SOLVAY

Applications of high resolution ICP-MS in the central analytical lab at SOLVAY

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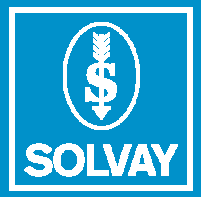


Introduction

Key tasks of the central analysis lab:

- Technical assistance (problem solving) to
  - Solvay research groups
  - SBUs (plants)
  - environmental department
  - external clients
- Development and harmonization of analytical methods between the different analytical labs within Solvay
- Follow new developments in analytical chemistry

➡ few routine analyse

➡ samples can be virtually any Solvay raw material, intermediate or finished product

3 SECTORS

PLASTICS

- PVC
- PEEK
- Polysulfones (PSU)
- Polyphenylene sulfide (PPS)
- Polyamide-imide (PAI)
- Polyarylamide (PA)
- Polyphtalamide (PPA)
- Fluoroelastomers
- Fluorin. polymer fluids (PFPE)
- PVDF, PFA, PTFE, ETFE…
- PVDC
- Polymer compounds (PE, PP, PVC) …

CHEMICALS

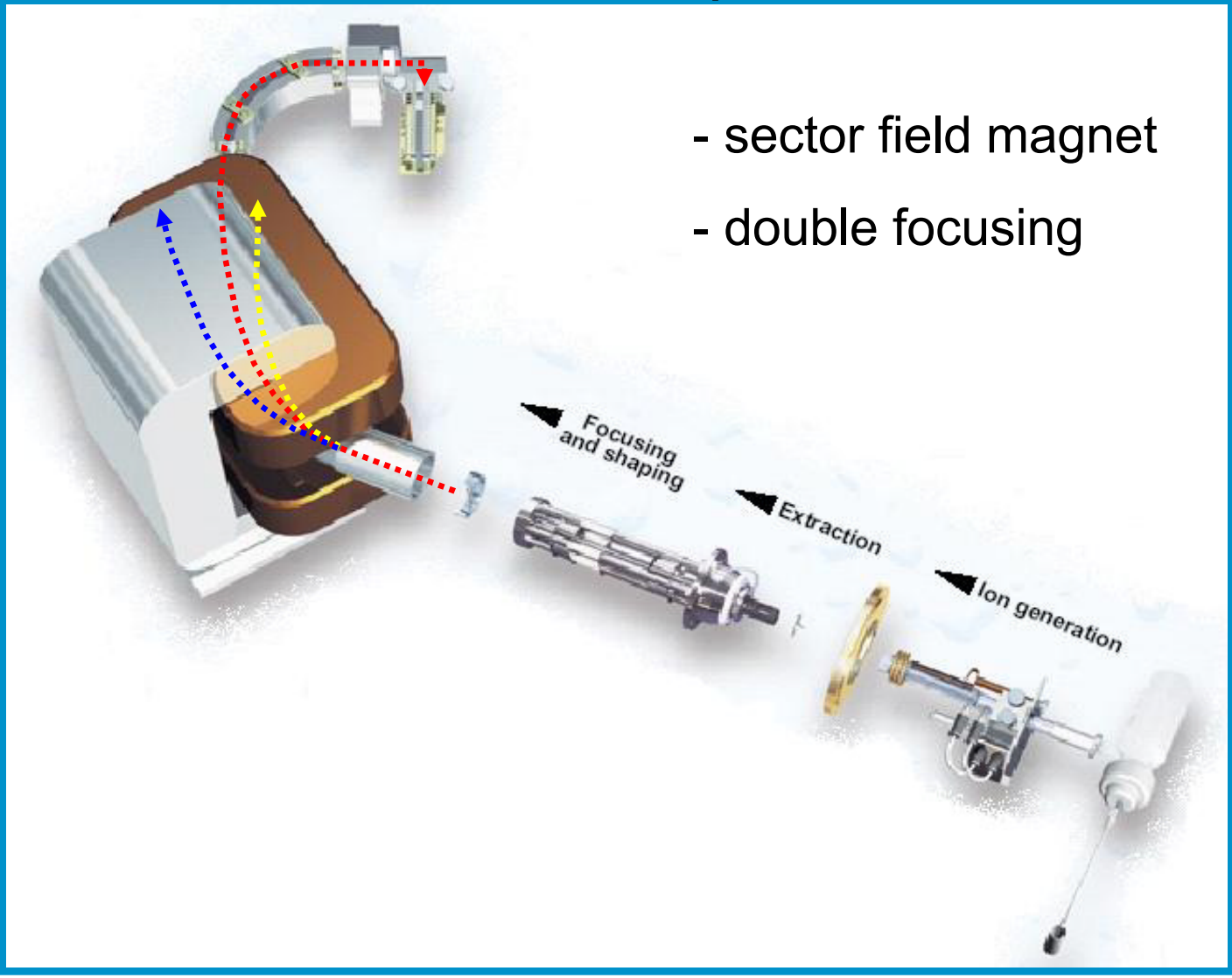
- Soda ash (Na_2CO_3)
- Sodium bicarbonate ($NaHCO_3$)
- Caustic soda (NaOH)
- Ba & Sr salts
- Caprolactones
- Glycerol & polyglycerol
- Chlorinated organics & inorganics
- H_2O_2
- Peracetic acid
- Persalts
- $CaCO_3$ & Mg salts
- Fluorinated molecules
- Organics …

PHARMA

- Cardiometabolics
- Neurosience
- Flu vaccines
- Pancreatic enzymes
- Gastroenterology
- Women’s and men’s health

High resolution ICP-MS: what, when and why?

