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Dealing with Difficult Samples

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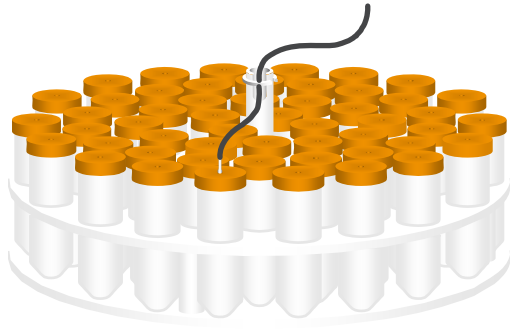
Mars – Instrument Configuration

One System Does it All



- Digestion / Extraction / Hydrolysis / Dissolution
- Options:
 - Dual IR Temperature (Xpress)
 - Fiber Optic Temperature
 - Internal pressure (ESP)
 - Batch Pressure (UPS)
 - Stirring
 - Electronic Notebook Option - SynergyPrep

Major Vessel Offerings



XP 1500 Plus

Primary Sample Types

- High Temperature Nitric Digestions
 - Examples :High temperature plastics, oils, polymers such as Kevlar. Carbon based catalysts. Rare earth oxides
- Aqua Regia digests, HCl, HF digests to provide a completely sealed environment.



MARSHpress

Simple to use, 3 part vessel



Vessel



Cap



Pressure Seal



MarsXpress Vessel Option

- No Pressure Temperature Connections
- Batch up to 40 samples
- Moderate Pressure and Temperature
- PFA or TFM liner
- Fastest Cooling
- Simple 3 part Vessel
- Available in 55mL or 75mL, 10mL, 20mL volume
- Perfect for tissues, soils, sludges, feeds, fertilizers

Contamination

- Still the biggest single cause of incorrect results!
- Can easily be managed with
 - Careful sample handling techniques and dedicated clean areas
 - Use of adequate quality reagents, standards and water
 - Pre-washing/leaching of all sample and standard containers
- Requires common sense and good procedures that are rigidly adhered to

Geological sample preparation and digestion

Resistant materials – sample preparation is often difficult

1) Acid dissolution – HF/HNO₃/HCl or HF/HClO₄

- Pros – Simple method, fast, moderate solids level
- Cons – “Free” HF, loss of Si

2) Fusion – 1:10 with flux e.g. borates, carbonates, Na peroxide

- Pros – “complete” analysis
- Cons – high dissolved solids, risk of contamination, large sample dilution, high matrix content

Geochemical Analysis: Lithium Metaborate Fusions

- A 0.25 g aliquot of finely ground sample was transferred to a clean platinum crucible
- Using a polythene rod, the sample was mixed with 1.25 g of high purity Lithium Metaborate
- The mixture was fused in a muffle furnace for 30 minutes at a temperature of 1000°C (45 minutes for resistant samples)
- Add 100 ml of 5 % nitric acid and place on a magnetic stirrer for 1 - 2 hours or until dissolution is complete
- Transfer to a 250 ml volumetric flask with deionized water and dilute to volume



Application Note: 40758

Analysis of Geological Samples using ICP

Key Words:
 • ICP
 • ICP-MS
 • Geological analysis
 • Lithium
 • Metaborate fusion
 • 210Cu⁶⁴Sn

Introduction
 The analysis of geological samples falls into two distinct groups each with different requirements. Complete or "whole rock" analysis is used in both pure and applied research geology to characterize rock types. Traditionally, complete alkalic analysis has been the concern of academically oriented studies. Sample numbers are usually limited while the emphasis is on the number of elements to be determined and the precision of results. The most important area of applied geochemistry is in the field of mineral exploration. In this application, samples of soil and rocks are spontaneously collected from large areas of land with a view to identifying small pockets or anomalies where the concentration of some element is higher than the average. These high concentrations are usually indicative of mineral deposits, which sometimes have no surface evidence. The most important elements are the common rare elements such as Cu, Fe, Ni, Zn and Fe in addition, other elements known as pathfinders are determined. The pathfinders are elements associated with the deposit which become more widely dispersed than the target elements making them easier to detect and less likely to be masked by the sampling strategy.

Key Instruments Used
 An iCAP 6500 Radial ICP Emission spectrometer equipped with concentric nebulizer and cyclonic spray chamber was used for this work. The iCAP 6500 series is the first generation of Thermo Electron Corporation's new breed of ICP emission spectrometer with high-resolution Echelle optics and much improved Charge Repulsion Device (CRD). Advancements in CCD technology allow this detector to feature higher sensitivity and lower noise than any of its predecessors. The radial plasma instrument was chosen to reduce matrix interference. The instrument configuration is detailed in Table 1.

PARAMETER	DETAILS
Sample tubing	Orange/white sample, white/white drain
Pump speed	50 gpm
Nebulizer type	Standard concentric
Nebulizer Argon flow	0.85 L/min
Spray Chamber	Standard cyclonic
Sampler tube	1.5 mm
Optics Orientation	Radial
ICP Power/Power	1000 W
Purge Gas	Argon
Carrier gas flow	0.2 L/min
Auxiliary gas flow	0.5 L/min

Table 1. Instrument Parameters

Method
Reagents and potential equipment:
 Nitric Acid (e.g. 42) approximately, Analytical grade.
 Lithium Metaborate, purified for fusion.
 Platinum crucible.
 Polythene rod.
 Melting furnace capable of a sustained temperature of 1000 °C.
 Magnetic stirrer.
 Volumetric flasks.
 1000 ppm single element stock standards for each element required.
 Crucible tongs suitable for use with platinum crucibles.

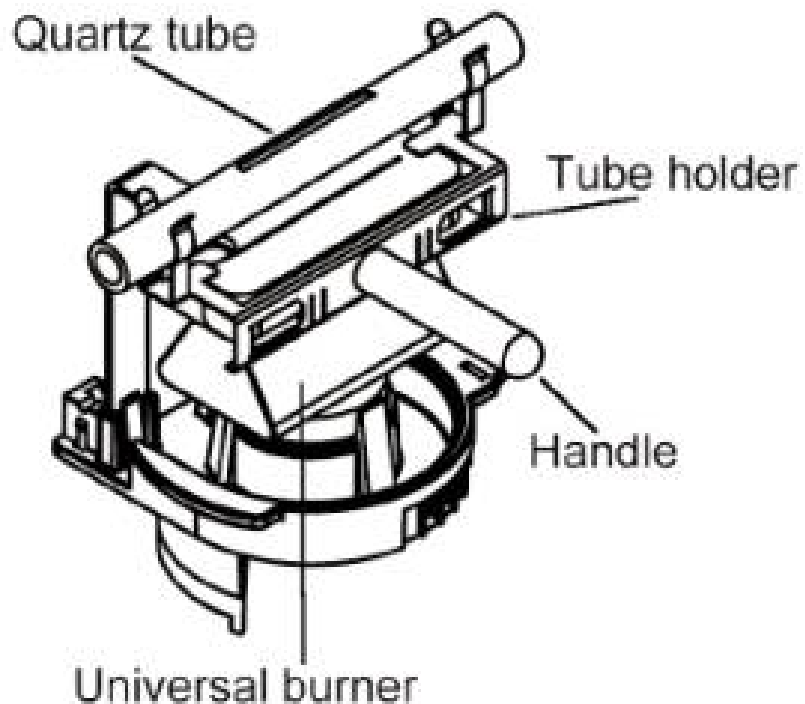
Principle
 0.25 g of finely ground sample was mixed with 1.25 g of lithium metaborate in a platinum crucible and fused in a muffle furnace. The resulting melt was dissolved in dilute nitric acid then diluted with deionized water. Emission signals from the elements of interest were measured directly with ICP using matrix-matched standards. Simultaneous background correction was used to overcome any background drift.

