

Trace element analysis of geological materials by ICP-MS I

DSP analytical geochemistry

C9067

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EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

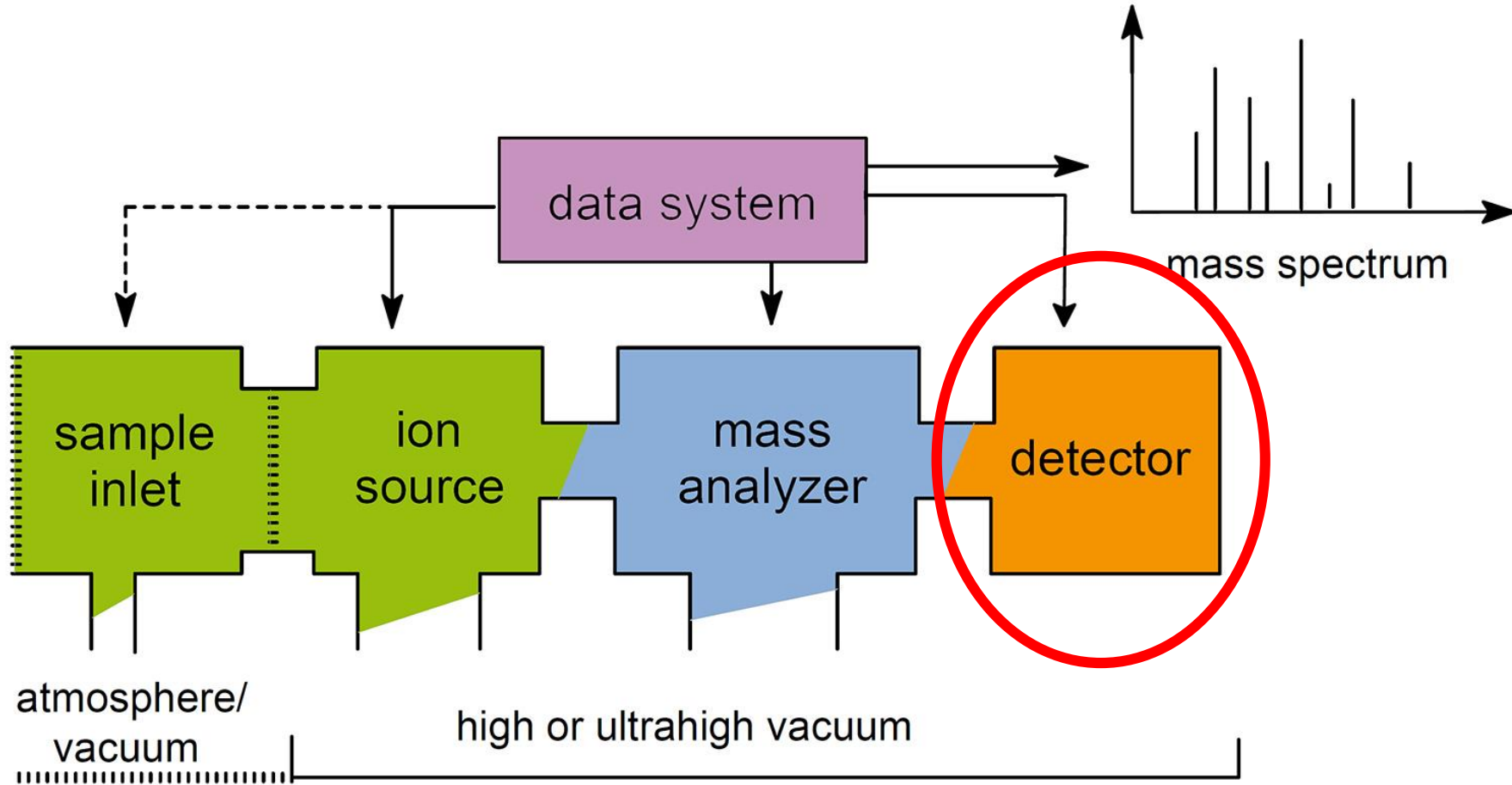


MINISTERSTVO ŠKOLSTVÍ,
MLÁDEŽE A TĚLOVÝCHOVY

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

Outline

1. Mass spectrometry. General introduction and history.
2. Ion sources for mass spectrometry. Inductively coupled plasma.
3. Interface. Ion optics. Mass discrimination. Vacuum system.
4. Spectral interferences. Resolution, ion resolution calculations.
5. Mass analyzers. Elimination of spectral interferences.
6. Non-spectral interference.
7. Detectors, expression of results.
8. Introduction of samples into plasma.
9. Laser ablation for ICP-MS.
10. Excursion in the laboratory.



1000 mbar 10⁻⁵ to 10⁻⁶ mbar 10⁻⁶ to 10⁻⁹ mbar

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Detectors

for ICP-MS

- Detection system — an important area of the mass spectrometer that **counts the number of ions** emerging from the mass analyzer.
- The detector **converts the ions into electrical pulses**, which are then counted by its integrated measurement circuitry.
- **The magnitude of the electrical pulses corresponds to the number of analyte ions present in the sample.** Trace element quantitation in an unknown sample is then carried out by comparing the ion signal with known calibration or reference standards.

Detectors

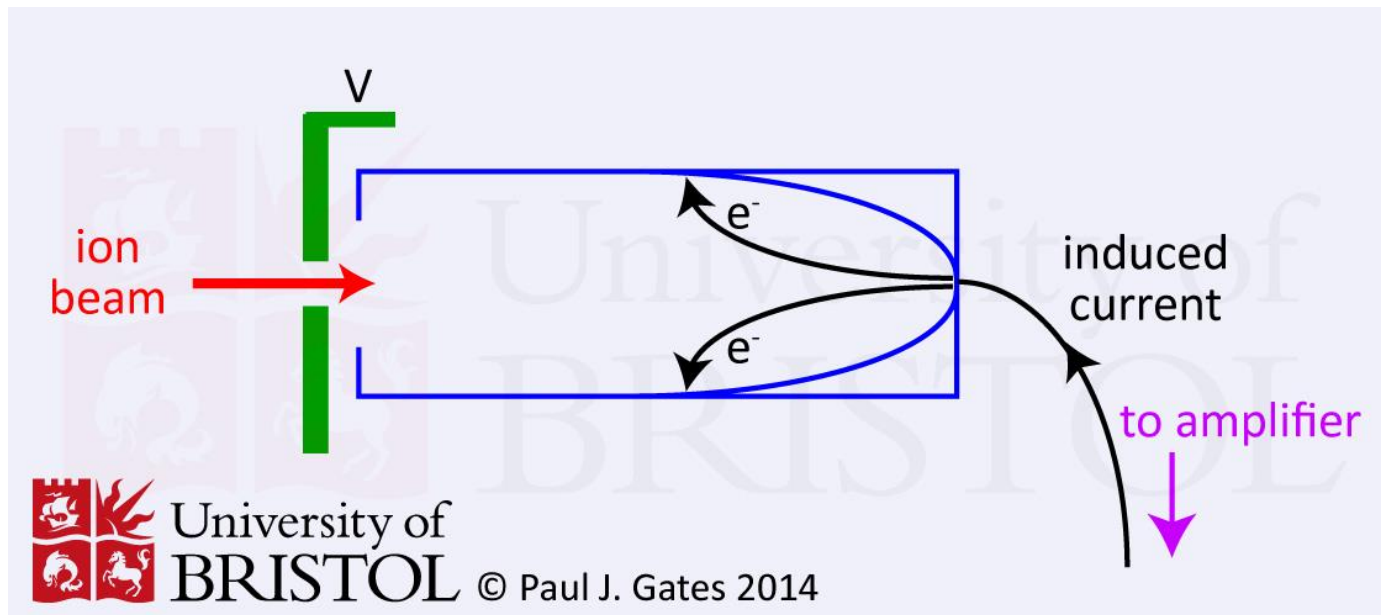
for ICP-MS

- For some applications where ultratrace detection limits are not required, the ion beam from the mass analyzer is directed into a **simple metal electrode (channeltron)**, or **Faraday cup**.
- The most common type is **discrete dynode electron multiplier**.

