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Contribution to the certification of B, Cd, Cu, Mg and Pb in a synthetic water sample, by use of isotope-dilution ICP–MS, for Comparison 12 of the International Measurement Evaluation Programme

Abstract The contribution of the Institute for Reference Materials and Measurements to the certification of the B, Cd, Cu, Mg, and Pb content of a synthetic water sample used in Comparison 12 of the International Measurement Evaluation Programme (IMEP-12) is described. The aim of the IMEP programme is to demonstrate objectively the degree of equivalence and quality of chemical measurements of individual laboratories on the international scene by comparing them with reference ranges traceable to the SI (Système International d'Unités). IMEP is organized in support of European Union policies and helps to improve the traceability of values produced by field chemical measurement laboratories. The analytical procedure used to establish the reference values for the B, Cd, Cu, Mg, and Pb content of the IMEP-12 sample is based on inductively coupled plasma–isotope-dilution mass spectrometry (ICP–IDMS) applied as a primary method of measurement. The measurements performed for the IMEP-12 study are described in detail. Focus is on the element boron, which is particularly difficult to analyze by ICP–MS because of potential problems of low sensitivity, high mass discrimination, memory effects, and abundance sensitivity. For each of the certified amount contents presented here a total uncertainty budget was calculated using the method of propagation of uncertainties according to ISO (International Organization for Standardization) and Eurachem guidelines. For all investigated elements with concentrations in the low µg kg^{-1} and mg kg^{-1} range (corresponding to pmol kg^{-1} to the high µmol kg^{-1} level), SI-traceable reference values with relative expanded uncertainties (k=2) of less than 2% were obtained.

Keywords IDMS · ICP–IDMS · IMEP · Certification · Uncertainty budget

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Introduction

International comparability of measurements is essential in many cross-border issues concerning international trade, environment, and political matters. The International Measurement Evaluation Programme (IMEP), coordinated by the Institute for Reference Materials and Measurements (IRMM) [1], offers measurement laboratories a tool for improving the reliability of chemical measurements. Unlike some other interlaboratory comparisons, in which results are compared with consensus values (i.e. derived from participants' results), in an IMEP comparison the participants' results are evaluated against metrological reference values. IMEP reference values should not just be taken "at face value", because they have proven uncertainty and traceability via a link to the international metrology community, i.e. BIPM–CCQM (Bureau International des Poids et Mesures–Comité Consultatif pour la Quantité de Matière) [2]. The IMEP program is open to all laboratories and full confidentiality is guaranteed. Because the participants are asked to use their routine methods when analyzing the IMEP intercomparison samples, IMEP gives a picture of the "state of practice" in chemical measurements.

Previous IMEP comparisons have focused on trace elements in water [3], trace and minor constituents in human serum [4], trace elements in polyethylene [5], and lead in wine [6]. Comparison 12 of the International Measurement Evaluation Programme (IMEP-12) is again focused on "trace elements in water". The sample matrix chosen for this IMEP comparison is similar to drinking water, which is one of the most important and most frequently analyzed matrices in trace analysis. The choice of the elements to be analyzed, and their concentrations, was made with regard to European legislation (e.g. directive 98/83/EC [7]) and the capability to provide reference values. These reference values were established by a collaboration of five reference laboratories each with a proven record in the application of isotope-dilution mass spectrometry (IDMS). The contribution of the IRMM to the certification of the concentration of B, Cd, Mg, Pb, and

Cu in the IMEP-12 water sample is described herein. The analytical procedure is based on ICP–IDMS, used as a primary method of measurement. For each element, a comprehensive measurement uncertainty was evaluated using the method of propagation of individual uncertainty components.

