Determination of technologically critical elements (TCE) in environmental and clinical samples by ICP-MS

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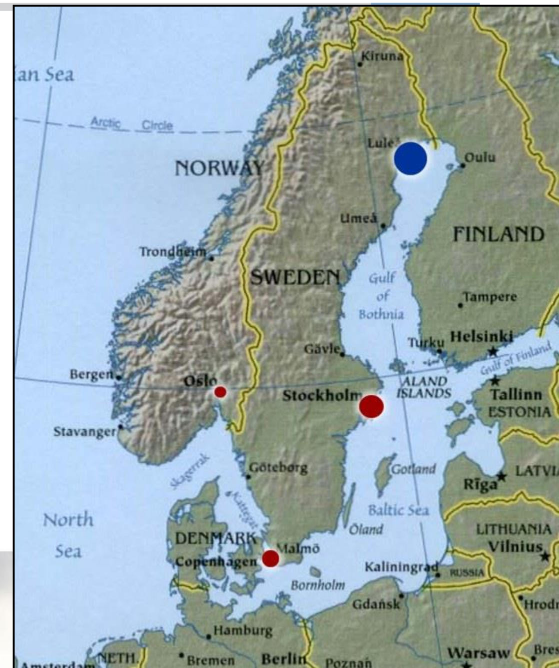
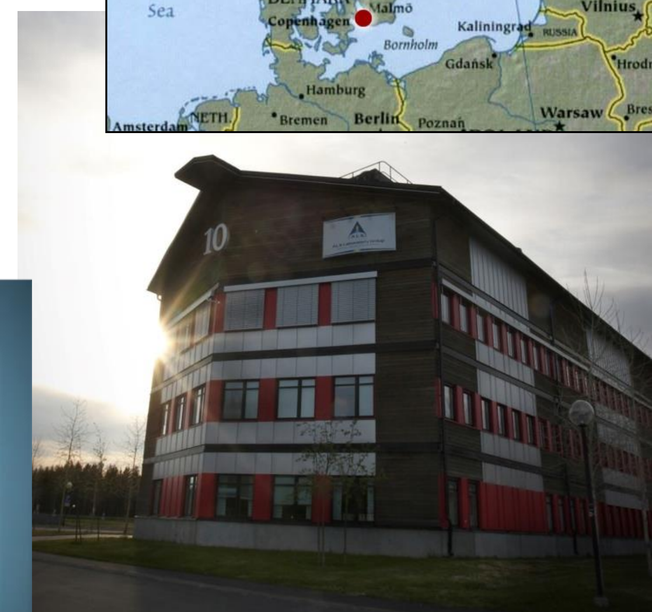
Luleå laboratory

- Part of ALS group (>300 laboratories worldwide)
- Focus areas: ultra-trace multi-elemental determinations and isotope ratio measurements
- >130 000 samples annually
- Close co-operation with LTU resulting in 200 publications





What are TCEs?

Trace elements that are **key components for the development of new technologies** and thus undergoing a significant change in their cycle at the Earth's surface due to their increase use in a variety of applications. Their impact on their biogeochemical cycles and potential biological and human health threats needs to be further explored. For most of these elements, the present understanding of their concentrations, transformation and transport in the different environmental compartments is **scarce and/or contradictory.**

What are TCEs?

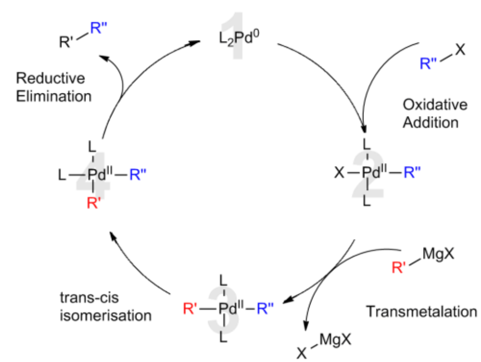
www.webelements.com

Key: element name / **atomic number** / symbol / atomic weight (mean relative mass)

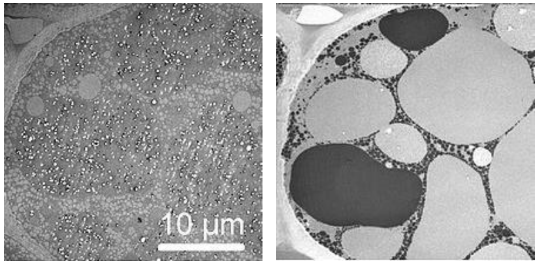
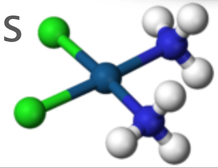
	1	2		3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	hydrogen 1 H 1.0079																		helium 2 He 4.0026
	lithium 3 Li 6.941	beryllium 4 Be 9.0122												boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
	sodium 11 Na 22.990	magnesium 12 Mg 24.305												aluminium 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
	potassium 19 K 39.098	calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80
	rubidium 37 Rb 85.468	strontium 38 Sr 87.62		yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.96	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29
	caesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
	francium 87 Fr [223]	radium 88 Ra [226]	89-102 **	lawrencium 103 Lr [262]	rutherfordium 104 Rf [267]	dubnium 105 Db [268]	seaborgium 106 Sg [271]	bohrium 107 Bh [272]	hassium 108 Hs [270]	meitnerium 109 Mt [276]	darmstadtium 110 Ds [281]	roentgenium 111 Rg [280]	ununbium 112 Uub [285]	ununtrium 113 Uut [284]	ununquadium 114 Uuq [289]	ununpentium 115 Uup [288]	ununhexium 116 Uuh [293]	ununseptium 117 Uus —	ununoctium 118 Uuo [294]

*lanthanoids	lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.06
**actinoids	actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

What are TCEs used for?

Element	Uses
Ru	Electronics 
Rh	Catalytic convertors 
Pd	Catalytic convertors Catalysts 

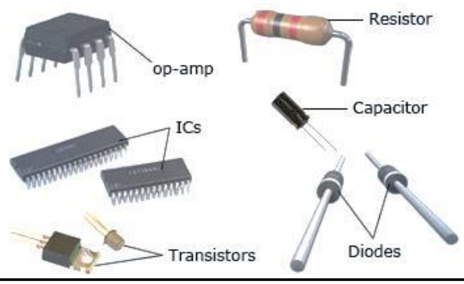
What are TCEs used for?

Element	Uses
Os	Staining, organic synthesis 
Ir	Electronics 
Pt	Catalytic convertors  Pharmaceuticals 

What are TCEs used for?

Element	Uses
Ce	Lighter flints Catalytic convertors 
Pr	Aircraft engine alloys 
Nd	Magnets 

What are TCEs used for?

Element	Uses
Ga	Computer chips Semi-conductors 

What are TCEs used for?

What are TCEs used for?

- Authentication of money

Problems to be solved

Understanding environmental processes including biogeochemical cycles of the TCEs

Assessment of exposure of humans to these elements and their compounds through air, water, and food, and potential ecological and human health threats (eco-toxicology)

Analytical challenges for quantitative and screening purposes

Environmental analysis

Determination of TCEs in environmental matrices

- Quantitate recovery at preparation stages
- Preventing losses during analysis
- Optimization of instrumental conditions (low oxides)
- Right resolution settings
- Matrix separation if necessary
- Analyte specific introduction (Os, Ge)

Ga, Ge, In, Nb, Ta, Te, Tl

Ir, Os, Pd, Pt, Rh

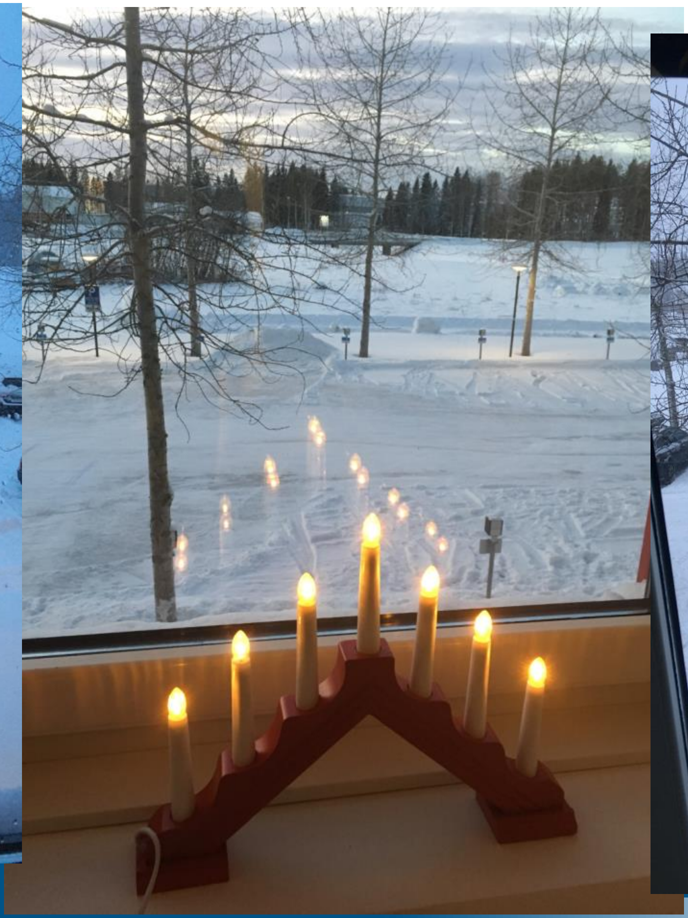
Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Y, Yb

Why Luleå?