Principle of HR-ICP-MS (Thermo Element2)



When do we use (HR-)ICP-MS?

low detection limits needed
and/or
only a small sample quantity available

Why a high resolution instrument?

wide diversity of analysis requests and sample matrices, very few routine

- **great variety of (unexpected) spectral interferences**
- **avoid optimization of a reaction/collision cell parameters for every new analysis request**

Examples of applications with HR-ICP-MS

1. Metal ultra-trace impurities in ultrapure fluoropolymers

2. Metals pollutants in effluents from soda ash plants

Example 1: ultrapure fluoropolymers

FLUOROPOLYMERS

PVDF, PFA, perfluoroelastomers…

- high temperature resistance
- very resistant towards corrosive reagents

  (UPW, acids, H_2O_2, …)
- can be produced with high purity

  (low cations & anions, no stabilizers, plasticizers or additives)
- good ageing resistance
- can be moulded or extruded

very well suited for liquid distribution systems in semiconductor industry…

… but they are demanding samples for an inorganic analyst

- typical trace metal concentrations in high purity PVDF: sub-ppb to at most a few hundred ppb

Method of choice: ICP-MS

- difficult to get into solution

SEMI®* GUIDELINES

*Semiconductor Equipment and Materials International

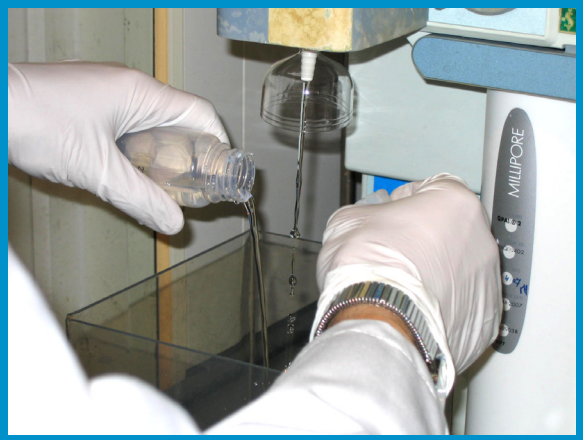
- **SEMI F40 & F57: leachout tests for surface extractable contaminants**
  - in water, H_2O_2, … at 20-85 °C
  - specifications for 16 cations (+ 7 anions + TOC) for 7 days leachout in water at 85 °C
- **SEMI F48: bulk trace metals analysis in polymers**
  - digestion in closed vessel or by dry ashing
  - list of 20 elements

e.g. leachout test on fluoroelastomer O-rings:

Comparison between

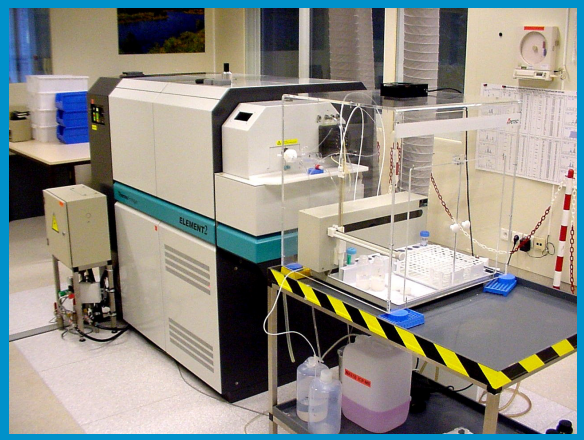
- 1 month leaching in **ultrapure H2O** at 80 °C
- 1 month leaching in **“Piranha fluid”** at 80 °C

  “Piranha fluid” = u.p. H_2SO_4 96% / u.p. H_2O_2 30% 3:1 (v/v)
- 1 week leaching in u.p. **49% HF** at room temperature



Rinsing 10 x 2 min

Leachout
in duplicate + 3 proced. blanks



Measurement by
HR-ICP-MS

Lab environment

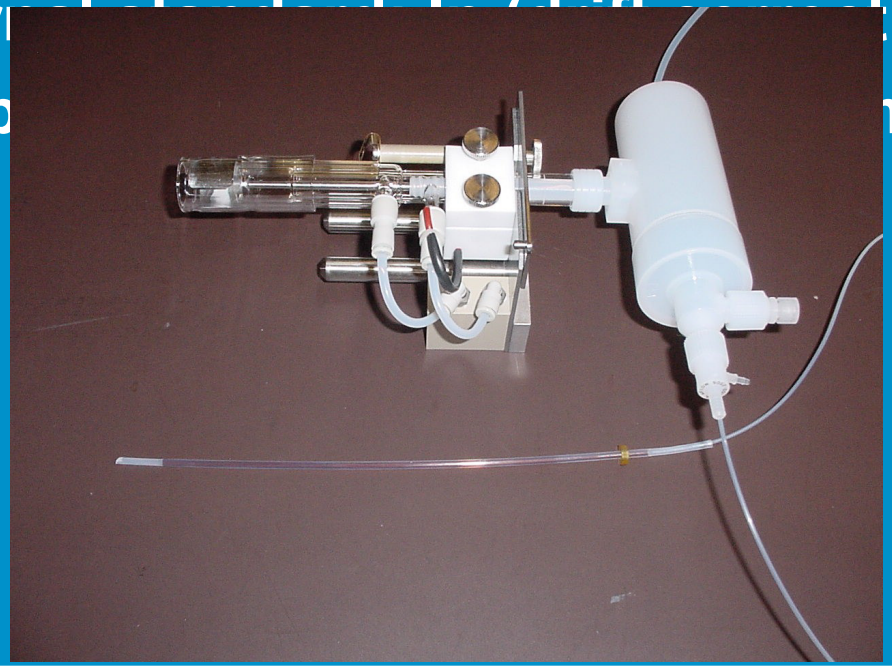
sub-µg/l trace level analysis
needs a
clean working environment !