Thermo ELECTRON CORPORATION

AA Accessories - STAT



- Improved flame sensitivity up to 3 to 5 times
- Ideal for rapid screening analysis
- Very easy to use

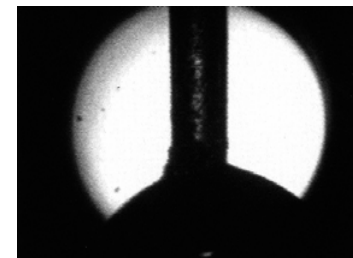
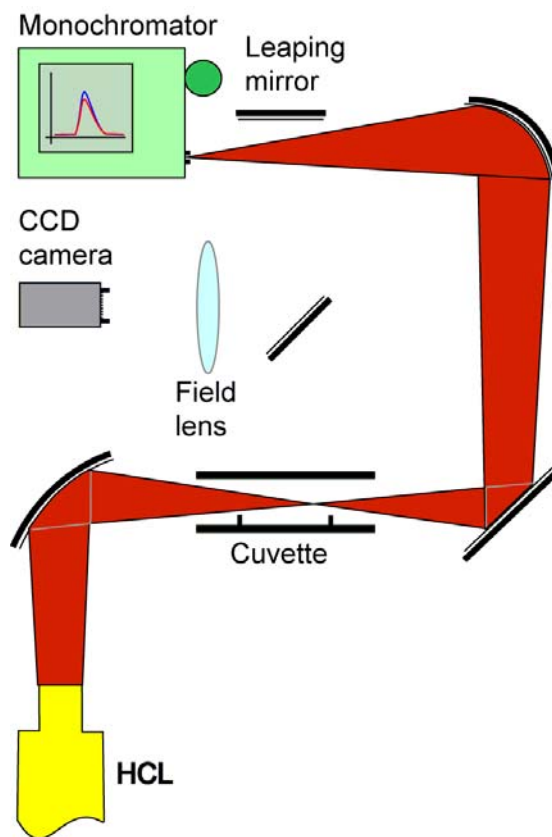


Flame characteristic concentrations

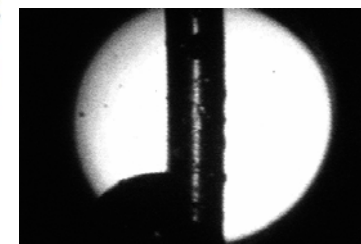
	50mm (mg/L)	100mm (mg/L)	STAT (mg/L)
Ag	0.03	0.02	0.01
As	0.24	-	0.06 (H ₂)
Bi	0.29	0.13	0.07
Cd	0.03	0.01	0.004
Cu	0.04	0.02	0.01
Pb	0.07	0.05	0.03
Zn	0.008	0.005	0.003

Graphite Furnace TeleVision AA Option

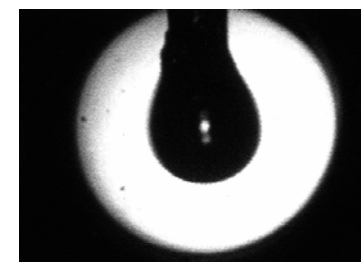
- Faster and easier furnace method development capability
- High definition video image within Windows software may be stored for future use
- Optimisation of critical parameters:
 - *injection depth*
 - *hot injection temperature*
 - *droplet deposition*
 - *dry and ash temperature*
 - *tube clean optimisation*
 - *platform alignment*
- Perfect training tool



Correct depth



Capillary too low



Capillary too high

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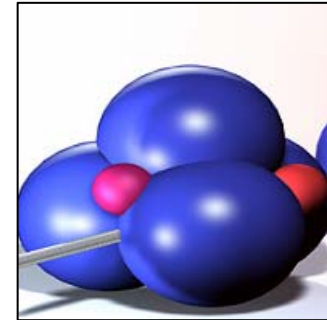
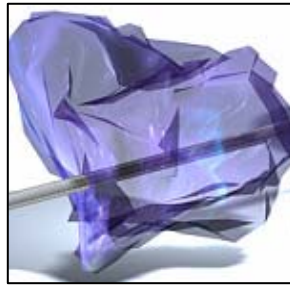
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Dealing with Difficult Samples in ICP-OES

Topics to be covered -

- Types of interferences common to ICP-OES

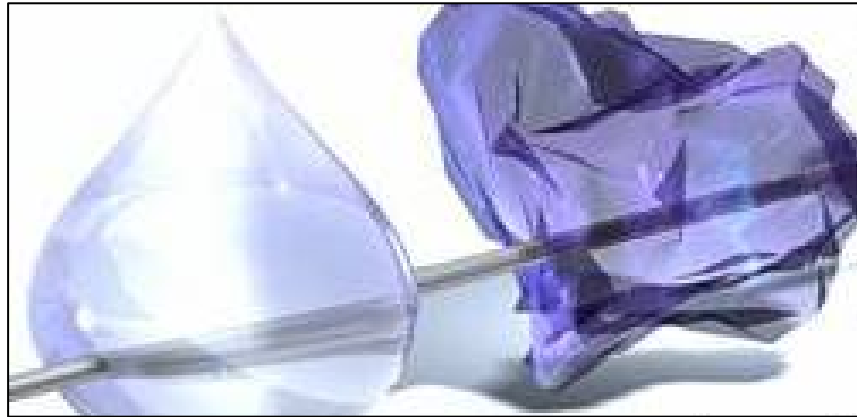
- *Physical*
- *Chemical*
- *Spectral*



- *How to overcome these interferences using method development and software tools*

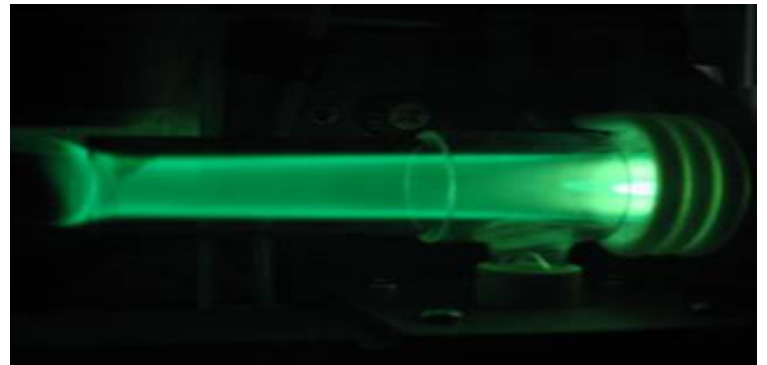
1- Physical Interferences

A characteristic difference between sample and standard which affects sample introduction or nebulisation



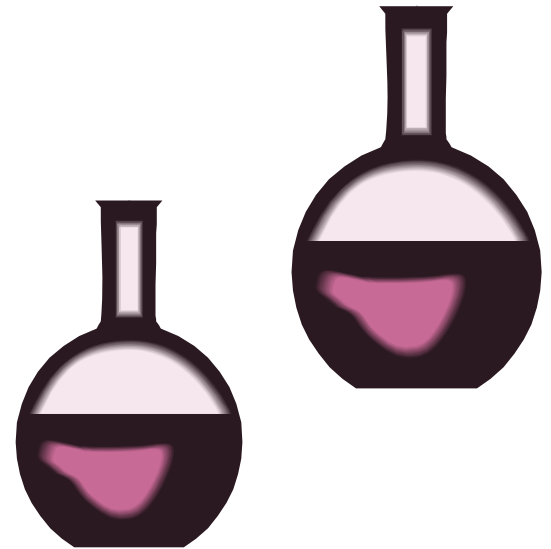
Examples of Physical Interferences

- Viscosity
- High Dissolved Solids (density)
- Acid type or concentration
- Surface tension
- Organic solvents