October

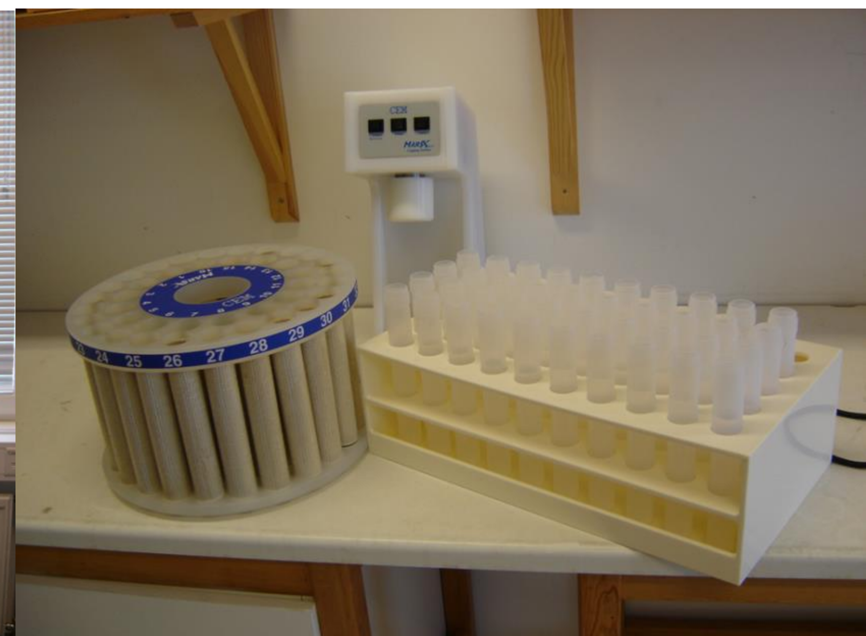
January

April



Before MS

- Sample collection
- Homogenization – representative sub-sample, contamination
- Digestion – recovery from matrix, (co)precipitation and volatile losses, contamination
- Column separation – purification efficiency, yield, contamination
- Evaporation/re-dissolution – recovery, contamination



Sensitivity in LRM, cps per 1 µg l^{-1}

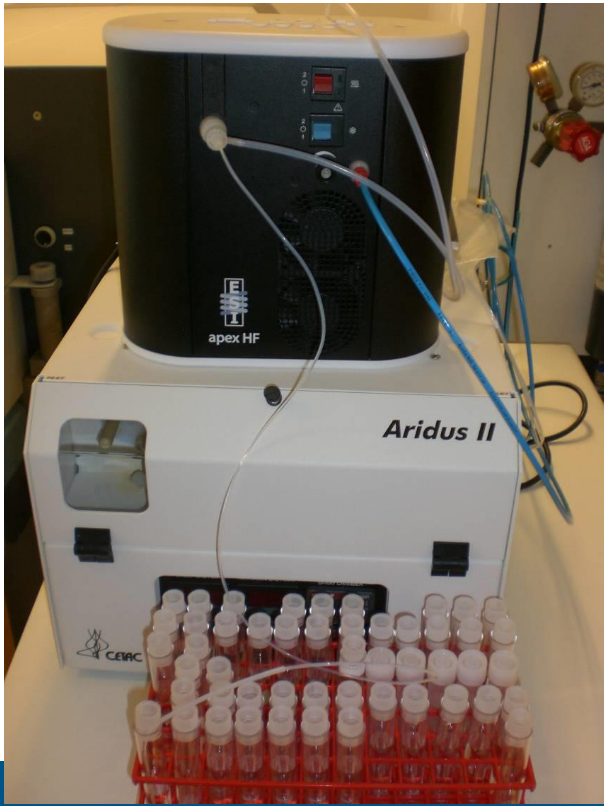
- Cell ICP-QMS: 2-10 10^5
- ICP-SFMS, standard set-up: $2x10^6$
- ICP-SFMS, X skimmer, methane: $6x10^6$
- ICP-SFMS, X skimmer, Aridus: $2x10^7$
- ICP-SFMS, Jet interface, APEX: $1.2x10^8$

$1.2x10^8$ cps/ppb correspond to **120 cps/ppq**

High efficiency nebulizers – Aridus II and Apex HF

- Intensity gain by efficient utilization of sample solution
- 'Dry' plasma – much lower O, H and OH interferences
- Great signal stability for low-matrix solutions

- Losses of volatile elements (Hg, Se, As, Os, B)
- Low matrix tolerance
- Long memory