Class 10000 clean room

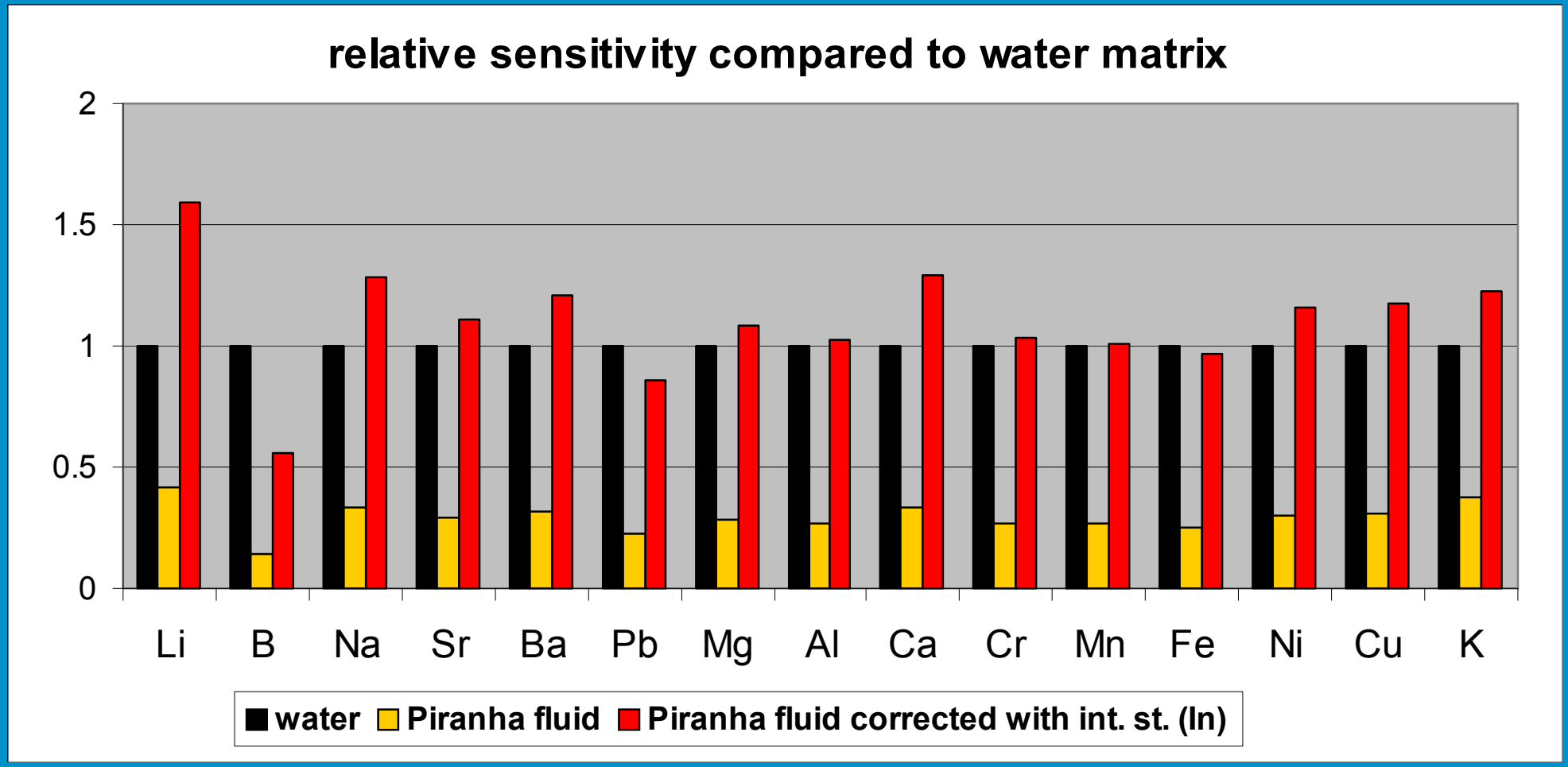
FEP bottles

ICP-MS Measurements:

- Dilution before the measurements:
  - H_2O matrix: no dilution
  - 49% HF and “Piranha fluid”: 10 x dilution
- Sample introduction system:
  - H_2O and “Piranha fluid”: quartz, Pt cones
  - HF: HF-resistant, Pt cones
- Inter[illegible]ion)
- Calib[illegible]matching



Matrix effect in 10x diluted Piranha fluid



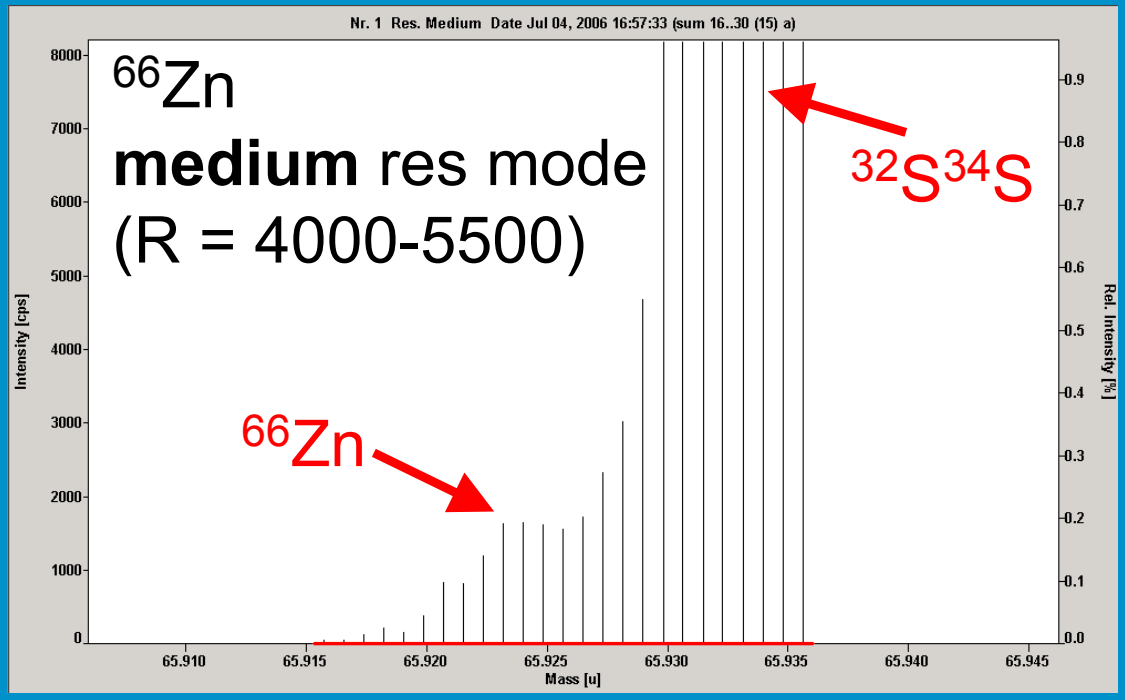
Matrix matching is necessary !!!