Theoretical

Isotope-dilution mass spectrometry (IDMS)

The analytical procedure used for the certification of B, Cd, Mg, Pb, and Cu in the synthetic water sample of IMEP-12 is based on isotope-dilution mass spectrometry [8, 9, 10, 11], used as a primary method of measurement. The corresponding equation is used as basis for the calculation of the content [8]:

$$c_x = \left(\frac{m_y}{m_x}\right) \cdot c_y \cdot \left(\frac{R_y - K_b \cdot R_b}{K_b \cdot R_b - R_x}\right) \cdot \left(\frac{\sum_{i=1}^{n} R_{xi}}{\sum_{i=1}^{n} R_{yi}}\right) - \left(\frac{Bl}{m_x}\right) \tag{1}$$

In Eq. (1), m_y and m_x are the masses, c_y and c_x the amount contents and R_{yi}, R_{xi} are the isotope ratios of spike and sample, respectively. R_b is the isotope ratio of the isotope diluted sample (the blend) and K_b is the K-factor (K is defined as $K = R^{certified}/R^{observed}$) of the blend, which is used to correct for the mass discrimination of the instrument. Bl is the procedural blank for the element. Because there is large variation in the natural isotopic composition of B and Pb, the isotopic composition and the atomic weight of these elements in the sample were determined experimentally. The isotopic compositions and atomic weights of Cd, Cu, and Mg in the sample were taken from IUPAC tables [12, 13].

Experimental

Sample

The IMEP-12 water samples were obtained from the Institute of Agrobiotechnology (IFA, Tulln, Austria). The main batch was synthetically prepared by gravimetric addition of standard solutions to purified water; it was then homogenized and bottled in precleaned 100-mL polyethylene bottles. The concentrations of the elements to be measured were adjusted to be comparable with relevant legal limits [7] for drinking water.

Instrumentation

All measurements were performed with an Elan 6000 quadrupole ICP–MS (Perkin–Elmer Sciex, Ontario, Canada) using the pulse-counting acquisition mode. For sample introduction, a low flow concentric nebulizer (MicroMist, Glass Expansion, Camberwell, Australia) was used in combination with a small cyclone spray chamber. This sample-introduction system was chosen with particular regard to boron measurements, because of its better wash-out characteristics compared with those of the instrument's standard Scott type spray chamber [14].

Chemicals and reference materials

Subboiled water was prepared by distilling water obtained from a Milli-Q system (Millipore, Bedford, MA, USA) in a quartz still under subboiling conditions. Subboiled HNO_3 was similarly prepared from p.a. grade HNO_3 from Merck (Darmstadt, Germany). Water produced by a Milli-Q system equipped with a special ion-exchanger cartridge for boron removal was used for boron determination. The 2% nitric acid solution, prepared from subboiled HNO_3 and Milli-Q water, which was used for spike and blend dilution, was checked for its boron blank level by semiquantitative ICP–MS analysis.

The details of the certified reference materials used for IDMS of all the elements described are listed in Table 1. For Pb, in particular, two different isotopic reference materials were used for K-factor determination – NBS-981 for determination of the K-factor for the sample isotopic composition and NBS-982 for the K-factor for blend isotope ratio measurements.

Materials

To minimize blank contributions and contamination risks in trace analysis at ng g^{-1} levels, clean and non-adsorbing materials are required for sample-treatment and storage. Acids, water, and spike materials were stored in Teflon bottles; samples, blends, blanks, and elemental standard solutions were stored either in Teflon bottles, PE-bottles, or PE centrifuge tubes. The cleaning procedure for all equipment (bottles, syringes, pipette tips, and centrifuge tubes) consisted of four consecutive steps – an ethanol/water (1/9) bath (24 h), an acid bath (10% HNO_3, 24 h), a second acid bath (10% HNO_3, 24 h), and a Milli-Q water bath (24 h). Between each step the material was rinsed with Milli-Q water and, after cleaning,