Detectors

Faraday cup

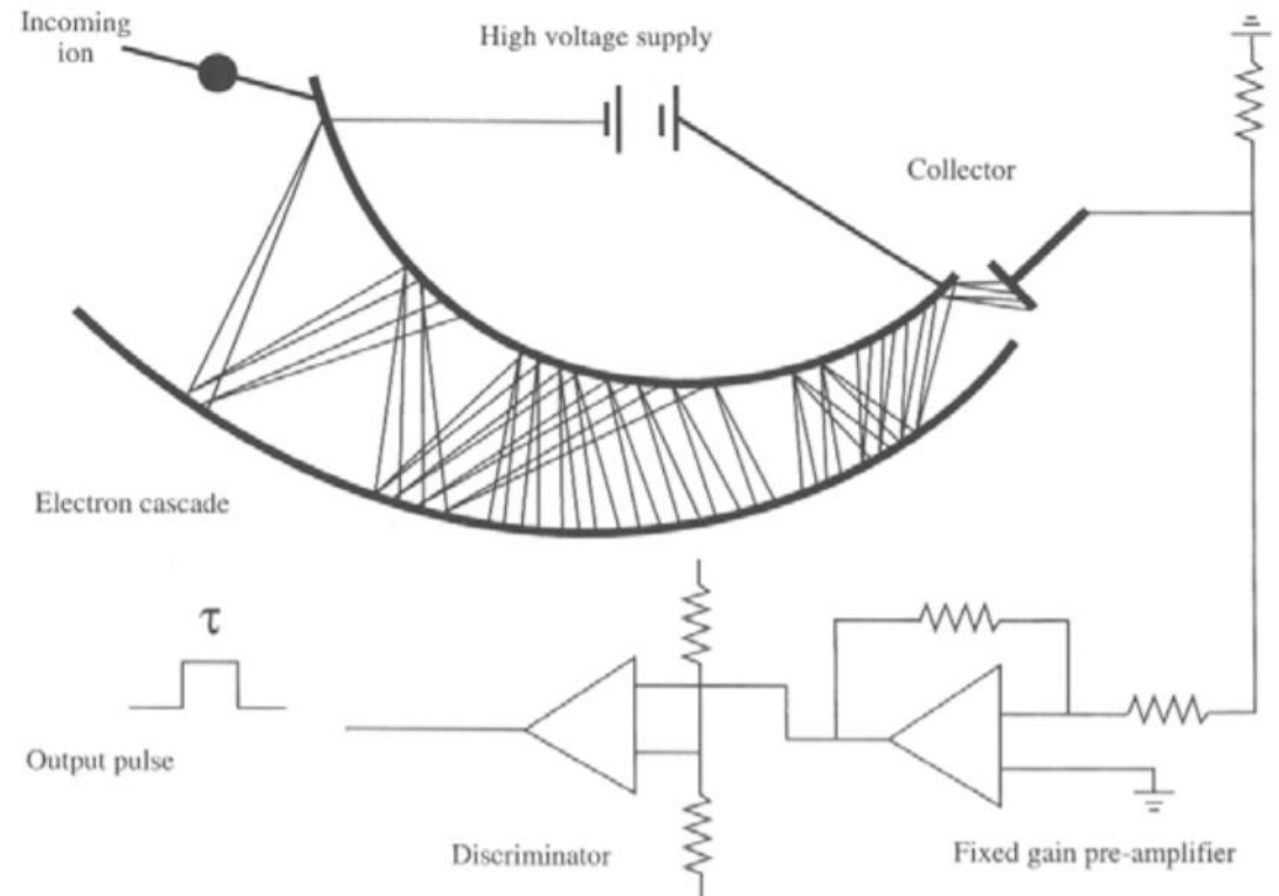
The incident ion strikes the dynode surface which emits electrons and induces a current which is amplified and recorded. The dynode electrode is made of a secondary emitting material like CsSb, GaP or BeO.



Detectors

Channel electron multiplier

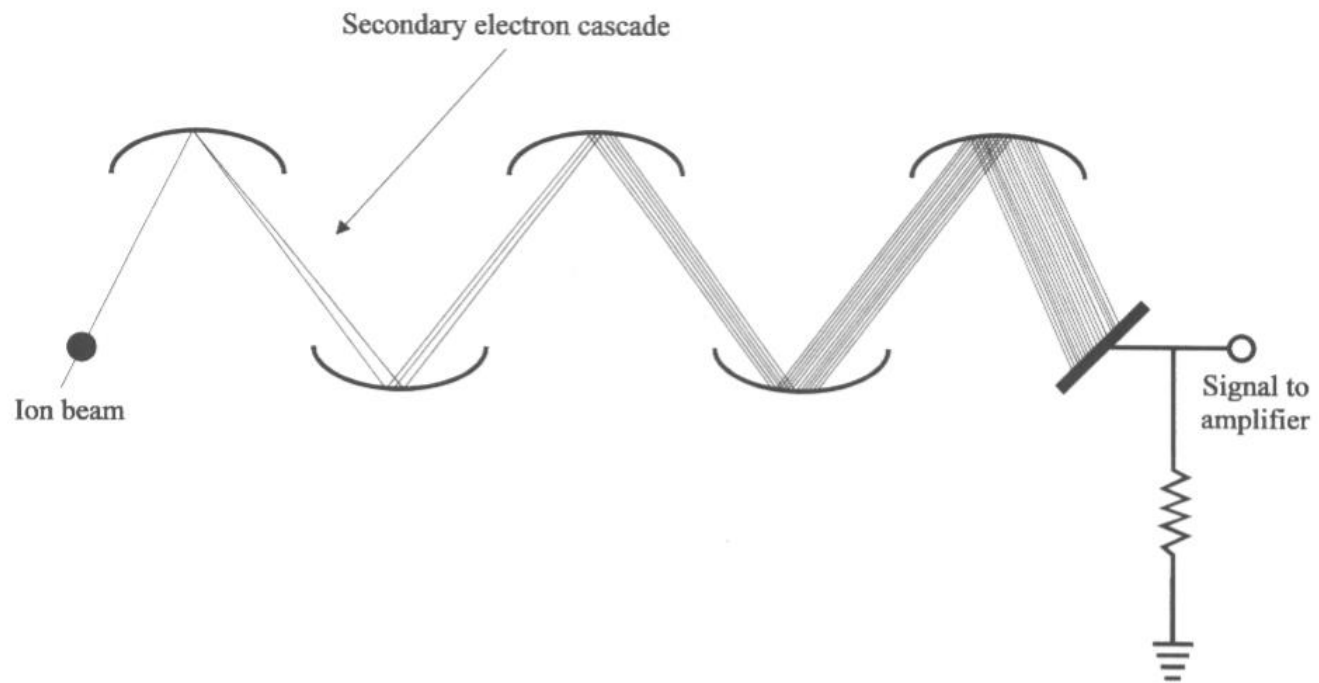
- Curved ('horn' shaped) continuous dynode where amplifications occur through repeated collisions with the dynode surface.
- Open glass cone coated with a semiconductor type material — that generates electrons from ions impinging on its surface.



