行政院所屬各機關因公出國人員出國報告書
（出國類別：開會研習）

參加「感應耦合電漿垂直加速飛行時間質譜儀教育訓練」報告

服務機關：行政院衛生署藥物食品檢驗局
姓名職稱：陳石松副研究員
派赴國家：澳洲 墨爾本省 佛蘭斯頓
出國期間：中華民國 99 年 10 月 25 至 10 月 29 日
報告日期：中華民國 99 年 12 月 10 日

目次

摘要

本局於本年度引進新一代設計之 Optimass 9500感應耦合電漿垂直加速飛行時間質譜儀(Inductively coupled plasma orthogonal acceleration time-of-flight mass spectrometer，ICP-oaTOF-MS)，期望用以改善解決目前採用四極柱式ICP-MS分析某些元素所遇到的干擾問題，利用TOF-MS的技術可以同步蒐集所有元素及其同位素質譜的資訊，用以加強分析數據之正確性；因為 oaTOF-MS是用於ICP-MS領域中為較新且前瞻性的技術，故要求製造廠 GBC Scientific Equipment Pty Ltd.及台灣總代理利泓科技有限公司於交貨前，提供到澳洲工廠研習相關技術課程，希望順利導入此分析技術於食品藥物化學分析領域之應用。

此次研習課程係由澳洲GBC公司產品經理亦是ICP-oaTOF-MS設計小組之原創者 Dr. Flynn授以該設備之工作原理、特性、調機技術、基本維護等專業技術，並與Dr. Flynn於食品藥物化學分析領域應用需求上之交流，希望能達到引用新技術並進而能改良目前之分析方法。併將研習成果帶回本局轉授予其他相關業務之同仁，俾使此次出國研習獲得最大之效益。

壹、目的

四極柱式 ICP-MS技術於1980年代已經開始商用化，目前此類 ICP-MS的技術已臻於成熟，但由於四極柱式的質譜分析器的物理限制，以致四極柱式ICP-MS的解析度仍無法有效分離複合離子（polyatom）或相同質荷比之同位素（isotope）干擾物。故於1990年代後期，四極柱式ICP-MS的發展大多著墨如何在質譜分析器前加上並改良可降低干擾的篩選器或反應器，但也因爲是利用碰撞之物理方式或加入反應性氣體以化學方法避免干擾，因此也只能針對某些特定元素做優化，卻必須同步犧牲其他元素的感度，直到目前，四極柱式 ICP-MS元件之進化仍有些許更新，但是仍無法避免先天上設計的限制。另因爲四極柱式ICP-MS是採用篩選質荷比的方式進行掃描式分析，故分析不同元素之間的時間差也是一個無法有效克服的問題，因此在擴充直接進樣的分析技術上就面臨穩定性差及分析元素數受限制的瓶頸。

GBC Scientific Equipment Pty Ltd.於 1995年成功的將感應耦合電漿與垂直加速質譜儀做結合而生產目前世界上唯一一套「感應耦合電漿垂直加速質譜儀，ICP-oaTOF-MS」，並成功的取得世界專利，ICP-MS得以出現完全不同技術層面的新設計，GBC改變了軸向加速式 ICP-aaTOF-MS的解析度不佳及抑制干擾差的問題，而發展出 Optimass系列的高解析度感應耦合電漿垂直加速質譜儀，而軸向加速式 ICP-TOF-MS則於 2000年年代消失於化學分析儀器市場。

此次訓練課程目的爲：1. 學習 ICP-oaTOF-MS的原理技術。2. 實際上機進行操作及調校優化離子光學及質譜分析器。3. 了解 ICP-oaTOF-MS擴充配件及於食品藥物化學領域的應用。4. 與 Dr. Flynn作經驗交流分享。

貳、過程

一、行程與工作記要

日期	工作記要
99 年 10 月 24 日	啓程
99 年 10 月 25 日	■ GBC Scientific 公司及組裝廠介紹參觀 ■ ICP-oTOFMS 原理介紹 ■ ICP-oTOFMS 儀器硬體介紹 & 實機參觀介紹
99 年 10 月 26 日	■ ICP-oTOFMS 操作軟體介紹& 基本實機操作 ■ ICP-oTOFMS 進階應用課程(I) ➢ HPLC 物種分析應用介紹
99 年 10 月 27 日	■ ICP-oTOFMS 進階應用課程(II) ➢ Laser Ablation 雷射固體直接進樣系統介紹 ➢ 有機溶質進樣系統介紹 ➢ ETV 微量石墨原子化進樣系統介紹
99 年 10 月 28 日	■ ICP-oTOFMS 細部零件維護課程(I) ➢ 電漿產生器、Torch 及週邊系統之安裝維護 ➢ 進樣系統及週邊系統之安裝維護 ➢ Cones Interface 總成之安裝維護
99 年 10 月 29 日	■ ICP-oTOFMS 細部零件維護課程(II) ➢ Smartgate 離子遮罩總成之安裝維護 ➢ TOF Mass 偵測器及飛行腔之維護 ➢ 真空系統之安裝維護 ■ 故障排除及遠端控制支援 ■ Q & A
99 年 10 月 30 日	回程

二、訓練課程日期及地點

訓練課程由 10 月 25 日起至 29 日止共計 5 天。上課地點於 GBC Scientific Equipment Pty Ltd. 公司會議室及 Optimass 9500 工廠生產線儀器測試區，由亞太區經理 Paul Liberatore 及 Optimass 產品經理 Dr. Andrew Flynn Saint 負責教授相關課程。

三、訓練課程內容

訓練課程包涵從儀器設計原理，軟、硬體之介紹，到儀器基本操作及最佳化調整，再到基本維護及故障除等內容，由於課程講授模式採段落式說明及實機實體操作對照相互穿插說明，故將此次課程整合後分段說明：

(一)、 Optimass9500 主要組件及功能：

A、Plasma Generator(電漿產生器)：包含 RF Generator 及 Torch 組件，其功能爲產生電漿炬，提供能量將樣品碎裂成壹價離子；RF 的頻率爲 27MHz 的原因是此頻率下所產生的壹價離子較 40MHz 的 RF(主要目的是激發離子產生特異發射光譜線)高很多，因此 ICP-MS 多採 27MHz RF 產生器。

B、Interface (電漿錐體界面)：其中包含三層錐體及兩道真空系統，其功能係將電漿內極高的陰離子及電子等篩選掉，只讓待測之陽離子進入質譜檢測系統；

i. 第一及第二道錐體，負責篩選只讓中心離子束進入後面光學系統，其中的空腔抽以一般真空 1~2 torr 使得部分干擾離子亦能被抽析離開降低背景，此道錐體可以換成雙層式錐體，藉由更換內層錐心之材質(Pt or Ni)可避免 HF 之侵蝕或避免欲分析元素之背景干擾問題(如 Fe 等)

ii. 第二道及第三道錐體中間空腔則可提供約 10-4torr 的真空，可讓背景在此降到更低的程度

iii. 第三道 Cone 通以較高的負電壓，可以將大部分電子及陰離子推開，而通負電的第三層 Cone 能將陽離子引聚進入孔洞進入離子光學(Ion Optics)部分提高陽離子數量已增加感度

iv. 三層錐體界面爲 GBC 的首創，目前其他廠商之新機型亦升級改採三層錐

C、**Ion Optics**(離子光學腔)：利用內部的各種光圈、電磁場供應系統，讓離子束能形成所需的形狀，以增加質譜的空間聚焦性，提高元素質譜解析度，並可去除干擾物質。

D、**Orthogonal Accelerator**(垂直加速器)：將離子束通已電場使其產生垂直加速度，進入質譜飛行腔體。

E、**Blanker**(背景抑制系統)：SMARTGATE 背景抑制系統放置在離子第一空間聚交點，可以將不要的離子移除，降低質譜背景干擾情形，並可保護質譜偵測器，避免遭受過量離子衝撞而感度衰減。

F、**Flight Chamber**(飛行腔)：欲分析元素之離子經過 Samrtgate 之刪選後，歲進入此高真空(5*10^{-6} torr)之腔體中做物理性分離，原子序的小的會先通過，反之亦反之；Optimass 9500 的飛行腔提供了 1.2 m 的飛行距離，且離子採拋物線路線飛行，離子間的斥力感擾較少、飛行距離較長數倍(四極柱通常爲 0.25~0.3m)，因此造就了優於四極柱 3~5 倍的質譜解析度。

G、**Detector**(偵測器)：Discrete dynode multiplier 爲一個與 Agilent 共用的元件，作動方式有點類似光電倍增管，但差異的是 Discrete dynode multiplier 是一個裸露的元件(PMT 有用石英管封包)，故需安置於飛行腔中受到高真空的保護，其中 Discrete dynode multiplier 使用了 22 到放大極板，因此一個離子撞擊可以產生大於 10^{7} 電子訊號，因此感度是相當高的，但也因爲感度之高，Smartgate blanker 的設定就更顯重要，過多的干擾離子長期送入偵測器中，會讓 Discrete dynode multiplier 的壽命減短，否則此偵測器壽命基本都達 3~5 年以上(依據樣品特性會有差異)。

(二)、 可擴充配件及應用說明

A、高壓液相層析系統(HPLC)：GBC 本身亦有生產 HPLC 系統，因此亦可擴充 LC-ICP-MS 的應用作物種分析，唯獨較不同的是，Optimass 9500 可以作的物種分析是全譜的同步分析，也因爲可以做全譜的分析，因此如果在流動相溶液加入內標準品同時分析內標作爲校正指標，Optimass9500 可提

B、雷射剝蝕系統（Laser Ablation，LA）：目前用在元素分析的直接進樣裝置有兩種，一個是電弧剝蝕，另一個是雷射剝蝕；前者電弧剝蝕最大的問題在於放置樣品後仍需形成導電通路才可使用，故幾乎只用於金屬產業；而 Laser Ablation 則是以提供超高密度短波長雷射做爲剝蝕能量來源，因此樣品的導電性就不是問題；Laser Ablation 技術雖發展一段時間，但是於 ICP-MS 的應用上，仍受到瓶頸，原因無他，就是因爲目前市場上多是以四極柱式 ICP-MS 作元素分析，但是四極柱式 ICP-MS 的分析速度遠不及 Laser Ablation 蝕刻樣品的差異性；而 Optimass9500 每秒可以蒐集 29000 個全元素質譜才有能力判別真實樣品差異下的數據，且因爲全元素質譜，故能同步分析全元素含量及其同位素比，是目前除多通道高解析度感應耦合電漿質譜儀(MC-HR-ICP-MS)以外能達到相同功能的設備，因此 Laser Ablation 搭配上 Optimass 9500 ICP-oaTOF-MS 才能真正發揮該效能，未來亦可引進此設備做食品化學材料減檢測使用，朝向開發綠色快速檢測方法發展。

C、電熱氣化裝置(Electrothermal vaporizers，ETV)：電熱氣化裝置爲類似石墨爐原子吸收光譜儀的石墨加熱模組，它可以升溫程式將樣品的基質(水分、有機質等)先利用乾燥及灰化的處理過程，將樣品做一個預處理，再將其原子化後以載流氣體導入 Optimass 9500 ICP-oaTOF-MS 中檢測，如此一來這些物質的干擾則可以大大降低。此外本模組優點有二：一是樣品量只需要 50~100uL，二來可以用重複注射乾燥濃縮（Hot Injection）做樣品濃縮的功能，因此 ETV-ICP-MS 非常適合用於液態檢體或臨床醫學生化檢體分析以及有機質干擾甚多的樣品。Optimass 9500 如果搭配這類配件時，可以直接表現出不同元素被瞬間加熱的兩秒鐘之間，不同的原子化時間(溫度不同)裂解出來的時間差可以完全被表現出來，可同時驗證石墨爐 AAS 的理論參數，而此類配件亦不適合四級柱式 ICP-MS 搭配使用，因爲瞬間氣化僅有兩秒鐘，只有 Optimass 9500 這種 ICP-oaTOF-MS 可以符合這種瞬間取樣的應用需求；爲此類配件尚爲量產化，GBC 將該公司

(三)、　其他說明：

GBC 亦提供包括重金屬分析、物種分析及重金屬指紋比對（**Fingerprinting**）等 Application note 及參考文獻資料作爲本局未來應用 Optimass 9500 ICP-oaTOF-MS 檢測食品及藥品中重金屬分析及物種分析等之參考。

參、研習心得

(一)、 感應耦合電漿垂直加速飛行時間質譜儀具有同步全譜檢測等優點，特別適合獲取瞬時信號的訊息，配合相關分析技術，可降低基質干擾，提高檢驗結果之準確度。

(二)、 以同位素稀釋法（isotope dilution method）配合感應耦合電漿垂直加速飛行時間質譜儀應用於食品及藥品中重金屬檢驗可獲得更高準確度之檢測結果。

(三)、 以高壓液相層析系統配合感應耦合電漿垂直加速飛行時間質譜儀應用於物種分析可同步獲得多元素物種之檢測結果。

(四)、 以雷射剝蝕系統直接進樣配合感應耦合電漿垂直加速飛行時間質譜儀開發綠色快速檢測方法可省略樣品前處理之步驟，避免消化前處理時污染或待測元素之漏失。

(五)、 以電熱氣化裝置配合感應耦合電漿垂直加速飛行時間質譜儀可直接進行液態檢體或臨床醫學生化檢體分析以及有機質干擾甚多的樣品，避免消化前處理時污染或待測元素之漏失，及減少有機質干擾。

肆、建議

一、利用感應耦合電漿垂直加速飛行時間質譜儀探討並建立以同位素稀釋法檢測食品及藥品中重金屬之標準檢驗方法。

二、本局有關食品中重金屬物種分析目前僅完成砷物種及甲基汞分析，未來希望利用感應耦合電漿垂直加速飛行時間質譜儀可同步全譜檢測之特性，進行多元素物種分析之研究。

三、雷射剝蝕感應耦合電漿質譜法及電熱氣化感應耦合電漿質譜法具直接進樣、無污染、快速之優點，未來亦可引進此設備作爲食品及藥品化學檢測使用，朝向開發綠色快速檢測方法發展。

四、本局有關重金屬微量分析設備已達國際水準，未來應精進相關研究，培養研究人才，並積極參與相關研討會及實驗室間共同試驗等國際交流活動，以提升本局國際知名度。

伍、附件

一、研習會課程與講義。

GBC Optimass Ion Optics

- All ICP-MS requires ion optics to transport ions effectively to the analyser
- How do ion optics work?
- Optimass unique 3 cone interface
- Optimass unique ion optics

All ICP-MS has some form of Ion Optics

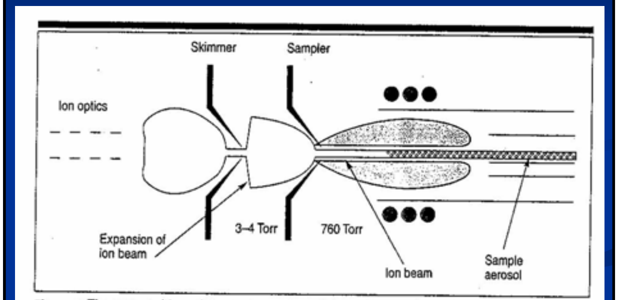
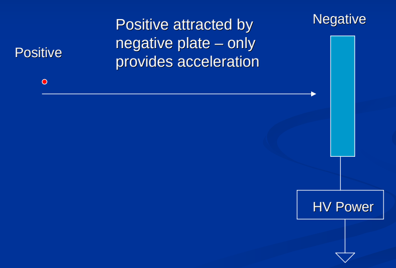


Figure 6. The composition of the ion beam is maintained, assuming a neutral plasma.