Table 1 Certified reference materials used in the measurement process

Element	CRM	Description	Use
B	IRMM-610[a]	^{10}B Enriched isotopic CRM	Sample spiking
	IRMM-611[a]	Natural isotopic CRM	K-Factor determination
Cd	IRMM-622[a]	^{111}Cd Enriched isotopic CRM	Sample spiking
Mg	IRMM-638[a]	^{26}Mg Enriched isotopic CRM	Sample spiking
	IRMM-637[a]	Natural isotopic CRM	K-Factor determination
Pb	NIST SRM 991 dil.[b]	^{206}Pb Enriched isotopic CRM	Sample spiking
	NBS-981[b]	Common Pb isotopic standard	K-Factor determination
	NBS-982[b]	Equal-Atom Pb isotopic standard	K-Factor determination
Cu	IRMM-632	^{65}Cu Enriched isotopic CRM	Sample spiking
	IRMM-633	Natural isotopic CRM	K-Factor determination

[a]Certified for isotopic composition and amount
[b]Prepared gravimetrically from solid material

dried on a class 10 clean bench. Because boron is a particularly problematic element, with regard to contamination, the Teflon bottles used for spike dilution, blend preparation, and monitoring of the procedural blank were checked before use for their boron level by semiquantitative ICP–MS analysis.

Fig. 1 Dependence of copper isotope ratio on sodium concentration in a blend solution
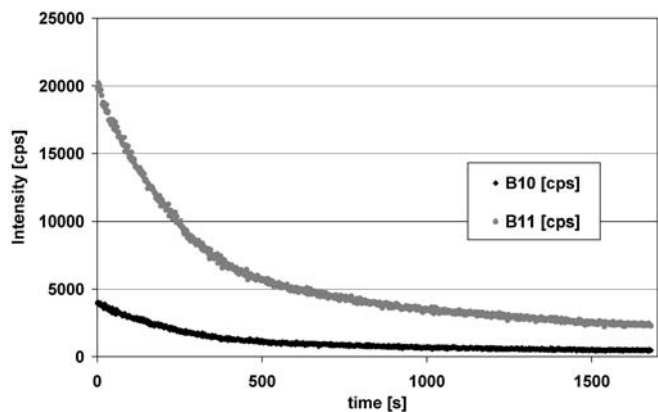
Fig. 2 Boron background signal decrease immediately after plasma ignition

In addition to the risk of contamination from materials, the risk of airborne contamination from dust particles during sample treatment is also significant at the ng g^{-1} concentration level and must be minimized. All sample-processing steps were therefore performed in the ultra-clean chemical laboratory (UCCL) [15], a clean room environment for sample preparation available at the IRMM.
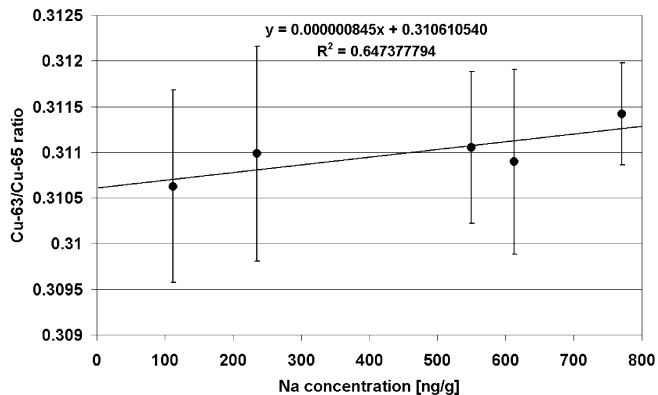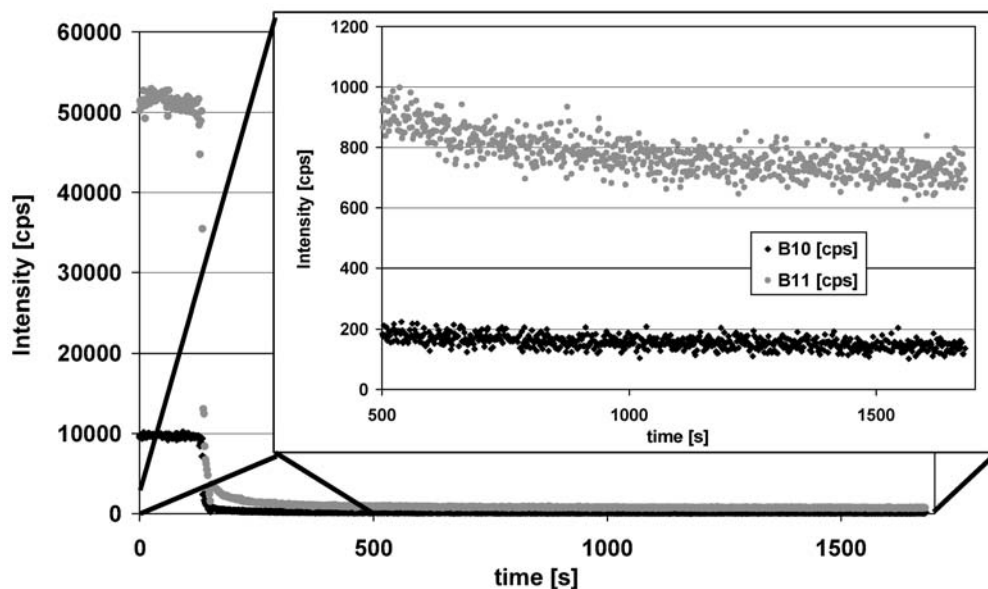
Effect of ArNa$^+$ interference on the copper result