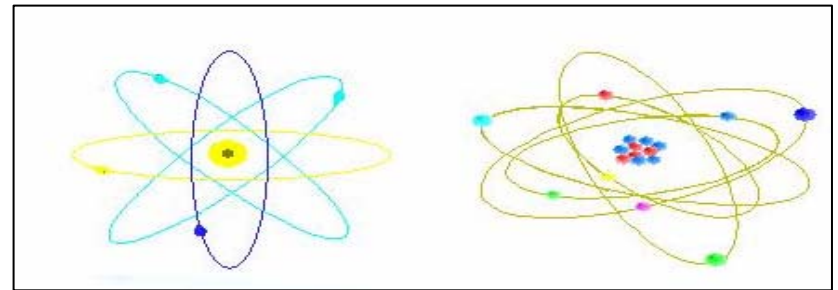
Solving Physical Interference Problems

- Dilution (degrades detection limits)
- Matrix matching (must be known to be effective)
- Internal Standardisation
- Method of Standard Additions



Use of Internal Standards

- Internal standards are dynamic drift corrections used to correct for physical differences in samples and standards by referencing all samples to the same element performance
- A correction is then applied to the sample in accordance with the suppression or enhancement of signal experienced by the Internal standard Element
- Internal Standards must be referenced to elements that will react the same way in the plasma, i.e. they are all UV, or all ionic lines



Internal Standard Requirements

- Not present in samples
- Added precisely and accurately to all solutions,
 - use the Internal Standard Mixing Kit to ensure accurate and constant flow
- Must be affected in the same manner as analytes
 - i.e. all UV, all hard lines etc.
- Line must be interference free
- Background correction must be used

Internal Standards



iTEVA and Internal Standard Set up cont.

- The elements are then referenced to the Internal Standard, taking care to reference UV elements to a UV Internal Standard and matching the states (ionic or atomic wherever possible)

	Line	Rel int	State
✓	371.030 {91}	7000000	II

Internal Standards

Internal Standard Lines

Referencing Lines

Y 371.030 {91}* Ti 334.941 {101}

⏪ ⏩

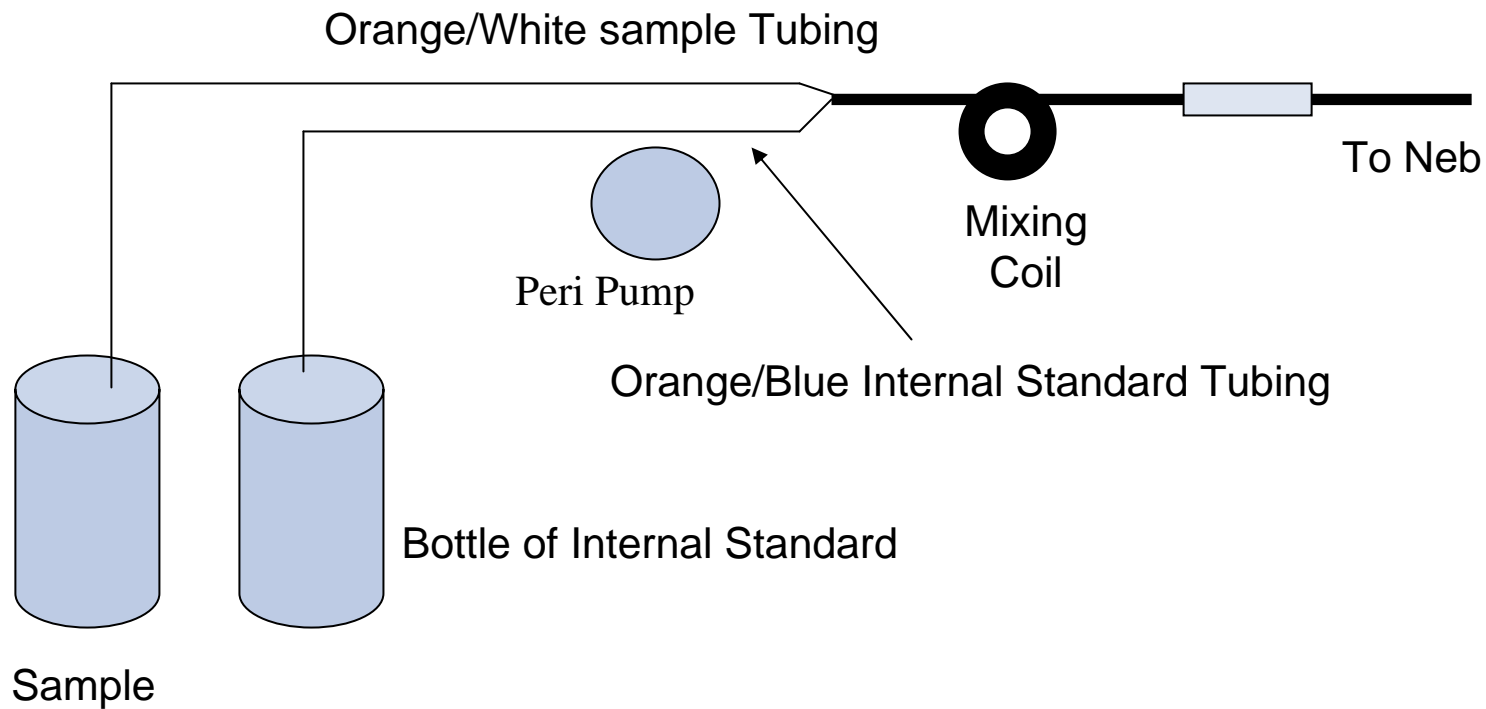
Example -

Yttrium 371.030 (State II – Ionic) referenced to :

Titanium 334.941 (State II)

	Line	Rel int	State
✓	334.941 {101}	5000000	II

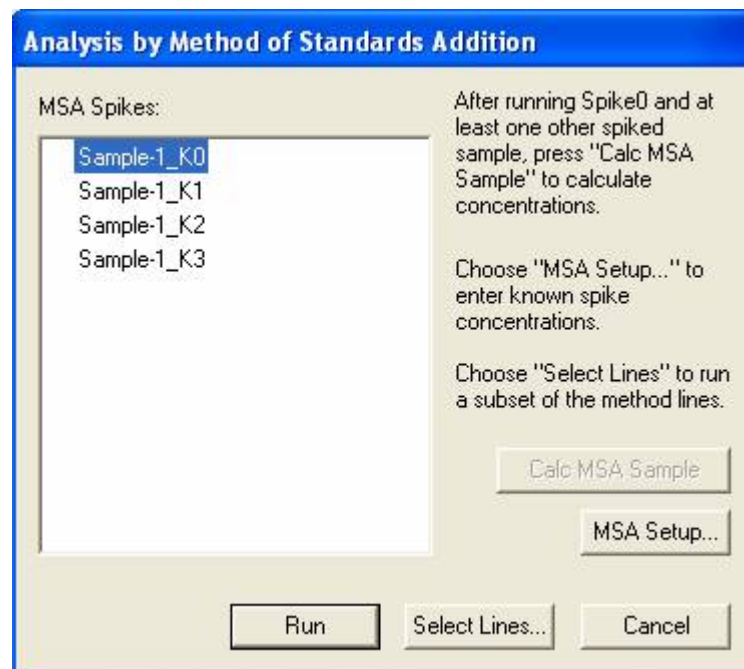
Internal Standard Mixing Kit for ICP-OES



