

16.05.2018

ISOTOPE DILUTION MASS SPECTROMETRY

applied as primary method of measurement
with examples from the ENVCRM project

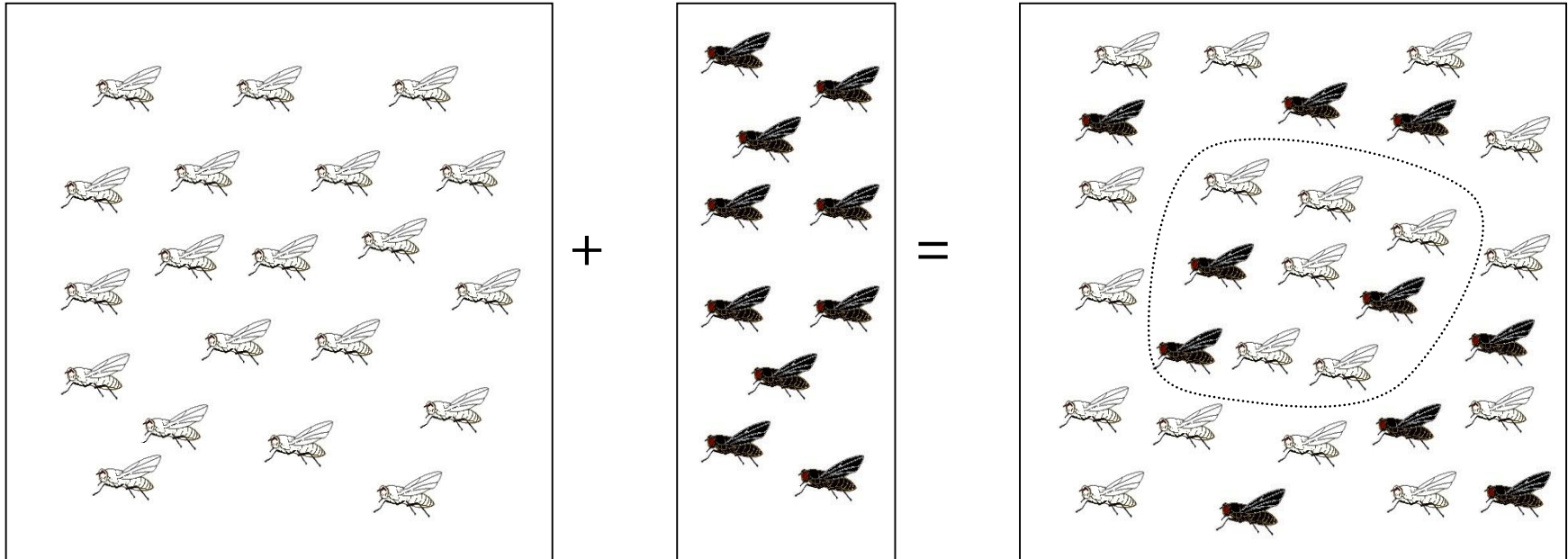
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Principle illustrated by “Fly dilution”

“Fly dilution”

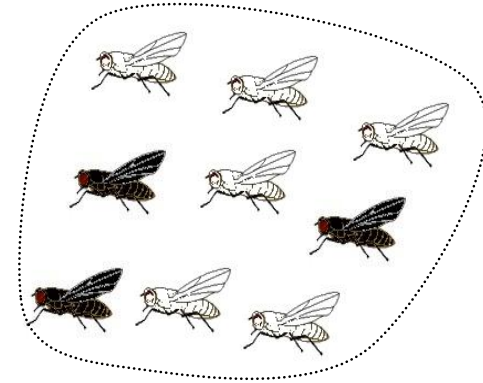


To an existing, normal population of white Tsetse-Flies

Jackson adds a known quantity of marked (black) flies

After mixture of both populations, sampling takes place (dotted line)

Sample composition



$$\frac{\text{marked flies in the sample}}{\text{non marked flies in the sample}} = \frac{\text{all marked flies}}{\text{all non marked flies}}$$



$$\frac{3}{6} = \frac{10}{\text{all non marked flies}} \Rightarrow \text{all non marked flies} = \frac{6 \cdot 10}{3} = 20$$

