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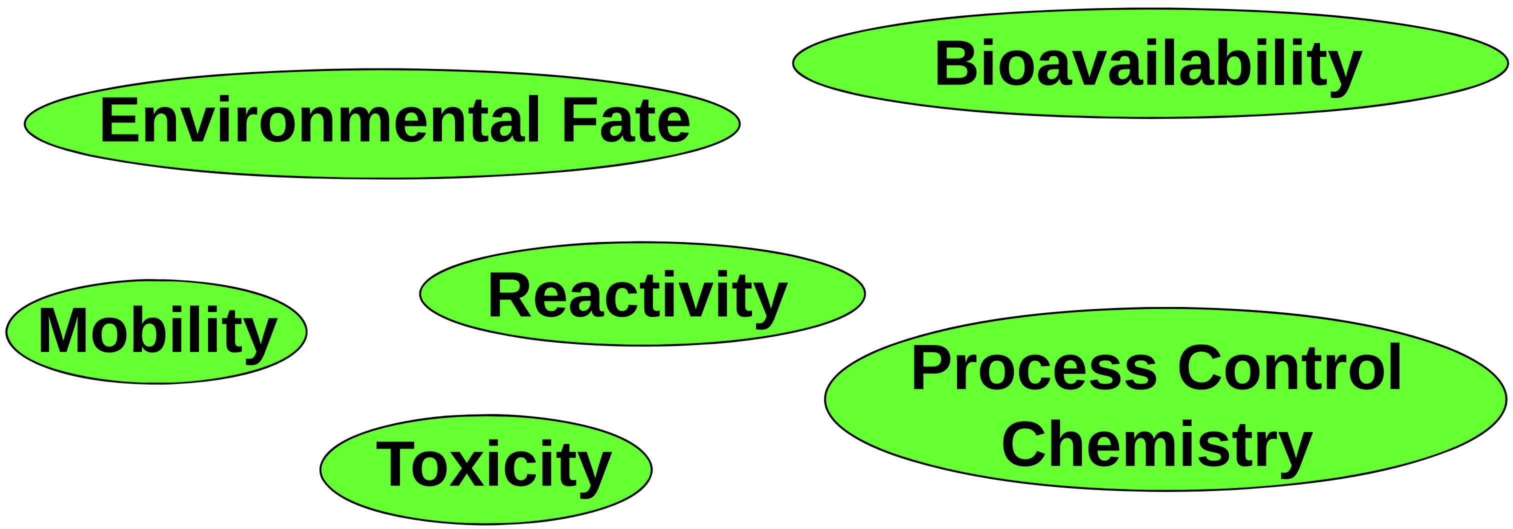
IC-ICP/MS…A New Direction

The world leader in serving science

Why is Speciation Analysis Important?

- Elemental speciation data can reveal valuable information in addition to total element concentrations:

  bioavailability, mobility, metabolic processes, biotransformations and toxicity implications



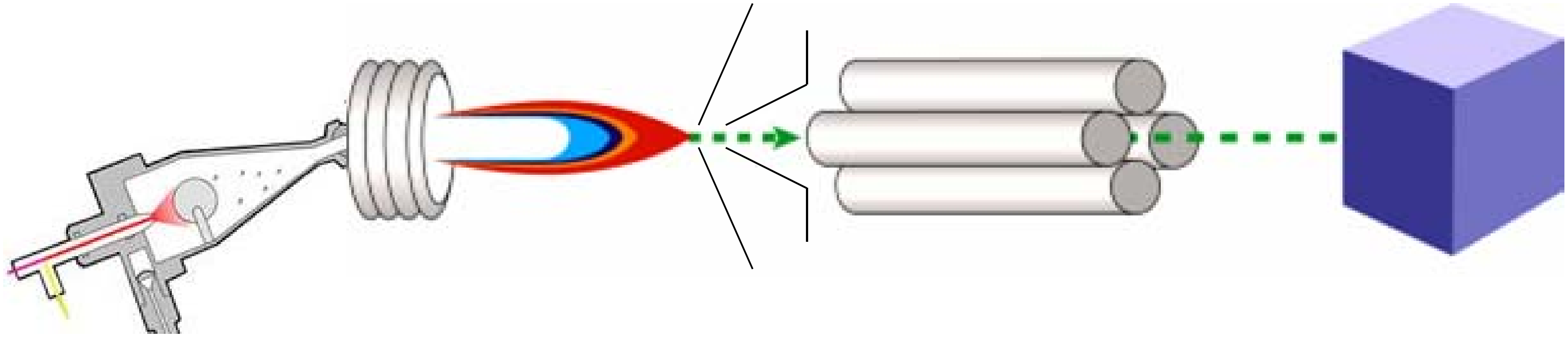
- Elemental speciation enables the significance of total elemental concentrations to be understood more clearly

Relevance of elemental speciation *

- **Environmental risk analysis**
  - hazard identification, exposure assessment
- **Waste management**
  - information to facilitate remediation
- **Occupational health and hygiene**
  - Toxic exposure, e.g. Hexavalent Chromium
- **Toxicology, pharmacy, medicine, clinical chemistry and biology**
  - enzymes (Zn), vitamins (Co), metallo-proteins (Se), metallo-drugs (Pt), toxins (As, Hg, Cr(VI), Cd, Pb) and their metabolic forms.
- **Nutritional sciences**
  - a better understanding of chemical forms of trace elements in food and their subsequent behaviour in the digestive tract.
- **Drinking water industry**
  - toxicity of trace elements (e.g. Al, As, Cr) present in the raw water depend strongly on their speciation (e.g. As(III)/As(V)).
- **Food industry**
  - improve the quality of their products.
- **Chemical industry**
  - chemical activities of reagents, catalysts, products, by-products and impurities are species dependent.
- **Petrochemical industry**
  - metalloporphyrins and other metal species are present in fossil fuels show species dependent behaviour in refinery
- **Semiconductor industry**
  - process chemicals used are organometallic compounds or metalloid compounds of high toxicity, calling for strict control

* www.speciation.net

ICP-MS in a nutshell



- Most elements possible (around 80)
- Elemental and isotopic information given
- Concentration range ppq (pg/L) to mid-ppm (100s mg/L)
- Rapid analysis – 2-6 minutes per sample
- Good precision – ~2% RSDs

