行政院所屬各機關出國報告
（出國類別： 實習 ）

九十年度聯合技術訓練計畫

「光化學評估測站操作運轉」

服務機關：行政院環境保護署
出國人　職稱：技正
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出國地區：美國
出國期間：九十年七月二十二日至九十年八月四日
報告日期：九十年八月二十七日

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行政院及所屬各機關出國報告提要

出國報告名稱：九十年度聯合技術訓練計畫「光化學評估測站操作運轉」

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出國計畫主辦機關/聯絡人/電話：經濟部國際合作處/盧美雅/23513855

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關鍵詞：光化學

內容摘要：如后。

摘要

臺灣地區現階段已建置完成七十二座空氣品質監測站，藉由此一二十四小時自動化監測系統，環保署得以即時監控各地區空氣品質狀況，並透過傳播媒體及資訊網路等提供大眾相關空氣品質資訊，除於空氣品質劣化時得適時採取緊急應變措施，降低造成之危害，且提供各項污染防制措施參考資料，以利空氣品質之改善。惟近年來，由於工商交通業之發達，使空氣中之污染物成份更趨複雜，有機化學溶劑大量應用於工業生產過程，致亞熱代高溫環境之台灣地區，經常曝露於高量之有機揮發氣體（VOCs）中。VOCs除引起光化反應外，對人體健康如呼吸系統及造血細胞病變等危害影響更為嚴重。鑑於有機揮發氣體為對流層臭氧（tropspheric ozone）產生之先驅化合物，依歷年來環保署監測資料分析顯示，除懸浮微粒(PM_{10})外，0_3的濃度亦經常超過國家大氣品質標準。因此，為進一步瞭解臭氧形成相關理、化特性，除臭氧濃度監測作業外，對其前趨物質之揮發性有機污染物，宜儘速加強監測，以建立完整之臭氧排放資料庫，提供空氣品質惡化及污染防制因應策略應用

參考。本次出國計畫，除瞭解美國最新環境空氣品質監測現況外，並針對臭氧前趨物監測相關技術如光化評估監測站(PAMS)之應用發展與儀器操作運轉維護進行觀摩實習，以提供國內臭氧監測及光化測站運轉管理應用參考。

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壹、目的：

（一）拜訪美國環保署地方分支機構及州政府與地區環保單位，以瞭解法規制定現況。

（二）美國光化評估監測站設置運轉及操作維護技術觀摩實習。

（三）瞭解光化評估監測儀器商品化應用情形及主要污染分析技術原理。

貳、實習行程

本次赴美實習行程如下表，實習單位主要包括加州地區環保機關、PAMS 測站及儀器製造公司等，見聞敘述如後。

實習行程表

預定起訖日期	天數	到達地點	詳細工作內容
七月二十二日	一	舊金山	台北搭機抵達 SFO
七月二十三日至二十五日	三	舊金山	拜訪 USEPA Region9 in SFO 及 CEPA Air Resource Board、與 SMAQMD 等環保單位，瞭解及觀摩空氣品質監測現場作業、實驗室分析與光化測站運轉情形
七月二十六日至二十七日	二	丹佛	舊金山搭機往丹佛路程、拜會科州環保單位（APCD）及參觀空氣品質監測站，並拜會 EPA region 8 in Denver
七月二十八日至二十九日	二	丹佛	週末
七月三十日至八月一日	三	洛山磯	丹佛搭機往洛山磯，拜會 SBAPCD 、Tetra Tech 環境顧問公司、SCAQMD 等地區環保單位及參觀空氣品質監測與光化測站運轉
八月二日	一	洛山磯	拜訪 Entech Instrument

			及 XonTech Inc 公司，討論儀器發展應用現況及參觀儀器設備
八月三日至四日	二	洛山磯-Taipei	相關資料整理及搭機返台

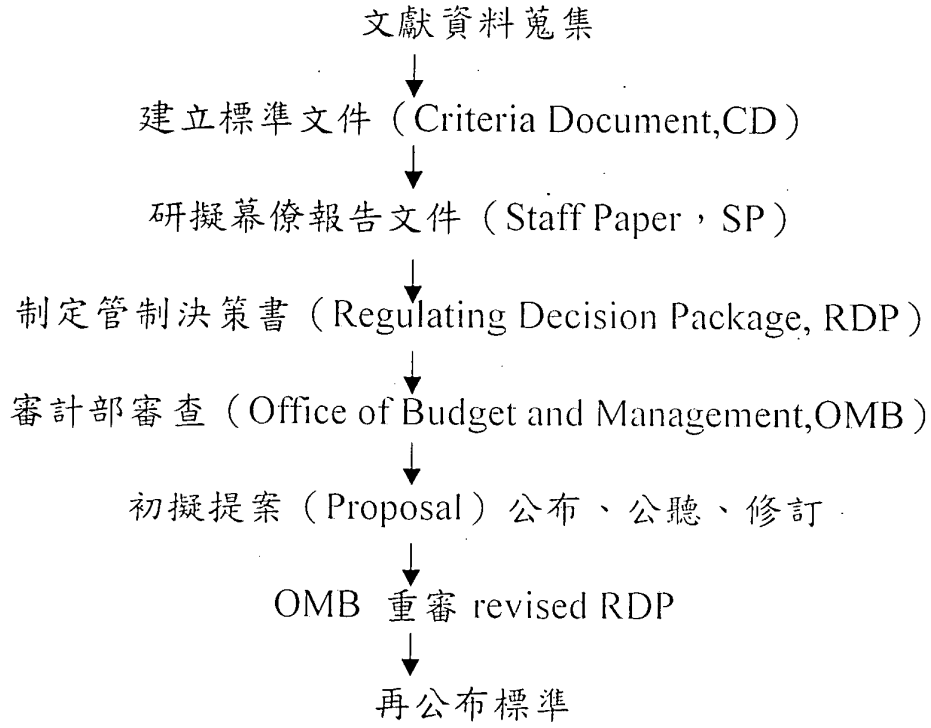
參、美國臭氧空氣品質標準現況

一、法規標準制訂程序

美國環境標準之制定過程極為複雜且耗時，整個制定和修正作業除明訂完成期程，對人類健康影響之相關科學研究報告數據資料，並詳加收集分析整理，提供朝野人士包括環保相關單位人員及民間組織與專家學者等參與審閱評估，俾廣納各界意見，使相關法規更為完善且易於推動落實執行。

臭氧標準制定作業流程第一要項為標準文件（Criteria Document,CD）之建立，主要係參考既有科學文獻資料，經由署外專家學者及空氣清淨法顧問團（Clean Air Scientific Advisory Communities, CASAC）之評估建議，再由研發處（Office of Research and Development，ORD）及環境評估室（Environmental Criteria and Assessment Office）進一步增修，並經 CASAC 審核後定案。標準文件建立後環保署空氣品質規劃及標準處（OAQPS）即針對相關意見及內容進行曝露風險評估分析，且著手撰擬幕僚文件（Staff Paper,SP）與研提方案，經過進一步嚴謹之科學驗證評估後，製成管制決策書（Regulating Decision Package, RDP）供署長決策訂定。署長所提決策標準須經審計部審查通過後才能將提案公布於

Federal Register，並召開公聽會，廣納各界意見及修正。相關作業流程兼顧影響民眾福址相關資訊蒐集與人體健康科學驗證為立法之依據，其主要作業流程圖如下：



二、臭氧空氣品質標準

美國臭氧空氣品質標準自 1971 年分別以人體健康影響及生態保護二大基準考量，訂定主要標準及次要標準為光化學氧化物（Photochemical Oxidants）濃度一年不得超過 0.08ppm 一小時。其中主要標準訂定依據係以洛杉磯地區呼吸系統疾病和光化學氧化物相關研究為主，次要標準以污染物對植物生長及產量影響為考量。1979 年則修訂為最大每小時平均 0.12ppm 臭氧濃度，且超過

次數一年不得大於一次。由於 1980 年起相關研究報告陸續指出臭氧較長時間之曝露對人體健康影響遠大於一小時之曝露情形，故建議修正現行標準。此外，依環境法對相關法規須定期修正之規定，美國環保署終於在 1996 年起藉由冗長嚴謹科學驗證及公開審閱步驟，提案修訂現行環境臭氧標準，並於 1997 年公布最新標準，重新界定以濃度基準考量制定主要標準為 0.08ppm-8hrs 平均，次要標準亦比照主要標準規定。評估品質是否符合標準，以三年之年第四日高值平均不可超過 0.08ppm。

表 3.1 美國國家 O_3 空氣品質標準（NAAQS）修正沿革

Year	Primary （一級） NAAQS	Secondary（次級） NAAQS
1971	1 hr 0.08ppm	同一級標準
1977	1 hr 0.12ppm （連續 3 年不得超過 3 次）	同一級標準
1993	重申 1977 年 NAAQS 規定標準	重申 1977 年 NAAQS 規定標準
1997	8 hr 0.08ppm （3 年之年第四高值平均值規定）	同一級標準

肆、美國光化學評估監測（PAMS）執行現況

一、設置源起

光化學評估監測站之設置，主要源於 1990 年美國清淨空氣法修正案（Clean Air Act Amendment, CAAA）第一篇（Title 1）182（C）節，要求各地方政府對都市地區空氣品質未達新定標準者，加強監測其臭氧(O_3)，氮氧化物(NOx)、羰基(carbonyl)成份和揮發性有機污染物(VOCs)等臭氧前驅物，以取得更詳盡且具代表性之臭氧污染監測資料。除 1992 年聯合國經濟理事會要求歐洲各國進行類似監測計畫，美國聯邦政府及各州並依規定執行相關措施，針對臭氧、VOCs 和 NOx 的進行監測改善作業規劃，同時美國聯邦條例(40 CFR 58)，並要求各州在臭氧未達到標準（A>120ppb O_3 1-hr exceedance；B>80ppb O_3 8-hrs average）的區域設立光化學污染物評估監測站的監測網，以獲取更多有關臭氧和其前驅物的空氣品質資料，提供空氣污染防治相關單位，對於空氣污染品質標準評估、污染追蹤及管制策略之研擬參考。環境週界臭氧及其前驅物濃度監測資料，並可提供建立 VOCs 等污染物管制清單，掌握未來空氣品質變化趨勢，且配合光化學污染物分析模式之建立與資料分析應用，除提昇各州空氣品質監測站設置規劃管理有效

評估，強化國家週界空氣品質標準(NAAQS)資料之完整性，且對各州依法規要求各項執行成效提供最具經濟效益之掌控。

二、數據品質目標須求(Data Quality Objectives；DQOs)

空氣監測數據品質目標(DQOs)定訂，一般係依決策制定目的所能賴以接受之環境監測資料品質的準確（或不確定性）程度而言。監測數據大體而言並無法百分之百準確提供對資料之實際應用須求，所以對於資料的變異必須加以權衡修正及適當的處理。舉例而言，下風處的臭氧濃度未必百分百一定高或低於上風處，由於氣象條件的變化，一天之中的臭氧濃度極可能造成兩個最高值。因此，採樣監測嚴謹的規劃設計，才有可能將誤差範圍控制在決策定訂可接受一定程度之內。

PAMS 計畫主要目的包括未達空氣品質標準地區之管制策略擬訂（包括污染源種類分布及模式分析評估）、管制策略執行成效評估、排放源追蹤（管制清單及污染特性建立）、環境趨勢評估及人體曝露評估等，以下就各類監測目的訂定數據品質目標，分述如下：

(一) DQO1—污染物成份分析及分布評估

為空氣污染控制策略、經濟效益和污染物散佈機制評估目的，

提供環境周界具有代表性及實用性之特定 VOCs 種類和分布之空氣品質資料。其數據品質目標說明如下：

1.1）PAMS 測點資料，必須能夠反應日夜間污染物形成狀況，若確有日夜雙高濃度存在時，則須達到 80%的信賴區間。

1.2）PAMS 測點資料，必須能夠反應日夜間污染物濃度變化情形，若確有變化存在時，則須達到 80%的信賴區間。

(二) DQO2—模式評估

為建立及修正光化學污染物分析模式，提供區域正確的氣象資料和空氣品質資料。其數據品質目標說明如下：

2.1）所提供的 VOCs，臭氧，NOx 和氣象等資料必須依法規規定方式執行，包含選址、操作和資料的品質標準。

(三) DQO 3 –防制成效評估

建立具代表性環境監測資料及污染物排放清單，提供污染防制成效評估及瞭解污染來源與環境之衝擊，其數據品質目標說明如下：

3.1）#2 測站所收集的總揮發性有機污染物(Total VOCs)監測資料必須超過五年以上的量測時間，且足以表現出 3%以上的年趨勢代表資料(上風或下風)，在 80%信賴區間。

3.2）#2 測站所收集的 VOCs 的監測混雜的資料，必須能夠顯現出連續兩年的季平均 20%的變化情形(上風或下風)，如果存在變化時，應落在 80%的信賴區間。

(四) DQO 4 –排放趨勢分析

量測數據主要用於日後對調整前後的污染趨勢分析。

4.1）都會區不同人口分布類型之複雜的 VOCs、臭氧、NOx 和氣象監測資料，必須能夠反應出一年的下風地區趨勢的 80%信賴區間狀況，直到其改善達空氣品質標準。

(五) DQO 5 –空氣品質標準修訂

針對特殊污染物在國家環境空氣品質標準新增訂定參考之監測數據，其數據品質目標說明如下：

5.1）臭氧(和 NO_2)監測必須符合國家監測站(NAMS)或區域監測站(SLAMS)的相關規定，包含選點，操作和資料的品質標準。

(六) DQO 6 –毒性污染物增修

對法規規定及未規定之污染物適當地點之量測，以提供暴露評估及法規標準之訂定須求，其數據品質目標說明如下：

6.1）#2 測站所提供各種 VOCs 的量測資料，必須能夠提供年平均資料在±50%以內濃度資料的 80%的信賴區間。

三、測站選址原則

光化學評估監測網設立的主要目的，在提供未達臭氧標準地區所需要的 VOCs、臭氧、NO_x 和氣象等監測資料，以進一步瞭解污染之發生與提供解決方案。為滿足前述監測計畫目標需求，最小的監測網規劃應至少要包含四到五個站：

站＃1 — 上風與背景特徵測站。

本站主要在建立上風處背景資料及臭氧傳送與前驅物質貢獻程度相關資訊。站址宜設在早上臭氧前驅物濃度最高的盛行上風方向，且足以反應都會尺度之上風處邊緣地區。

站＃2 —最高臭氧前驅物濃度測站。

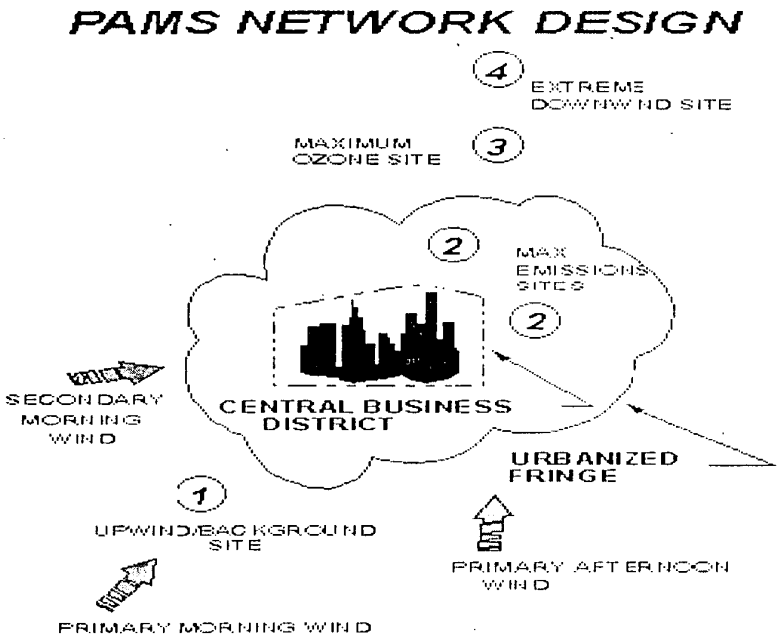
本站以監測都會區內臭氧前驅物排放的型態與量。測站位置應選在與選站＃1 的早上盛行風方向下風處且緊鄰都會工業區或主要排放源的邊界下風處。如果地區太大時，應在早上第二盛行風方向增設一個本類型測站。

站＃3 — 最高臭氧濃度測站。

本站主要在監測從最高臭氧前驅物排放的下風處形成的最高臭氧濃度。本站應設在離都會區邊緣約 15 至 50 公里處。

站＃4 —遠下風測站。

本站旨在瞭解臭氧及其前驅物的長程傳送與對其他較遠地區之貢獻程度。本站應設在下午的盛行下風方向且足以反應都會尺度之下行風的邊緣。



四、 美國現行光化學評估監測站網

1997 年美國國家空氣品質標準的修訂中，原擬取消 O_3 濃度 1 小時的標準，惟因大部分地方政府機關的反對，最後仍決定在 226 個地區 (和 38 個未達標準的區域)維持適用 1 小時的標準規定。現階段在 38 個 1 小時值未達標準的區域中，24 個區域，不論其未達標準程度輕重，一律視為光化學評估監測站的主要標的區域。這 24 個區域共涵蓋 8 千 4 百萬的人口，惟考量光化學評估測站的彈性規定，允許部分緊鄰地區合併執行，所以實際整個監測站網共計 22

個區，包括約 78 個監測站，詳如下表：

表 4.4.1 美國光化學評估監測站的地點及分類

Nonattainment Areas Subject to PAMS	Classification
Atlanta, GA	Serious
Baltimore, MD	Severe
Baton Rouge, LA	Serious
Boston-Lawrence-Worcester, MA-NH	Serious
Chicago-Gary-Lake County (IL), IL-IN-WI[1]	Severe
Dallas-Fort Worth, TX	Serious
El Paso, TX	Serious
Greater Connecticut, CT	Serious
Houston-Galveston-Brazoria, TX	Severe
Los Angeles-South Coast Air Basin, CA[2]	Extreme
Milwaukee-Racine, WI[1]	Severe
New York-New Jersey-Long Island, NY-NJ-CT	Severe
Phoenix, AZ	Serious
Philadelphia-Wilmington-Trenton, PA-NJ-DE-MD	Severe
Portsmouth-Dover-Rochester, NH-ME	Serious
Providence-Pawtucket-Fall River, RI-MA	Serious
Sacramento, CA	Severe
San Diego, CA	Serious
San Joaquin Valley, CA	Serious
Santa Barbara-Santa Maria-Lompac, CA	Serious
SE Desert Modified AQMA, CA[2]	Severe
Springfield, MA	Serious
Ventura County, CA	Severe
Washington, DC-MD-VA	Serious

(1) Chicago and Milwaukee are combined into one PAMS area referred to as Lake Michigan.

(2) Los Angeles-South Coast and SE Desert Modified AQMA are combined into one PAMS area referred to as South Coast-SEDAB.

五、光化學評估監測項目及頻率

美國環保署對 PAMS 之 VOCs 定義為在 25℃時蒸汽壓大於 0.14 mm 汞柱的非甲烷 aliphatic 及芳香烴化合物。主要為 2 到 12 個碳數的有機物。1990 年亞特蘭大首先依據都會區的含量及其生成臭氧的能力研擬提供一份 VOCs 的建議

名單，並於 1994 年修正。新修正名單中加入 6 個含量較高的芳香烴化合物取代其中 6 個含量較低的 oleifin 化合物。1998 年公佈的最新 56 種 VOCs，如表 7.2。其與'94 年的名單相較主要的差別在於將不穩定的化合物 2-methyl, 1-pentene 從名單中剔除。另外加入了 1-hexene 和 dodecane 兩化合物作為滯留時間之查核 。dodecane 亦可作為 12 個碳化合物回收率之指標。

環保署規定 PAMS 主要量測項目除臭氧(O_3)，氮氧化物(NOx)、地表和上風處的氣象資料外，還包括揮發性有機污染物(VOCs)等。大部分測站以每三個小時或一個小時量測頻率，針對 56 種碳氫化合物進行監測。#2 測站則必須另以每三個小時的頻率收集 3 種羰基化合物(甲醛、乙醛、丙酮)。這些污染物被歸類為十種的危害性空氣污染物。對於臭氧(O_3)，氮氧化物(NOx)和地表的氣象條件則須以每小時的連續監測頻率進行量測。

地表氣象監測至少包括風速、風向、溫、濕度，其中每一監測區域，應有一個站量測太陽輻射、紫外線、氣壓及降雨量。高空氣象監測則需在每一個區域測站設置一座

以瞭解平行風速、風向、溫度及混合層高度等。

表 4.5.1 美國於 1998 年公佈的最新 56 種 VOCs

AIRS Parameter Code	Target Compound Name	Code Parameter AIRS	Target Compound Name
43203	Ethylene	43249	3-Methylhexane
43206	Acetylene	43250	2,2,4-Trimethylpentane(isooctane)
43202	Ethane	43232	n-Heptane
43205	Propylene	43261	Methylcyclohexane
43204	Propane	43252	2,3,4-Trimethylpentane
43214	Isobutane	45202	Toluene
43280	1-Butene	43960	2-Methylheptane
43212	n-Butane	43253	3-Methylheptane
43216	trans-2-Butene	43233	n-Octane
43217	cis-2-Butene	45203	Ethylbenzene
43221	Isopentane	45109	m/p-Xylene
43224	1-Pentene	45220	Styrene
43220	n-Pentane	45204	o-Xylene
43243	Isoprene(2-methyl-1,3-butadiene)	43235	n-Nonane
43226	trans-2-Pentene	45210	Isopropylbenzene(cumene)
43227	cis-2-Pentene	45209	n-Propylbenzene
43244	2,2-Dimethylbutane	45212	m-Ethyltoluene(1-ethyl-3-methylbenzene)
43242	Cyclopentane	45213	p-Ethyltoluene(1-ethyl-4-methylbenzene)
43284	2,3-Dimethylbutane	45207	1,3,5-Trimethylbenzene
43285	2-Methylpentane	45211	o-Ethyltoluene(1-ethyl-2-methylbenzene)
43230	3-Methylpentane	45208	1,2,4-Trimethylbenzene
43245	1-Hexene*	43238	n-Decane
43231	n-Hexane	45225	1,2,3-Trimethylbenzene
43262	Methylcyclopentane	45218	m-Diethylbenzene
43247	2,4-Dimethylpentane	45219	p-Diethylbenzene
45201	Benzene	43954	n-Undecane
43248	Cyclohexane	43141	n-Dodecane*
43263	2-Methylhexane	43102	TNMOC**
43291	2,3-Dimethylpentane	43000	PAMHC***

* These compounds have been added as calibration and retention time standards primarily for the purpose of retention time verification. They can be quantitated at the discretion of the user.

** Total Nonmethane Organic Compounds

*** PAMS Hydrocarbons

六、採樣監測頻率及設置需求

光化學評估監測站設置種類及採樣頻率，主要係依人口分布數

量考量規定，如下表：

Population of MSA/CMSA	Freq-type	Site location
Less than 500,000	A or C	(1)
	A/D or C/F	(2)
500,000 to 1,000,000	A or C	(1)
	B/E	(2)
	A or C	(3)
1,000,000 to 2,000,000	A or C	(1)
	B/E	(2)
	B/E	(2)
	A or C	(3)
Greater than 2,000,000	A or C	(1)
	B/E	(2)
	B/E	(2)
	A or C	(3)
	A or C	(4)

Type	Requirement
A	8 3-hour samples every third day
	1 24-hour samples every sixth day
B	8 3 hour samples everyday
	1 24-hour sample every sixth day(year-round)
C	8 3-hr samples 5 hio-event/prev days/every 6th day
	1 24-hour sample every sixth day

Type	Requirement
D	8 3-hour samples every third day
E	8 3 hour samples everyday
F	8 3-hr samples 5 hio-event/prev days/every 6th day

Years/After Promulgation	Number sites operating	Operating Site Location Recommendation
1	1	2
2	2	2,3

3	3	1,2,3
4	4	1,2,3,4
5	5	1,2,2,3,4

七、執行現況檢討建議

由於大氣中 VOCs 成份複雜且濃度甚低，分析前必需經過濃縮聚焦的過程，以取得適量之分析濃度。除毛細管層析為最常用的分析方法外，臭氧前趨物分析技術樣品的收集，公布方法分為冷凍收集及吸附劑收集兩種型式，採樣方法以採樣瓶(Canister)與多重吸附管最為常用。標準方法包括在 TO-15 及 TO-17 等。由於冷凍濃縮及冷凍聚焦兩個步驟皆需消耗相當量的冷媒（每小時必須至少採集 40 分鐘的樣品；目前有液態 N_2 、CO_2、電冷式三種冷凍方式），且鋼瓶清洗過程易遭污染，故目前加州多數 PAMS 測站採樣後仍須送回實驗室分析。而分離過程中不同層析管柱長度與靜相厚度影響其對化合物之分析效率，故冷媒使用量亦造成相當影響。常用之 BP1 等級的管柱，靜相厚度必須要 3mm （50 公尺長），才能在低於室溫下有效分離 C_2-C_4 化合物。靜相厚度為 1mm 的管柱較不易在低於室溫下達到理想的分離效果。若採雙管柱法用 BP-1 分離 6 碳以上的化合物（圖 4.1 ），PLOT 管柱分離六個碳以下的化合物（圖 4.2）如此可不用冷媒，惟 PLOT 管柱對水及極性分子較敏感，

會造成峰寬及滯留時間之改變。

由於各州 PAMS 測站皆已運轉多年，環保署現行策略為加強數據品保之控管。諸如鋼瓶清洗步驟、實驗室比對、儀器校正等。另 2000 年 3 月美國環保署與地方環保機關協辦的一次研討會中，州和地區環保單位檢討指出現行 PAMS 執行相關問題包括執行目標未集中焦點及資料量、設置需求量、目標化和物過多與品保未確實等，州及地方環保單位並紛紛建議提出改善措施。

八、修正後監測目標

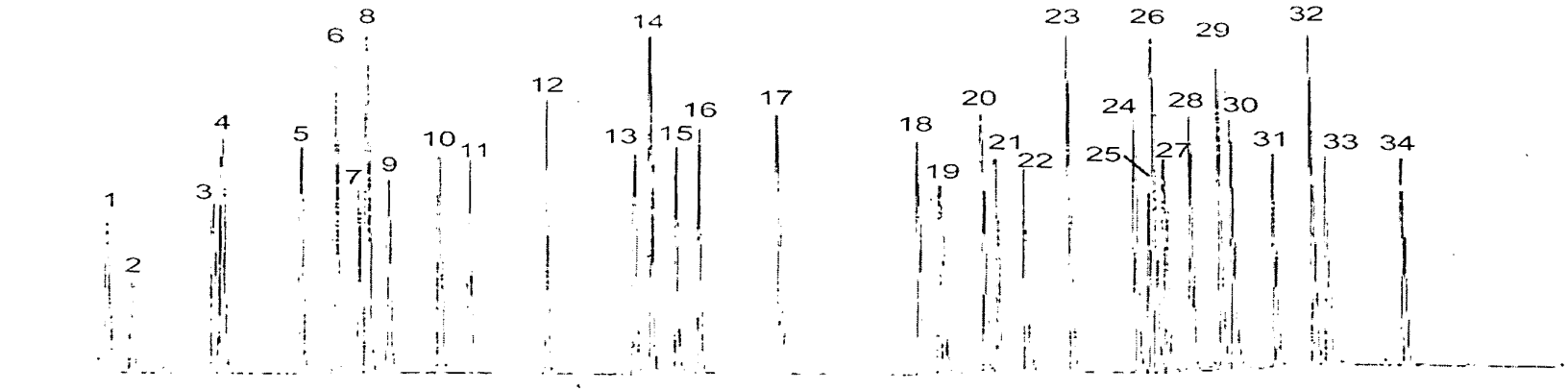
依前述所提建議，環保署重新簡化設定光化監測站設置主要目的為追蹤及改善污染排放控制策略，協助評估臭氧控制計畫，包括主要貢獻污染源及其它參數鑑定、趨勢變化、傳輸特性、強化排放資料庫及污染事件預測等。

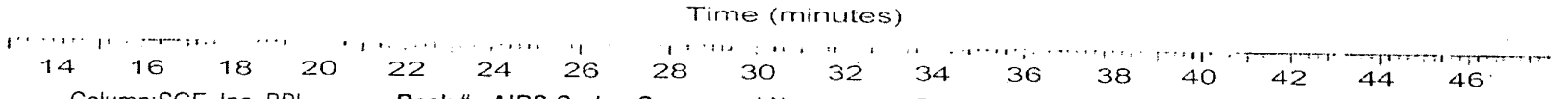
另考量光化監測站可能利於相關計畫之執行，包括在空氣中毒化物、支援模式、主要趨勢、NOx 排放及環境濃度等特性瞭解及 PM&RH 評估與特殊研究等方面。

九、經費需求

自 1992 年 PAMS 先趨計畫執行迄今，環保署聯邦基金已投資 8 千 8 百萬美元在其建置與操作運轉。州政府與地區環保單位相關

基金項下並已投入類似經費。估計每年共約耗費 2 千 4 百萬美元，在 PAMS 相關計畫執行應用。

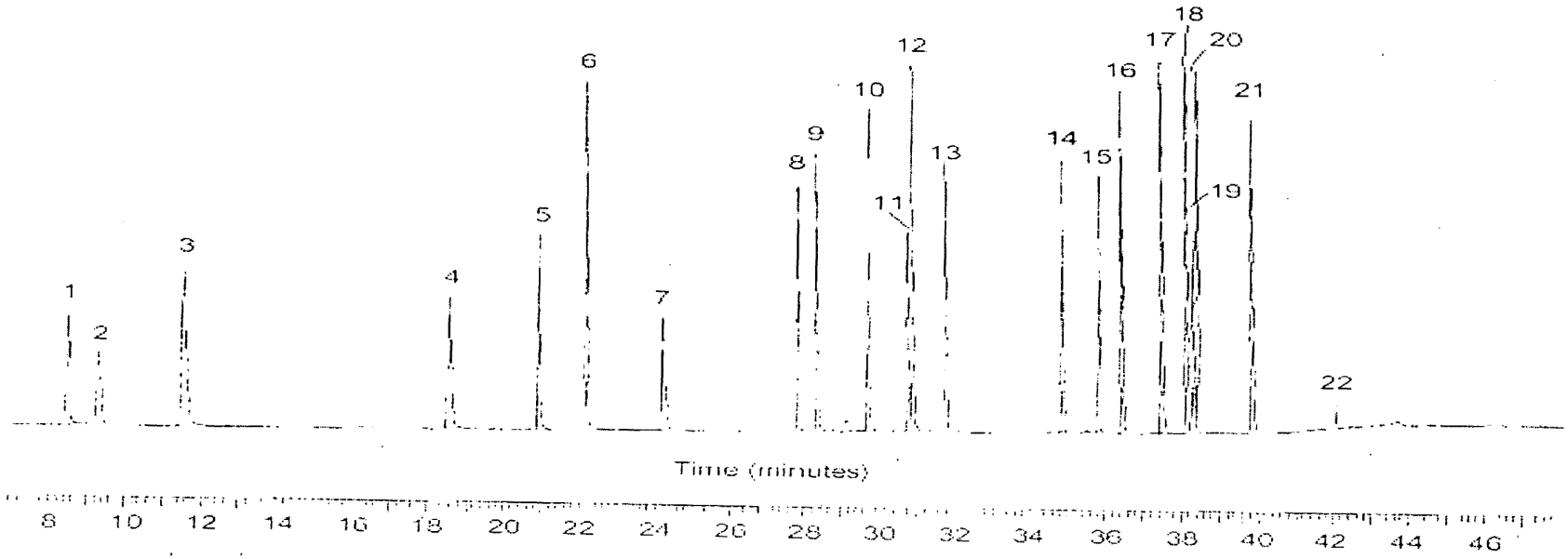




Column:SGE, Inc. BPI,
50m x 0.22mm x 1µm
Carrier:Helium, ~2.5ml/min
Initial Temp:45°C, 15 minutes
Rate 1:5°C/min.
Temp 2:170°C
Rate 2:15°C/min.
Final Temp:200°C, 6 minutes

Peak #	AIRS Code	Compound Name	Peak #	AIRS Code	Compound Name
1	43231	Hexane	18	45203	Ethylbenzene
2	N/A	Unknown	19	45109	m/p-Xylene
3	43262	Methylcyclopentane	20	45220	Styrene
4	43247	2, 4-Dimethylpentane	21	45204	O-Xylene
5	45201	Benzene	22	43235	n-Nonane
6	43248	Cyclohexane	23	45210	Isopropylbenzene
7	43263	2-Methylhexane	24	45209	n-Propylbenzene
8	43291	2, 3-Dimethylpentane	25	45212	m-Ethyltoluene
9	43249	3-Methylhexane	26	45213	p-Ethyltoluene
10	43250	2, 2, 4-Trimethylpentane	27	45207	1, 3, 5-Trimethylbenzene
11	43232	n-Heptane	28	45211	o-Ethyltoluene
12	43261	Methylcyclohexane	29	45208	1, 2, 4-Trimethylbenzene
13	43252	2, 3, 4-Trimethylpentane	30	43238	n - Decane
14	45202	Toluene	31	45225	1, 2, 3-Trimethylbenzene
15	43960	2-Methylheptane	32	45218	m-Diethylbenzene
16	43253	3-Methylheptane	33	45219	p-Diethylbenzene
17	43233	n-Octane	34	43954	n-Undecane

圖4.1 以BP-1分離6個碳以上的化合物



Rate 1:5°C/min
Temp 2:170°C
Rate 2:15°C/min
Final Temp:200° C, 6 minutes

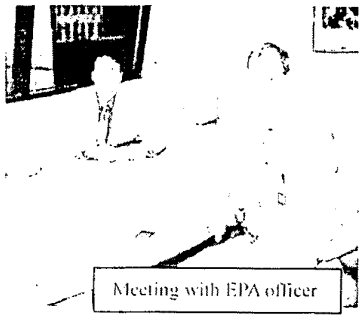
4	43205	Propylene	15	43224	1-Pentene
5	43214	Isobutane	16	43227	cis-2-Pentene
6	43212	n-Butane	17	43244	2, 2-Dimethylbutane
7	43206	Acetylene	18	43284	2, 3-Dimethylbutane
8	43216	trans-2-Butene	19	43263	2-Methylpentane
9	43280	1-Butene	20	43230	3-Methylpentane
10	43217	cis-2-Butene	21	43243	Isoprene
11	43242	Cyclopentane	22	43246	2-Methyl-1-Pentene

圖 4.2 以 PLOT 管柱分離六個碳以下的化合物

伍、科羅拉多與加州空氣品質作業概況

一、科羅拉多州：

本次行程為瞭解美國聯邦政府對整體臭氧監測作業之管理，特安排至一平均臭氧濃度表現較佳之科州(非 O_3 Non attainment area）進行對照比較，並拜訪位於丹佛市之州政府環保單位 Colorado Department of Public Health and Environment 負責空氣品質監控作業之 Air Pollution Control Division (APCD) 與聯邦環保署 EPA Region8。


Meeting with EPA officer

丹佛市至 2000 年人口總計約 2,400,570，由於氣候環境舒適，入口有逐年增加之趨勢。其空氣品質主要污染物為 CO，其中 78.6%來自交通、工業製程及汽油燃燒產生等。懸浮微粒（Particulate matter）則 59%來自風吹沙塵（冬季道路灑沙防止車輛因下雪路滑；過去使用鹽易造成木製橋樑受損）(Fugitive dust）及道路揚塵，一般為大於 10μm 以上，至於較細小懸浮微粒（Pm2.5 以下）則大多人為造成（包括電廠、汽機車柴油及壁爐），由於西部地區較為乾燥且冬天山區燃木合併其它污染源之產生，形成之細微粒因

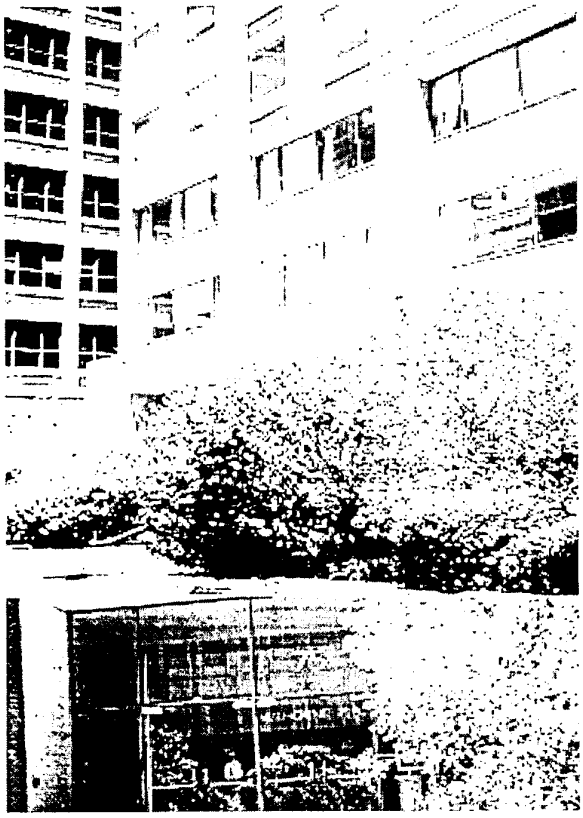
scatter light 作用，經常導致丹佛市"Brown Cloud"之現象，影響視覺(visibility)，民眾遂要求州政府需對 Visiblility 進行監控預報，1990 科州爰訂定視野標準為 0.076/Km (7.6% of light in the air blocked)，量測方法包括：Camera system(densitometry calculate slide)、Transmissometer & Nephelometer (比濁計)。另科州在臭氧方面主要來自交通排放、工業用 Paint 溶劑等 CH 化合物釋放，經夏季高溫及光之作用產生之二次污染，並未有超過排放標準之現象。

※圖示丹佛市空品測站美觀建築可供國內設置參考

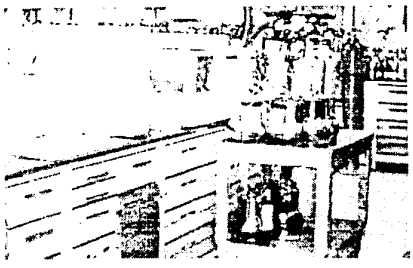
二、加州

加州總計現有人口 32,000,000，共分為十二個空品區(參考氣象條件、地型及污染源擴散影響面)，其中有 8 個

區為聯邦環保署歸納為O_3空氣品質標準未達成區域（Non-attainment area），為美國地區比例最高之地區，因此本次行程特安排觀摩其臭氧相關監測作業。

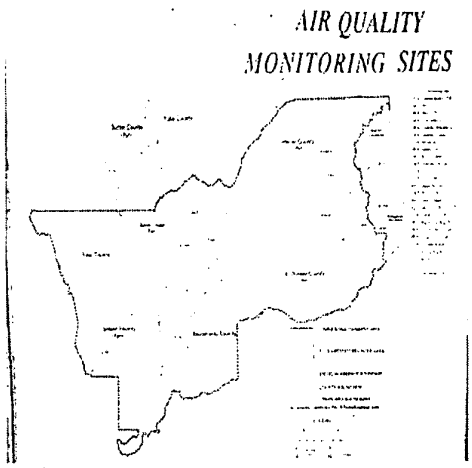


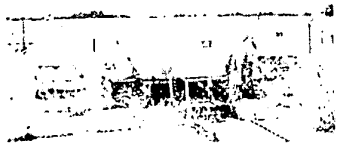
聯邦環保署 Region 9 位於舊金山市區，總計 6,000,000 人口居住，負責相關法規制定及空品策略及相關研究計畫執行，並審核及督導州政府空品達成計畫推動執行。加州州政府環保單位位於 Sacramento 市區，其空氣品質作業由 Air Resource Board 負責，設有相關監測實驗及檢驗室，包括 canister 清洗室及一 NIST traceable 臭氧光度計，



進行相關儀器之認證，主要業物為相關法規訂定及研究計畫執行與督導地區環保單位空品監測作業。由於 Sacramento

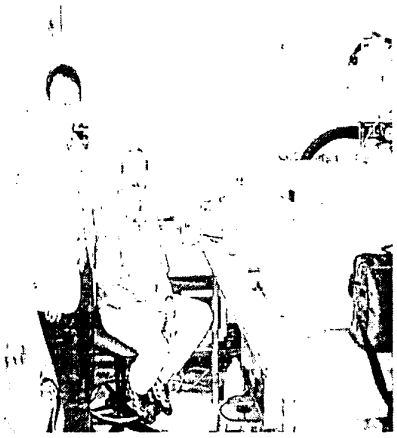
為環保署列為臭氧空氣品質極嚴重（severe）未達成區域，依規定應提出臭氧加強監測計畫並設置光化學評估測站，行程特參訪 Sacramento Metropolitan Air Quality Management District（AQMD），負責 Sacramento 大都會區空氣品質實際監測作業，轄區共 10 個空氣品質監測站，分別依污染源分布及人口數需求設置相關監測設備，現場共參觀二個 full equipment 空氣品質監測站，一交通測站（依人口規定需求設置）；設備與本署大同小異， 其中有關光化測站（PAMS）計 4 個，分別依環保署規定於污染源上下風等處設置 TypeI, II, II. III 型測站及一座上空氣象雷達觀測站，*Lower Atmosphere Profiling Radars（可外加 4 個 Radio Acoustic Sounding System（RASS）（利用聲波 915MHz-1290MHz 釋放 120m-5Km 經大氣結構之不同反射接收其溫差）*





Santa Barbara 位於加州南端，1997 年被環保署列為

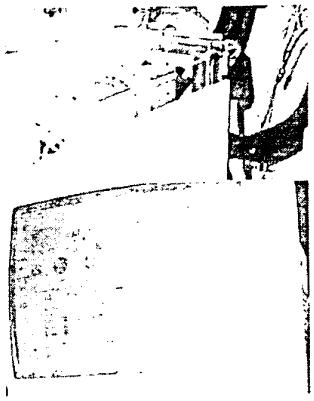
為另一空氣品質嚴重（serious）未達成區域，(3-40 days exceed state sd; 1-6 days exceed National 1hr sd/yr) 雖在 1997-99 El Nino & La nina 造成空品改善現象，惟臭氧污染尚未整體改善，目前設有一座光化學評估站，由 Santa Barbara air pollution control district（SBAPCD）負責操作運轉，利用 Canister 採樣方式及 Entech 前濃縮系統配合 GC-FID 線上分析。每三天進行一次八個三小時採樣之作業（七到九月間執行；每月皆能涵蓋假日及分例假日監測）。



Lab Canister 採樣分析

South Coast air basin 轄區涵蓋六個郡市包括洛山磯市（LA），橙市（orange），Reverside, San bernardino 及部份 Meteorological & geographic similar EX Salton air basin, Mojave Desert，

總面積計 10743mile^2，人口 15 百萬，空氣品質由 SCAQMD 負責 *6 個光化站*實際操作執行，整體空氣品質 Smog 相當嚴重，由於地面 O_3 經海風吹向山邊，再經逆溫層暖空氣向下推動

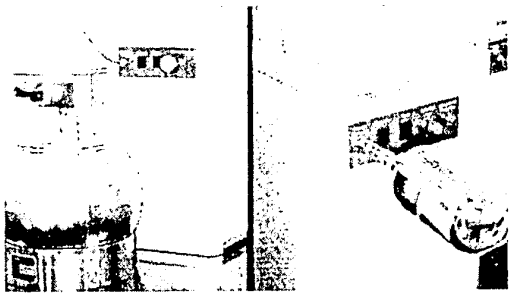


造成此一煙霧現象，環保署列為極端（Extreme）至極（Severe）嚴重臭氧未達成區域，州政府因此投入相當多的經費加強臭氧監控。除每三天收集八個三小時樣品，每六天並需有一次 24 小時連續採樣，儀器使用包括 XonTech 及 EnTech 之前濃縮系統。對水份及 CO_2 排除效果相當良好。

陸、**Entech Instruments** 氣相層析儀器研發公司

本次實習特地參訪總公司位於加州 Simi Valley 市的氣相層析儀器製造廠 **Entech Instruments Inc.,** 特別是針對環境空氣中低濃度揮發性有機氣體的濃縮系統研發應用進行瞭解。Entech 公司研發生產之揮發性有機氣體前濃縮系統主要應用於環保、工業及政府實驗部門。特參關其研發之液態氮冷卻前濃縮系統及真空加溫採樣鋼瓶清洗校正過程。

前濃縮系統可應用於無法直接注射進氣相層析儀之樣品如空氣中低濃度之氣態樣品、凝膠或乳液及固體樣品等聚焦後迅速注入氣相層析儀層析管柱內，達到各樣品成份最大溶出分離效益。

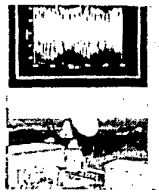


樣品的收集主要包括採樣吸附管、不銹鋼瓶及流量調節器等，其中並以 Silionite 塗敷在氣鋼壁，避免樣品附著於鋼瓶內壁，影響採樣收集效率。高量恒定採樣接頭(Large Volum Static Headspace)允許食品臭味、香味及塗敷物品等超低量(sub-ppb)樣品濃度濃縮至數百毫升濃度於 Headspace。

Entech 公司環境監測相關產品皆能符合美國環保署毒性氣體採樣方法規定，包括 TO1, TO2, TO3, TO12, TO14, and

其產品特色為前濃縮系統使用三階補集聚焦 3 traps stage(Cryon trap, Tenax trap, Back flush)CTD(cold trap dehydration) & MPTMicroscale purge&trap)--(-180 度 C-230)，可在 90% CO_2 環境下進行分析，幾乎所有流程皆塗敷矽化物減少管避吸附干擾，可作連續性及即時性分析(hrly)對極性與非極性分子皆可補捉偵測。70% R Humidity 25 度 C 狀況下，18ul/1sample H20 產生，且 1cc/1000cc sample 揮發 at RT，因此本系統設計對水份及 C02 干擾情形做最佳之處理，以提昇檢測數據之精確性能。

柒、**Xon Tech Inc.,**



XonTech 總公司位於加州 Van Nuys，為一高科技顧問公司，主要經費在國防設備之研發，其中僅 3%投資於環境科學研究。其在 VOC 分析儀器方面研發產品之特色在於非液態淡冷卻濃縮系統之應用，廣泛被應用於周界環境空氣品質監測，包括美國環保署曾使用該產品進行相關揮發性氣體之採樣研究計畫。

其前濃縮（pre-concentration）系統源自美軍紅外線飛彈設備之改良，除由二個多重吸附劑(Tenax-GR/Carbotrap)進行第一次補捉，並配合 dry He purge to remove H_2O, 再經特殊設計之 Stirling-cooled (-165 度 C)進行二次補捉及聚焦。由於該項產品與 PE ATD400 同樣前濃縮不需使用液態氮進行冷卻濃縮，因此適用於周界空氣品質採樣。相關研究包括在加拿大一項比對發現，其對 VOC 中 1, 3-butadiene, benzene, ethylbenzene & o-xylene/styrene 等與鋼瓶採樣分析有極佳之一致性，惟 hexane, N-octane

值有偏高現象（原因未明），1996 年美國環保署在田納西州一次試驗比對發現，其偵測極限值（MDL）較 PE ATD400 為低(0.1ppbv--0.5ppbv QA Objectives) Relative %Dif 10%--25%，且PE 對濕度較為敏感，並且對 2,3-dimethylbutane 有遺漏偵測現象。

捌、Perkin Elmer 儀器概述

光化學測站長程目標在累積空氣中揮發性有機物(VOCs)之變化數據，並與地理、氣象等環境資訊結合建立適當模式，以提供污染控制等應用參考。監測系統主要包括採樣與前濃縮設備、臭氧前驅物分析儀及其它附屬周邊設備。

系統以每小時採樣頻率針對清靜空氣法案（CAA）規定之臭氧先驅物進行量測。採樣流量為 15ml/min 抽 40 分鐘共 600ml 以確保乙炔（Acetylene）不會透出。VOCs 濃縮於 ATD400 之電子冷卻濃縮阱（-30^0C），濃縮阱內充填適當吸附劑，以便定量濃縮的 C_2-C_{12} 之揮發性有機物。快速加溫及逆吹之攜行氣體隨後將 VOC 帶入臭氧前驅物分析儀。

臭氧前驅物分析儀由兩組層析管柱（BP1 及 Al_2O_3 Plot）藉獨特之 Dean's Switch 設計使其分離並於不需使用液態冷凝劑狀態下分析 C2 至 trimethyl benzenes 成分。對 BP1 無法分離之低分子量碳氫化合物，於 45^0C 時被導引至 Al_2O_3 Plot 並加以分離及通過火焰離子偵測器（FID2）量測。沸點較高之成分

則於 BP1 分離後導入第一組火焰離子偵測器（FID1）量測。

分析儀偵知訊號經 NCI 902 數據界面接收後轉為數位訊號輸出至 Turbochrom 層析電腦程式中進行數據處理。

玖、結論與建議

自然界中，原本臭氧即普遍存在大氣平流層（15~30 公里）中，除吸收有害的紫外線(UV)，且維持大氣結構之平衡，對地球上的生物具相當保護作用。惟近地表對流層所形成之臭氧，卻是直接威脅人類健康以及農作物之生長。由於近地表臭氧主要是由交通與工廠固定源所排放之氮氧化物(NO_x)與逸散性有機化合物(VOCs)經光化作用的途徑而產生。由於這些污染物均具擴散與傳送特性，對環境造成之衝擊不僅是污染源中心的都會區空氣品質劣化而已，郊區下風處甚或偏遠地區的空氣品質已蒙受其害。由於先進各國已漸趨感受到其對人民生命財產嚴重之威脅，過去幾十年來，紛紛投注大量人力與財力，尋求臭氧相關改善控制策略，以解決因應此一環境污染之課題。

美國環保署近 10 年來在臭氧監測方面更是投入相當之經費人力，研究臭氧先驅化合物之形成機制與加強臭氧監控，做法頗值得我國參考。

本次行程安排考量期程緊湊，為兼顧路程之順暢便捷及計畫需求，訪習單位以美國西岸為主，並參考美國現行空氣品質對臭氧污染狀況相關改善要求，特拜訪科羅拉多

州 O_3 空氣品質標準達成區域及加州之未達成區域，加以對照比較。共計參訪單位包括二個中央 EPAregion 8 & 9、二個州政府環保單位（California Air resource Board & Colorado Department of public health & Environment APCD）及三個地方等環保單位（Sacramento Metropolitan AQMD、SBAPCD、SCAQMD）與二家儀器製造公司（Entech、Xontech）。主要參訪實習心得及建議依儀器應用及行政規劃策略說明如下：

一、儀器應用：

（一）東西岸儀器應用明顯差異，目前瞭解為加州大部分地區設置期程較早之故，惟因各類型儀器研發皆有其優缺點及特殊性能，對不同之 VOC 成分各有其優劣解析效果，故在使用方面宜針對主要污染成分特性，審慎評估後，並進一步比較分析選擇應用。

（二）國內高濕環境下，對儀器解析度及 VOC 定量干擾極大，過量水份會干擾 FID 訊號，造成基準線及尾線訊號上升。除前濃縮系統在除水及 CO_2 排除效果方面應多加評估外，定量時並應注意逆吹補集以避免濃度低估情形。

（三）使用吸附劑應審慎考量吸附效率與溫度之控制，一般

而言吸附性越強,其熱脫附溫度需求越高(如tTenax, Carbon Molecular sieve 等 300 度 C 之熱脫附),不良之吸附作用會造成分析成份之損失(如 Nafion 半滲透管吸附對極性分子具親合性使用效果不佳)。

(四) ambient air have similar retention time 易造成不準確之定量及判斷。

(五) insufficient cooling during pre-injection period may cause inefficient trapping of organic compounds especially C_2-C_3。

(六) trap Temp well below set -172^0 CH_4, O_2 & CO_2can be trapped, 其中 CH_4, O_2 造成 baseline perturbation, CO_2 造成 plugging problems.

(七) Mass Flow Controller (MFC) 應定期留意,避免造成流量錯誤而影響結果產生。

(八) 其它問題包括 dirty jets, plugged jets, and improper flame gas flows.

Setting carrier, hydrogen, & makeup gases should be performed whenever the peak signature changes (peak broadening, multiple peaks or significant changes

in retention times）並注意儀器之定期維護

（九）Plot 層析管柱應注意 High carier flow rate(>8ml/min He)會造成基線 Spikes 因 Polymerblown into FID Carrier FL 以(5ml/min)為佳。

（十）加州地區之監測站大部份仍使用鋼瓶採樣，於現場或送回實驗室分析。現場分析資料一般皆可透過遠端遙控軟體系統提供環保單位人員進行監控作業。

二、規劃應用策略

由於本署光化測站設置尚在初期測試階段，相對美國之七八年執行成效宜借鏡其經驗，避免重蹈覆徹。美國目前各州已針對光化站要求環保署提出相關檢討改善事項，主要包括：

（一） 執行目標未能集中焦點

（二） 資料收集需求量過多（April-Sept）

（三） 監測目標化和物太多（57 種先趨化合勿；德州更訂定 81 種化合物）

（四） 測站設置需求量過多（2-5 個站）

（五） 遲未收集到真正必需之污染物資料

（六） 測站設址未必符合需求

（七） 數據品質未確保

（八） 資料未被充份應用

未來本署在推動光化測站之同時，建議明確界定監測數據使用目標，審慎評估核心監測作業之需求數量，且加強人員訓練，提昇數據品質，並落實資料之應用管理，以達成空氣品質改善之目標。

附　錄

一、實習照片剪輯

二、USEPA O_3 Emission Trends 1997

三、USEPA 臭氧前驅物採樣相關規定

四、ARB SOP for NMOC by GC-FID

五、SMAQMD PAMS 計畫及設備等相關資料

六、CDPHE-APCD 空污監測簡報資料

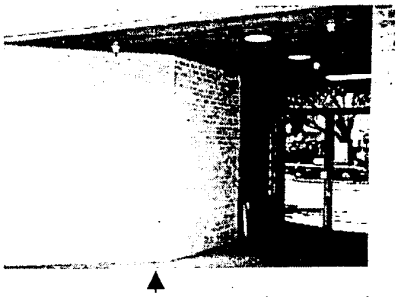
七、SBAPCD 2001 Clean Air Plan

八、Entech Product

九、ZonTech Product

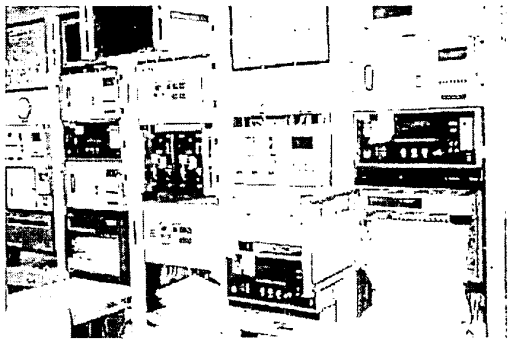
附錄一

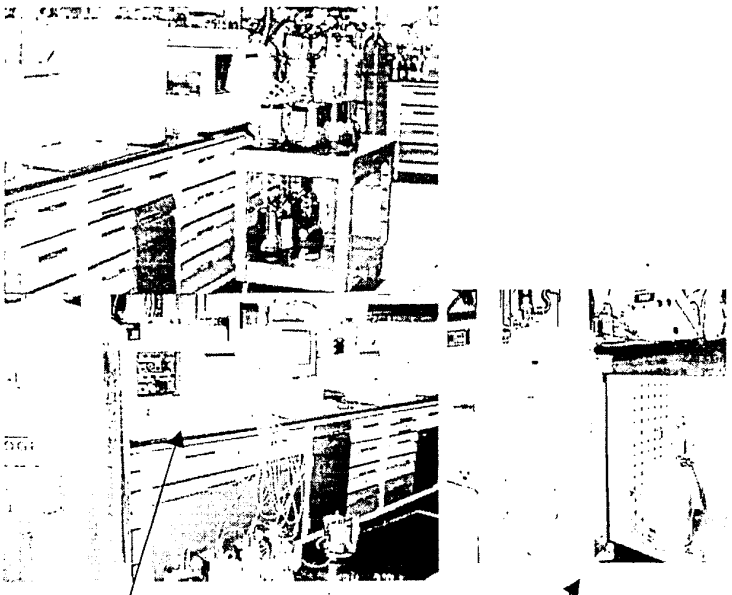
實習相關照片剪輯：



加州環保單位（ARB）

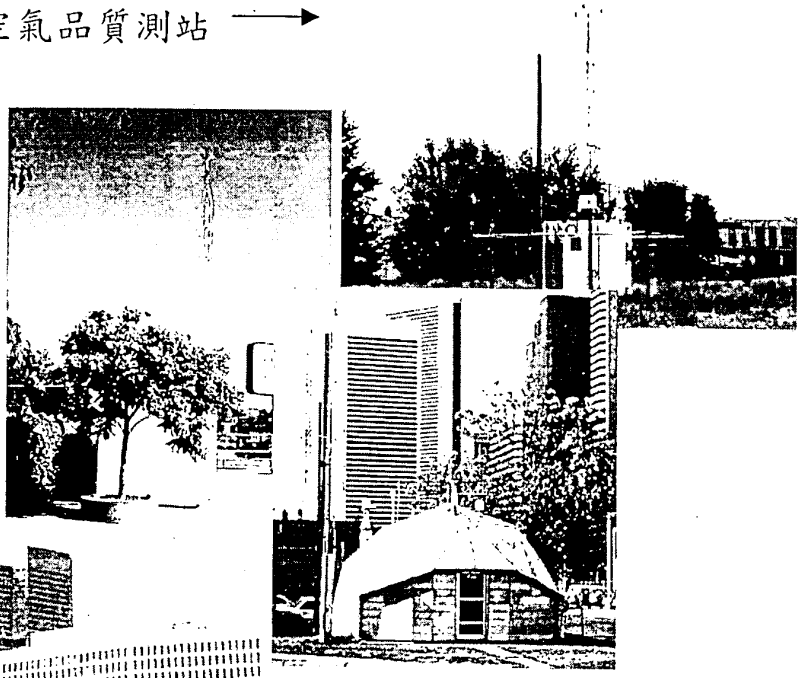
及監測檢驗分析室⟶





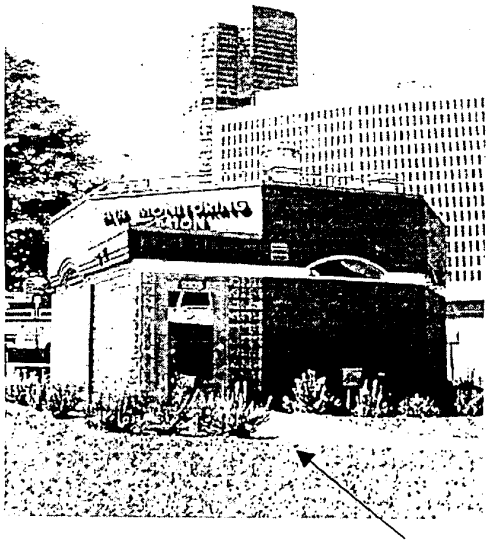
VOC 實驗室 GC 分析作業及採樣鋼瓶清洗過程

科羅拉多州 APCD
一般空氣品質測站 →

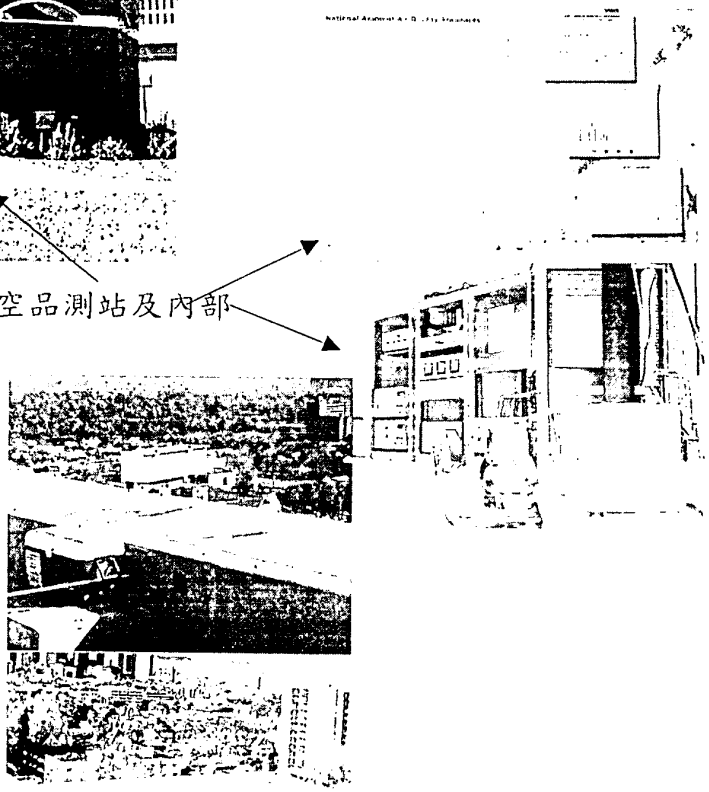


COAPCD
交通測站→

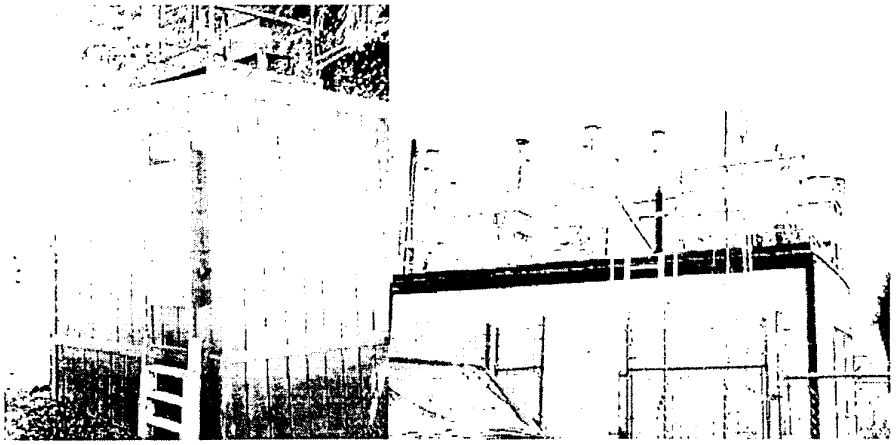
舊有測站風貌



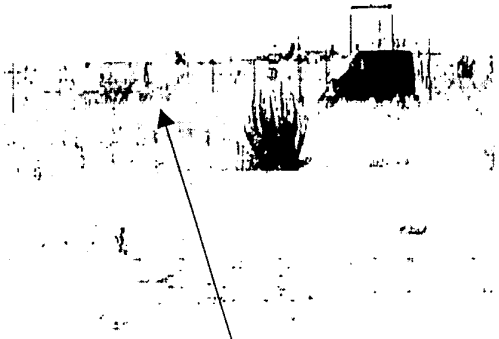
丹佛市 2000 改建後空品測站及內部



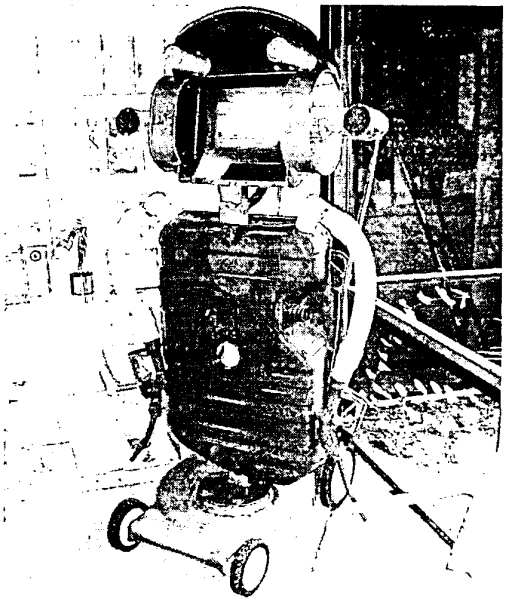
聯邦大樓
Transmissometer
（Visibility）



SMAQMD 空氣品質監測站

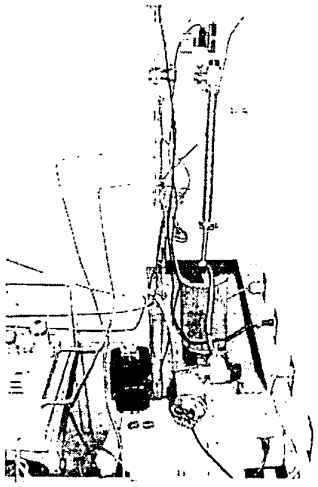


SMAQMD upper air 氣象測站及測站接收端 ⟶

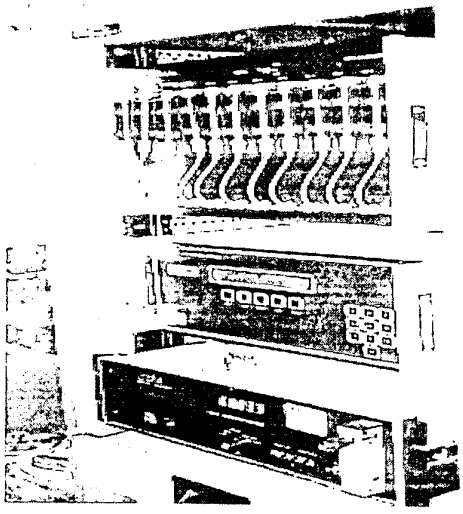


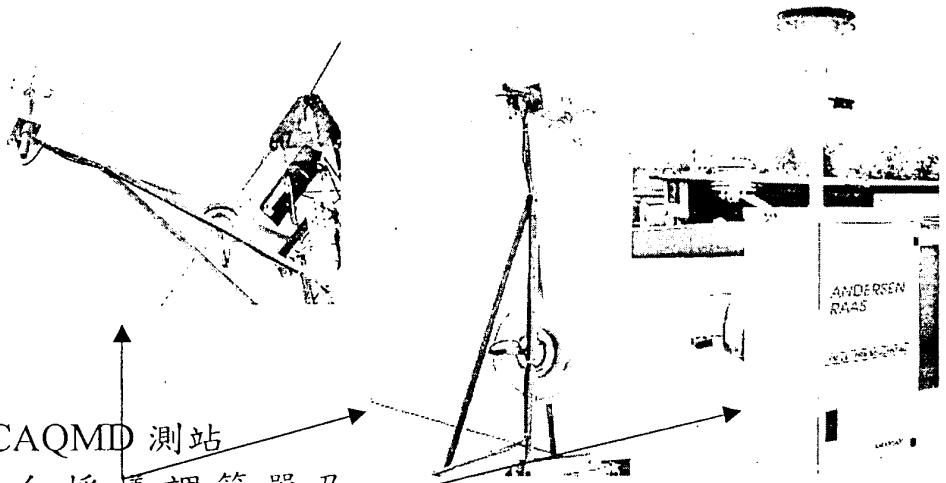
Santa Barbra 利用各類回收物品製成之空氣品質活動文宣系統，巡迴各社區學校進行清淨空氣宣導，廣獲各界好評。

SBAPCD 採樣管線



羰基化合物採樣儀

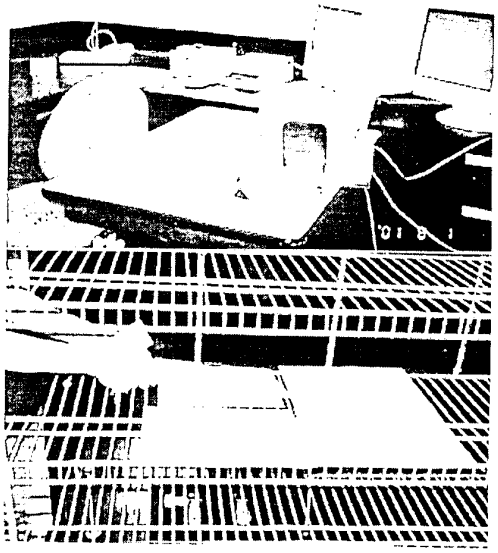


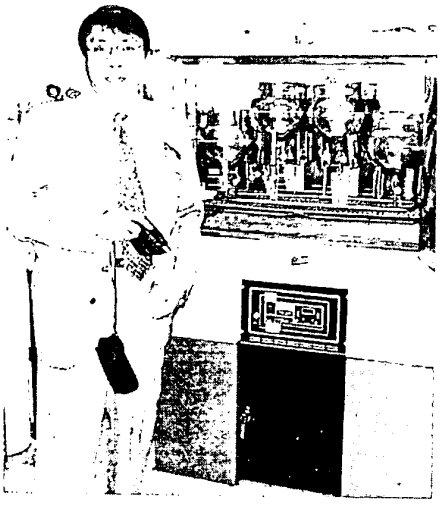


SCAQMD 測站
風向採樣調節器及
PM10 採樣器

SCAQMD voc 實驗室 GC 分析作業

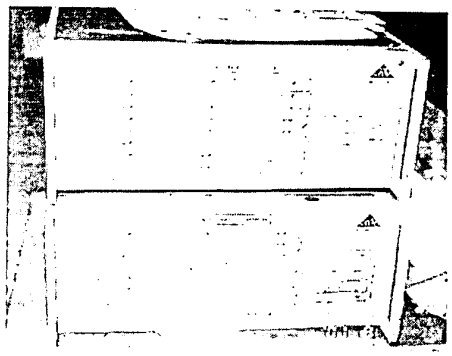
SCAQMD 六位數懸浮微粒稱重分析無塵室



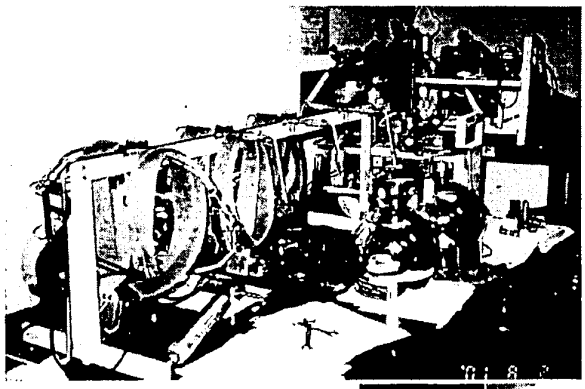


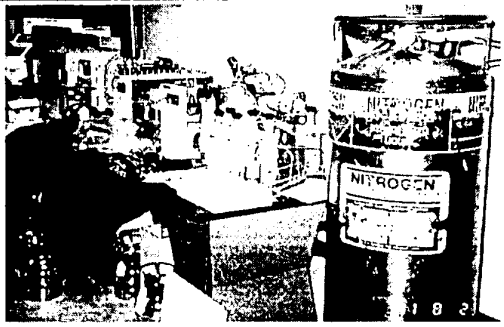
Souuth Coast AQMD 採樣鋼瓶清洗作業（Vaccum Pressure）

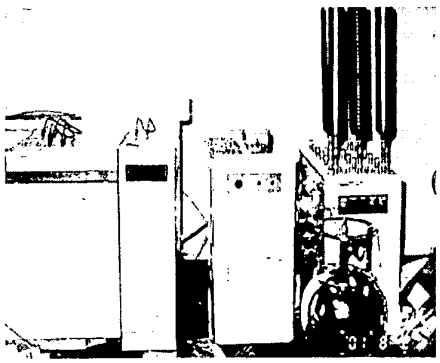
SCAQMD 羰基化合物連續採樣設備

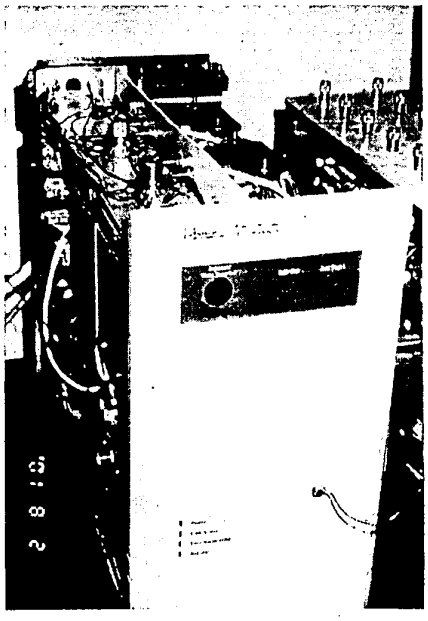


Entech VOC 分析設備

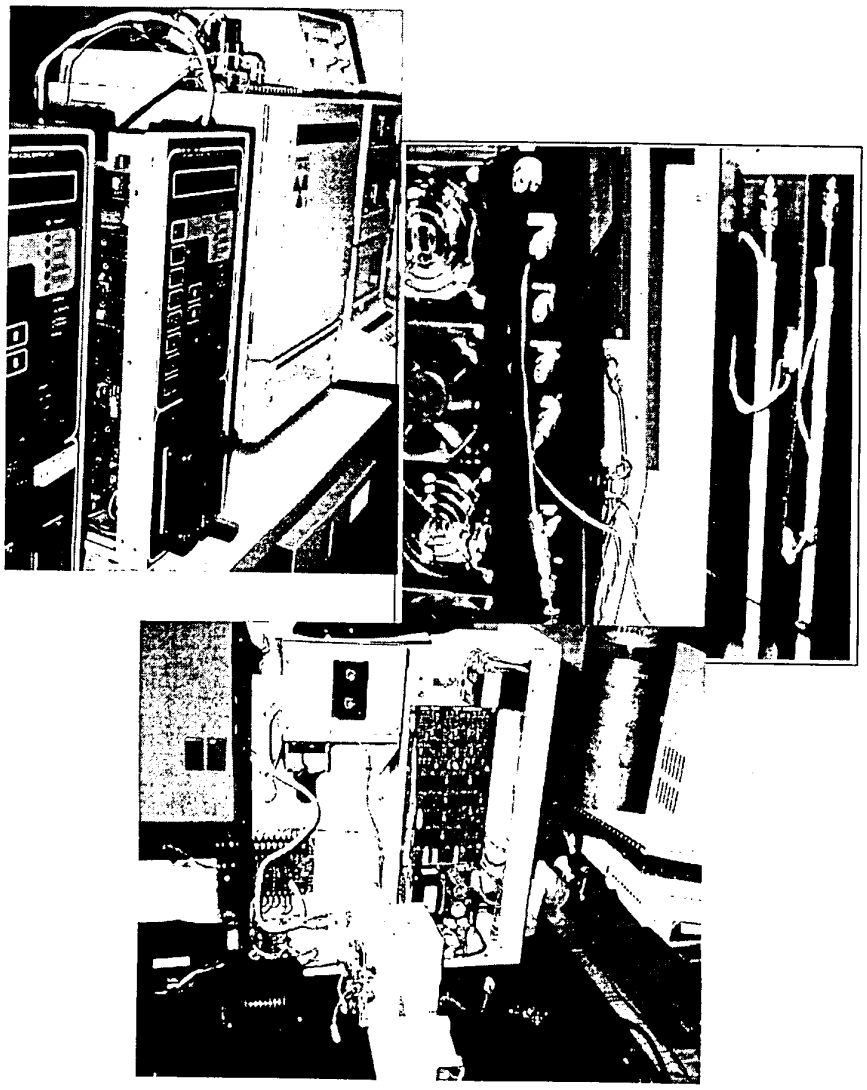








Xon Tech VOC 分析設備



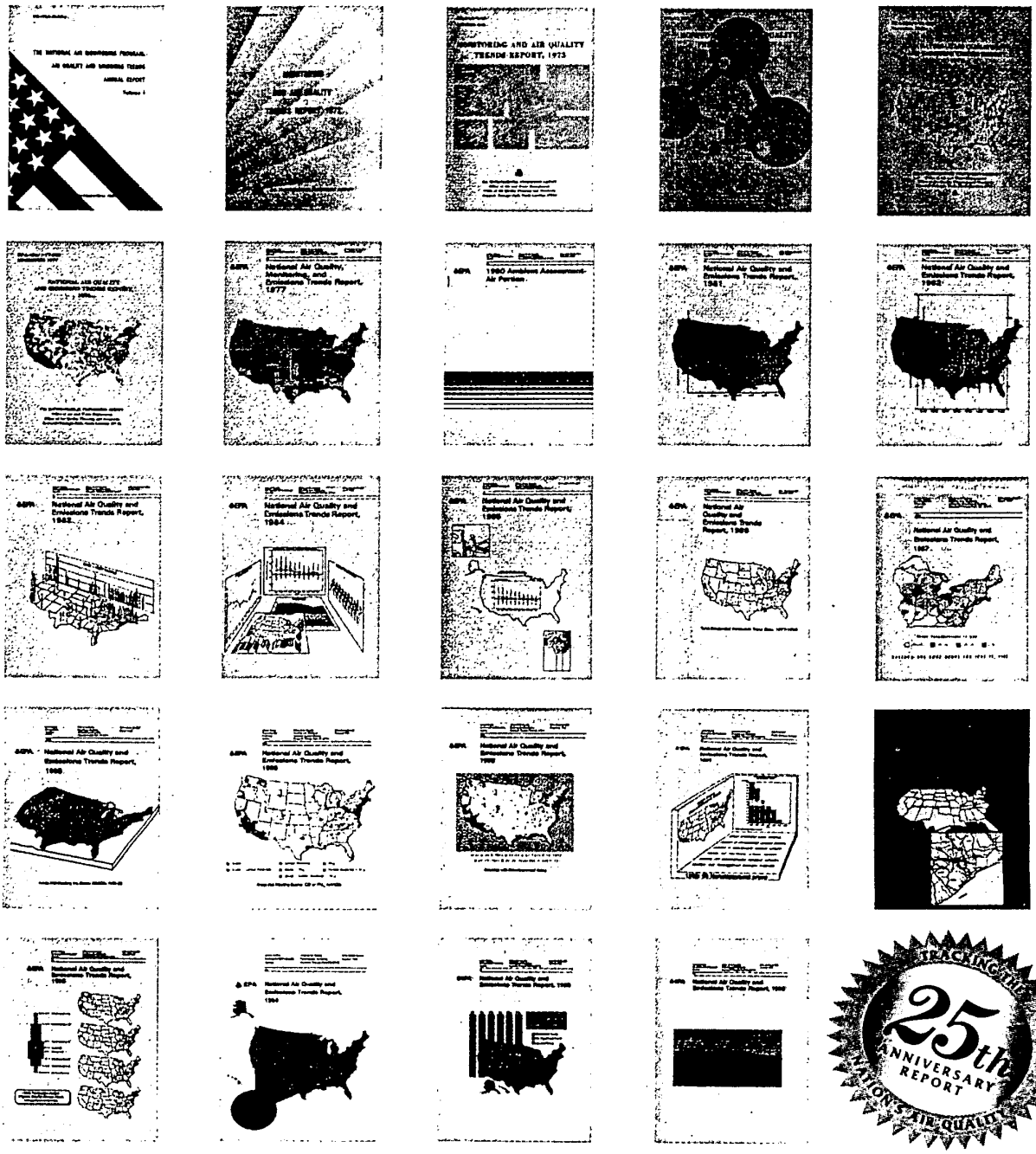
附錄二

United States Environmental Protection Agency | Office of Air Quality Planning and Standards Research Triangle Park NC 27711 | EPA 454/R-98-016 December 1998

Air

EPA

National Air Quality and Emissions Trends Report, 1997



Ozone

- **Air Quality Concentrations**

1988–97	19%	decrease (1-hr)
	16%	decrease (8-hr)
1996–97	no	change (1-hr)
	1%	decrease (8-hr)

- **Emissions**

1988–97	20%	decrease
1996–97	no	change

Nature and Sources

Ground level ozone has remained a pervasive pollution problem throughout the United States. Ozone is formed readily in the atmosphere by the reaction of VOCs and NO_x in the presence of heat and sunlight, which are most abundant in the summer. VOCs are emitted from a variety of sources including: motor vehicles, chemical plants, refineries, factories, consumer and commercial products, other industries, and natural (biogenic) sources. NO_x is emitted from motor vehicles, power plants, other sources of combustion and natural sources including lightning and biological processes in soil. Changing weather patterns contribute to yearly differences in ozone concentrations. Ozone and the precursor pollutants that cause ozone also can be transported into an area from pollution sources found hundreds of miles upwind.

Health and Environmental Effects

Ozone occurs naturally in the stratosphere and provides a protective layer high above the Earth. At ground-level however, it is the prime ingredient of smog. Short-term (1–3 hours) and prolonged (6–8 hours) exposures to ambient ozone concentrations have been linked to a number of health effects of concern. For example, increased hospital admissions and emergency room visits for respiratory causes have been associated with ambient ozone exposures.

Exposures to ozone can make people more susceptible to respiratory infection, result in lung inflammation, and aggravate pre-existing respiratory diseases such as asthma. Other health effects attributed to short-term and prolonged exposures to ozone, generally while individuals are engaged in moderate or heavy exertion, include significant decreases in lung function and increased respiratory symptoms such as chest pain and cough. Children active outdoors during the summer when ozone levels are at their highest are most at risk of experiencing such effects. Other at-risk groups include adults who are active outdoors (e.g., outdoor workers) and individuals with pre-existing respiratory disease such as asthma and chronic obstructive lung disease; within each group there are individuals who are unusually responsive to ozone. In addition, long-term exposures to ozone present the possibility of irreversible changes in the lungs which could lead to premature aging of the lungs and/or chronic respiratory illnesses.

Ozone also affects vegetation and ecosystems, leading to reductions in agricultural and commercial forest yields, reduced growth and survivability of tree seedlings, and increased plant susceptibility to disease, pests, and other environmental stresses (e.g., harsh weather). In long-lived species, these effects may become evident only after several years or even decades, thus, having the potential for long-term effects on forest ecosystems and habitat quality for wildlife and endangered species. Further, ozone injury to the foliage of trees and other plants can decrease the aesthetic value of ornamental species as well as the natural beauty of our national parks and recreation areas.

Primary and Secondary 1-hour Ozone Standards

In 1979, EPA established 1-hour primary and secondary standards for ozone. The level of the 1-hour primary NAAQS is 0.12 ppm daily maximum 1-hour O_3 concentration that is not to be exceeded more than once per year on average. The secondary standard is identical to the primary standard. To encourage an orderly transition to the revised O_3 standards, the 1-hour standards will no longer apply to an area once EPA determines that the area has air quality data meeting the 1-hour standards. In 1998, EPA revoked the 1-hour O_3 NAAQS in 2918 counties in the United States leaving 225 counties where the 1-hour standard still applies.[13,14]

Primary and Secondary 8-hour Ozone Standards

On July 18, 1997, EPA established an 8-hour O_3 primary standard to protect against longer exposure periods that are of concern for both human health and welfare (vegetation).[15] The level of the national 8-hour primary and secondary ambient air quality standards for ozone is 0.08 ppm, daily maximum 8-hour average over 3 years. The standards are met when the 3-year average of the annual fourth-highest daily maximum 8-hour ozone concentration is less than or equal to 0.08 ppm.[15] EPA will designate ozone nonattainment areas for the 8-hour ozone NAAQS by July, 2000.[16]

National 10-Year Trends

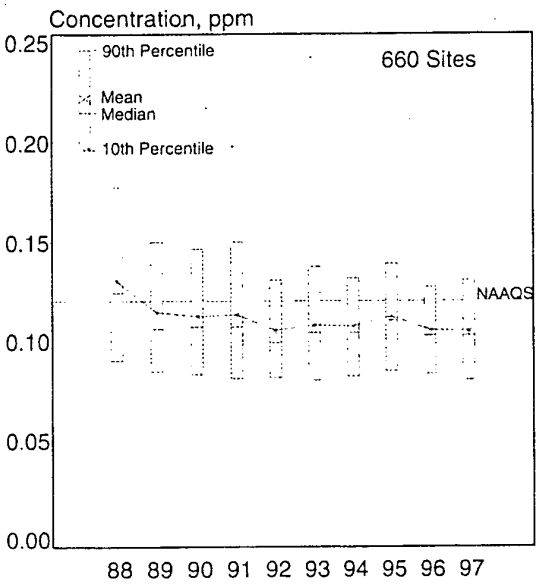
Because the 1-hour and 8-hour NAAQS have different averaging times and forms, two different statistics are used to track ambient O_3 air quality trends. For the 1-hour O_3 NAAQS, Figure 2-24 presents the national trend in the annual second-highest daily maximum 1-hour O_3 concentration at 660 monitoring sites. The inter-site variability for annual second highest daily maximum 1-hour O_3 concentrations is graphically shown by the 90th percentile, median, composite mean, and 10th percentile concentrations in Figure 2-24. This figure shows that during the past 10-years, higher concentrations have declined more rapidly (the 90th percentile concentration is down 28 percent), while the 1997 national composite average daily maximum 1-hour ozone concentration is 19 percent lower than the 1988 level. The composite mean concentration is unchanged between 1996 and 1997.

Although not shown, the composite average estimated exceedance rate (i.e., the average number of days when the daily maximum 1-hour average concentration exceeds the level of the 1-hour NAAQS) has declined 86 percent since 1988. As noted in previous reports, this statistic, which is simply a count of the number of times the level of the NAAQS has been exceeded, can vary significantly from year to year. Between 1996 and 1997, the national composite mean of the average number of exceedances of the ozone NAAQS declined 30 percent, primarily as a result of the 61 percent decrease in the exceedance rate at sites in California.

For the 8-hour ozone NAAQS, Figure 2-25 presents the trend in the annual fourth-highest 8-hour daily maximum O_3 concentration at the same 660 sites. The trend in the 8-hour O_3 statistic is similar to the 1-hour trend, although the concentration range is smaller. As measured by the composite mean concentration across all 660 sites, annual fourth-highest 8-hour average concentrations decreased 16 percent since the peak year of 1988. Although, the 8-hour national composite mean concentration decreased 1 percent between 1996 and 1997, the higher concentration sites, as shown by the 90th percentile concentrations, increased 2 percent since 1996.

Ambient O_3 trends are influenced by year-to-year changes in meteorological conditions, population growth, VOC to NO_x ratios, and changes in emissions from ongoing control measures. This 10-year trends period, with peak ozone years at both endpoints, demonstrates the importance of accounting for year to year variability in meteorological conditions when assessing ozone trends.[17,18] Previous *Trends Reports* have discussed an EPA statistical model, based on the Weibull probability distribution, that attempts to account for meteorological effects and helps to normalize the resulting trend estimates across years.[18] The model, applied on an individual metropolitan area basis, includes a trend component that adjusts the annual rate of change in ozone for concurrent impacts of meteorological conditions, including surface temperature and wind speed. Figure 2-26 displays the model results for both the 1-hour and 8-hour trends statistics averaged across 41 metropolitan areas. While the ambient monitoring data reflect the year-to-year variability in ozone conducive conditions, the meteorologically adjusted ozone trend provides a better indicator of the impact

Figure 2-24. Trend in annual second-highest daily maximum 1-hour O_3 concentrations, 1988-1997.



of emissions changes. For these 41 metropolitan areas, the adjusted trend for both averaging times shows continued improvement with an average decrease in O_3 concentrations of about 1 percent per year since 1986.

Figure 2-27 shows the 10-year change in ambient ozone concentrations among urban, suburban and rural monitoring sites. The highest ambient O_3 concentrations are typically found at suburban sites, consistent with the downwind transport of emissions from the urban center. During the past 10 years, the composite mean O_3 concentration decreased 23 percent at 117 urban sites and declined by 21 percent at 292 suburban sites. The 1997 composite mean concentration at 234 rural sites is 17 percent lower than the 1988 level.

EPA also announced that it intends to expand the rural ozone monitoring network and to explore opportunities to work with other federal agencies to develop a coordinated and long-term rural monitoring network.[15] One of the ways EPA is accomplishing this is the Clean Air Status and Trends Network (CASTNet) which was developed in response to the CAAA of 1990 requiring implementation of a national network to measure national status and trends. The CASTNet O_3 network, which consists of a total of 69 sites (50 CASTNet and 19 National Park Service (NPS) sites), was designed, in part, to provide information on the distribution of O_3 across rural areas of the United States.

CASTNet sites are considered regionally representative, and thus able to define geographic patterns of rural ozone across the United States. Meteorological variables also are recorded continuously and

Figure 2-25. Trend in annual fourth-highest daily maximum 8-hour O_3 concentrations, 1988-1997.

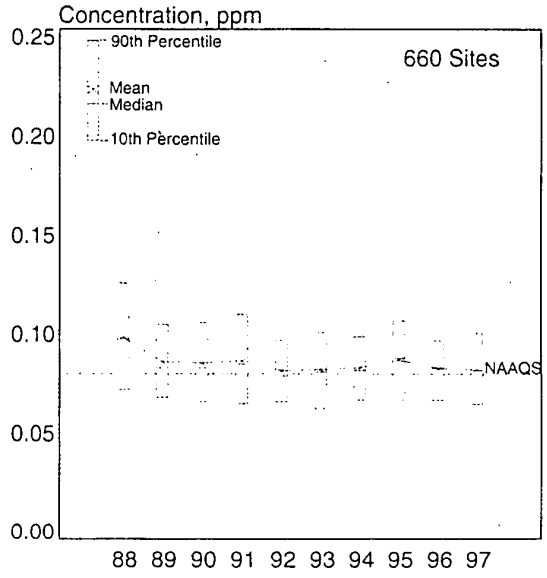


Figure 2-26. Comparison of actual and meteorologically adjusted trends in 1-hour and 8-hour 99th percentile O_3 concentrations, 1988-1997.

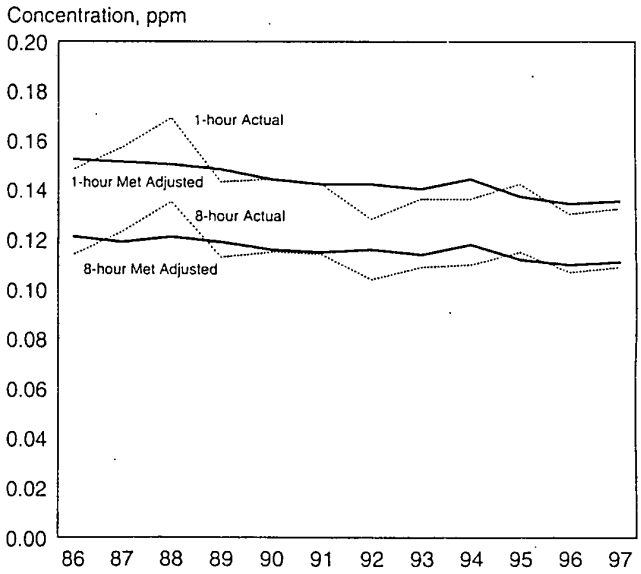


Figure 2-27. Trend in annual second-highest daily maximum 1-hour O_3 concentrations by location, 1988-1997.

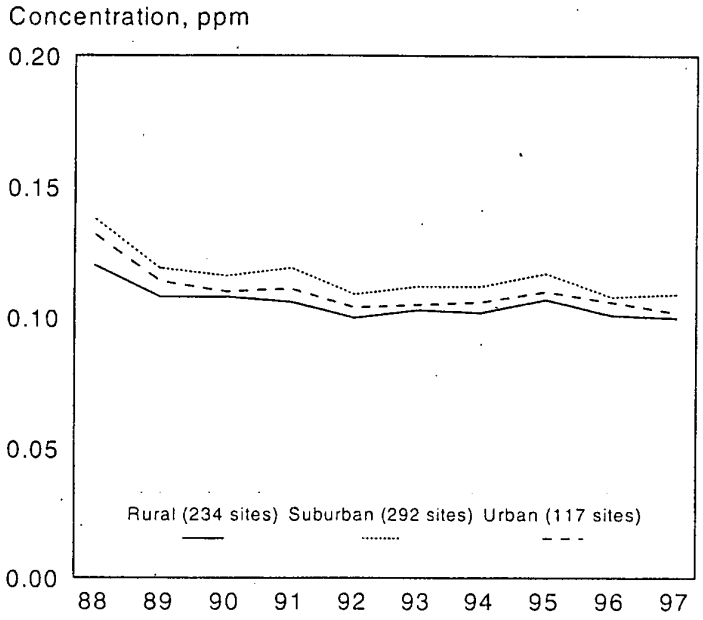
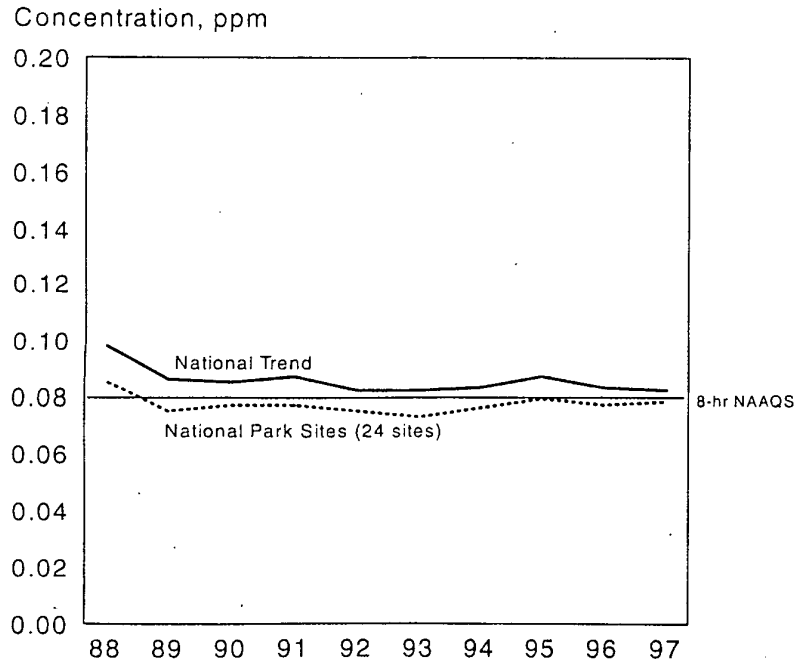


Figure 2-28. Trend in annual fourth-highest daily maximum 8-hour O_3 concentrations in National Parks, 1988-1997.



reported as hourly averages. See Chapter 7: Acid Deposition for more information concerning CASTNet.

Because several other federal agencies have a similar need to understand how ozone impacts the resources they manage, EPA is also working with these agencies to identify better ways to leverage existing monitoring and data collection and analysis efforts. For example, a special subset of rural environments, all national parks and wilderness areas exceeding 5,000 acres, were designated as Class I areas in the 1977 amendments to the CAA. These areas are accorded a higher degree of protection under the CAA provisions for the prevention of significant deterioration. The CAA further directs the federal land managers to protect air-quality related values (AQRVs). Sufficient monitoring data are available to assess 10-year trends in ambient O_3 concentrations at 24 NPS sites. Figure 2-28 compares the 10-year trend in the composite mean of the annual fourth highest 8-hour O_3 concentration at these 24 Class I sites with the national O_3 trend. Nonparametric regression was used to assess the statistical significance of the 10-year trend in 8-hour ozone concentrations for the composite mean across all 24 NPS sites, and at each of the NPS sites. Although the 1997 composite mean O_3 concentrations is 8 percent lower than the 1988 value, there is no statistically significant trend in the composite mean O_3 concentration at these NPS sites. On an individual site basis, only two sites, both in the Great Smoky Mountains National Park, had statistically significant upward trends. Although not statistically

significant, of the remaining 22 sites, 11 sites had downward slopes, 8 upward and 3 showed no change. (See Chapter 3: Criteria Pollutants - Metropolitan Area Trends, for a description of the non-parametric regression procedure.)

Enhanced Ozone Monitoring (PAMS)

Section 182(c)(1) of the CAA called for improved monitoring of ozone and its precursors, VOC and NO_x, to obtain more comprehensive and representative data on ozone air pollution. Responding to this requirement, EPA promulgated regulations in February 1993 to initiate the Photochemical Assessment Monitoring Stations (PAMS) program.[19] The PAMS program requires the establishment of an enhanced monitoring network in all ozone nonattainment areas classified as serious, severe, or extreme. Currently, 24 of the remaining 38 nonattainment areas for the 1-hour O_3 NAAQS are subject to PAMS; these areas are identified in Figure 2-29.

Each PAMS network consists of as many as five monitoring stations, depending on the area's population. These stations are carefully located according to meteorology, topography, and relative proximity to emissions sources of VOC and NO_x. Each PAMS network generally consists of four different types of monitoring sites (Types 1, 2, 3, and 4) designed to fulfill unique data collection objectives. Type 1 sites are located upwind of the metropolitan area to measure ozone and precursors being transported into the area. Type 2 sites, referred to as maximum precursor emissions impact sites, are designed to collect data on the type and magnitude of ozone precursor emissions emanating from the metropolitan area and are typically located immediately downwind of the central business district. Type 3 stations are intended to measure maximum ozone concentrations and are sited farther downwind of the urban area than the Type 2 sites. Type 4 PAMS sites are located downwind of the nonattainment area to assess ozone and precursor levels exiting the area and potentially contributing to the ozone problem in other areas. In addition to the surface monitoring sites, each PAMS area also is required to monitor upper air meteorology at one representative site.

Regulations allow a 5-year transition or phase-in schedule for the program at a rate of at least one station per area per year. The first official year of implementation for PAMS was 1994. As of August 1998, there were 78 operating PAMS sites. The data collected at the PAMS sites include measurements of ozone, NO_x, total non-methane organic compounds (TNMOC), a target list of VOC species including several carbonyls, plus surface and upper air meteorology. Most PAMS sites measure 56 target hydrocarbons on an hourly or 3-hour basis during the PAMS monitoring season. Included in the monitored VOC species are 10 compounds classified as hazardous air pollutants (HAPs). The PAMS program is the only federally mandated initiative that requires routine monitoring of HAPs; for more information on HAPs see Chapter 5: Air Toxics. All PAMS stations measure ozone, NO_x, and surface meteorological parameters on an hourly basis. In general, the PAMS monitoring season spans the three summer months when weather conditions are most conducive for ozone formation. EPA allows states flexibility in network design and sampling plans in recognition of the fact that each PAMS area has its own unique characteristics and demands. For more information on the PAMS networks, data col-

Figure 2-29. Metropolitan areas subject to the PAMS program.

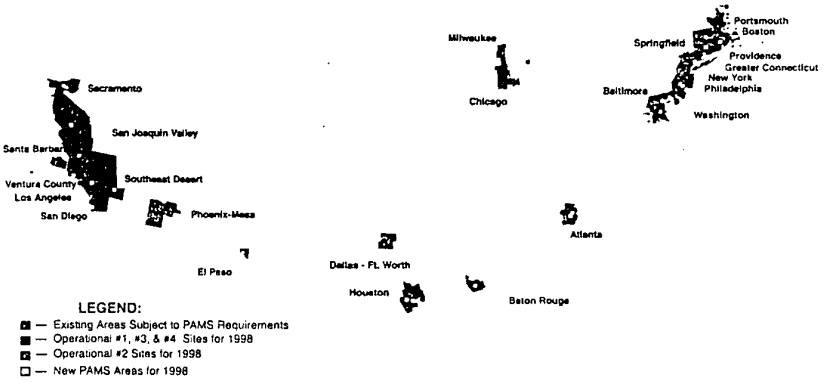
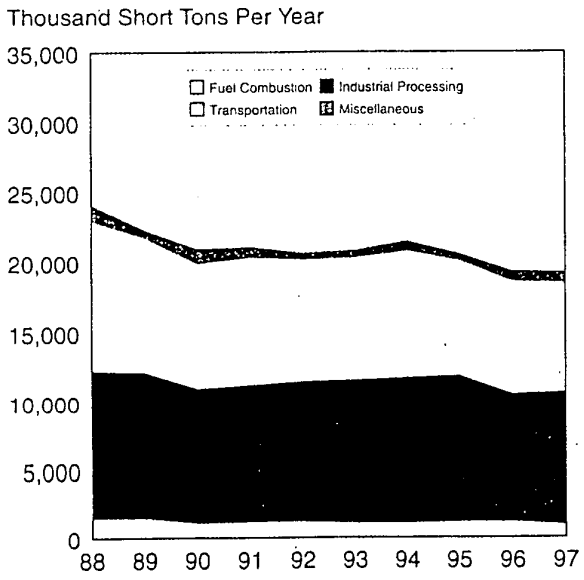


Table 2-3. Summary of changes in O_3, NO_x and TNMOC at PAMS sites, 1996-1997.

Pollutant	Number of Sites			Median Percent Change
	Total	Up	Down	
O_3 2nd daily max 1-hr	69	-	-	1%
NO_x—Summer 6–9am mean	52	8	9	0%
TNMOC—Summer 6–9am mean	42	6	9	-2%

Note: The numbers shown in the "Up" and "Down" categories refer to the number of sites in which the change in summer 6–9am, mean concentrations between the years referenced is a statistically significant increase or decrease (as determined by a t-test with a significance level of .05). The total number of sites ("Total") may not equal the sum of the corresponding "Up" and "Down" categories.

Figure 2-30. National total VOC emissions trend, 1988–1997.



lected, and analyses of the data, see the EPA PAMS web site at **http://www.epa.gov/oar/oaqps/pams.**

PAMS data provide the opportunity for state and local air pollution control agencies to effectively evaluate ozone nonattainment conditions, confirm attainment/nonattainment decisions, identify cost-effective control strategies, evaluate population risk exposure, and develop ozone and ozone precursor trends. The measurements have proven extremely valuable in verifying ozone precursor emissions inventories and in corroborating estimates of area-wide emissions reductions. The data can be used to evaluate, adjust, and provide input to the photochemical grid models used to develop ozone control strategies, as well as demonstrate their success.

Table 2-3 shows second daily maximum 1-hour O_3 concentrations and summer 6–9am mean NO_x and TNMOC concentrations for all reporting PAMS sites for the most recent 2-year period. Morning periods for NO_x and TNMOC are shown since those time frames are generally thought to be an appropriate indicator of anthropogenic emissions. In general, total VOC declined notably between 1994 and 1997, though most of the reductions occurred in the first 2 years, especially between 1994 and 1995. Previous editions of the *Trends Report* highlighted these reductions (as well as corresponding declines in selected VOC species) and attributed them, at least in part, to mobile source controls, specifically the implementation of reformulated gasoline (RFG). Between 1996 and 1997, total VOC only declined slightly (2 percent). NO_x concentrations at PAMS sites were even flatter. The median site concentration is unchanged between 1996 and 1997; only a third of the reporting sites had a significant change in either direction with a fairly even split between sites that showed increases and those that showed declines.

Emissions Trends

Figure 2-30 shows that national total VOC emissions (which contribute to ozone formation) from anthropogenic sources decreased 20 percent between 1988 and 1997. National total NO_x emissions (the other major precursor

to ozone formation) increased 1 percent between 1988 and 1997. Recent control measures to reduce emissions include regulations to lower fuel volatility and to reduce NO_x and VOC emissions from tailpipes.[20] The effectiveness of these control measures is reflected in the 28 percent decrease in VOC emissions from transportation sources. VOC emissions from highway vehicles have declined 37 percent since 1988, while highway vehicle NO_x emissions have declined 8 percent since their peak level in 1994. Nationally, the two major sources of VOC emissions are industrial processes (51 percent) and transportation sources (40 percent) as shown in Figure 2-31. Solvent use comprises 66 percent of the industrial process emissions category and 34 percent of total VOC emissions. The emissions totals by source category and year can be found in Table A-5.

As required by the CAA, a cleaner burning fuel (RFG) has been sold since January 1, 1995 in those areas of the country with the worst ozone or smog problems. RFG is formulated to reduce automotive emissions of ozone-forming pollutants and toxic chemicals and is estimated to reduce both VOC and toxic emissions by more than 15 percent.[21] RFG sold during the summer ozone season has lower volatility than most conventional gasoline.[22] The RFG program is mandated year-round in 10 areas of the country (Los Angeles, San Diego, Hartford, New York, Philadelphia, Chicago, Baltimore, Houston, Milwaukee, and Sacramento). Besides these required areas, several other parts of the country exceeding the ozone standard have voluntarily entered the RFG program.[22]

Figure 2-31. VOC emissions by source category, 1997.

