

# Analytical Methods in Exploration Geochemistry

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Exploration**07**

# Choosing the analytical method(s)

- Total or partial elemental composition
- Elements and detection limits required
- Matrix suitable for method
- Accuracy and precision required: 'fit for purpose'
- Representative size of sample or size limitation
- Non-destructive analysis
- Cost

# Common Methods

- Digestion of sample (acid digestion or fusion) and **ICP-MS, ICP-ES, AAS**
- Element-specific methods (e.g. F by fusion and ISE)
- **INAA**
- **XRF (fused disc and pressed pellet)**

*Always state the sample digestion AND the analytical technique:  
This describes the methodology, NOT the technique alone!*

# Sample decomposition

- **Aqua regia, 'partial'**: 3:1 HCl: HNO<sub>3</sub>, highly oxidising.



Targets sulphides; native Au, Pt, Pd; arsenides, selenides, tellurides; carbonates; most sulphates; some oxides (e.g. U) and their hydrates (e.g. Fe, Mn); some silicates; organically bound elements. Minerals hardly attacked include barite, chromite, gahnite, cassiterite, ilmenite, rutile, sphene, monazite, zircon, garnet.

- **"Four-acid", HF-HClO<sub>4</sub>-HNO<sub>3</sub>-HCl, 'nearly total'**: Most silicates dissolve but minerals above still may be partial. Often not total for REEs, Al, Ba, Ta, Nb, Hf, Sn, Cr, W, Fe. Si volatilises as do Cr, As, Sb, Au *sometimes* (dependent on conditions)
- **Li meta/tetra-borate fusion**: excellent total digestion, with bead dissolved in HNO<sub>3</sub> but DLs in ICP-MS are compromised by dilution to lower TDS
- **Sodium peroxide fusion**: for refractory minerals/ores and sulphides, results in very 'clean' matrix for analysis

# From Hall, *Explore Newsletter*, 2000: Aqua regia data across labs

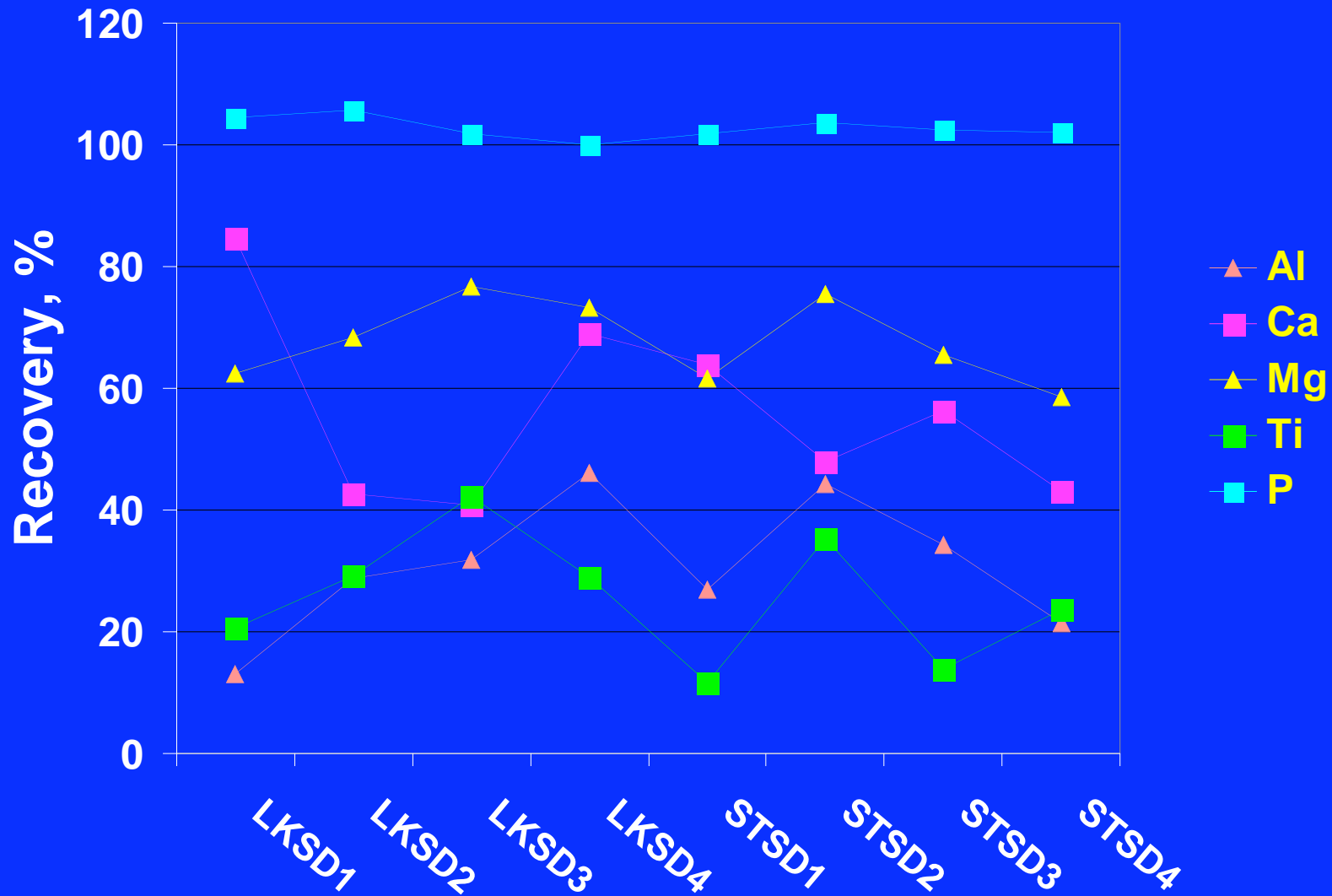
~ 20 labs

<u>Element</u>	<u>Mean ± SD</u>	<u>Element</u>	<u>Mean ± SD</u>
Al, %	1.87±0.25, LKSD-2	Mn, ppm	950±70, TILL-1
As, ppm	23±6, LKSD-2	Ni, ppm	44±4, LKSD-3
Ba, ppm	110±5, STSD-2	P, ppm	1290±99, LKSD-2
Ca, %	1.64±0.07, STSD-1	Pb, ppm	40±7, LKSD-2
Cd, ppm	1.2±0.3, LKSD-1	Sb, ppm	2.0±1.0, STSD-1
Co, ppm	11±1, STSD-4	Sr, ppm	41±5, LKSD-2
Cr, ppm	30±3, TILL-1	Ti, ppm	1070±202, STSD-4
Cu, ppm	43±3, STSD-2	V, ppm	48±8, TILL-1
Fe, %	2.0±0.1, TILL-3	Zn, ppm	192±11, STSD-3
Mg, %	0.92±0.10, LKSD-3		

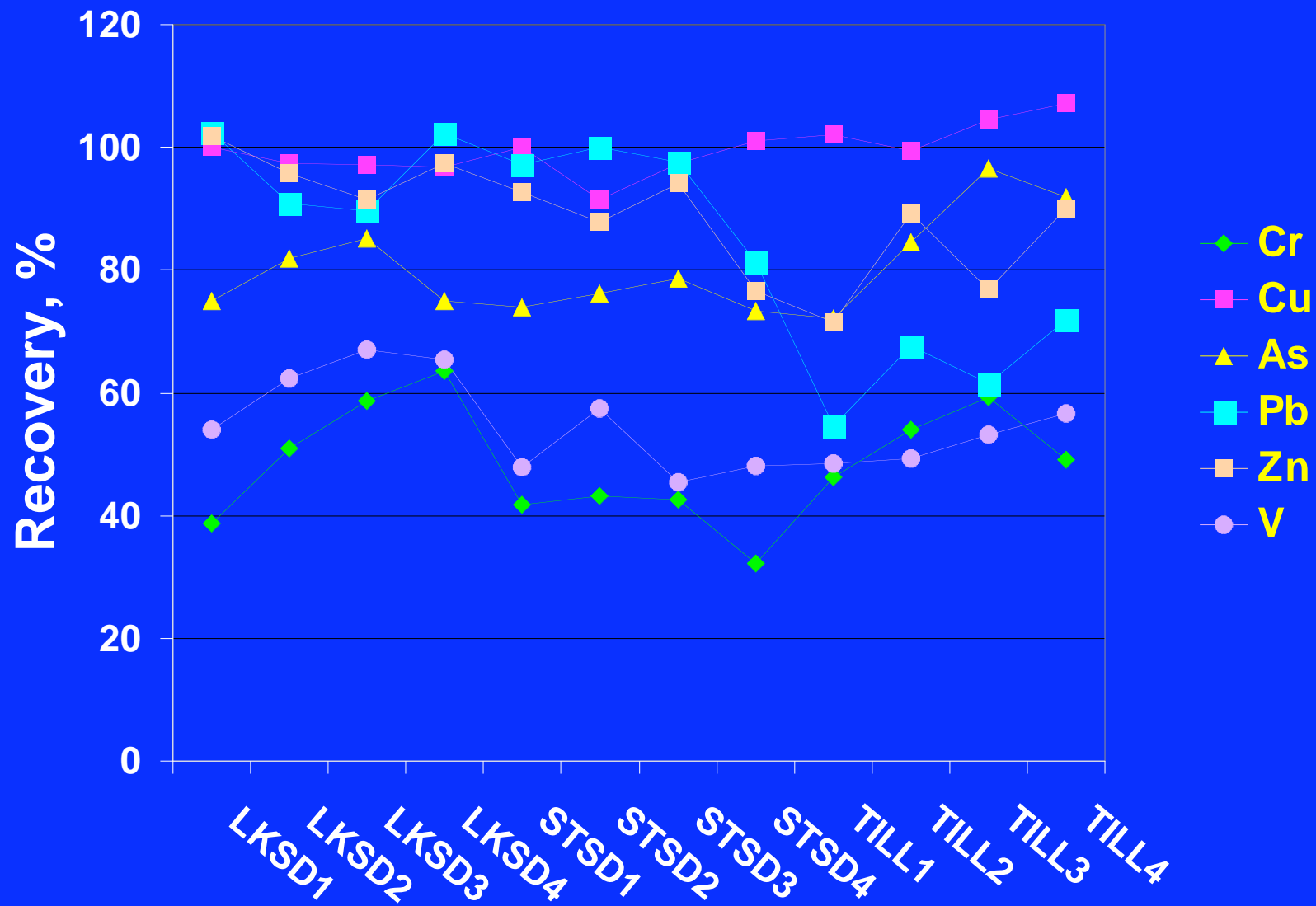
Aqua regia digestions varied in heating time, from 2 to 4 h (usually at 90°C) and in contact time prior to heating from 1 h to overnight.

Several laboratories employed the Lefort aqua regia, but as the results agreed well (within expected analytical limits) with those by aqua regia, they were included in the compilation.

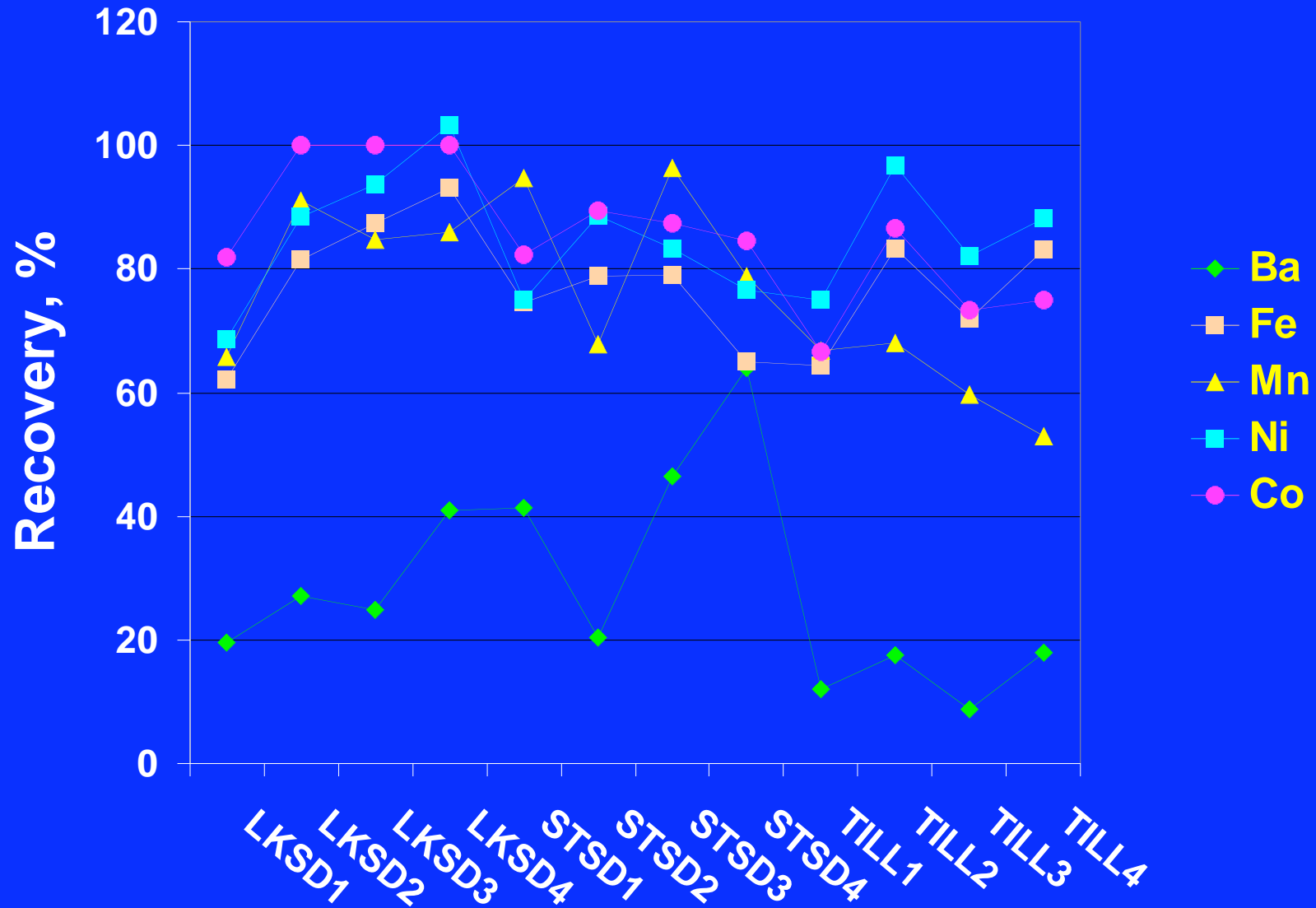
# Recovery in Aqua Regia



# Recovery in Aqua Regia

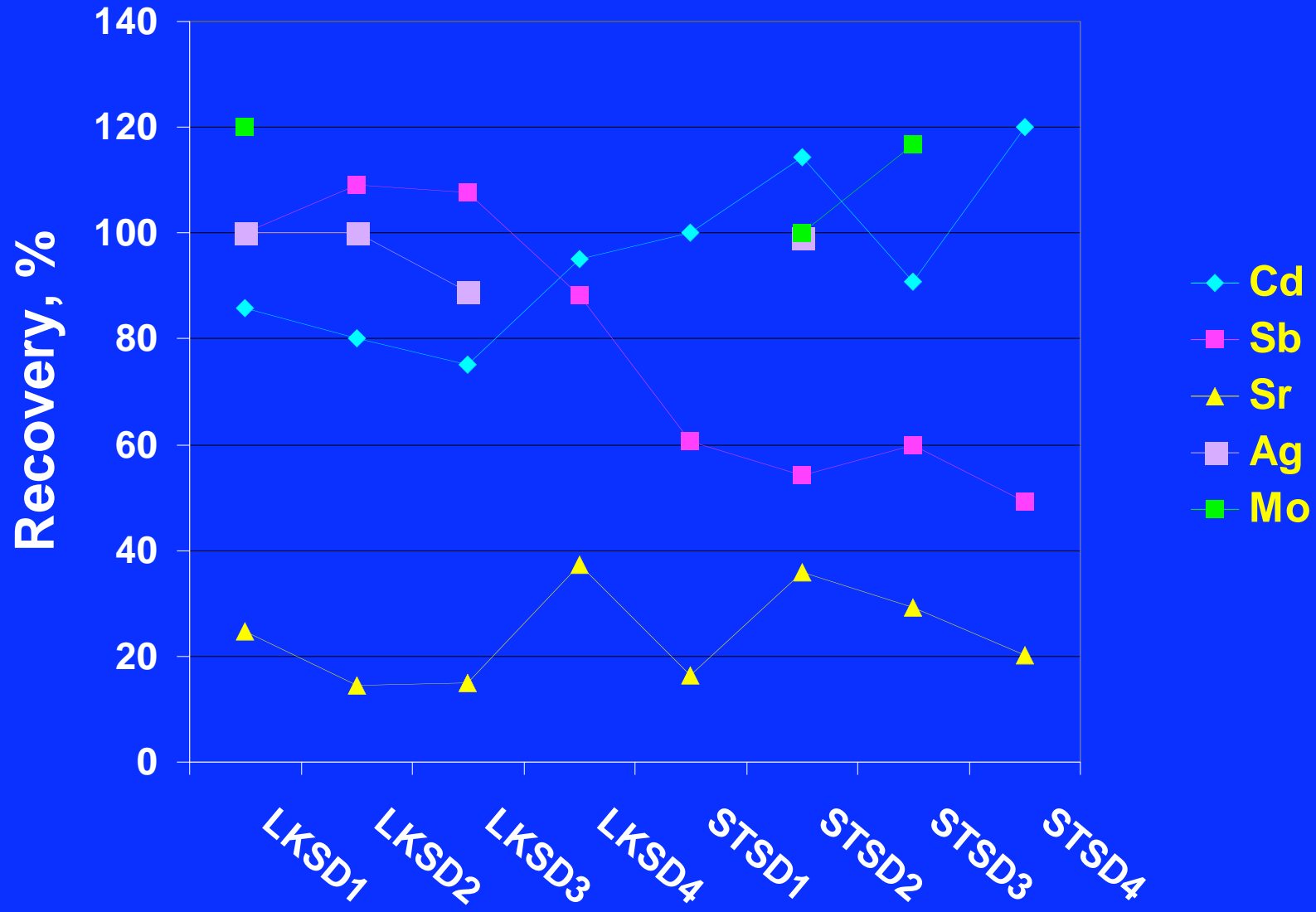


# Recovery in Aqua Regia





# Recovery in Aqua Regia



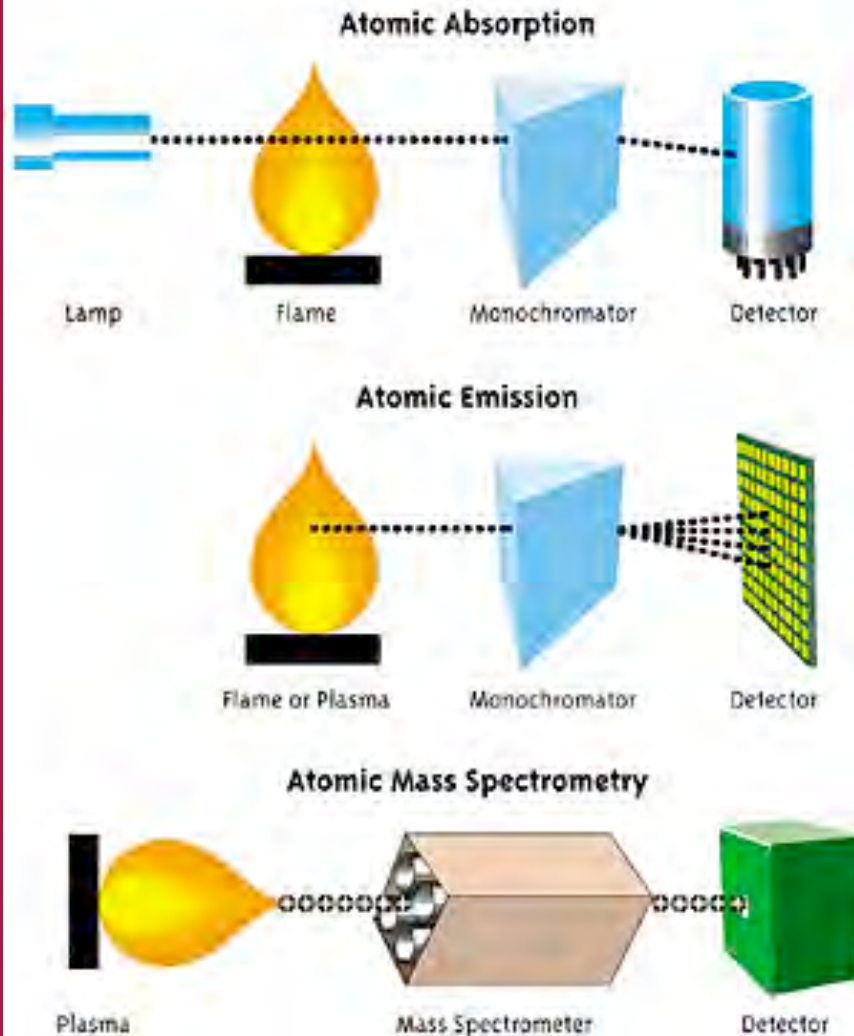
# From Hall, *Explore Newsletter*, 2000

*Range in recoveries of elements by aqua regia in 12 Canmet CRMs:  
LKSD, STSD and TILL series*