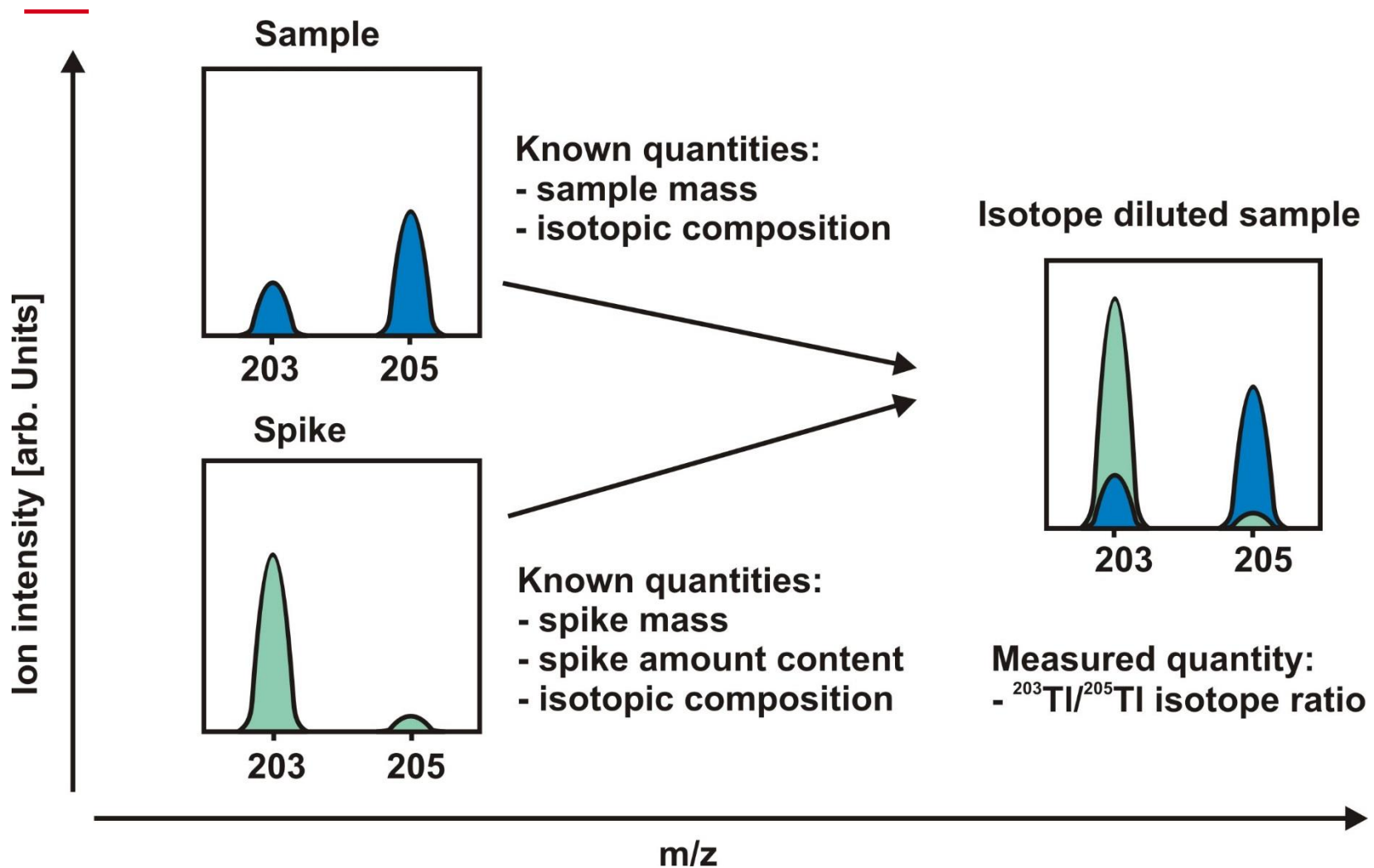
Requirements for fly dilution

-
- ▶ **Knowledge:** about the quantity of marked and released flies
 - ▶ **Confirmation:** of white and black Tsetse-Flies being homogenous distributed
 - ▶ **Ability:** to identify and separate white and black flies
 - ▶ You must **not miscount**

Isotope dilution mass spectrometry (IDMS)

Principle, performance & equation system

Principle of isotope dilution mass spectrometry



-
- ☺ Losses of analyte do not affect the accuracy of the result
 - ☺ Nearly matrix independent
 - ☺ Major (%) to ultra-trace components (< pg/g)
 - ☺ Elements, species and compounds
 - ☺ Various matrices
 - ☺ High trueness together with smallest uncertainty
 - ☺ Potential to be a primary method of measurement
 - ☹ Not a non-destructive method
 - ☹ Complete isotopic exchange needs to be guaranteed
 - ☹ At least two isotopes are needed, which are free from any interferences

$$\rightarrow w_x = w_{y,b} \cdot \frac{M_x \cdot m_y}{M_b \cdot m_x \cdot a_{x,b}} \cdot \frac{(R_y - R_{xy})}{(R_{xy} - R_x)}$$

Equation only consists of the **isotope ratio of the blend**, the **masses of sample and spike** as well as **known or tabulated quantities**.

The result can easily be calculated and the set-up of an uncertainty budget is straight forward.

