

iCAP 6000 Series – Applications Part 1 - Mining and Metals

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Topics to be covered -

- Method development features –
 - Hardware
 - Software automation
 - Technical support
- Routine applications and their performance –
 - Geochemical
 - Metals and Materials
 - Petrochemical (organics)
- Integrated sampling options – USN, Hydride, SSEA and Laser



iCAP 6000 Method development features - Hardware

- An efficient kitchen area makes sample handling and maintenance simple
- Pre-configured application specific sample introduction kits allow the analyst to change easily from one application to another
- Integrated accessories enable effortless enhanced analytical capabilities



Pre-configured Sample kits for every application

Standard Kit –
Complete kit for normal
aqueous solutions up to 3 %
m/v dissolved solids



Hydrofluoric Acid Kit -
All components in contact
with HF solutions are
composed of resistant
plastics or alumina ceramic

High Solids Kit -
For analysis of solutions of up to
20 % m/v dissolved solids.
Optional argon humidifier for
ultimate high solids tolerance



Organics/Volatile Kit –
Spray chamber with baffle
(optional jacketed)

Method development features - Software

The screenshot displays the iTEVA Analyst software interface. On the left is a navigation tree with categories like Status, Analysis Preferences, Automated Output, Report Preferences, Checks, Sequence Automation, Source Settings, Internal Standards, Standards, Elements, and Method Reports. The main window shows a periodic table with Nickel (Ni) selected. A pop-up window titled 'Periodic table' displays the element's details: Ni Nickel, atomic number 28, and atomic weight 58.710000. Below this is a table of spectral lines for Nickel, with the first line (221.647) selected. To the right of the table is a list of 'Interferences for Ni (221.647)'. At the bottom of the pop-up, there are options for 'Intelli-Frame' (checked), 'Max Integration Time' (30 seconds), and 'WL Range' (Low selected).

Line	Rel int	State
221.647 (452)	600000	II
231.604 (446)	600000	I
341.476 (99)	300000	I
216.556 (456)	250000	II
232.003 (445)	250000	I
352.454 (96)	250000	I
361.939 (93)	200000	I
230.300 (446)	150000	II
243.789 (138)	50000	II
217.467 (455)	0	II

Interferences for Ni (221.647)			
W	221.601	II	50000
V	221.603	III	1800
Ir	221.603	I	2000
Re	221.616	II	1000
W	221.630	II	6000
Ni	221.647	II	600000
Os	221.652		7000
Mo	221.661	II	1000
Si	221.667	I	200000
Nb	221.670		1000
Ir	221.705	II	1200
Rb	221.708	II	2778
Nb	221.723		2000
Co	221.728	II	4000
Pt	221.734	I	3000

- iTEVAs' method development tools –
55,000 wavelength line library
Comprehensive Interferent Database for each line
Intuitive method creation template

Reduced Analysis Times

Maximum analyst flexibility with two analysis modes -

Speed or Precision

- Speed mode analyses all axial, then all radial
- Precision mode analyses in the “traditional” mode, per replicate
- Time savings on real samples =
Speed Mode = 60 seconds per sample
Precision Mode = 90 seconds per sample
- Intelligent rinse and sipper step ahead autosampler functions reduce overall running time

Analysis Mode:

Speed

Precision



iCAP Applications and their performance

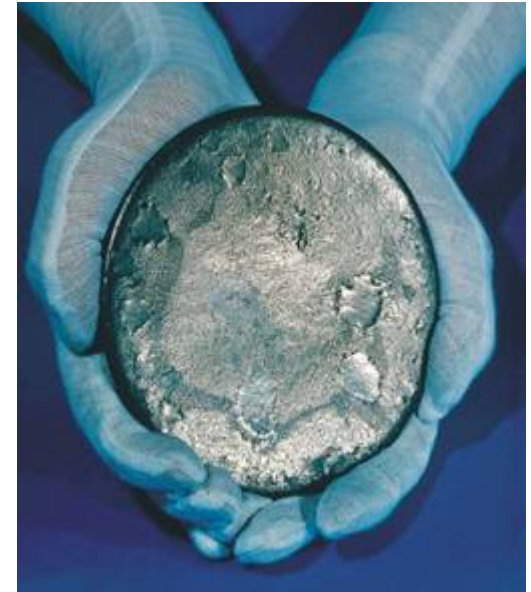
- Available application notes to get the analyst up and running with full method guidelines and published achievable Method Detection Limits
- Pre-configured Application specific sample introduction kits
- Details of environmental, geological, organics, metallurgy and foodstuffs applications



Metallurgy and Materials

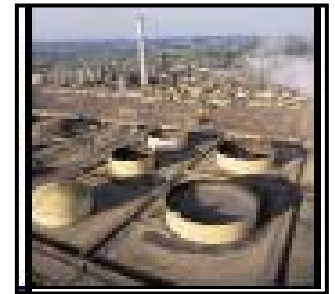
Typical samples -

- Steels and Alloys
 - Precious metals – PGMs
 - Bulk Materials – bronzes and brasses
 - Miscellaneous materials – e.g. catalyst substrates
 - Traces - contaminants
-
- Typically uses a Radial iCAP