When sodium is present in a sample, ArNa$^+$ can be formed during ICP–MS measurements, resulting in isobaric overlap on mass 63. This induces a change in the ^{63}Cu/^{65}Cu isotope ratio measured by ICP–MS, thereby affecting the results of copper determination by IDMS. Semiquantitative measurements revealed that the Na concentration in the IMEP-12 sample was about 70 times the Cu concentration. A preliminary study was, therefore, performed to investigate the effect on the Cu isotope ratio and the copper amount content determined by IDMS.

First, a test blend solution with a ^{63}Cu/^{65}Cu isotope ratio and a concentration similar to the blends to be measured was prepared by use of the original IMEP-12 sample and the IRMM-632 spike. After dilution, this solution was analyzed for its mass 63/mass 65 ratio by ICP–MS. A sodium standard solution was then added to the diluted blend solution and the isotope ratio was measured again. This was repeated four times. A dilution of the IRMM-633 natural Cu CRM was measured together with the test blend for K-factor determination. Additionally, the Na standard solution was checked for its copper blank by measuring the intensity on ^{65}Cu in the Na standard solution. This was used to correct for the Cu blank contribution introduced to the test blend when spiking with sodium.

Figure 1 shows the dependence of mass 63/mass 65 ratio (corrected for instrumental background, mass discrimination, and the copper blank of the sodium standard) on the sodium concentration in the test blend. Vertical bars on the graph indicate the experimental standard deviation of the isotope ratio measurement. The contribution of ArNa$^+$ to the intensity on mass 63 results in a positive correlation between the mass 63/mass 65 ratio and the sodium concentration.

The slope of the linear regression indicates an increase in the mass 63/mass 65 ratio of 0.85×10^{-6} ng^{-1} g Na in the solution. The sodium content of the blend solutions (~200 ng g^{-1}) increases the measured 63/65 ratio of the blend by 0.00017, or 0.055%. Thus ArNa$^+$ interference results in an apparent increase of 0.065% in the Cu content.

Fig. 3 Wash-out of a 25 ng g^{-1} boron standard solution on the Elan 6000 equipped with MicroMist nebulizer and cyclone spray chamber

Preliminary investigation of boron analysis by ICP–IDMS

In addition to the contamination risks associated with its ubiquitous nature, boron measurement by ICP–MS is difficult for other reasons; this can affect the results from boron determination by IDMS. Boron isotope ratio measurements by ICP–MS suffer from low sensitivity (about 2000 cps per ng g^{-1} for the Elan 6000), high mass discrimination (K-factor ~1.2 to 1.4 for the Elan 6000, depending on the ion-lens voltage), long wash-out time, and sensitivity problems for carbon-containing samples [14].