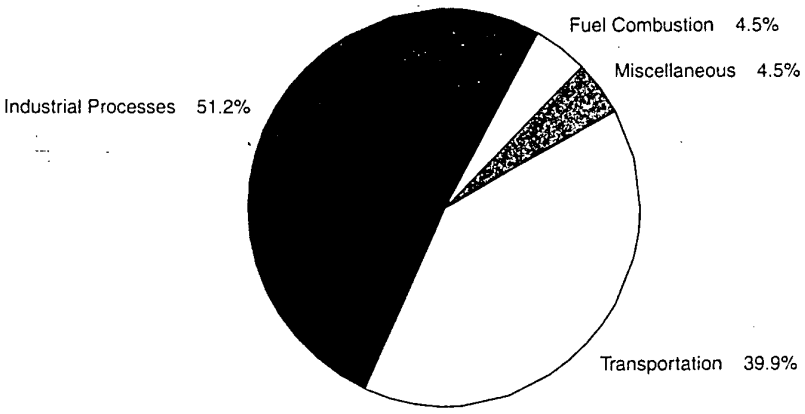


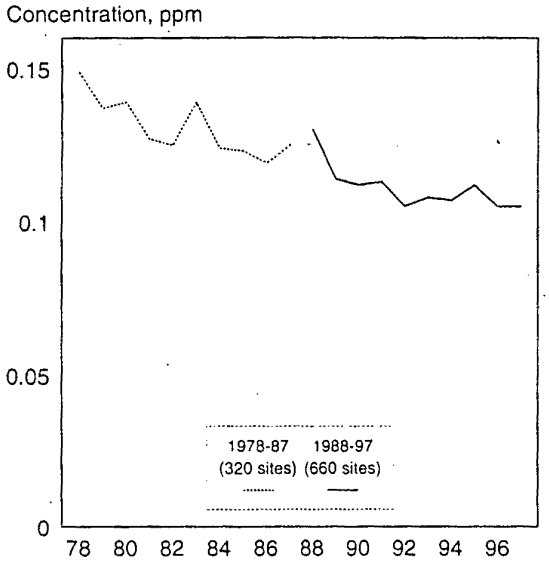
Table 2-4. Biogenic sources of VOC emissions by region.

Region	VOC	Source
Southwestern United States	Isoprene	Oak (mostly), citrus, eucalyptus
	Monoterpenes	Pine, citrus, eucalyptus
Northeastern United States	Isoprene	Oak (mostly), spruce
	Monoterpenes	Maple, hickory, pine, spruce, fir, cottonwood

In addition to anthropogenic sources of VOCs and NO_x, there are natural or biogenic sources of these compounds as well. Table 2-3 shows the different predominant plant species responsible for VOC emissions in different parts of the country for two major biogenic species of concern, isoprene and monoterpenes. Though we are not able to control the level of these natural emissions, when developing ozone control strategies, their presence is an important factor to consider. Biogenic NO_x emissions are associated with lightning and biological processes in soil.

On a regional basis, biogenic VOC emissions can be greater than anthropogenic VOC emissions. Biogenic NO_x emissions, on the other hand, are less than 10 percent of total NO_x emissions. EPA's estimates of total U.S. VOC emissions from biogenic sources are based on the Biogenic Emissions Inventory System—Version 2 (BEIS2).[23,24] A recent national estimate for annual total biogenic VOCs from vegetation

Figure 2-32. Trend in annual second-highest daily maximum 1-hour O_3 concentrations, 1978-1997.



is 29 million short tons, while biogenic nitric oxide emissions are estimated at 1.5 million short tons.[25] Biogenic emissions are influenced by fluctuations in temperature, with the highest emissions occurring in the summer when temperatures are highest. For example, an increase of 10 degrees Celsius (°C) can result in over a two-fold increase in both VOC and NO_x. Research in the area of biogenic emissions continues, and changes in emission estimates are to be expected and should be viewed with an uncertainty of at least a factor of two.

National 20-Year Trends

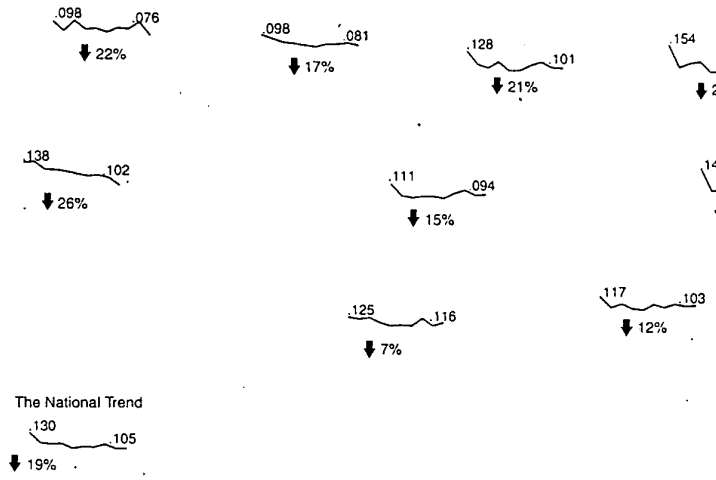
Long-term, quantitative ambient ozone trends are difficult to estimate due to changes in network design, siting criteria, spatial coverage and monitoring instrument calibration procedures during the past two decades. For example, in Figure 2-32 the first year of the early trends period, 1978, corresponds to the use of the old calibration procedure where concentration levels are less certain. Because only a few sites have monitored continuously for two decades, the 20-year trends line in Figure 2-32 is composed of two segments; 238 sites with complete data during the first 10 years, 1978–1987, and 660 sites meeting the data completeness criteria in the most recent 10 years, 1988–1997. Nationally, peak 1-hour O_3 concentrations, as measured by the composite mean of the annual second highest daily maximum 1-hour O_3 concentrations, declined 30 percent since 1978. Figure 2-32 clearly shows the peak ozone years of 1980, 1983, 1988 and 1995.

Regional Trends

The map in Figure 2-32 shows regional trends in 1-hour O_3 concentrations during the past 10 years, 1988–1997. The trends statistic is the composite mean of the annual second-highest daily maximum 1-hour O_3 concentration averaged across all sites in each EPA region with at least eight years of ambient O_3 measurements. Figure 2-34 shows the 10-year trends in the composite mean of the annual fourth-highest daily maximum 8-hour concentration. The trends for both the 1-hour and 8-hour trends statistics are similar, however, the magnitude of the reductions is larger for the annual second-highest 1-hour daily maximum O_3 concentrations as compared to the annual fourth-highest daily maximum 8-hour concentrations. Every EPA region recorded 10-year declines in composite mean 1-hour and 8-hour peak O_3 concentrations.

The greatest improvement in air quality occurred in Northeast, Mid-Atlantic, North Central and Pacific regions. The changes in O_3 concentrations since last year reflect the regional differences in meteorological conditions across the country. Summer 1997 statewide temperature and precipitation ranks are shown in Figure 2-35 based on preliminary meteorological data available from National Oceanic aand Atmospheric Administration (NOAA).[26] No state was within the top ten warm category and only eight states ranked within the warm third of the temperature distribution. Preliminary data indicate that Summer 1997 was the sixth coolest on record for Georgia and the ninth coolest since 1895 for both Mississippi and South Carolina. Nine states ranked within the top ten dry portion of the historical distribution for Summer 1997 including the fourth driest summer since 1895 for Virginia and Maryland and the fifth driest summer season for

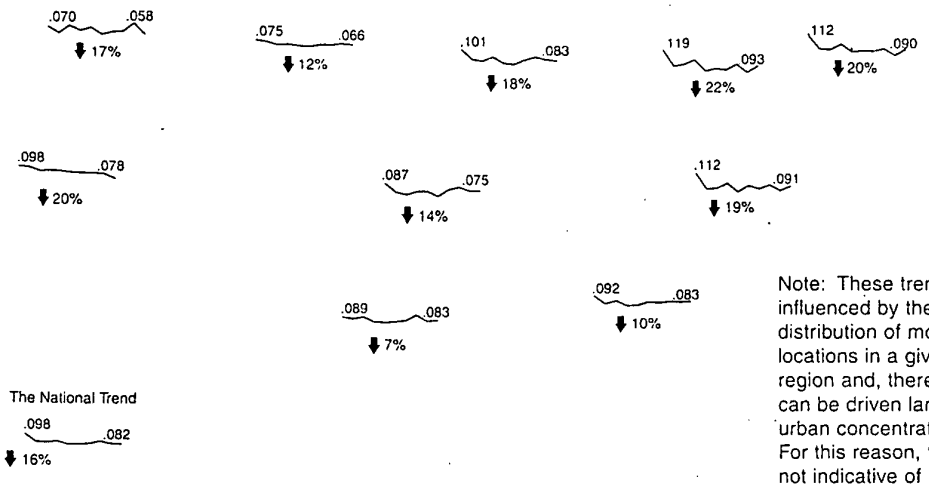
Figure 2-33. Trend in O_3 second maximum 1- hour concentrations by EPA Region, 1988-1997.



Alaska is in EPA Region 10; Hawaii, EPA Region 9; and Puerto Rico, EPA Region 2.
Concentrations are ppm.

Note: These trends are influenced by the distribution of monitoring locations in a given region and, therefore, can be driven largely by urban concentrations. For this reason, they are not indicative of background regional concentrations.

Figure 2-34. Trend in O_3 fourth maximum 8-hour concentration by EPA Region, 1988-1997.



Alaska is in EPA Region 10; Hawaii, EPA Region 9; and Puerto Rico, EPA Region 2.
Concentrations are ppm.

Note: These trends are influenced by the distribution of monitoring locations in a given region and, therefore, can be driven largely by urban concentrations. For this reason, they are not indicative of background regional concentrations.

New Jersey. Fifteen other states ranked within the dry-third of the distribution. It was the second wettest summer since records began for California and the ninth wettest summer on record for Montana.[26]

Addressing The Ozone Transport Issue

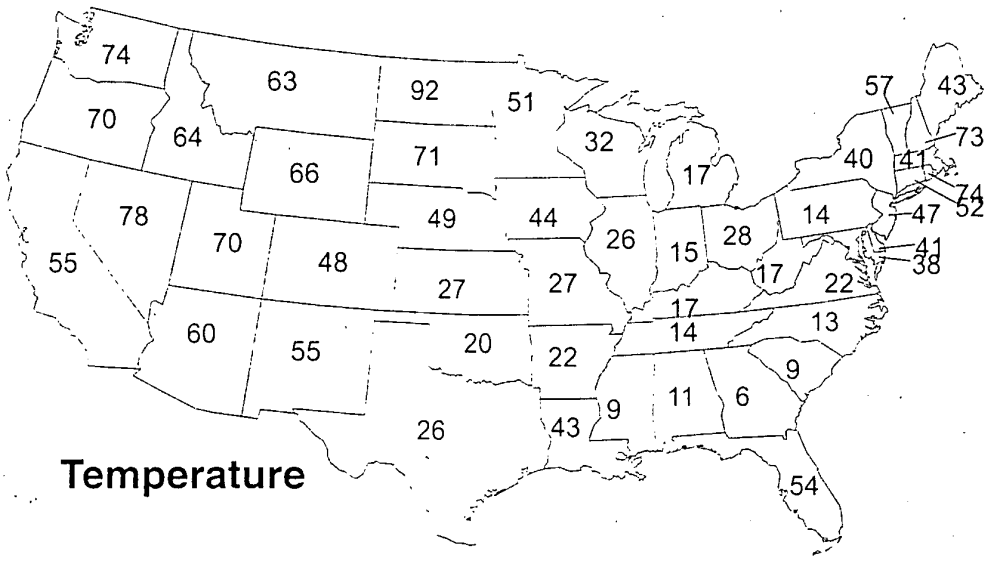
In recognition of long-standing regional ozone problems in the Northeastern United States, the 1990 CAAA established the Ozone Transport Commission (OTC) and the Northeast Ozone Transport Region which includes 12 states. Since that time, several other regional groups have formed to study various aspects of the problem and to try to identify acceptable solutions. EPA continues to be a contributor, partner, or interested party in each of these efforts. The most significant recent developments occurred as a result of a 2-year effort known as the Ozone Transport Assessment Group (OTAG), EPA worked in partnership with state and local government agencies in the 37 easternmost states, industry, and academia to address ozone transport. The extensive modeling analysis conducted by OTAG showed the significant contribution of transported precursor emissions to nonattainment of the ozone NAAQS. As a result of OTAG's findings on the role of nitrogen oxides as a precursor to ozone formation, EPA published a rule in October 1998 (commonly known as the NO_x SIP Call) that called for reductions in summertime NO_x emissions to reduce the regional transport of ozone.[10] The NO_x SIP Call sets (1) a model cap-and-trade program, (2) statewide NO_x emission budgets, and (3) proposed revisions to the acid rain program October 1998. More detailed information on the OTAG process and details on information generated by the OTAG workgroups are available on the OTAG web page at **http://www.epa.gov/ttn/otag**.

Other regional groups that have addressed regional ozone problems include the Lake Michigan Ozone Study (LMOS), the Southern Oxidant Study (SOS), the Southern Appalachian Mountain Initiative (SAMI), and the North American Research Strategy for Tropospheric Ozone (NARSTO). For more information on these groups, see **www.epa.govairprogm/oar/oaqps/airtrans/regional.html**.

1997 Air Quality Status

The map in Figure 2-36 presents the highest second daily maximum 1-hour concentration by county in 1997. The accompanying bar chart to the left of the map reveals that in 1997 approximately 48 million people lived in 77 counties where the annual second daily maximum 1-hour O_3 concentration was above the level of the 1-hour ozone NAAQS. These numbers represent an increase from the totals reported last year (39 million people living in 52 counties) with ozone concentrations above the level of the ozone NAAQS in 1996. As noted previously, meteorological conditions in some regions of the country were more conducive to peak O_3 formation in 1997, than in 1996. The map in Figure 2-36 shows large spatial differences, with higher O_3 concentrations typically found in Southern California, the Gulf Coast, and the Northeast and Northcentral states. Historically, the highest 1-hour concentrations are found in Los Angeles, however, 1997 is the first year that the highest 1-hour concentrations in Houston exceeded the levels recorded in Los Angeles.

Figure 2-35. Summer 1997 statewide temperature ranks (Source: NOAA, 1997).



Note: 1 = coldest/driest ; 103 = warmest/wettest

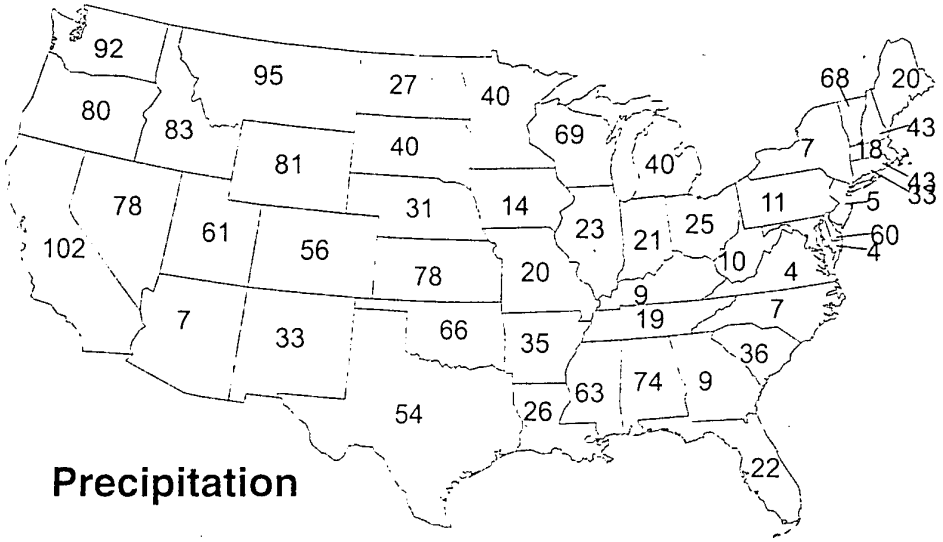
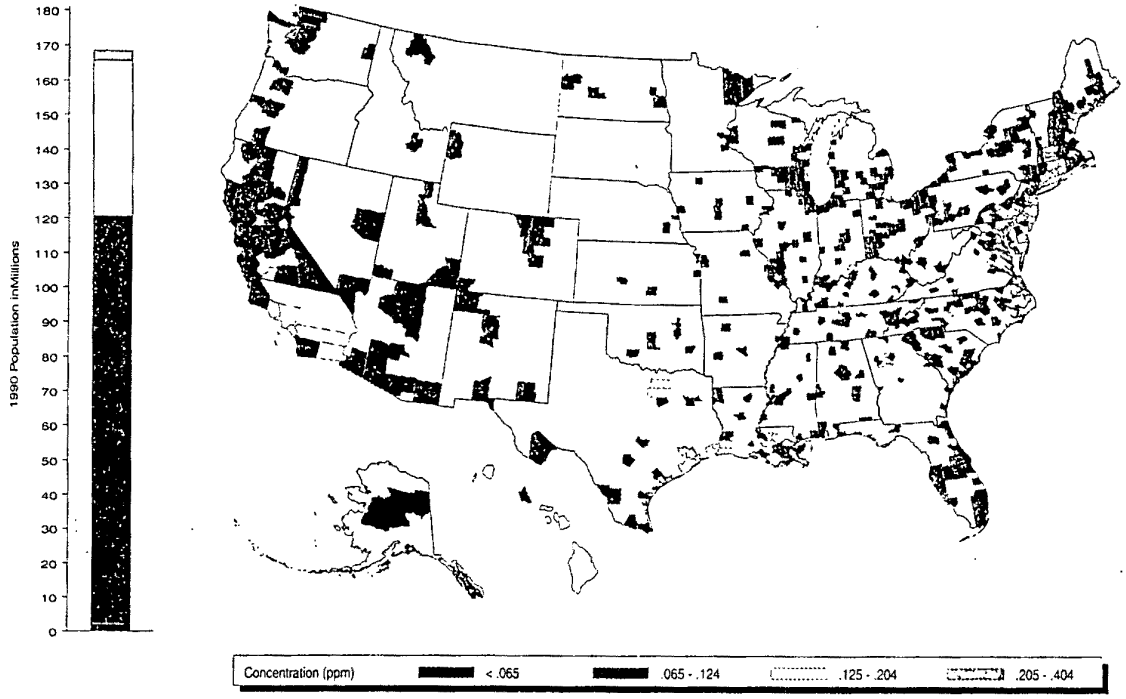


Figure 2-36. Highest second daily maximum 1-hour O_3 concentration by county, 1997.



United States
Environmental Protection
Agency

National Exposure
Research Laboratory
Research Triangle Park, NC 27711

EPA/600-R-98/161
September 1998

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Research and Development

EPA

TECHNICAL ASSISTANCE DOCUMENT FOR SAMPLING AND ANALYSIS OF OZONE PRECURSORS

Technical Assistance Document for Sampling and Analysis of Ozone Precursors

September 30, 1998

U.S. Environmental Protection Agency
National Exposure Research Laboratory
Human Exposure and Atmospheric Sciences Division
Research Triangle Park, North Carolina, NC 27711

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Section 1.0
Introduction

Section 182 (c)(1) of the 1990 Clean Air Act Amendments (CAAA) required the Administrator to promulgate rules for enhanced monitoring to obtain more comprehensive and representative data on ozone air pollution. The Environmental Protection Agency (EPA) has revised the ambient air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations (40 CFR Part 58)[1] to include provisions for enhanced monitoring of ozone (O_3), oxides of nitrogen (NO_x), volatile organic compounds (VOCs), selected carbonyl compounds, and monitoring of meteorological parameters. The revisions require States to establish Photochemical Assessment Monitoring Stations (PAMS) as part of their existing State Implementation Plan (SIP) monitoring networks in ozone nonattainment areas classified as serious, severe, or extreme.

The principal reasons for requiring the collection of additional ambient air pollutant and meteorological data are the lack of successful attainment of the National Ambient Air Quality Standard (NAAQS) for O_3, and the need to obtain a more comprehensive air quality data base for O_3 and its precursors. Analysis of the data will help the EPA understand the underlying causes of ozone pollution, devise effective controls, and measure improvement. Data acquired from enhanced ambient air monitoring networks will have a variety of uses, which may include:

- Developing, evaluating, and refining new O_3 control strategies;
- Determining NAAQS attainment or non-attainment for O_3;
- Tracking VOCs and NO_x emissions inventory reductions;
- Providing photochemical prediction model input;
- Evaluating photochemical prediction model performance;

- Analyzing ambient air quality trends; and
- Characterizing population exposure to VOCs and O_3.

1.1 Purpose

The Technical Assistance Document (TAD) for Sampling and Analysis of Ozone Precursors was initially published in October 1991. The document was intended to provide guidance to those responsible for implementing PAMS. Since the initial publication, there has been a draft revision in October 1994 to Sections 2.0, 4.0, and 5.0 and a revision to Section 6.0 in June 1995, all of which were included in Appendix N of the PAMS Implementation Manual. Since these revisions, there have been significant advances in the methodology used to measure the components and parameters of interest at PAMS. These advances have necessitated this revision of the TAD.

The purpose of this document is to provide guidance in support to the enhanced ozone monitoring revisions in 40 CFR Part 58. The document provides technical information and guidance to Regional, State, and local Environmental Protection Agencies responsible for measuring O_3 precursor compounds in ambient air. Sampling and analytical methodology for speciated VOCs, total nonmethane organic compounds (NMOC) and selected carbonyl compounds (i.e., formaldehyde, acetaldehyde, and acetone) are specifically addressed. The document also addresses methodology for measuring NO_X, as required by PAMS, and discusses issues associated with the collection of total reactive oxides of nitrogen (NO_y) and meteorological measurements.

The technical guidance provided for measuring O_3 precursors is based on emerging and developing technology. Guidance for automated applications, in particular, is based on experience obtained from the application of this technology during the beginning years of PAMS implementation. Because these methods are based on emerging technology and reflect state-of-

the-art, they will be subject to continuing evaluation and improvements or clarifications in the future.

Users should consider this guidance a basic reference to assist in developing and implementing their PAMS monitoring program. The technical assistance document is prepared in a document control format to accommodate revisions that are anticipated as the emerging technologies develop.

1.2 Organization

The guidance provided in Section 2 of this document addresses the measurement of volatile organic O_3 precursors and includes method descriptions for manual and automated sample collection and analysis. Detailed discussions are presented on selected topics such as which volatile organic O_3 precursors to measure, critical chromatography issues, moisture control, data validation, Quality Control and Quality Assurance, AIRS data entry, and how canister sampling should be approached.

Section 3 discusses the measurement of total NMOC using Method TO-12 from the Compendium of Methods for Sampling and Analysis of Toxic Organic Compounds in Ambient Air.[2] Measurement of total NMOC by Method TO-12 has limited application to the implementation of the 40 CFR Part 58 requirements, but Method TO-12 is included because of its applications to canister cleanliness verification, application to alternative monitoring strategies, and use in O_3 prediction models. Alternative monitoring strategies involve the use of canister and/or automated Method TO-12 complemented with an extensive canister sampling and manual VOCs speciation analysis program.

Section 4 addresses the measurement of NO_X and issues associated with NO_y. Section 5 addresses the measurement of selected carbonyl compounds using Compendium Method TO-11A from the Compendium of Methods for Sampling and Analysis of Toxic Organic Compounds in Ambient Air and includes new information regarding the methodology and issues

associated with the measurement of carbonyl compounds. Section 6 provides guidance for PAMS meteorological monitoring, which is essential to the PAMS program. Note that all sections of this Technical Assistance Document are intended to be independent. Figures, tables, and text are therefore repeated as necessary.

1.3 Summary of the Monitoring Regulations

The 1990 CAAA required EPA to promulgate regulations to enhance existing ambient air monitoring networks. Existing SIP stations are identified as State and Local Agency Monitoring Stations (SLAMS) and National Air Monitoring Stations (NAMS). The enhanced O_3 monitoring stations are a subset to SLAMS and identified as Photochemical Assessment Monitoring Stations (PAMS).

The monitoring revisions by EPA required changes to 15 separate Sections, Subparts, or Appendices of 40 CFR Part 58, and varied in complexity and impact on State and local agencies. The areas of the revised 40 CFR Part 58 regulations most relevant to enhanced ambient air monitoring are operating schedules, PAMS methodology, and quality assurance. Section 58.13 of 40 CFR Part 58 contains the operating schedule for SLAMS, NAMS, and PAMS. This section requires sampling for VOCs and carbonyl compounds according to the monitoring period and minimum monitoring network requirements specified in Sections 4.3 and 4.4 of Appendix D of the revised regulations.[1]

Unlike the SLAMS and NAMS design criteria which are pollutant-specific, PAMS design criteria are site specific. Design criteria for the PAMS network are based on selection of an array of site locations relative to O_3 precursor sources and predominant wind direction associated with peak O_3 events. Four PAMS site types are described in the regulations. The number and type of monitoring sites and sampling requirements is dependent on the population of the Metropolitan Statistical Area (MSA) or Consolidated Metropolitan Statistical Area (CMSA). The specified minimum sampling requirements for VOCs and carbonyl compounds for each site type are presented in Table 1-1. Monitoring for O_3 and NO_X (including NO and NO_2)

Table 1-1 . PAMS Minimum Monitoring Network Requirements

Population of MSA/CMSA[1]	Required Site Type	Minimum VOCs Sampling Frequency[2]	Minimum Carbonyl Compounds Sampling Frequency[2]
Less than 500,000	(1)	A or C	-
	(2)	A or C	D or F
500,000 to 1,000,000	(1)	A or C	-
	(2)	B	E
	(3)	A or C	-
1,000,000 to 2,000,000	(1)	A or C	-
	(2)	B	E
	(2)	B	E
	(3)	A or C	-
More than 2,000,000	(1)	A or C	-
	(2)	B	E
	(2)	B	E
	(3)	A or C	-
	(4)	A or C	-

[1]Whichever area is larger.

[2]Frequency requirements are as follows:

A = Eight 3-hour samples every third day and one additional 24-hour sample every sixth day during the monitoring period.

B = Eight 3-hour samples every day during the monitoring period and one additional 24-hour sample every sixth day year-round.

C = Eight 3-hour samples on the 5 peak O_3 days plus each previous day, eight 3-hour samples every sixth day and one additional 24-hour sample every sixth day during the monitoring period.

D = Eight 3-hour samples every third day during the monitoring period.

E = Eight 3-hour samples on the 5 peak O_3 days plus each previous day and eight 3-hour samples every sixth day during the monitoring period.

F = Eight 3-hour samples on the 5 peak O_3 days plus each previous day, eight 3-hour samples every sixth day and one additional 24-hour sample every sixth day during the monitoring period.

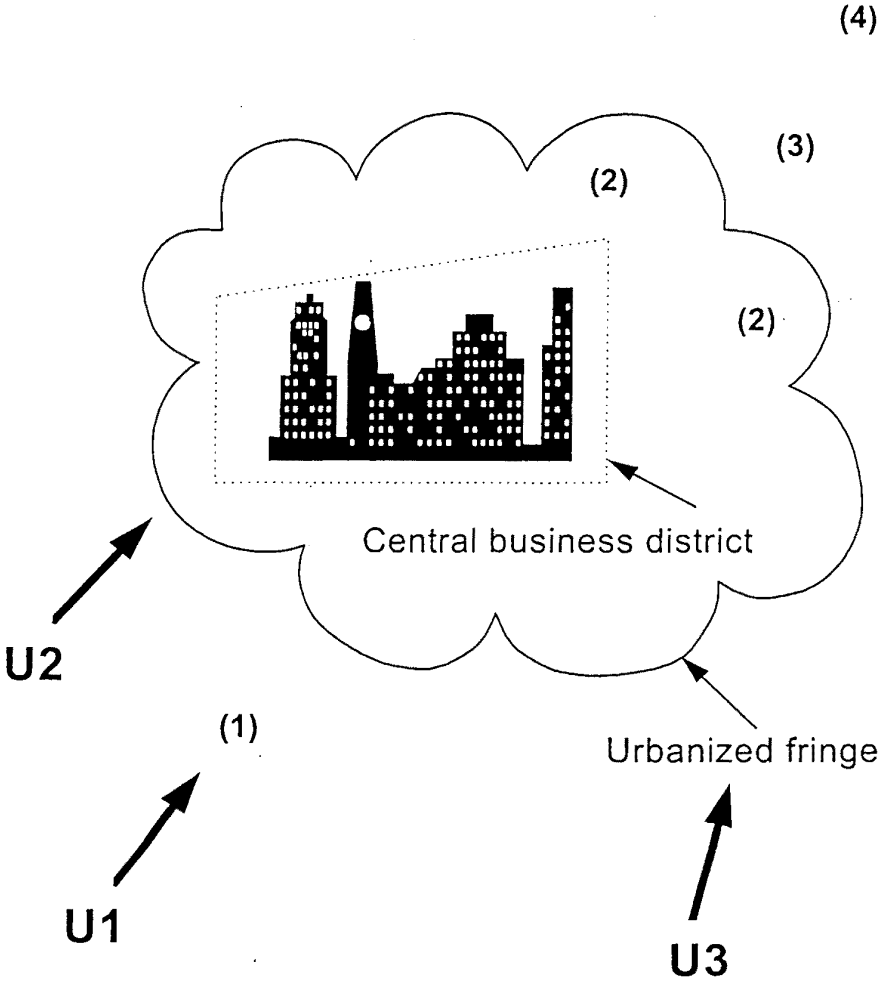
requires continuous measurements. The sampling schedule applicable to a specific area is dependent on population and PAMS site types. Specific monitoring objectives are associated with each sampling location. An example of an isolated area network design shown in Figure-1-1 identifies the location of the four PAMS site types referred to in Table 1-1.

The EPA has also prepared a guidance document on enhanced O_3 monitoring network design and siting criteria[3] which provides assistance regarding the number of PAMS required, station location, and probe siting criteria. The PAMS site types are described below.

Type (1) PAMS characterize upwind background and transported O_3 and precursor concentrations entering the MSA or CMSA and are used to identify those areas subjected to overwhelming transport. Type (2) PAMS monitor the magnitude and type of precursor emissions in the area where maximum O_3 precursor emissions are expected and are also suited for monitoring urban air toxic pollutants. Type (3) PAMS characterize O_3 precursor concentrations occurring downwind from the area of maximum emissions. Type (4) PAMS characterize extreme downwind transported O_3 and its precursor concentrations exiting the area and identify those areas which are potential contributors.

Appendix A of 40 CFR Part 58 references the Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV (Revised March, 1995) - Ambient Air Specific Methods[4] for general quality assurance recommendations for PAMS. Quality assurance procedures for VOC, NO_X, O_3 , and carbonyl and meteorological measurements must be consistent with EPA guidance. This guidance, and other information from appropriate sources, including Section 2.8 of this document, should be used by States in developing a Quality Assurance program.

Isolated Area Network Design



Note:
U1 and U2 represent the first and second most predominant high ozone day morning wind direction.
U3 represents the high ozone day afternoon wind direction.

o:\g\morr\3797\pams\isolated.ppt

(1), (2), (3), and (4) are different types of PAMS sites (See Table 1-1).

Figure 1-1. Isolated Area Network Design

Appendix C of 40 CFR Part 58 requires that methods used for O_3 and NO_X be reference or equivalent methods. Because there are no reference or equivalent methods promulgated for VOC and carbonyl measurements, Appendix C of the revisions refers agencies to this guideline document for direction.

Appendix C of the revisions would also allow the use of approved alternative VOC measurement methodology (including new or innovative technologies). This provision requires States that pursue alternatives to the methodology described herein to provide details depicting rationale and benefits of their alternative approach in their network description as required in 40 CFR Part 58, Section 58.40 - PAMS Network Establishment.

1.4 References

1. U.S. Environmental Protection Agency. Code of Federal Regulations. Title 40, Part 58. Ambient Air Quality Surveillance, Final Rule Federal Register, Vol. 58, No. 28, February 12, 1993.

2. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Compendium Method TO-12. *Method for the Determination of Non-Methane Organic Compounds (NMOC) in Ambient Air Using Cryogenic Preconcentration and Direct Flame Ionization Detection (PDFID).* EPA-600/4-89/017. Research Triangle Park, NC: U.S. Environmental Protection Agency, 1988.

3. *Photochemical Assessment Monitoring Stations Implementation Manual.* EPA-454/B-93-051. Research Triangle Park, NC: U.S. Environmental Protection Agency, 1994.

4. *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV - Ambient Air Specific Methods.* EPA 600/4-77-27a. U.S. Environmental Protection Agency, 1977. Revised March, 1995.

Section 2.0

Methodology for Measuring Volatile Organic Compound Ozone Precursors in Ambient Air

In accordance with the provisions for the enhanced O_3 ambient monitoring network requirements specified in 40 CFR Part 58, Subpart E,[1] this section provides guidance and method descriptions for measuring volatile organic compounds (VOCs) that are considered to contribute to the formation of ozone in the right atmospheric conditions. Information and guidance are provided to assist in the development, implementation, and use of these methods for designing a VOC measurement program consistent with the requirements of the enhanced O_3 monitoring rule. Areas addressed include:

- A review of the network monitoring requirements;
- A list of target VOCs to be measured;
- Chromatography issues associated with peak identification and quantification;
- Automated and manual methodology for collecting and analyzing samples;
- The minimum requirements of a Quality Assurance (QA) and Quality Control (QC) program;
- Guidance for validating data from automated GC systems; and
- Submitting data into the AIRS AQS data base.

Measuring VOCs is a complex process involving the application of gas chromatographic techniques for qualitative and quantitative determination of individual hydrocarbon compounds and an estimation of total non-methane organic compound (TNMOC) content in ambient air. Two methods are presented for collecting and analyzing VOC samples: an automated method (Section 2.4) and a manual method (Section 2.5). Ideally, agencies responsible for designing, implementing, and operating their O_3 monitoring networks will satisfy

their monitoring requirements by using some combination of the automated and manual gas chromatographic approaches. Even if agencies primarily choose the automated methodology, manual sampling and analysis capability are needed to fulfill the 24-hour sample requirement; verify the proper operation of the automated systems; characterize the quality of the collected data; address the identification of unknown compounds; and enhance the representativeness of the monitoring network.

Users are ultimately responsible for equipment selection, set-up, parameter optimization, and preparation of Standard Operating Procedures (SOPs) for their specific network. Because of the complexity of the measurement process and the numerous choices of instrumentation (e.g., sampling equipment, gas chromatographs, data acquisition hardware and software, etc.), the method descriptions presented are generic. Background information on the potential benefits and limitations of the methods are also provided.

2.1 Network Monitoring Requirements

The minimum sampling frequency requirements for speciated VOC monitoring are prescribed in 40 CFR Part 58, Subpart E, Appendix D - Network Design for State and Local Air Monitoring Stations (SLAMS), National Air Monitoring Stations (NAMS), and Photochemical Assessment Monitoring Stations (PAMS). Section 4.3 - Monitoring Period requires, at a minimum, that O_3 precursor monitoring be conducted annually throughout the months of June, July, and August when peak O_3 values are expected. Section 4.4 - Minimum Monitoring Network Requirements specifies the minimum required number and type of monitoring sites and sampling frequency requirements based on the population of the affected MSA/CMSA or nonattainment area, whichever is larger. These monitoring requirements are outlined in Table 1-1. The minimum speciated VOC sampling frequency requirements are summarized by site type below:

- Site Type 1 - Eight 3-hour samples every third day and one additional 24-hour sample every sixth day during the monitoring period; or eight 3-hour samples on

the five peak O_3 days plus each previous day and eight 3-hour samples and one 24-hour sample every sixth day, during the monitoring period.

- Site Type 2 - (population less than 500,000) - Same as Site Type 1.
- Site Type 2 - (population greater than 500,000) - Eight 3-hour samples every day during the monitoring period and one additional 24-hour sample every sixth day year around.
- Site Type 3 - (population greater than 500,000) - Same as Site Type 1.
- Site Type 4 - (population more than 2,000,000) - Same as Site Type 1.

Either of the two VOC methods (automated or manual) described in this section is capable of satisfying the sampling frequency and sample integration requirements. Samples collected for either method should represent a time-integrated average for the required sampling period. It is important to understand that the 3-hour sample integration period is a maximum requirement in the sense that samples can be collected more frequently at shorter sampling intervals (i.e., three 1-hour periods) but not less frequently for longer sampling intervals.

The manual methodology, where samples are collected in canisters, is primarily applicable to the less frequent sampling required for site Types 1, 3, and 4 (i.e., eight 3-hour samples every third day or during peak O_3 events) and the 24-hour sample requirement. The automated method, which allows for direct on-line sample collection, is primarily applicable to the more frequent sampling requirements for Site Type 2 (eight 3-hour samples every day during the monitoring period). The automated method provides a viable option for the continuous collection of hourly samples. Though not required, continuous collection of hourly samples also offers a more definitive assessment of the temporal and diurnal distribution of VOCs. Although it is possible to use the manual methodology for Site Type 2 sampling requirements, it is not practical due to the large number of SUMMA® canisters required.

2.2 Target Volatile Organic Compound Ozone Precursors

For the purposes of this document, the term VOCs refers to gaseous aliphatic and aromatic nonmethane organic compounds that have a vapor pressure greater than 0.14 mm Hg at 25 °C, and generally have a carbon number in the range of C_2 through C_{12}. Many of these compounds play a critical role in the photochemical formation of O_3 in the atmosphere. Volatile organic compounds are emitted from a variety of sources. In urban areas, the dominant source may be automobiles. Table 2-1 presents the target VOCs which could be measured and reported to satisfy the requirements of 40 CFR Part 58, Subpart E. Users should consider these target compounds in developing their measurement systems and monitoring approach, and initially report and submit results for these compounds into the Aerometric Information Retrieval System (AIRS) as described in Section 2.6.2 of this document. The VOCs listed in Table 2-1 were selected primarily based on their abundance in urban atmospheres and their potential role in the formation of O_3. Polar compounds are not included on the target list due to their surface adsorption characteristics and the difficulty in measuring these compounds using the methodology designed for nonpolar hydrocarbons. The methodology described in this document is designed to measure the more abundant non-polar hydrocarbons or VOCs.

The target list in Table 2-1 is not definitive or all-encompassing, but should be used as a guideline for implementation that should evolve as the monitoring program matures. As experience is gained in the collection of data regarding the abundance of specific VOCs at each site, target compounds may be deleted from the list depending on the frequency of occurrence. If additional compounds are identified and occur at high frequency, they should be added to the list of PAMS target compounds.

The compounds listed in Table 2-1 are presented in the order of their expected chromatographic elution from a J&W® DB™-1 non-polar dimethylsiloxane capillary analytical column. The AIRS parameter code for each compound is also given in Table 2-1. Compounds

Table 2-1. Target Volatile Organic Compounds

AIRS Parameter Code	Target Compound Name	AIRS Parameter Code	Target Compound Name
43203	Ethylene	43249	3-Methylhexane
43206	Acetylene	43250	2,2,4-Trimethylpentane (isooctane)
43202	Ethane	43232	*n*-Heptane
43205	Propylene	43261	Methylcyclohexane
43204	Propane	43252	2,3,4-Trimethylpentane
43214	Isobutane	45202	Toluene
43280	1-Butene	43960	2-Methylheptane
43212	*n*-Butane	43253	3-Methylheptane
43216	*trans*-2-Butene	43233	*n*-Octane
43217	*cis*-2-Butene	45203	Ethylbenzene
43221	Isopentane	45109	*m/p*-Xylene
43224	1-Pentene	45220	Styrene
43220	*n*-Pentane	45204	*o*-Xylene
43243	Isoprene (2-methyl-1,3-butadiene)	43235	*n*-Nonane
43226	*trans*-2-Pentene	45210	Isopropylbenzene (cumene)
43227	*cis*-2-Pentene	45209	*n*-Propylbenzene
43244	2,2-Dimethylbutane	45212	*m*-Ethyltoluene (1-ethyl-3-methylbenzene)
43242	Cyclopentane	45213	*p*-Ethyltoluene (1-ethyl-4-methylbenzene)
43284	2,3-Dimethylbutane	45207	1,3,5-Trimethylbenzene
43285	2-Methylpentane	45211	*o*-Ethyltoluene (1-ethyl-2-methylbenzene)
43230	3-Methylpentane	45208	1,2,4-Trimethylbenzene
43245	1-Hexene*	43238	*n*-Decane
43231	*n*-Hexane	45225	1,2,3-Trimethylbenzene
43262	Methylcyclopentane	45218	*m*-Diethylbenzene
43247	2,4-Dimethylpentane	45219	*p*-Diethylbenzene
45201	Benzene	43954	*n*-Undecane
43248	Cyclohexane	43141	*n*-Dodecane*
43263	2-Methylhexane	43102	TNMOC**
43291	2,3-Dimethylpentane	43000	PAMHC***

* These compounds have been added as calibration and retention time standards primarily for the purpose of retention time verification. They can be quantitated at the discretion of the user.

** Total Nonmethane Organic Compounds

*** PAMS Hydrocarbons

with lower boiling points typically elute first on this analytical column, followed by the heavier, higher molecular weight components with higher boiling points. Concentrations of the target VOCs and unknown compounds (unidentified peaks) are calculated in units of parts per billion Carbon (ppbC). The concentration in ppbC for a compound can be divided by the number of carbon atoms for that compound to estimate the concentration in parts per billion volume (ppbv). The target compound list in Table 2-2 has also been separated and classified into categories based on structure. The categories include paraffins (alkanes and cycloalkanes), olefins (alkenes and cycloalkenes), aromatics (arenes), and alkynes. Because the compound proved to be unstable and decomposed in the calibration gas cylinder, 2-methyl-1-pentene was replaced on the list of PAMS target volatile organic compounds by 1-hexene. *n*-Dodecane was added as a late-eluting retention time marker.

2.2.1 *Total Nonmethane Organic Compound (TNMOC) and PAMS Hydrocarbons (PAMHC)*

The TNMOC measurement is the unspeciated total concentration of VOCs (typically C_2 through C_{12}) in ambient air. This measurement supplements the O_3 precursor compound measurements and is used for O_3 models that do not require speciated hydrocarbon measurement input. This estimate can be made using either the automated or manual techniques described in Sections 2.4 and 2.5, respectively. An estimate of the TNMOC in ppbC is determined as the sum of all identified and unidentified gas chromatographic peaks in the C_2 through C_{12} range as eluted from the analytical column and detected by the flame ionization detector (FID). The concentration in ppbC of TNMOC is calculated by taking the total area count measured and applying the response factor for propane, the primary calibration compound. The C_2 through C_{12} retention time window should be established and periodically verified by analyzing ethylene or acetylene (C_2) and dodecane (C_{12}). These compounds may be incorporated in the retention time or calibration standard.

Table 2-2. Target VOC Compound Classification

Alkyne	Paraffin
Acetylene	Isopentane
	3-Methylheptane
Aromatic	2-Methylheptane
Styrene	*n*-Octane
m/p-Xylene	2,3,4-Trimethylpentane (isooctane)
o-Xylene	Ethane
Toluene	Propane
Ethylbenzene	Isobutane
n-Propylbenzene	*n*-Nonane
1,2,4-Trimethylbenzene	*n*-Butane
1,3,5-Trimethylbenzene	2,2,4-Trimethylpentane
1,2,3-Trimethylbenzene	*n*-Hexane
Benzene	*n*-Pentane
Isopropylbenzene (cumene)	3-Methylpentane
m-Ethyltoluene (1-ethyl-3-methylbenzene)	2-Methylpentane
p-Diethylbenzene	Cyclopentane
o-Ethyltoluene (1-ethyl-2-methylbenzene)	2,3-Dimethylbutane
p-Ethyltoluene (1-ethyl-4-methylbenzene)	Methylcyclopentane
m-Diethylbenzene	2,4-Dimethylpentane
	2,2-Dimethylbutane
Olefin	*n*-Heptane
1-Hexene*	3-Methylhexane
1-Butene	2,3-Dimethylpentane
Isoprene (2-methyl-1,3-butadiene)	Cyclohexane
1-Pentene	2-Methylhexane
trans-2-Butene	Methylcyclohexane
cis-2-Butene	*n*-Decane
trans-2-Pentene	*n*-Undecane
cis-2-Pentene	*n*-Dodecane*
Propylene	
Ethylene	

*These compounds have been added as calibration and retention time standards primarily for the purpose of retention time verification. They can be quantitated at the discretion of the user.

Compendium Method TO-12, preconcentration direct flame ionization detector (PDFID) techniques described in Section 3.0 of this document and in Appendix C, may also be used to determine TNMOC. Method TO-12 measures carbon-containing compounds from the sample as concentrated by cryogenic trapping and thermal desorption directly into a FID. The FID response is typically calibrated using propane to give a per-carbon response in area counts per ppbC. Compounds with a carbon number greater than C_{12} may be transferred and detected using the Method TO-12 technique. Because of inherent differences between the "summation of peaks" and PDFID approaches, the two approaches do not provide equivalent TNMOC results and are not directly comparable. Since the vapor pressure of carbon-containing compounds decreases with increasing molecular weight, compounds with a carbon number above C_{12} are not expected to contribute significantly (more than a few percent) to the TNMOC value.

A subgroup of TNMOC, PAMHC is the sum of peak areas for only the PAMS target compounds. Both TNMOC and PAMHC are valuable data components and the ratio PAMHC/TNMOC may indicate the conversion of ozone precursors to carbon-containing products resulting from atmospheric chemistry.

The PAMHC parameter itself is of limited value because the PAMS target list may change by geographic area. Also, PAMHC provides a broad measure of compounds that is often not substantially different from TNMOC. PAMHC could be used by a state or agency measuring only listed compounds, and then calculating the percent of unidentified compounds as:

$$\text{Percent Unidentified} = \frac{\text{TNMOC} - \text{PAMHC}}{\text{TNMOC}} * 100$$

Alternatively, PAMHC can be used to determine the percentage of the total made up by the listed compounds.

$$\text{Percent Identified} = \frac{\text{PAMHC}}{\text{TNMOC}} * 100$$

This ratio for a given PAMS site usually stays within a range characteristic of the site, subject to seasonal variation.

2.3 Chromatography Discussion and Issues

The following section discusses the basic operating principles of the gas chromatography with flame ionization detection (GC/FID) methodology used to measure ambient VOCs either as an independent analytical system or as part of an automated sampling/analytical system. Related chromatography issues or concerns regarding peak identification and quantitation, sample moisture removal, calibration, primary and retention time standard preparation and humidification, and analytical column selection and configuration are also discussed.

2.3.1 Gas Chromatography with Flame Ionization Detection

Gas chromatography with flame ionization detection is the established analytical technique for monitoring VOCs in ambient air. The sensitivity, stability, dynamic range, and versatility of GC/FID systems make them extremely effective in measuring very low concentrations of VOCs. The gas chromatograph may be an independent analytical system or a component of an automated sampling/analytical system.

Typically, a sample taken from an urban environment contains more than 100 detectable compounds that may reasonably be separated into quantifiable peaks. These compounds are generally present at concentrations varying from less than 0.1 ppbC to greater than 500 ppbC with the typical concentration ranging between 0.1 to 50 ppbC. Detection of typical urban concentration levels generally requires that samples be passed through a preconcentration trap to concentrate the compounds of interest and separate them from components of the sample that are not of interest (i.e., air, methane, water vapor, and carbon dioxide).

The GC/FID systems required for VOC measurement consist of the following principal components:

- Sample introduction;
- Sample conditioning for moisture removal (optional);
- Sample concentration;
- Sample focusing for optimal sample injection and improved chromatographic separation (optional);
- Gas chromatography; and
- Flame ionization detection.

An air sample may be introduced to the measurement system directly from ambient air, an integrated canister, or a calibration gas cylinder. The sample is optionally passed through a sample conditioning system for moisture removal and then concentrated using an adsorbent or glass bead trap that is cryogenically cooled using liquid nitrogen, liquid carbon dioxide, or thermoelectric closed-cycle coolers. The concentrated sample is then thermally desorbed and introduced into the carrier gas prior to being introduced to the analytical column. Sample refocusing is optional and may be performed using a cryogenically or thermoelectrically cooled secondary trap. Sample refocusing may also occur at the head of the cryogenically cooled analytical column. Sample focusing is used to concentrate the desorbed sample into a narrow band for injection onto the capillary GC analytical column. The focused sample is thermally desorbed rapidly and injected onto the analytical column of the gas chromatograph as a "plug," which maximizes GC column resolution and results in improved C_2 and C_3 chromatographic separation and peak shape. Sample focusing is effective when low carrier gas flow rates (1-2 mL/minute) are used. The analytical column separates the sample into individual components based on the distribution equilibrium between the mobile (carrier gas) and stationary (liquid column coating) phases. The separated components elute from the column and enter the FID, where a signal is generated based on carbon response. The time of elution and detection

(retention time) is the primary basis for the identification of each compound. Retention time units are typically expressed in minutes and are specific to the conditions of the GC system used. The identification of sample components is determined by matching the known retention times of the components in a retention time standard with those in the sample. It is desirable to confirm GC peak identification periodically using a mass spectrometric detector, if available.

The FID is the most widely used, universal GC detector. As a general observation, the FID provides good sensitivity and uniform response to *n*-alkanes based on the number of carbon atoms in the compound. For unsaturated, cyclic, or aromatic hydrocarbons, the FID response is less predictable. The FID is, therefore, well suited for ambient air analysis since a majority of VOCs in ambient air are hydrocarbons. This uniformity of FID response to *n*-alkanes simplifies calibration in that a single hydrocarbon compound (e.g., propane) can be used to calibrate the detector response for all hydrocarbons.[2,3] This FID response characteristic also provides for the unique capability of estimating the concentrations of not only the target peaks (identified) but also the unidentified components of the sample. Some automated GC systems require a two-component calibration mixture (e.g., propane and benzene) due to the use of dual analytical columns. By summing all identified and unidentified chromatographic peak areas, a useful estimate of the concentration of TNMOC is provided. The FID also has a broad linear dynamic range of response, allowing for the analysis of samples with concentrations ranging from picogram (using preconcentration) to microgram quantities of hydrocarbons.

Modern GC technology, coupled with sophisticated data acquisition and processing software, provides for reasonable estimates of both the identity and quantity of the target species to the extent that the analytical column is capable of separating them and the system has been adequately characterized and calibrated. The retention characteristics of the analytical column must be determined for each target compound using pure components or mixtures of pure components diluted with a humidified inert gas.

2.3.2 *Identification and Quantification Issues*

Although the peak identification and quantification expected with GC/FID systems is acceptable for meeting the objectives of PAMS, the GC/FID technique has some inherent limitations. Chromatographic systems using GC/FID rely primarily on the practical use of retention times to make compound identifications for each chromatographic peak. Commercial GC/FID systems configured for VOC analyses must be suitably designed to provide stability of system parameters to ensure consistent retention times for confident peak identification.

Gas chromatographic peak misidentifications typically occur as a result of retention time shifting and interferences due to co-eluting non-target compounds. Modern GC capillary columns are generally capable of adequately separating the targeted compounds; however, co-elution of unidentified species with the targeted species can and does occur. The identification and quantitative uncertainty resulting from co-elution will depend on the type of unidentified compound and the abundance relative to the affected target VOC. The target VOCs are exclusively hydrocarbons which are primarily emitted into the atmosphere by mobile sources and generally dominate most urban samples. Concentration estimates for substituted hydrocarbon species such as oxygenated or halogenated hydrocarbons using FID are uncertain since these compounds do not respond to the FID solely on a per carbon basis. Generally, the identification and quantification of a targeted compound will not be significantly affected unless a substituted species, at a significant concentration, co-elutes with the target compound.

The potential for target compound identification errors can be reduced or eliminated by:

- Ensuring that the measurement system is fully optimized and characterized as discussed in Section 2.3.7, Pre-Measurement Chromatographic System Verification;
- Designating chromatographic reference peaks and using relative retention times for peak identification (Section 2.7.1, Data Validations);
- Using dual-column configurations to provide improved resolution (Section 2.3.5, Column Configuration);

- Having an experienced chromatographer conduct visual inspection of the chromatograms at some practical frequency to verify proper system operation;
- Reviewing the chromatographic data using computer-based exploratory software designed to improve and validate the GC data and determine outliers;
- Periodically re-analyzing samples on a different well-characterized GC system to identify co-eluting compounds; and
- Periodically confirming peak identification using more definitive GC/MS techniques.

Quantitative errors can be reduced by careful attention to quality control (calibration details and system blanks), frequent response checks using canister samples containing target compound mixtures of known concentration, and periodic performance audits or proficiency studies using independent reference materials. Analytical system blank analysis of humidified, ultra zero air is performed to characterize the background concentration of VOCs present in the measurement system. If unacceptable levels of background system contamination occur the data will be quantitatively compromised. Sources of contamination can be related to the:

- Source of humidified, ultra zero air;
- Sample to trap transfer line;
- Carrier gas and filters; and
- Analytical columns.

The effort devoted to peak identification, confirmation, and quantification is important to the quality of the collected data. Users must determine the appropriate level of effort to devote to this activity based on their specific needs and capabilities.

2.3.3 Sample Moisture Issues

The accurate identification and quantitation of trace level VOCs in ambient air generally require the use of sample concentration techniques for sample enrichment to enhance instrument sensitivity. The effects of moisture must be considered in any measurement program where sample concentration is required. Cryogenic concentration techniques are commonly used, especially for light hydrocarbons. The vast difference in boiling points of the C_2 and C_{12} hydrocarbons also may require the use of sub-ambient chromatography to adequately separate the entire range of compounds. The co-collection of moisture in the concentration trap and subsequent injection of water onto the analytical column can cause a number of problems and adversely affect the overall quality of the data generated. These problems include:

- Cryogenic trap freezing which results in reduced sample flow or trap blockage;
- Chromatographic column plugging due to ice formation and subsequent retention time shifting, peak splitting, and poor peak shape and resolution which result in incorrect peak identification and peak naming;
- Chromatographic column deterioration (especially with Al_2O_3 columns);
- Baseline shifts due to elution of the water profile;
- FID flame extinction;
- Poor reproducibility and precision of the data generated;
- Competition for active sites and adverse effects on adsorbent concentration traps; and
- Suppression of the FID signal.

In addition, if "cold spots" exist in the sample concentration or transfer system, water can collect and cause sample carryover or "ghost" peaks in subsequent sample analyses. This carryover may affect the data by causing chromatographic interferences which affect the resolution, identification, and quantitation of the components of interest.

Moisture removal from the sample stream prior to sample concentration minimizes these problems and also allows larger sample volumes to be concentrated, thus providing greater detection sensitivity. Moisture related problems can be alleviated by various water management methods that include Nafion® driers (Perma-Pure® Inc., Toms River, NJ), selected condensation at reduced temperatures, selective temperature desorption, non-cryogenic hydrophobic adsorbent sample concentration traps, dry gas purging, and selective multibed sorbent trapping. However, some methods used to remove moisture from the sample may result in the loss of polar VOCs which affects the TNMOC measurement. This effect is variable, based on drier efficiency and compound selectivity. A drier that minimizes both polar VOC loss and the potential for introducing contaminants into the system should be considered.

Nafion® driers are commonly used for ambient air sample drying, and are discussed in Compendium Method TO-14.[4] The Nafion® membrane consists of a hygroscopic copolymer of tetrafluoroethylene and a perfluorosulfonic acid that is coaxially mounted within a larger Teflon® or stainless steel tube. The humid sample stream is passed through the membrane tube, allowing water to pass through the walls by a process called "perevaporation" into a dry nitrogen (N_2) or air purge stream that is counter-currently flowing through the annular space between the membrane and the outer tube. Variables that determine the drying efficiency include the surface area of the membrane used, sample flow rate or sample residence time in the dryer, pressure or vacuum of the sample and purge flow rate, temperature, and sample humidity. Depending upon the variables affecting drying efficiency, Nafion® drier water removal efficiency ranges of 80-95% have been reported.[5,6,7]

Nafion® drying devices have shown demonstrated losses of certain polar VOCs (amines, ketones, alcohols, and some ethers).[8,9] This reduction in recovery of polar VOCs significantly affects TNMOC measurements made using a Nafion® drier. Reduction in recovery of polar VOCs by drying can reduce the TNMOC measurement by 20-30% in typical ambient air samples. Nafion® driers have also caused rearrangement of several monoterpenes (α-pinene and β-pinene) but have no effect on the recovery of isoprene.[6] Hydrocarbons, chlorinated or fluorinated hydrocarbons, esters, aldehydes, and some ethers are unaffected by the drier.[8,5,10]

Recent information[11] discusses issues reported when using Nafion® driers shortly after heating to regenerate the drier by removing residual water vapor and organic compounds, in order to improve drier efficiency. Heating can significantly affect the sample integrity of the C_4-C_6 alkenes and cause compound losses and rearrangement. The degree of loss and rearrangement is dependent on length of time and the temperature used for drier regeneration, as well as sample humidity. Isoprene may be lost without reappearance of an equivalent amount of carbon. In the case of C_6 alkenes, new, unidentified peaks may emerge in the retention time area of the original peaks. Heating had no effect on C_2-C_3 alkenes, C_2-C_{10} alkanes, cycloalkenes, and aromatics. The effects of heating are reversed if the drier is immediately purged with clean, dry nitrogen or air at a flow rate of 50 cc/minute for at least three hours. Heating of Nafion® driers for regeneration should be avoided and is not recommended for PAMS. If the drier shows a loss of efficiency as determined by recovery of the target compounds in the retention time standard, the drier should be replaced. To improve efficiency and prevent memory effects, the drier should be replaced at least seasonally or more frequently as needed. Information on the use of Nafion® drying devices is presented in EPA Compendium Method TO-14[4] or EPA Compendium Method TO-15, entitled *Determination of Volatile Organic Compounds (VOCs) in Air Collected-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)* (see Appendix A).

Sample drying using selective condensation at reduced temperatures is performed by selectively condensing moisture at a reduced temperature from the sample stream during thermal desorption from the sample concentration trap. This method of drying has been evaluated for recoveries of compounds having a wide range of volatilities and was found to give good recovery, reproducibility, and acceptable chromatography when operated at 15°C.[12]

Studies have been done incorporating the use of controlled vaporization of VOCs off glass bead traps at ambient and reduced temperatures, non-cryogenic hydrophobic adsorbent sample concentration traps, dry gas concentration trap purging at selected temperatures,[13] and dual sorbent trapping systems to selectively reduce sample moisture.[14,15,16] Techniques for drying an ambient air sample have been combined, including dry purging after collection on solid sorbent, loss of water by breakthrough when collecting on solid sorbents, and sample

splitting.[17,18] These novel approaches to mitigating the effects of moisture should be evaluated to determine any limitations or negative effects prior to incorporating them into any VOC measurement system. EPA Method TO-15 (see Appendix A) has recently been added to the EPA Compendium of Methods for the Determination of Toxic Organics in Ambient Air and describes different techniques for drying ambient air samples. One of the main goals of this method was to use drying methods that would not affect polar VOCs as drastically as the Nafion® driers.

2.3.4 Calibration Standards

Calibrating a GC/FID system to measure VOCs requires two distinctly different types of calibration mixtures: a primary standard to calibrate detector response for gas chromatographic peak quantitation (primary calibration standard) and a qualitative mixture of known hydrocarbon compounds to determine gas chromatographic peak retention times (retention time standard).

2.3.4.1 Primary Calibration Standard

The GC/FID response is calibrated in ppbC using a propane primary calibration standard referenced to a National Institute of Standards and Technology (NIST) Standard. A propane and benzene mixture is recommended for systems that utilize dual columns or column switching configurations that use two FIDs. Standard Reference Materials (SRMs) from NIST and Certified Reference Materials (CRM) from specialty gas suppliers are available for this purpose. NIST currently has a fifteen component ambient non-methane organics in nitrogen SRM available (SRM 1800) for use as a reference or primary calibration standard. SRM 1800 contains both propane and benzene. Less expensive working standards needed for calibration verification over the range of expected concentrations can be prepared by the user or purchased from a gas supplier, provided they are periodically referenced to a primary SRM or CRM. The primary calibration standards must be humidified to reflect the ambient air matrix being analyzed. A procedure for preparing humidified standards is given in Section 2.3.4.3.1. A procedure for diluting standards is given in Section 2.3.4.3.2. Based on the uniform carbon

response of the FID to hydrocarbons, the response factor determined from the propane or benzene primary calibration standard is used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

It is also feasible to incorporate the primary calibration standard into the retention time standard described below by confirming the concentration of propane and benzene in the retention time mixture using a primary SRM or CRM.

2.3.4.2 Retention Time Calibration Standard

The retention time calibration standard is a multiple-component mixture containing all target VOCs at varying concentration levels. The retention time calibration standard is a humidified working standard used during the initial setup of the GC/FID system to optimize critical peak separation parameters and determine individual retention times for each of the target compounds. The retention time calibration standard is also used during the routine operation of the GC/FID system as a QC standard for verifying these retention times.

The response of the GC/FID to selected hydrocarbons in this standard can be used to monitor system performance and determine when system maintenance or recalibration of the FID using the primary calibration standard is necessary. Proper operation of the FID according to the manufacturer's specifications produces a linear response across the chromatographic range. The concentration of each compound in the retention time standard need not be directly referenced to the SRM or CRM (as is the case for the primary calibration standard); rather, the concentration of each compound can be determined with reasonable accuracy using the FID propane or benzene carbon response factor from the calibrated GC system. If the propane and benzene in the retention time mixture are used for primary calibration, then both must be directly referenced to an SRM or CRM. To reference a working standard to an SRM or CRM, the analytical system is calibrated with the SRM or CRM, then the working standard is analyzed against the SRM or CRM calibration. If necessary, a correction factor for the working standard is calculated.

A multiple-component high pressure mixture containing the target VOCs can be obtained from a specialty gas supplier. Multiple-component mixtures can also be prepared by the user to confirm the peak identifications using the retention time standard. The retention time standard must be humidified for use as discussed in Section 2.3.4.3.

2.3.4.3 Calibration Standard Preparation

The primary propane and benzene calibration standards must be humidified to ensure integrity and stability. Water vapor has been shown to improve the stability of low pressure VOC gas mixtures in SUMMA® canisters.

A stock multiple-component retention time calibration standard containing the compounds of interest may be prepared at a concentration level approximately 100 times that of the anticipated working standard concentration. The stock standard can be prepared by blending gravimetrically weighed aliquots of neat liquids or by adding aliquots of gaseous standards with an inert diluent gas. The aliquot of each compound should be introduced through a heated injector assembly into an evacuated SUMMA® passivated stainless steel canister or other inert container. For the neat liquid aliquots, the pre-injection and post-injection syringe weights are recorded, and the difference used to determine the amount of liquid actually transferred to the canister. Following injection of all neat liquid and gaseous components, the canister is pressurized to at least 2 atmospheres above ambient pressure with clean, dry N_2. Concentrations are calculated based on the amount of compounds and diluent injected and the final canister pressure, using ideal gas law relationships.

The stock retention time calibration standard is used to prepare humidified retention time working standards at the ppbC level. It is not necessary to determine exact component concentrations in the multi-component mixture because the working retention time standard should not be used to determine compound specific response factors. However, the approximate concentration of the stock standard must be known in order to prepare the working retention time standards. Preparation of the working standards is accomplished by syringe injection of a

gaseous aliquot of the stock standard into a SUMMA® passivated stainless steel canister or other inert canister, and subsequently humidifying for use.

2.3.4.3.1 Procedure for Humidification

The relative humidity of the air in a canister is an important issue with respect to the storage stability and recovery of VOCs. A study using SUMMA® passivated canisters under varying pressures, relative humidities (RHs) and different VOC residence times has shown that humidification of canisters improves the recovery of higher molecular weight, less volatile components.[19] The study showed that RH levels above 18% were required for improved compound recovery. Another study using SUMMA® passivated canisters showed that a relative humidity of at least 15% was necessary to ensure complete recovery of 41 chlorinated, brominated and aromatic compounds at concentrations of 2 to 4 ppbv.[20] There is some evidence that canisters lined with fused silica (SilcoCan™, Restek, Inc. Bellefonte, PA) do not have a minimum requirement for humidity, as do the SUMMA® polished canisters.[21]

The relative humidity of air taken from a humidified canister can vary over a significant range. For example, as shown in Figures B-1 and B-2 of Appendix B (also see Reference 22),[22] if 18L of air at 75% RH is sampled, the air subsequently released from the canister will vary from 33% RH at 30 psig (first sample taken) to 100% RH at 0 psig. This knowledge is important since the retention times of individual gas chromatographic peaks and the response factors of some types of gas chromatographic detectors change appreciably with sample humidity. A second concern is the loss of water-soluble VOCs either to condensed water or to water consolidated in drops on the canister interior surface. For the example given above, after the canister is filled with 18L of ambient air at 75% RH, 55% of the water in the fully pressurized canister (30 psig) will be condensed on the canister interior surface and 45% will be in the gas phase. As sample is removed from the canister the water adsorbed will be replenished by evaporation of the condensed water. The ratio of H_2O in the gas phase (maintained at the equilibrium vapor pressure by evaporation from the wall) to the amount of air in the canister will increase and the RH will increase. If the RH of the ambient sample is high enough (>70% RH)

then there will still be condensed water inside the canister even when the canister pressure is reduced to atmospheric pressure. The reader can gain a better appreciation for the variation in RH of gas released from a canister by assuming various RH values for ambient air and using Figures B-1 and B-2 in Appendix B.

In general, the amount of water in a given volume of air at a specified RH is calculated by using the ideal gas law and a table of water vapor pressures (Table 2-3.)[23] The ideal gas law applied to calculating the amount of water required to humidify 6 liters of air to 100% RH at 21°C and one atmosphere (zero psig) of pressure is:

$$PV = nRT \qquad \textbf{(2-1)}$$

$$n = \frac{PV}{RT}$$

Where:

n	=	moles of H_2O
V	=	canister volume, 6 L
P	=	vapor pressure of H_2O, atm
T	=	temperature in K, 21 °C + 273 = 294K
R	=	ideal gas constant, 0.08205 L-atm/K mole

Converting the vapor pressure of H_2O in mm at 21 °C to atm:

$$\frac{18.65\,\text{mm}}{760\,\text{mm/atm}} = 0.02454\ \text{atm}$$

Table 2-3. Vapor Pressure of Water at Various Temperatures, mm Hg

Temp °C	0.0	0.2	0.4	0.6	0.8
10	9.209	9.33	9.458	9.585	9.714
11	9.844	9.976	10.109	10.244	10.380
12	10.518	10.658	10.799	10.941	11.085
13	11.231	11.379	11.528	11.680	11.833
14	11.987	12.144	12.302	12.462	12.624
15	12.788	12.953	13.121	13.290	13.461
16	13.634	13.809	13.987	14.166	14.347
17	14.530	14.715	14.903	15.092	15.284
18	15.477	15.673	15.871	16.071	16.272
19	16.477	16.685	16.894	17.105	17.319
20	17.535	17.753	17.974	18.197	18.422
21	18.650	18.880	19.113	19.349	19.587
22	19.827	20.070	20.316	20.565	20.815
23	21.068	21.234	21.583	21.845	22.110
24	22.377	22.648	22.922	23.198	23.476
25	23.756	24.039	24.326	24.617	24.912
26	25.209	25.509	25.812	26.117	26.426
27	26.739	27.055	27.374	27.696	28.021
28	28.349	28.680	29.015	29.354	29.697
29	30.043	30.392	30.745	31.102	31.461
30	31.824	32.191	32.561	32.934	33.312
31	33.695	34.082	34.471	34.864	35.261
32	35.663	36.068	36.477	36.891	37.308
33	37.729	38.155	38.584	39.018	39.457
34	39.898	40.344	40.796	41.251	41.710
35	42.175	42.644	43.117	43.595	44.078
36	44.563	45.054	45.549	46.050	46.556
37	47.067	47.582	48.102	48.627	49.157
38	49.692	50.231	50.774	51.323	51.879
39	52.442	53.009	53.580	54.156	54.737

Substituting values in the above equation:

$$\frac{(0.02454\ \text{atm})(6\text{L})}{(0.08205\ \text{L - atm/K mole})(294\text{K})}$$

n = 0.00610 moles of H_2O required for 100% RH in the canister.

To calculate the moles of H_2O required for a given relative humidity multiply the value of *n* by the RH expressed as a fraction (e.g., 20% = 0.2) and convert to the number of mg of H_2O. Express the number of mg as an equal number of μL since 1.0 mg of water occupies 1.0 μL. Thus:

$$0.00610\ \text{moles} \times 0.2 \times 18\ \frac{\text{gm}}{\text{mole}} \times 1000\ \frac{\text{mg}}{\text{gm}} \times \frac{1.0\ \mu\text{L}}{1.0\ \text{mg}} = 22.0\ \mu\text{L}$$

The number of μL to be added for other sample volumes scales linearly with volume, e.g., for a sample volume of 18L, multiply the number of μL to be added to 6L by the ratio 18/6 = 3. Hence, the number of μL to be added to a canister in order to simulate the sampling of 18 L of sample air at 21°C and 20% RH is 66 μL. Figure 2-1 can be used to approximate the amount of water in 1 L of air at temperatures from -30°C to 40°C at 75% and 100% RH. The values in the figure also scale linearly with sample volume.

Based on the studies of SUMMA®-passivated canisters, low pressure (30 psig) calibration standards prepared in canisters ideally should have at least a certain minimum amount of water vapor (20% relative humidity) to ensure sample integrity but not enough water to cause condensation of water vapor in the canister (33% relative humidity). Using Equation 2-1, the amount of liquid water that must be added to a 6L canister (pressurized to 18 L with dry air) to achieve these conditions at 21°C (70°F) is between 66 and 110 μL. This range will of course

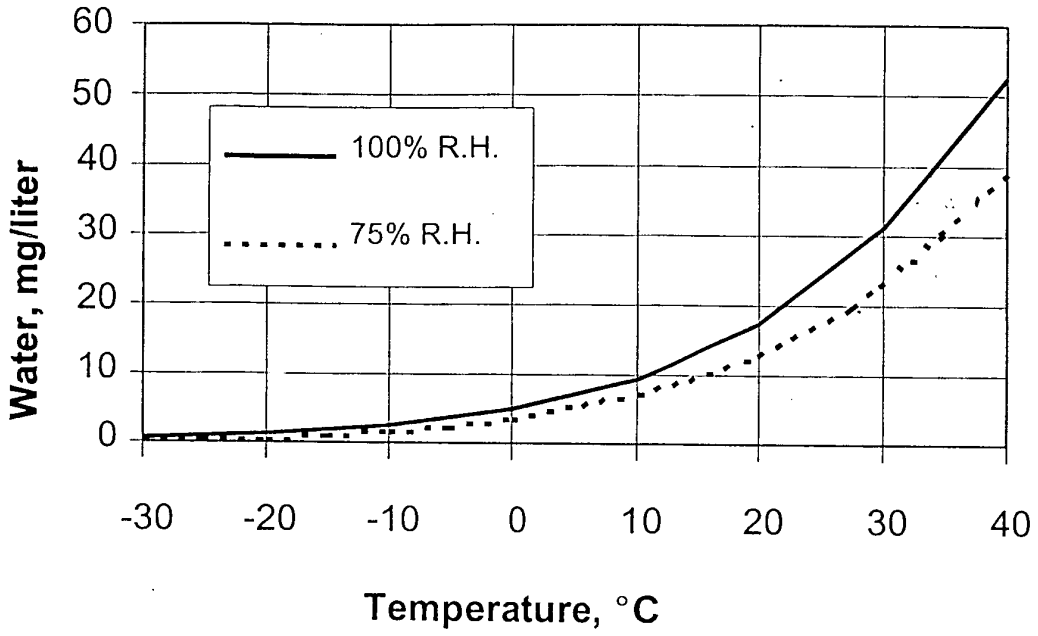


Figure 2-1. Water Content of Air at 75% and 100% Relative Humidity Over a Range of Temperatures

Amount of water is expressed as mg/liter. The density of water under standard conditions is 1 g/mL. Thus 1 mg of water occupies a volume of 1 µL. For a dry six-liter canister sample at 25°C, approximately (23 x 6) µL of water would be need to be added to achieve 100% relative humidity. Pressure is measured at the exit of the canister.

Figure adapted from Tipler, A. "Water Management in Capillary Gas Chromatographic Air Monitoring Systems." In *Proceedings of the 1994 U.S. EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants*, Research Triangle Park, NC, 1994.

vary slightly with the sample temperature (and atmospheric pressure) and should be recalculated for specific conditions. If excess water is added to the canister, water will condense inside the canister. However, the presence of condensed water is not observed to have any effect on the recovery of the non-polar PAMS target compounds and an excess of water vapor has often been used in practice when only non-polar compounds are of interest.

A detailed procedure for humidifying non-polar canister calibration standards prepared from dry stock high-pressure cylinder gases is given below. Two simple methods can be used to humidify calibration gas:

- Direct injection of water into the canister before filling with dry calibration gas; and
- Injection of water into the canister through a stainless steel union tee, then filling with dry calibration gas.

Both procedures incorporate active temperature controlled heating of the gas transfer line to 90°C. Heating ensures that the higher molecular weight compounds are transferred quantitatively and not adsorbed onto the stainless steel tubing during gas transfer. Heat also keeps the water injected through the stainless steel tee from condensing on the surfaces.

The following materials are needed:

Two-stage, non-corrosive, ultra high purity regulator - the regulator must have stainless steel diaphragms and inert seats and seals to prevent air diffusion and adsorption of low concentration trace level gases.

¼-Inch stainless steel tubing and union tee - chromatographic grade stainless steel, fused silica-lined stainless steel, or nickel are all recommended tubing material choices. A stainless steel union tee should be used.

High purity water - HPLC or spectrophotometric-grade high purity water.

Cord heater - 110 VAC rated for metal contact, with a 300-watt heat capacity minimum.

Temperature controller - active temperature controller operating on a thermocouple feedback loop.

Figure 2-2 shows the configuration of the materials for direct injection and Figure 2-3 shows the configuration of the materials for union tee injection.

Direct Injection of Water into the Canister—To humidify calibration standards by direct injection, follow these steps:

1) Insert an inert 10-mm septum into the ¼-inch nut on top of the canister valve and hand tighten to seat the septum.

2) Fill a glass syringe with the desired volume of high purity water for the canister size used. Open the canister valve slightly while quickly injecting the water, allowing the vacuum to draw the water into the canister.

3) Close the valve and remove the cap. The canister is now ready to be filled with dry calibration gas. Any remaining water droplets in the canister valve will be carried into the canister by the flow of dry calibration gas.

4) Install the correct CGA type high purity regulator onto the calibration gas cylinder. Install a ¼-inch stainless steel male connector to connect the female NPT thread on the regulator to the ¼-inch stainless steel tubing. Install a length of ¼-inch stainless steel tubing to connect the canister to the connector fitting on the regulator.

5) Leak check the entire system by capping the ¼-inch tube outlet and pressurizing the system to the desired final canister pressure. Close the pressure regulator and monitor pressure changes. If the pressure drops, check all fitting connections.

6) Loosely attach the canister so that a complete seal is not achieved. With the valve closed, purge the entire system before use by opening and closing the pressure regulator at least three times, allowing the excess gas to escape past the incomplete seal. As an option, a stainless steel toggle shutoff valve may be installed between the canister and gas transfer tube to vent the purge gas.

7) Wrap the transfer tubing with a cord heater and plug it into the active temperature controller. Activate the temperature controller and the system to equilibrate (for 5 to 10 minutes) at a setting of about 90°C.

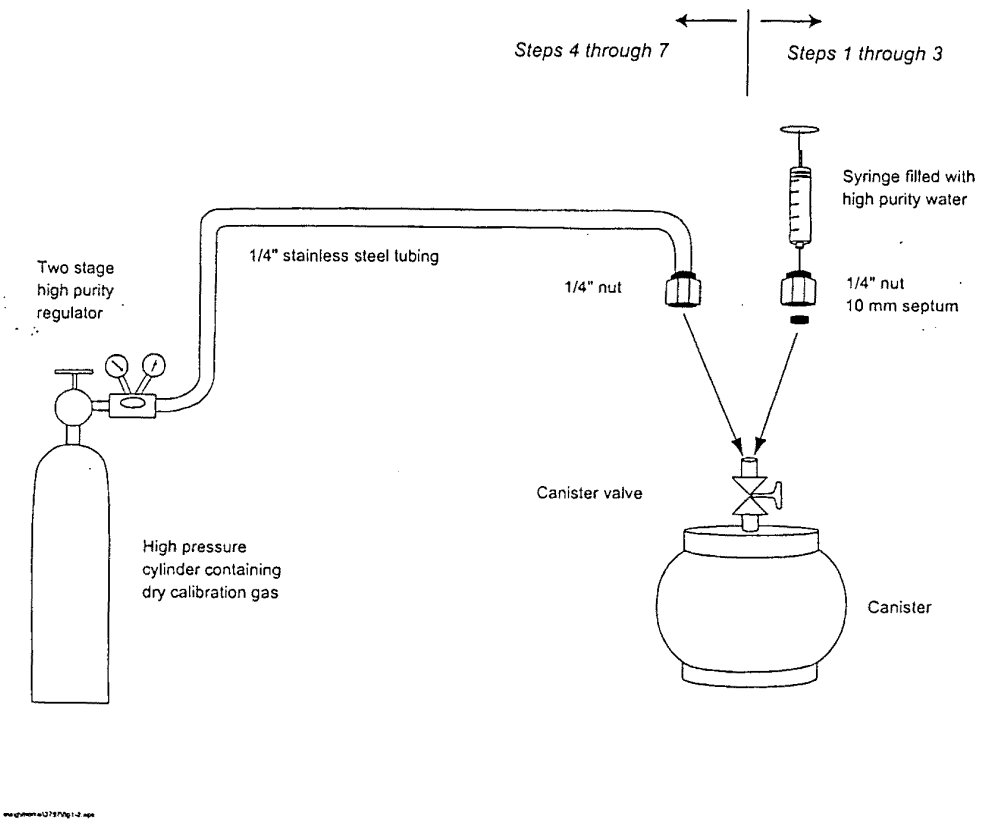


Figure 2-2. Configuration of Materials to Perform Direct Injections of Water into the Canister Before Filling with Dry Calibration Gas

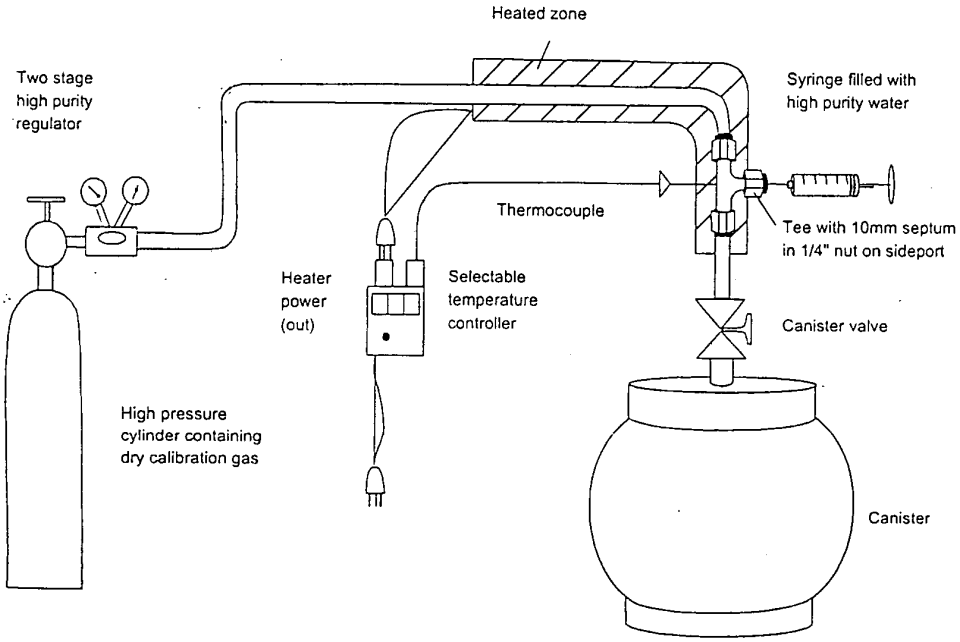


Figure 2-3. Configuration of Materials to Perform Injection of Water Through a Heated Tee While Filling with Dry Calibration Gas

8) Tighten the canister nut and set the delivery pressure gauge on the regulator to the desired final canister pressure. Fill the canister and allow it to sit overnight for static equilibration.

Union Tee Injection of Water into the Canister—To humidify calibration standards in canisters using a stainless steel union tee, follow these steps:

1) Install the correct CGA type high purity regulator onto the calibration gas cylinder. Install a ¼-inch stainless steel male connector to connect the female NPT thread on the regulator to the ¼-inch stainless steel tubing.

2) Install a length of ¼-inch stainless steel tubing to connect the canister to the connector fitting on the regulator. Install a ¼-inch stainless steel union tee at the end of the tubing and place an inert 10-mm septum in the ¼-inch nut on the side of the tee. Hand tighten the nut to seat the septum.

3) Leak check the entire system by capping the ¼-inch union tee outlet and pressurizing the system to the desired final canister pressure. Close the pressure regulator and monitor pressure changes. If the pressure drops, check all fitting connections.

4) Loosely attach the canister so that a complete seal is not achieved. With the valve closed, purge the entire system before use three times by opening and closing the pressure regulator at least three times, allowing the excess gas to escape past the incomplete seal. As an option, a stainless steel toggle shutoff valve may be installed between the canister and gas transfer tube to vent the purge gas.

5) Tighten the canister nut and wrap the transfer line and union tee with the cord heater and plug it into the active temperature controller. Activate the temperature controller and the system to equilibrate (for 5 to 10 minutes) at a setting of about 90°C.

6) Fill a glass syringe with the desired volume of high purity water for the canister size used. Open the canister valve slightly, insert the syringe into the septum and quickly inject the water.

7) Set the delivery pressure gauge on the regulator to the desired final delivery pressure and open the canister valve completely to allow the gas to fill the canister to the desired pressure.

8) When the final pressure is achieved, close the toggle valve, turn off the temperature controller, and close the regulator. Allow the canister valve to cool

before closing. The valve may become hot due to thermal conductivity. **Note: Do not close the canister valve when it is hot because the Viton® ring will be distorted and the valve damaged.**

9) Allow the canister to sit overnight for static equilibration.

10) Calculate the volume of water to be added using equation 2-1.

2.3.4.3.2 Calibration Standard Dilution Procedure

In order to prepare multiple concentration levels from the primary calibration standard for system calibration, the calibration gas may be diluted according to the basic procedure. This dilution procedure involves volumetric dilution based on pressure and is provided here as a simplified, proven means of accurately preparing diluted calibration standards. Calibration gases may also be diluted by dynamic flow dilution, or by using commercially available dilution systems.

The primary calibration standard is initially humidified as described in Section 2.3.4.3.1. The standard is diluted with ultra high purity nitrogen. Stainless steel fittings and chromatographic grade stainless steel tubing are used for all connecting lines and fittings. The primary calibration gas is transferred into a canister for dilution. The calibration gas must be humidified as described in Section 2.3.4.3.1. The initial pressure of the canister is measured. The canister is then diluted to the desired pressure and the final canister pressure is measured. Equilibration and static mixing are allowed to take place for at least 18 hours prior to analysis. The calculated dilution factor is used to determine the final concentration value for the calibration standard.

Dilution equipment is commercially available; a dilution apparatus can also be assembled in the laboratory. The dilution apparatus shown in Figure 2-4 requires the materials described below for assembly.

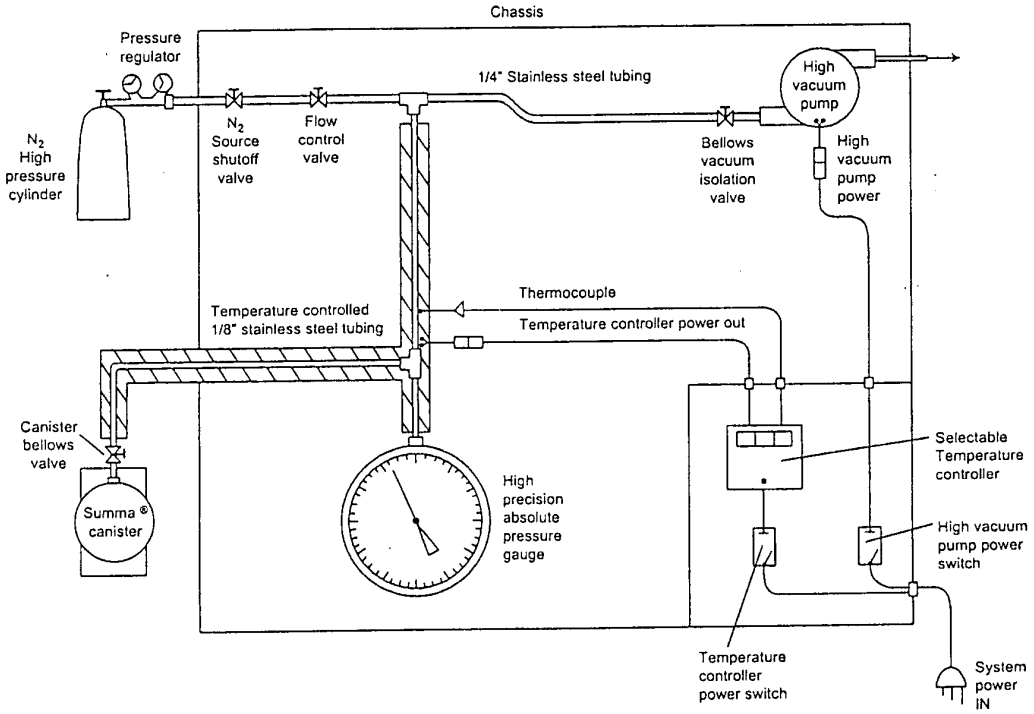


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Figure 2-4. Calibration Standard Dilution System

Ultra high purity grade nitrogen or air - 99.9999% purity or equivalent, hydrocarbon free.

Hydrocarbon trap - available from chromatographic supply vendors to remove trace impurities from high pressure cylinder gases.

¼-inch and ⅜-inch stainless steel tubing and union tees - chromatographic grade stainless steel, fused silica-lined stainless steel, or nickel are all recommended tubing material choices.

Cord heater - 110 VAC rated for metal contact, with a 300-watt heat capacity minimum.

Temperature controller - active temperature controller operating on a thermocouple feedback loop.

N_2 source shutoff valve - a stainless steel bellows assembly designed valve. When the shutoff valve is closed, the dilution gas cylinder and regulator are isolated during purge evacuation of the system. When the shutoff valve is opened, the valve is used to apply dilution gas to the system for controlled introduction.

Flow control valve - a stainless steel micro-metering needle designed valve, used to introduce dilution gas into the system at a controlled flow rate.

Bellows vacuum isolation valve - a stainless steel bellows assembly designed valve. When closed, the bellows vacuum valve isolates the high vacuum pump from the system. When opened, the valve is used to apply vacuum, from the high vacuum pump, to the system.

High precision absolute pressure gauge - a compound pressure gauge used to measure the pressure in the system and the calibration canister in both positive and negative pressure modes. The pressure gauge must be able to measure pressure from 40 psig to 5 mm Hg absolute.

High vacuum pump - An oil-less diaphragm pump used to apply vacuum to the system. The pump must be able to create vacuum to 5 mm Hg absolute.

Once a dilution system is available, the basic steps for standard dilution are described below:

1) Turn the temperature controller on and allow the system to equilibrate at 100° C. Open the main dilution gas cylinder valve. Set the delivery pressure using the

second gauge on the pressure regulator to approximately 10 pounds per square inch gauge (psig) pressure over the desired final canister pressure using the pressure control knob on the regulator.

2) Zero the absolute pressure gauge by adjusting to zero.

3) Connect the calibration gas canister to be diluted to the dilution apparatus.

4) Turn on the high vacuum pump and the active temperature controller.

5) With the canister bellows valve and the N_2 source shut-off valve closed, open the bellows vacuum isolation valve. Allow vacuum throughout the system to stabilize at the lowest vacuum achievable by the pump to purge all residual gas from the system.

6) Once stabilized, close the bellows vacuum isolation valve. Open the canister bellows valve and allow the pressure in the system to equilibrate to the initial canister pressure.

7) Measure the initial pressure of the canister from the absolute pressure gauge. Record the initial canister pressure.

8) Close the flow control valve and open the N_2 source shut-off valve. Slowly open the flow control valve while monitoring the absolute pressure gauge. The slower the canister is filled, the easier it is to meet the final target pressure.

9) Continue to fill the canister until the final set point is achieved. Allow the absolute pressure gauge needle to equilibrate before reading the final pressure of the canister.

10) Once the canister has filled to the desired pressure, close the flow control valve, the N_2 source shut-off valve, and lastly the canister bellows valve. Turn off the vacuum pump and the active temperature controller.

11) Disconnect the canister, close the main valve on the dilution gas cylinder.

12) The canister should sit for at least 18 hours before analysis or further dilutions are performed to allow for static mixing and equilibration.

Calculations—The following calculations are used to determine the target final pressure (Equation 2-2) and dilution factor (Equation 2-3). The calculations do not account for barometric pressure and temperature changes, which are expected to be negligible.

$$P_{fa} = \frac{C_i (P_i + 14.696)}{C_f} \qquad (2\text{-}2)$$

where:

P_{fa} = Final Diluted Absolute Pressure, psia

C_i = Initial Concentration, ppbC

P_i = Initial Gauge Pressure, psig

C_f = Final or Target Diluted Concentration, ppbC

14.696 = Atmospheric Pressure, psi

Example:

To dilute a 30 ppbC calibration standard in a canister with an original pressure of 5 psig (19.696 psia) to a final concentration of 15 ppbC, what is the target diluted pressure?

$$P_{fa} = \frac{30 \text{ ppbC } (5 \text{ psig} + 14.696 \text{ psi})}{15 \text{ ppbC}}$$

$$= 39.39 \text{ psia}$$

To convert psia to psig (the measured value), subtract 14.696:

39.39 psia - 14.696 = 24.70 psig

$$DF = \frac{P_{ia}}{P_{fa}} \qquad (2\text{-}3)$$

where:

P_i = Initial Gauge Pressure, psig

P_{ia} = Initial Absolute Pressure, psia = P_i + 14.696

P_f = Final Gauge Pressure, psig

P_{fa} = P_f + 14.696

DF = Dilution Factor

P_{fa} = Final Absolute Pressure, psia

Example:

Continuing with the example above, what is the dilution factor for the 30 ppbC standard which was diluted to a final pressure of 24.70 psig? What is the final concentration of the standard?

$$P_{ia} = P_i + 14.696$$
$$= 5 \text{ psig} + 14.696$$
$$= 19.696 \text{ psia}$$

$$P_{fa} = P_f + 14.696$$
$$= 24.7 \text{ psig} + 14.696$$
$$= 39.40 \text{ psia}$$

$$DF = \frac{P_{ia}}{P_{fa}}$$
$$= \frac{19.696}{39.40}$$
$$= 0.499$$

$$\text{Standard Concentration} = C_i * DF$$
$$= 0.499 * 30 \text{ ppbC}$$
$$= 14.97 \text{ ppbC}$$

where:

C_i = Initial concentration, ppbC

2.3.5 Column Configurations

The chromatographic column configurations generally used for VOC monitoring programs incorporate single-column, single-detector, or dual-column, dual-detector applications. The simplest analytical column configuration involves the use of a single column with a single FID. However, this configuration imposes limitations on the overall separation of the selected target VOCs. Analyzing the full range of C_2 through C_{12} target hydrocarbons using a single analytical column may result in less than optimal separation for either the light or heavy hydrocarbons, depending on the analytical column chosen. For example, to improve resolution of the C_2 through C_4 hydrocarbons, a thick liquid-phase fused silica or Porous Layer Open Tubular (PLOT) column at sub-ambient column oven temperatures may be desirable. However, PLOT columns generally result in less than optimal resolution of the C_5 through C_{12} hydrocarbons. Likewise, PLOT columns increase retention times of the C_{10} through C_{12} hydrocarbons and require longer sample analysis time. If the heavier hydrocarbons are not eluted from the thick phase or PLOT columns, the TNMOC measurement may be affected, and carryover and ghost peaks may result.

In order to improve the separation characteristics for the light hydrocarbons (C_2 through C_4) as well as the heavier hydrocarbons (C_5 through C_{12}), a dual-column, dual-detector configuration should be considered. In this case, two columns can be judiciously selected to provide optimal separation of both light and heavy hydrocarbons without sub-ambient column oven temperatures. Because both columns are generally contained in one gas chromatographic oven for automated applications, columns must be selected that will provide the desired separation with a single GC oven temperature program. Dual column systems may be configured with the analytical columns in parallel, operating either concurrently or sequentially. Pre-column

and post-column switching valves and the Deans®[24] switch have been used to accommodate these dual-column configurations.

2.3.6 Column Selection

Column selection for analysis of the target VOCs is dictated by the target compound resolution requirements and other practical and cost considerations, such as the need to minimize cryogen consumption and total sample analysis time. Selecting columns that will provide the desired separation of the C_2 through C_4 hydrocarbons without cooling the column oven to sub-ambient temperature decreases cryogen consumption significantly.

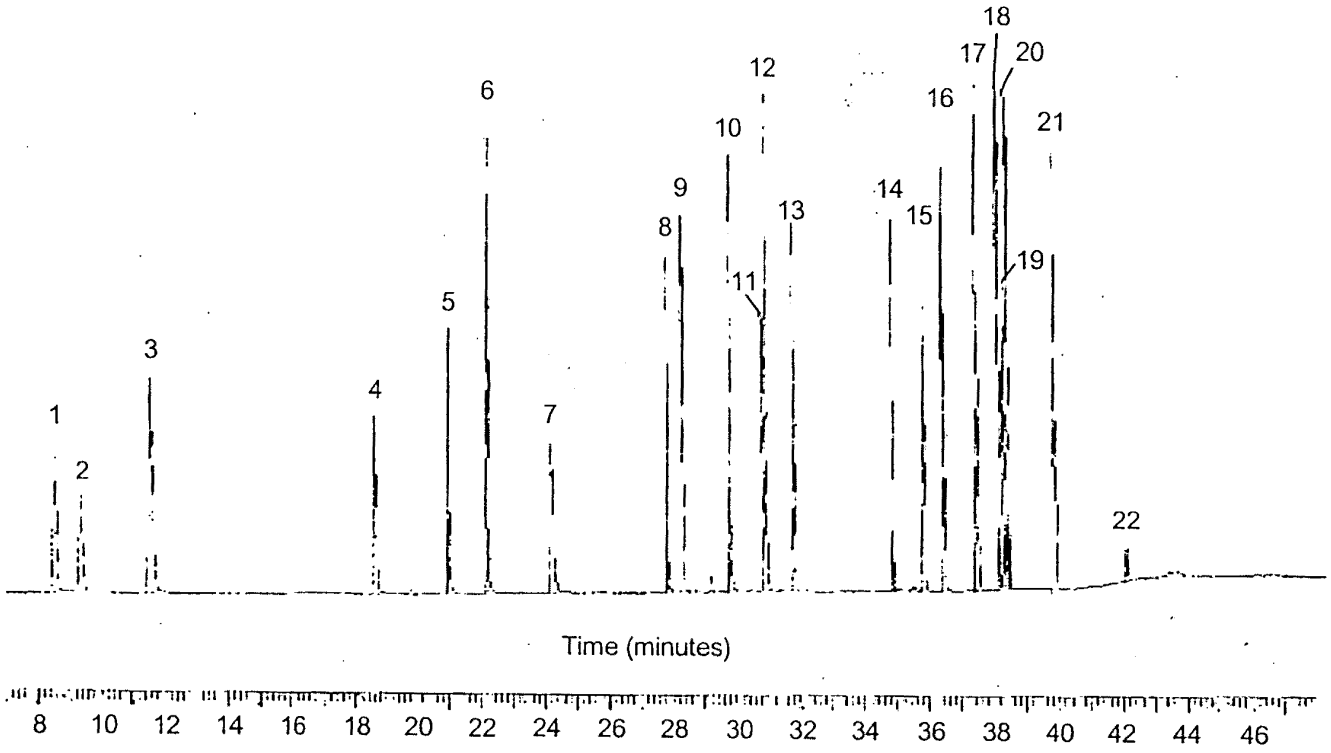
Several columns suitable for either single- or dual-column applications are discussed below. The columns described have been used in either a single- or dual-column configuration in conjunction with a single- or dual-FID for separation of the C_2 through C_{12} hydrocarbons. The column conditions described are recommendations provided from laboratory applications or conditions determined by the manufacturer to provide adequate separation of the VOCs of interest. However, these conditions must be evaluated and optimized to verify acceptable peak resolution prior to use.

The C_4 through C_{12} hydrocarbons may be resolved using a 0.32 or 0.22 millimeter (mm) inside diameter (I.D.), 50 meter (m) long SGE, Incorporated BP1 fused silica column with a 1-micrometer dimethyl polysiloxane coating. This column generally does not provide adequate separation of the C_2 and C_3 hydrocarbons even at sub-ambient column oven temperatures. However, the column can provide adequate separation of the C_2 and C_3 hydrocarbons if the coating is 3 μm thick and Electronic Pressure Control is used along with sub-ambient column oven temperatures. Under these conditions, a single column can be used for all of the target hydrocarbons. Other compatible columns include the J&W DB™-1, Hewlett-Packard HP-1, Chrompack CP-SIL 5 CB, Restek RTx-1, and the Supelco SPB-1. The DB™-1 column has been historically and extensively used in ambient air applications. The SGE BP1 column can be used in conjunction with a 0.32 mm I.D., 50 m, Porous Layer Open Tubular (PLOT) fused silica

analytical column with a 5-micrometer Hewlett-Packard Al_2O_3/KCl or Al_2O_3/Na_2SO_4 coating. The Al_2O_3/Na_2SO_4 column is slightly more polar than the Al_2O_3/KCl and provides optimal resolution of the C_4 hydrocarbons. The PLOT column provides acceptable light hydrocarbon separation under the same column oven temperature program conditions used for the DB™-1 column but does not provide complete separation and elution of C_9 through C_{12} hydrocarbons. Other compatible columns include the J&W GS-Alumina™ Al_2O_3/KCl and Al_2O_3/Na_2SO_4. However, alumina PLOT columns from different manufacturers may not be directly interchangeable and may require some method modification due to the variation in column selectivity.

Because the alumina layer is active, PLOT Al_2O_3 analytical columns are very susceptible to polar compounds such as water, which causes column deactivation and shifting of peak retention times. Moisture and other polar compounds must be removed from the sample stream using a membrane drier or other drying device. If manual sample analysis using a single PLOT Al_2O_3 column is performed, sequential analyses or the use of separate GC systems may be considered to optimize and obtain complete C_2 through C_{12} separation and elution. Figures 2-5 and 2-6 are example chromatograms of retention time calibration standards containing the PAMS target compounds as eluted from the 0.32 mm I.D., 50 m, 5 micrometer, Al_2O_3/Na_2SO_4 PLOT and 0.22 mm I.D., 50 m, 1 micrometer, SGE, Incorporated BP1 columns. Since these columns have been successfully used by others, users should give primary consideration to these column types during their column selection process. Figure 2-7 shows a representative ambient air sample analyzed on a PLOT column; Figure 2-8 shows the same sample analyzed on a BP1 column. Peaks are numbered on the chromatograms, identified peaks are listed in Table 2-4.