Sample preparation – Metallurgy

- Microwave digestion – safe and efficient, sometimes requires HF for siliceous
- Direct Acid digestion – quick, but may not fully digest the sample, Siliceous materials require HF digestion
- Hot plate digestion – traditional, time consuming technique
- The use of a stabiliser such as Citric acid is sometimes required for volatile elements



Application Notes – Metallurgy

Application Note: 40758

Determination of Trace Elements in Steels and Alloys using ICP

Key Words
• ICP
• ICP OES
• Alloys
• Microwave digestion
• Steels

Introduction

Steel and iron alloys are among the most flexible and widely used metals in industry. They can be formed, drawn, cast or turned to shape with a wide range of finishes such as polishing, plating or simply painting. This flexibility means that they have found a wide range of applications from constructional use to surgical implements.

The properties of the steel can be enhanced or changed to suit the application depending on the constituent elements. For example, Ni, Cr and Mn give corrosion resistance while C will improve the hardness of a cutting edge.

In order to maintain consistent quality of the steel it is necessary to determine the trace element composition very accurately. ICP-OES is an ideal technique for this analysis since the wide linear dynamic range allows for the determination of minor and trace elements simultaneously without the need for additional dilution or pre-concentration techniques resulting in a considerable time saving.

Samples are traditionally prepared by dissolution using nitric acid in an open beaker. However, this approach can be quite time consuming with resultant samples and result in partial loss of some elements. More recently dissolution in sealed vessels has been used allowing higher temperatures and pressures to be obtained, aiding in the dissolution of the sample. The use of microwave power, rather than a conventional oven, further increases the efficiency of the digestion, and shortens the time required.



Principle

A 0.5 g mass of sample was digested with a mixture of nitric and hydrochloric acids in a high pressure microwave digestion system. The emission signals from the resulting sample solutions were measured directly using ICP-OES. Simultaneous background correction was used to overcome any background shifts.

Instrumentation

An iCAP 6000 Radial ICP Emission spectrometer equipped with concentric nebuliser and cyclonic spray chamber was used for this work. The iCAP 6000 series is the first generation of Thermo Electron Corporation's new breed of ICP emission spectrometers with high-resolution Echelle optics and much improved Charge Injection Device (CID). Advancements in CID 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.

PARAMETER	SETTING
Pump tubing	Orange/wellie sample, white/wellie drain
Pump speed	25 gpm
Nebuliser	Standard concentric
Nebuliser Argon flow	0.8 L/min
Spray Chamber	Standard optima
Centre tube	1.5 mm
Source Orientation	Radial
RF Forward Power	1150 W
Purge Gas	Argon
Coolant gas flow	12 L/min
Auxiliary gas flow	0.8 L/min

Table 1. Instrument Parameters

Reagents

Reagents and equipment
Nitric acid 65-70%, Analytical grade
Hydrochloric acid 35% w/w, Analytical grade
1000 ppm single element stock standards for each element required
Microwave digestion system
Volumetric flask

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Steels and Alloys – Radial

- Method fully described with microwave digestion procedure and analysis parameters required
- High matrix tolerance even with standard sample introduction kit
- No special plasma parameters required :
1150W Plasma
0.6L/min nebuliser

Geochemical Analysis: Accuracy and MDLs

ELEMENT	ZRM 476-3 MEASURED %	ZRM 476-3 EXPECTED %	GBW 01323 MEASURED %	GBW 01323 EXPECTED %
Cr 205.552 nm	0.0649	0.0648 ± 0.0012	0.368	0.389 ± 0.006
Cu 327.396 nm	0.2349	0.2445 ± 0.0025	0.276	0.277 ± 0.009
Mn 279.482 nm	1.009	0.987 ± 0.008	1.46	1.44 ± 0.02
Ni 231.604 nm	0.0576	0.0549 ± 0.0014	0.161	0.166 ± 0.004
P 178.284 nm	0.0901	0.0908 ± 0.0023	0.011	0.013 ± 0.001
Ti 334.941 nm	0.0202	0.0222 ± 0.0005	0.268	0.285 ± 0.006
V 268.796 nm	0.0101	0.0115 ± 0.0002	0.148	0.158 ± 0.005

ELEMENT	3 σ METHOD DETECTION LIMITS (ppb)
Cr 205.552 nm	1.3
Cu 327.396 nm	4.3
Mn 279.482 nm	11.1
Ni 231.604 nm	1.7
P 178.284 nm	6
Ti 334.941 nm	0.5
V 268.796 nm	4

Sample Introduction Kits - Metallurgy

- Standard Kit (Duo or Radial)
 - *Complete kit for normal aqueous solutions up to 3 % m/v dissolved solids*
- High Solids Kit
 - *Designed for analysis of solutions containing up to 20 % m/v dissolved solids*
 - *The 2mm centre tube and high solids nebuliser allows for the easy analysis of majors*