Comparison of equations: Vogl (2007)

Pitfalls in IDMS

-
- ▶ **Systematic errors or not corrected bias for weighings**
 - ▶ Moisture or water content of the sample
 - ▶ Evaporation of solutions, electrostatic effects etc.
 - ▶ **No complete isotopic equilibrium between sample & spike**
 - ▶ Incomplete digestion
 - ▶ Different species during separation
 - ▶ **Systematic errors or not corrected bias when determining isotope ratios**
 - ▶ Dead time effects when using pulse counting systems
 - ▶ Mass fractionation in mass spectrometer
 - ▶ Contaminations

- ▶ Moisture or water content in the sample has to be considered
 - ▶ Classical oven drying method
 - ▶ Karl-Fischer-Titration
 - ▶ Commercial moisture analyzer
- ▶ Reduce static charges when weighing plastic container
 - ▶ Commercial tools
 - ▶ Blow out gun with ionized nitrogen
- ▶ Consider air buoyancy
 - ▶ Depends on the different densities
 - ▶ Leads to a bias of the weighed object
 - ▶ For a sample density $\approx 10^3$ kg/m (e.g. water) the resulting bias is $\approx 10^{-3}$ relative

Equation for buoyancy correction

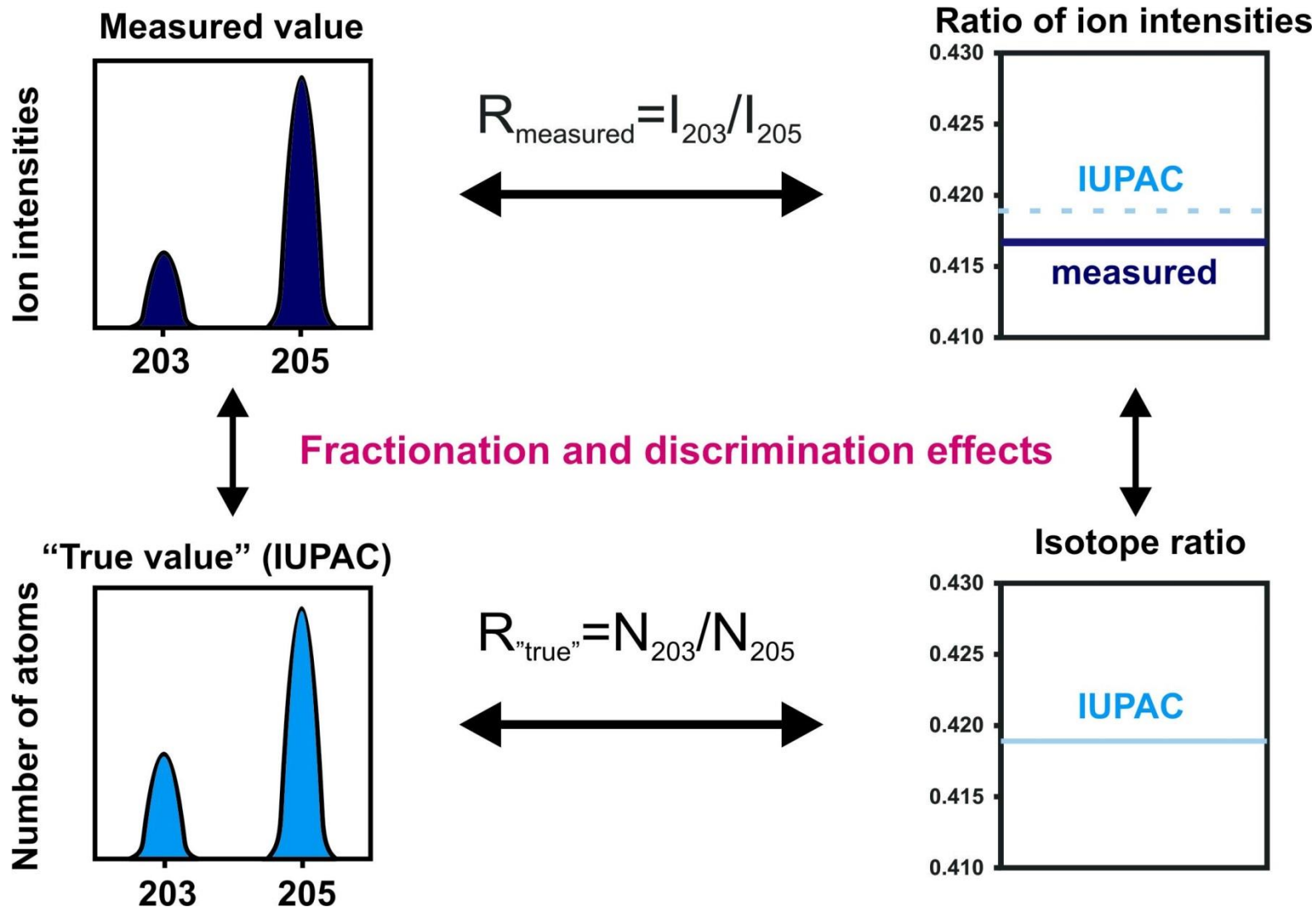
$$m_x = m_{x,obs} \cdot \frac{\left(1 - \frac{\rho_{air}}{\rho_{bal}}\right)}{\left(1 - \frac{\rho_{air}}{\rho_x}\right)}$$