Stationary phase selectivity is neither completely understood nor easily explained. Using a simplification, selectivity can be considered the ability of the stationary phase to differentiate between two compounds by virtue of a difference in their chemical and/or physical properties. Stationary phase and solute factors such as polarizability, solubility, magnitude of dipoles and hydrogen bonding influence selectivity. In many cases, more than one factor will be

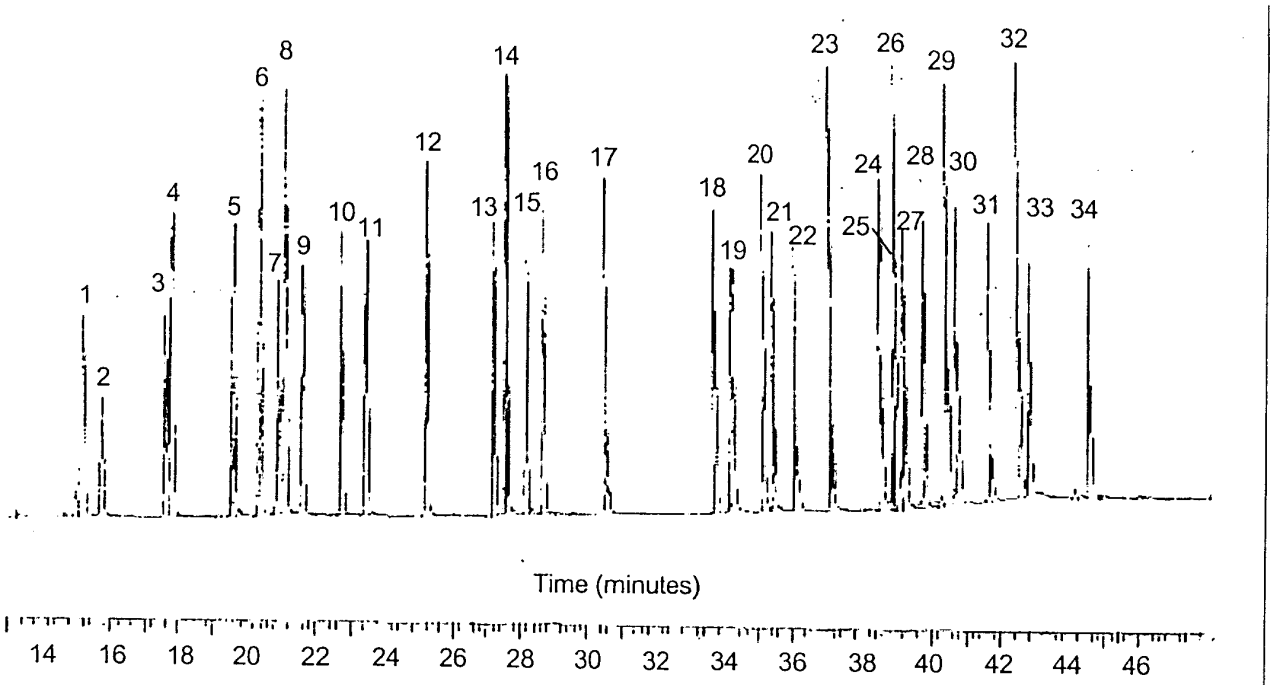


Column:	HP Al_2O_3/Na_2SO_4 50m x 0.32mm x 5µm
Carrier:	Helium, ~2.5ml/min
Initial Temp:	45°C, 15 minutes
Rate 1:	5°C/min
Temp 2:	170°C
Rate 2:	15°C/min
Final Temp:	200° C, 6 minutes

Peak #	AIRS Code	Compound Name	Peak #	AIRS Code	Compound Name
1	43202	Ethane	12	43221	Isopentane
2	43203	Ethylene	13	43220	n-Pentane
3	43204	Propane	14	43226	trans-2-Pentene
4	43205	Propylene	15	43224	1-Pentene
5	43214	Isobutane	16	43227	cis-2-Pentene
6	43212	n-Butane	17	43244	2, 2-Dimethylbutane
7	43206	Acetylene	18	43284	2, 3-Dimethylbutane
8	43216	trans-2-Butene	19	43263	2-Methylpentane
9	43280	1-Butene	20	43230	3-Methylpentane
10	43217	cis-2-Butene	21	43243	Isoprene
11	43242	Cyclopentane	22	43246	2-Methyl-1-Pentene

o:\g\morr\3797\pams\compoun1.ppt

Figure 2-5. Example Chromatogram for the PAMS Target Compounds from the PLOT Analytical Column



Column:	SGE, Inc. BPI, 50m x 0.22mm x 1µm
Carrier:	Helium, ~2.5ml/min
Initial Temp:	45°C, 15 minutes
Rate 1:	5°C/min.
Temp 2:	170°C
Rate 2:	15°C/min.
Final Temp:	200°C, 6 minutes

Peak #	AIRS Code	Compound Name
1	43231	Hexane
2	N/A	Unknown
3	43262	Methylcyclopentane
4	43247	2, 4-Dimethylpentane
5	45201	Benzene
6	43248	Cyclohexane
7	43263	2-Methylhexane
8	43291	2, 3-Dimethylpentane
9	43249	3-Methylhexane
10	43250	2, 2, 4-Trimethylpentane
11	43232	n-Heptane
12	43261	Methylcyclohexane
13	43252	2, 3, 4-Trimethylpentane
14	45202	Toluene
15	43960	2-Methylheptane
16	43253	3-Methylheptane
17	43233	n-Octane

Peak #	AIRS Code	Compound Name
18	45203	Ethylbenzene
19	45109	m/p-Xylene
20	45220	Styrene
21	45204	O-Xylene
22	43235	n-Nonane
23	45210	Isopropylbenzene
24	45209	n-Propylbenzene
25	45212	m-Ethyltoluene
26	45213	p-Ethyltoluene
27	45207	1, 3, 5-Trimethylbenzene
28	45211	o-Ethyltoluene
29	45208	1, 2, 4-Trimethylbenzene
30	43238	n - Decane
31	45225	1, 2, 3-Trimethylbenzene
32	45218	m-Diethylbenzene
33	45219	p-Diethylbenzene
34	43954	n-Undecane

o:\g/mon/3797/pams/compoun2.ppt

Figure 2-6. Example Chromatogram for the PAMS Target Compounds from the BP1 Analytical Column

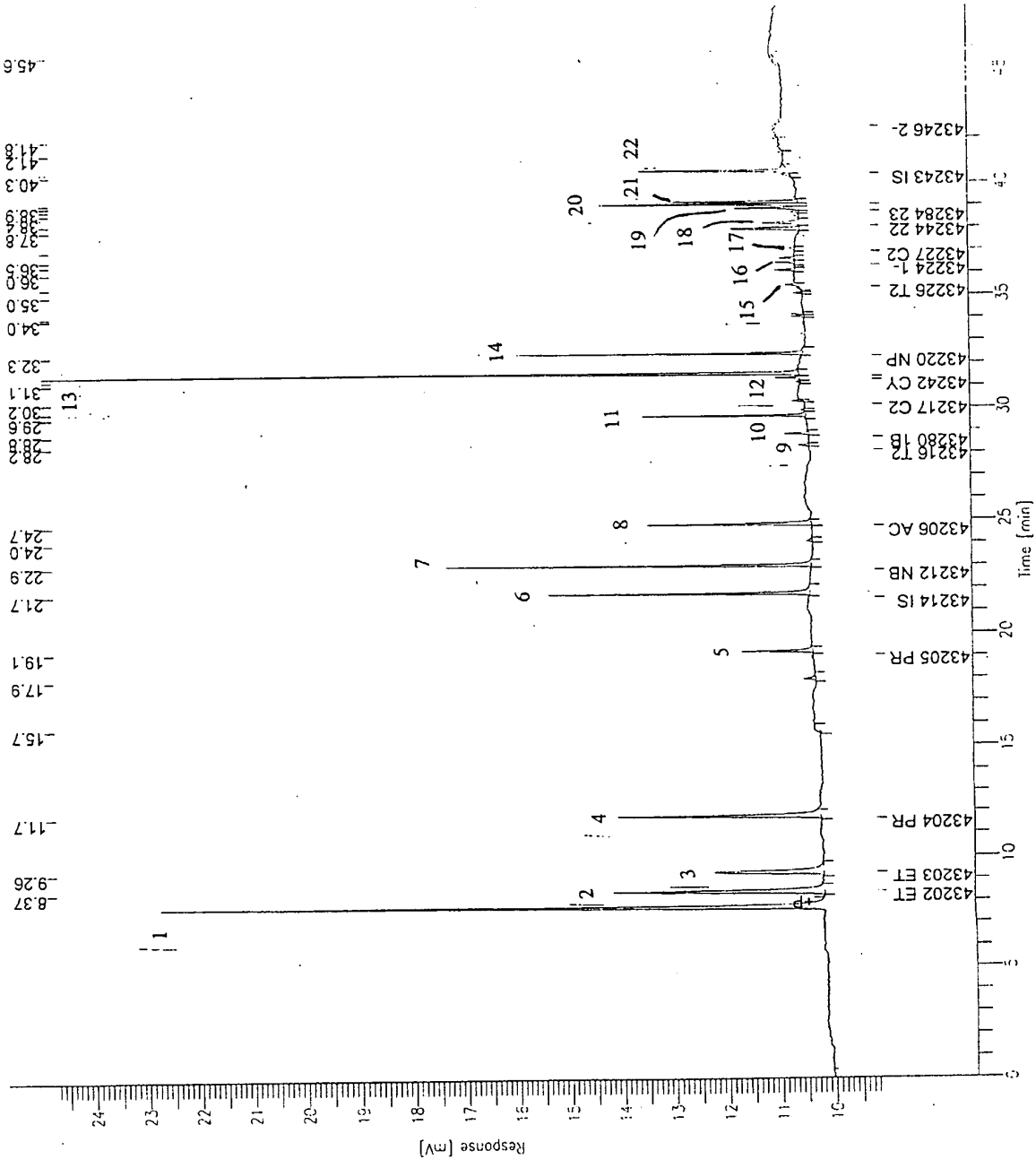


Figure 2-7. Representative Ambient Air Sample Analyzed on a PLOT Column

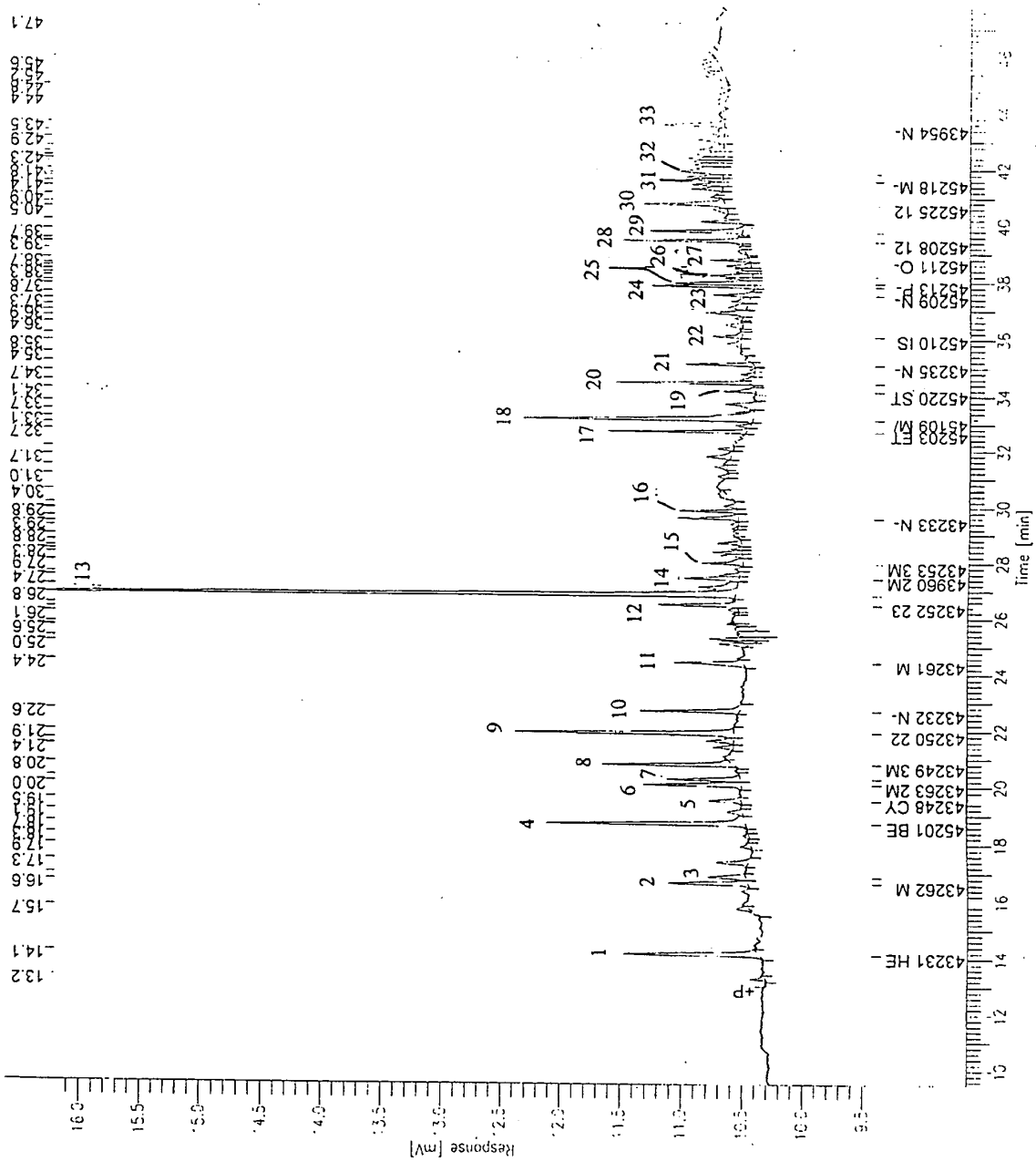


Figure 2-8. Representative Ambient Air Sample (same as Figure 2-6) Analyzed on a BP-1 Column

Table 2-4. Peak Identifications, Ambient Air Sample

PLOT Column		BP1 Column	
Peak Number	**Peak Identification**	**Peak Number**	**Peak Identification**
1	ethane	1	hexane
2	unidentified	2	methylcyclopentane
3	ethene	3	2,4-dimethylpentane
4	propane	4	benzene
5	propylene	5	cyclohexane
6	isobutane	6	2-methylhexane
7	*n*-butane	7	2,3-dimethylpentane
8	acetylene	8	3-methylhexane
9	*trans*-2-butene	9	2,2,4-trimethylpentane
10	1-butene	10	*n*-heptane
11	unidentified	11	methylcyclohexane
12	*cis*-2-butene	12	2,3,4-trimethylpentane
13	cyclopentane	13	toluene
14	isopentane	14	2-methylheptane
15	*trans*-2-pentene	15	3-methylheptane
16	1-pentene	16	*n*-octane
17	*cis*-2-pentene	17	ethylbenzene
18	2,2-dimethylbutane	18	*m/p*-xylene
19	2,3-dimethylbutane	19	styrene
20	2-methylpentane	20	*o*-xylene
21	3-methylpentane	21	*n*-nonane
22	isoprene	22	isopropylbenzene
		23	*n*-propylbenzene
		24	*m*-ethyltoluene
		25	*p*-ethyltoluene
		26	1,3,5-trimethylbenzene
		27	*o*-ethyltoluene
		28	1,2,4-trimethylbenzene
		29	*n*-decane
		30	1,2,3-trimethylbenzene
		31	*m*-diethylbenzene
		32	*p*-diethylbenzene
		33	*n*-undecane

significant, so there will be multiple selectivity influences. Unfortunately, information about most compound characteristics, such as the strength of hydrogen bonding or dipoles, is not readily available or easy to determine. This lack of physical data makes it difficult to accurately predict and explain the separation obtained for a particular column and set of compounds. Some generalizations, however, can be made. The DB1 nonpolar phase (dimethyl polysiloxane) is the most nonpolar siloxane stationary phase available. In most cases, compounds will elute from this column primarily in order of increasing boiling point. However, both vapor pressure and solubility in the stationary phase influence the exact elution order.

PLOT chromatography is accomplished through the gas/solid adsorption interactions between the solutes and the solid adsorbent coated on the column tubing wall. The aluminum oxide (Al_2O_3) surface is deactivated using KCl or Na_2SO_4. Stationary phase polarity is based on the relative retention of saturated and unsaturated hydrocarbons. The more polar column will result in unsaturated compounds being more retained relative to the saturated hydrocarbons. The Na_2SO_4 deactivation of the Al_2O_3 results in a slightly more polar column than the KCl deactivation.

There are some alternative columns that can be used to separate C_2 through C_{12} hydrocarbons for both single- or dual-column approaches. The column selection process should be based on the capability of the column to separate the VOCs listed in Table 2-1 in conjunction with desired overall sample analysis time and cryogen use. The manufacturer-recommended conditions and carrier gas flow rates should be evaluated and optimized to verify acceptable peak resolution prior to use. When choosing alternate columns, the user should consult directly with the analytical column manufacturer for advice regarding column characteristics, optimum gas chromatographic oven temperature programs, carrier gas flow rates, and other operational considerations.

The following columns are alternatives for single-column, C_2 through C_4 hydrocarbon separation and may require sub-ambient temperature conditions to achieve adequate separation:

1. J&W DB™-1 with a 5-micron dimethyl siloxane phase thickness, an internal diameter of 0.32 mm, and a length of 60 m. The recommended oven temperature program is -60°C for 2 minutes then to 180°C at 8°C per minute. The final oven temperature is maintained for 13 minutes for a total analytical run time of 45 minutes.

2. J&W GS-Q® fused silica PLOT capillary column with an internal diameter of 0.53 mm and a length of 30 m. The recommended oven temperature program is 40°C for 4 minutes to 200°C at 10°C per minute. The final oven temperature is maintained for 5 minutes for a total analytical run time of 25 minutes. The GS-Q® column is not affected by water.

The following columns are alternatives for single-column, C_5 through C_{12} hydrocarbon separation and may require sub-ambient oven temperature conditions to achieve adequate separation:

1. Restek® RTx-502.2 capillary fused silica column with a 3-micron phase thickness, an internal diameter of 0.53 mm, and a length of 105 m. The recommended GC oven temperature program is 35°C for 10 minutes to 200°C at 4°C per minute. The final oven temperature is maintained for 7 minutes, which results in a total analytical run time of 58 minutes. This column is capable of separating the C_4 through C_{12} hydrocarbons without the need for sub-ambient column oven temperatures.

2. J&W DB™-624 capillary fused silica column with a 3-micron stationary phase thickness, an internal diameter of 0.53 mm, and a length of 75 m. The recommended oven temperature program is 35°C for 8 minutes to 200°C at 10°C per minute. The final temperature of 200°C is maintained for 3 minutes, which results in a total analytical run time of 27.5 minutes.

3. Restek® RTX-1 capillary fused silica column with a 3-micron dimethylsiloxane phase thickness and an internal diameter of 0.32 mm and a length of 60 m. The recommended oven temperature program is -25°C for 4 minutes then to 175°C at 4°C per minute, then to 220°C at 22°C per minute. The final oven temperature is maintained for 5 minutes for a total run time of about 60 minutes. The Electronic Pressure Control program is 18.3 psi for 5 minutes then to 37.5 psi at 0.35 psi/minute. Total program time is about 61 minutes.

A combination of these light and heavy hydrocarbon separation columns may be used to accommodate dual-column approaches.

2.3.7 *Pre-measurement Chromatographic System Verification*

Prior to making speciated VOC measurements using an automated GC system, the level of system operation must be thoroughly documented. Information collected during this process is important in characterizing the system operation and establishing a baseline for performance. The information from the pre-measurement system verification is used to determine system specific target analyte retention times, relative retention times, identification of co-eluting compounds and matrix effects, internal standard retention times, interferences, and detection limits.

2.3.7.1 Retention Times and Relative Retention Times

The rigorous sampling frequency requirements and large data sets associated with PAMS require the use of an automated GC system with FID, and presume the commercial availability of such systems. These systems must rely on the practical use of retention times and relative retention times for qualitative peak identification. Commercial GC/FID systems are designed to provide stable system parameters that ensure adequate peak identification based on the use of retention times.

Retention time is the time at which the component elutes from the analytical column and reaches the detection device. The retention of a compound will be determined by its distribution equilibrium between the stationary and mobile phases, i.e., the distribution ratio. Retention time units are typically expressed in minutes and this time is specific to the conditions of the GC system used.

When dealing with complex target analyte lists, as in the case of PAMS measurements, preparing multiple retention time standards that contain 10-15 target analytes that are of known retention order and well separated by retention time will simplify peak identification and retention time assignment. These standards must be analyzed to determine specific retention times for the target compounds and resolve chromatographic issues relative to the instrument

conditions, analytical column(s), and chromatographic conditions used. Retention time is widely applied in chromatography and based on the information gathered from standards. When the retention times for a GC system are verified, it is important for the system to be operated for a period to allow equilibration and retention time stabilization to occur. Several standards should be analyzed over a period of days to assess retention time variability and system stability. The retention time variability is used to establish retention time windows for each component. It is very important that standards be prepared in humidified air, at a relative humidity similar to the samples being analyzed.

The identification of sample components is determined by matching the retention times of the components in the standard with those in the sample. This procedure provides the chromatographer with a certain degree of confidence that the correct peak has been accurately identified. Peak identification by retention time is adequate for the PAMS network requirements. A compound's retention time is characteristic, though not unique. It is, therefore, possible for other compounds to have the same retention time. The presence of co-eluting compounds or missed peak identifications cannot be completely excluded. Periodic confirmation of peak identification and quantification using more definitive techniques, such as GC/MS, is encouraged.

Retention times are typically stable and reproducible, but they are subject to system variability. To account for any retention time variations, relative retention time (RRT) can be used to aid in assigning peak identifications. Many commercial GC systems incorporate the use of relative retention times for peak identification in their data acquisition and processing software. On most commercial GC systems, the use of RRT for peak identification is easy to implement. An adjusted or relative retention time can be determined by using both reference or internal standard peaks. Reference peaks are those components of the sample that are typically present in the sample matrix (reference peaks of opportunity). Internal standard peaks are components subsequently added to the sample that are uncommon to the sample matrix. The relative retention time of a target compound (a), as compared with a reference compound (b), may be calculated as:

$$RRT = \frac{RT_a}{RT_b} \qquad (2\text{-}4)$$

where:

RT_a = retention time of the target compound

RT_b = retention time of the reference peak

The relative retention time of a compound determined in this manner will vary with temperature and the analytical column stationary phase, but should otherwise be independent of other analytical conditions. The relative retention time method of peak identification works well when the target compound elutes relatively close to the reference peak used and retention time shifting is linear. The use of reference peaks in several retention time windows is only recommended to compensate for retention time shifting that is not linear. The use of too many reference peaks may actually compromise the ability of the data system to adequately identify the target peaks consistently.

A retention time reference peak should be chosen that;

- Is always or typically present in the sample matrix;
- Is in the same general retention time area or carbon number range of the chromatogram;
- Shows chromatographic behavior similar to target components (sharp peak shape); and
- Is well separated from other components in the sample matrix.

Suggested retention time reference peaks include propane, toluene, benzene, and butane, or other compounds appropriate to the individual PAMS site.

2.3.7.2 Internal Standards

When GC analysis is performed on a continuous basis at an often unattended or remote site, fluctuations in ambient temperature and other factors can cause variations in instrument performance and chromatographic retention times. Changes in ambient conditions can cause small changes or variations in carrier gas flow rate, column temperature, detector response, sample injection volumes, and sample moisture content. Use of internal standards can help to minimize the influence of GC system variability. Internal standards are often also used as reference peaks for determining relative retention times.

The internal standard should be added to the cryofocusing or adsorbent sample collection system, concurrent with sample collection, to minimize the effects of the sample matrix. The chief difficulty in using internal standards for VOC analysis lies in finding an internal standard that does not interfere with the sample constituents. Characteristics that must be considered when choosing a suitable internal standard include:

- Components that are uncommon in ambient air;
- Ease and reproducibility in handling and introducing into the GC system;
- Similar in chemical and physical properties to those compounds being analyzed;
- Moderate volatility and low vapor pressure comparable to the expected retention times and concentrations of the sample hydrocarbons;
- Does not interfere with the measurement method;
- Complete resolution from all other components present in the sample;
- Stable under the conditions and method used; and
- Does not react with components of the measurement system.

Perfluorotoluene (PFT) is a compound that meets these characteristics and has been used as an internal standard for air monitoring programs.

Separation of the internal standard compound from other compounds normally found in the sample must be accomplished using the measurement system and methods implemented by the user to accomplish sample analyses. Typical ambient air samples are very complex and contain numerous components. Verification of the internal standard performance and retention time characteristics using the GC system chosen must be determined using actual ambient air samples. A suitable internal standard can be analyzed concurrently with the sample to adjust for variations in retention time and detector response.

2.3.7.3 Identification of Co-Eluting Compounds and Matrix Effects

Another important part of pre-measurement chromatographic system verification is the determination and effect of possible co-eluting compounds and other sample matrix effects on the ability to find reference peaks, make peak identification, and ultimately to quantitate target analytes.

Blank samples that contain humidified zero air should be analyzed to establish the GC system background and determine the level of contamination or artifacts. Blank or zero air samples should not contain the target VOCs at a concentration greater than the detection limit. Any significant levels of contamination or artifacts that interfere with the retention times of target analytes must be addressed or documented prior to sample analysis. Information from the analysis of standards containing target analytes can then be used to determine where co-eluting compounds may occur. Co-elution issues can be resolved by optimizing the chromatographic conditions of the system, such as carrier gas linear velocity and column oven temperature.

Further information regarding co-eluting compounds in samples not identified by zero air analyses may be obtained using GC/MS. When used under similar conditions (column type, temperature program, etc.), the GC/MS provides valuable information to aid the user in confirming peak identification and determining the presence of co-eluting compounds and other unknowns. When GC/MS is used for confirmation, it is important to ensure that the system sensitivity or detection limits are equivalent to the O_3 precursor GC/FID system being used.

2.3.7.4 Detection Limits

The development of methods to measure trace levels of organic compounds in ambient air and the need for the ability to measure extremely low concentration levels for risk assessment purposes requires that the analytical system detection limits for the target compounds be established for the analytical system used. The analytical detection limit must meet the measurement quality objectives given in Section 2.8. The detection limit is one of the most important performance characteristics of an analytical system. The GC system detection limit should not be determined until a complete, specific, and well defined analytical method has been developed. All sample processing steps used in the analytical method must be included in the experimental determination of the detection limit. Refer to Section 2.8 for guidance on the approach to establishing VOC detection limits for PAMS. If the analytical method detection limit does not meet the quality objectives, the sensitivity of the GC system and methodology used may not be adequate and should be re-evaluated and improved prior to use for O_3 precursor monitoring programs.

2.4 Automated Method for Collecting and Analyzing Volatile Organic Compound Ozone Precursor Samples

The minimum monitoring network requirements for enhanced O_3 monitoring are described in Section 4.4 of 40 CFR Part 58, Subpart E, Appendix D, and are also discussed in Section 2.1 of this document. The rigorous sampling frequency requirements of enhanced O_3 monitoring (e.g., eight 3-hour samples every day during the monitoring period) makes automated GC methodology a viable, cost-effective approach for obtaining VOC measurements at all sites within a network. An automated GC system offers an additional advantage in its inherent capability to provide short-term (e.g., 1-hour) measurements on a continuous basis for long time intervals.

The following description of automated methodology is based on currently available commercial automated GC systems and is described in general terms. The intent is to provide

guidance on the configuration and operation of automated GC systems, not to serve as a Standard Operating Procedure (SOP). Alternative approaches using custom fabricated automated systems are acceptable. This guidance should be used to define equipment specifications and prepare system specific SOPs consistent with the 40 CFR Part 58 enhanced O_3 monitoring requirements. The users must recognize that they are responsible for optimization and characterization of the critical parameters for their specific GC system (consistent with the manufacturers' instructions, if applicable).

The GC system must be capable of automated sample collection, analysis, and data acquisition on site and must be housed in a temperature-controlled shelter. The primary components of an automated GC are a sample introduction system, sample conditioning system (for moisture removal), sample concentration system (for sample enrichment), cryofocusing trap (as an option for improving peak shape and resolution), gas chromatograph with FID(s), and a data acquisition and processing system. Commercially available systems incorporate many variations of the primary components of an automated GC system.

The purpose of Section 2.4 is to describe the sample collection, sample analysis, system operation, system calibration, and system specifications for an automated GC system. The sample probe and manifold, sample introduction, sample conditioning, and sample concentration systems are discussed in Sample Collection, Section 2.4.1. Sample cryofocusing, gas chromatography, and data acquisition and processing are discussed in Sample Analysis, Section 2.4.2. This guidance should be used to define automated GC specifications for procurement and to develop and implement a network monitoring program consistent with the 40 CFR Part 58 enhanced O_3 monitoring requirements.

2.4.1 Sample Collection

Samples collected for automated analysis should represent a time-integrated average for the required sampling period. In the case where an integrating canister is used to collect the sample, the canister should be filled at a constant flow rate over the full integration period minus

the time required to transfer a sample to the primary trap and purge and evacuate the canister. In the case where the sample is collected directly onto the primary concentration trap, the sample should be collected at a constant flow rate for the full integration period minus the time required to desorb the sample onto a secondary trap or onto the analytical column and perform system operations to accommodate the next sample collection. The minimal sample integration time required to constitute a 1-hour sample is 40 minutes. Additional provisions must be made to meet the 24-hour sample requirement. A manual approach to 24-hour sample collection and analysis is discussed in Section 2.5.

The O_3 precursor compounds are collected from a sample manifold with a probe and introduced into the automated GC system. Water may be removed from the sample stream as discussed in Section 2.3.3 and then the VOCs concentrated onto a primary sample collection trap. The concentrated sample is thermally desorbed onto a secondary cryofocusing trap (optional) or onto the head of the cooled GC column to focus the desorbed sample into a small volume or "plug." The sample volume is then desorbed for analysis by the GC/FID system.

2.4.1.1 Sample Probe and Manifold

A sample probe and manifold assembly should be used to provide a representative air sample for collection and subsequent analysis. Sample probe and manifold assemblies are commercially available or can be custom fabricated. Examples of typical sample probe and manifold assemblies are presented below. If automated calibration techniques that periodically flood the manifold with calibration standards are to be applied for the criteria pollutants, a separate manifold would be required to support the VOC and carbonyl components of the PAMS program.

The sample probe is constructed of glass that is approximately 1 inch in outside diameter (O.D.). The inlet of the sample probe is configured with an inverted funnel, approximately 4 inches O.D. The sample manifold is constructed of glass, approximately 1 and ½ inches O.D. The manifold has ports used for sample distribution. The number of ports located

on the manifold must be equal to or greater than the total number of monitoring systems to which sample will be delivered. To reduce the potential for bias, the port nearest to the inlet of the manifold should be reserved for VOC sampling.

Teflon® bushings are used to connect sample lines to the manifold. Because the manifold and ports are constructed of glass, care must be taken to not place excessive stress on the assembly to avoid breakage. For VOC sampling, the sample lines should be constructed of 1/8 inch O.D. stainless steel tubing. The 1/8 inch tubing is flexible and will accommodate the flow rates typically associated with VOC sample collection. The sample lines should be kept as short as possible to reduce sample transfer time.

A blower and bleed adapter are located at the exit end of the sample manifold. The blower is used to pull sample air through the probe and manifold and the bleed adapter is used to control the rate at which the sample air is pulled through the manifold. An excess of sample air is pulled through the sample probe and manifold to prevent back diffusion of room air into the manifold and to ensure that the sample air is representative of outside ambient air. Sample air flow through the sample probe and manifold should be at least two times greater than the total air flow being removed for collection and analysis by all systems on the manifold.

The vertical placement of the sample probe and inlet funnel should be at a height of 3 to 15 meters above ground level. Because the O_3 monitoring requirements involve multiple-pollutant measurements, this range serves as a practical compromise for probe position. In addition, the probe inlet should be positioned more than 1 meter, both vertically and horizontally, away from the housing structure. The probe inlet should be positioned away from nearby obstructions such as a forest canopy or building. The vertical distance between the probe inlet and any obstacle should be a least two times the height difference between the obstacle and the probe inlet. Unrestricted air flow across the probe inlet should occur within an arc of at least 270 degrees. The predominant and second most predominant wind direction must be included in this arc. If the probe inlet is positioned on the side of a building, a 180 degree clearance is required. More specific details of probe positioning are presented in the "PAMS Implementation

Manual."[25] The glass probe should be reinforced or supported along the straight vertical axis of the assembly. Typically this support is provided by routing the probe shaft through a rigid section of metal or plastic tubing that is secured to the housing structure.

The manifold can be positioned in either a horizontal or vertical configuration. Figure 2-9 presents the manifold assembly in the vertical configuration. Figure 2-10 presents the manifold assembly in the horizontal configuration. If the horizontal configuration is used, the sample ports must point upward so that material that may be present in the manifold will not be transferred into the sample lines.

With continuous use the sample probe and manifold can accumulate deposits of particulate material and other potential contaminants. The sample probe and manifold should be cleaned to remove these materials. The recommended frequency for cleaning is quarterly. To clean the assembly, disconnect the sample lines and blower from the manifold. The sample lines and blower are not cleaned. For safety, electric power to the blower should be terminated until the cleaning process is completed. Disassemble the individual components by disconnecting the probe, manifold, collection bottle, and coupling devices from each other. The individual components should then be cleaned using heated high purity distilled water and a long handled bottle brush. The components should then be rinsed with the distilled water and allowed to dry completely before reassembling. If required, mild glass cleaner or detergent can be used to clean particularly dirty components. However, care should be taken to select cleaners and detergents that are advertised to have low organic compound content and the number of rinses performed should be increased to ensure that all associated residues are removed.

2.4.1.2 Sample Introduction

The air sample can be introduced to the automated GC system directly from the air sample manifold using a mass flow controller or other flow control device at a constant flow rate over the prescribed sample integration time. As an alternative, the air sample may be collected into an integrating canister at a constant flow rate over the prescribed sample integration time,

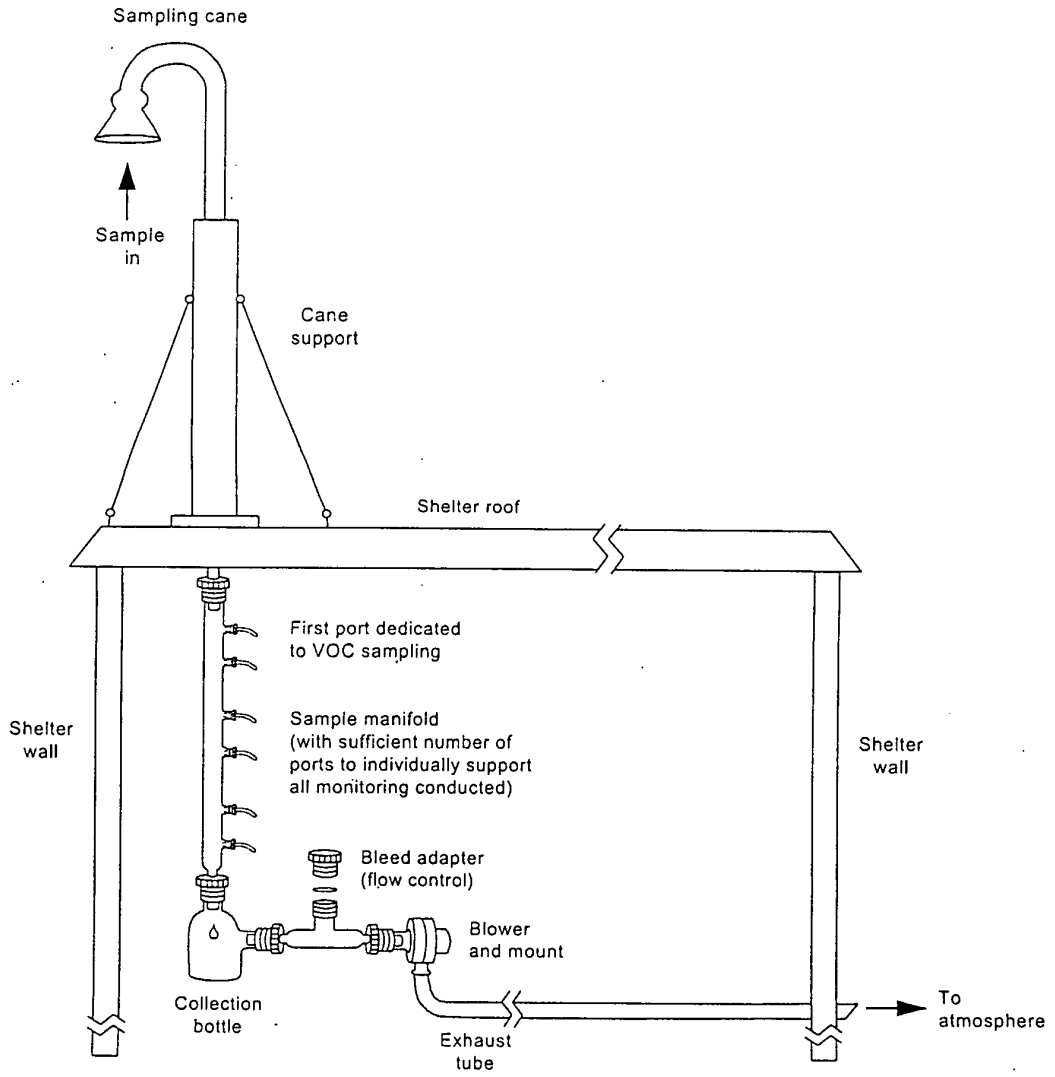


Figure 2-9. Vertical Configuration

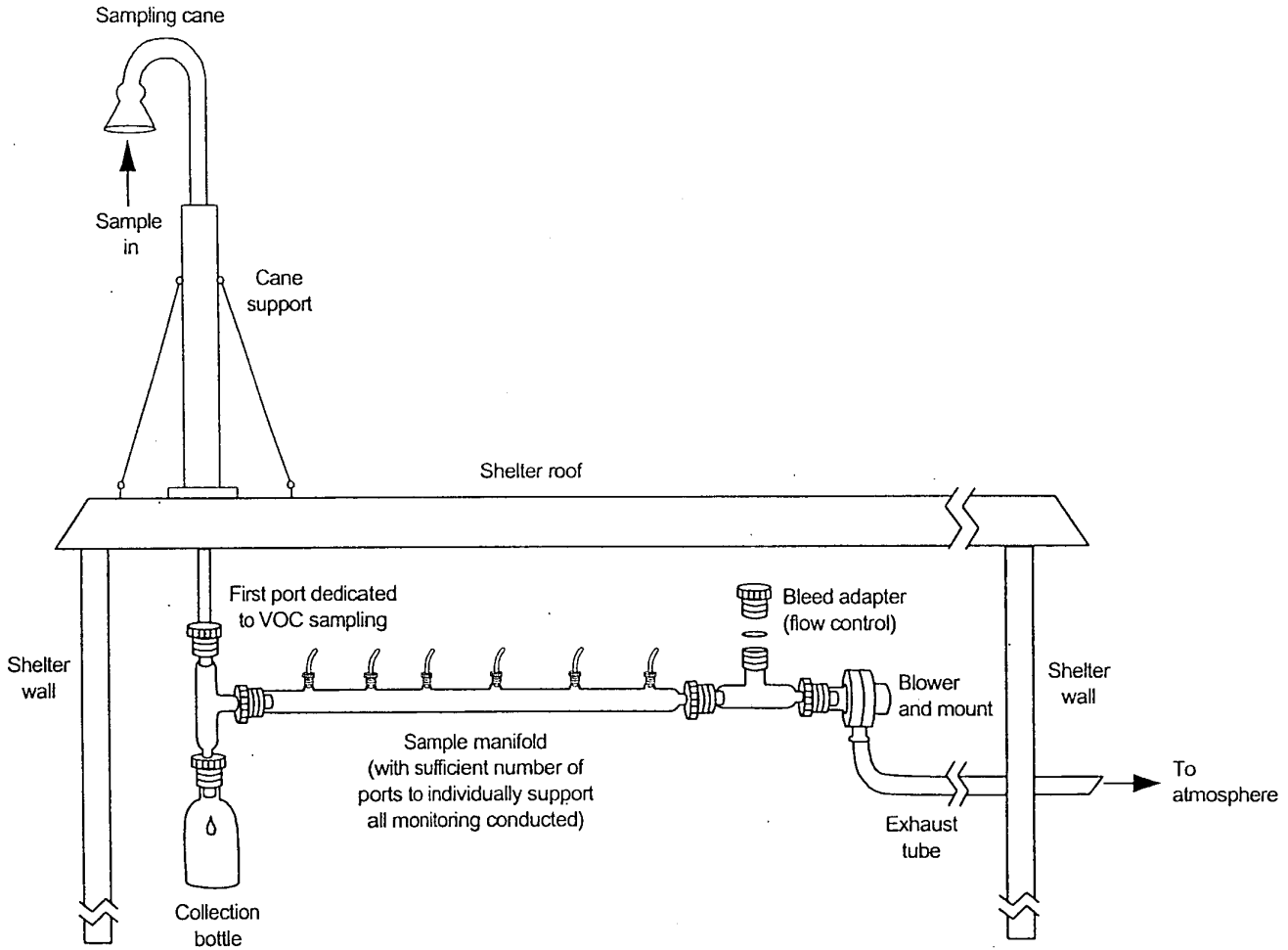


Figure 2-10. Horizontal Configuration

and then supplied to the sample concentration trap at the end of the integrating period. For purposes of calibration and proficiency studies, and to meet the 24-hour sampling requirements, samples may also be introduced directly from pressurized SUMMA® canisters.

2.4.1.3 Sample Conditioning

Moisture is removed from the sample stream for automated GC analysis to prevent or reduce the detrimental effects of moisture on the primary concentration trap, analytical column(s), and detector(s) as described in Section 2.3.3. Moisture removal also allows for analysis of larger sample volumes, which provides lower detection limits, and is crucial to the measurement of very low concentration VOCs.

Some commercially available automated GC systems incorporate the use of Nafion® membrane sample drying devices. New developments in moisture removal include controlled temperature vaporization, selective temperature condensation, hydrophobic concentration traps, and micro-scale purge-and-trap. The loss of polar VOCs may result from moisture removal using some of these techniques and this loss of polar VOCs may significantly affect the TNMOC measurement. The user must characterize the effects of their particular sample conditioning method on the TNMOC measurement and target VOCs of interest.

2.4.1.4 Sample Concentration

Ambient air samples are primarily concentrated using multi-bed sorbent or cryogenically-cooled deactivated glass bead traps. Sampling time and flow rate are typically used to determine the total volume concentrated onto the primary trap. Multi-bed sorbent traps (Carbotrap® and Carbosieve®) or cryogenically cooled glass bead traps are required to efficiently collect the complete range (C_2 through C_{12}) of VOCs for O_3 precursor monitoring.

Samples are collected onto sorbent traps at ambient temperature or the traps are cooled using liquid cryogen (H_2, CO_2, Ar) or Peltier® electronic cooling devices to improve collection

efficiency. Ideally, sorbent traps selectively adsorb only the trace VOCs and do not interact with the atmospheric constituents (i.e., CO_2) or introduce any contaminants into the system. Sorbent traps may also be designed to eliminate water vapor by using hydrophobic sorbent materials.

Sample concentration using glass bead traps requires a trapping temperature of -185°C. Trapping at a temperature above -185°C will result in the loss of early-eluting C_2 compounds such as acetylene, ethane, and ethylene. Trapping at a temperature below -185°C can result in the collection of methane and oxygen, and can have an adverse effect on chromatography. These traps are typically cooled using liquid cryogen (N_2 or Ar). This cooling process is commonly known as cryogenic concentration or cryotrapping, and is the oldest and best known of the techniques for collecting C_2 through C_{12} VOCs. The glass beads provide surface area for collection of the VOCs at the cryogenic trapping temperature.

2.4.2 Sample Analysis

Following sample collection and concentration, the sample is thermally desorbed directly onto the analytical column(s). The analytical column may be cryogenically cooled to aid in focusing the desorbed sample into a narrow band prior to chromatographic separation. The analytical column chromatographically separates the sample into components for subsequent detection by the FID. The signal from the FID is then acquired and processed using a PC-based data acquisition and processing system.

2.4.2.1 Sample Focusing or Cryofocusing

The sample cryofocusing step is optional and may not be employed in all commercially available automated GC systems. The secondary cryofocusing trap is used to focus the desorbed sample from the concentration trap into a "plug" for injection onto the analytical column. Cryofocusing improves the peak separation and in particular the resolution of C_2 and C_3 hydrocarbons. This technique is especially helpful when the sample is desorbed from the concentration trap at low flow rates.

Cryofocusing traps incorporate the use of fused silica tubing that is cooled using liquid cryogen. The fused silica tubing is wide-bore (0.32 mm I.D.) or megabore (0.53-mm I.D.) deactivated fused silica tubing that is cooled to approximately -185°C. Cryofocusing traps may be packed to increase the surface area and improve the focusing of the sample band.

2.4.2.2 Gas Chromatography

The gas chromatograph contains the analytical column(s) of choice for PAMS VOC analysis. Refer to Sections 2.3.5 and 2.3.6 for guidance on column configuration and selection. Commercially available GC systems are typically configured with the appropriate analytical column(s) to separate the VOCs of interest. However, the user must determine if the system meets the enhanced O_3 monitoring requirements and specifications (Section 2.4.4) prior to procurement. The user must also characterize the performance of the system operation prior to use. Commercial GC systems may incorporate the use of single or dual-column configurations (in series or parallel) that may require sub-ambient oven temperature programs. It is important to note that systems that eliminate the need for sub-ambient column oven temperatures reduce the overall cryogen consumption of the system. New developments in carrier gas electronic pressure programming and control have greatly improved peak resolution and retention time stability for some automated GC systems.

Automated GC systems employ the use of a PC-based data acquisition and processing system for peak integration and quantitation. Data acquisition and processing systems are comprised of hardware and software that perform data acquisition, peak detection and integration, peak identification by retention time, post-run calculations and quantitation, calibration, peak reintegration, user program interfacing, and hard copy output. Data are automatically stored on magnetic media (e.g., hard disk or floppy diskette).

The GC data acquisition and processing software is developed and supplied by the GC manufacturer and should contain the necessary algorithms to acquire, integrate, and identify the chromatographic peaks by retention time. The system should be capable of producing an

electronic and hard copy report file that contains the information needed to identify the sample and a listing of all peaks detected in the chromatogram. This listing should contain the peak name if it is a target compound. All detected peaks (both target and unidentified) should be reported with a concentration, in ppbC, and a retention time. The listing should also contain the TNMOC estimate calculated by summing the concentrations of all peaks (both target and unidentified) detected in the chromatogram. See Section 2.6.1 for a more detailed discussion on data processing capabilities of automated GC systems.

2.4.2.3 Analytical System Calibration

The detector response of the analytical system should be calibrated with multiple level propane primary standards over the expected sample concentration range. Benzene is suggested as a second primary standard to calibrate dual-column systems. These dual-column systems employ a Deans®[24] switch or other column switching techniques. Benzene may also be used to quantitate the target compounds when using a single-column approach. The primary calibration standard is used to generate a response factor per carbon atom for determining the concentration of each target VOC, as well as the TNMOC. It is impractical and unnecessary to determine compound specific response factors for each of the target VOCs presented in Table 2-1 because the carbon response of the FID to these compounds is approximately linear.

For a known, fixed sample volume, concentration is proportional to the area under the chromatographic peak. The area is converted to ppbC using the following equation:

$$C_A = RF(AC) \qquad (2\text{-}5)$$

where:

C_A = Concentration (ppbC)
RF = Response Factor, ppbC/area count
AC = Area Counts

The response factor (RF) is an experimentally determined calibration constant (ppbC/area count), and is used for all compound concentration determinations. The response factor is determined by the analysis of the primary standard using the following equation:

$$RF = \frac{3(C_B)}{MAC} \qquad (2\text{-}6)$$

where:

3	=	Carbon Atoms in Propane (6 when benzene is used as a second calibration standard)
C_B	=	Concentration of the NIST Propane Standard (ppbv)
MAC	=	Mean Area Count, determined from the analyses of multiple levels or multiple injections of the primary standard

The retention time of target compounds is determined by analyzing the retention time calibration standard as described in Section 2.3.4.2. This standard is analyzed in triplicate, at a minimum, to establish the correct retention times and retention time windows for the peaks of interest.

The primary standard (Section 2.3.4.1) is used to perform a calibration check of the analytical system in order to determine system variability and overall performance. The calibration and retention time checks may be performed concurrently using the retention time calibration standard. The compound concentrations and retention times should compare within the limits of the data quality objectives established for the monitoring program. If they do not, the analytical system should be recalibrated.

2.4.3 System Operation

This section provides guidance and general operating considerations for initial system set-up, optimization of sampling parameters, and field operation for automated GC systems.

2.4.3.1 Initial System Set-up

During the initial set-up of the automated system several parameters must be evaluated to optimize the operating conditions. Critical parameters include, but are not limited to, the sample collection flow rate and sample integration time, sample concentration and desorption conditions, oven temperature program parameters, detector calibration, and the peak detection and integration methods used by the data acquisition and processing system. These parameters are optimized by varying the operating conditions to achieve the best resolution and detection of the target VOCs using primary calibration and retention time calibration standards.

Prior to making VOC measurements using an automated GC system, the baseline performance of the system must be thoroughly documented. The information from the system baseline characterization is used to determine system specific target compound retention times, relative retention times, identification of co-eluting compounds and matrix effects, internal standard retention times, interferences, and detection limits. Subsequent calibrations and retention time QC checks should be verified against the system baseline to identify trends or excursions from acceptable performance. See Section 2.3.7 for a discussion of pre-measurement system characterization.

Users should anticipate a minimum of six months for initial setup, configuration, familiarization, and development of SOPs prior to the field implementation of an automated GC system. The system should initially be set up by the manufacturer and demonstrate adequate system stability and performance. Under terms of agreement for purchase, the manufacturer should be required to provide a detailed instruction manual for system operation and to meet the specifications as defined by the user. For a set of primary system specification guidelines see Section 2.4.4.

2.4.3.2 Sampling Parameters

Determination of optimum sampling parameters is dependent on field conditions (i.e., expected compound concentration ranges, humidity, temperature, etc.), desired sensitivity, cryogen consumption, and sample trapping efficiency. During the setup period, these sampling parameters should be evaluated to determine the optimum conditions for each. Primary sampling parameters are the sample collection frequency (1 sample each hour) and the minimum sample collection or integration time (40 minutes).

For hourly sampling, the minimum sample collection or integration time is 40 minutes. A sample collection volume of 200 to 600 mL is recommended. The sample volume used requires a trade-off between the required detection limit and potential moisture interference problems. Longer sample integration times may be implemented by using an intermediate sample collection or integration device. This device usually consists of a sample integration vessel configured to provide integrated collection of one sample while the previously collected sample is being analyzed. Advantages to using an intermediate sample integration device include longer integration times and reduced cryogen use during the concentration step of sample analysis.

2.4.3.3 Field Operation

The automated GC system should be installed in a temperature-controlled shelter at the field location. Detailed SOPs for field operation of the automated GC system must be developed. The SOPs should be based on information obtained during the set-up and familiarization period and the requirements of the monitoring program. Refer to QA/QC Section 2.8.3.1 for a more detailed discussion of SOP development. The system should be maintained by a qualified operator who should perform the routine operational and quality control functions as specified in the SOPs. Critical operational checks should be performed as frequently as practical. Operational parameters should be adjusted, if necessary, so that the data quality objectives are met. It is recommended that all adjustments to the operational parameters

be documented in a laboratory notebook. Primary calibration and retention time checks should be performed routinely according to the minimum QC requirements given in Section 2.8. Retention time calibration checks are performed to provide retention time reference information for validating compound identifications. The retention time calibration standard can also be used to track the FID response to determine when recalibration is necessary.

2.4.4 System Specifications

A set of primary specifications is provided below to conduct the evaluation for procurement of an automated GC/FID system. It is imperative that the enhanced O_3 monitoring network requirements for this type of system be compared against vendor offers to ensure that appropriate systems are procured. Primary system specifications are presented below. Additional system specifications may be added at the discretion of the user.

- The automated GC/FID system must be able to meet the sampling frequency requirements as prescribed in 40 CFR Part 58, Subpart E, Appendix D, and the sample integration requirements as discussed in Section 2.1 of this document (minimum sample integration time of 40 minutes to comprise a 1-hour sample). The manual methodology described in Section 2.5 is required for collection of the one 24-hour sample every sixth day.

- Cryogen consumption is a primary consideration for system procurement. Transport and delivery of liquid cryogen to the site may be impractical. The amount of liquid cryogen consumed by the system will determine the frequency of site visits and impact the cost for site operation and the level of data capture. Systems that utilize electronic cooling devices should be strongly considered if all other user specified requirements are satisfied.

- To avoid cross contamination, the system must demonstrate system background levels that are below the 0.2 ppbC estimated detection level for each VOC target species and 3 ppbC for TNMOC.

- The system must demonstrate the ability to separate the target VOCs of interest (C_2 through C_{12}) and provide an adequate estimate of the TNMOC value. Refer to Section 2.2.1 for a discussion of TNMOC.

- To ensure adequate peak identification and quantitation by retention time, the system must incorporate operating parameters that provide stable retention times. Observed retention time drift must be less than 0.1 minutes.

- The sample conditioning device, used to remove moisture from the sample stream and reduce the effects of moisture on the system, must minimize both polar VOC losses and the potential for introducing contaminants into the analytical system.

- The minimum level of quantitation (LOQ) must be 3.0 ± 0.2 ppbC for propane and correspond to an FID signal that is 3 to 5 times the baseline noise.

- The system should incorporate microprocessor control and battery backup capability to ensure that all programmed control activities for sample collection and analysis will be retained should the system power be interrupted. The system should automatically resume all operations once power is restored to the system to improve the level of data capture. Although not a requirement, the capability to log and report system interruptions (date, time, and type of failure) is advantageous.

- The system operation should be flexible enough to allow sample collection and analysis parameters to be easily modified to meet changes in network monitoring frequency and sample integration times as required.

- Expedient and responsive vendor support is a key consideration. The user should specify that the vendor maintain an adequate supply of replacement parts and a staff of qualified service technicians to ensure that the minimum number of sampling events are missed should a system failure occur. The user should specify that the vendor guarantee that parts and components be delivered to the site within 2 working days from the placement of the order. The user should also specify that the response to automated GC system service calls be received within 24 hours of placement and the system be placed in acceptable working order within 7 days of the service request.

- The vendor must provide an in-depth, detailed manual covering all aspects of the automated GC/FID system (i.e., operation, maintenance, etc.), initial system setup, user training, and demonstrate adequate system performance.

2.5 Manual Method for Collecting and Analyzing Volatile Organic Compounds

The manual methodology for obtaining volatile organic compound (VOC) measurements involves collecting time-integrated, whole air canister samples for subsequent

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California Environmental Protection Agency

Air Resources Board

SOP MLD 032

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF NON-METHANE ORGANIC COMPOUNDS IN AMBIENT AIR BY GAS CHROMATOGRAPHY USING DUAL CAPILLARY COLUMNS AND FLAME IONIZATION DETECTION

Engineering and Laboratory Branch
Monitoring and Laboratory Division

First Approved Date of SOP: October 1, 1996
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Revision Number: 3.1

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STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF NON-METHANE ORGANIC COMPOUNDS IN AMBIENT AIR BY GAS CHROMATOGRAPHY USING DUAL CAPILLARY COLUMNS AND FLAME IONIZATION DETECTION

1. SCOPE

This document describes the method for analysis of non-methane organic compounds (NMOC) in ambient air. The method is developed from and based upon EPA-600/625/R-96/010b and SOP No. MLD032 Revision 3.0. Method MLD032 is a modified version of USEPA Compendium Method Toxic Organics (TO)-14A. It involves the cryogenic pre-concentration of volatile organic compounds (VOCs), of which many are involved in photochemical formation of ozone in atmosphere. VOCs are defined as aliphatic and aromatic compounds having a vapor pressure greater than 0.10 Torr at 25^0C and 760 mm Hg. The Environmental Protection Agency (EPA), under Section 182 of the 1990 Clean Air Act Amendments (CAAA) revised the air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations (40 CFR Part 58) to include provisions for the States to establish Photochemical Assessment Monitoring Stations (PAMS) as part of State Implementation Plan (SIP) in ozone non-attainment areas classified as serious, severe, or extreme. This method addresses 56 recommended target compounds (range of C_2 through C_{12}, Table 1 pg. 18) to satisfy the requirements of 40 CFR Part 58, Subpart E. This method applies under most conditions encountered in sampling of whole air samples into SUMMA™ passivated stainless steel canisters, and also addresses the water removal by Nafion™ dryer before analysis.

2. SUMMARY OF METHOD

Ambient air is sampled over a three-hour period and collected in an evacuated, clean SUMMA™ passivated stainless steel canister. A pressurized mode, using a XonTech 910A sampler, is used during sample collection. A sample of air is drawn through a sampling train that regulates the rate and duration of sampling. A record of field information is sent back to the Engineering Laboratory Brach (ELB), Organics Laboratory Section along with the sample for immediate analysis. Upon arrival to the laboratory, the canister sample is equilibrated to room temperature for at least one hour before it is leak checked. The integrity of the canister pressure is validated by using a calibrated gauge. All information from the canister is documented in the login protocol, as well as into Laboratory Information Management Systems (LIMS).

A 300 cc ambient air sample is introduced into the automated gas chromatography (GC) system from the pressurized canister to the concentrator through 1/16" stainless steel tubing with the aid of a mass flow controller (MFC) and a vacuum system. The MFC

digital meter readout, that is attached to the Sierra MFC within the GC, provides a visual indication of the proper sample flow during sampling. Automated sampling of up to 16 canister samples can be accomplished using a multi-position automated sampler. The sample passes through the Nafion™ dryer, to remove moisture (H_2O vapor) from gas streams without the loss of PAMS target compounds. The dried sample is trapped within the 1/8" nickel tubing filled with silanized glass beads (60/80 mesh) at -172^0C. The desired NMOC components are immobilized (solidified), while oxygen (O_2), carbon monoxide (CO), and methane (CH_4) pass through the vent. The sample in the injector is purged with nitrogen (N_2) followed by isolation, rapid heating and injection onto the column.

3. INTERFERENCES AND LIMITATIONS

3.1 All compounds are identified by their corresponding retention times. Compounds in ambient air that have similar retention times may co-elute causing inaccurate quantifications, as well as misidentification.

3.2 Excess moisture, especially with large sample volumes, not removed by an in-line Nafion™ dryer and trapped with the sample, can interfere with the FID signal, producing elevated baseline and tailing. Correction by data system integration can offset most of these effects. Also, high levels of water can cause trap blockage, not allowing complete sample loading and must be avoided. Blockage can be detected by elevated pressure readings on purge gases during trap flushing. Injecting smaller sample volumes can minimize this problem.

3.3 Due to possible carryover effects, a blank analysis should be performed immediately after analyzing samples with high concentrations of VOCs (i.e., outside the calibration range).

3.4 Insufficient cooling within the cryotrap during the pre-injection period may cause inefficient trapping of organic compounds, especially C_2 compounds and propane. Check to ensure that during the thermal stabilization period that the trapping

3.5 temperature reaches -172^0C and is maintained. If the trap temperature deviates well below the set temperature, CH_4, O_2, and CO_2 can be trapped and cause detector problems. CH_4 and O_2 can cause baseline perturbations, and CO_2 can cause plugging problems.

3.6 Improper use of the MFC, especially when introducing a specific sample volume into the system, will produce significant errors in the final results. Periodically observe the MFC s actual sampling rate from the MFC s digital flow meter readout to ensure that there is agreement, and that these settings are at the calibrated range for the instrument. It should also be noted that air streams with high levels of CO_2 (>10%) can cause significantly lower volumes to be sampled, and should not be used with MFC sampling.

3.7 Other typical problems encountered are dirty FID jets, plugged jets, and improper flame gas flows. Optimization, involving setting the carrier, hydrogen, and makeup gases, should be performed whenever the peak signature changes (peak broadening, multiple peaks, significant changes in retention times). It is also important that the optimal instrument settings are recorded and maintained. In addition, preventive maintenance should be performed at least once a year.

4. APPARATUS

4.1 An Ultra-Trace Hydrocarbon System (UTHS), employing a Varian Model 3600*Cx* (GC) system (from Lotus Consulting) equipped with the following:

i. Sampling hardware (16-port multipostion automated sampler).

ii. Gas pneumatics with High Performance Valves (Valco Instruments-high temperature, low internal volume version with operating temperature, range of +100°C to 350°C).

iii. Inert nickel contact surfaces and low-volume nickel or stainless steel interconnecting tubing.

iv. 1/8" nickel tubing concentrator trap with adsorbent silanized glass beads (60/80 mesh).

v. Three capillary columns, a J&W Scientific 15m DB-1 and a 60m DB-1 with 0.32mm ID, 1 micron film thickness, and a Chrompack 50m Al_2O_3/Na_2SO_4 porous layer open tubular (PLOT) capillary column with 0.32mm ID, 5 micron film thickness.

vi. Dual flame ionization detectors (FIDs), both composed of 0.02" ceramic flame tips.

vii. A continuous self-regenerating dryer (Nafion™, Perma Pure Inc.).

Note: *The principles of gas chromatography and a brief overview of appropriate detector are documented in Appendix II.*

viii. High performance digital flow controllers for accurate and reproducible flow regulation. A pressure regulator is set in parallel to minimize flow upsets during valve switching and to prevent system pressure from dropping below the set pressure. The digital flow controllers and pressure regulator are installed in the heated pneumatics compartment, which is heated isothermal at 45°C.

Note: *Pressure gauges or electronic pressure readouts (EPRs), give a visual display of column pressure and are used for carrier gas monitoring and problem diagnostics (displayed on the pneumatics panel in front of the GC).*

ix. A Sierra Model 840 MFC (0-5 VDC output) calibrated to deliver a constant flow rate from 0 to 100 sccm/min± 3% for N_2 or air with an inlet pressure of 80 psig. The MFC readout display (Sierra Instruments, Inc.) is set at 50% of the 100 sccm/min output or 50 sccm/min for flow control.

x. An inline sample pressure regulator ("Go" Valve), to minimize pressure upsets during sampling.

4.2 Carrier Gas Filter Supelpure™ HC 2-2445 and Sulpelpure™ O_2 2-2449 or equivalent.

4.3 A Varian GC Star Workstation, PC based, IBM compatible, for GC system control, automation, and method editing.

Note: *For a detailed description of Star Chromatography Workstation, See Appendix III.*

4.4 A Perkin-Elmer Nelson 2700 Chromatography data system, IBM PC based, for data collection, storage, and quantitation. Appendix I.

4.5 A Perkin-Elmer Nelson 900 Series Analog/Digital Converter (model 970).

4.6 Leak-free stainless steel canisters of the desired volume (eg., 6L), with interior surfaces treated by the SUMMA passivation process.

4.7 A vacuum pump that can continuously draw air through the inlet manifold, at a rate greater than 10L/min.

4.8 Teflon tubing (1/8" OD x 1/16" ID, 0.030 wall) and brass fittings for autosampler-to-canister connections.

5 MATERIALS

5.1 Before each set of sample analyses it is necessary to introduce a blank (e.g., zero air, ultra-pure air, or ultra-pure N_2) into the system in the same manner as a sample.

5.2 A Standard Reference Material 1800 (SRM-1800), certified by the National Institute of Standards and Technology (NIST), containing fifteen Toxic "VOC s" in N_2 (Table 2, pg. 19), is used for daily one-point calibrations of the GC instruments. All concentrations are given in a molar ratio for a given compound, relative to the total of all constituents or nanomole/mole (parts per billion-ppb). Trace hydrocarbon concentrations have

assigned units of **ppb Carbon (ppb C)**. This unit is derived by multiplying ppb volume/volume (ppb v/v) by the number of carbons in the molecule of analyte. In our dual column GC system, the C_2-C_4 compounds are calibrated with **Propane (C_3)**. This NIST mix is also used in multipoint analysis to establish a linear dynamic range, as well as the limit of detection (LOD) of the instrument.

5.3 A control sample, PAMS Retention Time cylinder (e.g., Spectra Gas Supply Inc., Alpha, NJ), containing 56 components, is used for retention time calibration and daily quality control.

5.4 Nitrogen, Grade 5 or ultra-pure ($\geq$99.9999% pure), is used as a FID make-up gas, fore-flushing gas, and as a counter-flow drying gas in the Nafion™ dryer.

5.5 Helium, Grade 5 or ultra-pure ($\geq$99.9999% pure), is used as a carrier gas.

5.6 Helium, Grade 5 or lower purity, is used as a valve actuator gas.

5.7 Liquid Nitrogen is used for cryogenic preconcentration and sub-ambient GC analysis. Also head-space nitrogen is used for system blank analysis.

5.8 Hydrogen, Grade 5 or ultrapure is used as a detector fuel gas.

5.9 Zero Air, is used as a flame ionization detector oxidant.

5.10 High Performance Liquid Chromatography (HPLC) grade water (150μL H_2O in 6L canister) is used for humidification of the standard hydrocarbon mix, the control mix, and any other in-house hydrocarbon gaseous mixtures injected into SUMMA™ passivated canisters. This is done in order to simulate humidified ambient air samples, as well as minimize active surface sites inside the canister.

5.11 Isopropyl alcohol/water (1:1), is used for leak detection (external applications only).

6 INSTRUMENT CONFIGURATION AND PARAMETERS

6.1 The analytical system and automation configurations are shown in Figures 1, 2, and 3. The valving diagrams depict the system configuration for normal operation including the use of a MFC for sample introduction and the use of 8134 SSV relay for ports 1-16 of the autosampler. Valves A, B, C and D are configured to *off* positions (-) for normal operation i.e., ready/standby. On the left side of the GC instrument there is a switch for manual sample purge, which activates relay **3** and turns valve B *on*. This can be used to manually condition the sample lines, evaluate MFC output flow, or to set the pressure of the inline "Go" valve. Also located on the left side panel of the GC instrument is a toggle switch that operates valve B. This toggle switch is normally set to the "disable" position since all calibrations are done by external standard analysis, but it can be set to "enable" for an internal standard/spike sample analysis. On the right side

of the GC instrument there is a button for manually advancing the stream selector valve for ports 1-16. This option is used when leak-checking and/or troubleshooting the alignment of streams in the 16-port valve.

6.2 There are six separate temperature zones for which there are parameters entered in Star Workstation: **GC Injector A** (not used), **GC Injector B** (Cryotrap), **GC Auxiliary** (Valve B, C, D), **GC Column** (Valve A, Analytical Capillary Columns), **GC Detector Heater A** (FID), and **GC Detector Heater B** (not used). There is one additional external temperature zone for the 16-port 8134 SSV, set manually at 130°C.

Note: *The temperature setting for injector B does not correspond to the true temperature of the injector. A graph is provided (Figure 4) which illustrates the relationship between the injection setting in the Star Workstation, and the true temperature of the concentration trap.*

6.3 Sample Volume Injection

A sample volume of 300 standard cubic centimeters (sccm) is achieved by collecting the sample for 6.00 minutes at a rate of 50 sccm/min. The process for achieving the proper volume of sample for injection is fully automated by the use of a Relay Time Program, which is part of the Varian GC Star Chromatography Workstation software, version 4.51. The location of the valves for a Varian 3600 *Cx* GC analytical system as well as the layout for the pneumatic controls is shown in Figure 1. Table 3A lists the relays and their corresponding functions. Table 3B lists the valve actuators employed in this system along with their corresponding degree of rotation.

6.4 3600GC Running Parameters:

6.4.1 GC Injectors:

GC Injector A: *Not Used*

Injectors A and B must be specified as temperature programmable to ensure proper hardware description.

Injector Type	*: Temperature Programmable*
Injector Oven	*: Off*
Initial Temperature	*: 50°C (by default)*
Initial Hold Time	*: 0.00 minutes*

GC Injector B: *Cyrotrap*

Injector Type	*: Temperature Programmable*
Injector Oven	*: On*
Initial Temperature	*: -172°C (set –72)*

Injector Hold Time : *0.50 minutes*

Temperature Program 1:

Final Temperature : *200°C (set 250)*
Rate : *250°C /min*
Hold Time :*58.0 minutes*
Coolant to Injector : *Yes*
Coolant Timeout : *60.00 minutes*

The concentrator trap has a volume of approximately 500 μL. This low volume facilitates a rapid heating/cooling cycle (from –172°C to 200°C) with minimum temperature overshoots/undershoots at set points. A typical temperature profile of a concentrator trap is shown in Figure 5.

6.4.2 **GC Auxiliary:** *Valve B, C and D*

Must be set with a high enough temperature to ensure that there is no sample condensation (max. temp. ≤ 350°C).

Auxiliary Injector Type : *Isothermal*
GC Auxiliary Oven on? :*Yes*
GC Auxiliary Description : *Valves B, C, D*
Initial GC Auxiliary Temperature : *175°C*
Initial GC Auxiliary Hold Time :*0.00 minutes*

6.4.3 **GC Column:** Valve A, Analytical Capillary Columns

There are three capillary analytical columns (one serving as a pre-column) installed in the GC oven as well as Valve A.

Column Oven On? : *Yes*
Initial Column Temperature : *0°C*
Initial Column Hold Time : *2.00 minutes*
Thermal Stabilization Time : *2.00 minutes*
Coolant to Column Valve On? : *Yes*
GC Column Program End Time : *60.00 minutes*

Temperature Program 1:

Final Temperature : *90°C*

Rate : *3.0°C /min*
Hold Time : *1.00 minutes*

Temperature Program 2:

Final Temperature : *200°C*
Rate : *5.0°C /min*
Hold Time : *5.00 minutes*

6.4.4 GC Column Parameters

There are three capillary columns in the GC oven. The first column is a J&W 15m DB-1 with 0.32 mm ID and 1 micrometer film thickness. Its function is to separate the $C_2 - C_4$ components from the C_5 - C_{12} components. The other two capillary columns separate components within the two respective groups. The column used for the speciation of C_2-C_4 components is a PLOT column, a 50m Al_2O_3 /Na_2SO_4 Chrompack column, with 0.32mm ID and 5 micron film thickness. The second analytical column, used for the speciation of $C_5 - C_{12}$ compounds, is a J&W 60m DB-1 column with 0.32 ID and 1 micron film thickness. Column parameters are given in the Star Chromatography Workstation GC 3600 Module of the analytical method in order for the instrument to calculate the linear velocity of the carrier gas and other base-level parameters prior to analysis.

Column A Parameters:

Installed? : *Yes*
Length : *50.00 meters (PLOT Column)*
Diameter : *320.0 microns*
Carrier Gas : *Helium*

Column B Parameters:

Installed? : *Yes*
Length : *60.00 meters (DB-1 Column)*
Diameter : *320.0 microns*
Carrier Gas : *Helium*

6.4.5 GC Detectors:

Heater A:

Detector Heater On? : *Yes*
Detector Temperature : *250°C*

Heater B:

Detector Heater On? : *No*
Detector Temperature : *50^{0}C (By default)*

GC Detector A:

Detector Type : *FID*
Detector On? : *Yes*
Attenuation : *8*
Detector Range : *12*
Autozero at GC Ready? : *Yes*

GC Detector B:

Detector Type : *FID*
Detector On? : *Yes*
Attenuation : *8*
Detector Range : *12*
Autozero at GC Ready? : *Yes*

Note: *Only one heating block is used in our GC (Heater A), which contains both Detector A and Detector B. There is no Heater B. However, settings for both Heater A and Heater B are entered in Star Chromotography Workstation because this is necessary in order for the software to run properly. Also, settings are entered for the attenuation which is only used for stripchart recorders, which we no longer use.*

6.4.6 Autosampler:

Autosampler Type : *8134 SSV*

6.4.7 GC Relays Time Program:

Relay Time Program? : *Use*

	Time(min)	*Relay#*
Start Oven temp. program	*0.00*	- - - -
Isolation of the trap/heat trap	*0.01*	- - - +4
Injecting sample onto PLOT	*1.50*	- - - -
Injecting sample onto DB-1	*3.40*	+1 - - -

[X] *Return Relays to Initial Conditions at Run End*

6.4.8 GC Stripchart:

Stripchart On? : *No*

6.4.9 Gas Flow Settings*

He- Carrier Gas	*: 5.00 ccm/min ± 0.3 mL/min*
N_2 – Nafion™ Counterflow	*: 200 ccm/min***
Make-up Gas	*: 25.0 ccm/min ±1mL/min*
H_2 – FID Fuel Gas	*: 30.0 ccm/min ± 1 mL/min*
Air- FID Oxidant	*: 300 ccm/min ± 10 mL/min*

* *All flows set with GC oven at 100°C*
** *Minimum of 3 X Sample Flow Rate*

6.4.10 Gas Cylinder Pressure Requirements:

He- Carrier Gas	*: 80 psig*
*He- Valve Actuator**	*: 65 psig*
N_2 – Nafion™, Purge	*: 80 psig*
Make-up Gas	
H_2 – FID Fuel Gas	*: 40 psig*
Air- FID Oxidant	*: 65 psig*

* *A separate supply gas tank is recommended for valve actuators to minimize spikes on the FID from pressure pulses when valves are turned. We recommend using He as a valving gas, not N_2 or air, because it produces crisper valve actuation.*

7. NMOC SPECIATED ANALYSIS PROCEDURE

7.1 Sample pre-injection period (PIP)- Figures 2A through 2F

Ambient air, calibration standards and control samples in SUMMA™ passivated canisters are connected to the autosampler using appropriate tubing and fittings. To evacuate or purge the lines manually, press the manual sample purge button located on the left side of the instrument panel (which rotates valve B to the *on* **(+3)** position). After assuring the connections are leak-free, the valves of the sample containers can be opened.

		lines by purging them with the new sample, and also allows time for the MFC to stabilize at 50 sccm/min. See Figure 2B.
1.00 min	- +2 +3 -	Valve B and C are activated to the *on* position **(+3, +2)**. The sample flow is directed through injector B (cryotrap) , which is at 172^{0}C. At this point effective sample loading begins. See Figure 2C.
7.00 min	- +2 - -	Valve C is *on* **(+2)** and valve B is *off* **(- 3)**. The effective sample loading is terminated. The sample flow dead-ends, allowing N_2 to pure the sample in the trap and the interconnecting lines of any gases that are bound to surfaces (e.g., O_2, CO, CH_4). These gases will be flushed by N_2, through the MFC and then out of the vacuum. **Note**: *By controlling the timed events activating valve B **(+3)** and turning off valve B **(-3)**, the sample volume can be varied.* See Figure 2D.

Time	Actuation Events	Valve Events
7.30 min	- +2 - +4	Valve B is deactivated **(-3)** and valve C and D are *on* **(+2, +4)**. The trap (injector B) is isolated and N_2 is redirected through the MFC, through the flow meter, and out to vacuum. Activation of valve D **(+4)** prompts PE Nelson 2700 to begin acquiring data (Turbochrom Chromatography Workstation, ver. 4.1.2f12). See Figure 2E.
7.35 min	- - - +4	Valve C is deactivated (-2) and valve D is *on* **(+4)**. The trap (injector B) remains isolated and the GC system is ready for the positive time events or post-injection period. See Figure 2F.

7.2 Sample injection/post-injection period (Figures 3A-3C)

7.2.1 All timed events for post sample injections are edited in ***.mth** files with Method Editor in the Star Chromatography 3600 Workstation.

Time	Actuation Events	Valve Events
0.01 min	- - - +4	Valve D is *on* **(+4)**. The trap is isolated while being heated to 200^{0}C (set at 250 at the rate of 250^{0}C /min). See Figure 3A.
1.50 min	- - - -	Valve D is *off* **(-4)**. The trap is open and in series with the PLOT column i.e., the heated sample is purged by primary He into the GC oven, through the DB-1 pre-column where the C_2-C_4 compounds are separated from the C_5-C_{12} compounds and are injected onto the PLOT column. See Figure 3B.
3.40min	+1 - - -	The trap is in series with the DB-1 column *via* actuation of valve A **(+1)**, the C_5-C_{12} compounds are carried through the DB-1 pre-column and injected directly onto the DB-1 analytical column. This timing may require adjustments due to changes in columns and/or column flows. The switch is made to allow 1,3-butadiene to be last component eluting off of the Alumina PLOT column. See Figure 3C.

8. ANALYSIS

In general, the sequence of analysis for Engineering Laboratory Branch methodology, including the requirements of quality control, is as follows:

1. System blank
2. Calibration
3. Control sample
4. Ambient samples
5. Sequence duplicate/replicate

6. Check or cross-duplicate sample

8.1 A system blank, consisting of either ultrapure zero air, headspace liquid nitrogen, or ultrapure N_2 gas, is analyzed prior to calibration to detect system contamination. System blanks must not have any interfering peaks greater than the LOD (1.0 ppb C) for any individual analyte of interest before proceeding to the next step.

8.2 A daily system calibration is performed with a 15 component certified NIST33762, SRM 1800-14A externally traceable primary gas standard mix (Figure 6A page 37 and Figure 6B page 38). The standard is prepared in a humidified (injection of 150 microliters of HPLC grade water under vacuum) SUMMA™ passivated canister that is analyzed after a system blank and before any ambient samples. The NIST standard offers calibrating standards for **propane** and **benzene** in concentrations applicable to ambient air analysis. A single point calibration is established for each sequence using a single analysis of the external standard at 300 sccm (mL) volume. There is no "averaging" of the daily response factors. The FID detector response, in area counts, is directly related to a known concentration of the analyte (i.e., propane and/or benzene), and is used to calibrate the instrument each time it is used. After the analysis of the standard run, the response factor (Rf) is calculated as follows:

Rf = (Std.Conc.)/Std. Area Count
i.e., Propane = (16.2 $\pm$ 0.6 ppb C) / Area Count
i.e., Benzene = (31.2 $\pm$ 1.2 ppb C) / Area Count

Note: *The concentrations of propane and benzene in the NIST SRM 1800 standard mix are listed as $\pm$ 0.2 nmole/mole. This uncertainty is due to imprecision in the preparation and analysis of the standard.*

8.3 A control sample (1997 PAMS Retention Time cylinder, Spectra Gas Supplies Inc.) is analyzed before any ambient air samples and is used for retention time calibration and for daily quality control (Figures 7A, 7B). This gas mixture contains 56 compounds (C_2-C_{12}), of which 14 compounds are evaluated as daily control limits, as defined in the MLD Laboratory Quality Control Manual, Revision 2.3 (1997). Each control sample result is plotted daily on a control chart (Table 7).

8.4 Ambient samples are introduced and analyzed under the same conditions as the calibration standard and the retention time standard. The resultant peaks are identified by their retention times and quantified relative to the certified values of propane (PLOT) and benzene (DB-1) in the NIST standard.

8.5 Duplicate analyses (analysis of the same sample by the same instrument) are performed on at least 10% of the ambient samples analyzed. Data for concentrations in excess of the limit of detection ($\geq$ LOD) are recorded. The percent difference of the duplicate analyses are recorded, and values that are $\geq$ 5X LOD and exceed the maximum percent difference (see 9.03 for formula) for an analyte are included in the Quality Control report.

8.6 Cross duplicate analyses (analysis of the same sample by different GC instruments) are performed on at least 10% of all ambient samples. Cross duplicate analyses are evaluated under the same conditions as the duplicate analyses.

9. QUALITY CONTROL

9.1 A system blank consisting of either humidified Ultra-pure zero-air, or Grade 5 N_2 is run once daily prior to calibration to check for any system contamination (background). System blank must also be run after any sample that contains high concentrations of analytes (exceeding the linear range of the detection), to eliminate any possible carry-over and bias on the next analysis in sequence. If the system blank contains any interfering peak that is greater than 1.00 ppb C for any targeted analyte, or the sum of all targeted peaks for both analytical columns exceeds 20 ppb C (or 10 ppb C per column) the following corrective actions will be taken:

1. Check system for leaks: Most contamination that is observed in the system blank is due to leaks, especially when the gases that serve the GC instrument have been changed. Look for obvious source of contamination especially the items that have been changed recently.

2. Clean system with wet air: Purging out the GC system with several runs of humidified air to reduce and to eliminate any source of contamination in order to meet the acceptable criteria for system blank.

3 Bake-out sample trap/system: Run the GC system at elevated temperature zones.

4. Repeat analysis.

9.2 Prior to the analysis of ambient samples but after the system blank, single point calibration (daily calibration) is performed. The NIST standard (SRM 1800-14A) provides propane and benzene as certified externally traceable primary standards for calibrating PLOT and DB-1 columns respectively. The acceptance criterion for daily calibration is that the Rf value must be within $\pm$10 relative percent difference (RPD) of average Rf for each calibrating compound. Attention must be given to changes in Rf values that may indicate instrument, standard gas mix, or detector sensitivity changes. Following corrective action should be made if the above criterion is not met:

1 Repeat daily calibration analysis.

2 Check FIDs for leaks and gas flows: Detector sensitivity changes are mostly contributed to leaks in the detector and changes in gas flows.

Make sure that the gas cylinder pressure requirements are met and that the gas flow settings have not been altered. If all the settings are correct, but the flow requirements are not met, check for the leak source and correct the problem. Document the corrective action taken, and repeat the daily calibration analysis.

3. Prepare new calibration standard sample and repeat the analysis: Prepare a new NIST standard sample (humidified with 150$_{\mu}$L H_2O) and re-run the daily calibration.

4. Repeat multi-point analysis: If all the corrective actions listed above do not produce the desired result, then verify the linear dynamic range of the FID detectors, by preparing and running new calibration standards. Verify that the expected precision, accuracy, and LOD are also not compromised. The calculated precision, accuracy and the LOD must be equal to or better than the established criteria prior to the PAMS season.

9.3 A control sample (1997 PAMS Retention Time cylinder, Spectra Gas Supplies Inc.) is analyzed before any ambient air samples and is used for retention time calibration and for daily quality control. This gas mixture contains 56 compounds (C_2-C_{12}), of which 14 compounds are evaluated as daily control limits and are plotted daily on a control chart. Control limit levels are established based on calculated standard deviation (std) of at least 20 measurements of the control sample analyzed during the pre-season period. The limits are set as follows:

UCL (Upper Control Limit)	=	+3*std of Mean Value
UWL (Upper Warning Limit)	=	+2*std of Mean Value
Mean or Assayed Value	=	
LWL (Lower Warning Limit)	=	-2*std of Mean Value
LCL (Lower Control Limit)	=	-3*std of Mean Value

If results of the control sample fall outside the Control Limits (UCL/LCL) for any compound, the control sample is reanalyzed. If the second results are also outside of the Control Limits, the analysis is discontinued, the Supervisor notified, and the cause of the problem investigated. All data, during the period of analyses is invalidated for those particular compounds that are outside the Control Limits.

An additional QC check of retention time windows for all 14 target analytes is performed using a retention time standard (control sample). This provides a comprehensive check of retention time windows and peak identification for all target VOCs. The retention time should not vary by more than 0.1 minutes. This chart is updated weekly and is used to indicate trends in qualitative performance of the GC.

9.4 Duplicate analysis of ambient samples is performed daily on at least 10% of the total ambient samples analyzed. The relative percent differences (RPD) of duplicate results for each target compound are recorded for all targeted compounds. The maximum allowable percent difference (MAPD) for any analyte with concentration equal to or greater than 5.0 ppb C should not be greater than 25%. If any targeted compounds fail to meet this criterion, the results of the compound is invalidated for the whole sequence.

9.5 Cross duplicate analyses (using the same method of analysis of the same sample by different GC instrument) are performed on at least 10% of the total samples analyzed. The cross duplicate table is updated weekly ($\geq$ LOD are recorded for all target compounds). The same acceptance criteria used for duplicate analyses is applied for cross duplicate analysis.

10. METHOD SENSITIVITY, PRECISION, AND ACCURACY

10.1 Multipoint analysis must be performed prior to the start of the NMOC season to verify the linear dynamic range of the FID response (Table 5A-Propane, Table 6A-Benzene). Hydrocarbon concentrations in ambient air can vary over a wide range , from very low ppb C to ppm C (parts per million). A strong positive correlation over the expected operating range ensures accurate results at other concentration levels . FIDs usually exhibit linearity over a 10^7 range (range set is 10^{-12} amps/millivolts at 50-microsecond time constant for speciated NMOC analysis). Multipoint analysis is performed with at least four (4) concentration levels over the linear range of the instrument. Each concentration level is measured at least three (3) times. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient (r). The linearity of calibration curve is verified when the coefficient r is greater than 0.98. If an ambient concentration of any compound exceeds the defined linear range of that compound, the sample must be diluted (so that the diluted component has a detector response within the defined linear range), reanalyzed, and the concentration recalculated for that particular compound.

10.2 As defined in the Laboratory Quality Control Manual, Revision 2.3 (1997) the Limit of Detection (LOD) is the Method Detection Limit (MDL), which is the minimum concentration of a substance that can be measured and reported with 99% confidence. The MDL is given in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as the product of the standard deviation (seven replicate measurements of the analyte of interest at a concentration near but less than 5 ppb C) times the expected detection limit (1 ppb C) and the value of 3.14 (Student t value for 99% confidence for seven values). See Table 4.

$$\mathbf{LOD = [std_{n=7}] * 3.14}$$

Multipoint calibration and LOD calculation must be performed under each of the following conditions:

a.) prior to every NMOC season
b.) when system maintenance is performed
c.) when minor modifications are done that may change the expected precision accuracy, and/or LOD of the measurement
d.) when a major modification is performed that may change the analytical equipment configuration, operating conditions , analyte target list, change in matrix or reagents that may change the precision, accuracy, and LOD calculation.

10.3 A duplicate/replicate analysis is the analysis of the same sample extract twice in one sequence. Duplicate samples are chosen at random, and should account for at least 10% of the total ambient samples analyzed. Method variability can be estimated from duplicate mesurements. To make a comparison of two values, Percent Difference (%D) is a more meaningful statistic than RSD. The duplicate/replicate pairs are evaluated based on the following formula:

$$\%D = [y-x/y+x] * 200$$

Where %D is the percent difference, the x and y represents the corresponding concentrations of an analyte for original and duplicate analyses.

10.4 The QA section provides the laboratory with performance audits (reference standards submitted in canisters as "blind" audits) to assess the accuracy of the data generated by the instrumentation. A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measure value divided by the audit value, and is expressed as a percentage, as illustrated below:

%Audit Accuracy= [(Audit Value – Measured Value) / Audit Value] * 100

The reference value for an accuracy standard should be a certified reference material (CRM) or traceable to a standard reference material such as a NIST Standard Reference Material (SRM). Federal regulations require State and Local air monitoring agencies to perform annual accuracy checks.

Table 1. PAMS Target VOCs

AIRS Code	Target Name	AIRS Code	Target Name
43203	Ethylene (Ethene)	43249	3-Methylhexane
43206	Acetylene (Ethyne)	43250	2,2,4-Trimethylpentane
43202	Ethane	43232	n-Heptane
43205	Propylene (Propene)	43261	Methylcyclohexane
43204	Propane	43252	2,3,4-Trimethylpentane
43214	Isobutane	45202	Toluene
43280	1-Butene	43960	2-Methylheptane
43212	N-Butane	43253	3-Methylheptane
43216	Trans-2-Butene	43233	n-Octane
43217	Cis-2-Butene	45203	Ethylbenzene
43221	Isopentane (2-Mebutane)	45109	m/p-Xylene
43224	1-Pentene	45220	Styrene
43220	N-Pentane	45204	o-Xylene
43243	Isoprene	43235	n-Nonane
43226	trans-2-Pentene	45210	Isopropylbenzene
43227	cis-2-Pentene	45209	n-Propylbenzene
43244	2,2-Dimethylbutane	45212	m-Ethyltoluene (1-Ethyl-3-Methylbenzene)
43242	Cyclopentane	45213	p-Ethyltoluene (1-Ethyl-4-Methylbenzene)
43284	2,3-Dimethylbutane	45207	1,3,5-Trimethylbenzene
43285	2-Methylpentane	45211	o-Ethyltoluene (1-Ethyl-2-Methylbenzene)
43230	3-Methylpentane	45208	1,2,4-Trimethylbenzene
43245	1-Hexene*	45238	n-Decane
43231	n-Hexane	45225	1,2,3-Trimethylbenzene
43262	Methylcyclopentane	45218	m-Diethylbenzene
43247	2,4-Dimethylpentane	45219	p-Diethylbenzene
45201	Benzene	43954	n-Undecane
43248	Cyclohexane	43141	n-Dodecane*
43263	2-Methylhexane	43102	TNMOC
43291	2,3-Dimethylpentane	43000	PAMHC

Table 2. Certified Concentration Values for SRM 1800

Cylinder ALM033762

SRM 1800					
No.	Compound	nmole/mole			Concentration (ppbC)
1	Ethane	5	±	0.2	10.2
2	Propane	5	±	0.2	16.2
3	Propene	5	±	0.2	15.6
4	Isobutane	6	±	0.2	22.0
5	n-Butane	5	±	0.2	21.2
6	Isobutene	6	±	0.2	22.0
7	2-Methyl Butane	6	±	0.2	29.0
8	n-Pentane	5	±	0.2	25.5
9	1-Pentene	5	±	0.2	25.5
10	n-Hexane	5	±	0.2	31.8
11	Benzene	5	±	0.2	31.2
12	n-Octane	5	±	0.2	40.8
13	Toluene	5	±	0.2	36.4
14	ortho-Xylene	5	±	0.2	40.8
15	n-Decane	5	±	0.2	51.0

Table 3A. Function of Valves for Varian GC 3600*Cx* System

Valve #	Function	Event	Rotation
A	Trap in series with PLOT	-1	Counterclockwise
	Trap in series with DB-1	+1	Clockwise
B	N_2 purge on	-3	Counterclockwise
	Sx flow on	+3	Clockwise
C	He carrier gas to trap	-2	Counterclockwise
	Sx to trap	+2	Clockwise
D	Trap in series	-4	Counterclockwise
	Trap is isolated	+4	Clockwise

Table 3B. List of Valve Actuators for Varian GC 3600CX System

Relav #	Number of Valve Ports	Actuator Rotation
A	4	90^0
B	10	36^0
C	6	60^0
D	4	90^0

Table 5A. Multipoint Calculations for Propane

Linear Range:	129.6ppb

ppbC =>	1.4	4.1	5.4	10.8	16.2	24.3	32.4	48.6	129.6
Vol (cc) =>	25	75	100	200	300	450	600	900	2400
Area (ac) =>	ac	ac	ac	ac	ac	ac	ac	ac	ac
1st Run	2800	8186	10974	22072	32886	49664	66741	100908	268150
2nd	2773	8212	11056	22229	32994	49693	67072	101323	266835
3rd	2758	8236	11041	22118	33416	49734	67000	101129	265346
4th	2786	8306	11029	22100	33106	49854	66846	101450	
5th	2840				33145				
6th	2877								
7th	2770								
8th									
9th									
Mean (ac) =	2801	8235	11025	22130	33109	49736	66915	101203	266777
Std.Dev (ac) =	43.0	51.5	35.7	68.8	199.1	83.6	149.3	236.6	1402.9
% RSD =	1.54	0.63	0.32	0.31	0.60	0.17	0.22	0.23	0.53
# Obs. =	7	4	4	4	5	4	4	4	3

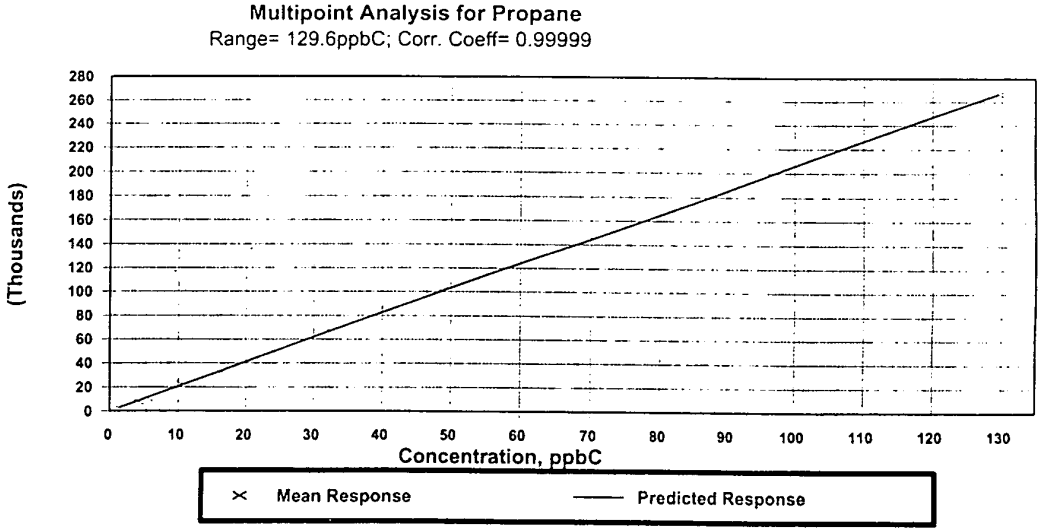


Table 5B. LOD Calculations for Propane

Linear Regression Line
Y(Area) = x(Area/Conc.) *X(Conc.) + b(Area)

Conc. ppbC	AC	Estimated AC	
0.01		-4.1286419E-16	Estimated
0		-12.06	Values
1.4	2801	2770	
4.1	8235	8335	
5.4	11025	11117	
10.8	22130	22247	
16.2	33109	33376	
24.3	49736	50071	
32.4	66915	66765	
48.6	101203	100153	
129.6	266777	267095	

**** Regression Output:

Constant	-12.1	y-intercept, b, in ac
Std Err of Y Est	453.7	
R Squared	0.99997	Regression Coefficient
No. of Observations	9	
Degrees of Freedom	7	
X Coefficient(s)	2061.01	slope, x, in ac/ppbC
Std Err of Coef	3.99	

R Correlation Coefficient 0.99999

LOD Calculations

X-Intercept [-(b/a)]	=	0.006 ppbC
Std. Dev. of Response at Low	=	43.042 ac
Slope of the Regression Line	=	2061.015 ac/(ppbC)
3 * (Std. Dev.)/(Slope)	=	0.063 ppbC
LOD Estimate	=	| X-Intercept | + 3(Std. Dev./ Slope)
	=	0.07 ppbC
Lowest Standard Conc/LOD Es	=	19.7

Or if the lowest level is more than 5 X LOD then the following formula apj

RSD [Std. Dev. / Mean]	=	0.0154
3*(RSD)	=	0.0461
Calculated LOD	=	|X-Intercept| + 3(RSD)|X-Intercept|
	=	0.01 ppbC

US EPA Method TO-15

SHM1600
Propane
2800
2773
2758
2786
2840
2877
2770

Known ppb C	1.4
Rf (ppb C/ Mean ac)	0.00050

	Propane
Mean (ac)	2800.57
Std (ac)	43.042
n	7

3 * (Std. Dev.) * Rf 0.068

	Propane
Calc. LOD (ppb C)	0.07

Table 6A. Multipoint Calculations for Benzene

Linear Range: 249.6 ppbC

ppbC =>	2.6	7.8	10.4	20.8	31.2	46.8	62.4	93.6	249.6
Vol (cc) =>	25	75	100	200	300	450	600	900	2400
Area (ac) =>	ac	ac	ac	ac	ac	ac	ac	ac	ac
1st Run	5028	15918	21823	43558	64952	98965	133252	203502	545543
2nd	5273	15997	21427	44579	65230	99269	133380	204543	545811
3rd	5112	16030	21514	43557	64997	99230	133685	204756	545788
4th	5238	16041	21474	43804	65227	99355	133465	205032	
5th	5072				65744				
6th	5218								
7th	5248								
8th									
9th									
Mean (ac) =	5170	15997	21560	43875	65230	99205	133446	204458	545714
Std.Dev (ac) =	97.3	55.6	179.2	483.8	314.6	168.1	182.1	668.2	148.2
% RSD =	1.88	0.35	0.83	1.10	0.48	0.17	0.14	0.33	0.03
# Obs. =	7	4	4	4	5	4	4	4	3

Multipoint Analysis for Benzene

Range= 249.6ppbC; Corr. Coeff= 0.99998

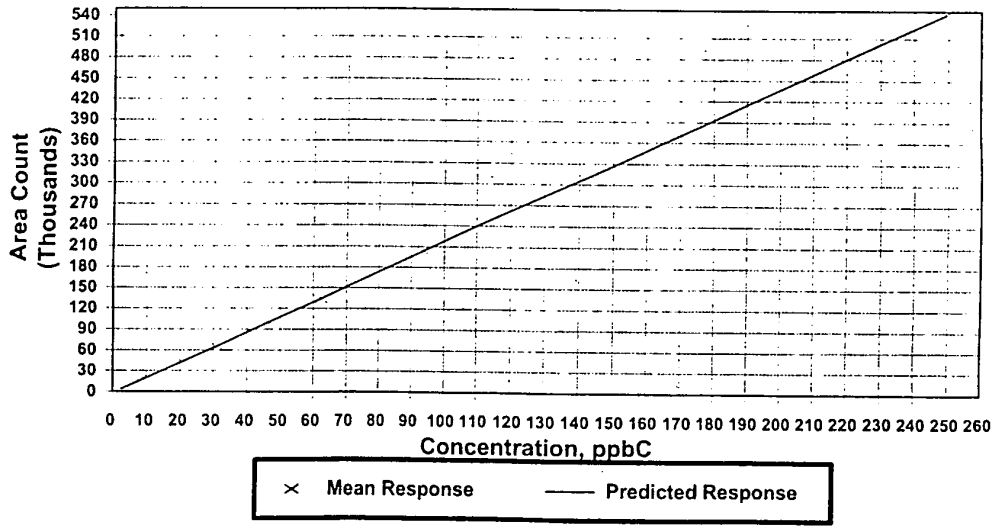


Table 6B. LOD Calculations for Benzene

US EPA Method TO-15

SRM1800
Benzene
5028
5273
5112
5238
5072
5218
5248

LOD Calculations:

X-Intercept [-(b/a)]	=	*0.855*	ppbC
Std. Dev. of Response at Lowes	=	97.256	ac
Slope of the Regression Line	=	2192.538	ac/(ppbC)
3 * (Std. Dev.)/(Slope)	=	*0.133*	ppbC
LOD Estimate	=	| X-Intercept | + 3(Std. Dev./ Slope)	
	=	0.99	ppbC
Lowest Standard Conc/LOD Est	=	2.6	

Known ppb C	2.6
Rf (ppb C/ Me	0.00050

Or if the lowest level is more than 5 X LOD then the following formula applies:

RSD [Std. Dev. / Mean]	=	0.0188	
3*(RSD)	=	0.0564	
Calculated LOD	=	|X-Intercept| + 3(RSD)(|X-Intercept|)	
	=	0.90	ppbC

	Benzene
Mean (ac)	5169.86
Std (ac)	97.256
n	7
3.143*Std*Rf	0.154

	Benzene
lc. LOD (ppb C	0.15

Linear Regression Line
Y(Area) = a(Area/Conc.) * X(Conc.) + b(Area)

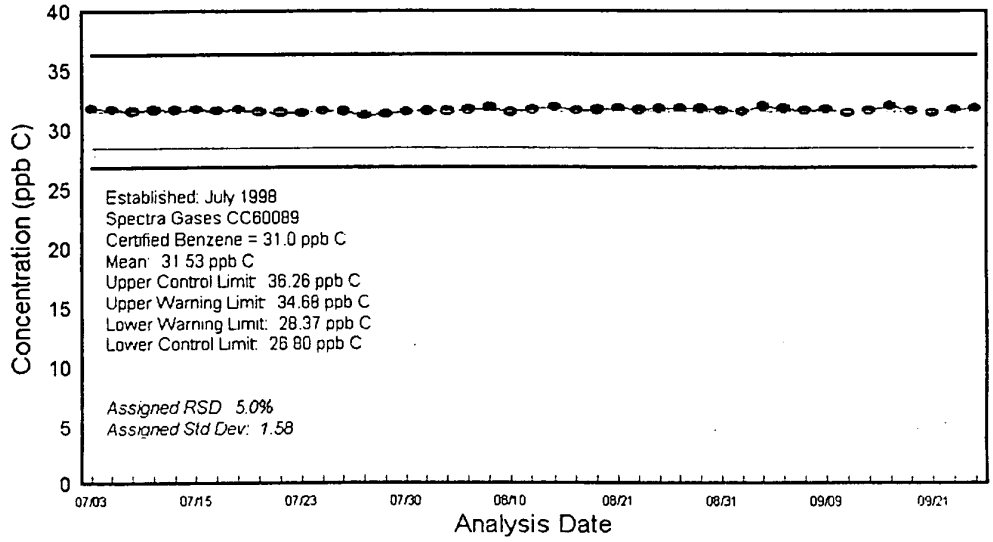
Conc. ppbC	AC	Estimated AC	
0.85		-9.392487E-14	Estimated
0		-1874.21	Values
2.6	5170	3826	
7.8	15997	15228	
10.4	21560	20928	
20.8	43875	43731	
31.2	65230	66533	
46.8	99205	100737	
62.4	133446	134940	
93.6	204458	203347	
249.6	545714	545383	

X-Intercept (-b/a)	0.855	x-intercep X(Conc.)
Y-Coefficient(s)	0.000	slope, 1/a, in ppbC/ac

•••• Regression Output:

Constant	-1874.2	y-intercept, b, in ac
Std Err of Y Est	1221.1	
R Squared	0.99995	Regression Coefficient
No. of Observations	9	
Degrees of Freedom	7	
X Coefficient(s)	2192.54	slope, a, in ac/ppbC
Std Err of Coef.	5.57	
R Correlation Coefficient	0.99998	

Table 7. Control Charts for Benzene and Propane



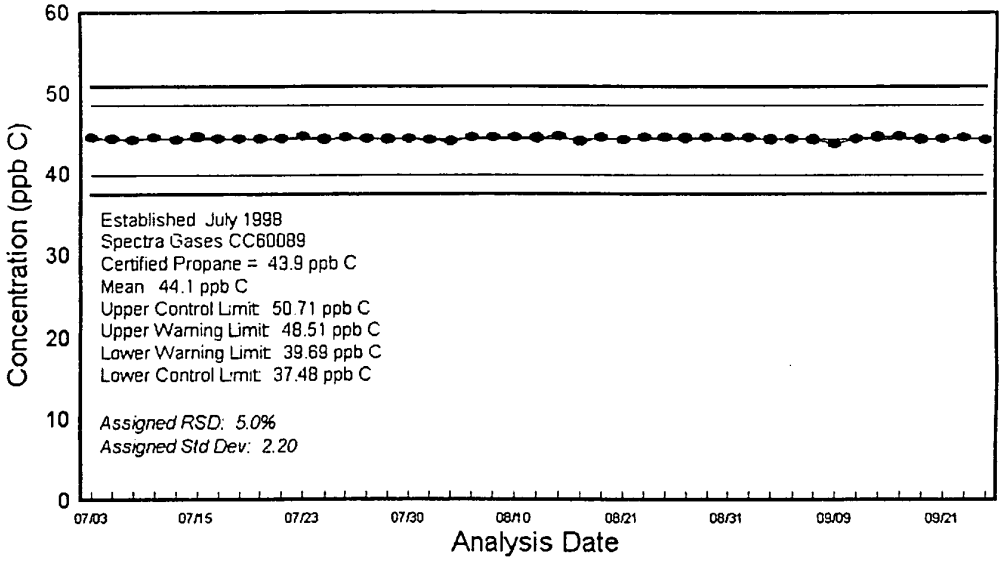


Figure 1. Varian 3600Cx GC Analytical System

MLD032 - NMOC Speciated VOC Analysis

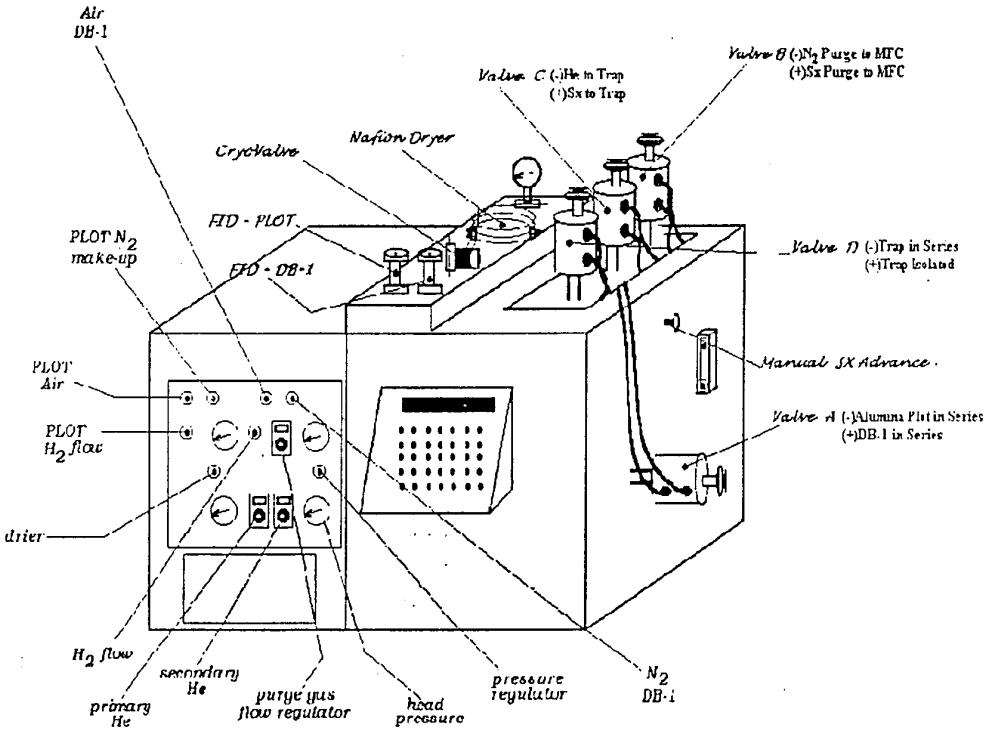


Figure 2A. Pre-Injection Time Events

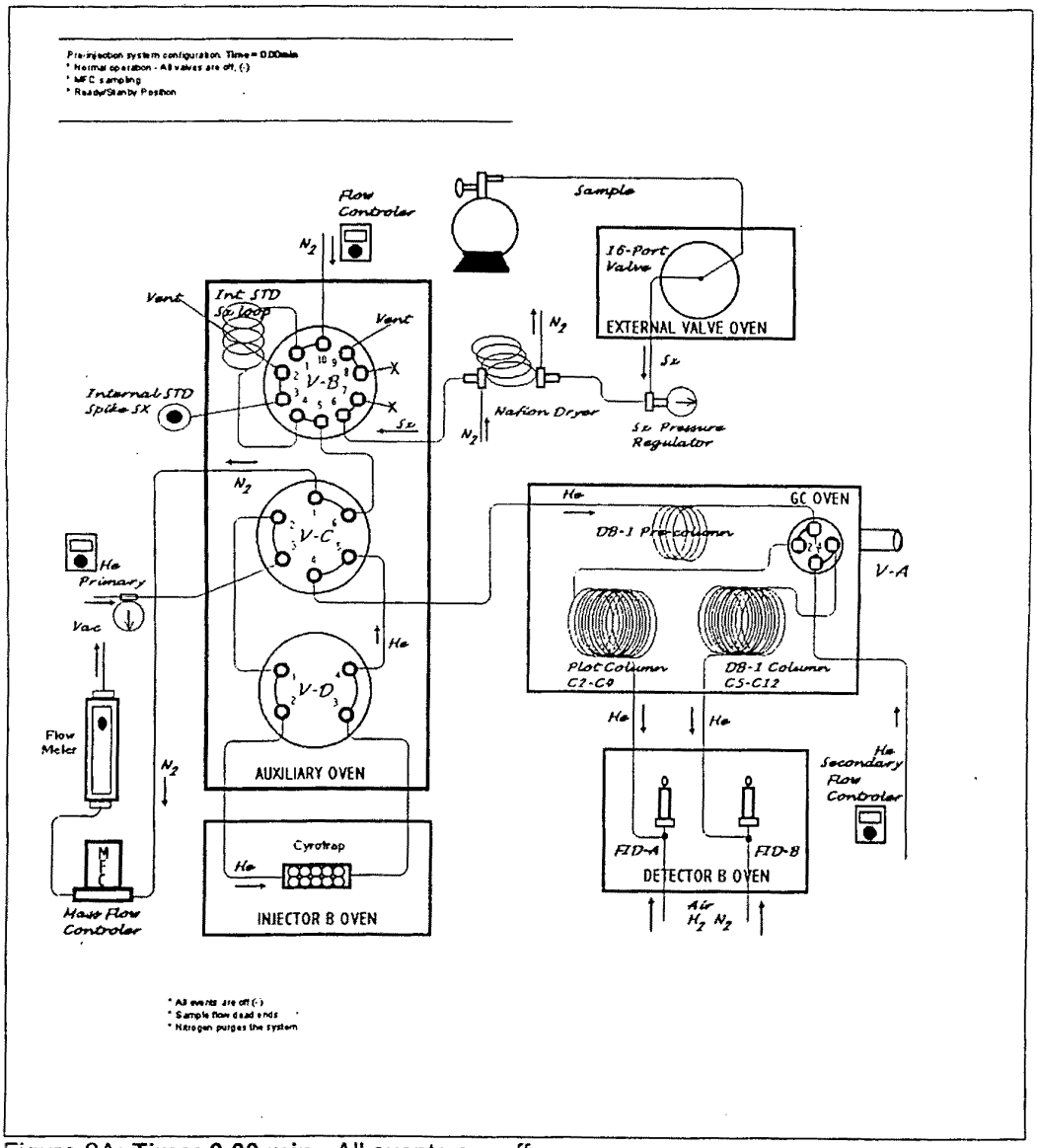


Figure 2A: **Time: 0.00 min** –All events are off

Figure 2B. Pre-Injection Time Events

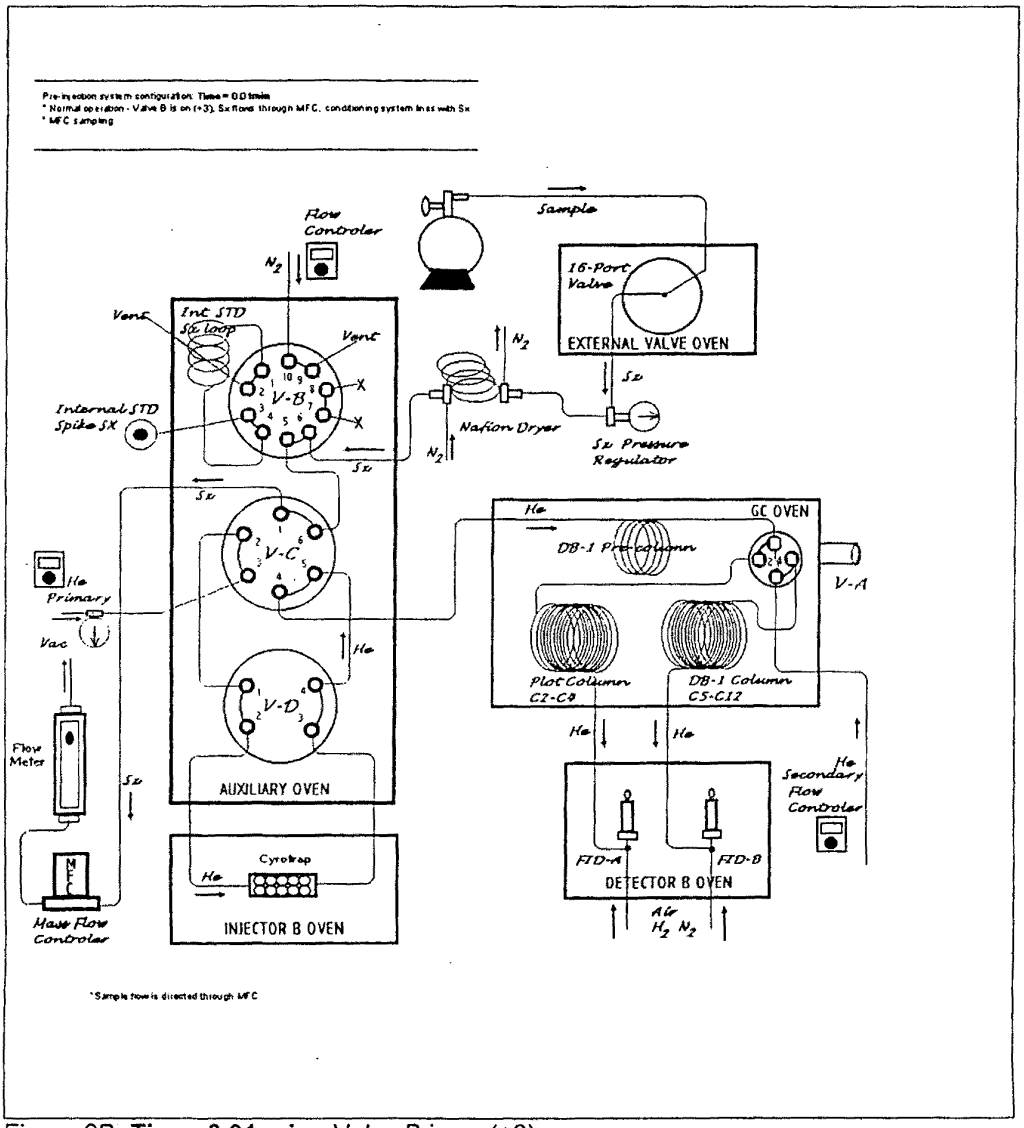


Figure 2B: **Time: 0.01 min** –Valve B is on (+3)

Figure 2C. Pre-Injection Time Events

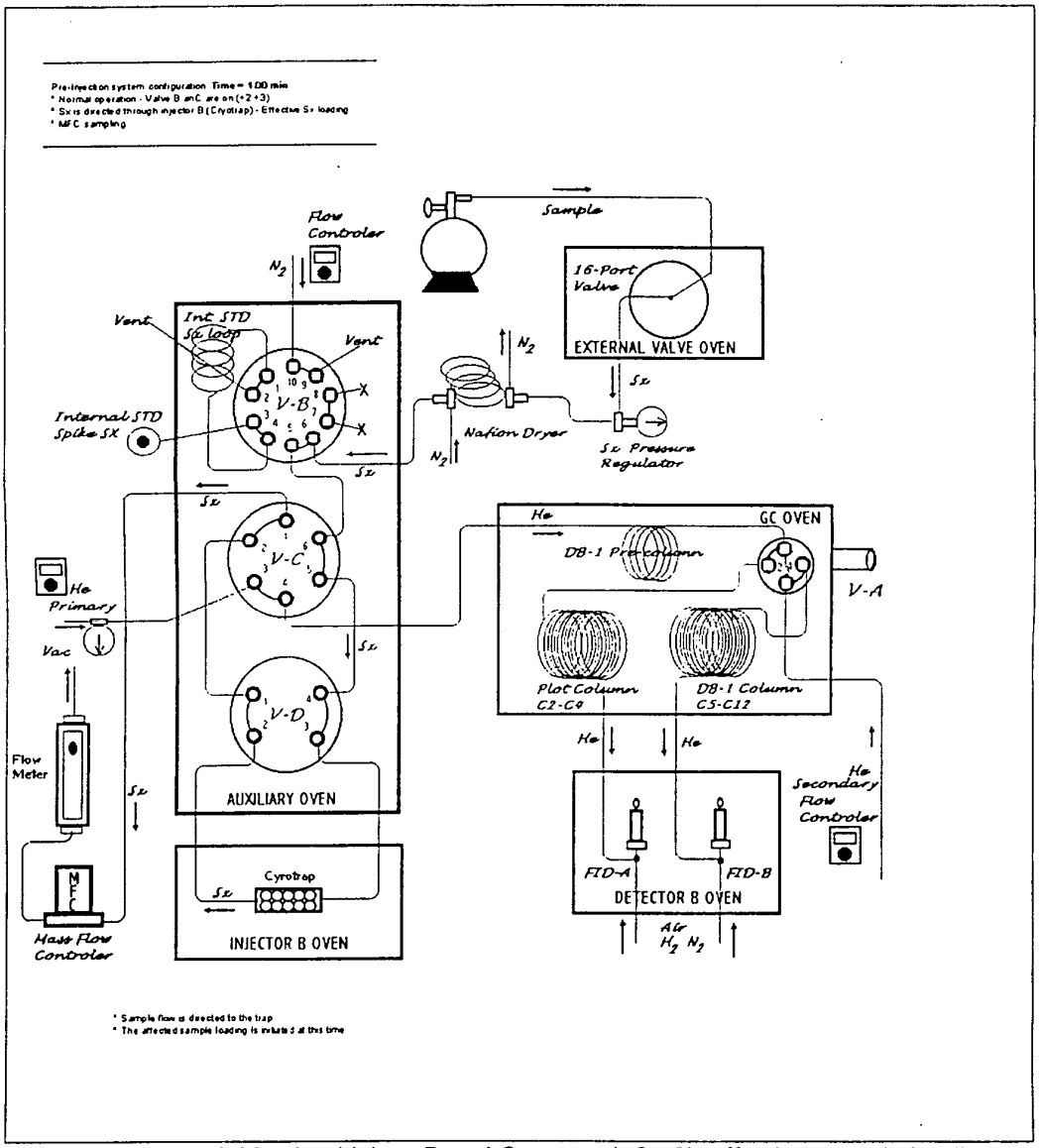


Figure 2C: **Time: 1.00 min** –Valves B and C are on (+2 +3), effective sample loading.