Geological

Typical samples -

- Rock samples, sediments, slags, ceramics, cements
 - Survey work, quality control, raw material screening
 - Robust
 - Matrix tolerant
 - Stability
 - Detection limits (traces)
-
- Typically uses a Radial iCAP



Geological sample preparation and digestion

Resistant materials – sample preparation is often difficult

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

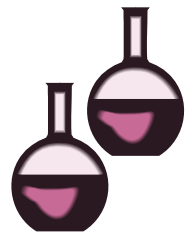
- Pros – Simple method, fast, moderate solids level
- Cons – “Free” HF, loss of Si or incomplete dissolution

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



Geochemical Applications: Optimisation

- 6300 Radial and 6300 Duo
- Optimise pump speed, neb flow & viewing height (radial)
- Plasma parameters
 - RF power 1100
 - Coolant flow 12 lpm fixed
 - Auxiliary flow 0.5 or 1 lpm
 - Nebuliser flow 0.15 - 0.2 MPa
 - Pump speed 40-50rpm = 1.4-1.6 ml/min
 - 15 seconds integration time



Geochemical Analysis: Accuracy 1

ELEMENT	AC-E MEASURED %	AC-E EXPECTED %
Al	7.42	7.78 ± 0.03
Ba	52 ppm	55 ppm ± 2.6
Ca	0.22	0.24 ± 0.014
Cu	4 ppm	4 ppm ± 0.9
Fe	1.65	1.77 ± 0.014
K	3.40	3.73 ± 0.02
Mg	0.013	0.02 ± 0.006
Mn	436 ppm	449 ppm ± 15.5
Ni	Not determined	Not determined
Si	31.83	32.88 ± 0.03
Ti	0.06	0.07 ± 0.02
Zn	207 ppm	224 ppm ± 6
Zr	781 ppm	780 ppm ± 20

ELEMENT	MAG-1 MEASURED %	MAG-1 EXPECTED %
Al	8.43	8.68 ± 0.16
Ba	461 ppm	480 ppm ± 41
Ca	0.96	0.98 ± 0.07
Cu	31 ppm	30 ppm ± 3
Fe	4.77	4.76 ± 0.42
K	2.78	2.95 ± 0.14
Mg	1.80	1.81 ± 0.06
Mn	734 ppm	759 ppm ± 70
Ni	49 ppm	53 ppm ± 8
Si	23.20	23.56 ± 0.45
Ti	0.44	0.45 ± 0.04
Zn	118 ppm	130 ppm ± 6
Zr	127 ppm	130 ppm ± 13

Geochemical Analysis: MDLs

ELEMENT 3σ METHOD DETECTION LIMITS (ppb)

Al	6.7
Ba	0.1
Ca	3.7
Cu	0.9
Fe	3.4
K	13.3
Mg	0.3
Mn	0.2
Ni	1.6
Si	19.6
Ti	1.0
Zn	0.4
Zr	0.8

Application Notes – Geological

Application Note: 40758

Analysis of Geological Samples using ICP

Key Words

- ICP
- ICAP 6500
- Geological analysis
- Utilities
- Metallurgical Analysis
- J18 coils box

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 in the characterization of rock types. Traditionally, complete lithium 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 rock are systematically collected from large areas of land with a view to identifying small pockets or anomalies where the concentration of some elements 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 ore elements such as Cu, Fe, Ni, Zn and Sn 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 missed by the sampling strategy.



Procedure

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 shifts.

Instrumentation

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 Injection Device (CID). Advancements in CID 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	SETTING
Pump tubing	Orange/white sample, white/white drain
Pump speed	50 gpm
Nebulizer type	Standard concentric
Nebulizer Argon flow	0.95 L/min
Spray Chamber	Standard options
Carrier tube	1.5 min
Source Orientation	Radial
RF Forward Power	1150 W
Plasma Gas	Argon
Carrier gas flow	12 L/min
Auxiliary gas flow	0.5 L/min

Table 1. Instrument Parameters

Method

Reagents and potential equipment

Nitric Acid, e.g. 1.42 approximately, Analytic grade.
Lithium Metaborate, purified for fusions.
Platinum crucible
Polyfuse rod
Muffle 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.