The wash-out time of the instrument was investigated during preliminary experiments performed using the same MicroMist nebulizer-cyclon spray chamber sample-introduction system that was later used for the blend measurements. Immediately after plasma ignition a high background signal is observed (Fig. 2), an effect which has also been described by Demuth and Heumann [14]. As a consequence, before starting boron measurements in the ng g^{-1} concentration range the sample introduction system was rinsed for at least 2 h after plasma start-up to stabilize the instrumental background.

During the measurements, however, the wash-out time after aspiration of a standard solution containing 25 ng g^{-1} of boron was observed to be approximately 1000 s (Fig. 3) with the sample-introduction system described. After every sample measurement, therefore, a rinsing period of 1000 s was used, followed by measurement of a blank solution.

The abundance sensitivity between $^{12}C^+$ and $^{11}B^+$ for the Elan 6000 ICP–MS was investigated while aspirating a 25 ng g^{-1} boron standard solution. Separation of the signals on mass 11 and mass 12 was sufficient. The same investigation was performed using a dilution of the IMEP-12 sample, again resulting in sufficient separation of $^{12}C^+$ from $^{11}B^+$. The results prove that for the IMEP-12 sample, a synthetic water sample containing only small amounts of carbonates and no dissolved organic carbon, no abundance sensitivity problems occur.

Analytical procedure for the IDMS experiments

Calculation of the amount of spike added

Preliminary measurements on the IMEP-12 sample were performed by ICP–MS using both external calibration and a semiquantitative measurement procedure. On the basis of the results obtained and the certified data of the spike material the optimum blend ratio for each element was calculated as a compromise between the lowest error magnification factor [9], sufficient counting rate above the instrumental background, and minimization of dead-time effects. For all elements, 8–10 g sample was spiked gravimetrically with 0.5–4 g of spike solution. For magnesium the sample had to be diluted gravimetrically by a factor of 50 before spiking, to furnish the optimum blend ratio. For the elements B, Pb, and Cd, present at much lower concentrations in the IMEP-12 sample, the respective spike solutions had to be diluted by factors of 10 (B, Cd) and 20 (Pb). The blend ratios thus obtained were: ~0.3 for $^{63}Cu/^{65}Cu$, ~0.5 for $^{24}Mg/^{26}Mg$, ~5 for $^{206}Pb/^{208}Pb$, ~0.11 for $^{110}Cd/^{111}Cd$, and ~2 for $^{10}B/^{11}B$. Six blends were prepared gravimetrically for each element.

Blend dilution and ICP–MS measurements

Typically, the optimum ICP–MS counting rate for the most abundant isotope is ~200,000 cps with regard to uncer-

Table 2 ICP–MS conditions for the isotope ratio measurement of B, Cd, Cu, Mg, and Pb

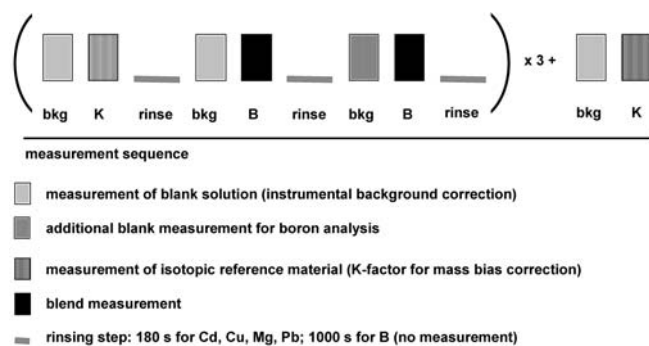| Condition	Value
Spray-chamber	Cyclone, quartz
Nebulizer	MicroMist
Sample flow rate	0.4 mL min^{-1}
Plasma gas flow	14.8 L min^{-1}
Auxiliary gas flow	0.70 L min^{-1}
Nebulizer gas flow	0.94 L min^{-1}
Plasma power	1200 W
Sensitivity per ng g^{-1}	~2000 cps (B), ~18,000 cps (Mg), >100,000 cps (Pb)
Background on mass 220	<10 cps
Lens voltage (autolens off)	7.7 V (Mg, B), 9.0 V (Cd, Cu), 12.0 V (Pb)