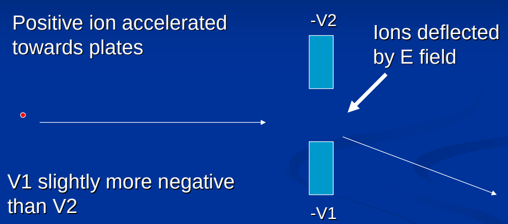
How do Ion Optics Work

- Use electromagnetic fields to change direction of motion of ions moving in vacuum
- In MS use only electrostatic – not mass selective

How do Ion Optics Work

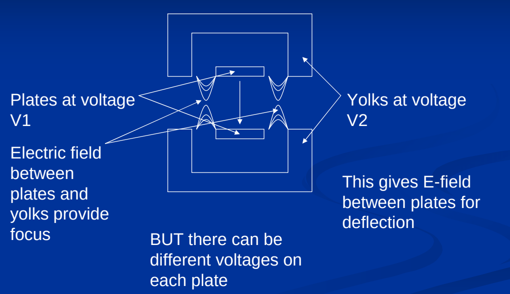


How do Ion Optics Work

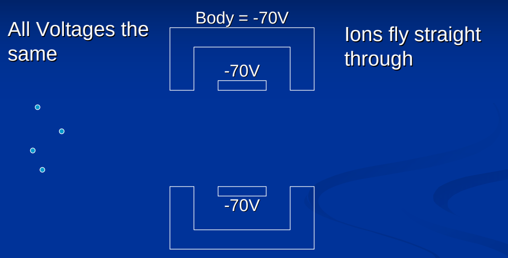


This is the basis of ion optics

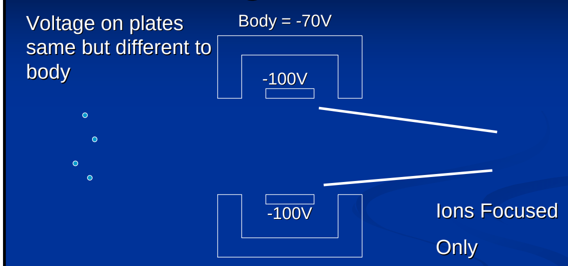
Optimass Ion Optics configuration



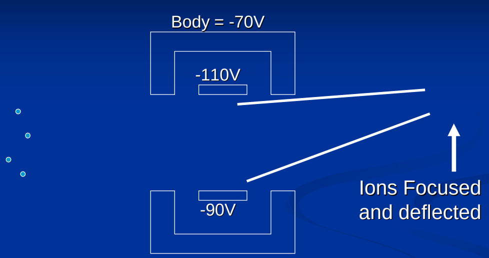
Focusing and Deflection



Focusing and Deflection



Focusing and Deflection



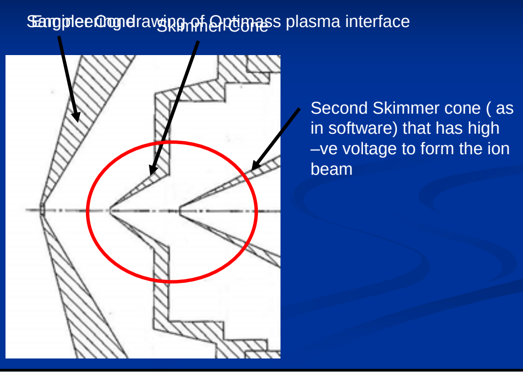
Voltage on plates slightly different - Mean = 100V

Def = 10V

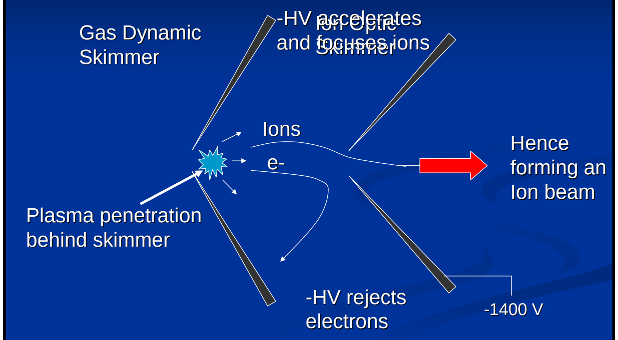
Major components of Optimass Ion Optics

- From plasma to ion beam
- Front End Ion Optics – form the ion beam from plasma
- Y and Z deflection and focussing (vertical and horizontal) to create "ribbon" beam
- Vacuum conductivity restrictor
- Presentation of beam to OA

From plasma to ion beam



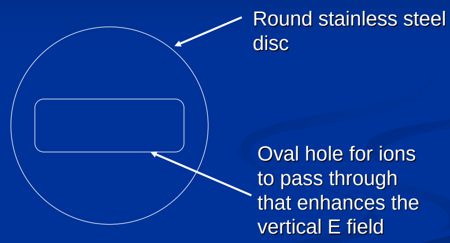
Optimass – Front End Ion Optics



GBC Optimass 9500 ion optics

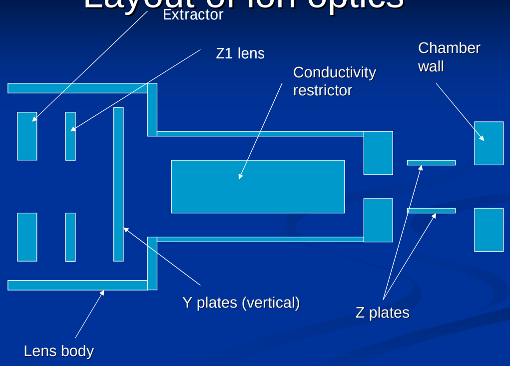
- Optimass 9500 requires a unique beam shape
- Most ICP-MS require a beam with cylindrical symmetry (round)
- Optimass 9500 requires a beam that is “ribbon” shaped
- This requires special ion optics

GBC Ion Optic Element



This is used for the extractor and Z1 electrode

Layout of ion optics



Actual Layout

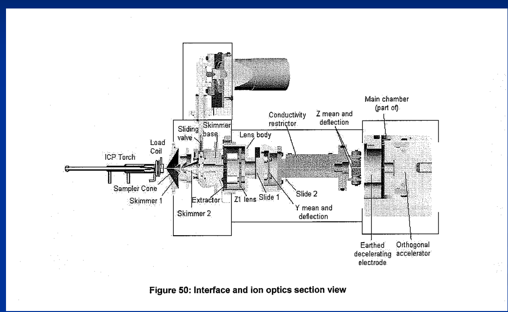
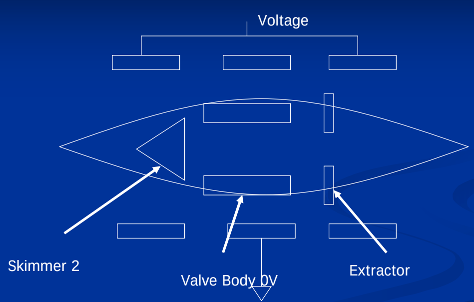
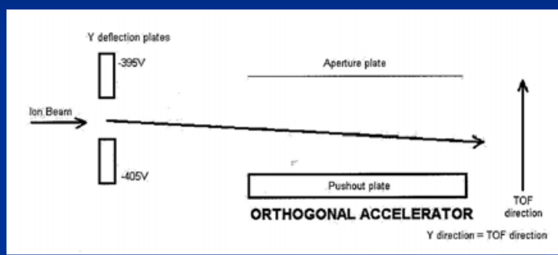


Figure 50: Interface and ion optics section view

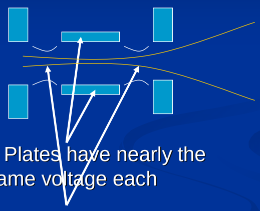
Optimass - Front End Optics



Y deflection



Idea of Z - Plates

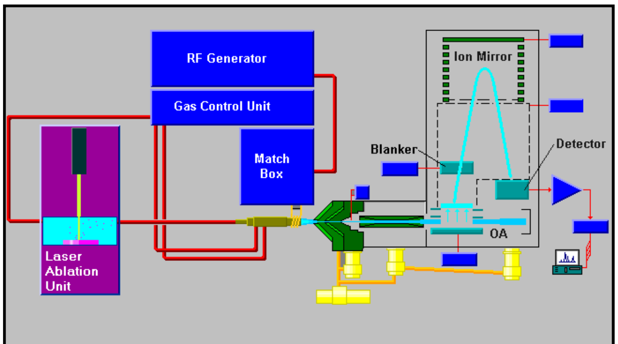


Summary

- Optimass ion optics are electrostatic only
- They convert the plasma to an ion beam
- They deflect and focus the ion beam to form a "ribbon" shaped beam
- This is a tall narrow beam for maximum sensitivity and best resolution

Application

Measurement of Isotope Ratio with Laser Ablation ICP MS



Scheme of ICP-oa-TOF mass spectrometer with Laser ablation sampling

Problems of LA - ICP MS

•In some conditions fractionation of species can be very severe.

•Precision of measurements is strongly impaired by signal fluctuations caused by large particulates in the sample flow.

Advantages of LA ICP oa-TOF MS

- Isotopes of every element are represented in the particulates proportionally.
- Their signals behave synchronously.
- The ratio of isotope signals measured simultaneously has high precision.

Advantages of LA ICP oa-TOF MS.

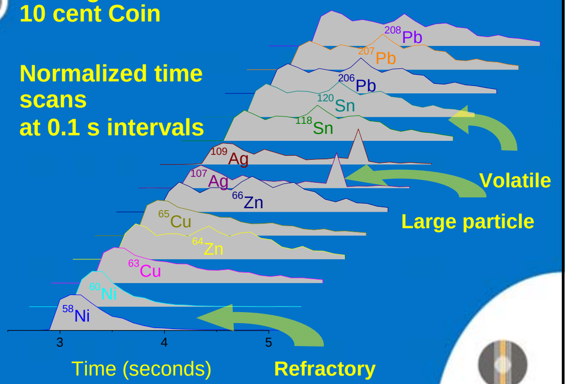
•It provides efficient simultaneous recording of ALL masses.

•The composition of large particles can be investigated

•Time response of different elements ablated in a single laser shot can be studied.

A Single Laser Shot of an Australian 10 cent Coin

Normalized time scans at 0.1 s intervals



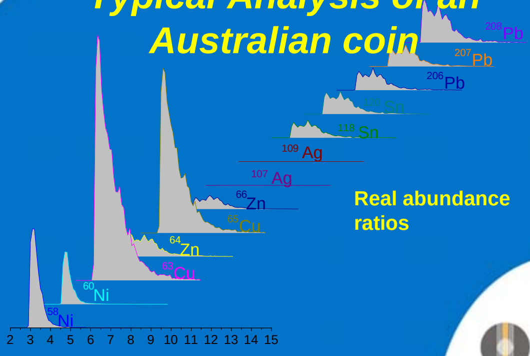
Fractionation Analysis

- All refractory and volatile species are appearing in the scan simultaneously
- The volatile species remain longer as they are represented in larger particles, which have longer transportation time.
- Short duration peaks of some elements indicate the arrival of large particles

ICP-orthogonal Time of Flight mass Spectrometers

www.gbcsci.com

Typical Analysis of an Australian coin



Real abundance ratios

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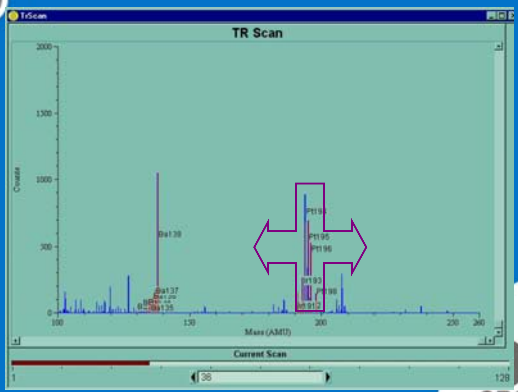

ICP-orthogonal Time of Flight mass Spectrometers

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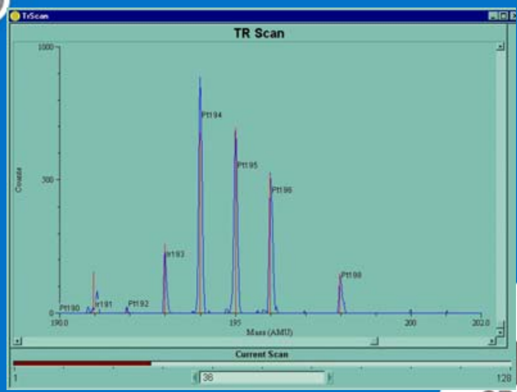
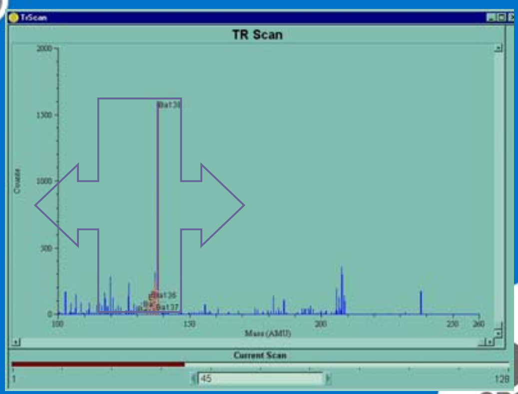


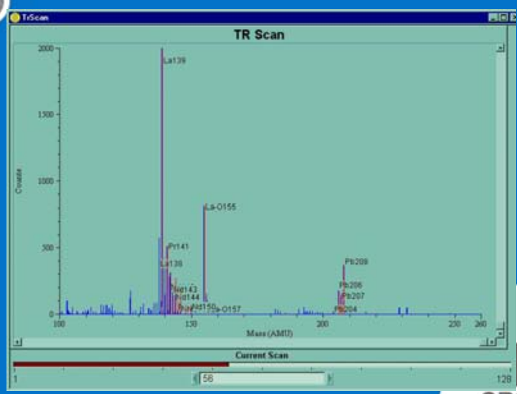
ICP-orthogonal Time of Flight mass Spectrometers

www.gbcsci.com



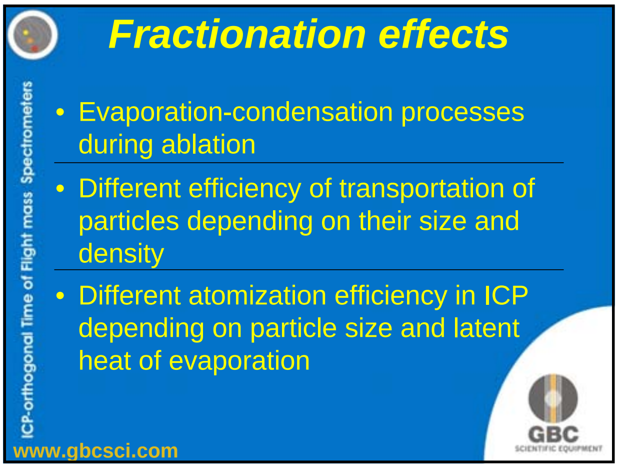
ICP-orthogonal Time of Flight mass Spectrometers

www.gbcsci.com



ICP-orthogonal Time of Flight mass Spectrometers

www.gbcsci.com


Fractionation effects
• Evaporation-condensation processes during ablation
• Different efficiency of transportation of particles depending on their size and density
• Different atomization efficiency in ICP depending on particle size and latent heat of evaporation
ICP-orthogonal Time of Flight mass Spectrometers
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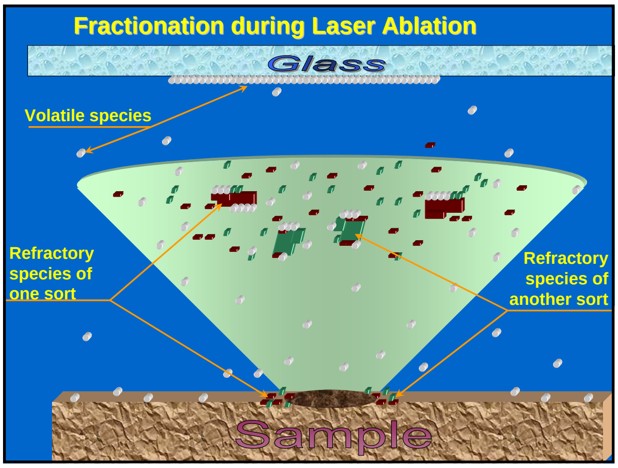
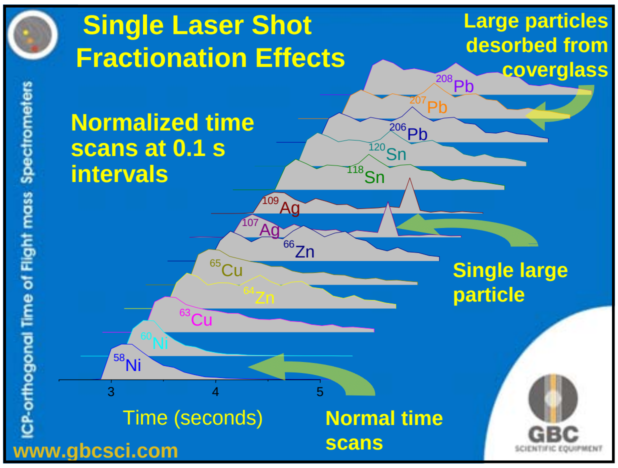
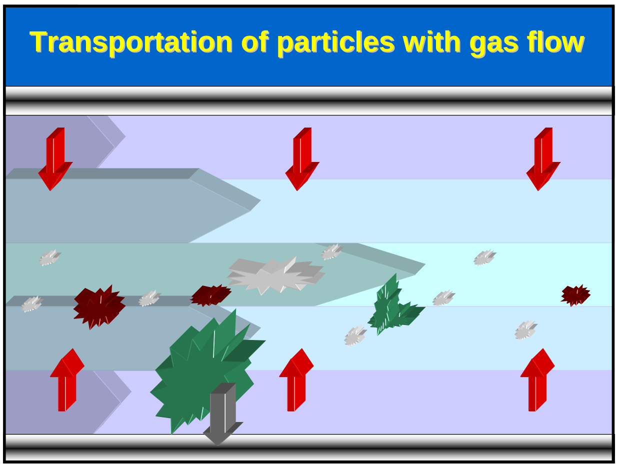
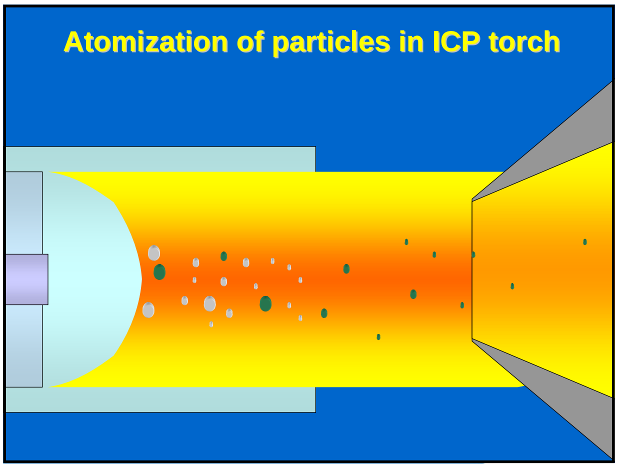
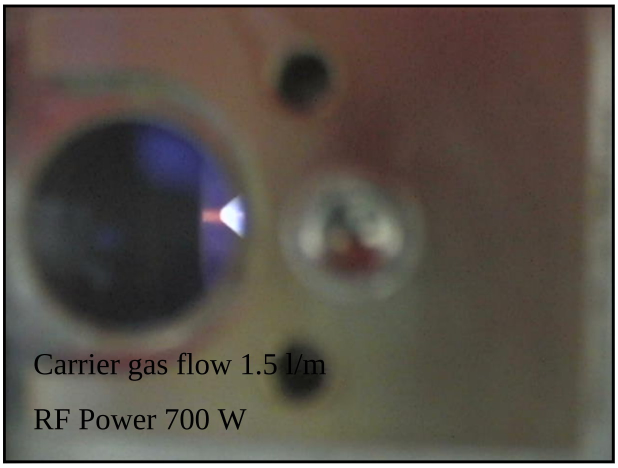
SCIENTIFIC EQUIPMENT