Vogl et al. (2010)

Isotope ratio measurements

Mass bias, interferences & matrix effects

Isotope ratio or ion current ratio?



Correction of mass fractionation and discrimination effects

- ▶ External: Isotope reference materials, IUPAC, standard-sample-bracketing



Sample	$R_{cor}^{Sa} = K \cdot R_{measured}^{Sa}$
Standard	$K = \frac{R_{certified}}{R_{measured}}$

- ▶ Single IDMS, only blend isotope ratio measured

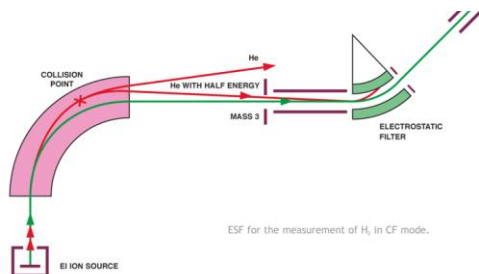
$$w_x = w_{y,b} \cdot \frac{M_x \cdot m_y}{M_b \cdot m_x \cdot a_{x,b}} \cdot \frac{(R_y - K \cdot R_{xy})}{(K \cdot R_{xy} - R_x)}$$

- ▶ Single IDMS, all isotope ratios measured

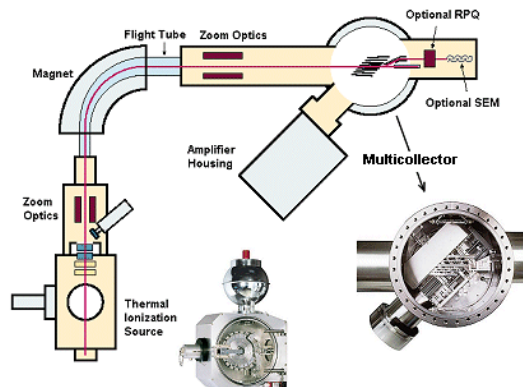
$$w_x = w_{y,b} \cdot \frac{M_x \cdot m_y}{M_b \cdot m_x \cdot a_{x,b}} \cdot \frac{(K \cdot R_y - K \cdot R_{xy})}{(K \cdot R_{xy} - K \cdot R_x)}$$

Selected Mass Spectrometers

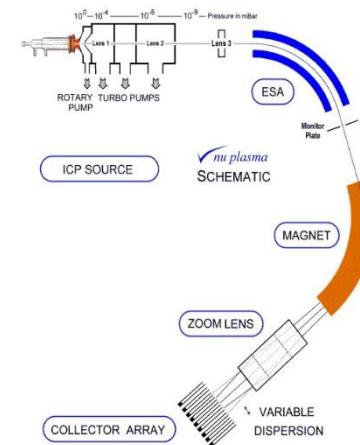
Stable Isotope Ratio MS (IRMS)



MC-TIMS



MC-ICPMS



Mass Spectrometer	Typical Repeatability in %
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Q-ICPMS

0.1 – 0.5

HR-ICPMS

0.05 – 0.2

MC-ICPMS

0.005 – 0.02

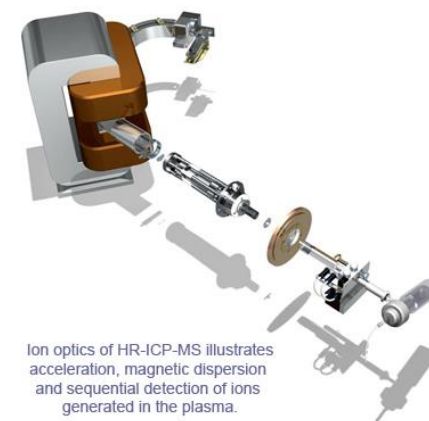
MC-TIMS

0.005 – 0.05

IRMS

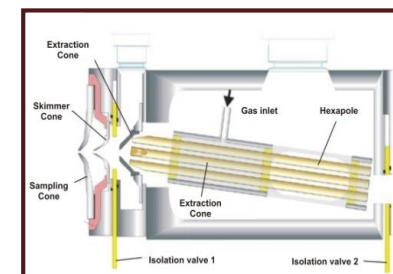
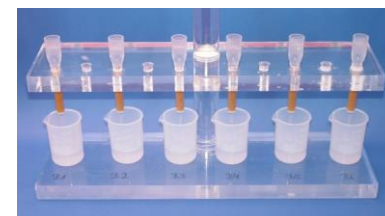
0.0005 – 0.05