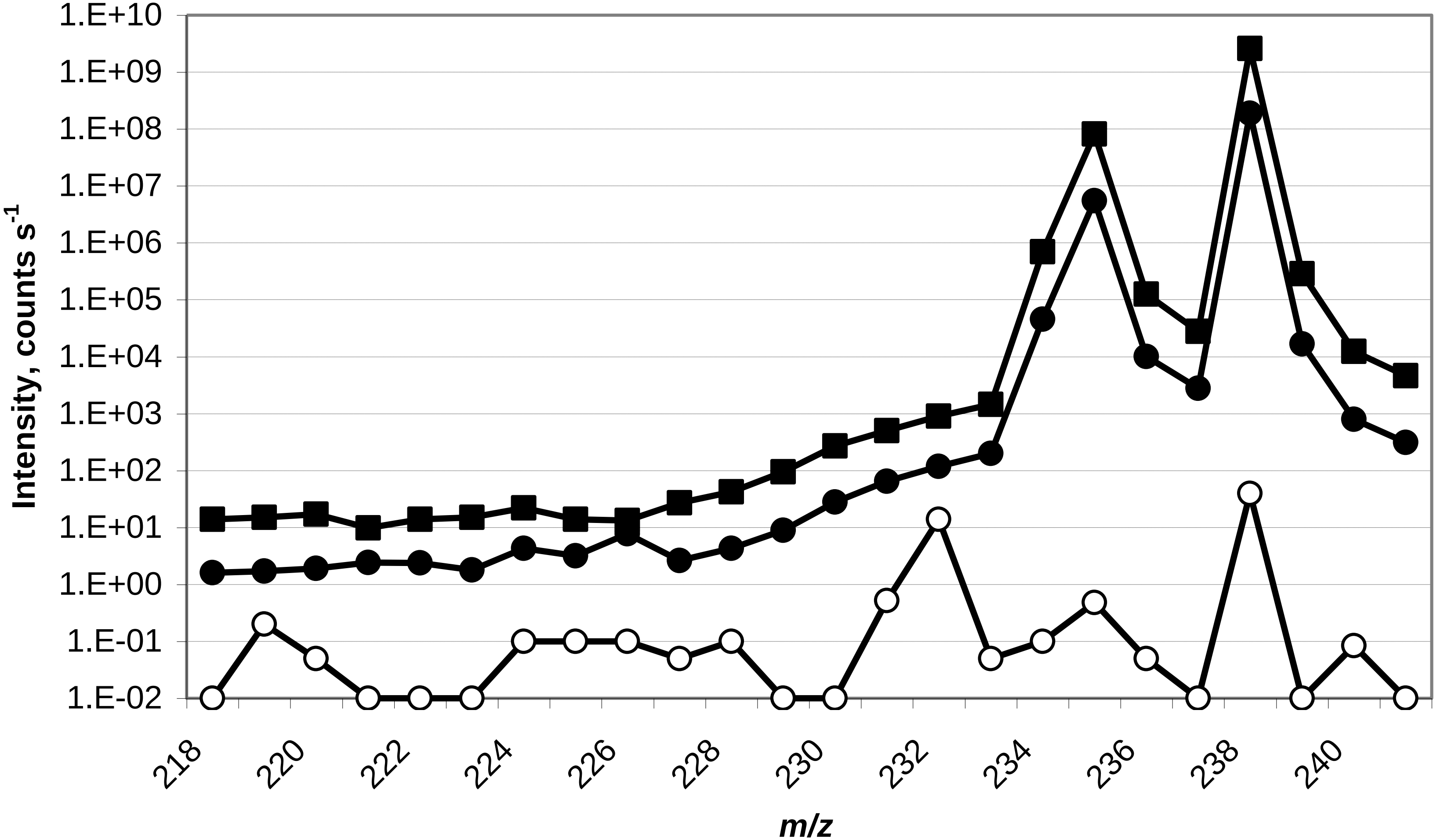


Spectral interferences on ^{103}Rh

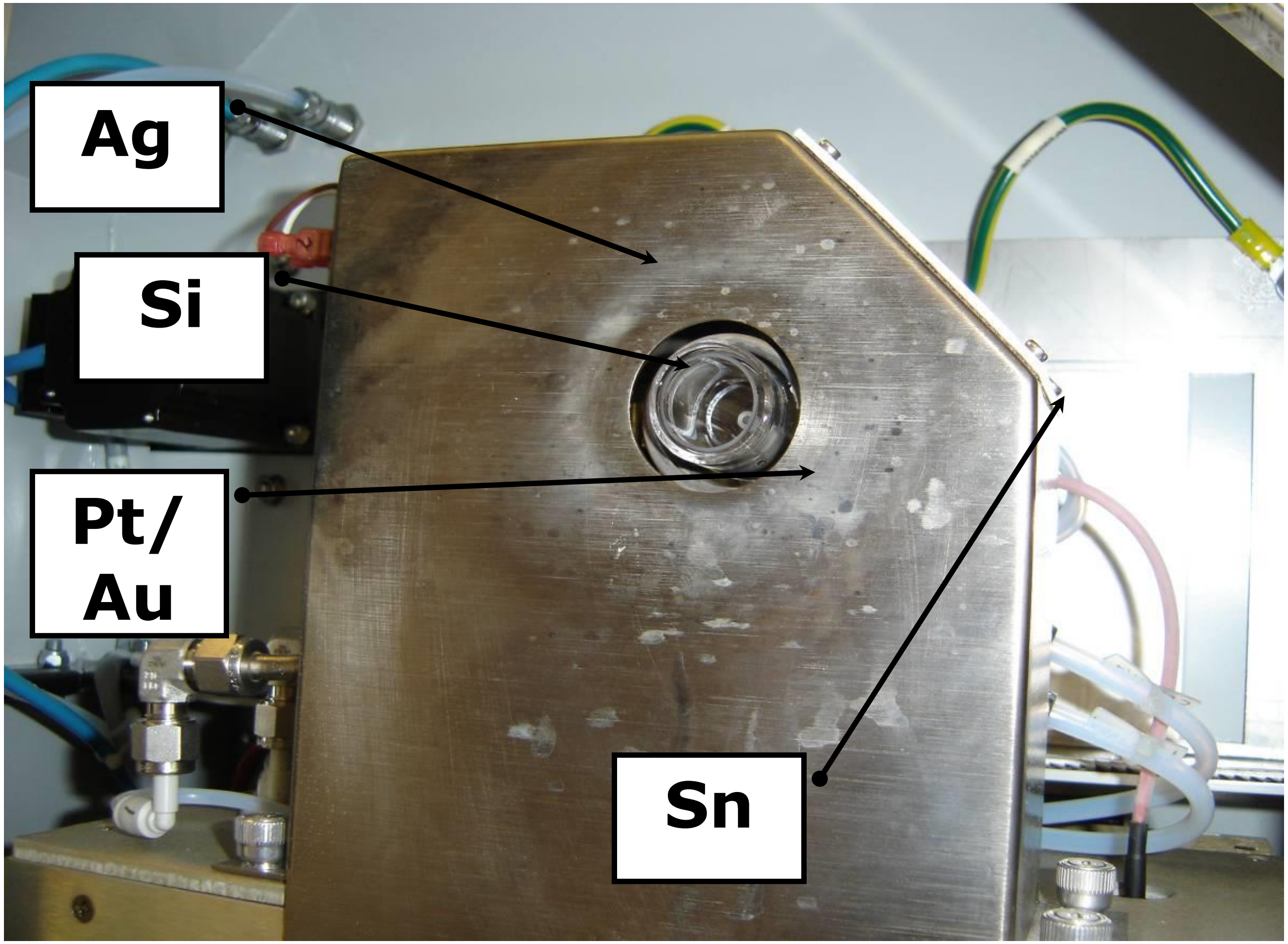
- $^{206}Pb^{++}$
- $^{87}Rb^{16}O^{+}$, $^{87}Sr^{16}O^{+}$, $^{86}Sr^{16}OH^{+}$
- $^{63}Cu^{40}Ar^{+}$, $^{65}Cu^{36}Ar^{+}$, $^{67}Zn^{36}Ar^{+}$
- $^{23}Na^{40}Ar^{40}Ar^{+}$, $^{23}Na^{40}Ar^{40}Ca^{+}$, $^{23}Na^{40}Ca^{40}Ca^{+}$
- $^{66}Zn^{37}Cl^{+}$, $^{68}Zn^{35}Cl^{+}$
- $^{32}S^{34}S^{37}Cl^{+}$, $^{33}S^{33}S^{37}Cl^{+}$, $^{34}S^{34}S^{35}Cl^{+}$, $^{34}S^{34}S^{34}SH^{+}$
- $^{96}Mo^{7}Li^{+}$, $^{97}Mo^{6}Li^{+}$, $^{40}Ar^{35}Cl^{12}C^{16}O^{+}$

The majority of spectral interferences can be eliminated using high resolution capabilities of ICP-SFMS

Tailing


1.E+10
1.E+09
1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
Intensity, counts s-1
218
220
222
224
226
228
230
232
234
236
238
240
m/z

Torch and interface may release



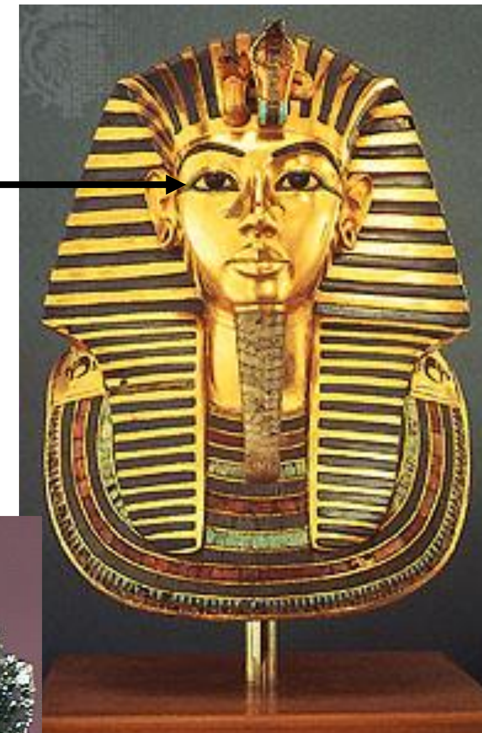
Personnel issues

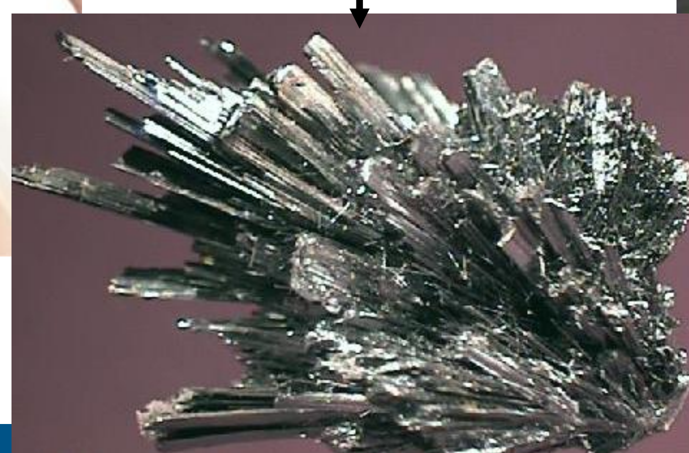
Spot the common denominator?