Detectors

Discrete dynode electron multiplier

- series of discrete dynodes maintained at increasing potentials resulting in a series of amplifications.
- Ions pass the conversion dynode and strike the initial amplification dynode surface producing an emission of secondary electrons which are then attracted either to the second dynode, or into the continuous dynode where more secondary electrons are generated in a repeating process ultimately resulting in a cascade of electrons.
- Linear range up to 9 orders

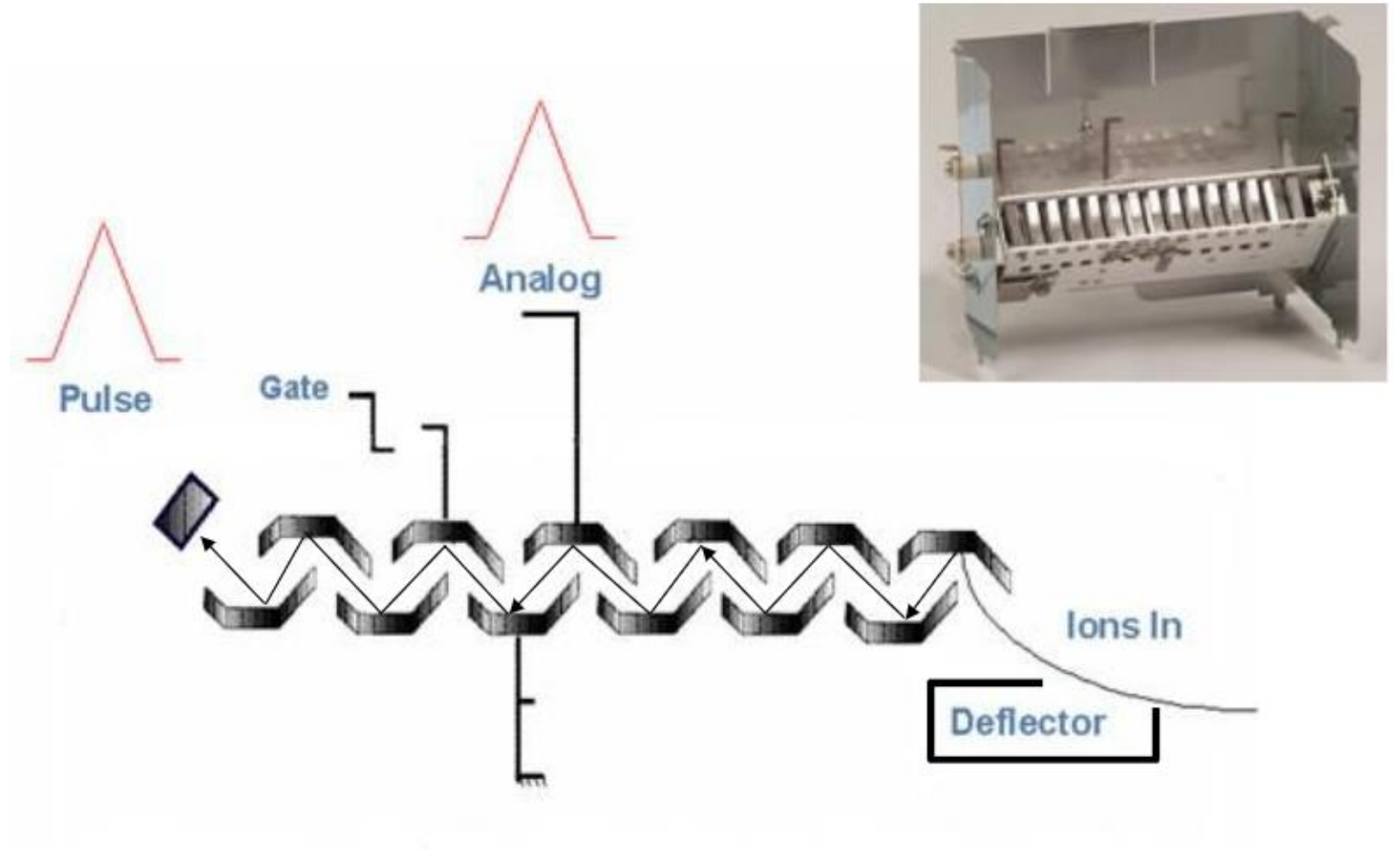


Detectors

Electron multiplier

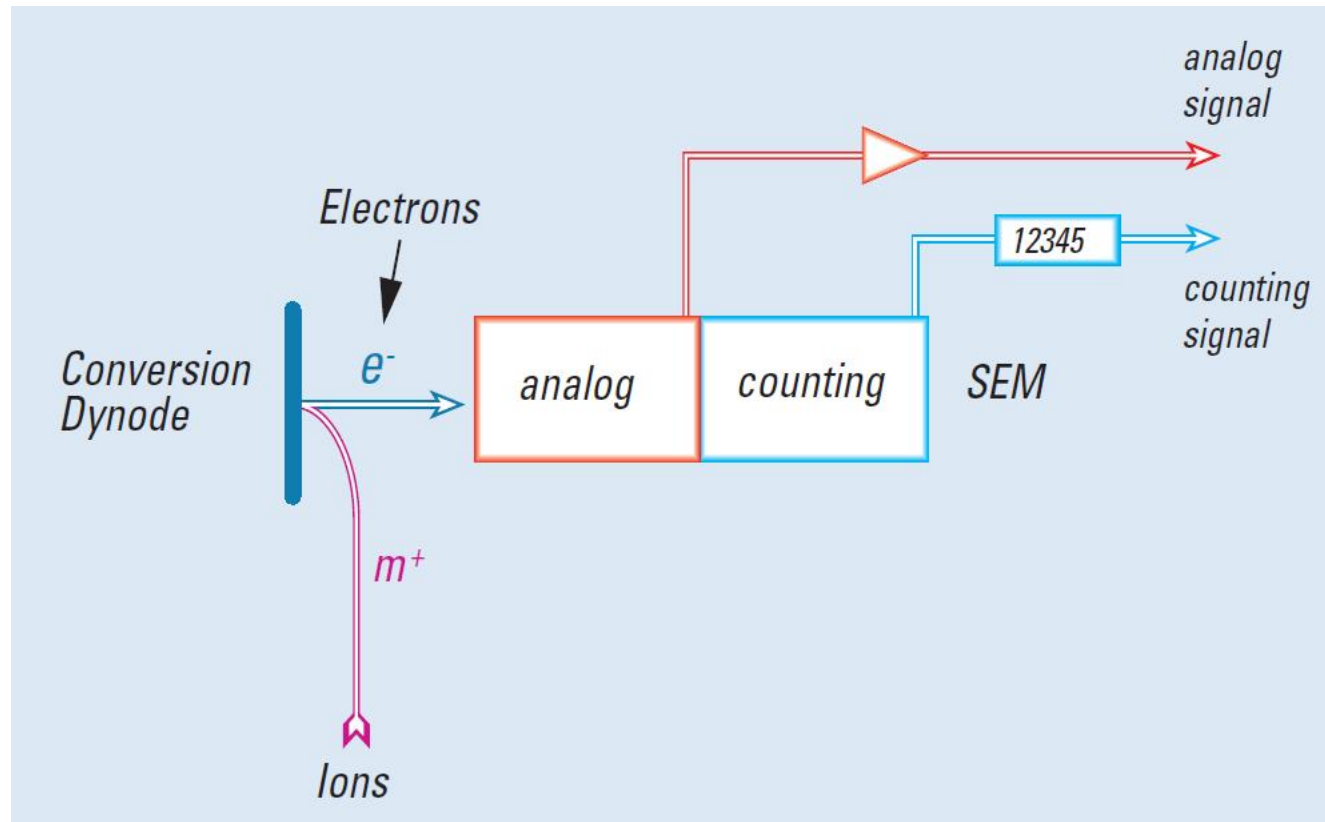
Working in dual mode:

- **pulse** – small ion signals
- **analog** – higher ion fluxes



Detectors

Analog + counting mode



HR ICP MS Element2

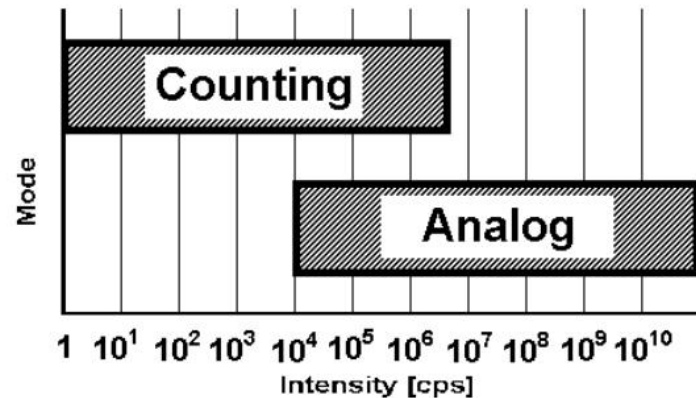
- discrete dynode detection system that enables the quantification of both trace and major elements.
- mass independent detector response, enabling **fully automatic cross calibration** between the counting and analog modes.
- manufacturer recommendation for isotope ratios - **with the minor isotope in counting mode and the abundant isotope in analog mode the highest precision and accuracy can be obtained.**
- **We prefer measuring all isotopes in counting mode which means appropriate sample dilution!!!**

Detectors

Analog + counting mode

HR ICP MS Element2

Dynamic range



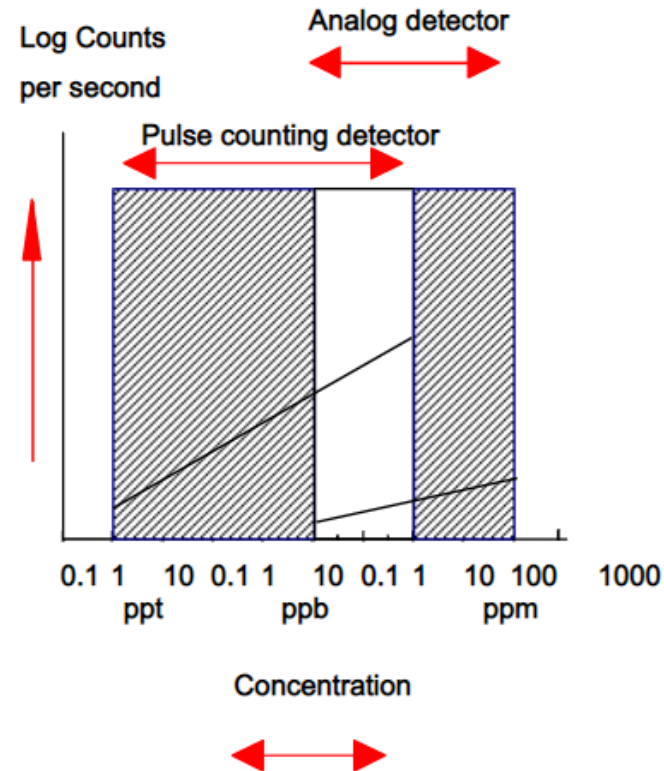
For the digital counting mode, the concentrations should generally not be greater than 100 µg/l at a resolution of R=300 for the upper mass range. **The upper limit of the count rate for the digital counting mode is about $5 \cdot 10^6$ cps**; at higher count rates, measurements must be made in the analog mode. The linearity of the calibration function, and the acceptable working ranges need to be checked for each particular application.

In the analog mode, the concentration limits are in the mg/l range.

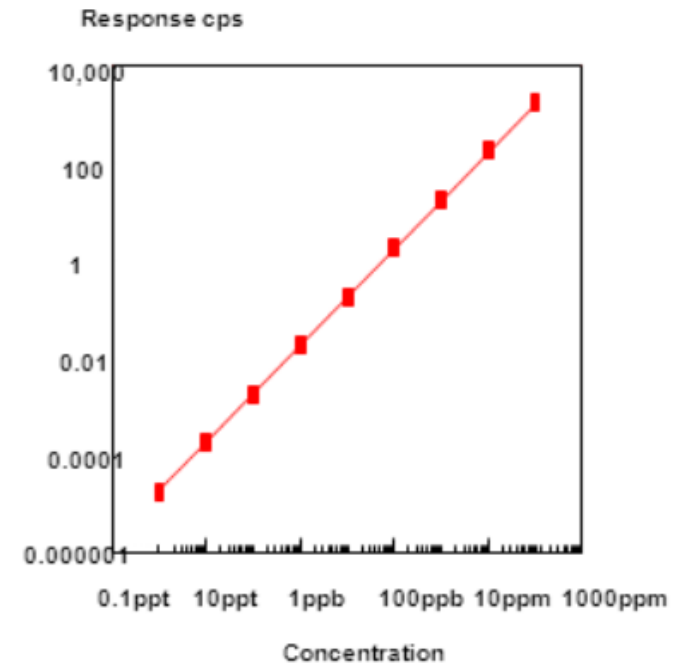
Detectors

Analog + counting mode

After cross calibration, the two curves are normalized, which means the detector is suitable for concentration levels between 0.1 ppt and 100 ppm — typically 8 - 9 orders of magnitude for most elements.