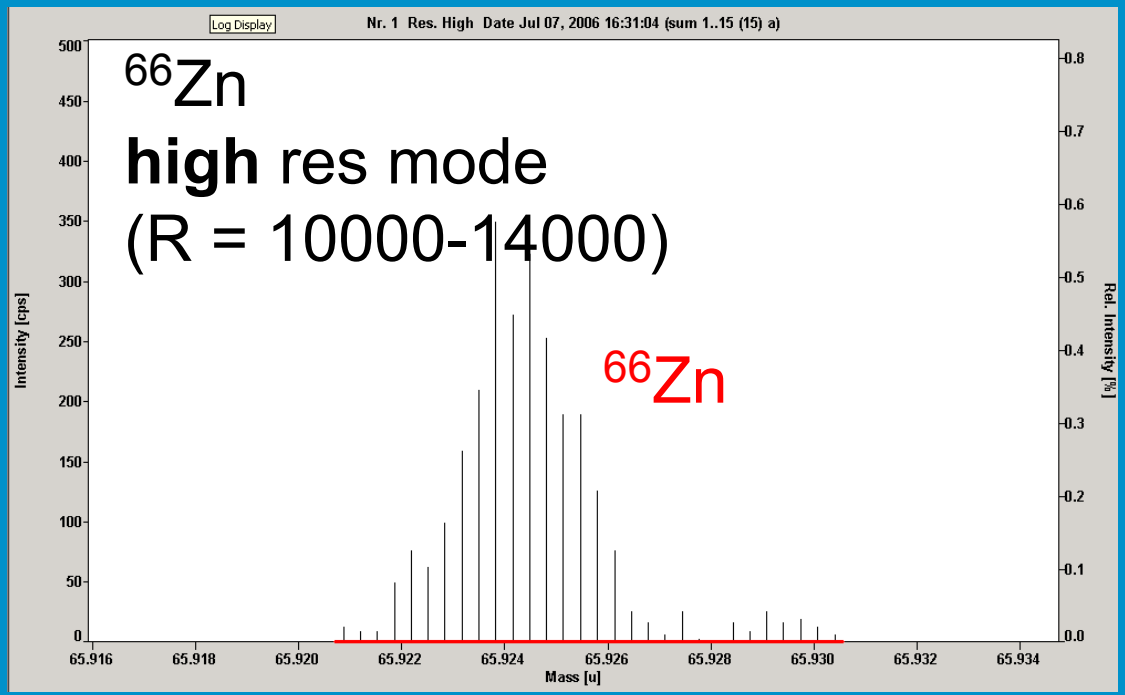
Interferences:

e.g. ^{66}Zn interfered in 10x diluted Piranha fluid by

$^{32}S^{34}S$	R = 4742
$^{34}S^{16}O_2$	R = 2083
$^{32}S^{16}O^{18}O$	R = 1644

Piranha fluid =
H_2SO_4 96% / H_2O_2 30%
3:1 (v/v)





Results: comparison WATER – PIRANHA – 49% HF

extractable conc., nomalized to average in WATER (=1)

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Bulk trace metals in high purity PVDF: analytical procedure (SEMI F48)

Samples

Sampling

Calcination of 1-20 g
on Bunsen in duplicate
+ crucible blanks

+ muffle furnace 585 °C, 6-12 h

Residue recovery:

residue taken up in 2 ml conc. u.p. **HCl**

↓

evaporation till dryness on hotplate

↓

residue taken up in 1 ml hot conc. u.p. **HNO_3**

↓ + Sc,In,Bi

brought to volume (20-50ml) with u.p. H_2O
in FEP bottle

↓

measurement by HR-ICP-MS (external calibration)

Method detection limits

The method detection limits are mainly determined by:

- contamination of the instrument by other sample matrices
- the amount of sample available (dilution factor)
- the cleanliness of the procedure blanks (crucibles)

LOD (3σ) for 10 g PVDF in 50 ml

	LOD (3σ) (ppb)	
	instrum.	proced.
Li (LR)	0.1	0.6
Na (LR)	1	1
Sr (LR)	0.004	0.01
Zr (LR)	0.003	5
Mo (LR)	0.001	0.1
Sn (LR)	0.01	0.3
Ba (LR)	0.005	0.06
Pb (LR)	0.004	0.3
Mg (MR)	0.05	0.2
Al (MR)	0.3	8