Figure 2D. Pre-Injection Time Events

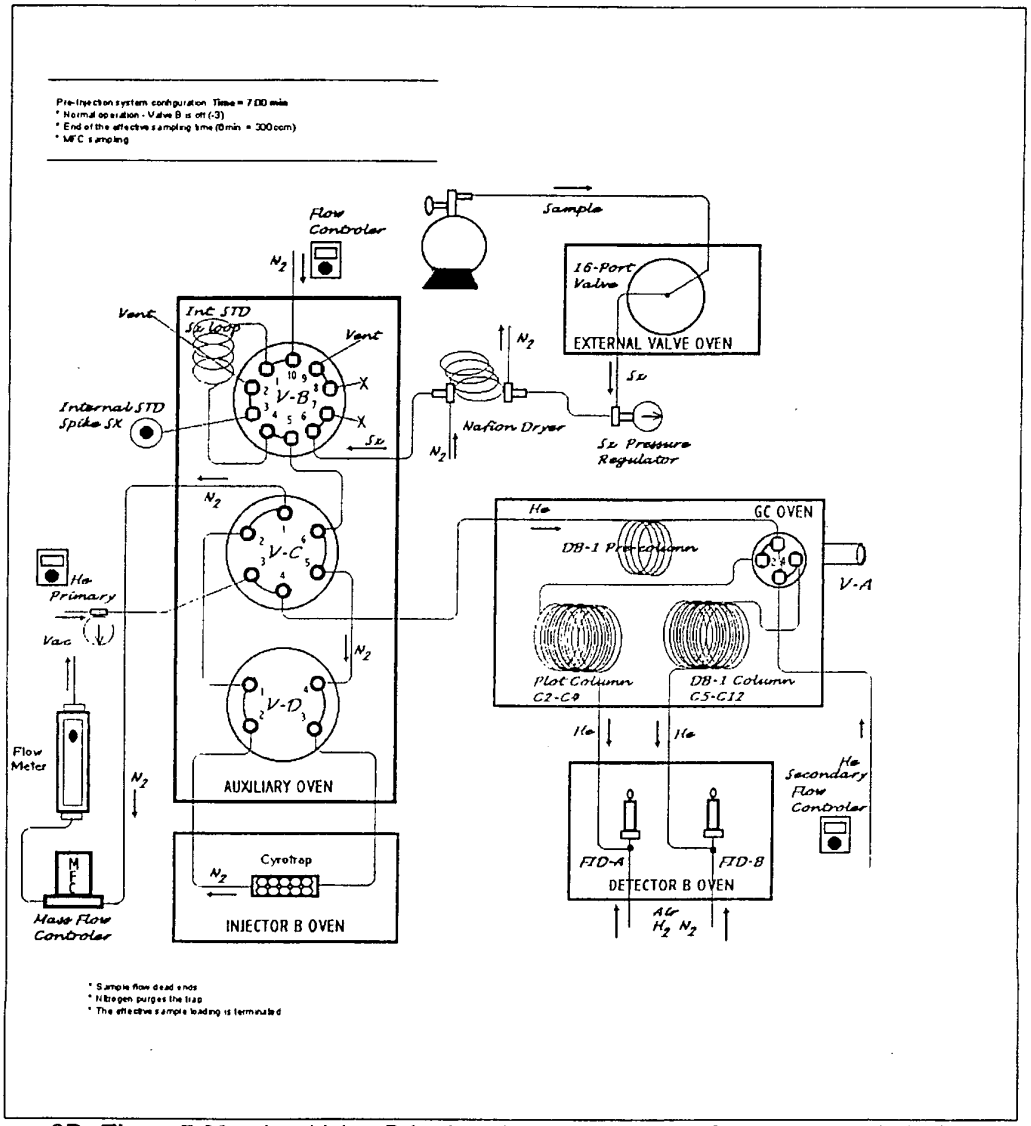


Figure 2D: **Time: 7.00 min** –Valve B is deactivated (-3), end of sampling period. The trap is purged with nitrogen.

Figure 2E. Pre-Injection Time Events

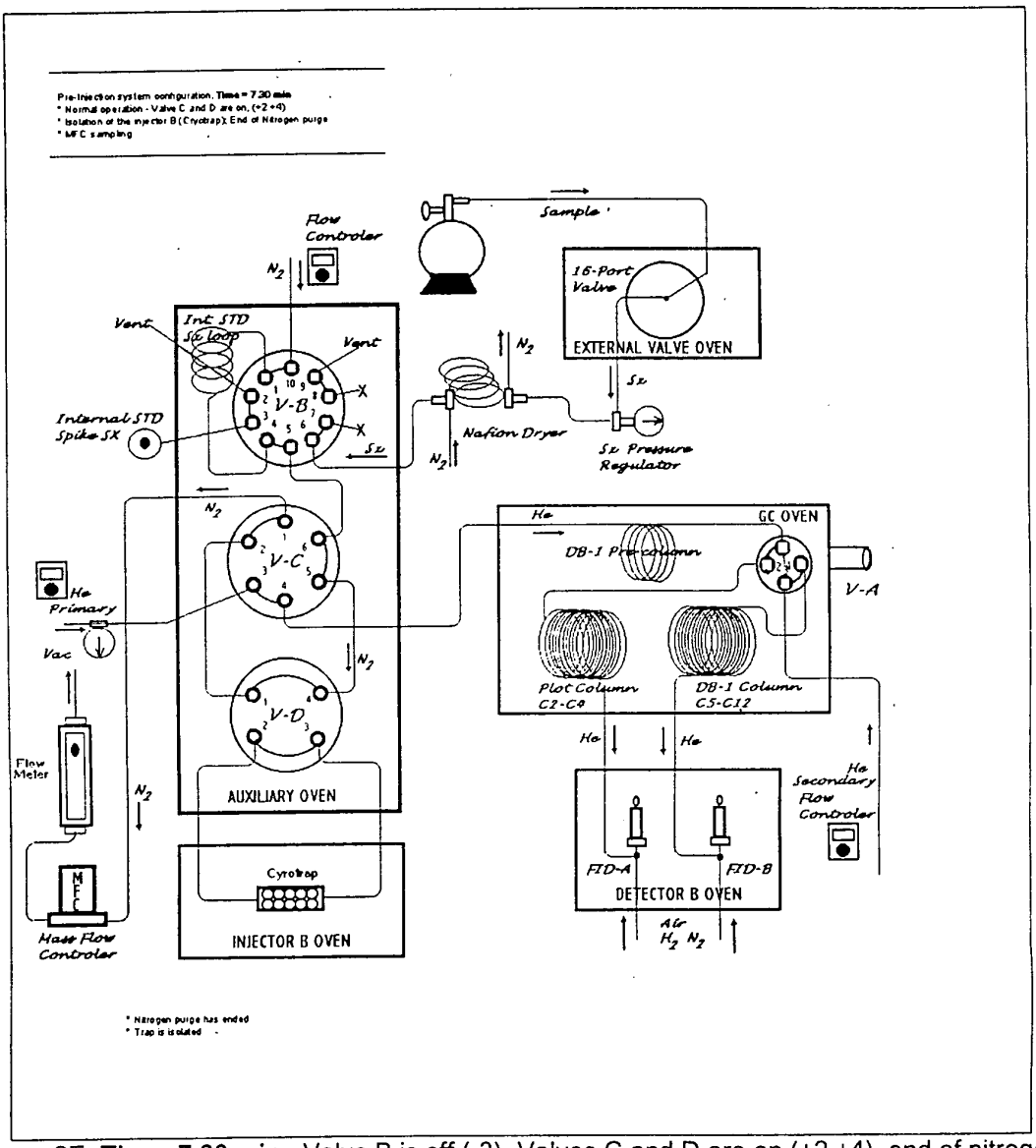


Figure 2E: **Time: 7.30 min** –Valve B is off (-3), Valves C and D are on (+2 +4), end of nitrogen purge of the trap. The trap is isolated and ready for heating.

Figure 2F. Pre-Injection Time Events

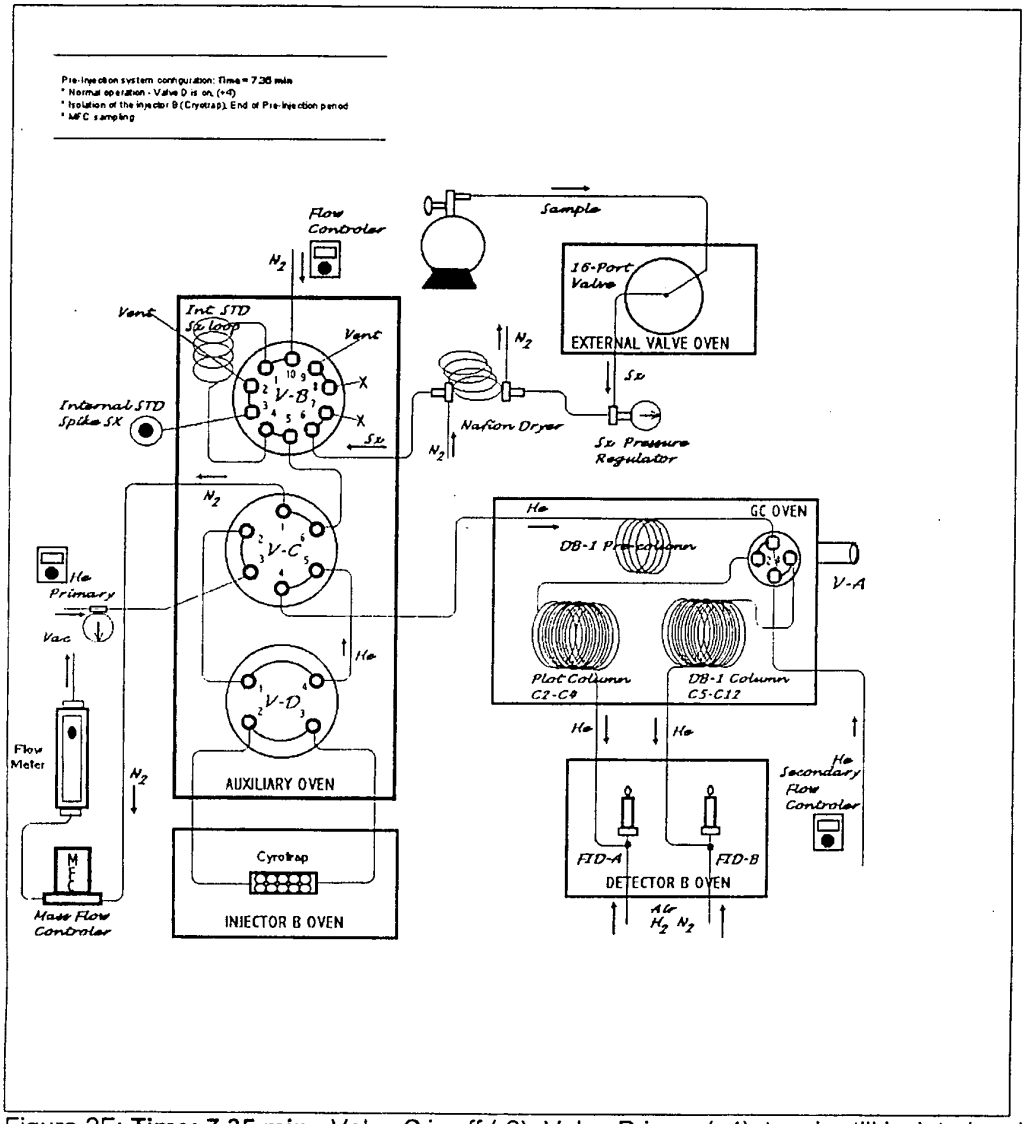


Figure 2F: **Time: 7.35 min** –Valve C is off (-2), Valve D is on (+4), trap is still isolated and this is the end of pre-injection program.

Figure 3A. Post-Injection Time Events

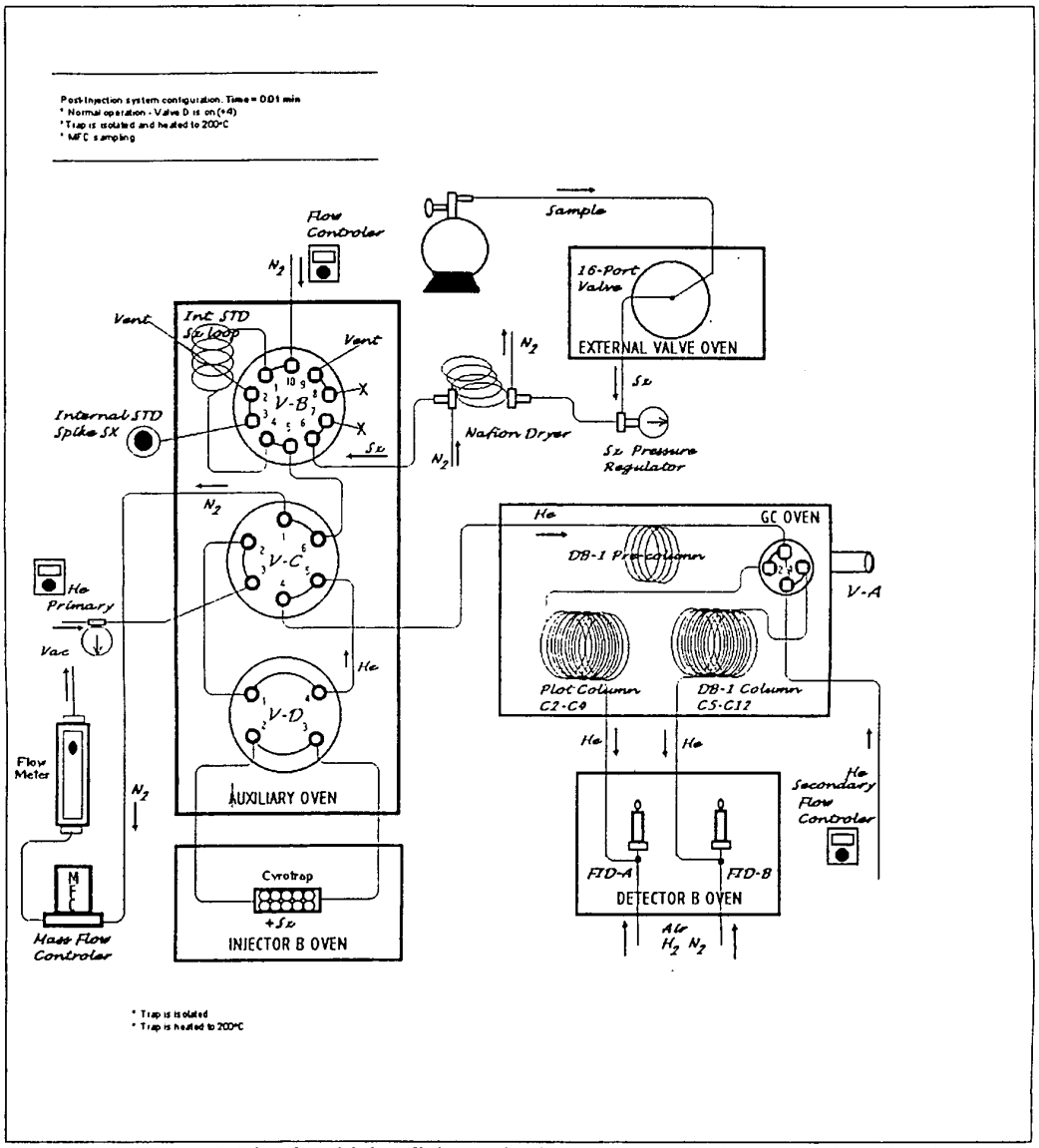


Figure 3A: **Time: 0.01 min** –Valve D is on (+4), the trap is isolated and is being heated.

Figure 3B. Post- Injection Time Events

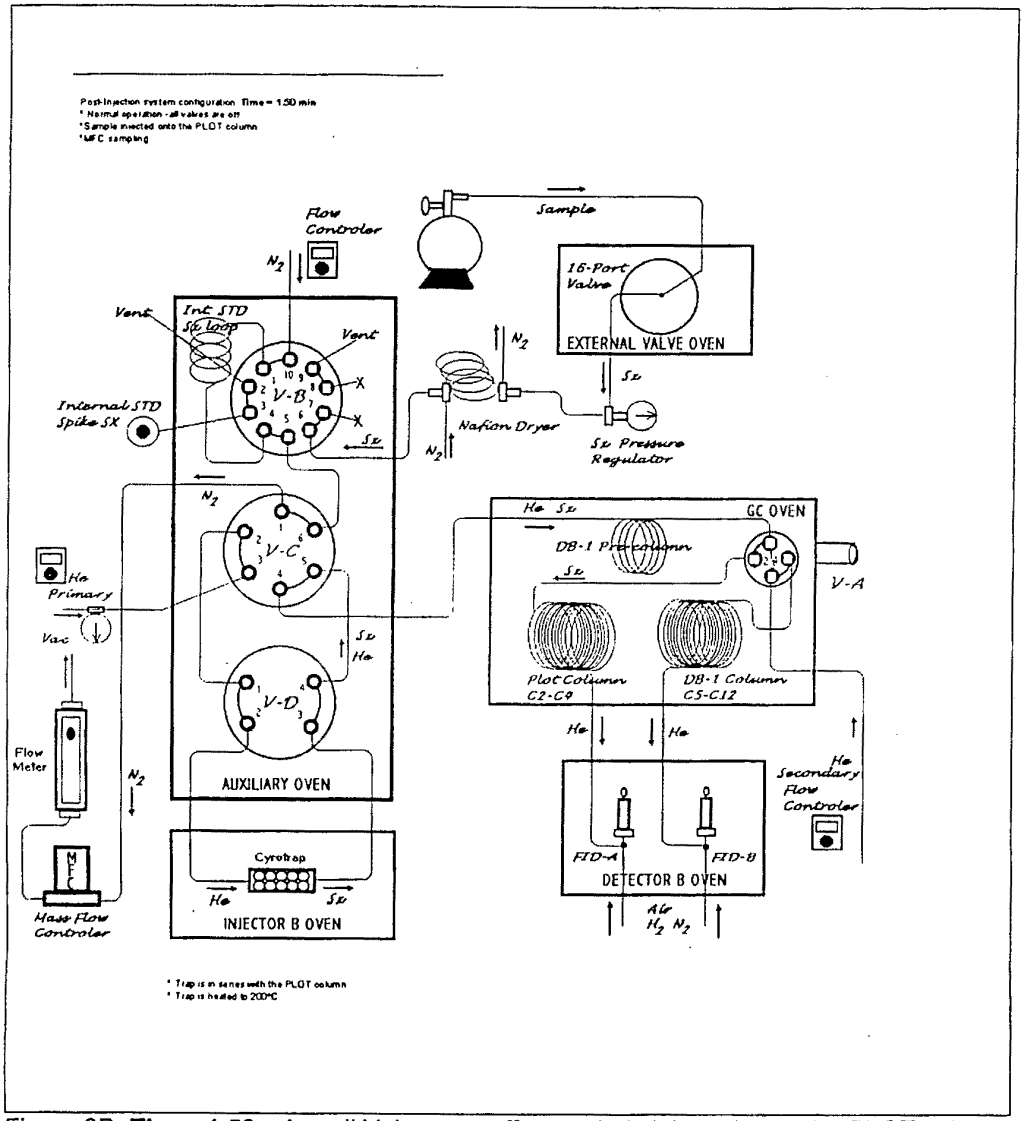


Figure 3B: **Time: 1.50 min** –all Valves are off, sample is injected onto the PLOT column.

Figure 3C. Post-Injection Time Events

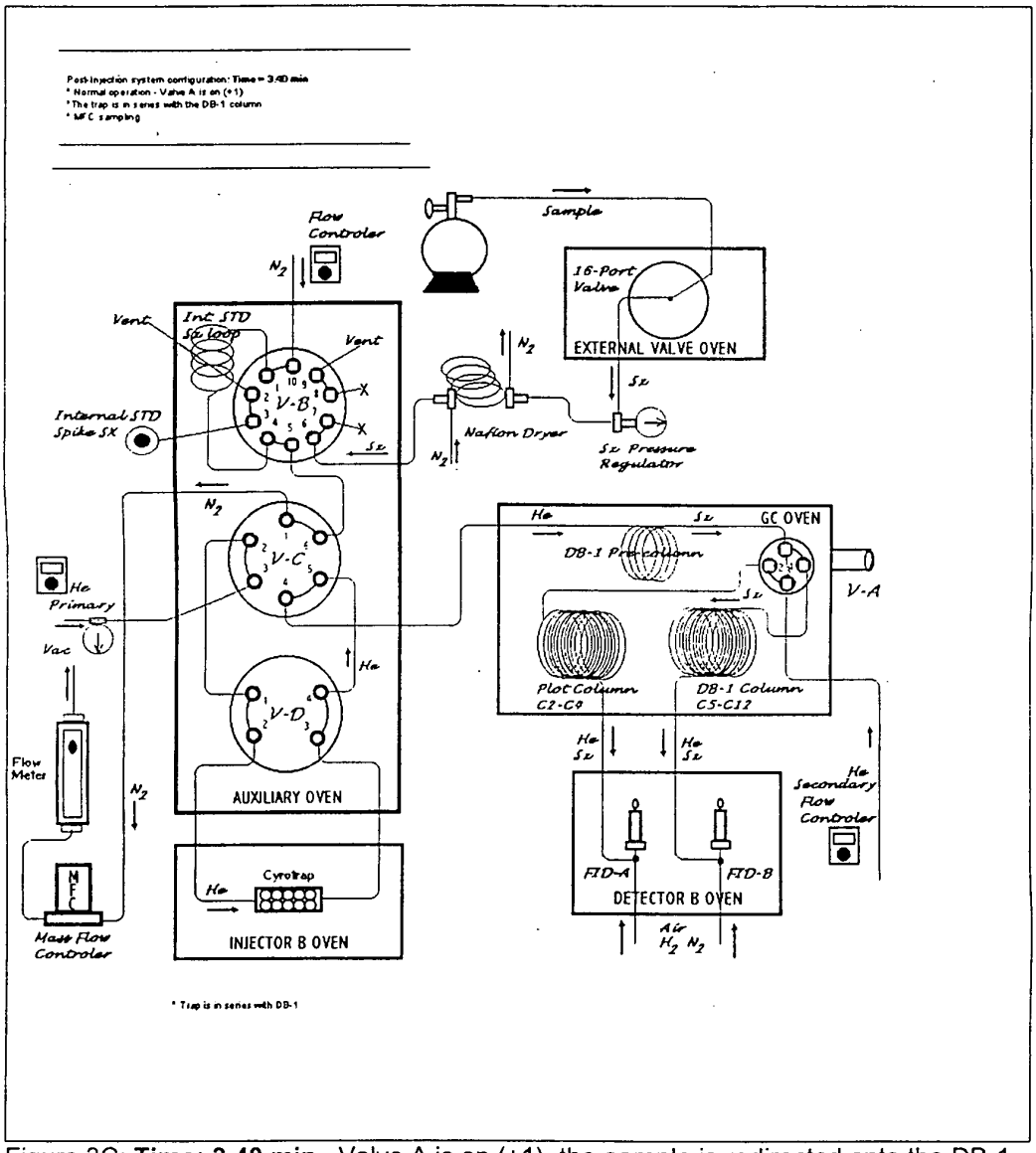


Figure 3C: **Time: 3.40 min** –Valve A is on (+1), the sample is redirected onto the DB-1 column.

Figure 4. Injector B Temperature Conversion

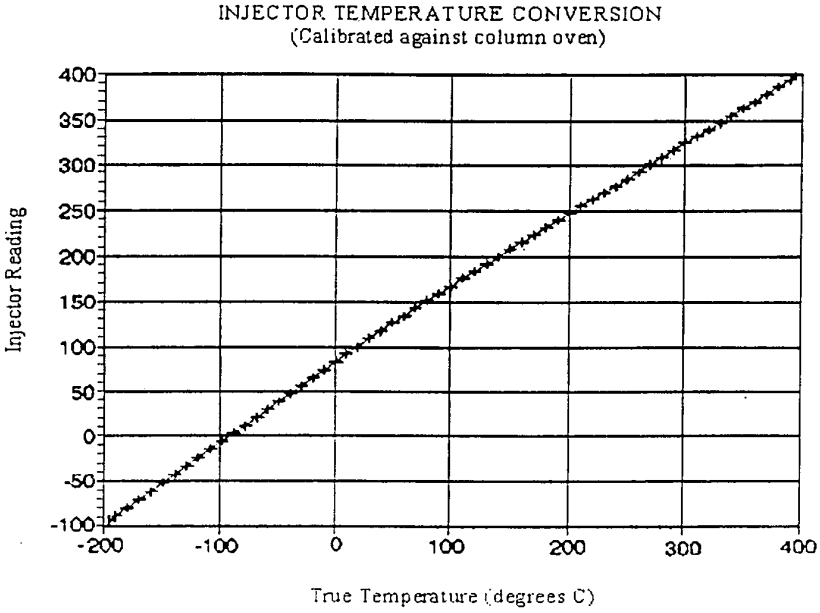


Figure 5. Injector B Temperature Profile

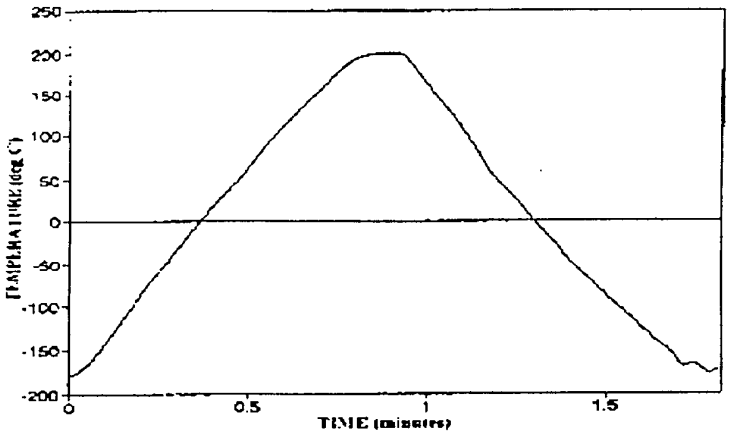


Figure 6A. NIST SRM 1800 VOC Standard

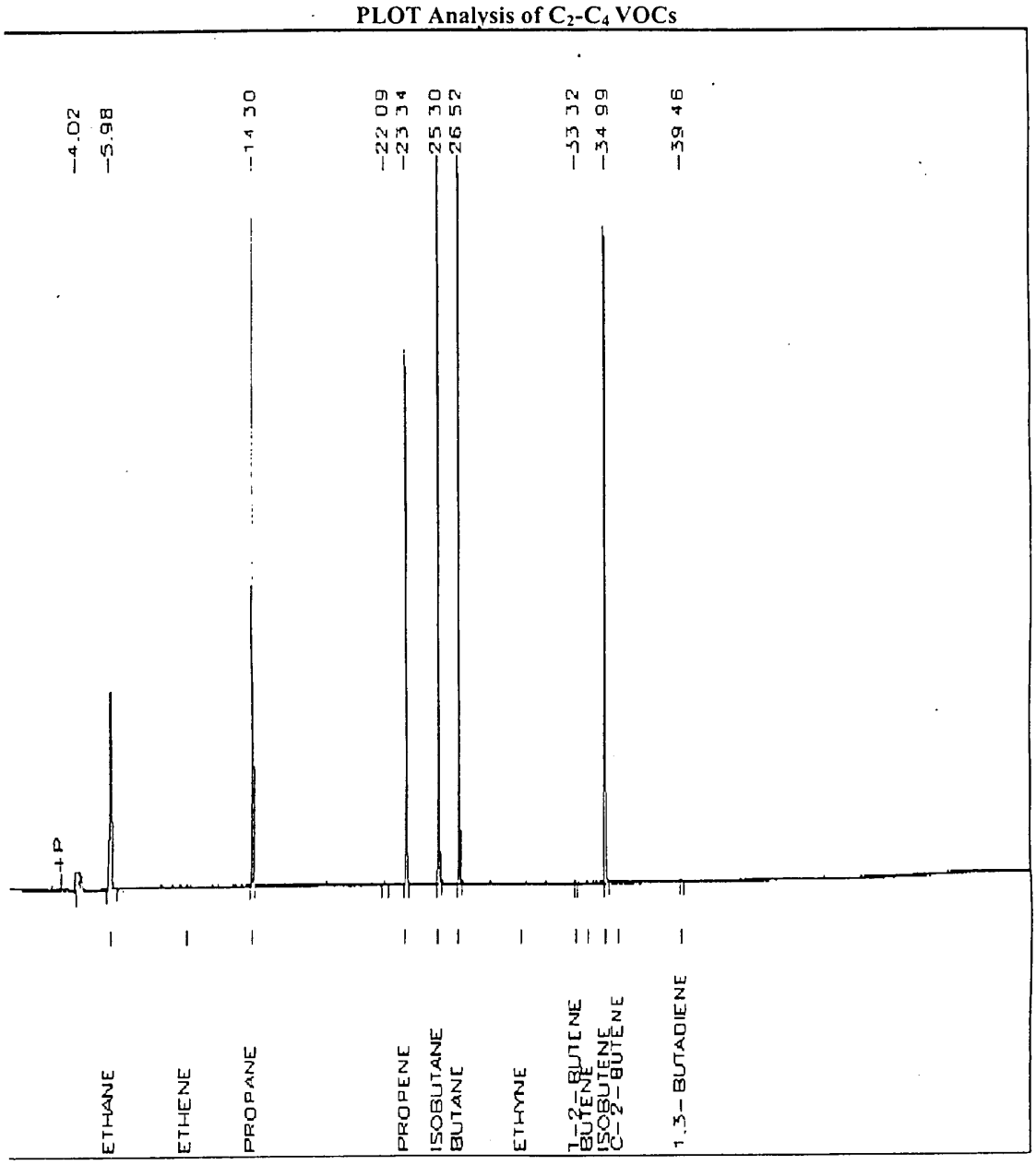


Figure 6B. NIST SRM 1800 VOC Standard

DB-1 Analysis of C_5-C_{10} VOCs

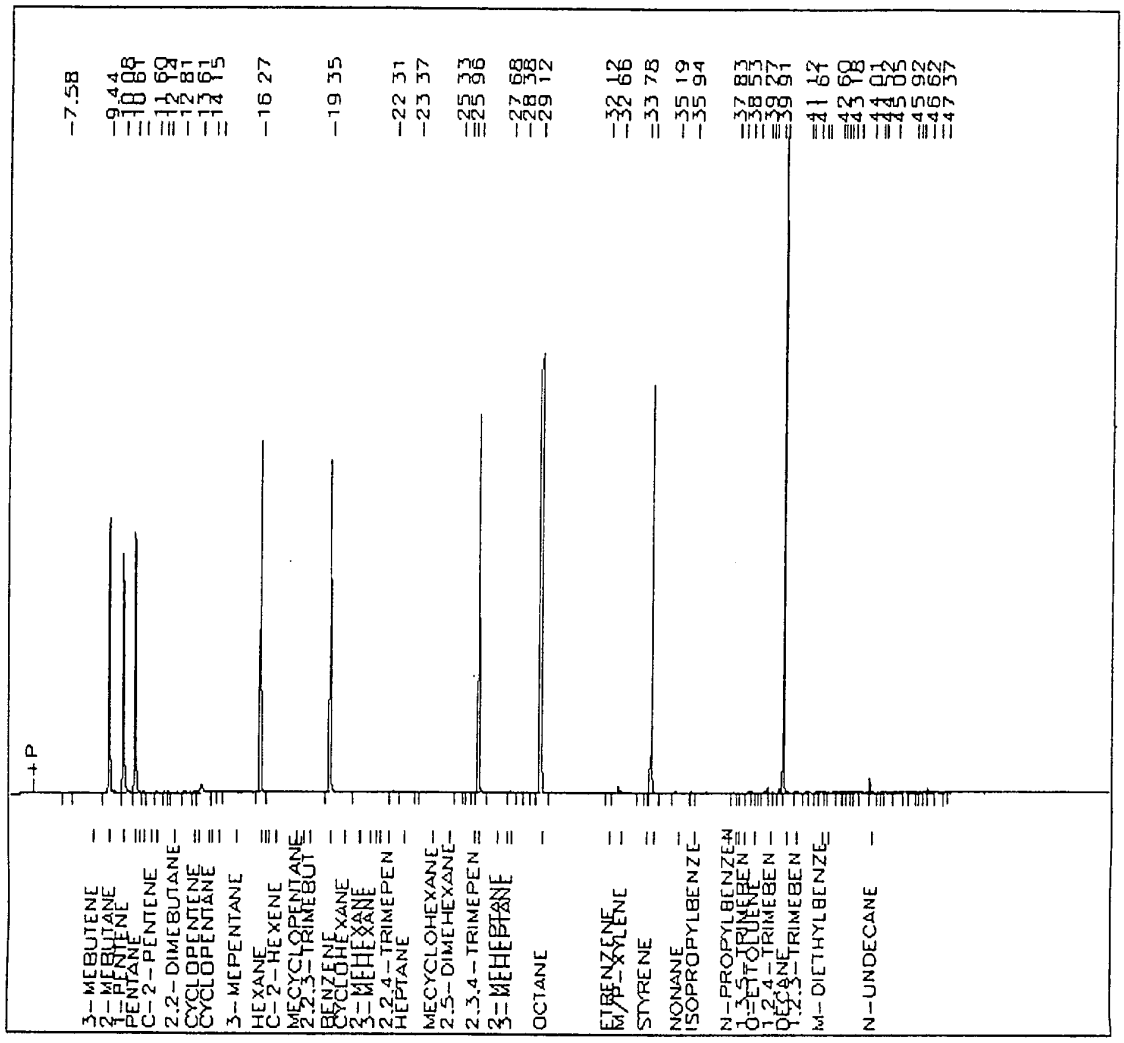


Figure 7A. PAMS Retention Time Standard (CC60089)
PLOT Analysis of C_2-C_4VOCs

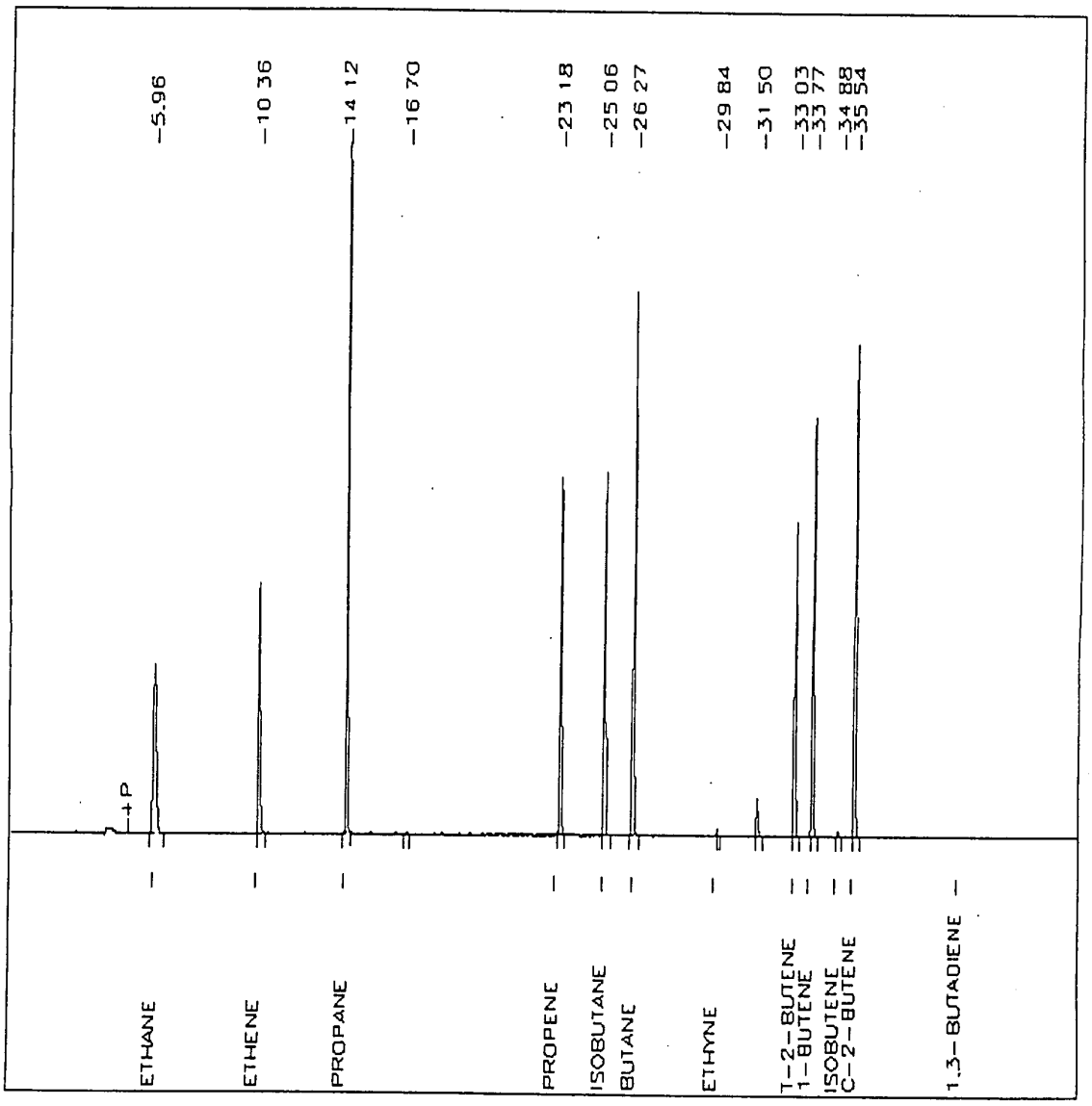


Figure 7B. PAMS Retention Time Standard (CC60089)

DB-1 Analysis of C_5-C_{12} VOCs

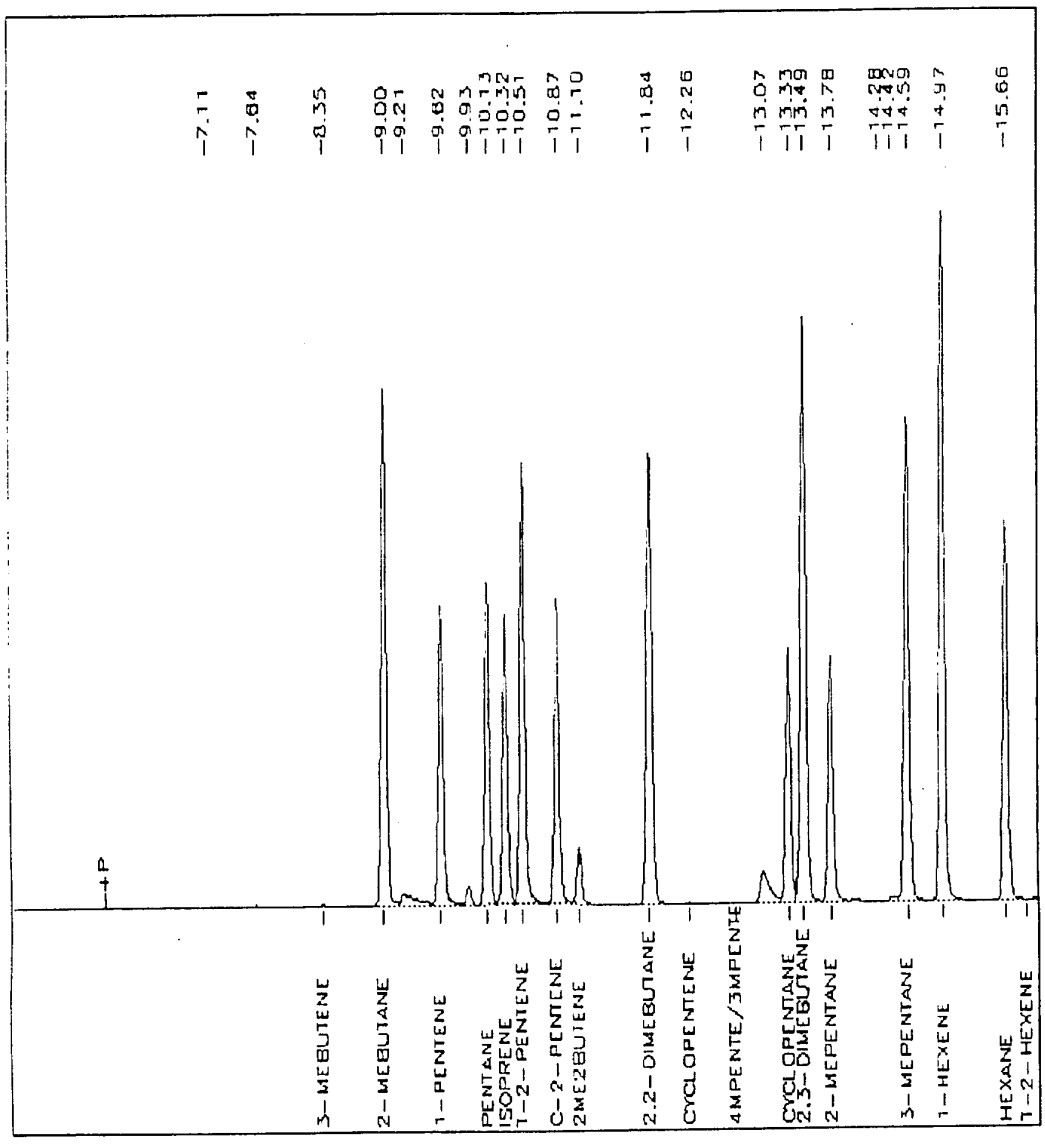


Figure 7B. PAMS Retention Time Standard (CC60089)

DB-1 Analysis of C_5-C_{12} VOCs

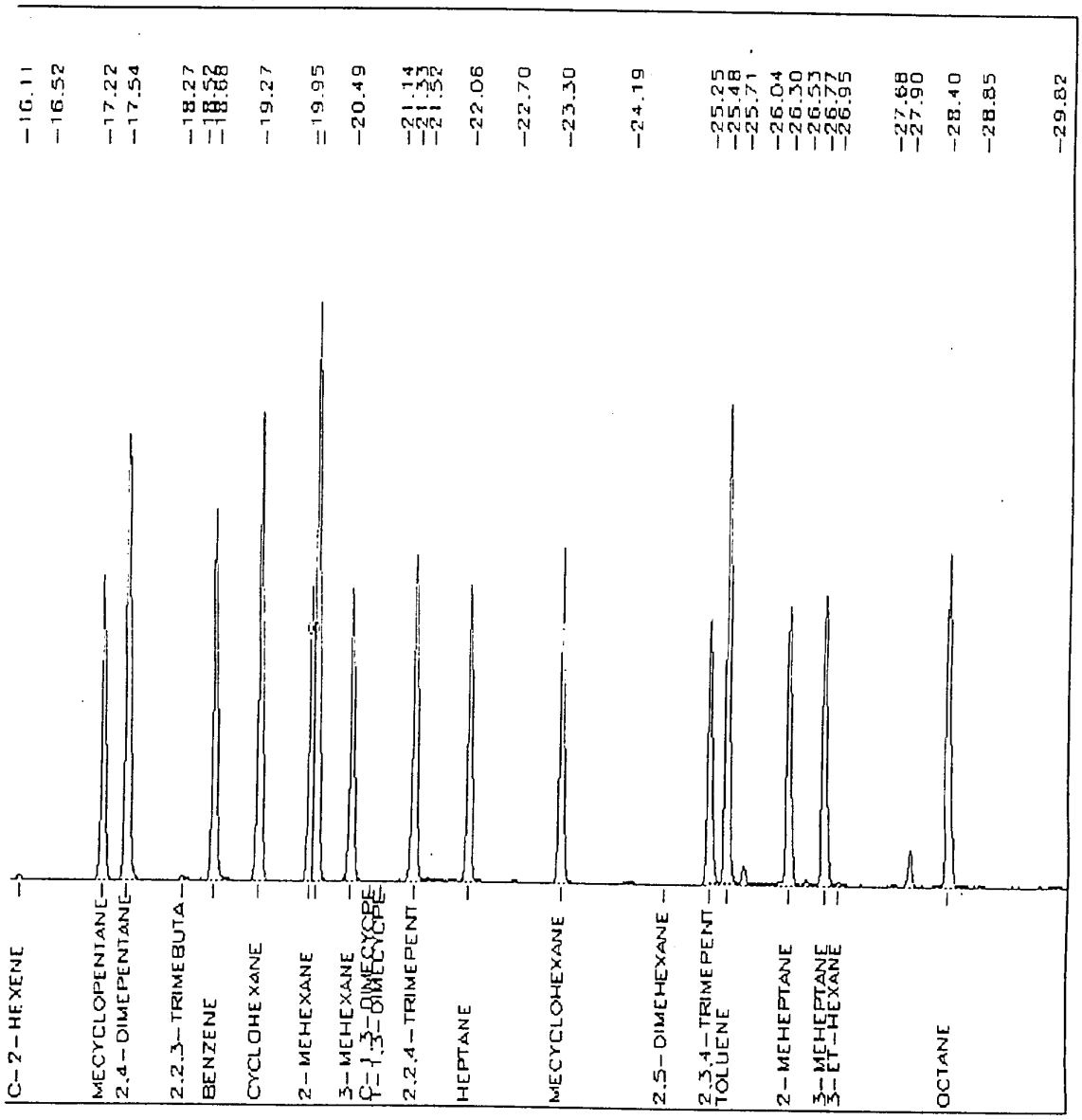
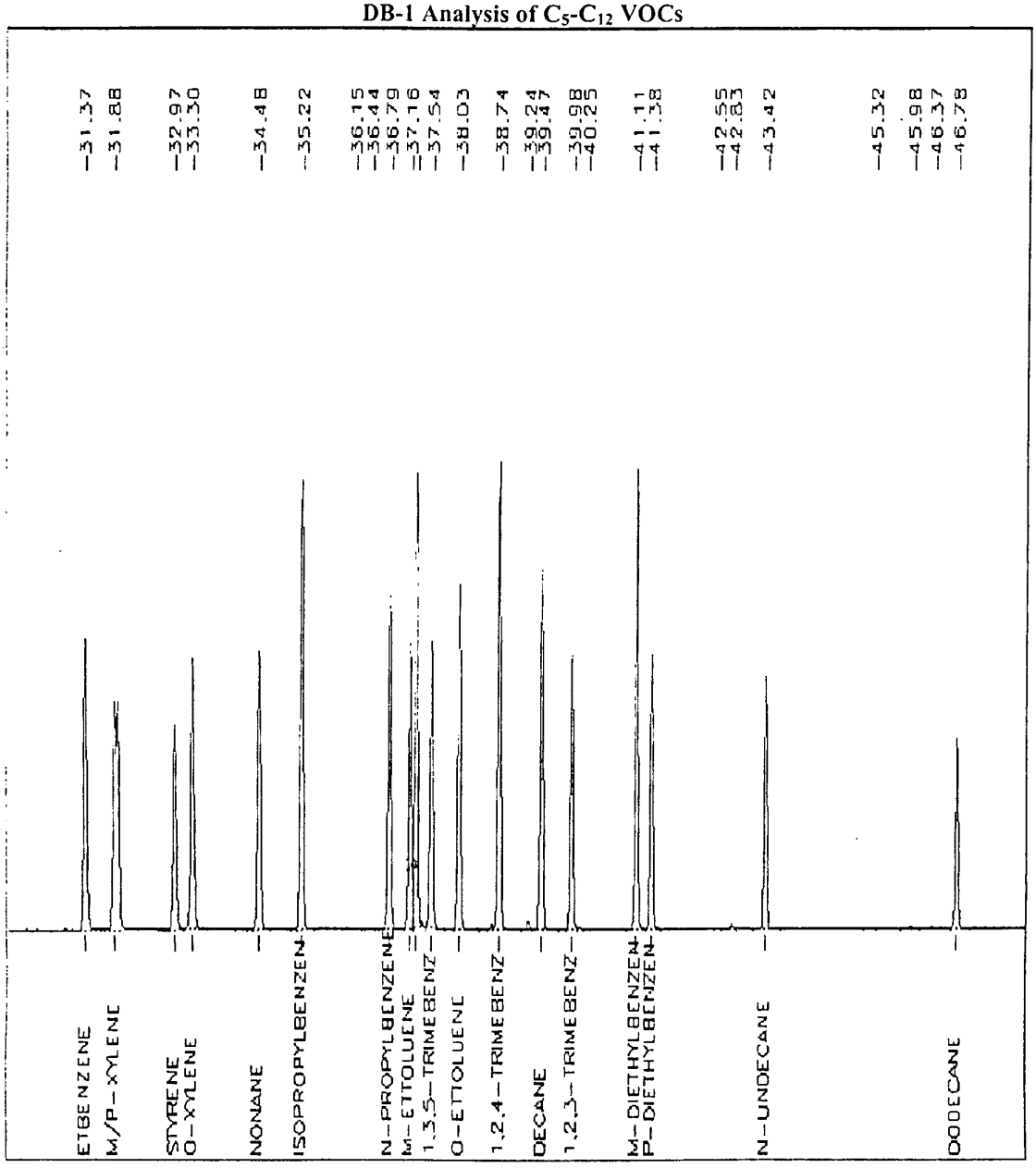


Figure 7B. PAMS Retention Time Standard (CC60089)
DB-1 Analysis of C_5-C_{12} VOCs



APPPENDIX I

TURBOCHROM - NELSON 2700 DATA SYSTEM

TURBOCHROM CHROMATOGRAPHY SYSTEM by PE Nelson: Turbochrom (Ver. 4.1<2fl2>) is a Microsoft Windows spreadsheet driven system. Here is a brief explanation of NMOC speciated chromatography setup for acquiring data, report formats, editing calibration methods, editing sequence files, incorporating Rf s, batch reprocessing the raw data files and creating peak summary reports.

The Navigator window is a graphical representation of the major functions in Turbochrom. The icons and menus along with their respective functions are as follows:

BUILD

Method This is where you can edit (non-graphically) the calibrating as well as acquiring method for any GC instrument.

Sequence Build This is where you can edit or build sequences.

Graphic Edit This allows you to graphically edit methods using a ***.raw** file.

ANALYSIS

Setup In this window you can edit the setup of the instruments, including the sequence and method files used and where created data files are stored.

Hands On This allows you to control instrument settings.

VIEW

Modify Here you can modify the active sequence or active method.

Details Lets you view detailed information about every instrument configured on your system.

Status Shows the current status of every instrument configured on your system.

Real-Time Plot This option allows you to view data points in real time.

REPROCESS

Results Allows you to reprocess ***.raw** data files with the calibrating method.

Batch Allows you to reprocess a number of ***.raw** data files at a time with the calibrating method.

Summary Here you can create a report which summarizes the results for an entire sequence by component.

DISPLAY

Chromatograms This option allows you to view multiple chromatograms and do overlays or other comparisons.

Spectra This is not used.

MENUS

Run Menu This controls single or multiple runs.

Applications Menu Here you can access any add-on applications, such as TC2ASCII.

Help Menu Allows you to get help for Turbochrom.

Instruments The instruments panel lists the instruments configured on the system. In our case there are three instruments listed:
Instrument_**B** (HC16)
Instrument_**C** (HC20)
Instrument_**D** (HC22)

INSTRUMENT

There are presently three instruments that are configured with PE Nelson 2700 Chromatography system: Instrument_B (HC16), Instrument _C (HC20), and Instrument_D (HC22).

System configuration is performed in the Configuration window (Config Icon), which allows you to edit the **F**ile menu (edit default printer), **C**olors command (defines colors for various screens), **I**nstrument command (edit configuration of all instruments connected to the computer), **P**ath menu (define where the data, methods and sequence can be stored), and **O**ptions menu (preferences in Graphic Method Editor, initialization

of any 900 Series Interface). The Configuration summary for the GC instruments in the PC is as follows:

Instr. No.	IEEE Add.	Instr. Type	Instr. Name	Autosamler Type
1	0	PEN900	Instr._**B**_HC16	None
2	1	PEN900	Instr._**C**_HC20	None
3	2	PEN900	Instr._**D**_HC22	None

There are three types of paths configured for each instrument: **1.** *System path* - path names of the directories that Turbochrom searches to find method (***.mth**) and sequence (***.seq**) files; **2.** *Program path* - drive and directory where the configuration, program, and library files are located; **3.** *Component defaults path* - DEFAULT.CMP file that contains default values that Turbochrom uses for editing new components to the method. Currently, paths configuration for the three instruments are set as follows:

Program Path	C:\TC4-2f12
System Path 1	C:\TC4-2f12\data16
System Path 2	C:\TC4-2f12\data20
System Path 3	C:\TC4-2f12\data22
Component defualts path	C:\TC4-2f12

FILE NAME FORMAT

The Nelson 2700 system (Turbochrom) uses 8 characters to form the file base name, three of which are reserved for numbering the data files and one for appending the duplicate analysis. By default, one can edit the **MMDD****** (i.e., **JN12**), where Turbochrom will append the cycle number and a letter for duplicate analysis MMDD****** (i.e., **001a**). To ensure that the base file name is unique and is indicative of the instrument that is generating the raw data file, 5 characters are used to form the file base name. The cycle of injection number is appended to the selected base name manually and the data files are stored on the specified drive and subdirectory. The same base name is used for storing raw (***.raw**) and result (***.rst**) files, where the three character extension differentiates one file from another. If a duplicate file name exists, a lower case "a" will be automatically appended to the cycle of injection number and will distinguish the file as being a second analytical run for the same sample in the sequence. To prevent any confusion and to allow easy identification of data, the following naming convention is used:

1. Use only a 5 character base name for data runs.
2. The first two characters will be a month code.
3. The third and fourth characters will be a date code.

4. The fifth character will be an instrument code: B - Instrument HC16; C Instrument HC20; D - Instrument HC22
5. The sixth through ninth character is manually assigned by the operator and represents the sample number for the base name.

MONTH CODES

JAN = **JA** JUL = **JL**
FEB = **FB** AUG = **AU**
MAR= **MR** SEP = **SE**
APR = **AP** OCT = **OC**
MAY= **MY** NOV =**NO**
JUN = **JN** DEC = **DE**

INSTRUMENT CODES

METHOD 002 = **A**
METHOD 012 = **Z**
METHOD 013 = **D**
METHOD 032 = **B/C/D** (3 instruments)

EXAMPLE: **SE08D004** Would be September 8th - Instrument HC22, Method MLD032 Speciated NMOC Analysis, cycle/injection number 4.

SAMPLE NAME FORMAT:

Within a sequence or during a manual download you must enter a sample name. The format for this is as follows:

* Generally a system blank or a sample of Grade 5 Nitrogen or equivalent is run as the first sample of the day to insure that the system is free of contamination.

* Enter system blank as: **BLK**

* The calibration NIST SRM1800 standard (ALM033762) with certified values for propane and benzene is run, labeled: **STD33762**

* The 15 component retention time standard that validates the calibration of the instruments is run, and is labeled: **CTL60089**

Once samples have been logged into LIMS, their corresponding data will be updated and transferred. A sample is identified in LIMS as being part of the NMOC analysis by the first 2 characters (i.e., **NM**) of the sample name. The rest of the LIMS numbers will be limited to 6 characters and the 7th character is used as a replicate code. If this is left blank, it represents the first analysis. A-J represents the 1st through 9th replicates. For example, if the LIMS number is **NM000125A *BF***, the NM distinguishes this sample as NMOC, the following 6 characters are additional LIMS numbers, which are followed by a capital letter "A"(replicate code), followed by a single space and then the sample location or other information. The example above is the first replicate of a Bakersfield sample having a LIMS number of NM000125A.

Turbochrom Method File

CHANNEL A: *Calibration Method for DB-1 Analysis*

Turbochrom Method File : C:\DATA16\HC16.MTH
Created by : SSR On : 5/26/98 04:00 PM
Edited by : SSR On : 5/26/98 05:03 PM
Description : Speciated NMOC HC16B Method

Instrument Conditions : Not Applicable

Instrument Control Method :
Instrument name : HC16B - Channel A

Interface Parameters :
Delay Time : 0.00 min.
Run Time : 60.00 min.
Sampling Rate : 2.0000 pts/s
Interface Type : 900
Analog Voltage Input : 1000 mV
Data will be collected from both channels

Timed Events :
There are no timed events in this method

Real Time Plot parameters :
Channel A -- Pages : 1 Offset : 0.100 mV Scale : 10.000 mV
Channel B -- Pages : 1 Offset : 0.100 mV Scale : 10.000 mV

Processing Parameters :
Bunch Factor : 4 point
Noise Threshold : 5 micro Volts
Area Threshold : 24.00 micro Volts
Peak Separation Criteria
Width Ratio : 0.200
Valley-to-Peak Ratio : 0.010

Exponential Skim Criteria
Peak Height Ratio : 5.000
Adjusted Height Ratio : 4.000
Valley Height Ratio : 3.000

Baseline Timed Events :
Event #1 - -P at 0.000
Event #2- +P at 6.000

Annotated Replot Parameters :

Offset & Scale determined automatically

Scale Factor	: 1.00000000
Number of Pages	: 3
Plot Title	: Chromatogram
X-Axis Label	: Time [min.]
Y-Axis Label	: Response [mV]
Orientation	: Landscape
Retention Labels	: Peak Crest
Component Labels	: Actual Time
Start Time	: 5.00
End Time	: 52.00

Report Format Files :

No report format files given

User Programs :

No user programs will be executed

Global Information :

Default Sample Volume	: 1.000 ppb C
Quatitation Units	: ppb C
Void Time	: 0.000 min.
Corrected amounts during calibration	: Yes
Rejected outliners during calibration	: No

An External Standard calibration will be used

Unknown peaks will be quatitated using a response factor of 1.000000

Component Information : Channel A

3-MeButene

Component Type	: Single peak Component
Retention Time	: 8.350 min.
Search Window	: 0.00 s, 3.00%
Reference Component	: 2-MeButane

Find largest peak in window

Quantitation will be done using response factor = 1.000000

2-MeButane

Component Type	: Single peak Component
Retention Time	: 9.010 min.
Search Window	: 0.00 s, 2.00%

Reference Component:

Find peak closest to expected RT in window

Quantitation will be done using response factor = 1.000000

1-Pentene

Component Type : Single peak Component
Retention Time : 9.640 min.
Search Window : 0.00 s, 2.00%
Reference Component: 2-MeButane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Pentane

Component Type : Single peak Component
Retention Time : 10.140 min.
Search Window : 0.00 s, 2.00%
Reference Component: 2-MeButane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Isoprene

Component Type : Single peak Component
Retention Time : 10.330 min.
Search Window : 0.00 s, 2.00%
Reference Component: 2-MeButane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

t-2-Pentene

Component Type : Single peak Component
Retention Time : 10.520 min.
Search Window : 0.00 s, 2.00%
Reference Component : 2-MeButane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

c-2-Pentene

Component Type : Single peak Component
Retention Time : 10.860 min.
Search Window : 0.00 s, 2.00%
Reference Component: 2-MeButane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

2Me2Butene

Component Type : Single peak Component
Retention Time : 11.110 min.
Search Window : 0.00 s, 2.00%
Reference Component: 2-MeButane
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

2,2-DiMeButane

Component Type : Single peak Component
Retention Time : 11.810 min.
Search Window : 0.00 s, 5.00%
Reference Component : 2-MeButane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Cyclopentene

Component Type : Single peak Component
Retention Time : 12.280 min.
Search Window : 0.00 s, 0.50%
Reference Component : 2-MeButane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

4MPente/3Mpente

Component Type : Single peak Component
Retention Time : 12.770 min.
Search Window : 0.00 s, 0.50%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Cyclopentane

Component Type : Single peak Component
Retention Time : 13.340 min.
Search Window : 0.00 s, 1.00%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

2,3-DiMeButane

Component Type : Single peak Component
Retention Time : 13.510 min.
Search Window : 0.00 s, 1.50%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

2-MePentane

Component Type : Single peak Component
Retention Time : 13.790 min.
Search Window : 0.00 s, 2.00%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

3-MePentane

Component Type : Single peak Component
Retention Time : 14.610 min.
Search Window : 0.00 s, 2.00%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

1-Hexene

Component Type : Single peak Component
Retention Time : 14.980 min.
Search Window : 0.00 s, 2.00%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

Hexane

Component Type : Single peak Component
Retention Time : 15.680 min.
Search Window : 0.00 s, 2.00%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

t-2-Hexene

Component Type : Single peak Component
Retention Time : 15.870 min.
Search Window : 0.00 s, 0.50%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

c-2-Hexene

Component Type : Single peak Component
Retention Time : 16.120 min.
Search Window : 0.00 s, 0.50%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

MeCycloPentane

Component Type : Single peak Component
Retention Time : 17.230 min.
Search Window : 0.00 s, 1.50%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

2,4-DiMePentane

Component Type : Single peak Component
Retention Time : 17.560 min.
Search Window : 0.00 s, 2.00%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

2,2,3-TriMeButane

Component Type : Single peak Component
Retention Time : 18.290 min.
Search Window : 0.00 s, 0.50%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

Benzene

Component Type : Single peak Component
Retention Time : 18.710 min.
Search Window : 0.00 s, 1.50%
Reference Component:
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Cyclohexane

Component Type : Single peak Component
Retention Time : 19.300 min.
Search Window : 0.00 s, 1.50%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

2-MeHexane

Component Type : Single peak Component
Retention Time : 19.970 min.
Search Window : 0.00 s, 0.30%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

2,3-DiMePentane

Component Type : Single peak Component
Retention Time : 20.050 min.
Search Window : 0.00 s, 0.30%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

3-MeHexane

Component Type : Single peak Component
Retention Time : 20.520 min.
Search Window : 0.00 s, 1.50%
Reference Component : Benzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

c-1,3-DiMeCycPenta

Component Type : Single peak Component
Retention Time : 20.750 min.
Search Window : 0.00 s, 0.50%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

t-1,3-DiMeCycPenta

Component Type : Single peak Component
Retention Time : 20.890 min.
Search Window : 0.00 s, 0.50%
Reference Component : Benzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

2,2,4-TriMePentane

Component Type : Single peak Component
Retention Time : 21.350 min.
Search Window : 0.00 s, 1.50%
Reference Component : Toluene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Heptane

Component Type : Single peak Component
Retention Time : 22.090 min.
Search Window : 0.00 s, 1.50%
Reference Component : Toluene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

MeCycloHexane

Component Type : Single peak Component
Retention Time : 23.330 min.
Search Window : 0.00 s, 1.50%
Reference Component : Toluene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

2,5-DiMeHexane

Component Type : Single peak Component
Retention Time : 24.650 min.
Search Window : 0.00 s, 0.50%
Reference Component : Toluene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

2,3,4-TriMePentane

Component Type : Single peak Component
Retention Time : 25.280 min.
Search Window : 0.00 s, 1.00%
Reference Component : Toluene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

Toluene

Component Type : Single peak Component
Retention Time : 25.520 min.
Search Window : 0.00 s, 1.50%
Reference Component:
Find largest peak in window
Quantitation will be done using response factor = 1.000000

2-MeHeptane

Component Type : Single peak Component
Retention Time : 26.330 min.
Search Window : 0.00 s, 1.00%
Reference Component : Toluene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

3-MeHeptane

Component Type : Single peak Component
Retention Time : 26.810 min.
Search Window : 0.00 s, 1.00%
Reference Component : Toluene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

3-Et-Hexane

Component Type : Single peak Component
Retention Time : 26.990 min.
Search Window : 0.00 s, 0.50%
Reference Component : Toluene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Octane

Component Type : Single peak Component
Retention Time : 28.440 min.
Search Window : 0.00 s, 1.50%
Reference Component : Toluene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

EtBenzene

Component Type : Single peak Component
Retention Time : 31.410 min.
Search Window : 0.00 s, 1.00%
Reference Component : Toluene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

m/p-Xylene

Component Type : Single peak Component
Retention Time : 31.930 min.
Search Window : 0.00 s, 1.00%
Reference Component:
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Styrene

Component Type : Single peak Component
Retention Time : 33.020 min.
Search Window : 0.00 s, 0.50%
Reference Component : m/p-Xylene

Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

o-Xylene

Component Type : Single peak Component
Retention Time : 33.340 min.
Search Window : 0.00 s, 0.50%
Reference Component : m/p-Xylene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Nonane

Component Type : Single peak Component
Retention Time : 34.520 min.
Search Window : 0.00 s, 1.00%
Reference Component : m/p-Xylene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

IsoPropylBenzene

Component Type : Single peak Component
Retention Time : 35.260 min.
Search Window : 0.00 s, 1.00%
Reference Component : n-PropylBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

n-PropylBenzene

Component Type : Single peak Component
Retention Time : 36.830 min.
Search Window : 0.00 s, 1.00%
Reference Component:
Find largest peak in window
Quantitation will be done using response factor = 1.000000

m-EtToluene

Component Type : Single peak Component
Retention Time : 37.200 min.
Search Window : 0.00 s, 0.30%
Reference Component : 1,2,4-TriMeBenzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

p-EtToluene

Component Type : Single peak Component
Retention Time : 37.310 min.
Search Window : 0.00 s, 0.30%
Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

1,3,5-TriMeBenzene

Component Type : Single peak Component
Retention Time : 37.580 min.
Search Window : 0.00 s, 0.50%
Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

o-EtToluene

Component Type : Single peak Component
Retention Time : 38.070 min.
Search Window : 0.00 s, 1.00%
Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

1,2,4-TriMeBenzene

Component Type : Single peak Component
Retention Time : 38.780 min.
Search Window : 0.00 s, 0.50%
Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Decane

Component Type : Single peak Component
Retention Time : 39.510 min.
Search Window : 0.00 s, 0.50%
Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

1,2,3-TriMeBenzene

Component Type : Single peak Component
Retention Time : 40.020 min.
Search Window : 0.00 s, 1.00%

Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

m-diethylbenzene

Component Type : Single peak Component
Retention Time : 41.150 min.
Search Window : 0.00 s, 0.30%
Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

p-diethylbenzene

Component Type : Single peak Component
Retention Time : 41.410 min.
Search Window : 0.00 s, 0.30%
Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

n-undecane

Component Type : Single peak Component
Retention Time : 43.460 min.
Search Window : 0.00 s, 0.50%
Reference Component : 1,2,4-TriMeBenzene
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

Dodecane

Component Type : Single peak Component
Retention Time : 46.460 min.
Search Window : 0.00 s, 2.00%
Reference Component : 1,2,4-TriMeBenzene
Find largest peak in window
Quantitation will be done using response factor = 1.000000

CHANNEL B: *Calibration Method for PLOT Analysis*

Turbochrom Method File : C:\DATA16\IC16.MTH
Created by : SSR On : 5/26/98 04:00 PM
Edited by : SSR On : 5/26/98 05:03 PM
Description : Speciated NMOC HC16B Method

Instrument Conditions : Not Applicable

Instrument Control Method :

Instrument name : HC16B - Channel B

Interface Parameters :

Delay Time : 0.00 min.
Run Time : 50.00 min.
Sampling Rate : 2.0000 pts/s
Interface Type : 900
Analog Voltage Input :1000 mV
Data will be collected from both channels

Timed Events :

There are no timed events in this method

Real Time Plot parameters :

Channel A -- Pages : 1 Offset : 0.100 mV Scale : 10.000 mV
Channel B -- Pages : 1 Offset : 0.100 mV Scale : 10.000 mV

Proccessing Parameters :

Bunch Factor : 2 point
Noise Threshold : 9 micro Volts
Area Threshold : 45.00 micro Volts

Peak Separation Criteria
Width Ratio : 0.200
Valley-to-Peak Ratio : 0.010

Exponential Skim Criteria
Peak Height Ratio : 5.000
Ajusted Height Ratio : 4.000
Valley Height Ratio : 3.000

Baseline Timed Events :
Event #1 - -P at 0.000
Event #2- +P at 3.000

Annotated Replot Parameters :
Offset will be autozeroed
Plot Scale: 10.000 mV

Number of Pages	: 1
Plot Title	: Chromatogram
X-Axis Label	: Time [min.]
Y-Axis Label	: Response [mV]
Orientation	: Landscape
Retention Labels	: Top of Plot
Component Labels	: Actual Time
Start Time	: 3.00
End Time	: 50.00

Report Format Files :
No report format files given

User Programs :
No user programs will be executed

Global Information :

Default Sample Volume	: 1.000 ppb C
Quatitation Units	: ppb C
Void Time	: 0.000 min.

Corrected amounts during calibration : Yes

Rejected outliners during calibration : No
An External Standard calibration will be used
Unknown peaks will be quatitated using a response factor of 1.000000

Component Information : Channel B

Ethane

Component Type	: Single peak Component
Retention Time	: 5.970 min.
Search Window	: 0.00 s, 5.00%
Reference Component	: Propane

Find largest peak in window
Quantitation will be done using response factor = 1.000000

Ethane

Component Type	: Single peak Component
Retention Time	: 10.430 min.
Search Window	: 0.00 s, 5.00%
Reference Component	: Propane

Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

Propane

Component Type : Single peak Component
Retention Time : 14.290 min.
Search Window : 0.00 s, 5.00%
Reference Component:

Find largest peak in window
Quantitation will be done using response factor = 1.000000

Propene

Component Type : Single peak Component
Retention Time : 23.380 min.
Search Window : 0.00 s, 1.00%
Reference Component : Propane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Isobutane

Component Type : Single peak Component
Retention Time : 25.335 min.
Search Window : 0.00 s, 1.00%
Reference Component : Propane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Butane

Component Type : Single peak Component
Retention Time : 26.540 min.
Search Window : 0.00 s, 1.00%
Reference Component : Propane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Ethyne

Component Type : Single peak Component
Retention Time : 30.200 min.
Search Window : 0.00 s, 3.00%
Reference Component : Propane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

t-2-Butene

Component Type : Single peak Component
Retention Time : 33.290 min.
Search Window : 0.00 s, 0.50%
Reference Component : Propane

Find largest peak in window
Quantitation will be done using response factor = 1.000000

Butene

Component Type : Single peak Component
Retention Time : 34.010 min.
Search Window : 0.00 s, 0.50%
Reference Component : Propane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

Isobutene

Component Type : Single peak Component
Retention Time : 35.090 min.
Search Window : 0.00 s, 1.00%
Reference Component : Propane
Find peak closest to expected RT in window
Find largest peak in window
Quantitation will be done using response factor = 1.000000

c-2-Butene

Component Type : Single peak Component
Retention Time : 35.740 min.
Search Window : 0.00 s, 3.00%
Reference Component : Propane
Find peak closest to expected RT in window
Quantitation will be done using response factor = 1.000000

1,3-Butadiene

Component Type : Single peak Component
Retention Time : 40.060 min.
Search Window : 0.00 s, 3.00%
Reference Component : Propane
Find largest peak in window
Quantitation will be done using response factor = 1.000000

SEQUENCE

Turbochrom Sequence File : C:\TC4-2F12\DATA16\APR23B.SEQ
Created by : SSR on : 5/27/98 10:45 AM
Edited by : SSR on : 5/27/98 10:47 AM
Description : Not Applicable

Number of Times Edited : 1
Sequence File Header Information:
Number of Rows : 5
Instrument Type : 760 / 900 Series Intelligent Interface
Injection Type : SINGLE

Sequence Sample Description

Sequence Sample Descriptions - Channel A

Row	Sample Name	Sample Number	Study Amount	Sample Amount	ISTD Method	Instrum. Method	Process Format	Calib File	Report File	Raw File
1 Sample	BLK	1	1.000	1.000	hC16	hC16	hC16	HC16	AP23B001	AP23B001
2 Sample	STD33762	2	1.000	1.000	hC16	hC16	hC16	HC16	AP23B001	AP23B001
3 Sample	CTL60089	3	1.000	1.000	hC16	hC16	hC16	HC16	AP23B001	AP23B001
4 Sample	NM000125	4	1.000	1.000	hC16	hC16	hC16	HC16	AP23B001	AP23B001
5 Sample	NM000125A	5	1.000	1.000	hC16	hC16	hC16	HC16	AP23B001	AP23B001

Sequence Sample Descriptions - Channel B

Row	Sample Name	Sample Number	Study Amount	Sample Amount	ISTD Method	Instrum. Method	Process Format	Calib File	Report File	Raw File
1 Sample	BLK	1	1.000	1.000	IC16	IC16	IC16	IC16	BP23B001	BP23B001
2 Sample	STD33762	2	1.000	1.000	IC16	IC16	IC16	IC16	BP23B001	BP23B001
3 Sample	CTL60089	3	1.000	1.000	IC16	IC16	IC16	IC16	BP23B001	BP23B001
4 Sample	NM000125	4	1.000	1.000	IC16	IC16	IC16	IC16	BP23B001	BP23B001
5 Sample	NM000125A	5	1.000	1.000	IC16	IC16	IC16	IC16	BP23B001	BP23B001

Turbochrom Report Format File -- C:\TC4-2F12\DATA16\HC16.RPT
Created by : SSR on : 5/2/96 11:36 AM
Edited by : SSR on : 5/26/98 04:00 PM
Number of Times Edited : 24
Report Title:
INSTRUMENT B (HC16)-CHANNEL A - DB-1 COLUMN
User Report Header:
HC16.MTH - DB1 Chromatograph of Speciated NMOC - 1998 Season
User Report Footer: No user footer will be printed

Report Format Options:
System Header

A medium default header will be printed
Compressed mode
The report body will be in 132 column mode
Report Body Options
Identified components
Unidentified peaks
Missing components will be listed in the main report
Miscellaneous Options
Report Area Reject = 0.00

Report Columns:

Column : 1 -- Peak Number Width : 3
Label 1 : 'Peak ' Label 2 : '#'
Precision: 0 Total Column: NO Expression:

Column : 2 -- Retention Time Width : 7
Label 1 : 'Time ' Label 2 : '[min]'
Precision: 3 Total Column: NO Expression:

Column : 3 -- Component Name Width : 12
Label 1 : 'Component ' Label 2 : 'Name'
Precision: 0 Total Column: NO Expression:

Column : 4 -- Adjusted Amount Width : 10
Label 1 : 'Concentration ' Label 2 : 'ppbC'
Precision: 3 Total Column: YES Expression:

Column : 5 -- Peak Area Width : 12
Label 1 : 'Area ' Label 2 : '[uV.s]'
Precision: 2 Total Column: YES Expression:

Column : 6 -- Baseline Code Width : 3
Label 1 : 'BL ' Label 2 : ''
Precision: 0 Total Column: NO Expression:

Column : 7 -- Area to Height Ratio Width : 6
Label 1 : 'Area/Height ' Label 2 : '[s]'
Precision: 2 Total Column: NO Expression:

Column : 8 -- Reference Peak Width : 20
Label 1 : 'Reference ' Label 2 : 'Component'
Precision: 0 Total Column: NO Expression:
Column : 9 -- Relative RT Width : 7

Label 1 : 'Rel. RT ' Label 2 : ''
Precision: 2 Total Column: NO Expression:

APPENDIX II

GAS CHROMATOGRAPHY

A. Gas Chromatographic Methods

Gas chromatographic (GC) methods are highly sophisticated microanalytical procedures. They should be used only by analysts experienced in the techniques required and competent to evaluate and interpret the data.

1. Gas chromatograph:

a) Principle -- In gas chromatography a mobile phase (a carrier gas) and a stationary phase (column packing or capillary column coating) are used to separate individual compounds. The carrier gas is nitrogen, argon-methane, helium, or hydrogen. For packed columns, the stationary phase is a liquid that has been coated on an inert granular solid, called the column packing, that is in borosilicate glass tubing. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven, and detector is maintained. Stationary-phase material and concentration, column length and diameter, oven temperature, carrier-gas flow, and detector type are the controlled variables. When the sample is introduced into the column, the organic compounds are moved through the column by carrier gas. They travel through the column at different rates, depending on differences in partition coefficients between the mobile and stationary phases.
b) Interferences-- Some interferences in the GC analysis occur as a result of sample or carrier gas contamination, or because large amounts of a compound injected into the GC, linger in the detector. Methylene chloride, chloroform, and other halocarbon and hydrocarbon solvents are ubiquitous contaminants in environmental laboratories. Strenuous efforts should be taken to isolate the analytical system from laboratory areas where these or other solvents are in use. Sources of interference originating in the chromatograph, and countermeasures, are as follows:
* Septum bleed -- This occurs when compounds used to make the septum on the injection port of the GC bleed from the heated septum. These high-molecular-weight silicon compounds are distinguished readily from compounds normally encountered in environmental samples. Nevertheless, septum bleed can be minimized by using septum sweep in which clean carrier gas passes over the septum to flush out the "bleed" compounds.
* Column bleed -- This term refers to the loss of column coating or the breakdown of products when the column is heated. This interference is more prevalent in packed columns, but also occurs to a much lesser extent in capillary columns. It occurs when the column temperature is high or when water or oxygen is introduced into the system. Solvent injection can damage the

stationary phase by displacing it. Certain organic compounds acting as powerful solvents, acids, or bases can degrade the column coating. Injection of large amounts of certain surface-active agents may destroy GC columns.
* Ghost peaks -- These peaks occur when an injected sample contains either a large amount of a given compound, or a compound that adsorbs to the column coating or injector parts (e.g., septum). When a subsequent sample is injected, peaks can appear as a result of the previous injection. Eliminate ghost peaks by injecting a more dilute sample, by producing less reactive derivatives of a compound that may interact strongly with the column material, by selecting a column coating that precludes these interactions, or by injecting solvent blanks between samples.

2. Detectors:

A) Flame ionization detector -- The flame ionization detector (FID) is widely used because of its high sensitivity to organic carbon-containing compounds. The detector consists of a small hydrogen/air diffusion flame burning at the end of a jet. When organic compounds enter the flame from the column, electrically charged intermediates are formed. These are collected by applying a voltage across the flame. The resulting current is amplified by an electrometer and then measured. The response of the detector is directly proportional to the total mass entering the detector per unit time and is independent of the concentration in the carrier gas.

The FID is perhaps the most widely used detector for gas chromatography because of several advantages: 1) it responds to virtually all organic carbon-containing compounds with high sensitivity (approximately 10^{-13} g/ml); 2) it does not respond to common carrier gas impurities such as water and carbon dioxide; 3) it has a large linear response range (approximately 10^{7}) and excellent baseline stability; 4) it is relatively insensitive to small column flowrate changes during temperature programming; 5) it is highly reliable, rugged, and easy to use; and 6) it has low detector dead volume effects and a fast response. Its limitations include: 1) it gives little or no response to noncombustible gases and all noble gases; and 2) it is a destructive detector that changes the physical and chemical properties of the sample irreversibly.

B) Mass spectrometer -- The mass spectrometer (MS) has the ability to detect a wide variety of compounds, coupled with a capacity to deduce compound structures from fragmentation patterns. Among the different types of mass spectrometers, the quadrapole has become the most widely used in water and wastewater analysis.

The mass spectrometer detects compounds by ionizing molecules into charged species with a 70-eV beam. The ions are accelerated toward the quadrapole mass filter through a series of lenses held at 0 to 200V. The differently sized,

charged fragments are separated according to mass-to-charge ration (related to molecular weight) by means of the quadrapole, which uses varying electric and radiofrequency (rf) fields. The quadrapole is connected to a computer, which varies these fields so that only fragments of one particular mass-to-charge ratio

(+/- 0.5) can traverse the quadrapole at any one time. As the ions leave the quadrapole they are attracted to the electron multiplier. Because the electric and the rf fields are cycled every few seconds, a fragmentation pattern is obtained. Each cycle is called a mass scan. Most chemicals have unique fragmentation patterns, called mass spectra. The computer contains, and can search, a library of known mass spectra to identify tentatively an unknown compound exhibiting a particular spectrum. Authentic compounds are used for confirmation after tentative identifications have been made.

Background mass interference can result from the ability of the mass spectrometer to detect any ions created in its ion volume (up to a specified mass). Any compounds continuously present in the source will be detected. Some mass ions are always present due to air components that leak into the system, such as oxygen (masses 16 and 32), nitrogen (masses 14 and 28), carbon dioxide (mass 44), argon (mass 40), and water (mass 18), or to helium carrier gas (masses 4 and 8), or to diffusion pump oil vapors.

APPENDIX III
VARIAN STAR CHROMATOGRAPHY WORKSTATION

The Varian Star Chromatography Workstation operates under Windows 95. The Star Chromotography Workstation controls the GC instruments, automates data collection and analysis, and documents the results of a chromatographic run. It uses four primary applications to perform specific tasks:

1. System Control and Automation
2. Method Editor
3. Interactive Graphics and Data Handling
4. Reports

The Interactive Graphics/Data Handling and Report Generating will not be addressed here since PE Nelson 2700 Data System (Turbochrom) is the primary interactive software used at this time. Also, the scope of Appendix III is directed only for speciated NMOC analysis and only addresses set parameters for Method MLD032. For general application of Star Workstation software, please refer to the Ultra Trace Hydrocarbon System Operator s Manual by Lotus Consulting (1993).

System Control and Automation: Part 1

This is the 1° station for the instrument. It reports on the status of the instrument and on its configuration. It also allows you to run methods for a particular set of samples. From this window, one can access and edit three main types of files: method file (***.mth**), sample file (***.smp**), and sequence file (***.seq**).

The basic configuration for GC Star Workstation consists of up to four GC systems, with one Analog-to-Digital Converter (ADC) Board installed in the PC for each GC (i.e., each GC is cabled to its own ADC Board). Before any sample injection can be made, the instrument must be properly configured. The bus address of each module appears at the bottom of its icon. The bus address of GC3600 (Instrument Control/Auto Control Module box) should always be one number greater than the bus address of its ADC Board.

Method MLD032 is configured with instrument #1 which is identified as Varian 3600*Cx* - NMOC16. Auto Control Module Address GC3600 17 and ADCB Address 16 are set addresses and are also configured with instrument #1. To configure or to confirm the configuration of the instrument, click mouse cursor on 'Instrument' and set the following parameters for instrument #1:

Instrument	: HC16B
Operator	: Your Name
Max Errors	: 99 (number of non-fatal errors)

Open Instrument #1/HC16B: 'System Control - Varian 3600 -HC16B - Status' - window that the operator will usually monitor during the run. It provides the

current status of the instrument and allows one to access and to modify all the system parameters for a sample run.

Open 'File'Sequence File
Method File
Sample List File
Sample Log File
Printer Setup...
Save Active Method...
Exit

Open 'Method File'...
New...
Open...

Select New or Open depending upon whether method **NMOC16.mth** already exists as a file. By taking the steps listed above, the operator has entered into the Method Editor. Note: Any of the 4 major functions can be accessed from another active function.

Method Editor:

Edit NMOC16.MTH:
1. ADCBoard-Module 16
2. ADCBoard-Data Handling-Module 16.A*
3. ADCBoard-Data Handling-Module 16.B*
4. 3600GC-Module 17

* Not used

1. Open 3600GC-Module 17:
3600 GC Injector
3600 GC Auxiliary
3600 GC Column
3600 GC Detectors
3600 AutoSampler
3600 GC Relays
3600 GC Stripchart

Edit each of the items listed for 3600 Module - 17 and set the parameters listed below:

3600 GC Injector A:

Injector Type	: Temperature Programmable
Injector Heater	: Off
Initial Temp.	: 50°C
Hold Time	: 0.00 minutes

3600 GC Injector B:

Injector Type	: Temperature Programable
Injector Heater	: On
Initial Temp.	: -172°C (set -72)

Hold Time : 0.50 minutes

Temp. Program 1
Rate : 250°C/min.
Final Temp. : 200°C (set at 250)
Hold Time : 58.0 min.
Coolant valve : On
Coolant timeout : 60.00 min.

GC Auxiliary:

Auxiliary Type : Isothermal
Auxiliary Heater : On
Description : Valves B,C,D
Initial Temp. : 175°C
Hold Time : 0.00 min.

3600 GC Column:

Column Oven : On
Initial Temp. : 0°C
Hold Time : 2.00 min.
Stabilization : 2.00 min.
Coolant to Column : On
Coolant Timeout : 60.00 min.

Column Program 1
Rate : 3°C/min.
Final Temp. : 90°C
Hold Time: 1.00 min.

Column Program 2
Rate : 5°C/min.
Final Temp. : 200°C
Hold Time : 5.00 min.

3600 GC Detectors:

Detect. Heater : On
Set Temp. : 250°C
Detector Type A : FID (On)
Detector Type B : Not used (Off)
Time Program : No
Detector Type A : Range 12
Attenuation : 8*
A/Z On : Yes

*__Note__: *The attenuation value in the 3600 GC detectors window changes the output signal to the stripchart recorder. We are currently not using the stripchart recorder and therefore the attenuation setting is not applicable in our method.*

3600 AutoSampler:

AutoSampler Type: 8134 SSV

Note: Up to 16 samples can be analyzed with the optional multi-position automated sampler. Separate external temperature control is used to heat the autosampler 130°C.

3600 GC Relays: Relay Time Program: Use

Time	Relays
0.00 min.	- - - -
0.01 min.	- - - **+4**
1.50 min.	- - - -
3.40 min.	**+1** - - -

[X] Return Relays to Initial Cond. at End Run

3600 GC Stripchart: Stripchart :Off
Time Program :No

2. Open ADCBoard - Module 16

ADCB - Set Conditions (set end time for run)
ADCB Detector Information (doc. of detectors)

ADCB - Set Cond.

End Time	: 60.00 minutes
Channel A	: FID
Channel B	: FID
Channel A Full Scale	: Alumina
Channel B Full Scale	: DB-1
Zero Display at the Start	: Yes

Detector Info.

Detector Bunch Rate	: 8 pts (5Hz)
Noise Monitor Length	: 64 bunched points
Data File Name	: MMDDB *

* MM = Month; DD = Day; **B** =designated for MLD032 HC16
i.e., MR01B = March 01 MLD032 NMOC speciated analysis

Edit Bakeout16.MTH

1. 3600GC-Module 17

2. ADCBoard-Data Handling-Module 16.A*
3. ADCBoard-Data Handling-Module 16.B*
* Not used

Note: *For convenience and the ease of creating a new method, copy NMOC16.MTH and edit only the following parameters listed below. Save method as* ***Bakeout16.mth****.*

3600 GC Injector A:
Injector Type: : Temperature Programmable
Oven on : no
Initial Temp. : 50°C
Hold Time : 0.00 minutes
Coolant Time Out. : Infinite
End Time : 69.00 min.

3600 GC Injector B:
Injector Type: : Temperature Programmable
Initial Temp. : 250°C
Hold Time : 69.00 minutes
Oven on : yes
Coolant Time Out. : Infinite

3600 GC Auxiliary:
Injector Type : Isothermal
Oven on : Yes
Initial Temp. : 175°C
Hold Time : 0.00 minutes

3600 GC Column:
Column Oven : On
Initial Temperature : 50°C
Hold Time : 0.00 minutes
Thermal Stabilization: 2.00 minutes
GC Coolant Column : No
Coolant Time Out : Infinite

Column Program 1
Rate : 30°C/min.
Final Temp. : 200°C
Hold Time : 64.00 min.

3600 GC Detectors: Same as NMOC16.mth.

3600 GC AutoSampler: Same as NMOC16.mth.

3600 GC Relays:
Relay Time Program: Use

Time	Relays
0.00 min.	**+1** -2 -3 -4

[X] Return Relays to Initial Cond. at End Run

3600 GC Stripchart: Same as NMOC16.mth.

Detector Info Data File Name : Star

Edit Idle16.MTH

1. 3600GC-Module 17
2. ADCBoard-Data Handling-Module 16.A*
3. ADCBoard-Data Handling-Module 16.B*

* Not used

Note: For convenience and the ease of creating a new method, copy NMOC16.MTH and edit only the following parameters listed below. Save method as **Idle16.mth.**

3600 GC Injector A:

Injector Type:	: Temperature Programmable
Oven on	: No
Initial Temp.	: 50°C
Hold Time	: 0.00 minutes
Coolant Time Out.	: Infinite
End Time	: 69.00 min.

3600 GC Injector B:

Injector Type:	: Temperature Programmable
Initial Temp.	: 250°C
Hold Time	: Infinite
Oven on	: Yes
Coolant Time Out.	: 30.00 minutes

3600 GC Auxiliary: Same as NMOC16.mth

3600 GC Column:

Initial Temp.	: 100°C
Hold Time	: Infinite
Therm. Stablization:	2.00 minutes
Coolant to Column	: Yes
Coolant Time Out	: 30.00 minutes

3600 GC Detectors: Same as NMOC16.mth

3600 AutoSampler: Same as NMOC16.mth

3600 GC Relays: Relay Time Program: Use **+1**

3600 GC Stripchart: Same as NMOC16.mth

Detector Info.: Data File Name : Idle

System Control and Automation: Part 2

In the 'System Control - Varian 3600 - HC16B window it is time to build a SampleList file and a Sequence file.

Edit SampleList File: New...Sample List Selection Type: 8134 SSV

NMOC16B.SMP:

Sample list or Sample File list is required by System Control for identifying what kind of sample is being injected and the order of sample injection (when performing a series of injections). In the displayed 'NMOC16B.SMP-SampleList' window there are the following parameters that need to be defined:

1. Sample Name
2. Sample Type
3. Cal. Level
4. # Inj.
5. Injection Notes
6. AutoLink
7. Stream
8. Relay Program
9. Amount Std.
10. Unidentified Peak Factor
11. Multiplier
12. Divisor

1. Sample Name: Use same format for base names as in PE Nelson 2700 Data System (Appendix I).

2. Sample Type: Use 'Analysis' as default for all samples. The system calibration and report generation will be done by PE Nelson 2700 Data System (Appendix I).

3. Cal. Level: Not applicable - all samples are set for analysis. Calibration is done by PE Nelson 2700 Data System (Appendix I).

4. # Inj.: Allows you to set the number of injections (i.e., number of analysis) to be performed on that particular sample.

5. Injection Notes: User defined

6. AutoLink: N.A.

7. Stream: Identify the port (stream) number for the corresponding sample.

8. Relay Program: Discussed below in text.

9. Amount Std: Use 1.0000 as a default value.

10. Unidentified Peak Factor: Use 0.0000 as a default value.

11. Multiplier: Use 1.0000 as a default value.

12. Divisor: Use 1.0000 as a default value.

Note: *These values are set in the 'Defaults...' window (click on the defaults button in the SampleList window). These parameters are common to all entries in the Sample List with the exceptions of Sample Name, # Inj., and Stream, which are edited directly in the SampleList window.*

8. Relay Program: In the 'Defaults...' window click on 'Relays...' button and open '8134 SSV Relay Program'. A 300 sccm aliquot of standard, control or ambient air sample is introduced into the GC

from the automated preconcentration system by means of the relay time program set below as follows:

Time (min.)	Relay 1	2	3	4
0.00	-	-	-	-
0.01	-	-	**+3**	-
1.00	-	**+2**	**+3**	-
7.00	-	**+2**	-	-
7.30	-	**+2**	-	**+4**
7.35	-	-	-	**+4**

Note:(-) sign = off position; (+) sign = on position

Save or update the default settings, and return to the 'NMOC16B.SMP - SampleList' window. Complete the sample list and Save as...NMOC16B.SMP.

Note: To run a dilution of a particular sample or a multipoint analysis of speciated NMOC analytes, edit the relay time program in the NMOC16B.SMP. as follows:

1. Identify the sample that requires dilution.
2. Identify the stream that the particular sample is attached to.
3. Log-in the sample in the SampleList, using default parameters.
4. Click on the stream number (select with mouse) and edit the relays in the SampleList window. Do not edit the relays under the default window because these are set for 300 cc sample volume common to all entries in the SampleList.
5. Edit the time between activating Valve B (**+3**) and turning off Valve B (**-3**), thus varying the effective sample loading. Leave other time events as default values.
6. Save the changes made. Only the selected stream will have saved edited parameters, whereas the rest of the samples in the SampleList file will have default values.

Bakeout16.SMP:

Bakeout16.smp is a sample file that is appended to Bakeout16.MTH. Bakeout16.mth calls for injection of the sample and requires a separate sample file that has defined parameters that differ from the .SMP file discussed above. In the New...SampleList window, log in the name of the sample as 'Bakeout' sample. Use all the default values (as discussed previously) and edit Relays...:

Time (min.)	Relay 1 2 3 4
0.00	+1 - - -

All the relays are in off-position except for valve A (+1), and no sample is injected into the column (sample flow dead-ends, N_2-purge gas flows through the mass flow controller and flow meter and He-carrier gas flows through the cold trap and through the column to the detector). Valve A is on to keep the trap in series with the DB-1 column, as to prevent any external contamination of the PLOT column. The purpose of the "Baking-out" the system is to remove any contamination (e.g., volatile and semi-volatile residues) by elevating the temperatures of different temperature zones for short periods of time.

Idle16.SMP:

Create an Idle sample list file for Idle16.mth by copying the Bakeout16.smp and Save As Idle16.smp.

Edit New Sequence:

The Sequence (*.seq) file is responsible for the coordination and execution of a number of operations. The *.seq file consists of list of *.mth file/*.smp file pairs in order of execution. By applying different strategies in building the *.seq file, one can:

1. Run each SampleList using a different method
2. Run a series of Sample Lists using the same method
3. Run one Sample List run by variety of methods

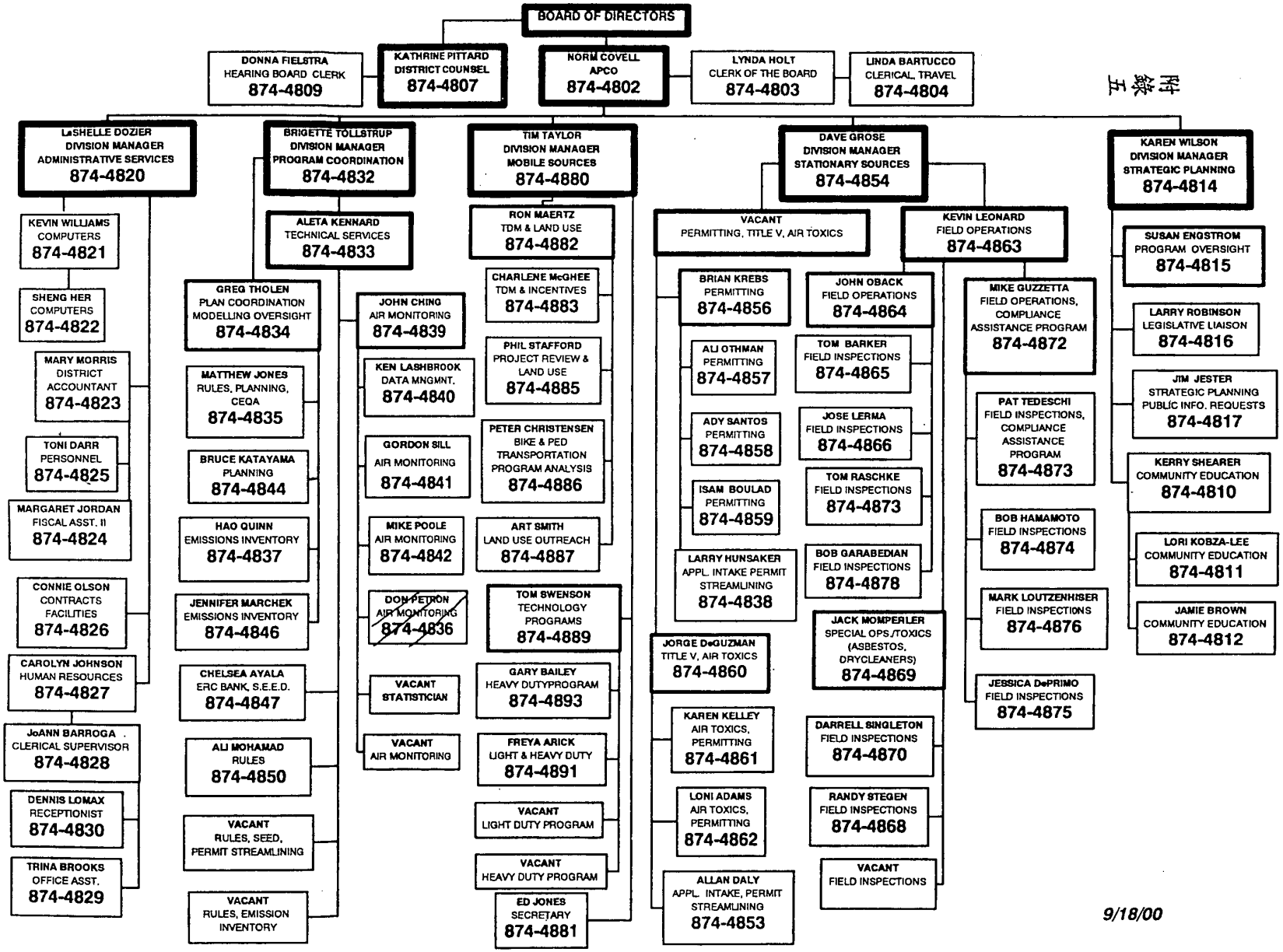
In the new Sequence window, click on desired cell in the column. The default path is displayed with a file name that is highlighted. Either type in the path name or use a Browse button. The typical .SEQ for NMOC16B.SEQ run is as follows:

	Method	SampleList/Log	Action
1.	C:\Star**NMOC16.MTH**	C:\Star**NMOC16B.SMP**	Inject

2. C:\Star**Idle16.MTH** C:\Star**Idle16B.SMP** Inject

Select the File and Save As...NMOC16B.SEQ. To activate a .SEQ, select File/Sequence File (NMOC16B.SEQ) and Activate a System Control Sequence dialog box. When a sequence is started, System Control performs a series of checks on the method and SampleList files. If any of these checks fails, System Control aborts the *.seq and indicates the cause within message boxes or entries to the Sequence Log.