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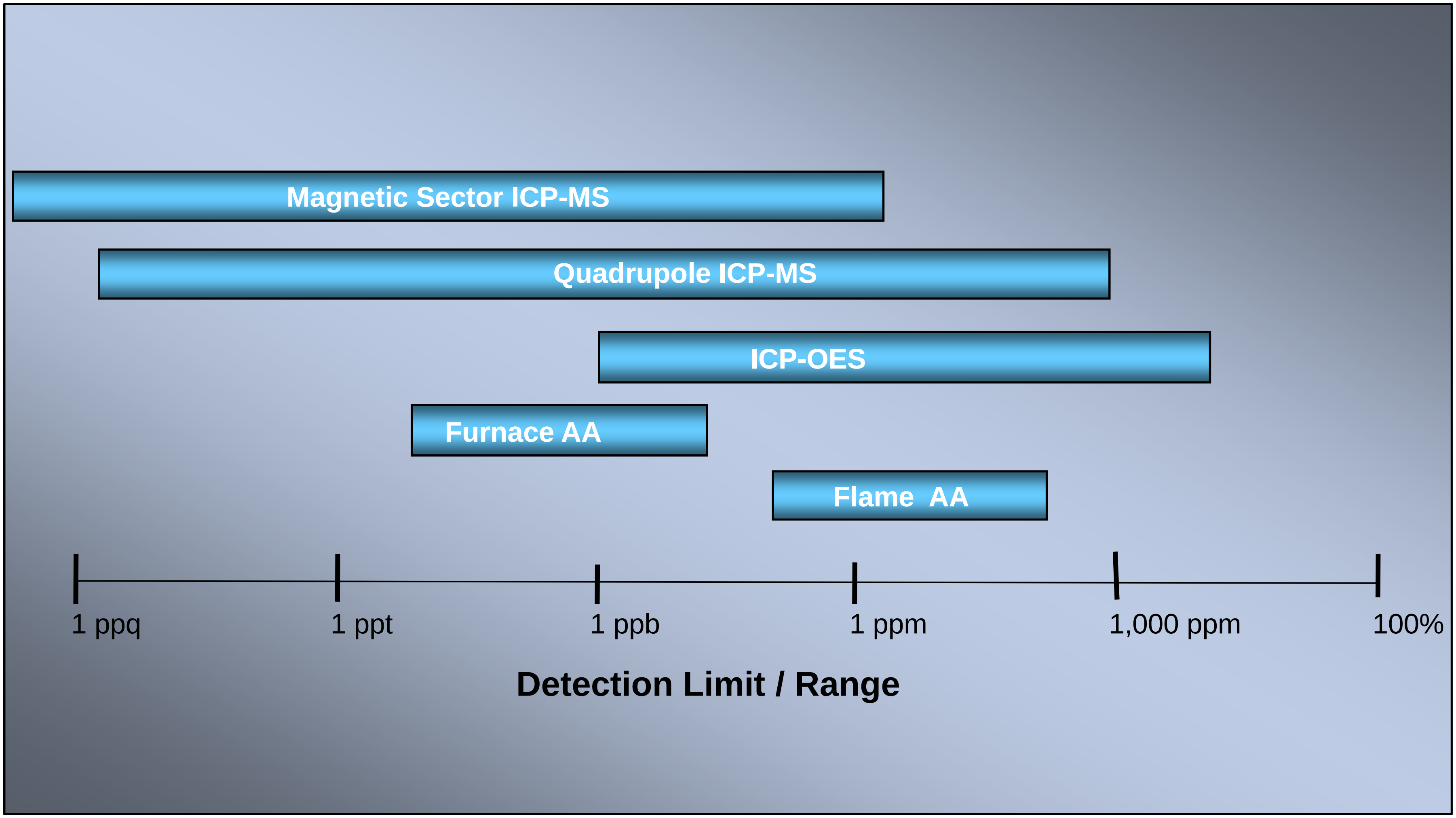
Performance Characteristics



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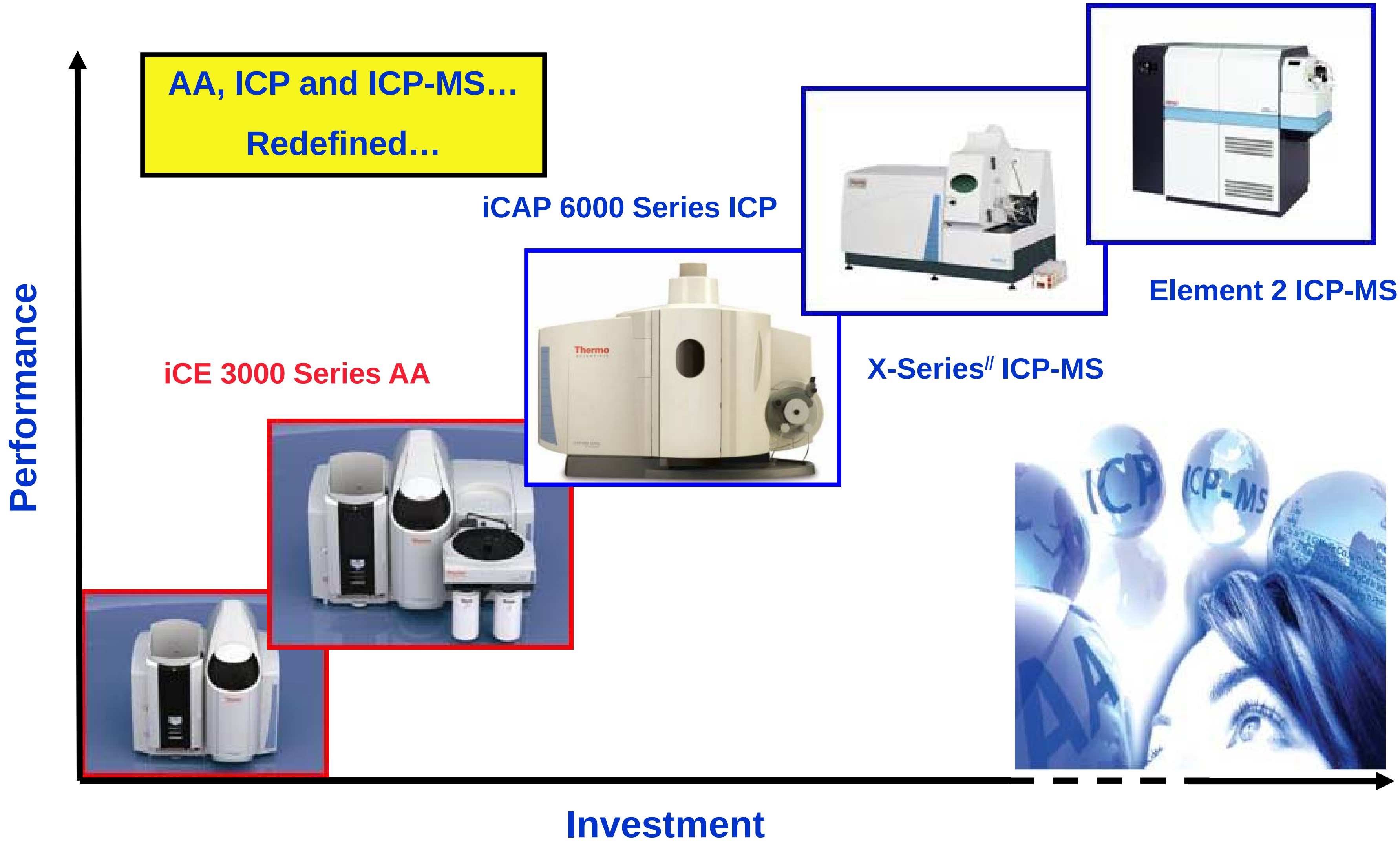
Trace Elemental Analysis Product Range