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Lithium Metaborate Fusions – Radial iCAP

- High matrix tolerance even with standard sample introduction kit
- No special plasma parameters required to analyse fusions :
 - 1150W Plasma
 - 0.65L/min nebuliser

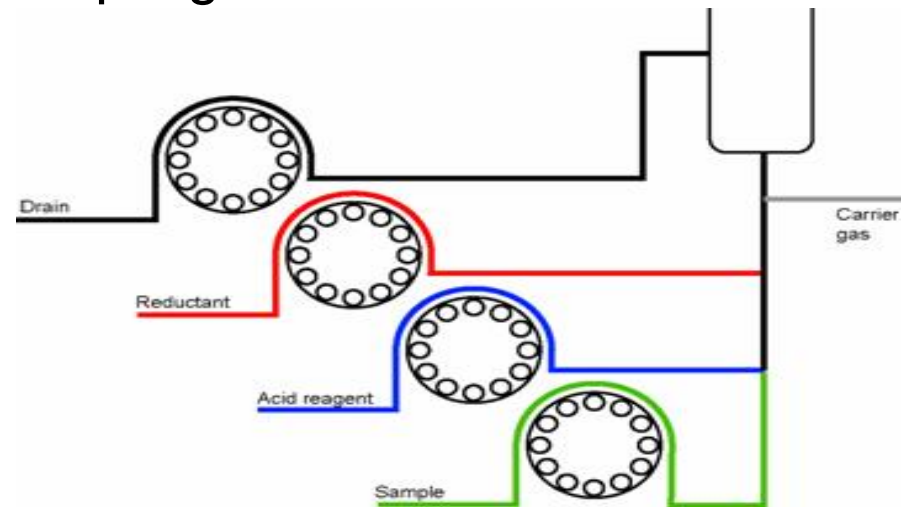
Sample Introduction Kits - Geological

- Standard Kit (Duo or Radial)
 - *Complete kit for normal aqueous solutions up to 3 % m/v dissolved solids*
- High Solids Kit
 - *Designed for analysis of solutions containing up to 20 % m/v dissolved solids*
 - *Use in conjunction with the argon humidifier for ultimate high solids tolerance*



Accessories for iCAP

- Ultrasonic nebuliser – for enhanced detection limits
- Hydride generator – either integrated for iCAP 6500 or basic system for iCAP 6300 for enhanced detection of hydride elements
- SSEA – Separate Sampling Excitation Accessory for solid sampling
- Laser – Laser ablation for solid sampling



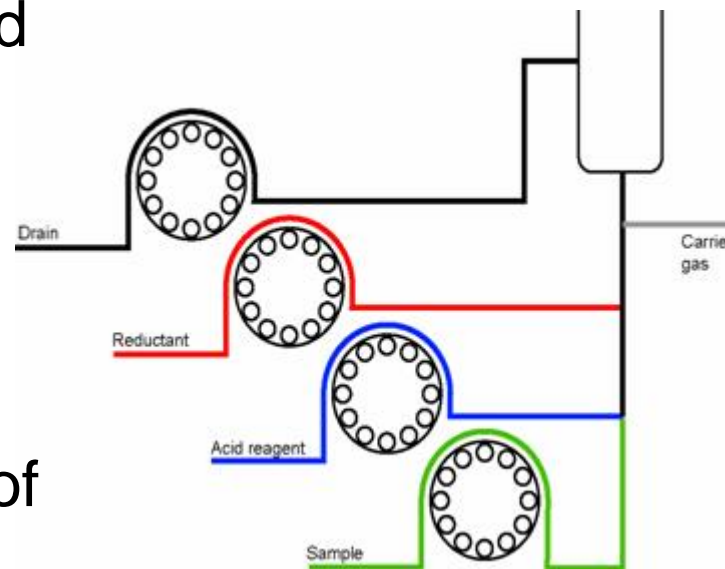
Integrated Accessories for the iCAP 6500

Enhanced Hydride Generation Accessory

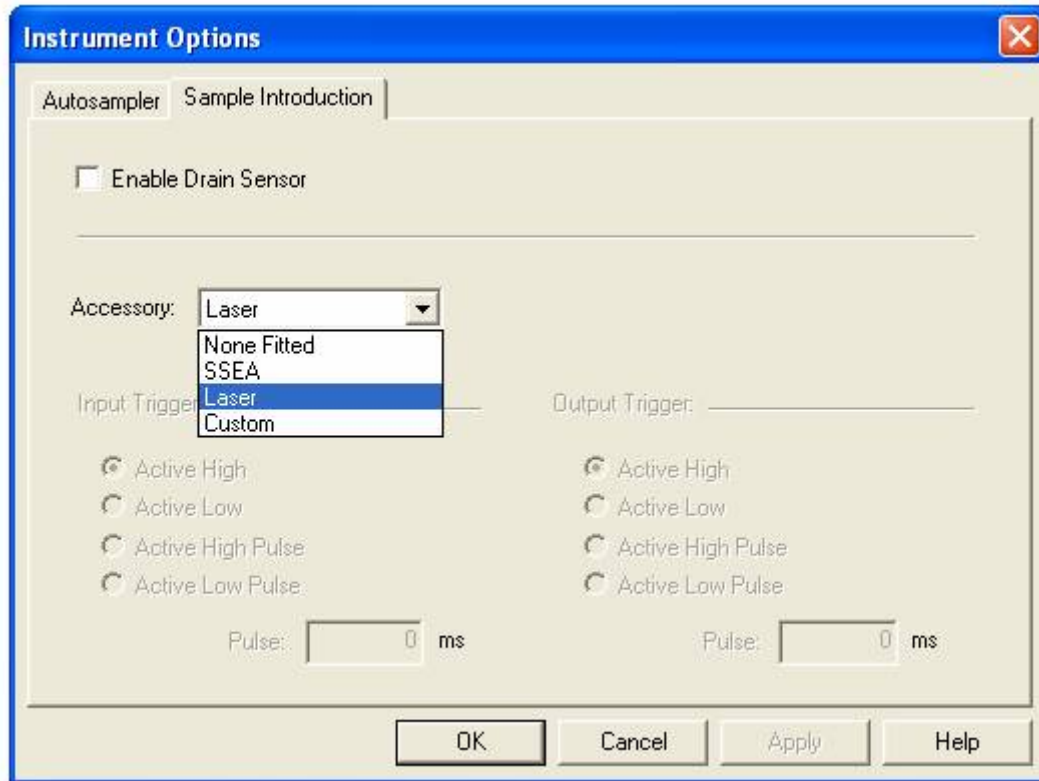
Gas Liquid Separator which connects directly to the iCAP 6500 four channel peristaltic pump

