AAs, ICP-OES or ICP-MS

Which one is fitted for your Application

AA ICP ICPMS which technique should I use?

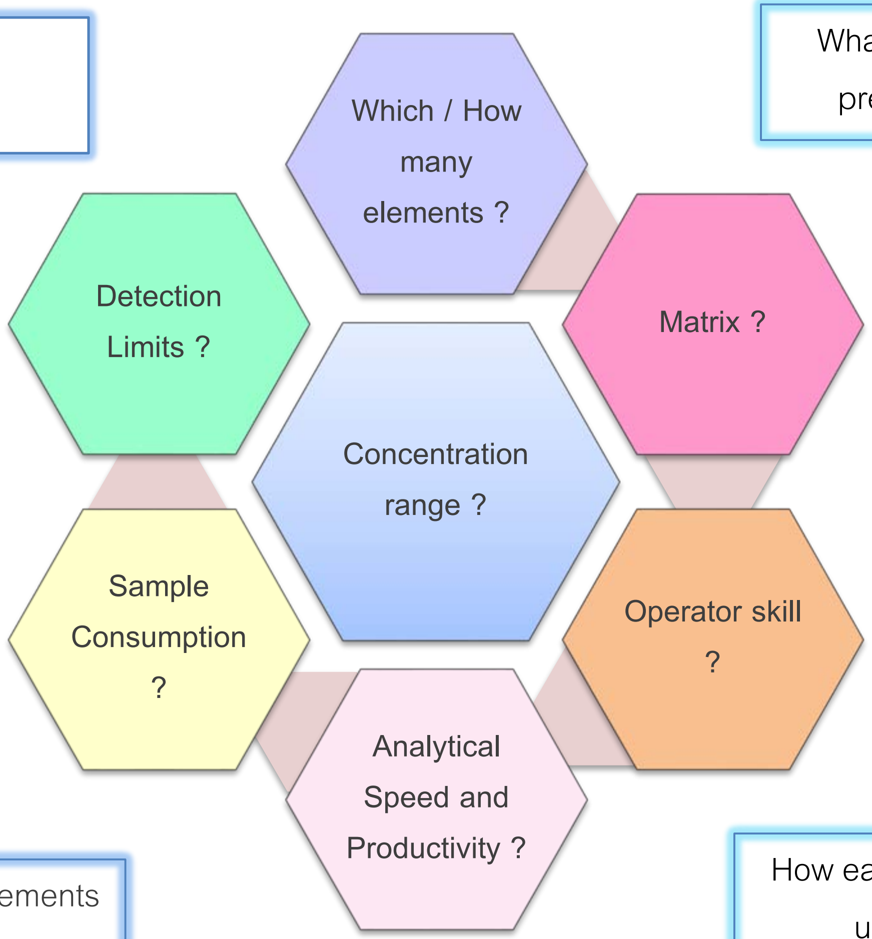
Which

technique?

AA ICP ICPMS which technique should I use?

Understanding how each technique works

What are the accuracy and precision requirements?



Which / How many elements ?

Detection Limits ?

Matrix ?

Concentration range ?

Sample Consumption ?

Operator skill ?

Analytical Speed and Productivity ?

Do I need to analyses multiple elements in a single sample?

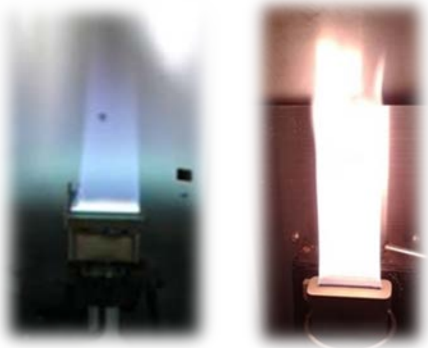
How easy is the instrument to set-up, maintain and run?

Understanding how each technique works

Atomic Absorption Spectrometry (FAAS)

- Air/acetylene or a nitrous oxide/acetylene flame is used to evaporate the solvent and dissociate the sample into its component atoms
- When light from a hollow cathode lamp (selected based on the element to be determined) passes through the cloud of atoms, the atoms of interest absorb the light from the lamp. This is measured by a detector, and used to calculate the concentration of that element in the original sample.

2600°C with the N_2O/acetylene flame



- Compounds of the alkali metals, and many of the heavy metals such as Pb or Cd and transition metals : Mn, Ni are all atomized with good efficiency with either flame type, with typical FAAS detection limits in the *sub-ppm range*.

☒ Refractory elements : V, Zr, Mo and B which do not perform well with a flame source, even with the N_2O/acetylene flame, is insufficient to break down compounds of these elements. As a result, flame AAS sensitivity for these elements is not as good as other elemental analysis techniques.

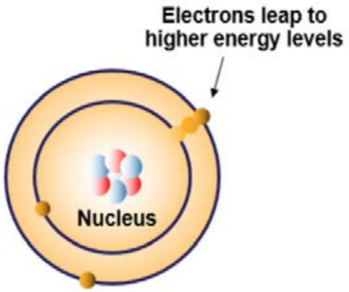


Figure 1. Excitation of an atom

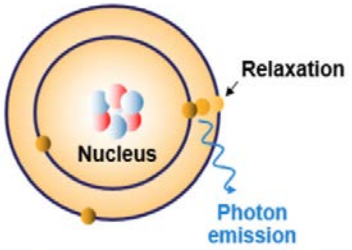
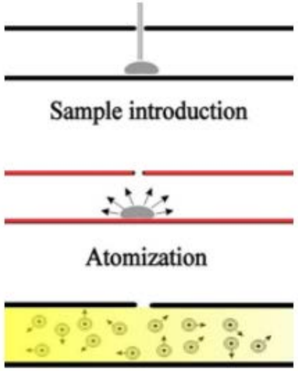


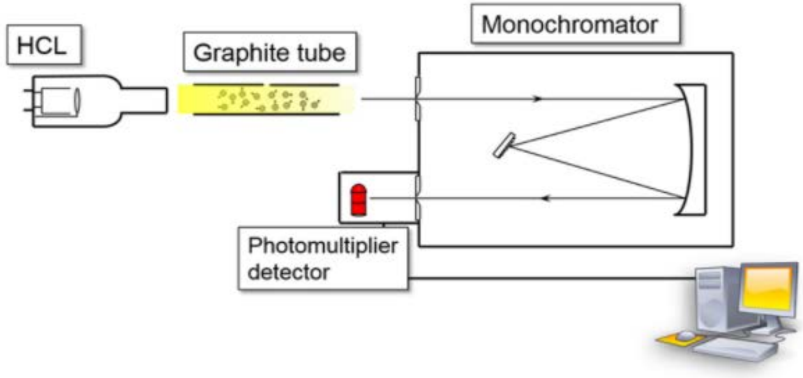
Figure 2. Relaxation and photon emission of an atom

Understanding how each technique works

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

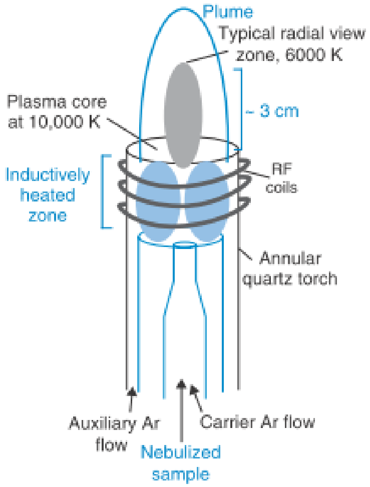
This technique is essentially the same as flame AA, except the flame is replaced by a small, electrically heated graphite tube, or cuvette, which is heated to a temperature up to 3000°C to generate the cloud of atoms. The higher atom density and longer residence time in the tube improve furnace AAS detection limits by a factor of up to 1000x compared to flame AAS, down to the *sub-ppb range*. However, because of the temperature limitation and the use of graphite cuvettes, refractory element performance is still somewhat limited.





Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

- A plasma will excite the atoms and ions that travel through it. When an atom or ion is excited, its electrons jump from a lower to higher energy level. Upon relaxation of these electrons to their initial 'ground' state, energy is emitted in the form of photons. The emitted photons possess wavelengths that are characteristic of their respective elements
- A detector measures the intensity of the emitted light, and calculates the concentration of that particular element in the sample
- Temperatures as high as 10,000°C, where even the most refractory elements are atomized with high efficiency. As a result, detection limits for these elements can be orders of magnitude lower with ICP than with FAAS techniques, typically at the 1-10 parts-per-billion level.
- Simultaneous ICP instruments can screen for up to 60 elements in a single sample run of less than one minute



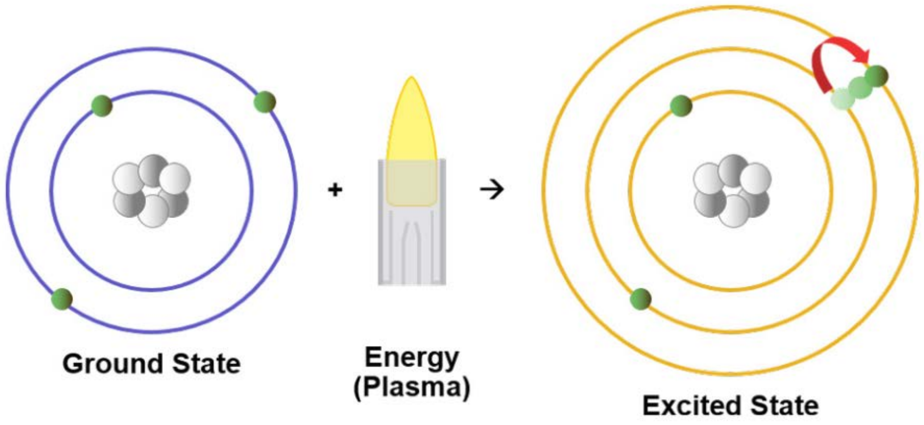
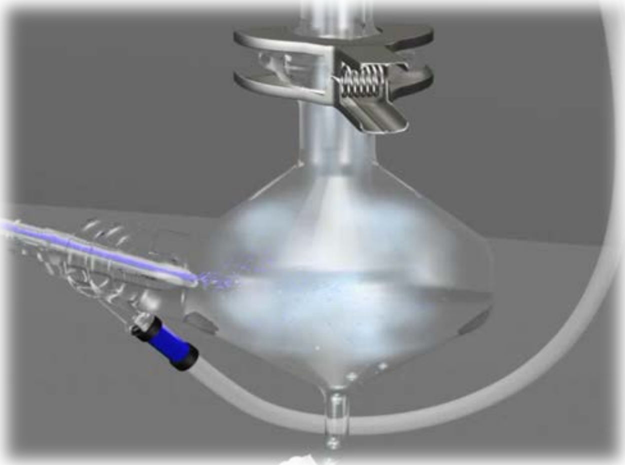
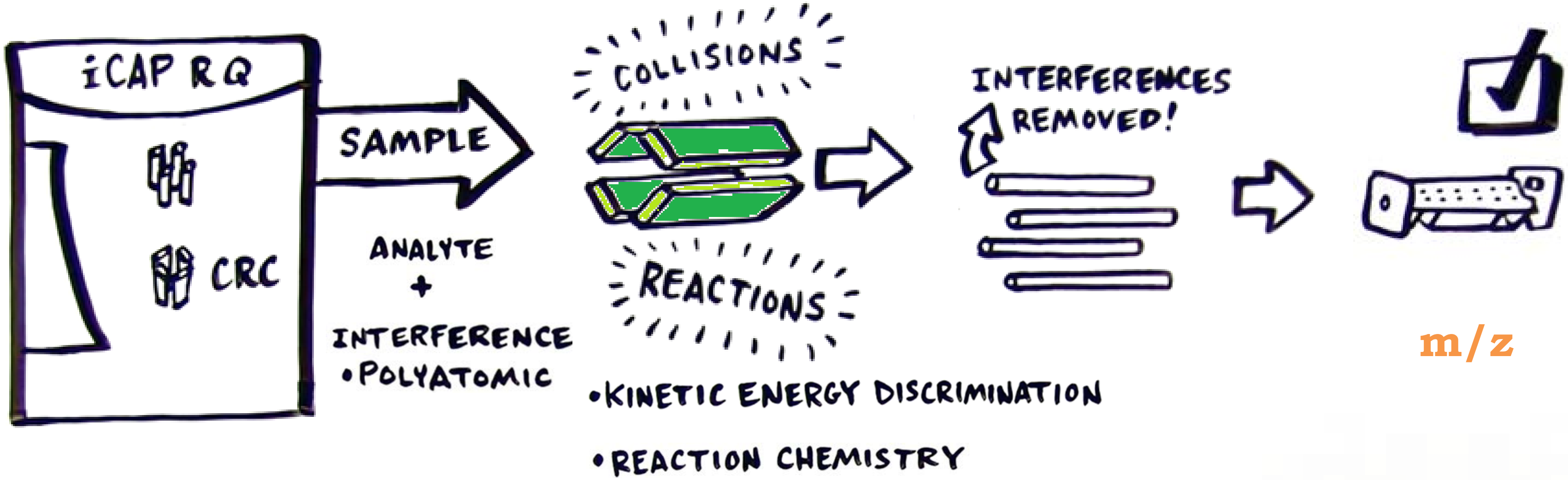
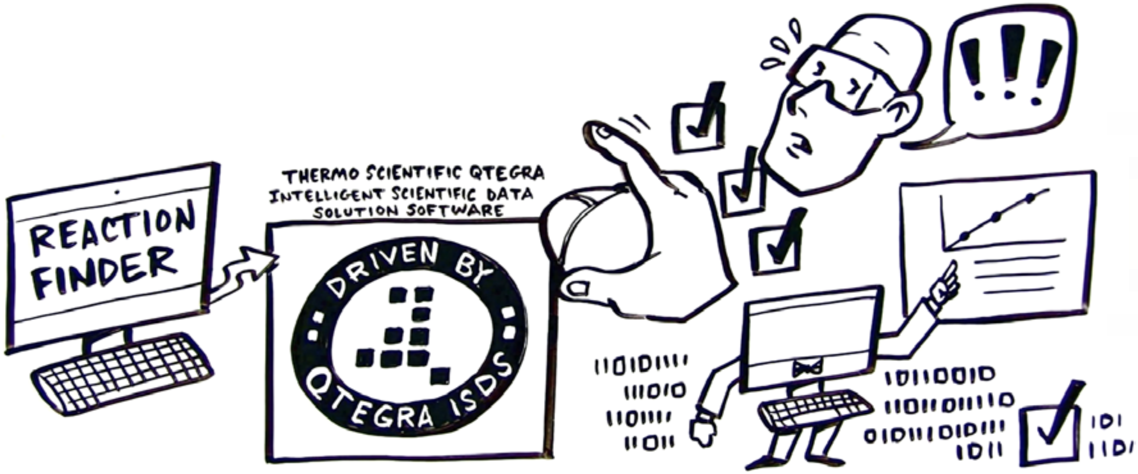


Figure 1. Excitation of an atom by a plasma.