Internal Standard is mixed at a 1 to 5 ratio with Sample

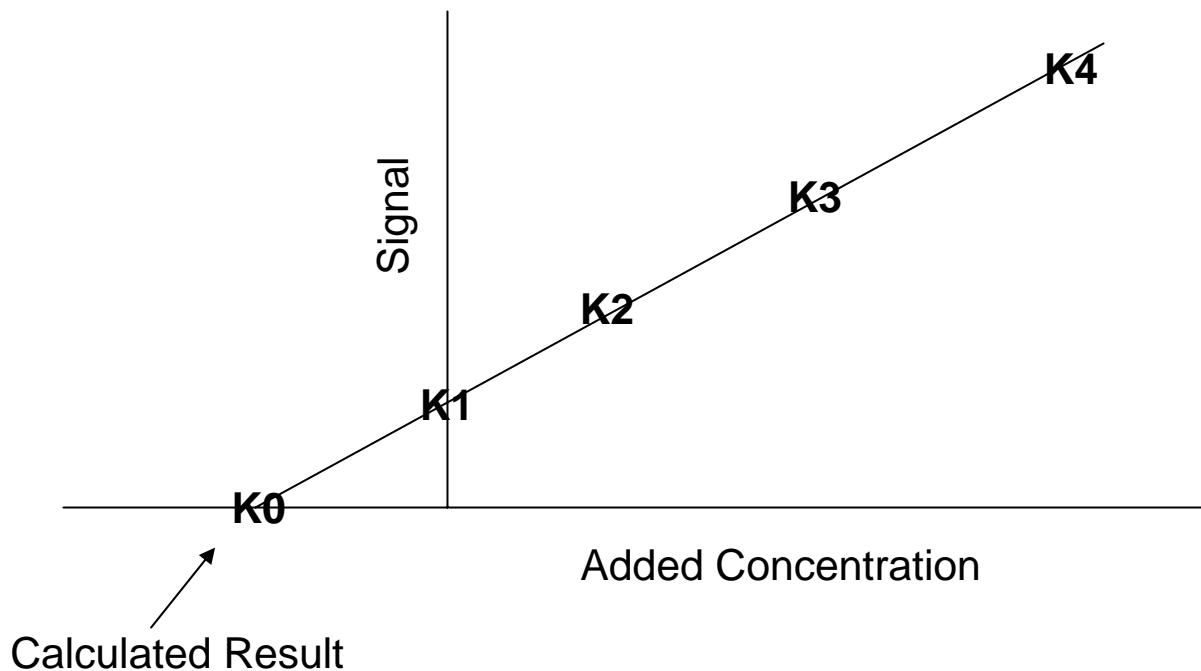
Method of Standards Addition

- Used to overcome physical interferences, or when the matrix is entirely unknown
- The unknown sample K0 is spiked with known additions of an element(s)
- After the sample and at least 1 spike have been run, the software can determine the concentration in the unknown K0



	Spike 0	Spike 1	Spike 2	Spike 3
Cd	0.000	1.000	2.000	3.000
Fe	0.000	1.000	2.000	3.000

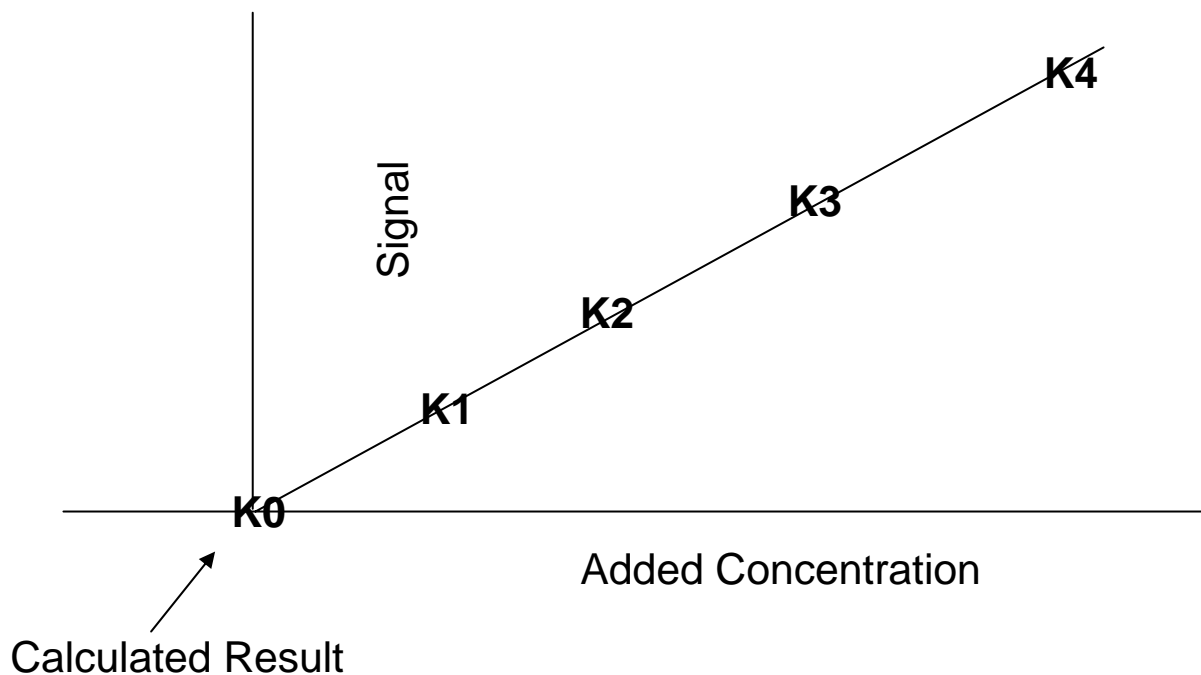
Method of Standards Addition explained



Requires Linearity

ALL SIGNAL MUST BE FROM ANALYTE

Curve becomes matrix matched calibration curve



Requires Linearity

ALL SIGNAL MUST BE FROM ANALYTE

2 - Chemical Interference

A sample matrix characteristic which causes an analyte to behave differently in the sample and standard



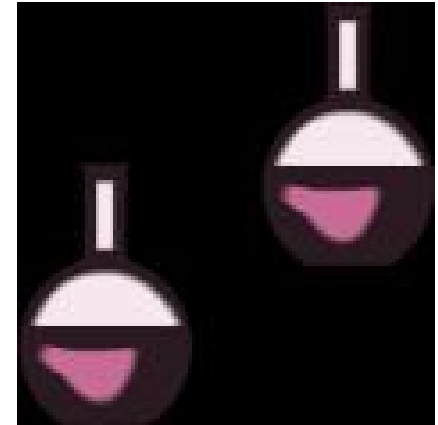
Examples of Chemical Interferences

- Ionisation (Na, K, Rb, Cs, Li)
- Molecular formation (i.e. oxides)
- Plasma Loading



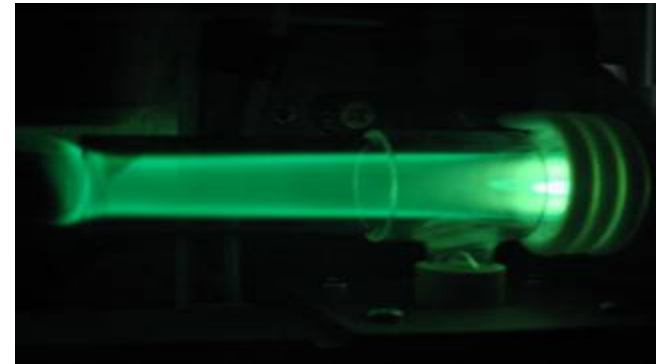
Solving Chemical Interference Problems

- Dilution (degrades detection limits)
- Matrix Matching
- Internal Standardisation (can reduce plasma loading)
- Optimise Plasma
- Oxygen Addition for Organics