HR-ICPMS

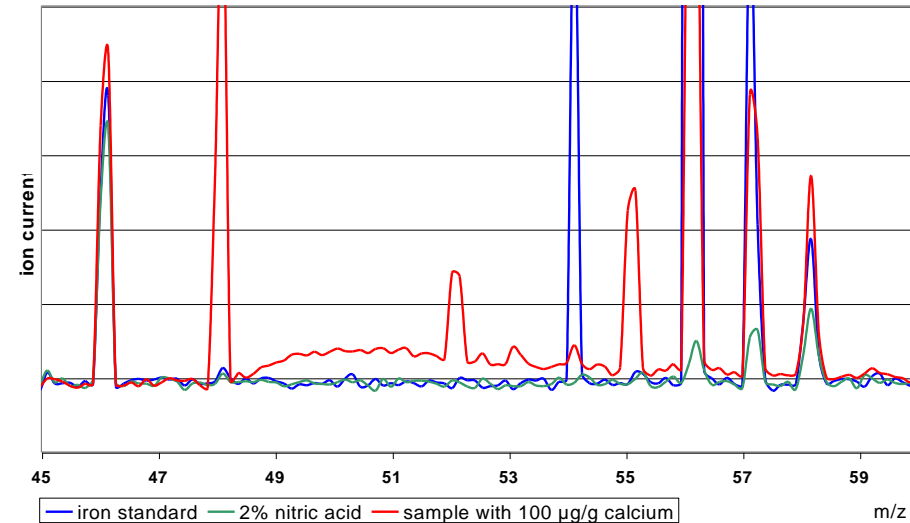
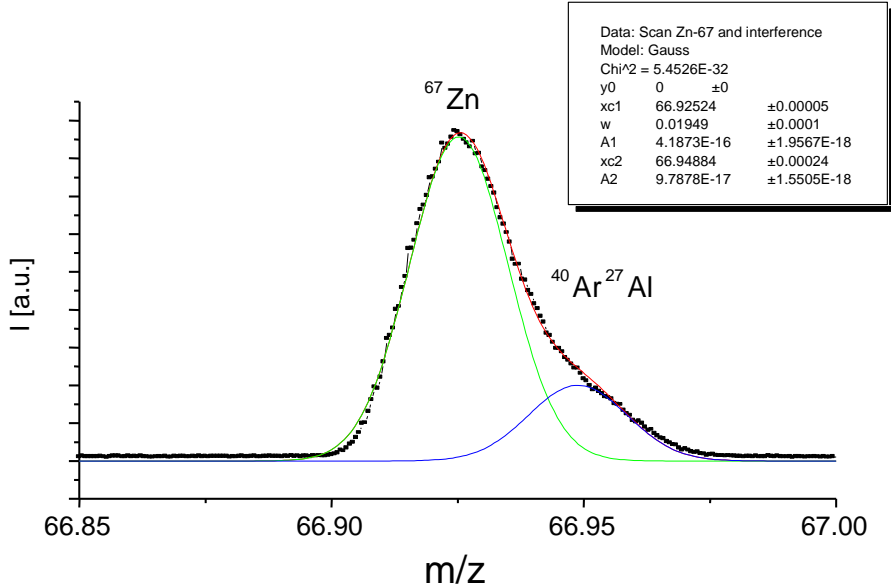


Isobaric and molecular interferences and their removal

- ▶ Best way to avoid spectral interferences is prior chemical separation: removal of matrix-based interferences and of matrix effects
- ▶ Use of higher mass resolution capabilities: removes interferences such as ArO^+ , ArCl^+ , ArNa^+ , O_2^+ , but sensitivity drops to $\approx 2\%$ at a resolution of 10000
- ▶ Use of collision and reaction cell technology: energy spread is reduced, but also multi-element capability, often interferences are only reduced
- ▶ Last possibility: Mathematical correction models, introducing additional uncertainty



Trace-matrix separation or not?