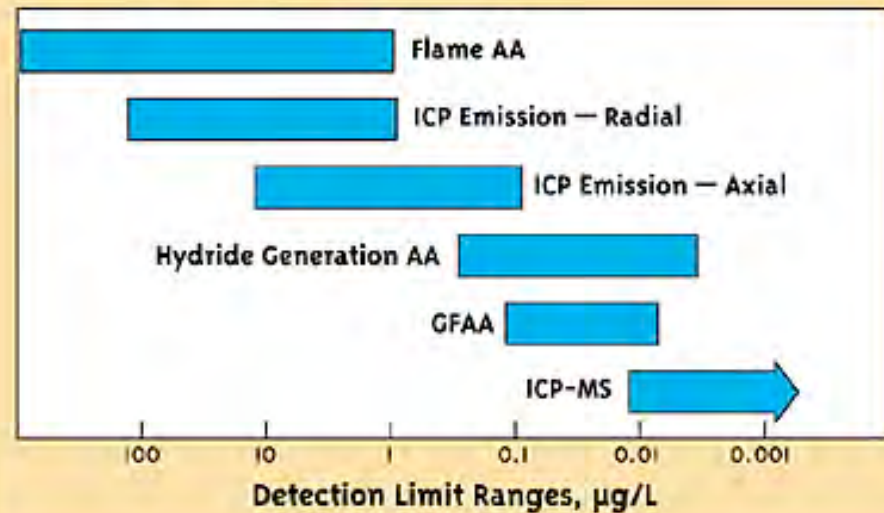
	<u>Range, %</u>		<u>Range, %</u>
Al	13-46	Mn	53-95
As	72-97	Ni	69-100
Ba	9-64	P	100
Ca	41-85	Pb	55-100
Cd	75-100	Sb	49-100
Co	67-100	Sr	15-37
Cr	32-64	Ti	12-42
Cu	92-100	V	46-67
Fe	62-93	Zn	71-100
Mg	59-77		

# The Basics of AAS, ICP-ES and ICP-MS

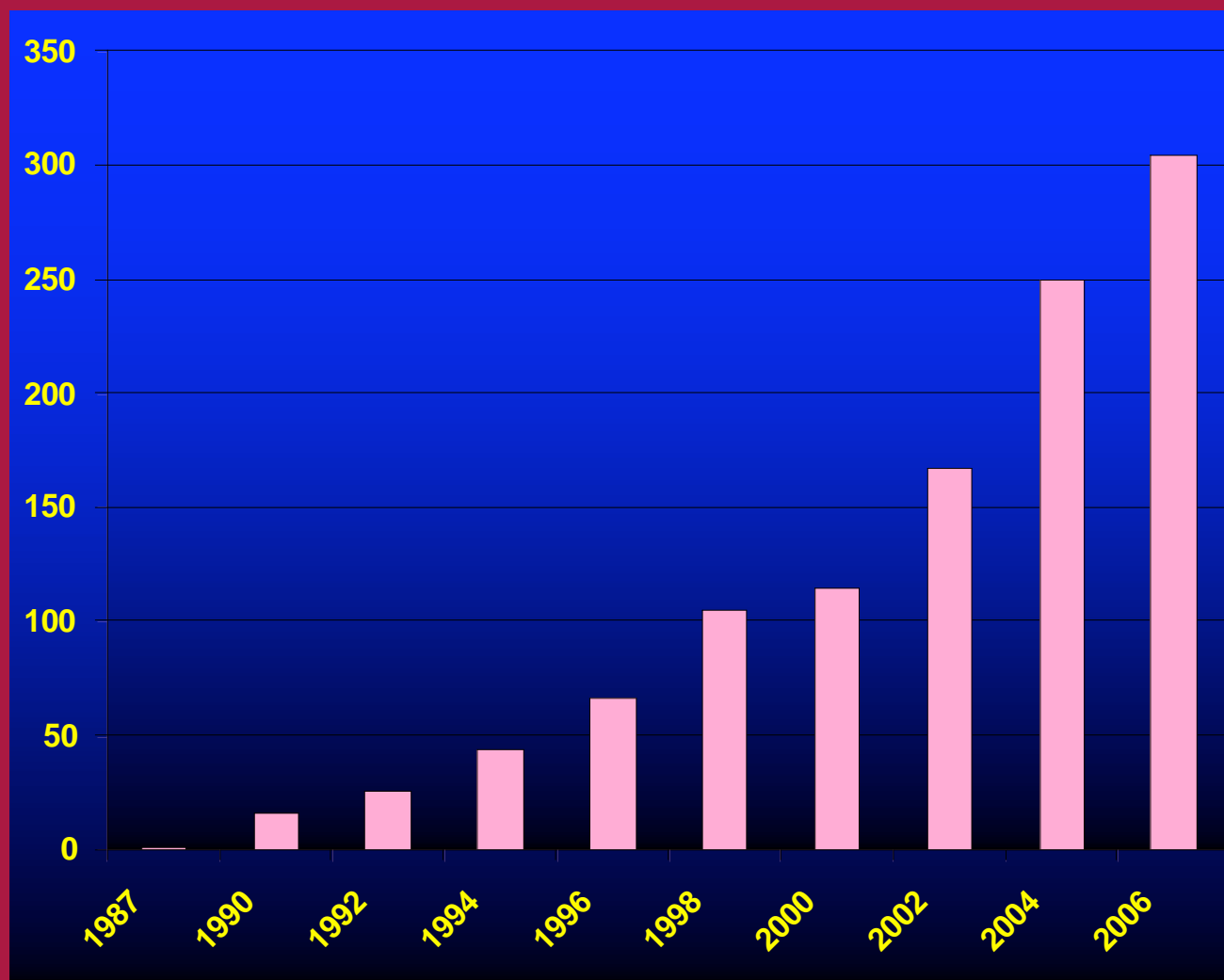
**Figure 1**  
Schematic Diagrams of the Principles of Atomic Absorption, Atomic Emission, and Atomic Mass Spectrometry



**Figure 2**  
Typical Detection Limit Ranges for the Major Atomic Spectroscopy Techniques

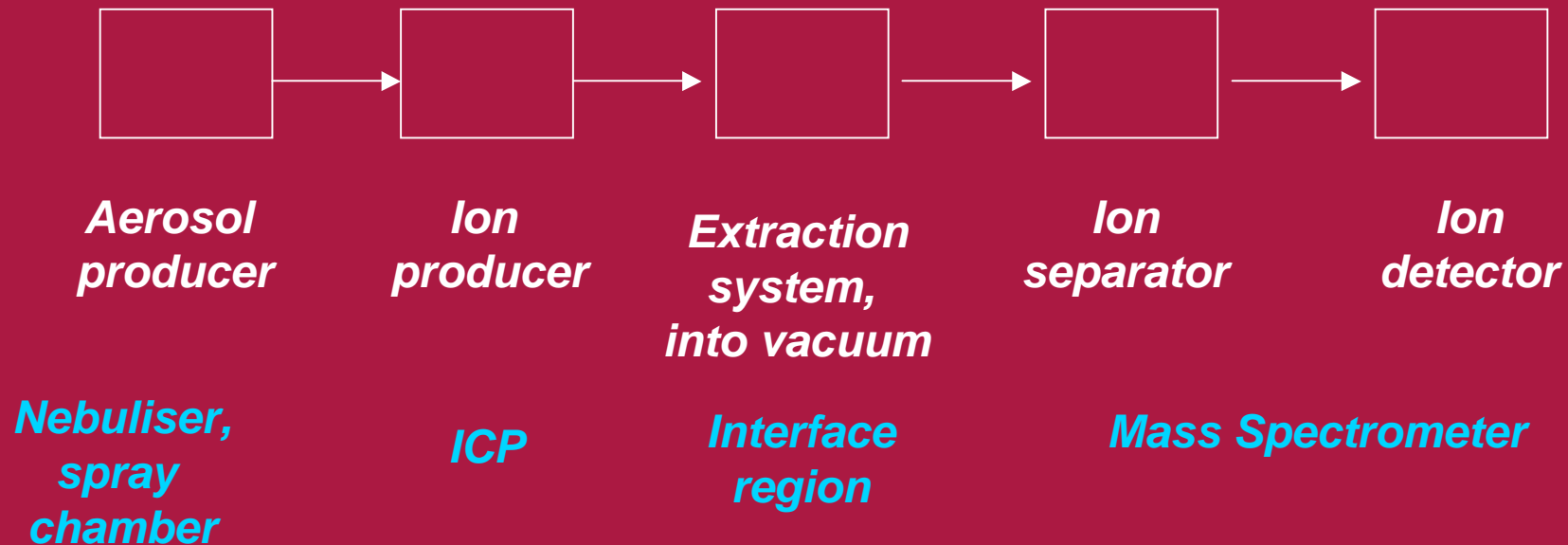


## 'ICP-MS' (in abstract, title or keyword) papers in Earth and Environmental Sciences (Scopus) by year

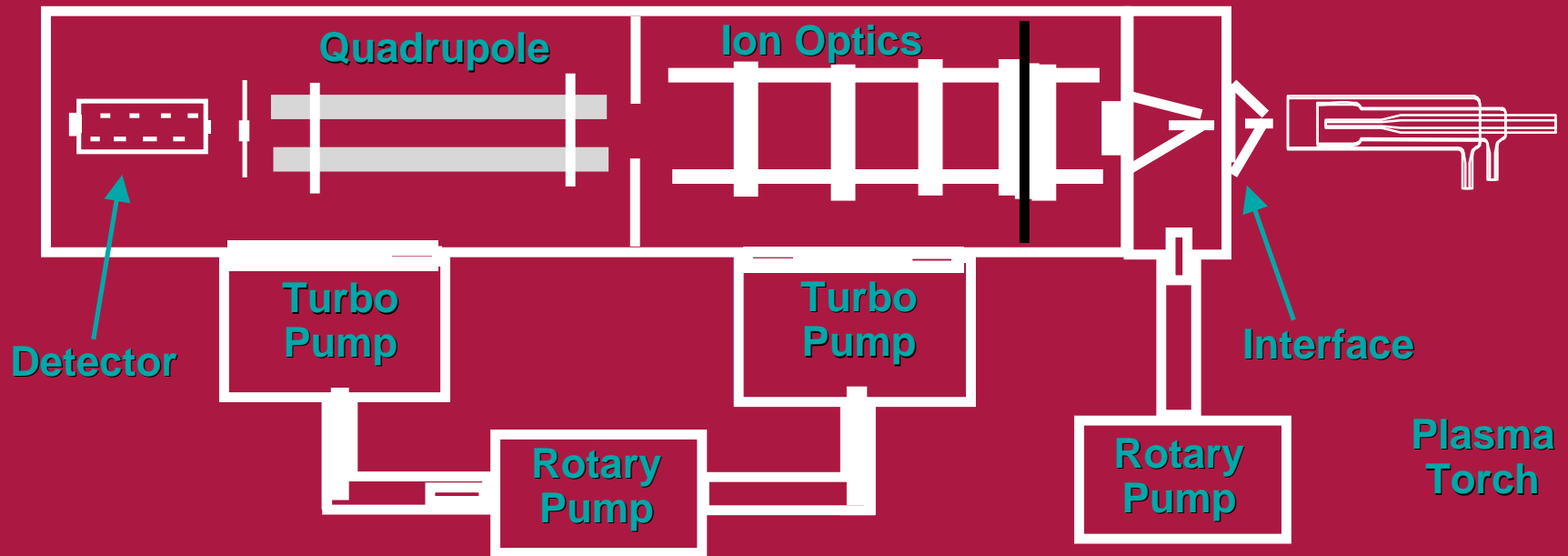


(Majority of 'ICP-MS' papers are in the Chemistry field of journals)

# Routine quadrupole-ICP-MS



# Quadrupole ICP-MS

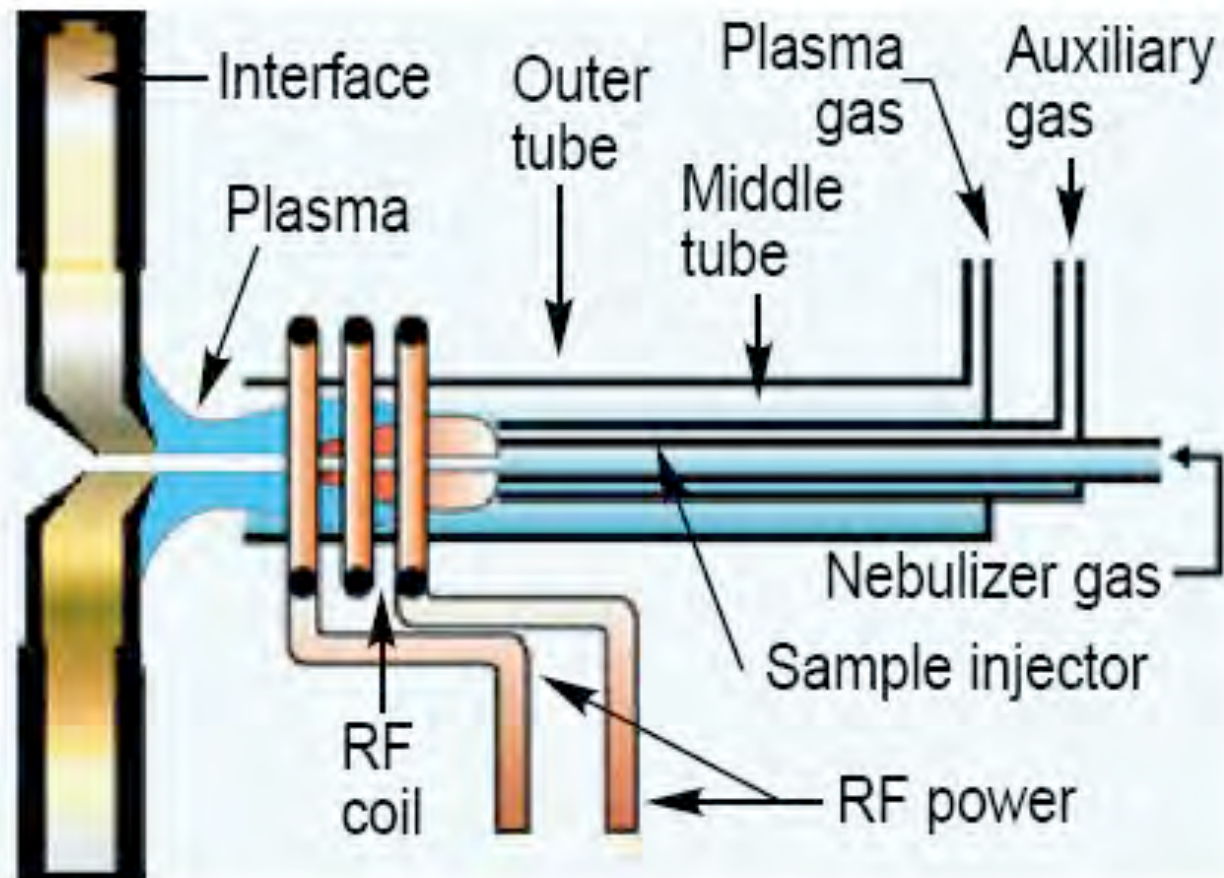


# Sample Introduction System: *Achilles Heel of ICP-MS (and ES)*

- Comprises the **nebuliser** and **spray chamber** to (1) transfer sample solution to ICP and (2) reduce droplet size to 5-10  $\mu\text{m}$  entering ICP
- **Nebulisers**: unlike ES, need to limit TDS to  $<0.2\%$  so use concentric (for 'clean' samples), cross-flow (for higher TDS, more rugged) or less commonly, microflow (0.1 ml/min, cf 1 ml/min) configurations
- **Spray chambers**: Scott double-pass most common, cyclonic also available. Usually cooled to 2-5  $^{\circ}\text{C}$  for thermal stability of sample, minimise concentration of solvent in the ICP and minimise formation of oxides

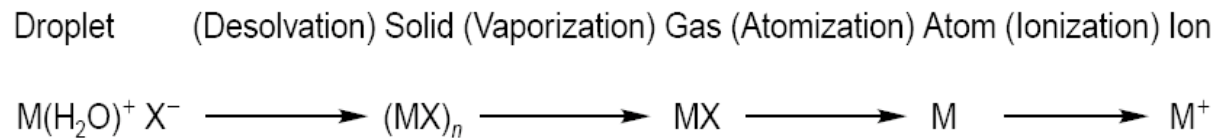
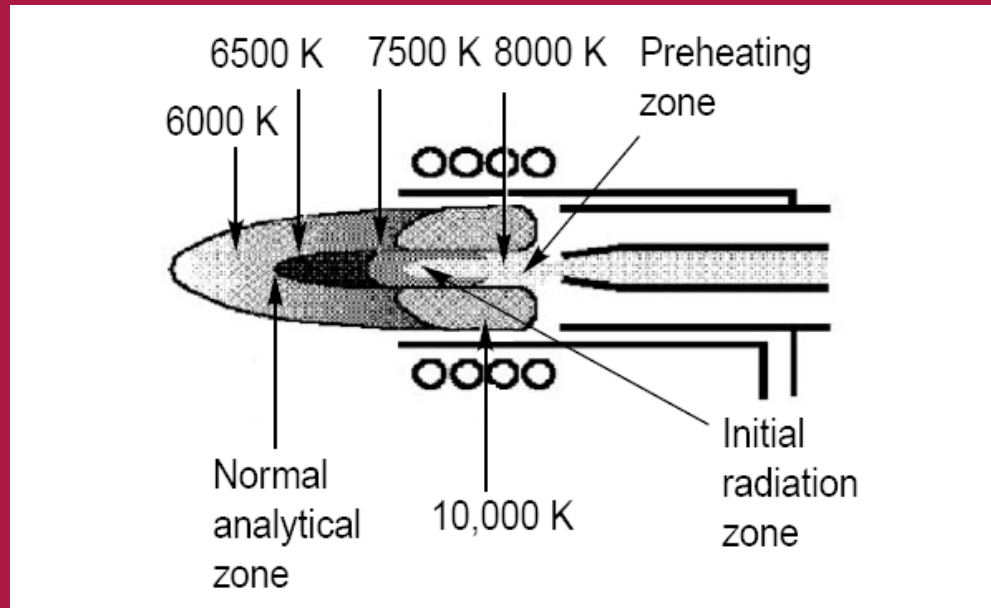
*Only ~ 2% of the analyte reaches the ICP!*