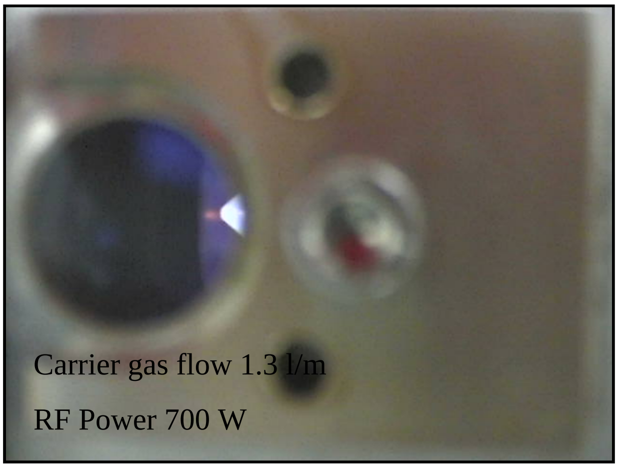

Fractionation during Laser Ablation
Glass
Volatile species
Refractory species of one sort
Refractory species of another sort
Sample

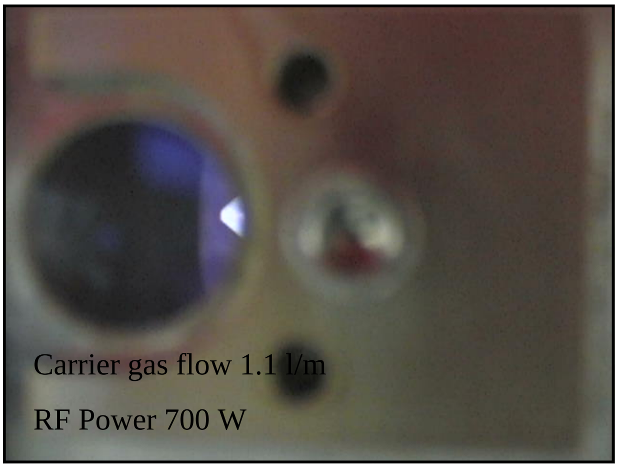

Single Laser Shot Fractionation Effects
Large particles desorbed from coverglass
Normalized time scans at 0.1 s intervals
208Pb
207Pb
206Pb
120Sn
118Sn
109Ag
107Ag
66Zn
65Cu
64Zn
63Cu
60Ni
58Ni
Single large particle
3
4
5
Time (seconds)
Normal time scans
ICP-orthogonal Time of Flight mass Spectrometers
www.gbcsci.com
GBC
SCIENTIFIC EQUIPMENT

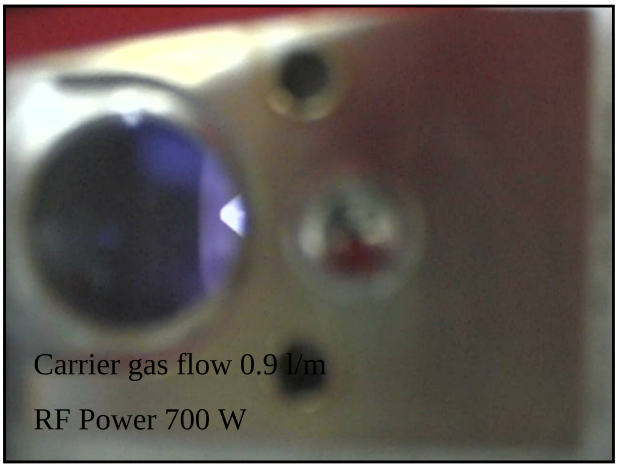

Transportation of particles with gas flow

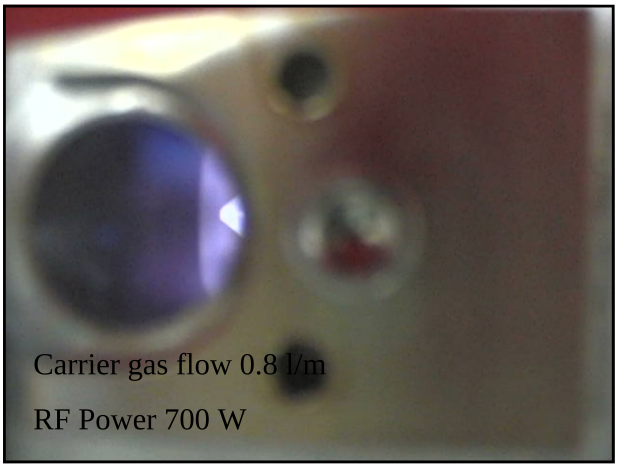

Atomization of particles in ICP torch

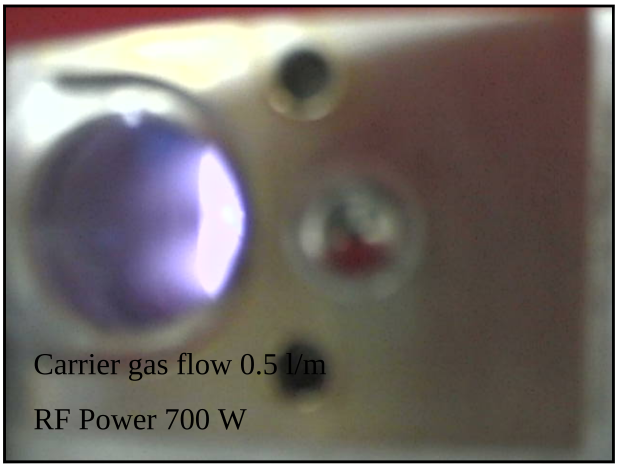

Carrier gas flow 1.5 l/m
RF Power 700 W











Precision of Isotopes Ratios

- Measuring individual isotopes results in high RSD’s
- However, isotope ratio precision is improved by an order of magnitude due to simultaneous nature of orthogonal TOF MS
- No sacrifice of your analysis time will occur

ICP-orthogonal Time of Flight mass Spectrometers

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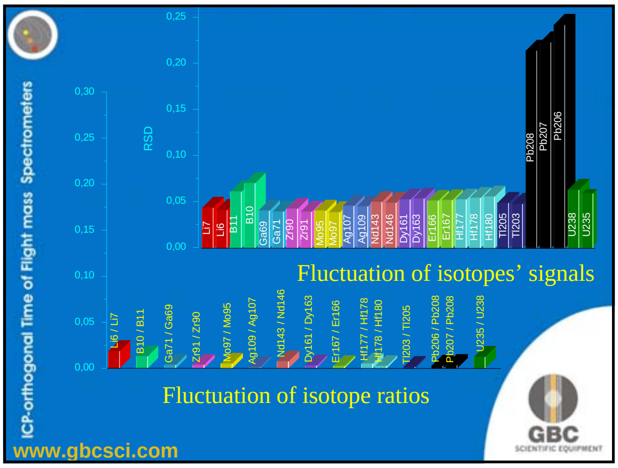

ICP-orthogonal Time of Flight mass Spectrometers

Conclusions

- A Superior method of measuring isotope ratio in LA-ICP based analysis
- Orthogonal TOF allows efficient monitoring of all masses for a single laser shot
- Orthogonal TOF reveals fractionation and other temporal effects not observed in typical quadrupole based analysis

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OPTIMASS 9500
2nd GENERATION Orthogonal Time of Flight ICP- MS

A NEW Speed Benchmark in ICP-MS Analysis

ICP-orthogonal Time of Flight mass Spectrometers

www.gbcsci.com

OptiMass 9500…

www.gbcsci.com

ICP-MS OVERVIEW

- First commercialised in 1983
- Multi-element analysis at ppt levels
- Wide elemental coverage
- Isotopic information
- Environmental, clinical, semiconductor, metallurgical, nuclear and geochemical industries

ICP-orthogonal Time of Flight mass Spectrometers

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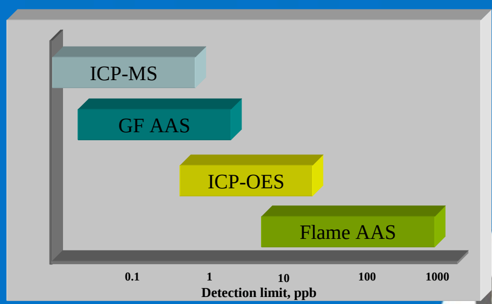
Relative Detection Limits



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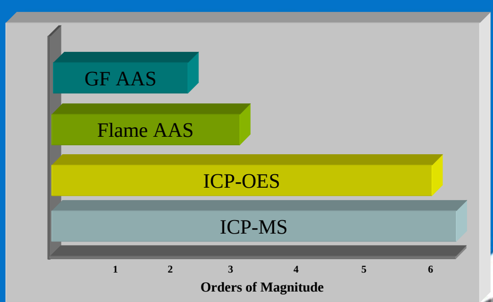
Analytical Working Ranges



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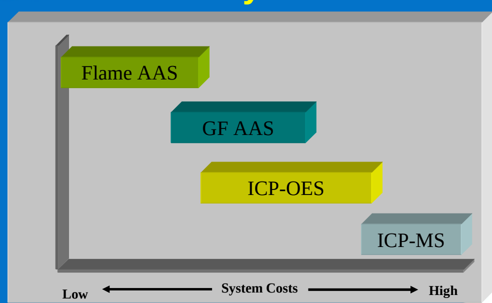
Relative System Costs



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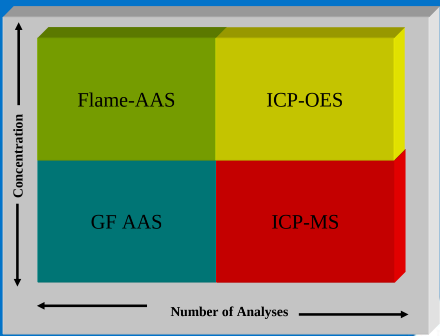
Guide to Selection



ICP-orthogonal Time of Flight mass Spectrometers

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	ICP-MS	ICP-OES	FLAME AAS	FURNACE AAS
Elements	116	75	68	50
Isotope Analysis	yes all	no	no	no
Detection Limits	ppt	ppb	ppb/ppm	ppb
Sample Throughput	All masses 45 sec/sample	30 elements <4 min/sample	1 element 9 sec/sample	1 element 2 – 3 min/sample
Linear Dynamic Range	10^7	10^6	10^3	10^2
Precision	0.5 – 2%	0.3 – 2%	0.1 – 1%	1 – 5%
Interferences				
Spectral	few	common	almost none	few
Matrix	moderate	almost none	moderate	many
Ionization	minimal	some	some	minimal
Mass Effects	some	NA	NA	NA
Isotope	yes	none	none	none
Methodology				
Dissolved Salts	<10%	<40%	<20%	>20%
Sample consumption	low	moderate/high	high	very low
Semi – Quant	yes	yes	no	no
Retrosp Semi Quant	yes	no	no	no
Fingerprinting	yes	no	no	no
Method Development	moderate	moderate	easy	difficult
Data interpretation	moderate	moderate	easy	easy
Routine Operation	moderate	easy	easy	easy
Unattended Operation	yes	yes	no	no
Operating costs	medium/high	medium	low	medium
Combustable gases	no	no	no	no

ICP-ortho

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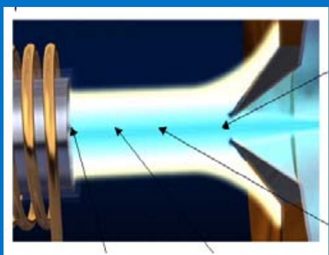
The ICP Torch



Analytes present as M^+ ions

Atoms are formed and then ionized

Aerosol is Dried

Particles are decomposed and dissociated

ICP-orthogonal Time of Flight mass Spectrometers

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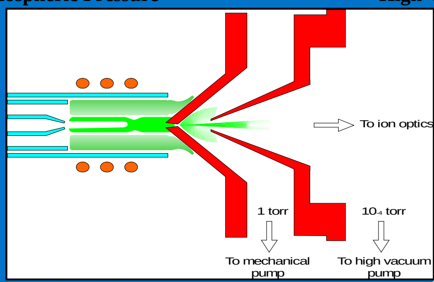
Torch and Interface

Atmospheric Pressure → High Vacuum



ICP-orthogonal Time of Flight mass Spectrometers

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Different mass analysers

- Quadrupole analyser – uses resonant motion of ions in RF field to allow only one mass to pass at a time.
- Magnetic Sector uses magnetic field to allow one mass to pass at a time.
- Time-of-Flight - uses the fact that different mass ions take different times to move over a pre-determined distance th allows all masses to be analysed simultaneously.

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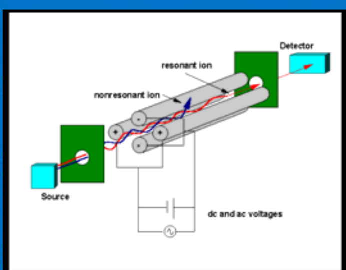
Quadrupole Mass Spectrometer



- Quadrupole Mass Filter
- Low Resolution
- Trade off between resolution and transmission - increasing resolution decreases sensitivity over entire mass range

ICP-orthogonal Time of Flight mass Spectrometers

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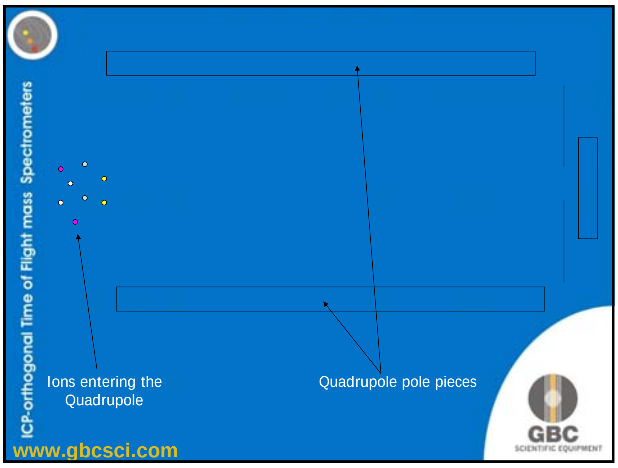
ICP-orthogonal Time of Flight mass Spectrometers
Ions entering the Quadrupole
Quadrupole pole pieces
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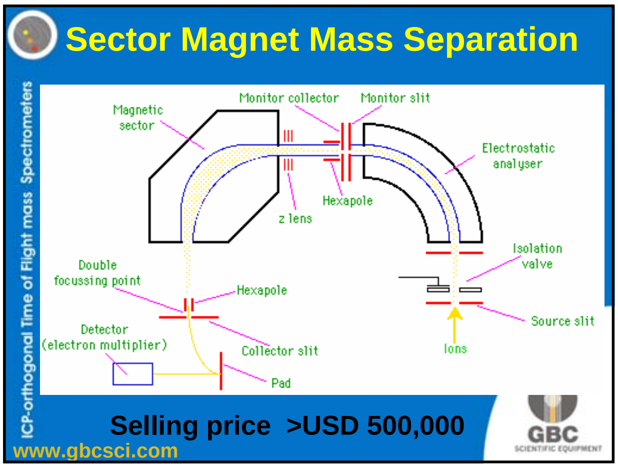
Sector Magnet Mass Separation
ICP-orthogonal Time of Flight mass Spectrometers
Magnetic sector
Monitor collector
Monitor slit
Electrostatic analyser
Hexapole
z lens
Isolation valve
Double focussing point
Hexapole
Source slit
Detector (electron multiplier)
Collector slit
Ions
Pad
Selling price >USD 500,000
www.gbcsci.com
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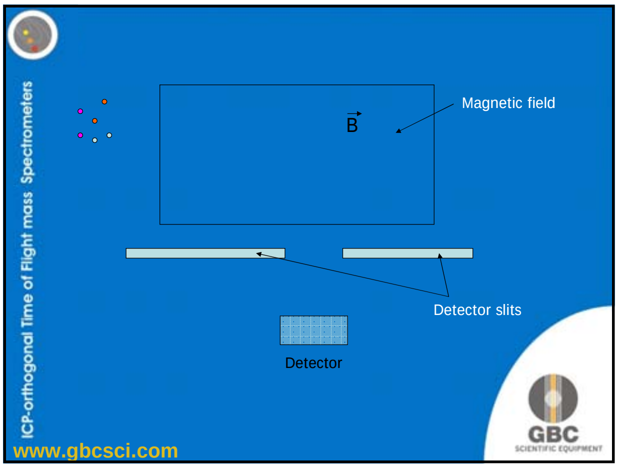
ICP-orthogonal Time of Flight mass Spectrometers
B
Magnetic field
Detector slits
Detector
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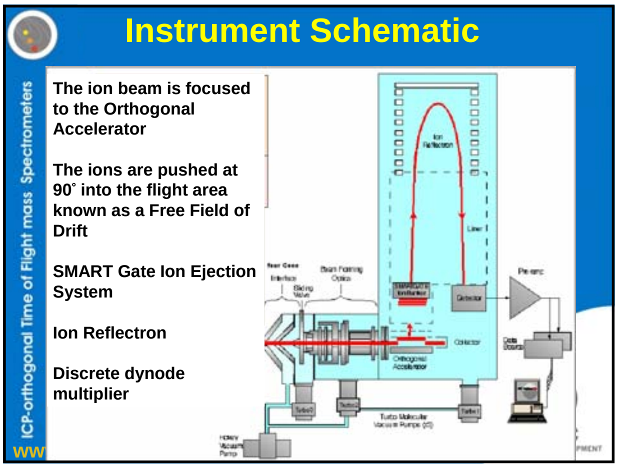
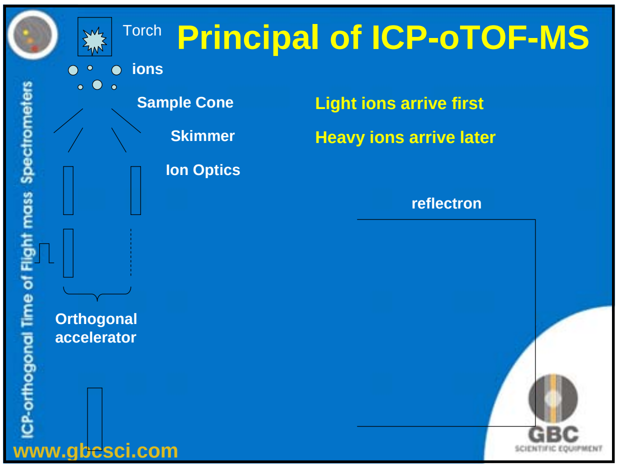