Stibnite

Antimonite

Sb_2S_3

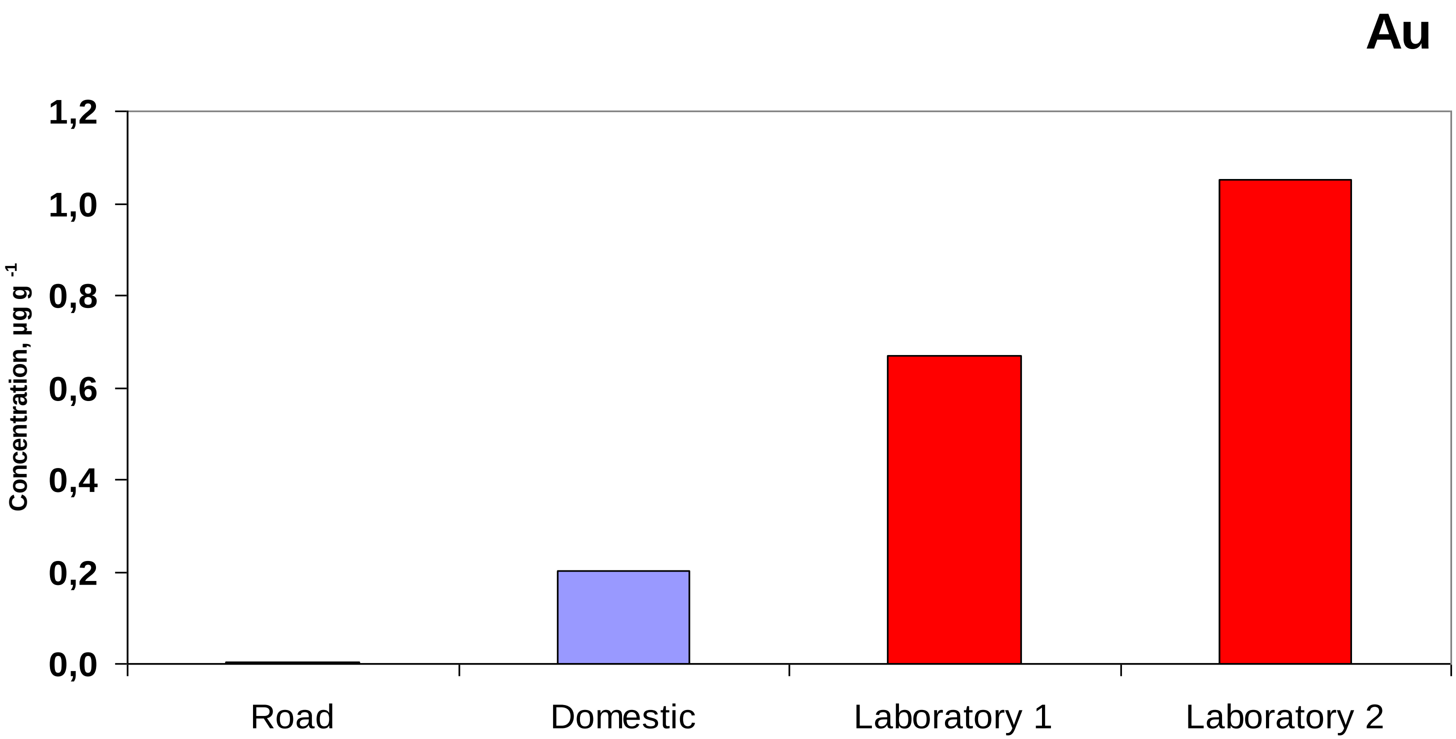




'Metall-free' dispenser

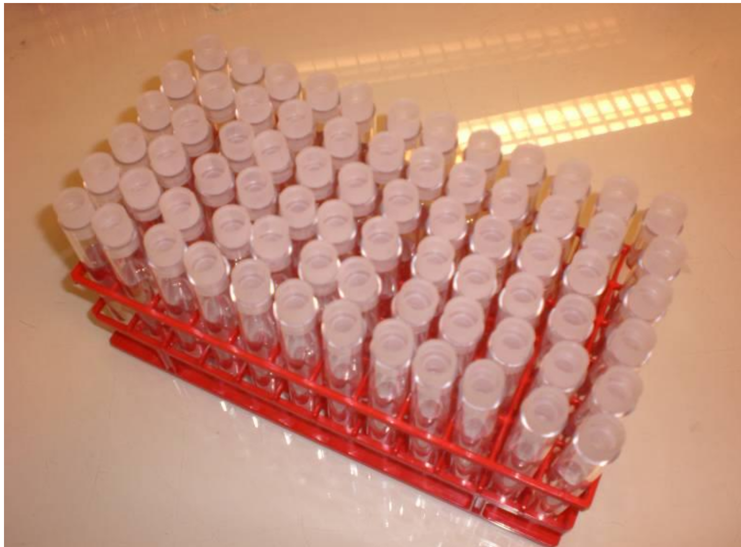
- Faster and more convenient way to handle relatively large sample volumes (>5 ml)
- Contaminates sample with **Pt** and **Ir** at ppt level, Pd and Au at ppq level because of Pt-Ir valve spring

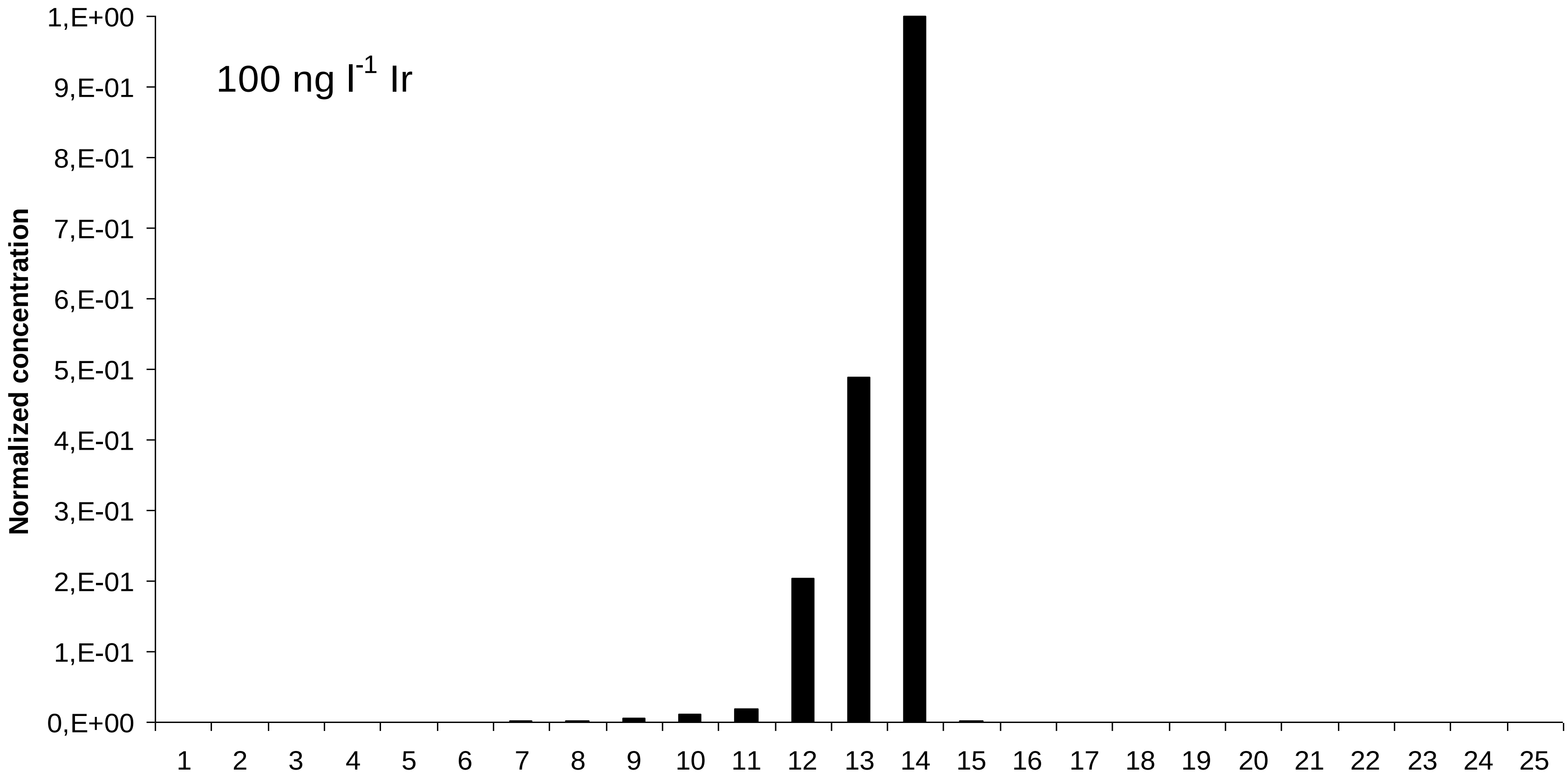
Concentrations of ‘rare’ elements are enriched in laboratory dust