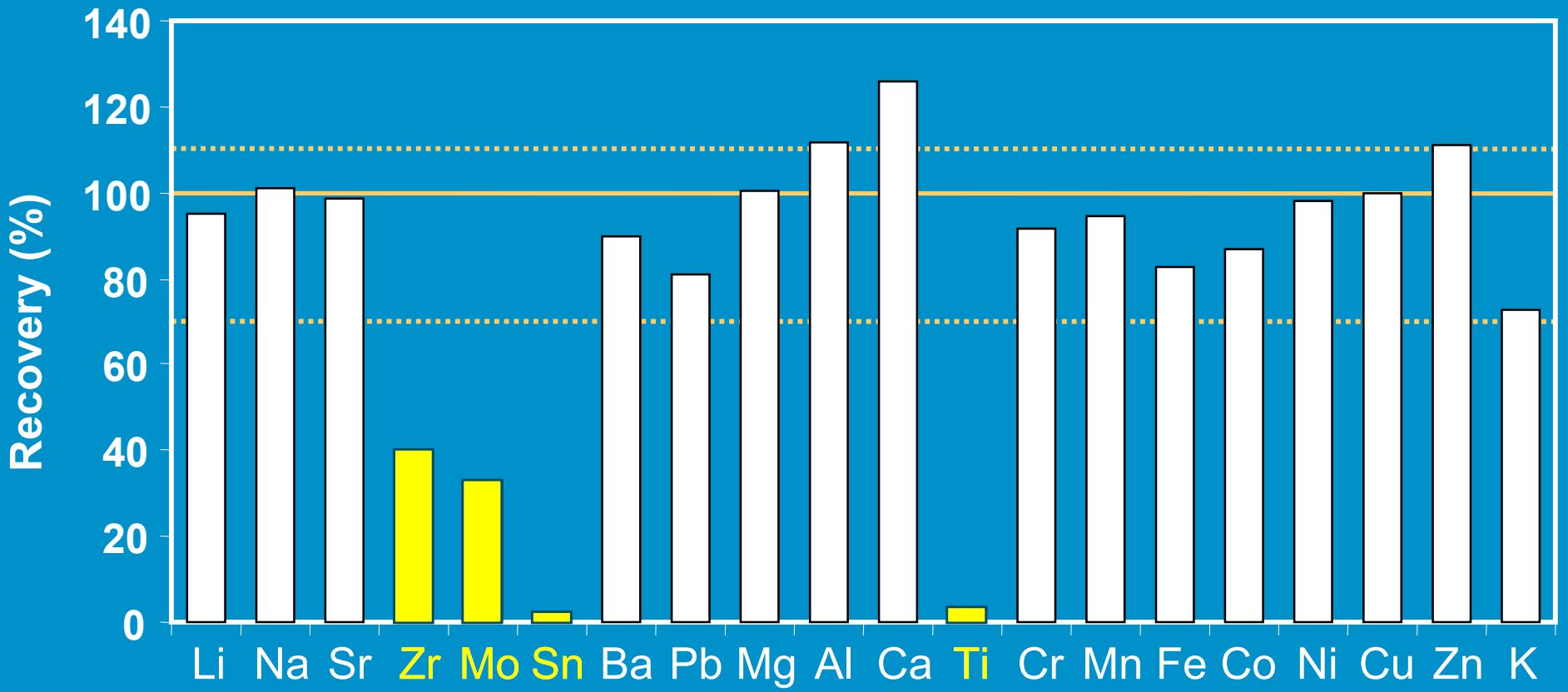
	LOD (3s) (ppb)	
	instrum.	proced.
Ca (MR)*	1	4
Ti (MR)	0.04	0.8
Cr (MR)	0.01	0.6
Mn (MR)	0.002	0.03
Fe (MR)	0.05	1
Co (MR)	0.01	0.04
Ni (MR)	0.2	0.7
Cu (MR)	0.03	(8)
Zn (MR)	0.07	4
K (HR)	0.12	0.5