Chemical forms of metals

REDOX FORMS	ORGANOMETALLIC COMPOUNDS	BIOMOLECULE
As(III)/As(V)	Methyl-Hg	Se amino acids
Se(IV)/Se(VI)	Butyl and Phenyl-Sn	Arsenosugars
Cr(III)/Cr(VI)	Alkyl Pb	Metalloproteins

DIFFERENCE OF

Toxicity, Bioavailability, Bioaccumulation and Mobility

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Environmental Contaminants and Legislation

- Many governing bodies are now recognizing that the elemental species and not necessarily the total concentration of an element should be controlled
    - Legislation and methods exist already for many organic pollutants (e.g. pesticides)
- Legislation for elemental species focuses on the more <u>toxic species</u>
- Future amendments to the Water Framework Directive in the EU will require maximal concentrations of 50 ppt for <u>Hg compounds</u> and 0.2 ppt for <u>Tributyl tin</u> in inland water systems

Element	Matrix	International Agency/Directive	Legislation
Hg	Fish	USEPA Criterion document 823-R-01-001	Criterion limit value of 0.3 mg/kg of $MeHg^+$ (concentration of MeHg+ in fish which is expected to be without appreciable risk to human health)
	Water	EU Water Framework Directive 2000/60/EC	Hg and its compounds listed as a priority hazardous substances < 50 ppt in inland waters
Sn	Water	EU Water Framework Directive 2000/60/EC	TBT listed as a priority hazardous substance < 0.2 ppt in inland waters
Br	Water	EU Water Framework Directive 2000/60/EC	Pentabromodiphenyl ether listed as a priority hazardous substance < 0.5 ppt

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HPLC-ICP-MS

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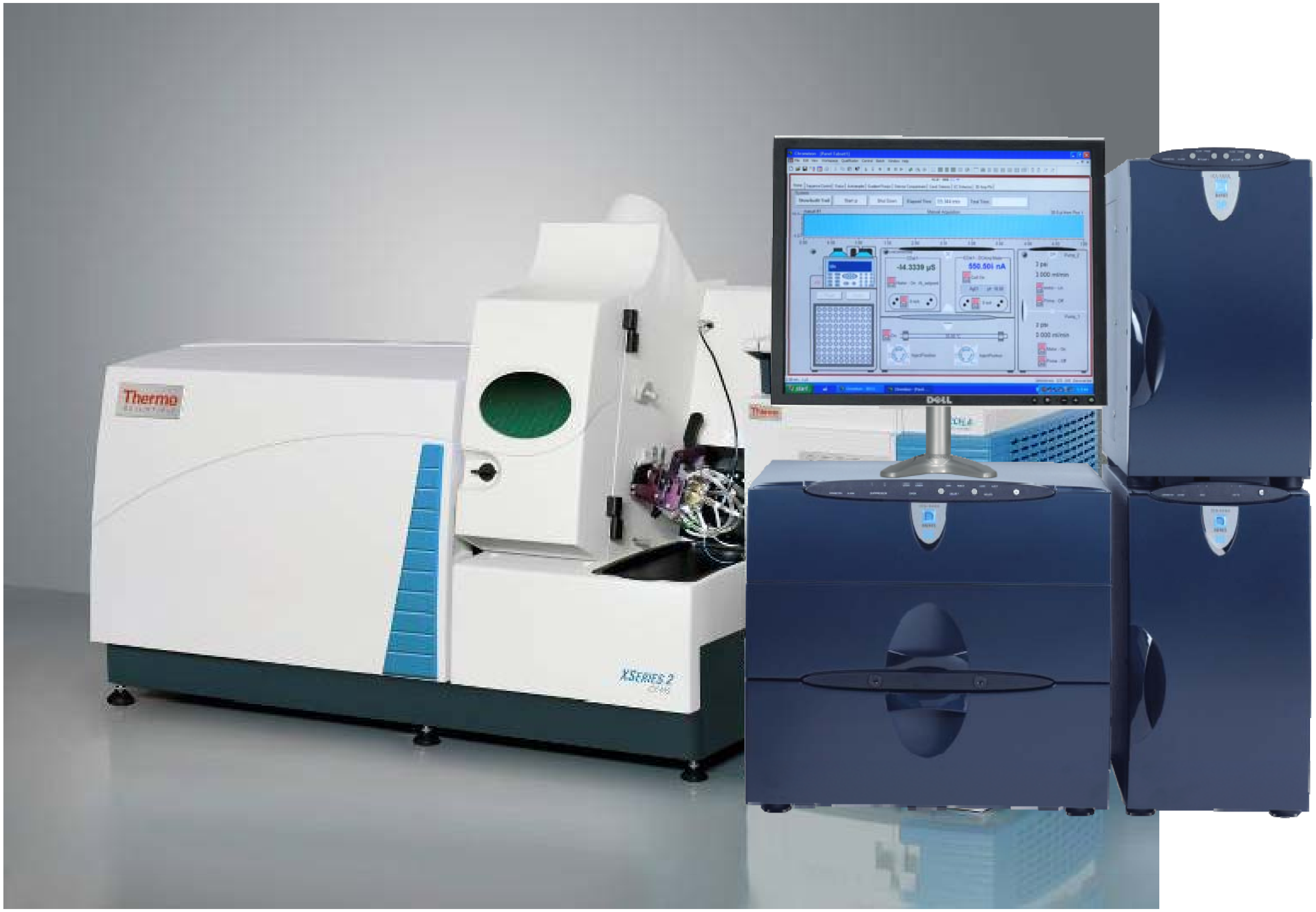
IC-ICP-MS