SACRAMENTO METROPOLITAN AIR QUALITY MANAGEMENT DISTRICT



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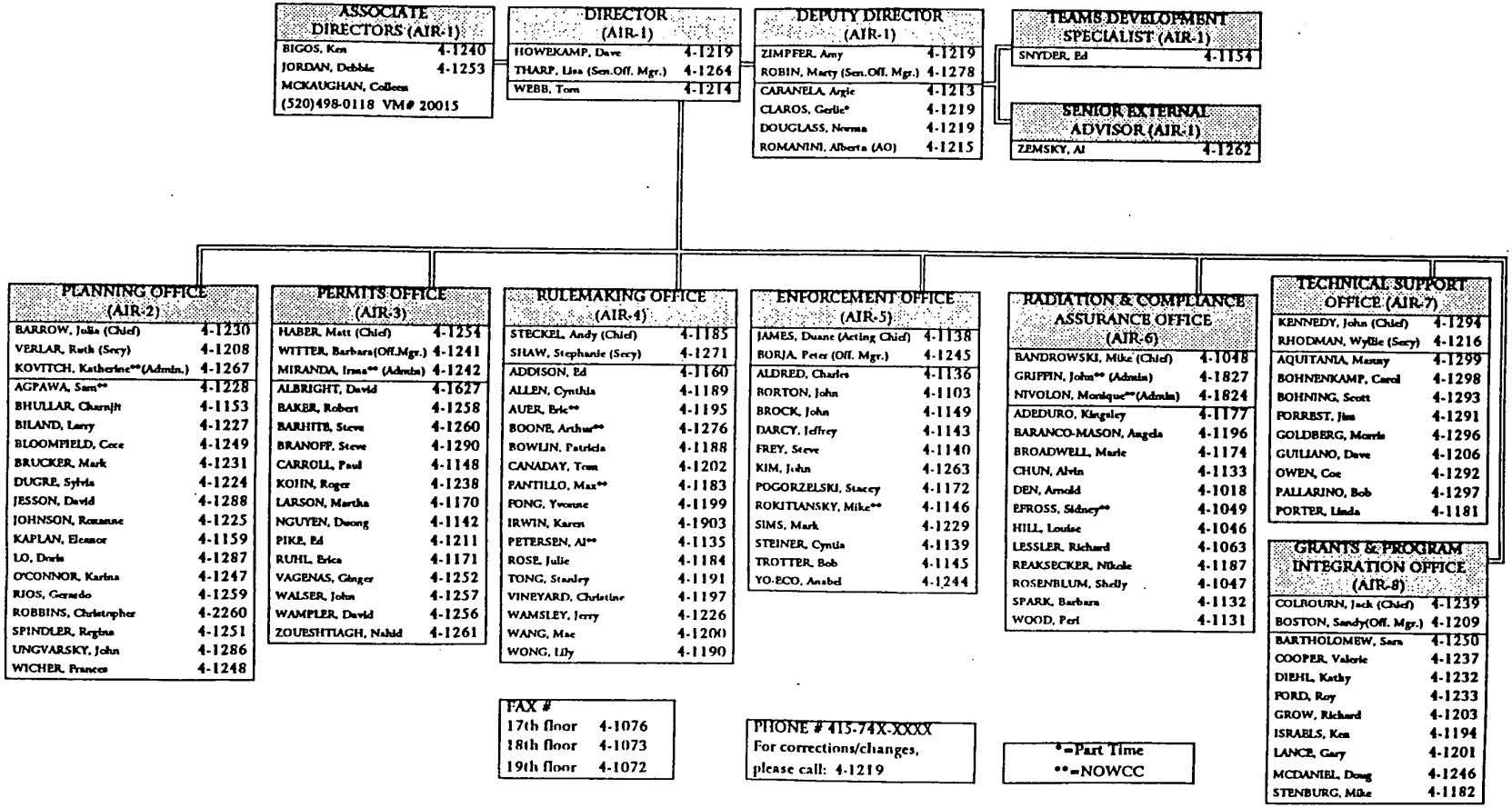
EPA
AIR DIVISION, REGION 9



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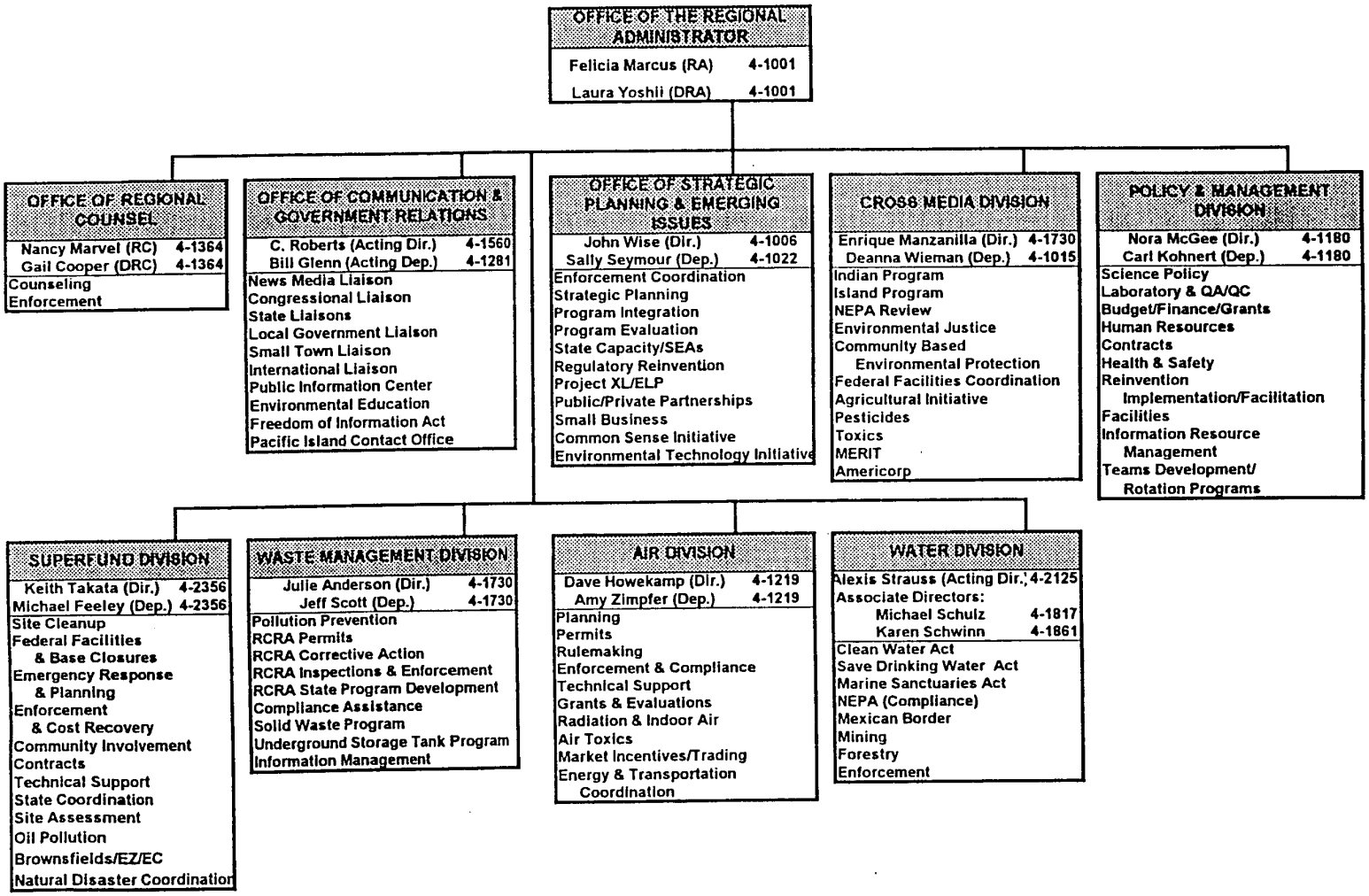
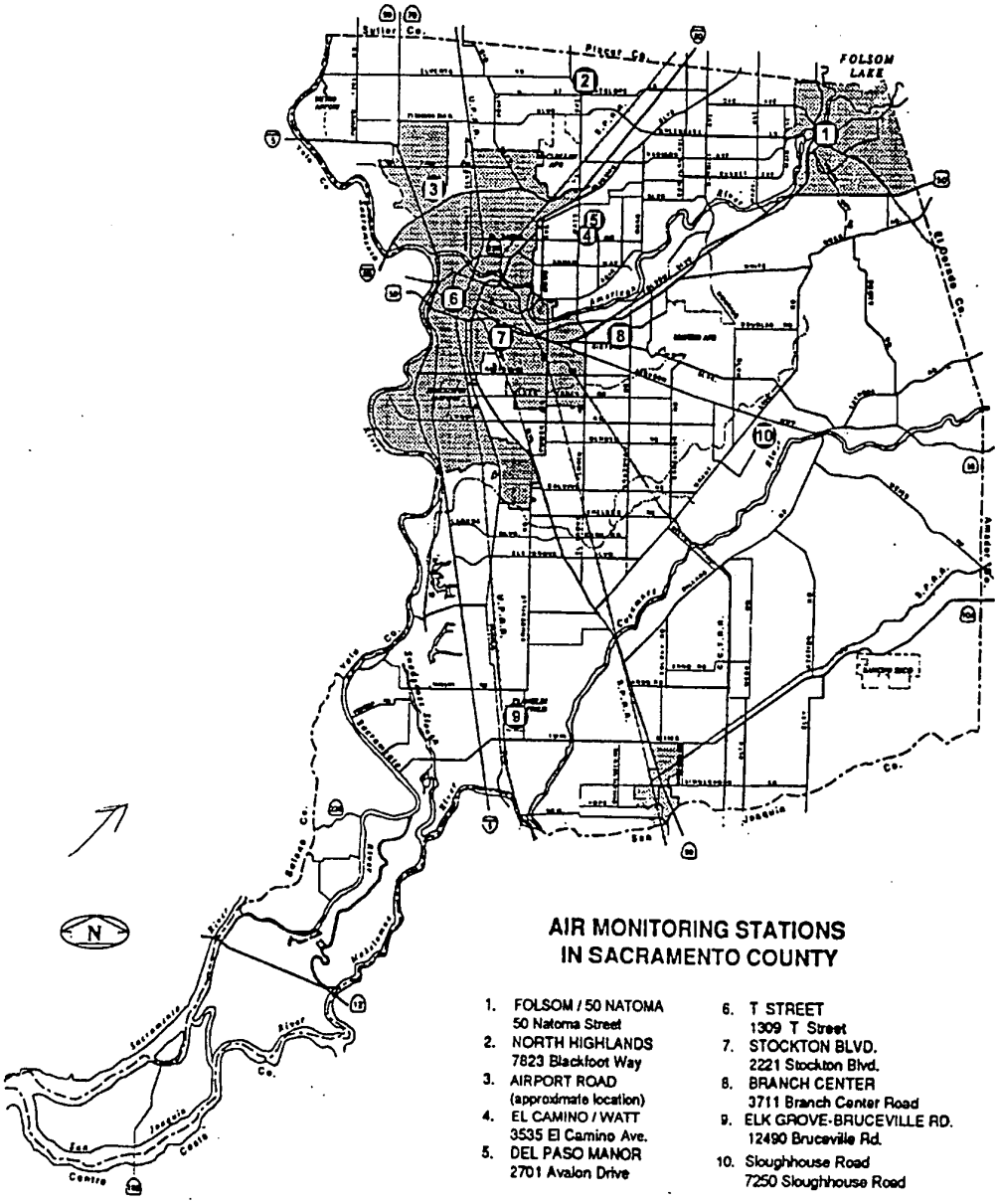
EPA REGION 9 ORGANIZATION CHART



Telephone: 415-74X-XXXX 01/26/99



AIR MONITORING STATIONS IN SACRAMENTO COUNTY

1. FOLSOM / 50 NATOMA
   50 Natoma Street
2. NORTH HIGHLANDS
   7823 Blackfoot Way
3. AIRPORT ROAD
   (approximate location)
4. EL CAMINO / WATT
   3535 El Camino Ave.
5. DEL PASO MANOR
   2701 Avalon Drive
6. T STREET
   1309 T Street
7. STOCKTON BLVD.
   2221 Stockton Blvd.
8. BRANCH CENTER
   3711 Branch Center Road
9. ELK GROVE-BRUCEVILLE RD.
   12490 Bruceville Rd.
10. Sloughhouse Road
    7250 Sloughhouse Road

SACRAMENTO METROPOLITAN AQMD
PROPOSED PAMS CALIFORNIA ALTERNATIVE PLAN III FOR SMAQMD
April 17, 2001

Listed below are changes proposed for the PAMS monitoring network in Sacramento County, for the summer 2001 ozone season. If these changes are approved, the proposed changes will be effective July 1, 2001.

For Type I Site- Elk Grove- Bruceville:

a) During the months of July-September:

Collect four (4) 3-hr VOC canister samples (speciated) on episode days. Sampling times will be 5 am - 8 am, 8 am - 11 am, 12 noon - 3 pm, 4 pm - 7 pm, PST on episode days.

VOC canister sampling on episode days will provide data on the day prior to an expected Federal O3 exceedance and the day of the expected Federal O3 exceedance. These data will be collected on days that are of interest to photochemical modelers/PAMS statisticians, and on days that are possible upwind ozone precursor transport days.

b) Continue year-round: Continuous NMOC monitoring using TECO 55C.

For Type II- Primary Site- Sacramento- Airport Road:

a) Delete VOC canister sampling.

We reviewed 1998 and 1999 total NMHC concentration data (from speciated canisters) from Airport Road (Type II- Primary) and Del Paso Manor (Type II- Secondary). Using time series plots, we compared the total NMHC concentrations, during the same sampling period and on the same day, collected at these Type II sites. We found that the number of VOC samples, where total NMHC was higher at Del Paso Manor compared to Airport Road, occurred with an approximate ratio of 2 to 1. This trend of the number of VOC samples where Del Paso Manor NMHC concentrations was greater than the Airport Road concentrations was true during all sampling periods and during both 1998 and 1999.

Comparing the highest seasonal NMHC concentrations between these two sites, Del Paso Manor had much higher peak concentrations compared to Airport Road in 1998, during all sampling periods. In 1999, the highest seasonal Del Paso Manor NMHC concentrations were slightly higher compared to Airport Road, during all sampling times.

For these reasons, we feel that VOC canister sampling at Airport Road is a low priority and Del Paso Manor should be redesigned as the Type II-Primary site.

11 pm - 2 am PST	1998	1999
# Samples w/ DPM > AIR	20	19
# Samples w/ AIR > DPM	10	11

5 am - 8 am PST	1998	1999
# Samples w/ DPM > AIR	21	19
# Samples w/ AIR > DPM	8	12

12 noon - 3 pm PST	1998	1999
# Samples w/ DPM > AIR	20	18
# Samples w/ AIR > DPM	9	13

4 pm - 7 pm PST	1998	1999
# Samples w/ DPM > AIR	22	21
# Samples w/ AIR > DPM	6	10

b) Continue year-round: Continuous NMOC monitoring using TECO 55C.

For Type II- Secondary Site- Sacramento- Del Paso Manor:

a) During the months of July-September:

Collect four (4) 3-hr VOC canister samples (speciated) on both trend and episode days. A trend day is defined as once every third day sampling. Sampling times will be 11 pm - 2 am, 5 am - 8 am, 12 noon - 3 pm, 4 pm - 7 pm, PST, on trend days.

Sampling times will be 5 am - 8 am, 8 am - 11 am, 12 noon - 3 pm, 4 pm - 7 pm, PST, on episode days. Sampling times are different between trend days and episode days, since modelers wanted an additional canister sample during the late morning hours (8 am - 11 am, PST) on episode days, so the California PAMS Districts removed the 11 pm - 2 am canister run for episode days.

Data from trend and episode days are comparable, since three out of the four sample periods have the same sample times (5 am - 8 am, 12 noon - 3 pm, and 4 pm - 7 pm, PST).

Collect four (4) 3-hr Carbonyl cartridges on both trend and episode days. Sampling times will be 11 pm - 2 am, 5 am - 8 am, 12 noon - 3 pm, 4 pm- 7 pm, PST, on trend days. Sampling times will be 5 am - 8 am, 8 am - 11 am, 12 noon - 3 pm, 4 pm - 7 pm, PST, on episode days.

b) Continue year-round: Continuous NMOC monitoring using TECO 55C.

For Type III- Folsom- Natoma Street:

a) During the months of July-September:

Collect two (2) 3-hr VOC canisters (speciated) on trend days. Sampling times will be 5 am - 8 am, 4 pm - 7 pm, PST, on trend days.

Collect four (4) 3-hr VOC canisters on episode days. Sampling times will be 5 am - 8 am, 8 am - 11 am, 12 noon - 3 pm, 4 pm - 7 pm, PST, on episode days.

b) Continue year-round: Continuous NMOC monitoring using TECO 55C.

For Upper-Air Profiler site at Elk Grove- Bruceville:

Continue year-round monitoring of upper-level winds and temperature.

Episodic Monitoring:

Strive to collect VOC and carbonyl data on, up to five O3 episodes, during the PAMS VOC sampling season (July - September), each year. Each episode will consist of, at a minimum, two days (the day prior to the O3 exceedence and the day of the O3 exceedence). An O3 exceedence is defined as any day when the maximum 8-hr O3 mean is 0.085 or higher.

Number of VOC/Carbonyl samples to be collected:

a) Maximum number of VOC canisters: 180 trend + 80 episode canisters = 260 canisters/season.

b) Maximum number of Carbonyl cartridges: 120 trend + 40 episode cartridges = 160 cartridges/season.

Year-round Air Toxics sampling:

Year-round collection of an once every 12 day air toxics (24 hr) sample will be continued at the Roseville, CA site, operated by California Air Resources Board.

In reference to the new Urban Air Toxics Monitoring program, we have proposed to install one air toxics sampler at Del Paso Manor, this year. We propose that sampling begin in October 2001, using a once every 12 day sampling schedule, year-round, for collection of a 24 hr averaged canister sample.

Additions to PAMS field sampling and PAMS data analysis:

a) NOY monitoring: operate NOY samplers at two sites, during May-October. Tentative site locations are Bruceville and Sloughhouse.

b) PAMS data analysis projects for remainder of FFY 2000-2001 and FFY 2001-2002 (Target deadline for completion of data analysis project).

1) Perform QC/QA review on summer 2000 VOC data (May 31, 2001).
2) Perform QC/QA review on summer 1999 VOC data (July 31, 2001).
3) Perform QC/QA review on summer 1998 VOC data (Sept 30, 2001).
4) Perform proposed Central California Ozone Study (CCOS) data analysis work. Data analysis projects to be determined jointly by CARB and the Districts, during spring 2001. Data analysis will commence, when CCOS releases these data for use by the study participants (Sept 30, 2002).
5) Determine 1-hr and 8-hr O3 trends: long-term trends, weekend O3 effect, any shifts in location of O3 peaks (Dec 31, 2001).
6) Conduct Exploratory PAMS data analysis on 1998-2000 VOC data (species fingerprint, time series, scatter plots for each PAMS site and time of day)(May 31, 2002).
7) Develop methodologies for determining VOC and NOX limitations for each site (Sept 30, 2002).

Please note that the QC/QA review is the data validation process carried out prior to conducting any PAMS data analysis.

c) U.C. Berkeley is proposing to operate an automated GC/MS, for collection of hourly VOC data, at or near the Folsom-Natoma (Type III) site, during summer 2001. This project is contingent on space, electric power, and access considerations. If the hourly VOC data collected, during summer 2001, meets their future study needs, hourly VOC monitoring may continue into future years. If not, the automated GC/MS will be removed.

If you have any questions, please contact me at (916) 874-4839.

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Sacramento, CA. 95814
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MODEL 55C

DIRECT METHANE, NON-METHANE HYDROCARBON ANALYZER

INSTRUCTION MANUAL
P/N 14999

THERMO ENVIRONMENTAL INSTRUMENTS INC.
8 WEST FORGE PARKWAY
FRANKLIN, MASSACHUSETTS 02038

TELEPHONE: (508) 520-0430
FACSIMILE: (508) 520-1460

1-18-99

CHAPTER 1
INTRODUCTION

Thermo Environmental Instruments is pleased to supply the Model 55C Direct Methane, Non-Methane Hydrocarbon analyzer. We are committed to the manufacture of instruments exhibiting high standards of quality, performance, and workmanship. Service personnel are available to assist with any questions or problems that may arise in the use of this instrument.

The Model 55C is a back-flush gas chromatography (GC) system designed for automated measurement of methane and non-methane hydrocarbons. Unlike instruments that measure only methane and total hydrocarbons, the back-flush GC method used by the Model 55C provides a direct measurement of non-methane concentrations. This allows accurate and precise measurement of low levels of non-methane hydrocarbons (NMHC), even in the presence of methane at much higher concentrations.

In addition to a GC based separation and measurement system, the Model 55C offers flexible menu driven software, automatic calibration, self-testing, RS-232 based remote operation and diagnostics, plus the full support of Thermo Environmental Instruments' worldwide customer service network.

PRINCIPLE OF OPERATION

The Model 55C's measurement of methane and non-methane hydrocarbons is based on the well developed science of gas chromatography and utilizes a proprietary column system developed specifically for this application. Gas chromatography is a proven analytical tool that was initially developed in the 1950's and is now the most widely applied separation technique in analytical laboratories. A detailed discussion of chromatographic theory goes beyond the scope of this manual, and is not necessary for operation of the Model 55C. However, a basic understanding of chromatographic principals may be helpful for instrument setup and troubleshooting. For initial installation and operation, the user should become familiar with the sampling system, the gas flow patterns, the analog signal outputs, and the hydrocarbon detection and measurement methods described in this chapter. For those who are interested in a more complete description of the chromatographic process, a detailed explanation can be found in most textbooks on analytical instrumentation.

The Model 55C is an automated batch analyzer which repeatedly collects and analyzes small amounts of the sample stream drawn in by the pump. Central to the instrument's operation is an eight port, two position, rotary valve which is used to introduce the gas sample into the analyzer and to control the flow of gases through the chromatographic column.

As illustrated in Figure 1-1, the rotary valve is designed in a circular configuration with the eight ports, or connection points, spaced equally around the periphery of the valve body. Internally, the valve includes a cone shaped "rotor" at the hub, which has a set of 4 channels or grooves cut in the surface. Each channel connects two adjacent ports. The rotor can be shifted to either of two positions to provide two different gas flow configurations. For example, port number two can be connected to either port number one or port number three, while port number three can be connected to port number two or port number four.

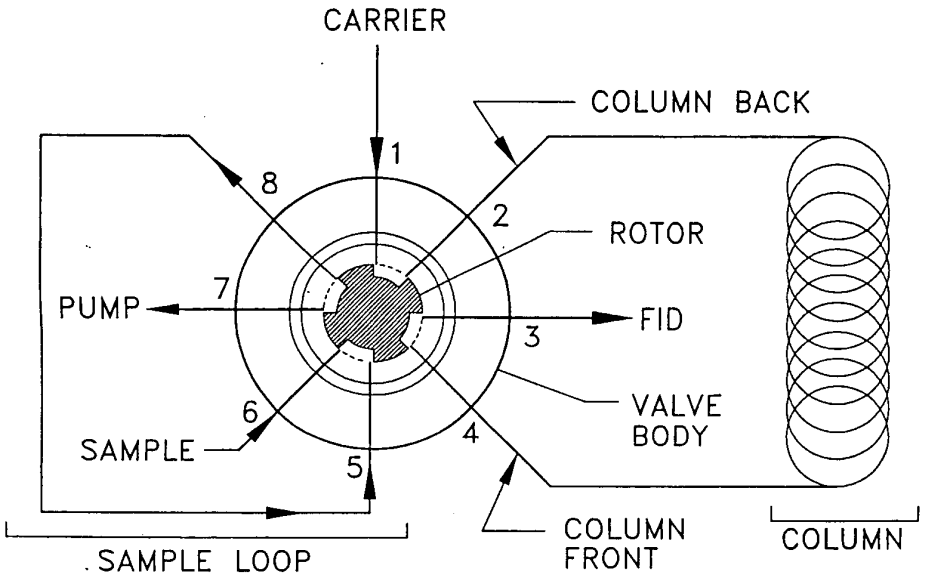


Figure 1-1. Rotary Valve Configuration

In the Model 55C, the two valve positions are referred to as "INJECT" and "BACKFLUSH" and they provide the following connections:

INJECT		BACKFLUSH	
Carrier Inlet	→ Sample Loop	Carrier Inlet	→ Column (back)
Sample Loop	→ Column (front)	Column(front)	→ FID
Column (back)	→ FID	Pump (-)	→ Sample Loop
Pump (-)	→ Sample Inlet	Sample Loop	→ Sample Inlet

Between analyses, or while running in the stand-by mode, the rotary valve is left in the BACKFLUSH position. In this position, sample gas is continuously pulled through the sampling loop, which is simply a coil of empty tubing, This flow configuration is illustrated in Figure 1-2A. To start the analysis, the rotary valve is switched to the INJECT position, as shown in Figure 1-2B. This action connects the carrier inlet to the sample loop and introduces the gas sample that was in the loop into a flowing stream of inert "carrier gas."

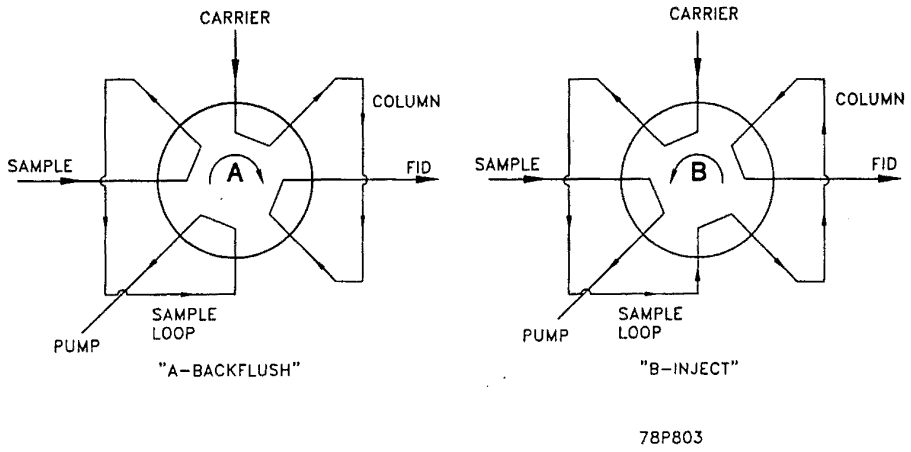


Figure 1-2. 8-Port Rotary Valve, Backflush and Inject Positions

The carrier gas sweeps the sample from the loop and into the front, or "inject" end, of the separation column. It should be noted that the column is physically located in a separate oven which is run at 65° C. As the sample is carried down the column, the various components move at different speeds, as determined by their physical and chemical properties. Due to its low molecular weight and high volatility, methane moves faster than other organic compounds and is the first to emerge from the opposite end of the column. Upon leaving the column, the methane flows back through the rotary valve and then to the flame ionization detector, or FID. The methane is measured by the FID and its signal is converted into a concentration by comparison with the signal produced by a calibration gas. The FID used in the Model 55 is similar to those seen in many laboratory instruments and uses a hydrogen flame to ionize organic molecules in the carrier gas. This is a well established method that is sensitive and reliable for measurement of most organic compounds.

Once the methane peak has been detected, the rotary valve is automatically returned to the original BACKFLUSH position, illustrated in Figure 1-1A. Note that at this point the direction of carrier gas flow through the column has reversed, and that the sample loop has been switched out of the carrier stream and back into the sampling system. With the reversal of carrier flow in the column, the non-methane hydrocarbons are "back-flushed" out and carried to the FID for measurement. As the NMHCs reach the FID, they create a signal which is proportional to the total NMHC concentration and can be converted to a ppm reading by comparison with the signal generated by a known standard.

If the FID signal is continuously monitored with a chart recorder, the output will create a chromatogram showing one peak for methane and a second peak that represents the combined non-methane hydrocarbons. A typical chromatogram obtained from the analysis of a standard mixture containing 2 ppm each of methane and propane is shown in Figure 1-3.

As indicated in the diagram, the methane peak reaches a maximum approximately 17 seconds after injection, and is preceded by a smaller peak which represents oxygen. The 17-second elapsed time between injection and the top of the methane peak is referred to as the methane retention time (C1-Rt) and is critical for proper operation of the instrument. The non-methane peak, as shown in Figure 1-3, will generally be lower and wider than the methane peak, and it can have varying retention times depending on operating conditions and composition of the sample.

In the automatic, or continuous, operating mode, the Model 55C initiates the next analysis by injecting another sample as soon as the non-methane measurement is complete. The time required for analysis of one sample is about 70 seconds. However, if rapid analysis times are not required, the instrument cycle time can be slowed by specifying an extended SAMPLING TIME in the PARAMETERS menu.

For applications with limited sample volume, such as those involving sample collection in Tedlar® or Teflon® bags, the Model 55C may be set to "SINGLE ANALYSIS" mode. In this mode, the analyzer completes one analysis and then pauses for operator input.

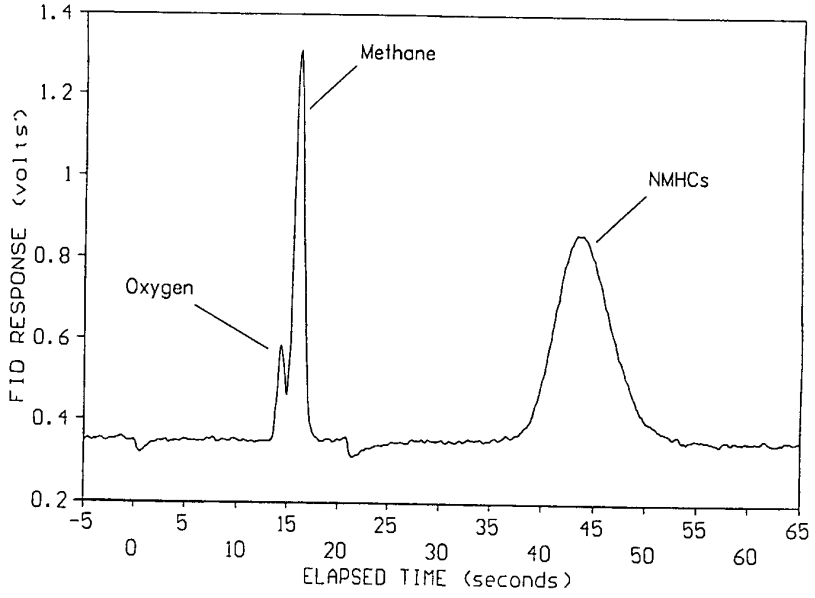


Figure 1-3. Typical Model 55C Span Gas Chromatogram

The Model 55C is calibrated using a mixture of methane and non-methane hydrocarbons which simulates the actual sample. In most applications, propane is a good choice for the non-methane component. Instrument calibration may be initiated manually or may be performed automatically at user specified intervals. Calibration is achieved by flooding the sample inlet with span gas. Methane concentrations are measured using peak height, measured from baseline references taken before and after the oxygen and methane elute from the column. Due to the variability in peak shapes and retention times, NMHCs are quantified based on peak area rather than height. Note that, because the instrument takes several references during each analysis, a separate zero gas is not required for calibration.

Methane and non-methane hydrocarbon concentrations are reported on the front panel digital display as methane and NMHC, respectively. Concentration units are the same as those used in calibration, and may be set to display parts per million (ppm) or parts per million carbon (ppmc), depending on the software version that is installed. The front panel display also includes the time the sample was injected, the instrument operating mode, and various status messages.

Separate analog outputs on the rear panel indicate the results of the most recent methane and non-methane analysis. A third output provides a continuous indication of the FID signal (the chromatogram). Other rear panel connections allow for remote operation of the unit, either by dedicated control lines or with a bi-directional RS-232 computer link.

Performance specifications and a description of important instrument parameters are listed on the following pages. A plumbing schematic is presented in Figure 1-4, below.

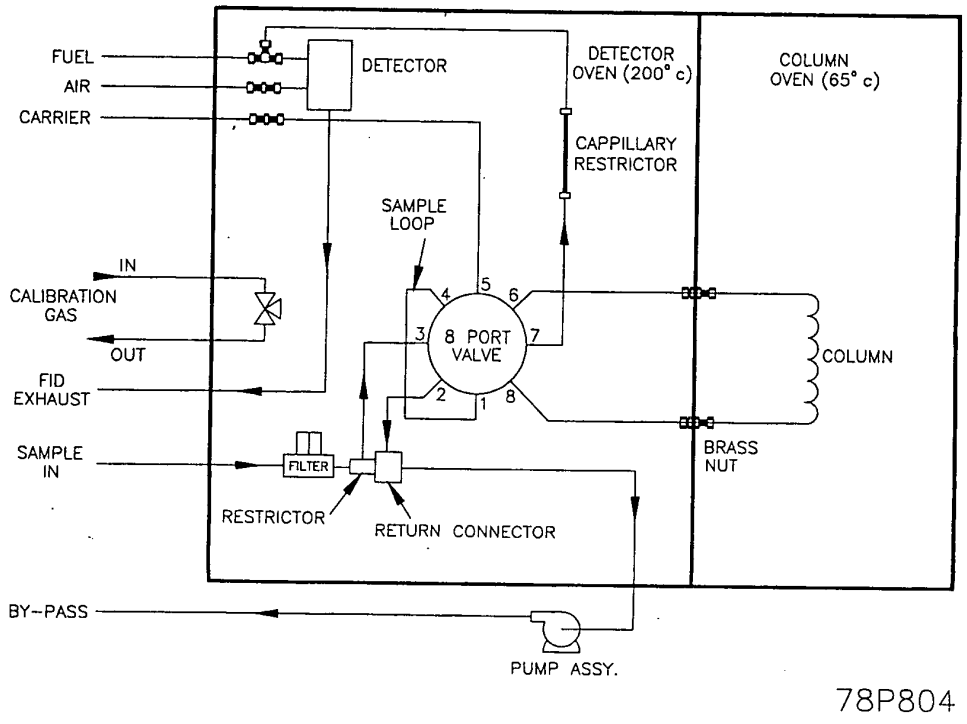


Figure 1-4. Model 55C Flow Schematic

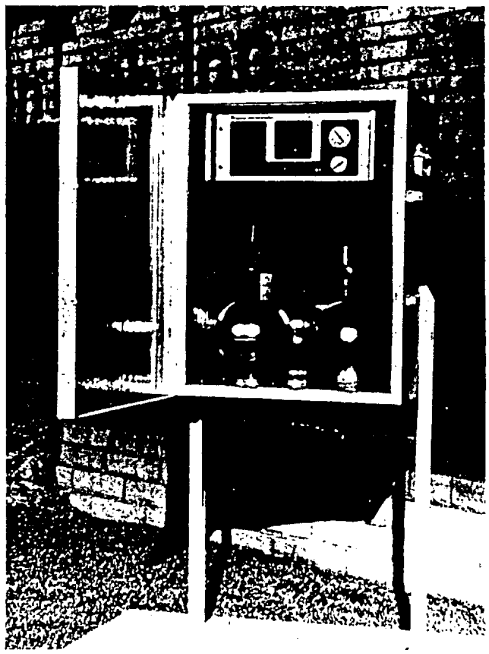
SPECIFICATIONS

Measurement Ranges: (C1 and NMHC set independently) (Other ranges optional)	0 - 20 ppm 0 - 200 ppm 0 - 2000 ppm
Recorder Ranges - User Selectable:	1 - 2000 ppm
Limits of Detection:	20 ppb methane, 50 ppb NMHC as propane
Analysis Time:	70 seconds (approximate)
Accuracy:	±2% of measured value
Precision:	±2% of measured value
Drift (without auto calibration):	±2% of span
Ambient Operating Temperature:	15° C - 35° C
Sample Temperature:	Ambient to 80° C (standard) (higher temperatures optional)
Analog Outputs:	Separate outputs for C1, NMHC, THC and chromatogram. Current outputs optional.
Digital Outputs:	RS-232
Alarm Systems:	Methane Concentration NMHC Concentration Calibration Failure System Failure
Sample Flow Rate:	0.5 liter/minute minimum
Power Requirements:	90-110 VAC @ 50/60 Hz 105-125 VAC @ 50/60 Hz 210-250 VAC @ 50/60 Hz
Support Gases:	HC Free Air (200 - 300 cc/min) N_2 carrier (35 cc/min) H_2 Fuel (25 cc/min) Span Mix (2-liter/calibration)
Physical Dimensions: Weight:	16.75" (W) X 8.62" (H) X 23" (D) 60 lbs.

MODEL 910A

910A/912

PROGRAMMABLE CANISTER SAMPLER



- *Automatic Operation*—saves time and money
- Specified by California Air Resources Board to collect samples of air toxics at field monitoring sites for subsequent lab analysis
- Does not degrade air sample—all wetted components of non-reactive materials
- Mass flow controller maintains constant, yet adjustable, flow rate
- Wide range of programmable sampling times
- Front panel access to all controls and indicators
- Digital display of flow rate
- Elapsed time meter shows actual sampling time
- Automatic restart after power failure
- Use with wind directional controller
- System is certified clean before shipment
- Easy to install, operate and maintain

XonTech, Inc.
6862 Hayvenhurst Avenue, Van Nuys, California 91406
(818) 787-7380

SPECIFICATIONS

Feature	Model 910	Model 910A
Gas Container Used	Bag	Summa electropolished cannister
AC Requirements	115V, 50/60 Hz, 1 amp	115V, 50/60 Hz, 4.9 amps
Dimensions	17"W x 13"D x 7"H	17"W x 13"D x 12¼"H
Weight	25 lbs.	45 lbs.
Pump	Bellows, 300 series stainless steel with teflon & Viton seals	Bellows, 300 series stainless steel with teflon & Viton seals
Pump Output Pressure	———	10 or 25 psig.
Flowrate	Adjustable from 8 to 100 cc/min	Adjustable from 8 to 100 cc/min
Flowrate Precision	Better than 0.5 cc/min.	Better than 0.5 cc/min.
Flowrate Accuracy	Better than 2 cc/min.	Better than 2 cc/min.
Timer Cycle	7 days	7 days
Sample Time	Selectable from 1 min to 7 days	Selectable from 1 min to 7 days
Elapsed Sample Time	Counter displays actual sample time in hours, minutes and tenths of a minutes	Counter displays actual sample time in hours, minutes and tenths of a minute
Timer Display	Continuous digital display of clock time, day of week, switching status	Continuous digital display of clock time, day of week, switching status
Fittings	Swagelok ¼" stainless steel	Swagelok ¼" stainless steel

CALL OR WRITE TODAY!

XonTech, Inc.

6862 Hayvenhurst Avenue, Van Nuys, California 91406
(818) 787-7380 TWX 910-495-1725 FAX (818) 786-4275

XONTECH MODEL 912 MULTI-CANISTER SAMPLING ADAPTER

GENERAL DESCRIPTION

The XonTech Model 912 Multi-Canister Sampling Adapter is designed to route gas samples to or fro up to 16 canisters. An internal time base is used to step a rotary valve from canister to canister at user-selected rate. The Model 912 will also accept timing signals from the XonTech Model 910A an 911A canister samplers.

FEATURES

The XonTech Model 912 is designed with the following features:

- 16 port rotary valve with electric actuator. Stainless steel and inert nonporous fluoropolyme construction. 1/8" stainless steel, zero dead volume, fittings.
- Stainless steel tubing throughout.
- 1/8" stainless steel swagelok inlet/outlet fittings.
- Switch-selectable sample time. 1/2 to 4 hours per sample (1 to 8 hours per sample optional). Wi also accept timing signals from XonTech Model 910A and 911A canister samplers.
- Can be used to route sample gas to or from up to 16 canisters.
- 19" rack-mount chassis with front panel mounted position indicator and controls.

SPECIFICATIONS

- Time base accuracy: 0.01% for 0 to 70o C.
- Size: 7" X 19" X 15"
- Weight: 18 Lbs.
- Power: 115 VAC, 2 amps max.
- Maximum pressure: 200 psi.

APPLICATIONS

- Sampling frequency requirements for VOC under proposed Enhanced Ozone Monitoring (EOM Regulations.
- Sequential sampling for VOC (with selectable sampling period).

Price per unit $2854

XonTech carries Dr. Rasmussen's 'Summa' electropolished canisters.
We can get you quantity discount and cheaper prices.

EPA Type SUMMA® Canister

Specifications

1. Canisters meet all requirements of EPA Compendium Method TO-14.

2. General Features:

   6-liter canister, 9-inch diameter, 20 ga. wall, type 304SS. Internally passivated by SUMMA® electropolish process; fitted with base ring-stand and valve guard/handle; equipped with one Nupro SS4H high vacuum ultra-clean bellows valve and ¼-inch Swagelok® connecting fittings. Helium leak-tested to 1 x 10^{-9} std cc/sec and guaranteed to be clean to <0.2 ppbv per hydrocarbon species and air toxics.

3. Special Features:

   1. SUMMA® electropolishing done internally after welding the container together. No unpassivated weld scar seams exposed internally. 100% passivation of all internal surfaces; no active sites.

   2. Entry port 3/8-inch NPT makes it easy to disassemble and visually inspect the condition of the inside of the canister after multiple usage.

   3. Large entry port facilitates re-polishing to rejuvenate the internal surface. No cutting and re-welding of the canister is required.

   4. Change-over from 1-valve to 2-valve purge-tube configuration done easily with wrench in the field if necessary. 2-valve assembly allows flow-through purge. Monitoring fill rate via -30 to +60 span gauge conveniently done using gauge on one of the valves.

   5. Packaged in double-walled reusable individual mailing cartons. Canisters shipped 4 to a box for consolidated shipments. No need to acquire special shipping cartons.

   6. All canisters are individually tested to pass EPA TO-12 method at <20 ppbvC.

For more information:

XonTech, Inc.

MATTHIAS YOONG, Ph.D.
Manager, Environmental
, Systems Group

6562 HAYVENHURST AVENUE, VAN NUYS, CALIFORNIA 91406
TEL: (818) 787-7380 FAX: (818) 786-4275

XONTECH MODEL 925

CARBONYL SAMPLER

OPERATIONS MANUAL

XonTech, Inc.

6862 HAYVENHURST AVENUE, VAN NUYS, CALIFORNIA 91406

XONTECH MODEL 925

CARBONYL SAMPLER

OPERATIONS MANUAL

August, 1995

XonTech, Inc.
7027 Hayvenhurst Avenue
Van Nuys, CA. 91406
(818) 787-7380

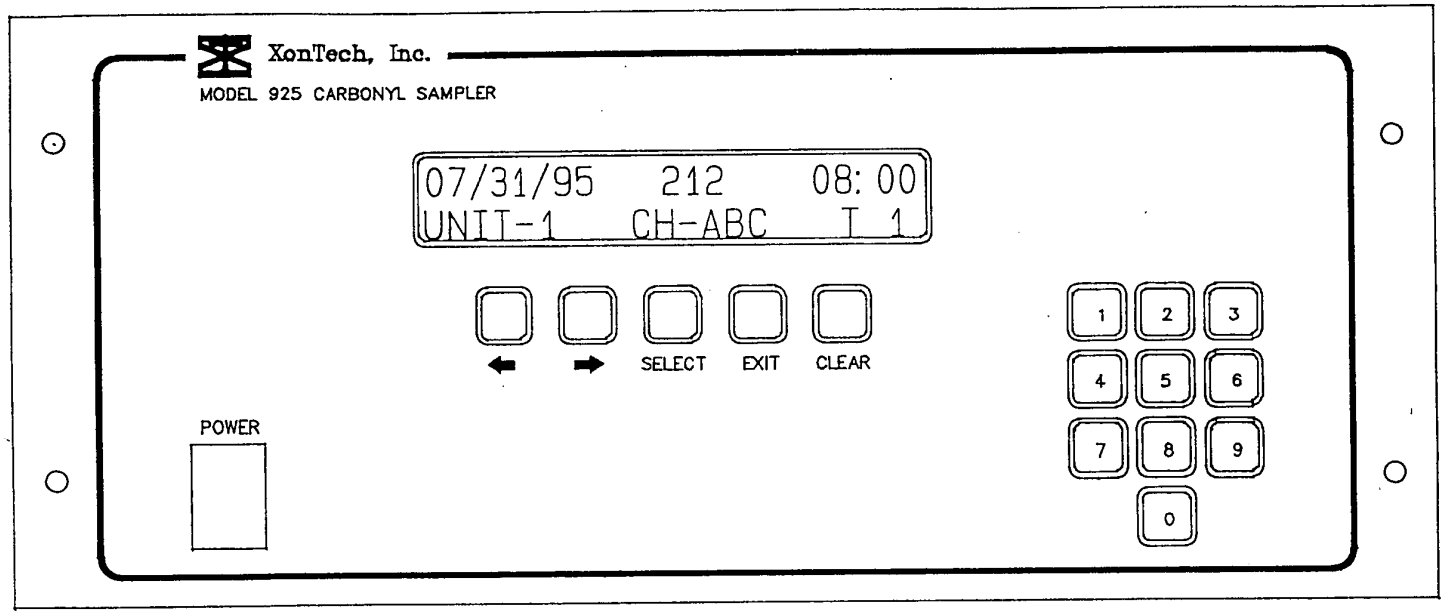
1. GENERAL DESCRIPTION

XonTech, Inc. Model 925 is an automatic system for trapping aldehydes and ketones in ambient air using adsorbent cartridges. The system is microprocessor controlled and consists of a "control unit" and a sampling "tube unit". As an option, each control unit can operate up to four tube units. The system meets the requirements of USEPA T0-11 method. That is, it can be programmed for one 24-hour continuous sample, eight 3-hour samples, one collocated 3-hour sample and a field blank. The system is so versatile that each of these sampling channels can be programmed independently for different selectable flowrates or start/end times as required. Because of this versatility, the system can meet different sampling schedules and requirements which would otherwise be difficult. Several low molecular weight aldehydes and ketones in ambient concentration have been reported by Tejada et al. (Arnts R.R. and Tejada S.B., '2,4-DNPH Coated Silica Gel Cartridge Method for Determination of Formaldehyde in Air', Env. Sc. and Tech. 22, 1989, p1428-1430.)

FORMALDEHYDE	Isovaleraldehyde
ACETALDEHYDE	Valeraldehyde
Acrolein	o-Tolualdehyde
ACETONE	m-Tolualdehyde
Propionaldehyde	p-Tolualdehyde
Crotonaldehyde	Hexanaldehyde
Butyraldehyde	2,5-Dimethylbenzaldehyde
Benzaldehyde	

1.1 The Control Unit

The control unit contains the microprocessor, the LCD display, keyboard and the mass flow controllers. Sequences for controlling sampling in the tube unit(s) are selected or programmed from the control unit or via a modem. All sampling duration, start time, start date, and flows are selectable via the control unit keyboard.



MODEL 925 CARBONYL SAMPLER FRONT PANEL

(Figure 1)

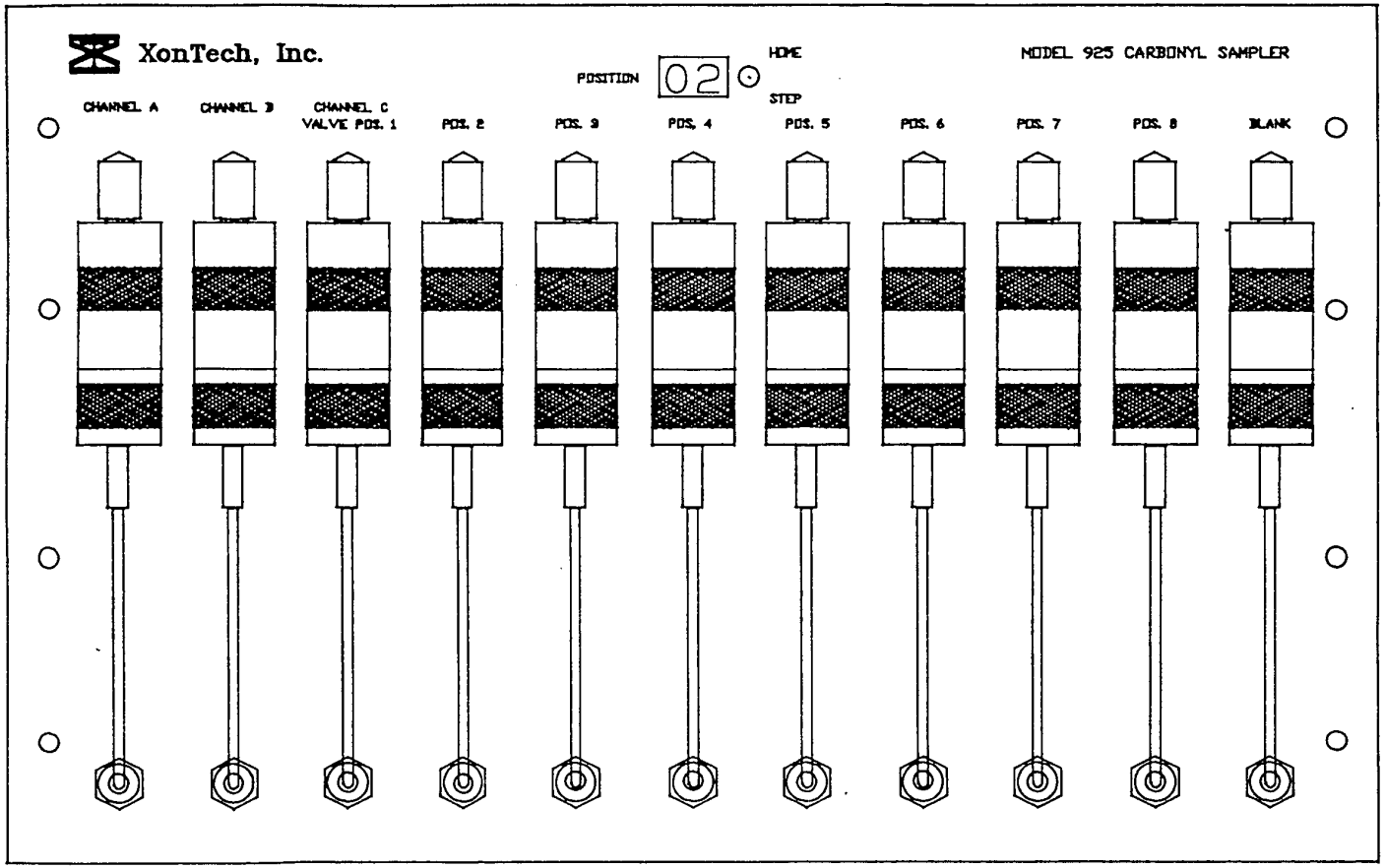
1.2 The Tube Unit

The tube unit contains the eight position rotary valve, position indicator, solenoids, denuder oven, temperature controller, and cartridge holders with quick-connect fittings. The tube unit is heated to 60°C to prevent any cold spots which may be cause for condensation. All sample cartridges in the tube unit when not sampling are sealed at both ends. The sample path upstream of the cartridge is constructed of stainless steel. Solenoid valves are stainless steel with viton o-rings. The sample pump is an oil-free vacuum pump rated at 5 liter/min. at -25" Hg.

1.3 Features

The XonTech Model 925 Carbonyl sampler is designed for automatic collection of carbonyl compounds. User friendly software simplifies application and maintenance procedures. Some of the features are:

- A leak test program to provide quick check of the system prior to sampling.
- An RS232 modem port on the control module for communication to be established between the control unit and a remote personal computer which can have access to all operator inputs and displays.
- Various sample holders for different types of cartridges. Holders protect cartridges from exposure to sunlight.
- Power fail is flagged and the sampling valve will advance to the proper channel when power is restored.
- A flow error is flagged when a flow error > or < 10% of the set flow occurs.
- An elapsed time counter for each sampling channel.
- Control unit and tube unit are heated to prevent condensation.
- Control unit and tube unit are standard 19" rack mountable.
- One control unit will operate up to four tube units.
- Meets the requirements of USEPA Method T0-11 sampling, each tube unit having a 24 hour sampling channel, a collocated sampling channel, eight 3-hourly sampling channels and a field blank.
- Flow rate, sampling duration and start date are selectable.
- Optional weather-resistant enclosure for a control unit and two tube units are available.



MODEL 925 TUBE UNIT FRONT PANEL

(Figure 2)

1.4 Specifications

The Model 925 is a microprocessor controlled carbonyl sampler. The instrument consists of a control unit and a tube unit. The control unit can operate up to 4 tube units.

Sample Channels

- One 24 hour channel.

  Programmable start time, date and duration.

- One collocated channel.

  Programmable start time, date and duration.

- Eight "X" hour channels (typically set to 3 hours).

  Programmable start time, date and duration for all 8 channels.

- One field blank tube holder.

Clock

- Battery-backed clock and microprocessor memory retains time, date and sampling program during periods of power failure.

- The sampling valve used to select the 8 "X" hour sample channels will advance to the proper channel when power is restored.

Electronic Mass Flow Controllers (3)

- 24 hour channel - adjustable from .15 to 1.50 liter/min full scale. (Practical range is .15 to 1.35 liter/min.)

- Collocational/24 hour channel - adjustable from .15 to 1.5 liters/minute full scale. (Practical range is .15 to 1.35 liter/min.)

- 8 "X" hour channels - adjustable from .15 to 1.5 liters/minute full scale. (Practical range is .15 to 1.35 liter/min.)

Denuder Oven

- A denuder oven with programmable temperature controller is provided in each tube chassis, the temperature is adjustable from ambient to +70°C. The rotary valves, the solenoid valves, and all sampling tubes are likewise heated.

- Filter type denuder holder optional.

Elapsed Time Display

- Elapsed time can be displayed for the 24 hour collocated and 8 "X" hour channels to show the total sampling time of each sample.

Power Failure Display

- The default display screen indicates if a power failure has occurred. The duration of the power failure can then be displayed for all channels.

- A power failure is defined as a loss of AC power for more than 2 minutes.

Low Flow Display

- The default display screen indicates if a flow error has occurred. The duration of the flow error can then be displayed for all channels.

- A flow error is defined as a flow that varies $\pm$10% of the set flow within the practical range of .15 to 1.35 liters/min.

- The elapsed time counter for the affected channel will stop accumulating time during conditions of low flow.

Temperature Control

- Control box temperature is sensed and used to control an internal heater or fan to keep the flow controllers within their operating temperature range.

Remote Control

- A RS-232 modem port is provided on the control unit. An optional modem allows communications to be established between the 925 control unit and a remote personal computer. The remote computer has access to all 925 operator inputs and displays. This allows the 925 to be programmed remotely and re-programmed for episode sampling.

Sample Integrity

- All sample tubes are sealed on both ends when not sampling.

- All tubing and fittings upstream of the sample tubes are stainless steel. Solenoid valves are stainless steel with viton o-rings.

Available Tube Holders

- Sep-Pak Classic (Waters).
- 2 X Sep-Pak Classic.
- Sep-Pak Plus (Waters).
- 2 X Sep-Pak Plus.
- NIOSH type tubes.

Sample Pump

- Oil-free system vacuum pump rated 5 liters/minute at -25"Hg.

Packaging

- Control unit.

  Contains the microprocessor, display, keyboard and mass flow controllers.

  7" high X 19" wide X 13" depth, 25 lbs., 19" rack mountable.

- Tube unit.

  Contains the 8 position rotary valve and position indicator, solenoids, denuder oven, temperature controller and tube/filter holders with quick-connect fittings.

  14" high X 19" wide X 13" depth (tube fittings extend an additional 2.5" from rear panel), 35 lbs., 19" rack mountable.

Expansion

- One control unit will control up to 4 tube units (40 sample tubes total).

Options

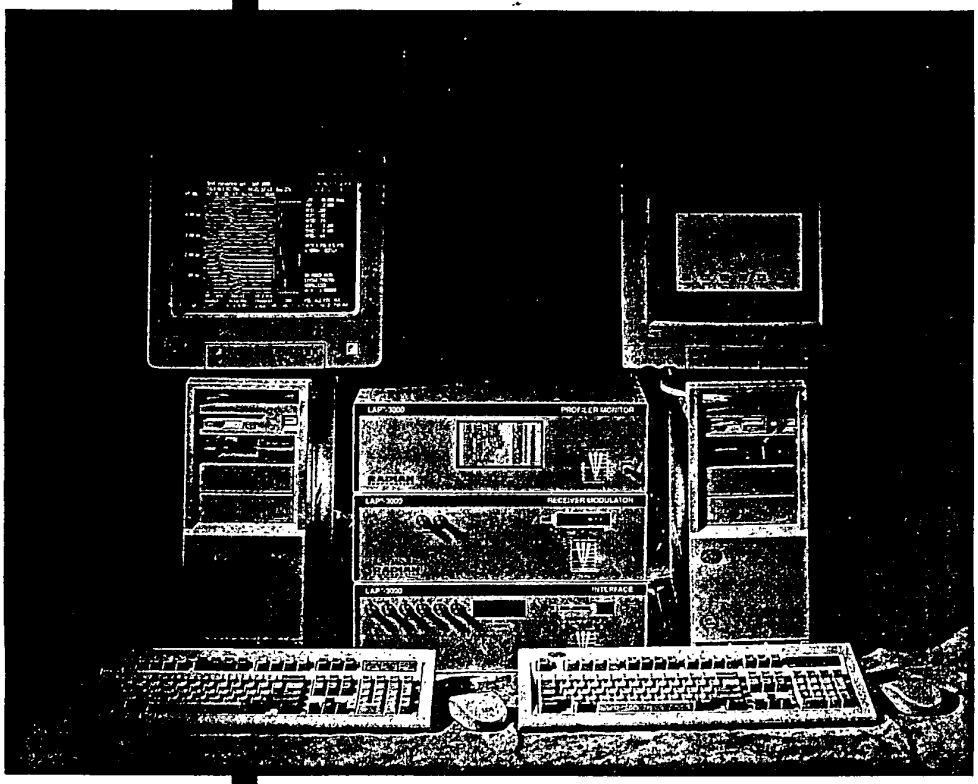
- Weather-resistant enclosure for one control unit and two tube units.
- Fan aspirated sample manifold.
- Additional tube unit.
- Modem.

Lower Atmosphere Profiling Radars

for Wind and Temperature Data

Technology from NOAA's Environmental Research Laboratories and

RADIAN CORPORATION
ELECTRONICS DIVISION



The LAP™-3000

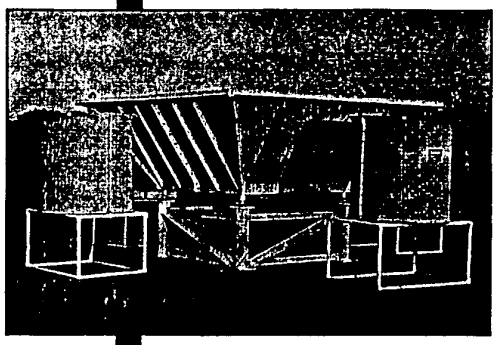
Lower Atmosphere Profiler

In 1991 Radian Corporation and Sonoma Technology, Inc. entered into a Cooperative Research and Development Agreement (CRADA) with the U.S. National Oceanic and Atmospheric Administration's (NOAA) Environmental Research Laboratories (ERL). The goal: To commercialize NOAA/ERL's newly developed UHF radar wind and temperature atmospheric profilers designed to use PC technology. In 1993 ERL received the Federal Laboratory Consortium Award for technology transfer for this project. The resulting product line, beginning with the 915-MHz LAP™-3000 Lower Atmosphere Profiler, is now the world's accepted standard for UHF radar profilers. Subsequent Radian development has made the same radar processor technology available at 449 MHz, 482 MHz, and 1290 MHz, with options that tailor the technology for our customers' unique requirements.

LAP™-3000 Options

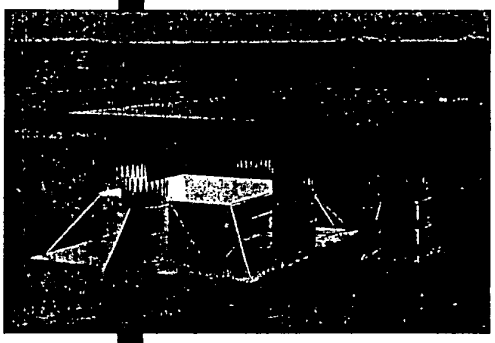
RASS

The Radio Acoustic Sounding System (RASS) is an option that can be added to the LAP™-3000 to obtain virtual temperature profiles, a temperature measurement that is uncompensated for humidity or pressure. RASS is composed of four acoustic sources, one placed on each side of the profiler. Notice the new antenna support stand designed for easy maintenance.



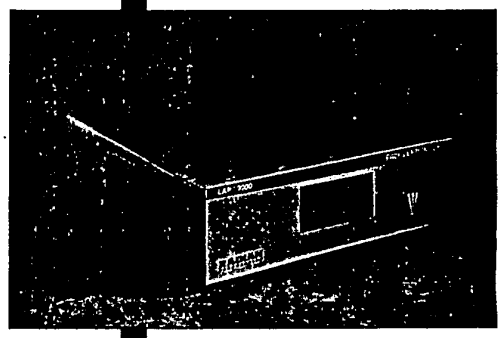
Expanded Antenna Configuration

The standard four-panel antenna configuration delivers data from 120 meters to a range between 2 and 5 kilometers, depending on atmospheric conditions. Extending the radar's aperture by using nine panels in the antenna configuration improves the radar's signal-to-noise ratio, refining the quality of the data in marginal conditions.



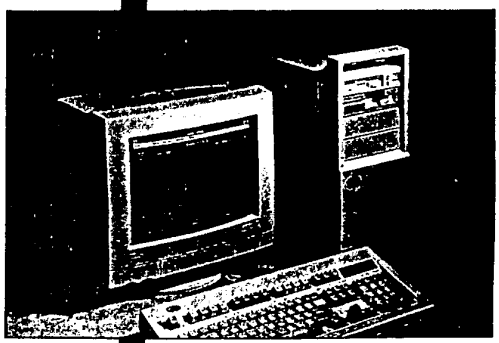
Profiler Monitor

The profiler monitor is a stand-alone processor and data acquisition subsystem designed to monitor the health of the LAP™-3000, assist maintenance personnel with fault diagnosis, and even shut down the system should certain critical conditions exceed pre-set limits. Diagnostic documentation accompanies the profiler monitor.



Gateway

Gateway is a software tool set for remotely supervising and controlling the profiler. With Gateway, you can transfer data files from one or several profilers, as often as you wish. Then you can verify the data with quality control algorithms and process the data into a variety of graphic formats for printing or displaying.



And More

Ask for details concerning other options such as the 50-MHz system, optical disk storage systems, trailer-mounted antenna systems, and specialized documentation.

RADIAN CORPORATION ELECTRONICS DIVISION

For more information contact or call:

Lower Atmosphere Profiler
1-800-RADARWP

Radian Corporation
Electronics Division
2990 Center Green Ct. S.
Boulder, CO 80301
(303) 443-2378
FAX (303) 443-1628

Sonoma Technology Inc.
5510 Skylane Blvd.,
Suite 101
Santa Rosa, CA 95403
(707) 527-9372

International Sales:
5801 Lee Highway
Arlington, VA 22207 USA
(703) 533-8555
Telex: 892532 REPUBLIC
FAX: (703) 533-3190

RADIAN CORPORATION

STi
Sonoma Technology Inc.

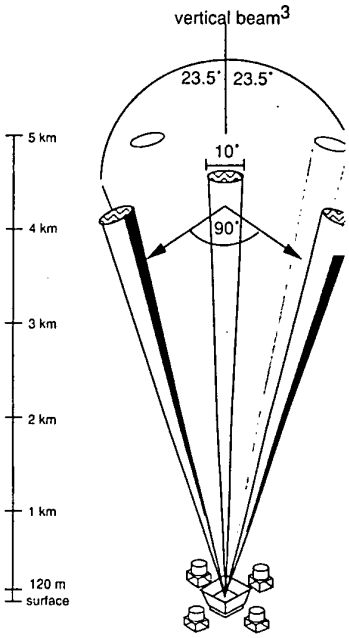
Cooperative Research & Development Agreement

LAP™-3000 Specifications (915, 1290 MHz)

Minimum Height[1]	120 m
Maximum Height[2]	2-5 km
Spatial Resolution	
with 400 ns pulse	60 m
with 700 ns pulse	100 m
with 1400 ns pulse	200 m
with 2800 ns pulse	400 m
Wind Speed Accuracy	< 1 m/s
Wind Direction Accuracy	< 10°
Averaging Time	3-60 minutes
Power Output	500 W peak
Antenna	Electrically steerable micropatch phased array panels
Aperture	2.7 m² (4 panels) 6.1 m² (9 panels)

Specifications for RASS (~2 kHz)

Minimum Height[1]	120 m
Maximum Height[2]	1-2 km
Spatial Resolution	
with 400 ns pulse	60 m
with 700 ns pulse	100 m
with 1400 ns pulse	200 m
with 2800 ns pulse	400 m
Temperature Accuracy	1°C
Averaging Time	3-60 minutes
Acoustic Source	Four compression drivers, parabolic reflectors
Aperture	1.2 m² x four

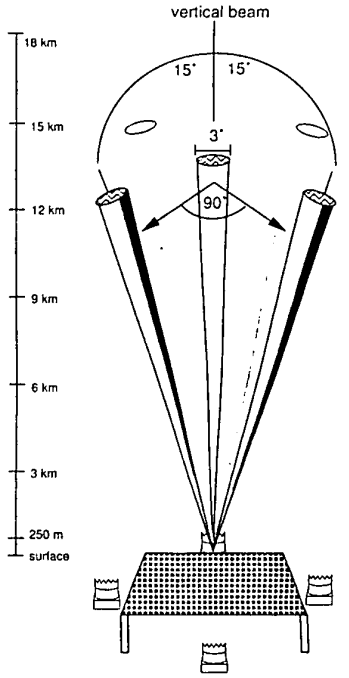


LAP™-16000 Specifications (449, 482 MHz)

Minimum Height[1]	250 m
Maximum Height[2]	12-18 km
Spatial Resolution	
with 700 ns pulse	100 m
with 1700 ns pulse	250 m
with 3300 ns pulse	500 m
with 6700 ns pulse	1000 m
Wind Speed Accuracy	< 1 m/s
Wind Direction Accuracy	< 10°
Averaging Time	3-60 minutes
Power Output	16 kW peak
Antenna	120-element coaxial-collinear array
Aperture	144 m²

Specifications for RASS (~1 kHz)

Minimum Height[1]	250 m
Maximum Height[2]	6-8 km
Spatial Resolution	
with 700 ns pulse	100 m
with 1700 ns pulse	250 m
with 3300 ns pulse	500 m
with 6700 ns pulse	1000 m
Temperature Accuracy	1°C
Averaging Time	3-60 minutes
Acoustic Source	Four compression drivers, parabolic reflectors
Aperture	1.8 m² x four



[1] Dependent on clutter environment & availa radio frequency emission bandwidth
[2] Dependent on atmospheric conditions
[3] Beam Pattern shown for standard 4-panel antenna

RADIAN
CORPORATION

LAP®-3000 1995 DOMESTIC PRICE LIST

The 1995 prices for standard 915 MHz LAP®-3000 Lower Atmosphere Profiler systems are listed below. Prices are FOB Boulder, Colorado, and do not include applicable taxes, packing, shipping, or installation.

Standard 915 MHz LAP®-3000 Lower Atmosphere Profiler:

Option - 00	3-Beam 2.7 m^2 antenna	$137,500
Option - 01	5-Beam 2.7 m^2 antenna	+4,500
Option - 02	5-Beam 6.1 m^2 antenna	+39,500
Option - 03	1290 MHz LAP®-3000	+9,000
Option - 10	Radio Acoustic Sounding System	+26,500
Option - 20	Profiler Monitor System/O&M Manual	+22,500
Option - 30	Gateway Hardware/Software Toolset	+14,500
Option - 31	Additional Gateway Software License	+2,500
Option - 32	Hub Remote User Hardware/Software	+7,500
Option - 33	Additional Hub License	+2,500
Option - 40	Extended Archiving Optical Disk	+6,500
Option - 41	Full On-Line UPS	+3,500
Option - 42	Antenna Trailer (2.7 m^2 only)	+18,500

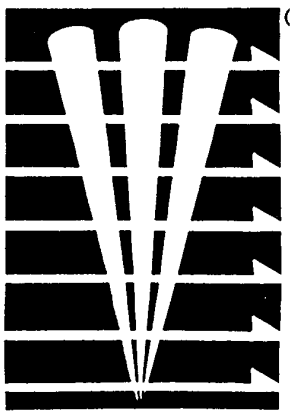
LEASE/PURCHASE FACTORS

	Monthly Rental as of % of Purchase Price	Purchase Credits as of % Total Lease Paid In	Remaining to Buy Out as a % of Purchase Price
1 Month	15	50%	92.5%
3 Months	12	50%	82.0%
6 Months	10	50%	70.0%
12 Months	8	50%	52.0%

For other options and services including spare parts, installation, and training please consult factory at 1-800-RADARWP.

University discounts are available.

All prices subject to change without notice.



PAMS DATA ANALYSIS WORKSHOP: ILLUSTRATING THE USE OF PAMS DATA TO SUPPORT OZONE CONTROL PROGRAMS

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U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Presented for:
California Air Resources Board & EPA Region IX
Sacramento, CA

May 1997

STI-997100-1719-WD7

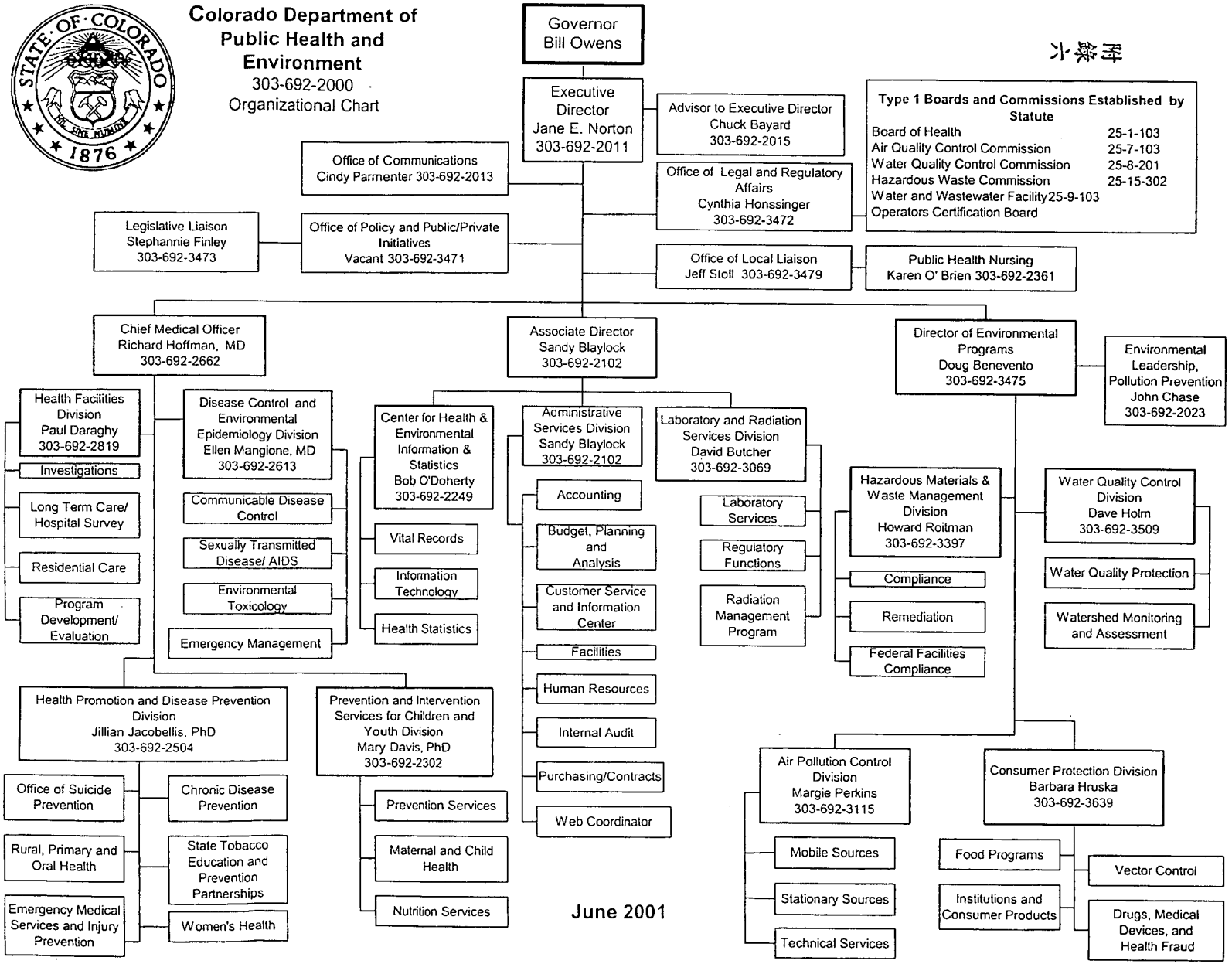
PAMS DATA USES

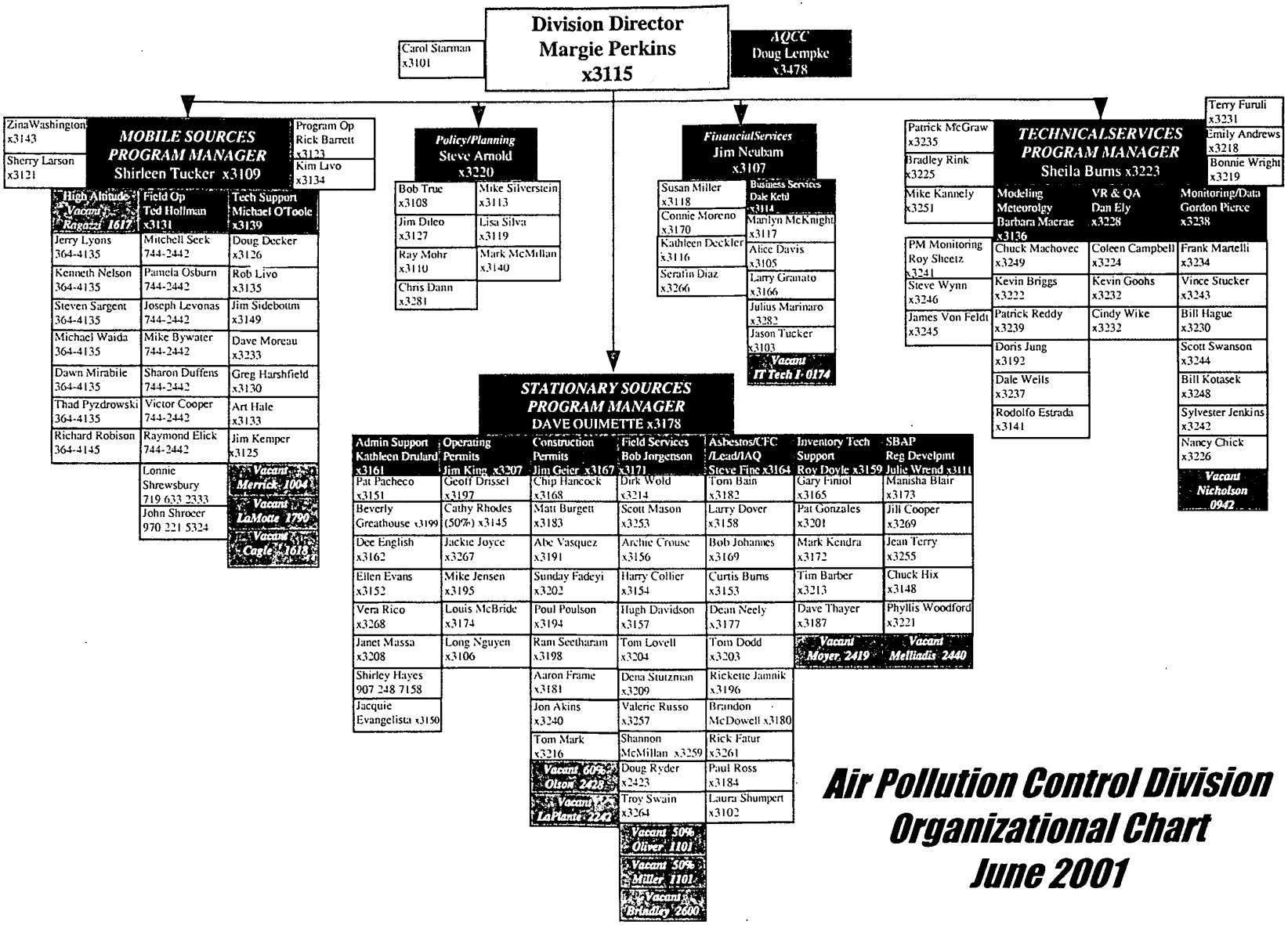
- Corroborate precursor emission inventories
- Assess changes in emissions; corroborate emissions reductions (SIP control strategy evaluation)
- Assess ozone and precursor trends
- Provide input to models; evaluate models (NAAQS attainment and control strategy development)
- Evaluate population exposure

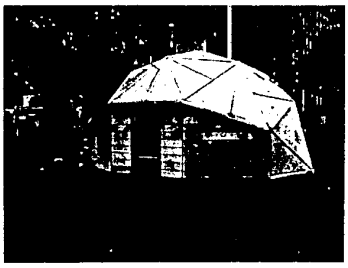
Colorado Department of Public Health and Environment

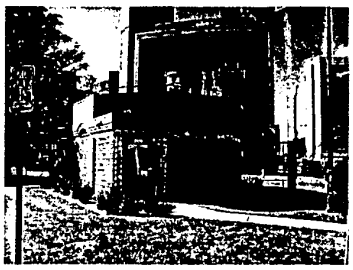
303-692-2000

Organizational Chart




Division Director
Margie Perkins
x3115
Carol Starman x3101
AQCC
Doug Lempke
x3478
MOBILE SOURCES PROGRAM MANAGER
Shirleen Tucker x3109
ZinaWashington x3143
Sherry Larson x3121
Program Op
Rick Barrett x3123
Kim Livo x3134
High Altitude
Vacant
Ragazzi 1617
Field Op
Ted Hoffman x3131
Tech Support
Michael O'Toole x3139
Jerry Lyons 364-4135
Kenneth Nelson 364-4135
Steven Sargent 364-4135
Michael Waida 364-4135
Dawn Mirabile 364-4135
Thad Pyzdrowski 364-4135
Richard Robison 364-4145
Mitchell Seek 744-2442
Pamela Osburn 744-2442
Joseph Levonas 744-2442
Mike Bywater 744-2442
Sharon Duffens 744-2442
Victor Cooper 744-2442
Raymond Elick 744-2442
Lonnie Shrewsbury 719 633 2333
John Shroeer 970 221 5324
Doug Decker x3126
Rob Livo x3135
Jim Sidebottm x3149
Dave Moreau x3233
Greg Harshfield x3130
Art Hale x3133
Jim Kemper x3125
Vacant
Merrick 1004
Vacant
LaMotte 1790
Vacant
Cagle 1618
Policy/Planning
Steve Arnold
x3220
Bob True x3108
Jim Dileo x3127
Ray Mohr x3110
Chris Dann x3281
Mike Silverstein x3113
Lisa Silva x3119
Mark McMillan x3140
FinancialServices
Jim Neubam
x3107
Susan Miller x3118
Connie Moreno x3170
Kathleen Deckler x3116
Serafin Diaz x3266
Business Services
Dale Ketel x3114
Marilyn McKnight x3117
Alice Davis x3105
Larry Granato x3166
Julius Marinaro x3282
Jason Tucker x3103
Vacant
IT Tech I 0174
Patrick McGraw x3235
Bradley Rink x3225
Mike Kannely x3251
PM Monitoring
Roy Sheetz x3241
Steve Wynn x3246
James Von Feldt x3245
TECHNICALSERVICES PROGRAM MANAGER
Sheila Burns x3223
Terry Furuli x3231
Emily Andrews x3218
Bonnie Wright x3219
Modeling Meteorolgy
Barbara Macrae x3136
VR & QA
Dan Ely x3228
Monitoring/Data
Gordon Pierce x3238
Chuck Machovec x3249
Kevin Briggs x3222
Patrick Reddy x3239
Doris Jung x3192
Dale Wells x3237
Rodolfo Estrada x3141
Coleen Campbell x3224
Kevin Goohs x3232
Cindy Wike x3232
Frank Martelli x3234
Vince Stucker x3243
Bill Hague x3230
Scott Swanson x3244
Bill Kotasek x3248
Sylvester Jenkins x3242
Nancy Chick x3226
Vacant
Nicholson 0942
STATIONARY SOURCES PROGRAM MANAGER
DAVE OUIMETTE x3178
Admin Support
Kathleen Drulard x3161
Pat Pacheco x3151
Beverly Greathouse x3199
Dee English x3162
Ellen Evans x3152
Vera Rico x3268
Janet Massa x3208
Shirley Hayes 907 248 7158
Jacquie Evangelista x3150
Operating Permits
Jim King x3207
Geoff Drissel x3197
Cathy Rhodes (50%) x3145
Jackie Joyce x3267
Mike Jensen x3195
Louis McBride x3174
Long Nguyen x3106
Construction Permits
Jim Geier x3167
Chip Hancock x3168
Matt Burgett x3183
Abe Vasquez x3191
Sunday Fadeyi x3202
Poul Poulson x3194
Ram Seetharam x3198
Aaron Frame x3181
Jon Akins x3240
Tom Mark x3216
Vacant 60%
Olson 2420
Vacant
LaPlante 2270
Field Services
Bob Jorgenson x3171
Dirk Wold x3214
Scott Mason x3253
Larry Dover x3158
Archie Crouse x3156
Curtis Burns x3153
Hugh Davidson x3157
Tom Lovell x3204
Dena Stutzman x3209
Valerie Russo x3257
Shannon McMillan x3259
Doug Ryder x2423
Troy Swain x3264
Vacant 50%
Oliver 1101
Vacant 50%
Miller 1101
Vacant
Brindley 2600
Asbestos/CFC /Lead/IAQ
Steve Fine x3164
Tom Bain x3182
Larry Dover x3158
Bob Johannes x3169
Curtis Burns x3153
Dean Neely x3177
Tom Dodd x3203
Rickette Jamnik x3196
Brandon McDowell x3180
Rick Fatur x3261
Paul Ross x3184
Laura Shumpert x3102
Inventory Tech Support
Roy Doyle x3159
Gary Finiol x3165
Pat Gonzales x3201
Mark Kendra x3172
Tim Barber x3213
Dave Thayer x3187
Vacant
Moyer 2419
SBAP Reg Develpmt
Julie Wrend x3111
Manisha Blair x3173
Jill Cooper x3269
Jean Terry x3255
Chuck Hix x3148
Phyllis Woodford x3221
Vacant
Melliadis 2440
Air Pollution Control Division
Organizational Chart
June 2001





New CAMP Building

What is CAMP? CAMP stands for Continuous Air Monitoring Project. The CAMP station is one the oldest continuously operated air monitoring sites in the country. The original building was a 30-year old geodesic dome that was intended to be a temporary structure. It stood as the new building does on one of the City of Denver's Triangle Parks that run along Broadway.

What were our goals for a new CAMP? We wanted to replace the deteriorating original structure with a building designed to meet current scientific needs while remaining versatile enough to facilitate the use of future monitoring technologies. We also wanted the architectural style to harmonize with both old and new downtown building styles.

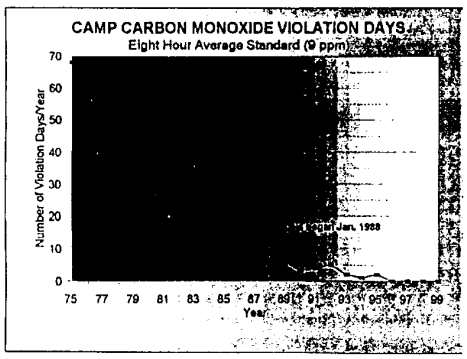
How did we get here? The new CAMP has been more than four years in the making. The many steps included securing a new lease with the City of Denver, identifying monitoring program needs, requesting and receiving funding from the Colorado legislature, selecting an architect and building design, putting the project out to bid, selecting the contractor, demolishing the old structure, and completing the new facility.

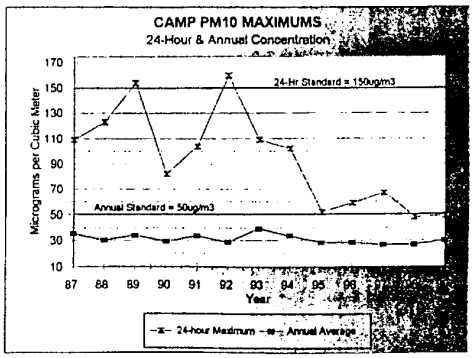
Features of the new facility:

- A flat roof with ample space and power for roof-top air sampling
- Interior access to the roof for improved staff safety
- Expanded instrument/monitor space
- Vestibule with public information displays and materials
- Improved energy efficiency
- Specialized lighting: the building can be automatically illuminated with red lights to indicate a pollution advisory or blue lights to indicate good air quality.
- Cost: The new CAMP facility cost $215,000 to complete. This cost included site work like ADA-accessible sidewalks, landscaping, and street lights.

Scientifically, what does CAMP provide?

- CAMP provides measurements of carbon monoxide, nitrogen dioxide, sulfur dioxide, PM_{10}, $PM_{2.5}$, lead, wind speed and wind direction, and air temperature. A real-time $PM_{2.5}$ monitor and toxics sampling are new this year. CAMP is the only location in the state where these new measurements are being taken.
- CAMP is considered a maximum concentration site for carbon monoxide. Therefore, data from CAMP (shown below) serves as proof that the Denver-metropolitan area is complying with federal health-based standards.

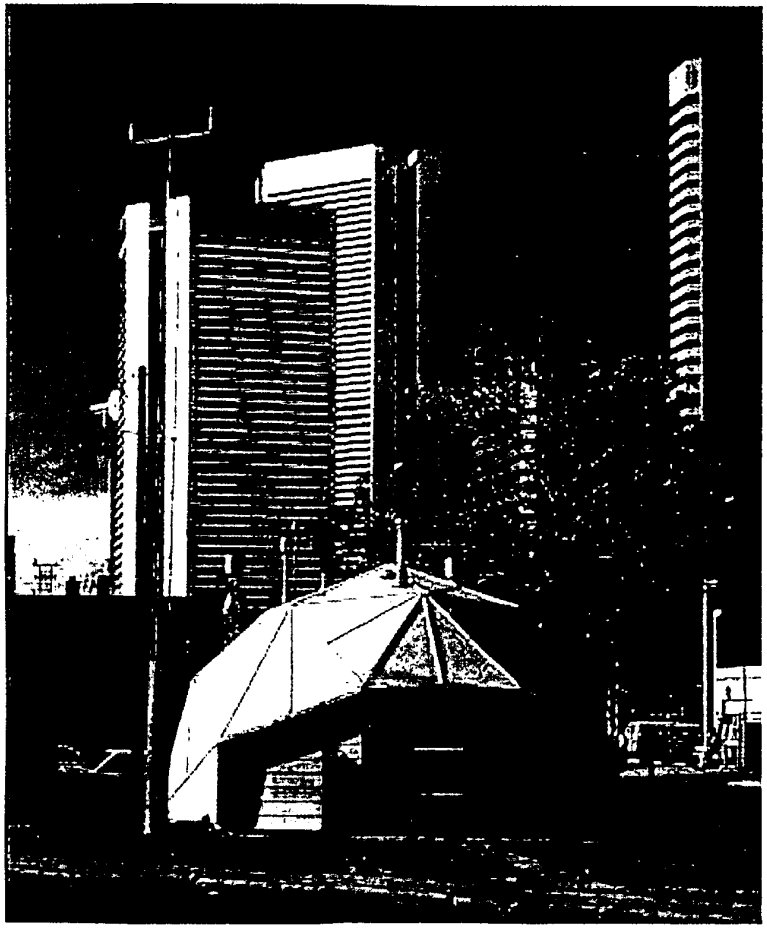




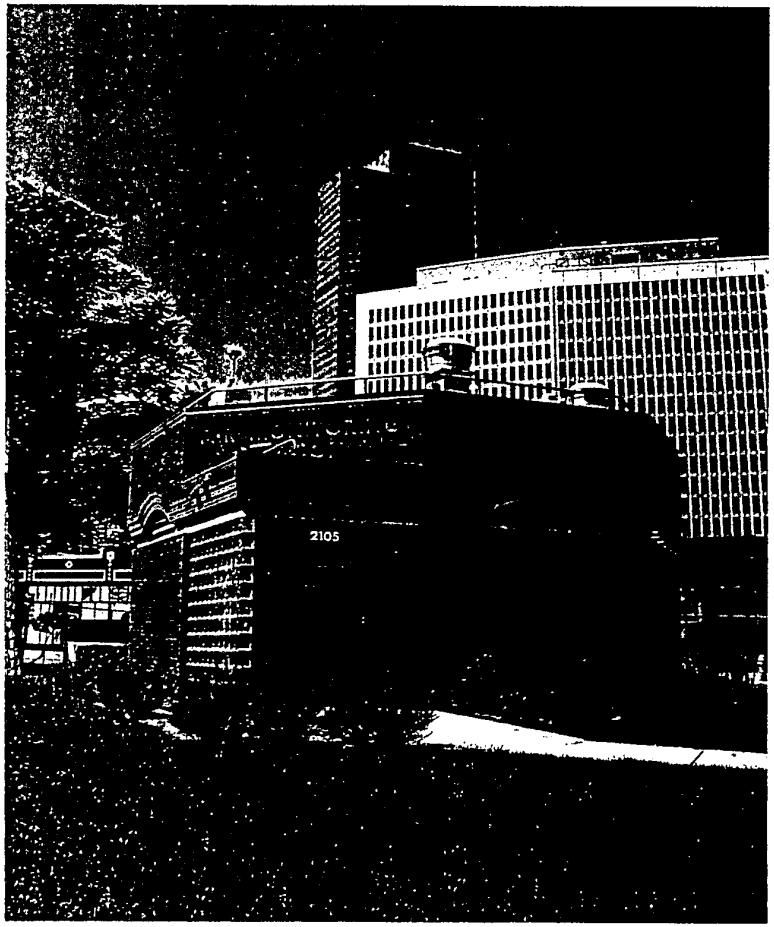

CDPHE-APCD
Technical Services Program
Presentation to
DRCOG, 7/26/2001

CAMP Site --- 2105 Broadway

Old building, 1965-1999



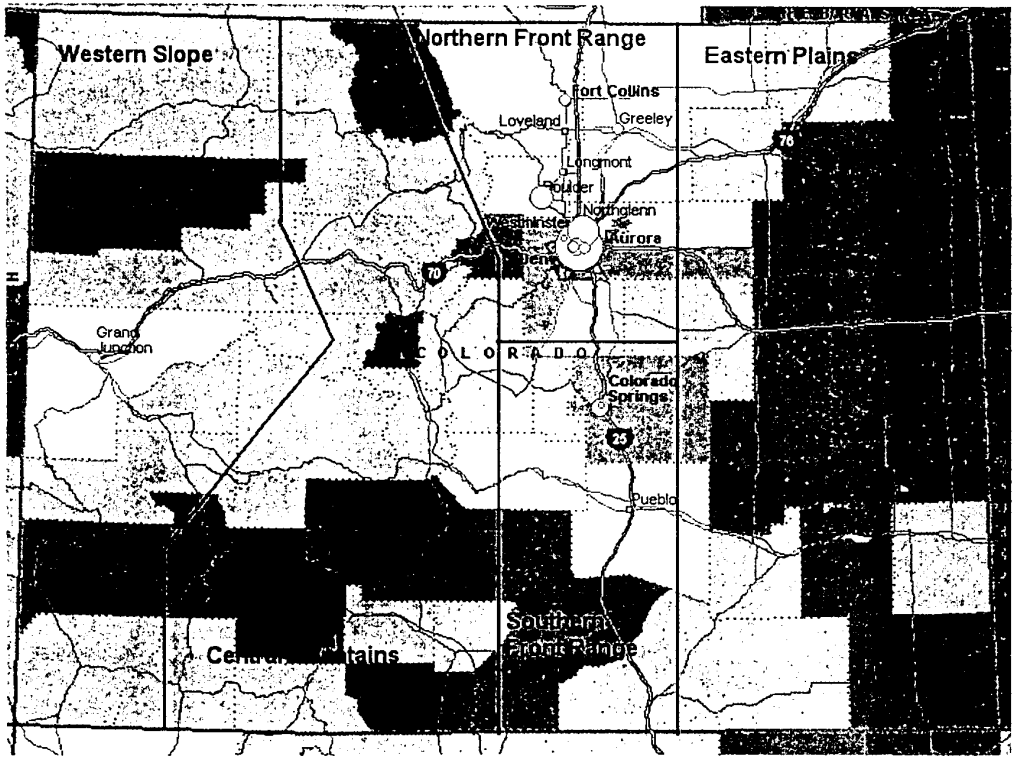
New building, 2000 onward

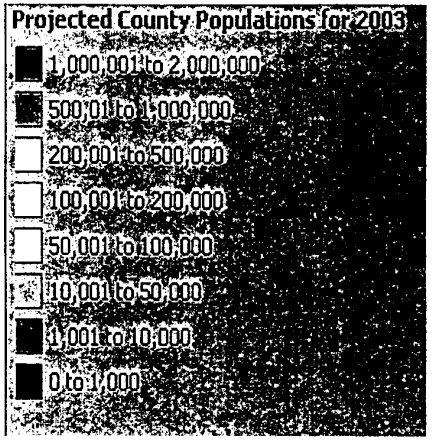


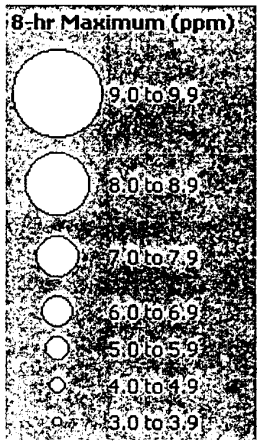
National Ambient Air Quality Standards

POLLUTANT	AVERAGING TIME	STANDARD
Carbon Monoxide (CO)	1 Hour	35 ppm
	8 Hour	9 ppm
Ozone (O_3)	1 Hour	current: 0.12 ppm
	8 Hour	proposed: 0.08 ppm
Nitrogen Dioxide (NO_2)	Annual Arithmetic Mean	0.053 ppm
Sulfur Dioxide (SO_2)	Annual Arithmetic Mean	0.030 ppm
	24 Hour	0.14 ppm
Particulates (PM_{10})	Annual Arithmetic Mean	50 $\mu g/m^3$
	24 Hour	150 $\mu g/m^3$
Fine Particulates ($PM_{2.5}$)	Annual Arithmetic Mean	proposed: 15.0 $\mu g/m^3$
	24 Hour	proposed: 65 $\mu g/m^3$
Lead (Pb)	Calendar Quarter Average	1.5 $\mu g/m^3$
Total Suspended Particulates (TSP)	Annual Geometric Mean	old standard: 75 $\mu g/m^3$
	24 Hour	old standard: 260 $\mu g/m^3$

Colorado Carbon Monoxide Monitoring in 2000





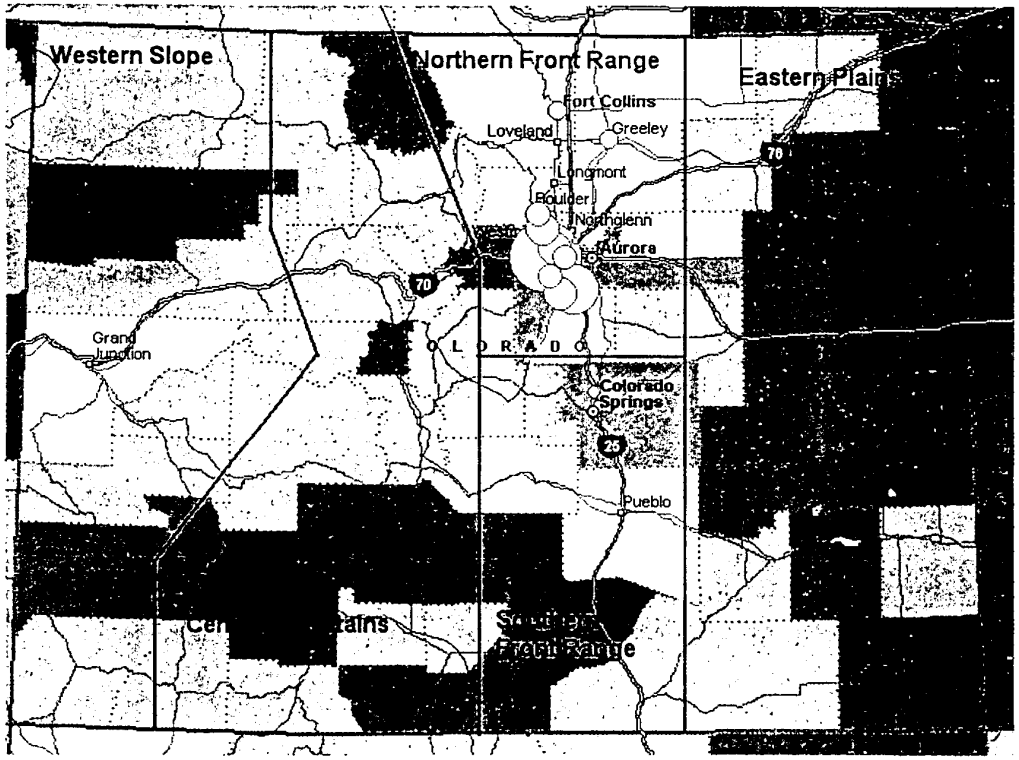


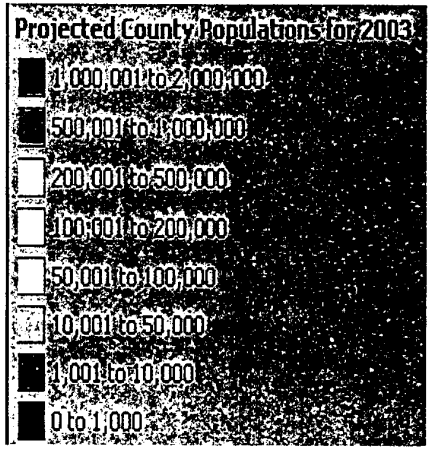
Colorado Carbon Monoxide Monitoring in 2000

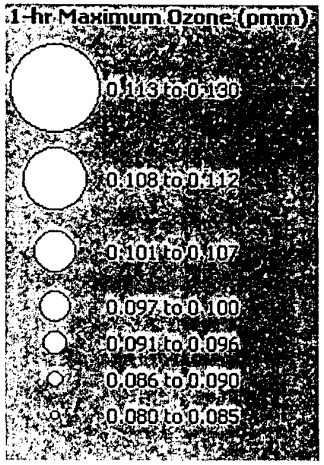
	1-hr Max	1-hr 2nd Max	8-hr Max	8-hr 2nd Max
Eastern Plains				
N/A			No monitors in this region.	
Northern Front Range				
Denver CAMP 2105 Broadway	17.1 ppm	12.8 ppm	8.5 ppm	8.2 ppm
Southern Front Range				
Colorado Springs 690 W. Hwy 24	8.5 ppm	8.2 ppm	5.1 ppm	4.2 ppm
Central Mountains				
N/A			No monitors in this region.	
Western Slope				
Grand Junction 12 St. & North Ave.	6.9 ppm	6.8 ppm	4.4 ppm	4.1 ppm
Statewide				
Denver CAMP 2105 Broadway	17.1 ppm	12.8 ppm	8.5 ppm	8.2 ppm

Carbon Monoxide Standards: **1-hour = 35 ppm, 8-hour = 9 ppm**

Colorado Ozone Monitoring in 2000





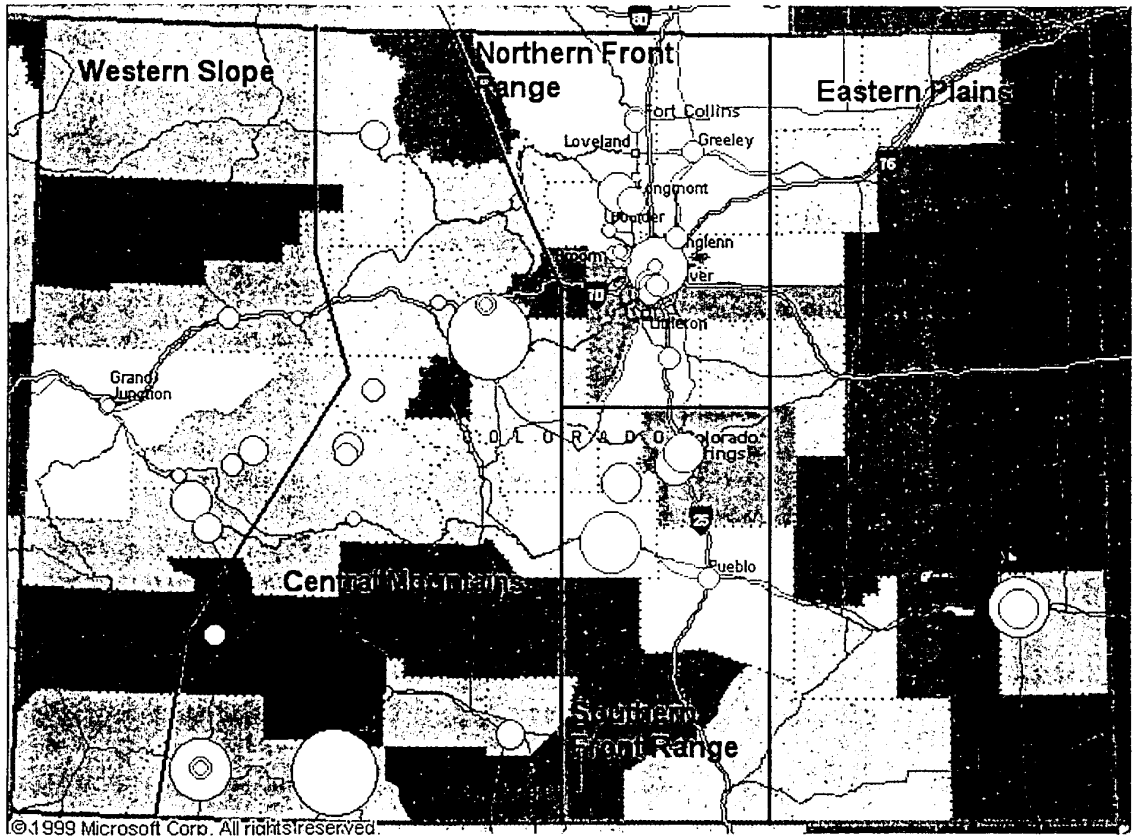


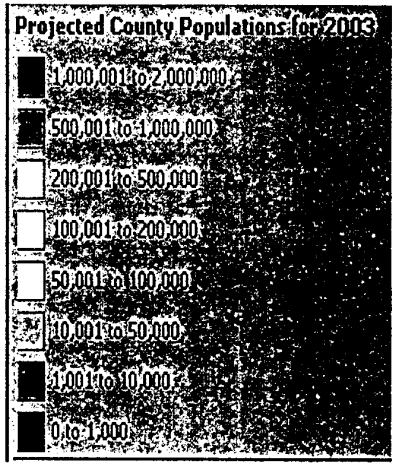
Colorado Ozone Monitoring in 2000

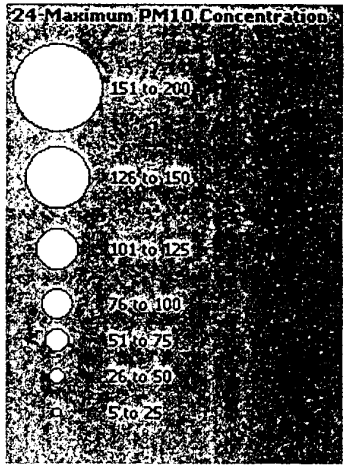
		1-hr Max		1-hr 2nd Max
Eastern Plains				
	N/A		No monitors in this region.	
Northern Front Range				
	NREL, 20th St. & Quaker Ave.	0.118 ppm		0.107 ppm
Southern Front Range				
	Colorado Springs, USAFA, Rd 640	0.088 ppm		0.088 ppm
Central Mountains				
	N/A		No monitors in this region.	
Western Slope				
	N/A		No monitors in this region.	
Statewide				
	NREL, 20th St. & Quaker Ave.	0.118 ppm		0.107 ppm
	Highlands Res. 8100 S. University Blvd	0.111 ppm		0.097 ppm