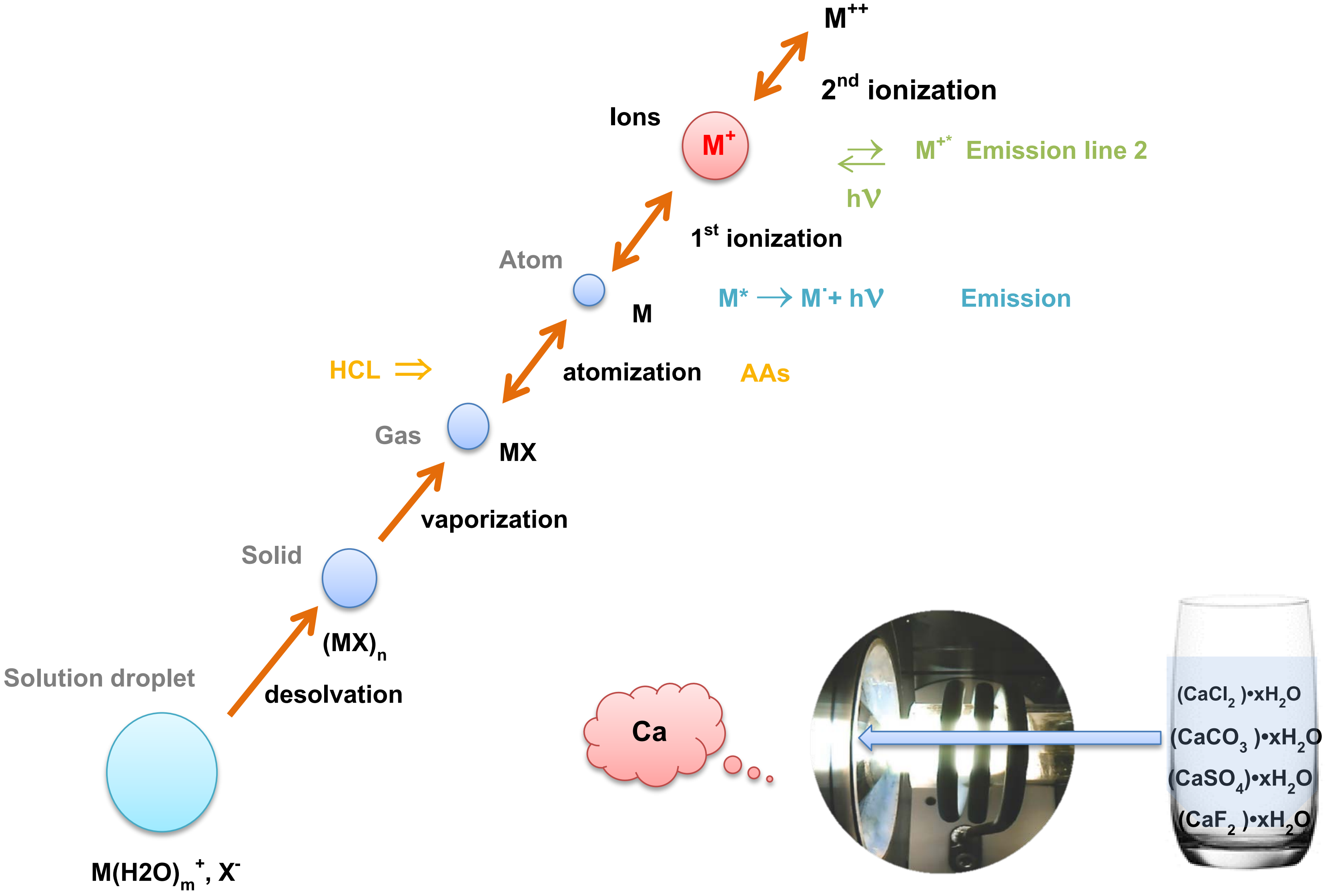


Inductively Coupled Plasma Mass Spectrometry (ICP-MS)





Atomization and Ionization



M^{++}

2nd ionization

Ions

M^{+}

$\rightleftarrows$ M^{+*} Emission line 2

$h\nu$

1st ionization

Atom

M

$M^* \longrightarrow M^{\cdot} + h\nu$ Emission

HCL $\Rightarrow$

atomization AAs

Gas

MX

vaporization

Solid

$(MX)_n$

desolvation

Solution droplet

$M(H2O)_m^{+}, X^{-}$

Ca

$(CaCl_2)\cdot xH_2O$

$(CaCO_3)\cdot xH_2O$

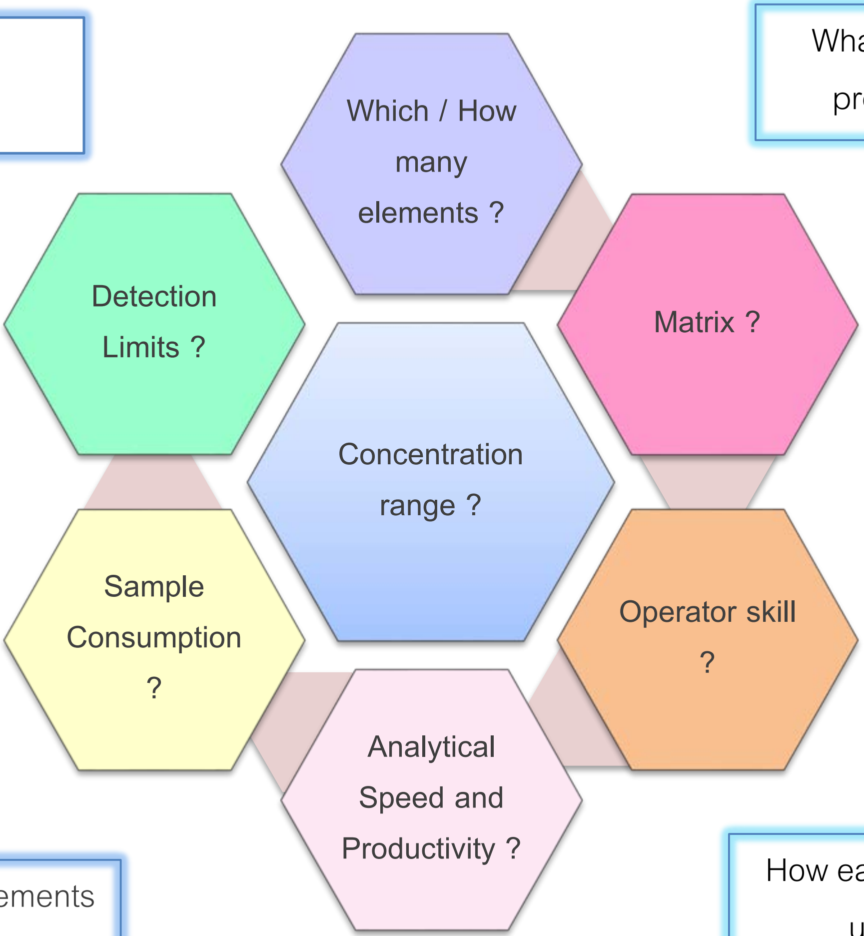
$(CaSO_4)\cdot xH_2O$

$(CaF_2)\cdot xH_2O$

AA ICP ICPMS which technique should I use?

Understanding how each technique works

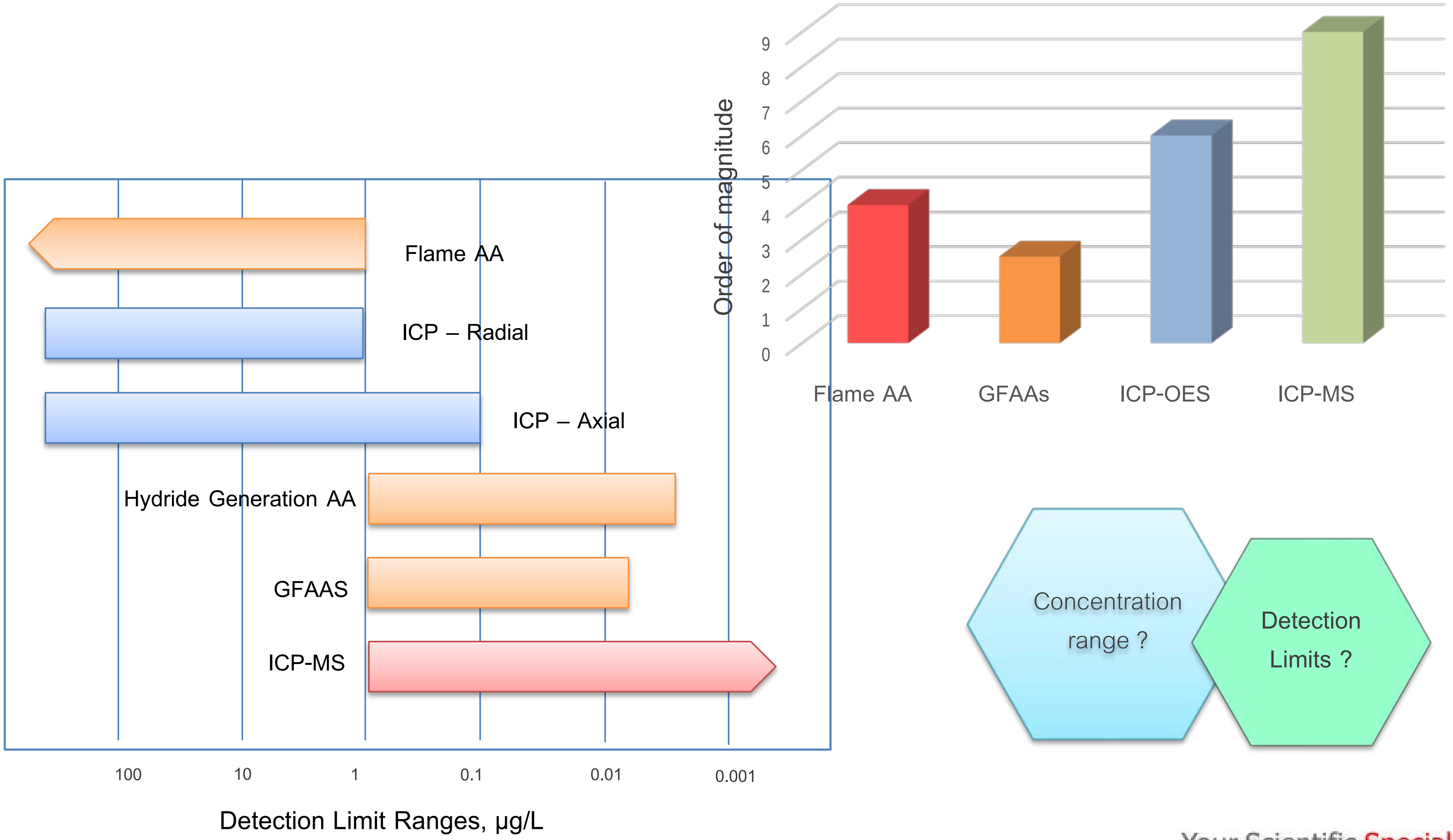
What are the accuracy and precision requirements?



Do I need to analyses multiple elements in a single sample?

How easy is the instrument to set-up, maintain and run?

Detection Limits and Dynamic range



Concentration range ?

Detection Limits ?