Instrument Schematic
ICP-orthogonal Time of Flight mass Spectrometers
The ion beam is focused to the Orthogonal Accelerator
The ions are pushed at 90° into the flight area known as a Free Field of Drift
SMART Gate Ion Ejection System
Ion Reflectron
Discrete dynode multiplier


Principal of ICP-oTOF-MS
ICP-orthogonal Time of Flight mass Spectrometers
Torch
ions
Sample Cone
Skimmer
Ion Optics
Light ions arrive first
Heavy ions arrive later
reflectron
Orthogonal accelerator
www.gbcsci.com
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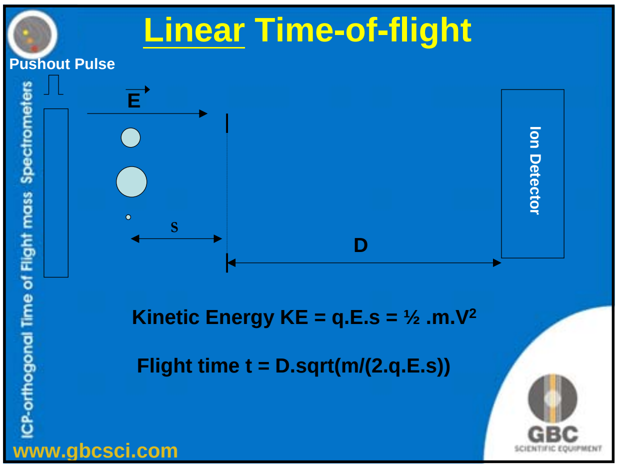
Linear Time-of-flight
ICP-orthogonal Time of Flight mass Spectrometers
Pushout Pulse
E
s
D
Ion Detector
Kinetic Energy KE = q.E.s = ½ .m.V²
Flight time t = D.sqrt(m/(2.q.E.s))
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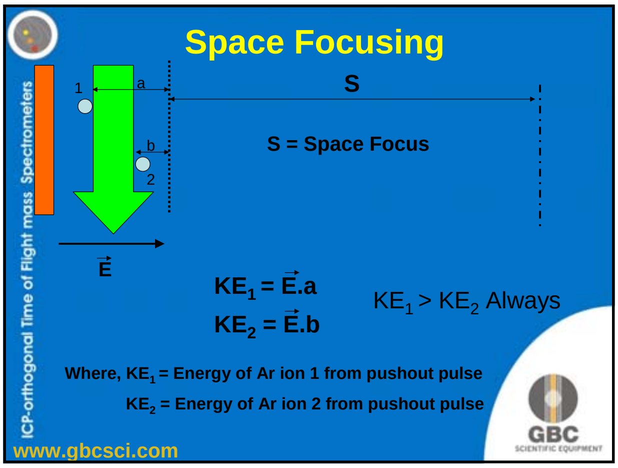
Space Focusing
ICP-orthogonal Time of Flight mass Spectrometers
1
a
b
2
S
S = Space Focus
E
KE1 = E.a
KE2 = E.b
KE1 > KE2 Always
Where, KE1 = Energy of Ar ion 1 from pushout pulse
KE2 = Energy of Ar ion 2 from pushout pulse
GBC SCIENTIFIC EQUIPMENT
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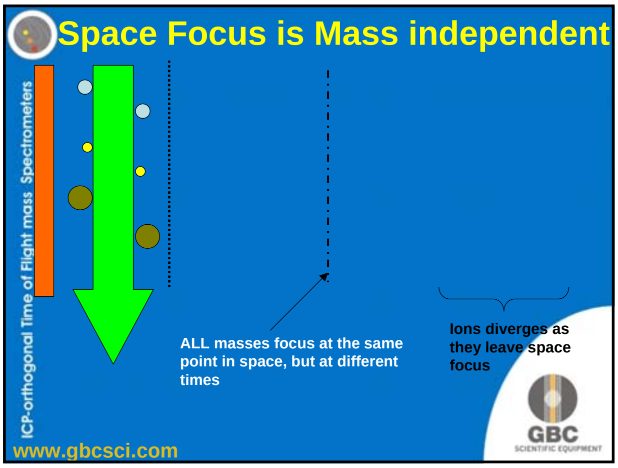
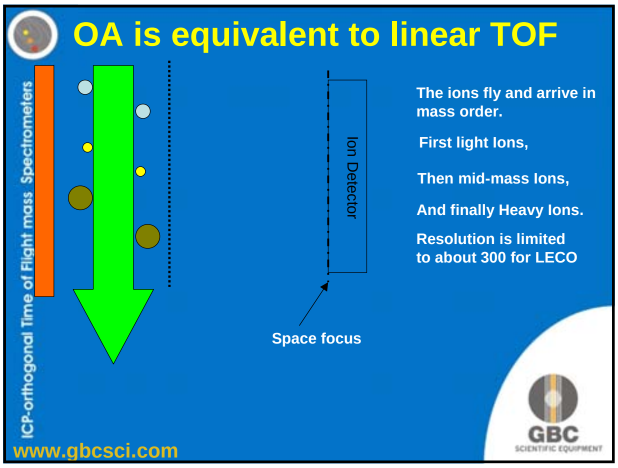
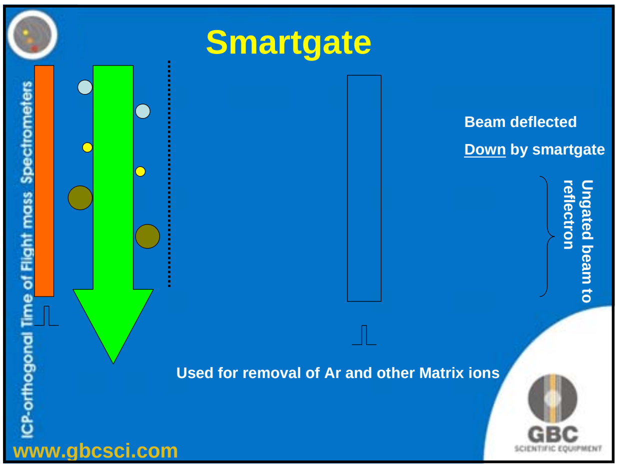
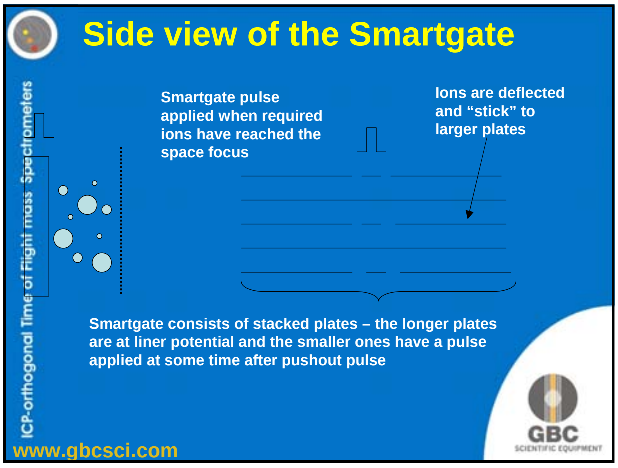

Space Focus is Mass independent
ICP-orthogonal Time of Flight mass Spectrometers
ALL masses focus at the same point in space, but at different times
Ions diverges as they leave space focus
GBC SCIENTIFIC EQUIPMENT
www.gbcsci.com


OA is equivalent to linear TOF
ICP-orthogonal Time of Flight mass Spectrometers
Ion Detector
The ions fly and arrive in mass order.
First light Ions,
Then mid-mass Ions,
And finally Heavy Ions.
Resolution is limited to about 300 for LECO
Space focus
GBC SCIENTIFIC EQUIPMENT
www.gbcsci.com


Smartgate
ICP-orthogonal Time of Flight mass Spectrometers
Beam deflected
Down by smartgate
Ungated beam to reflectron
Used for removal of Ar and other Matrix ions
GBC SCIENTIFIC EQUIPMENT
www.gbcsci.com


Side view of the Smartgate
ICP-orthogonal Time of Flight mass Spectrometers
Smartgate pulse applied when required ions have reached the space focus
Ions are deflected and "stick" to larger plates
Smartgate consists of stacked plates – the longer plates are at liner potential and the smaller ones have a pulse applied at some time after pushout pulse
GBC SCIENTIFIC EQUIPMENT
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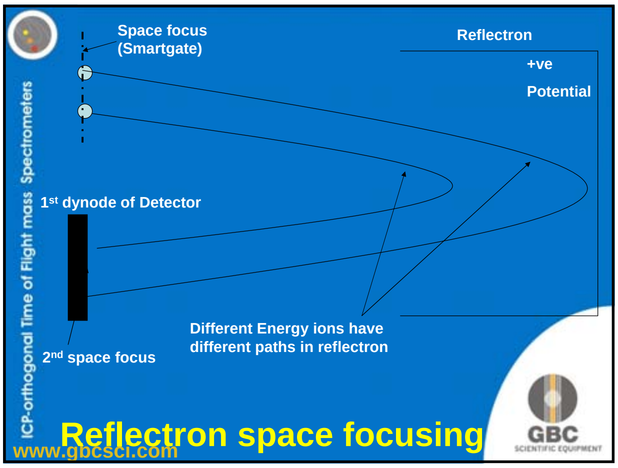
Space focus (Smartgate)
Reflectron
+ve
Potential
ICP-orthogonal Time of Flight mass Spectrometers
1st dynode of Detector
2nd space focus
Different Energy ions have different paths in reflectron
Reflectron space focusing
GBC SCIENTIFIC EQUIPMENT
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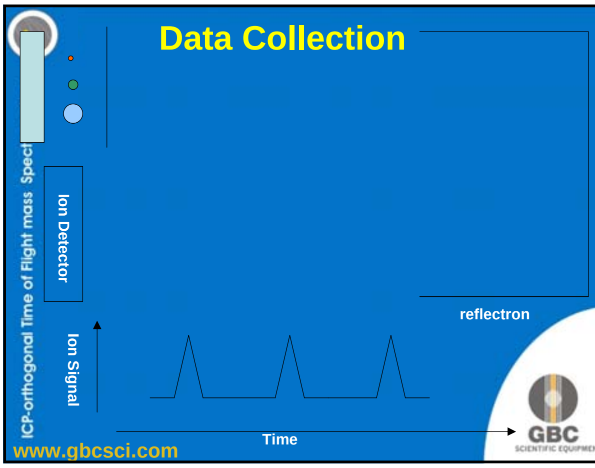
Data Collection



Orthogonal Acceleration

- Provides a well defined start
- Space focus provides means of Ar removal
- Utilizes ions energy to “fly” ions to detector
- Detector “looks” 90º to beam direction – lower background.

ICP-orthogonal Time of Flight mass Spectrometers
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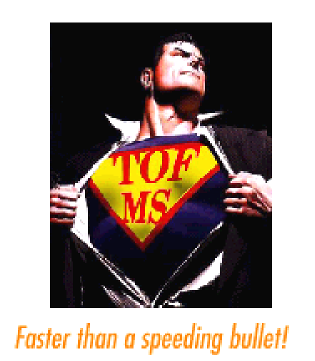
TIME-OF-FLIGHT MS

Why is TOF so sort after today ?

Because it is

FAST !



ICP-orthogonal Time of Flight mass Spectrometers
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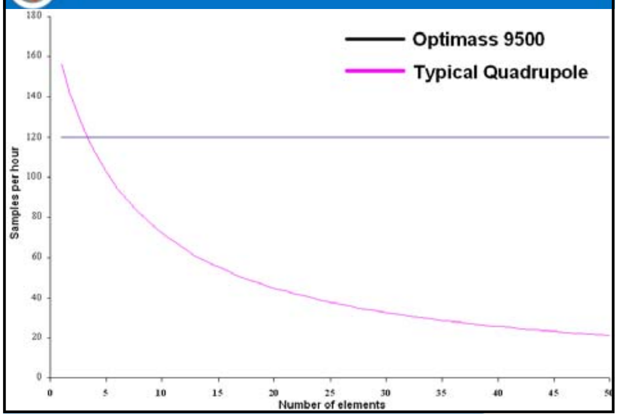
Optimass 9500 - Ultra High Speed



Typical Detection Limits for the Optimass 9500

Full Mass Range Detection Limits from 10s Acquisition

Element(s)	DL
V, Mn, Co, Rb, Sr, Y, Zr, Nb, Rh, Ag, In, Sc, Ba, Ce, Tb, Ho, Ta, Pb, Bi, U	<1ng/L
Li, Mg, Al, Ti, Cu, Ga, Mo, Pr, Nd, Re, Pt, Au	<10ng/L

ICP-orthogonal Time of Flight mass Spectrometers
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GBC Time of Flight ICP-MS

- Orthogonal Acceleration TOF Analyzer
- 27.12 MHz Solid State RF Generator
- 4 Stage Fully Interlocked Vacuum System
- Continuous or Transient Sample Introduction Systems Compatibility
- Windows XP Operating Software
- Benchtop Design

ICP-orthogonal Time of Flight mass Spectrometers
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ICP Time-of-Flight MS

- Simultaneous full mass range coverage (1 to 260 amu)
- Full mass range time profiling sampling for transient signals
- Improved Isotope ratio precision
- Simultaneous internal standardization using 4 channel peristaltic pump

Resolution

- Resolution in time-of-flight MS is defined as

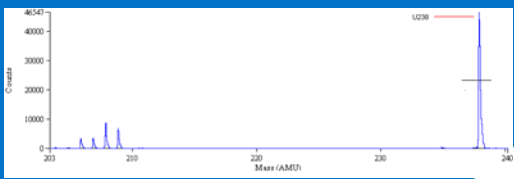
$$R = M/\Delta M = T/(2\Delta T)$$

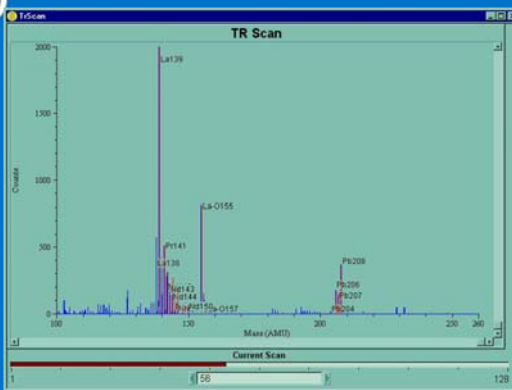
- Resolution is mass dependant

$$T = k(M)^{1/2}$$

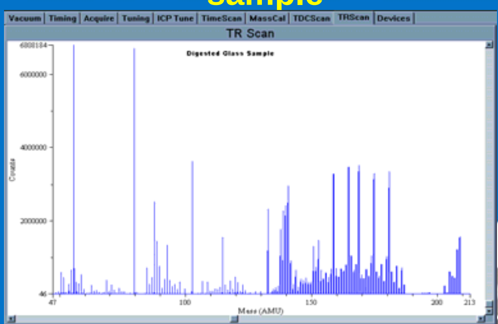
Resolution ≈ 2000 U_{238}

Quadrupoles typically give 400 - 600
Magnetic Sectors give ≈ 10,000

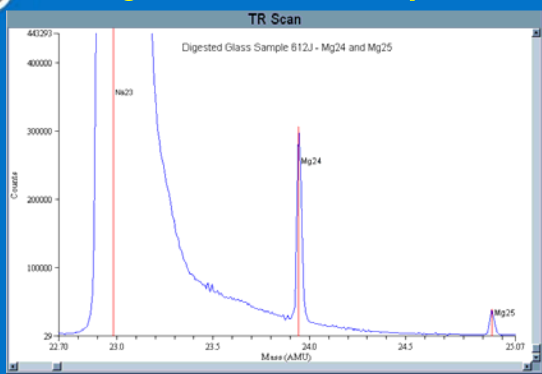




Complete Elemental Mass Spectrum –Digested Glass sample



Digested Glass sample



Digested Glass sample

	55Mn	24Mg	25Mg	86Sr	88Sr	90Zr	91Zr
OptiMass8000 Values	34070	122231	104224	75975	70386	32846	36760
STD Deviation	1863	6697	6494	3555	2255	1555	1917
Compared Quadrupole Value	38135	Na		68856	63140	33528	37036
STD Deviation	1637			1516	2106	3425	3890

	121Sb	137Ba	138Ba	SumPb	69Ga	71Ga
OptiMass8000 Values	29147	33316	30380	24865	31045	35493
STD Deviation	1940	2008	1359	1731	1612	1920
Compared Quadrupole Value	33078	37936	RuO2	34766	27836	33112
STD Deviation	2182	1903		2956	1728	2246

	85Rb	140Ce	147Sm	178Hf
OptiMass8000 Values	29156	34990	35341	33721
STD Deviation	1606	1514	1986	1944
Compared Quadrupole Value	26952	35794	36332	35124
STD Deviation	1191	2092	2122	2121

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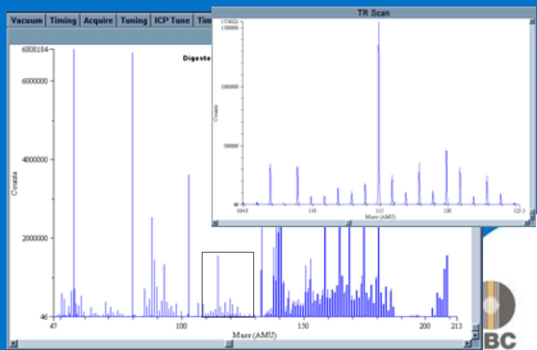
What is in this sample?



