

A convenient and economic approach to achieve SI-traceable reference values to be used in drinking-water interlaboratory comparisons

Olaf Rienitz · Detlef Schiel · Bernd Güttler ·
Michael Koch · Ulrich Borchers

Received: 25 June 2007 / Accepted: 24 September 2007 / Published online: 23 October 2007
© Springer-Verlag 2007

Abstract Metrologically traceable reference values add an essential benefit to interlaboratory comparisons: unlike consensus values, they can be used to establish national and international comparability. Furthermore, the participating laboratories obtain a reliable and unbiased benchmark to check their results for accuracy. Usually, metrologically traceable reference values are obtained by so-called *primary methods* which demand excessive efforts at great expense. Within the framework of two national drinking-water interlaboratory comparisons (proficiency testing rounds), a new approach to provide metrologically traceable reference values was applied. It is solely based on existing data which were collected during the comparison itself. Lead (Pb) measurements serve as an example to show how metrologically traceable reference values were derived from the lead amount added during sample preparation and the amount of lead already present in the drinking-water matrix used to prepare these samples. Within this approach, the matrix content is calculated in a way similar to a standard addition experiment. An uncertainty budget for the reference value was set up which

describes the link to the corresponding SI units. Isotope dilution mass spectrometry (IDMS) as a primary method was used to validate this approach in the case of cadmium, chromium, copper, lead, and nickel.

Keywords Metrological traceability · Drinking water · Proficiency testing · Reference values · Heavy metals

Introduction

Within the scope of European harmonization, the comparability of measurement results is increasingly demanded. An example is the Drinking Water Directive 98/83/EC [1]. Metrological traceability ensures international comparability. A way to achieve comparability is the implementation of a traceability chain to the SI units via national standards. National standards are developed and provided by National Metrology Institutes (NMIs). In the field of analytical chemistry, the NMIs are also responsible for dissemination of these national standards to set up at least the first link of the traceability chain [2].

In addition to the use of reference materials (RMs) or even certified reference materials (CRMs) for calibration purposes, proficiency testing (PT) rounds are used to verify the measurement results. Therefore in Germany, all laboratories concerned with drinking-water monitoring regularly have to participate in interlaboratory comparisons. The German drinking water directive [3] establishes the corresponding legal basis in conjunction with a recommendation issued by the German Federal Environment Agency (UBA) [4].

Two interlaboratory comparisons addressing heavy metals in drinking water are discussed in detail taking lead as an example to show a convenient way to generate

O. Rienitz (✉) · D. Schiel · B. Güttler
Physikalisch-Technische Bundesanstalt (PTB),
Metrologie in der Chemie, Bundesallee 100,
38116 Braunschweig, Germany
e-mail: olaf.rienitz@ptb.de

M. Koch
Institut für Siedlungswasserbau,
Wassergüte und Abfallwirtschaft (ISWA),
Universität Stuttgart, Bandtäle 2, 70569 Stuttgart, Germany

U. Borchers
IWW Rheinisch-Westfälisches Institut für Wasserforschung
gemeinnützige GmbH, Moritzstraße 26, 45476 Mülheim,
Germany

metrologically traceable reference values solely based on data collected during these comparisons. The PT provider usually prepares the samples used by adding appropriate amounts of the analyte elements to natural drinking water (matrix). As this addition is done volumetrically or gravimetrically, the added amount is well-known, especially if certified RMs are used. Even though the matrix content of the analyte elements is low, reference values have to include these matrix contents along with their measurement uncertainties to become traceable. Therefore the matrix contents have to be measured and their uncertainties have to be estimated.

Measuring these matrix contents directly is often a challenging task and yields poor uncertainties. The experimental design of the discussed comparisons, however, offers a totally different way to obtain the matrix contents. To avoid cheating and to check their measurement capabilities over a certain range, the participants are provided with randomly selected samples out of a pool of up to 12 concentration levels covering nearly two orders of magnitude. This complex design can be taken advantage of by regarding and evaluating the comparison as a standard addition. The gap between the measured values and the added concentration arises from the matrix content. Therefore the measurement results of the participants themselves provide the missing piece needed to complete the reference value without any additional measurements.

Refusing the straightforward use of consensus values as metrologically traceable ones, but applying them to introduce a minor correction to the previously incomplete reference values seems to be a contradiction. The special properties of standard addition are able to smooth this out. For example: the result of a standard addition experiment remains totally unaffected by recovery problems, because the slope and the y -intercept are changed by exactly the same factor. However, there may exist constant biases misleading the standard addition. To rule this out and to prove the whole approach experimentally, IDMS as a primary method was applied to determine reference values that are independent of the sample preparation.