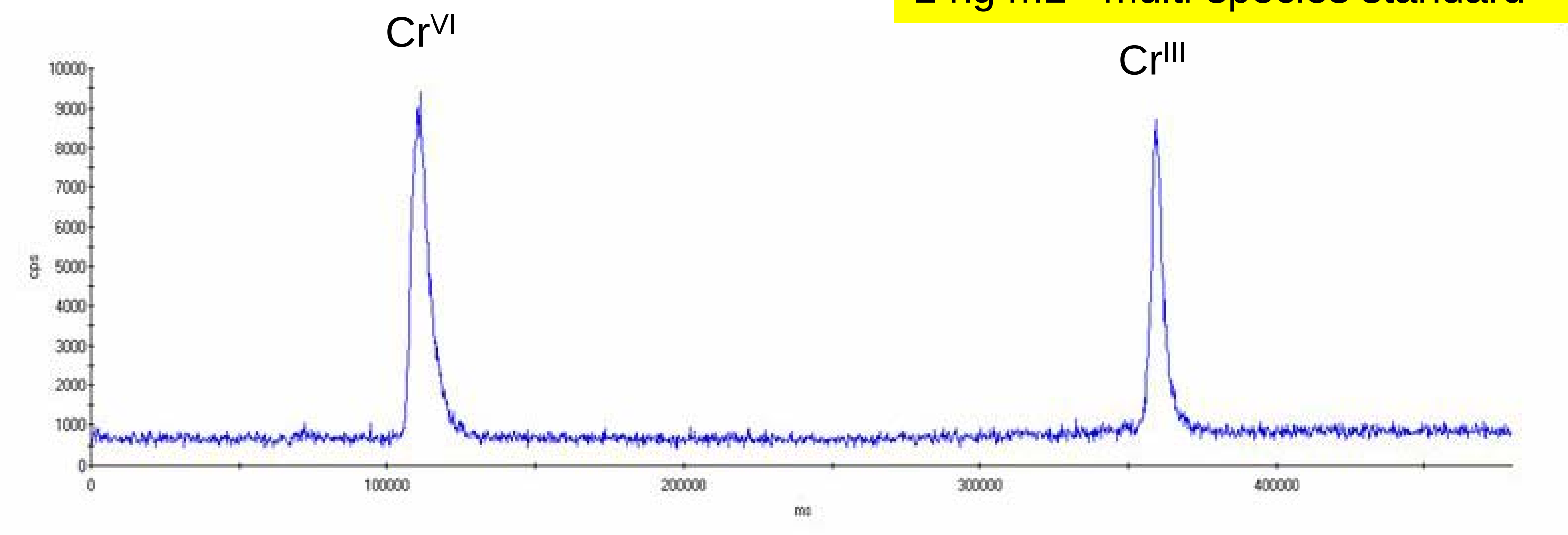
Typical IC/HPLC-ICP-MS Applications

Element	***Species***	***Matrices***	***Scientific Sector***
Cr	Chromium III & VI	Water, air particulates, cement	Environment, industry, nutrition, occupational exp.
As	Organoarsenic compounds	Fish, water, sediments, urine, hair	Nutrition, environment, exposure
Se	Organoselenium	Yeast, garlic, urine	Agroindustry, nutrition, pharma, clinical
Hg	Inorganic mercury, organomercury	Fish, sediments, water, urine, blood	Environment, Clinical
Sn	Organotins	Fish, sediments, water, plastics	Environment, industry
Fe	Iron II & III	Bacteria, soils, water	Environment, clinical, nutrition
Cu, Zn, Cd	Phytochelatins, metallothioneins	Plant tissues, brain & kidney tissue	Agroindustry, clinical

Speciation of Chromium Using HPLC-ICP-MS

- Thermo Scientific Surveyor HPLC Conditions
  - Commercial standards prepared in deionised water
  - 100 µL injection volume
  - Dionex IonPac CS5A (2 x 250 mm) plus guard column CG5A (2 x 50 mm)
  - Gradient elution (0.3 to 1 M nitric acid, flow rate = 0.5 mL/min)
- X Series^{II} ICP-MS Conditions
  - Peltier cooled Spray Chamber, PlasmaScreen and Xt interface
  - HPLC Coupling Kit

2 ng mL^{-1} multi-species standard



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Figures of Merit for Chromium Speciation Analysis

Recovery of Cr^{VI} from a dust filter

Sample	CrVI
DF 198	0.521
DF 198 + 5 ng/mL	4.664

Method Detection Limits

Cr Species	3 sigma DL (ng/mL)	Absolute DL (pg)
Cr^{VI}	0.08	8
Cr^{III}	0.105	10.5

Quantitative analysis of cement and airborne particulate

Application Note: 40807

Chromium Speciation in Cement Extracts and Airborne Particulates using HPLC Coupled with the XSeries*II* ICP-MS

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Key Words
- Airborne Particulates
- Cement
- Chromium
- HPLC
- ICP-MS

This application note describes the use of an HPLC-ICP-MS instrument package from Thermo Electron Corporation to enable the determination of chromium species in cement extracts and airborne workplace particulates. Chromium species were separated on-line prior to ICP-MS detection using a cation exchange stationary phase in conjunction with a 100 % aqueous acidic mobile phase. The HPLC-ICP-MS methodology was validated using a CRM (BCR CRM-545, welding dust). Method detection limits (MDLs) and limits of quantification (LOQ) were determined using the 3σ and 10σ models respectively based on repeat injections of the calibration blank (n=5).

Introduction

Oxidation state and chemical form are important factors which influence the toxicity, bioavailability and mobility of chromium. For example, trivalent chromium (Cr^{III}) is essential for many biochemical mechanisms in contrast to hexavalent chromium (Cr^{VI}) which is highly toxic due to its high oxidation potential and ability to attack the skin, respiratory and digestive systems. To date there is an increasing requirement for methodologies to enable sensitive, quantitative chromium speciation analyses in order to determine concentrations of toxic and/or non-toxic species and to better understand the implications of total chromium concentrations.

Chromium is employed in a number of industrial applications (e.g. chromium plating, stainless steel production, paint, pigment and cement manufacture) and occupational exposure issues have prompted the implementation of a number of directives for the protection of employers in the workplace. According to the European Commission (EC) directive 2003/53/EC, wet cement should contain no more than 2 ppm hexavalent chromium and according to the directive 2000/53/EC, no more than 2 g of hexavalent chromium can be used in anti-corrosion coatings on road vehicles. Additionally, the 'occupational health and safety administration' (OSHA) have recently proposed a permissible exposure limit of 0.5 µg/m³ Cr^{VI} in workplace atmospheres (OSHA method

HPLC-ICP-MS configuration

A Finnigan™ SpectraSYSTEM™ HPLC pump with AS3500 autosampler were coupled to the XSeries*II* ICP-MS using the Thermo Electron HPLC-ICP-MS Coupling Kit (P/N 4600485) and Finnigan SpectraSYSTEM HPLC Wiring Harness (P/N 4600488). The XSeries*II* was operated under standard hot plasma conditions using a one-piece quartz torch with 1.5 mm ID injector and PlasmaScreen™ option. The spray chamber was cooled to 2°C with the optional Peltier cooling device. PlasmaLab and Xcalibur™ software packages were used in conjunction with the External Trigger Card (P/N 4600261) to enable automated HPLC accessory control using bi-directional communications and intelligent peak integration facilities. The associated HPLC parameters and analytical conditions for HPLC-ICP-MS are shown overleaf in Table 1.