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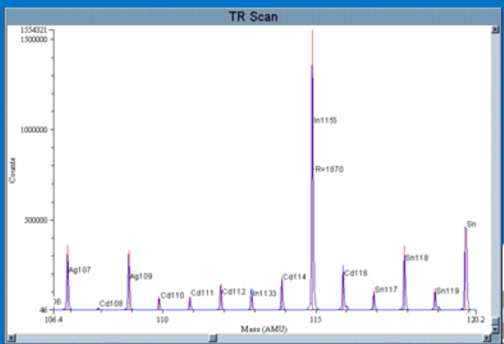
Elemental Fingerprint



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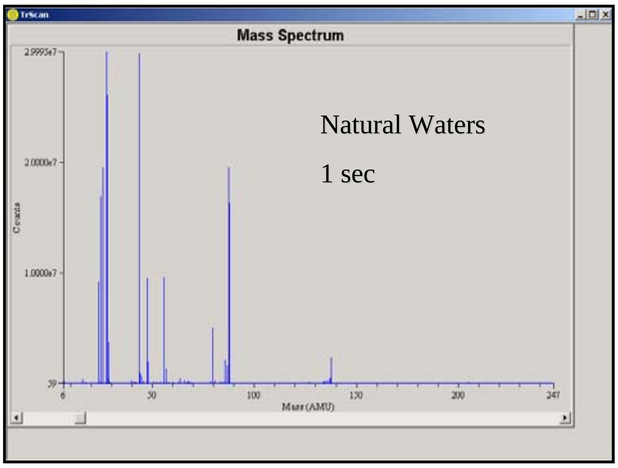

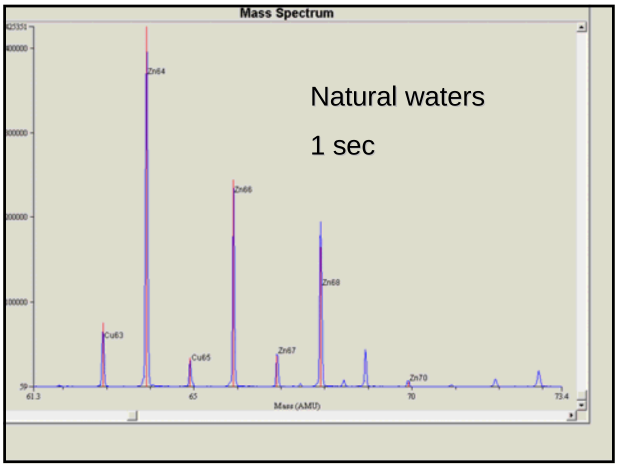

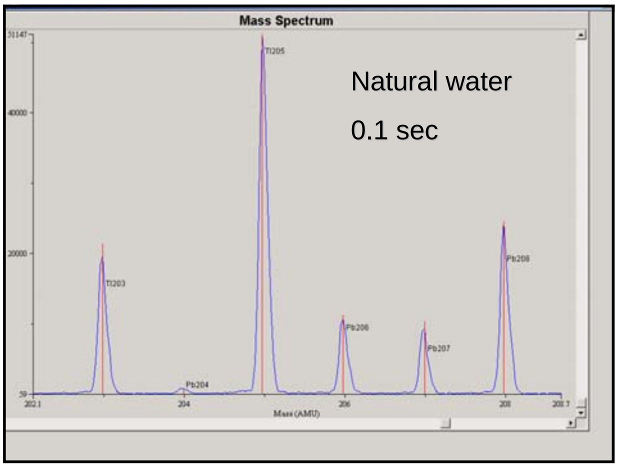

Summary of Performance Specifications

ICP-orthogonal Time of Flight mass Spectrometers

- Resolution up to ≈ 2000 (m/z=238)
- Simultaneous full mass range coverage (1 to 260 amu)
- 3-5s detection limits 1-10 ng/L
- Background 1-3 counts/s/mass
- Dynamic range 10^6 orders
- CeO/Ce <1% and Ba^{++}/Ba^{+} <1%

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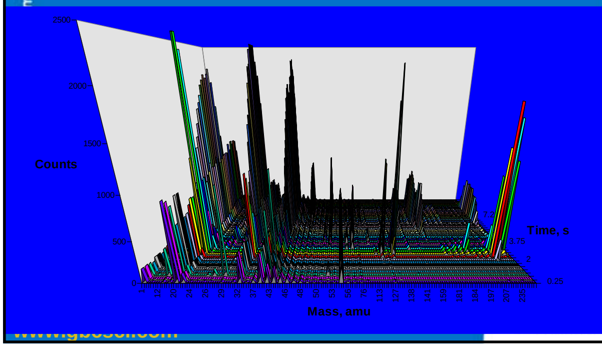
ETV Signal Time Profiling @ Full Mass Range



Powerful Windows XP Software

ICP-orthogonal Time of Flight mass Spectrometers

- **Modular Designed User Interface**
- **Easy to Set Up Method**
- **Full Computer Control of Parameters**
- **Data Export Capability to Common Third Party Packages**
- **Status Panels for Instrument Diagnostics**

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Powerful Windows XP Software new features

ICP-orthogonal Time of Flight mass Spectrometers

- **Auto Optimization**
- **Semi Quantitative Analysis (SQ)**
- **Retrospective Semi Quantitative (RSQ)**
- **Spectral Fingerprinting**

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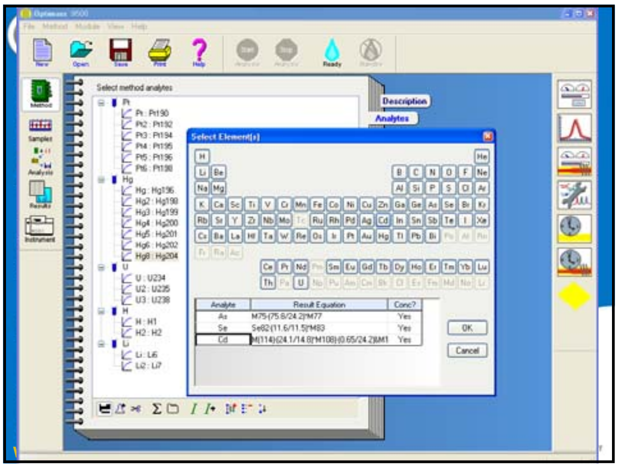
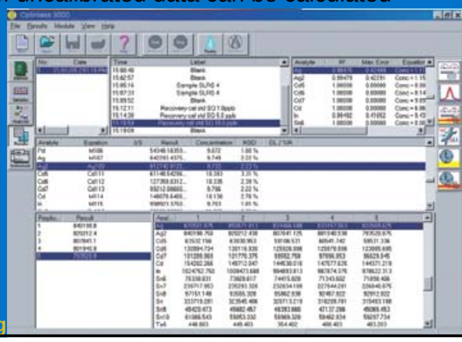


Semi Quantitative (SQ)

ICP-orthogonal Time of Flight mass Spectrometers

By using factory defined RSF, concentrations of uncalibrated data can be calculated



Retrospective Semi Quantitative (RSQ)

As the Optimass 9500 ALWAYS takes all data from mass 1 to 260 amu then at any future time any of peak not previously calibrated can be quantified using RSQ.

Optimass 9500 collects data today for the questions you may ask tomorrow.

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Fingerprinting

By using a statistical algorithm, a spectrum can be compared to a reference spectrum.

The software generates a value between 0 (no match) to 1 (perfect match).

Useful for comparing scene of crime results to criminal's personal effects.

As the Optimass 9500 is portable, can be used on site for so called "dirty weapons" to determine radio nuclides.

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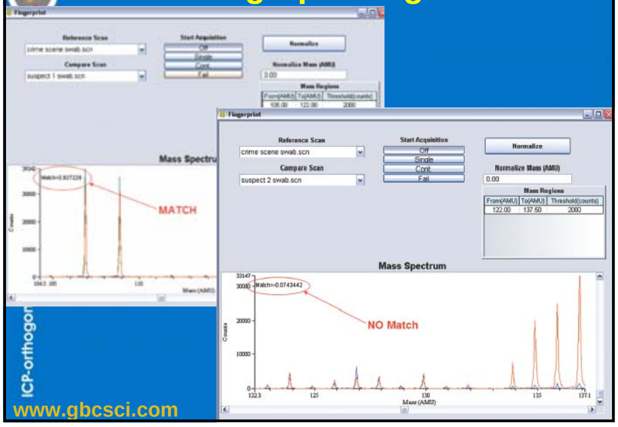
Fingerprinting



ICP-orthogon

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Auto Optimisation

The Auto Optimisation software optimises over 22 conditions to obtain best sensitivity – automatically.

Plasma Conditions, Torch Position, Beam energy and other focussing parameters are automatically optimised.

ICP-orthogonal Time of Flight mass Spectrometers

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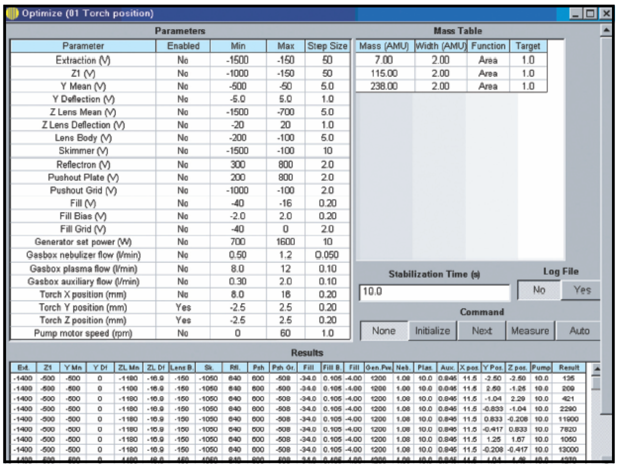
GBC SCIENTIFIC EQUIPMENT



Optimize (01 Torch position)

Parameters

Parameter	Enabled	Min	Max	Step Size
Extraction (V)	No	-1500	-150	50
Z1 (V)	No	-1000	-150	50
Y Mean (V)	No	-500	-50	5.0
Y Deflection (V)	No	-5.0	5.0	1.0
Z Lens Mean (V)	No	-1500	-700	5.0
Z Lens Deflection (V)	No	-20	20	1.0
Lens Body (V)	No	-200	-100	5.0
Skimmer (V)	No	-1500	-100	10
Reflectron (V)	No	300	800	2.0
Pushout Plate (V)	No	200	800	2.0
Pushout Grid (V)	No	-1000	-100	2.0
Fill (V)	No	-40	-16	0.20
Fill Bias (V)	No	-2.0	2.0	0.20
Fill Grid (V)	No	-40	0	2.0
Generator set power (W)	No	700	1600	10
Gasbox nebulizer flow (l/min)	No	0.50	1.2	0.050
Gasbox plasma flow (l/min)	No	8.0	12	0.10
Gasbox auxiliary flow (l/min)	No	0.30	2.0	0.10
Torch X position (mm)	No	8.0	16	0.20
Torch Y position (mm)	Yes	-2.5	2.5	0.20
Torch Z position (mm)	Yes	-2.5	2.5	0.20
Pump motor speed (rpm)	No	0	60	1.0

Mass Table

Mass (AMU)	Width (AMU)	Function	Target
7.00	2.00	Area	1.0
115.00	2.00	Area	1.0
238.00	2.00	Area	1.0

Stabilization Time (s): 10.0

Log File: No Yes

Command: None Initialize Next Measure Auto

Results

Ext.	Z1	Y Mn	Y Df	ZL Mn	ZL Df	Lens B.	Sk.	Rfl.	Psh	Psh Gr.	Fill	Fill B.	Fill	Gen.Pw.	Neb.	Plas.	Aux.	X pos.	Y Pos.	Z pos.	Pump	Result
-1400	-500	-500	0	-1180	-16.9	-150	-1050	640	600	-508	-34.0	0.105	-4.00	1200	1.08	10.0	0.846	11.5	-2.50	-2.50	10.0	135
-1400	-500	-500	0	-1180	-16.9	-150	-1050	640	600	-508	-34.0	0.105	-4.00	1200	1.08	10.0	0.846	11.5	2.50	-1.25	10.0	209
-1400	-500	-500	0	-1180	-16.9	-150	-1050	640	600	-508	-34.0	0.105	-4.00	1200	1.08	10.0	0.846	11.5	-1.04	2.29	10.0	421
-1400	-500	-500	0	-1180	-16.9	-150	-1050	640	600	-508	-34.0	0.105	-4.00	1200	1.08	10.0	0.846	11.5	-0.833	-1.04	10.0	2290
-1400	-500	-500	0	-1180	-16.9	-150	-1050	640	600	-508	-34.0	0.105	-4.00	1200	1.08	10.0	0.846	11.5	0.833	-0.208	10.0	11900
-1400	-500	-500	0	-1180	-16.9	-150	-1050	640	600	-508	-34.0	0.105	-4.00	1200	1.08	10.0	0.846	11.5	-0.417	0.833	10.0	7820
-1400	-500	-500	0	-1180	-16.9	-150	-1050	640	600	-508	-34.0	0.105	-4.00	1200	1.08	10.0	0.846	11.5	1.25	1.67	10.0	1050
-1400	-500	-500	0	-1180	-16.9	-150	-1050	640	600	-508	-34.0	0.105	-4.00	1200	1.08	10.0	0.846	11.5	-0.208	-0.417	10.0	13000

GBC Time Of Flight ICP-MS

- Sets a NEW Benchmark in Speed of Routine Analysis
  - 120 samples/hour
  - Full Mass Range
  - No compromise in sensitivity or precision
- The ULTIMATE tool for Multi-element Transient Signal Analysis

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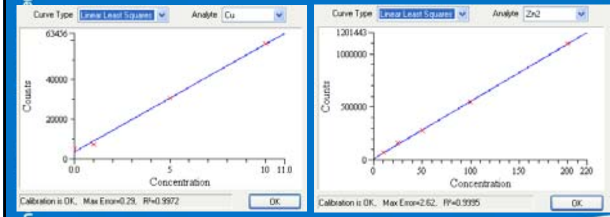
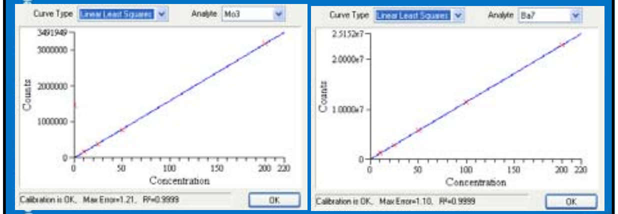
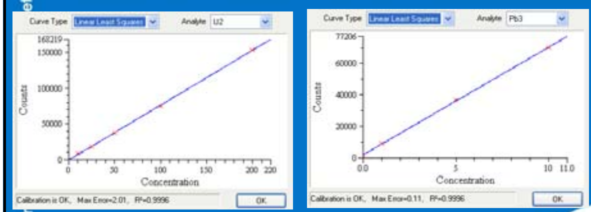
USEPA 200.8 calibration



USEPA 200.8 calibration



USEPA 200.8 calibration



USEPA 200.8 Results

Elements	Certified Result	Result
Al	54 ± 4	52.0
Sb	0.23 ± 0.04	0.24
As	0.68 ± 0.06	0.690
Ba	12.2 ± 0.6	12.60
Be	0.007 ± 0.002	0.006
Cd	0.012 ± 0.002	0.012
Cr	0.33 ± 0.02	0.343
Co	0.033 ± 0.006	0.029
Cu	1.81 ± 0.08	1.730
Pb	0.086 ± 0.007	0.093
Mn	3.37 ± 0.18	3.440
Mo	0.21 ± 0.02	0.190
Ni	0.67 ± 0.08	0.69
Se	n/a	0.23
Ag	n/a	0.13
Tl	n/a	0.14
Th	n/a	0.19
U	0.05 ± 0.003	0.049
V	0.32 ± 0.03	0.330
Zn	0.93 ± 0.10	0.98

USEPA 200.8 Results

Elements	Certified Result (ppb)	Result (ppb)
Ca	6.2 ± 0.2	6.13
Mg	1.6 ± 0.1	1.57
K	0.68 ± 0.02	0.67
Na	2.4 ± 0.2	2.33
Fe	103 ± 5	104.22
Sr	26.3 ± 3.2	26.340