Response for Indium

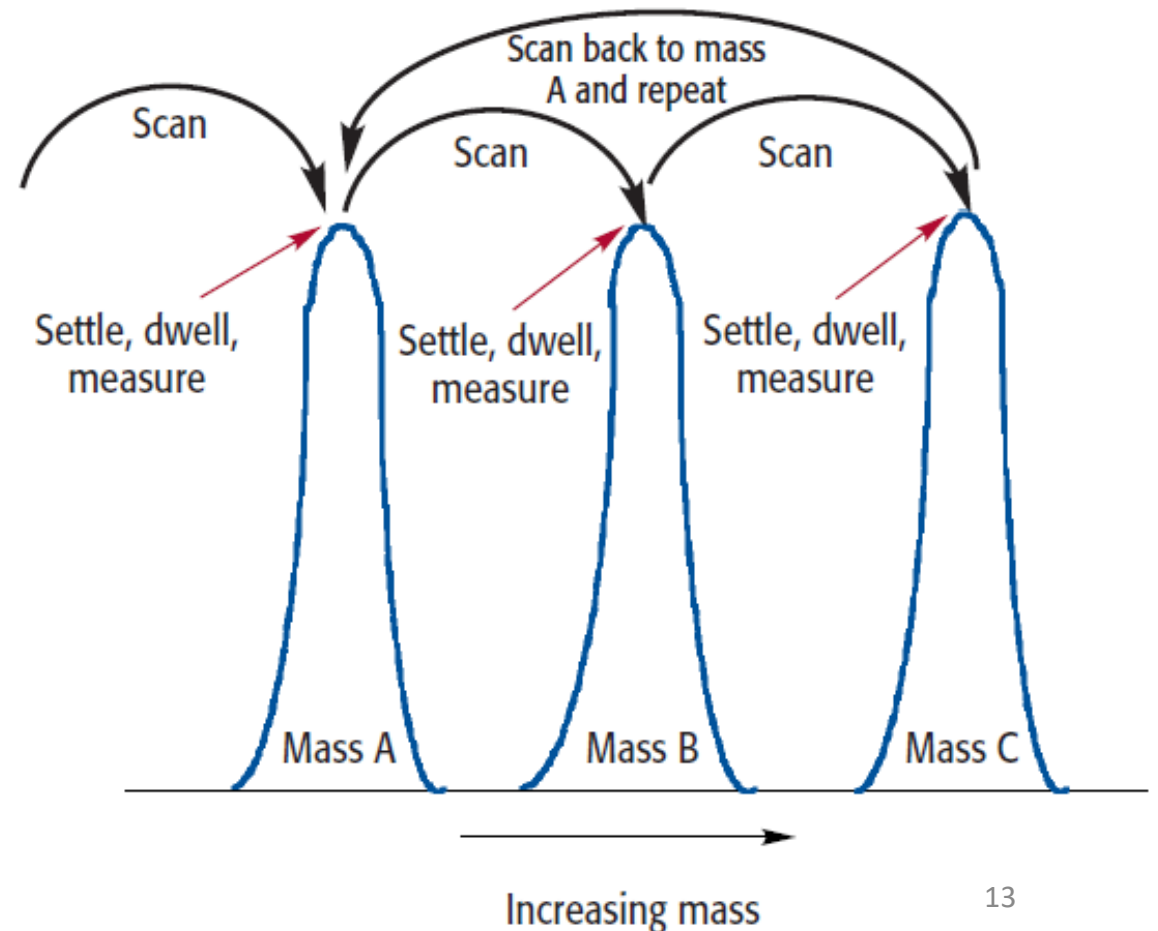


Detectors

Electron multiplier

Quadrupole is scanned to mass A. The electronics are allowed to settle (**settling time**) and left to dwell for a fixed period of time at one or multiple points on the peak (**dwell time**); intensity measurements are then taken (based on the dwell time). The quadrupole is then scanned to masses B and C and the measurement protocol repeated. The complete multielement measurement cycle (**sweep**) is repeated as many times as needed to make up the **total integration per peak**.

Scanning protocol of a multielement scan of three different masses.



Detectors

Electron multiplier

Impact of integration time on the overall analysis time for Pb isotope ratios.

Dwell time (ms)	Number of sweeps	Integration time (s)/mass	%RSD, ²⁰⁷Pb/²⁰⁶Pb	Analysis time for 9 reps
25	220	5.5	0.25	2 min 29 s
25	500	12.5	0.19	6 min 12 s
25	700	17.5	0.17	8 min 29 s

More ions that are counted = the better the precision will be.

Detectors

Dead time

The dead time of a detector is defined as the **minimum time interval that two consecutive counts must be separated in order to be recorded as two different events**. The effect of having a dead time in a detector used to monitor counting rates is that the measured counting rates will be lower than the real ones. However, the real counting rate can be determined from the measured one if the dead time of the detector is known.

Dead time changes with life of a detector and for accurate isotopic ratio measurement must be determined. It is performed on the measured intensities (counts per second) using the equation:

$$I_{\text{cor}} = \frac{I_{\text{exp}}}{1 - I_{\text{exp}} \times \tau}$$

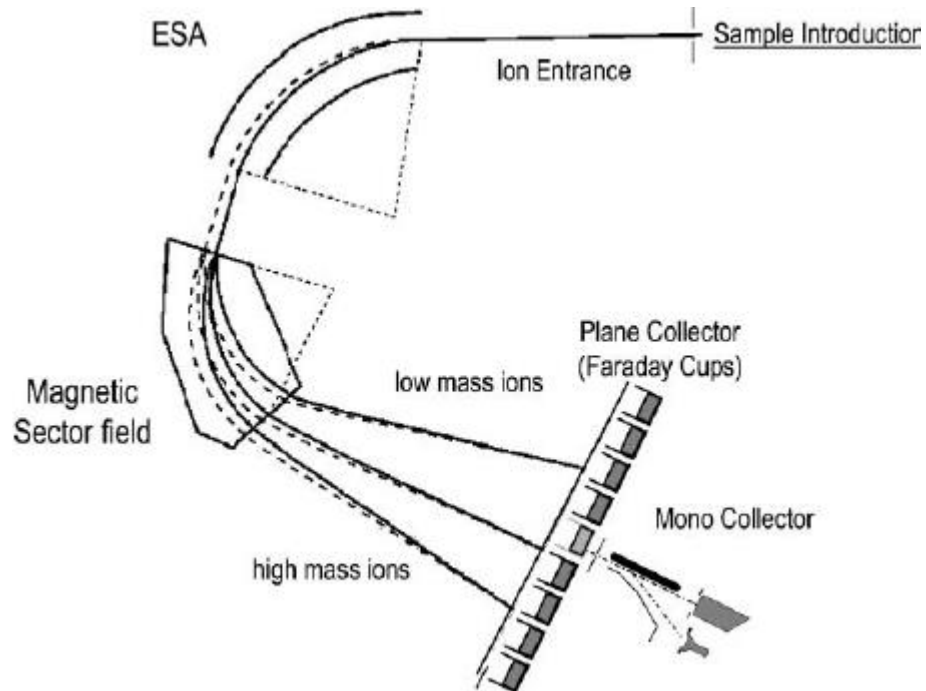
I_{cor} and I_{exp} are the corrected and experimental intensities, and τ is the dead-time (in seconds).

It is prudent to check this internal correction by measuring the isotope ratios of a standard solution at different concentration levels and updating the detector deadtime value in the software.

Detectors

multicollector

MC-ICP-MS: These instruments have similar sensitivities and can achieve precision for isotope ratio measurements in the range of 0.001–0.002%.



Isotope ratio – $^{87}\text{Sr}/^{86}\text{Sr}$ obtained by ablation SRM NIST 1486 by LA-ICP-(Q)MS.
Certified ratio: 0,70931

$^{87}\text{Sr}/^{86}\text{Sr}$	RSD
0,78304	10,4
0,68258	3,8
0,71015	0,1
0,69038	2,7
0,73036	3,0
0,81509	14,9



Quadrupole filter is not suitable for isotope ratio measurements?