*Ca42

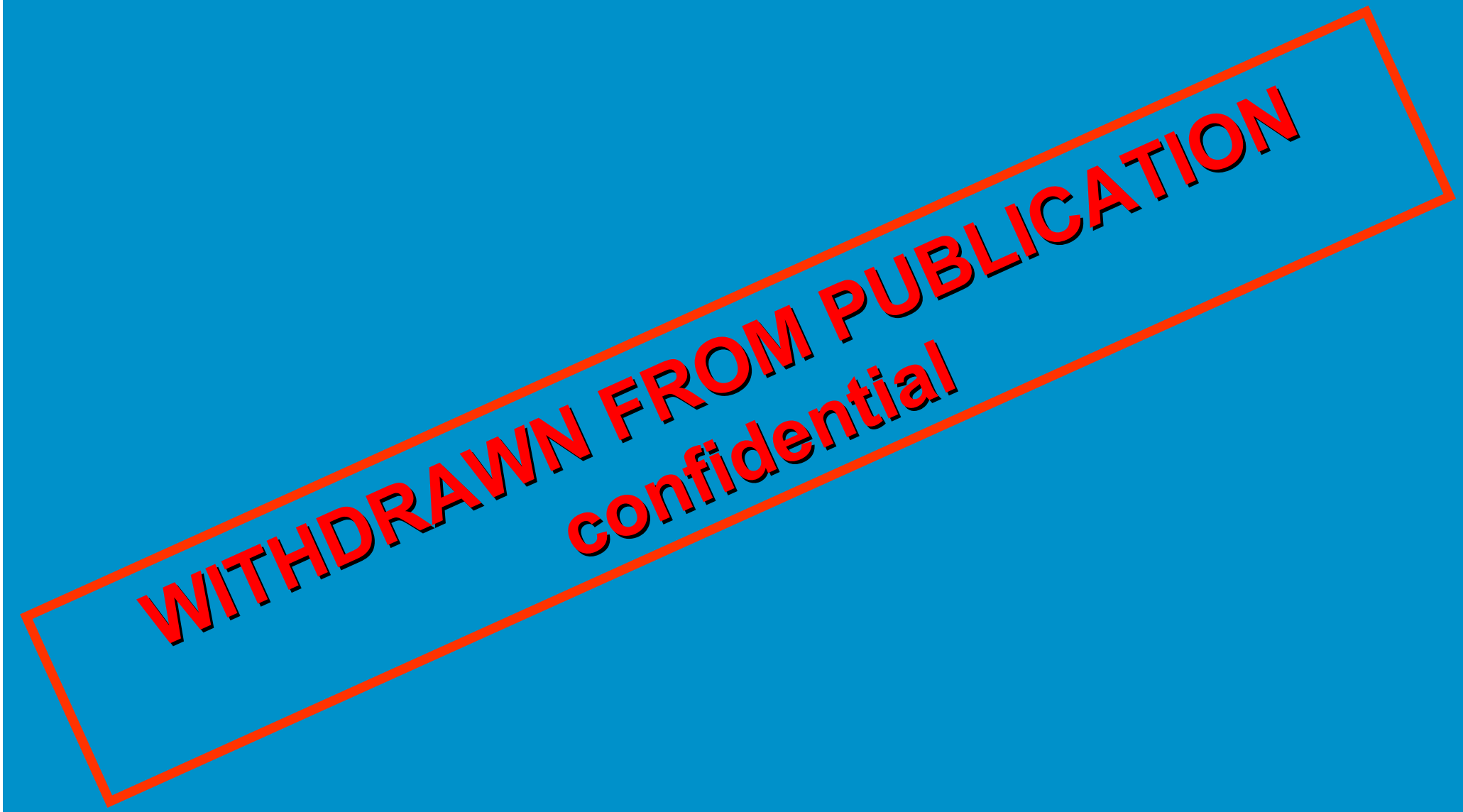
Analyte recovery

100 ppb spike

(Merck VIII + 1 g/l Merck stand. sol. for Ti, Zr, Mo, Sn)



Example 2: Trace metals in a > 100 g/l $CaCl_2$ + NaCl matrix



Determination of metals in a > 100 g/l CaCl2 + NaCl matrix

- solutions contain > 100 g/l $CaCl_2$ + NaCl
- 60-150 x dilution and acidification (HNO_3) before analysis
- use of a second sample introduction system (quartz) to avoid memory effects on Na or Ca determinations in other sample types
- matrix difficult to matrix match → calibration by standard addition
- internal standard(s) for drift correction
- heavy Ca and Na matrix → many severe spectroscopic interferences

Some potential interferences in a CaCl2 + NaCl (+SO_4^{2-}) matrix:

	Measuring mode to separate interferences	
	Medium resolution	**High resolution**
^{27}Al		
^{52}Cr	$^{36}Ar^{16}O$, $^{38}Ar^{14}N$, $^{35}Cl^{17}O$, $^{35}Cl^{16}O^{1}H$	
^{53}Cr	$^{37}Cl^{16}O$, $^{35}Cl^{18}O$, $^{38}Ar^{14}N$	
^{55}Mn	$^{40}Ar^{14}N^{1}H$, $^{96}K^{16}O$	
^{54}Fe	^{54}Cr, $^{40}Ar^{14}N$, $^{37}Cl^{16}O^{1}H$	
^{56}Fe	$^{40}Ar^{16}O$, $^{40}Ca^{16}O$	
^{57}Fe	$^{40}Ar^{16}O^{1}H$, $^{40}Ca^{16}O^{1}H$	
^{59}Co	$^{36}Ar^{23}Na$, $^{43}Ca^{16}O$	
^{58}Ni	^{58}Fe, $^{42}Ca^{16}O$	
^{60}Ni	$^{44}Ca^{16}O$, $^{23}Na^{37}Cl$, $^{43}Ca^{16}O^{1}H$	
^{61}Ni	$^{44}Ca^{16}O^{1}H$, $^{38}Ar^{23}Na$, $^{23}Na^{37}Cl^{1}H$	
^{63}Cu	$^{40}Ar^{23}Na$, $^{40}Ca^{23}Na$?	
^{65}Cu	$^{40}Ar^{23}Na$, $^{32}S^{33}S$	
^{64}Zn	^{64}Ni, $^{44}Ca^{18}O$, $^{32}S^{32}S$, $^{32}S^{16}O_2$	
^{66}Zn	^{64}Ni, $^{44}Ca^{18}O$, $^{34}S^{16}O2$	$^{32}S^{34}S$
^{67}Zn	$^{35}Cl^{16}O_2$	
^{68}Zn	$^{35}Cl^{16}O^{17}O$	$^{34}S^{34}S$
^{75}As		$^{40}Ar^{35}Cl$, $^{40}Ca^{35}Cl$
^{111}Cd		
^{118}Sn		
^{200}Hg		
^{207}Pb		

Interferences:

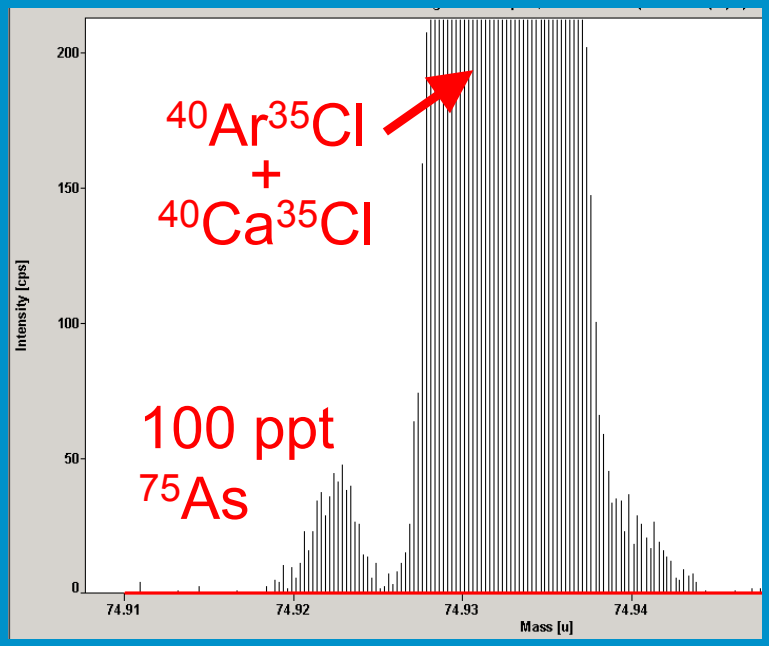
e.g. ^{75}As interfered in a 2.7 g CaCl2 + NaCl solution by

$^{40}Ar^{35}Cl$ R = 7773

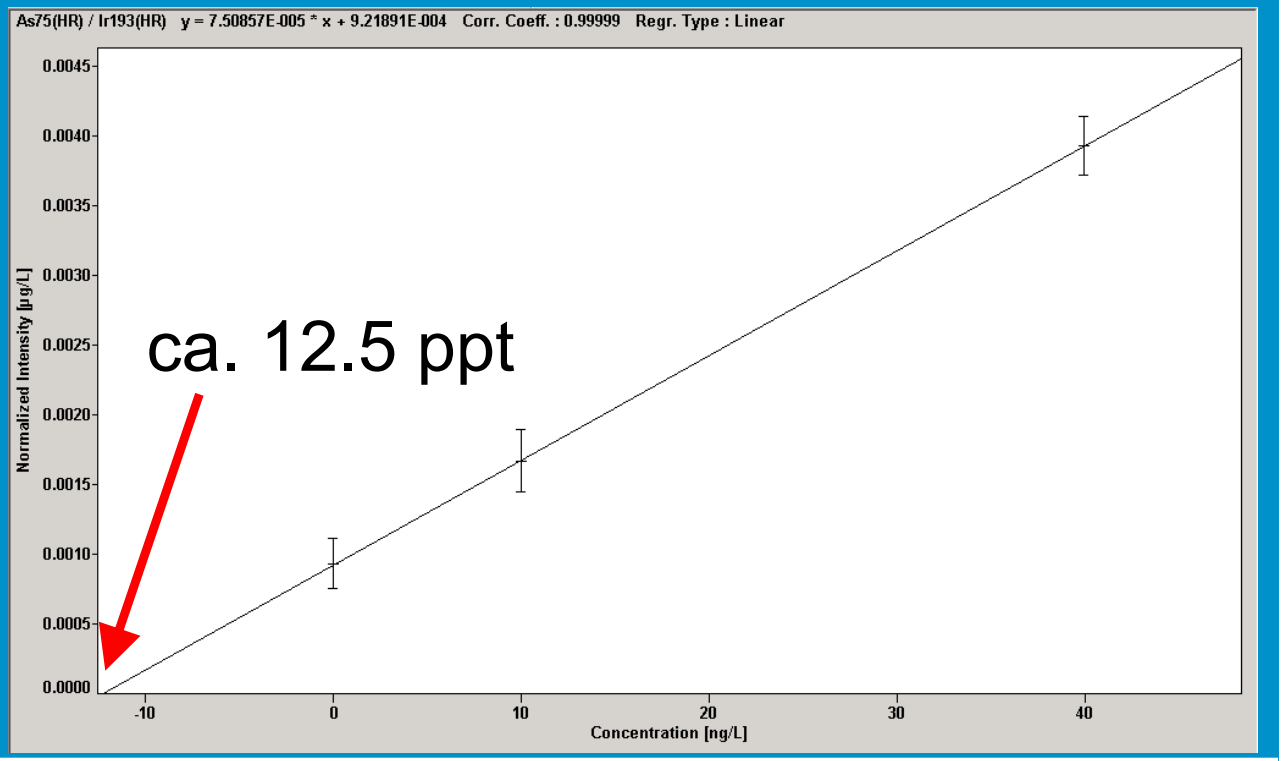
$^{40}Ca^{35}Cl$ R = 7613

➡ Measured in high resolution mode (R > 10000)

