Determination of Elemental Mass Fractions Using Isotope Dilution Mass Spectrometry (IDMS)

Keywords

IDMS, mass spectrometry, trace element contents, primary method of measurement

Quantities and items tested

Determination of elemental mass fractions and amount of substances in solid and liquid samples.

Elements: B, Mg, S, Cr, Fe, Ni, Cu, Zn, Ga, Ag, Cd, Sn, Sb, Ba, Hg, Tl and Pb

Matrices: metals, metal alloys, environmental samples, food samples, sediments, serum, polyethylene and aqueous samples.

a) Mass fractions of elements and trace elements (g/kg resp. mol/kg)

b) Absolute amounts of substances (g resp. mol)

Testing range						Uncertainty of results			
a)	10^{1} to 10^{-3}	g/kg	resp.	10^{-1} to 10^{-5}	mol/kg	from	0.1 %	to	2 %
	10^{-3} to 10^{-6}	g/kg	resp.	10^{-5} to 10^{-9}	mol/kg	from	0.5 %	to	5 %
b)	10^{-3} to 10^{-5}	g	resp.	10^{-4} to 10^{-7}	mol	from	0.1 %	to	2 %
	10^{-5} to 10^{-7}	g	resp.	10^{-7} to 10^{-9}	mol	from	0.5 %	to	5 %

Fields of application

Reference procedure for the determination of the mass fraction of elements and trace elements.

Certification of reference materials, as there are trace elements in matrix materials, single element solutions, enriched isotopes.

Calibration and validation of all analytical procedures for the determination of the amount of substance or the elemental mass fraction not being used as an absolute or primary method of measurement.

Methodology and instrumentation

Weighing of sample and spike by calibrated highly accurate analytical balances. Sample preparation and analyte separation by highly developed separation procedures (e.g. ion exchange procedure). Mass spectrometric measurements using a thermal ionization mass spectrometer and an inductively coupled plasma mass spectrometer, both equipped with a multi-collector array for highly accurate isotope ratio measurements.

Qualification and quality assurance

Widespread knowledge and experience based on participation in certification of reference materials and international interlaboratory comparisons for more than 15 years (see Further information for details). Thus broad knowledge in calculating measurement uncertainties.

Quality assurance is carried out by regular participation in interlaboratory comparisons.

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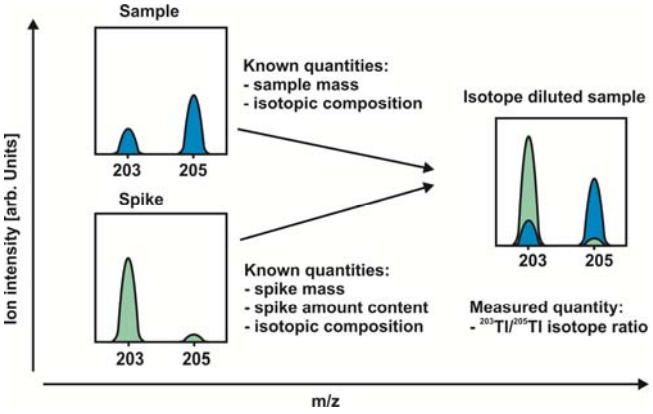
Further information

General

Isotope dilution mass spectrometry is considered to be one of the most powerful and most accurate methods for determining amounts of substance. This is clearly demonstrated by equation 2. Contrary to other calibration approaches IDMS will not directly suffer from long-time changes or drifts in instrument sensitivity. Moreover as soon as the isotopic exchange between sample and spike is guaranteed losses of analyte do not affect the analytical result. Both advantages are based on the fact that IDMS requires only isotope ratio measurements. Isotope ratios, however, are largely unaffected by instrumental drifts or setup and by matrix, unless there is no isobaric interference.
The "Consultative Committee for Amount of Substance“ (CCQM), the world’s highest institution for Metrology in Chemistry, considers IDMS as most important “Primary Method of Measurement” for amount determination. The total combined uncertainty, according to ISO and EURACHEM guidelines, can easily be calculated based on eqn. 1. Applying it correctly, IDMS has the potential to be a primary method of measurement yielding SI-traceable values in the most direct way with combined uncertainties significantly smaller than obtainable by other methods.

Principle



In principle all elements of the periodic system having two natural isotopes can be analyzed by IDMS as long as they can be measured by mass spectrometry. Moreover even mono-isotopic elements can be determined, if they feature a long-lived radionuclide such as iodine-129. In the figure on the left the principle of IDMS is exemplary shown for thallium. A sample with known isotopic composition but unknown element content is mixed with an accurately known amount of spike. This spike contains the element in a non-natural isotopic composition; ideal is an enrichment of the rarest natural isotope. After complete mixing of sample and spike the new isotope ratio R_B will be determined by mass spectrometry. This isotope ratio R_B can be calculated as follows (equation 1):

$$R_M = \frac{N_{sa} \cdot a_{sa,a} + N_{sp} \cdot a_{sp,a}}{N_{sa} \cdot a_{sa,b} + N_{sp} \cdot a_{sp,b}}$$

Modifications lead to equation 2:

$$w_{sa} = \frac{M_{sa} \cdot m_{sp}}{a_{sa,b} \cdot M_b \cdot m_{sa}} \cdot w_{sp,b} \cdot \left(\frac{R_{sp} - R_M}{R_M - R_{sa}} \right)$$

Hereby a_{sa} and a_{sp} are the known abundances of the isotopes a and b in sample and spike, respectively, and N_{sp} is the known amount of spike atoms, whereas N_{sa} is the unknown amount of analyte atoms in the sample. $w_{sp,b}$ and w_{sa} are the corresponding amount contents of spike isotope in the spike and analyte element in the sample, R_{sp} and R_{sa} are the isotope ratios of isotope a and b in spike and sample and m_{sp} and m_{sa} are the corresponding weights. M_{sa} is the molar mass of the analyte element in the sample and M_b the molar mass of isotope b. Consequently the measurand is R_B, the isotope ratio of the blend. w_{sa}, the wanted quantity, can now be calculated easily.

Thus IDMS only requires the measurement of isotope ratios. Guaranteeing the complete isotopic exchange and avoiding or correcting respectively mass spectrometric interferences, the advantages compared to other methods are quite obvious:

- Losses of analyte do not change the analytical result.
- Nearly no influences by matrix effects, as only isotope ratios have to be measured and both isotopes will be affected in the same way.
- Primary method of measurement, this means high accuracy and small measurement uncertainties.

Qualification

Regular and successful participation in the worldwide highest metrological key comparisons between the National Metrological Institutes (NMI), run by "Comité Consultatif pour la Quantité de Matière (CCQM)", representing the Federal Republic of Germany. Moreover, participation in different certifications of reference materials of BAM, the "Institute for Reference Materials (IRMM)", the "Bureau Communautaire de Référence (BCR)" and other institutions.