# The ICP

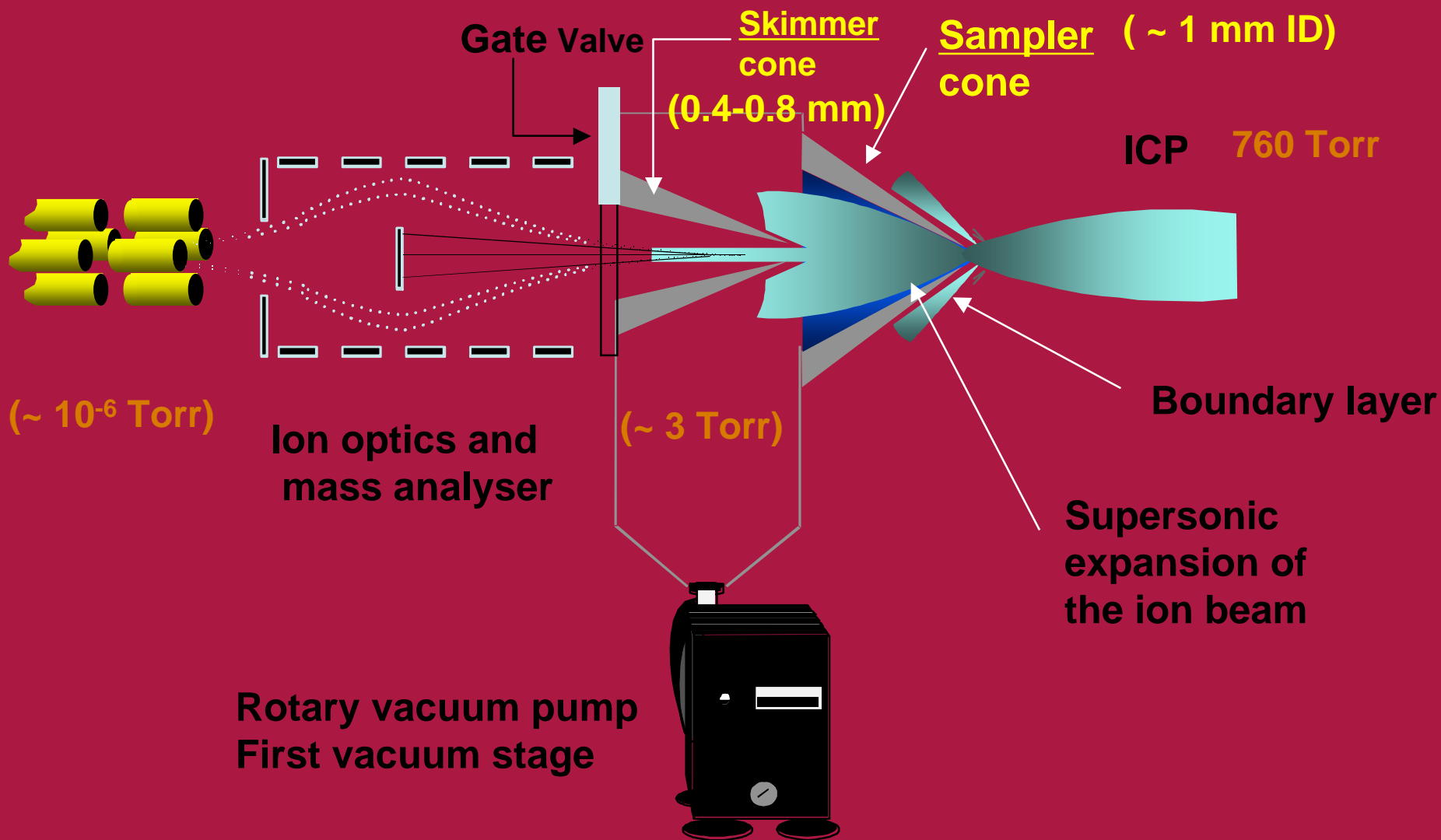




# Changes of analyte in the ICP

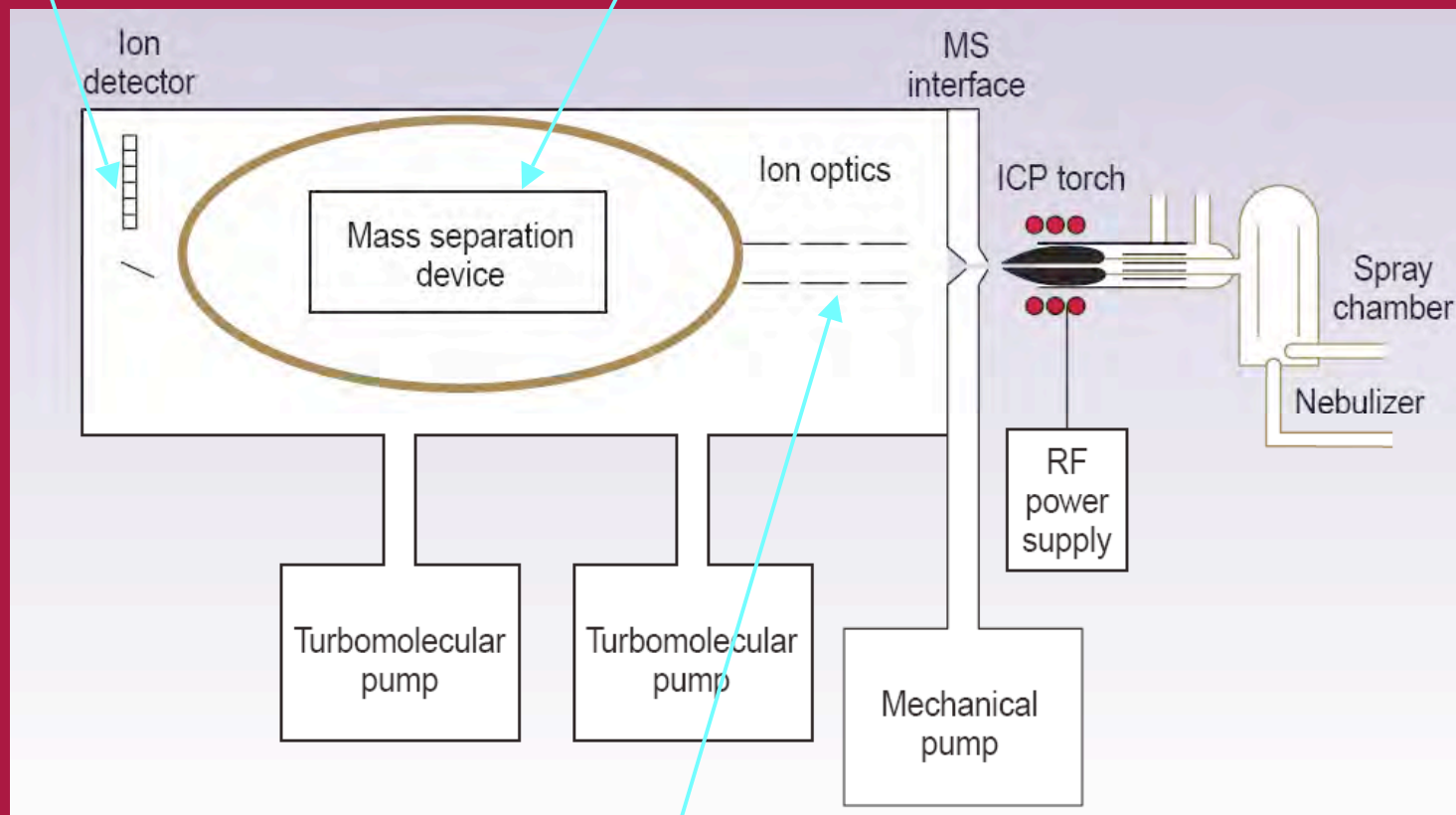


# ICP-MS Interface



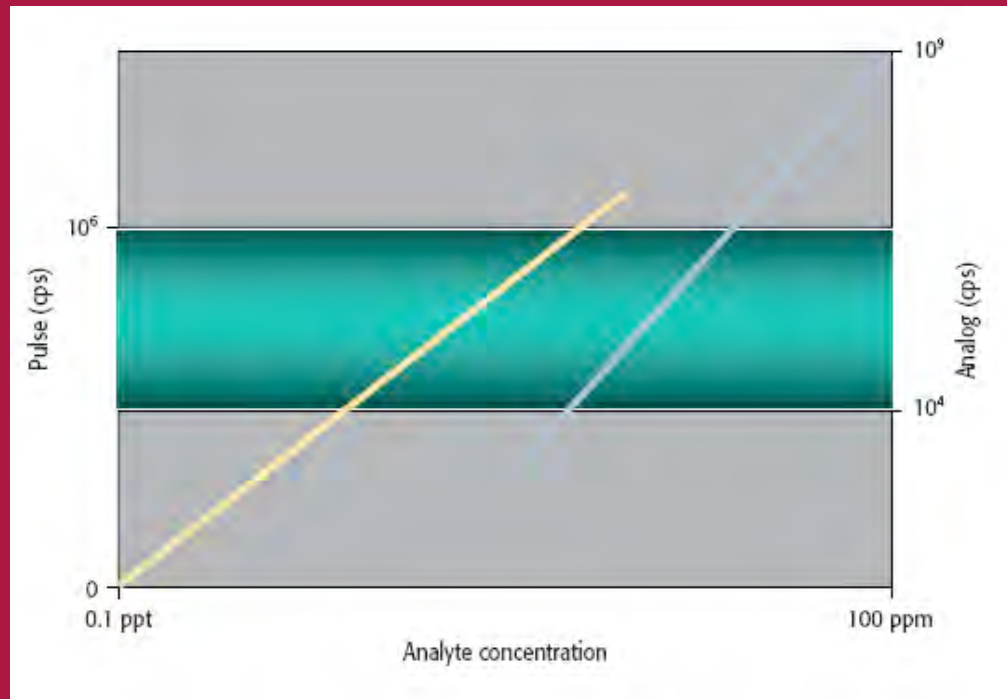
**Detector: Now a diode has replaced the CEM**

**MS: quadrupole in this case, comprising 2 pairs of rods; RF is scanned on 1 pair and voltage on the other to allow specific ions to pass sequentially to the detector**



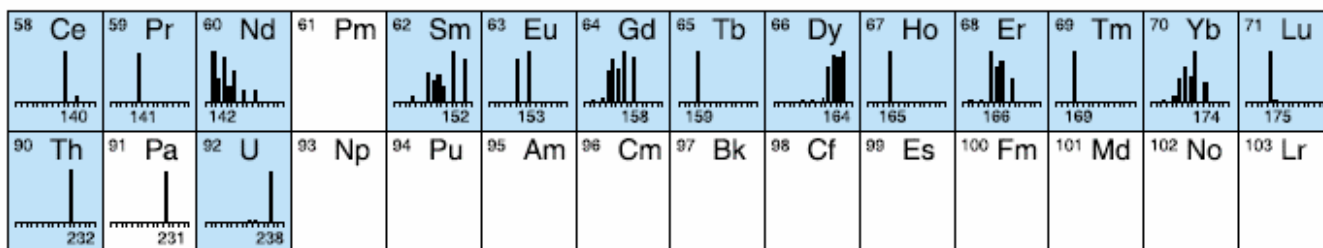
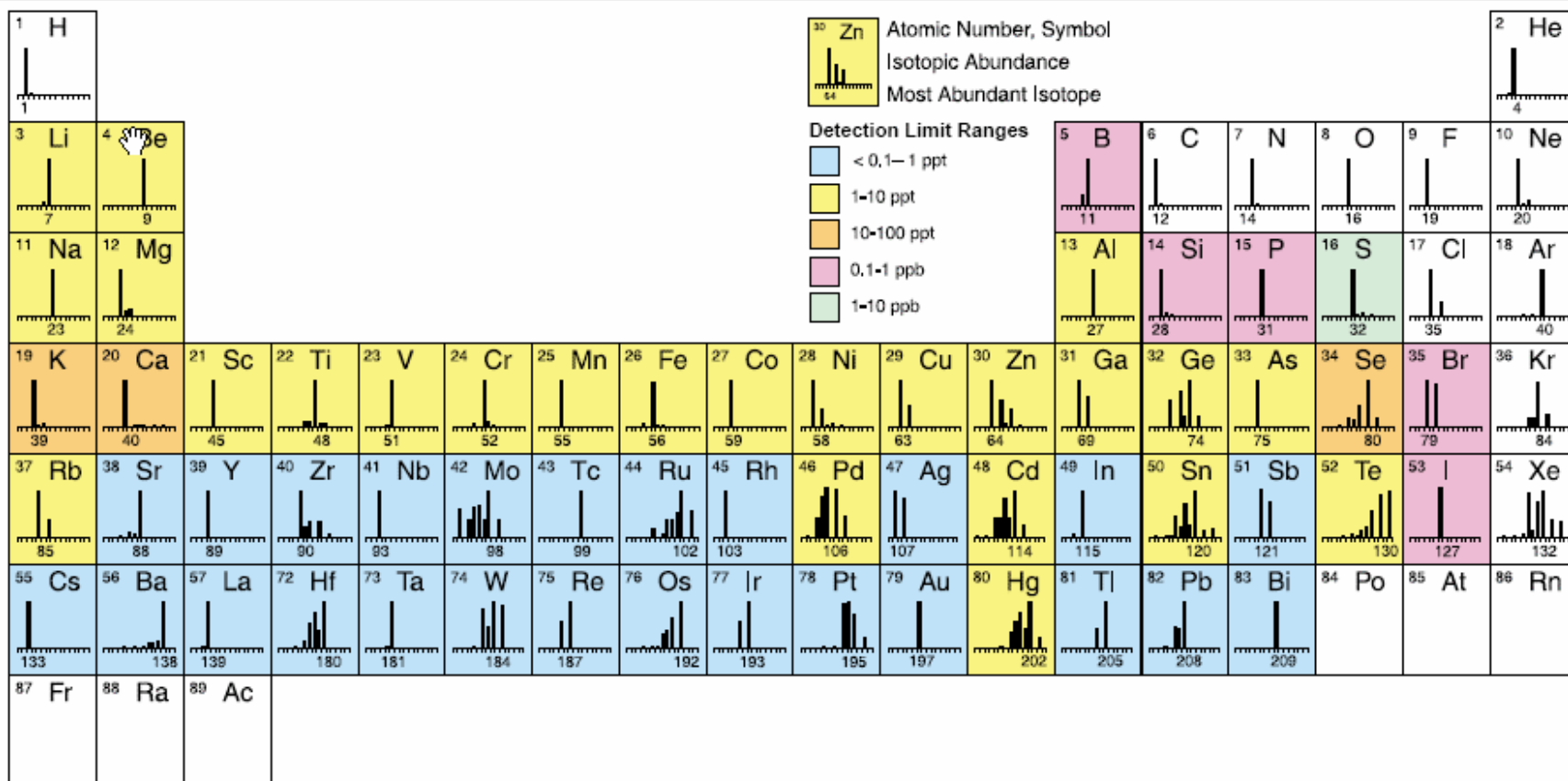
**IO: to transfer the analytes at optimum KE to the mass analyser, eliminating particulates, neutral species and photons**

# The dual mode discrete dynode detector in ICP-MS: 0.1 ppt to 100 ppm!!



*No need for two scans,  
only cross-calibration of the two counting modes*

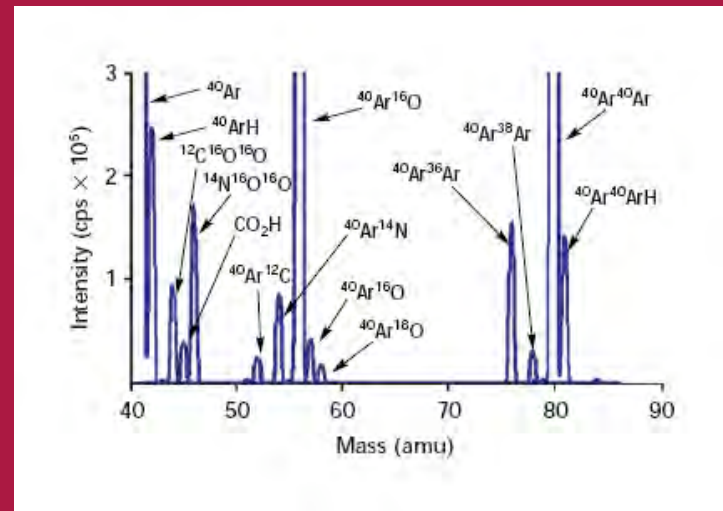
# Instrumental detection limits by ICP-MS



# Interferences in ICP-MS

Spectral, are most important.  
Opposite is spectrum of H<sub>2</sub>O  
from 40 to 85 amu

To mitigate, use correction equations,  
'Cool' plasma (small group of elements)  
or Collision Cell



## Physical matrix interferences:

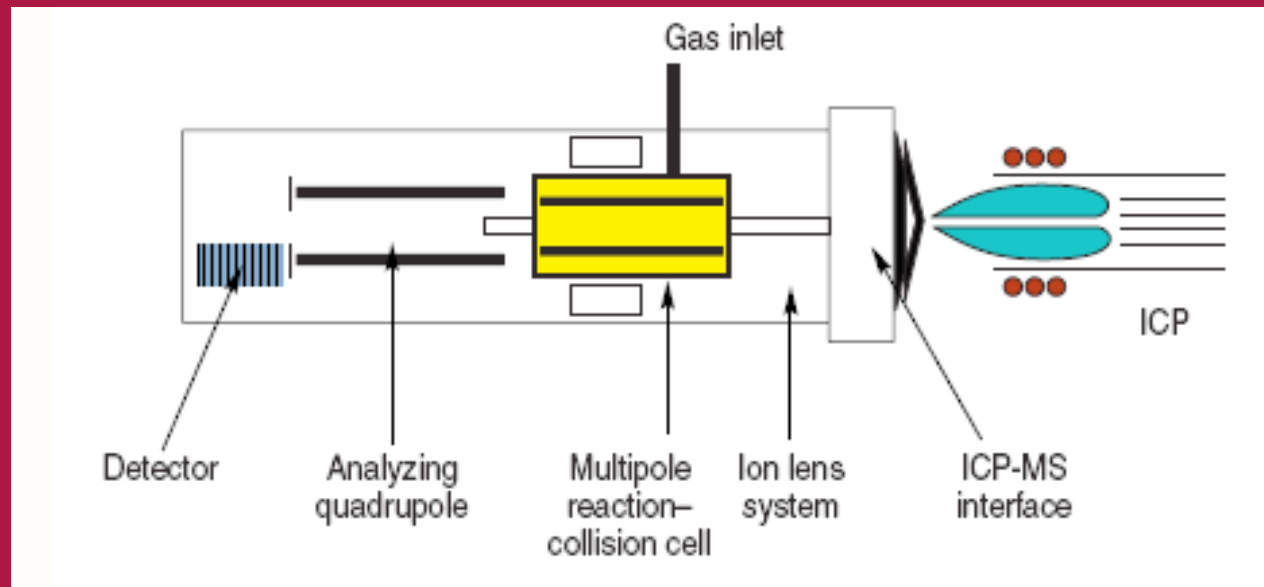
(1) transport effects in introduction system and (2) in the ICP itself.