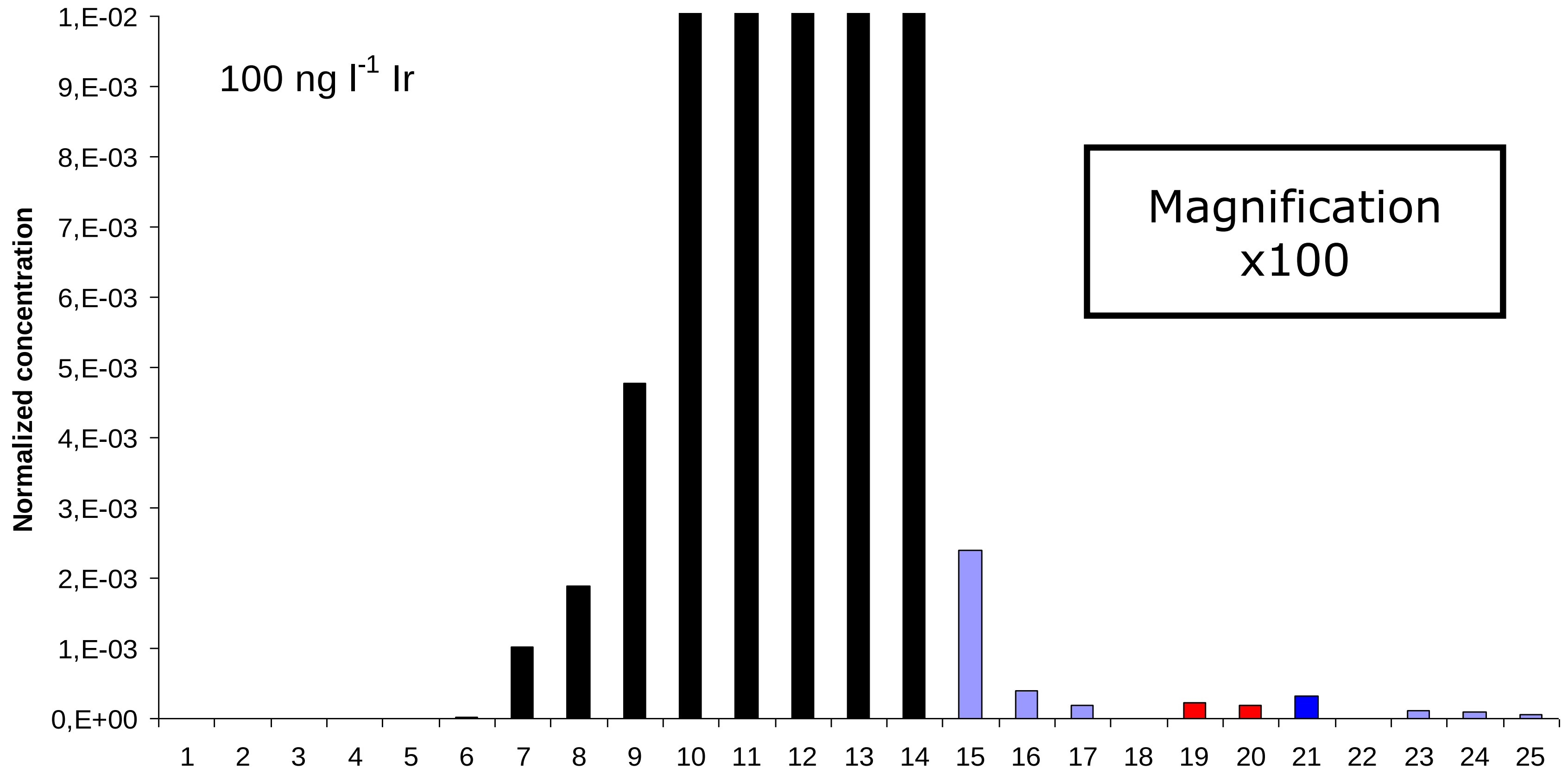


Dedicated areas for ultra-trace preparations

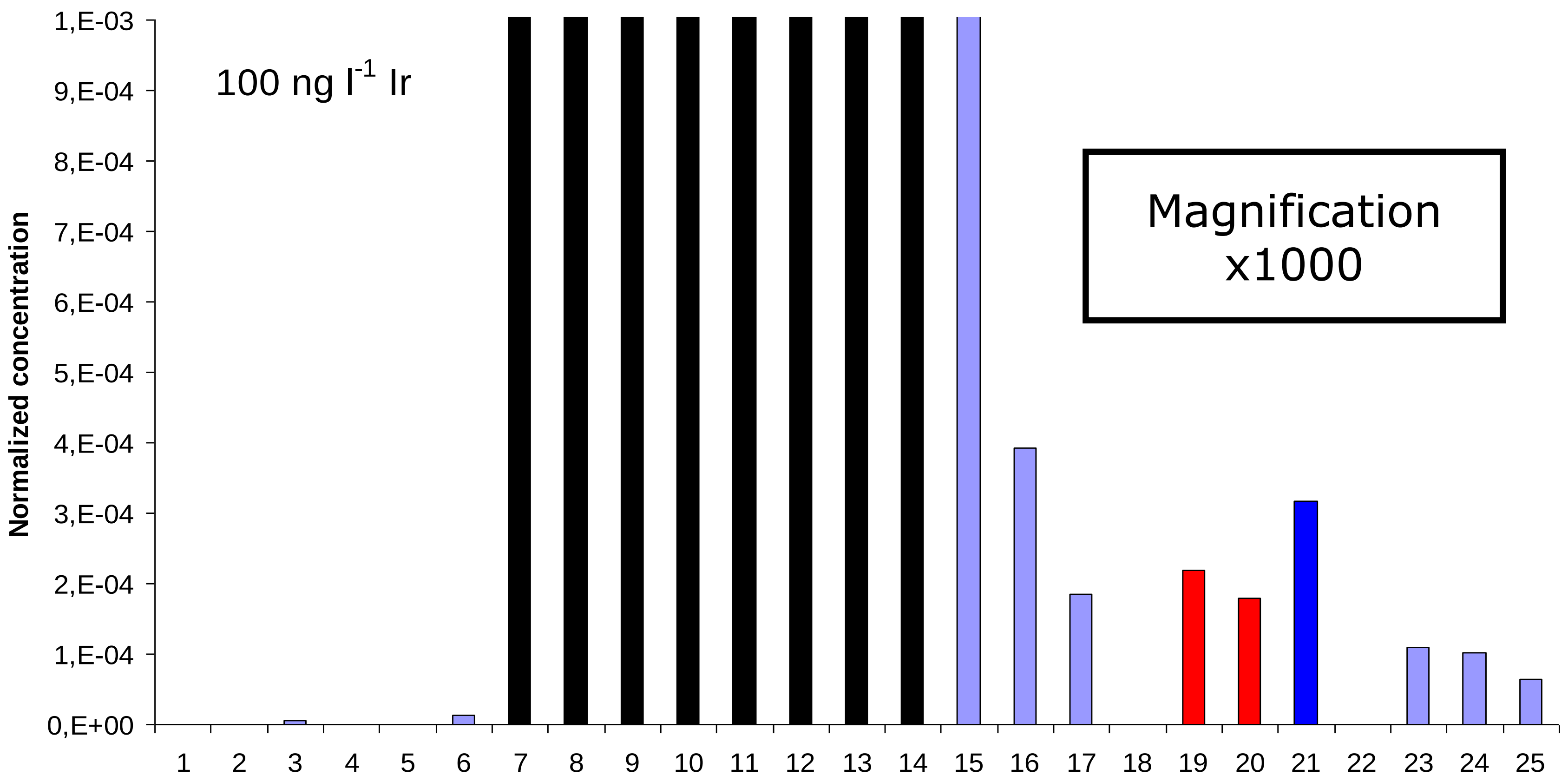
Applications dictate choice of tube materials