Ozone Standard : **1-hour = 0.12 ppm**

Colorado PM_{10} Monitoring in 2000





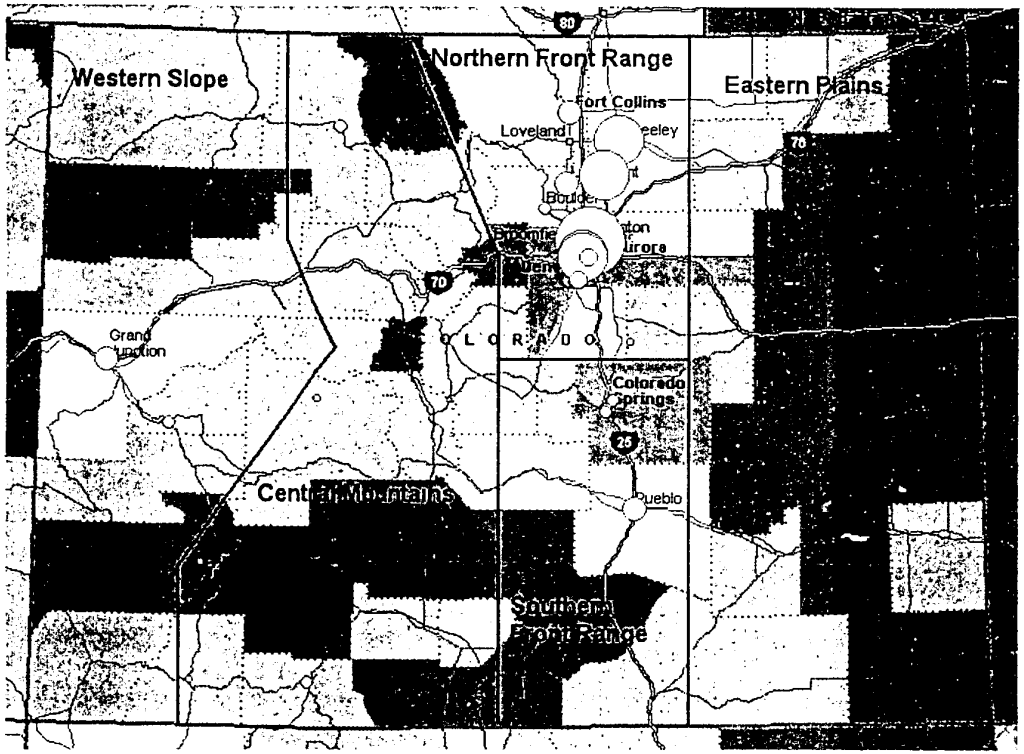


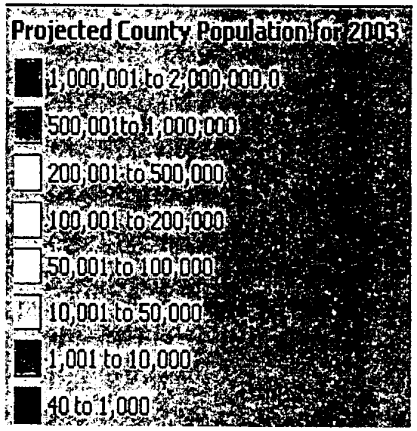
Colorado PM_{10} Monitoring in 2000

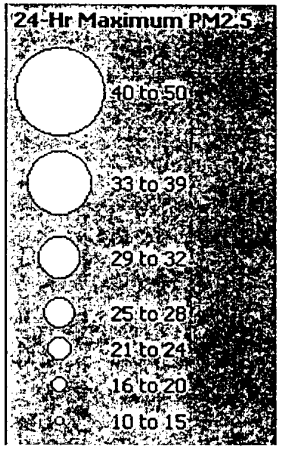
	Maximum	2nd Maximum	Annual Average
Eastern Plains			
Lamar, 100 2nd Ave.	137 μg/m³	136 μg/m³	29 μg/m³
Northern Front Range			
Adams City, 4301 E. 72nd Ave.	135 μg/m³	134 μg/m³	43 μg/m³
Southern Front Range			
Canon City, Courthouse	133 μg/m³	36 μg/m³	17 μg/m³
Central Mountains			
Breckenridge, Courthouse	182 μg/m³	71 μg/m³	22 μg/m³
Western Slope			
Olathe, 327 4th St.	104 μg/m³	87 μg/m³	30 μg/m³
Statewide			
Breckenridge, Courthouse	182 μg/m³	71 μg/m³	22 μg/m³
Pagosa Springs, 486 San Juan	165 μg/m³	87 μg/m³	28 μg/m³

PM_{10} Standards: **24-hr = 150 μg/m³** , Annual Average = **50 μg/m³**

Colorado $PM_{2.5}$ Monitoring in 2000





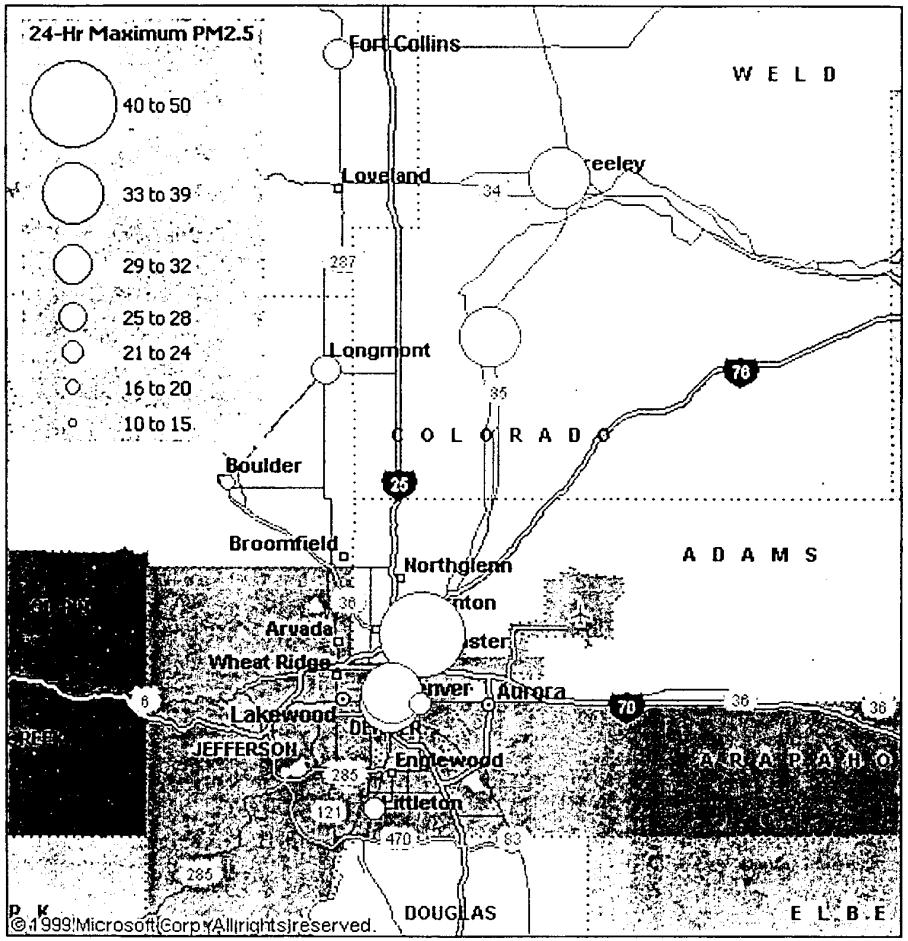


Colorado $PM_{2.5}$ Monitoring in 2000

	Maximum	2nd Maximum	Annual Average
Eastern Plains			
No monitoring in this region			
Northern Front Range			
Adams City, 4301 E. 72nd Ave.	40.4 μg/m³	23.3 μg/m³	10.8 μg/m³
Southern Front Range			
Pueblo, 211 D St.	25.3 μg/m³	22.1 μg/m³	7.9 μg/m³
Central Mountains			
Pagosa Springs, 486 San Juan	20.6 μg/m³	16.7 μg/m³	6.7 μg/m³ *
Western Slope			
Grand Junction, 515 Patterson Rd.	27.5 μg/m³	25.3 μg/m³	7.2 μg/m³
Statewide			
Adams City, 4301 E. 72nd Ave.	40.4 μg/m³	23.3 μg/m³	10.8 μg/m³
Platteville, 1004 Main St	39.0 μg/m³	22.4 μg/m³	9.0 μg/m³

$PM_{2.5}$ Standards: **24-hr = 65 μg/m³ , Annual Average = 15 μg/m³** *** : Incomplete data**

Northern Front Range $PM_{2.5}$ Monitoring



Denver – Boulder Region
Census Data

- 1990 Population = 1,848,319
- 2000 Population = 2,400,570

  (+29.9 percent change from 1990)
- 2010 Population estimate = 2,807,947

  (+17.0 percent change from 2000)

(from Colorado Demography Section)

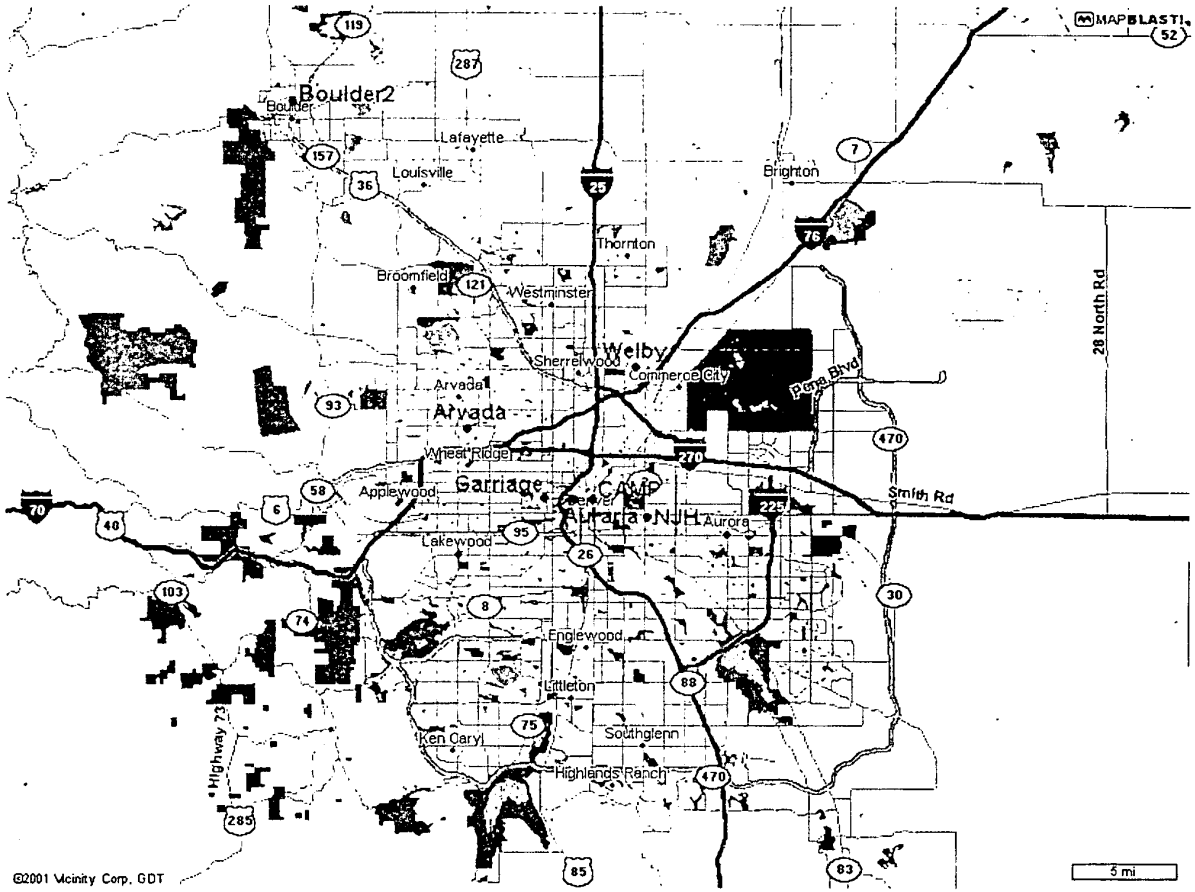
EPA Requirements under 40 CFR Part 58

- Carbon Monoxide
  - If population > 500,000 then need 2 sites
- Ozone
  - If population > 200,000 then need 2 sites
- Nitrogen Dioxide
  - If population > 1,000,000 then need 2 sites
- Sulfur Dioxide
  - If population > 1,000,000 then need:
    - 2-4 sites if low concentration area
    - 4-8 sites if medium concentration area
    - 6-10 sites if high concentration area

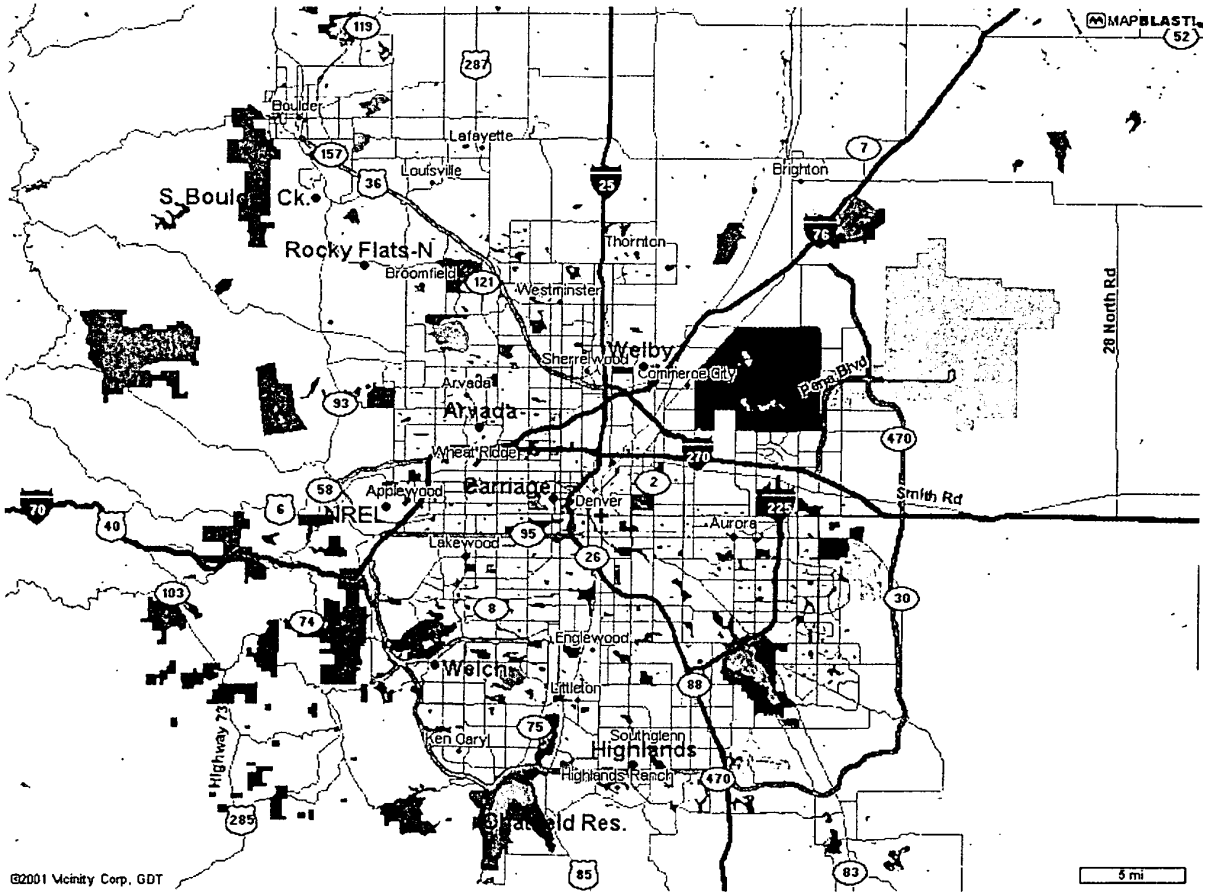
EPA Requirements under 40 CFR Part 58

- PM_{10}
  - If population > 1,000,000 then need:
    - 2-4 sites if low concentration area
    - 4-8 sites if medium concentration area
    - 6-10 sites if high concentration area
- $PM_{2.5}$
  - If population > 2,000,000 and < 4,000,000 then need 4 sites
- Lead
  - Need one site in largest city in the State.

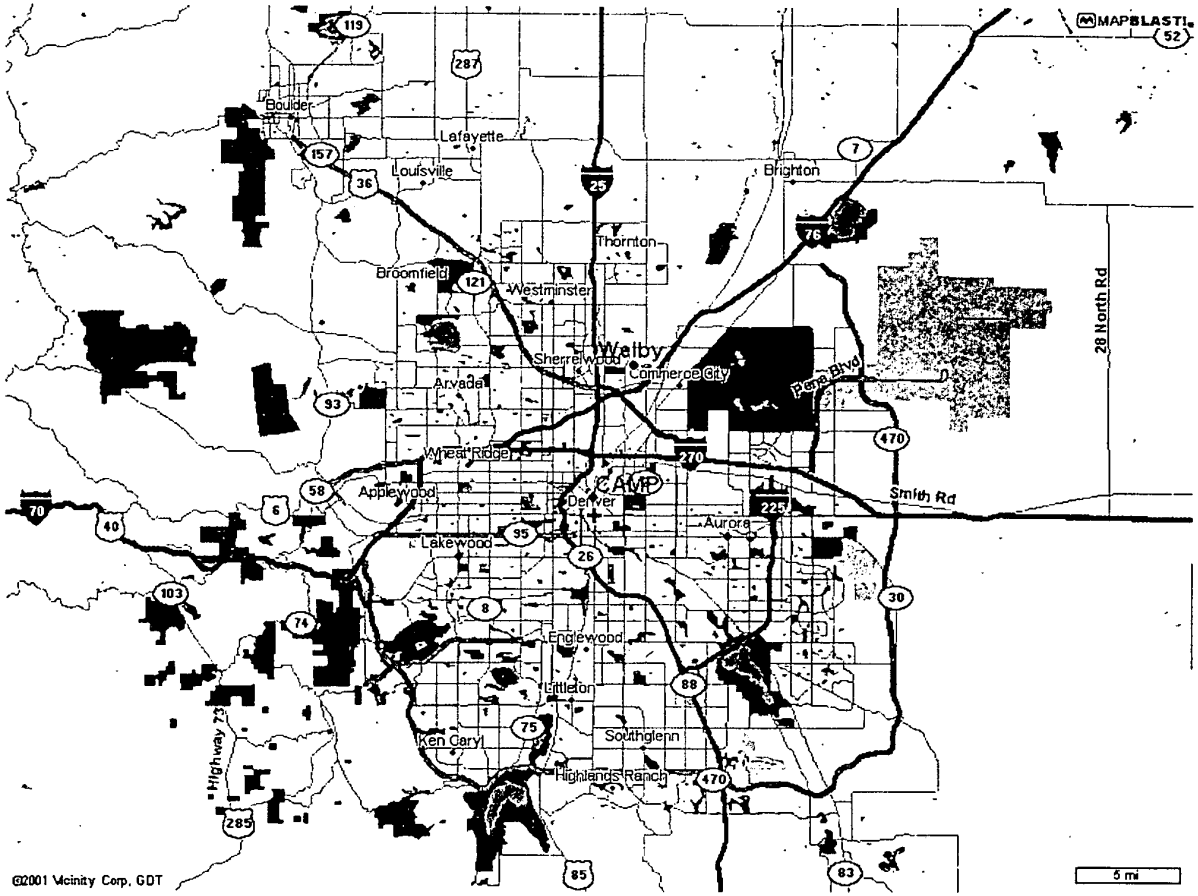
Denver Metro Area
Monitoring Sites – Carbon Monoxide



Denver Metro Area
Monitoring Sites – Ozone



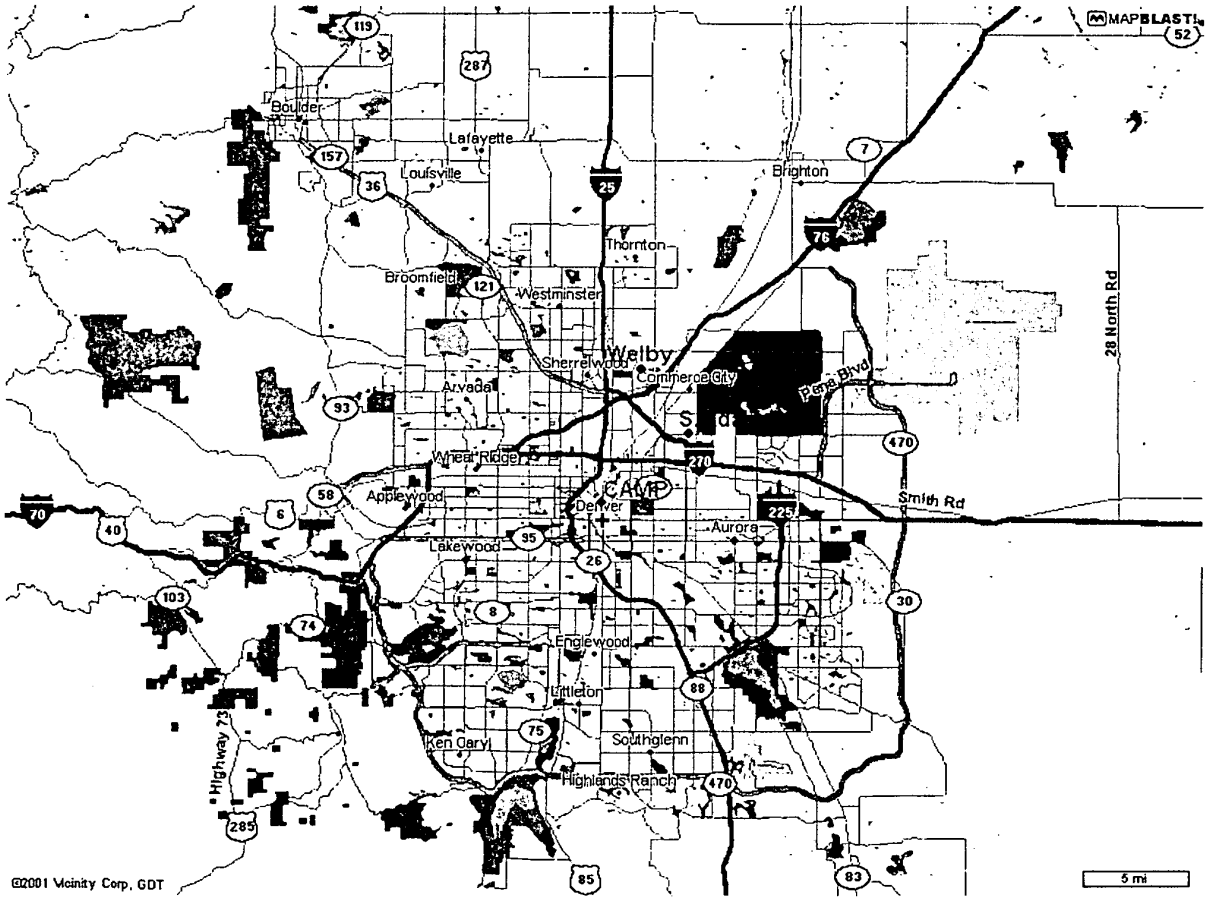
Denver Metro Area
Monitoring Sites – Nitrogen Dioxide



7/26/01

APCD Technical Services Program

Denver Metro Area
Monitoring Sites – Sulfur Dioxide



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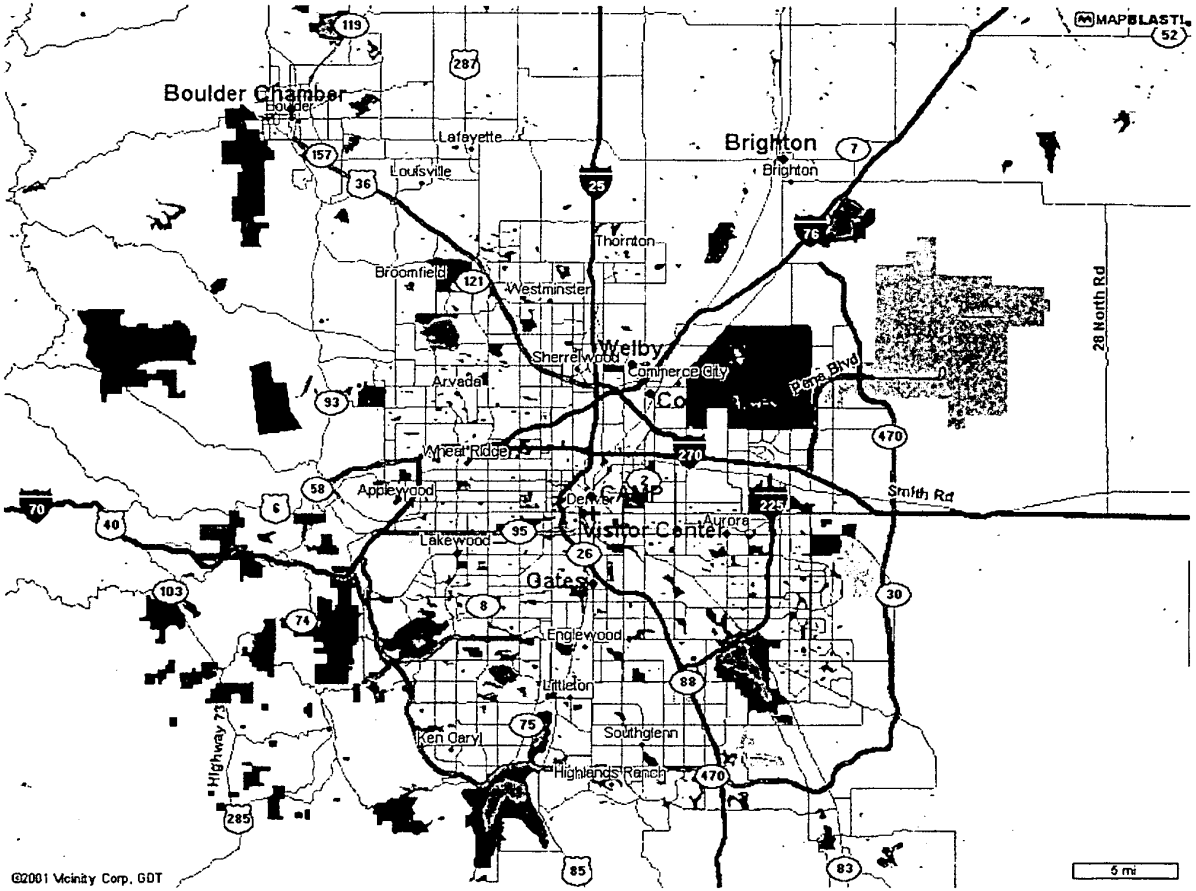
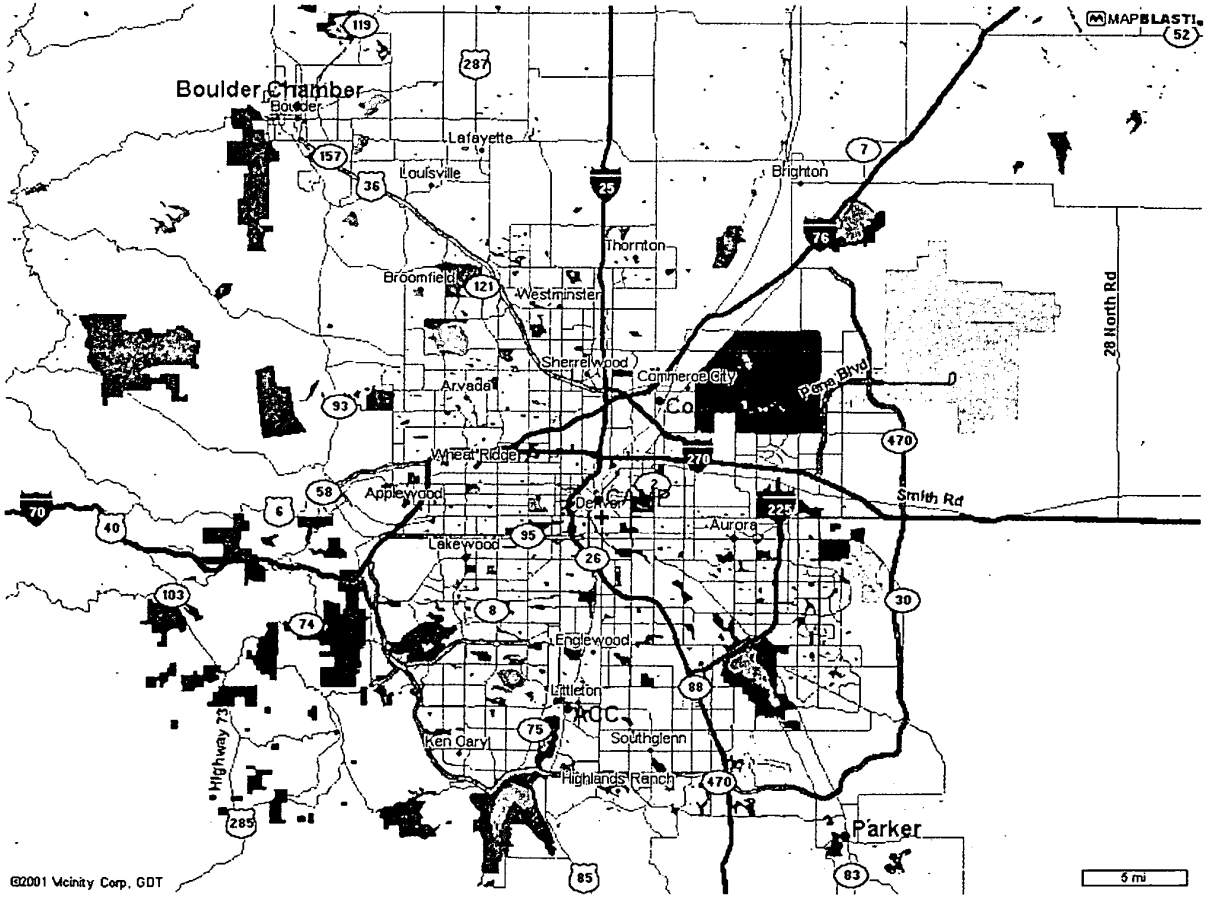
APCD Technical Services Program

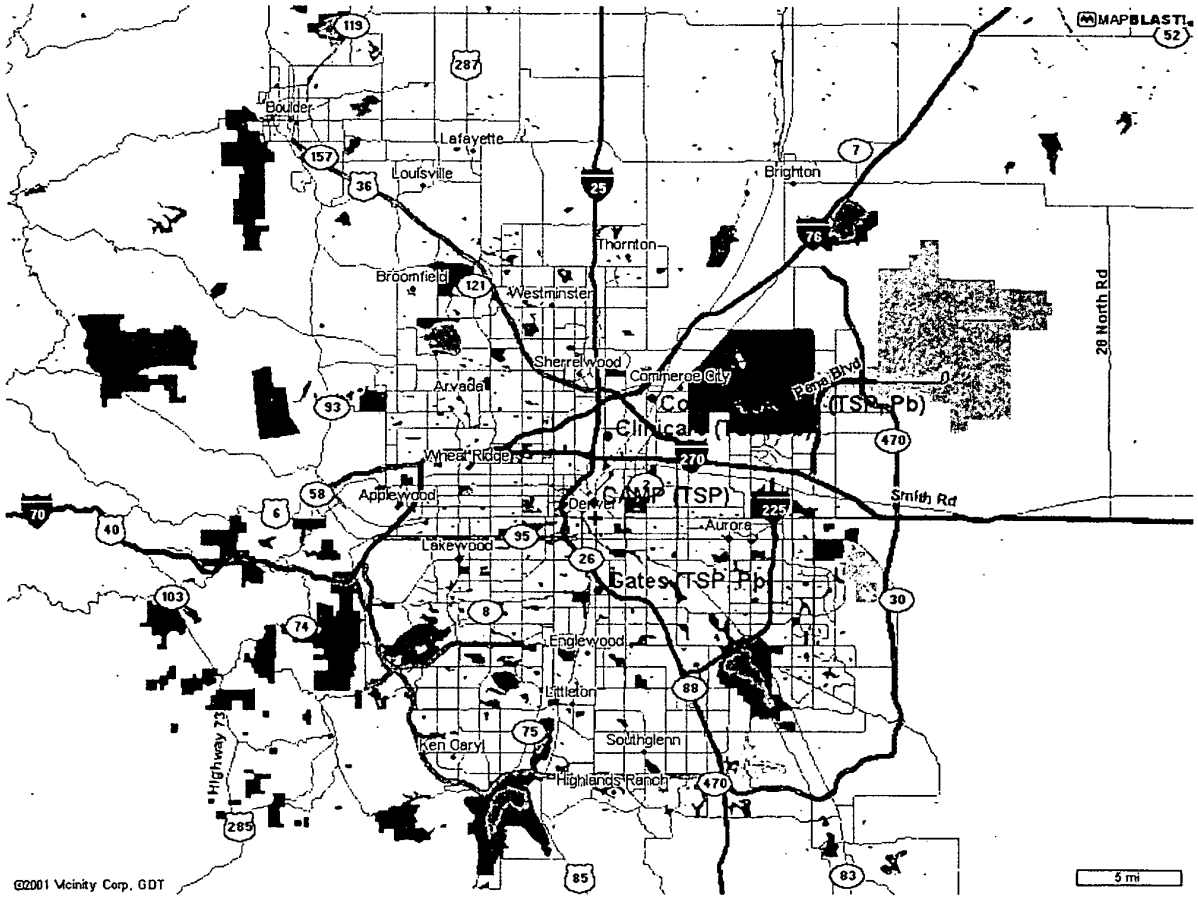
Denver Metro Area
Monitoring Sites – PM10



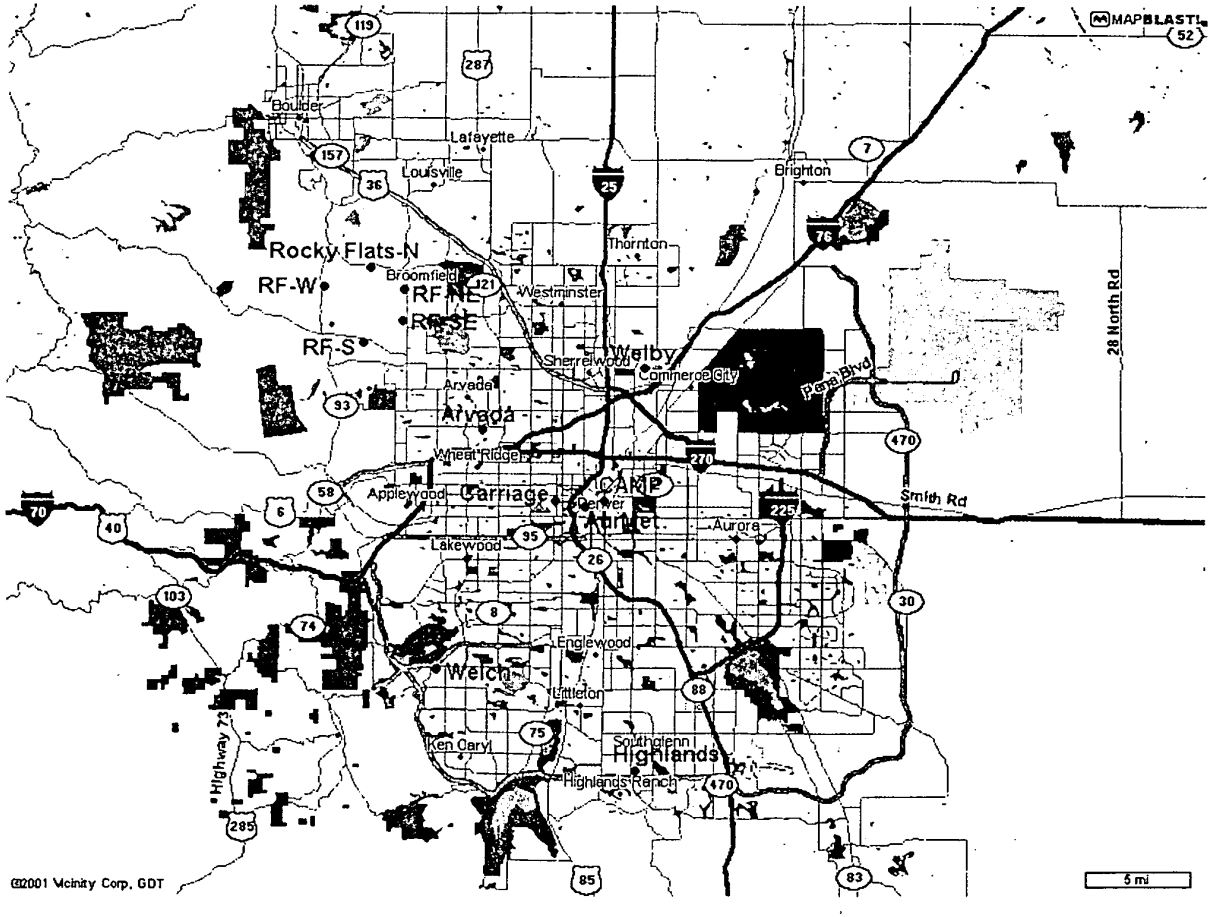
Denver Metro Area
Monitoring Sites – PM2.5



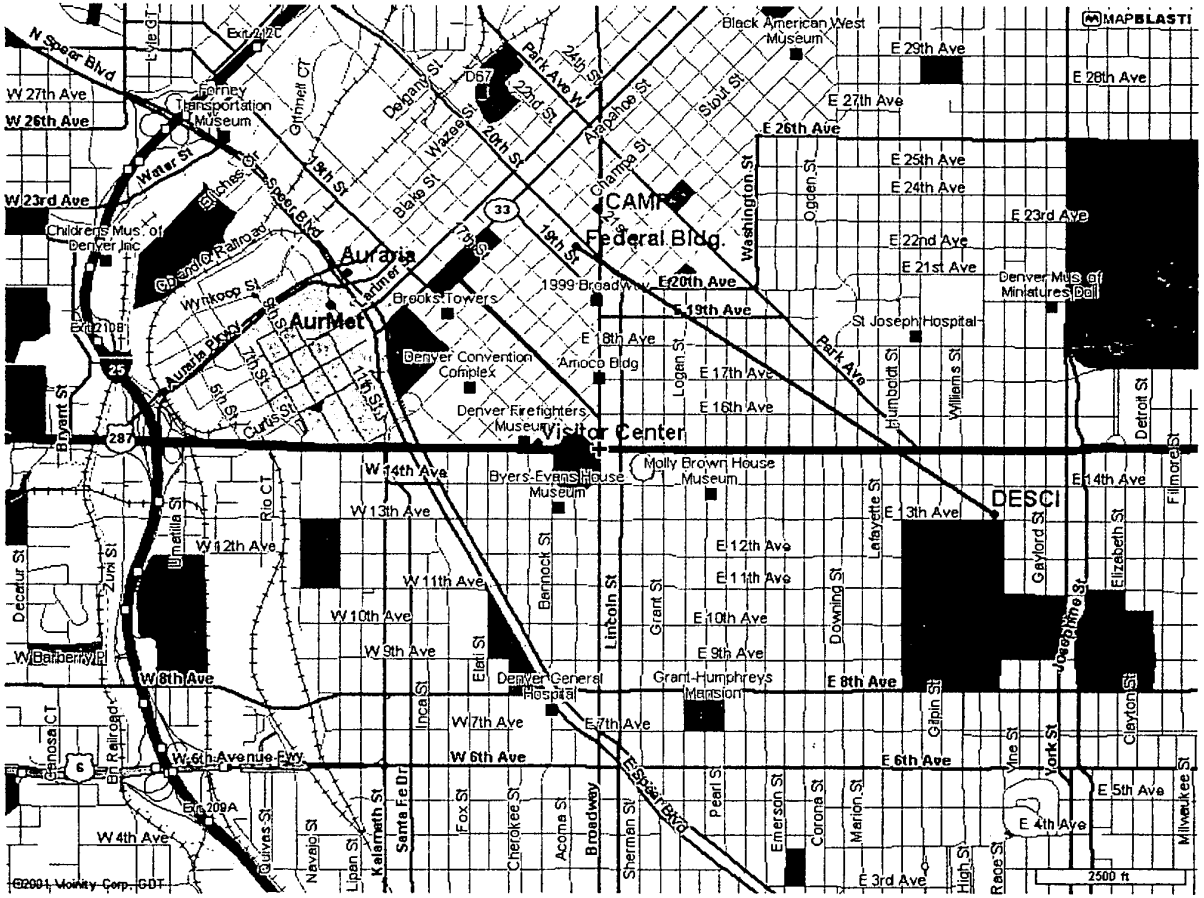
Denver Metro Area
Monitoring Sites – TSP and Lead



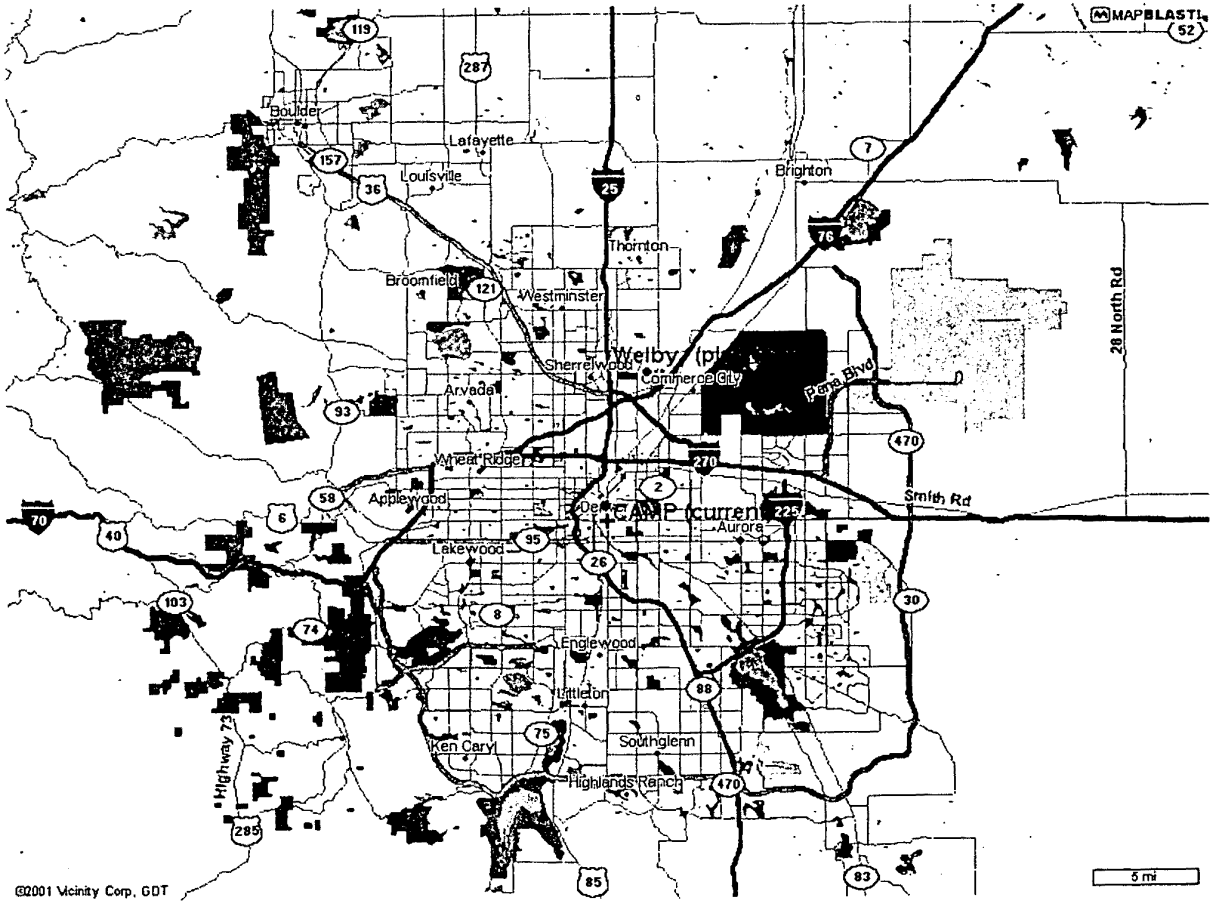
Denver Metro Area
Monitoring Sites – Meteorology



Denver Metro Area
Monitoring Sites – Visibility



Denver Metro Area
Monitoring Sites – Air Toxics



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2001 Clean Air Plan

Santa Barbara County's plan to maintain the federal 1-hour ozone standard and attain the state 1-hour ozone standard

DRAFT

August 2001

Santa Barbara County
Air Pollution Control District

Santa Barbara County
ASSOCIATION OF
GOVERNMENTS

EXECUTIVE SUMMARY

INTRODUCTION

Air quality in Santa Barbara County continues to improve, with 1999 being one of the cleanest years on record. In fact, our air quality has improved to the point that it is clean enough to meet the federal 1-hour ozone standard. This milestone is clear evidence that Santa Barbara County residents are breathing cleaner air and it allows us to request the United States Environmental Protection Agency (USEPA) to declare us as an attainment area for the federal 1-hour ozone standard. For the USEPA to take this action, we must develop and adopt a plan that documents how we achieved clean air and how we will continue to keep it clean. Continuing progress toward clean air is a challenge that demands participation by the entire community. A clean air plan represents the blueprint for air quality improvement in Santa Barbara County. A clean air plan's goals are to explain the complex interactions between emissions and air quality and to design the best possible emission control strategy in a cost-effective manner. This 2001 Clean Air Plan also represents a partnership among the Air Pollution Control District (APCD), the Santa Barbara County Association of Governments (SBCAG), the California Air Resources Board (ARB), the USEPA, local businesses, and the community-at-large to reduce pollution from all sources: cars, trucks, industry, consumer products, and many more.

We have made remarkable progress in cleaning our air; the number of days on which we experience unhealthful air quality in Santa Barbara County has been reduced by over 80 percent from 1990 to 2000 despite substantial increases in population and vehicle miles traveled. The community should be proud of these accomplishments to date in reducing air pollution. This 2001 Clean Air Plan reflects a commitment to continue this progress and bring truly clean air to all of the residents of Santa Barbara County.

This 2001 Clean Air Plan addresses both state and federal clean air act mandates. More specifically, this Plan addresses all federal planning requirements for "Maintenance" areas, including a demonstration that we attained the federal 1-hour ozone standard and a demonstration that we will continue to attain the federal standard through 2015. In addition, this Plan re-establishes on-road mobile source reactive organic compounds and oxides of nitrogen emission

budgets for the purposes of transportation conformity. This Plan also provides a three-year update to the APCD's 1991 Air Quality Attainment Plan, the 1994 Clean Air Plan, and the 1998 Clean Air Plan for the state ozone standard, as required by the 1988 California Clean Air Act.

WHY IS THIS PLAN BEING PREPARED?

This Plan is being prepared to formally request USEPA to redesignate Santa Barbara County as an attainment area for the federal 1-hour ozone standard. From 1997 through 2000, ozone concentrations measured throughout Santa Barbara County were clean enough to meet this standard. This milestone allows us to request the USEPA to redesignate Santa Barbara County as an attainment area for the federal 1-hour ozone standard. For this to happen, we must have an approved Maintenance Plan that includes an attainment emissions inventory, future year projections of the inventory demonstrating continued attainment, a commitment to continue air monitoring, procedures to verify continued attainment, and contingency provisions that will promptly correct any violation of the federal ozone standard that occurs after redesignation.

Additionally, state law requires that our state planning requirements must be evaluated every three years. To coordinate all applicable state and federal planning requirements, this Plan integrates the technical and policy issues associated with both the state and federal 1-hour ozone standards. This Plan therefore satisfies both state and federal planning requirements.

WHAT IS NEW IN THIS PLAN REVISION?

Each clean air plan revision represents a snapshot in time, based on the best available current information. This Plan is similar to the 1998 Clean Air Plan but includes significant new information. Some key new elements are:

- Updated local air quality information (1999 and 2000);
- An attainment emission inventory (1999);
- Identification of every feasible emission control measure as part of the overall emission control strategy; and
- A Maintenance demonstration for the federal 1-hour ozone standard (through 2015).

HOW WAS THIS PLAN REVISION PREPARED?

We prepared this plan in partnership with SBCAG, ARB, and USEPA. SBCAG provided future growth projections, developed the transportation control measures, and estimated the on-road mobile source emissions. ARB provided information on statewide mobile sources and consumer product control measures. USEPA provided information on the status of the control efforts for federally regulated sources.

To help provide important local policy and technical input on APCD clean air plans and rules, the APCD Board of Directors established the Community Advisory Council. Starting in July of 2000, the CAC considered various components of this Plan at their monthly meetings. The information and guidance provided by the Community Advisory Council was, on many occasions, directly incorporated into this Plan. APCD staff also conducted public workshops to obtain direct public input on the Plan.

WHAT ARE THE HEALTH EFFECTS OF OZONE?

The health effects of ozone focus on the respiratory tract. Asthma, bronchitis and other respiratory disorders are worsened by high ozone concentrations. High ozone concentrations can be especially harmful to children, the elderly, people with respiratory illnesses, and people who exercise outdoors. Long-term exposure to moderate levels of ozone can damage even healthy people's lungs. Ozone air pollution is also bad for the economy by increasing health care expenses, loss of work due to illness, and damage to agricultural crops, buildings, paint, and rubber.

IS AIR QUALITY IMPROVING?

Santa Barbara County's air quality is improving, as measured ozone concentrations continue to decline. In 1999, for example, our monitoring stations recorded only three exceedances of the more health protective state ozone standard and only one exceedance of the federal 1-hour ozone standard. This represents the cleanest year on record! During 2000, we experienced 6 exceedances of the state 1-hour ozone standard and one exceedance of the federal 1-hour ozone standard. Figure EX-1 shows the number of state and federal ozone standard exceedances from 1990 through 2000.

The most important feature of Figure EX-1 is the decline of state 1-hour ozone standard exceedances since 1990 by over 80 percent.

WHAT ARE THE KEY FEDERAL REQUIREMENTS THAT THIS PLAN ADDRESSES?

To grant our request for redesignation, USEPA must address the five criteria contained in Section 107(d)(3)(E) of the federal Clean Air Act Amendments as described below. They must:

- Determine that the national ambient air quality standard for ozone has been attained.
- Fully approve our applicable implementation plan under Section 110(k).
- Determine that the improvement in air quality is due to permanent and enforceable reductions in emissions.
- Determine that we have met all applicable requirements for the area under Section 110 and Part D.
- Fully approved our Maintenance Plan, including contingency provisions, for our area under Section 175A.

In addition, this Plan re-establishes on-road mobile source reactive organic compounds and oxides of nitrogen emission budgets for the purposes of transportation conformity. These emission budgets will be used to evaluate conformity of future transportation improvement plans and programs to ensure that they are consistent with this 2001 Plan.

WHAT ARE THE KEY STATE REQUIREMENTS THAT THIS PLAN ADDRESSES?

Key requirements of the California Clean Air Act that this Plan addresses are the Triennial Progress Report (H&SC Section 40924(b)) and the Triennial Plan Revision (H&SC Section 40925(a)). Additionally, the Plan must provide an annual 5 percent emission reduction of ozone precursors or, if this cannot be done, include every feasible measure as part of the emission control strategy. Finally, state law requires this Plan to provide for attainment of the state ambient air quality standards at the earliest practicable date (H&SC Section 40910).

HOW HAS THE EMISSION INVENTORY CHANGED?

In this 2001 Plan, an updated emission inventory was developed for 1999. This inventory serves as our attainment emission inventory and is used to forecast emissions for 2005, 2010, and 2015. The 1999 attainment inventory was developed in accordance with ARB and USEPA policies and procedures and represents the most up-to-date inventory established for Santa Barbara County. The emissions inventory follows the organizational structure developed by ARB and assigns all air pollution sources into one of four categories. The four categories are stationary sources, area-wide sources, mobile sources, and natural sources. On-road mobile source emissions are estimated with the latest approved computer models, vehicle registration information, and emission factors.

WHERE DOES OUR HUMAN-GENERATED AIR POLLUTION COME FROM?

Figure EX-2 shows the attainment emission inventory for 1999. This figure presents the estimated emissions of reactive organic compounds and oxides of nitrogen (precursors that combine to form ozone) generated locally from human activities and does not include emissions on the Outer Continental Shelf or those from natural sources (seeps and vegetation). The largest contributor to our locally generated air pollution is on-road mobile sources (cars and trucks) that combine to contribute over 60 percent of the reactive organic gases and 88 percent of the emissions of oxides of nitrogen. Other mobile source (planes, trains, boats), the evaporation of solvents, combustion of fossil fuels, surface cleaning and coating, and petroleum production and marketing combine to make up the remainder. Figure EX-3 shows the attainment emission inventory for the Outer Continental Shelf, where the majority of reactive organic gas and oxides of nitrogen emissions comes from mobile sources (i.e., international marine vessels).

HAS THE OVERALL CONTROL STRATEGY CHANGED?

The overall combined reactive organic compounds and oxides of nitrogen control strategy adopted in the 1998 Clean Air Plan continues in this 2001 Plan, with the addition of eight new or revised stationary source control measures and updated transportation control measures. The 1998 Clean Air Plan contained: (1) the control measures needed to meet federal requirements for attaining the federal 1-hour ozone standard, (2) additional control measures needed to address state requirements

and attain the state 1-hour ozone standard, and (3) further study measures. This 2001 Plan evaluates each of the further study measures identified in the 1998 Clean Air Plan and sets a schedule for adoption of those measures that were determined to be feasible. This Plan also provides updated information on emission control measures approved under the 1994 California State Implementation Plan.

DOES THE PLAN SHOW THAT WE WILL MAINTAIN THE FEDERAL 1-HOUR OZONE STANDARD?

This Plan demonstrates that we will maintain the federal 1-hour ozone standard through 2015. The demonstration is based on an attainment emission inventory assessment of the overall control strategy proposed in the Plan. However, the impacts of transported pollution from areas and sources outside of our local control (e.g., international marine vessels), may impact our ability to achieve this projected milestone. We must also recognize that varying weather conditions can effect local air quality concentrations.

DOES THE ELECTRICITY CRISIS IMPACT THIS 2001 PLAN?

The electricity crisis in California may affect this 2001 Plan's redesignation effort. If blackouts occur on smoggy days, there will likely be an increase in ozone precursor emissions from emergency backup generators. We also expect that there will be an increase in emissions from power plants and "peakers" throughout the state. These potential increases in emissions are not accounted for in this 2001 Plan because the emission increases and their impacts are very difficult to predict. Therefore, while the electricity crisis may ultimately affect our local air quality, it is not specifically addressed in this 2001 Plan.

Figure EX-1

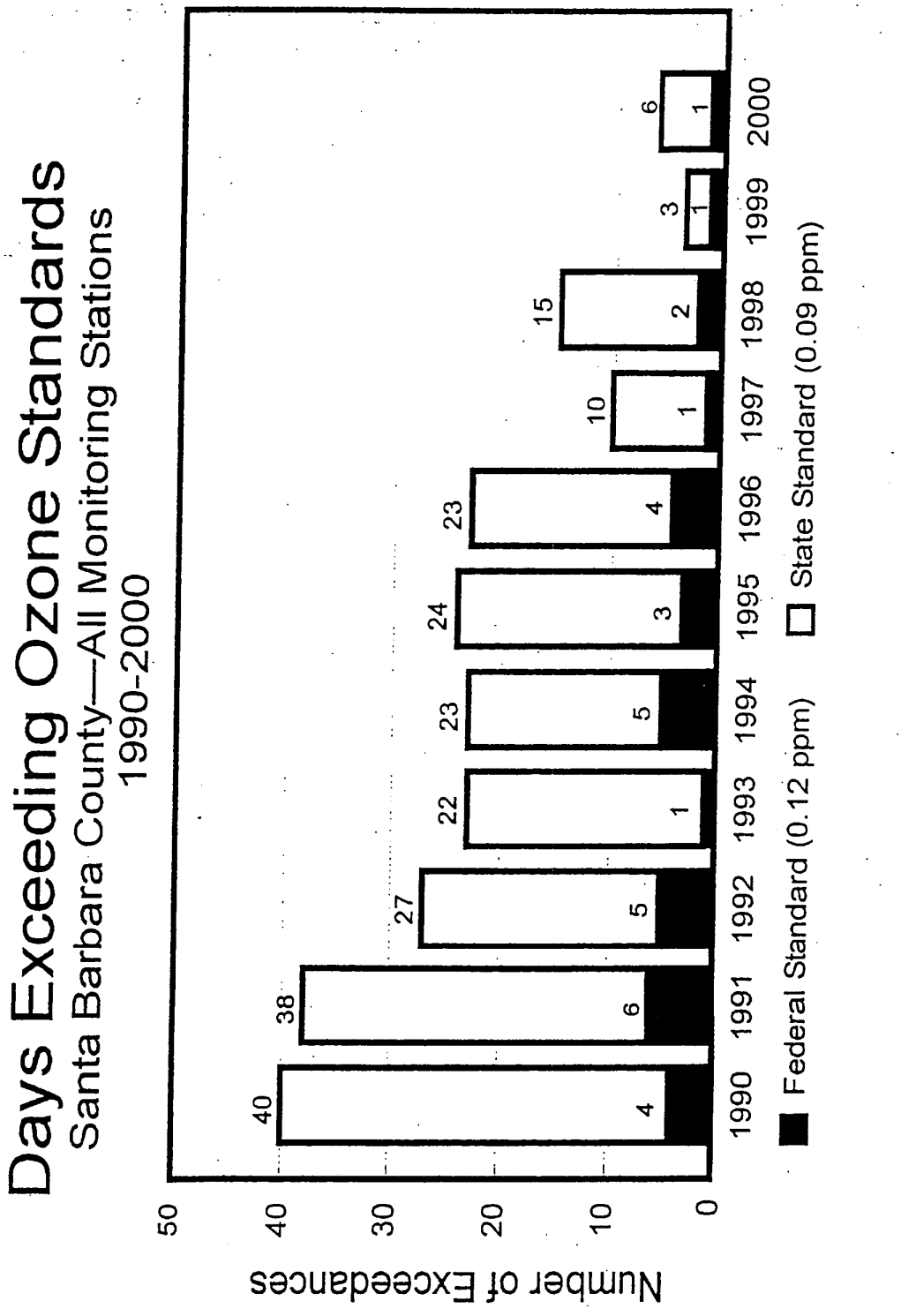
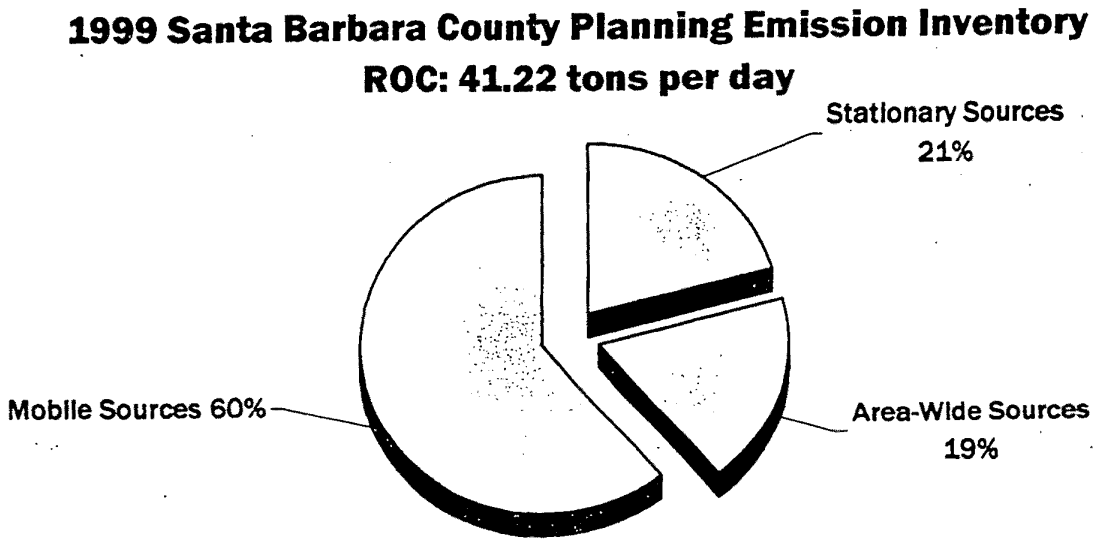

Days Exceeding Ozone Standards
Santa Barbara County—All Monitoring Stations
1990-2000
Number of Exceedances
0
10
20
30
40
50
40
4
38
6
27
5
22
1
23
5
24
3
23
4
10
1
15
2
3
1
6
1
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
Federal Standard (0.12 ppm)
State Standard (0.09 ppm)

Figure EX-2


1999 Santa Barbara County Planning Emission Inventory
ROC: 41.22 tons per day
Stationary Sources
21%
Mobile Sources 60%
Area-Wide Sources
19%

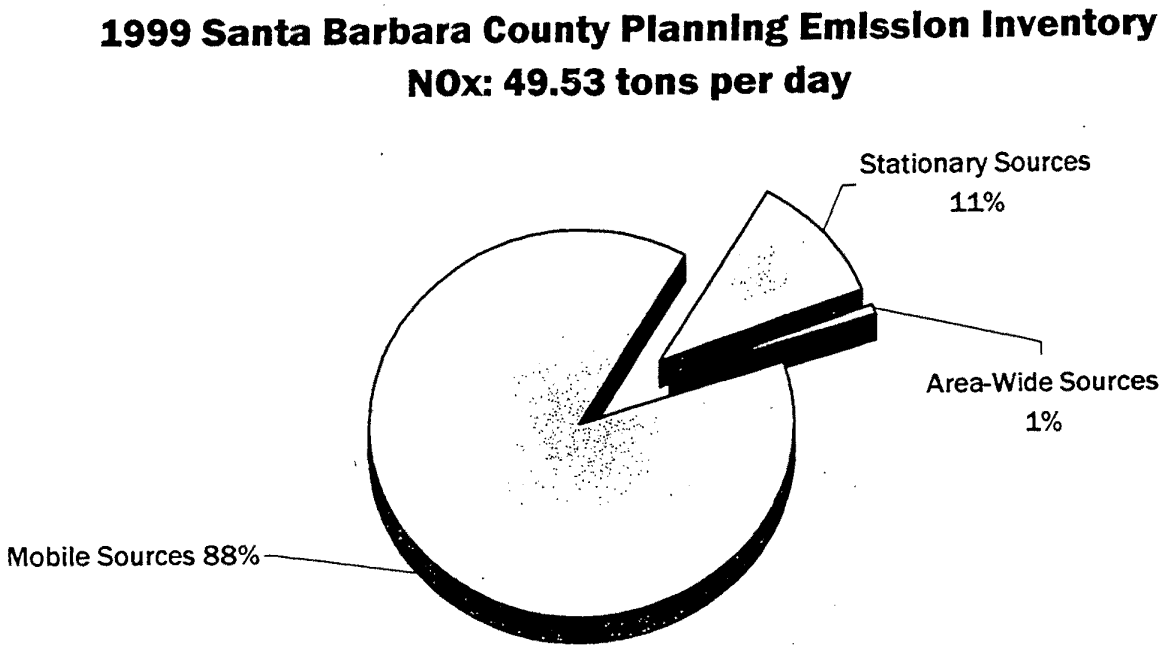
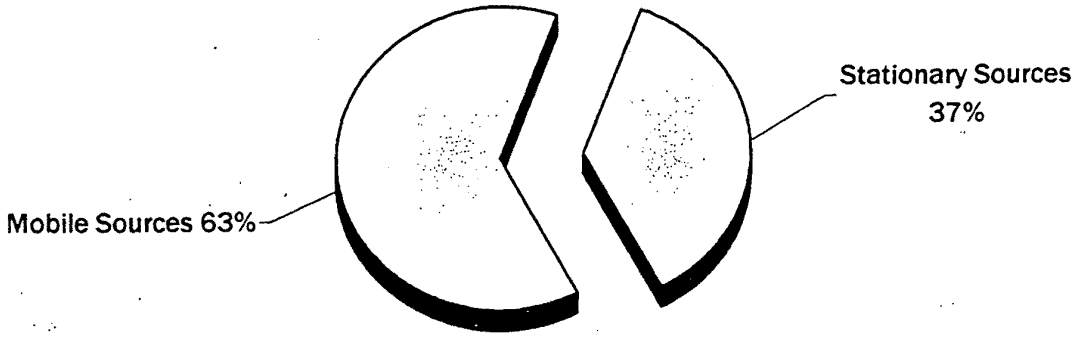
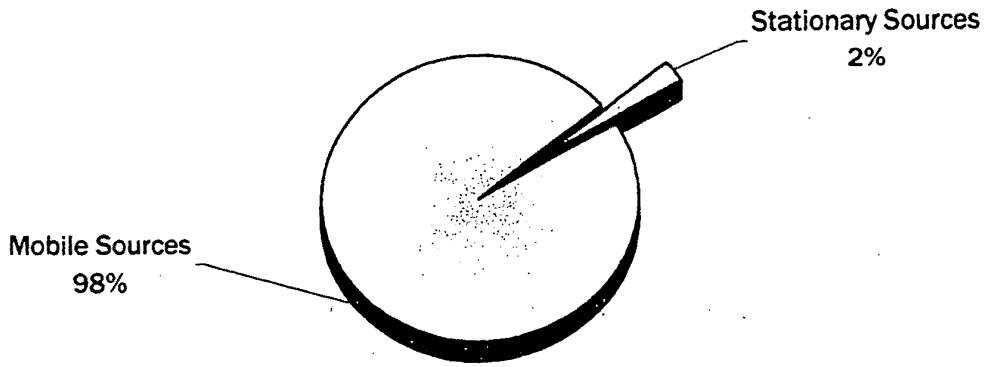

1999 Santa Barbara County Planning Emission Inventory
NOx: 49.53 tons per day
Stationary Sources
11%
Area-Wide Sources
1%
Mobile Sources 88%

Figure EX-3

1999 OCS Planning Emission Inventory
ROC: 2.84 tons per day



1999 OCS Planning Emission Inventory
NOx: 29.08 tons per day



CHAPTER 1

INTRODUCTION

Purpose

Current State and Federal Planning Requirements

Summary of Attainment Planning Efforts

Plan Organization

1. INTRODUCTION

1.1 PURPOSE

The purpose of this 2001 Clean Air Plan (2001 Plan) is to chart a course of action that will ensure clean air for the residents and environment of Santa Barbara County. Clean air is fundamental to good public health; it enhances the environment and contributes to the attractiveness of the area to residents, businesses, and visitors. Fortunately, our air quality has been improving through implementation of several air quality plans. These plans have been developed for Santa Barbara County as required by both the 1998 California Clean Air Act (State Act) and the 1990 Federal Clean Air Act Amendments (Federal Act).

Santa Barbara County's air quality has historically violated both the state and federal ozone standards. Ozone concentrations above these standards adversely affect public health, diminish the production and quality of many agricultural crops, reduce visibility, and damage native and ornamental vegetation. Under both the Federal Act and the State Act, the measured ozone concentrations in the county resulted in our classification as a "moderate" nonattainment area. The county continues to be classified as a "moderate" area under the State Act, but was re-classified as a "serious" ozone nonattainment area under the Federal Act on December 10, 1997, for failure to attain the federal 1-hour ozone standard by our November 15, 1996, attainment date.

However, more recent data, collected from 1997 through 1999, show that every monitoring location in Santa Barbara County complied with the federal 1-hour ambient air quality standard for ozone. Achieving this milestone has two important results:

1) The residents of Santa Barbara County are breathing cleaner air, and
2) We are now able to submit a redesignation request and Maintenance Plan to the United States Environmental Protection Agency (USEPA) to become an attainment area for the federal 1-hour ozone standard.

Specifically, this 2001 Plan addresses all federal planning requirements for "Maintenance Plans" and provides for ongoing maintenance of the federal 1-hour ozone standard through the year 2015. The Plan also formally requests that USEPA re-designate Santa Barbara County as an attainment area for the federal 1-hour ozone standard. In addition, this 2001 Plan re-establishes on-road mobile source reactive organic compounds (ROC) and oxides of nitrogen (NO_x) emission budgets to address the requirements of transportation conformity. Finally, this 2001 Plan provides a three-year update to the 1991 Air Quality Attainment Plan, the 1994 Clean Air Plan and the 1998 Clean Air Plan for the state ozone standard, as required by the State Act. Many of the local control measures proposed in this plan satisfy the "every feasible" measure requirements of the State Act and serve as "contingency" measures for the Federal Act. If we experience a "violation" of the federal 1-hour ozone standard during the planning horizon of this 2001 Plan, we will evaluate and expedite the implementation of the "contingency" measures outlined in this plan.

1.2 CURRENT STATE AND FEDERAL PLANNING REQUIREMENTS

Section 175A of the Federal Act requires that areas prepare a plan to provide for maintenance of the federal 1-hour ozone standard for at least 10 years after an area is redesignated to an attainment area. This 2001 Plan is the forth major planning effort under the Federal Act and also complies with the triennial progress report and plan revision requirements under the State Act. A complete summary of all state and federal Clean Air Act requirements that apply to Santa Barbara County is provided in Chapter 10.

The first step in the development of a Maintenance Plan is to determine an "attainment inventory" for Santa Barbara County against which to compare future predicted emissions for 2005, 2010, and 2015. Since we attained the federal 1-hour ozone standard during the 1997-1999 period, we developed emission inventories for 1999 for both ROC and NOx. The attainment inventory methodology assumes that the emission levels experienced in Santa Barbara County during 1999 are adequate to keep measured ozone concentrations below the federal 1-hour ozone standard. The maintenance demonstration must show that

all predicted future year emission levels in 2005, 2010, and 2015 are below the attainment inventory established for 1999.

Failure to fully meet the requirements of the Federal Act can lead to federal intervention in our local air pollution control program. Loss of federal highway funds and increased emission offset requirements for new stationary sources are possible outcomes under the mandatory sanctions imposed for failure to meet Federal Act requirements. Failure to maintain the federal 1-hour ozone standard through 2015 could also result in the USEPA reclassifying Santa Barbara County back to a nonattainment area. The strategy outlined in this 2001 Plan is structured in such a way as to minimize the probability of these events. However, if Santa Barbara County is unable to maintain the federal 1-hour ozone standard through 2015 due to the impacts of transported pollution from areas outside our local control, we may request that the USEPA consider these circumstances when evaluating future designations. This request would be based upon a USEPA policy, dated July 17, 1998, on the extension of attainment dates for downwind transport areas.

California law mandates that APCDs periodically revise and update attainment plans to achieve the state 1-hour ozone standard as expeditiously as practicable. The efforts being undertaken for this 2001 Plan also address attainment of the state 1-hour ozone standard, which is more protective of public health than the federal 1-hour ozone standard. This 2001 Plan will therefore satisfy all state triennial planning requirements. This Plan will also assist us in the comprehensive planning effort envisioned by the California Air Resources Board (ARB) for 2003.

This 2001 Plan will be forwarded to the ARB for their review and approval before being submitted to the USEPA as a revision to the State Implementation Plan (SIP). The USEPA must approve both the Maintenance Plan and redesignation request in order to redesignate Santa Barbara County as an attainment area for the federal 1-hour ozone standard.

1.3 SUMMARY OF ATTAINMENT PLANNING EFFORTS

Several prior air quality plans have been prepared for Santa Barbara County. The first clean air plan for Santa Barbara County was the 1979 Air Quality Attainment Plan (1979 AQAP) which was updated in 1982. These two plans were prepared in response to mandates established by the federal Clean Air Act of 1977. At that time only the southern portion of the county, the region south of the Santa Ynez Mountains, violated the federal 1-hour ozone standard. The 1982 update predicted attainment of the federal ozone standard by 1984, but acknowledged that the county's ability to attain the federal ozone standard was uncertain because pollution generated on the OCS was not considered in the Plan.

The predicted attainment of the federal ozone standard did not occur. As a consequence, the USEPA called for an update to the 1982 Air Quality Attainment Plan on March 17, 1986. On May 26, 1988, the USEPA issued a subsequent mandate that our planning efforts address air quality for the entire county. This new mandate was issued in response to the failure of many regions of the country to attain the federal 1-hour ozone standard by 1987. In response, the APCD prepared the 1989 Air Quality Attainment Plan (1989 AQAP), which was adopted by the APCD Board of Directors in June of 1990 and was designed to bring the southern portion of the county into attainment with the federal 1-hour ozone standard.

The APCD also prepared a 1991 Air Quality Attainment Plan (1991 AQAP). This plan was required by the State Act to bring the entire county into attainment of the more health protective California ozone standard. The APCD Board of Directors adopted the 1991 AQAP in December 1991 and ARB approved it in August 1992.

In 1990, Congress amended the federal Clean Air Act (Federal Act). The Federal Act required Santa Barbara County, as a "moderate" nonattainment area, to submit a Rate-of-Progress Plan to the USEPA by November 15, 1993, and an attainment demonstration by November 15, 1994. The 1994 Clean Air Plan (1994 CAP) that contained these required elements was adopted by the APCD Board of Directors and formally submitted to the

USEPA on November 15, 1994. The 1994 CAP included: amendments to the 1993 Rate-of-Progress (1993 ROP) Plan; an attainment demonstration of the federal ozone standard by 1996; a request for re-designation from a nonattainment area to an attainment area for the federal ozone standard; and a plan to show maintenance of the federal ozone standard through the year 2006. The 1994 CAP also provided a three-year update to the 1991 AQAP for the state ozone standard, as required by the State Act.

On January 8, 1997, the USEPA approved several elements of the 1994 CAP, including the amendments to the 1993 Rate-of-Progress Plan, the base year emission inventory, and the control strategy. USEPA did not approve the attainment demonstration element due to violations of the federal 1-hour standard that occurred during 1994-1996. This element was withdrawn from the 1994 CAP submittal. Similarly, the USEPA never acted upon the maintenance plan element due to the measured violations of the federal 1-hour ozone standard.

On December 10, 1997, the USEPA issued a final action finding that Santa Barbara County had not attained the federal 1-hour ozone standard by the statutory attainment date for "moderate" nonattainment areas of November 15, 1996. As a result, the entire Santa Barbara County nonattainment area was reclassified as a "serious" nonattainment area by operation of federal law. The USEPA action mandated that we continue progress toward the federal 1-hour ozone standard through the development of a revised Clean Air Plan. The 1998 CAP was adopted by the APCD Board of Directors on December 17, 1998, and forwarded by the ARB to the USEPA on March 19, 1999. The 1998 CAP addressed all the new federal planning requirements for "serious" nonattainment areas and was approved by the USEPA on August 14, 2000 (65 FR 49499-49501).

A summary of Santa Barbara County's state and federal planning activities beginning with the 1991 AQAP is presented in Table 1-1.

1.4 PLAN ORGANIZATION

Chapter 2, Local Air Quality, provides a summary of Santa Barbara County's air quality, and discusses the nature and extent of the ozone problem.

Chapter 3, Emission Inventory, establishes an "attainment inventory" for Santa Barbara County by quantifying the emissions of reactive organic compounds and oxides of nitrogen for 1999. This emission inventory is tailored to meet federal requirements.

Chapter 4, Emission Control Measures, provides an overview of the APCD's control measures. In addition, the chapter summarizes all ARB's emission reduction programs that reduce emissions in Santa Barbara County. This chapter identifies the status of each control measure in relation to both state and federal requirements.

Chapter 5, Transportation Control Measures, describes all transportation related control measures, and identifies their applicability to both state and federal requirements.

Chapter 6, Emission Forecasting, details the forecast procedures used to develop future year emission inventories for 2005, 2010, and 2015.

Chapter 7, Redesignation Request and Maintenance Plan, formally requests the USEPA to redesignate Santa Barbara County in attainment of the federal 1-hour ozone standard and provides a demonstration that we will continue to maintain the standard through 2015.

Chapter 8, Implementation Support Activities, identifies and discusses other APCD programs and policies that facilitate continued progress toward attainment of state and federal ozone standards.

Chapter 9, Land Use Strategies, discusses the connection between land use development and air quality and sets forth specific policies and sustainable ways in which air pollution impacts of growth can be minimized.

Chapter 10, State and Federal Clean Air Act Requirements, provides an overview of all state and federal Clean Air Act planning requirements and discusses how the work completed in conjunction with this 2001 Plan complies with all applicable requirements.

Chapter 11, State Mandated Triennial Progress Report and Triennial Plan Revision, summarizes how the development and adoption of the 2001 Plan satisfies the triennial update requirements of the California Clean Air Act.

Chapter 12, Public Participation, summarizes all public input received during the development of this 2001 Plan.

In addition to the above chapters, three appendices document and support the 2001 Plan. These include the following:

Appendix A:	*Emission Inventory and Forecasting Documentation*
Appendix B:	*Stationary Source Control Measure Documentation*
Appendix C:	*Transportation Control Measure Working Papers & On-Road Mobile Source Emissions Analysis*

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U.S. Environmental Protection Agency: Clean Air Act Reclassification; California Santa Barbara Nonattainment Area; Ozone. 40 CFR Part 81, December 10,1997.

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Table 1 - 1

Comparison of the 1991 AQAP, 1993 ROP Plan, 1994 CAP, 1998 CAP and the 2001 Plan

	1991 AQAP	1993 ROP Plan	1994 CAP	1998 CAP	2001 Plan
Mandates	California Clean Air Act of 1988	Federal Clean Air Act Amendments of 1990	Federal Clean Air Act Amendments of 1990 California Clean Air Act of 1988.	Federal Clean Air Act Amendments of 1990 California Clean Air Act of 1988	Federal Clean Air Act Amendments of 1990 California Clean Air Act of 1988
Air Quality Standards	The state 1-hour ozone standard is 0.09 parts per million. An area is designated nonattainment based on a calculated "design day" value.[1]	The federal 1-hour ozone standard is 0.12 parts per million. An area is designated non-attainment if it violates the standard more than three times in three years at a single monitoring station.	Addresses both the state 1-hour ozone standard (0.09 parts per million) and the federal 1-hour ozone standard (0.12 parts per million)	Addresses both the state 1-hour ozone standard (0.09 parts per million) and the federal 1-hour ozone standard (0.12 parts per million)	Addresses both the state 1-hour ozone standard (0.09 parts per million) and the federal 1-hour ozone standard (0.12 parts per million)
Region Covered	All of Santa Barbara County failed to attain the state 1-hour ozone standard. The 1991 AQAP covered the entire county.	Under the Federal Clean Air Act of 1990, all of Santa Barbara County failed to attain the federal 1-hour ozone standard.	Under the Federal Clean Air Act of 1990, all of Santa Barbara County failed to attain the federal 1-hour ozone standard. The 1994 CAP covers the entire county and the Outer Continental Shelf.	The USEPA re-classified the entire county as a "serious" nonattainment area. The 1998 CAP covers the entire county and the Outer Continental Shelf.	The Maintenance Plan and re-designation request covers the onshore area of Santa Barbara County.
Emission Inventory	A 1987 baseline inventory of emission sources county-wide was developed, but excluded sources in the Outer Continental Shelf.	A 1990 baseline inventory of emission sources county-wide was prepared, not including sources in the outer continental shelf. Also, an "emission budget" for ROG was established.[2]	A 1990 baseline inventory of emission sources county-wide was developed, which included an updated inventory of Outer Continental Shelf sources. Also, an "emission budget" for ROG and NO_x was established.	A 1996 baseline inventory of emission sources county-wide has been developed, including an updated inventory of Outer Continental Shelf sources. The 1996 inventory will be used to update the 1990 emissions and to forecast the 1999 and 2005 emissions. Also, an "emission budget" for ROG and NO_x was established.	A 1999 baseline inventory of emission sources county-wide has been developed, including an updated inventory of Outer Continental Shelf sources. The 1999 inventory will be used to develop a "carrying capacity" and to forecast 2005 and 2015 emissions. Also, an "emission budget" for ROG and NO_x are re-established.
Plan Summary	The 1991 AQAP was required to reduce ROG and NO_x emissions by 5% per year until the state 1-hour ozone standard was achieved, or to have included all feasible control measures.	The 1993 ROP Plan was required to achieve a 1996 ROG emission inventory, which is 15% less than the 1990 adjusted base year ROG emission inventory.	The 1994 CAP was required to demonstrate attainment of the federal 1-hour ozone standard by 1996; document amendments to the 1993 ROP Plan; initiate the federal re-designation process; and satisfy state triennial update requirements.	The 1998 CAP is required to demonstrate attainment of the federal 1-hour ozone standard by 1999 and show a 24% reduction in ROG emissions between 1990 and 1999. This 1998 CAP also satisfies state planning requirements.	The 2001 Plan contains a Maintenance Plan and re-designation request for the federal 1-hour ozone standard. This 2001 Plan also satisfies state planning requirements.

[1] The design day value is called the one-in-one year recurrence rate value, and is based on a statistical analysis that essentially discounts any pollution episodes expected to occur just once per year.

[2] An emission budget is a ceiling for future transportation ROG and/or NO_x emissions.

CHAPTER 2

LOCAL AIR QUALITY

Introduction

Climate of Santa Barbara County

Air Quality Monitoring

Attainment Pollutants

Discussion of Pollutants Which Violate Standards

Conclusions

2. LOCAL AIR QUALITY

2.1 INTRODUCTION

This chapter provides the background for this Clean Air Plan by presenting an overview of the climate and current air pollution levels in Santa Barbara County. This information is important for understanding the factors that influence air quality in the county, and for assessing progress towards attainment of air quality standards.

There are two related terms that are used frequently in this chapter: standard *exceedance* and standard *violation*. A *standard exceedance* occurs when a measured concentration exceeds any applicable air quality standard. A *standard violation* occurs after a certain number of exceedances have been measured and is dependent on the standard in question. For example, a federal 1-hour ozone standard violation occurs when four federal ozone standard exceedances are measured during a three-year period at a single air monitoring station. Attainment and nonattainment designations are based on violations of standards.

The next section of this chapter, Section 2.2, discusses the local climate of Santa Barbara County in terms of precipitation, temperatures, winds, and inversions, and their relationship to air quality. Section 2.3 describes the air quality monitoring network in the county. Section 2.4 briefly discusses attainment pollutants and Section 2.5 examines ozone and particulate matter in greater detail. Finally, Section 2.6 highlights the conclusions of the chapter.

2.2 CLIMATE OF SANTA BARBARA COUNTY

Air quality in Santa Barbara County is influenced by both the local topography and the meteorological conditions of the area. Surface and upper-level wind flow varies both seasonally and geographically in the county and inversion conditions common to the area can affect the vertical mixing and dispersion of pollutants. It should be emphasized that the prevailing wind flow patterns in the county are not necessarily those that cause high ozone values. In fact, high ozone

values are often associated with unusual wind flow patterns. Meteorological and topographical influences that are important to air quality in Santa Barbara County are as follows:

- Semi-permanent high pressure that lies off the Pacific Coast leads to limited rainfall (around 18 inches per year), warm, dry summers and relatively damp winters. Maximum summer temperatures average about 70 degrees Fahrenheit near the coast and in the high 80s to low 90s inland. During winter, average minimum temperatures range from the 40s along the coast to the 30s inland. Additionally, cool, humid, marine air causes frequent fog and low clouds along the coast, generally during the night and morning hours in the late spring and early summer. The fog and low clouds can persist for several days until broken-up by a change in the weather pattern.

- In the northern portion of the county (north of the ridgeline of the Santa Ynez Mountains), the sea breeze (from sea to land) is typically northwesterly throughout the year while the prevailing sea breeze in southern portion of the county is from the southwest. During summer, these winds are stronger and persist later into the night. At night, the sea breeze weakens and, as air adjacent to the surface cools, it descends down the coastal mountains and valleys, resulting in light land breezes (from land to sea). The alternation of the land-sea breeze cycle can sometimes produce a "sloshing" effect, where pollutants are swept offshore at night and subsequently carried back onshore during the day. This effect is exacerbated during periods when wind speeds are low.

- The terrain around Point Conception, combined with the change in orientation of the coastline from north-south to east-west can cause counterclockwise circulation (eddies) to form east of the Point. These eddies fluctuate temporally and spatially often leading to highly variable winds along the southern coastal strip. Point Conception also marks the change in the prevailing surface winds from northwesterly to southwesterly.

- Santa Ana winds, which are dry northeasterly winds that occur primarily during fall and winter, but occasionally in spring. These are warm, dry winds blown from the high inland desert that descend down the slopes of a mountain range. Wind speeds associated with

Santa Ana's are generally 15-20 mph, though they can sometimes reach speeds in excess of 60 mph. During Santa Ana conditions, pollutants emitted in Santa Barbara, Ventura County, and the South Coast Air Basin (the Los Angeles region) are moved out to sea. These pollutants can then be moved back onshore into Santa Barbara County in what is called a "post Santa Ana condition." The effects of the post- Santa Ana condition can be experienced throughout the county. Not all post Santa Ana conditions, however, lead to high pollutant concentrations in Santa Barbara County.

- Upper-level winds measured at Vandenberg Air Force Base once each morning and afternoon are generally from the north or northwest throughout the year, but occurrences of southerly and easterly winds do occur in winter, especially during the morning. Upper-level winds from the south and east are infrequent during the summer. When they do occur, they are usually associated with periods of high ozone levels. As with the surface winds, upper-level winds can move pollutants that originate in other areas into the county.

- Surface temperature inversions (0-500 ft) are most frequent during the winter, and subsidence inversions (1000-2000 ft) are most frequent during the summer. Inversions are an increase in temperature with height and are directly related to the stability of the atmosphere. Inversions act as a cap to the pollutants that are emitted below or within them and ozone concentrations are often higher directly below the base of elevated inversions than they are at the earth's surface. For this reason, elevated monitoring sites will occasionally record higher ozone concentrations than sites at lower elevations. Generally, the lower the inversion base height and the greater the rate of temperature increase from the base to the top, the more pronounced effect the inversion will have on inhibiting vertical dispersion. The subsidence inversion is very common during summer along the California coast, and is one of the principle causes of air stagnation.

- Poor air quality is usually associated with "air stagnation" (high stability/restricted air movement). Therefore, it is reasonable to expect a higher frequency of pollution events in the southern portion of the county where light winds are frequently observed, as opposed to the North County where the prevailing winds are usually strong and persistent.

2.3 AIR QUALITY MONITORING

The State of California has established ambient air quality standards to protect human health. The federal government has also established health-based standards ("primary" standards), which are generally less protective of public health than state standards. In addition, the federal government has established "secondary" standards to protect public welfare. State and federal standards have been established for ozone, carbon monoxide, nitrogen dioxide, sulfur dioxide, suspended particulate matter 10 micrometers or less in size (PM_{10}), and lead. On July 18, 1997, federal standards were promulgated for ozone (8-hour) and suspended particulate matter 2.5 micrometers or less ($PM_{2.5}$) in size. These two standards were successfully challenged before the U.S. Court of Appeal for the District of Columbia Circuit and are currently under review by the U.S. Supreme Court. In addition, California has standards for sulfates, hydrogen sulfide, vinyl chloride, and visibility-reducing particles. All applicable state and federal standards are shown in Table 2-1.

Monitoring of ambient air pollutant concentrations is conducted by the ARB, APCD and industry. Monitors operated by the ARB and the APCD are part of the State and Local Air Monitoring System (SLAMS). The SLAMS monitors are located to provide local and regional air quality information. Monitors operated by industry, at the direction of the APCD, are called Prevention of Significant Deterioration (PSD) stations. PSD stations are required by the APCD to ensure that new and modified sources under APCD permit do not interfere with the county's ability to attain and maintain air quality standards. Historically, ambient air quality monitoring stations have operated in North County and San Luis Obispo by the Environmental Research Foundation (ERF), which is a non-profit organization funded by local industry. Methods and procedures used in monitoring follow guidelines prescribed by the ARB and the USEPA to ensure consistency with the standards.

Figure 2-1 shows the locations of all past and present monitoring stations that have operated in Santa Barbara County. Many of the sites depicted in Figure 2-1 have been de-commissioned, but are presented here for informational purposes. The installation dates, status, and parameters measured for all stations are listed in Table 2-2. Several of the stations have been in operation for

more than 12 years and some for over 20 years. Figure 2-2 presents a summary of the current monitoring network.

2.3.1 ENHANCED MONITORING

On December 10, 1997, the USEPA reclassified the Santa Barbara County one-hour ozone non-attainment area from "moderate" to "serious." That action precipitated the requirement to establish a Photochemical Assessment Monitoring Station (PAMS) program. This USEPA funded program involves collecting low-level (3,500 feet) upper-air meteorological measurements utilizing an upper-air radar wind profiler, ten meter wind speed and direction, atmospheric temperature, relative humidity, total solar and sky radiation, barometric pressure, carbonyl sampling, speciated hydrocarbon sampling (72 compounds), and oxides of nitrogen and ozone measurements. As agreed with USEPA, PAMS data are collected from equipment installed at the APCD Goleta office; upper-air measurements are taken at the Santa Barbara Airport.

In addition to the APCD's PAMS program, the ARB is conducting $PM_{2.5}$ monitoring at their downtown Santa Barbara and Santa Maria sites, which began in 1999. A third sampler will be installed around the end of year 2000 near the San Rafael Wilderness and operated by the federal land manager.

With the recent promulgation of regional haze regulations, the USEPA is drafting guidance on regional haze or visibility monitoring to be instituted under the Interagency Monitoring of Protected Visual Environments (IMPROVE) program. An IMPROVE site is scheduled to be co-located with the $PM_{2.5}$ site located near the San Rafael Wilderness. The $PM_{2.5}$ monitoring regulations in 40 CFR Part 58 allow the use of the IMPROVE protocol for the purpose of characterizing background or transported levels of $PM_{2.5}$.

2.4 ATTAINMENT POLLUTANTS

The federal Clean Air Act establishes air quality standards for the following "criteria" air pollutants: ozone, nitrogen dioxide, sulfur dioxide, carbon monoxide, PM_{10}, and lead. State standards also exist for each of these criteria pollutants. In addition, state standards are in place for visibility reducing particles, sulfates, hydrogen sulfide and vinyl chloride. With the exception of ozone and PM_{10}, Santa Barbara County is in compliance with all state and federal air quality standards. Health effects information and historical concentrations of attainment pollutants have been documented in several air quality plans including the 1991 Air Quality Attainment Plan, the 1994 Clean Air Plan and the 1998 Clean Air Plan.

2.5 DISCUSSION OF POLLUTANTS THAT VIOLATE STANDARDS

As discussed in the air quality overview, Santa Barbara County violates the state PM_{10} standard and has historically violated both state and federal ozone standards. The following sections provide a more in-depth discussion of these pollutants.

2.5.1 OZONE

Ozone has been monitored in the county for over 25 years. Data collected at these stations, in conjunction with the various air quality studies performed in the region provide valuable insight into the county's ozone problem. The following sections use this information to discuss ozone formation and health effects, peak ozone levels, the geographical extent of ozone exceedances in the county, seasonal variability of ozone exceedances and the area's ozone classification.

Ozone is formed in the atmosphere through a series of chemical reactions involving oxides of nitrogen (NOx), reactive organic gases (ROG), and sunlight occurring over a period of several hours. The major source of NOx in the county is combustion of fossil fuels for transportation, energy and heat. ROG sources include natural seeps of oil and gas, solvents in paints, consumer and industrial products, automobiles, natural vegetation, and processes in the petroleum industry. Since ozone is not emitted directly into the atmosphere, but is formed as a result of chemical

reactions in the atmosphere, it is classified as a "secondary" pollutant and is considered "regional" because it occurs over a wider area than that in which the pollutants are emitted. Because ozone-forming photochemical reactions take time, peak ozone levels are often found several miles or more downwind of major source areas. This is particularly true when winds are persistent from one direction.

The health effects of ozone focus on the respiratory tract. Asthma, bronchitis and other respiratory disorders are worsened by high ozone concentrations. Eye irritation, nausea, headaches, coughing and dizziness are other symptoms of ozone exposure. Ozone also interferes with photosynthesis, thereby damaging natural and ornament vegetation, and agricultural crops.

Figure 2-3 presents the number of state (1-hour) and federal (1-hour and 8-hour) ozone exceedances measured in the county from 1990 through 1999 for all monitoring stations in continuous operation during the last 10 years. As seen in the figure, Santa Barbara County experienced between 3 and 40 days per year on which the state ozone standard was exceeded and 1 to 6 days per year on which the federal 1-hour standard was exceeded. Figure 2-3 also presents the number of exceedances of the new federal 8-hour ozone standard that is more protective of public health than the existing federal 1-hour standard, but slightly less protective of public health than the state 1-hour ozone standard.

The most striking feature of Figure 2-3 is the dramatic drop in ozone exceedances from 1996 to 1999. In fact, 1999 was the cleanest year on record in Santa Barbara County. It should be pointed out that various weather conditions that existed between 1997 and 1999 may have contributed to improved air quality. El Nino conditions existed during 1997 and 1998, which were followed by La Nina conditions during 1999. Both these conditions may have inhibited poor air quality during this period. A more detailed discussion of ozone air quality in Santa Barbara County is provided in Section 2.5.1.3.

2.5.1.1 New Federal 8-Hour Ozone Standard

In addition to the federal 1-hour ozone standard, the USEPA promulgated (July 18, 1997) a new 8-hour ozone standard (0.08 ppm) that is generally more protective of public health. Compliance with the new standard is judged by taking the average of the 4th highest 8-hour concentration, each year, for a 3-year period.

On May 14th 1999, an appeals court placed the 8-hour standard on hold, pending further clarification from USEPA on how it determined the level of the standard. The court stated that the factors EPA used to determine the degree of public health concern were reasonable, but found that USEPA did not clearly specify the rationale for selecting the standard. The court left the 8-hour standard in place, but prevented USEPA from implementing it. The court did, however, note that although USEPA cannot implement the standard, the Clean Air Act requires EPA to finalize designations to fulfill its statutory obligations. USEPA and the Department of Justice requested a review of the case before the Supreme Court. The Supreme Court has recently agreed to review the case.

The Clean Air Act requires states to submit recommendations on initial air designations and boundaries for the new federal 8-hour ozone standard. On March 23, 2000, the ARB approved recommendations for submittal to USEPA. Table 2-3 provides 8-hour ozone design value calculation using data from 1997 through 1999. Based on these monitoring data, Santa Barbara County will be designated as attainment for the federal 8-hour ozone standard.

2.5.1.2 Peak Ozone Levels

According to USEPA policy, the 4th highest 1-hour ozone concentration measured at a particular monitoring station during a three-year period constitutes the design value for that station. These design values are used to classify the attainment status of Santa Barbara County pursuant to the federal Clean Air Act Amendments of 1990. Santa Barbara County was originally classified as 'moderate' nonattainment based on ozone concentrations recorded in the county from 1987 to 1989.

Santa Barbara County was required to develop the 1994 Clean Air Plan to comply with the federal 1-hour ozone standard by the statutory attainment date for "moderate" areas of November 15, 1996. Based on 1994 through 1996 monitoring data, three sites in the county continued to violate the federal 1-hour ozone standard, prompting USEPA to reclassify Santa Barbara County as a "serious" nonattainment area for the 1-hour ozone standard. The "serious" re-classification triggered the development of the 1998 Clean Air Plan to provide for attainment of the federal 1-hour ozone standard by November 15, 1999.

Table 2-4 summarizes the four highest ozone values recorded in Santa Barbara County from 1997 through 1999 at all monitoring locations. As seen in the table, the maximum recorded 1-hour ozone concentrations range from 73 to 137 ppb. The highest federal design value is 108 ppb, which is less than the concentration considered to be in excess of the federal 1-hour ozone standard (125 ppb). This shows that Santa Barbara County has complied with the federal 1-hour ozone standard for this three-year period.

For the state ozone standard, attainment is also based on a design value. The definition of the state design value, however, differs considerably from the federal design value definition. The state design value is the highest measured concentration remaining at a given site after all measured concentrations affected by extreme concentration events are excluded. Extreme concentrations are determined through statistical calculations that provide an Expected Peak Daily Concentration (EPDC). The EPDC is the concentration that statistically is estimated to recur once per year and is based on the most recent three-year period for which air quality data are available. Concentrations that are higher than the EPDC are identified as being caused by extreme events and are not considered violations of the state standard. It is the concentration that is equal to or lower than the EPDC that is considered the state design value for each monitoring site. Based on the state design value, Santa Barbara County continues to violate the state ozone standard.

2.5.1.3 Ozone Standard Exceedances

Figures 2-4 and 2-5 present ozone exceedance data throughout the county for selected SLAMS and PSD stations. The majority of the SLAMS stations have been in operation since 1980, while the PSD stations were installed in the mid to late 1980's. The figures, however, show SLAMS and PSD data from the period of 1990 to 1999 to assess trends during the past ten years.

Figure 2-4 shows the variability of ozone standard exceedances at the SLAMS stations in the county. Stations located in the south coast area experience a greater number of exceedances compared to north county, where the Santa Ynez station generally measures a higher number of exceedances than other north county sites.

Figure 2-5 shows selected PSD stations around the county. This figure reveals that there are areas in the county that experience a greater number of ozone standard exceedances than indicated by the SLAMS stations. For example, Las Flores Canyon - Site 1, and Paradise Road have experienced from 3 to 24 state ozone standard exceedances and up to 6 federal standard exceedances per year. In general, areas of south county experience less healthful air quality than areas to the north and west. Paradise Road, at the eastern end of the Santa Ynez Valley however, has experienced a significant number of days with unhealthful air quality.

To gain a better understanding of ozone exceedances across the county, the APCD performed a study entitled, "Selection, Classification, and Analysis of Ozone Violations in Santa Barbara County" (SBCAPCD, 1990). The primary focus of the study was to assess the geographical and meteorological patterns associated with ozone standard exceedances.

Eighteen ozone exceedances were grouped into five categories based on the geographical extent of the observed exceedance: Countywide, Paradise Road, Lompoc, south county, and Carpinteria. Meteorological data during the ozone episodes were then compiled and the data were analyzed. Results of the 1990 study show that ozone exceedances in Santa Barbara County occur under diverse meteorological conditions and that the topography of the county plays an important role in the distribution of ozone exceedances.

Additionally, the APCD has prepared an update to the 1990 study that analyzes ozone exceedances between 1990 and 1999. In contrast to the previous study, the current analysis looks at all federal exceedances that have occurred in the past 10 years without primary regard to the spatial or geographical extent of the exceedance. After reviewing the meteorology associated with all federal exceedances, it was apparent that the focus of the study should be placed on comparing meteorological differences between high ozone events that have occurred in summer against those that have occurred in spring and fall.

Some important conclusions from the current study are:

- There are contrasting meteorological conditions that occur between episodes that occur during summer to those that occur during spring and fall. The primary difference between summer and spring/fall episodes is that summer events are characterized by weak onshore pressure gradients while spring/fall events are characterized by moderate offshore gradients.

- A greater frequency of southeasterly winds aloft occurs during spring/fall events than during summer episodes. Southeasterly winds aloft suggest potential transport of pollutants from Ventura County and/or the Los Angeles Basin, which may be mixed with locally generated pollution leading to high ozone concentrations. Some episodes, regardless of season, also showed indications of transport at the surface from areas to the southeast of Santa Barbara County.

- Transport plays a role in some of the ozone exceedances experienced in Santa Barbara County. Federal exceedances appear to be related to a combination of meteorological conditions that are conducive to high ozone formed locally and to transport from outside the county.

- Given the widespread nature of exceedances of the state ozone standard in the county, and given that the entire San Luis Obispo County, Santa Barbara County, and Ventura County

area is nonattainment for the state 1-hour ozone standard, the evidence suggests that emissions generated locally contribute to some degree to the regional problem.

2.5.2 PM_{10} (Particulate Matter)

Santa Barbara County violates both the state PM_{10} 24-hour and annual standards. PM_{10} is produced either by direct emission of particulates from a source (primary PM_{10}), or by formation of aerosols as a result of chemical reactions in the atmosphere involving precursor pollutants (secondary PM_{10}). The sources of PM_{10} can also be categorized as natural or resulting from human activity. Based on emissions data, the largest single source of PM_{10} emissions in the county is entrained paved road dust. Other major sources include dust from construction and demolition, tilling dust (agricultural), entrained road dust from unpaved roads, natural dust and sea-salt, and particulate matter released during fuel combustion.

Particulate matter with an aerodynamic diameter of 10 microns or less (PM_{10}) is generated by a wide variety of sources, including wind blown dust, wildfires, dirt roads, construction sites, internal combustion engines and agriculture. Particulate matter is a respiratory irritant. Large particles are effectively filtered in the upper respiratory tract. Small particles (under 10 microns), however, can cause serious health effects. The chemical makeup of the particles is an important factor in determining the health effect.

PM_{10} has been measured consistently at both SLAMS and PSD stations since 1986 with measurements at the Santa Maria Library SLAMS site going back to 1985. Figure 2-6 presents the maximum 24-hour average concentration measured each year and the annual geometric mean for the Santa Barbara and Santa Maria SLAMS sites. As shown in the figure, both the state 24-hour and state annual PM_{10} standards are exceeded in the county. Santa Barbara County is currently designated nonattainment for the state PM_{10} standard. The county does not exceed the federal 24-hour PM_{10} standard. Figure 2-7 presents the annual arithmetic mean PM_{10} concentrations measured in Santa Maria, where highest annual values are usually recorded. As shown from this figure, Santa Barbara County complies with the federal annual PM_{10} standard.

To investigate the county's PM_{10} problem, the APCD started a specialized sampling and analysis study in 1989 called the Santa Barbara County Particulate Matter Emission Reduction Study. The study collected and analyzed ambient samples of PM_{10} at a number of sites located throughout the county to identify chemical constituents. The study identified potential source characteristics and assessed control strategies for reducing PM_{10} concentrations. The major findings of the study include: 1) background sources (primarily sea-salt) are major contributors to PM_{10} concentrations; 2) on average, 70% of the locally generated PM_{10} (primary) is directly emitted; 3) locally generated geological dust and motor vehicle exhaust are the most significant sources of primary PM_{10} in the county; and 4) potential control measures should concentrate on these primary sources of PM_{10}.

Although Santa Barbara County has developed an excellent database for PM_{10} attainment, there is much additional work to be performed. Non-traditional controls (e.g., controls for fugitive dust) will have to be evaluated along with the more traditional controls. Therefore, attainment of the state PM_{10} standards may depend on the development of innovative control technologies and their effectiveness upon implementation. In any case, implementation of ozone control measures adopted in the 1998 Clean Air Plan, and ozone precursor (ROG and NO_x) emissions reductions required by the California Clean Air Act will result in PM_{10} air quality benefits by reducing secondary PM_{10}. Some progress is already underway, but additional steps will have to be taken to attain the state PM_{10} standards.

2.5.3 New Federal $PM_{2.5}$ (Fine Particulate Matter) Standard

On July 18, 1997, EPA revised the primary and secondary air quality standards for particulate matter by establishing annual and 24-hour $PM_{2.5}$ standards and also revised the form of the existing 24-hour PM_{10} standard. The $PM_{2.5}$ standards are set at 65 ug/m^3 for 24-hour and 15 ug/m^3 for an annual average.

As with the 8-hour ozone standard, the revised federal particulate standard was challenged before the U.S. Court of Appeals. On May 14, 1999 the Court ruled that the new $PM_{2.5}$ standards shall remain in place, but vacated the revised course particle (PM_{10}) standard. As such, the pre-existing PM_{10} standard continues to apply. It should be noted that there still is uncertainty with regard to the

$PM_{2.5}$ standard and the Court has asked for additional information to decide whether the $PM_{2.5}$ standards shall remain in place or be vacated. USEPA is currently preparing a health effects study for fine particulate matter and, since the $PM_{2.5}$ standard remains in place, $PM_{2.5}$ monitoring is being done locally and nationwide. The health effects study and data from the monitoring program will be used to determine the nature and extent of particulate matter pollution to support the review of the standard.