Designed to enhance the detection limits for As, Se, Bi, Hg, Sb, Sn and Te to sub ppb levels

Four dedicated channels for sample, acid blank, reductant and drain, with optimized pump tubing size to ensure the correct mixture of sample to reductant



New Accessory Control

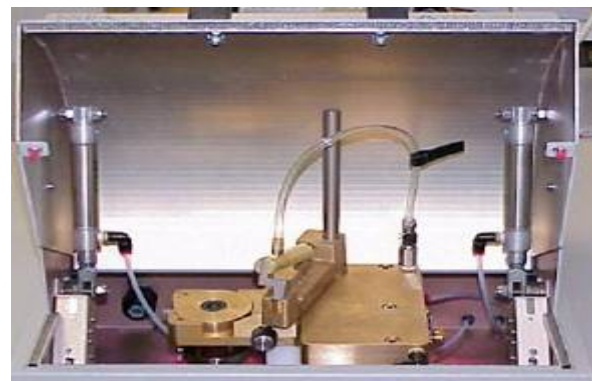


- iCAP 6500
- Enable Drain Sensor option for accessories
- Automatic handling of supported accessories
- Simplified accessory control for unsupported
 - Select type
 - Com port
 - Trigger type

Integrated accessories – SSEA

SSEA – Separate Sample and Excitation Accessory Direct analysis of conductive samples

A spark ablates the solid conductive sample and the resulting cloud of atoms is carried to the plasma via an argon stream



Fully supported by iTEVA, controls the SSEA power functions, all the triggering is automatic



Sample Options:

Repeats:

Gas flush time: seconds

Preburn time: seconds

Analysis Mode: Speed Precision

Source:

Sample Intro:

Plasma View:

Auto-Increment Sample Names

Use Sample Weight Corrections

Sample Introduction Settings:

Frequency:

Power level:

Door Trigger: First Repeat Only Each Repeat

Laser Ablation – New Wave and CETAC models

- Historically used with ICP-MS
- Used for examination of artefacts, fluid inclusions or depth profiling
- Applications require high sensitivity
- New generation of “large spot” lasers
- Latest ICP’s have higher sensitivity
- Bulk analysis and traces now possible with ICP-OES



Relative Sensitivities - ICP-OES

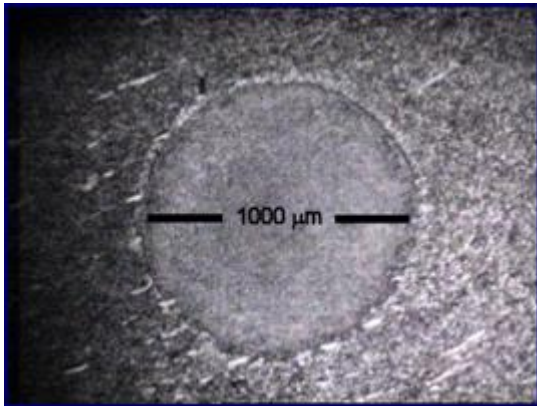
Sample to Plasma

Aqueous Transport \cong 300 μ g/sec (H₂O)
[1ml/min, 2% transport efficiency]

Laser (750 μ m spot) \cong 3 μ g/sec (SiO₂)
[500nm/shot, 10Hz, 15% transport efficiency]

cps/ppm

[50,000] $\xrightarrow{100X \text{ Dilution}}$
[500] = [500]



1000 μ m spot in NIST 610 Glass

With large spot ablation aqueous and laser ablation detection limits are approaching parity for many elements in the solid