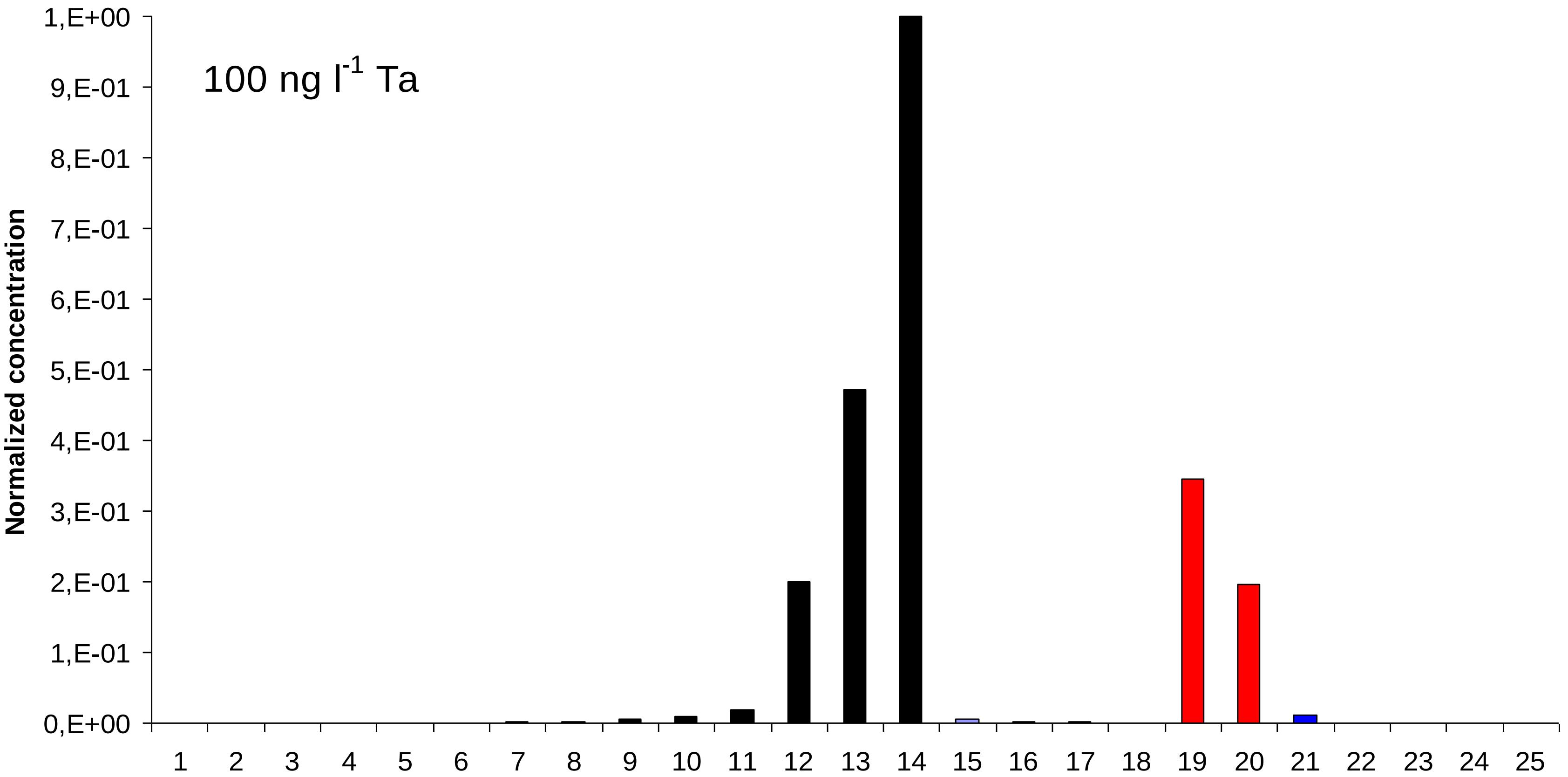



100 ng l-1 Ir
Normalized concentration
1,E+00
9,E-01
8,E-01
7,E-01
6,E-01
5,E-01
4,E-01
3,E-01
2,E-01
1,E-01
0,E+00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25



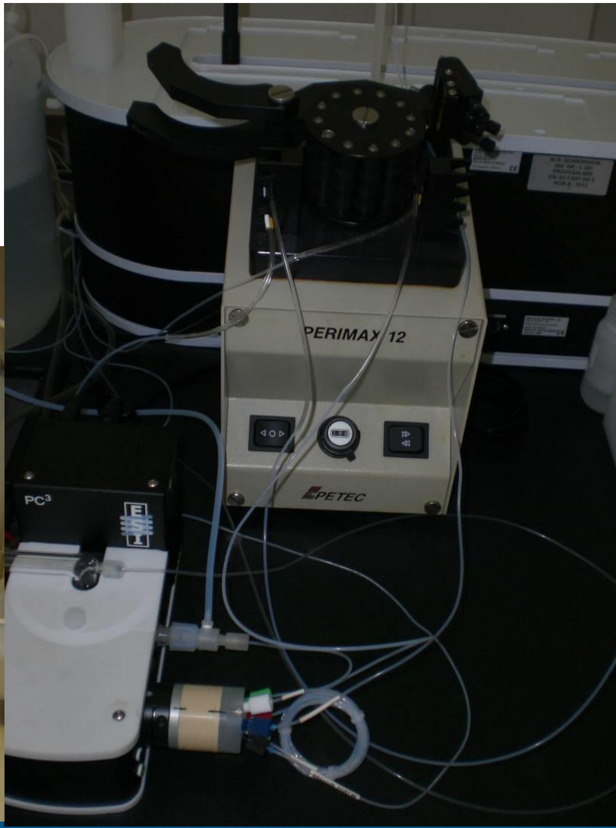
100 ng l-1 Ir
Magnification x100
Normalized concentration
1,E-02
9,E-03
8,E-03
7,E-03
6,E-03
5,E-03
4,E-03
3,E-03
2,E-03
1,E-03
0,E+00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


1,E-03
9,E-04
8,E-04
7,E-04
6,E-04
5,E-04
4,E-04
3,E-04
2,E-04
1,E-04
0,E+00
Normalized concentration
100 ng l-1 Ir
Magnification x1000
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25


100 ng l-1 Ta
Normalized concentration
1,E+00
9,E-01
8,E-01
7,E-01
6,E-01
5,E-01
4,E-01
3,E-01
2,E-01
1,E-01
0,E+00
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25

Memory effects

- In tubing – min. length and strong rinse solutions
- In spray chamber – low-volume or DIN, matrix optimization (suppression of volatile species formation)
- On cones – use 'Si-trick'
- Inside MS – wait…