Detectors

SF-ICP-MS

- fast electric scanning mode (EScan) - magnetic field is kept constant and scanning is performed electrically by varying the accelerating voltage and the ESA high voltage
- the low mass resolution mode with flat top peaks
- peak jump (scan time ~ 0.1 s), points per peak – 1-3 for LA (TRA), 3-10 for SN
- detection mode - counting
- dead time changes with life of a detector and for accurate isotopic ratio measurement must be determined

Datovani_230612.met - Method Editor - Thermo ELEMENT

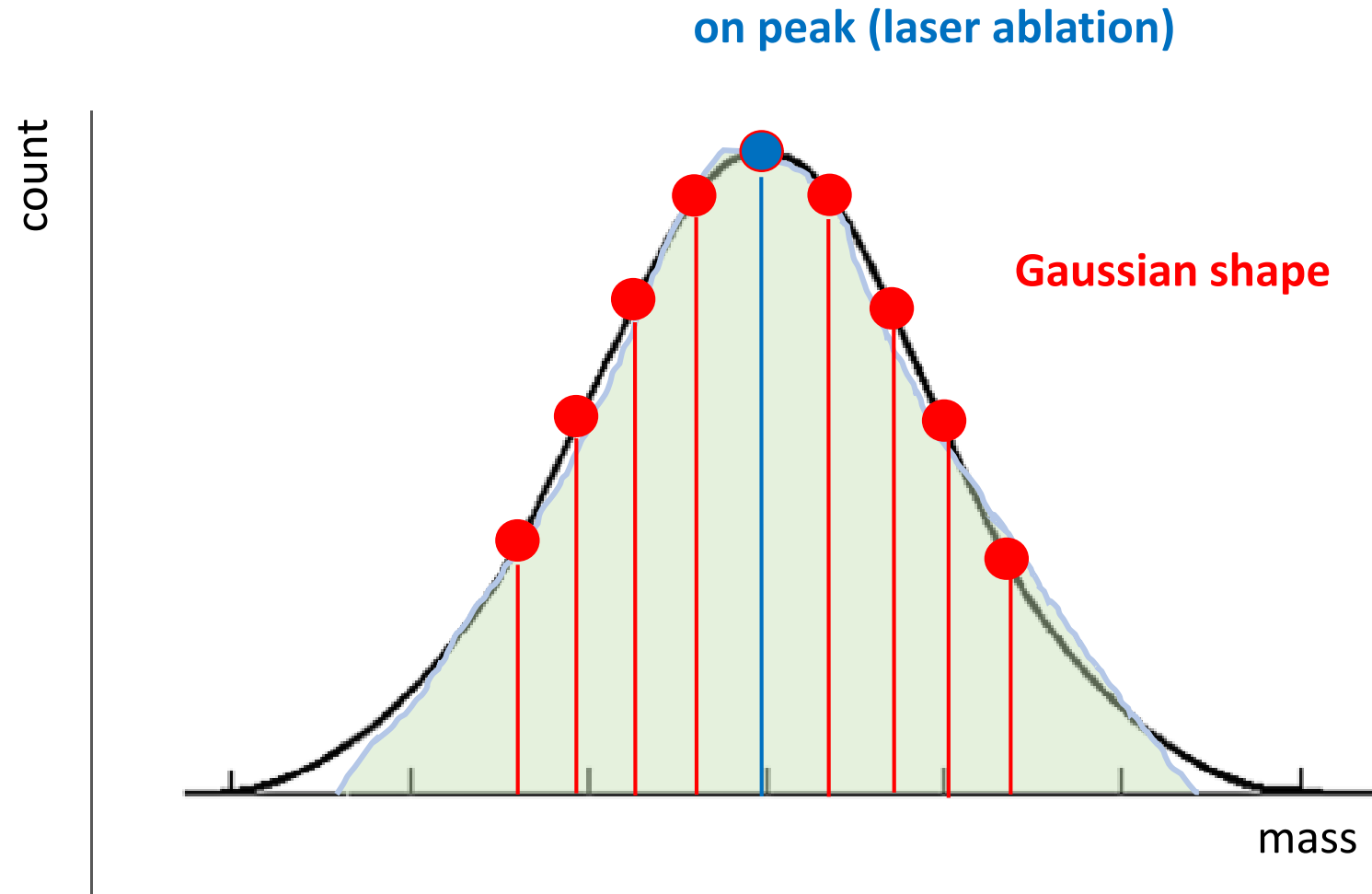
File Edit Setup View Resolution Interference Correction Plot Help

Resolution: Low Runs: 420 Estimated Total Time: [h:min:s] 00:00:48
Mode: 1 Passes: 1

Method Data			Interference Correction			Quality Control												
Entry	Locked	Isotope	Calib Threshold	Accurate Mass	Method Mass Offset	Mass Window	Mass Range	Magnet Mass	Settling Time	Sample Time	Samples Per Peak	Segment Duration	Search Window	Integration Window	Scan Type	Detection Mode	Integration Type	IS Index
1	No	Pb204	0	203.9725	0.0000	1	203.969 - 203.976	203.972	0.001	0.0100	100	0.010	0	1	EScan	Counting	Average	
2	No	Pb206	0	205.9739	0.0000	1	205.970 - 205.977	203.972	0.001	0.0150	100	0.015	0	1	EScan	Counting	Average	
3	No	Pb207	0	206.9753	0.0000	1	206.972 - 206.979	203.972	0.001	0.0300	100	0.030	0	1	EScan	Counting	Average	
4	No	Pb208	0	207.9761	0.0000	1	207.973 - 207.980	203.972	0.001	0.0100	100	0.010	0	1	EScan	Counting	Average	
5	No	Th232	0	232.0375	0.0000	1	232.034 - 232.041	203.972	0.001	0.0100	100	0.010	0	1	EScan	Both	Average	
6	No	U235	0	235.0434	0.0000	1	235.039 - 235.047	203.972	0.001	0.0200	100	0.020	0	1	EScan	Counting	Average	
7	No	U238	0	238.0502	0.0000	1	238.046 - 238.054	203.972	0.001	0.0100	100	0.010	0	1	EScan	Both	Average	
*																		

Signal evaluation

Peak reading



Results expression

arithmetic mean, standard deviation

Table 3
Average trace element concentrations ($\mu\text{g g}^{-1}$) in the *L. sinensis* shells from different depths of Nam Co 8 by spot analysis.

Core depth (cm)	Age (cal BP)	Sr	Ba	U	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	LREE/HREE ^a
31	250	4830	1400	16.6	6.63	15.6	1.66	6.97	0.93	0.31	0.63	0.13	1.17	–	–	0.14	0.97	0.13	–
46	450	5140	413	11.5	3.16	5.64	0.64	3.12	0.64	0.15	0.68	0.12	0.64	0.14	0.50	0.077	0.46	0.078	5.0
151	2550	2100	245	12.5	4.49	7.56	0.58	3.32	0.61	0.16	0.59	0.089	–	0.14	0.45	–	0.33	–	–
211	4650	1540	278	8.17	7.36	16.6	1.66	7.22	1.80	0.30	1.66	0.24	1.38	0.22	0.67	0.12	0.63	0.092	6.9
216	4700	1490	274	11.9	8.09	16.6	1.66	7.90	1.76	0.34	2.54	0.25	1.76	0.27	0.82	0.083	0.72	0.085	5.6
236	5950	1370	266	24.3	9.72	22.4	3.02	11.4	2.34	0.59	2.54	0.34	2.15	0.51	1.07	0.17	1.17	0.18	6.1
256	6550	1400	319	10.8	6.29	13.9	1.51	5.70	1.16	0.22	1.04	0.17	0.91	0.19	0.56	–	0.38	0.051	–
261	6750	1610	174	12.0	4.88	9.41	1.07	4.73	1.17	0.27	2.05	0.23	1.27	0.28	0.68	0.11	0.48	0.068	4.2

The concentrations in this table were obtained by the average values of two or three *L. sinensis* shells from each depth. The concentrations of some rare earth elements were not detected by the spot analyses (–).

^a LREE/HREE: the total concentration of La, Ce, Pr, Nd, Sm and Eu divided by that of Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu in a single shell.

Results expression

arithmetic mean, standard deviation

Table 1

Average REE + Y concentrations ($\mu\text{g/g}$) measured for NIST612 and BCR-2 standards by LA-ICP-MS with respective reference data (Pearce et al., 1997; GeoReM database: <http://georem.mpch-mainz.gwdg.de>, Jochum et al., 2005).