To mitigate, use internal standardisation but can be dangerous if the IS is not close in mass or IP, alternatively matrix-match or dilute

## Space-charge effects in the ion optics:

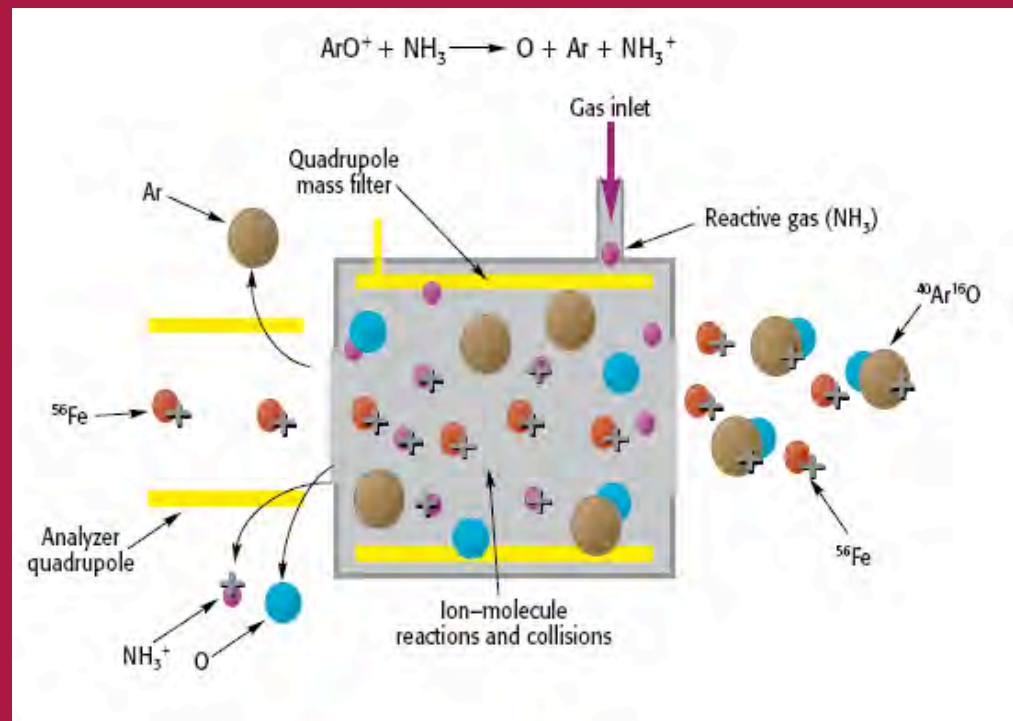
Lighter elements are lost (defocussed) in transmission through the lenses  
Voltages are applied to the ion lenses to mitigate

# Collision or Reaction Cell Technology: to remove spectral interferences

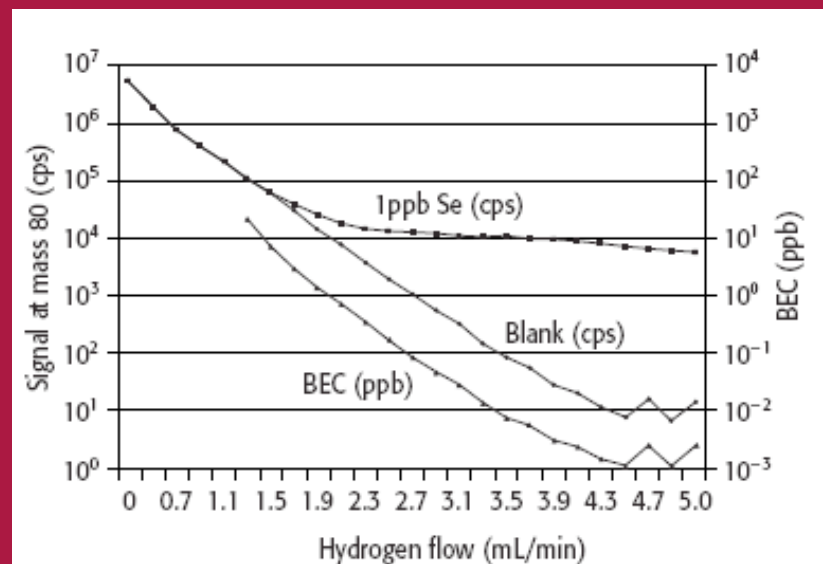


*Gas such as  $H_2$ , He, Xe,  $NH_3$  is passed into the cell (which is a quad, hex or octapole operated in an RF mode) to react with analyte ion beam via collisions, thus producing different species*

**- Removal of ArO by collision with NH<sub>3</sub> molecules, in analysis for Fe**



**-Removal of Ar<sub>2</sub> species which interferes with Se at mass 80, note the blank background (Ar<sub>2</sub>) decreasing with H<sub>2</sub> flowrate**

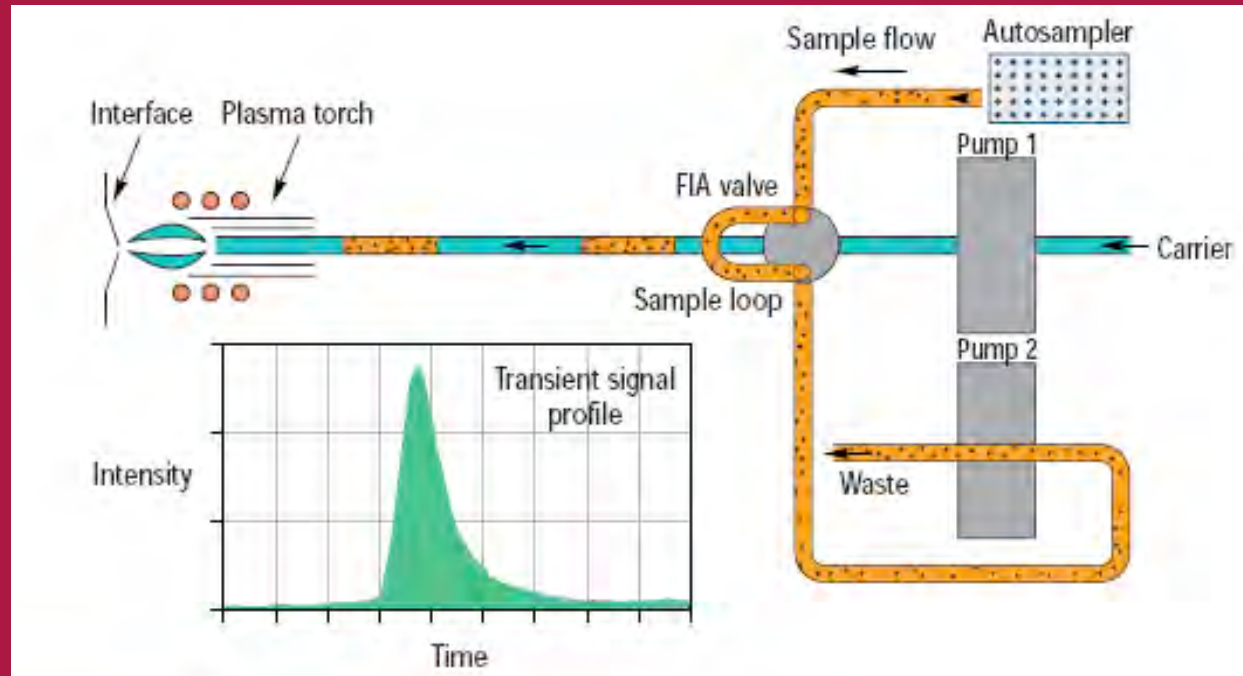




# Sample Introduction Alternatives

- Ultrasonic nebulisers (with desolvation)
- **Direct Injection Nebuliser (DIN) into centre of ICP, for  $\mu\text{l}$  amounts and as interface for IC**
- Hydride generators (As, Se, Te, Bi, Ge)
- **Laser ablation**
- Graphite Furnace (GF) or Electrothermal Vaporisation (ETV)
- **Direct insertion of solid sample into the centre of plasma (not commercialised)**
- Flow injection analysis (FIA)

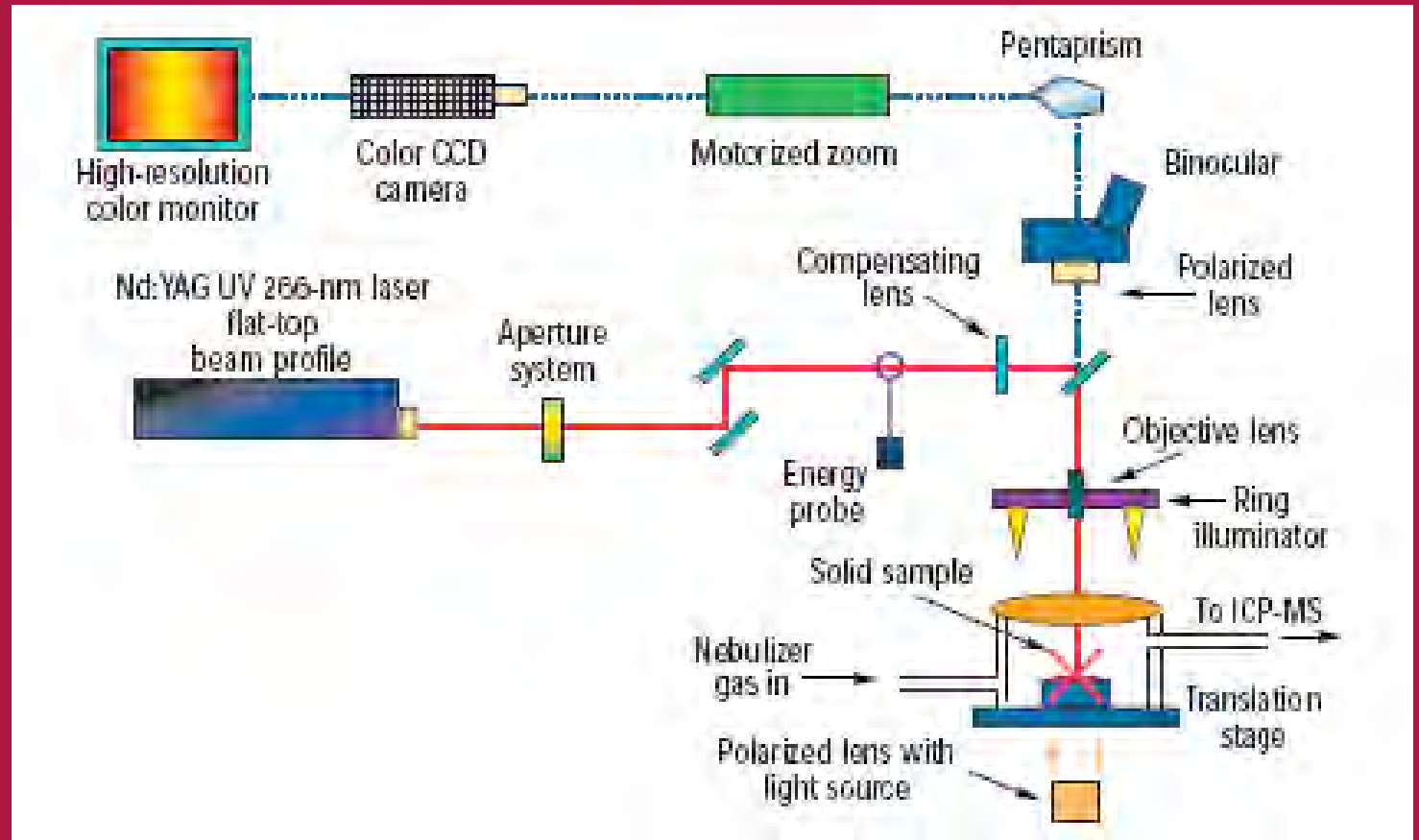
# Flow injection analysis (FIA)



*Automated introduction of a discrete sample aliquot into a flowing carrier stream, allows for: automatic addition of reagents, limited contamination through handling, improved ICP stability, interface to hyphenated techniques such as IC*

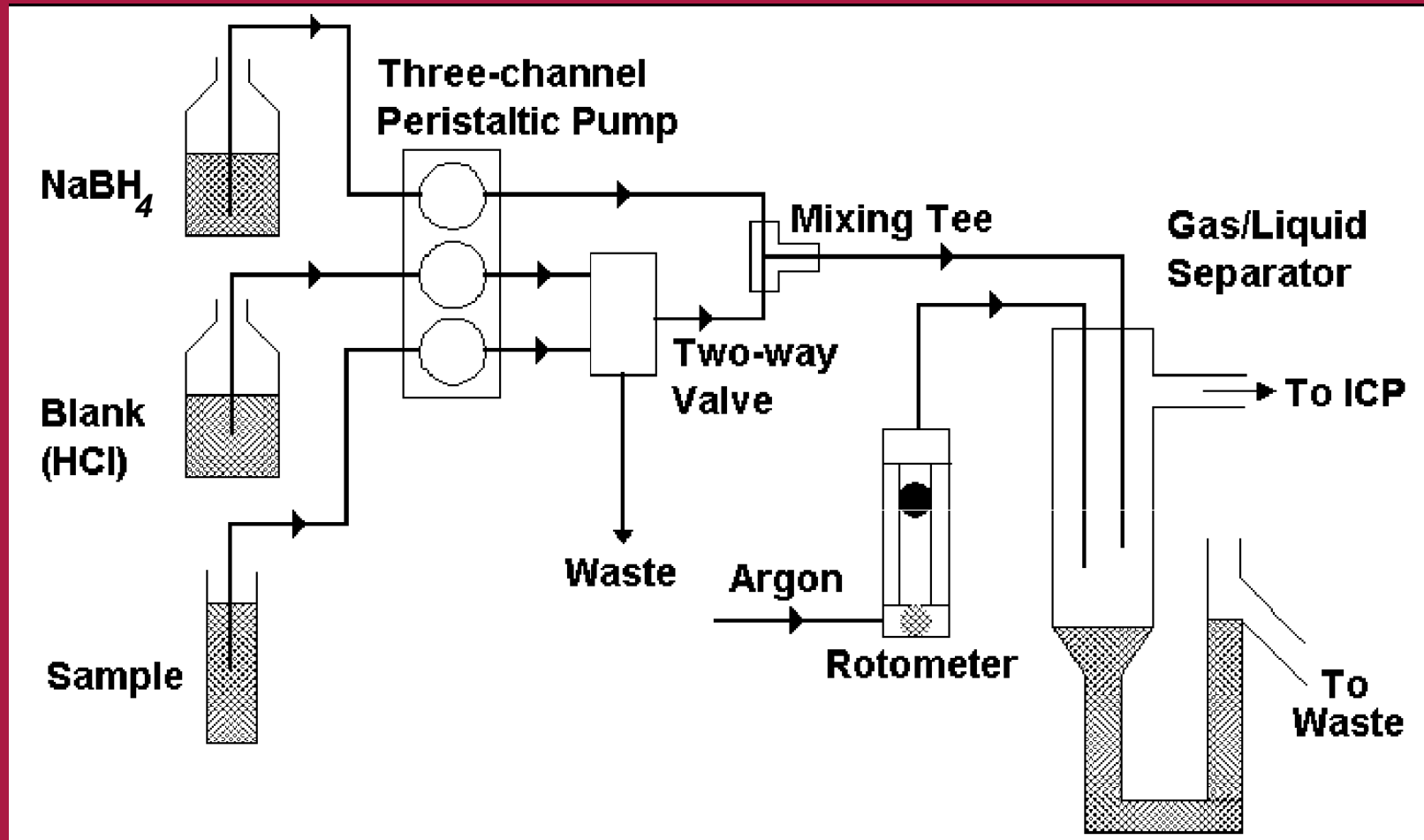
# Laser ablation ICP-MS

*Cetac's system*



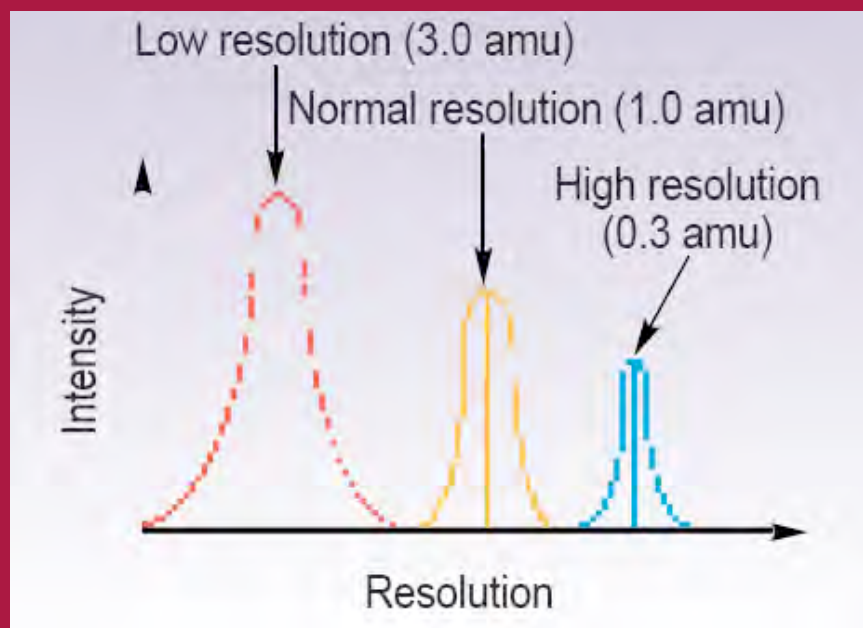
*Although advantages over nebulisation are obvious (no digestion, fewer interferences), but its real strength is in spatial mapping of elements and their ratios, in grains, inclusions, coatings etc*

# Hydride generation (HG), for ICP-MS or -ES



# Resolution and sensitivity

- Resolution of Quad is ~ 0.7-1 amu
- Resolving Power,  $R = m / \Delta m$  (mass difference of 2 resolved peaks); this is usually <300 for the Quad
- Higher the resolution, the lower the sensitivity, so one has to compromise

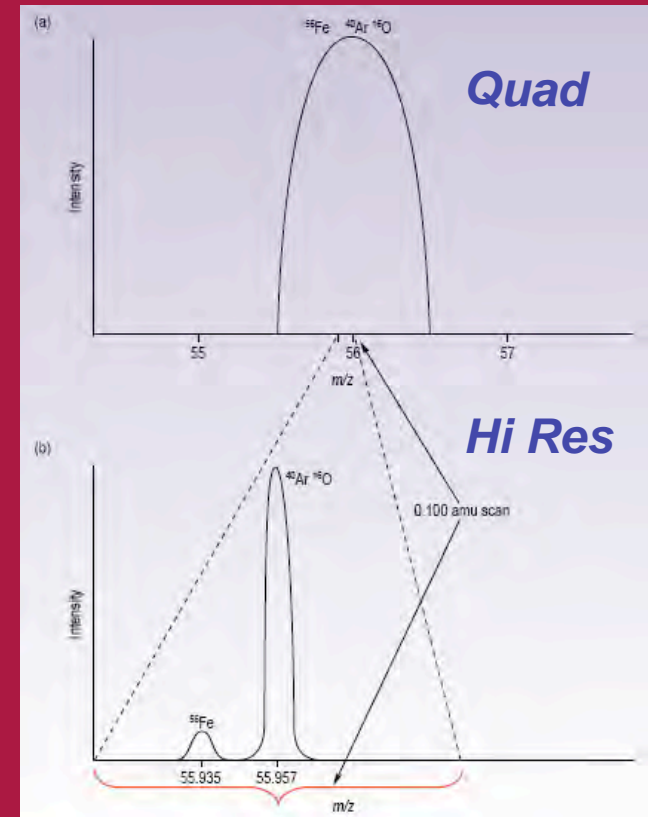
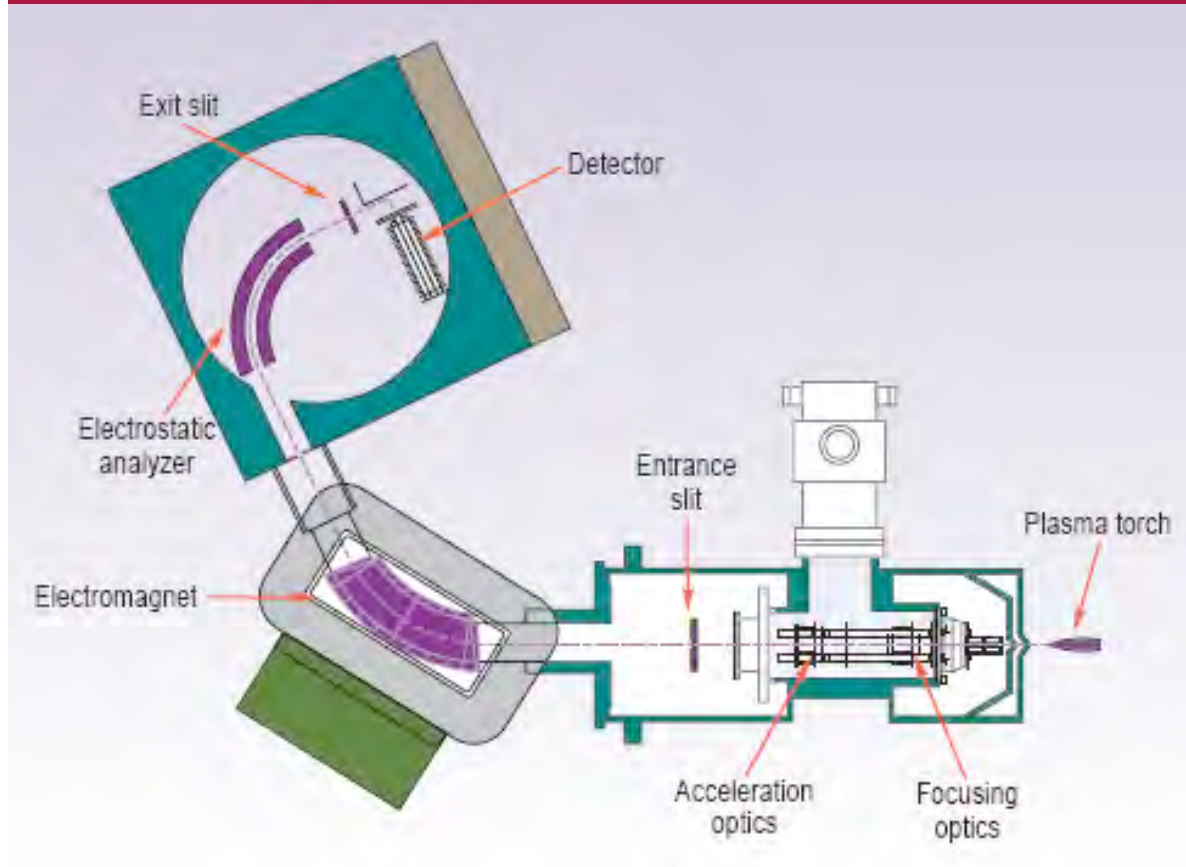