The characteristics, sources, and potential health effects associated with larger or "coarse" particles (from 2.5 to 10 micrometers in diameter) and smaller or "fine" (smaller than 2.5 micrometers) can be very different. Coarse particulates generally come from windblown dust and dust kicked up from mobile sources. Fine particulates are generally associated with combustion processes as well as being formed in the atmosphere as a secondary pollutant through chemical reactions. From a health perspective, fine particles are more likely to penetrate deeply into the lungs and increase respiratory symptoms and disease, decrease lung function, and alter lung tissues and structures and respiratory tract defense mechanisms.

$PM_{2.5}$ is monitored at two locations in Santa Barbara County, one at the Santa Maria Library, and the other in downtown Santa Barbara. As noted earlier, a third sampler will be installed near the San Rafael Wilderness in 2000. Once the data have been processed, USEPA will be designating attainment and nonattainment areas (action expected between 2002 and 2005) with State Implementation Plans due starting in the year 2005.

2.6 CONCLUSIONS

Santa Barbara County has historically violated both state and federal health standards for ozone and state standards for PM_{10}. The County continues to violate both the state 1-hour ozone standard and state PM_{10} standard. The County is in compliance with all other applicable state and federal ambient air quality standards.

Analyses of 1997 through 1999 monitoring data shows that Santa Barbara County has complied with the federal 1-hour ozone standard. In addition, data from this period show that Santa

Barbara County has complied with the federal 8-hour ozone standard although the fate of the standard is still being considered in the courts. Santa Barbara County has also made progress toward the state 1-hour ozone standard although remains out of compliance with the standard. While 1997 through 1999 were the cleanest years on record, various meteorological conditions existed during the three-year period that were conducive to good air quality.

Ozone studies prepared by the APCD have shown that ozone exceedances can occur under a wide variety of meteorological conditions. Additionally, based on analyses of ozone episodes occurring during the past ten years (1990 through 1999), there is an indication that federal exceedances may be related to meteorological conditions that are conducive to high ozone formed locally combined with transport of pollutants from outside the county. The analyses also suggest that our airshed may be able to support ozone concentrations in excess of the state ozone standard, but that an additional influx of pollution due to transport is characteristic of federal ozone exceedances.

Table 2-1
Ambient Air Quality Standards

Pollutant	Averaging Time	California Standards[1]	National Standards[2]	
		Concentration[3]	Primary[2,4]	Secondary[2,5]
Ozone	1 Hour	0.09 ppm (180 ug/m^3)	0.12 ppm (235 ug/m^3)	Same as Primary Std.
	8 Hour		0.08 ppm (157 ug/m^3)	Same as Primary Std.
Carbon Monoxide	8 Hour	9 ppm (10 mg/m^3)	9 ppm (10 mg/m^3)	Same as Primary Stds.
	1 Hour	20 ppm (23 mg/m^3)	35 ppm (40 mg/m^3)	
Nitrogen Dioxide	Annual Average	--	0.053 ppm (100 ug/m^3)	Same as Primary Stds.
	1 Hour	0.25 ppm (470 ug/m^3)	--	
Sulfur Dioxide	Annual Average		80 ug/m^3 (0.03 ppm)	
	24 Hour	0.04 ppm[6] (105 ug/m^3)	365 ug/m^3 (0.14 ppm)	--
	3 Hour	--		1,300 ug/m^3 (0.5 ppm)
	1 Hour	0.25 ppm (655 ug/m^3)		--
Suspended Particulate Matter (PM_{10})	Annual Geometric Mean	30 ug/m^3	--	--
	24 Hour	50 ug/m^3	150 ug/m^3	Same as Primary Stds.
	Annual Arithmetic Mean	--	50 ug/m^3	
Particulate Matter ($PM_{2.5}$)	Annual Arithmetic Mean		15 ug/m^3	Same as Primary Stds.
	24 Hour		65 ug/m^3	Same as Primary Stds.
Sulfates	24 Hour	25 ug/m^3		--
Lead	30 Day Average	1.5 ug/m^3	--	--
	Calendar Quarter	--	1.5 ug/m^3	Same as Primary Std.
Hydrogen Sulfide	1 Hour	0.03 ppm (42 ug/m^3)		--
Vinyl Chloride (chloroethene)	24 Hour	0.010 ppm (26 ug/m^3)		--
Visibility Reducing Particles	1 Observation	In sufficient amount to reduce the prevailing visibility[7] to less than 10 miles when the relative humidity is less than 70%		--

Table 2-1 (Concluded)

NOTES:

1. California standards for ozone, carbon monoxide, sulfur dioxide (1 hour), nitrogen dioxide and particulate matter - PM_{10}, and visibility reducing particles are values that are not to be exceeded. The sulfur dioxide (24-hour), sulfates, lead, hydrogen sulfide, and vinyl chloride are not to be equaled or exceeded.

2. National standards, other than ozone and those based on annual averages or annual arithmetic means, are not to be exceeded more than once a year. The ozone standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above the standard is equal to or less than one.

3. Concentration expressed first in units in which it was promulgated. Equivalent units given in parenthesis are based upon a reference temperature of 25° C and a reference pressure of 760 mm of mercury. All measurements of air quality are to be corrected to a reference temperature of 25° C and a reference pressure of 760 mm of mercury (1,013.2 millibar); ppm in this table refers to ppm by volume, or micromoles of pollutant per mole of gas.

4. National Primary Standards: The levels of air quality necessary, with an adequate margin of safety to protect the public health. Each state must attain the primary standards no later than three years after that state's implementation plan is approved by the Environmental Protection Agency.

5. National Secondary Standards: The levels of air quality necessary to protect the public welfare from any known or anticipated adverse effects of a pollutant. Each state must attain the secondary standards within a "reasonable time" after the implementation plan is approved by the EPA.

6. At locations where the state standards for ozone and/or suspended particulate matter are violated. National standards apply elsewhere.

7. This standard is intended to limit the frequency and severity of visibility impairment due to regional haze and is equivalent to a 10-mile nominal visual range when relative humidity is less than 70 percent.

TABLE 2-2
AIR QUALITY MONITORING STATIONS - OPERATIONAL STATUS AND PARAMETERS MEASURED

	SITE	TYPE	START	END	PARAMETERS													
					O_3	NO_2	SO_2	CO	THC	H_2S	TSP	PM_{10}	ROC	WS	VWS	WD	AMT	TRS
N 1	Santa Maria Refinery	PSD	2-1-87	10-31-92										■		■		
N 2	Bonita School Road	PSD	2-1-87	10-31-92			■							■		■		
N 3	West Main Street	PSD	2-1-87	11-1-89			■							■		■		
N 4	Guadalupe	PSD	2-1-87	11-1-89			■							■		■		
N 5	Casmalia Hills	PSD	2-1-87	10-31-92			■							■		■		
N 6	Santa Maria (SM) Values for SM include these sites																	
	Main Street	SLAMS	Pre-1980	10-81	■		■							■		■		
	McClelland	SLAMS	01-82	09-87	■		■											
	Broadway	SLAMS	09-87	•	■		■					■						
N 7	Battles	PSD	09-85	11-30-95	■	■			■	■			■	■	■	■	■	
N 8	Santa Maria - Briarwood	ERF	3-1-79	12-31-90			■				■							
N 9	Santa Maria - Glacier Ln.	ERF	3-1-79	12-31-90		■	■			■								
N 10	Airox Road	PSD	09-86	11-87	■	■	■		■		■	■	■	■	■	■	■	
N 11	Watt Road	SLAMS	01-83	05-88	■	■	■	■			■			■		■		
	VAFB Watt Road	PSD	05-01-92	3-1-97	■	■	■	■	■			■	■	■	■	■	■	
N 12	Lompoc HS & P	PSD	09-85	•	■	■	■		■				■	■	■	■	■	
N 13	Lompoc HS & P Odor	PSD	1-1-88	•						■				■		■	■	
N 14	Herado Road	SLAMS	03-82	10-86	■	■	■	■			■			■		■		■
N 15	Lompoc (LOM) Values for LOM include these sites																	
	Lompoc - G Street	SLAMS	07-80	04-83	■		■				■			■		■		
	Lompoc - H Street	SLAMS	06-83	•	■	■	■	■			■	■		■		■		
N 16	VAFB STS	PSD	02-87	•	■	■	■	■	■		■	■	■	■	■	■	■	
N 17	Point Arguello	PSD	09-85	11-30-95	■	■			■				■	■	■	■	■	
N 18	Lompoc - Jalama	ERF	3-1-79	12-31-90			■				■			■		■		
S 19	Jalama Beach	PSD	11-85	11-30-95	■	■	■		■		■	■	■	■	■	■	■	
S 20	Pt. Conception	PSD	12-86	•	■	■	■				■	■		■	■	■	■	
S 21	Government Pt.	PSD	02-85	01-31-92	■	■	■	■	■		■	■	■	■	■	■	■	
N 22	GTC B	PSD	06-87	•	■	■								■	■	■	■	
S 23	Gaviota West	PSD	09-84	•	■	■	■		■		■	■	■	■	■	■	■	
S 24	Gaviota Odor West	PSD	7-1-88	•						■				■		■	■	
S 25	GTC A	PSD	09-85	11-30-95	■	■	■				■	■		■	■	■	■	■
S 26	Gaviota East	PSD	12-87	•	■	■	■		■		■	■	■	■	■	■	■	
S 27	GTC C	PSD	06-87	•	■	■	■		■		■	■	■	■	■	■	■	
S 28	Gaviota Odor East	PSD	7-1-88	•						■				■		■	■	■
S 29	Molino	PSD	04-84	06-87	■	■	■		■		■	■	■	■	■	■	■	
N 30	Santa Ynez Airport	SLAMS	09-80	•	■									■	■	■	■	

TABLE 2-2
AIR QUALITY MONITORING STATIONS - OPERATIONAL STATUS AND PARAMETERS MEASURED

	SITE	TYPE	START	END	PARAMETERS													
					O_3	NO_2	SO_2	CO	THC	H_2S	TSP	PM_{10}	ROC	WS	VWS	WD	AMT	TRS
	Las Flores Canyon (LFC)																	
	Values for LFC																	
	include these sites																	
S 31	LFC Site 1	PSD	01-88	*	■	■	■	■	■			■	■	■		■	■	
S 32	LFC Site 2	PSD	4-1-88	1-31-99		■	■					■		■		■	■	
S 33	LFC Site 3	PSD	1-15-88	1-31-99		■	■					■		■		■	■	
S 34	ARCO Site 4	PSD	07-86	08-87	■	■	■		■		■	■	■	■	■	■	■	
	LFC Site 4	PSD	1-1-88	3-31-99										■	■	■	■	
	LFC Odor								■				■					
S 35	Popco (POP)															■	■	
	Values for POP																	
	include these sites																	
	Popco North	PSD	06-01-91	3-31-99						■								■
	Popco South	PSD	06-01-91	3-31-99						■								
	Popco Met	PSD	06-01-91	02-28-93			■							■		■	■	
S 36	El Capitan	PSD/SLAMS	Pre-1980	*	■	■			■	■		■		■	■	■	■	■
S 37	Naples	PSD	6-1-87	3-91					■		■	■	■	■	■	■	■	
S 38	Ellwood	PSD	09-85	10-31-92										■		■		
S 39	West Campus (WC)													■		■		
	Values for WC																	
	include these sites				■	■	■		■		■	■	■		■		■	
	ARCO Site 2	PSD	12-85	10-87	■	■	■		■	■	■	■	■		■		■	
	Exxon Site 10	PSD	06-88	*	■	■	■		■	■	■	■	■	■	■	■	■	
S 40	Ocean Road (ARCO, Site 1)	PSD	11-85	10-87	■	■	■	■			■			■		■	■	
S 41	Goleta	SLAMS	Pre-1980	*										■		■		
S 42	Cathedral Oaks	SLAMS	Pre-1980	10-82	■													
N 43	Paradise Road	PSD	01-86	*	■	■								■	■	■	■	
S 44	Santa Barbara (SB)																	
	Values for SB																	
	include these sites																	
	State Street	SLAMS	Pre-1980	01-83	■	■	■	■	■		■			■		■		
	Canon Perdido	SLAMS	02-83	06-88	■	■	■	■	■		■							
	West Carrillo	SLAMS	06-88	*	■	■	■	■			■	■		■		■	■	
S 45	Carpinteria	PSD	09-85	*	■	■								■	■	■	■	
S 46	ARCO - Platform Holly	PSD	8-1-86	11-1-87										■	■	■	■	

PARAMETERS

O_3	Ozone
NO_2	Nitrogen Dioxide
SO_2	Sulfur Dioxide
CO	Carbon Monoxide
THC	Total Hydrocarbon
H_2S	Hydrogen Sulfide
TSP	Total Suspended Particulate

PARAMETERS

PM_{10}	Particulate Matter (less than 10. microns)
ROC	Reactive Organic Compounds
WS	Wind Speed
VWS	Verticle Wind Speed
WD	Wind Direction
AMT	Ambient Temperature
TRS	Total Reduced Sulfur

*	- still in operation as of January 1998
S	- station located in south county
N	- station located in north county
SLAMS	- state and local air quality monitoring station
PSD	- prevention of significant deterioration station
ERF	- Environmental Research Foundation

2001 Monitoring Schedule

1/6-Day &1/3-Day Monitoring Schedule for TSP, Pb, PM-10, PM-2.5, and VOC

[ ] = 1/6 schedule

January

Su	M	Tu	W	Th	F	Sa
	[1]	2	3	4	5	[6]
[7]	8	9	10	11	12	[13]
14	15	16	17	18	[19]	20
21	22	23	24	[25]	26	27
28	29	30	[31]			

February

Su	M	Tu	W	Th	F	Sa
				1	2	3
4	[5]	[6]	7	8	9	10
11	[12]	13	14	15	16	17
[18]	19	20	21	22	23	[24]
25	26	27	28			

March

Su	M	Tu	W	Th	F	Sa
				1	[2]	3
4	5	6	7	[8]	9	10
11	12	13	[14]	15	16	17
18	19	[20]	21	22	23	24
25	[26]	27	28	29	30	31

April

Su	M	Tu	W	Th	F	Sa
[1]	2	3	4	5	6	[7]
8	9	10	11	12	[13]	14
15	16	17	18	[19]	20	21
22	23	24	[25]	26	27	28
29	30					

May

Su	M	Tu	W	Th	F	Sa
		[1]	2	3	4	5
6	[7]	8	9	10	11	12
[13]	14	15	16	17	18	[19]
20	21	22	23	24	[25]	26
27	28	29	30	[31]		

June

Su	M	Tu	W	Th	F	Sa
					1	2
3	4	5	[6]	7	8	9
10	[11]	[12]	13	14	15	16
17	[18]	19	20	21	22	[23]
[24]	25	26	27	28	29	[30]

July

Su	M	Tu	W	Th	F	Sa
1	2	3	4	5	[6]	7
8	9	10	11	[12]	13	14
15	16	17	[18]	19	20	21
22	23	[24]	25	26	27	28
29	[30]	31				

August

Su	M	Tu	W	Th	F	Sa
			1	2	3	4
[5]	6	7	8	9	10	[11]
12	13	14	15	16	[17]	18
19	20	21	22	[23]	24	25
26	27	28	[29]	30	31	

September

Su	M	Tu	W	Th	F	Sa
						1
2	3	[4]	5	6	7	8
9	[10]	11	12	13	14	15
[16]	17	18	19	20	21	[22]
23	24	25	26	27	[28]	29
30						

October

Su	M	Tu	W	Th	F	Sa
	1	2	3	[4]	5	6
7	8	9	[10]	11	12	13
14	15	[16]	17	18	19	20
21	[22]	23	24	25	26	27
[28]	29	30	31			

November

Su	M	Tu	W	Th	F	Sa
				1	2	[3]
4	5	6	7	8	[9]	10
11	12	13	14	[15]	16	17
18	19	20	[21]	22	23	24
25	26	[27]	28	29	30	

December

Su	M	Tu	W	Th	F	Sa
						1
2	[3]	4	5	6	7	8
[9]	10	11	12	13	14	[15]
16	17	18	19	20	[21]	22
23	24	25	26	[27]	28	29
30	31					

Santa Barbara County APCD
Carbonyl Sample Cartridge
Custody and Data Form

Run Day:

	Installation		Removal			
	Operator:		Operator:			
	Date:		Date:			
Cartridge Number	Po No	Start Time	End Time	Verify Run Time	Avg Flow LPM	Volume Liters	Elasped Time (min)
	1	12:00 AM	2:59 AM				
	2	3:00 AM	5:59 AM				
	3	6:00 AM	8:59 AM				
	4	9:00 AM	11:59 AM				
	5	12:00 PM	2:59 PM				
	6	3:00 PM	5:59 PM				
	7	6:00 PM	8:59 PM				
	8	9:00 PM	11:59 PM				
	Duplicate	9:00 AM	11:59 AM				
	Blank	NA	NA				

PAMS GC Operating Procedures
Summer 2001

Entech Smart Lab Software

1. Start up the 7000 Sequence Table if it is not running. Check for a task bar item called "NT7000 sequence table". If it is not running double click on the icon on the desktop labeled "NT7000 concentrator".
2. Load the normal run day sequence by selecting "open" and then select c:\smart\autosamp.seq. The following table should appear.

Sample Name	Inlet #	Auto Pos	Samp Vol.	Cal Std Vol.	Method	Time
Amb1	1	1	400	0	C:\smart\focus3.mpt	02:40
Std	1	1	0	400	C:\smart\focus3.mpt	04:10
Amb2	1	1	400	0	C:\smart\focus3.mpt	05:40
Blank	1	1	0	0	C:\smart\focus3.mpt	07:10
Amb3	1	1	400	0	C:\smart\focus3.mpt	08:40
Amb4	1	1	400	0	C:\smart\focus3.mpt	11:40
Amb5	1	1	400	0	C:\smart\focus3.mpt	14:40
Amb6	1	1	400	0	C:\smart\focus3.mpt	17:40
Amb7	1	1	400	0	C:\smart\focus3.mpt	20:40
Std	1	1	0	400	C:\smart\focus3.mpt	22:10
Amb8	1	1	400	0	C:\smart\focus3.mpt	23:40
Blank	1	1	0	0	C:\smart\focus3.mpt	23:00

3. If the "time" column does not appear, click on the button labeled "Mode Real"
4. Highlight the first line and click on the "Go" button.
5. Verify that the "real time" sampler is working by selecting the button labeled "real".

6. The real time set up should look as follows. The time closest to the current time should be highlighted. If it is not configured it should be set up as follows:

MFC Flow = 30 sccm
Evac Time = 10 min.
Time:
00:00
03:00
06:00
09:00
12:00
15:00
18:00
21:00

7. To close the real time set up screen, click on the "Real" button again.
8. To see monitor the operation of the Preconcentrator, you can click on the "View" button. Another window will appear showing a diagram of the pre-concentrator and all of the temp, pressures and flows.

HP Chemstation Software Set-up

A total of four different methods are used in the Hewlett Packard chemstation software. The methods name and their use are defined below:

METHOD NAME	USED FOR
DUALSB1	Sample runs with no pause before next run
SB1PAUSE	Sample runs with 90 min pause before next run
DELAY	Used to delay system until scheduled start time
STANDBY	Used after sampling to put system in standby

Setting up the sequence

1. Open the instrument 1 Online. Look for the item in the task bar labeled "Instrument 1 (online)". If it is not opened, double click on the icon on the desktop labeled "Instrument 1 (online)".
2. View the sequence table by selecting the following from the menu:
   a. Sequence
   b. Sequence table...
3. The following table should show up. Change the file names for the sample run day. If any of the lines are different, change them back to this default or flowed the instructions in the next step.

Line	Vial	Sample Name	Method	Injection	Sample Type	Inj Vol.	Data File
1	1	Amb1	DUALSB1	1	Sample		YYMMDDA1
2	2	Rstd	DUALSB1	1	Sample		YYMMDDC1
3	3	Amb2	DUALSB1	1	Sample		YYMMDDA2
4	4	Blank	DUALSB1	1	Sample		YYMMDDB1
5	5	Amb3	SB1PAUSE	1	Sample		YYMMDDA3
6	6	Amb4	SB1PAUSE	1	Sample		YYMMDDA4
7	7	Amb5	SB1PAUSE	1	Sample		YYMMDDA5
8	8	Amb6	SB1PAUSE	1	Sample		YYMMDDA6
9	9	Amb7	DUALSB1	1	Sample		YYMMDDA7
10	10	Rstd	DUALSB1	1	Sample		YYMMDDC2
11	11	Amb8	SB1PAUSE	1	Sample		YYMMDDA8
12	12	standby	STANDBY	1	Sample		Bogus1

Data file names represent the sampling day date (YYMMDD) and sample type where:

A= Ambient sample
C= Calibration (Retention Standard)
B= Blank

The ending number represents the time of day for that particular sample day. Note that the numbers in the data file names corresponds to the sample name on this sequence table, as well as the sample name used in the Entech 7000

4. If the sequence table has been modified you can load the default by doing the following from the menu:
    a. Sequence
    b. Load sequence...
    c. Run2001.s
    software sequence table.
5. If the computer asks to save the sequence, select "No".

Starting the Sequence

The GC is started using the Chemstation Scheduler.
Verify that the method is on "standby". The middle pull down window will show which method is loaded.

1. Select ChemStation Scheduler under the View menu if it is not already open in the task bar.
2. Change the date for the run day date (typically tomorrow)
3. Change the time to 02:45
4. In the Command Field type "StartSequence".
5. The Mode field will by default be "Do Once".
6. Tab to a new line.
7. Click on the Save button and then minimize the window.

Last minute checks

1. Verify that the method is "standby".
2. Open the retention time cylinder valve.
3. Verify that the Liquid nitrogen valves are open.
4. Verify that the Hydrogen valve is open.
5. Verify that your shoes are tied.

Shut – down procedures

The Shut down procedure should be used the day following the run day. Typically these procedures are done at 8:00 am except on weekend when they can be done anytime before 11 pm.

1. Press the "abort" menu item on the "Instrument 1 (online)" program.
2. Press "stop" button on the "NT7000 Sequence Table" program.
3. Follow Retrieval Procedures for the Carbonyl Sampler
4. Close retention time cylinder valve.
5. Check liquid Nitrogen supply and order for next run if needed.

Carbonyl Sampler Set-up Procedures
Summer 2001

The Carbonyl sampler will run every third during the months of July, August and September. The days will coincide with the sampling schedule for the PAMS days.

Carbonyl Set-up Procedures

1. The set up procedures should be performed the day before the sample run day. Typically, we set-up for the next day at 4 pm. This can vary especially on weekends.
2. Retrieve 10 new cartridges from the "un-exposed" jar in the refrigerator in the inspector's lab.
3. Put a cartridge number sticker label on each filter and put the duplicate number label on the sample form for the appropriate port. There is one form for each sample day.
4. Make sure there is a cartridge in ports 1 – 8, channel 2 (collocated), and the blank. Verify that each connection is secure and that the numbers match the port numbers on the sample form.
5. Switch sampler to program mode (If it is not there already).
6. Press the "Port" key.
7. It should ask, "Cycle in Date Mode". Make sure this is "Date" mode and change if it is not.
8. Use the right arrow to scroll through each port and change the date to the next run day. Use the up and down arrow to change the appropriate numbers.
9. Keep using the right arrow to scroll through all of the ports. After the last port it will ask, "Print Cycle Data". Before you answer this, verify that the Hyperterm capture program is on. Look on the task bar for Atec Carbonyl or to start the capture program, double click on the icon on the desktop labeled Atec Carbonyl.ht. When you select "Yes", the printout will be displayed on the hyperterm display. Look over the print out to verify that the sampler is programmed correctly.
10. When everything is ready, switch to "Run" mode.

Carbonyl Retrieval Procedures

1. The retrieval procedures should be performed the day after the sample run day. Typically this is done at 8 am except for weekends and holidays which that time can vary.
2. Switch the sampler to program mode.
3. Verify that the Hyperterm capture program is on. Look on the task bar for Atec Carbonyl or to start the capture program, double click on the icon on the desktop labeled Atec Carbonyl.ht.
4. Under the "Transfer" menu, select "capture text". A screen will appear asking the file name. Save the file in e:\Atec Capture\yymmdd.txt (yy is the year, mm is the month, and dd is the day of the run).
5. Press the "print" button and and the data will scroll on the screen.
6. After the data is finished, under the "transfer" menu select "capture text" and then "stop".
7. Go to the e:\Atec Capture folder. There is a shortcut on the desktop.
8. Find the file and print it out.
9. Unload each cartridge and fill out the sample form for each port/cartridge. The information needed will be obtained from the printout.
10. Tape the printout to the back of the sample form.
11. Put the cartridges in the "exposed" sample jar in the refrigerator in the inspector's lab.

Received 4/27/97
Expires 4/27/97

Table 1.

Certified Concentration Values for NMOC Mixture: SRM 1800

Compound	Concentration nanomole/mole (ppb)[a]	ppb C
(1) Ethane	5.1 ± 0.2	→ 10.2
(2) Propane	5.4 ± 0.2	→ 16.2
(3) Propene	5.2 ± 0.2	→ 15.6
(4) iso-Butane	5.5 ± 0.2	→ 22.0
(5) n-Butane	5.3 ± 0.2	→ 21.2
(6) iso-Butylene (isobutene)	5.5 ± 0.2	→ 22.0
(7) ~~iso-Pentane~~ (2-MeButane)	5.8 ± 0.2	→ 29.0
(8) n-Pentane	5.1 ± 0.2	→ 25.5
(9) 1-Pentene	5.1 ± 0.2	→ 25.5
(10) n-Hexane	5.3 ± 0.2	→ 31.8
(11) Benzene	5.2 ± 0.2	→ 31.2 * Calculated
(12) n-Octane	5.1 ± 0.2	→ 40.8
(13) Toluene	5.2 ± 0.2	→ 36.4
(14) ortho-Xylene	5.1 ± 0.2	→ 40.8
(15) n-Decane	5.1 ± 0.2	→ 51.0

PLOT

DB-1

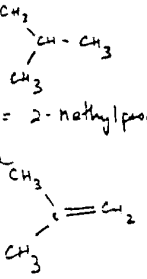
New Peaks

[a]Each of the certified compounds of the gas mixture is reported as the molar ratio of that compound relative to the total of all other constituents.

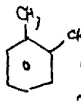
Isobutane = 2-Methylpropane

Toluene Methylbenzene

Isobutylene = 2-methylpropene

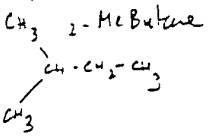


o-Xylene



ortho (1,2)
meta (1,3)
para (1,4)

Isopentane



2-MeButane

Santa Barbara County
Air Pollution Control District

On the Air

Santa Barbara County
Air Quality News
Issue 61
March-June 2001

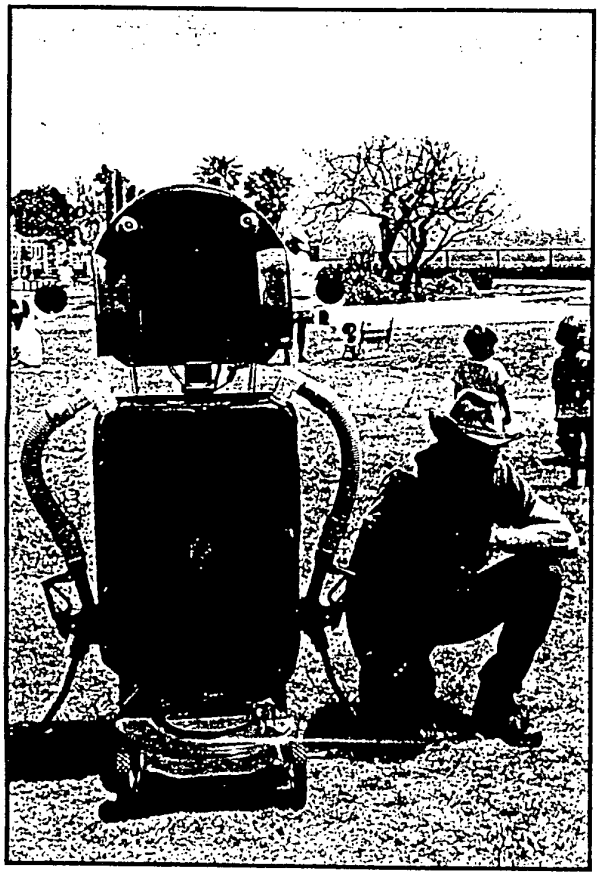
Smog Season is Here

Smog season is here. In Santa Barbara County, our highest levels of ozone (the principal component of smog) occur between April and October, when our air most frequently does not meet health-based ozone standards. Our air continues to violate the state standard for ozone. We attained the federal ozone standard at the end of 1999, and successfully stayed in attainment through the year 2000. However, the margin is slim. Different weather patterns and additional pollution could cause our county to go out of attainment of the federal standard again. If this happens, our local businesses will face additional regulations that are required for areas that don't meet the federal standard.

Enclosed with this issue is a chart that explains the Air Quality Index (AQI), a new way of reporting air quality. Ozone is the pollutant of most concern here, so we report the AQI for ozone. To view ozone data and the AQI, updated hourly, and to see charts of violations of ozone standards to date this year, check out "Today's Air Quality" on our website at **www.sbcapcd.org.**

This year, we face a new concern as we enter smog season — we are also entering the period of peak energy demand, and may experience energy shortages and rolling blackouts. These can result in significant additional air pollution. During blackout conditions, older, normally seldom-used power plants operate more hours without adequate pollution controls, and high-polluting emergency diesel generators are used.

(continued on page 2)



Clean Air Month, Earth Day, and APCD's New Kiosk

Kites filled the skies over Shoreline Park in Santa Barbara and Oxnard Beach Park on May 6, as APCD, the American Lung Association of Santa Barbara and Ventura Counties, and the Ventura County Air Pollution Control District celebrated Clean Air Month this year. "When people see these kites in the sky, we hope it reminds them that our air is a precious resource requiring protection and commitment," said APCD Director Doug Allard. Kids made clean-air pledges and received free kites, and adults entered to win a free electric bike at the *Flight for Life* events.

APCD's new kiosk also put in an appearance at the Shoreline Park event (see photo). **R2P2** (Robot Resource for Pollution Prevention) is an interactive kiosk with information on air pollution narrated by celebrities. The computer system, originally developed as *Air World* by the Ventura County Air Pollution Control District, has been customized with information specific to Santa Barbara County. APCD first introduced this version of *Air World* on a computer at the Santa Maria Valley Discovery Museum last

(continued on page 2)

Inside...

- The Air We Breathe
- Energy Conservation
- Board Roundup
- Clean-Air Vehicles
- Diesel Generators
- Dry Cleaner Training
- Car-free and Carefree

Smog Season (cont'd from page one)

Diesel-powered backup generators represent one of the dirtiest possible ways to generate electricity.
In addition to producing smog-forming pollutants, these generators produce diesel soot, also known as diesel particulate, which is considered the number one airborne carcinogen in California (for more information, see "Think Twice About Diesel Generators" in *Business Focus*).

It's especially important this summer that we do all we can to reduce air pollution. Here's how you can help:

❖ ***Conserve energy,*** and use energy during off-peak hours (after 6 PM in summer). Minimize the use of air conditioning, which pulls a large amount of electrical energy, and use compact fluorescent light bulbs to cut your energy bill (see article page three, for more).

❖ ***Drive less.*** Even considering additional pollution from older power plants and diesel generators, cars and trucks remain the major source of smog-forming pollution in our county. Choose to walk, bicycle, take the bus, share a ride, or telecommute.

❖ ***Combine car trips.*** Much of the pollution a car will cause occurs during the cold start, as the catalytic converter does not operate at full efficiency until the car warms up. This means that one trip with three short stops will pollute much less than three separate trips.

❖ ***Consider making your next car a clean-air car.*** There are many choices on the market today. Look for a car that has been classified as a ZEV (Zero Emission Vehicle), (SULEV) Super Ultra Low Emission Vehicle or ULEV (Ultra Low Emission Vehicle).

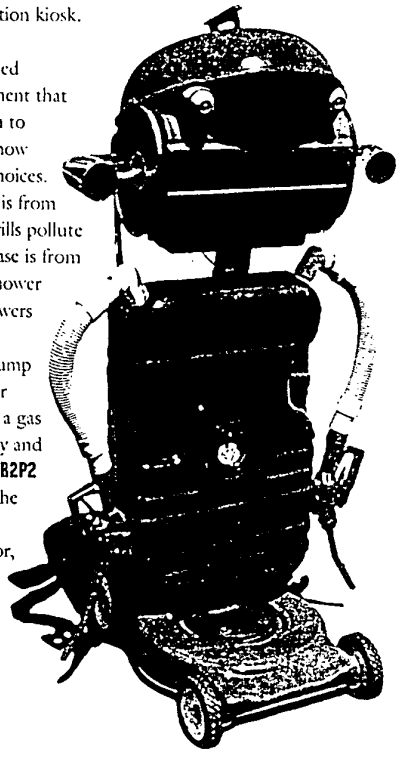
Help keep our air clean!

Clean Air Month and Earth Day (cont'd from page one)

May for Clean Air Month 2000. Artist Daniel Girard (shown in the cover photo) has since designed (and just completed) the new housing to make this a stand-alone information kiosk.

R2P2 is made of recycled materials from equipment that can cause air pollution to demonstrate that we now have more clean-air choices. For example, its head is from a charcoal grill (gas grills pollute much less), and the base is from a gas-powered lawn mower (electric and push mowers pollute less than gas mowers). Older gas pump nozzles (without vapor recovery systems) and a gas tank make up the body and arms. Girard also had **R2P2** powder-coated, with the coating and services donated by Permacolor, Inc. (using powdered paint instead of spray paint greatly reduces the amount of volatile organic compounds released into the air).

Kids at the Shoreline Park May 6 event got the first glimpse of **R2P2**, which APCD will display around the county at schools, businesses, and public agencies for weeks at a time.
To invite **R2P2** *to visit your facility, call 961-8800.*



APCD also celebrated Earth Day in April, participating at events in Santa Maria (at the new Natural History Museum) and Santa Barbara. At the Santa Barbara event, APCD, working with the Community Environmental Council, invited drivers of new clean-air cars to come to a Green Energy Leaders display and talk with people about their experiences with electric, hybrid gas-electric, and compressed natural gas vehicles.

Paul Cicilco of Santa Barbara County Vehicle Operations talks about the county's new gas-electric hybrid car at APCD's Green Energy Leaders display at Earth Day. The Toyota Prius has both a gas engine and an electric motor, and runs on gasoline, achieving a rated 52 miles-per-gallon (mpg) on city streets, and 45 mpg on the highway. The Prius is classified as a super ultra low emission vehicle (SULEV).

Energy Conservation Initiatives

APCD Board Roundup

Following are the highlights of the February, March and April Board meetings.

February

✓ Recognized APCD Inspector Glenn Gazdecki for a cost-saving suggestion on recertification training.

✓ Received and filed reports on: APCD customer service surveys; the Ventura County APCD land use conference; and permit, inspection, and the air quality impacts of the state's energy crisis.

March

✓ Executed grant agreements for the purchase of low-emission burners for two agricultural boilers, and a low-NOx diesel engine for a 10-wheeler dump truck.

✓ Received and filed the 2000 annual report on the Air Toxics "Hot Spots" Program, and approved the program budget for FY 2001-2002.

April

✓ Adopted a resolution proclaiming April 22, 2001 as Earth Day, May as Clean Air Month, and May 19-27 as Bike Week.

✓ Received a report regarding APCD assistance with applications for air quality mitigation funds by the City of Guadalupe.

✓ Transferred the Clean Air Express Commuter Bus Program administration to Santa Barbara County Association of Governments, and approved the associated agreements.

A coalition of local environmental organizations, businesses, and government agencies, including APCD, is working on several initiatives to promote energy conservation. Starting June 30, declared Energy Conservation Day, the coalition is recommending that energy users:

❖ ***Change three light bulbs.*** Compact fluorescent light bulbs (CFLs) are easy to use, and can be found at most home improvement stores. While slightly more expensive than traditional bulbs, CFLs can last for a year or longer, are more convenient, and can save up to $60 in electricity use over their lifetime. Start by replacing the 60 to 100W bulbs that you use several hours a day.

❖ ***Check settings.*** Thermostats should be set at 74 to 78 degrees in the summer, refrigerators at 38 to 42 degrees, and freezers at 0 to 5 degrees. Find the lowest water heating setting comfortable for your household – try 120 degrees (or "warm"). Consider putting your air conditioning system on a timer to ensure that it is not on when you are out of the building.

For more information and tips, visit www.greendifference.org. The campaign is organized by the Nuclear Age Peace Foundation, the Community Environmental Council, APCD, The Gas Company, The Sustainability Project, Get Oil Out!, and Environmental Defense Center, and will continue with ongoing events and initiatives.

Additional resources:
Qualifying for the California 20/20 rebate:
www.savepower.lbl.gov.

Search for a grant, rebate, or incentive to help save energy or use alternate energy sources:
www.consumerenergycenter.org/rebate/index.php.

Good general information:
www.flexyourpower.ca.gov.a

Award for *The Air We Breathe*

In April, APCD's new 15-minute video ***The Air We Breathe*** received an Award of Distinction from The Videographer Awards, a national awards program for video production. Coordinated by Bobbie Bratz of APCD, the video was written, produced and directed by Daniel Girard of Heyoka Studios.

Call 961-8800 to invite APCD to make a presentation to your group and show the video, or to receive a copy of the video to show at your organization or facility.

APCD Inspector Fred White (below) answered questions about air pollution at APCD's booth at the Santa Maria Earth Day event at the new Natural History Museum.

Air Pollution Control District Board

Supervisor Naomi Schwartz
First District
Santa Barbara County

Supervisor Susan Rose
Second District
Santa Barbara County

Supervisor Gail Marshall
Third District
Santa Barbara County

Supervisor Joni Gray
Fourth District
Santa Barbara County

Supervisor Tom Urbanske
Fifth District
Santa Barbara County

Councilmember Russ Hicks
City of Buellton

Councilmember Dick Weinberg
City of Carpinteria

Mayor Sam Arca
City of Guadalupe

Councilmember DeWayne Holmdahl
City of Lompoc

Councilmember Gil Garcia
City of Santa Barbara

Councilmember Larry Lavagnino
City of Santa Maria

Councilmember Ed Andrisek
City of Solvang

APCD Board Calendar

All meetings start at 2 p.m. For final meeting agendas, call the APCD Board Clerk, 961-8853.

July 19
Board of Supervisors
Hearing Room
511 East Lakeside Parkway
Santa Maria, CA 93455

August 16
Board of Supervisors
Hearing Room
105 East Anapamu Street
Santa Barbara, CA 93101

September 20
Board of Supervisors
Hearing Room
511 East Lakeside Parkway
Santa Maria, CA 93455

October 18
Board of Supervisors
Hearing Room
105 East Anapamu Street
Santa Barbara, CA 93101

Community Advisory Council

The APCD Community Advisory Council meets the second Wednesday of every month at the Days Motor Inn in Buellton. The public is welcome. For more information, call Linda Beard, 961-8853.

Promises Flying High

"I'll ride my bike to school more," or "I'll walk to my friend's house," are some of the clean-air pledges kids made at a recent event at Shoreline Park in Santa Barbara. Kids (and adults) decorated free kites with pictures and pledges as part of Clean Air Month events sponsored by APCD, the American Lung Association of Santa Barbara and Ventura Counties, and the Ventura County Air Pollution Control District (see page one article).

Santa Barbara County
Air Pollution Control District

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Goleta, CA 93117
(805) 961-8800

Business Assistance
(805) 961-8868

Daily Air Quality Report
(805) 961-8802

Complaints/Public Information
(805) 961-8800

World Wide Web
www.sbcapcd.org

E-Mail
apcd@sbcapcd.org

On the Air is a bimonthly newsletter published by the Community Assistance Section of the Santa Barbara County Air Pollution Control District.

For further information on items in this newsletter, or to be added to our subscription list, please call Bobbie Bratz, 961-8890 or Email bratzb@sbcapcd.org.

Our Vision: Clean Air

Santa Barbara County
Air Pollution Control District

Business Focus

Business Oriented Air Quality News • March–June 2001

Running on Clean Energy

Clean-Air Vehicles

Twenty-four clean-air vehicles make up part of the fleet of the Housing and Residential Services Department of the University of California at Santa Barbara (UCSB). Shown above are: eight compressed natural gas trucks in the back row; eight electric Ford Ranger pickup trucks and one electric converted Ford Escort in the next row; two Honda Civic GX natural gas vehicles in the second row; and five electric grounds maintenance vehicles in the front row.

Mark Rousseau (above-right), Energy and Environmental Manager for the UCSB Housing and Residential Services Department brought one of UCSB's Honda GX natural gas vehicles to display at APCD's booth at Earth Day in Santa Barbara. Honda calls the GX "the cleanest car on earth," claiming that the tailpipe emissions are cleaner than the surrounding air on a smoggy day.

Think Twice About Diesel Generators

Standby diesel generators represent one of the dirtiest – and most toxic – ways to generate electricity. They should only be used under emergency conditions, when there is no alternative.

Diesel exhaust contains carcinogenic diesel particulate, which represents our state's most significant toxic air pollution problem. California Air Resources Board estimates that operation of one uncontrolled one-megawatt diesel generator for only 250 hours per year results in a 50 percent increase in cancer risk for residents within one city block.

A recent study by South Coast Air Quality Management District found that diesel particulate accounted for 71 percent of the total cancer risk from toxic air pollution in the Southern California region covered by that agency. The study is one of the most comprehensive studies of urban toxic air pollution ever performed.

Diesel generators also produce nitrogen oxides (NOx), a smog-forming pollutant. Per megawatt hour of electricity generated, standby diesel generators

(continued on back)

Santa Barbara County
Air Pollution Control District

Business Update

Page

Attention: Dry Cleaners

The California Air Resources Board is holding a Dry Cleaner Air Toxic Control Measure (ATCM) Training at the San Luis Obispo Air Pollution Control District office on *Thursday, July 26, 2001.*

The original certification course (*required* for new operators) is a full day course, and is subject to cancellation due to lack of attendance. If you are interested, please register as soon as possible.

The re-certification course (*required* for those who were last trained in 1998) is a half-day course. A fee will apply for both courses. Operators will be required to bring to the class a halogenated hydrocarbon detector used in their shops for leak detection.

❖ *To register for the training, contact the California Air Resources Board Course Registrar in the Compliance Division at (916) 322-8272 or by email at cdtrain@arb.ca.gov.*

❖ *If you have any questions about the training and whether or not you need to attend, please contact John Garnett of APCD at 961-8935, or by email at garnettj@sbcapcd.org. You may also contact the course instructor, Tom Raschke of the California Air Resources Board, at traschke@arb.ca.gov.*

❖ *For directions to the location of the training, contact the San Luis Obispo APCD at (805) 781-5912.*

Note: *Permit Fees and Asbestos Fees will be increasing as of July 1, 2001. See:* www.sbcaped.org/new.htm *for information on new rates.*

Charge It!

APCD now accepts credit card payments for permit fees, rules request fees, variance fees, and most other kinds of charges. APCD accepts Master Card, VISA, and Discover credit cards. For more information, contact Martha Gibbs at 961-8820, or by email at gibbsm@sbcapcd.org

Clean Energy (Cont'd from front)

produce 50 to 60 times the amount of NOx produced (per megawatt hour generated) by California's typical mix of gas-powered power plants.

Backup generators should only be used when absolutely necessary. Some generator installations may require permits, including APCD permits, or land use, fire, or building entitlements, and associated inspections.

Alternatives

Conserve energy: This is the first and most effective weapon against rolling blackouts. Search for a grant, rebate, or incentive here: www.consumerenergy-center.org/rebate/index.php.

Shift power use to off-peak hours: You are less likely to experience power interruptions during off-peak hours.

Plan ahead: Make a plan for rolling blackouts so you are prepared.

Use battery backup power: Uninterruptible Power Supply (UPS) systems can keep computer servers and networks operational until they can be shut off safely.

If you must have additional backup power: Buy or rent the smallest unit you can use, use it only when absolutely necessary, and consider the following options (in this order):

❖ A natural gas or propane fired unit with catalytic controls

❖ A natural gas or propane fired unit without catalytic controls

❖ A gasoline-fired unit with catalytic controls

❖ A gasoline fired unit without catalytic controls

❖ A diesel-fired unit manufactured after January 1996 that is certified to meet EPA and CARB Tier 1 Emission Standards, and is equipped with an exhaust particulate filter system.

Car-free and Carefree in Santa Barbara

In April, the Take a Vacation from Your Car project, led by APCD and the American Lung Association of Santa Barbara and Ventura Counties, launched a new website to help visitors get to, and around, the Santa Barbara area without a car. The project aims to promote car-free transportation options to tourists in order to reduce air pollution and alleviate traffic congestion. Many other partners are participating. For more information, check out:

santabarbaracarfree.org

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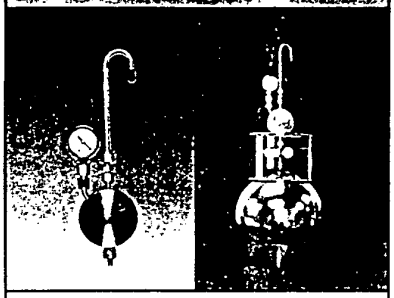
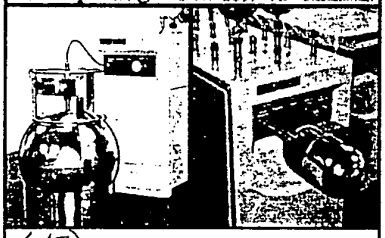
New, Improved Passive VOC Sampling Inlet



- Improved air sampling inlet for determining average VOC concentrations.
- Flow stability over a wider temperature range(-20°C to 50°C).
- Superior recovery of TO14 Compounds.

Circle #100 for more information

Improved Data Reliability Using Automated Surrogate Spiking into Canisters

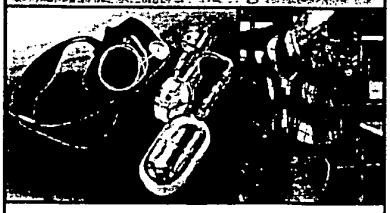


Now incorporate the same surrogate spiking used for water and soil methods when analyzing canister air samples.

- The 7032 and 4600 automatically inject surrogate either to target pressure or target dilution factor.
- Helps protect data reliability while providing ISO14000 acceptable Quality Assurance.

Circle #101 for more information

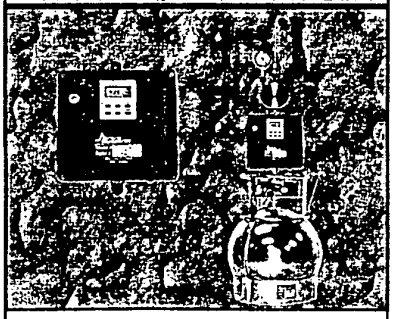
The Power of Canister Sampling Technology Now Available for Personal Monitoring



- Perform personal exposure monitoring without pumps or batteries.
- Silonite ™ coated canisters allow greater recovery of workplace chemicals, including sulfur compounds.
- Elimination of extraction solvents allows direct analysis by GCMS for better reliability.

Circle #102 for more information

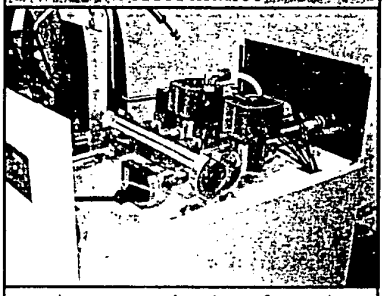
Automatically Start and Stop Air Sampling with this Low Cost Timer



- Program start / stop times for precise sampling events.
- Allows multiple sites to coordinate sampling times.
- Up to 10 start / stop events.
- Battery lasts several months on a single charge.

Circle #103 for more information

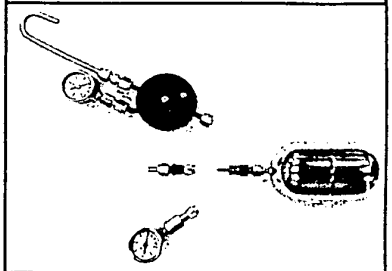
New Features Improve 3100 Canister Cleaner Performance



- Automates cleaning of any size canister.
- All welded internal manifold improves high vacuum capabilities.
- SmartLab control software allows recording of system pressure, vacuum, and canister temperatures during cleaning.

Circle #104 for more information

Sampling Sulfur Gases Has Never Been Easier or More Reliable



- Silonite ™ coated MiniCans and samplers allow recovery of sulfur compounds at PPB through PPM levels.
- Holding times of 1-2 weeks for H_2S and Mercaptans.
- Ideal for process monitoring, stack/landfill gas, odor analysis, and personal monitoring.

Circle #105 for more information

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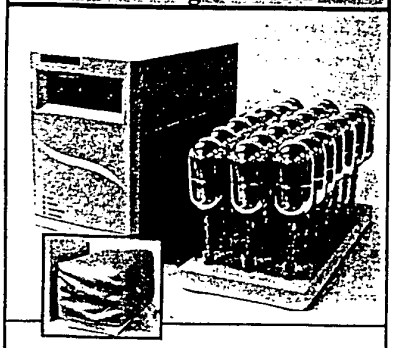
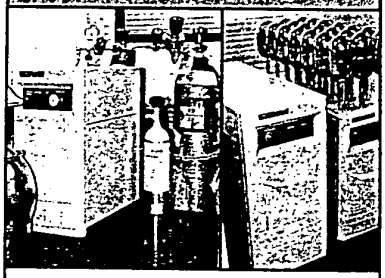
Maximize Sample Throughput by Adding a 3121 MiniCan Cleaning Manifold



- Clean 21 MiniCans at a time.
- Vacuum tight miniature quick connects allow fast loading and unloading.
- Heater covers entire canister.

Circle #106 for more information

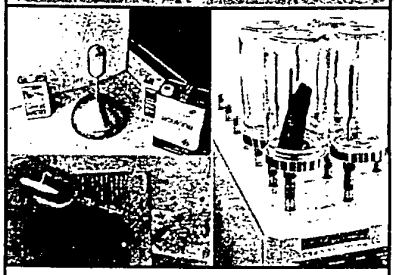
Laboratory Support for Sulfur Compound Analysis



- Complete systems available for PPM to sub-PPB level analysis.
- Dynamically dilute fresh PPB standards from PPM level cylinders as needed with the 4600 Diluter.
- Automated analysis of up to 21 samples.

Circle #107 for more information

New Support for Arson Investigation



- Quickly collect accelerant vapors.
- Large Volume Headspace Analysis (LVHA) allows fast accelerant determination directly from debris, eliminating charcoal adsorption step.
- Obtain results while crime scenes are still secure.

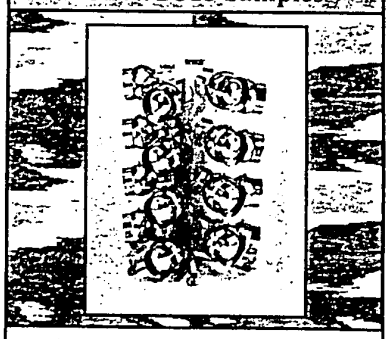
Circle #108 for more information

Tube Desorption and Direct Syringe Injection Option for the 7100 Preconcentrator

- Thermally desorb 1/4" x 4.5" sorbent tubes when performing EPA Methods TO1, TO2, and TO17.
- Perform high flow, splitless syringe injections of 0.1 - 10cc sample volumes.
- Silonite coated lines allow recovery of reactive compounds and reduced carryover.

Circle #109 for more information

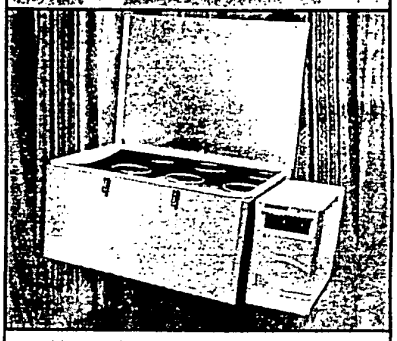
Improve Laboratory Throughput of TO14/TO15 Samples



- Automates the analysis of 16 SUMMA or Silonite ™ passivated canisters.
- All positions automatically leak checked before analysis.
- Exclusive double flushing insures lowest possible carryover.

Circle #110 for more information

6-Position 6L Canister Oven Reduces Cleanup Times



- Heats the entire canister during cleanup.
- Manifold lines are electropolished and kept hot to reduce VOC adsorption.
- Optimized for 6L cans, but will clean all cans from 1L to 15L.

Circle #111 for more information

Entech Instruments Inc. • 2265 A Ward Ave. • Simi Valley CA 93065 • 805-527-5939 • 805-527-5687 Fax • www.entechinst.com

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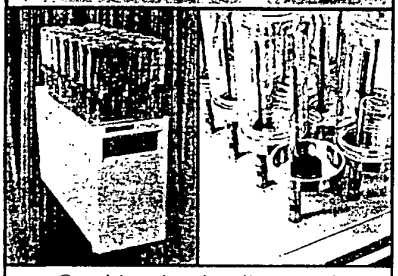
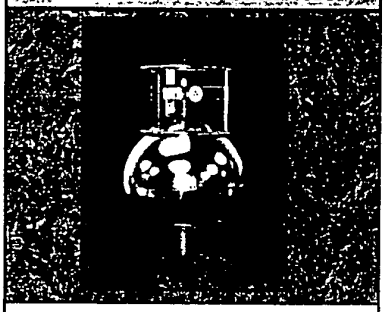
Large Volume Headspace Analyzer



- Combine the cleanliness and reproducibility of static head space analysis with the sensitivity of purge & trap.
- Perform outgassing studies:
  - Food & Preservative Testing
  - Product QA
  - Fragrance Analysis
  - Material Testing

Circle #112 for more information

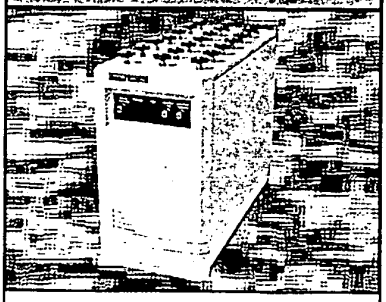
Advance your Technology with Silonite™ Coated 6L Stainless Steel Canisters



- For collection and storage of TO14 and TO15 analytes.
- Utilizes Nupro bellows valves for leak tight operation.
- Optional Silonite ™ coated valve for sulfur sampling and analysis.

Circle #113 for more information

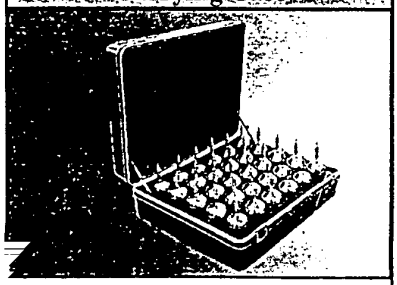
Automate Tedlar Bag Analysis While Improving Reproducibility



- Highly reproducible GC inlet system featuring "tool free" connections to SKC Tedlar bags.
- Loop injection or optional sample preconcentration.
- Works with all GC Instruments.

Circle #114 for more information

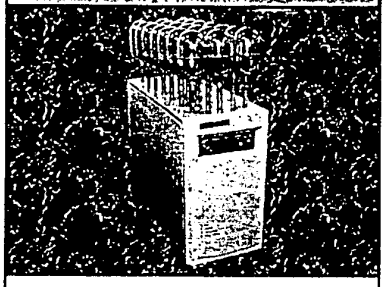
Ship and Store MiniCans in this Convenient Space Saving Carrying Case



- Light yet durable carrying case simplifies shipping of 30 MiniCans and flow controllers.
- Easily stores on shelf or under bench.
- Improves field portability when collecting multiple samples.

Circle #115 for more information

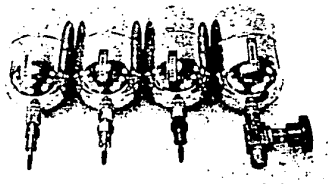
MiniCan Autosampler Automates Canister Analysis While Minimizing Lab Space Requirements



- Analyze 21 MiniCans Unattended.
- Ideal for analysis of VOC's, sulfur compounds, and fixed gases.
- Maximize QA using unique surrogate spiking feature.

Circle #116 for more information

MiniCan ™ Canisters Improve Air Lab Efficiency While Lowering Costs



- Quick connect valve allows loading of autosamplers or cleaning systems in minutes.
- Smaller, lighter design greatly reduces shipping costs relative to larger canisters.
- 0.4L MiniCans are ideal for PPB and PPM level analysis.

Circle #117 for more information

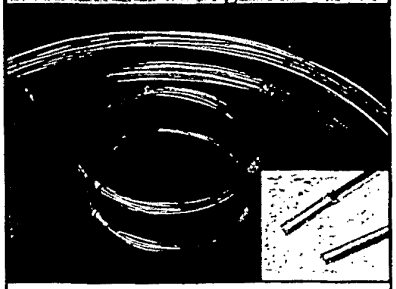
ENTECH INSTRUMENTS INC.

Entech Product Focus

Your Source for VOC Monitoring Solutions

800/555-8034
805/527-5939
805/527-5687 Fax

Silonite™ Coating Maximizes the Inertness of Stainless Steel Tubing



- New coating technology provides inertness of fused silica on stainless steel surfaces.
- Improves recovery of reactive compounds.
- Available in 1/32", 1/16", 1/8" and 1/4" OD.

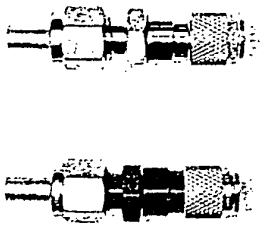
Circle #118 for more information

Check out Entech's Solutions for Soil Gas Sampling and Analysis

- Collect soil gas using either surface or probe sampling.
- Automated analysis of core samples using large volume headspace analysis.
- MiniCan samplers allow storage of soil gas for weeks without loss of VOCs.

Circle #119 for more information

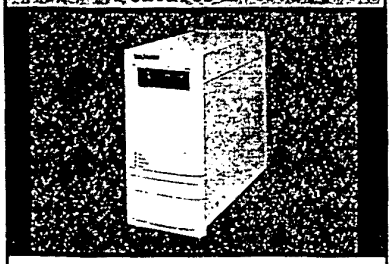
New Critical Orifice Samplers Reduce Cost and Size of Canister Samplers



- Low cost canister sampling solution.
- Ideal for short term, integrated sampling (1 to 30 minutes).
- Available for 6L canisters (1/4" Swagelock) and MiniCans (Miniature Quick Connect).

Circle #120 for more information

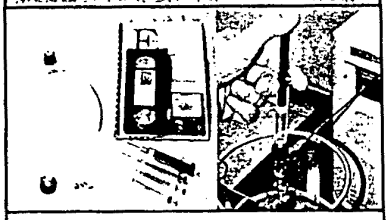
Third Generation Preconcentration System Provides Best Features Ever!



- Automates the preconcentation and GCMS injection of gas phase VOC's.
- Most advanced water / CO_2 elimination technology available.
- Ideal for environmental monitoring, large volume headspace analysis(foods, flavors, fragrances), sulfur analysis.

Circle #121 for more information

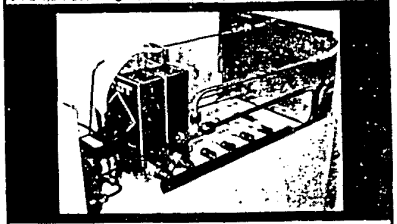
Static Dilution Kit Allows 4600 to Make Virtually Any Gas Phase Standard



- Prepare custom standards from inexpensive neat compounds.
- Utilizes Entech's ESP Windows Software to create dilution SOP's.
- Final pressurization of canister standard is under SmartLab® control through the 4600 Windows control software.
- Ideal for special projects that require analysis of new compounds.

Circle #122 for more information

Dilute a Wide Range of Standards Using the 4600 Dynamic Diluter



- The 4600 utilizes 2 - 6 mass flow controllers to dynamically dilute standards to PPB levels.
- Unique back-pressure regulator and post-mixer splitting help maintain constant outlet concentrations during canister filling.
- Can be attached directly to the 7100 Preconcentrator for fresh standards on demand.

Circle #123 for more information

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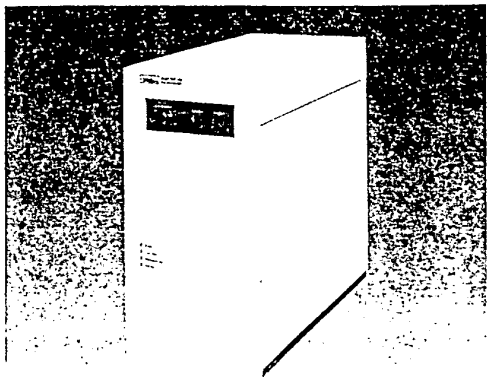
ENTECH INSTRUMENTS, INC.

Performance Specifications of the 7100 Preconcentrator

Unique Only to the Entech System:



- Has three traps built in to allow water and CO_2 removal using MPT and CTD techniques for analysis of ppb - ppt VOC's.
- Reproducibly samples 10 - 2000CC from canisters and Tedlar bags.
- Permits direct syringe injection of gas (i.e. cal std., BFB) without plumbing change.
- Built in self-diagnostics to analyze electronics and system components.
- Can analyze trace VOC's in over 90% CO_2.
- Can perform matrix spiking.
- Can be linked to up to two multi- position autosamplers and a purge & trap.
- Can analyze sub ppb level sulfur compounds using Extended Cold Trap Dehydration (ECTD) and GC/MS.
- Does not require an autosampler; four canister positions are built into the concentrator.
- Uses only 10 inches of linear bench space.
- Monitors pressure of sample, internal standards, flush gas, and calibration standard.
- Can pressure or vacuum leak test every canister connection prior to opening the canister valves for analysis.
- Compatible with Large Volume Headspace Analysis (LVHA) and MiniCan inlet systems.

Other Important Features:

- No solenoids or Mass Flow Controllers in sample path.
- Can analyze TO14 or TO15 analyte list simultaneously without any modification.
- Fused silica lined stainless tubing. Nearly the entire flow path is fused silica lined.
- QA/QC reports are saved after every run and monitor 51 parameters to verify that all volumes, heated zones, flows, pressures, timed events etc. met operational setpoints.
- Can achieve detection limits of <0.2 ppbc for Title I compounds and <0.1 ppbv for Air Toxics.
- Can perform real time analysis every 1 - 8 hours.
- Can concentrate up to 600cc of 100% RH sample volumes with splitless injection into the GC.
- Improved system cleaning using VP Pulse™ technique.
- The Entech system is operated using a true Windows interface.

Entech Instruments, Inc. 2265-A Ward Avenue Simi Valley, CA 93065 Tel (805) 527-5939 FAX (805) 527-5687

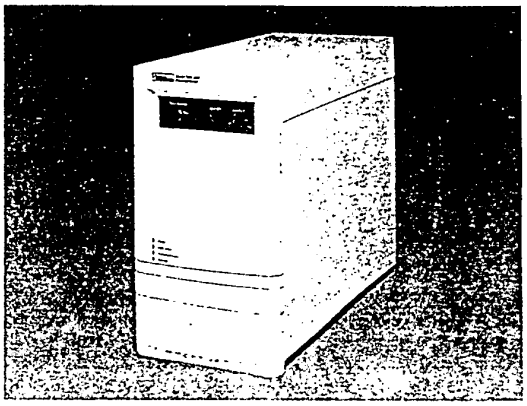
ENTECH 7100

AUTOMATED PRECONCENTRATOR

The analysis of gas-phase Volatile Organic Compounds (VOC's) by GC or GC/MS requires a reliable, reproducible means of quantitatively delivering the VOC's from the point of sampling to the capillary GC column. Analysis of ppm level VOC's in stack gas, landfill gas, auto exhaust, and headspace is accomplished by a fast injection of small, precisely measured volumes without exposure to active surfaces or dead-volume. Low-level ppb analysis of volatile compounds in ambient air, indoor air, industrial environments, or in headspace testing of flavors and frangrances requires larger sample volumes. The larger the sample size, the more critical it becomes to have multiple preconcentration stages to eliminate the CO_2 and water vapor before sample introduction into the gas chromatograph.

The 7100 Preconcentrator

The 7100 Preconcentrator represents the most sophisticated preconcentrator available today for the analysis of vapor phase Volatile Organic Compounds. Its unique three stages of concentration offer a wide spectrum of choices for preparing the sample for capillary GC analysis. Turn-key methods are available for both cryogenic and cryogenless operation to accommodate laboratory and mobile operating environments. Advanced water and CO_2 management systems provide superior analysis of polar and non-polar organics, while the inert, heated flow path allows recovery of hydrocarbons in the range of



Entech 7100

C_2-C_{15}. Four inlets are built into the 7100 that are available for direct sample introduction or as inlets for multi-position autosamplers. Internal traps are easily accessed from the top for fast replacement.

System Hygiene

Cleaning of any preconcentration system is necessary on a routine basis, especially if the inlet is exposed to high concentration samples. Rather than flushing lines to remove contaminants entrained in fittings and valves, the model 7100 utilizes a vacuum/pressure pulsing technique called VP-Pulse™ that actually pulls contaminants out of un-flushed "dead volumes" so they aren't left to slowly diffuse out and contribute to later sample analyses. With this procedure, acceptable blanks are obtained in a fraction of the time compared to constant pressure flushing. The sample path in the 7100 has also been designed

without solenoid valves so there are no cold regions with absorptive surfaces that can bleed contamination back into the flow stream. Silonite™ coated stainless steel tubing is used exclusively for all transfer tubing and traps exposed to the sample to minimize sample adsorption. These features are helpful in obtaining the lowest useable detection limits in a wide variety of matrices. Ultra-sensitive mass spectrometers are meaningless if there are interferences from previous samples.

Quality Assurance

The 7100 comes equipped with tools for validating system performance, including the ability to perform automated leak checking and matrix spiking. The 7100 also records critical parameters during each sample preconcentration to verify proper system operation, such as trapping flow rates, flow volumes, trap pressure drop, trapping temperatures, water management parameters, desorption temperatures and flows, autosampler position, and sample transfer times. The preserved history of each preconcentration can be used for internal QA, while providing a powerful diagnostic tool that helps keep the 7100 operating at maximum potential.

Leak Checking

A major source of error in GC inlet systems is the presence of leaks that go undetected. The 7100 performs automated leak-check using both pressure and vacuum techniques to insure that a leak-tight system exists before samples are analyzed. A report is generated giving the starting and ending pressure during the monitoring period. Leak checking can be done either by selecting individual sample ports, or by selecting a sequence table which defines a group of samples on the autosampler.

Matrix Spiking

GC or GCMS calibration is performed using carefully prepared standards in a clean matrix (N_2 or zero air). It is usually assumed that no interferences exist in actual samples that will change response factors or detection limits. However, this may not be the case. The true detection limit of benzene, for example, may be altered if it coelutes with a high concentration interferent that wasn't in the standard. The only way to determine whether interferences are changing response factors for target compounds in samples is to spike low levels of the analytical standard right into the sample matrix. By adding 1 ppb of target compounds to the sample being analyzed, for example, all responses should go up by about 1ppb. The 7100 makes this easy by allowing the co-preconcentration of analytical standard. This will add reassurances on the most critical of samples and can help uncover matrix interfences if they exist.

Sequential or Real Time Analysis

The 7100 can perform sample analysis sequentially as determined by the GC run time, or can be set up to run samples at a particular time of the day. For example, 24 runs can be started, one each hour, after which the system will loop back to the first sample position. For on-site analysis, air samples can be integrated into a single canister over 1-24 hours followed by an analysis and re-evacuation of the canister for continuous cycling.

SmartLab® Control Interface

The 7100 is controlled using the Entech SmartLab® control network operating under Microsoft Windows. The 7100 user interface includes screens for developing concentration METHODS and SEQUENCE TABLES for automated, multi-sample operation. SmartLab electronics can be swapped with electronics in other Entech SmartLab products, which simplifies the support strategy by reducing complexity and part count.

Features & Benefits

Analytical
- Superior H_2O and CO_2 management via advanced 3-stage trapping procedures.
- No cold-spots or solenoid valves in sample flow path.
- Optimized compound recovery through adjustable parameter settings.
- Silonite™ coated stainless steel flow paths maximize heavy and polar VOC recovery while reducing carryover.

Operational
- Supports matrix spiking and adds internal standard automatically.
- Performs automated leak-checks and instrument bake-outs.
- User-friendly Window based software operating on GC data system.
- Occupies only 9" of linear bench space.

Economy
- Fully automates VOC analysis.
- Pressure compensation allows 100 x calibration range from one standard mix.
- Four sample inlets for unattended operation.
- SmartLab technology reduces spare parts count.
- Compatible with low cost MiniCan canisters.

Serviceability
- Built-in diagnostic software for troubleshooting.
- Electronics are modular, socketed and easily accessible.
- Remote communication option via modem.
- Comprehensive instrument QA/QC report printed for each run.

Flexibility
- Compatible with most major GC models.
- May be interfaced with P&T for maximum GC/MS utilization.
- Accommodates canisters, tedlar bags, adsorbent traps and Large Volume Static Headspace (LVSH).
- Two autosamplers can be added to maximize throughput.

Typical Configurations

Application	*Analyzer*	*Water/C02 Elimination*	*Module 1*	*Module 2*	*Module 3*
Polar/Non-Polar AirToxics	GC/MS	MP&T	1/8" glass bead 04-11320	1/8" cryo sorbent 04-11330	on-column focusing
C_2-C_{12} Hydrocarbons	GC/FID	MP&T	1/8" GB/Sorb. 04-11340	1/8" cryo sorbent 04-11330	on-column focusing
Flavor and Frangrance Testing	GC/MS	MP&T	1/8" glass bead 04-11320	1/8" cryo sorbent 04-11330	on-column focusing
Sample from GC Injector Loop or P&T	GC/MS	None	NA	NA	on-column focusing
PPB H_2S/Mercaptans	GC/MS	ECTD	Empty Trap 04-11310	1/8" cryo sorbent 04-11330	on-column focusing
BTEX Analysis	GC/MS	Dry Purge	None or pass-thru	1/8" sorbent 04-11330	pass thru

MP&T = Microscale Purge & Trap ECTD = Extended Cold Trap Dehyration

7100 Specifications

Cryotrapping Modules:	Temperature range: -180°C to 230°C. Temperature rise: 360°/min. Module 2 cryotrap (P/N 04-01720) can be used alone for single stage concentrations, or with Module 1 (P/N 04-01710) for advanced H_20 and $C0_2$ management.
Cryofocusing Trap:	(P/N 04-01730) Internal megabore focusing trap. Trapping temperature to -190°C. Initial temperature rise 10,000°C /min decreasing rapidly to final value with no cold spots on entrance or exit of trap.
Mass Flow Controller:	(P/N 03-00200) 10 to 200 sccm.
Maximum Sample Volume:	2000 mls. 400 mls typical for ambient air.
Minimum Sample Volume:	10cc using pressure compensation algorithm.
Pressure Sensor:	(P/N 03-30120) 0-50 psia.
Sample Pressure:	Subambient (7 psia) to 35 psig.
Reproducibility:	3% for sample volumes over 100cc.
Heated Regions:	Maximum temperature of isothermal zones: sample transfer line (150°C), rotary valve block (180°C), Module 1 bulkhead (200°C), Module 2 bulkhead (200°C), GC transfer line (150°C).
Outputs:	2 TTL level optoisolated open-collector outputs as start signals for GC1 and GC2 (START DESORB for Purge & Trap control).
Inputs:	Contact closures or open-collector inputs for GC1 READY, GC2/P&T READY.
Aux 1:	External canister sampler control for continuous monitoring.
Aux 2:	External MFC control for real-time monitoring.
Size:	9" W x 18" H x 21" D.
Weight:	60 lbs (3-stage cryo modules installed).
Utilities:	POWER (120VAC, 50/60Hz) 1500VA
Gases:	Ultra High Purity (UHP) Helium, 20 to 60 psig. *Pulse Gas*: UHP Nitrogen or Zero Air. 15 to 50 psig. *Vacuum System:* 1 psia at 200 sccm (for cryogen based systems). *Coolant*: Liquid Nitrogen, 20 to 50 psig.

OPTIONS

P/N	DESCRIPTION
09-33203	Heated 4 Sample Inlet
7100-01	Single Tube Thermal Desorber
7100-04	Real Time Run Mode Sample Integrator
7032	MiniCan Autosampler, 21 Position
7032 LVSH	Large Volume Static Headspace Autosampler
7016CA	6L Canister Autosampler, 16 Position

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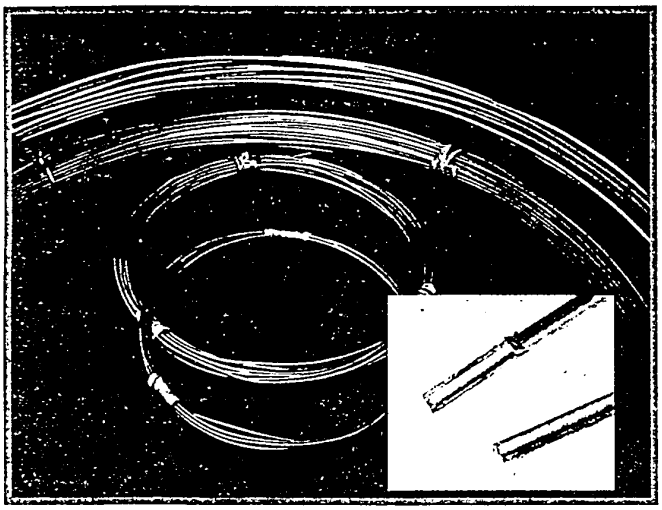
Silonite™ Tubing



Silonite Tubing - The Right Choice!

Silonite is a unique fused silica coating that reduces the surface activity of stainless steel. When applied to the inside of stainless steel tubing, chemical inertness is greatly improved. Combining the durability of stainless steel with the inertness of fused silica creates the perfect solution for real world chemical applications.

What makes Silonite so unique? Unlike other coatings, Silonite provides a thinner, higher density barrier that prevents chemicals from reaching the metal oxides on the interior tubing walls. The smooth coating results in an even, laminar flow creating a lower pressure drop while discouraging the deposition of high molecular weight contaminants. This helps to maintain a clean flowpath while preserving the inert, non-adsorptive properties of the tubing.

Since Silonite is 10-10,000 times thinner than glass lined or thick fused silica lined tubing. Silonite tubing can be bent to nearly any angle without fear of damaging the interior lining. Even the smallest sample loops or tightest bends around corners will not affect tubing inertness.

ENTECH
INSTRUMENTS, INC.
2265-A Ward Ave. Simi Valley, CA 93065
800/555-8034 FAX 805/527-5687

Features:

- Inert Silonite (fused Silica) coating.
- Dense coating prevents interaction with reactive metal oxides on tubing walls.
- Flexible, allowing virtually any bend radius.
- Better recovery of reactive organic compounds containing oxygen, nitrogen and sulfur.
- Smooth coating process reduces internal surface area of tubing.
- No Siloxane bleed.
- Does not require additional bonded phase to complete deactivation. Chemicals are transferred more quickly and at lower temperatures.

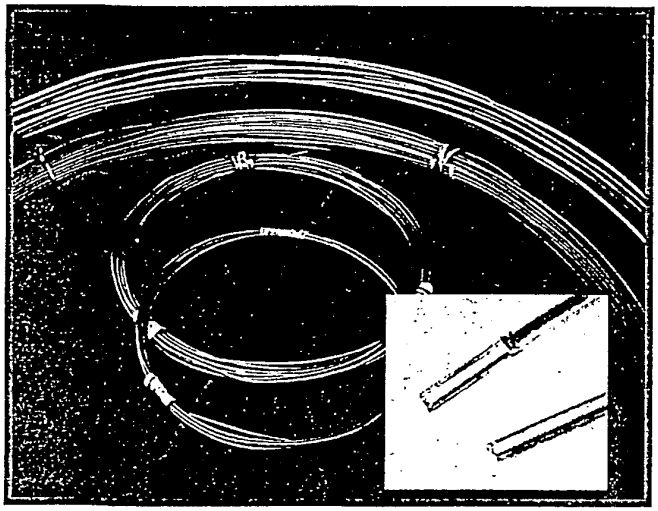
Applications:

- GC Transfer Lines
- Sample Loops
- Chemical Analyzers
- GC Inlet Systems (P&T, Headspace, Thermal Desorption)
- Chemical Processing
- Cylinder/Canister Purging

Ordering Information

Size (Od x ID)	P/N
1/32" x 0.02"	15-87020
1/16" x 0.04"	15-87140
1/8" x 0.085"	15-87280
1/4" x 0.21"	15-87421

Silonite™ Tubing



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ENTECH
INSTRUMENTS, INC.
2207 Agate Court, Simi Valley, CA 93065
800/555-8034 FAX 805/527-5687

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- Flexible, allowing virtually any bend radius.
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Applications:

- GC Transfer Lines
- Sample Loops
- Chemical Analyzers
- GC Inlet Systems (P&T, Headspace, Thermal Desorption)
- Chemical Processing
- Cylinder/Canister Purging

Ordering Information

Size (Od x ID)	P/N:	Qty(ft.)	Price/ft.
1/32" x 0.02"	15-87020	5-24	$8.00
		25-199	$5.00
		200+	$3.60
1/16" x 0.04"	15-87140	5-24	$8.00
		25-199	$5.00
		200+	$3.60
1/8" x 0.085	15-87280	5-24	$8.00
		25-299	$5.00
		200+	$3.60
1/4" x 0.21"	15-87421	5-24	$11.00
		25-199	$7.00
		200+	$5.00

ENTECH 4600

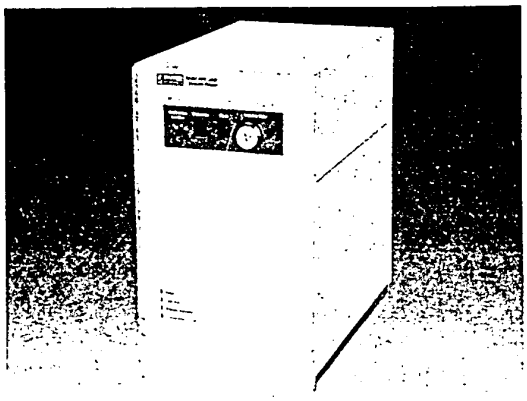
AUTOMATED DYNAMIC DILUTER

The analysis of Volatile Organic Compounds at ppm through sub ppb levels requires the generation of standards for instrument calibration. These standards can be prepared in passivated stainless steel canisters, Tedlar™ bags, or sorbent tubes, depending on the application to be calibrated. The most accurate procedure for obtaining ppb level standards is to dilute NIST-referenced standard mixtures contained in cylinders at low ppm levels. Accuracy can be maximized if the transfer is done under equilibrium conditions so initial losses on surfaces will not affect overall final concentrations. The only way to achieve this equilibrium is by performing dynamic dilutions.

The 4600 Dynamic Diluter

The 4600 Dynamic Diluter prepares analytical standards in canisters or Tedlar™ bags by blending 1-5 cylinders together with a diluent gas under mass flow control. The controlled flow streams are combined and then pass through a blending region to insure complete homogeneity before sampling into the canister or bag. The diluter can be given several minutes to reach equilibrium under the current temperature, pressure and flow before the stream is partially diverted into the storage receptacle. The remainder is vented out of a 35psig back pressure regulator which maintains a constant pressure in the manifold whether or not canister filling is occurring. Obtaining the required concentration at the outlet is done by setting up the method in the 4600 Windows™ application software and then down-loading to the diluter through the SmartLab® control network.

The 4600 can be ordered with a minimum of 2 mass flow controllers, one for diluent flow control (5000 sccm) and a second for a single standard cylinder (50 sccm). Additional flow controllers can be ordered for channels 3-6 which increase the number of cylinders being blended to 5. All MFC's have Kel-F seals to reduce impurities introduced into the flow path. The extra channels can be ordered with MFC's ranging from 10 to 1000 sccm.



Entech 4600

Sample Pressurizing

The 4600 can perform automated pressurizing of canisters to support static dilution standard preparation or to pressurize samples that were filled to less than 1 atmosphere during field sampling. A high accuracy sensor (± 0.3%) first measures the initial pressure, then fills to a requested final pressure and calculates the dilution factor. A second operating mode allows dilution by a constant factor of 1.5, 2, or 3 x. This conveniently eliminates the need to adjust concentration results separately for each sample. Pressurizing samples with a three component surrogate mixture can add further reliability to the results by validating the actual volume withdrawn from the sample canister during analysis.

Support for Static Dilution

The 4600 supports the preparation of custom standard blends when no cylinder standards are available. Static dilution option 4600-02 provides a convenient means for injecting a gas or liquid phase standard mixture directly into a canister while the 4600 software fills the canister with diluent or surrogate to a preset, final pressure. The extensive calculations required with this form of standard preparation are simplified using the Entech Standard Preparation software (ESP). Combining dynamic

and static dilution capabilities allows a laboratory to calibrate their GC or GCMS for virtually any VOC's needing to be quantified.

SmartLab® Control Interface

The 4600 is controlled using the Entech SmartLab® network. The interface includes screens for defining and running methods and for pressurizing samples or standards before analysis. Maximum flow rates for each channel can be changed for easy expansion or system optimization. The graphical interface simplifies operation and accelerates the user's understanding of operation principles.

Features

- Dynamically dilutes 2-6 cylinders (including diluent).
- Analytes well mixed before splitting into collection vessel.
- Maintains pressure, temperature, and flow equilibrium during canister filling.
- Controlled using SmartLab network.
- ESP software calculates flows in response to user requested concentrations.
- Optional canister sample pressurization feature for sample dilution and surrogate standard introduction.
- 2-Stage model (4620) allows dilution up to 1 million times for part-per-trillion standards generation.
- Start/Stop control of dilution process provided by 7100 Preconcentrator, giving freshly prepared standard on demand.
- Diluent can be pre-humidified for superior VOC transmission through manifold.
- All stainless steel interconnective manifold. Fused silica lined stainless manifolds available.

Part Number	Description
4600	Dynamic Diluter (with MFC's)
4620	2-Stage Dynamic Diluter (2 MFC's per stage)
45-10001	Control Network and Computer Interface
12-70010	10 Foot SmartLab Cable
12-70025	25 Foot SmartLab Cable
03-1xxxx	Extra MFC Channels with Kel-F Seals (xxxx specifies flow in standard cc/min)
11-20022	Extra SmartLab UNICARD PCB (required for 4 - 6 MFC's)
07-10040	Humidifying Chamber with Water Level Site Glass
4600-01	Canister Pressurizing Option
4600-02	Static Dilution Injector Kit
4600-03	Silonite Coated Internal Parts Option for Sulfur Anaylis
01-ESP	Entech Standard Preparation Software

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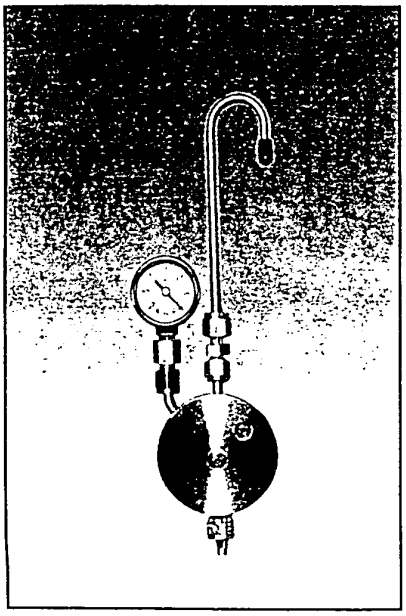
CS1200E Canister Sampler



Specifications:

OPERATING PRESSURE

Inlet:	Atmospheric
Outlet:	30" Hg Vac - 0 psig

TEMPERATURE RANGE

Operation: -10°C to 45°C
Cleaning: 20°C to 85°C

WEIGHT

1.6 lbs.

FLOW RESTRICTORS

		Fill Times (Hours)	
Code#	Part Number	6L Canister	0.4L MiniCan
1	39-23010	1	0.02 - 0.1
2	39-23030	3	0.1 - 0.3
3	39-23080	8	0.3 - 1
4	39-23240	24	1 - 3
5	39-24010	168 (1 week)	5 - 10

Features:

- Accurate filling of 6L stainless steel canisters with integration times from 1 hour to 1 week.
- Fills 400cc MiniCans in 3 minutes to 8 hours.
- Gauge built into controller for compact operation.
- Welded, electropolished sample flow path cleans up faster and is more leak tight.
- Sapphire flow elements provide stable operation from -10°C to 40°C.
- Replaceable glass frit filters maintain an inert flow path while eliminating particulates.
- Separate purge port allows fast cleanup without restrictor removal.
- Compatible with TM1000 battery operated digital timer for automatic start/stop field sampling.
- Silonite coating option for sulfur applications.

CS1200E Includes:

	Part Number
➤ Flow Controller	39-CS1200E-01
➤ Flow Restrictor	(see above)
➤ Glass Frit Filters	39-25100
➤ 30" Hg Vacuum Gauge	39-27500
➤ Electropolished 304 SS Inlet	39-CS1200E-02

Order the complete sampler using P/N 39-CS1200Ex, where x is the restrictor code listed above. For example, use P/N 39-CS1200E4 to receive a 24 hour, 6L canister passive sampler.

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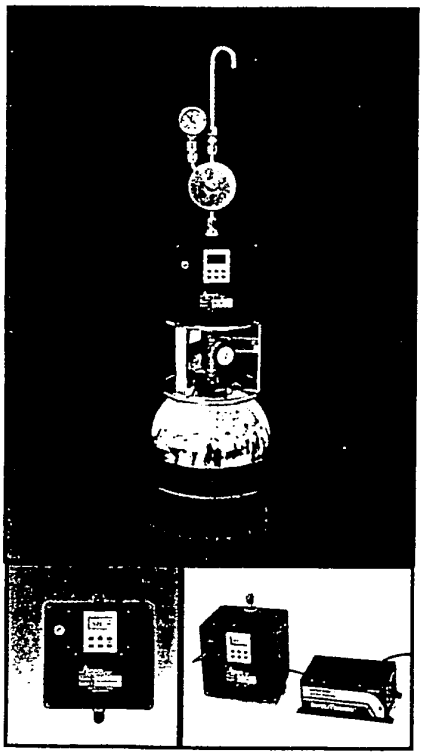
TM1000 Digital Timer



Top: TM1000 with 6L Canister and CS1200E flow controller. *Lower Right:* TM1000 being charged by TMR120.

The TM1000 is a low cost solution for automating VOC sampling into stainless steel canisters. Up to 10 start /stop events can be programmed to occur over a one week period with 1 minute sampling resolution. A low dead volume latching solenoid valve is used to turn flows on and off allowing long periods of operation with very little power consumption. A 12V battery is included that provides several weeks of operation and can be recharged without removal. The TM1000 is compatible with all common passive flow controllers, including the Entech model CS1200E (purchased separately).

Features:

- Compact, economical solution for timed sampling.
- One week timer with 1 minute resolution.
- Up to 10 start /stop events for simple or sophisticated sampling protocols.
- Latching valve prevents overheating and conserves power.
- 12V rechargeable battery (requires 39-TMR120 recharger).

Accessories:

Description	Part Number
➤ One Week Controller	39-TM1000
➤ 12 V Battery Recharger	39-TMR120
➤ Passive Flow Controller	39-CS1200E
➤ Locking Cabinet (30"x12 x13")	39-CAB1000
➤ 6L Fused Silica	29-10621

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ENTECH 3100

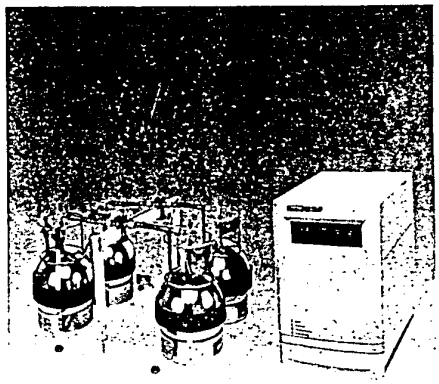
AUTOMATED CANISTER CLEANER

Fused silica lined stainless steel canisters are the preferred means of collecting VOC's at ppm to sub ppb levels in air for analysis in the laboratory. After sample analysis, the canisters must be cleaned for reuse by eliminating all gas-phase and surface bound contaminents. Failure to remove all of these contaminents will result in false-positive detection and poor quantification in future sampling events. In addition, heavier organics remaining in the canisters can result in build up on passivated surfaces which may increase VOC losses due to absorption.

The 3100 Canister Cleaner

The 3100 canister cleaning system adds simplicity and repeatability in the cleaning of SUMMA® and fused silica lined canisters. Multiple canisters are cleaned on a common manifold by cycling between evacuation and filling with clean air or nitrogen to "rinse" the contamination out of the canisters. Canister manifolds are made of 300 series stainless steel which eliminates VOC absorption during cleaning. Two on-line transducers monitor both pressure (0-50 psia) and vacuum (0-2000 mtorr) in the cleaning manifold. Three external canister manifold options are available, offering flexibility to research and production laboratories working with canisters and/or MiniCans.

During cleaning, canister evacuation is performed in two stages. The first stage utilizes a diaphragm pump to perform a rough evacuation of the canisters. A molecular drag pump then further reduces the vacuum down to the millitorr range. Both pumps are oil-free eliminating the need for isolation traps. After evacuation, canisters are refilled with humidified zero air or nitrogen to dilute any remaining impurities. Cycling between fill and evacuation effectively eliminates VOC contaminants.



Entech 3100 with a 4-Canister Manifold

Control of two separate heated zones is supported allowing method selection of canister cleaning temperatures when using the optional six 6L canister oven or the 21 position MiniCan heating mantle.

Silanizing / Surrogate Spiking

The 3100 can be configured to add surrogates or silanizing agents at the end of the cleaning process. Silanizing agents help to complete the passivation of fused silica-lined canisters and can improve stability of sulfur and nitrogen containing compounds. Silanizing also helps to restore inertness to surfaces after canisters have been exposed to harsh matrices.

Surrogates can also be automatically introduced at the end of the cleaning process. Introducing 0.001 atmospheres of a ppm level surrogate will result in ppb levels in the canister after field sampling providing validation of the sampling and analysis process with virtually no dilution of the sample.

Features

- Cleans up to 16 6L canisters or 42 MiniCans unattended.
- Choice of band heaters (105°C), six 6L canister ovens, or 21 MiniCan heater (140°C).
- Oilless pumps virtually eliminate potential for system contamination.
- Fill/evacuation cycling improves VOC removal.
- Digital representation of system pressure (0-50 psia) and vacuum (0-2000mtorr).
- Automatic leak-checking during cleaning.
- SmartLab® Windows-based control.
- Cleaning procedures easily defined, stored, and implemented.
- All stainless interconnective manifold.
- Option for introducing silanizing agents or surrogates.

Part Number	Description
Systems:	
3100	Cleaning System Controller
45-1000	Control Network and Computer Interface
07-10030	Humidification Chamber with Water Level Indicator
Pumps:	
10-20020	Dual Stage Diaphragm Pump
10-30020	Molecular Drag Pump (Internal to 3100)
Manifolds:	
3000-MN	4-Position Manifold (Order 1-4)
3000-MN8	8-Position "Stacking" Manifold (Order 1-2)
09-61006	6-Liter Canister Heaters (Order 1-16)
3121	21 Position MiniCan Cleaning Manifold
09-70010	Heated Enclosure for 3121
3000-OV6	Six Position 6L Canister Oven
Options:	
12-70010	10 Foot SmartLab Cable
12-70025	25 Foot SmartLab Cable
3100-01	Silane/Surrogate Spiking Option

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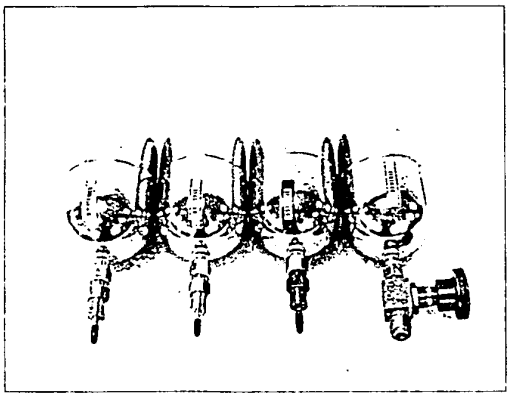
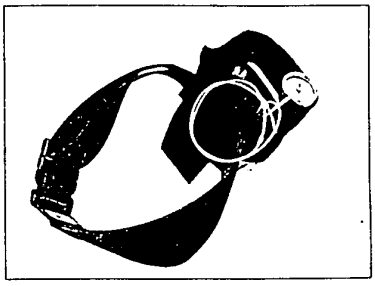
MC400/1000 MiniCan Canisters



Specifications:

Dimensions

	MC400	MC1000
Length:	7.3"	14.3"
Width:	2.75"	2.75
Volume:	0.4L	1.0L
Weight:	7.8 oz.	18 oz.



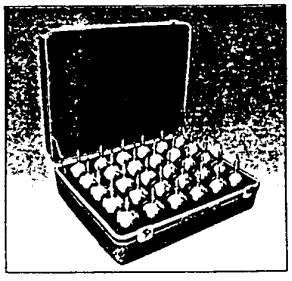
IH1200 MiniCan Personal Monitor

Features:

- No power needed for sampling. Vacuum draws in sample.
- Offers better recovery and QA than tube sampling technologies.
- Built in low volume quick connect fittings offer "no tool" connection to samplers, analyzers, and cleaning systems.
- Small size dramatically reduces storage space and shipping costs.
- Will not absorb VOC's. Can be cleaned and reused hundreds of times.
- Useable over a large concentration range.
- Durable and inexpensive.
- Silonite ™ coated MiniCans maximize recovery of all VOC's, including H2S and mercaptans.
- 21-position autosamplers and cleaning systems available for improved laboratory efficiency.

Applications:

- H2S & Mercaptans
- BTEX
- Landfill Gas
- Industrial Hygiene
- Personal Monitoring
- Indoor Air Quality
- Petroleum / Petrochemical
- Soil Gas
- Material Characterization
- Stack Gas
- Tank/Drum Head Space
- Site Investigation
- Ambient Air (MC1000L)



Carrying Case

Part Number	Description
29-MC400	0.4L Electropolished MiniCan
29-MC400L	0.4L Silonite™ MiniCan
29-MC400S	0.4L Silonite™ MiniCan for Sulfurs
29-MC400V	0.4L MiniCan w/ Nupro Valve
29-MC1000L	1.0L Silonite MiniCan
29-MC1000LV	1.0L Silonite MiniCan w/Nupro Valve
29-20000	0.4L MiniCan Carrying Case

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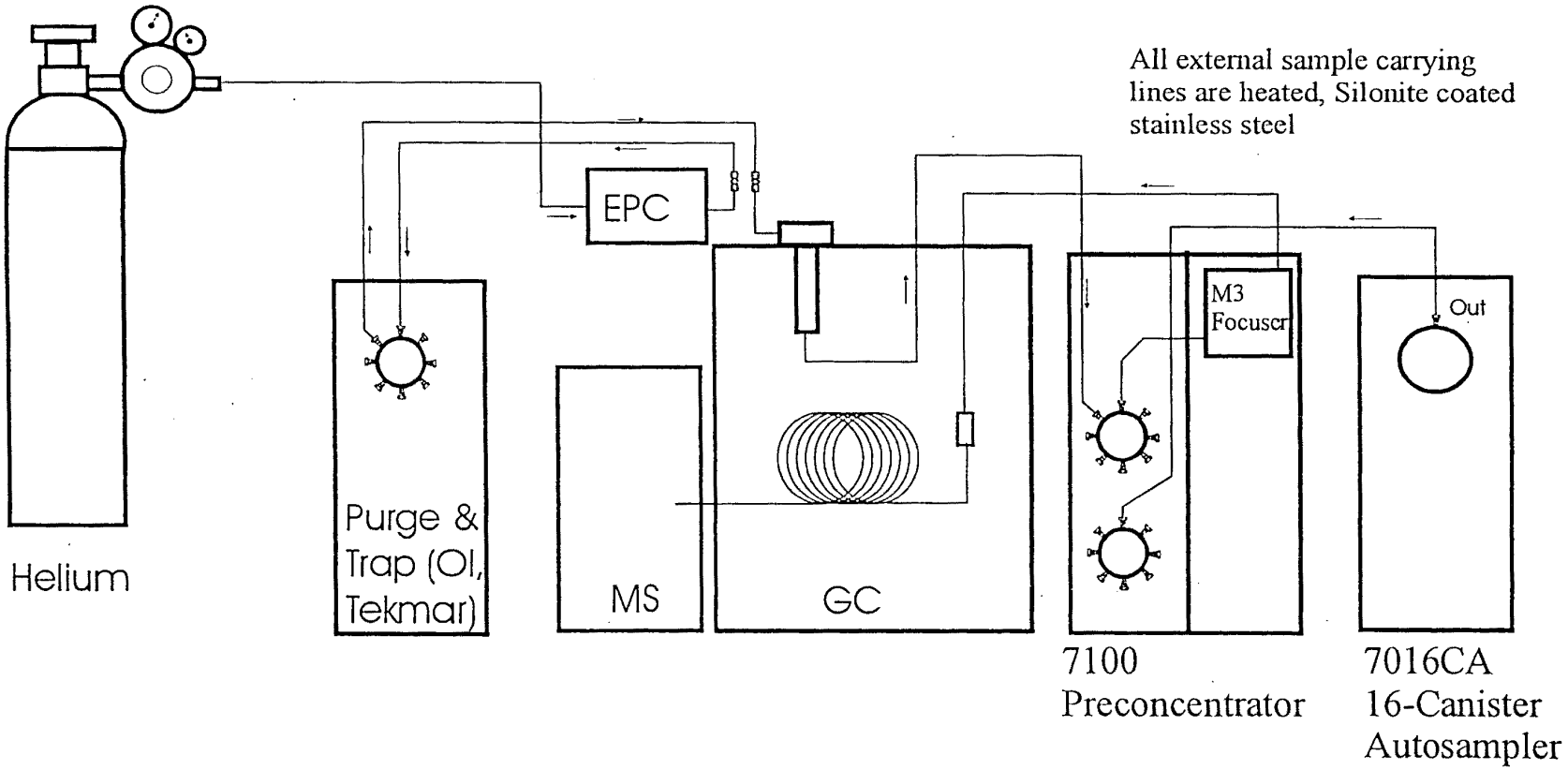
Plumbing the 7100 Air Preconcentrator into an HP597x/Purge & Trap System



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TO-14 Application Note

Bahman "Bob" Moezzi, Michael R. Winward,
Daniel B. Cardin
Entech Instruments, Inc.
Simi Valley, CA

Abstract

The Entech Model 7100 automated air concentrator and HP 5973 GCMS have been evaluated to show they meet the requirements of EPA Method TO14. Calibration and internal standards were prepared in stainless steel canisters and used to determine system reproducibility and method detection limits. The correlation coefficients showed excellent linearity between the five points for all compounds.

A method detection limit (MDL) study was performed using seven replicate injections and the MDLs were calculated. The values were in the range of 15 to 70 parts per trillion (ppbtv) for most compounds indicating that the VOC's listed in EPA Method TO14 could be analyzed at concentrations present in ambient air.

Introduction

Air pollution is an important global problem, especially in developing countries. A major part of air pollution is due to the presence of volatile organic compounds which are themselves toxic and may contribute to ozone formation.

In order to determine the concentration of volatile organic compounds (VOC's) in ambient air, samples can be collected in passivated stainless steel canisters and analyzed by Gas Chromatography/Mass spectrometry (GC/MS). Due to the low concentrations of VOC's in ambient air (generally sub-PPB), samples must be concentrated prior to analysis in order to detect the VOC's present.

The procedure for sampling and analyzing VOCs in ambient air is described in EPA Method TO14. The air is collected in passivated stainless steel canisters and analyzed by GC/MS. The toxicity of some VOC's has resulted in legislation mandating very low detection limits, in parts per trillion, for these compounds. Until recently, however, these very low detection limits could not be achieved. The presence of moisture and CO_2 in the sample, difficulties in managing large sample volumes, and limitations in GC/MS sensitivity are among the problems associated with reaching sub-PPB detection limits.

The application presented here describes an Entech Model 7100 air concentrator attached to a HP 6890/5973 GC/MS system. The Entech 7100 performs the concentration of VOC's with excellent water and CO_2 management and is capable of accurate measurement of small or large sample volumes with very good precision. It can be equipped with one or two 16 position autosampler(s) for unattended operation.

The SmartLab software controlling the preconcentator generates an extensive QA/QC report for each sample concentration performed, recording all actual runtime parameters. This QA/QC report can easily be accessed and can be used as a very useful diagnostic tool.

Experimental Parameters

The instrumental parameters are summarized in *Table 1.*

Table 1. Instrumental Parameters

Entech 7100 Concentrator

Module	Trap	Trap Temp(C)	Preheat Temp (C)	Desorb Temp (C)	Bake Temp (C)	Bake Time (Min)
1	Glass Bead	-150	20	20	130	5
2	Tenax	-50	----	180	190	5
3	Cryofocusing	-150	----	50-70	50-70	2

Additional Parameters:

Module 2 Desorb Time (min):	3.5
Module 3 Inject Time (min):	2

HP 6890 GC

Oven

Initial Temp:	35 C
Initial Time:	5 min
Ramp 1:	5 deg. C per min to 150 C
Ramp 1 Final Time:	0 min
Ramp 2:	15 deg C per Min to 220 C
Ramp 2 Final Time:	2 min

Column

HP-1 Methyl Siloxane
Length: 50 m, Diameter: 0.32 mm, Film Thickness: 1.0 um
Column Flow rate: 1.5 ml per min (constant flow)

HP 5973 MSD

Tune:	BFB autotune
Scan Parameters:	30 to 180 a.m.u., A/D = 2^4 for the first 6 minutes
	33 to 260 a.m.u., A/D = 2^3 for the rest of the run
Threshold:	150 counts
Solvent Delay:	none
EMV:	+200 over tune setting
Quad Temp:	150 deg C
Source Temp:	230 deg C

Tuning and Calibration

The tuning of the mass spectrometer was performed using the automated tune routine of the HP ChemStation software and was tuned to BFB (bromofluorobenzene) specifications.

Full scan data was collected to allow mass fragmentation patterns to be compared to an NIST spectral library for verification of compound identity. The mass spectrometer is initially set to start scanning at 30 amu to allow detecting of light compounds in the sample, such as methanol and hydrogen sulfide. After 6 minutes, the scan range is changed to 33-260 amu to avoid over exposure of the mass spectrometer electron multiplier to residual oxygen (32 amu) in the source.

For the calibration of the mass spectrometer, a certified TO14 gas standard from Matheson Gas Products containing 39 compounds in the mixture was used. The nominal concentration of each component of this mix was 1 ppm. This standard was diluted to 10 ppbv using an Entech Model 4600 Dynamic Diluter. A gas mixture of 4 internal standards (IS) and 3 surrogate compounds with a concentration of 20 ppbv for each compound was prepared and analyzed with all blanks, calibration standards, and samples. A five-point calibration was performed by analyzing 10, 40, 100, 400, and 1000 ml volumes of the 10 ppbv working standard. Small volume pressure compensation was used to correct any offset in volumes introduced due to sample pre-pressurization into the "non-zero" trap volumes, particularly when loading the 10 and 40 ml standard volumes. Using a nominal volume of 400 ml for sample analysis, the above volumes used for calibration correspond to a range of 0.25 to 25 ppbv. *Figure 1* shows the total ion chromatogram obtained when preconcentrating a 400 ml volume of 10 ppbv TO14 standard. *Figure 2* is a chromatogram of a blank run including 100 ml of internal standard and surrogate compounds at 20 ppbv.