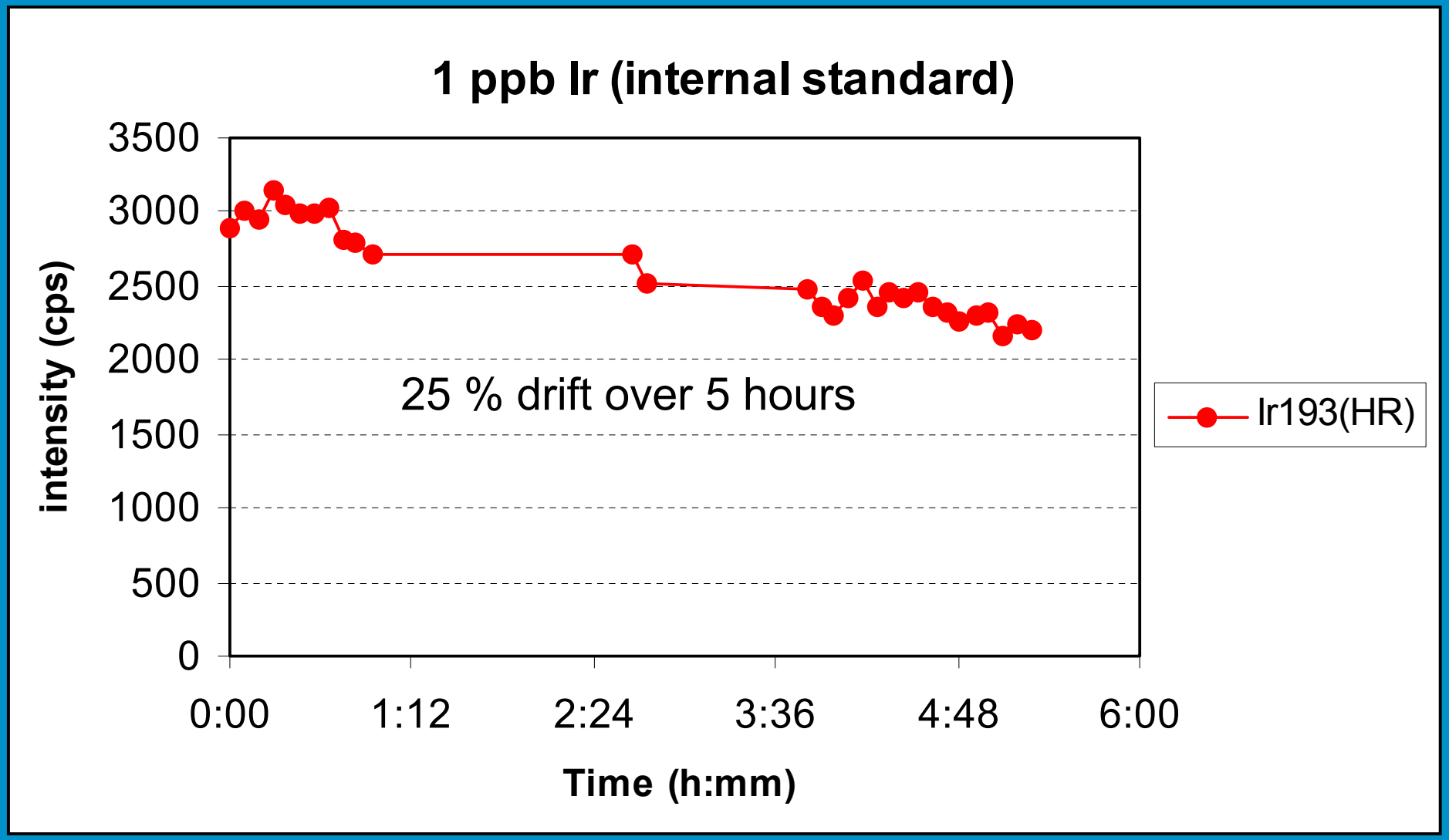
^{75}As 100 ppt in High Res mode



Calibration by stand. addition for ^{75}As (Ir as int.st.)



Signal drift in approx. 2.7 g/l CaCl2 + NaCl :



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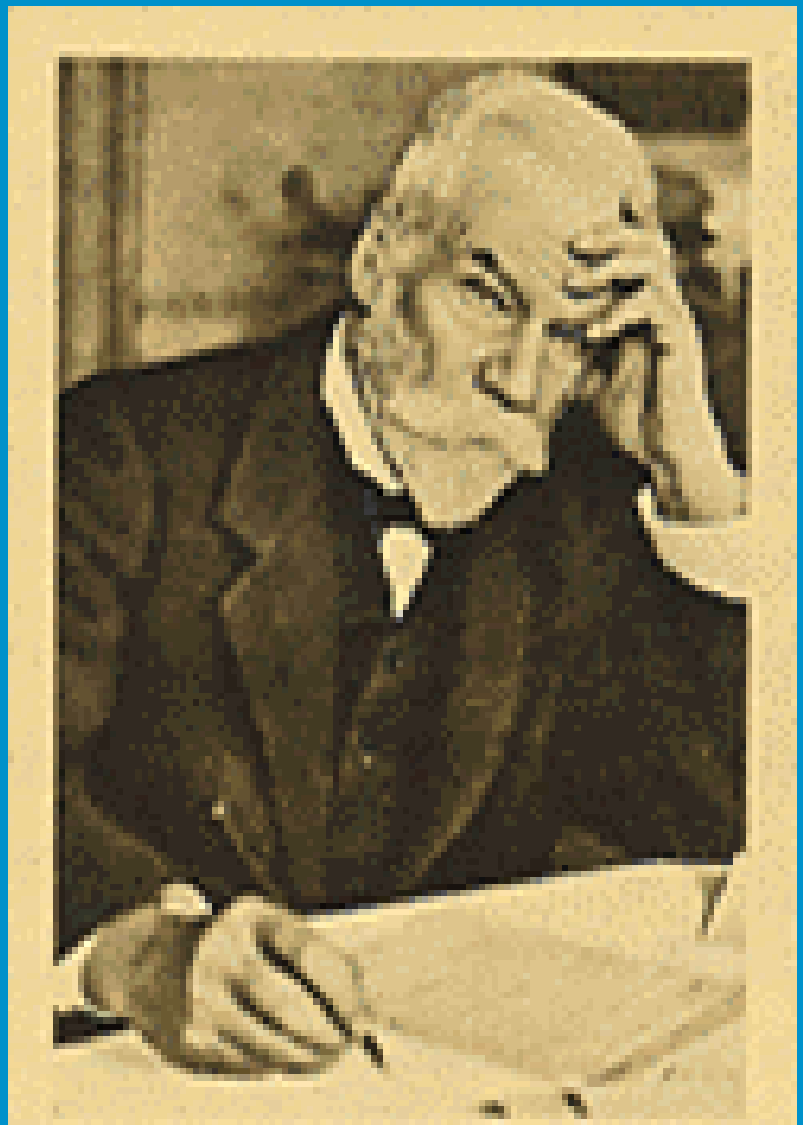

Ernest Solvay
1838 - 1922

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