# Resolution

Analyte	Interference	$ \Delta m $	m	R
$^{75}\text{As} = 74.92160$	$^{40}\text{Ar}^{35}\text{Cl} = 74.93123$	0.00963	75	7788
$^{56}\text{Fe} = 55.93494$	$^{40}\text{Ar}^{16}\text{O} = 55.95729$	0.02235	56	2505
$^{40}\text{Ca} = 39.96259$	$^{40}\text{Ar} = 39.96238$	0.00021	40	190476
$^{87}\text{Sr} = 86.90889$	$^{87}\text{Rb} = 86.90918$	0.00029	87	300000

*R for quad is < 300*

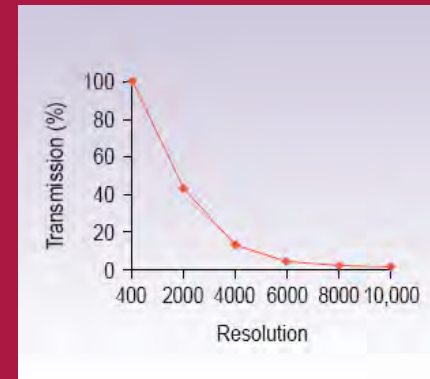
# HR (high resolution)-ICP-MS: double-focussing magnetic sector



*e.g. the 'Element 2'*

# Features of HR-ICP-MS

- Resolving power of ~ 300 to 3000 to 10,000 but sensitivity is still reduced at high R

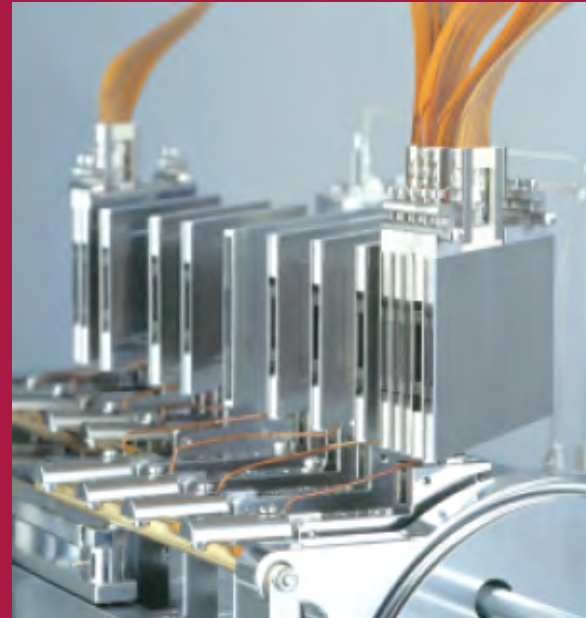


- Higher sensitivity (cf Quad). At low R, >100 mcps per ppm over bgd of ~0.1 cps (cf ~ 10 mcps per ppm over bgd of ~ 10 cps)
- Precision is better, at ~ 0.01-0.05% RSD at low R
- Less rugged than Quad, still significant downtime



# Multicollector ICP-MS

*Thermo's Finnigan  
'Neptune'  
(3<sup>rd</sup> generation MC-ICP-MS);  
the competitor, the 'Nu Plasma,'  
has 12 Faraday cups and  
3 discrete dynode EMs*

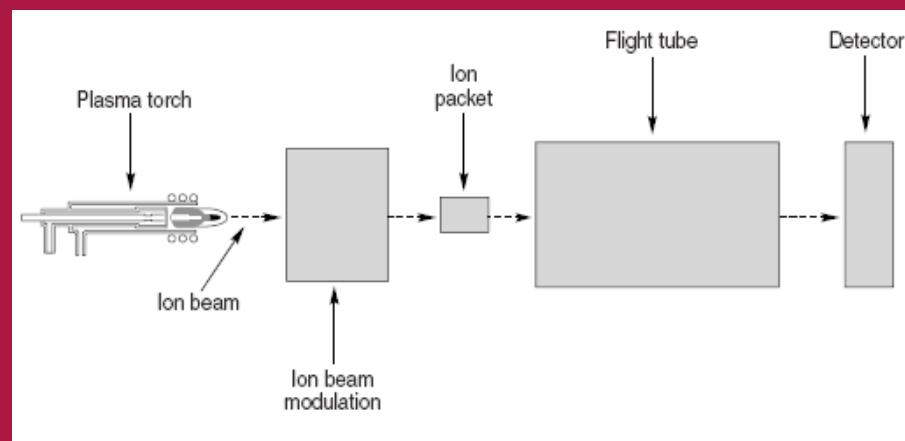


*Similar to the Element 2 but instead of a single detector there are 17 collectors in parallel: 1 fixed centre channel and 8 moveable collectors, each carrying a Faraday cup and 1 SEM, which are plug-in design (i.e. easy to change)*

# Time-of-flight (TOF) ICP-MS: all ions sampled at once

## *Advantages of simultaneous detection:*

- Multielement determinations of rapid transient signals generated by sampling accessories such as laser ablation and ETV devices
- High-precision, ratioing techniques such as internal standardization and isotope ratio analysis
- Rapid multi-element measurements, especially where sample volume is limited.



*Commercialised in 1998, still not many instruments*

# Features of ICP-MS

## Advantages

- Multi-element technique suitable for wide range of elements to sub-ppb DLs in the sample (ppt in solution); large linear dynamic range (analog and pulse-counting detector modes; don't have to dilute frequently)
- Ideally suited for ultratrace geochemical methods such as selective and sequential extractions, waters, vegetation.
- Most spectral interferences can be negated by judicious selection of isotope, correction algorithms and appropriate operating conditions.
- Isotope measurement!!!!

## Limitations

- The total dissolved salt (TDS) content of the analyte solution must be kept low (e.g. <0.2%) or instrument performance is adversely affected; dilution can lead to inadequate DLs for some elements.
- Technical expertise is required to mitigate spectral and non-spectral matrix effects.
- Ultrapure acids are required for leaches and digestions, thus increasing the cost of analysis.

# Aqua regia ICP-MS pkg: DLs in ppm

Ag	2 ppb	Fe	0.01%	Ni	0.1	Ti	.001%
Al	0.01%	Ga	0.1	P	.001%	Tl	0.02
As	0.1	Ge	0.1	Pb	0.01	U	0.1
Au	.2 ppb	Hf	0.02	Rb	0.1	V	2
B	1	Hg	5 ppb	Re	1 ppb	W	0.1
Ba	0.5	In	0.02	S	0.02%	Zn	0.1
Be	0.1	K	0.01%	Sb	0.02	Zr	0.1
Bi	0.02	La	0.5	Sc	0.1		
Ca	0.01%	Li	0.1	Se	0.1		
Cd	0.01	Mg	0.01%	Sn	0.1	+	
Co	0.1	Mn	1	Sr	0.5	REEs	~0.1
Cr	0.5	Mo	0.01	Ta	0.05	+	
Cs	0.02	Na	.001%	Te	0.02	Pt	2 ppb
Cu	0.01	Nb	0.02	Th	0.1	Pd	10 ppb

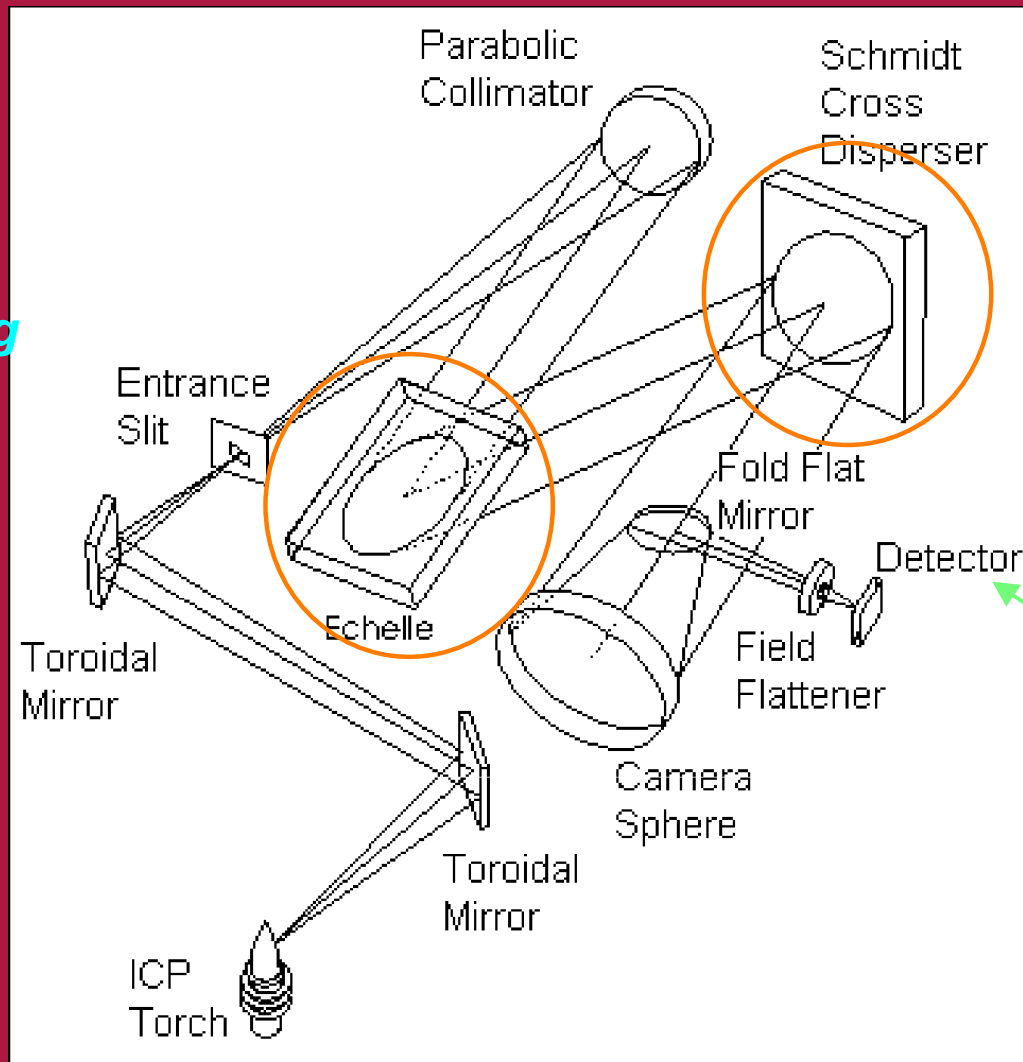
~\$20+ , additional charge for > 1 g sample weight

# ICP-ES

- Has gone through a revolution in the past decade, improving DLs and resolution
- **Most instruments now are simultaneous with echelle grating design**
- Spectral interferences (eg background shifts, direct overlap) corrected by simultaneous correction of background, alternate choice of line or inter-element correction (IEC) and non-spectral by matrix-matching (eg [EIE] such as Na, K, [acid])
- **Detection limits generally in low ppb range in solution**

# The Echelle mount: to separate wavelengths and spectral orders

*Echelle grating produces multiple orders of wavelengths*

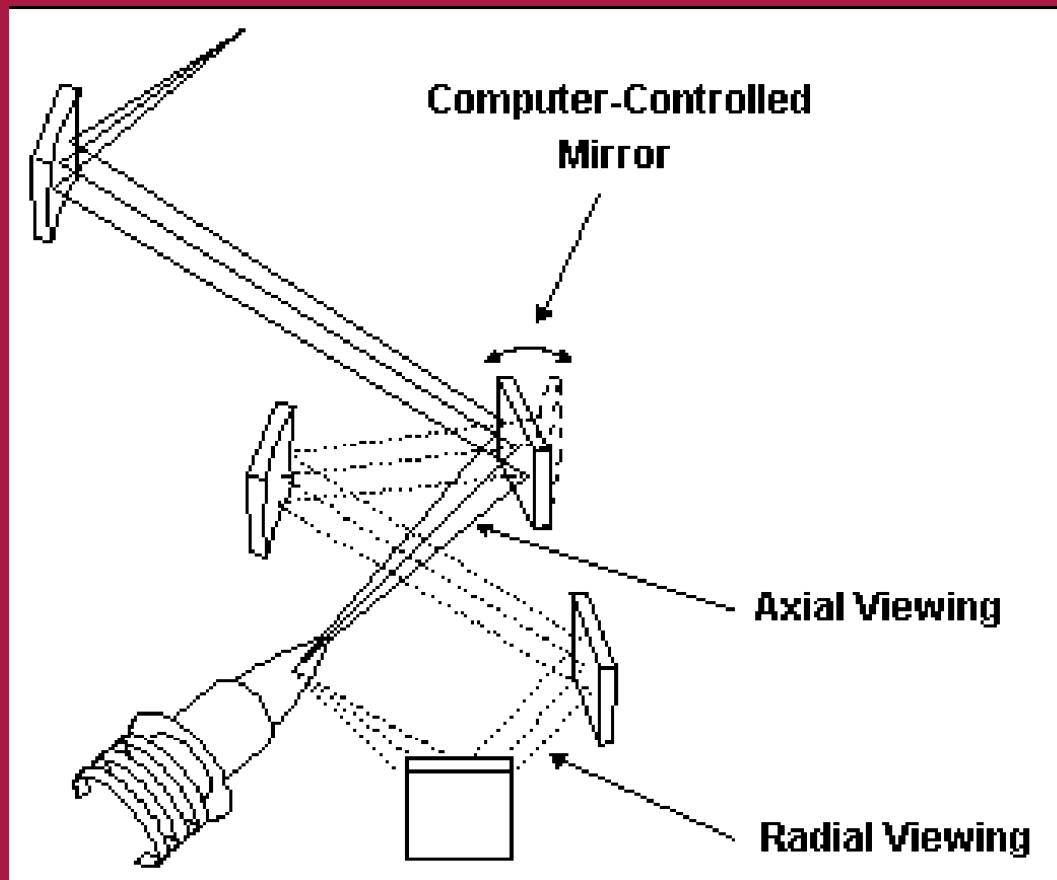


*2<sup>nd</sup> grating or prism cross-disperses multiple orders into a 2-dimensional array: an echellogram*

*Segmented array charge coupled device (SCD) > 230 lines*

*Superior efficiency and resolution cf to standard Paschen-Runge polychromators*

# Radial and axial viewing in ICP-ES



*Axial viewing of ICP:  
longer path length, thus  
better sensitivity (~x10).*

*It took ~ 15 yrs to really  
commercialise this, to  
understand and mitigate  
the increased interferences  
(eg, use of shear gas to  
remove tail plume)*

*Radial viewing: conventional*

# ICP-ES detection limits

Element	Wavelength (nm)	Detection Limit (ppb)	Element	Wavelength (nm)	Detection Limit (ppb)
Ag	328.068	.5	Mg	279.8	1.5
Al	396.152	0.9	Mn	257.61	0.1
As	188.98	3	Mo	202.03	0.5
As	193.696	4	Na	589.59	0.2
Ba	455.403	0.03	Ni	231.6	0.7
Ba	233.527	0.1	P	177.43	4
Be	313.107	0.05	Pb	220.34	1.5
Ca	396.847	0.01	Rb	780.03	0.01
Ca	317.933	0.8	S	206.83	3
Cd	214.439	0.2	Se	196.03	4
Co	238.892	0.4	Sn	189.93	2
Cr	267.716	0.5	Sr	407.77	0.02
Cu	327.395	0.9	Ti	336.12	0.5
Fe	238.204	0.3	Tl	190.79	2
K	766.491	0.3	V	292.4	0.7
Li	670.783	0.06	Zn	213.86	0.2
Mg	279.55	0.05			



# Improvement in DLs with Cetac's ultrasonic nebuliser, U-5000AT+

## ICP-ES, radial, in ppb

Element	Wavelength (nm)	Pneumatic Nebulizer (Cross-Flow)	U-5000AT+
Ag	328.06	2	0.3
Al	396.15	9	0.5
As	193.69	18	2
Be	313.04	0.3	0.02
Cd	214.43	2	0.2
Co	228.61	5	0.3
Cr	267.71	4	0.2
Cu	324.75	2	0.3
Mo	202.03	8	0.3
Ni	231.60	10	0.4
Pb	220.35	27	1
Sb	206.83	12	3
Se	196.03	20	1.3
Tl	190.80	22	5
V	292.40	2	0.2
Zn	213.85	2	0.2

Notes: Detection limits are based on 3 sigma, with a 10-second integration time. Instrument used was a Thermo Jarrell Ash ICAP 61.

## ICP-ES, axial, in ppb

Element	Wavelength (nm)	Pneumatic Nebulizer (GemCone)	U-5000AT+
Ag	328.068	1	0.03
Al	396.153	2	0.06
As	188.979	3	0.7
Ba	233.527	0.5	0.01
Be	313.107	0.1	0.009
Bi	233.061	2	0.2
Ca	317.933	2	0.03
Cd	228.802	0.1	0.02
Co	228.616	0.2	0.02
Cr	267.716	0.2	0.01
Cu	324.754	0.6	0.02
Fe	238.204	0.1	0.02
Mg	285.213	0.5	0.06
Mn	257.610	0.1	0.03
Mo	202.031	0.6	0.3
Ni	231.604	0.4	0.06
Pb	220.353	2	0.2
Sb	206.836	2	0.3
Se	196.026	3	0.5
Sn	189.927	1	0.4
Ti	334.940	0.2	0.006
Tl	190.801	2	0.5
V	290.880	2	0.02
Zn	213.857	0.2	0.03

Notes: Detection limits are based on 3 sigma, with a 20-second integration time. Instrument used was a Perkin-Elmer 4300DV ICP-OES.