Quadrupole takes 180 seconds for 20 elements

Optimass 9500 takes 25 seconds for 26 – ALL masses

Detection Limits

Element	Detection Limit (ppt)
Ag	<1
Al	<10
Au	<10
Ba	<1
Bi	<1
Ce	<1
Co	<1
Cu	<10
Ga	<10
Ho	<1
In	<1

Detection Limits

Element	Detection Limit (ppt)
Li	<10
Mg	<10
Mn	<1
Mo	<10
Nb	<1
Nd	<10
Pb	<1
Pr	<10
Pt	<10
Rb	<1
Re	<10

Detection Limits

Element	Detection Limit (ppt)
Rh	<1
Sc	<1
Sr	<1
Ta	<1
Tb	<1
Ti	<10
U	<1
V	<1
Y	<1
Zr	<1

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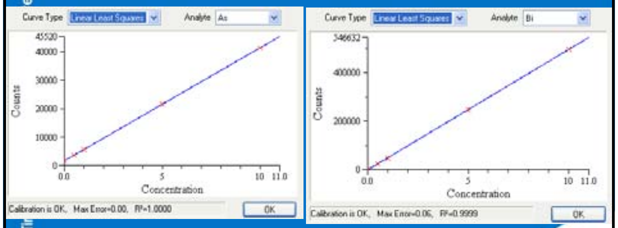
As analysis
(5 sec acquistion time)



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As analysis
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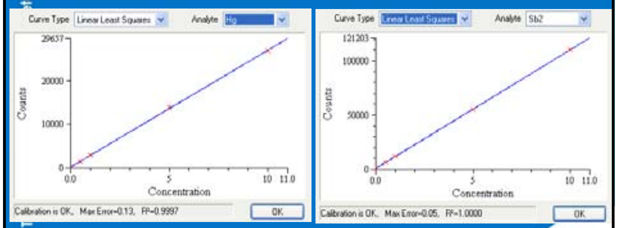

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As analysis
(5 sec acquistion time)

Sample	A (ppb)	B (ppb)
As	6.03	33.4
Bi	10.5	12.8
Hg	16.2	<0.02
Sb	23.1	22.6

For analysis time required for As results for Bi, Hg and Sb are also available with the Optimass 9500

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Contract Analytical Laboratory

- Employ over 700 people
- Analyse over 2 million samples per year
- Europe's largest analytical laboratories
- Responsible for drinking water quality for over 8 million people

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Requirements

- Faster sample throughput – currently GBC Optimass 9500 can analyse samples 5 times faster than competing instruments

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Commercial Lab applications

- Running real samples for a well known commercial lab
- Difficult matrix (1.6% Aqua Regia)
- Need for increased sample throughput and minimal down time.
- GBC set out to test these samples for our customer

ICP-orthogonal Time of Flight mass Spectrometers

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Test Schedule

- To run a batch of samples (200) TO determine LODs for user selected elements
- To run large batches of samples for extended period (1 month) on a daily basis to investigate any long down time issues

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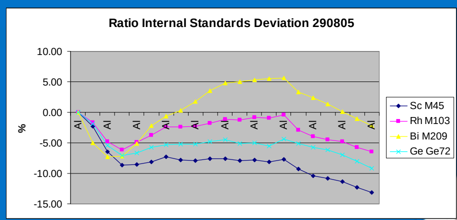
Long term stability test – The following stability run was performed over a 14 hour period. These are raw counts normalized to the first sample



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Limits of detection as requested by Commercial Laboratory

isotope	LOD	Req LOD	equation
Cr	0.06439	10.0	M52
Cu2	0.00331	10.0	Cu63
Ni	0.04450	1.0	M60
Zn	0.04911	2.0	M66
Pb	0.01314	0.2	M206 + M207 + M208
As2	0.57132	1.0	M75-3.132*M77+2.736*M82-2.760*M83
Mo7	0.00218	1.0	Mo100
Hg3	0.00078	0.2	Hg204
Se4	0.46328	0.8	Se78
Cd	0.00708	0.1	M114
B	0.11462	2.0	M11
Be	0.01669	2.0	M9
Tl	0.00343	2.0	M205
Te	0.04084	2.0	M130
Sc			M45
Rh			M103
Bi			M209
Ge			Ge72

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Accessories

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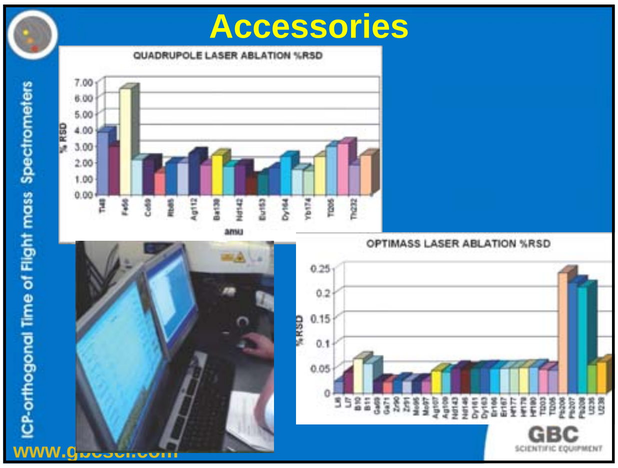
Accessories
QUADRUPOLE LASER ABLATION %RSD
% RSD
amu
OPTIMASS LASER ABLATION %RSD
%RSD
ICP-orthogonal Time of Flight mass Spectrometers
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Support
• PC anywhere is included and provides fast easy diagnostics from GBC factory
• Each country also has GBC trained service technician
• Modular electronics allows easy service and maintenance
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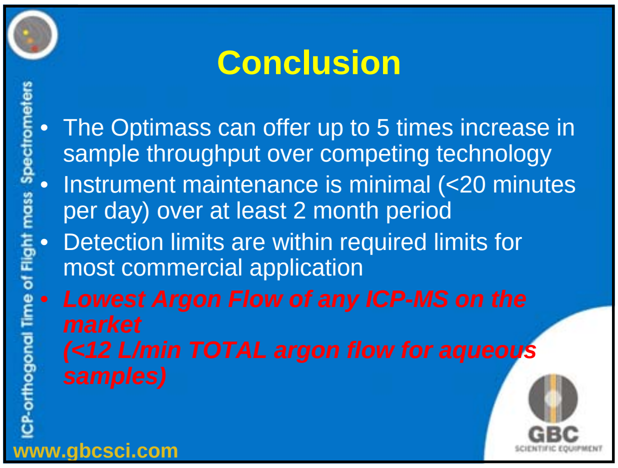
Conclusion
• The Optimass can offer up to 5 times increase in sample throughput over competing technology
• Instrument maintenance is minimal (<20 minutes per day) over at least 2 month period
• Detection limits are within required limits for most commercial application
• Lowest Argon Flow of any ICP-MS on the market
(<12 L/min TOTAL argon flow for aqueous samples)
ICP-orthogonal Time of Flight mass Spectrometers
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Recent application of the GBC Optimass 9500 ICP-oTOF- MS

- Time-of-flight mass spectrometry has been a successful techniques for the analysis of organic molecules for many years.
- More recently, Orthogonal time-of-flight mass spectrometry has found many applications in the inorganic analysis field.

- The development by GBC of the worlds first commercial ICP-oTOF-MS has lead to the application of this techniques to a number of different fields.
- The rise in the use of TOF for inorganic analysis has lead to many new applications of the ICP-MS techniques.
- TOF technology has also been adopted by the traditional ICP-MS community, including commercial laboratories

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Real World applications

- Stability of instrument to run routinely in a commercial laboratory environment.
- Need to provide required detection limits for real samples - aqua regia digested clay.
- Need to optimise TOF advantages – speed – true multi-element – to provide a real higher throughput analysis system.

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Alcontrol requirements

- Faster sample throughput – currently GBC Optimass 9500 can analyse sample 3 – 5 times faster than competing instruments
- Required detection limits in ppb range
- Minimal down time – excellent service response (24 hour max)
- Minimal daily maintenance

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Commercial Lab applications

- Running real samples for a well known commercial lab
- Difficult matrix (1.6% Aqua Regia) – Stability is an issue
- Need for increased sample throughput and minimal down time.
- GBC set out to test these samples for our customer

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Test Schedule

- To run a batch of samples (200) to determine LODs for user selected elements
- To run large batches of samples for extended period (1 month) on a daily basis to investigate instrument stability and any long down time issues

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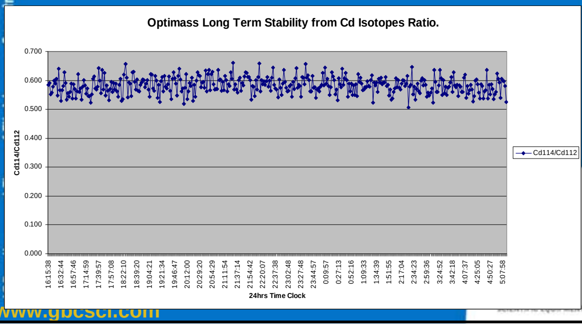
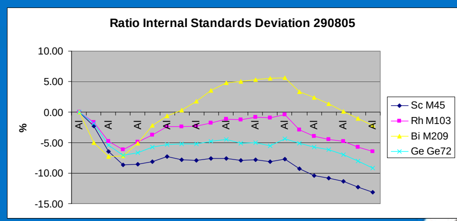
Long Term Stability



Long term stability test – The following stability run was performed over a 14 hour period. These are raw counts normalized to the first sample



isotope	LOD	Req LOD	equation
Cr	0.06439	10.0	M52
Cu2	0.00331	10.0	Cu63
Ni	0.04450	1.0	M60
Zn	0.04911	2.0	M66
Pb	0.01314	0.2	M206 + M207 + M208
As2	0.57132	1.0	M75-3.132*M77+2.736*M82-2.760*M83
Mo7	0.00218	1.0	Mo100
Hg3	0.00078	0.2	Hg204
Se4	0.46328	0.8	Se78
Cd	0.00708	0.1	M114
B	0.11462	2.0	M11
Be	0.01669	2.0	M9
Tl	0.00343	2.0	M205
Te	0.04084	2.0	M130
Sc			M45
Rh			M103
Bi			M209
Ge			Ge72

Limits of detection

As requested by Alcontrol

Conclusion

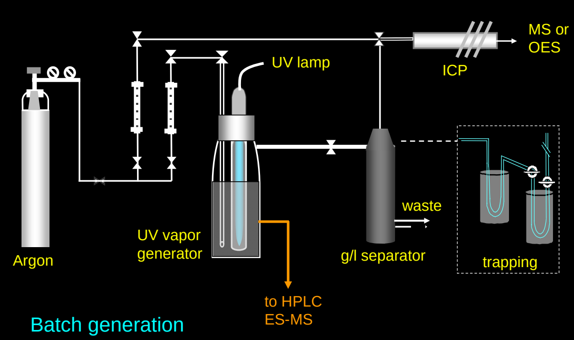
- The Optimass can offer a 3 – 5 times increase in sample throughput over competing technology
- Instrument maintenance is minimal (<20 minutes per day) over at least 2 month period
- Detection limits are within required limits for most commercial application

National Research Council Canada
Conseil national de recherches Canada
NRC·CNRC
Institute for National Measurement Standards

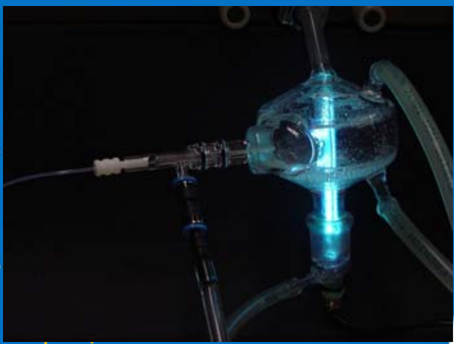
Photochemical Alkylation and Vapor Generation For Enhanced Sample Introduction Efficiency

R.E. Sturgeon, Z. Mester and X. Guo

Photochemical Vapor Generation



UV Reactive Spray Chamber



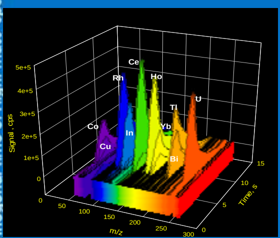
Enhancement Factors

1 ml/min 5 ppb Multielement Spike

	prop 1%	prop 5%	formic 1%	formic 5%	acetic 1%	acetic 5 %
Cu	0.6	2.1	0.9	2.4	1.0	
Ag	0.6	2.8	1.7	3.6	1.1	
Cd	0.6	2.8	0.8	3.1	0.9	
Pd	0.6	2.8	0.8	2.6	0.9	
Se	1.6	4.9	5.6	22.1	2.3	17.0
Ba	0.5	2.5	0.8	2.8	0.9	2.6
Co	0.5	2.1	0.9	2.7	1.0	
Hg	6.1	26.3	1.2	6.3	1.9	
I	1.1	3.8	0.9	2.7	1.4	
Bi	0.8	9.7	1.9	11	0.9	6.2
Pb	0.6	3.5	2.1	8.7	0.8	3.9
Ni	0.6	2.2	1.0	2.8	1.0	
Mg	0.6	1.6	1.1	2.3	1.2	

National Research Council Canada
Conseil national de recherches Canada

Institute for National Measurement Standards



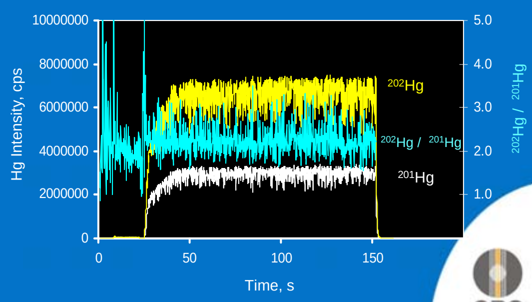
Isotope Ratio Precision with Transient Sample Introduction using ICP-oa-TOFMS

Scott Willie
Zoltán Mester
Ralph Sturgeon

32nd FACSS and 51st ICASS
Quebec City, October 9 - 13, 2005

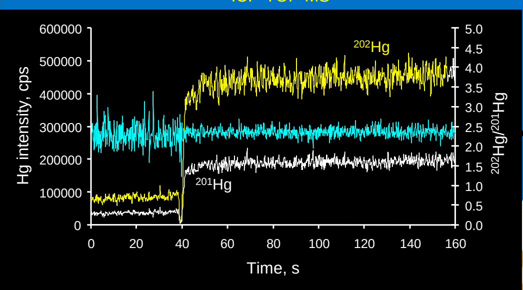
Steady-State CV Hg Generation

100 ppt Hg std
SF-ICP-MS



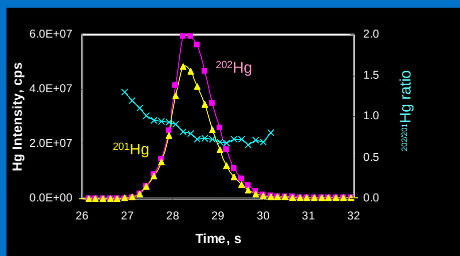
Steady-State CV Hg Generation

100 ppt Hg std
ICP-TOF-MS



Hg CV Generation: ^{201}Hg spike ORMS-3

SF-ICP-MS
CV with Au trap

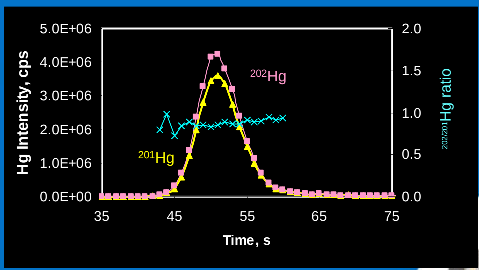


spectral skew is evident

Hg CV Generation: ^{201}Hg spike ORMS-3

ICP-TOF-MS

CV with Au trap



no spectral skew

Determination of Hg in ORMS-3 by CV ID-ICP-MS

pg / g, n = 4

	Steady-state	Au trap
SF-ICP-MS	12.75 ± 0.24	12.55 ± 0.41
TOF-ICP-MS	12.34 ± 0.11	12.65 ± 0.30

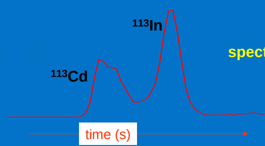
certified value : 12.6 ± 1.1

Practical Capabilities of TOF Mass Analyzers

- unlimited use of internal standardization (isotope ratios)
- reduction of multiplicative (correlated) noise
- ratio measurements “limited” by Poisson counting statistics
- multielement analysis of transients (10 - 100/s, no spectral skew)

Q-MS	USD 150,000	0.1 – 0.5 %
TOF-MS	USD <200,000	0.04 % (Ag, 200 ppb 20 s)
SF-MS	USD 500,000	0.01 – 0.1 %
MC-MS	USD 2,500,000	0.001 – 0.02 %

The Analytical Utility of Optimized Time Resolved ETV-ICP(TOF)MS Data Collection



Needed mass spectral resolution: 332,169

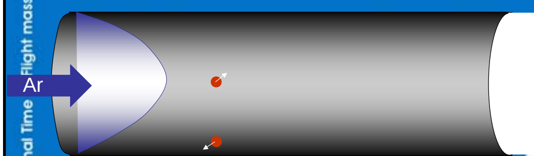
Gulay Ertas[1] and James A. Holcombe
Department of Chemistry and Biochemistry
University of Texas
Austin, Texas