Detection Limits

Element	Flame AAS (ppb)	GFAAS (ppb)	ICP AES *(Radial)* (ppb)	ICP AES *(Axial)* (ppb)	ICP-MS *(Quad)* (ppt)
Ag	2	0.05	2	0.5	0.01-0.1
Al	30	0.25	6	1.5	0.1-10
As	300	0.33	12	2	1-10
Au	8	0.15	6	0.6	0.01-0.1
B	500	43	0.5	0.2	10-100
Ba	20	0.4	0.2	0.04	0.01-0.1
Be	1	0.025	0.2	0.06	0.1-1
Bi	50	0.3	18	2	0.01-0.1
C			50		
Ca	1	0.04	0.03	0.03	1-100
Cd	1.5	0.02	1	0.1	0.01-0.1
Ce	100,000		8		0.01-0.1
Co	5	0.5	2	0.5	0.1-1
Cr	6	0.025	2	0.4	0.1-1
Cs	4	0.3	3200		0.01-0.1
Cu	3	0.07	2	0.3	0.1-1
Dy	40	1.8	0.3		0.01-0.1
Er	35	3.8	0.7		0.01-0.1
Eu	1.5	0.8	0.3		0.01-0.1
Fe	6	0.06	1	0.3	0.1-100
Ga	65	23	7		0.1-10
Gd	2000		3		0.01-0.1
Ge	100	0.5	10		1-10
Hf	2000		4		0.01-0.1
Hg	145	18	9	1.2	1-10
Ho	60		0.5		0.01-0.1
In	40	0.3	18		0.01-0.1
Ir	500	4	4		0.01-0.1
K	2	0.02	6.5	0.5	0.1-100
La	2000		0.02		0.01-0.1
Li	2	0.1	1		0.01-1
Lu	300		0.05		0.01-0.1
Mg	0.3	0.01	0.1	0.03	0.1-1
Mn	2	0.03	0.3	0.05	0.1-1
Mo	20	0.14	4	0.5	0.01-0.1
Na	0.3	0.05	1	0.2	0.1-100

Element	Flame AAS (ppb)	GFAAS (ppb)	ICP AES *(Radial)* (ppb)	ICP AES *(Axial)* (ppb)	ICP-MS (ppt)
Nb	2000		4		0.01-0.1
Nd	850		2		0.01-0.1
Ni	10	0.24	6	0.4	0.1-10
Os	100		5		0.01-0.1
P	4000	100	18	13	>1,000
Pb	10	0.04	14	1	0.01-0.1
Pd	10	0.5	2		0.01-0.1
Pr	5000		0.8		0.01-0.1
Pt	75	4.5	20		0.01-0.1
Rb	5	0.06	35		0.01-0.1
Re	800		11		0.01-0.1
Rh	3	0.4	5		0.01-0.1
Ru	100	0.75	4		0.01-0.1
S			20	28	>1,000
Sb	40	0.35	18	2	0.01-0.1
Sc	30		0.2	0.05	1-10
Se	500	0.65	20	5	1-100
Si	200	0.8	5	2	>1,000
Sm	750		7		0.01-0.1
Sn	95	0.6	0.1	0.01	0.01-0.1
Sr	2	0.1	0.1	0.01	0.01-0.1
Ta	1500		9		0.01-0.1
Tb	700	0.2	5		0.01-0.1
Te	30	0.5	27		1-10
Th			17		0.01-0.1
Ti	70	1.6	0.6	0.09	0.1-1
Tl	20	0.75	16	3	0.01-0.1
Tm	20		1.5		0.01-0.1
U	40000		3.5	0.4	0.01-0.1
V	50	0.7	2	0.5	0.01-10
W	750		17		0.01-0.1
Y	350		0.2		0.01-0.1
Yb	4	0.15	0.3		0.01-0.1
Zn	1.0	0.0075	1	0.06	0.1-10
Zr	1500		0.8		0.01-0.1

3 sigma detection limits in deionized water.

Precision

"Precision" is a measure of the confidence you can have in your measured results

Technique	Precision
Flame AAS	Short term : 0.1-1.0% Long term : 1-2% (2beam optic)
GFAAS	Short term 0.5-5% Long term : highly dependent on the tube type and condition
ICP-OES	Short term : 0.1-2% Long term : <1-5%
ICP-MS	Short term : 0.5-2% Long term : <4%

- Long-term precision in any of the techniques can be improved by more frequent instrument calibration or drift correction techniques. precision.
- The use of internal standardization can significantly improve precision in ICP and ICPMS

Speed of Measurement

- How many samples can a particular technique analyze in a given time?
- How many elements can be determined?

Analytical Speed and Productivity ?

Which / How many elements ?

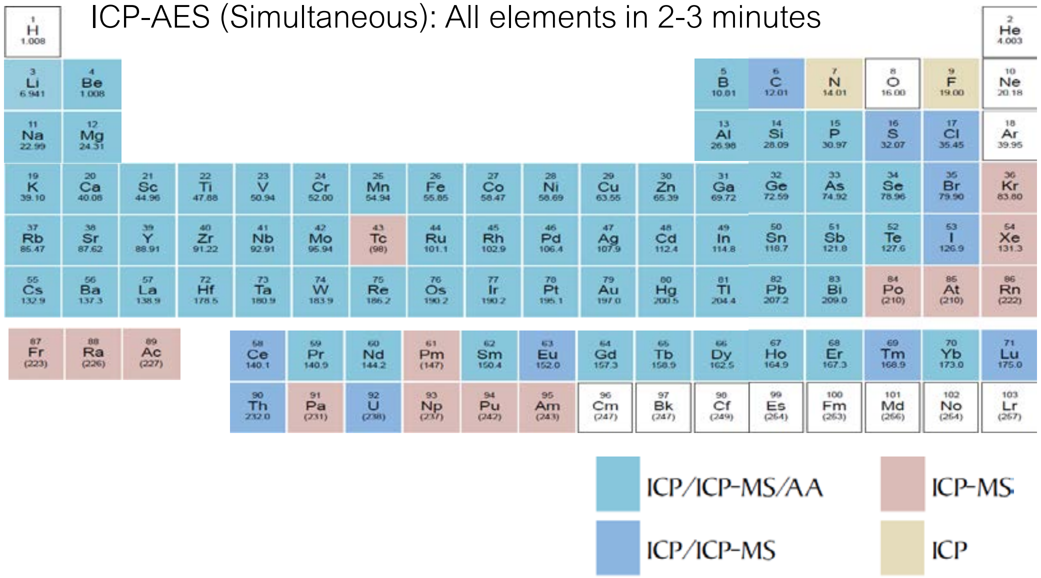
Sequential

- ICP-AES (Sequential): 5-6 elements per minute for each sample
- FAAS: 4 seconds per element for each sample
- GFAAS: 2-3 minutes per element for each sample

Simultaneous

ICP-MS: All elements in 2-3 minutes

ICP-AES (Simultaneous): All elements in 2-3 minutes



- For less than 5 elements per sample, FAAS is often the quickest technique, depending on the total number of samples.
- For 5-15 elements, sequential ICP-AES is the optimum choice.
- Above 15 elements, either ICP-MS or simultaneous ICP-OES is the best choice.
- GFAAS will always be the slowest of the techniques

Operating cost

FAAS

- acetylene/nitrous oxide gases
- compressed air source
- hollow cathode lamps
- reagents and standards
- power

GFAAS

- argon gas
- hollow cathode lamps
- graphite tubes and cones
- reagents and standards
- power
- cooling wa

ICP-OES

- argon gas
- quartz torches
- reagents and standards
- pump tubing
- power
- cooling water

ICP-MS

- argon gas
- quartz torc
- sampling and skim s
- reagents and stan
- pump tubing
- power
- cooling water

Summary of elemental analysis techniques

	Flame AAS	GFAAS	ICP-AES	ICP-MS
Detection limits	Very good for some elements	Excellent for some element	Very good for most elements	Excellent for most element
Sample throughput	10-15 secs per element	3-4 mins per element	1-60 element/minute	All elements/1 min
Dynamic range	10^3	10^2	10^6	10^{10}
Precision				
Short term Long term	0.1-1% 1-2% (2-beam)	0.5-5% 1-10%	0.1-2.0% 1-5%	0.5-2% 2-4%
Dissolved solids in sol	0.5-5%	>20% (Slurries)	0-20%	0.1-0.4%
Element applicable to	68+	50+	73	82
Sample volume required	Large	Very small	Medium	Very small to medium
Semi-Quantitative analysis	No	No	Yes	Yes

Summary of elemental analysis techniques

	Flame AAS	GFAAS	ICP-AES	ICP-MS
Ease of use	Very easy	Moderately easy	Easy	Moderately easy
Method development	Easy	Difficult	Moderately easy	Difficult
Capital costs	Low	Medium to high	High	Very high
Running costs	Low	Medium	High	High
Cost per elemental analysis				
High volume – few elements	Low	High	Medium	Medium
High volume – many elements	Medium	High	Low-Medium	Low-Medium

Field	Typical Applications	Commonly used Techniques		
		AA	ICP-OES	ICP-MS
Environmental	Water	⬜	🟨	🟥
	Soil	⬜	🟥	🟨
	Air	🟨	⬜	🟨
Food	Food safety	🟧	🟧	🟧
	Nutritional labeling	🟥	🟥	⬜
Pharmaceutical	Drug / Clinical	⬜	🟨	🟥
Petrochemical	Petroleum refining	🟥	🟥	🟥
	Lubricants and oil	⬜	🟥	⬜
Chemical / Industrial	QC/Product testing	🟨	🟥	🟨
Agriculture	Soil	🟧	🟥	⬜
Geochemical/Mining	Exploration	🟧	🟥	🟥
	Research	⬜	🟥	🟥
Bio-monitoring	Biological Fluids	🟨	⬜	🟥
Semiconductor	Wafers	⬜	⬜	🟥
	High-Purity Chemicals	🟨	⬜	🟥
Nuclear Energy	Low-level waste	⬜	🟨	🟨
	Process water	⬜	🟨	🟨
Renewable Energy	Biofuels	⬜	🟥	🟥
	Solar panels	⬜	🟥	🟨
Nano materials	Research	🟧	⬜	🟨

Frequency of Technique Used

⬜ 🟧 🟨 🟥

→

Applications

Which Instrument would you recommend for analysis of Trace Elements in Honey?

- Honey is predominantly fructose and glucose, combined with a mixture of other natural ingredients such as organic acids and enzymes. It also contains a small percentage of metals, including potassium, sodium, magnesium and calcium.
- The metal composition is geographically significant, as the majority of metals in honey are transferred from the soil to the plant or flower.
- Metals can also be transferred from other sources such as water aerosol spray and atmospheric pollution.

- The viscous and sugary nature of honey makes it a difficult substance for quantitative trace elemental analysis.
- Standards may require matrix matching to take into account the change in viscosity
- Acid digestion can be used to remove the organic material from the sample prior to dilution with water.

Application Notes 43060

The Analysis of Trace Elements in Honey by Flame and Graphite Furnace Atomic Absorption Spectrometry

Rebecca Price, Thermo Fisher Scientific, Cambridge, UK

Key Words
Atomic Absorption, Flame, Deuterium, Graphite Furnace, Honey, Zeeman

Key Benefits

- The robust flame sample introduction system allows dissolved honey samples to be run without blockage or contamination.
- The advanced furnace autosampler speeds up analysis by automatically preparing the working standards from a single master standard.
- The permanently aligned true dual atomizer enables rapid switching between flame and furnace methods.
- Deuterium and Zeeman background correction offer a flexible solution for the analysis of challenging matrices such as honey.

Summary

The Thermo Scientific iCE 3500 Atomic Absorption Spectrometer is the ideal solution for the analysis of major, minor and toxic elements in honey. The permanently aligned true dual atomizer allows robust and reliable analysis of major elements by flame, followed by accurate and precise determination of minor and toxic elements by graphite furnace.

Introduction

Honey is a sweet and viscous substance produced from the nectar and secretions of plants and flowers. The nectar is transported to a beehive by honey bees, where worker bees then add enzymes to create honey. Most honey is created from a variety of plants and flowers, though in some areas, where a particular plant or flower is in abundance, monofloral honey can be produced, and this is particularly valuable. Honey is typically advertised to the consumer by floral source or geographical location, however many honey products are blended from a variety of sources. This has resulted in a global market with hundreds of types of honey, each with unique taste, color and crystallization properties. In the EU, honey must adhere to strict composition criteria, including sugar, moisture and hydroxymethylfurfural (HMF) content.[1]

Sugar is often substituted with honey in the making of cake products. Not only is honey sweeter than sugar, and therefore used as a sugar alternative, it is also hygroscopic. This causes it to attract and hold water, resulting in deliciously moist baking products. Honey is predominantly fructose and glucose, combined with a mixture of other natural ingredients such as organic acids and enzymes. It also contains a small percentage of metals, including potassium, sodium, magnesium and calcium. The metal composition is geographically significant, as the majority of metals in honey are transferred from the soil to the plant or flower from which the nectar is collected. Metals can also be transferred from other sources such as water aerosol spray and atmospheric pollution. The metal profile of honey is therefore significantly important on three levels – for evidence of provenance, nutritional benefit and toxicological implications.