Accessories for solid sampling - Laser

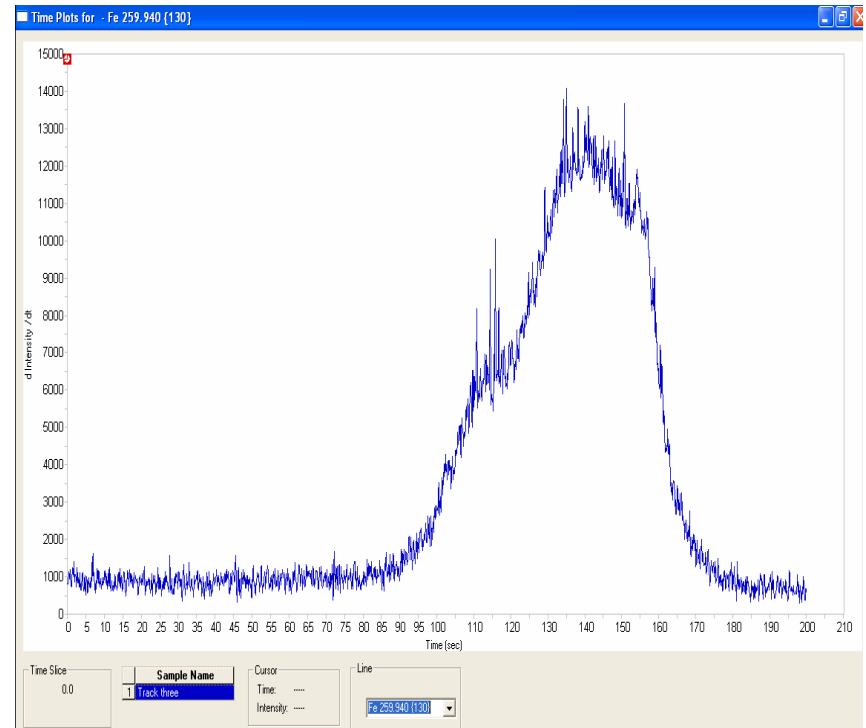
- CETAC and New Wave supported by iTEVA
- New software support to enable transient and steady state analysis for Laser
- Application note for LA – ICP due for release in Q3

Sample Introduction Settings:

Exposure Type:

Steady State

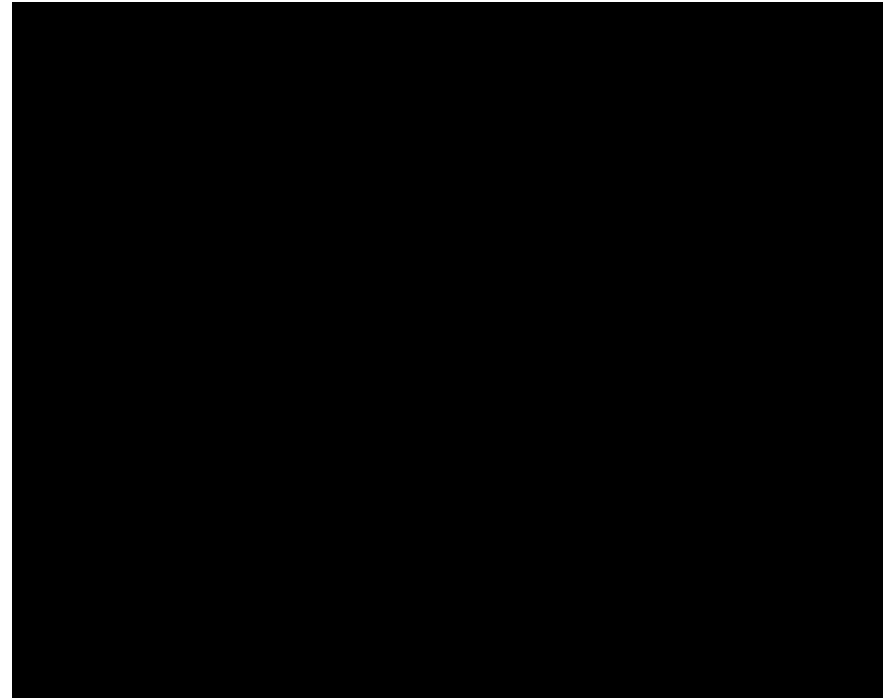
Transient



Conclusions

- iCAP – covers all applications with ease making any analysis routine
- Expert software and technical help means that the answer to your question is just a click away