CRM 545 WELDING DUST (40.2 ± 0,6 g/kg Cr^{VI})	**Cr^{VI} (g/kg)**	**Cr^{III} (g/kg)**
Mean of three replicate analyses of one extract	39.8 ± 0.5 g/kg	-
CEMENT	**Cr^{VI} (mg/kg)**	**Cr^{III} (mg/kg)**
1	5.21	-
2	7.07	-
3	14.53	-
4	11.16	-
5	0.011	0.013
6	1.20	1.80
SURFACE AREA DUST	**Cr^{VI} (µg/kg)**	**Cr^{III} (µg/kg)**
Extraction of soluble Cr^{VI}	70	13
Extraction of insoluble Cr^{VI}	1544	156
FILTERS - SPIKE RECOVERIES (100 ng Cr^{VI})	**Cr^{VI} (ng)**	**Cr^{III} (ng)**
Filter 1 spiked prior to extraction	105	-
Filter 2 spiked prior to extraction	90	-
Filter 3 spiked during extraction	97	-

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Where do we Need Speciation of Arsenic and Selenium

- Food Safety (Control of toxic substances, Nutrition)
  - Monitoring species in various food groups to route out possible ‘toxic’ foods/waters or find which foods are beneficial
  - Gastric digestion of foods, could lead to potentially new compounds which could be more toxic than the ingested form
  - Supplementation of selenium in both animal feeds and as supplements to the human diet should be controlled
  - Certain trade legislation limits inorganic arsenic content in fish
- Environment: Although many species have been identified, the identification of new species still plays an important role and could help us understand how species are accumulated, transformed and detoxified in plants/animals
- Clinical: analysis of blood, hair and urine can alert us to cases of poisoning

Chemical forms of As and their toxicity

CHEMICAL FORM	LD50 (mg/kg)
Arsenite (As(III))	14
Arsenate (As(V))	20
Arsine (AsH_3)	3
Monomethylarsonic acid (MMA)	700 - 1800
Dimethylarsinic acid (DMA)	700 - 2600
Arsenocholine	> 10000
Arsenobetaine	> 10000
Aspirin	1000 - 1600
Strychnine	16

LD50 rat: Lethal dose 50 (dose for which 50 % of a population is dead)

Chemical forms of Se and their toxicity

Relation between dose and toxicity

Necessary nutritional dose	50 - 200 µg /day
Limit nutritional dose	500 µg /day

Protective role for human health

- antioxidant
- cardiovascular disease

Chemical form and toxicity

Se(IV)	MLD = 3.5 mg/kg
Se(VI)	MLD = 5.5 mg/kg
Selenomethionine	MLD = 4.25 mg/kg
Selenocystine	MLD = 4 mg/kg

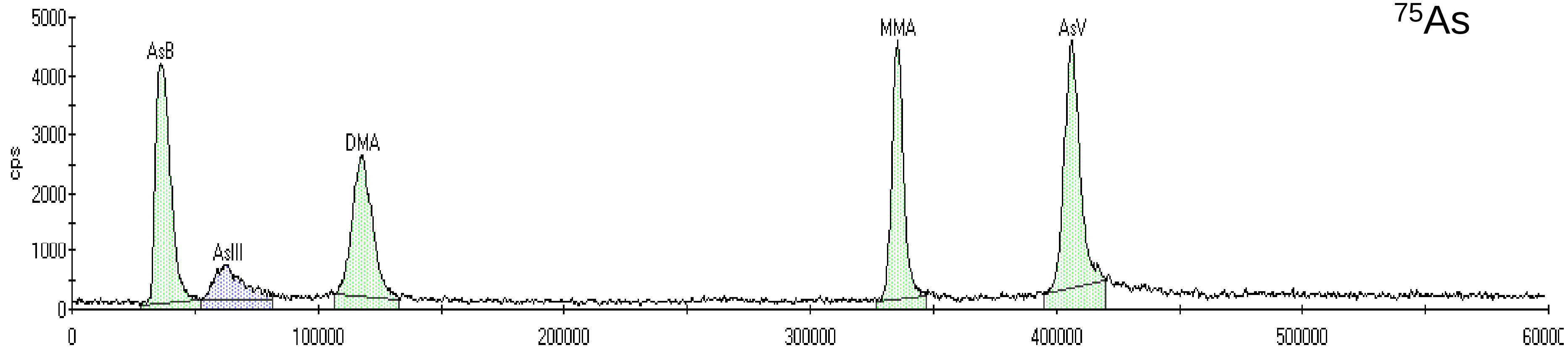
Other forms: Se(-II), Se(0), DMSe, DMDSe, $TMSe^{+}$, ...

Se supplementation: only the organic forms are biologically active

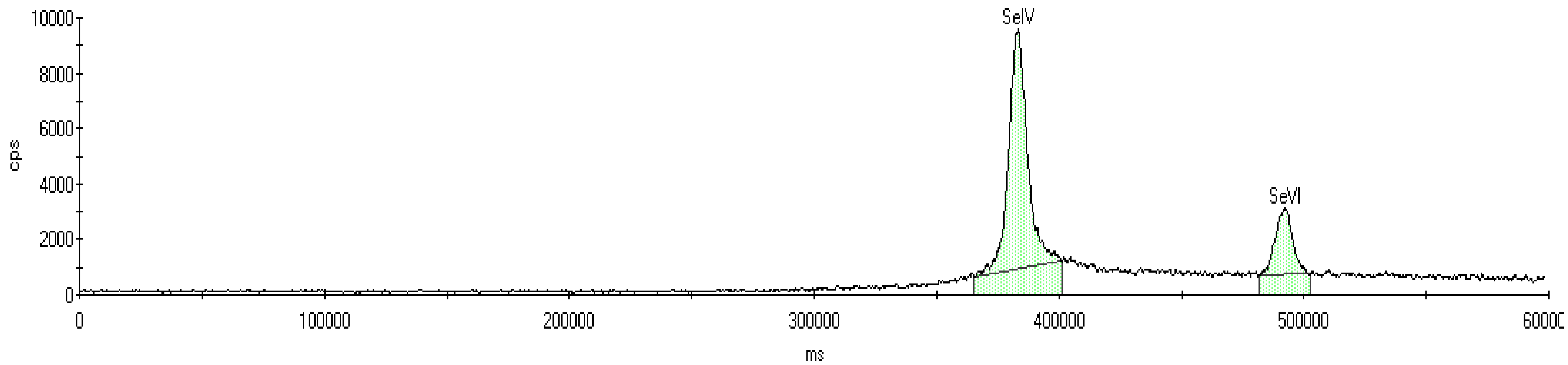
MLD: minimal lethal dose (death of one individual in a population)