Thermo
SCIENTIFIC

Analysis of Trace Elements in Honey by AAs

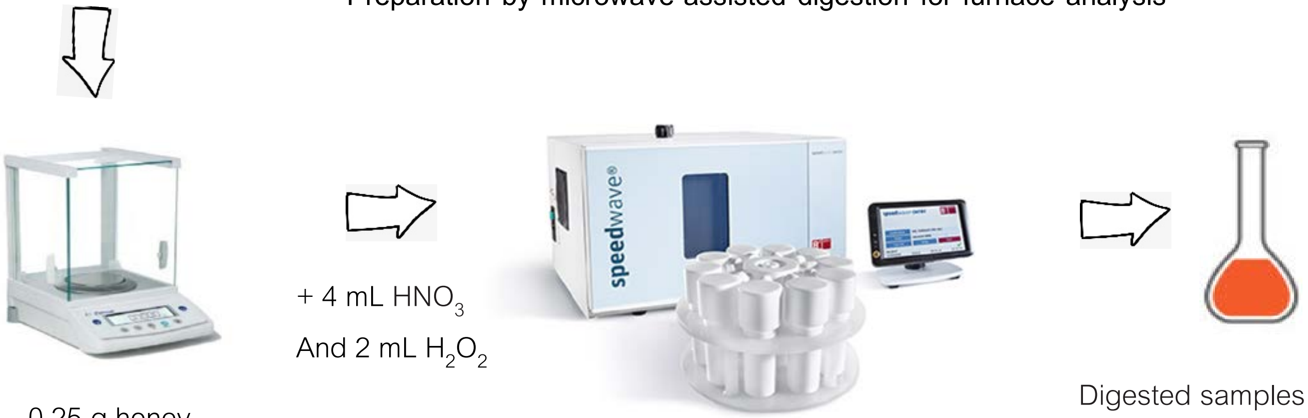
Preparation for Flame analysis

60 °C

1 g honey

diluted to 100 g with 1% HNO_3

Preparation by microwave-assisted digestion for furnace analysis



0.25 g honey

+ 4 mL HNO_3

And 2 mL H_2O_2

Digested samples were quantitatively transferred to 100 ml volumetric flasks

Analysis of Trace Elements in Honey by AAs

Flame method

Spectrometer Parameter	Magnesium	Sodium
Flame type	Air/Acetylene	
Fuel flow l/min	1.0	
Burner height / mm	8.6	6.2
Wavelength / nm	285.2	589.0
Bandpass / nm	0.2	
Background correction	Deuterium	None
Measurement time / s	4	
Number of resamples	3	
Calibration type	Segmented curve fit	

Furnace method

Spectrometer Parameter	Cadmium	Lead
Wavelength / nm	228.8	217.0
Cuvette	Electrographite	ELC (Extended Life Cuvette)
Dry temperature / °C	100	
Ash temperature / °C	800	
Atomize temperature / °C	1000	1200
Bandpass / nm	0.5	
Background correction	Zeeman	
Signal measurement	Transient Height	
Number of resamples	3	
Calibration type	Quadratic least squares fit	

Sample	Concentration in original honey sample / ppm	
	Magnesium	Sodium
Spanish Orange Blossom	9.26	16.9
Australian Eucalyptus	25.33	94.08
Brazilian Pure Set	25.14	42.83
	Spiked Honey	
Measured concentration in solution / ppm	0.196	0.187
% Recovery	96	92

Results

- Analysis by flame took only 12 seconds for a triplicate reading on a single sample .
- Cd and Pb were not detected in analyzed honey samples.
- Honey sample was prepared with a spike equal to 5 ppb in the diluted sample.

	Cadmium	Lead
Measured concentration in solution / ppb	4.66	5.49
% Recovery	93	110

Which Instrument would you recommend for analysis of Cadmium in Chocolate ?

Cadmium is a heavy metal used in a variety of applications, such as steel plating, as a pigment in plastics and glasses, and in the production of batteries. These industrial activities are the main route through which cadmium is released into the environment where it accumulates in water and soil, and subsequently plants, animals and fish through uptake and ingestion. One of the main routes of human exposure to cadmium is therefore through the ingestion of foodstuffs.

- Typical maximum levels of cadmium in foodstuffs are currently between *0.05 – 0.2 mg/kg* wet weight.
- The main ingredients in chocolate consist of cocoa, milk and fats, each of which is a potential source of cadmium.

Sample Preparation

0.3 g

+ 7 mL HNO_3 + 1 mL H_2O_2

Left to stand for 5 mins

diluted to 100 ml with DI water

1 mg/l cadmium sub-standard was prepared in deionised water for spiking of samples prior to digestion

Analysis of Cadmium in Chocolate by GFAAS

- 10 μg/l sub-standard was made up in 7% nitric acid and 1% hydrogen peroxide to matrix match to the digested samples.
- Blank and diluent were also prepared at 7% nitric acid and 1% hydrogen peroxide.
- A matrix modifier : 2 g/l of ammonium nitrate
- Cadmium was analyzed at 228.8 nm and Zeeman background correction

Furnace Method

Phase	Temperature / °C	Time / s	Ramp / °C/s
Dry	110	30	10
Ash	400	20	150
Atomize	1300	3	0
Clean	2500	3	0

Results for the analysis of cadmium in chocolate following analysis by GFAAS

Sample	Measured Concentration μg/l	Concentration in original sample mg/kg	Calculated Recovery Spiked / %
USA Origin, Milk	0.030	0.010	
USA Origin, Milk, Spiked	5.095		101
UK Origin, Milk	0.038	0.012	
UK Origin, Milk, Spiked	5.182		103
USA Origin, Dark	0.124	0.042	
USA Origin, Dark, Spiked	4.761		93

Analysis of toxic elements in drinking and bottled waters

China and India have seen a huge increase in the consumption of bottled water in the last decades

Chinese regulations:

GB 8537–2008 - Drinking natural mineral water

GB 17324–2003 - Hygienic standard of bottled purified water for drinking

GB 5749–2006 - Standards for drinking water quality

GB 3838–2002 - Environmental quality standard for surface water

Indian regulations:

IS 10500:2012 - Drinking Water

IS 13428:2005 - Packaged natural mineral water

IS 14543:2004 - Packaged drinking water (other than packaged natural mineral

Table 1. Maximum permissible levels in $mg \cdot kg^{-1}$.

Element	GB 8537-2008	GB 17324-2003	GB 5749-2006	GB 3838-2002 (I)[1]	IS 10500:2012	IS 13428:2005	IS 14543:2004
Arsenic	0.01	0.01	0.01	0.05	0.01	0.05	0.05
Cadmium	0.003	-	0.005	0.001	0.003	0.003	0.01
Chromium*	0.05	-	0.05	0.01	0.05	0.05	0.05
Copper	1	0.01	1	0.01	0.05	1	0.05
Iron	-	-	0.3	0.3	0.3	-	0.1
Lead	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mercury	0.001	-	0.001	0.00005	0.001	0.001	0.001
Nickel	0.02	-	0.02	0.02	0.02	0.02	0.02
Zinc	0.2	-	1	0.05	5	5	5

Analysis of toxic elements in drinking and bottled waters by ICP-OES

Thermo Scientific™ iCAP™ 7200 ICP-OES Duo with Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software

- Tap water sample from Dingpu river area, Shanghai
- Tap water sample from Jinqiao lake area, Shanghai
- Waterman (packaged drinking water)
- Nestle (natural mineral water)
- Evian (natural mineral water)

- Samples did not require any pre-treatment
- Samples were analyzed directly after preservation in 0.5% AR grade nitric acid (HNO_3)

Parameter	Setting
Pump Tubing	Sample Tygon® orange/white Drain Tygon® white/white
Pump Speed	45 rpm
Nebulizer	Glass concentric
Nebulizer Gas Flow	0.19 MPa
Spray Chamber	Glass cyclonic
Auxiliary Gas Flow	0.5 L·min^{-1}
Coolant Gas Flow	12 L·min^{-1}
Center Tube	2 mm
RF Power	1150 W
Plasma View	Axial
Exposure Time	5 s

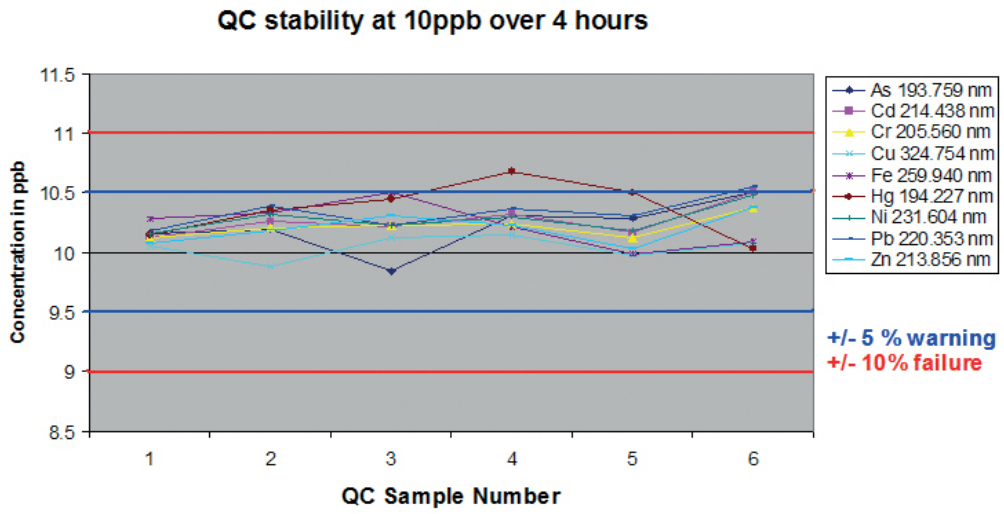
Analysis of toxic elements in drinking and bottled waters by ICP-OES

Averaged results and method detection limits in µg·kg-1.

Element and wavelength (nm)	MDL	Dingpu River	Jinquiao Lake	Waterman	Nestle	Evian
As 193.759	2.14	<DL	1.27	<DL	<DL	<DL
Cd 214.438	0.07	<DL	<DL	<DL	<DL	<DL
Cr 205.560	0.21	<DL	<DL	<DL	<DL	<DL
Cu 324.754	0.39	<DL	1.52	<DL	<DL	<DL
Fe 259.940	0.25	1.14	1.53	0.41	0.78	0.74
Hg 194.227	0.66	<DL	<DL	<DL	<DL	<DL
Ni 231.604	0.36	1.05	0.57	<DL	<DL	<DL
Pb 220.353	1.06	<DL	<DL	<DL	<DL	<DL
Zn 213.856	0.19	<DL	<DL	<DL	<DL	<DL

✓ All QC recoveries were within 10%

Stability of the 10 µg·kg-1 QC check over 4 hours



Analysis of trace elements in naphtha

- The analysis of trace elements in naphtha is important in petrochemical industry, especially in the cracking of hydrocarbons. The presence of trace elements can severely hamper this process as well as poison the catalysts used
- As can poison catalysts at trace concentrations (as low as 50 μg·kg-^{1}).
- As can cause problems with high temperature naphtha cracking tubes due to the formation of coke build-up.
- This build-up can result in the eventual failure of the tubes and subsequently reduce the production capabilities.
- Arsenic free naphtha is also the preferred feedstock for a number of downstream processes such as catalytic reforming, gasoline blending, and C5 and C6 isomerization.
- These processes are using platinum and palladium catalysts where the presence of arsenic would cause serious problems, poisoning the catalysts.

thermoscientific

Analysis of trace elements in naphtha using the Thermo Scientific iCAP 7000 Plus Series ICP-OES

Analysis of trace elements in naphtha using the ICP-OES

- Interferences from carbon based emissions can be reduced by optimizing the radial viewing height.
- IsoMist™ is a Peltier cooled spray chamber which was used in conjunction with a glass concentric nebulizer for this analysis : -10 °C

Parameter	Setting
Pump Tubing (Standard Pump)	Sample Solvent Flex orange/white Drain Solvent Flex white/white
Pump Speed	40 rpm
Nebulizer	Glass concentric
Nebulizer Gas Flow	0.45 $L\cdot min^{-1}$
Auxiliary Gas Flow	1.5 $L\cdot min^{-1}$
Coolant Gas Flow	12 $L\cdot min^{-1}$
Center Tube	1.5 mm
RF Power	1150 W
Radial Viewing Height	8 mm
Exposure Time	UV 15 s, Vis 5 s

Sample and standard preparation

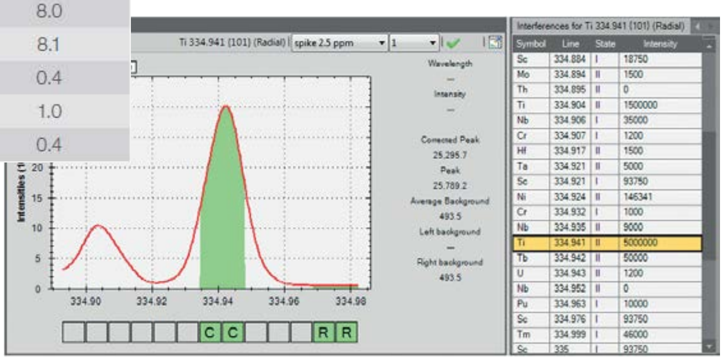
Solution	Concentration ($mg\cdot kg^{-1}$)		
	S-21+K	As	Hg
Low standard	0.96	0.95	0.97
High standard	4.88	4.90	4.89
Spike	2.34	2.37	2.36

Plasma aspirating naphtha after auxiliary and nebulizer gas flows have been optimized.