# Features of ICP-ES

## Advantages

- Multi-element technique suitable for wide range of elements to ~ ppb DLs in solution; large linear dynamic range ( $10^4$  to  $10^6$ )
- Most interferences can be negated by judicious selection of line, background correction, IECs, use of internal standards and appropriate operating conditions.
- Instruments are robust and relatively inexpensive, operation and methods are well documented.
- Can nebulise solutions much higher in TDS than in ICP-MS (in % range).
- Cheaper per analysis than ICP-MS

## Limitations

- Less sensitive than ICP-MS, should be used as a complementary technique for the same digested sample
- Need sample to be in solution

# Aqua regia ICP-ES pkg: DLs in ppm

---

Ag	0.2	Co	1	Mo	1	Th	1
Al	0.01%	Cr	1	Na	0.01%	Ti	0.01%
As	2	Cu	1	Ni	1	Tl	2
B	10	Fe	0.01%	P	.001%	U	10
Ba	1	Ga	10	Pb	2	V	1
Be	0.5	K	0.01%	S	0.01%	W	2
Bi	2	La	1	Sb	2	Zn	1
Ca	0.01%	Mg	0.01%	Sc	1	Zr	1
Cd	0.5	Mn	2	Sr	1		

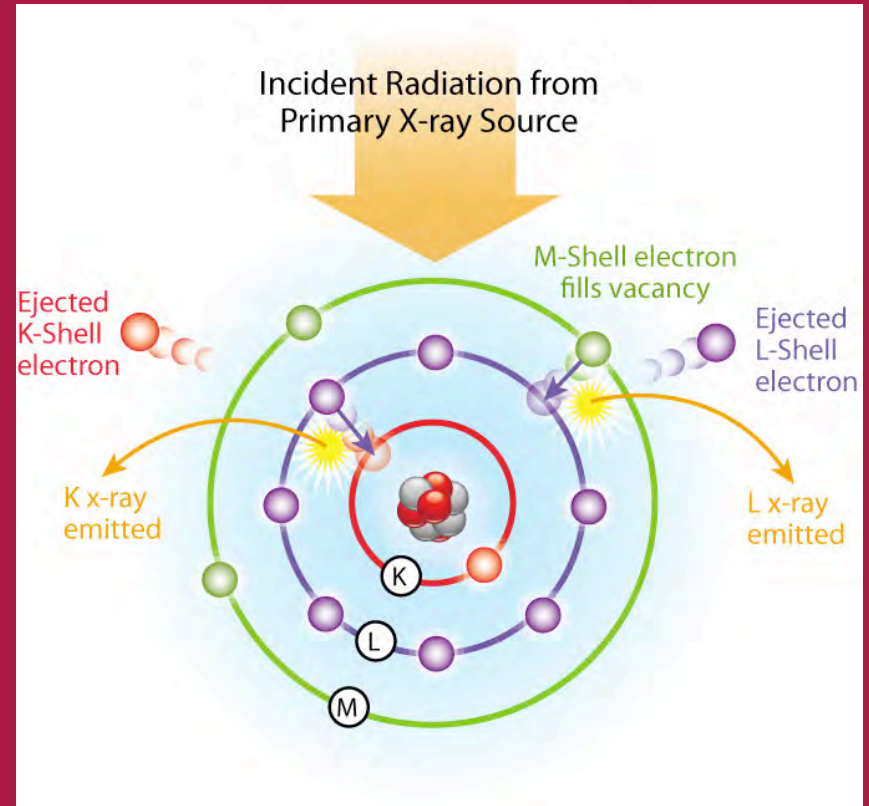
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*~\$11, additional charge for > 1 g sample weight*

*DLs of the same order for an HF-HClO<sub>4</sub>-HNO<sub>3</sub>-HCl digestion*

# Principle of XRF

- Incident high energy photons strike the atom, dislodging an electron from one of the atom's inner orbital shells.
- The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher quantum energy orbital shells.
- The electron drops to the lower energy state by releasing a characteristic fluorescent x-ray whose intensity is measured by a detector (e.g. NaI, proportional counter). Calibration curve is constructed using well characterised, appropriate SRMs
- Sample is prepared by  $\text{LiBO}_2$  fusion (majors, minors, some traces) or made into pressed pellets (traces)



# Features of XRF

## Advantages

- The fusion technique minimises particle size/matrix effects that could otherwise cause problems with the measurement process. Excellent for 'whole rock' analysis.
- Numerous trace elements can also be determined from the same fused disk, e.g. Y, Nb, Zr. The disks can be stored indefinitely.

## Limitations

- Fluorescent X-rays can be easily absorbed by the sample itself (self-absorption), also enhanced. Important to matrix match the calibration standards, or empirical correction factors must be applied.
- Lighter elements are not easily determined (less sensitive).
- With respect to the fusion, sometimes refractory minerals dissolve slowly and do not give satisfactory melts or discs.
- Samples high in sulphide minerals do not fuse well with lithium borate.
- Sensitivity not high for trace/ultra-trace analysis

# Typical pressed pellet XRF detection limits in ppm

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As	5	Mo	4	Sn	5	U	4
Ba	10	Nb	2	Sr	2	W	10
Bi	4	Rb	2	Ta	10	Y	2
Cr	5	Sb	4	Th	4	Zr	2
Ga	4	Se	2	Ti	5		

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*Above is from ALS/Chemex; Actlabs offers a slightly different grouping of elements, adding Co, Cu, Ni, Pb, S, V, Zn*

# Field-portable XRF

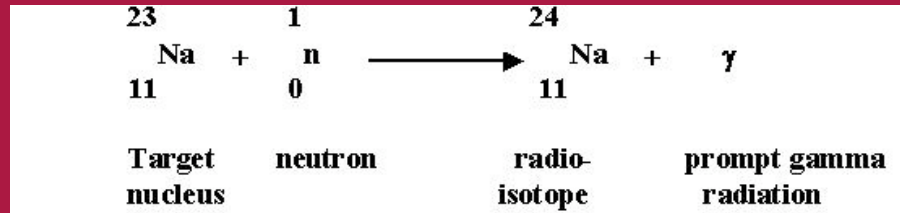
e.g. Thermo's Niton XL EDXRF,  
measures from Mg (12) to U (92)



Typically measure 1x1 cm  
to a depth of ~ 2 mm in soil,  
especially good for Pb in  
environmental surveys (EPA  
approved)

- Need different sources for different combinations of analyte elements
- Relatively new compact detectors (e.g. HgI<sub>2</sub>, Si-PIN, Si-DRIFT and CdZnTe) are ideal for portability but their resolution is inferior to the standard Si and Ge detectors
- Use fundamental parameter method for calibration
- Very fast, non-destructive but DLs are still in the ppm range and
- Accuracy (and precision) is limited by heterogeneity, moisture content, inconsistent sampling position, spectral overlap (eg Pb on As) and absorption/enhancement effects (should be taken care of by software)

# INAA: principle and features



- Irradiate 0.5-2 g sample in a vial with a flux of  $7 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$  for 15 min; wait a week, count with Ge detector. Flux monitored with wire on sample.
- **Simultaneous, multi-element, total, automated technique that does not require digestion and therefore there is little likelihood of contamination; interferences (not too many) are well documented; good precision and accuracy (SRMs)**
- On the negative side, there is not enough coverage of the Periodic Table at adequate detection limits and access to a reactor can be difficult! Also cost of ~ \$25 for the 'exploration' DLs and ~\$60 for the 'research' package (shown next)



# INAA package: DLs in ppm

---

Ag	5	Hf	1	Sm	0.1
As	0.5	Ir	5 ppb	Sr	500
Au	2 ppb	La	0.5	Ta	0.5
Ba	50	Lu	0.05	Tb	0.5
Br	0.5	Mo	1	Th	0.2
Ca	1%	Na	0.01%	U	0.5
Ce	3	Nd	5	W	1
Co	1	Ni	20	Yb	0.2
Cr	5	Rb	15	Zn	50
Cs	1	Sb	0.1		
Eu	0.2	Sc	0.1		
Fe	0.01%	Se	3		

---

# Whole-rock analysis

- Majors oxides (inc  $P_2O_5$ ) to 0.01%; MnO and  $TiO_2$  to 0.001%; by Li metaborate/tetraborate fusion and ICP-ES or XRF
- C and S to 0.01% by IR (Leco); LOI to 0.01%
- Trace elements by fusion/ICP-MS (especially for those in refractory minerals) and by 4-acid ICP-MS (better DLs but not always total)
- Can combine ICP-MS, ICP-ES, INAA and XRF for full coverage

# Au and PGEs

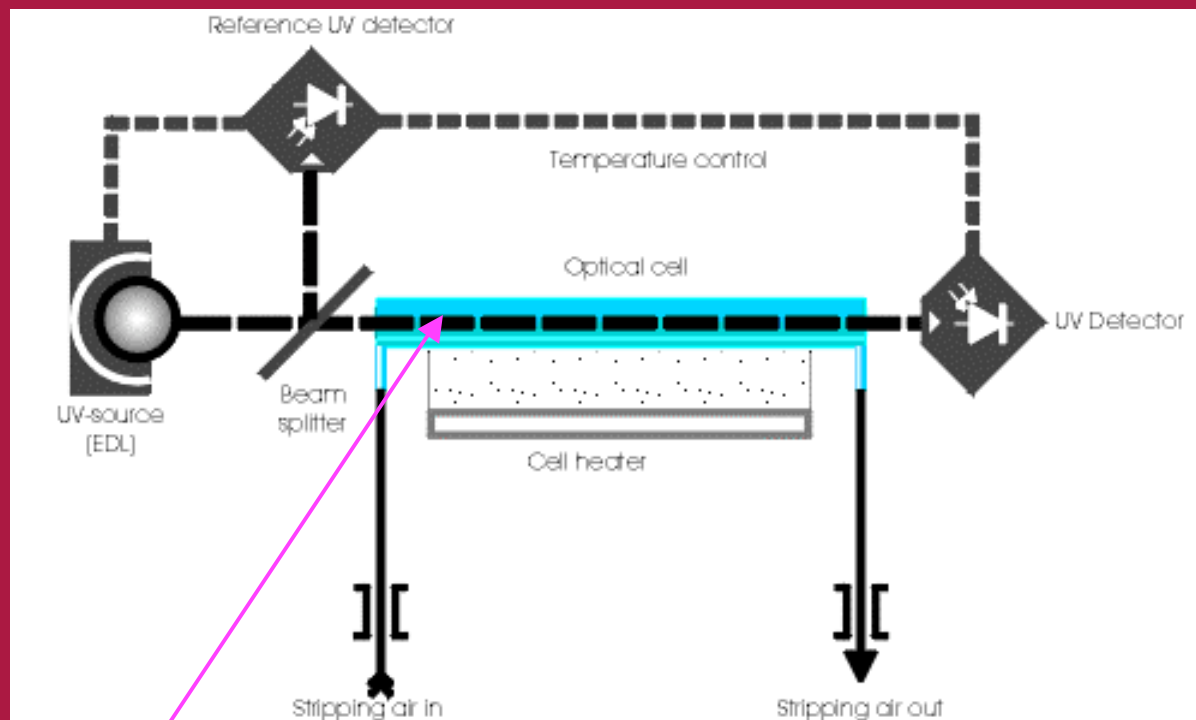
- Au by aqua regia/ICP-MS to ~ 0.2 ppb using weights from 2 to 30 g for ~ \$10. Not always total; should roast sample at ~500°C first if high in carbon and sulphides. Can determine Pt and Pd off same attack but digestion is likely partial (especially for Pt).
- Au by cyanide leach (BLEG) for 'free Au' using large sample weights (~ 1 kg or more), to DLs easily of < 1 ppb, if heterogeneity is a major concern.
- 'Metallics Sieve Analysis' for heterogeneous Au: 500 to 1000 g sample is sieved to 100-mesh. A Pb fire assay is carried out on a split (30 g) of the fine fraction (replicated) whereas the entire coarse fraction is subjected to FA. Weight of each fraction is used to compute the final result.

# Au and PGEs

- Lead fire assay ICP-MS with collection in Ag, using a 30-g sample, for Au (1 ppb), Pt (0.1 ppb), Pd (0.2 ppb), ~\$20. For a few \$ less, DLs of ~ 2-5 ppb. Rhodium can be collected in Au rather than Ag by Pb fire assay.
- NiS fire assay is used for all the PGEs; not amenable to Zn concentrates and not ideal for Au. With ICP-MS finish, DLs for ~ 1 ppb for Au, Pt, Pd, Re, Rh, Ru and Ir. Os volatilises ( $\text{OsO}_4$ ) during the digestion. With an INAA finish, DLs, in ppb, are Au-0.5, Pd-2, Pt-5, Re-5, Rh-0.2, Ru-5, Os-2, Ir-0.1. INAA DLs are compromised by high concentrations of Au, Sb and Cu. From ~\$150/sample.

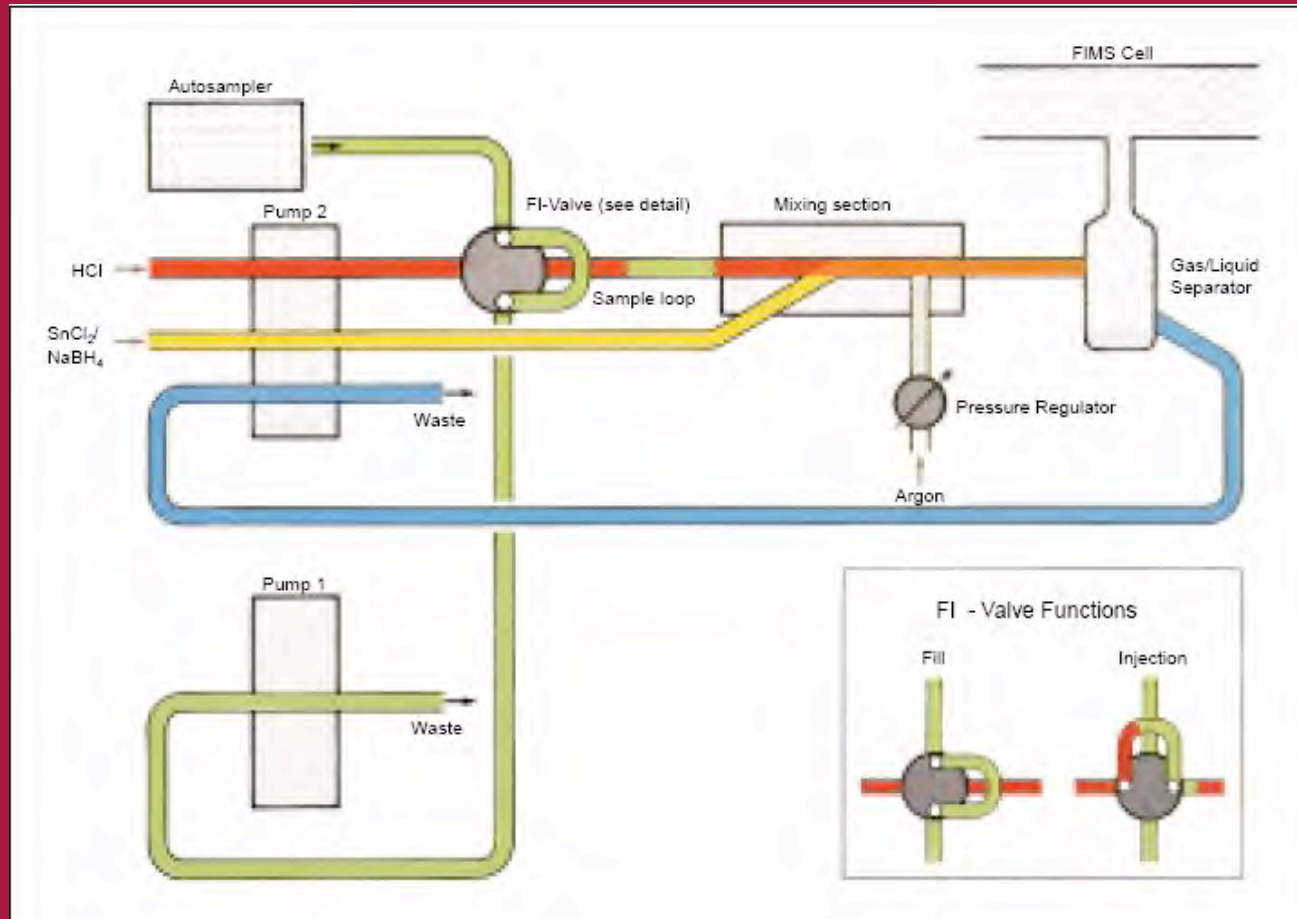
# Classic CV-AAS configuration for Hg

Reference beam to eliminate effects of drift



Long cell for better sensitivity, Beer's Law

# Perkin-Elmer FIMS 400 FI-CV-AAS for Hg

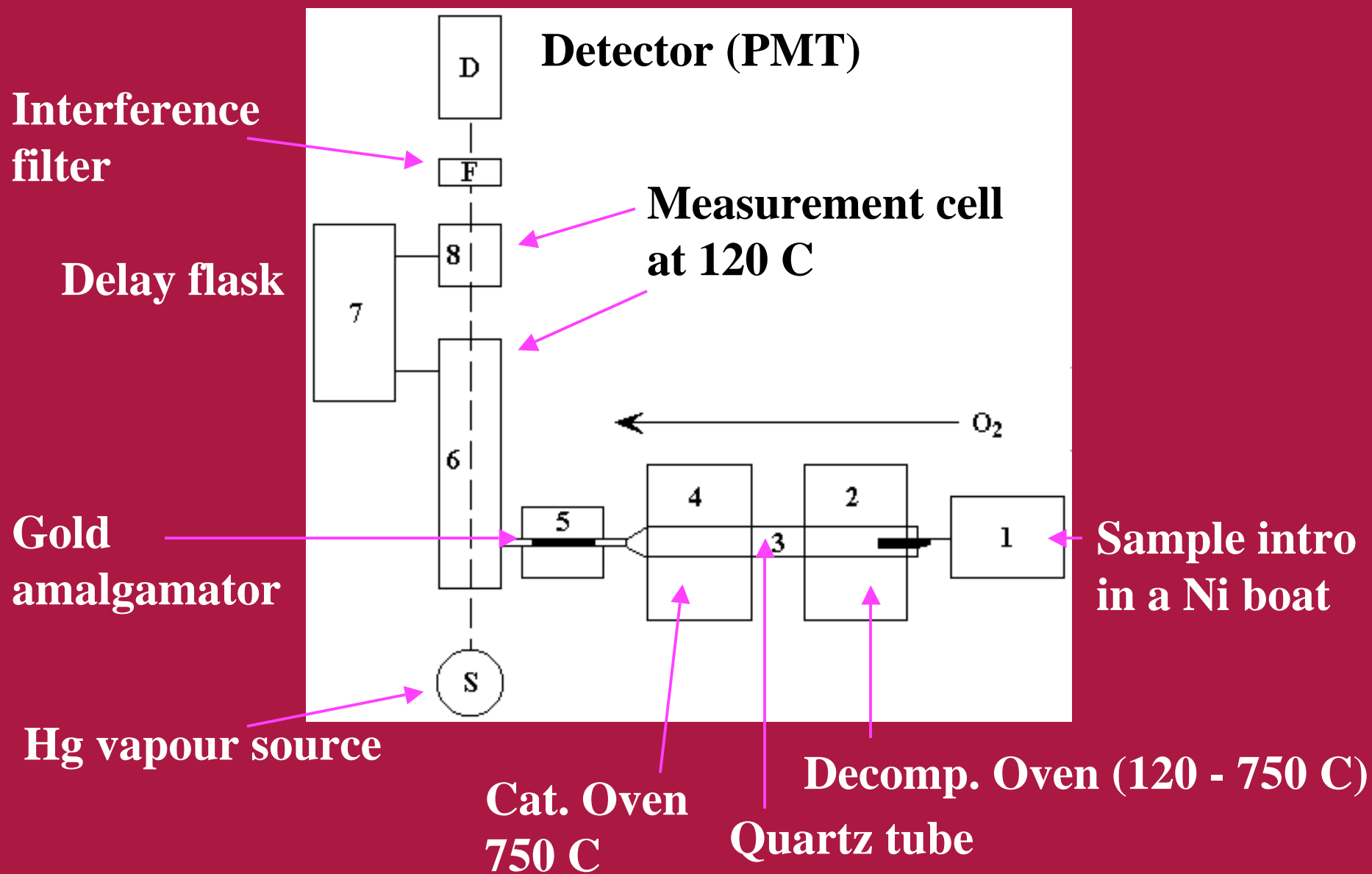


DL in solution of ~ 5 ppt Hg

# ***Direct determination of Hg in solids by pyrolysis***

- **Sample is heated in oxygenated atmosphere to liberate Hg (and other products);**
- **Volatiles are carried by flowing O<sub>2</sub> to the catalytic section of the furnace where oxidation is complete and halogens and N/S oxides are trapped;**
- **Decomposition products are carried to an amalgamator and system flushed with O<sub>2</sub>;**
- **Hg is released by heating into the cell of a CV-AA spectrometer at 253.7 nm.**

# Schematic of AMA-254 from Hall & Pelchat (1997)





# Pyrolysis CV-AAS

- **Highly sensitive (absolute DL of ~ 0.01 ng Hg, translates to < 0.1 ppb Hg), RSDs better than 5% over 33 reference materials (4-6250 ppb Hg);**
- **Eliminates errors inherent in digestions and is rapid (every 5 min);**
- **Milestone markets the 'DMA-80', Leco the 'AMA-254', and Nippon the MA-2000;**
- **This technique is the basis of EPA Method 7473, working range of 0.05 – 600 ng of Hg.**

# Hg in soil gas by Lumex's RA-915+ portable Hg analyser

*DL of 2 ng/m<sup>3</sup>*

*Can be converted  
for waters and solids*



# **Analysis of vegetation**

**Ashing (i.e. preconcentration) is no longer necessary to reach required detection limits, thanks to latest generation of ICP-MS**

# Vegetation: digestion approaches for ICP-MS or ICP-ES

- Oxidation via digestion (not dry ashing) to destroy organic C cpds
- Commonly  $\text{HNO}_3$  predigest at RT and then at  $\sim 130^\circ\text{C}$ , followed by  $\text{H}_2\text{O}_2$ . Take up in dilute  $\text{HNO}_3$  or  $\text{HNO}_3/\text{HCl}$  or  $\text{H}_2\text{O}$ .
- Older methods used  $\text{HNO}_3$  at  $\sim 100^\circ\text{C}$ , followed by  $\text{HClO}_4$  at  $\sim 200^\circ\text{C}$ . Take up in  $\text{HCl}$  or  $\text{H}_2\text{O}$ .
- Silicates often allowed to settle or centrifuged/filtered off. Alternatively can add HF as final step to digestion.