IC/HPLC-ICP-MS – CCT mode

^{75}As



^{80}Se



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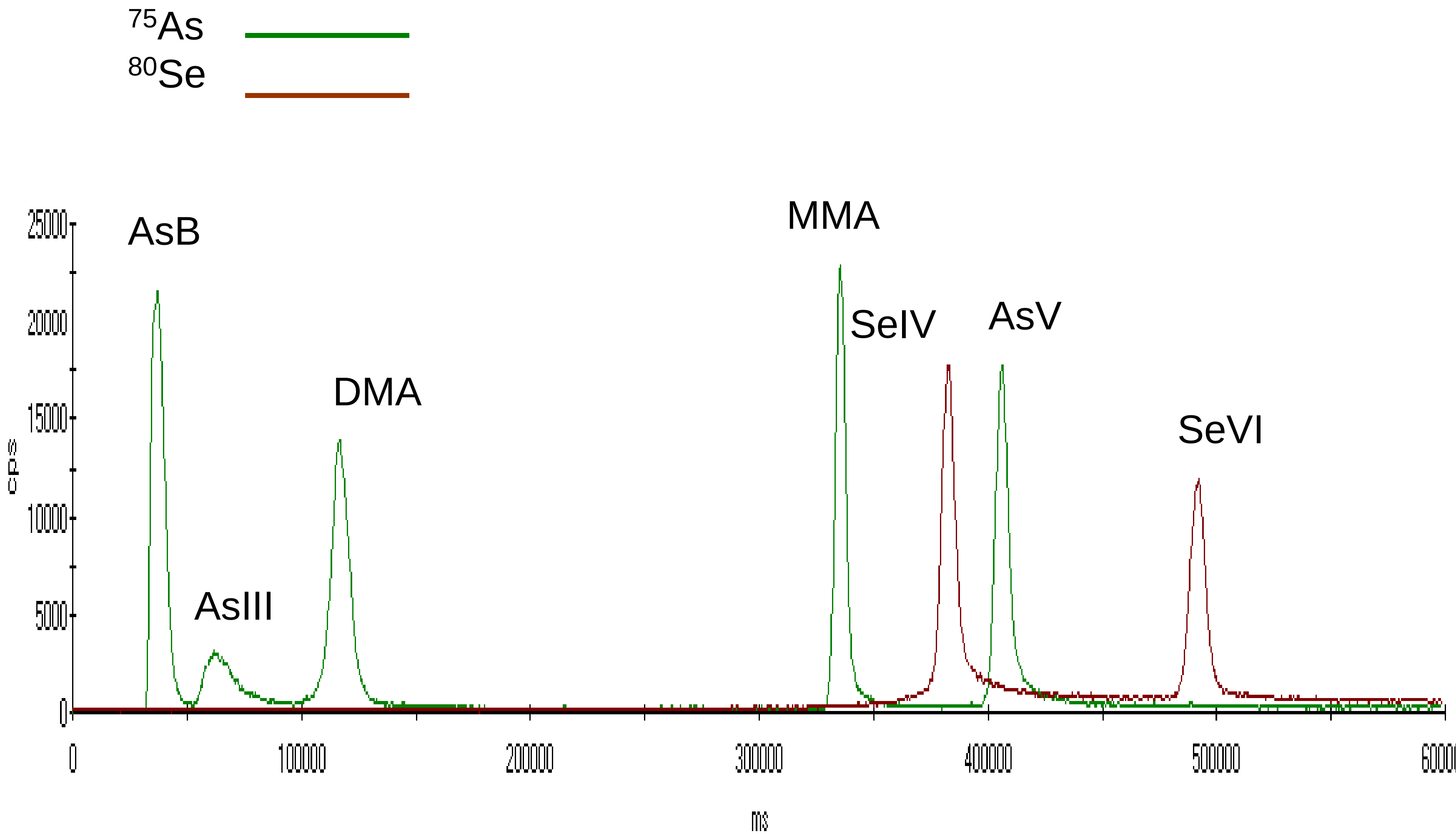
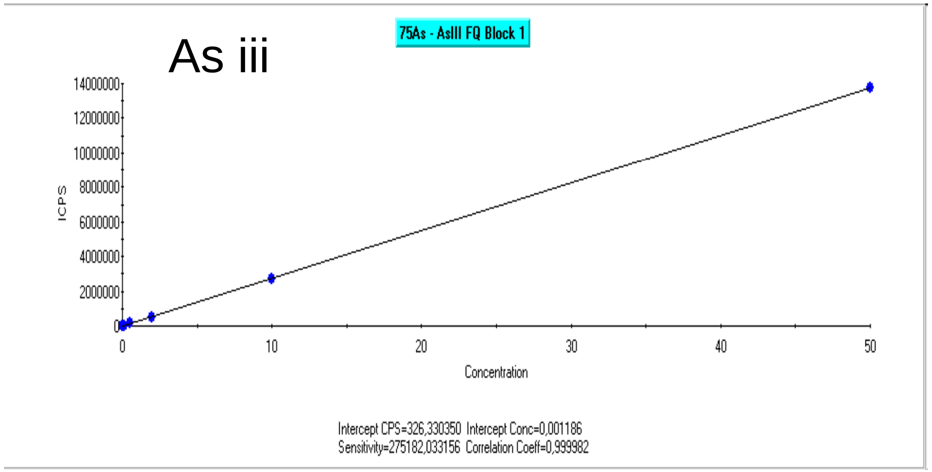
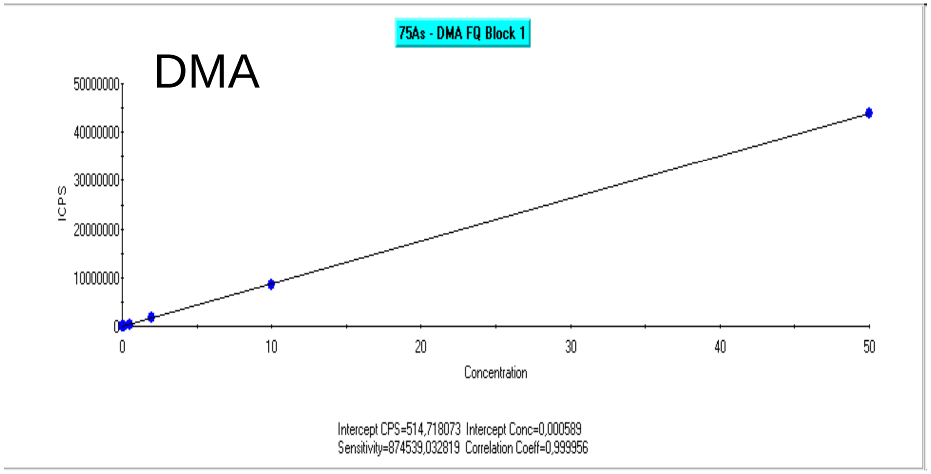
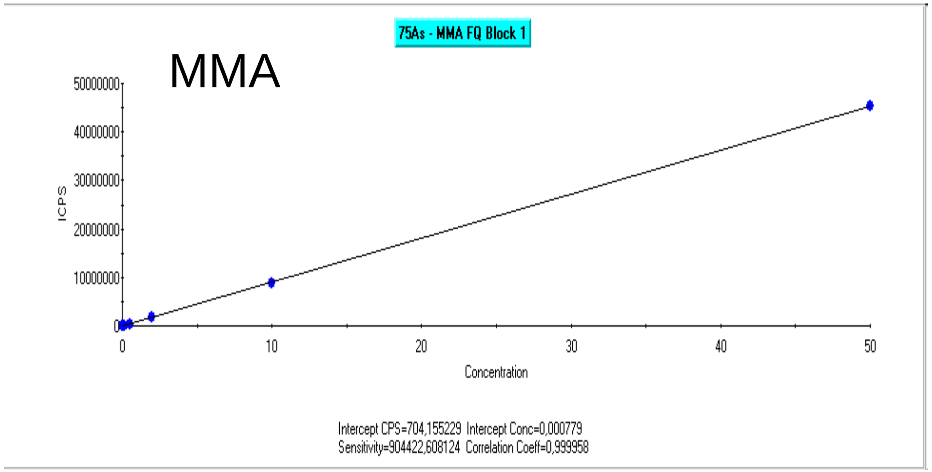
Overlaid ^{75}As and ^{80}Se Chromatograms for a 0.5 ppb Standard