Analysis of trace elements in naphtha using the ICP-OES

Element and wavelength (nm)	Spike concentration (mg·kg⁻¹)	Measured spike concentration (mg·kg⁻¹)	Spike recovery (%)	RSD on three replicates of the spike (%)	MDL (µg·kg⁻¹)
Ag 328.068	2.34	2.44	104	1.36	3.4
Al 396.152	2.34	2.46	105	1.20	7.9
As 189.042	2.37	2.39	101	0.25	7.4
B 208.893	2.34	2.44	104	0.58	13
Ba 455.403	2.34	2.40	103	0.86	0.2
Ca 393.366	2.34	2.44	104	0.33	0.1
Cd 228.802	2.34	2.37	101	0.28	0.6
Cr 267.716	2.34	2.34	100	0.57	1.0
Cu 324.754	2.34	2.44	104	1.15	1.3
Fe 259.940	2.34	2.34	100	0.35	1.9
Hg 184.950	2.36	2.38	101	0.44	2.7
Mg 279.553	2.34	2.39	102	0.22	0.04
Mn 257.610	2.34	2.34	100	0.38	0.3
Mo 202.030	2.34	2.35	100	0.19	2.7
Na 589.592	2.34	2.43	104	1.43	10
Ni 221.647	2.34	2.30	98	0.32	1.6
P 178.284	2.34	2.36	101	0.19	11
Pb 220.353	2.34	2.27	97	0.12	7.6
Si 212.412	2.34	2.39	102	0.46	8.0
Sn 189.989	2.34	2.27	97	0.92	8.1
Ti 334.941	2.34	2.37	101	0.40	0.4
V 309.311	2.34	2.37	101	0.39	1.0
Zn 213.856	2.34	2.35	100	0.01	0.4

- All element recoveries fall within acceptable limits of ±5% of the true values
- RSD of the three replicates of the spiked blank are below 1.5% for all elements.
- MDL are in the single digit µg·kg-1 range or lower.



Wavelength
—
Intensity
—
Corrected Peak
25,295.7
Peak
25,789.2
Average Background
493.5
Left background
—
Right background
493.5

Interferences for Ti 334.941 (101) (Radial)

Symbol	Line	State	Intensity
Sc	334.884	I	18750
Mo	334.894	II	1500
Th	334.895	II	0
Ti	334.904	II	1500000
Nb	334.906	I	35000
Cr	334.907	I	1200
Hf	334.917	II	1500
Ta	334.921	II	5000
Sc	334.921	I	93750
Ni	334.924	II	146341
Cr	334.932	I	1000
Nb	334.935	II	9000
Ti	334.941	II	5000000
Tb	334.942	II	50000
U	334.943	II	1200
Nb	334.952	II	0
Pu	334.963	I	10000
Sc	334.976	I	93750
Tm	334.999	I	46000
Sc	335	I	93750

Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) Software

Which technique?

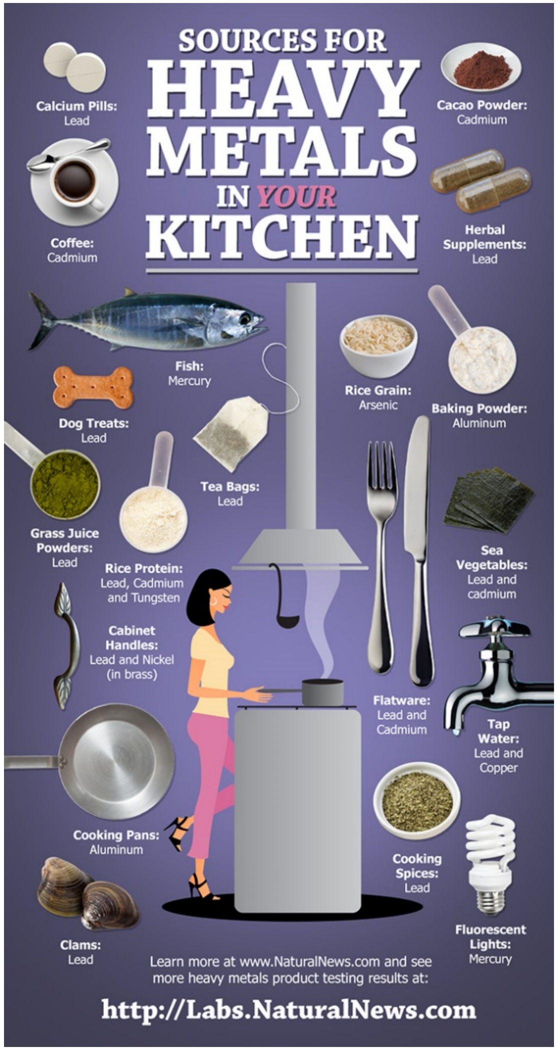
Which technique would you use for the analysis of total inorganic Mercury in urine and Lead in blood?? They do not have detection limits but would like to detect as low as possible

A fully quantitative research method for the analysis of Lead in whole blood

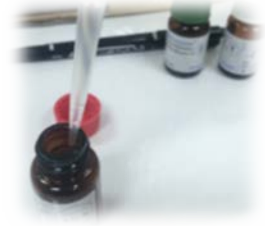
Dust, Paint, Soil, Industrial, Water, Toy, Food

- The United States Centers for Disease Control and Prevention (CDC) states that Blood Lead Levels (BLL) >70 µg/dL (700 ng/mL) can cause serious health effects.
- BLL as low as 10 µg/dL (100 ng/mL) are associated with cognitive development, growth, and behavioral issues in children between the ages of 1-5 years.

✓ As, Cd, Cr, Pb, Hg and Se in whole blood and Certified reference materials (Seronorm Trace Elements Whole Blood)



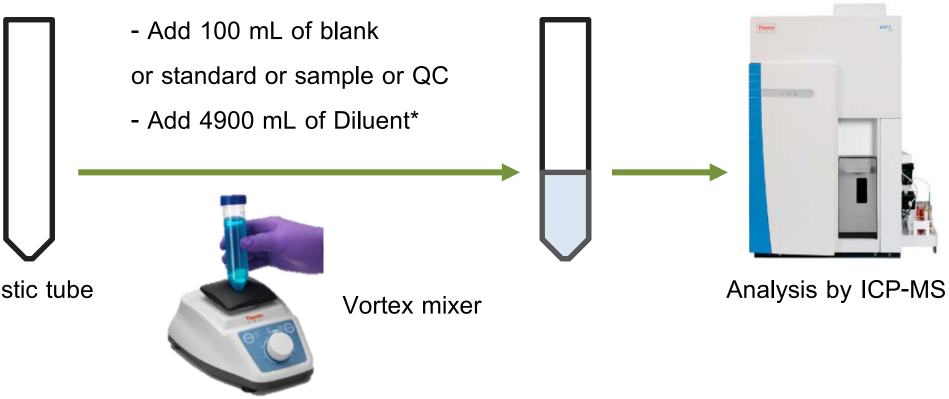
A fully quantitative research method for the analysis of Lead in whole blood using ICPMS



Add Ultrapure water

Vortex mixing for 15 minutes before use

Sample is 50 fold diluted with diluent



Plastic tube

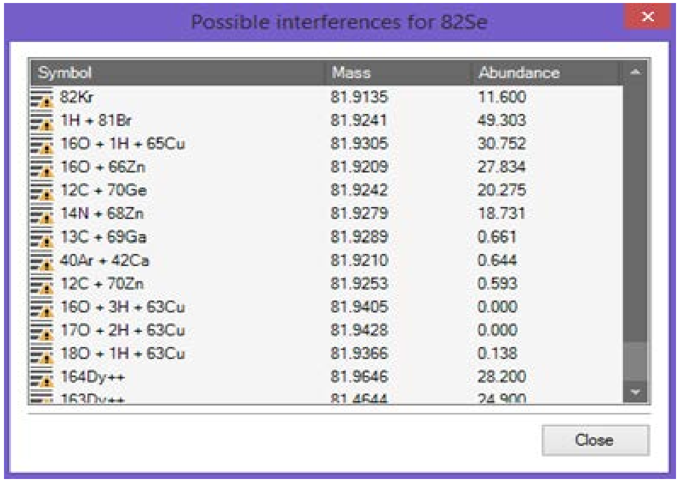
- Add 100 mL of blank or standard or sample or QC
- Add 4900 mL of Diluent*

Vortex mixer

Analysis by ICP-MS

* Tetramethylammonium hydroxide (TMAH, 1.5%), Hydrochloric acid (HCl, 1.5%), Ammonium Pyrrolidine dithiocarbamate (APDC), Triton-X and 0.1 µg/L of ^{103}Rh (Internal standard)

A fully quantitative research method for the analysis of Lead in whole blood using ICPMS



Possible interferences for 82Se

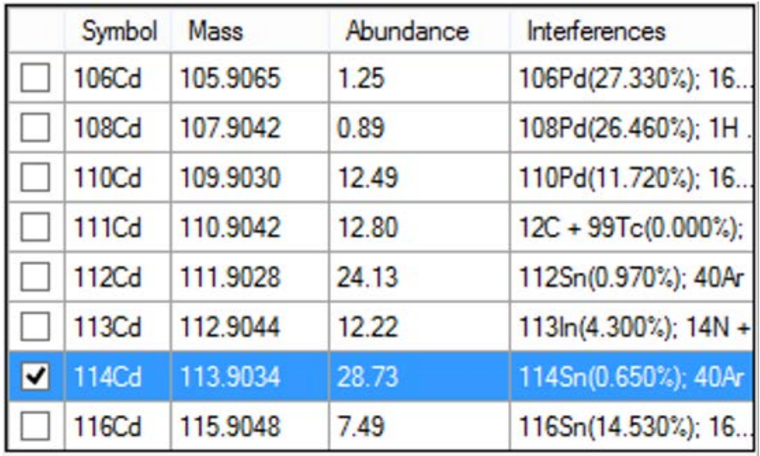
Symbol	Mass	Abundance
82Kr	81.9135	11.600
1H + 81Br	81.9241	49.303
16O + 1H + 65Cu	81.9305	30.752
16O + 66Zn	81.9209	27.834
12C + 70Ge	81.9242	20.275
14N + 68Zn	81.9279	18.731
13C + 69Ga	81.9289	0.661
40Ar + 42Ca	81.9210	0.644
12C + 70Zn	81.9253	0.593
16O + 3H + 63Cu	81.9405	0.000
17O + 2H + 63Cu	81.9428	0.000
18O + 1H + 63Cu	81.9366	0.138
164Dy++	81.9646	28.200
163Dy++	81.4644	24.900

^{82}Se is chosen based on less possible argon based interferences compare to ^{80}Se ($^{40}Ar_2^{+}$).

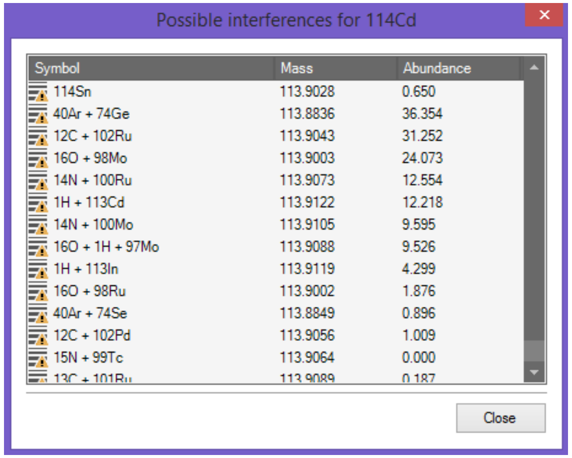
Selected analyte isotopes		
^{75}As	^{114}Cd	^{82}Se
^{52}Cr	^{202}Hg	
^{63}Cu	^{208}Pb	

Internal standard isotope
^{103}Rh

^{63}Cu is chosen based on it abundance.



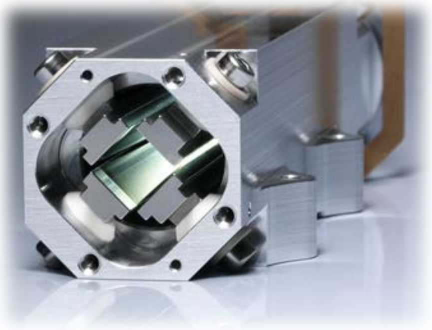
	Symbol	Mass	Abundance	Interferences
☐	106Cd	105.9065	1.25	106Pd(27.330%); 16..
☐	108Cd	107.9042	0.89	108Pd(26.460%); 1H .
☐	110Cd	109.9030	12.49	110Pd(11.720%); 16..
☐	111Cd	110.9042	12.80	12C + 99Tc(0.000%);
☐	112Cd	111.9028	24.13	112Sn(0.970%); 40Ar
☐	113Cd	112.9044	12.22	113In(4.300%); 14N +
☑	114Cd	113.9034	28.73	114Sn(0.650%); 40Ar
☐	116Cd	115.9048	7.49	116Sn(14.530%); 16..