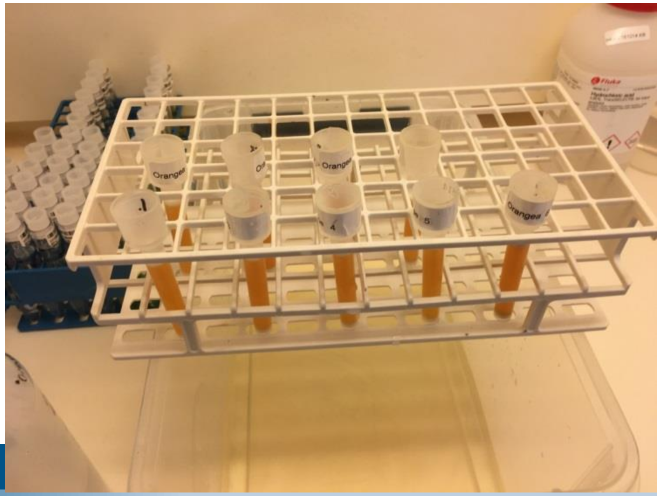
Clinical applications

TCEs in human brain, ng g^{-1} DW

	LOD	Median		LOD	Median		LOD	Median
Ga	0.05	0.07	**Ir**	0.005	0.004	**Ce**	0.008	1.8
Ge	0.7	2	**Os**	0.006	0.009	**La**	0.003	1.1
In	0.08	0.1	**Pd**	0.02	0.06	**Dy**	0.006	0.03
Ta	0.004	0.006	**Pt**	0.002	0.2	**Er**	0.002	0.006
Te	0.04	0.08	**Rh**	0.005	0.01	**Gd**	0.007	13
Tl	0.005	0.3	**Ru**	0.03	0.03	**Ho**	0.003	0.004

PGEs in body fluids

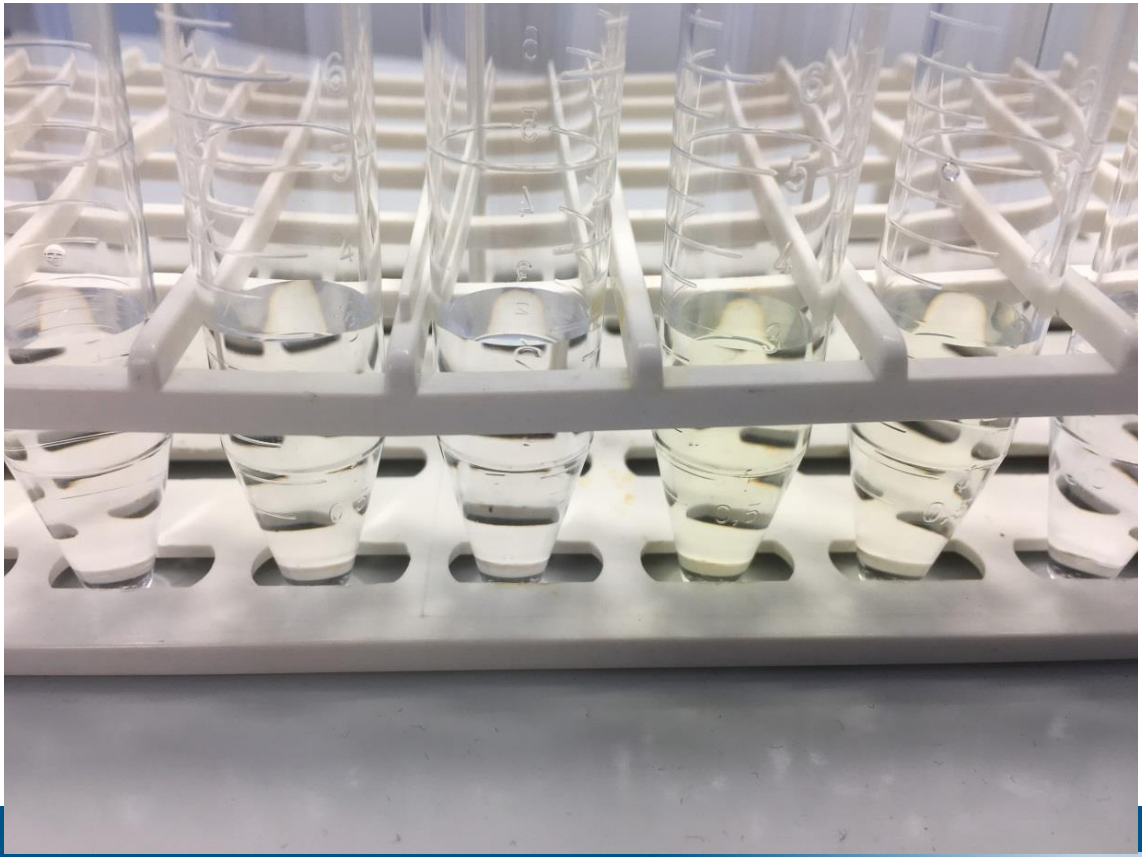
- Digestion with concentrated HNO_3 in Ultraclave (2-5 ml)
- Evaporation, dissolution in concentrated HCl
- Column separation using pre-cleaned AG 50W-X8 resin
- Quantitative (R>85%) recoveries of Au, Ag, Ir, Pd, Pt, Rh, Ru (As, B, Li, Sb, Te)
- Complete separation of Na, K, Mg, Ca, Fe, Rb, Zn, Cu, Sr, Ba, Pb
- DF < 1
- Aridus+ICP-SFMS (LR+HR)



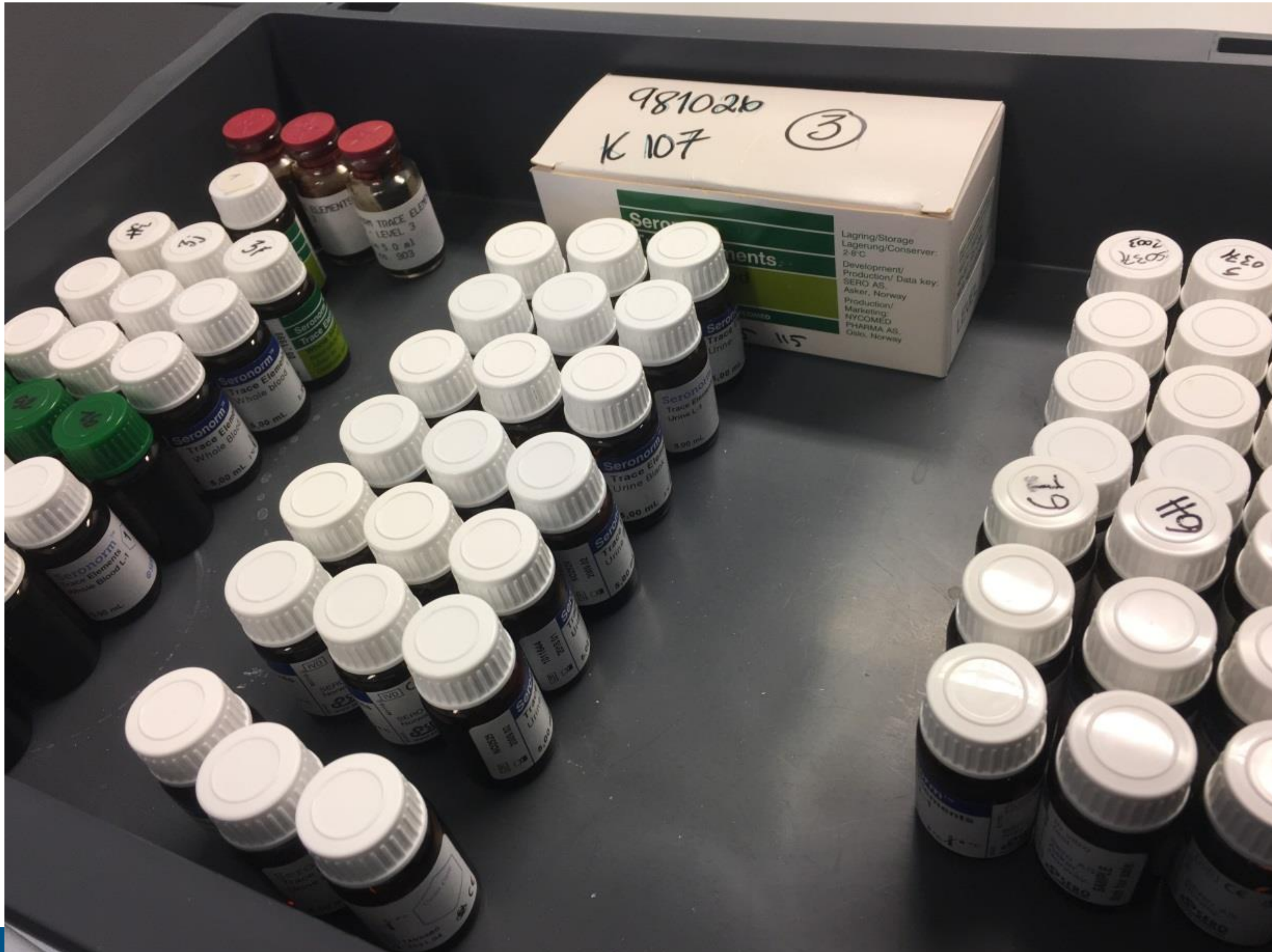
Separated fractions

LODs in the range 5-50 pg l^{-1}

20-200 times improvement compared to direct analysis after dilution



SERO AS test samples - pooled body fluids from Norwegian donors (first lots from 1990th)