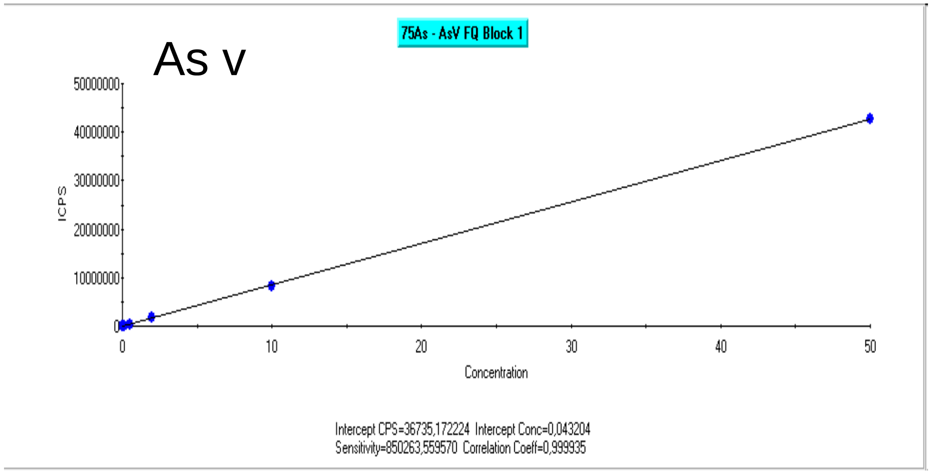


Fully Quantitative Calibration Curves for As-species









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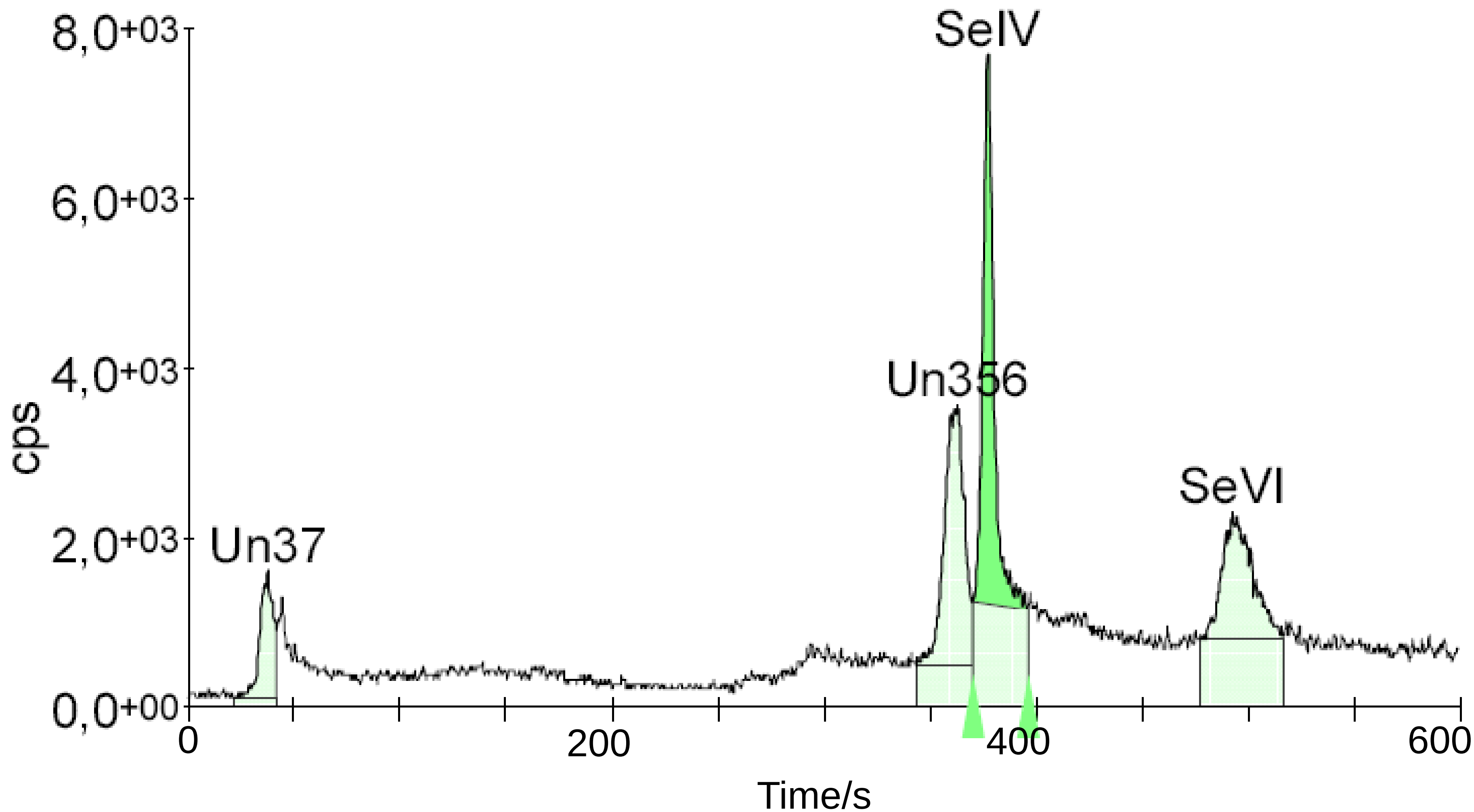
Aqueous Extracted Cooked King Prawn – ^{80}Se