Plasma Loading

- Complex matrix reduces energy available to excite analytes
- Affects ion lines more than atom lines
- May be element or wavelength sensitive
- Can employ selective internal standardisation
- May be affected by RF power and nebulizer pressure



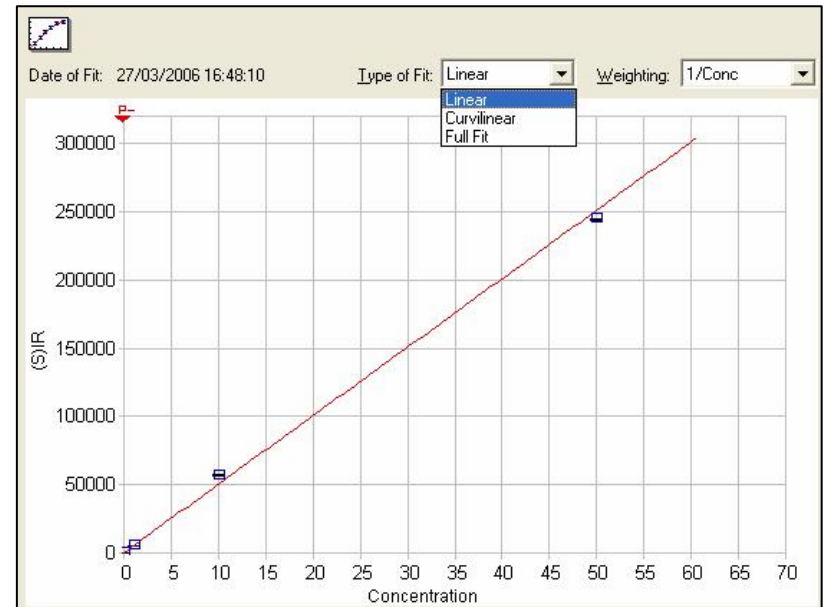
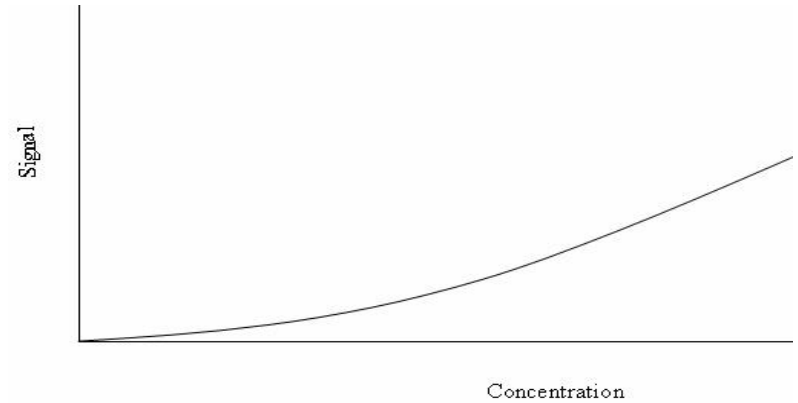
Ionisation Interferences – EIE effects



- As [M] increases, the electron concentration also increases shifting the equilibrium to the left
- Very common effect when analysing matrices with high concentrations of Alkali elements e.g. Na, Ca etc.

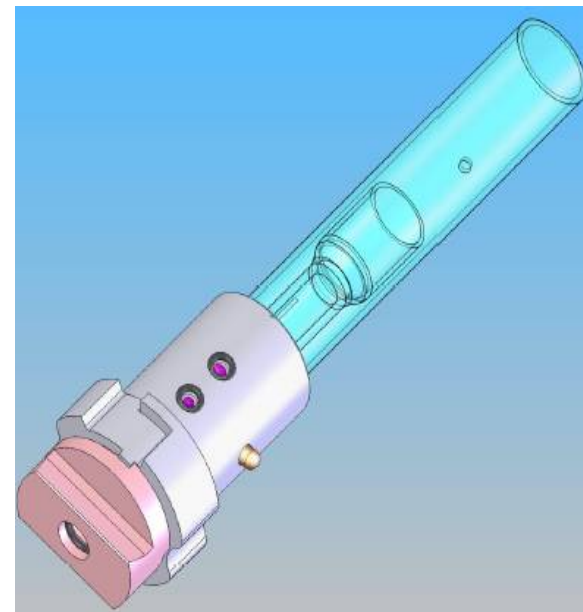
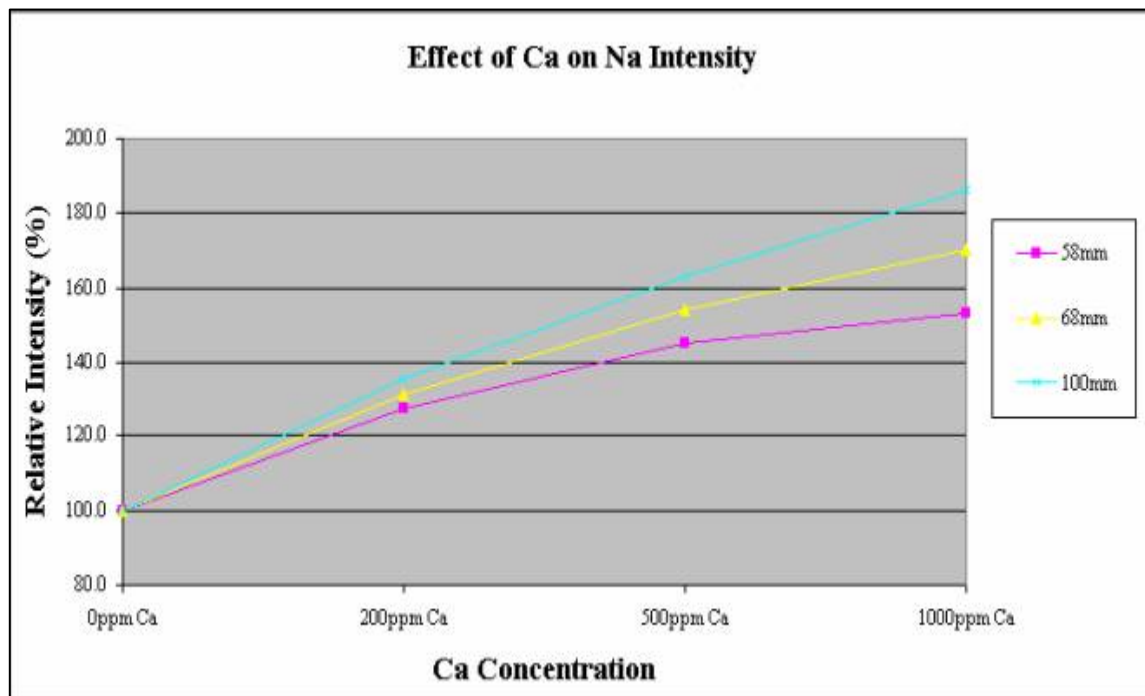
Easily Ionised Element Interference

- For a single element solution of an easily ionized element, positive curvature is seen when calibrating
- Solutions to EIE -
- Curve Fit through the entire range, iTEVA allows for polynomial fitting. Select the best fit for the curve
- Use an ionisation buffer e.g. Li or Cs salts to supply a constant amount of e⁻ to react in the plasma