iCAP – Your analysis solution

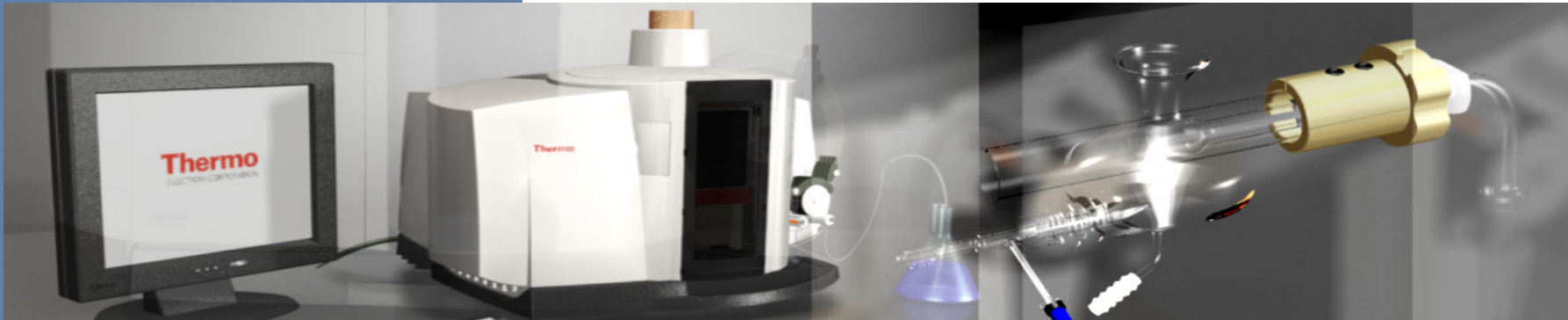


iCAP 6000 Series – Applications Part 1 - Mining and Metals

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How can we use iTEVA to help with method development for different applications?

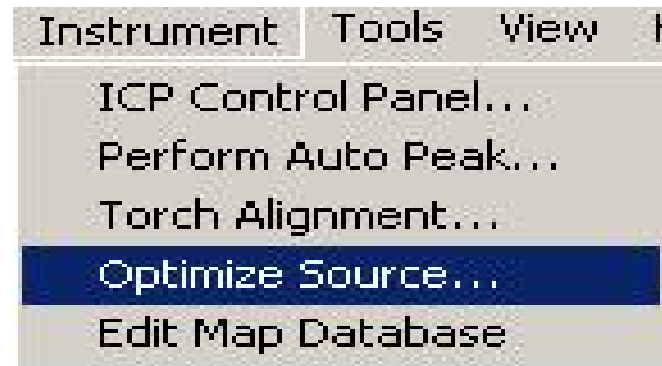
- iCAP 6500 Series allows automated method development using the “Optimise Source” routine
- The automated routine requires no user input except to aspirate a method solution
- Let’s see how this can help with a specific EPA method for soils and sludges - 6010, and its method development



Method specific software optimization packages

- Source optimization enables unattended method development with a simple automated routine
- Automatically optimizes RF power, Nebuliser gas flow, Pump speed, Coolant gas flow, Auxiliary gas flow (Radial Viewing Height is also included for Radial Instruments)

Example using EPA 6010 method for Soils and Sludges analysis



Source Optimization for methods

Optimize Source

Please aspirate a solution containing all the elements you wish to take part in the optimization.

By default, the source conditions for all lines in the method will be optimized.

Choose 'Select Lines' to optimize a subset of these lines.

Optimize For:

Best Signal
Best Signal
Best SBR
Best DL

RF Power
750 1350 750 - 1350 W

Nebulizer Gas Flow
0.30 1.50 0.0 - 1.5 L/min

Pump Speed
30 125 0 - 125 rpm

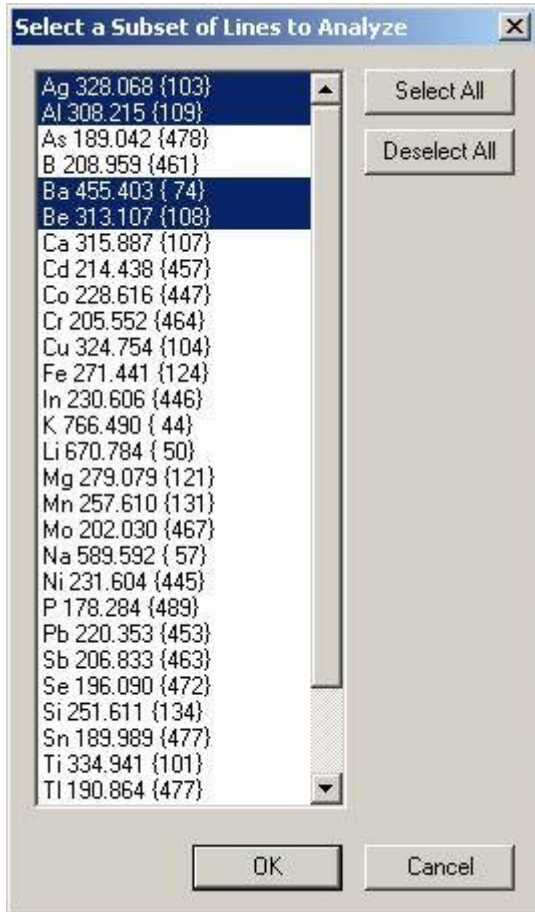
Coolant Gas Flow
12 20 10 - 20 L/min

Auxiliary Gas Flow
0.2 2.0 0 - 2 L/min

Run Select Lines... Close

- Optimize every parameter automatically – with user defined parameters
- Simply aspirate a method solution
- Optimize for Best Signal, Best Signal/Noise Ratio or Best DL (Best DL used in this case)

Source optimization continued..