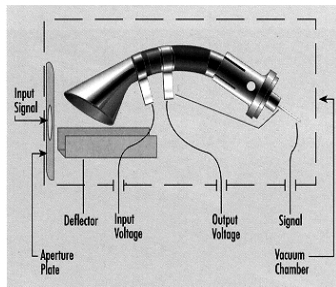
- ▶ $^{40}\text{Ar}^{27}\text{Al}$ interference on ^{67}Zn
- ▶ Required resolution (> 4000) reduces the intensity to 10 %
- ▶ Mathematical correction rises uncertainty
- ▶ **Yes, separation required**

- ▶ Ca matrix (100 mg/kg) caused disturbed back-ground
- ▶ This causes wrong blank correction
- ▶ Erroneous isotope ratio determinations
- ▶ **Yes, for multi-collector, maybe for single-collector IDMS**

More sources of error in isotope ratio measurement

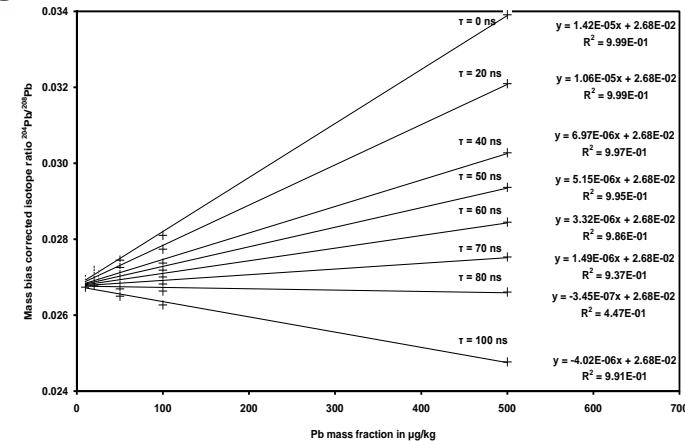
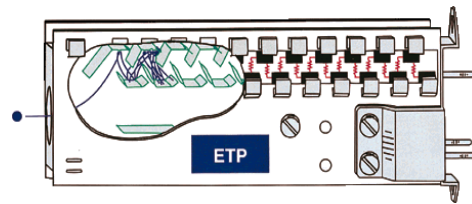
▶ Dead time effects for pulse counting systems

Nelms et al. (2001)



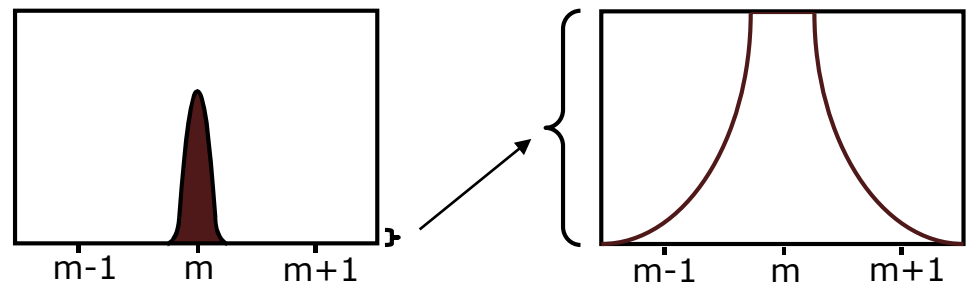
Input Voltage = -3000 Volts
Output Voltage = Ground
Signal = Ground

Aperture = -3000 Volts
Deflector = ± 400 Volts



▶ Abundance-Sensitivity

Intensity contribution to neighbour mass: $I(m \pm 1)/I(m)$
In ICP-MS commonly $\sim 10^{-5} - 10^{-6}$



▶ Contamination

Calibration strategies and measurement uncertainty

-
- ▶ Use of a certified spike from, e.g. IRMM, NIST: **Single IDMS**
 - ▶ Simple, straight forward
 - ▶ Largest measurement uncertainty
 - ▶ Calibration of spike using a primary assay: **Double IDMS**
 - ▶ More work but less expensive
 - ▶ Smaller measurement uncertainties
 - ▶ Calibration of spike using a primary assay and additionally matching the sample-spike-blend: **Matching IDMS**
 - ▶ Iterative approach, even more laborious
 - ▶ Smaller measurement uncertainties

Spike selection

- ▶ Commercial spikes: $u_{c,rel} \approx 1 \%$
- ▶ Spikes from NIST, IRMM or BAM: $u_{c,rel} \approx 0.1 \%$
- ▶ In-house produced spikes
 - ▶ Selection of enriched isotope, preferably metal form
 - ▶ Select suitable acids for dissolution and storage
 - ▶ Mass monitoring to correct for evaporation losses
- ▶ Spike characterization by reverse IDMS
 - ▶ Production of back-spike from pure element
 - ▶ Production of blends from spike & back-spike
 - ▶ Measurements, calculation & uncertainty budget



Achievable relative uncertainty down to 0.05 %



BAM primary materials

Single IDMS: uncertainty consideration

$$W_x = W_{y,b} \cdot \frac{M_x \cdot m_y}{M_b \cdot m_x \cdot a_{x,b}} \cdot \frac{(R_y - R_{xy})}{(R_{xy} - R_x)}$$