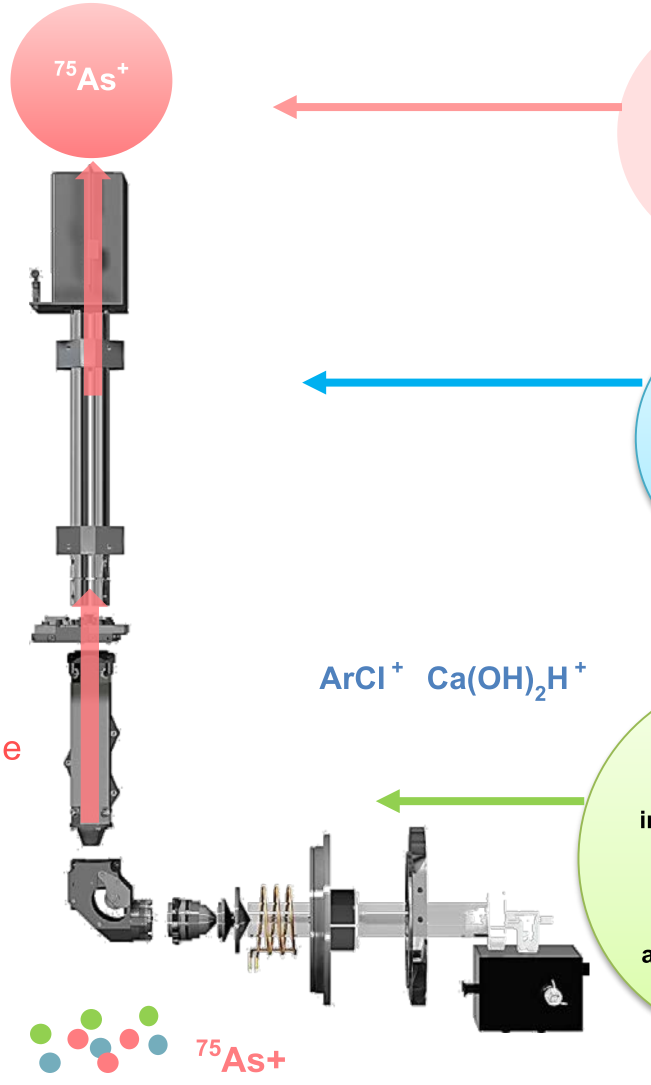
Possible interferences for 114Cd

Symbol	Mass	Abundance
114Sn	113.9028	0.650
40Ar + 74Ge	113.8836	36.354
12C + 102Ru	113.9043	31.252
16O + 98Mo	113.9003	24.073
14N + 100Ru	113.9073	12.554
1H + 113Cd	113.9122	12.218
14N + 100Mo	113.9105	9.595
16O + 1H + 97Mo	113.9088	9.526
1H + 113In	113.9119	4.299
16O + 98Ru	113.9002	1.876
40Ar + 74Se	113.8849	0.896
12C + 102Pd	113.9056	1.009
15N + 99Tc	113.9064	0.000
13C + 101Ru	113.9089	0.187

How to remove Polyatomic Interference?



Unique Flatapole Design



He KED mode

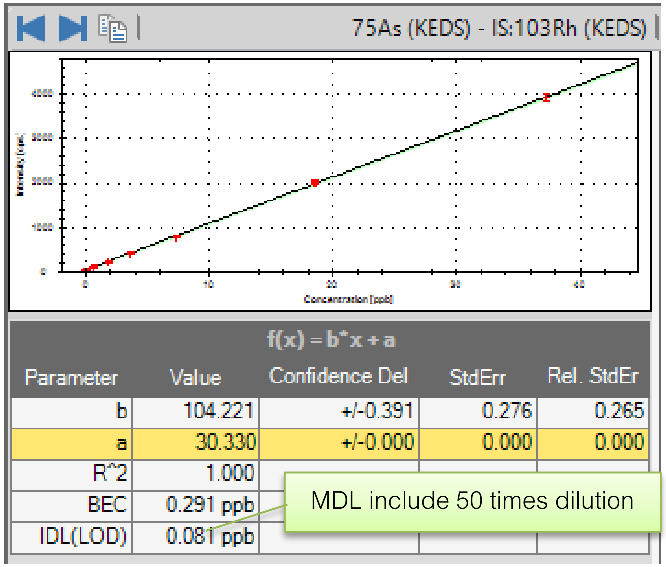
$40Ar35Cl^+$ $Ca(OH)_2H^+$

Comprehensive Interference Removal

Quadrupole isolates ions wanted for measurement

He KED filters out unwanted polyatomic interferences, based on difference in cross-sectional size of the analyte and polyatomic

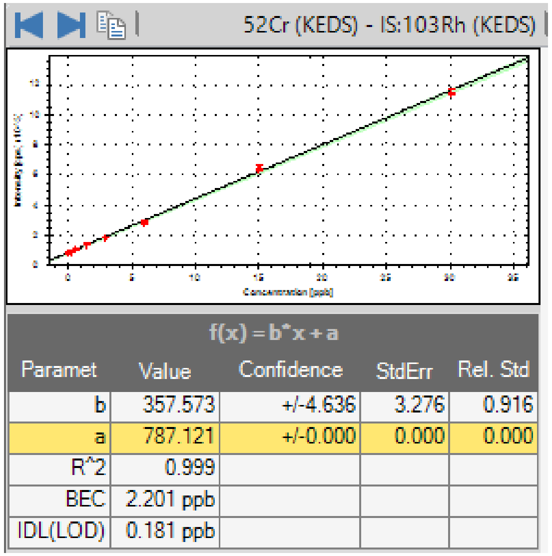
A fully quantitative research method for the analysis of Lead in whole blood using ICPMS



f(x) = b*x + a

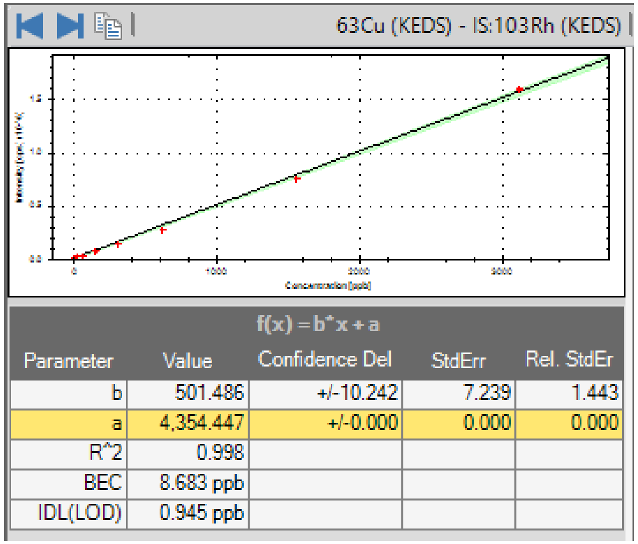
Parameter	Value	Confidence Del	StdErr	Rel. StdEr
b	104.221	+/-0.391	0.276	0.265
a	30.330	+/-0.000	0.000	0.000
R^2	1.000			
BEC	0.291 ppb			
IDL(LOD)	0.081 ppb			

MDL include 50 times dilution



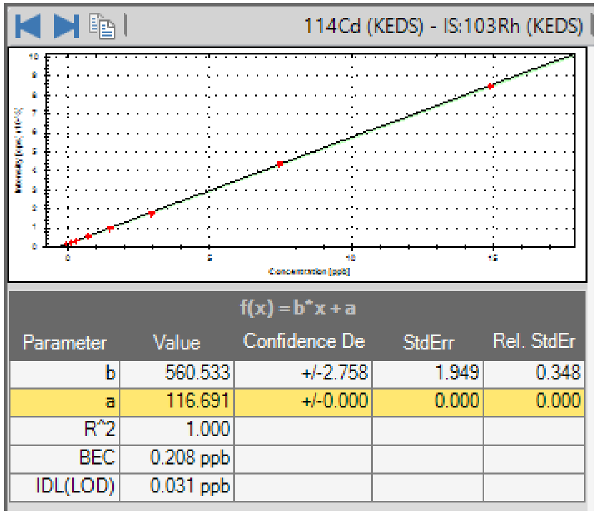
f(x) = b*x + a

Paramet	Value	Confidence	StdErr	Rel. Std
b	357.573	+/-4.636	3.276	0.916
a	787.121	+/-0.000	0.000	0.000
R^2	0.999			
BEC	2.201 ppb			
IDL(LOD)	0.181 ppb			



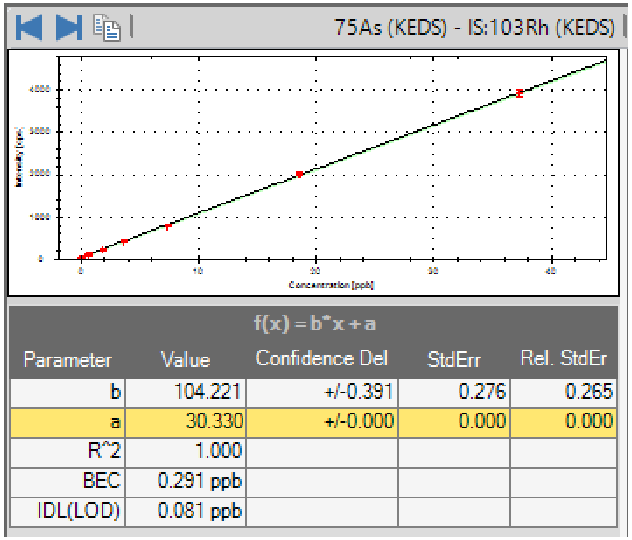
f(x) = b*x + a

Parameter	Value	Confidence Del	StdErr	Rel. StdEr
b	501.486	+/-10.242	7.239	1.443
a	4,354.447	+/-0.000	0.000	0.000
R^2	0.998			
BEC	8.683 ppb			
IDL(LOD)	0.945 ppb			



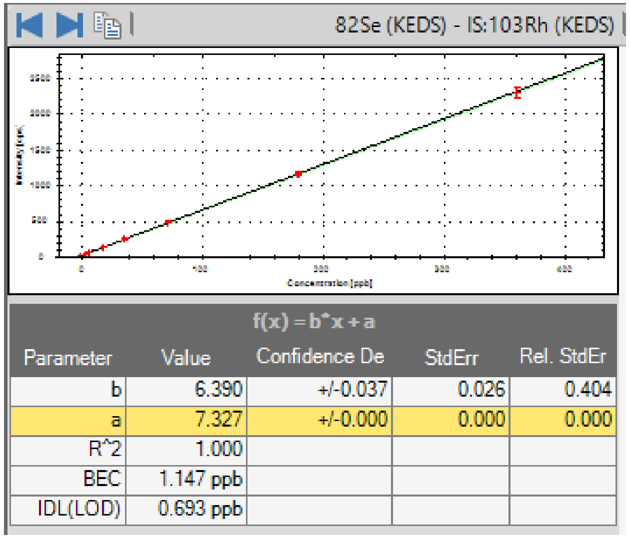
f(x) = b*x + a

Parameter	Value	Confidence De	StdErr	Rel. StdEr
b	560.533	+/-2.758	1.949	0.348
a	116.691	+/-0.000	0.000	0.000
R^2	1.000			
BEC	0.208 ppb			
IDL(LOD)	0.031 ppb			



f(x) = b*x + a

Parameter	Value	Confidence Del	StdErr	Rel. StdEr
b	104.221	+/-0.391	0.276	0.265
a	30.330	+/-0.000	0.000	0.000
R^2	1.000			
BEC	0.291 ppb			
IDL(LOD)	0.081 ppb			

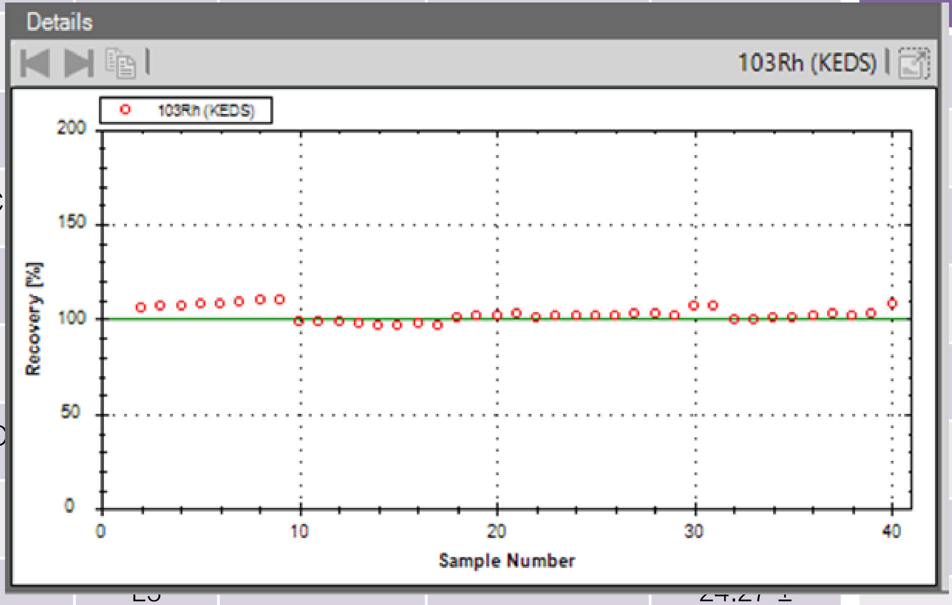


f(x) = b*x + a

Parameter	Value	Confidence De	StdErr	Rel. StdEr
b	6.390	+/-0.037	0.026	0.404
a	7.327	+/-0.000	0.000	0.000
R^2	1.000			
BEC	1.147 ppb			
IDL(LOD)	0.693 ppb			