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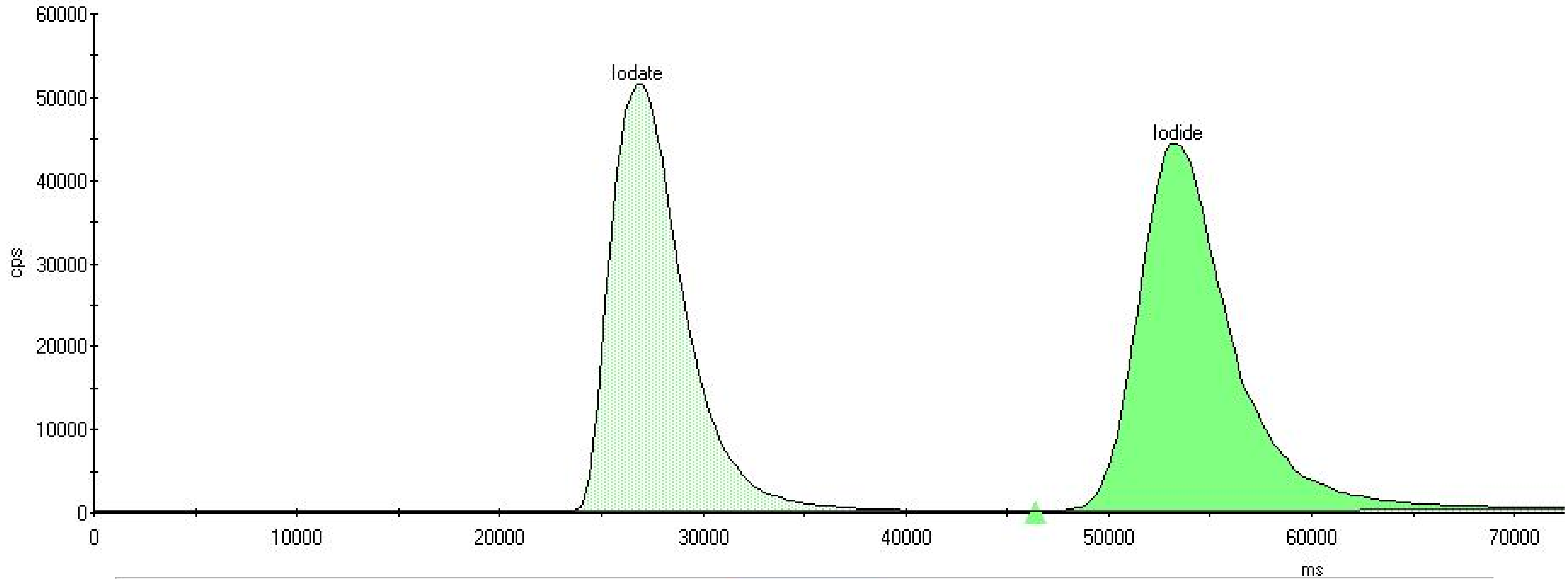
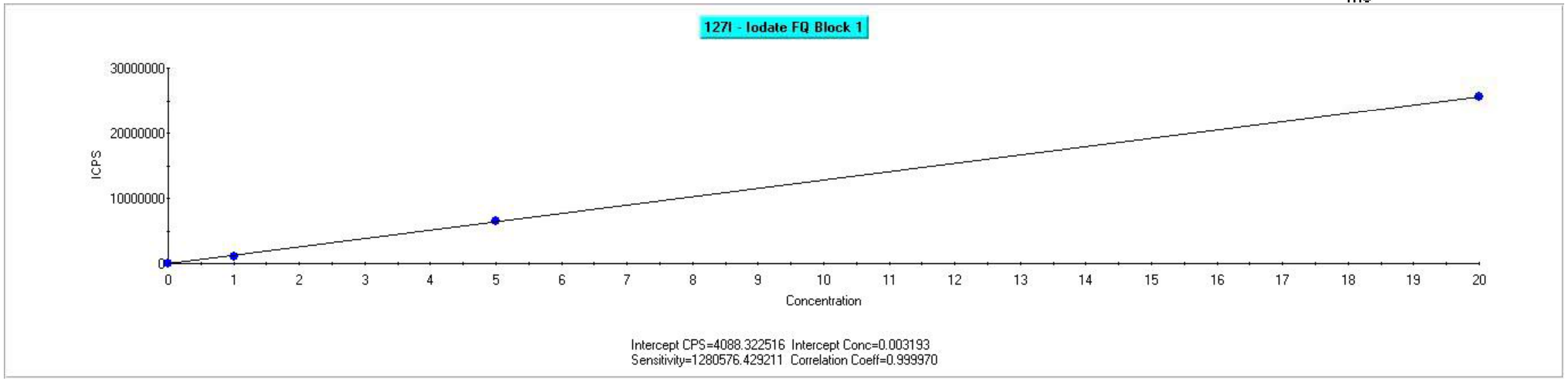
Future Capabilities: “New” Ions





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Conclusions

- Elemental speciation data can reveal valuable information in addition to total element concentrations:
  - bioavailability, mobility, metabolic processes, biotransformations and toxicity implications

- Elemental speciation using hyphenated ICP-MS is now a widely accepted routine analytical tool

- A single fast, reproducible and ultra sensitive IC-ICP-MS method for the multi-elemental speciation of both As and Se is possible