# Vegetation Round-Robin: Analytical methods, labs

Dry state testing

Each subset of  
48 samples (16x3)  
Dry  
1 g each

Lab 1  
HNO<sub>3</sub>/'AR'  
ICP-MS

Lab 2  
'Digestion in acid'  
HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>/HCl/HF  
HR-ICP-MS

Lab 3  
HNO<sub>3</sub>/HClO<sub>4</sub>  
HNO<sub>3</sub>/HClO<sub>4</sub>/HF  
ICP-MS

And 2 labs analysed 15-g pellets by INAA

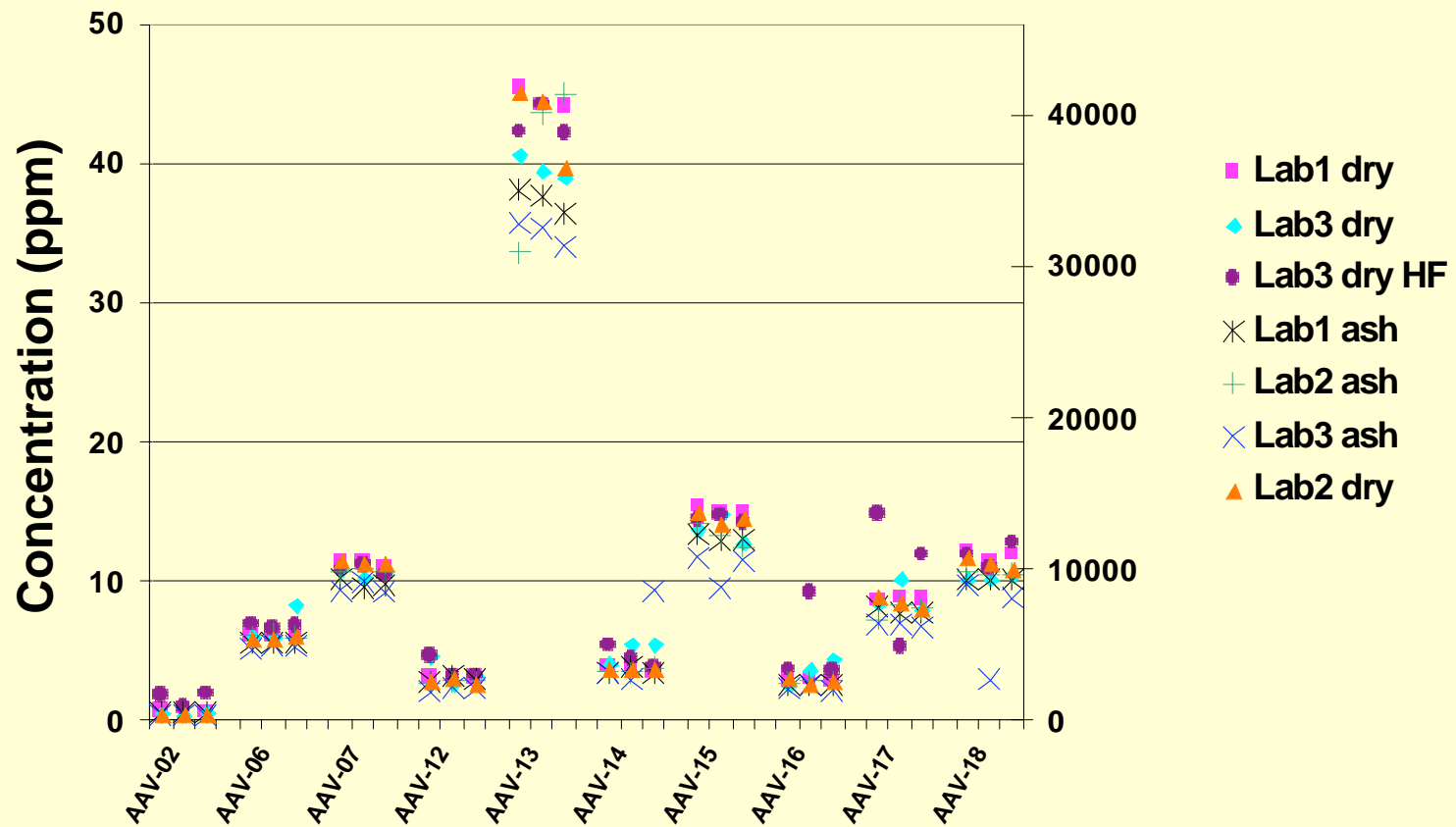
## Elements which show good/acceptable results across the both digestion and ashing methods and the labs

B, (Ba), Bi (>10 ppb), Ca, Cd, Ce, Co, Cs, Cu, Fe, Hg (dry), (K), La, Mg, Mn, Mo, Na (at levels > 100 ppm), Ni, P, (Pb), Rb, S (dry), Sr, Zn.

*( ) indicates perhaps one lab shows unusual behaviour but in general data ought to be good*

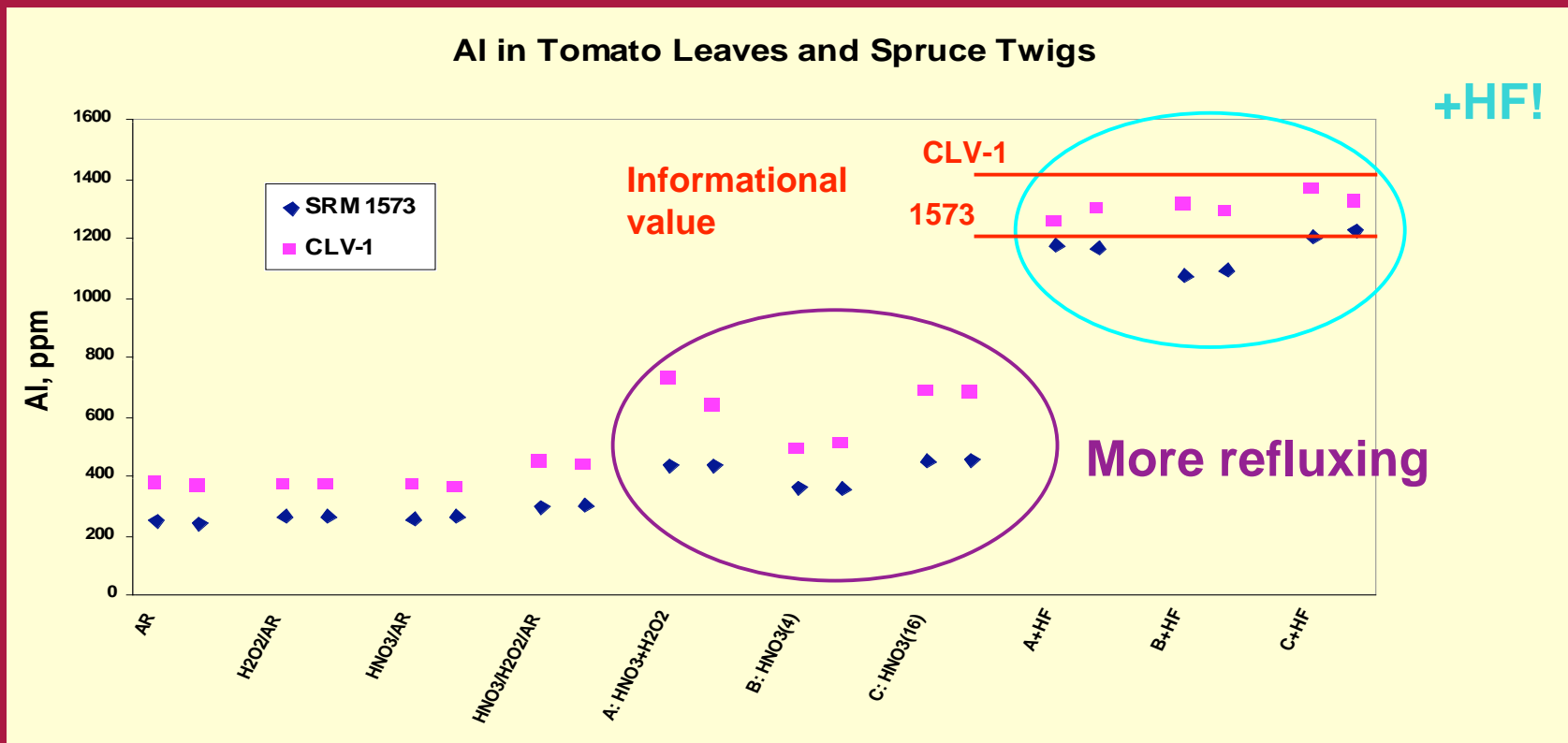
Good results for samples and controls, though numerous fliers in the Lab 3 dry (HF) data. Lab 1 tends to be a little high.

# Copper



# Elements which show variable recovery in the dry methods, particularly with HF present

High field strength and refractory elements such as Zr, Nb, Hf, Ti, Cr, Al



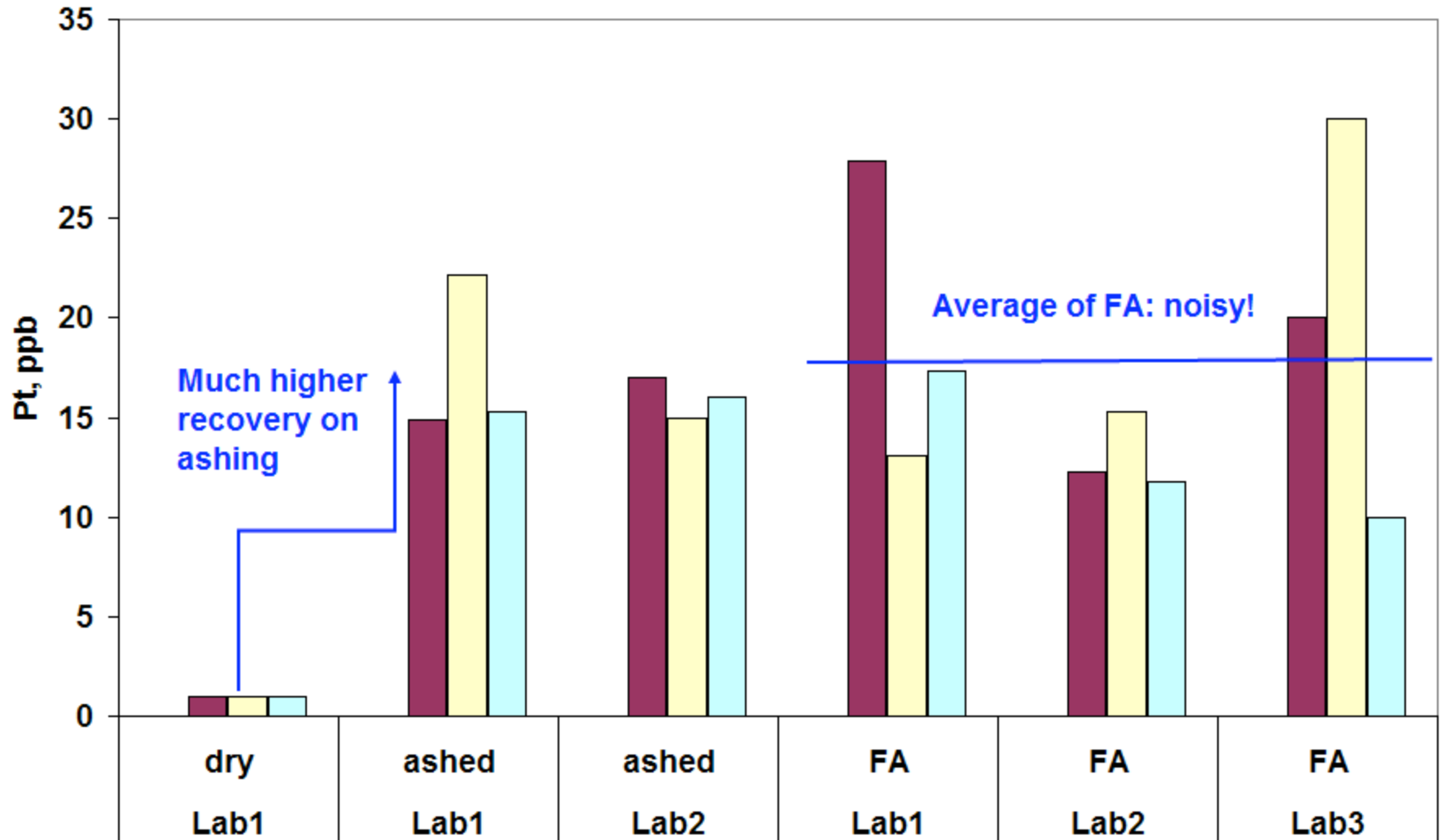


## Au in CRMs: slight bias between labs, no CRM Au values

CRM	Au, ppb		CRM	Au, ppb	
	Lab 1 dry	Lab 2 dry		Lab 1 dry	Lab 2 dry
B231	1.1	1.5	GBW07603	0.8	2.3
B231	1.7	1.7	GBW07603	0.8	1.9
B231	1.2	1.6	GBW07603	0.7	2.4
CRM-PN-A	0.7	1.7	GBW07604	<.2	0.9
CRM-PN-A	0.9	1.6	GBW07604	<.2	1
CRM-PN-A	0.9	2.2	GBW07604	<.2	0.5
GBW07602	<.2	1.7	NIST 1575a	0.4	0.7
GBW07602	0.9	1.6	NIST 1575a	0.3	1.6
GBW07602	<.2	1.3	NIST 1575a	0.8	0.7

*All are pine needles except 7602 and 7603 which are 'bush branches and leaves' and 7604 is 'poplar leaves'*

## Pt in spruce twigs, Rottenstone



1 g

15 g

15 g

50 g

# Summary of vegetation round-robin

**Digestion ICP-MS** across labs is fine for B, Ba, Bi (>10 ppb), Ca, Cd, Ce, Co, Cs, Cu, Dy, Er, Fe, Ga, Gd, Hg, K, La, Li, Mg, Mn, Mo, Na (>100 ppm), Nd, Ni, P, Pb, Pr, Rb, S, Sm, Sn, Sr, Tl, Y, Yb, Zn.

Elements which show **varied recovery amongst the labs** include Ag, Al, Cr, Hf, Na (at levels <100 ppm), Nb, Sb, Ti, W, Zr.

Elements where **HR sensitivity is useful** include Be, Bi, Ho, In, Lu, Nb, Re, Ta, Th, Ti, Tm, U, V, and W. **Quad ICP-MS sensitivity** is *almost* OK for As, Au, Be, Ho, Th, Ti, U, V, and W.

**Hydride-forming elements** (As, Bi, Ge, Sb, Se, Te) would be well determined by **HG-ICP-MS**

# **Hydrogeochemistry: sampling and analysis**

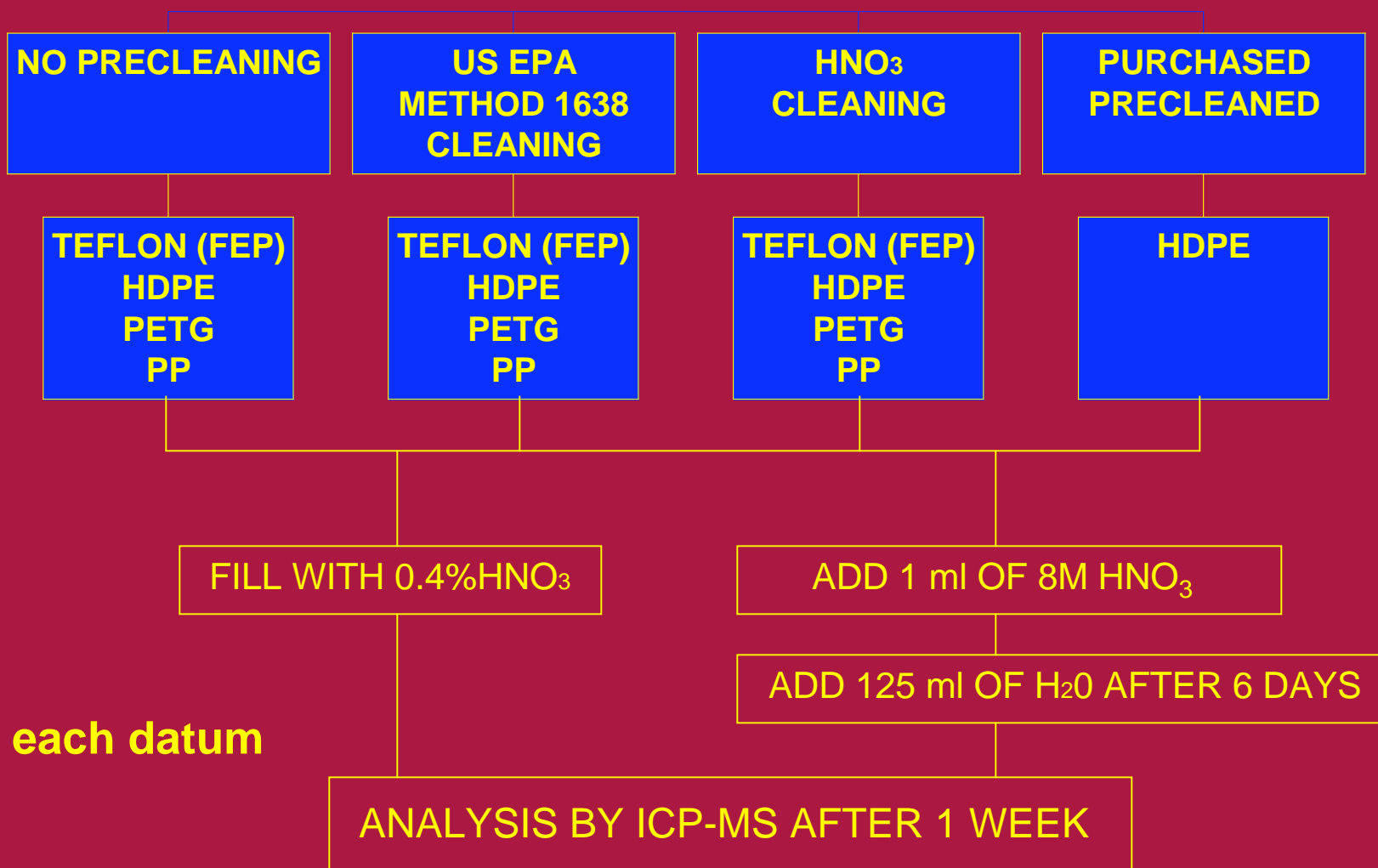
**Preconcentration techniques used  
in the '90s are not necessary now  
for most elements but take care with  
sampling, filtration and preservation**

# GSC Water Protocol Study

- *Parameters studied for their effect on measurement of Ag, Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Tl and Zn include:*
- **Test-tubes** used in experiment
- **Bottles** for collection, and **cleaning methods**
- **Filter (0.45 $\mu$ m) systems** (syringe, in-line and vacuum)
- **Preservation methods**

# BOTTLE TESTING

Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, Zn



N=5 for each datum

# Filter Systems (0.45 $\mu\text{m}$ ) tested (12 in total)

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## Designation

## Description

**G-1-S**

Ion chromatography Acrodisc,  
Supor membrane

**G-2-S**

Acrodisc GF, nylon with glass  
fibre prefilter

**G-3-S**

GHP Acrodisc, hydrophilic  
polypropylene

**M-1-S**

Sterivex capsule, hydrophilic  
Durapore (polyvinylidene  
fluoride, PDVF)