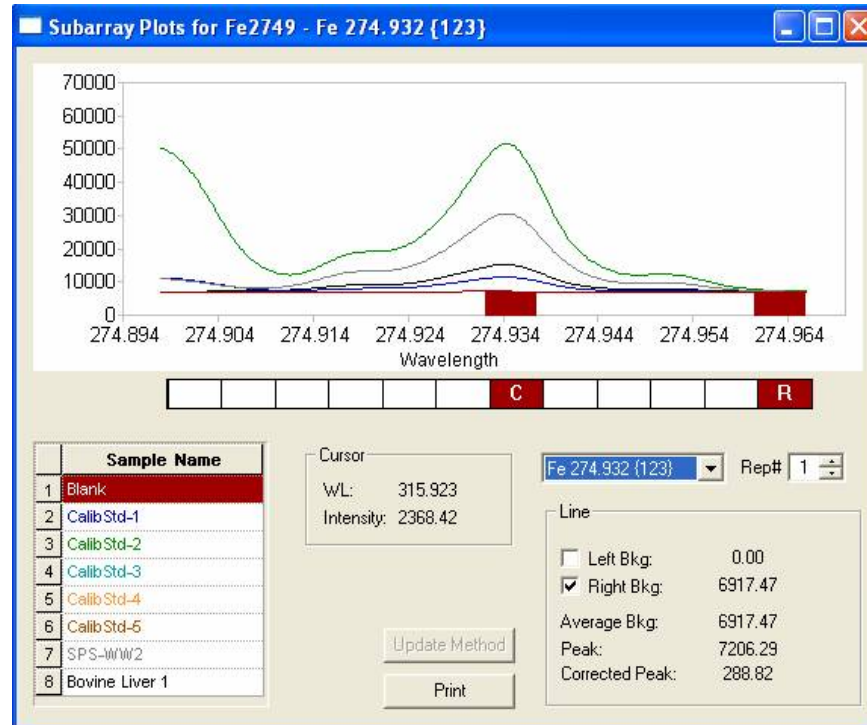
New torch design for iCAP – plasma loading tests

- New 58mm design
- Superior plasma loading confirmed a 45% improvement in EIE handling