Fig. 4 Sequence for blend isotope ratio measurement by ICP–MS

tainty propagation associated with the correction for dead-time and instrumental background [16]. The blend solutions were therefore diluted with 2% nitric acid by a factor of 3 (for Cd) up to a factor of 200 (for Mg), depending on the element. ICP–MS operating conditions are listed in Table 2.

The acquisition sequence described in Fig. 4 was applied to all blend isotope ratio measurements. With this sequence, any drift of the instruments mass discrimination over time can be monitored and corrected for ("bracketing approach"). For boron measurements an additional 2% nitric acid blank solution was measured between two successive blends to correct for differences between instrumental background caused by wash-out effects. For determination of the isotopic composition of B and Pb in the sample, the same measurement sequence as that applied to the blend solutions was used.

Uncertainty calculations

All measurement results in this work are given together with their combined uncertainties. These uncertainties were calculated according to the ISO/GUM [17] and Eurachem [18] guides by applying an uncertainty propagation procedure to individual uncertainty contributions. In addition to the uncertainty associated with the different quantities de-

scribed in Eq. (1), uncertainty components taken into account include uncertainty from the correction for dead-time and instrumental background, and, for Cu measurement, for the $ArNa^+$ interference [19]. In practice, a dedicated software program [20], based on the numerical method of differentiation described by Kragten [21], was used to calculate the combined uncertainty. The calculated combined uncertainties on the content are expanded with a coverage factor $k=2$.

Results and discussion

Procedural blank

The procedural blank was obtained by use of 2% HNO_3 treated in the same way as the samples and the spike solutions (the same dilution rates using identical vials and syringes). Calibration for the blank measurements was performed as an external one-point calibration using a 10 ng g^{-1} multi-element solution. The instrumental background was measured by using ultra-clean 2% nitric acid stock solution. The calculated absolute amounts of the procedure blanks used for blank correction of each element are listed in Table 3. Because the blank contribution was always less than 0.2% of the analyte signal, the uncertainty of the blank correction was not a major contribution to the total combined uncertainty of the measurements.

Table 3 Procedural blanks for B, Mg, Pb, Cu, and Cd, and their standard uncertainties ($k=1$)

Element	No. of determinations	Absolute blank amount (ng)	Analyte signal (%)
B	3	0.536±0.112	0.04
Mg	6	0.14±0.19	0.0017
Pb	6	0.17±0.03	0.18
Cu	6	0.018±0.020	0.0011
Cd	6	0±0.003	-[a]

[a]no significant blank signal measured

Table 4 Isotope ratio (corrected for mass discrimination), abundances, and atomic weight of boron in the IMEP-12 sample, and their uncertainties ($k=2$)

n	Ratio $^{10}B/^{11}B$	Abundance ^{10}B (%)	Abundance ^{11}B (%)	Atomic weight
6	0.2481±0.0016	19.88±0.10	80.12±0.10	10.8113±0.0010

Effect of spectroscopic interferences on the analytical result

The influence of $ArNa^+$ on the Cu isotope ratio measurement and thus on the amount of Cu determined by ICP–IDMS was studied under conditions which were very similar to those of the blend measurements. For the IMEP-12 sample with a sodium content of ~15 mg kg^{-1}, the effect on the Cu content was almost insignificant and found to be less than 0.1%. Separation of Cu from Na before copper isotope ratio measurement by ICP–MS, as described elsewhere [22], was, therefore, not necessary in this work. No correction was applied but an uncertainty contribution of 0.2% from the $ArNa^+$ interference was introduced into the uncertainty budget for copper as a conservative estimate (by introducing a multiplicative factor of 1±0.002).