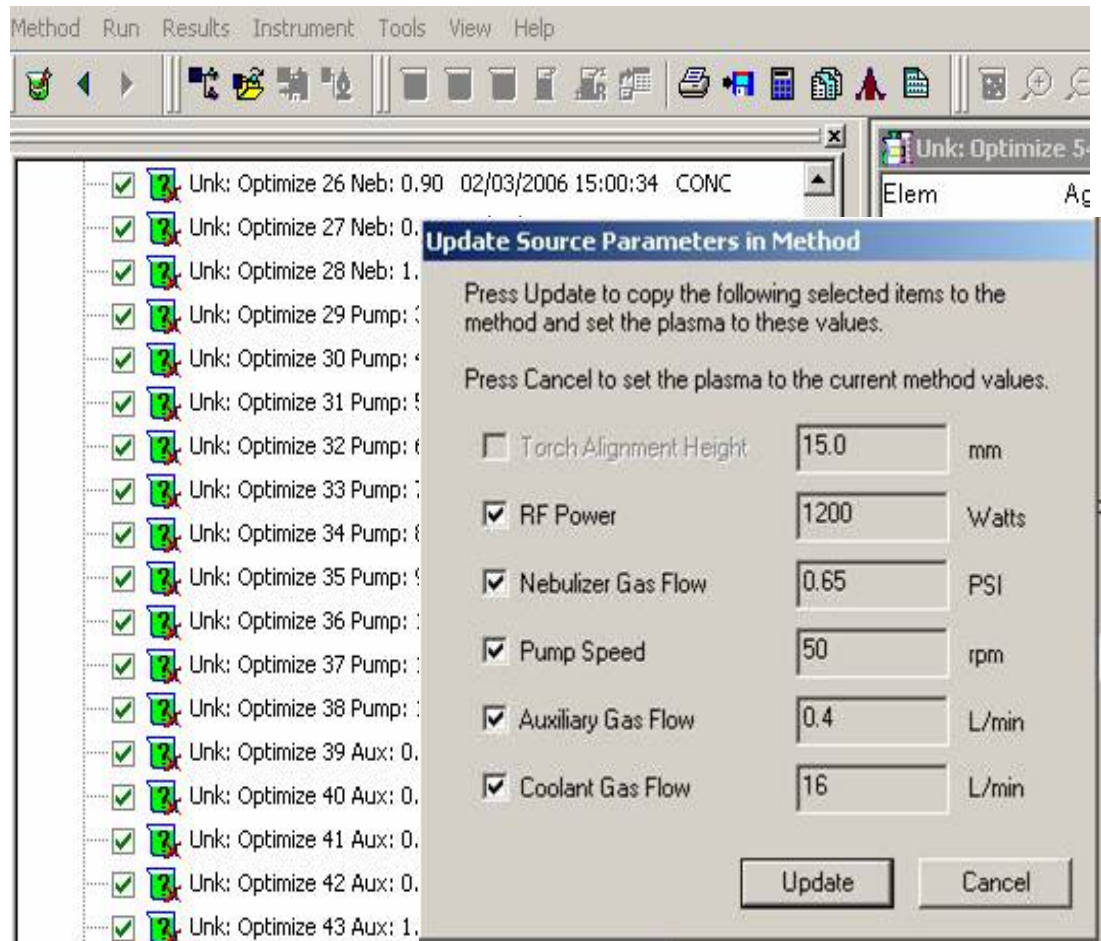


The analyst can specify which elements to optimize the method :

- choose your critical elements with the click of a button
or
- optimize for all elements in the method
- For this EPA Method, all elements were optimized (except Internal Standards Yttrium and Indium)

Source optimization continued..

- On completion, the analyst is presented with the results of the procedure
- The optimized values are displayed with the option to update the method



Source optimization concluded

The screenshot displays the 'Source Settings' window with the following parameters:

- Plasma Settings:** Includes a 'Get Current Conditions' button.
- Sample Pump:**
 - Flush Pump Rate: 50 rpm (range 0-125 rpm)
 - Analysis Pump Rate: 50 rpm (range 0-125 rpm)
 - Pump Stabilization Time: 0 s (range 0-1000 s)
 - Pump Tubing Type: Tygon Orange/White
- Source Settings:**
 - Wavelength Range: Low / Both (High is unchecked)
 - RF Power: 1200 W (range 750-1350 W)
 - Auxiliary Gas Flow: 0.4 L/min (range 0-2 L/min)
 - Nebulizer Gas Flow: 0.65 L/min (range 0.0-1.5 L/min)
 - Coolant Gas Flow: 16 L/min (range 10-20 L/min)

- The optimized values are automatically updated into the method
- As the procedure does not require any analyst input, it was run unattended
- The EPA 6010 method was optimized for all parameters (using default settings) and all 29 elements in 40 minutes!