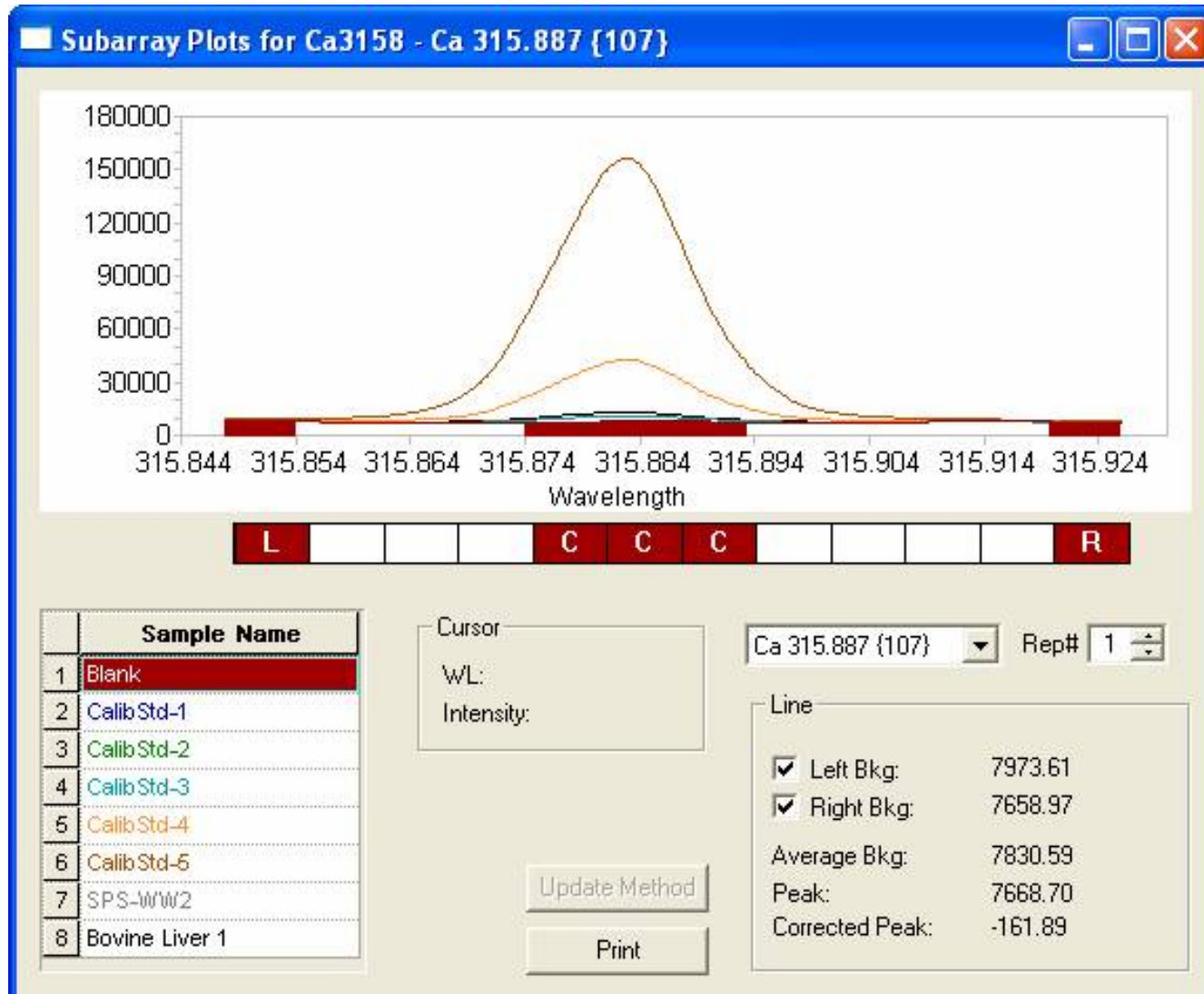


3 - Spectral Interferences

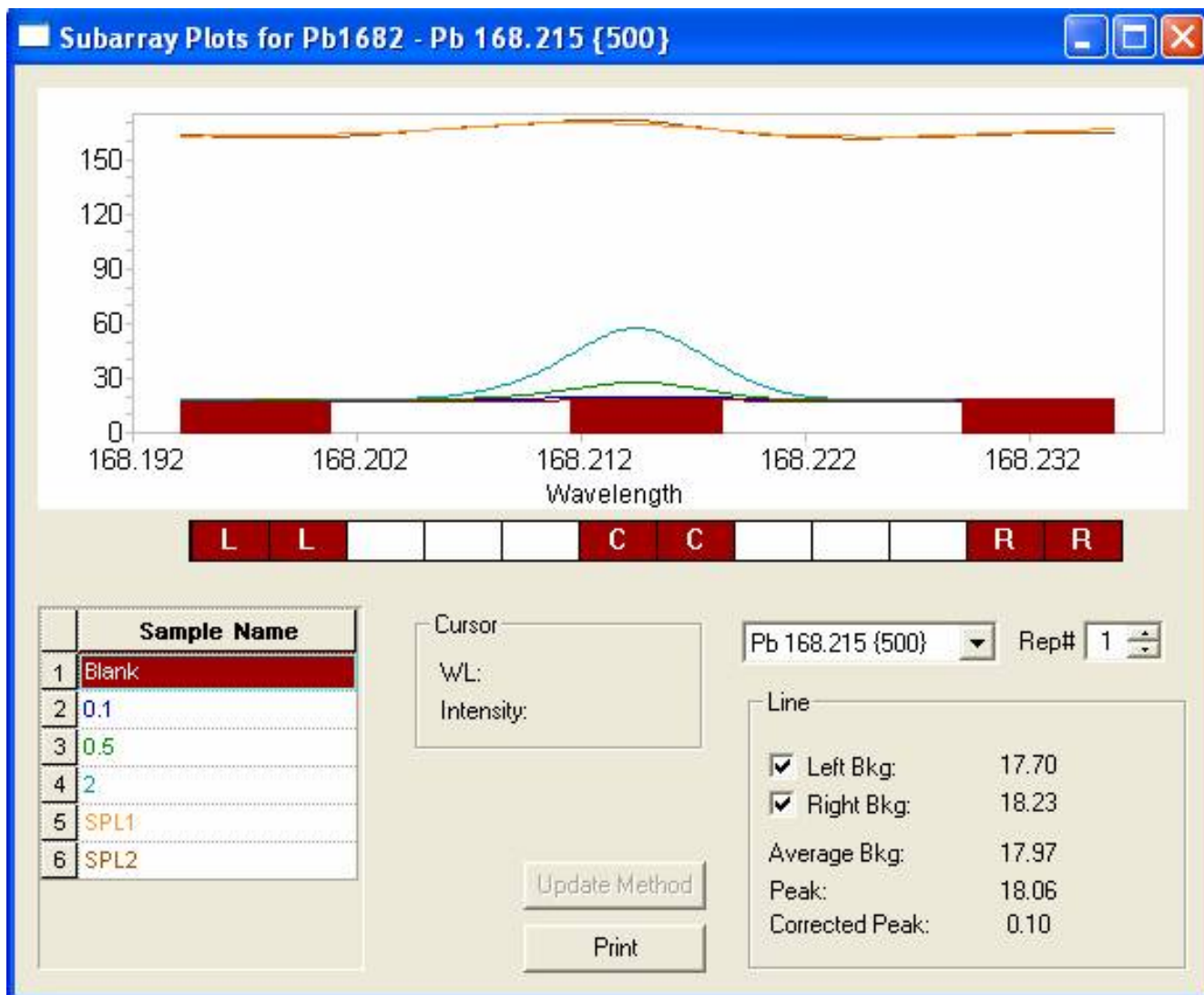
- Severe in ICP-OES
- Need to use off-peak background correction
- Interfering Element Correction (IEC)



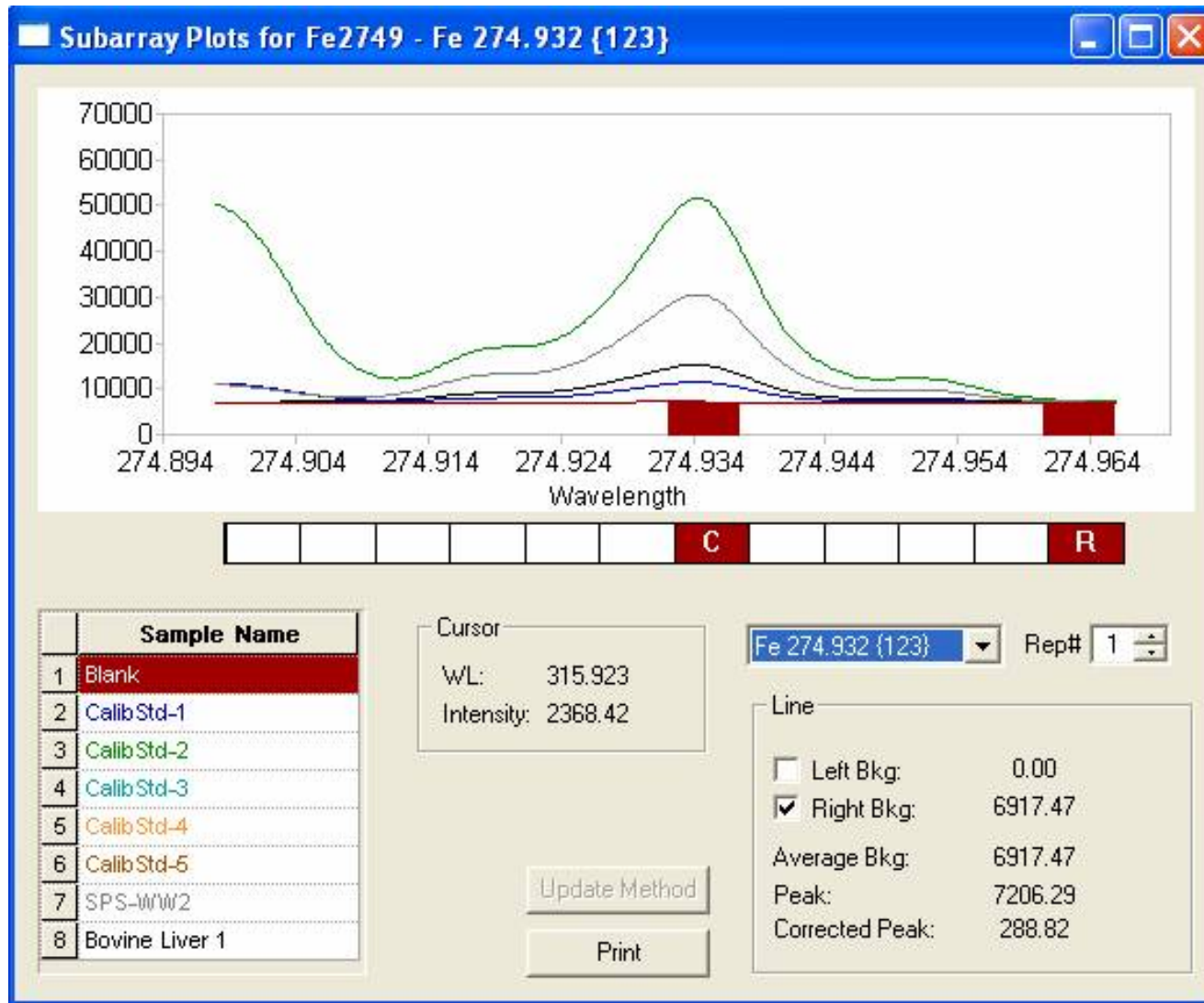
Ideal situation of no background shift or spectral interferences