Element	NIST612				BCR-2			
	This study		Pearce et al. (1997)		This study		GeoReM	
	Average (n = 11)	SD (%)	Preferred average	SD (%)	Average (n = 9)	SD ($\mu\text{g/g}$)	Preferred values	SD ($\mu\text{g/g}$)
La	36	2.75	35.77	2.15	24	0.3	24.9	0.2
Ce	38	2.58	38.35	1.64	51	0.6	52.9	0.2
Pr	37	2.31	37.16	0.93	6	0.1	6.7	0.1
Nd	35	1.97	35.24	2.44	27	0.5	28.7	0.1
Sm	37	1.40	36.72	2.63	6	0.2	6.58	0.02
Eu	34	1.34	34.44	1.59	1.8	0.05	1.96	0.01
Gd	37	2.60	36.95	1.06	6	0.2	6.75	0.03
Tb	36	3.05	35.92	2.68	1.0	0.03	1.07	0.03
Dy	36	2.14	35.97	0.82	6	0.1	6.41	0.05
Y	38	2.76	38.25	2.14	33	0.6	37	2
Ho	38	1.39	37.87	1.09	1.2	0.03	1.28	0.03
Er	37	1.17	37.43	1.5	4	0.1	3.66	0.01
Yb	40	1.01	39.95	2.86	3	0.1	3.38	0.02
Lu	38	1.08	37.71	1.95	0.5	0.02	0.503	0.009

Results expression

arithmetic mean, standard deviation

Table 2
Parameters evaluated for the proposed method.

Element	LOD ($\mu\text{g g}^{-1}$; n = 10)	LOQ ($\mu\text{g g}^{-1}$; n = 10)	Reference value NIST 614 ($\mu\text{g g}^{-1}$) [41]	Obtained value NIST 614 Mean \pm 1s ($\mu\text{g g}^{-1}$; n = 12)
Y	0.003	0.011	0.790 \pm 0.032	0.802 \pm 0.016
La	0.003	0.011	0.720 \pm 0.013	0.717 \pm 0.011
Ce	0.003	0.011	0.813 \pm 0.025	0.803 \pm 0.020
Pr	0.003	0.011	0.768 \pm 0.015	0.847 \pm 0.049
Nd	0.032	0.107	0.752 \pm 0.014	0.682 \pm 0.084
Sm	0.023	0.078	0.754 \pm 0.013	0.768 \pm 0.014
Eu	0.005	0.016	0.770 \pm 0.016	0.692 \pm 0.017
Gd	0.044	0.146	0.763 \pm 0.021	0.847 \pm 0.151
Tb	0.003	0.011	0.739 \pm 0.020	0.831 \pm 0.064
Dy	0.016	0.054	0.746 \pm 0.022	0.660 \pm 0.073
Ho	0.003	0.011	0.749 \pm 0.015	0.684 \pm 0.023
Er	0.009	0.031	0.740 \pm 0.017	0.829 \pm 0.046
Tm	0.002	0.008	0.732 \pm 0.020	0.746 \pm 0.018
Yb	0.017	0.055	0.777 \pm 0.021	0.692 \pm 0.054
Lu	0.004	0.014	0.732 \pm 0.018	0.782 \pm 0.029

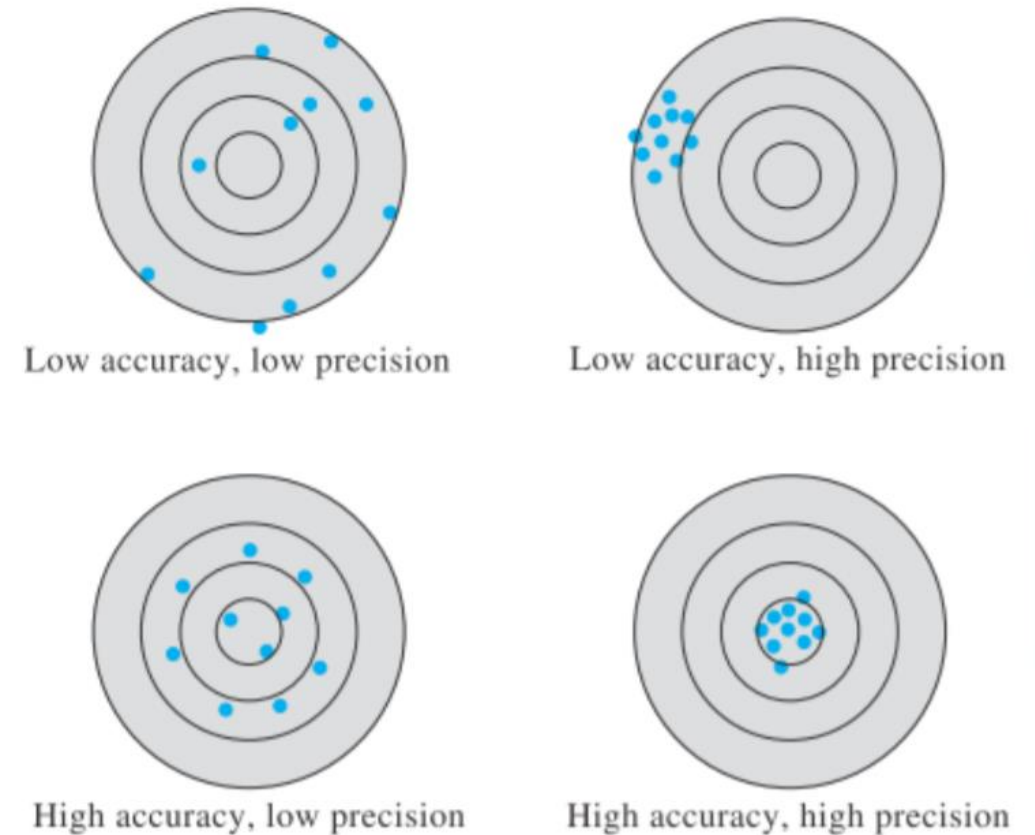
LOD (limit of detection); LOQ (limit of quantification).

Results expression

errors

- **Random errors** (indeterminate) – influence **precision**, causes data to be scattered more or less symmetrically around a mean value. Standard deviation, confidence interval (uncertainty)
- **Systematic errors** (determinate) – influence **accuracy**, causes the mean of a data set to differ from the accepted value (wrong calibration, interference ...) – (Student's t-test)
- **Gross errors** – influence precision and accuracy, occur only occasionally, are often large, are often the product of human errors; lead to outliers (test to detect outliers)

It is impossible to perform a chemical analysis that is totally free of errors or uncertainties.



Results can be precise without being accurate and accurate without being precise.

Results expression

Gaussian Distribution and Reference Range

Gaussian distribution (also known as normal distribution) is a bell-shaped curve, and it is assumed that during any measurement values will follow a normal distribution with an equal number of measurements above and below the mean value.

In a normal distribution the mean is zero and the standard deviation is 1.