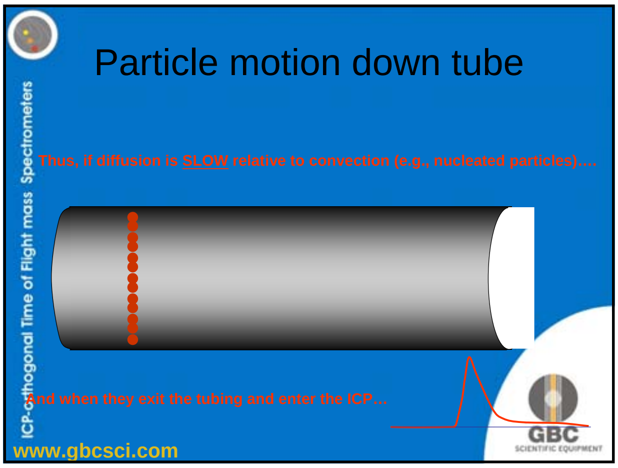
[1] Current address: Bilkent University; Ankara, Turkey

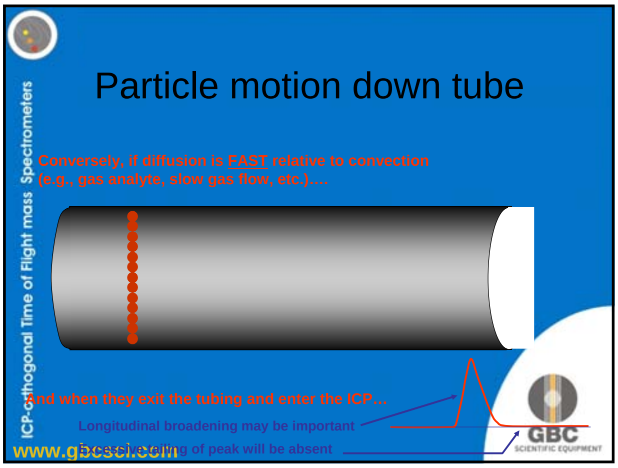
ETV for high resolution

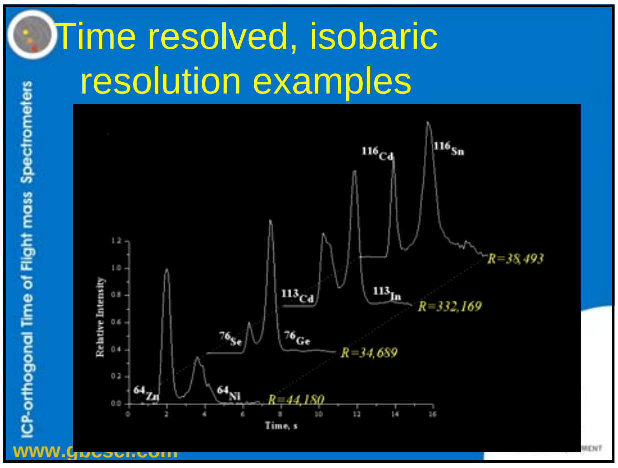
- Need to investigate particulate flow through ETV furnace
- ETV particles can be considered as a gas
- How does the flow regime effect the chemical resolution of the ETV.

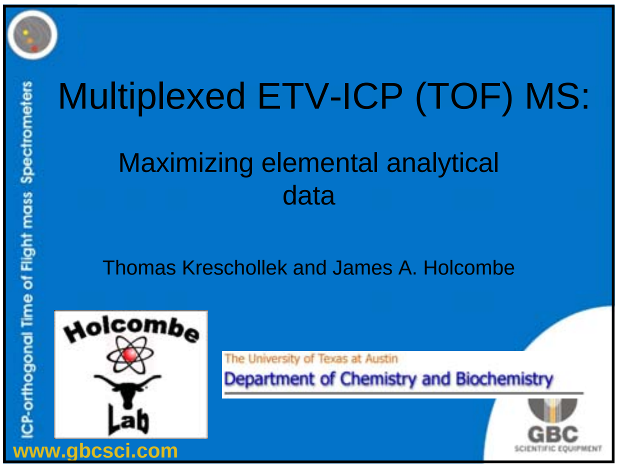
Particle motion down tube




Particle motion down tube
Thus, if diffusion is SLOW relative to convection (e.g., nucleated particles)….
And when they exit the tubing and enter the ICP…
ICP-orthogonal Time of Flight mass Spectrometers
www.gbcsci.com
GBC
SCIENTIFIC EQUIPMENT


Particle motion down tube
Conversely, if diffusion is FAST relative to convection
(e.g., gas analyte, slow gas flow, etc.)….
And when they exit the tubing and enter the ICP…
Longitudinal broadening may be important
Excessive tailing of peak will be absent
ICP-orthogonal Time of Flight mass Spectrometers
www.gbcsci.com
GBC
SCIENTIFIC EQUIPMENT


Time resolved, isobaric
resolution examples
Relative Intensity
Time, s
64Zn
64Ni
76Se
76Ge
113Cd
113In
116Cd
116Sn
R=44,180
R=34,689
R=332,169
R=38,493
ICP-orthogonal Time of Flight mass Spectrometers


Multiplexed ETV-ICP (TOF) MS:
Maximizing elemental analytical
data
Thomas Kreschollek and James A. Holcombe
Holcombe
Lab
The University of Texas at Austin
Department of Chemistry and Biochemistry
ICP-orthogonal Time of Flight mass Spectrometers
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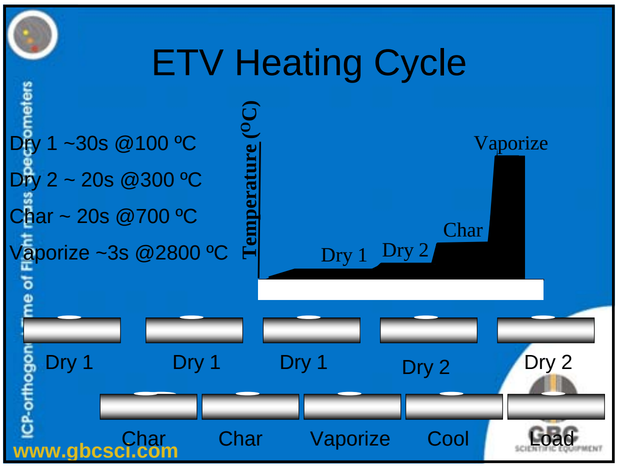
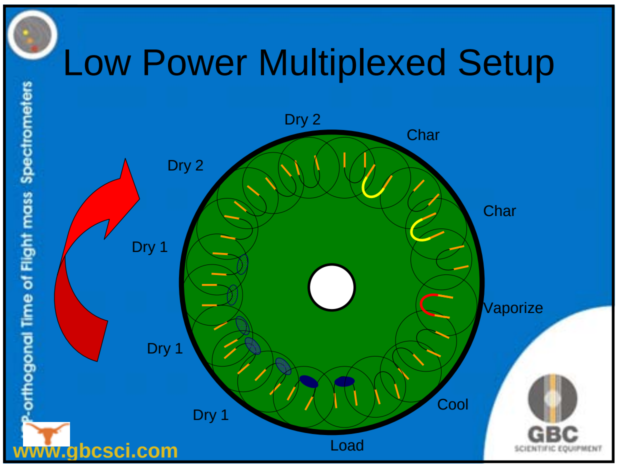
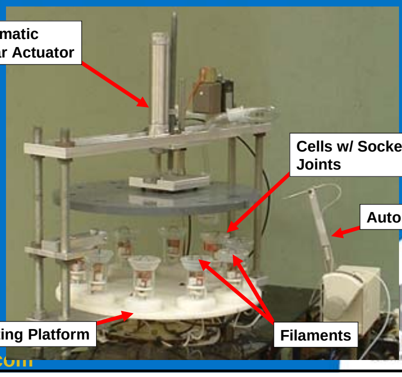

ETV Heating Cycle
Dry 1 ~30s @100 ºC
Dry 2 ~ 20s @300 ºC
Char ~ 20s @700 ºC
Vaporize ~3s @2800 ºC
Temperature (ºC)
Vaporize
Char
Dry 1
Dry 2
Dry 1
Dry 1
Dry 1
Dry 2
Dry 2
Char
Char
Vaporize
Cool
Load
ICP-orthogonal Time of Flight mass Spectrometers
www.gbcsci.com


Low Power Multiplexed Setup
Dry 2
Char
Dry 2
Char
Dry 1
Vaporize
Dry 1
Cool
Dry 1
Load
ICP-orthogonal Time of Flight mass Spectrometers
www.gbcsci.com
GBC
SCIENTIFIC EQUIPMENT

Multi-ETV Setup



ICP-orthogonal Time of Flight mass Spectrometers

www.gbcsci.com

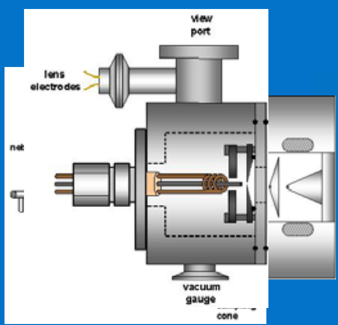
Development and Characterization of a Multi-functional Ionization Source for Time-of-Flight Mass Spectrometry

Brad C. Knippel, Lei Li, Glen P. Jackson, Douglas C. Duckworth

Chemical Sciences Division, Oak Ridge National Laboratory
Oak Ridge TN 37831

Oak Ridge National Laboratory
U. S. Department of Energy

New ORNL TOF ion source



ICP-orthogonal Time of Flight mass Spectrometers

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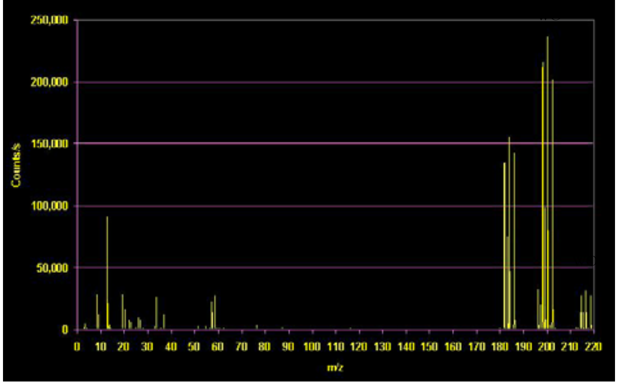
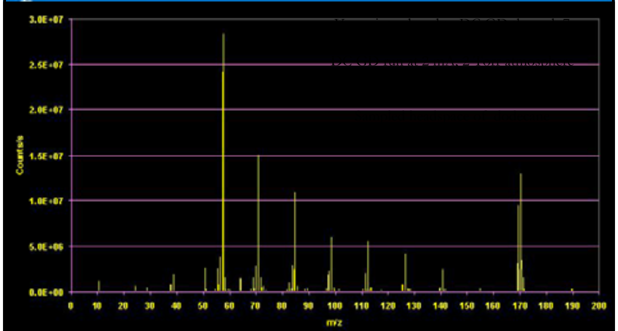
Solids Analysis – Glow Discharge Mode
Tungsten



Gaseous Analysis - Atmospheric Sampling
Glow Discharge Mode - Dodecane



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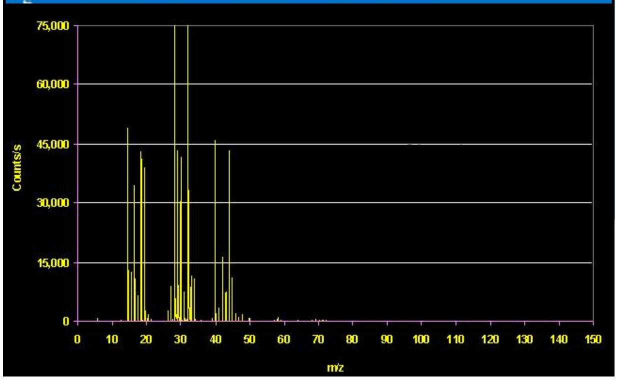
Liquid Analysis - Electrospray Mode
Tetrabutylammonium iodide



LA-ICP-TOF-MS analysis of Tephras

- Tephras are small (400 um) shards of volcanic glass that are used in geochronlogy of certain volcanic sites.
- Tephras are usually analysed by INAA which is expensive and time consuming.
- EMPA is also used but is found to be unreliable

ICP-orthogonal Time of Flight mass Spectrometers

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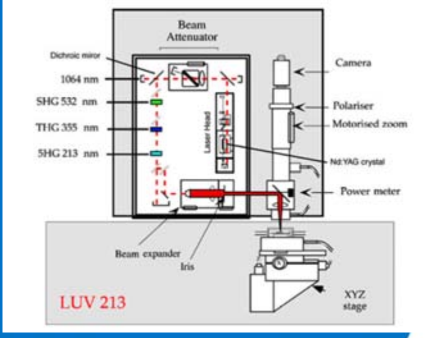

ICP-orthogonal Time of Flight mass Spectrometers

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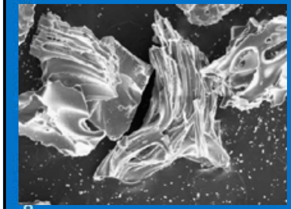
LA-ICP-MS example: tephrachronology (Dr. Jeffrey Knott, CSUF)



Shards from volcanic ash less than 0.5 mm diameter

Multiple ash beds (tuffs) from multiple volcanic centers are exposed in Death Valley, CA

Tephrachronology requires not only discriminating tuffs from different centers but different eruptions from the same center

ICP-orthogonal Time of Flight mass Spectrometers

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How does TOF help!

- TOF allows true multielement analysis of the tephra as it is ablated
- The information on all isotopes provides true multivariant statistical mapping.
- 100 tephra were analysed in 6 hours.
- This would take 6 weeks by INAA
- Conventional digestion ICP-MS would not capable of doing the job
- Neither INAA or Quad ICP-MS could be used for individual shard analysis

ICP-orthogonal Time of Flight mass Spectrometers

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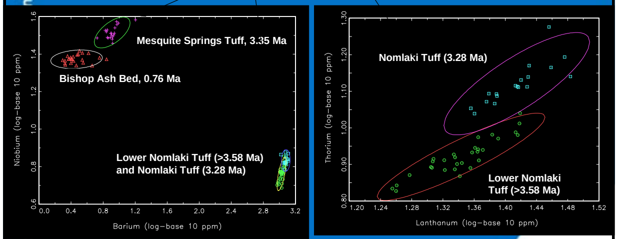
The very good statistics created by the speed of the TOF means that different eruptions at the same site can also be distinguished

The large amounts of data that are quickly collected means we can distinguish different sites on many different bivariant projections



Not only do the LA-ICP-MS data discriminate the four tuffs, including ones from the same volcanic center, they also agree very closely with previous analyses of bulk ash samples by solution ICP-MS and INAA.

ICP-orthogonal Time of Flight mass Spectrometers

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Conclusions

- The speed and multielement capability of the Optimass 9500 make it ideal for providing multiple bivariant elemental maps for statistical analysis
- The speed of data collection and also of individual analyse allows many samples to be analysed in a short time for better statistics
- The accuracy and precision of the instrument are more than adequate for this geochronological application

ICP-orthogonal Time of Flight mass Spectrometers

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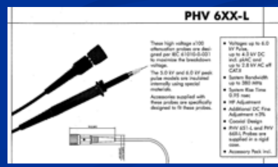
Optimass Service Modules

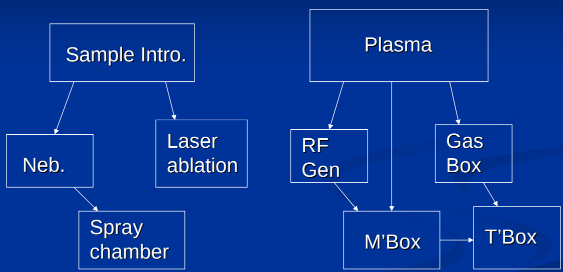
- Plasma – including interface
- Ion Optics – no light
- HV analyser –TOF
- Data collection and computer

Specialized tools

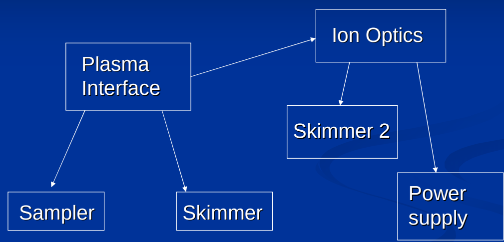
- Portable Oscilloscope - http://www.used-line.com/b2020p1pr0-used-portable-oscilloscopes.htm
- High voltage probe -



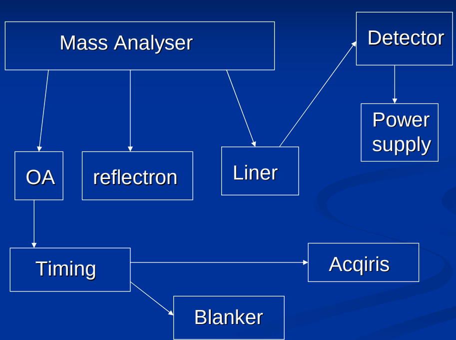
Sample intro and Plasma



MS Interface



Mass Analyser



Main Service Issues

The following slides will now give a brief summary of some of the common service issues that arise on an Optimass 9500

ALWAYS REMEMBER – most faults are in sample introduction

Sample Introduction

- GAS LEAKS – usually on joints external to Optimass – Nebuliser leak has biggest effect on sensitivity.
- SAMPLE LEAKS – easy to see and fix
- NEBULISER BLOCKAGE – usually at base but can be at tip – check both with magnifier – clean by back-flush with methanol using a syringe and tygon tubing.
- LASER ABALTION – refer to manufacturers manual