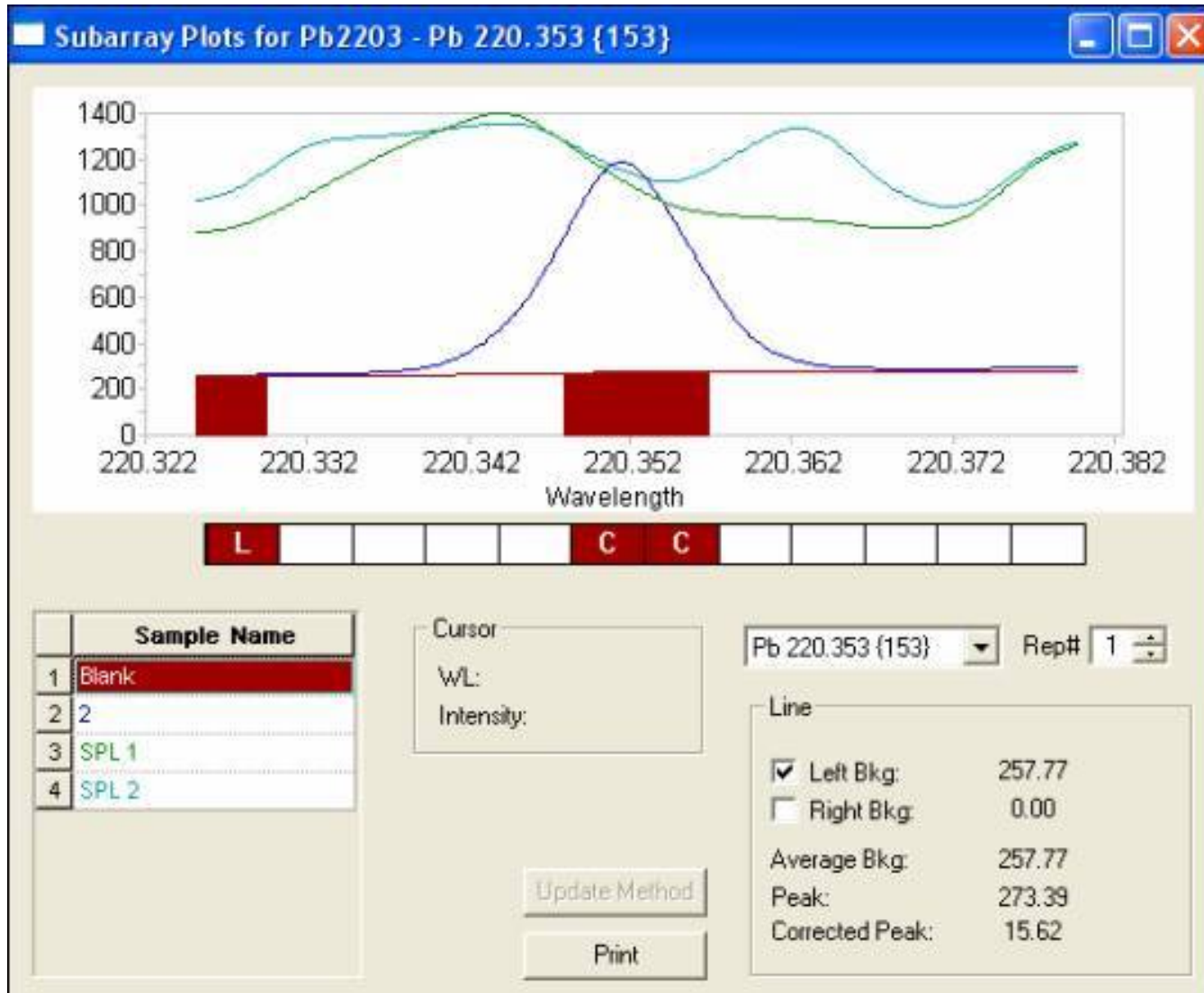
Large Background shift in Sample - Use Background correction points



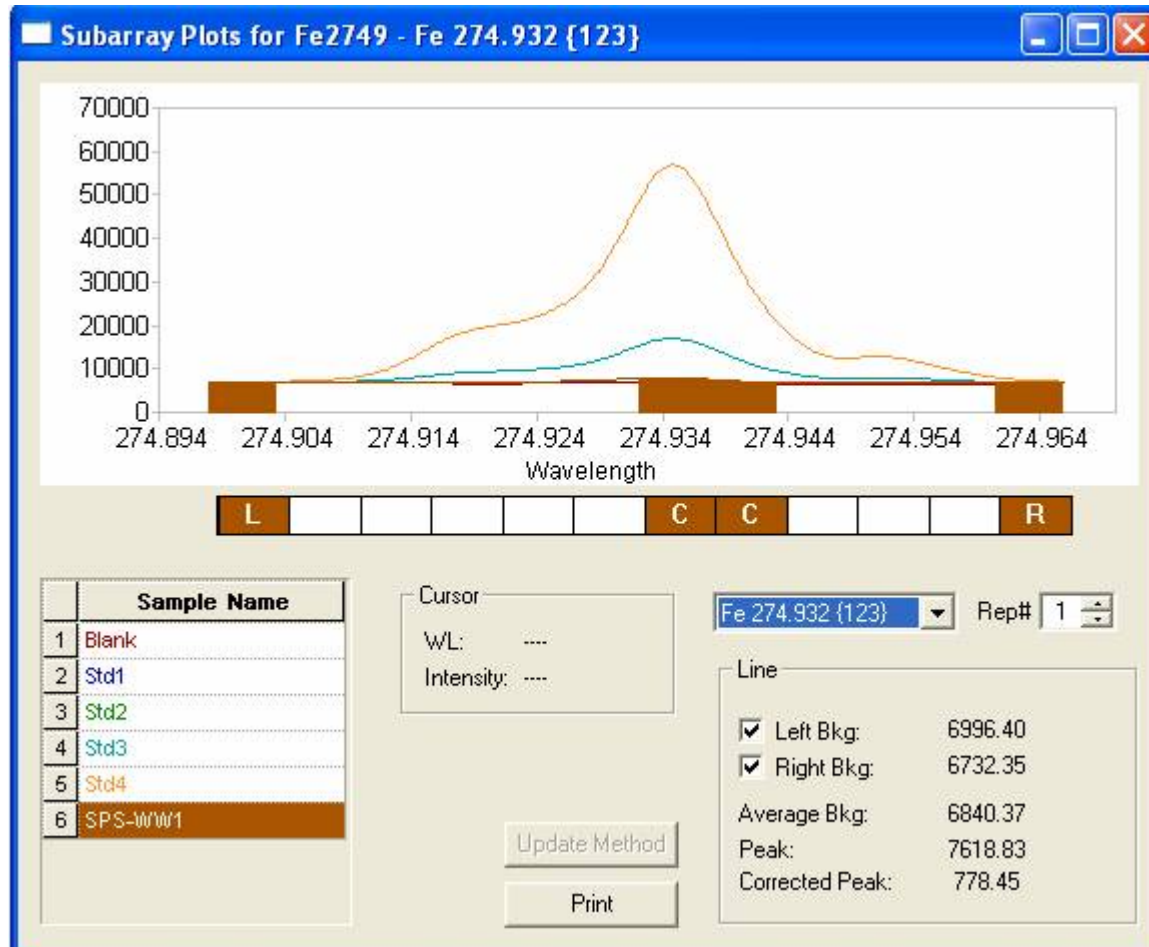
Spectral Interferences - nearby interference



Spectral Interferences – raised background and interferences

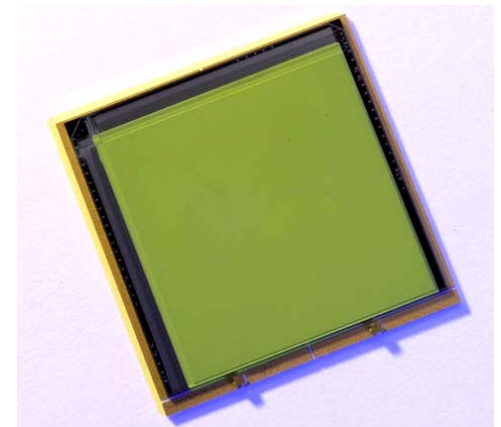


Spectral Interferences – direct spectral overlap



Solution: Pick another line

- iCAP 6000 CID 86 detector
 - 291,600 user accessible pixels
 - Imagine 291,600 photomultiplier tubes!
 - Complete Simultaneous Wavelength Coverage
 - 166.25 – 847.00nm
 - Most sensitive lines for Al167nm & Na 818nm
 - Uniform resolution across chip
 - Entire MIT, NIST Wavelength library available



Interfering Element Correction - IEC

- It applies a correction factor based on the apparent concentration of the interferent to every analysis
- IEC is used to correct for direct spectral overlaps
- Before setting up an IEC the analyst –
 - Needs to know what is interfering
 - To measure the interferent
- IEC's are dependent upon Background correction points, and they assume a linear relationship (as it applies a ratio)



Steps to determine an IEC

- Identify the interferent
- Add a primary line for the interferent to the method
- Analyse an appropriate concentration of the interferent (high purity, single element)
- Calculate IEC's if significant – the formula used is
$$\text{IEC} = k_1(x) + k_2(x)^2$$
- Where x is the concentration of the interferent
- Insert the IEC's into the method
- iTEVA will do all this for you....