**M-2-S**

Millex HV, hydrophilic  
Durapore

**M-3-S**

Millex-LS 5  $\mu\text{m}$  prefilter or  
Millex-SV

**M-4-S**

Millex, HN nylon

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**Recommended: Whatman all-plastic syringe  
with Millipore Durapore Capsule (M-1-S)  
or Millex Membrane (M-2-S) and HDPE bottle**





# PRESERVATION STUDY

Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Ti, Zn

## SELECTED BOTTLES

OTTAWA RIVER

RIDEAU RIVER

GATINEAU RIVER

H<sub>2</sub>O

FILTER 0.45 µm  
ACIDIFY TO 0.4%  
WITH HNO<sub>3</sub>

FILTER 0.45 µm  
ACIDIFY TO 0.4%  
WITH HNO<sub>3</sub>

FILTER 0.45 µm  
ACIDIFY TO 0.4%  
WITH HNO<sub>3</sub>

FILTER 0.45 µm  
ACIDIFY TO 0.4%  
WITH HNO<sub>3</sub>, SPIKE

All

ANALYSE IMMEDIATELY  
ANALYSE AFTER 1 DAY  
1 WEEK  
2 WEEKS  
3 WEEKS  
4 WEEKS

Stable

# Acidification impractical in the field.....

- Sampled 5 local rivers/streams, filtered and created acidified (0.4%  $\text{HNO}_3$ ) and unacidified subsets
- Tested element recovery in samples acidified after 2 months of storage and then left for 7 days in original bottle
- Used different [ $\text{HNO}_3$ ] of 0.4, 1, 2, 5, 10%
- Used HDPE, PP, FEP, PET, all in triplicate

**Elements not lost from any sample  
over 2-month period include:**

**B, Ba, Ca, K, Li, Mg, Mo, Na, Ni,  
Rb, S, Sb, Si, Sr, U, V**

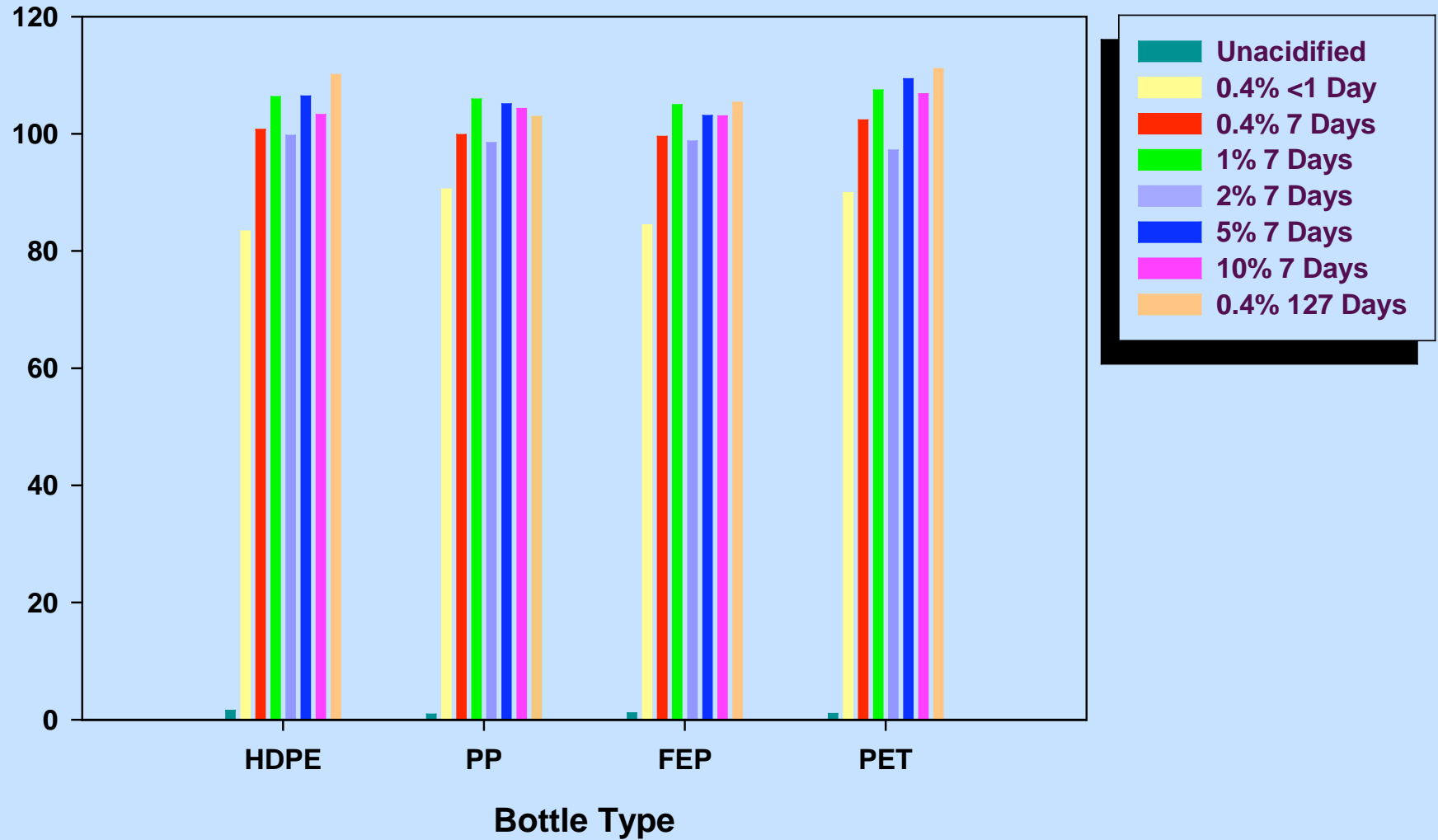
**Elements with greatest loss over  
2-month period include:**

**Mn, Fe, Al, Ti, Pb, REEs, Cu, Zn**

# Mn

Rivière La Blanche

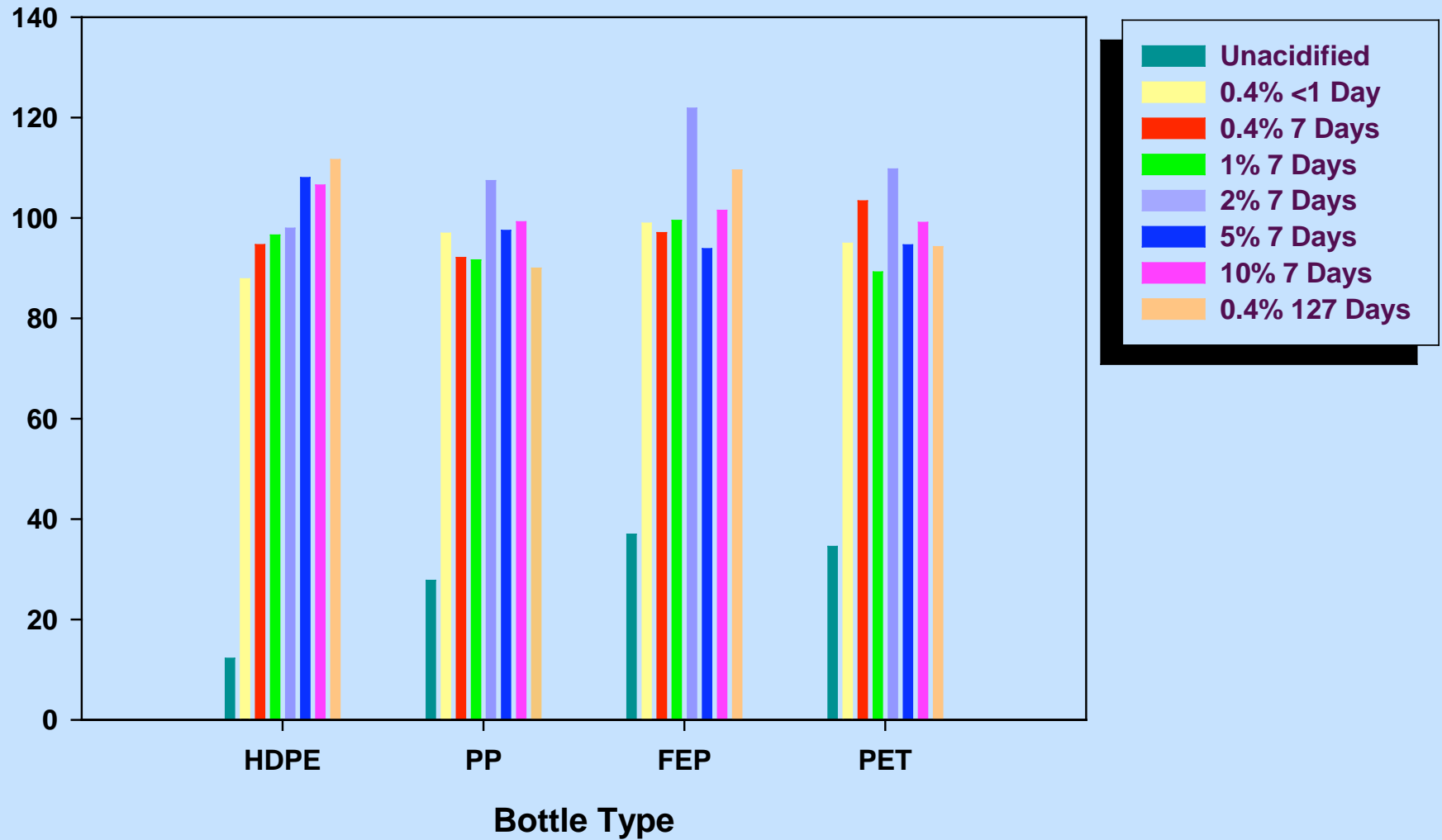
21 ppb  
DL 0.1 ppb



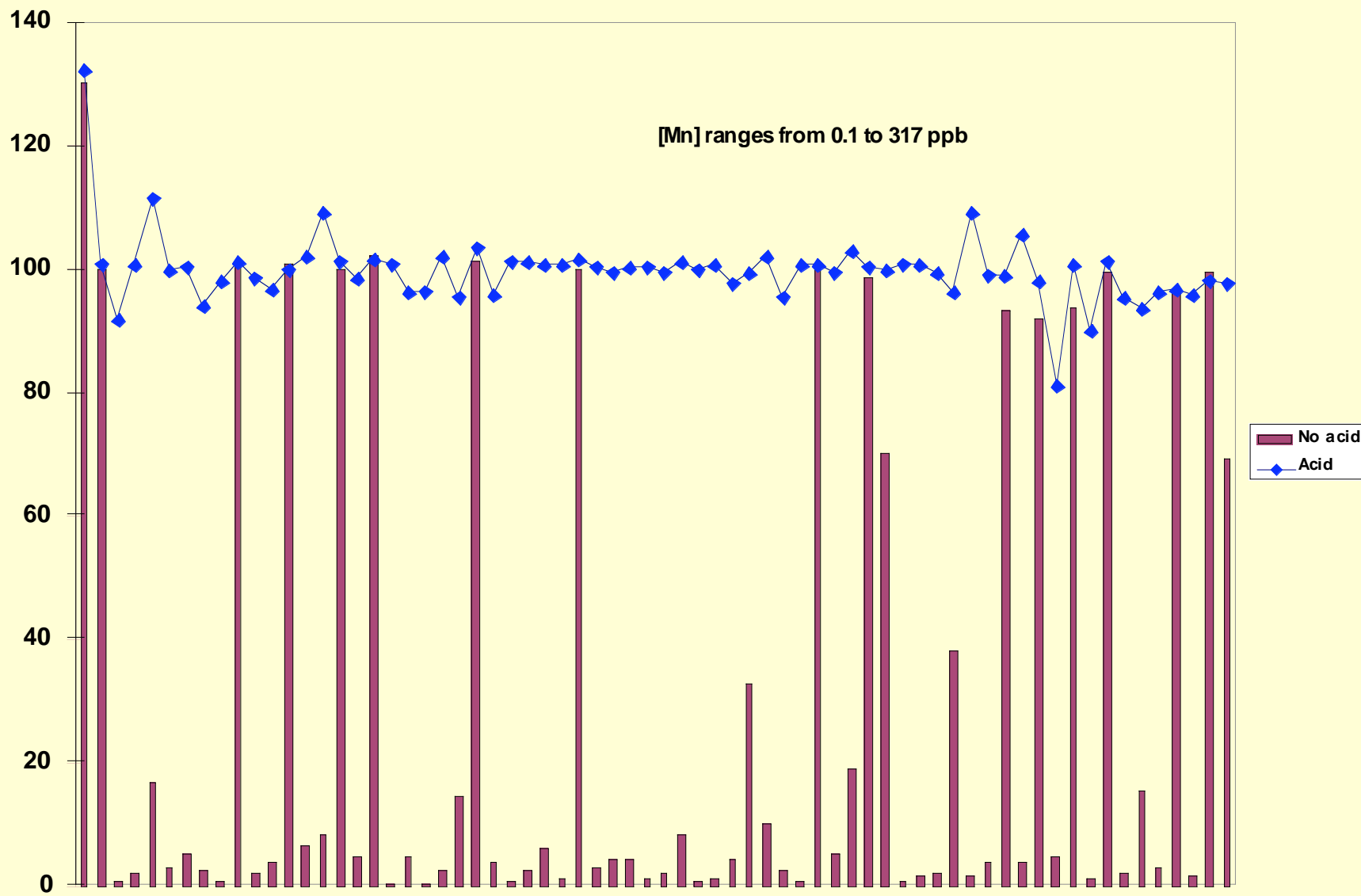
# Pb

Rideau River

60 ppt  
DL 10 ppt



# Recovery of Mn, %



# Halogens: the last frontier?

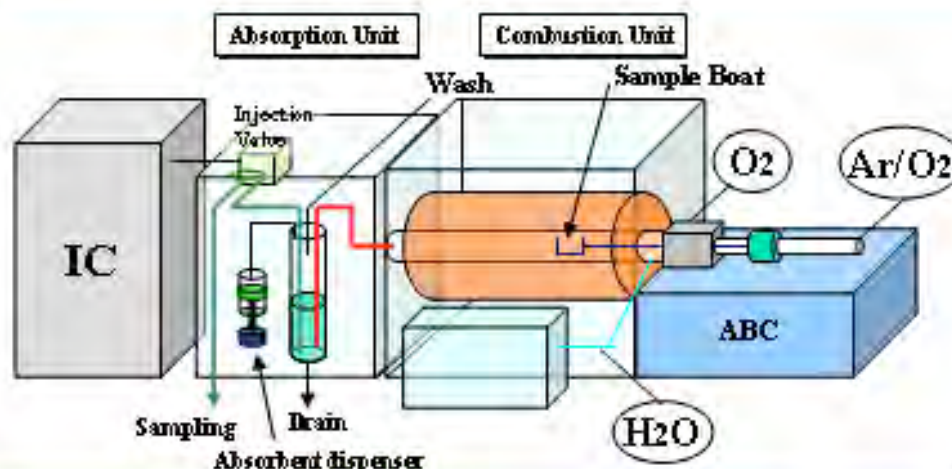
- **F** (DL of ~50 ppm) by fusion and ion-selective electrode
- **Br** by INAA (0.5 ppm) in the 'Au+' package but **Cl** (50 ppm) and **I** (20 ppm) can also be determined by INAA but under different conditions (and therefore separate charges)
- **Cl** by fusion and XRF but it is not in an XRF package
- In waters, use ion chromatography (IC) for DLs of 10-30 ppb for F, Cl, Br, NO<sub>2</sub>, NO<sub>3</sub>, PO<sub>4</sub>, SO<sub>4</sub> and following up on an old GSC methodology for F, Cl, S published in the 80s, ...we need to establish the following method

# Pyrolysis/IC for F, Cl, Br, I, S

- ~100 mg of sample
- Several min of pyrolysis time,
- ~15 min analytical
- DLs in order of 0.5 ppm

## AQF-100 Outline

Back to T.C. 

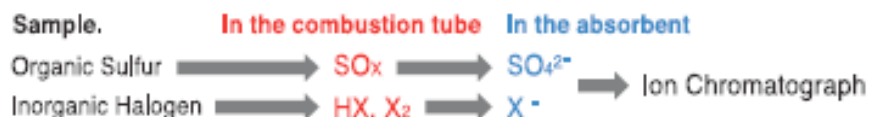


### \*\*\* Features \*\*\*

- Preparation - Combustion - Absorption - Injection are performed automatically.
- High precision by low possibility of contamination with the closing system.
- Better recovery **Combustion with humidification** (New Method, Patent Pending).

Mitsubishi Chemical Corporation  
DIA INSTRUMENTS CO., LTD.

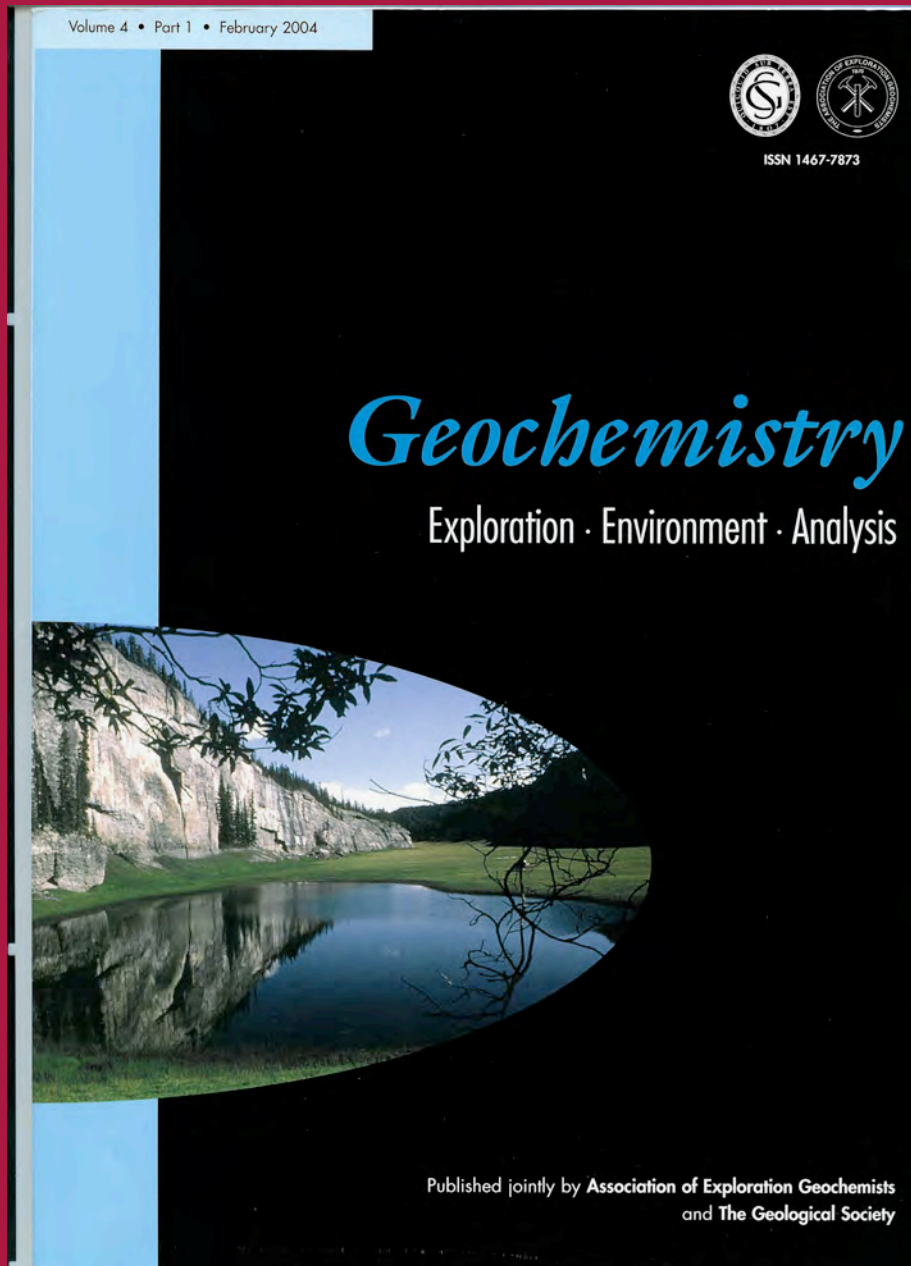
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Thank you!



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