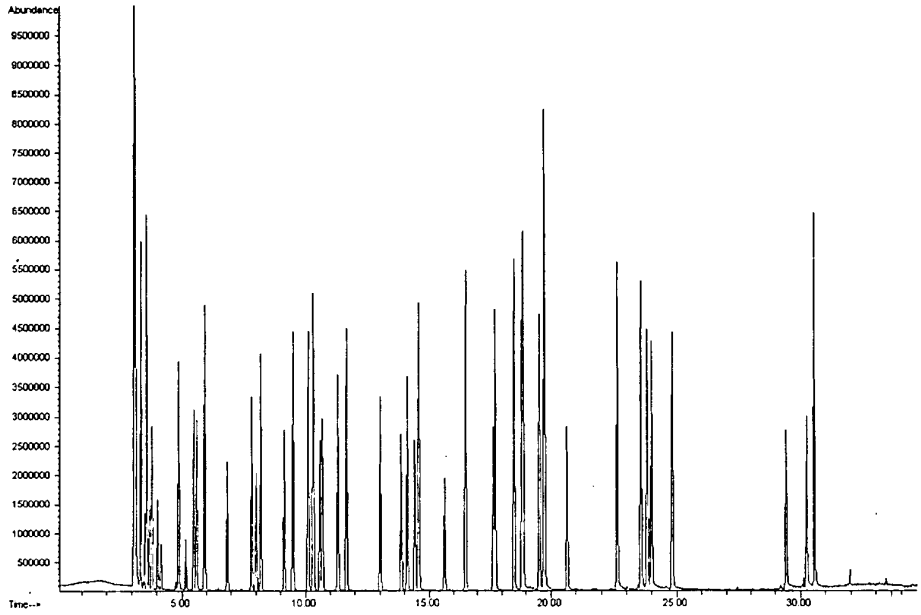


Figure 1
400cc of 10ppbv TO14 Standard

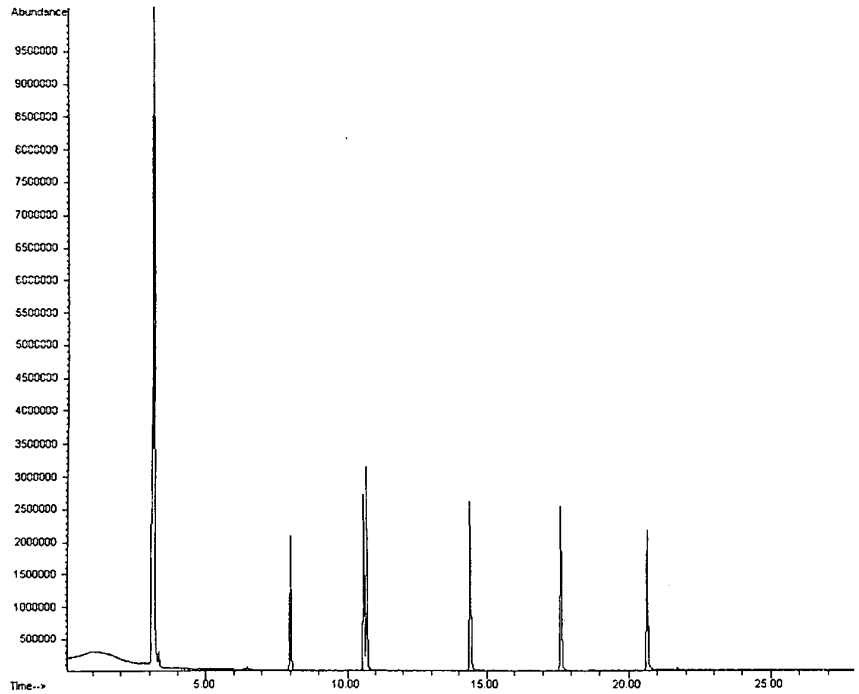
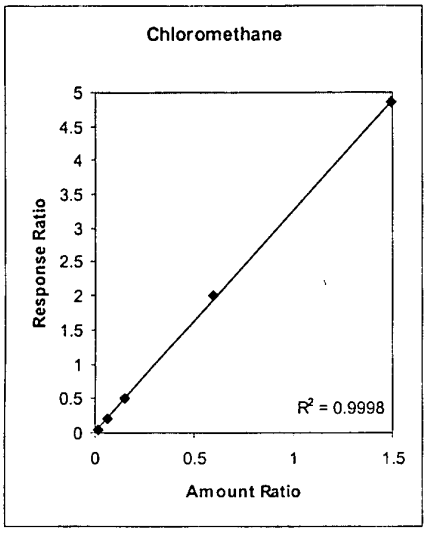


Figure 2
Blank Run

The calibration data for each compound were fitted to a line using the linear least square option in the HP ChemStation software. The correlation coefficients for the equations of all compounds were in the range of 0.999 to 1.000, except for one which was 0.995. These are very good results bearing in mind the wide range of concentration covered. The excellent correlation coefficients obtained demonstrate the ability of the 7100 preconcentrator to trap variable volumes reproducibly and deliver the VOCs quantitatively to the GCMS. Correlation coefficients are listed in *Table 2*. The calibration curves of a few compounds are shown in *Figure 3*.

Table 2. Correlation Coefficients

Compound	Retention Time	Correlation Coefficient
Dichlorodifluoromethane (Freon 12)	3.38	0.995
Chloromethane	3..51	1.000
1,2-Dichloro-1,1,2,2-tetrafluoethane (Freon 114)	3.61	0.999
Vinyl Chloride	3.70	1.000
Bromomethane	4.04	1.000
Chloroethane	4.19	1.000
Trichlorofluoromethane (Freon 11)	4.88	0.999
1,1-Dichloroethene	5.49	1.000
Methylene Chloride	5.60	1.000
Trichlorotrifluorethane (Freon 113)	5.93	1.000
1,1-Dichloroethane	6.85	1.000
cis-1,2-Dichloroethene	7.84	1.000
Chloroform	8.20	1.000
1,2-Dichloroethane	9.15	1.000
1,1,1-Trichloroethane	9.51	1.000
Benzene	10.12	0.999
Carbon Tetrachloride	10.33	1.000
1,2-Dichloropropane	11.30	1.000
Trichloroethene	11.65	0.999
cis-1,3-Dichloropropene	13.00	1.000
Trans-1,3-Dichloropropene	13.86	1.000
1,1,2-Trichloroethane	14.11	1.000
Toluene	14.57	0.999
1,2-Dibromoethane	15.63	1.000
Tetrachloroethylene	16.50	0.999
Chlorobenzene	17.73	1.000
Ethylbenzene	18.50	0.999
m,p-Xylene	18.87	0.999
Styrene	19.54	1.000
1,1,2,2-Tetrachloroethane	19.72	0.999
o-Xylene	19.74	0.999
1,3,5-Trimethylbenzene	22.65	1.000
1,2,4-Trimethylbenzene	23.57	1.000
1,3-Dichlorobenzene	23.82	1.000
1,2-Dichlorobenzene	24.00	1.000
1,4-Dichlorobenzene	24.82	1.000
1,2,4-Trichlorobenzene	29.43	0.999
Hexachloro-1,3-Butadiene	30.56	0.999



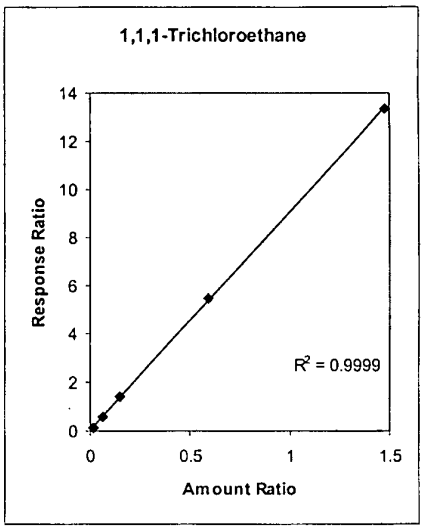
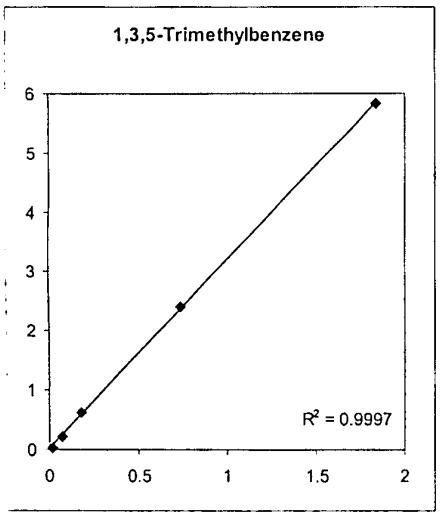
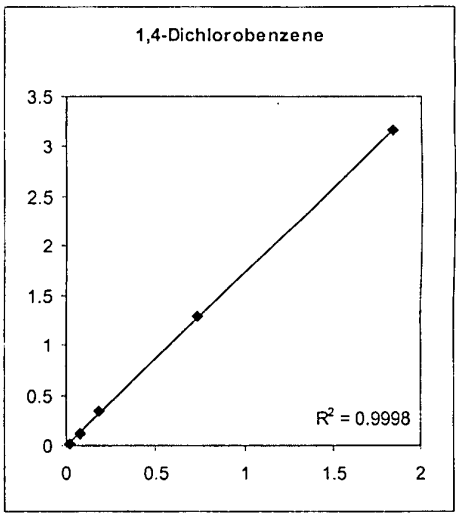


FIGURE 3





The TO14 working standard in a passivated stainless steel canister showed very good stability and no sign of deterioration during a period of 3 months.

Method Detection Limit Study

The method detection limits (MDL's) were determined by analyzing a low concentration TO14 standard seven times. In general, when doing MDL studies, a concentration of about 5 to 10 times greater than the expected MDL is used.

Seven replicate analyses were made by preconcentrating 100 mls of a 2 ppb standard to provide GCMS injection amounts equivalent to a 0.5 ppbv sample using the standard 400 cc volume. *Table 3* lists the expected concentration values along with the experimental values found for the TO14 compounds. In addition, the standard deviation (SD), MDL, and relative standard deviation (RSD) for each compound are tabulated in *Table 3*.

Internal Standards	Spike	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Average	S.D.	R.S.D.	MDL
1) Bromochloromethane		3667162	3756240	3530479	3524668	3559721	3542955	3509181	3584344	92049	3%	
17) 1,4-Difluorobenzene		14942367	15002683	14523439	14039643	14179460	14310568	13861642	14408543	437500	3%	
30) Chlorobenzene-d5		9838654	9941971	10484164	9330425	9012255	10066377	9302327	9710882	515399	5%	
43) 1,2-Dibromobenzene		3109859	3110723	3340881	2838287	3030643	3237331	2805079	3067543	195791	6%	
Surrogates												
20) Fluorobenzene		20.13	20.30	20.03	20.06	20.05	20.18	20.42	20.17	0.146	1%	
26) Toluene-d8		18.21	18.40	19.98	18.56	18.08	19.26	18.63	18.73	0.669	4%	
37) 4-Bromofluorobenzene		16.97	17.64	18.93	17.34	17.44	18.31	18.15	17.83	0.672	4%	
Target Compounds												
2) Dichlorodifluoromethane	0.57	0.64	0.67	0.64	0.65	0.66	0.66	0.66	0.65	0.011	2%	0.036
3) Chloromethane	0.60	0.64	0.65	0.62	0.63	0.65	0.61	0.63	0.63	0.015	2%	0.047
4) 1,2-Dichloro-1,1,2,2-tetrafluroethane	0.59	0.57	0.60	0.59	0.60	0.60	0.60	0.59	0.59	0.011	2%	0.035
5) VinylChloride	0.60	0.56	0.59	0.59	0.58	0.58	0.59	0.58	0.58	0.011	2%	0.034
6) Bromomethane	0.56	0.45	0.45	0.45	0.45	0.46	0.44	0.44	0.45	0.007	2%	0.022
7) Chloroethane	0.62	0.59	0.60	0.59	0.60	0.61	0.59	0.59	0.60	0.008	1%	0.025
8) Trichlorofluoromethane	0.60	0.60	0.61	0.61	0.60	0.62	0.61	0.59	0.61	0.010	2%	0.031
9) 1,1-Dichloroethene	0.57	0.54	0.56	0.56	0.56	0.56	0.55	0.55	0.55	0.008	1%	0.025
10) MethyleneChloride	0.66	0.63	0.67	0.64	0.65	0.63	0.64	0.64	0.64	0.014	2%	0.043
11) Trichlorotrifluoroethane	0.60	0.60	0.59	0.60	0.60	0.59	0.58	0.59	0.59	0.008	1%	0.024
12) 1,1-Dichloroethane	0.58	0.56	0.57	0.57	0.57	0.57	0.57	0.56	0.57	0.005	1%	0.015
13) cis-1,2-Dichloroethene	0.58	0.53	0.56	0.58	0.56	0.55	0.55	0.54	0.55	0.016	3%	0.050
14) Chloroform	0.63	0.62	0.66	0.65	0.64	0.63	0.66	0.65	0.64	0.015	2%	0.047
15) 1,2-Dichloroethane	0.59	0.53	0.55	0.53	0.52	0.54	0.53	0.53	0.53	0.010	2%	0.030
16) 1,1,1-Trichloroethane	0.59	0.56	0.57	0.58	0.56	0.57	0.55	0.56	0.56	0.010	2%	0.031
18) Benzene	0.60	0.57	0.61	0.58	0.58	0.58	0.58	0.60	0.59	0.014	2%	0.044
19) CarbonTetrachloride	0.59	0.55	0.58	0.56	0.57	0.57	0.55	0.56	0.56	0.011	2%	0.035
21) 1,2-Dichloropropane	0.61	0.59	0.59	0.60	0.59	0.60	0.60	0.59	0.59	0.005	1%	0.017
22) Trichloroethene	0.61	0.67	0.70	0.68	0.68	0.67	0.67	0.68	0.68	0.011	2%	0.034
23) cis-1,3-Dichloropropene	0.52	0.30	0.29	0.30	0.28	0.29	0.30	0.28	0.29	0.009	3%	0.028
24) trans-1,3-Dichloropropene	0.55	0.23	0.23	0.25	0.23	0.21	0.22	0.22	0.23	0.013	6%	0.039
25) 1,1,2-Trichloroethane	0.62	0.56	0.57	0.62	0.55	0.57	0.58	0.56	0.57	0.023	4%	0.072
27) Toluene	0.64	0.56	0.56	0.57	0.56	0.56	0.58	0.54	0.56	0.012	2%	0.038
28) 1,2-Dibromoethane	0.58	0.40	0.41	0.44	0.40	0.40	0.42	0.38	0.41	0.019	5%	0.059
29) Tetrachloroethylene	0.64	0.57	0.60	0.61	0.58	0.59	0.61	0.59	0.59	0.015	3%	0.047
31) Chlorobenzene	0.63	0.60	0.58	0.59	0.59	0.61	0.58	0.57	0.59	0.013	2%	0.042
32) Ethylbenzene	0.65	0.55	0.53	0.55	0.55	0.55	0.55	0.52	0.54	0.013	2%	0.039
33) m,p-xylene	1.24	1.03	0.98	1.04	1.06	1.04	1.05	0.99	1.03	0.030	3%	0.095
34) Styrene	0.63	0.33	0.34	0.37	0.37	0.36	0.37	0.35	0.36	0.016	5%	0.051
35) 1,1,2,2-Tetrachloroethane	0.65	0.56	0.54	0.54	0.60	0.59	0.57	0.56	0.57	0.023	4%	0.072
36) o-Xylene	0.65	0.53	0.50	0.51	0.55	0.56	0.53	0.51	0.53	0.022	4%	0.070
38) 1,3,5-Trimethylbenzene	0.74	0.49	0.48	0.47	0.53	0.54	0.49	0.48	0.50	0.027	5%	0.084
39) 1,2,4-Trimethylbenzene	0.70	0.46	0.42	0.44	0.48	0.45	0.44	0.42	0.44	0.021	5%	0.067
40) 1,3-Dichlorobenzene	0.73	0.53	0.51	0.52	0.53	0.53	0.51	0.50	0.52	0.012	2%	0.038
41) 1,2-Dichlorobenzene	0.71	0.45	0.40	0.45	0.44	0.42	0.41	0.44	0.43	0.020	5%	0.063
42) 1,4-Dichlorobenzene	0.74	0.58	0.55	0.56	0.61	0.60	0.56	0.56	0.57	0.023	4%	0.072
44) 1,2,4-Trichlorobenzene	0.65	0.54	0.52	0.51	0.51	0.56	0.50	0.58	0.53	0.030	6%	0.093
45) Hexachloro-1,3-Butadiene	0.55	0.78	0.76	0.69	0.77	0.78	0.72	0.75	0.75	0.034	4%	0.106

The MDL values found are in the range of 15 to 100 pptv. Since MDL's are based on precision, the calculated MDL's show an excellent reproducibility for Entech 7100/HP 5937 analytical system. These MDL's exceed EPA TO14 requirements and Contract Laboratory Program (CLP) contract required quantitation limits (CRQLs).

Conclusion

This study shows the superb performance of Entech Model 7100 preconcentrator in terms of accuracy and precision for EPA Method TO14 Compounds. The volume measurement accuracy was demonstrated by the very good agreement between the chromatographic peak areas and the volume of TO14 standard from 10 to 1000 mls. The consistency in the GCMS response for sample volumes up to 1000 mls indicates the ability of the 7100 Preconcentrator to remove most of the water used to humidify the TO14 standard without loss of analytes.

VOC Preconcentration Theory

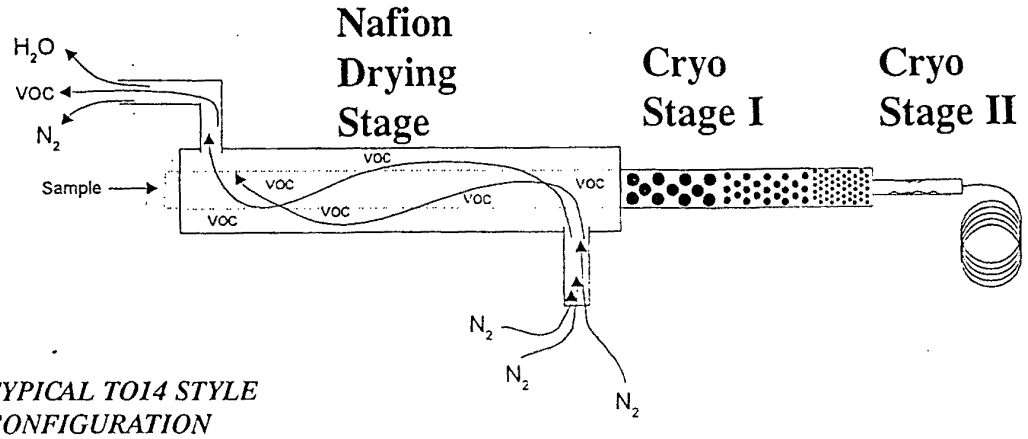
Technical issues that set the stage for practical solutions

By

Daniel B. Cardin

The analysis of Volatile Organic Compounds, or VOC's, at levels found in urban air requires an initial sample preconcentration to reach the detection limits imposed by EPA methods TO14 and TO15 (roughly 0.2 ppbv) using GC and GC/MS analysis. Enrichment of the VOC concentrations relative to the fixed gases found in air is accomplished by passing a known volume of air through a trap that selectively retains the organics while allowing bulk gases (primarily N_2, O_2, Ar) to pass through unimpeded. If a trap packing is used that has a low affinity for the targeted analytes, a reduction in the trapping temperature is required for quantitative retention of the VOC's on the trap. This increases the affinity for surfaces by decreasing vibrational and kinetic energies that would otherwise keep these compounds mobile. When a very weak sorbent is used, such as glass beads, the trapping temperature must be between -100 to -180°C depending on the list of analytes targeted. For TO14, a trapping temperature of -150°C is recommended. Sorbents for which VOC's exhibit higher affinity can perform the same sample enrichment near or at room temperature. Examples of such sorbents include Tenax and activated charcoal. The stronger the sorbent, the higher the necessary desorption temperature for recovery of the trapped organics. A minimum temperature difference between trapping and desorption of 150°C is common, although stronger sorbents such as Carbon Molecular Sieve can require desorption temperatures in excess of 300°C after ambient temperature sample collection.

To quantify the levels of VOC's in air, the mass of sample concentrated must be determined. It is often convenient to refer to a sample aliquot in terms of its volume rather than its mass, although it is assumed that this volume has been corrected to standard temperature and pressure (STP). Withdrawing a known standardized volume from a SUMMA-passivated canister is complicated by the varying pressures found in different canister samples. Two techniques have been developed and used routinely to measure sample volumes. The first determines sample mass indirectly by measuring the pressure difference in a vacuum reservoir of known volume before and after sample concentration. The reservoir is placed downstream of the trap and collects the major air components (N_2, O_2, Ar) that do



TYPICAL TO14 STYLE CONFIGURATION

not condense in the trap. The STP volume is calculated by the formula:

VT = (PD/14.696) x VR

where VT is Volume Trapped, PD is Pressure Differential in the reservoir before and after sampling, and VR is the Volume of the Reservoir.

A second measurement technique utilizes a Mass Flow Controller (MFC) to directly determine standardized volume per unit time. In practice, flow rate is converted to a volume either by waiting a required period of time or directly by integrating the actual flow output from the MFC. Integrating an MFC's output has the advantage of allowing sample volumes to be changed more easily and can also more readily detect trapping flow rate upsets due, for example, to excessive ice formation in the primary cryogenic trap. MFCs also allow the flow rate to remain constant during trapping unlike the vacuum reservoir technique where trapping flow rate drops as the pressure difference between the sample and vacuum reservoir decreases.

Water also has to be managed when concentrating large volumes. Roughly 18µl of water is recovered from every liter of sample concentrated that was initially at 70% Relative Humidity (RH) at 25°C. Since typical sample sizes are about 500cc, 9µl of water could end up on the analytical column and in the detector if not removed during preconcentration. That much water can foul up chromatographic resolution, reduce column life, and degrade performance of detectors. In particular, injections of over 1µl of water into a typical benchtop mass spectrometer will cause attenuation of analytes that co-elute with the water peak. The amount of sample at 70% RH that can be concentrated without water management/removal then is roughly 50-70cc.

Nafion Dryers have been utilized to remove moisture from air samples before initial concentration. Generally, a 1/16" OD x 4' length of Dupont engineered Nafion polymer is placed within a larger 1/8" tube to allow dry air to flow around the semipermeable polymer membrane. The humid air sample will hydrate the polymer and water will ultimately be transferred to the dry air stream in an attempt to set up an equilibrium water vapor pressure. Countercurrent flow of dry air through the dryer causes the sample leaving the dryer to be exposed to the driest section of the polymer.

Unfortunately, any compounds of interest are also lost in the Nafion Dryer due to both active and passive mechanisms. VOC's with -OH groups are lost almost quantitatively while other water-soluble compounds absorb into the membrane at rates that are dependent on the current level of hydration of the membrane making quantitation difficult. Also, since the Nafion polymer is relatively porous, light VOC's

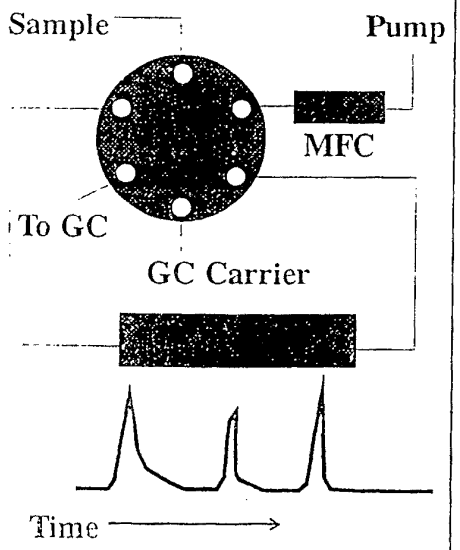
can diffuse through it adversely affecting their analytical precision and detection limits.

Alternate water management techniques have been developed that do not share limitations imposed by Nafion Dryers. Some of these are covered in the following sections.

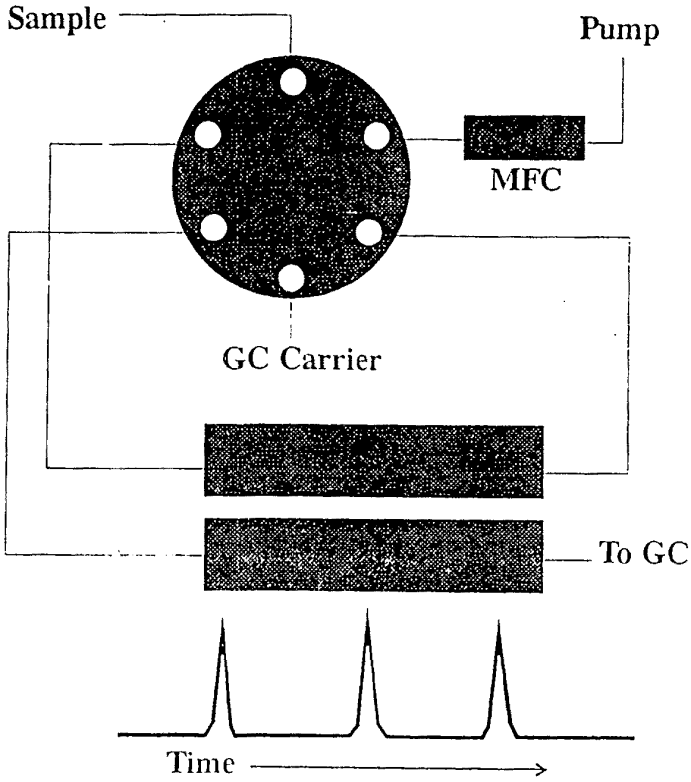
Single Stage Concentrations

One stage concentrations require the least amount of sophistication to perform as they simply use a single trap from which desorption is made directly onto the column. Pre-elimination of water using a Nafion Dryer may also be performed but does not constitute a concentration stage. Because of the volume of the 1/8" trap typically used for initial sample trapping, single stage concentrations require high column flow rates (>8cc/min) during desorption to allow rapid injection onto the analytical column. Even with high flow rates, however, a certain degree of peak tailing can be expected due to mixing in the high volume trap as desorption is occurring. This is similar to the "non-plug" flow that occurs if light VOC's are first desorbed into a GC injector rather than directly onto the analytical column.

SINGLE STAGE



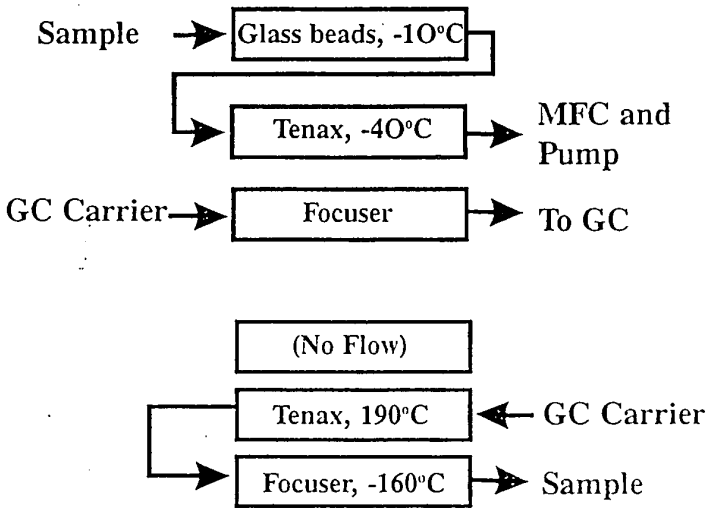
TWO STAGE



Two Stage Concentrations

To improve chromatographic resolution, a second concentration stage can be implemented to further reduce the sample volume. Using a megabore column (.53mm ID), the volume can be reduced to less than .01cc. Injections from this volume will occur very rapidly even at 1cc/min column flow rates. Combined with a Nafion Dryer, 2-stage concentrations provide an excellent approach for concentration and analysis of nonpolar and semi-polar VOC's.

COLD TRAP DEHYDRATION



Cold Trap Dehydration

As an alternative to Nafion Dryers, water can be removed by passing the sample through a cold region which promotes water condensation. The cold trap is held at a temperature between 0° to -50°C and is either unpacked or filled with glass beads. Cold Trap Dehydration can be an effective water management technique for analyzing polar and non-polar VOC's, especially in the presence of high CO_2 concentrations. Passing the sample first through a glass bead trap at -10 deg C will eliminate a sufficient amount of water to collect a 500cc sample for GC/MS analysis. A second trap, in line with the first, containing Tenax TA at -40 deg C will effectively trap the volatile organics while letting the CO_2 pass through to the mass flow controller and pump.

Although it can be applied to all air matrices, this technique is especially well suited for landfill gas, stack gas, and other sample types containing CO_2 levels in the 0.1 - 50% range.

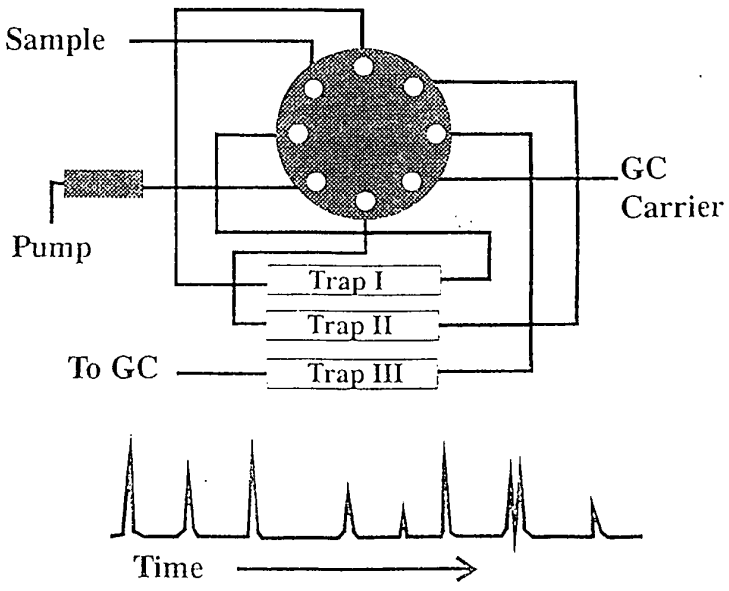
3-Stage Concentrations

The elimination of water vapor without the loss of polar VOC's is facilitated by adding a third concentration, or separation stage.

Microscale Purge And Trap

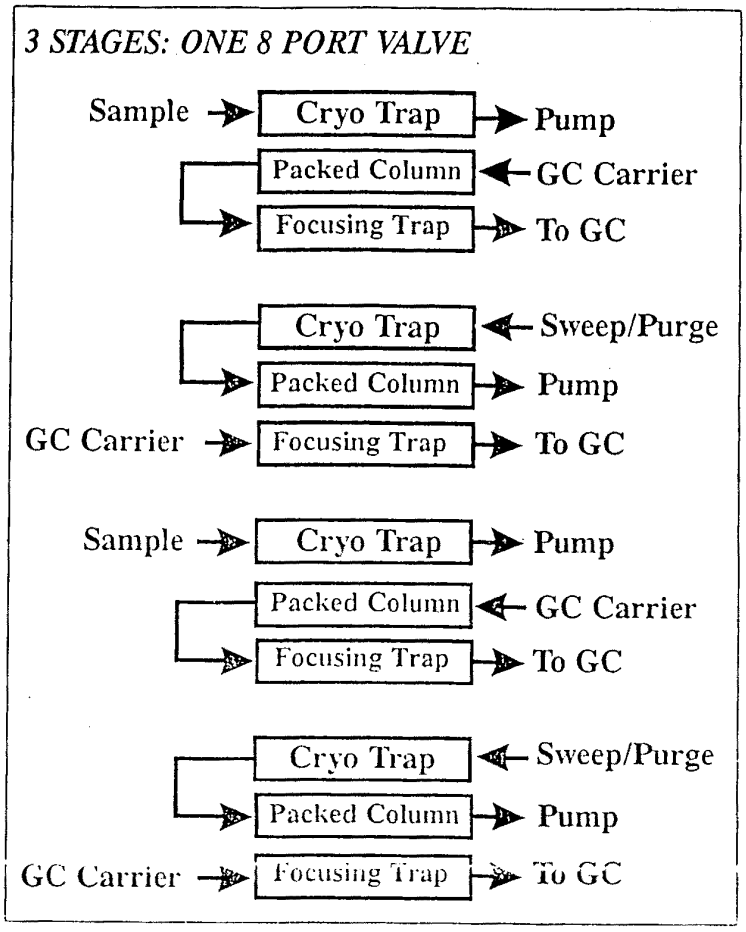
VOC's in ambient air exist at levels which are at least three orders of magnitude below their saturation point. Therefore, assuming there are no adsorptive surfaces, VOC's from a 1000cc sample volume should volatilize into a 1cc volume at room temperature after concentration if allowed to come to equilibrium. If this volume is actually flushed with 40 cc of inert gas at room

THREE STAGE



temperature, the VOC's could be quantitatively transferred to the gas phase. This is similar to the principle behind Purge and Trap Analysis of water samples. In the case of air, however, initial trapping of 1000cc would only yield 15-20µl of water rather than the 5000µl used in water analysis. The distribution of the condensed water on the glass beads in the trap should further facilitate the transfer of VOC's to the gas phase (i.e. the rate at which equilibrium is achieved).

A 3-stage concentration technique called Microscale Purge and Trap has been developed to analyze nonpolar VOC's in humid air. It is analogous to the Purge and Trap used in water analysis, only on a much smaller scale. The air sample is first concentrated to about a 0.5cc volume in a cryogenic trap. The trap is then heated to roughly room temperature and is held there while slowly passing helium or nitrogen through it to transfer these compounds to a secondary trap. The second trap is usually Tenax at about -10°C. Sweeping the VOC's from the first to the second trap with only 40cc of helium results in a transfer of less than 1 µl of water (40cc @ 100%RH) which can be handled quite readily by benchtop mass spectrometers. After transfer to the second trap, the VOC's can be back-flushed while heating to be further focused on an open-tubular focusing trap for rapid injection onto the analytical column.



Internal Standard Addition

Internal Standard is added directly to the first stage cryogenic trap either under mass flow control or by using a loop of known volume. MFC-controlled introduction is advantageous over loop injection as it remains consistent with the mechanism used to measure the sample volume. Since it is the ratio of the response of analyte to internal standard that is important, a short term drift in the mass flow controller output will be canceled out if the MFC is measuring both the sample and internal standard. If the MFC is just measuring the sample volume, an error could be introduced by any changing MFC response. This approach also reduces by one the number of rotary valves needed by the system.

Matrix Spiking

Matrix spiking can be an important investigative tool for discerning the effects that an actual air matrix has on analyte

response and detection limits. When small amounts of the target compounds are added to a sample containing varying concentrations of methane, water and CO_2, a challenge is placed on the analytical system that transcends the task of obtaining response factors from clean standards in a pristine nitrogen matrix. Water and CO_2 can affect trapping performance or cause pressure upsets upon desorption which can cause peak splitting or tailing. In addition, they may cause analyte retention time shifting and interference in the mass spectrometer. The only sure way to determine that target analytes are indeed detectable at 0.2 ppb is to co-inject a 0.2 ppb standard into an actual air sample. As a close approximation to direct canister introduction, the targets, sample and internal standard can be sequentially added to a preconcentrator. The original sample is, therefore, left unchanged.

Checking for matrix effects is obviously not necessary for every sample analyzed. However, new samples obtained from untested sources should be investigated thoroughly before assuming that matrix interferences will be insignificant.

System Leak Checking

The primary source of error in an otherwise properly designed preconcentration system is the presence of undetected leaks. Leaks can cause room air to get into the system resulting in high system blanks. It can also cause sample volumes to be incorrectly measured. In the case of 16-position autosamplers, a leak in the fittings connected to the canisters can permit all of the sample to leak out while waiting several hours for that position to deliver a sample into the preconcentrator. Worse yet, if the canister was originally at subatmospheric pressure, laboratory air can leak in allowing introduction of some solvents that may be several hundred times higher in concentration than in the original sample. Verification of a leak-free system can be done by pulling a vacuum throughout the system right up to the canister while the canister valve is closed. Isolating the system from the pump and recording the initial vacuum provides a baseline to which any pressure rise can be compared. Waiting a minute or so should be sufficient to see any pressure increase caused by a leak. Repeating for each of the autosampler positions where a canister sample is attached is facilitated by using commercially available automated preconcentrators that support this pressure tesing feature.

Quality Assurance

Verifying data quality is essential to any laboratory performing quantitative sample analyses. Failure to take all measures reasonably possible to assure that data reported by a laboratory is accurate places the reputation of that laboratory at risk.

The quality of a sample analysis can often be determined by adding surrogate standards to the sample before sample preparation and then assessing recovery relative to previous analyses or calibrations. Surrogate addition to SUMMA canisters can be more difficult than with waters and soils because the surrogate must pass through the canister isolation valve which could retain some of the high concentration spike if insufficiently flushed. Unfortunately, sufficient flushing can also further dilute the sample thereby affecting detection limits. Even with surrogates, information afforded the analyst is generally limited to whether the analysis worked or not, without answering the question "What went wrong?" if, indeed there was a problem.

The age of intercomputer connectivity offers a more elegant and sophisticated solution to quality assurance. These days, it is not enough for a microprocessor-based system to simply turn valves on and off while controlling temperatures and flows. The technology is available to feed this information back to the host "Data System" in the form of a report that shows what happened during every stage of an unattended TO14/TO15 preconcentration. Therefore, it is possible to maintain a record of the concentration data showing parameters such

as sample pressures, temperatures, and flow rates, Internal Standard pressures and flow rates, and trapping and desorption temperatures. Combined with the information a knowledgeable analyst can extract from GC or GC/MS data (chromatograms, calibration reports, control charts), there should be fewer analytical problems that go undetected.

System Contamination Concerns

Ambient level concentrations are typically quantified in the range of 1-100 ppbv, although TO14 blank certification is required down to 0.2 ppbv. Sampling locations range from Industrial/Urban atmospheres to low level tropospheric sampling far removed from any local sources. Conversely, source sampling involves collection directly at the site of VOC emission (stacks, landfills, etc.) where concentrations can be hundreds to millions of times higher. Based on a maximum carryover of 0.1% in a well designed system, one could expect to analyze a sample 1000 times higher than the 0.2 ppbv allowable TO14 blank level and still obtain a clean blank on the subsequent run. This would easily cover the expected ambient concentrations of VOC's. As pointed out, however, source level concentrations can be thousands of times higher than this. Under such conditions, system contamination is imminent.

One or more of the following can cause carryover in a concentration system:

- Adsorption
- Absorption
- Insufficient flushing between runs
- Unswept zones (dead volume)

Adsorption occurs if there is any affinity of the VOC's to the surfaces to which they are exposed. This can be reduced by heating exposed surfaces as well as by utilizing inert materials. Absorption can occur when VOC's are exposed to polymeric materials such as Teflon and Nafion which absorb and off-gas quite readily. Carryover caused by insufficient flushing can be eliminated by making sure that flushing of lines occurs all the way up to the next canister to be analyzed before concentrating a sample from it.

附錄九

PROGRAMMABLE CANISTER SAMPLER MODEL 910PC

The Model 910PC is a computer-controlled, programmable sampler that is designed to collect volatile organic compounds in ambient air. The method is based on collection of whole air samples into "Summa" electropolished canisters as outlined in USEPA T0-14/T0-15 Methods. A diaphragm pump is used to pressurize the sample canister up to 25 psi. A mass flow controller maintains a constant flow into the canister over the desired sample period. When sampling is not taking place the sample canister is isolated from the rest of the sampling system by a pulsed, magnetically latched solenoid valve. The use of a pulsed solenoid valve eliminates the temperature rise and out-gassing of organic compounds from the valve seat materials that might occur in a normally energized valve. All materials used in the sample path are non-reactive.

The XonTech Model 910PC sampler can be used with a XonTech Model 912 Multi-Canister Sampling Adapter to route air samples into up to sixteen canisters.

Scheduling for the XonTech Model 910PC sampler and optional Model 912 Multi-canister Sampling Adapter is controlled by an internal computer board. Sampling schedules are entered through the front panel keypad or from a remote computer via modem. Remote control of the sampling schedule allows the schedule to be altered when episode days are predicted. A "Reschedule" function allows a sampling schedule to be repeated at a later date without re-entering the scheduling information.

Time, date, pre-purge delay, flow set point and rate, average flow, pump and canister pressure, beginning and end pressure for all samples, elapsed time, sampling schedule, and power failure errors are displayed on the front panel display or on a remote computer via modem. A hard copy of the above parameters is printed on the front panel-mounted printer at the end of each sample period. A print-out of the schedule or sampling report can be requested from the front panel keypad or from a remote computer.

Sampling can be initiated manually from the front panel for the purposes of manual sampling, troubleshooting or to perform a "leak check" when connecting new canisters.

Recovery from a power failure is automatic, the sample pump will turn on and the sixteen port valve in the Model 912 will automatically advance to the correct position when power is restored.

XonTech, Inc.

ENVIRONMENTAL SYSTEMS GROUP
7027 HAYVENHURST AVENUE VAN NUYS, CA. 91406
(818) 787-7380 FAX: (818) 787-8132 http://www.xti.com/esg.html

The Model 910PC sampler can be operated remotely using its internal modem and a P.C. The remote P.C. is identical to instrument front panel operation with the exception that inverse video is used instead of underlining to identify the selected fields.

Also, three additional XonTech instruments (e.g. Model 925 Carbonyl sampler, Model 924 Automatic Multi-medium sampler) can share the single phone line normally available in the air monitoring station. To share the single phone line may require a XonTech manufactured Modem/Junction box.

The XonTech Model 910PC design is based on the field proven XonTech Model 910A sampler that is widely used by State and Federal agencies.

FEATURES:

Meets all PAMs and TO-14/TO-15 requirements.

Fits Standard 19 inch rack. Size: 7"H x 19"W x 15"D. Weight: 20 pounds.

Mass flow controller maintains constant and adjustable flow rate.

Does not degrade VOCs - all wetted components are non-reactive materials.

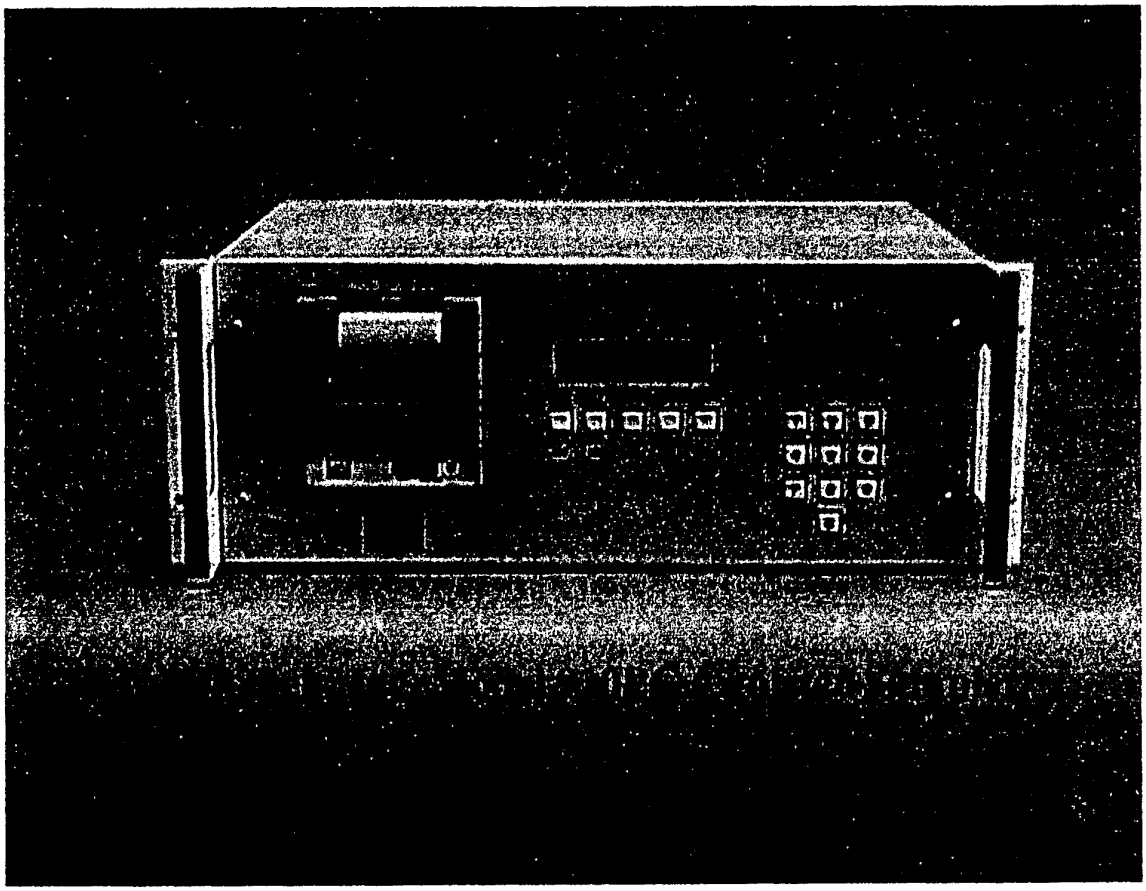
Programmable system purge prior to sampling.

Automatic restart after power failure.

Operating parameters and schedule are input using the front panel display and keypad. Battery back-up of clock/calendar, operating parameters, and sampling data.

Display and print: Time, Date, Purge Delay, Flow Rate, Flow Set, Flow Average, Total Volume, Elapsed Time, Pump Pressure, Canister Pressure, Start and End Pressure, Sampling Schedule.

Easy to install, operate and maintain.



PRICE LI

XonTech, Inc. 7027 HAYVENHURST AVENUE VAN NUYS, CALIFORNIA

EXPORT

May 10,

MODEL 910PC PROGRAMMABLE AIR SAMPLER

Model 910PC (Basic)	$ 8748.(

Remotely programmable AC operated air sampler configured for use with canisters. Standard Viton® diaphragm pump with an operating pressure of 30 psi. Front panel printer, LCD display and keypad. Programmable purge delay, flow rate and sampling schedule. Sample outlet valve is automatically closed during power failure. Standard flow range of the mass flow controller is 0 - 50 cc/min. If a different flow range is required, please specify when ordering. Please indicate your choice of modems, internal or external. See Junction Box/Modem below.

Model 910PC - CARB Option	$ 9047.(

The standard pump is replaced by a 30 psi, Teflon® diaphragm, pump (KNF # MPU781-N010-9.95).

Modification of system to 220V/50-60 Hz power requirement.	$ 500.0(
Model 910PC Outdoor Enclosure	$ 2219.(

Lockable, insulated enclosure with heater and fan for temperature control; satin white finish. The enclosure will hold (2) 6-liter canisters. The 910PC is mounted on slides for easy access. A stainless steel sampling probe is included. Removable legs for the enclosure put the 910PC at eye level.

Junction Box/Modem	$ 457.8

A Junction Box/Modem is available for field monitoring stations having multiple 910PC samplers or combinations of 910PC and Model 925 Carbonyl Samplers. The junction box allows up to four samplers to be connected to 1 telephone line. Requires an external 2400 baud modem.

Printer paper – 910PC printer paper, 20 rolls	$ 46.0
Printer Ribbon – 910PC printer ribbon, 6 ribbons	$ 58.0

PRICES ARE SUBJECT TO CHANGE WITHOUT NOTICE.

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CANISTER CLEANING SYSTEM
MODEL 960

USEPA TO-14/T0-15 methods for the determination of volatile organic compounds (VOCs) involves the use of "Summa" electropolished canisters for the collection of ambient air samples followed by analysis of the samples using gas chromatography technique. The methods also provide guidance on how to clean and certify canisters (T0-14/T0-15 or T0-12) by measuring the residual level of VOCs remaining after the cleaning process. Thus, the importance of thorough and proper cleaning of Summa cans before use cannot be overlooked.

A commercially available canister cleaning system is now available. The automated system utilizes repeated cycles of evacuation, fill, and bake at 120°C. The cycles are first performed using humidified air, followed by final dry air cycles. At the end of these cycles, the canisters are free of VOCs and are dry. The finishing step is to evacuate the canisters to < 0.05mm Hg using a high vacuum pump.

Two systems are available depending on the user's requirements. One system is a low vacuum system, i.e., the finishing step, evacuating the cans to 0.05mm Hg is performed separately. The purpose of the two step process is to allow the cleaning system to simply clean as many cans as possible. The finishing step, evacuating the cans to 0.05mm Hg, can be performed rapidly with a variety of high vacuum pumps. The other system is the high vacuum system where the finishing step is automated into the system after the cleaning cycles.

LOW VACUUM CANISTER CLEANING SYSTEM

This low vacuum cleaning system consists of a stainless steel oven capable of holding four 6-liter or eight 3.2-liter canisters. The oven is top-loading and mounted on a moveable rack. Two auxiliary units, each with the same capacity of four 6-l cans can be added. The system operates on 115V AC. Each control unit and auxiliary unit requires separate 115V, 15 amp AC circuits. Gauges, oven temperature controller, and switches are mounted on the top panel. An oven cover is provided and the cover allows the spheres of the canisters to be completely heated in the oven. The valves are outside the oven to minimize heat distortion of the valve seats. PFA tubing is used for connecting the vacuum manifold to the canisters. This allows visual observation of the condensed moisture on the tube during the humidified air cycle and absence of condensed moisture during the dry air cycle. Use of brass fittings and PFA tubing also minimizes the wear and damage to the stainless steel canister valve.

A humidifier comes with the system. The pump for the low-vacuum canister cleaning system is an oil-free diaphragm pump. Two options for the air inlet are offered. One option is for room air. The air is scrubbed with activated charcoal to remove VOCs and then pressurized to fill the cans via a diaphragm pump. The standard gas inlet in the system is for pressurized zero air or N_2 cylinder.

XonTech, Inc.

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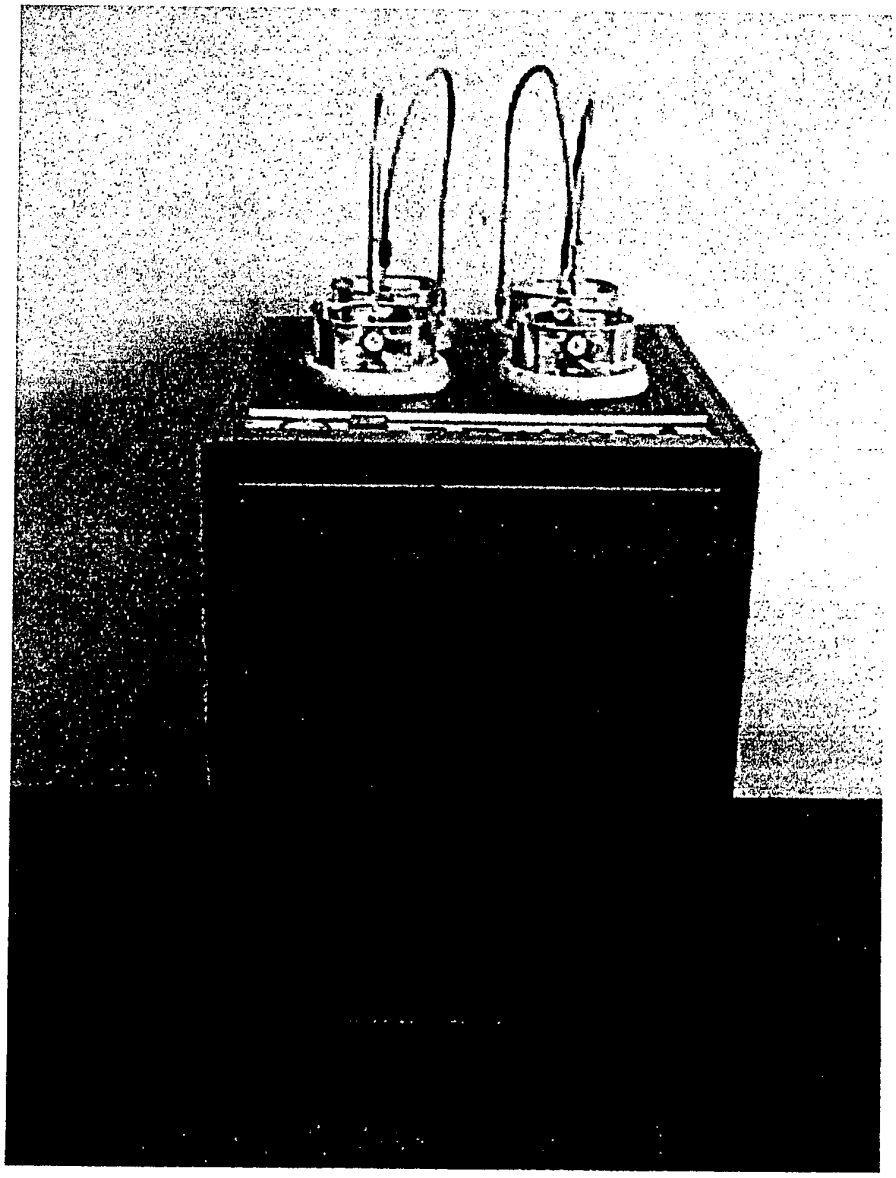
HIGH VACUUM CANISTER CLEANING SYSTEM

This high vacuum system is similar to that of the low vacuum system except a high vacuum pump is provided such that after the humidified and dry air cycles are completed, the system automatically switches on the high vacuum pump and evacuates the canisters to < 0.05 mm Hg. This system uses flexible stainless steel tubing for connection of the vacuum manifold to the canisters. The canister end of the flex tubing also has a short piece of PFA tubing and brass fittings to minimize the wear and damage of the stainless steel canister valve. A high vacuum gauge is also provided in the system.

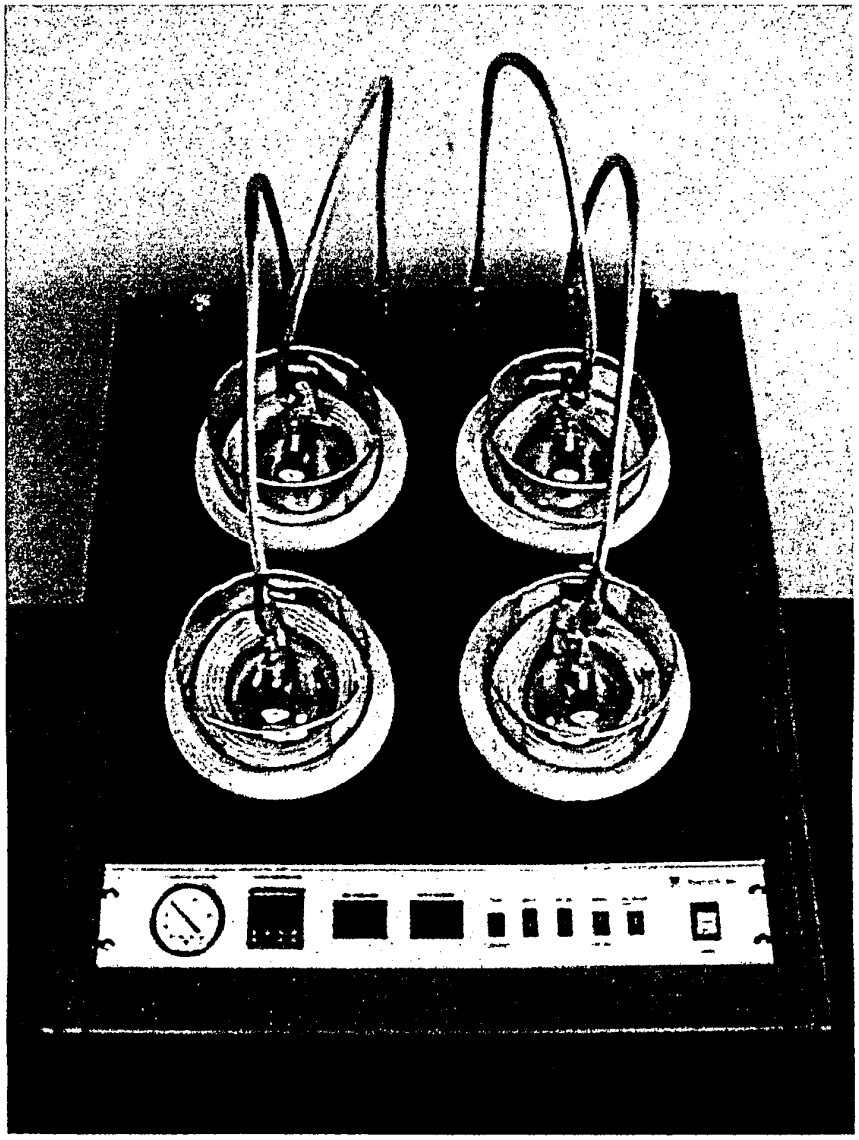
SPECIFICATIONS:

Control Unit Capacity:	4 - 6 liter canisters. 8 - 3.2 liter canisters.
Auxiliary Unit Capacity: (1 Control Unit will operate 2 auxiliary units)	4 - 6 liter canisters. 8 - 3.2 liter canisters.
Total System Capacity:	12 - 6 liter canisters. 24 - 3.2 liter canisters.
Canister Oven Operating Temp. Range:	Ambient to +120°C.
Canister Vacuum:	-20 inches of mercury.
Operator Controls:	* Power On/Off. * Number of Purge / Fill Cycles (humidified air) * Number of Purge / Fill Cycles (dry air) * "N" Cycle / Continuous. * Oven Temperature.
Indicators:	* Cycle #. * Time remaining in current cycle. * Canister Pressure / Vacuum. * Oven Temperature.
Wetted Materials:	Stainless steel, PFA, Viton.
Dimensions:	38"H x 26"W x 31"D.
Weight:	Control Unit ~ 300 pounds. Auxiliary Unit ~ 250 pounds.
Power Requirements:	Control Unit - 115 VAC, 60 Hz, 15 Amps. Aux. Unit - 115 VAC, 60 Hz, 12 Amps.

XONTECH INC. MODEL 960 CANISTER CLEANINGSYSTEM



XONTECH INC. MODEL 960 CANISTER CLEANINGSYSTEM



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EXPORT

Feb. 2001

MODEL 960 CANISTER CLEANING SYSTEM

(This system is not a stock item. It is a customized item and therefore requires a longer delivery time.)

Low Vacuum canister cleaning system Model #960LC - Control Unit only for four 6-liter canisters	$ 14599.00
High Vacuum canister cleaning system Model #960HC - Control Unit only for four 6-liter canisters	$ 23785.00
Auxiliary canister cleaning unit for four 6-liter canisters Model #960AU - This auxilliary unit works with Model #960LC or #960HC	$ 9108.00
Stainless steel manifold for cleaning one-liter canisters (set of 4). Each set allows the unit (#960LC, #960HC or #960AU) to clean sixteen one-liter canisters. Covers are included with the manifold.	$ 1566.00
Stainless steel oven extension for cleaning two 15-liter canisters. Covers and fiberglass insulating socks included.	$ 1142.00
Fiberglass insulating socks. (Set of 4) includes 4 outer and 4 inner socks.	$ 256.00
Modification of system for 220V/50-60 Hz power requirement.	$ 500.00

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PROGRAMMABLE CANISTER SAMPLER MODEL 910A

The Model 910A sampler is designed to collect volatile organic compounds in ambient air. The method is based on collection of whole air samples into a "Summa" electropolished canister as outlined in USEPA T0-14/T0-15 Methods. The Model 910A sampler is used for pressurized sampling up to 30 psi. A flow controller is chosen to maintain a constant flow into the canister over the desired sample period. The use of a pulse magnelatch valve avoids a substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sampling period. The temperature rise in the valve could cause out-gassing of organic compounds from the valve seat material.

The XonTech Model 910A sampler has proven to be field reliable and is widely used by State and Federal agencies. This sampler can be coupled with the XonTech Model 912 (16 port multi-canister valve).

FEATURES:

Meets all PAMs and T0-14/T0-15 requirements.

Standard 19 inch rack mountable.

Weight: 19 lbs. Size: 7"H x 19"W x 15"D.

Automatic system purge prior to sampling.

Does not degrade VOCs - all wetted components of non-reactive materials.

Mass flow controller maintains constant and adjustable flow rate. Digital display of flow rate.

Front panel access to all controls and indicators.

Elapsed timer shows actual sampling time.

Automatic restart after power failure.

Easy to install, operate and maintain.

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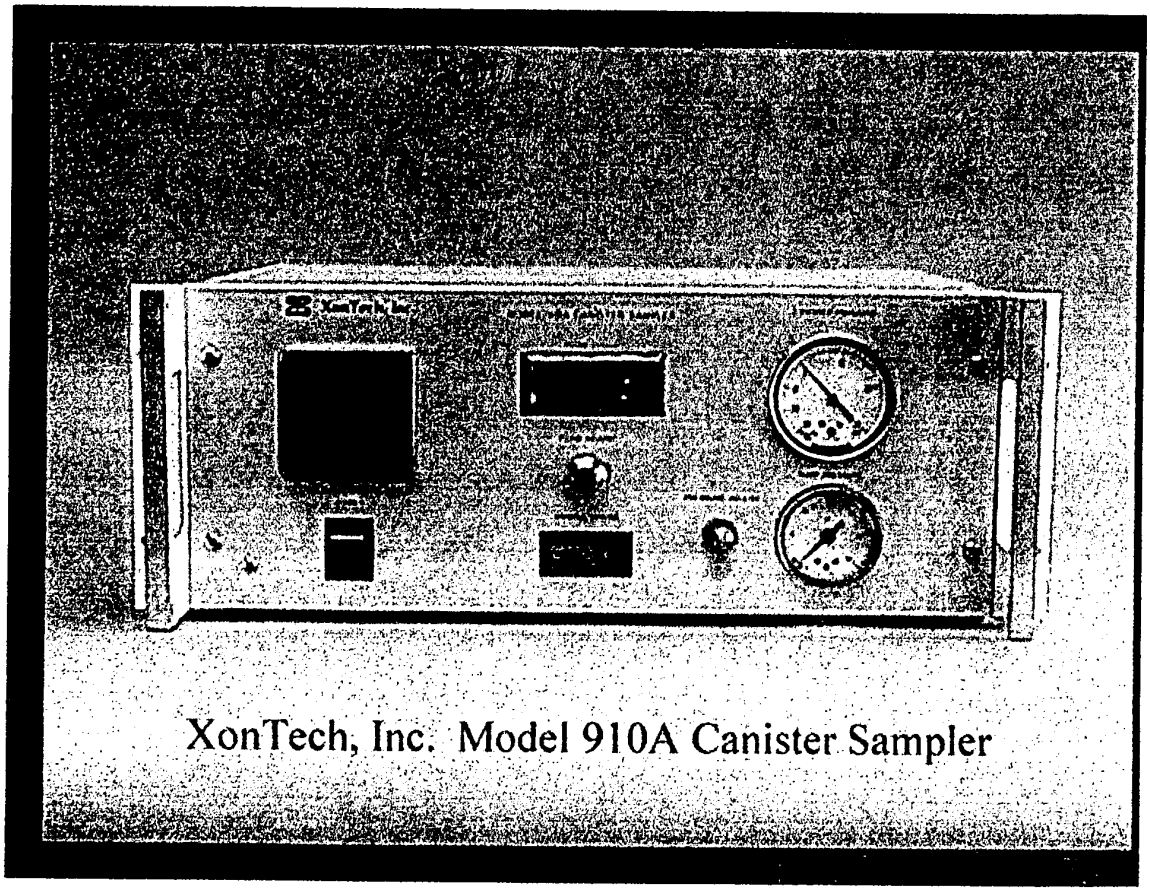

XonTech, Inc. Model 910A Canister Sampler

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XonTech, Inc. 7027 HAYVENHURST AVENUE VAN NUYS, CALIFORNIA

EXPORT

May 10, 2000

MODEL 910A PROGRAMMABLE AIR SAMPLER

Model 910A (Basic) Programmable AC operated air sampler configured for use with canisters. Standard diaphragm pump with an operating pressure not less than 30 psi. Front panel access to all controls and indicators. An automatic purge of the instrument for 1 minute before sampling is provided. Standard flow range of the mass flow controller is 0-50 cc/min. Please indicate if other flow range is required.	$ 7191.00
Model 910A - CARB This model has all the features of the Model 910A Basic except for the pump, which is a 30 psi KNF pump Model MPU781-N010-9.95. A purge delay circuit board is also added to the system for selectable purge time.	$ 7974.00
Modification of system to 220V/50-60 Hz power requirement.	$ 500.00

Options Available

Selectable purge delay board	$ 461.00
"CARB" pump, 30 psi Neuberger, PN: MPU781-N010-9.95	$ 859.00
Outdoor enclosure-lockable, insulated, with heater and fan for temp. control; satin white finish. The enclosure will hold (2) 6-liter canisters. The 910A is mounted on slides for easy access. A stainless steel sampling probe is included. Legs for enclosure allow instrument to be at eye level. Dimensions: 32 ½"H x 24 ½"W x 21 ¼"D	$ 2219.00

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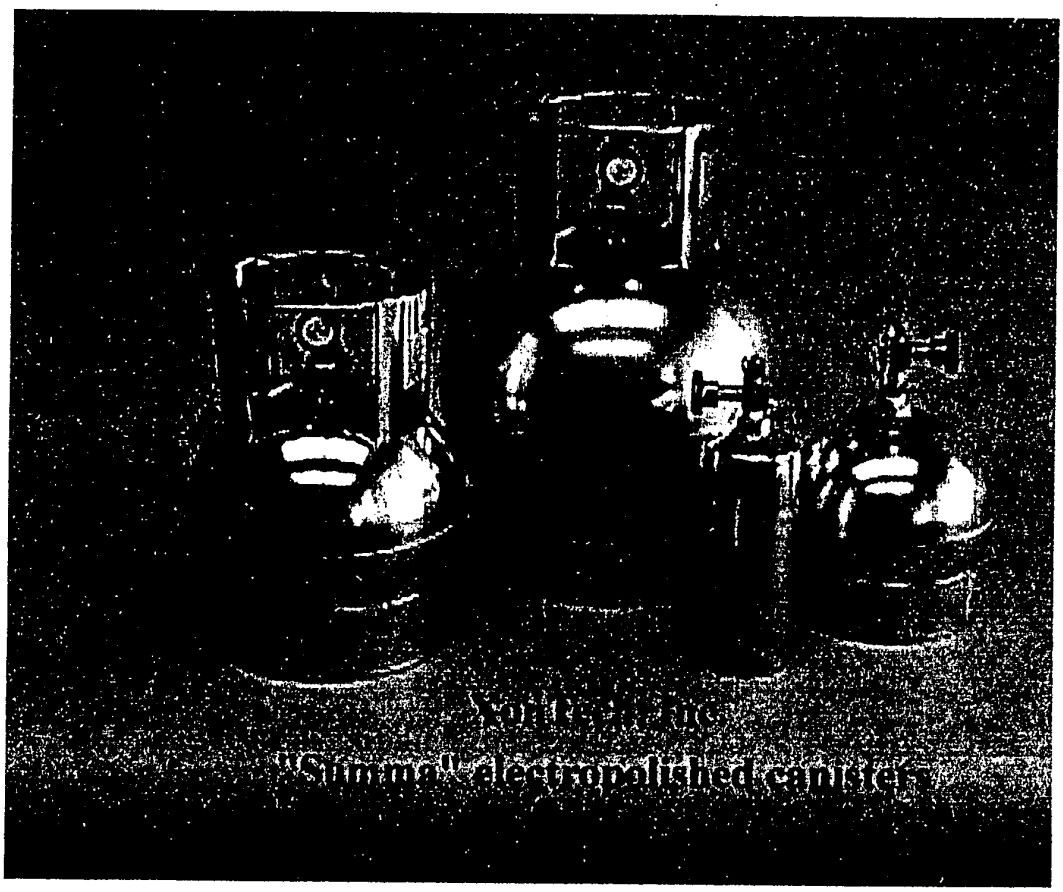
EPA Type SUMMA Canister Specifications



Specifications

1. Canisters meet all requirements of EPA Compendium Method T0-14/15.

2. **General Features:** 20 ga. wall, type 304SS. Internally passivated by SUMMA electropolish process; fitted with basering-stand and valve guard/handle; equipped with one Nupro SS4H high vacuum ultra-clean bellows valve and¼-inch SWAGELOK connecting fittings. Helium leak-tested to 1 x 10-9 std cc/sec. and guaranteed to be cleanto <0.2 ppbv per hydrocarbon species and air toxics.

3. **Special Features:**

3.2-liter	6 x 9-inch	7-inch sphere
6-liter	7 x 12-inch	9-inch sphere
15-liter	10 x 14-inch	12-inch sphere
32-liter	12 x 22-inch	

Dimensions Of Spherical Canisters

	3.2-liter	**6-liter**	**15-liter**
Total height	10.5"	12.5"	16.75"
Sphere	7"	9"	12"
Stand	2"	2.5"	2.5"
Handle/valve guard	not avail.	4.5"	4.5"
Plug & chain	incl.	incl.	incl.
Exit port	¼" Swagelok	¼" Swagelok	¼" Swagelok
Valve	SS4H, high vac. ultra clean	SS4H, high vac. ultra clean	SS4H, high vac. ultra clean
Anti valve rotation brkt.	incl.	incl.	incl.
Weight	3 lbs.	5.5 lbs.	10.5 lbs.

Back to XTI Home Page

SUMMA electropolishing done internally after welding the container together. No unpassivated weld scar seams exposed internally. 100% passivation of all internal surfaces; no active sites.

Entry port 3/8-inch NPT makes it easy to disassemble and visually inspect the condition of the inside of the canister after multiple usage.

Large entry port facilitates re-polishing to rejuvenate the internal surface. No cutting and re-welding of the canister is required.

Change-over from 1-valve to 2-valve purge-tube configuration done easily with wrench in the field if necessary. 2-valve assembly allows flow-through purge. Monitoring fill rate via -30 to +60 span gauge conveniently done using gauge on one of the valves.

Packaged in double-walled reusable individual mailing cartons. Canisters shipped 4 to a box for consolidated shipments. No need to acquire special shipping cartons.

All canisters are individually tested to pass EPA T0-12 method at <20 ppbvc.

Item

A. Spherical containers, EPA-SUMMA canisters

6-liter canister, 9-inch diameter, 20 ga. wall, type 304SS. Internally passivated by SUMMA electro-polish process; fitted with SS base ring and SS valve guard/handle; equipped with one Nupro SS4H high vacuum ultra-clean valve and ¼-inch SWAGELOK connecting fittings.

With purge-tube and 2 valves, or 1 valve with integral SPAN guage (-30 to +60 psig). Request quote.

B. Cylindrical Cans

850-mL canister, 3 x 8-inch, 20 ga. wall, type 304SS. Internally electropolished to provide passivated chrome-nickel oxide skin. Exceptionally inert surface fitted with a new miniature Nupro SS4H bellows stem valve and ¼-inch SWAGELOK connecting fittings. Cryogenic air sample storage bottle. Maximum internal pressure: 275 psig.

C. Tanks

Type 304SS, 14-18 ga. wall, internally passivated by electro-polish process and fitted with Nupro SS4H4 valves and SWAGELOK or CAJON VCR fittings. Special options available.

Sizes Available

PORTABLE WIND SECTOR CONTROLLED POWER SWITCHING SYSTEM MODEL 970

The Wind Sector Controlled Power Switching System consists of two parts: an electronics enclosure and a wind speed and direction sensor with portable tower and accessories.

The electronics enclosure is an insulated and heated aluminum enclosure that contains the wind speed and direction sensor interface logic, a 7 day, 22 event timer, in and out sector elapsed timers, and the power switching circuitry. The enclosure measures 12 ½" x 11 ¼" x 5 ½" and is provided with the mounting hardware necessary to attach it to the wind sensor tripod.

The wind sector and wind speed threshold is factory set to customer specifications (South +/- 150 degrees and 3 miles per hour). The sector and speed threshold can be adjusted by the operator in the field, a digital voltmeter is required to make this adjustment. A snap-action thermostat and 100 watt heater is used to keep the timer displays within their operating temperature range.

The power switching circuitry can supply a total of 12 amps at 115 VAC, 50/60 Hz to an external load. A 15 amp, 115 VAC input source is required. The output power is on if the timer is on, the wind direction is in sector, and the wind speed is above the wind speed threshold. A 25', 14 gauge, type SEOW line cord with molded plug supplies input power. Input power is routed through a GFCI/motor control circuit breaker to a solid-state relay that is controlled by the wind sector/threshold logic. The output of the solid-state relay is routed to three water-resistant connectors that are mounted on the enclosure wall. A 16 AWG, 12' long, outlet cord with receptacle is provided for each output connector.

A wind monitor provides wind direction and speed signals. A portable tripod is provided for wind sensor mounting.

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PRICE LIST

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DOMESTIC

May, 2000

MODEL 970 Portable Wind Sector Controlled Power Switching System

Model 970	$ 8352.00

Wind sector controlled power switching system consists of
Two parts: an electronic enclosure and a wind speed
and direction sensor with portable tower and accessories.

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PORTABLE CANISTER SAMPLER MODEL 911A

The Model 911A sampler is uniquely designed to collect air samples into 'Summa' electropolished canisters. It has been used to collect air samples for the characterization of emissions at landfills, surface impoundment, landspreading, drum burial or waste piles. It has also been used as a wind sector sampler at Superfund sites.

Sector sampling and data reduction technique can provide VOC data that indicate probable source emission identification. This technique is useful for short-term VOC screening of suspect sources or for long-term monitoring of the contribution from a specific source. Upwind/Downwind monitoring by the same sampler can eliminate the complexity of having sampling personnel manually operating samplers or physically moving them to sample in the appropriate wind condition.

FEATURES:

Field proven to be reliable, easy to install, operate and maintain.

Weight: 14 lbs; Size: 11¼"W x 12½"H x 5½"D; Battery or AC operated.

Does not degrade air sample; all wetted components of passivated stainless steel.

Pump consists of stainless steel head and non-lubricated Viton diaphragm. Sample pressurized to 25 psi.

Adjustable flow rate.

Chem-filmed white aluminum enclosure; lockable.

Specially designed parts to eliminate water condensation from clogging the flow controller and sample path.

Automatic pre-purge of sampling line before sampling into canister.

A 7-day, 36-events timer for programming start and end time.

Meets all PAMs network or TO-14/TO-15 requirements. (For network station, we suggest the Model 910A rack mountable unit.)

Accepts 0-5 volt signals from meteorology gear to function as sector sampler.

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OPTIONS:

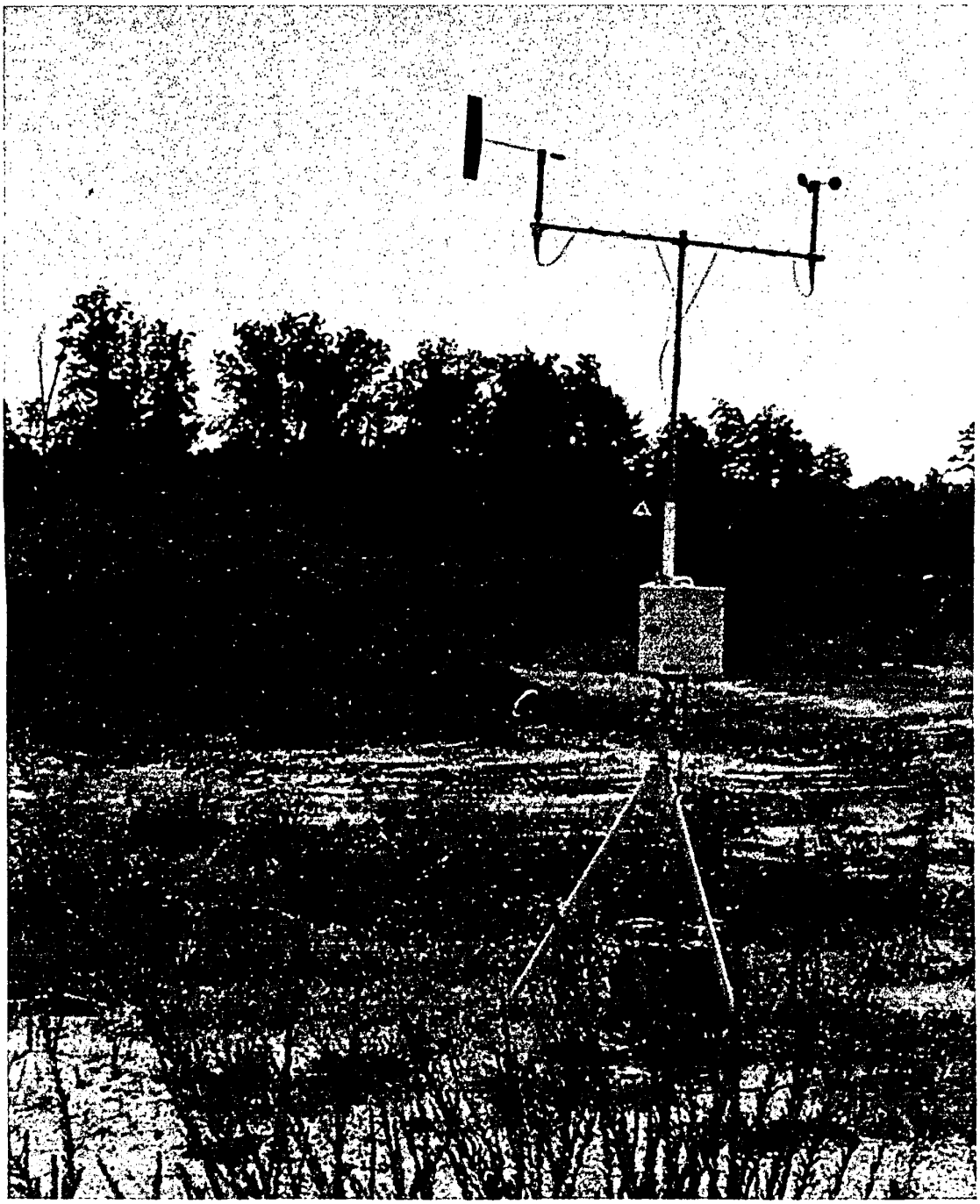
Sector Sampler

Use with wind directional sensor as sector sampler. Air sample is directed to the in-sector canister when the wind is blowing from the selectable sampling sector (practical limit is 45° - 315°) and to the out-sector canister when the wind is not blowing from the sampling sector.

Sector Sampler with Wind Speed Cut-off Option

This option provides all the features of the Sector Sampler plus an interface to a wind speed sensor which allows the selection of a minimum wind speed threshold (normally 1 mph). Sampling stops if the wind speed falls below the selected threshold.

XONTECH INC. MODEL 911A



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XonTech, Inc. 7027 HAYVENHURST AVENUE VAN NUYS, CALIFORNIA 9140

EXPORT

May, 10 200C

MODEL 911A PORTABLE CANISTER SAMPLER

Model 911A (Basic) $ 5287.00

The basic 911A is configured for manual operation and sampling to one canister. A 7 day, 10 events timer for programming of sample start and end time is included. The 911A is AC/DC operated. For battery operation, an automotive/marine battery of appropriate size is required. Standard flow range is 0 – 50 cc/min. For different flow ranges please specify when ordering. Mounting brackets, guy wires and masts are optional (they can be easily obtained in local hardware stores). For options or updates to other configurations, please see Options.

ncluded with the basic unit:

Stainless steel sampling probe.

AC adaptor.

Accessory cable for an external customer-supplied automotive or marine battery.

A connector (DAS OUTPUT) with "Sampler on" and "in/out-sector"signals is provided. These signals can be recorded by a customer supplied data acquisition system.

A connector is provided for the optional elapsed timers.

Model 911A with In/Out Sector Sampling Capabilities $ 6016.00

The 911A is configured to allow wind direction controlled sampling into two canisters, in-sector and out-sector. The ambient air sample is directed to the in-sector canister when the wind is blowing from the sampling sector. The ambient air sample is directed to the out-sector canister when the wind is not blowing from the sampling sector. The wind direction controller is sold separately. The accessories listed in the basic model are included.

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Model 911A witn In/Out Sector Sampling and Wind Speed Cut Off $7015.00

This option provides an interface to a wind speed sensor and allows the selection of a minimum wind speed threshold. Sampling stops if the wind speed falls below the selected threshold. Additionally, the following features are added:

The 911A can be operated with the XonTech wind speed and direction sensors or accept 0 to 5 volt signals from existing customer supplied wind sensors.

When used with a linear output wind direction sensor or 0 to 5 volt signal, the sampling sector is continuously variable from 0 to 360 degrees (practical limit is 45° - 315°). On-board controls are used to set the limits.

"Wind speed" and "wind direction" signals are added to the DAS OUTPUT connector.

The wind speed and wind direction sensors are sold separately. The accessories listed in the b model are included.

Options Available

Wind direction controller	$ 680.00
Wind speed sensor	$ 680.00
Cross arm for wind sensors	$ 162.00
Battery cable	$ 42.00
6-10 ft. quick deployment tripod for met sensors	$ 576.00
Single elapsed timer	$ 167.00
Dual elapsed timer (use with wind speed/direction options)	$ 269.00
Outdoor enclosure-lockable, insulated, with rack and slide mounting provisions, with removable legs, which when attached raises the instrument to eye level. The enclosure has ample space for two canisters or an auto/marine battery and one canister. The enclosure is finished with an epoxy based satin white paint. The instrument is also front panel mounted for easy access to indicators & controls.	$2219.00
Modification of system to 220V/50-60 Hz power requirement.	$ 500.00

MULTI-CANISTER SAMPLING ADAPTER MODEL 912

The XonTech Model 912 Multi-Canister Sampling Adapter is designed to route air samples to or from up to 16 canisters. An internal time base is used to step a rotary valve from canister to canister at a user-selected rate. The Model 912 accepts timing signals from the XonTech Model 910A or 911A canister samplers.

FEATURES:

16 port rotary valve with electric actuator. Stainless steel and inert nonporous fluoropolymer construction. 1/8" stainless steel, zero dead volume, fittings.

Stainless steel tubing throughout.

1/8" stainless steel Swagelok inlet/outlet fittings.

Switch-selectable sample time. ½ to 4 hours per sample (1 to 8 hours per sample optional). Will accept timing signals from XonTech Model 910A or 911A canister samplers.

Can be used to route sample gas to or from up to 16 canisters.

19" rack mount chassis with front panel mounted position indicator and controls.

SPECIFICATIONS:

Time base accuracy:	0.01% for 0 to 70°C.
Size:	7" H x 19" W x 15" D
Weight:	18 lbs.
Power:	115 VAC, 2 amps max.
Maximum pressure:	200 psi.

APPLICATIONS:

Sampling frequency requirements for VOC under proposed Enhanced Ozone Monitoring (EOM) Regulations.

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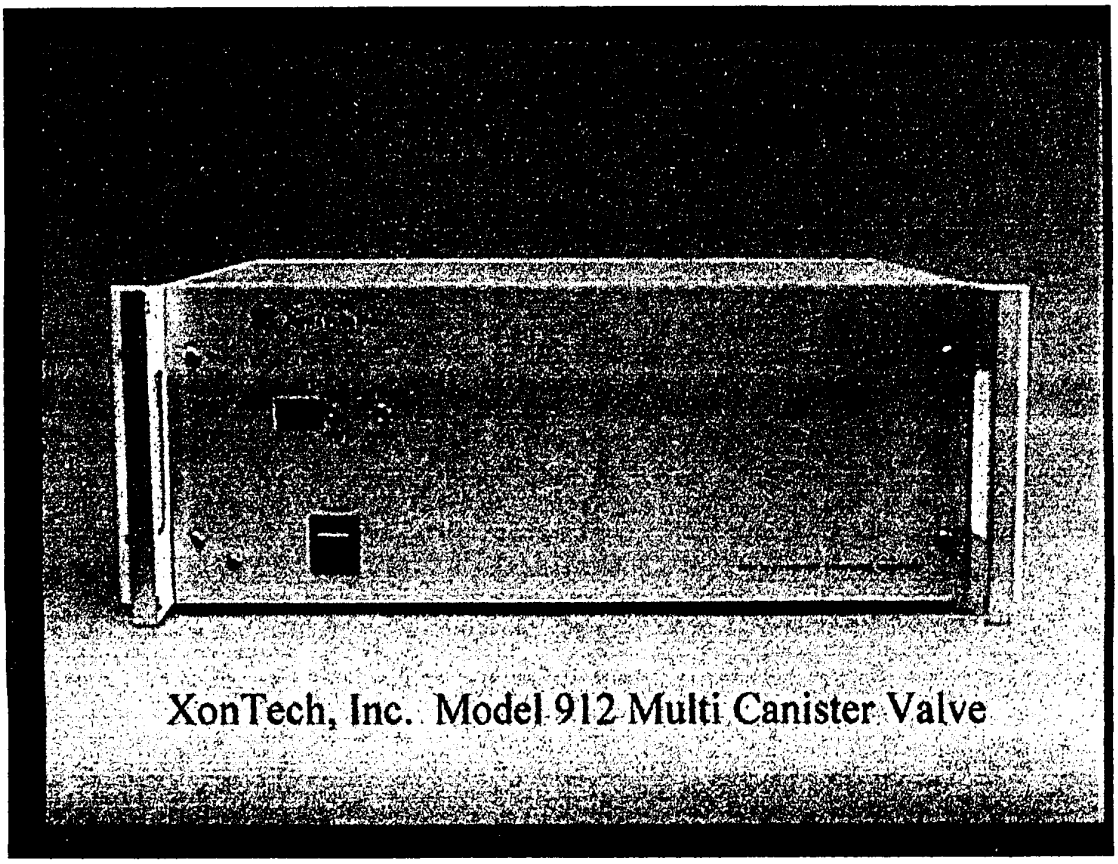

XonTech, Inc. Model 912 Multi Canister Valve

PRICE LIST

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May 10, 2000

MODEL 912 MULTI-CANISTER SAMPLING ADAPTER

Model 912	$ 4178.00

16-canister sampling adapter. Can be used in conjunction with Model 910A or Model 911A samplers. The Model 912 chassis is 19" rack mountable. Slides do not come with the unit.

PASSIVE AIR SAMPLER
MODEL 915

The Model 915 Passive Air Sampler is designed to collect air samples in remote locations in the absence of electric power or during sampling periods which prohibit an attendant being present.

The system is equipped with a battery operated, programmable timer, with seven day, thirty-six event pre-program capability. The timer pulses "latch" open a solenoid valve at the beginning of the pre-programmed sampling episode, and pulses "release" the solenoid valve closed at the end of the program. A manual override switch allows for operation without the need of a program cycle.

The sampler is constructed of a lightweight aluminum chassis, with a white powder coat finish, a lockable latching clasp, hanging brackets, and a carry handle. Fitted with ¼" stainless steel Swagelok tube fittings for inlet and outlet connections and a weather-tight connector for the battery charger.

The system is supplied with a stainless steel inlet assembly consisting of a length of ¼" tubing, an inverted funnel at the inlet, and a 15 micron particulate filter.

System installation is achieved by attaching the unit to the top of a 6-liter canister. If a smaller size canister is used, the system needs to be secured to a ½", 1" or 1 ½" pipe by means of the attached bracket and a U-bolt.

The battery reserve will sustain a standby condition for approximately 14 days, and a sampling state for about 6 days. The furnished battery charger will recharge the battery overnight. There is a small but continuous drain on the battery whenever it is connected to the system. During extended periods of non-usage, we recommend you charge the system and disconnect the battery by removing the lug from one of the battery terminals. Or alternatively, hang the unit in the vertical position and plug in the battery charger. The "float" condition will assure the system battery is not damaged due to a complete discharge of the battery, and the system will be maintained ready for use.

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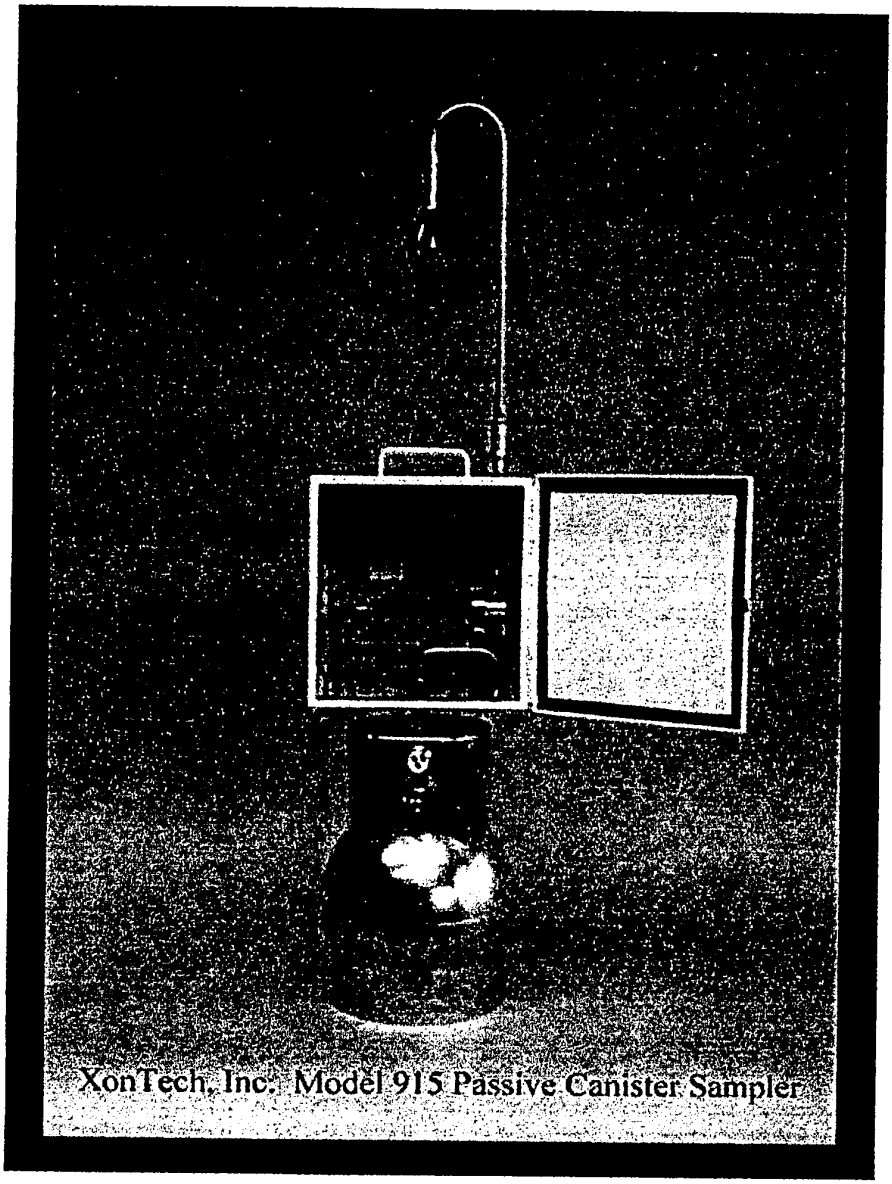

XonTech, Inc. Model 915 Passive Canister Sampler

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XonTech, Inc. 7027 HAYVENHURST AVENUE VAN NUYS, CALIFORNIA 9

EXPORT

Feb. 2001

MODEL 915 PASSIVE AIR SAMPLER

Model 915		$ 2282.00
	Passive air sampler includes programmable timer, flow controller, lightweight aluminum chassis with lockable latching clasp, and stainless steel cane.	

Spare parts:

TR-611S	Programmable Time Switch (Theben)	$ 237.60
SC423XL	Super-4 flow controller for low flow or 24 hour sampling	$ 672.00
	Additional orifices for 3 hour or 8-12 hour sampling	$ 144.00
455171V	Solenoid valve	$ 247.64
L-07263-00	SS 3" diameter sampling funnel with modified Press fit ¼" fitting	$ 100.70
SS-4F-T7-15	15 micron inline filter	$ 100.50
	Inlet assy. tube, SS ¼" OD, 18" total length	$ 69.30

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MODEL 924 TOXIC AIR SAMPLER

The newly designed Model 924 Toxic Air Sampler provides significant improvements to the discontinued Model 920.

An updated microcomputer and user interface provides more functions and user versatility; remote operation may be controlled by a personal computer and internal modem, user options include eight menus, episode schedule and reschedule capabilities, elapsed sampling periods, flow calibration (slope and intercept adjustments), system operation status (temperatures, flow rates, pump menu & vacuum status) for each sampling channel. The sampler is modular in design consisting of a sampling module, control module, and a pump module.

SAMPLING MODULE

The standard module comes with three sampling channels. An optional fourth sampling channel can be added. Each channel can accommodate either a 37mm or 47mm filter, or sorbent tube sampling medium with an actuation valve upstream, and an isolation valve downstream to protect the medium from pre-sampling exposure. The inlet height can be extended to 3 meters above ground, and the inlet is protected by a weather shield assembly.

CONTROL MODULE

The control module contains the microcomputer, mass flow controllers, front panel display, printer, keypad, system power supplies, all plumbing and electrical interconnections. Sampling start time, duration, date and flow are programmed for each channel and a sampling report is printed as each channel completes its sampling period. The sampling report contains time and date, ID#, channel #, start time, duration, total volume of air sampled, average flow, flow error, and duration of power off. A full report including all control settings, schedule, and sampling report can be requested. The control module enclosure is insulated. A heater and cooling fan maintain the enclosure within a selected temperature range.

PUMP MODULE

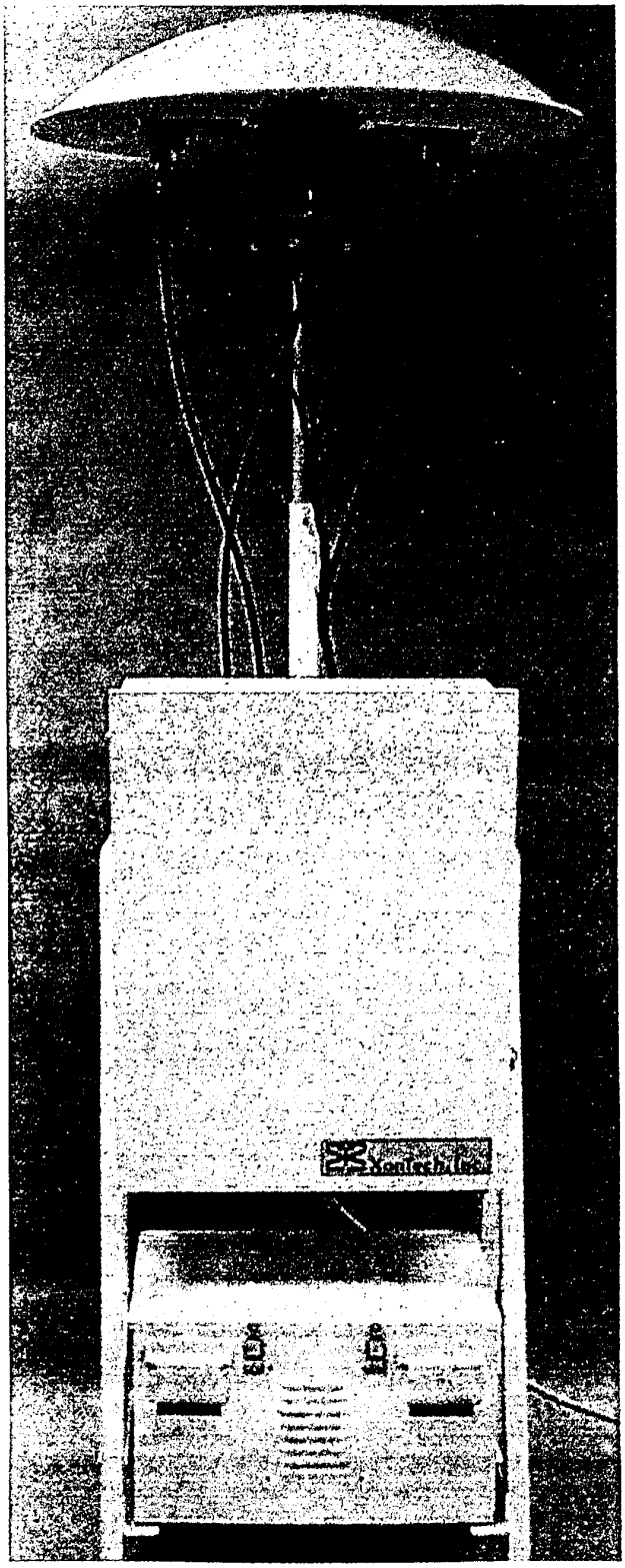
This module contains a vacuum pump which provides adequate capacity for simultaneous operation of all channels. The flow rate for the filter is 30 lpm and the sorbent tube is 2 lpm.

Features:
- Automated collection of air samples on a variety of media.
- Up to 4 channels of 37mm or 47mm filters or sorbent tubes, or combination of filters and tubes.
- Automatic reports for each channel.
- Power fail logging and recovery.
- User-friendly operator interface.
- Operation from a remote PC is identical to front panel operation.
- Easy to set up.

XonTech, Inc.

ENVIRONMENTAL SYSTEMS GROUP
7027 HAYVENHURST AVENUE VAN NUYS, CA. 91406
(818) 787-7380 FAX: (818) 787-8132

XONTECH, INC.MODEL 924 TOXIC AIR SAMPLER



PRICE LIST

XonTech, Inc. 7027 HAYVENHURST AVENUE VAN NUYS, CALIFORNIA 9140

EXPORT

Feb. 2001

MODEL 924 TOXIC AIR SAMPLER

# 924T3	Model 924 Toxic Air Sampler with three sorbent tube sampling Channels for Sep-paks or NIOSH tubes.	18,650
# 924T2	Model 924 Toxic Air Sampler with two sorbent tube sampling channels for Sep-paks or NIOSH tubes.	15,606
#924T1	Model 924 Toxic Air Sampler with one sorbent tube sampling channel for Sep-pak or NIOSH tube.	12,562
#924T3F3	Model 924 Toxic Air Sampler with three sorbent tube sampling channels. Each sorbent tube holder has a 37mm or 47mm aerosol filter holder upstream.	20,090
#924T2F2	Model 924 Toxic Air Sampler with two sorbent tube sampling channels. Each sorbent tube holder has a 37mm or 47mm aerosol filter holder upstream.	16,686
#924T1F1	Model 924 Toxic Air Sampler with one sorbent tube sampling channel. Each sorbent tube holder has a 37mm or 47mm aerosol filter holder upstream.	12,922
#924F3	Model 924 Toxic Air Sampler with three 37mm or 47mm filter sampling channels.	19,010
#924F2	Model 924 Toxic Air Sampler with two 37mm or 47mm filter sampling channels.	15,846
#924F1	Model 924 Toxic Air Sampler with one 37mm or 47mm filter sampling channel.	12,682

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#924TC	Sorbent tube sampling channel including actuation valve, 2 lpm mass flow controller and accessories.	3,044
#924TFC	Sorbent tube sampling channel with 37mm or 47mm aerosol filter holder upstream. Includes actuation valve, 2 lpm mass flow controller and accessories.	3,404
#924FC	37mm or 47mm filter sampling channel including actuation valve, 30 lpm mass flow controller and accessories.	3,164
	Modification of system for 220V/50-60 Hz power requirement.	500

AUTOMATED CARBONYL SAMPLER MODEL 925

The automated carbonyl sampler is designed to collect ambient aldehydes and ketones using sep-pak tubes to satisfy the requirements of the Enhanced Ozone Monitoring Network in accordance with Section 182 of the 1990 Clean Air Act. Its design permits easy handling for eight 3-hourly samples, a 24-hour integrated sample, a 3-hourly collocational sample, and a quality control blank. The sampler has a built-in denuder oven for attachment of a KI denuder for the removal of O_3.

APPLICATIONS:

Collection of air samples for carbonyls using DNPH cartridges, or VOCs using other absorbents.

Sampler is appropriate for monitoring stations, indoor or outdoor.

FEATURES:

Reliable, and unattended operations.

Eight 3-hourly samples, one 24-hour integrated sample, one 3-hourly collocational sample, and a field blank (sampling time is selectable from ½ to 4 hours).

Built-in ozone denuder oven with adjustable temperature up to 50° C.

Does not degrade air sample; all wetted components of non-reactive material.

Mass flow controller maintains constant, yet adjustable flow rate.

Front panel access to all controls and indicators.

Digital display of flow rate.

Elapsed timer shows actual sampling time.

Instruments mounted on standard 19" rack.

Environmentally controlled outdoor enclosure available.

Easy to install, operate and maintain.

XonTech, Inc.

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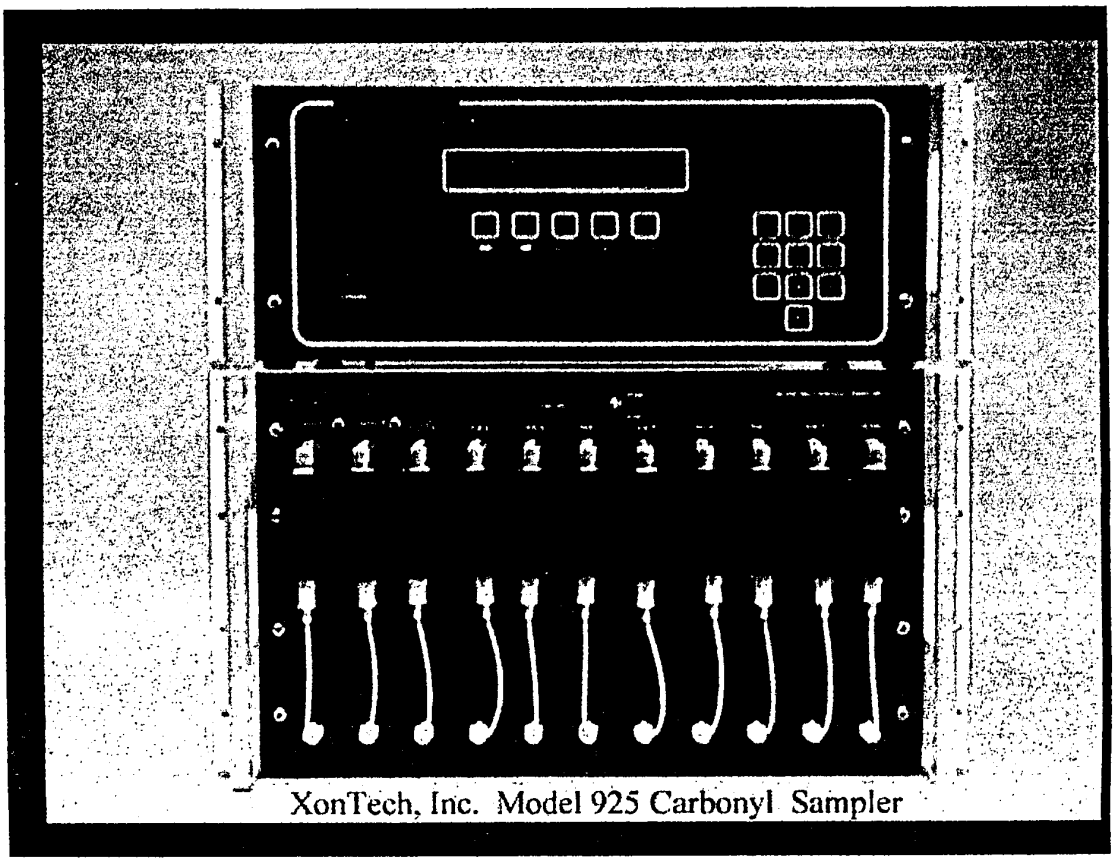

XonTech, Inc. Model 925 Carbonyl Sampler

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MODEL 925 AUTOMATED CARBONYL SAMPLER

Model 925	$15787.00
The Model 925 carbonyl sampler consists of one control module and one tube module. Instrument collects eight - 3 hour samples, one 24 - hour integrated sample, one 3 - hour collocational sample, and a field blank. The sampler has a built-in denuder oven. Also, each of the 10 sampling channels can be programmed for individual sampling times to meet different sampling requirements.	
Control module - contains microprocessor, electronics, mass flow controllers, LCD display, modem and cables. 7"H x 19"W x 13"D, 25 lbs., 19" rack mountable.	$ 8374.00
Tube module - contains 8 position rotary valve and position indicator, solenoids, denuder oven and temperature controller, electronics, and tube/filter holders. 4"H x 19"W x 13"D (tube fittings extend an additional 2.5" from rear panel), 5 lbs., 19" rack mountable.	$ 8346.00
Environmentally controlled outdoor enclosure. Lockable front and rear door, insulated with fan for temperature control. Enclosure will hold 1 tube and 1 control module. A fan aspirated sample manifold is provided. Legs for enclosure. Instrument to be at eye level. Enclosure is satin white finish.	$ 2416.00
Printer kit consisting of a light weight dot matrix printer (4"W x 4.5"L x 2"H) and an EPROM set which provides flow averages for all channels, total volume of air sampled in each channel, improved leak check procedure; prints control menu and schedule, sampling reports and others. The printer is not chassis or rack mounted but simply set on top of the 925 unit. For units with an outdoor enclosure, the printer is mounted on the back door.	$ 563.00
Modification of system for 220V/50-60 Hz power requirement.	$ 500.00

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