Ranges of PGE in human pooled biological fluids, ng l^{-1}

	Urin (n=8)		Blood (n=8)		Serum (n=6)	
	Min	Max	Min	Max	Min	Max
Ir	<0.005	0.03	<0.005	0.07	<0.005	0.03
Pd	<0.1	2	<0.1	0.4	<0.1	0.3
Pt	0.3	5	0.3	3	0.1	0.5
Rh	<0.05	0.5	<0.05	0.8	<0.05	0.1
Ru	<0.05	0.2	<0.05	0.1	<0.05	0.1

WHO: 'Background Pt levels in human blood are of the order of 0.1-2.8 µg l^{-1}'

Conclusions

- ICP-SFMS offers instrumental detection limits in low ppq range
- Ultimate technique for multi-element TCE determination in variety of matrices
- High-resolution capabilities are indispencible for accurate determination of Ge, Ru, Pd, Rh, Ir and Pt
- Analysis at endogenous levels in clinical samples wil require pre-concentration and optimized introductio systems

Thank you for your attention!

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Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Application of double-focusing sector field ICP-MS for determination of ultratrace constituents in samples characterized by complex composition of the matrix

Ilia Rodushkin [a,b], Cora Paulukat [b], Simon Pontér [b,*], Emma Engström [a,b], Douglas C. Baxter [b], Dieke Sörlin [b], Nicola Pallavicini [a,b], Katerina Rodushkina [c]

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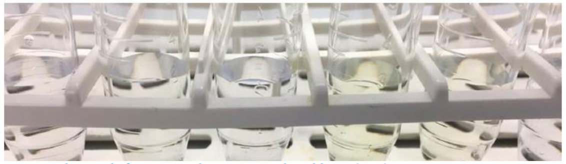
[b] ALS Laboratory Group, ALS Scandinavia AB, Aurorum 10, S-977 75 Luleå, Sweden
[c] Department of Chemistry, Uppsala University, Uppsala, Sweden

HIGHLIGHTS

- Determination of ultra-trace elements in snow, waters and clinical samples by ICP-SFMS.
- Combination of pre-concentration and matrix separation
- Concentration ranges of a variety of TCEs and other elements at ultra-trace levels in environmental sample matrices.

GRAPHICAL ABSTRACT



Spectrochimica Acta Part B 141 (2018) 80–84

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Analytical note

A concise guide for the determination of less-studied technology-critical elements (Nb, Ta, Ga, In, Ge, Te) by inductively coupled plasma mass spectrometry in environmental samples☆

Montserrat Filella [a,*], Ilia Rodushkin [b,c]

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[b] Division of Geosciences and Environmental Engineering, Luleå University of Technology, S-971 87 Luleå, Sweden
[c] ALS Laboratory Group, ALS Scandinavia AB, Aurorum 10, S-977 75 Luleå, Sweden

echnology-critical elements', mental matrices. Nowadays, ue of choice for measuring rd than often assumed. The died technology-critical ele-

Science of the Total Environment 624 (2018) 1634–1639

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Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Seasonal shift of diet in bank voles explains trophic fate of anthropogenic osmium?

Frauke Ecke [a,*], Åsa M.M. Berglund [b], Ilia Rodushkin [c], Emma Engström [c], Nicola Pallavicini [c], Erik Nyholm [b], Birger Hörnfeldt [a,1]

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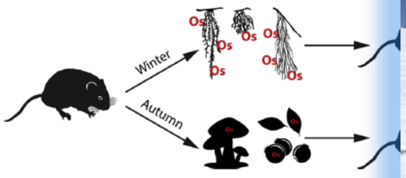
[c] ALS Scandinavia AB, Aurorum 10, SE-97775 Luleå, Sweden

HIGHLIGHTS

- Osmium concentrations in bank vole tissue shift seasonally.
- High osmium concentrations in bank voles are likely due to feeding lichens.
- Organ-to-body weight ratios indicate osmium-induced intoxication.

GRAPHICAL ABSTRACT



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International Journal of Hygiene and Environmental Health

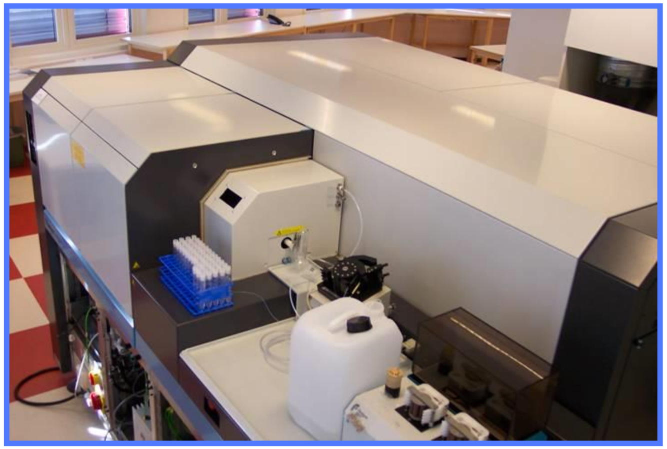
journal homepage: www.elsevier.com/locate/ijheh

Platinum, palladium, rhodium, molybdenum and strontium in blood of urban women in nine countries

Gerda Rentschler[a], Ilia Rodushkin[b], Milena Cerna[c,d], Chunying Chen[e], Florencia Harari[f], Raúl Harari[f], Milena Horvat[g], Frantiska Hruba[h], Lucie Kasparova[c], Kvetoslava Koppova[i], Andrea Krskova[c], Mladen Krsnik[j], Jawhar Laamech[k], Yu-Feng Li[e], Lina Löfmark[a], Thomas Lundh[a], Nils-Göran Lundström[l], Badiaa Lyoussi[k], Darja Mazej[g], Josko Osredkar[j], Krystyna Pawlas[m], Natalia Pawlas[m,1], Adam Prokopowicz[m], Staffan Skerfving[a], Janja Snoj Tratnik[g], Vera Spevackova[c], Zdravko Spiric[n], Anneli Sundkvist[l], Ulf Strömberg[a], Drazenka Vadla[n], Katerina Wranova[c], Soumia Zizi[k], Ingvar A. Bergdahl[l,o,*]

Instrumentation

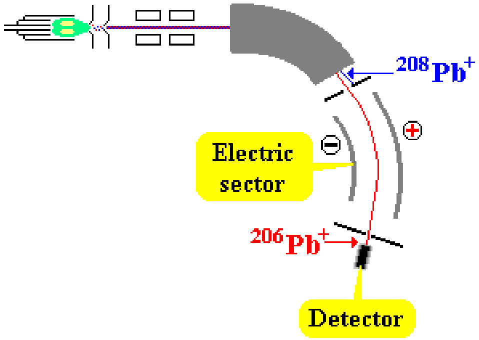
- 3 ICP-OES
- 14 ICP-SFMS
- 3 AFS
- 1 ICP-QMS
- 2 MC-ICP-MS



ICP-SectorFieldMS = HighResolution-ICP-MS = Double Focusing ICP-MS

- High ion transmission = high sensitivity
- Can be operated in high resolution mode(s)
- Flat-top peaks in low resolution
- Instrumental dark current <0.2 cps
- Flexible introduction system

- Relatively low matrix tolerance
- Large and heavy
- Expensive
- Requires experienced operators



Deodorants

- **Al, Cl, Zr, Hf, Si**

Aluminium Chlorohydrate, Aluminium Zirconium Tetrachlorohydrex Gly, Silica, Silica Dimethyl Silyate, Hf

All labware in contact with samples is acid cleaned

The Milestone UltraCLAVE

The next generation MW system

The UltraCLAVE Principle

The patented* Milestone UltraCLAVE achieves extraordinary performance capabilities by combining direct microwave heating in a high pressure reactor, which acts simultaneously as microwave cavity and vessel.

Lowest reported concentrations in body fluids