A fully quantitative research method for the analysis of Lead in whole blood using ICPMS

Element	CRM	Certified Value (ng/mL)	Acceptable range (ng/mL)	Found (± SD, n = 3) (ng/mL)
As	L1	2.4	1.4-3.4	2.77±0.09
C				
C				
	L3	23.2	18.5 – 27.9	24.27 ± 0.64



Element	CRM	Certified Value (ng/mL)	Acceptable range (ng/mL)	Found (± SD, n = 3) (ng/mL)
	L1	1.5	0.90 – 2.10	2.24 ± 0.24
	L2	16	9.60 – 22.40	20.47 ± 0.39
	L3	37.1	29.6 – 44.6	40.41 ± 1.55
	L1	10.2	6.00 – 14.40	10.68 ± 0.36
	L2	310	186 - 434	394 ± 13
	L3	447	401 - 493	536 ± 22
	L1	59	35 – 69	69.03 ± 0.59
	L2	112	66 – 158	131 ± 5
	L3	272	217 – 327	258 ± 8

Arsenic speciation in human urine by hyphenated

- The different As species can be classified as inorganic arsenic (iAs) and organic arsenic compounds.
- iAs as the sum of Arsenite As(III) and arsenate As(V) is a major concern for public health authorities worldwide.
- Drinking water, pesticides, wood preservatives, dust emission and disposal of industrial waste.
- Dietary : Cereals, rice or fruit and vegetables
- Exposure to iAs can result in a variety of adverse effects such as skin disorders, neuropathy, and lung, bladder and skin cancer.
- Organic species of As, such as arsenobetaine (AsBet), arsenocholine (AsChol) and arsenosugars, is primarily observed after consumption of fish or seafood and much less toxic

Simultaneous separation and quantification of six different As species in human urine samples.

- ✓ As(III)
- ✓ As(V)
- ✓ AsBet
- ✓ AsChol
- ✓ Dimethylarsinic acid (DMA)
- ✓ Monomethylarsonic acid (MMA)

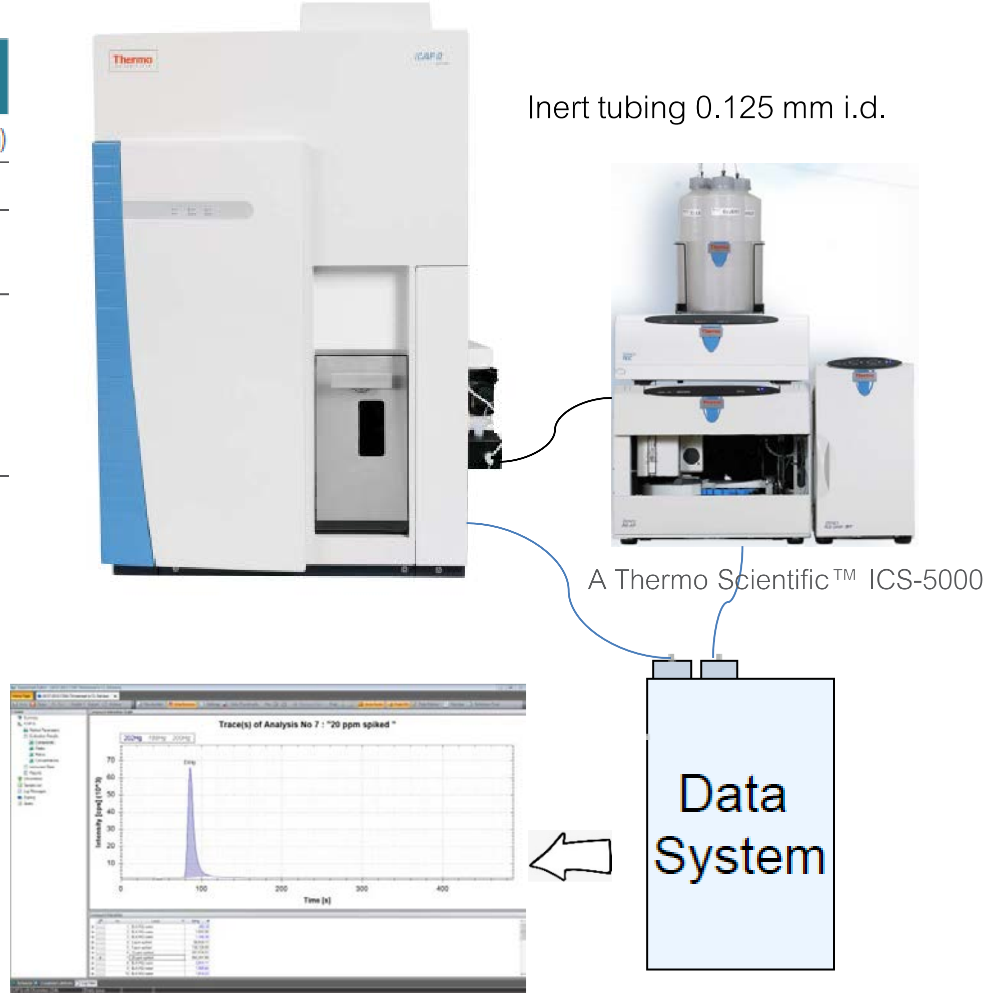
Arsenic speciation in human urine by hyphenated *IC and ICP-MS*

Table 1. Ion Chromatography operating conditions.

Parameter	Value			
Columns	Dionex IonPac AG7 (4x50 mm) and AS7 (4x250 mm)			
Injection Volume	100 µL			
Eluents	A: Ultrapure water B: 100 mM $(NH4)_2CO_3$ + 3% MeOH, pH 10.3			
Gradient	**Time min**	**Flow mL·min^{-1}**	**% A**	**% B**
	0-5	0.7	95	5
	5.1-10	1.5	70	30
	10.1-13	1.5	40	60
	13.1-14	0.7	95	5

Table 2. ICP-MS operating conditions.

Parameter	Value
Nebulizer	PFA-ST nebulizer, pumped at 40 rpm
Spraychamber	Quartz, cyclonic spraychamber cooled at 2.7 °C
Injector	2.5 mm i.d., Quartz
Interface	Ni cones with High Matrix (3.5 mm) insert
RF Power	1550 W
Nebulizer Gas Flow	1.17 L·min^{-1}
QCell settings	**KED**
Gas Flow	100% helium (99.999% Purity), 4.8 mL·min^{-1}
QCell Bias	-18 V
Quadrupole Bias	-21 V
Scan Settings	0.05 s dwell time per analyte, 14 minutes acquisition time



Inert tubing 0.125 mm i.d.

A Thermo Scientific™ ICS-5000

Data System

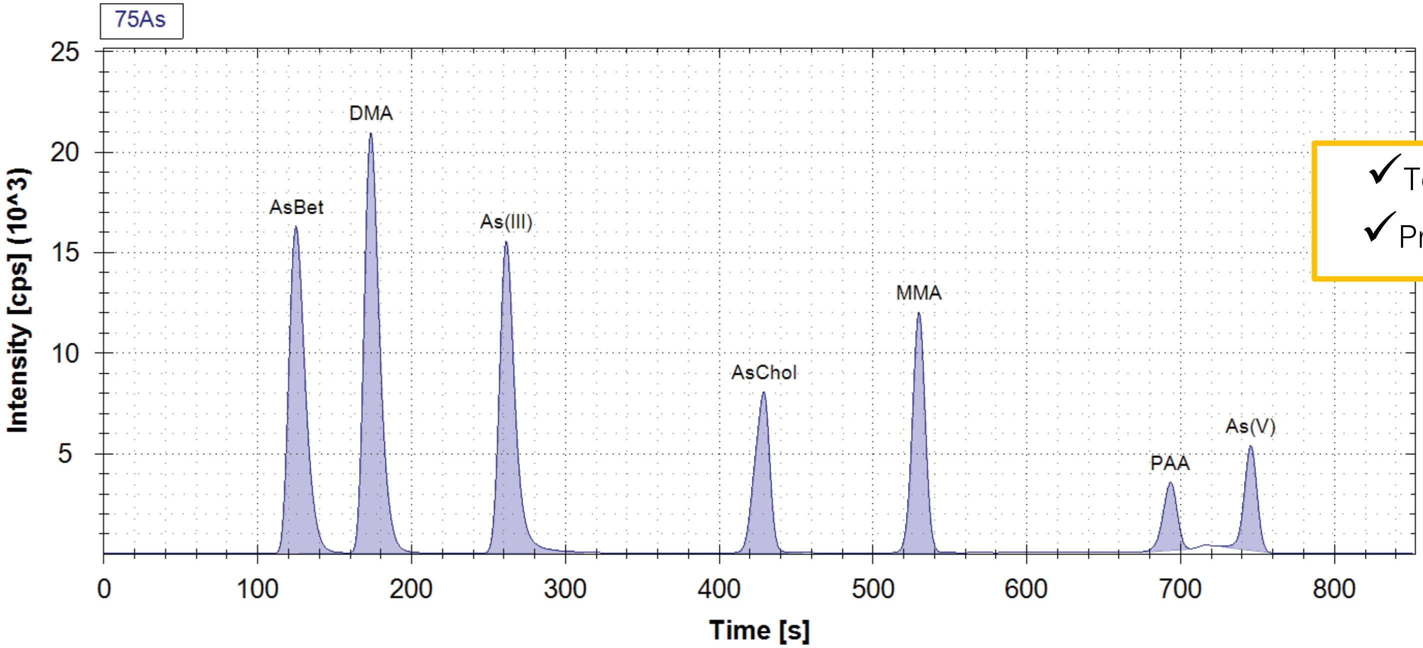
Arsenic speciation in human urine by hyphenated *IC and ICP-MS*

Sample preparation

a 0.45 µm PTFE membrane

2 mL of Urine → Diluted 1:5 with deionized ultrapure water

- Urine samples were spiked with 10 µg·L-1 of As(III), As(V), AsBet, AsChol, DMA and MMA to optimize the chromatographic separation
- 1 µg·L-1 of Phenylarsonic acid (PAA) as Internal standard

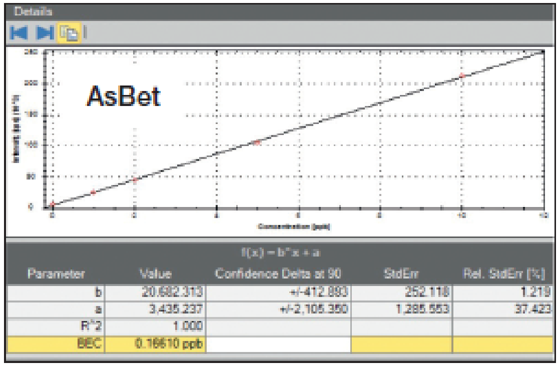


Chromatographic separation of all As species investigated in this study, including PAA used as internal standard

✓ Total time < 15 mins

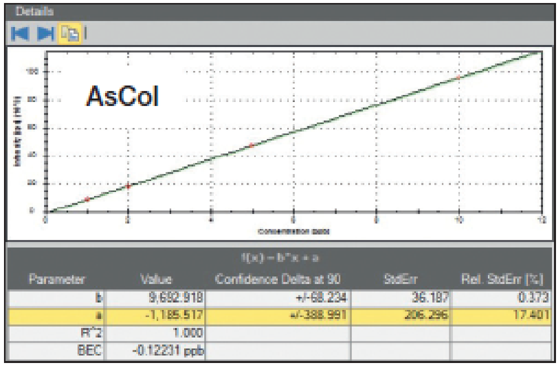
✓ Precision of RT < 4%

Arsenic speciation in human urine by hyphenated *IC and ICP-MS*



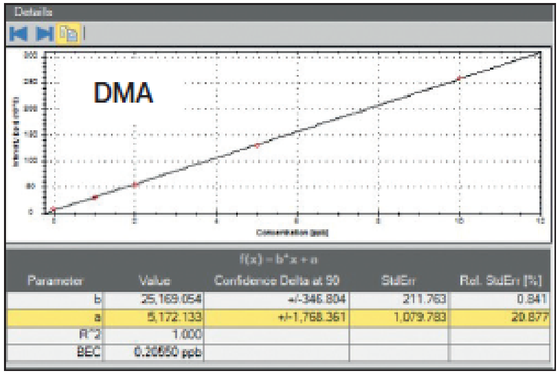
f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	20,692.313	+/-412.893	252.118	1.219
a	3,435.237	+/-2,105.350	1,285.553	37.423
R^2	1.000			
BEC	0.16610 ppb			



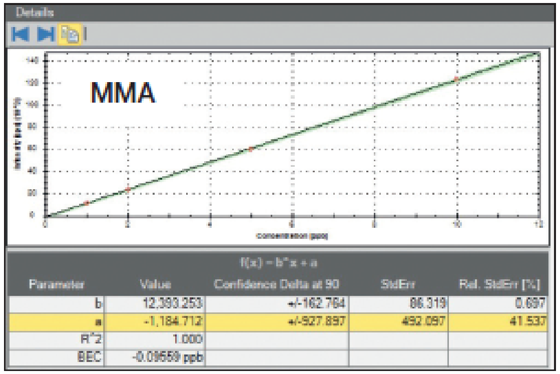
f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	9,692.918	+/-68.234	36.187	0.373
a	-1,185.517	+/-388.991	206.296	17.401
R^2	1.000			
BEC	-0.12231 ppb			