Parameter	Accuracy	$U_{c,rel}$
Masses	High	< 0.1 %
Isotope masses	Very high	< 0.0001 %
Atomic weights	High	< 0.05 %
Isotope abundances	Moderate / high	0.005 % to 5.0%
Observed isotope ratios	Moderate / high	0.01 % to 1 %
Spike concentration	Moderate	0.1 % to 1 %
Analyte mass fraction	Moderate	0.6 % to 2 %

Limiting factors

Double IDMS: uncertainty consideration

$$W_X = W_Z \cdot \frac{m_y \cdot m_z}{m_x \cdot m_{y'}} \cdot \left(\frac{R_y - R_{xy}}{R_{xy} - R_x} \right) \cdot \left(\frac{R_{zy} - R_z}{R_y - R_{zy}} \right)$$

Parameter	Accuracy	$u_{c,rel}$
Masses	High	< 0.1 %
Observed isotope ratios	Moderate / high	0.01 % to 1 %
Back-spike concentration	Moderate / high	0.05 % to 0.5 %
Analyte mass fraction	Moderate / high	0.05 % to 1 %

Limiting factor

This equation is valid as long as no isotopic variations occur in nature or in the samples.

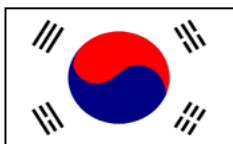
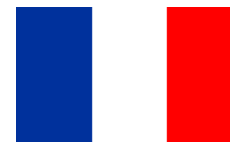
Application to soil analysis

Environmental application: CCQM-P15 „Lead in Sediment“

Sample:

- ▶ Organized by IRMM
- ▶ Sediment from the Channel
- ▶ Homogeneity and stability tested
- ▶ Material was used in parallel for IMEP-14

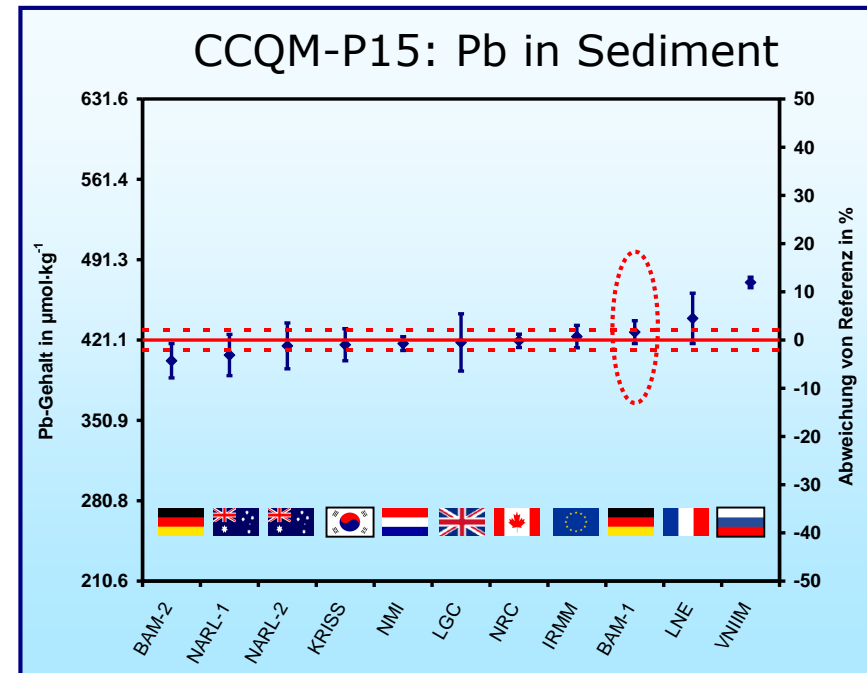
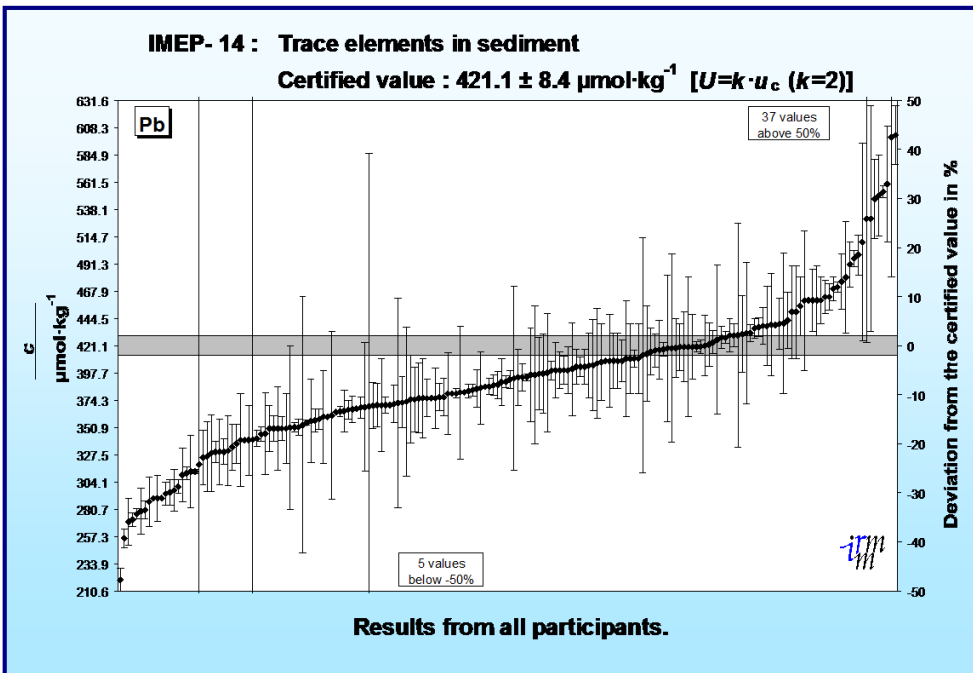
CCQM-P15 participants:



Analytical procedures:

- ▶ IDMS with TIMS, Q-ICP-MS and HR-ICP-MS
- ▶ Only BAM-2 used F-AAS

Environmental application: Comparison IMEP-14 with CCQM-P15



IMEP

- ▶ > 40 results are outside $\pm 50 \%$
- ▶ Many results do not overlap within the stated uncertainties
- ▶ Pb mass fraction $\approx 90 \text{ mg}\cdot\text{kg}^{-1}$

CCQM

- ▶ Standard deviation of all results is 4.4%
- ▶ VNIIM: may be considered as outlier

Sample preparation for soil candidate reference material EnvCRM

1 g of sample + 0.5 g each of the ^{61}Ni , ^{65}Cu , ^{113}Cd , ^{201}Hg and ^{206}Pb spike solutions

Addition of 6 mL HNO_3 , 2 mL HCl and 3 mL HF

Microwave assisted digestion: 20 min, 200°C

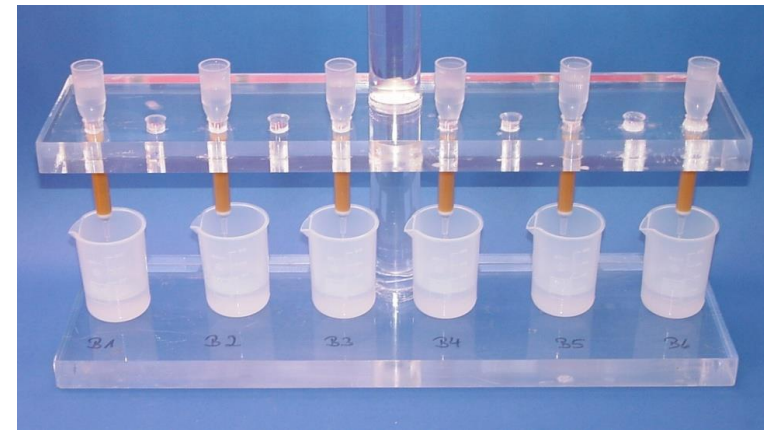
Centrifugation of the CaF_2 -precipitate

Evaporation of the solution to dryness (3x)

Analyte separation by chromatographic procedures

Evaporation to dryness (3x)

Isotope ratio measurements by TIMS or ICP-MS



- ▶ Crown-ether based resin for Pb
- ▶ Anion exchange resin AG 1X8 for Zn, Cd and Tl
- ▶ Resin with diacetyl dioxime groups for Ni

Results for soil candidate reference material EnvCRM

Element	Mass fraction / ($\text{mg}\cdot\text{kg}^{-1}$)			U_{rel}
	Value	u_c	U (k=2)	
Cd	0.05 - 5	< 0.005	< 0.01	0.57 %
Cr	50 - 200	< 1	< 2	1.2 %
Cu	20 - 100	< 0.2	< 0.5	0.44 %
Hg	0.1 - 1	< 0.002	< 0.005	0.91 %
Ni	20 - 100	< 0.2	< 0.5	0.52 %
Pb	20 - 100	< 0.2	< 0.5	0.34 %

-
- ▶ IDMS applied for elemental analysis is fully understood and completely under control, when
 - ▶ Isotopic equilibrium is guaranteed
 - ▶ A matrix separation is being carried out
 - ▶ IDMS is superior to other analytical procedures concerning
 - ▶ Trueness
 - ▶ Measurement uncertainty
 - ▶ SI traceability
 - ▶ Best results with double IDMS & matrix separation
 - ▶ IDMS is perfectly suited for reference measurements
-

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