Measurement of the isotopic composition for lead can be affected by an interference of ^{204}Hg with ^{204}Pb; ^{204}Hg can be present in the sample, but can also arise as a result of contamination of the plasma gas with traces of mercury. The isotope ratio $^{204}Pb/^{206}Pb$ measured for the determination of the Pb isotopic composition must, therefore, be corrected for ^{204}Hg interference. In the determination of the isotopic composition for lead in IMEP-12, however, the Hg contribution on mass 204 represents less than 1% of the ^{204}Pb-signal. This interference was corrected via the ^{201}Hg signal using the IUPAC abundances for Hg.

Concentrations and combined uncertainty

The experimentally determined isotope ratios of boron in the sample, its isotopic composition, and the derived atomic weight of boron, together with their expanded uncertainties ($k=2$) are listed in Table 4. The isotopic composition and the atomic weight of lead in the sample were determined in a similar manner.

The results obtained for the elements B, Cd, Cu, Mg, and Pb in the IMEP-12 samples are shown in Table 5. Accompanying quantities are expanded uncertainties ($k=2$). As is apparent from the results, the concentrations of all the elements investigated, which ranged from low µg kg^{-1} to mid mg kg^{-1} levels (corresponding to the pmol kg^{-1} to high µmol kg^{-1} range), could be measured with relative expanded uncertainties ($k=2$) between 0.8% (Mg) and 1.5% (Cd).

The distribution of the main contributions to the total uncertainty for the boron content is illustrated in Fig. 5. Unlike the other elements, the main contribution to the uncertainty for boron is the variation of the instrumental
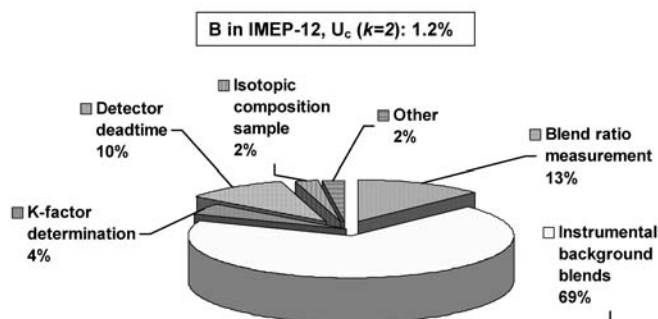
Table 5 Element concentrations and amounts in IMEP-12 with combined uncertainties ($k=2$), contribution to the certification done in this work, and reference values

Element	This work (µg kg^{-1})	This work (mol kg^{-1})	Reference values in IMEP-12 (mol kg^{-1})
B	130.9±1.5	(12.11±0.14)×10^{-6}	(12.11±0.24)×10^{-6}
Cd	4.624±0.068	(41.14±0.60)×10^{-9}	(40.78±0.82)×10^{-9}
Cu	220.3±1.9	(3.468±0.031)×10^{-6}	(3.412±0.068)×10^{-6}
Mg	(38.65±0.29)×10^3	(1.590±0.012)×10^{-3}	(1.590±0.032)×10^{-3}
Pb	8.746±0.080	(42.22±0.39)×10^{-9}	(42.27±0.85)×10^{-9}

Fig. 5 Main contributions to uncertainty in the measurement of boron content

background during blend measurement. For the other elements, the main contributions to the uncertainties are dead-time effects, the repeatability of the blend isotope ratio measurement, and the K-factor determination.

The results obtained by applying the IDMS method described in this work were combined with amounts measured for the IMEP-12 samples in four other IMEP Reference Laboratories to produce the IMEP-12 reference values [23]. In Table 5, the results obtained in this work are compared with the reference values. For all the elements agreement between the data is very good.

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