Plasma

- GENERATOR – New GBC generator – no failures yet – SEREN generator usually comms failure – return to SEREN.
- GAS BOX – valves “stick” – they need to be freed manually – Solenoid valve also “sticks” – replace valve.
- MATCHBOX – Arc erosion on shunt capacitor – capacitor does not move – Replace capacitor – lot of screws !!
- WATER LEAKS – usually plastic insulating tube in box – replace tubing

Torch Box

- TORCH – replace and align as manual
- GAS LINES - can get cut by door if customer is not careful
- SPARK – check spark WITH argon present – if no spark – check/replace coil

Interface

- Remove and clean cones as specified in manual

Ion Optics

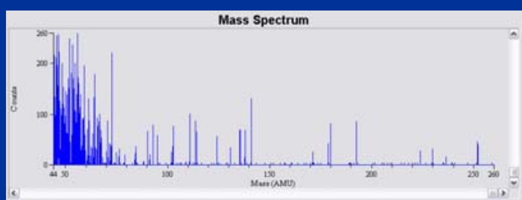
- Check for loss of voltages on the supplies in service panel – if lost – replace board

Analyser

- Usually if the analyser is working it will continue to work – if there are problems then check for voltages as with ion optics and replace board

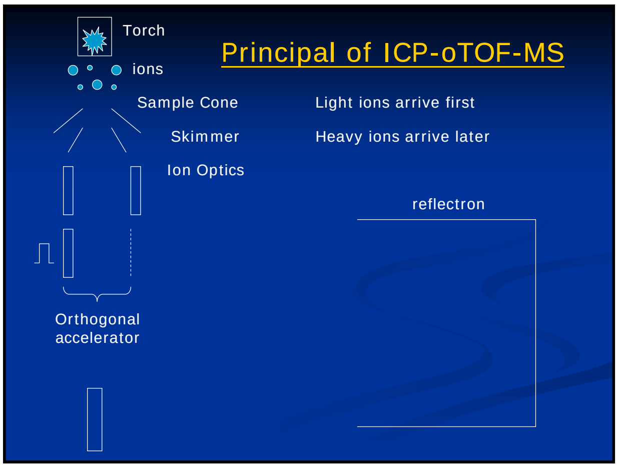
Blanker

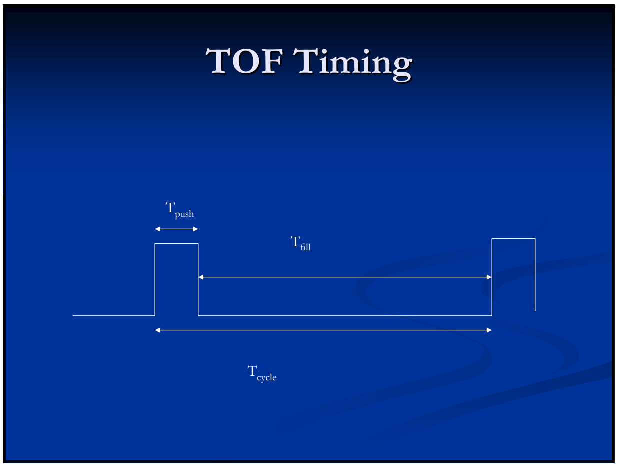
- One failure mode on the blanker is to blank everything

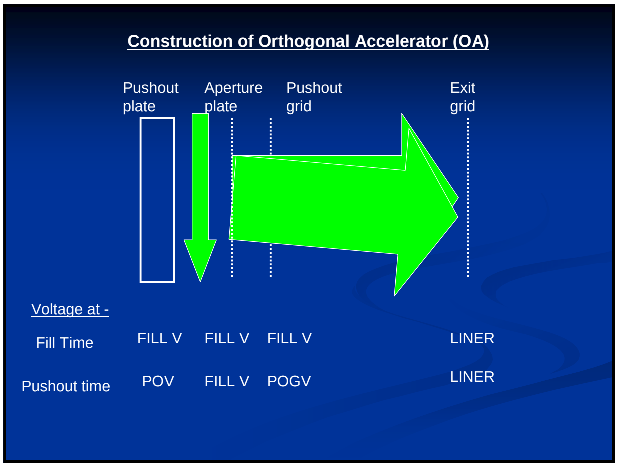


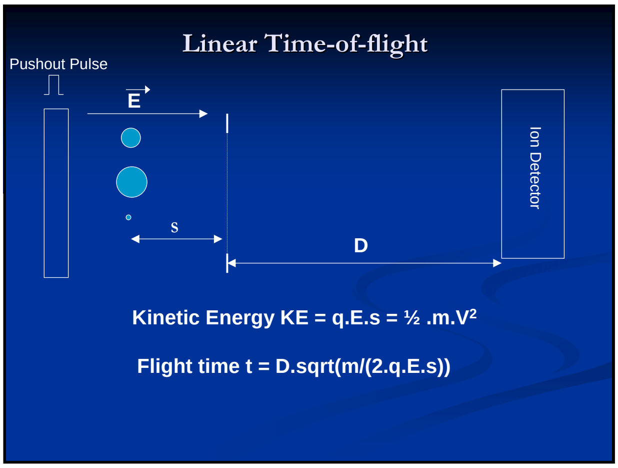
ICP Orthogonal Acceleration Time-of-Flight Mass Spectrometry

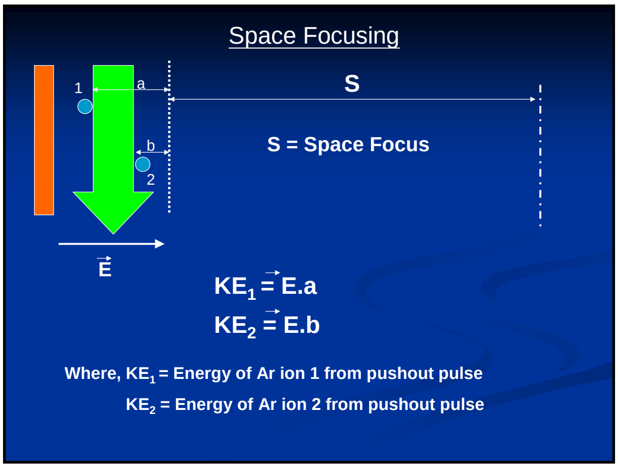
- Provides a well defined start
- Space focus provides means of Ar removal
- Utilizes ions energy to "fly" ions to detector
- Detector "looks" 90º to beam direction – lower background.

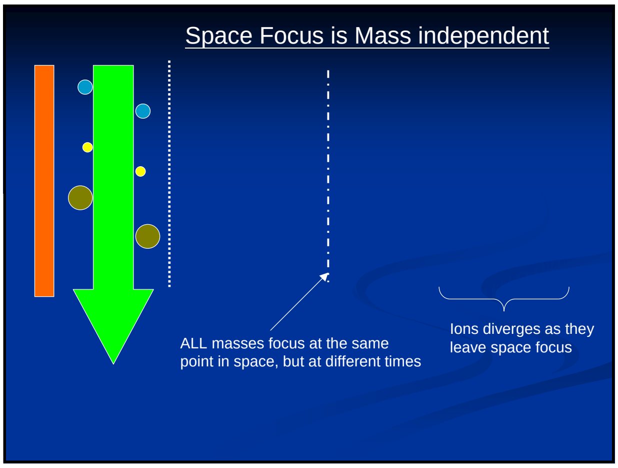


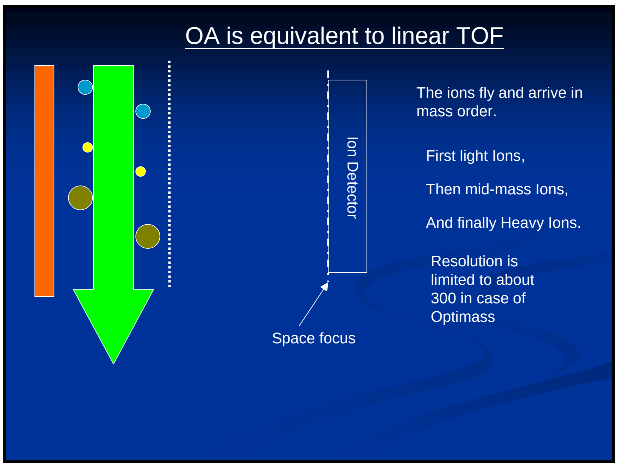


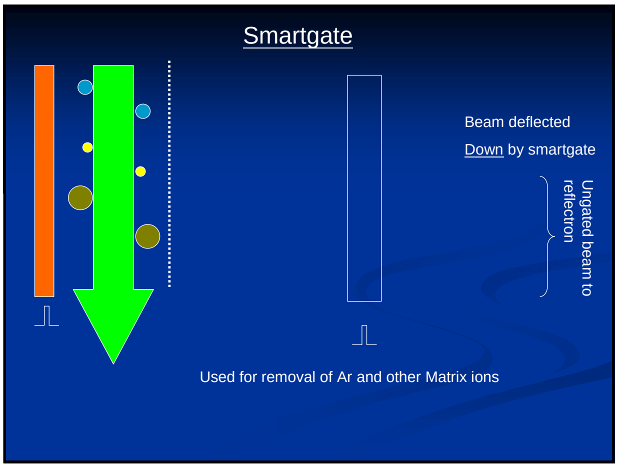


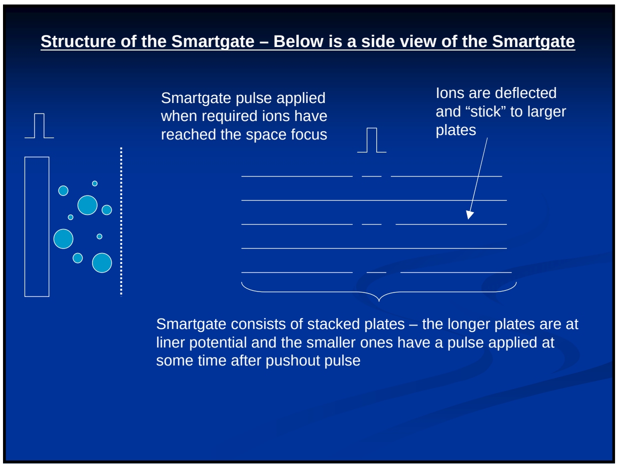


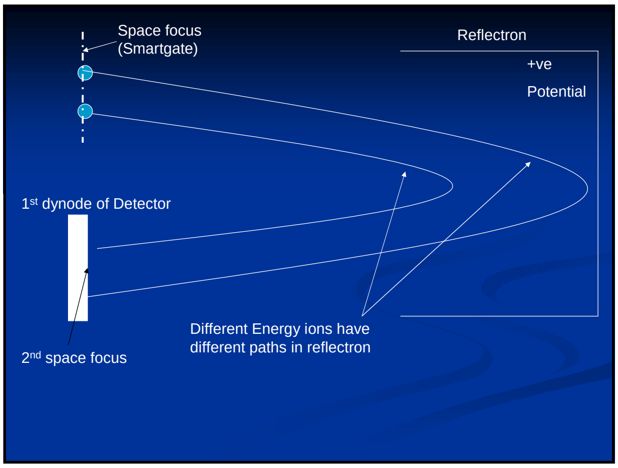


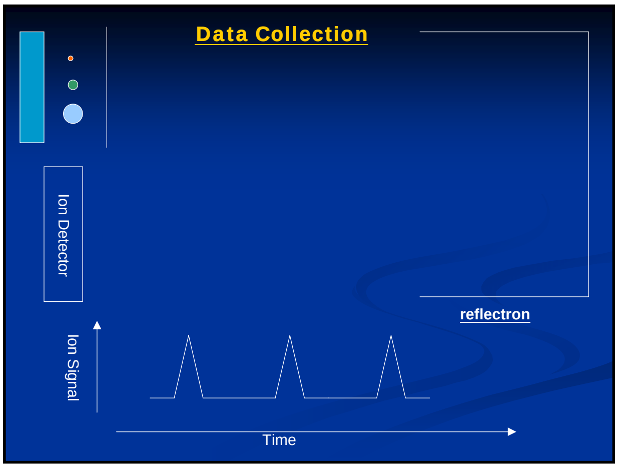

Space Focus is Mass independent
ALL masses focus at the same point in space, but at different times
Ions diverges as they leave space focus


OA is equivalent to linear TOF
Ion Detector
Space focus
The ions fly and arrive in mass order.
First light Ions,
Then mid-mass Ions,
And finally Heavy Ions.
Resolution is limited to about 300 in case of Optimass


Smartgate
Beam deflected
Down by smartgate
Ungated beam to reflectron
Used for removal of Ar and other Matrix ions


Structure of the Smartgate – Below is a side view of the Smartgate
Smartgate pulse applied when required ions have reached the space focus
Ions are deflected and "stick" to larger plates
Smartgate consists of stacked plates – the longer plates are at liner potential and the smaller ones have a pulse applied at some time after pushout pulse

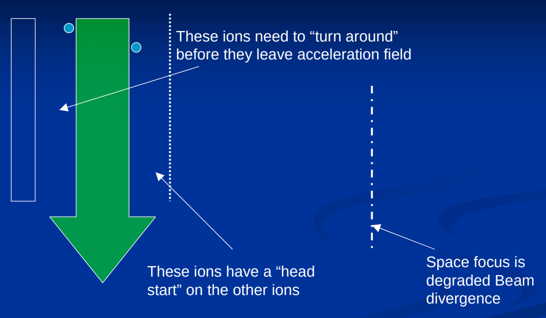

Space focus (Smartgate)
Reflectron
+ve
Potential
1st dynode of Detector
2nd space focus
Different Energy ions have different paths in reflectron


Data Collection
Ion Detector
reflectron
Ion Signal
Time

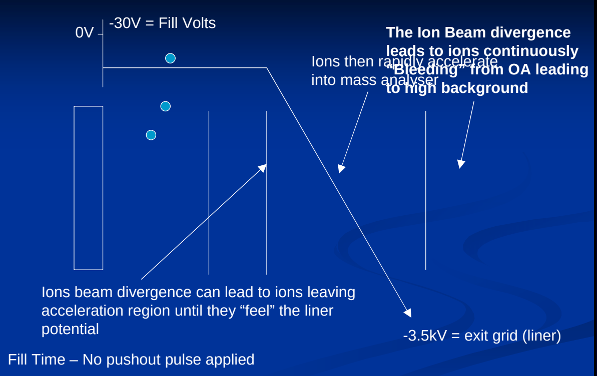
What can go Wrong!!

- “turn around” time – Bad with ICP (hot) ion source
- “ion bleeding” from OA – how to avoid
- OA charging and the use of “Fill Bias” voltage

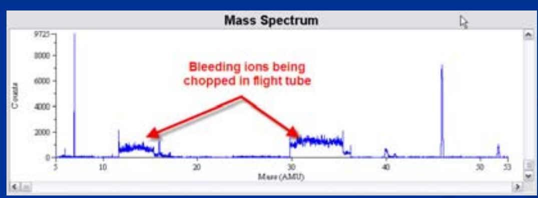
Ion Beam Divergence and “turn around” Time



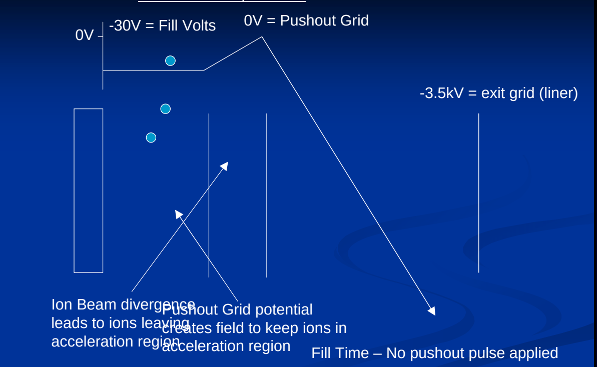
Ion “Bleeding” from OA



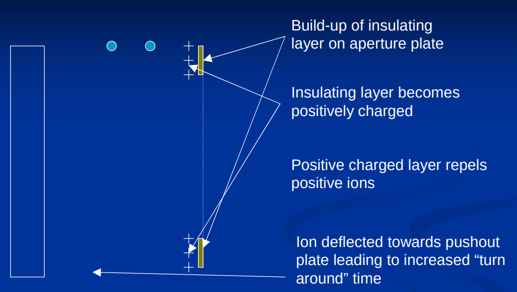
Ions bleeding from OA

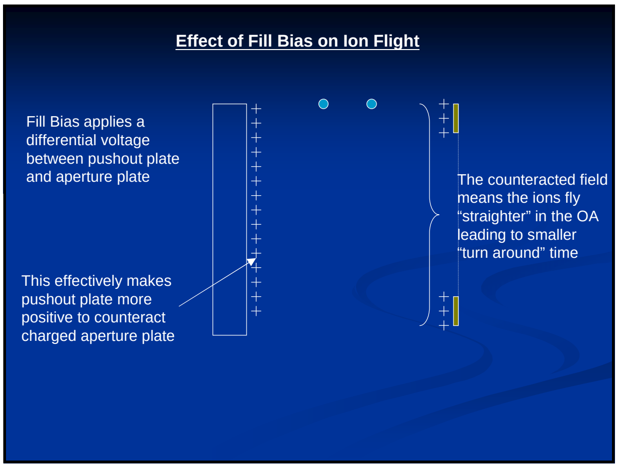


Pushout Grid potential



Effect of Fill Bias on Ion Flight





Conclusions

- DON’T PANIC !!!!!!!!!!!!!!!!!!!!!!!
- Always think before you act
- Use software and spectral feedback to diagnose problems
- Good Luck !