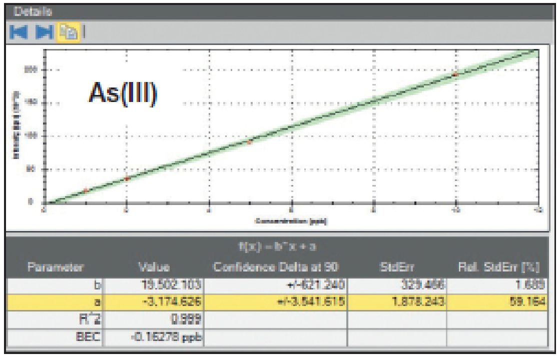
f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	25,169.054	+/-346.804	211.763	0.841
a	5,172.133	+/-1,768.361	1,079.783	20.877
R^2	1.000			
BEC	0.20550 ppb			



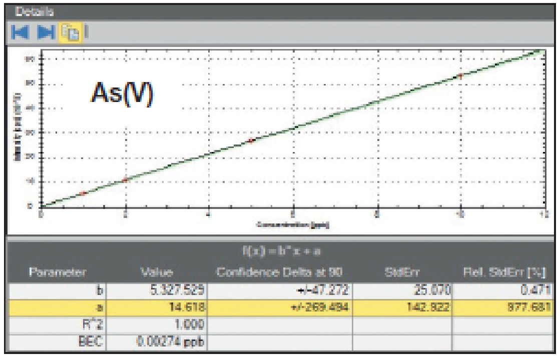
f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	12,393.253	+/-162.764	86.319	0.697
a	-1,184.712	+/-927.897	492.097	41.537
R^2	1.000			
BEC	-0.09559 ppb			



f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	19,502.103	+/-621.240	329.466	1.689
a	-3,174.626	+/-3,541.615	1,878.243	59.164
R^2	0.999			
BEC	-0.16278 ppb			



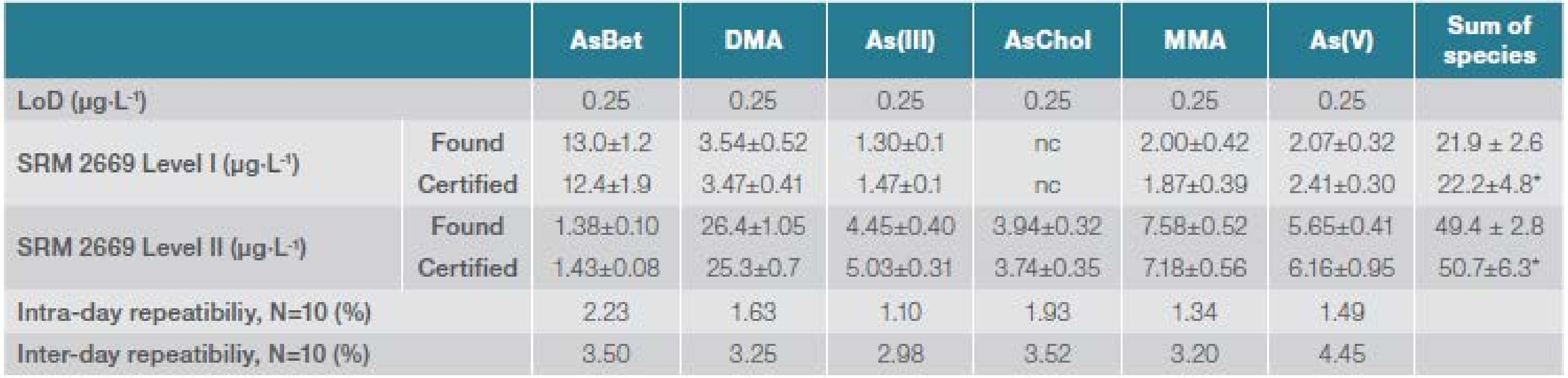
f(x) = b*x + a

Parameter	Value	Confidence Delta at 90	StdErr	Rel. StdErr [%]
b	5,327.529	+/-47.272	25.070	0.471
a	14.618	+/-269.494	142.922	977.681
R^2	1.000			
BEC	0.00274 ppb			

Calibrations of six As species in urine samples diluted 1:5 with deionized ultrapure water, with calibration levels at 1, 2, 5, 10 µg/L

✓ R^2 : 0.999-1.000 for all species.

Arsenic speciation in human urine by hyphenated *IC and ICP-MS*



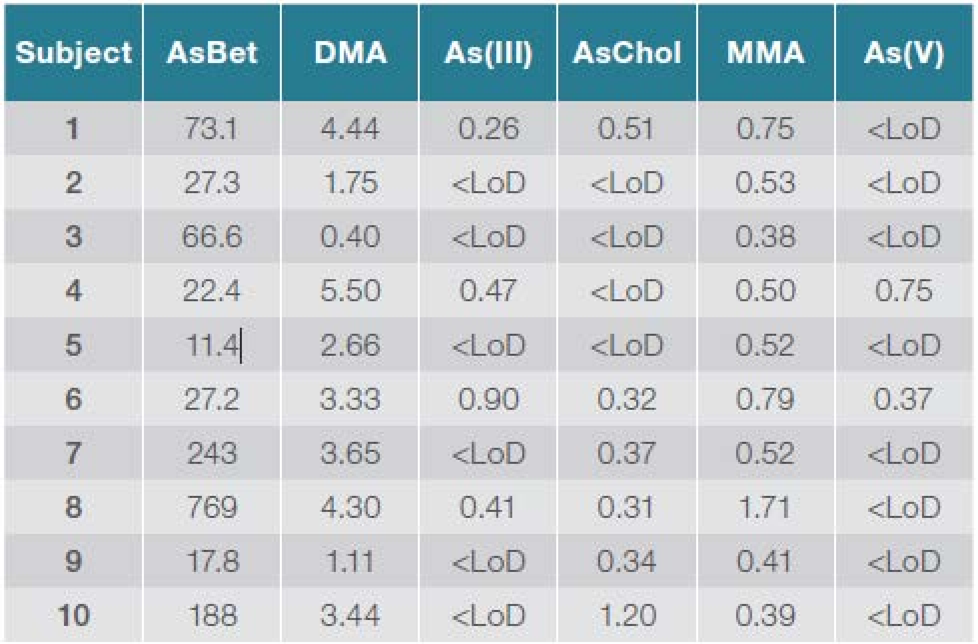
		AsBet	DMA	As(III)	AsChol	MMA	As(V)	Sum of species
LoD (μg·L⁻¹)		0.25	0.25	0.25	0.25	0.25	0.25	
SRM 2669 Level I (μg·L⁻¹)	**Found**	13.0±1.2	3.54±0.52	1.30±0.1	nc	2.00±0.42	2.07±0.32	21.9 ± 2.6
	Certified	12.4±1.9	3.47±0.41	1.47±0.1	nc	1.87±0.39	2.41±0.30	22.2±4.8*
SRM 2669 Level II (μg·L⁻¹)	**Found**	1.38±0.10	26.4±1.05	4.45±0.40	3.94±0.32	7.58±0.52	5.65±0.41	49.4 ± 2.8
	Certified	1.43±0.08	25.3±0.7	5.03±0.31	3.74±0.35	7.18±0.56	6.16±0.95	50.7±6.3*
Intra-day repeatibiliy, N=10 (%)		2.23	1.63	1.10	1.93	1.34	1.49	
Inter-day repeatibiliy, N=10 (%)		3.50	3.25	2.98	3.52	3.20	4.45	

Ten samples of urine spiked with the different As species at concentrations of 2 μg·L-1 each.

- ✓ LOD was 0.25 μg·L-1 for all the species
- ✓ Accuracy was in the ranges 86-107% for the Level I and 88-106% for the Level II materials.
- ✓ The intra-day and inter-day repeatability were on average 1.6% and 3.5%, respectively, for all the species.
- ✓ The sum of all As species accounted for 98.6% of the total certified As for the Level I and 97.4% for the Level II, respectively

Arsenic speciation in human urine by hyphenated IC and ICP-MS

Analysis of real samples (Urine of Children)



Subject	AsBet	DMA	As(III)	AsChol	MMA	As(V)
1	73.1	4.44	0.26	0.51	0.75	<LoD
2	27.3	1.75	<LoD	<LoD	0.53	<LoD
3	66.6	0.40	<LoD	<LoD	0.38	<LoD
4	22.4	5.50	0.47	<LoD	0.50	0.75
5	11.4	2.66	<LoD	<LoD	0.52	<LoD
6	27.2	3.33	0.90	0.32	0.79	0.37
7	243	3.65	<LoD	0.37	0.52	<LoD
8	769	4.30	0.41	0.31	1.71	<LoD
9	17.8	1.11	<LoD	0.34	0.41	<LoD
10	188	3.44	<LoD	1.20	0.39	<LoD

Concentrations in µg·L-1 of the six As species after the chromatographic separation.

- ☐ The results indicate that AsBet was the main arsenic species found in children's urine, representing about 90% of the total content of As found
- ☐ AsBet is a non-toxic species of marine food origin, even though As levels were found to vary strongly between 11.4 and up to 769 µg·L-1.
- ☐ sum of As(III) and As(V) was around or far less than 1 µg·L-1.

Thank you for your attention!

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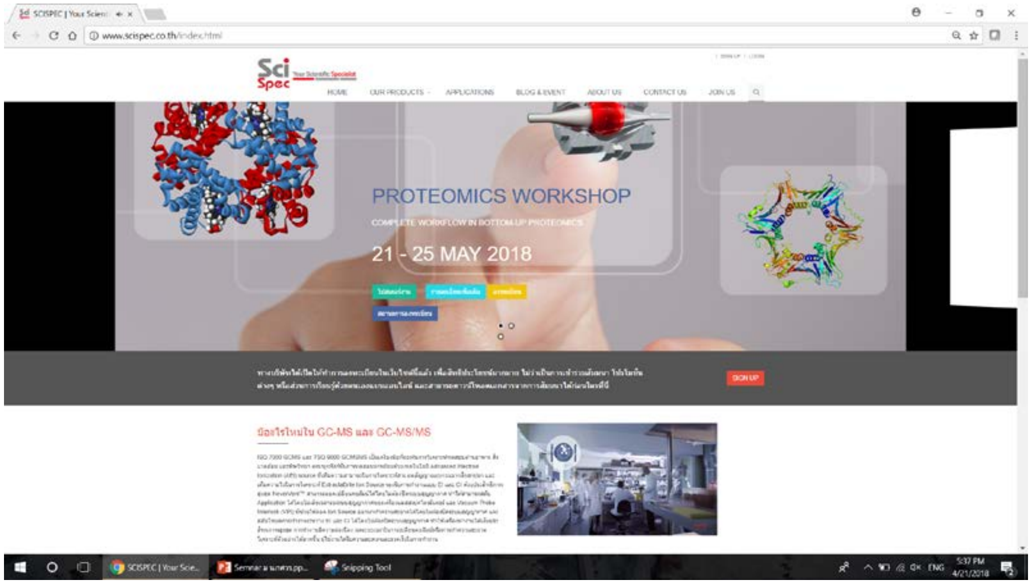

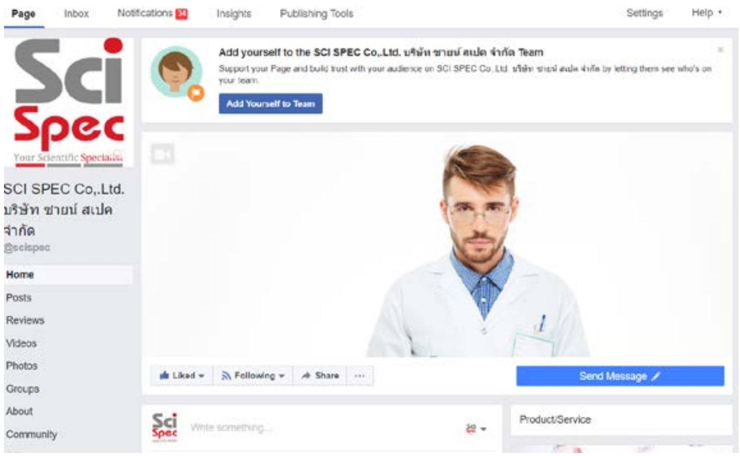

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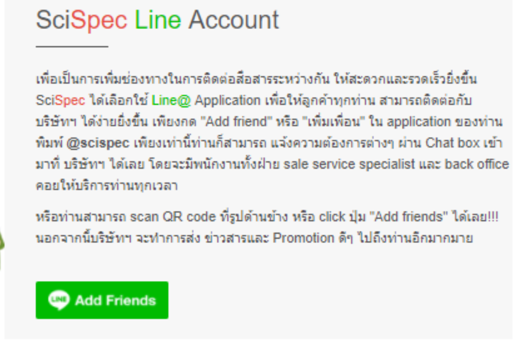

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