Normal distribution is characterized by two parameters:

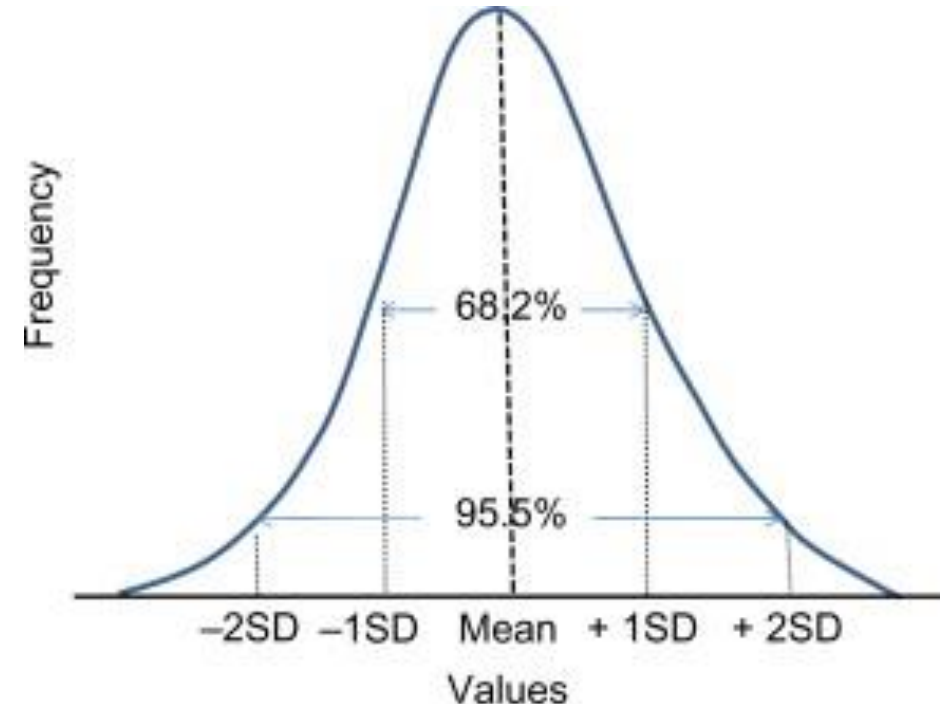
μ – mean value

SD (σ) – standard deviation

the mean value μ or SD cannot be determined => an estimate of these values is determined

Estimation of μ : median, arithmetic or geometric mean

Estimation of SD: range, standard deviation



Mean \pm 1 SD contain 68.2% of all values.

Mean \pm 2 SD contain 95.5% of all values.

Mean \pm 3 SD contain 99.7% of all values

Results expression

arithmetic mean, standard deviation

- **arithmetic mean** – almost eliminates the effect of random errors, use only in the case of normal distribution

$$\bar{X} = \frac{1}{n} \sum_{x=1}^n x_i$$

x_i – measured value; n – number of measurements

- estimation of the **standard deviation** for $n < 7$ using R

$$s = k_n \cdot R$$

k_n – tabulated values; $R = x_n - x_1$

- estimation of the **standard deviation** for $n > 7$

$$s = \sqrt{\frac{\sum_{i=1}^n \left(x_i - \bar{X} \right)^2}{(n-1)}}$$

x_i – measured value; \bar{X} – arithmetic mean;
 n – number of measurements

Results expression

arithmetic mean, standard deviation

- estimation of the **standard deviation** for $n < 7$ using R

$$s = k_n \cdot R$$

k_n – tabulated values; $R = x_n - x_1$

n	k_n
2	0.886
3	0.591
4	0.486
5	0.430
6	0.395
7	0.370
8	0.351
9	0.337
10	0.325

Example:

The following Cd contents were determined in the soil sample by ICP MS method:

14.2, 15.7, 14.9, 13.7, 15.1 ng/g

Express analytical result with SD.

Mean = 14.72, $R = 15.7 - 13.7 = 2$, $SD = 2 \cdot 0.43 = 0.86$

Cd: 14.72 ± 0.86 ng/g

Results expression

Limit of detection, limit of quantification

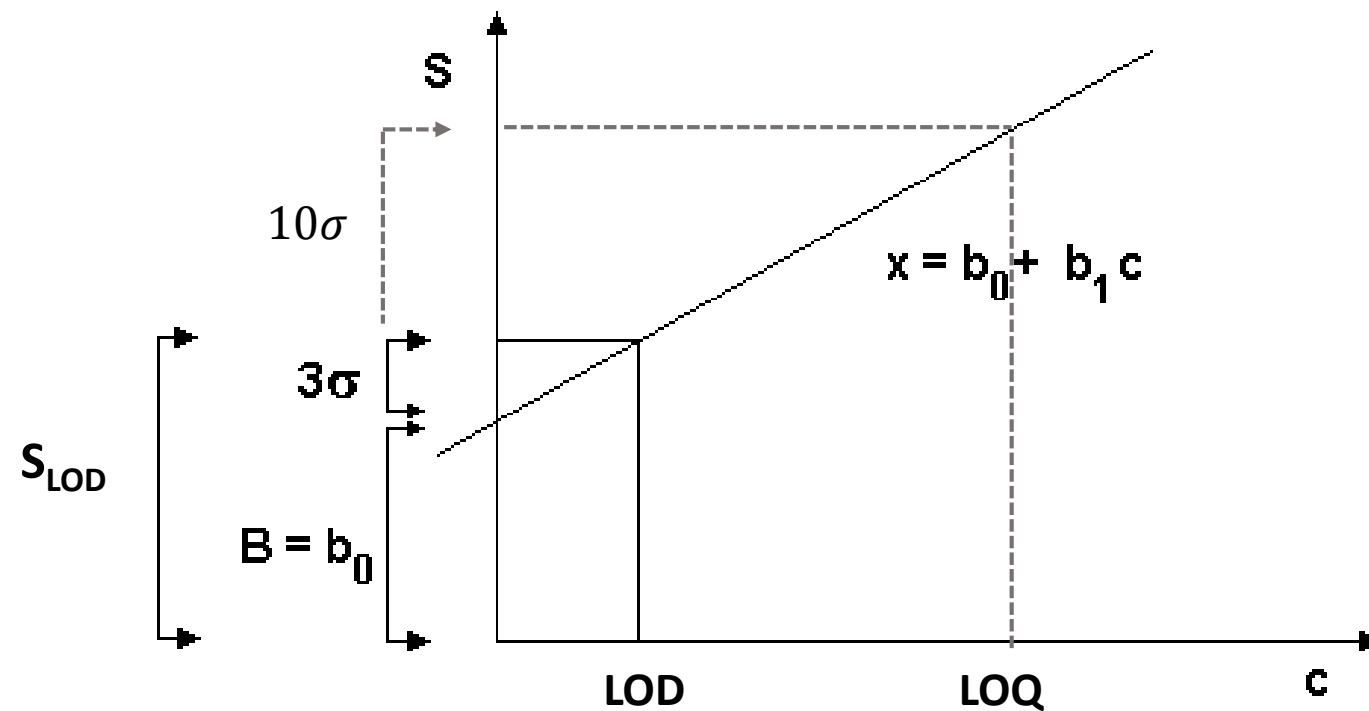
- **Limit of detection (LOD)** is defined as the smallest possible concentration that can be distinguished with a predetermined probability from random background fluctuations.
- We do not directly measure concentration, but the signal intensity. The relationship between signal and concentration is determined by **calibration**.
- Assuming that background fluctuations have a Gaussian distribution, the noise is expressed as the **standard deviation** of the distribution σ .
- **Limit of quantification (LOQ)** is the lowest concentration determined with **acceptable accuracy**, considering the statistical fluctuations between the background and an analytical signal.

$$\text{LOD} = \frac{3\sigma}{S}$$

$$\text{LOQ} = \frac{10\sigma}{S}$$

Results expression

Limit of detection, limit of quantification



Results expression

arithmetic mean, SD, LOD, LOQ

Table 2
Parameters evaluated for the proposed method.

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