Two different ways of sample preparation (volumetric and gravimetric) were scrutinized with respect to the

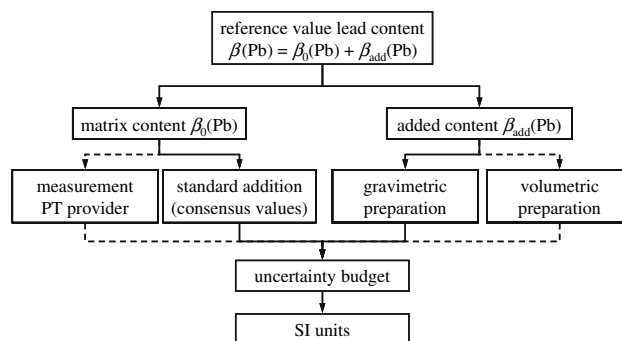


Fig. 1 Several possibilities of obtaining an SI traceable reference value $\beta(\text{Pb})$. *Solid line*: example using the added content $\beta_{\text{add}}(\text{Pb})$ from a gravimetric preparation combined with the content $\beta_0(\text{Pb})$ arising from the matrix calculated using the consensus values and the preparation

metrological traceability of the added analyte contents. The crucial point was to set up an equation describing the particular sample-preparation procedure. This so-called *mathematical model of the measurement* (model equation) was used to estimate the measurement uncertainty of the added amount of analyte according to the *Guide to the Expression of Uncertainty in Measurement* (GUM) [5].

Combining the added concentration of analyte β_{add} and the concentration β_0 arising from the matrix resulted in the desired reference value β (Fig. 1). The corresponding model equation needed in the uncertainty budget reflects also the traceability chain by linking the reference value directly to the purity of the applied certified reference material (standard).

Experimental

Drinking water samples

Volumetric preparation

The drinking water matrix for the preparation of the samples was directly taken from the public water distribution system after rinsing the relevant faucets thoroughly for several hours. A 10-L class A volumetric

Table 1 Symbols used in the volumetric sample preparation section

$\beta_{\text{add}}(\text{Pb})$	Added mass concentration of Pb in the sample ($\mu\text{g L}^{-1}$)	k_{res}	Correction for residual water in the flask after draining (1)
V_{pip}	Nominal volume delivered by the pipette used (mL)	V_{10}	Nominal volume of the 10 L glass volumetric flask (mL)
δV	Bias of the pipette (mL)	δV_t	Bias of the flask volume due to the temperature of the tap water (mL)
β_{ref}	Mass concentration of Pb in the certified standard solution (mg L^{-1})		

flask (Hirschmann, Duran) was filled roughly below its mark. After adding 300 mL nitric acid (Merck, Suprapur, 65%), a calibrated pipette (Eppendorf, Reference) was used to add 0.350–4.60 mL of certified standard solutions (Merck, Certipur, $(1\,000 \pm 2) \text{ mg L}^{-1}$) in order to adjust the desired concentration of the analytes of interest. After that, the flask was made up to the mark, again using tap water. It was drained into a 60 L HDPE vessel (Nalgene). Again the flask was filled up to its mark another five times, but solely using tap water. After intense homogenizing, the required number of aliquots of this pool was bottled. To calculate the uncertainty associated with the mass concentration, a mathematical model was set up (Eq. 3, symbols Table 1). This model takes into account the bias of the pipette determined during calibration, the residual water in the volumetric flask after draining, and the bias of the volumetric flask due to the tap water temperature which is different from the temperature the certified volume of the flask is valid for. A relative expanded uncertainty U_{rel} was calculated in the range 0.5–0.7 % associated with added lead mass concentrations $\beta_{\text{add}}(\text{Pb})$ of 6–80 $\mu\text{g L}^{-1}$.

$$\beta_{\text{add}}(\text{Pb}) = \frac{(V_{\text{pip}} + \delta V)\beta_{\text{ref}}}{6(k_{\text{res}}V_{10} + \delta V_t)} \quad (1)$$

Gravimetric preparation

An appropriate amount of 100–250 mg of lead(II) nitrate (Sigma Aldrich, $w_{\text{pur}} = 0.99999 \text{ g g}^{-1}$, unopened, factory packaged) was weighed (Sartorius, RC210D) into a beaker and dissolved using deionized water (Elga, Purelab ultra). The solution was transferred into a weighed 1-L volumetric flask, diluted with deionized water and acidified using 1 mL nitric acid (Merck, Suprapur, 65%) to yield about 1 000 g of a stock solution having a lead mass fraction of 80–170 $\mu\text{g g}^{-1}$, depending on the concentration level aimed at. The exact masses were measured on a balance (Sartorius, BA 3100P). Of the stock solution, 10, 25, or 50 g were weighed directly into another 1-L volumetric flask and, using deionized water,

diluted to an approximate—but exactly measured—amount of 500 g of the intermediate solution (Sartorius, BA 3100P). On a balance (Sartorius, F150S), a PE vessel was filled with a few liters of tap water. One hundred grams of the intermediate solution were added. After adding the desired amounts of all other elemental solutions and 20 mL nitric acid (65%), the vessel was filled to 35 L and the final mass was read. After homogenizing, the aliquots intended to be sent to the participants of the interlaboratory comparison were bottled. A 100 mL pycnometer was used to gravimetrically (Sartorius, RC210D) determine the density of the samples which was used to calculate the added lead mass concentration. The preparation was described with a mathematical model (Eq. 2, symbols Table 2) that incorporates the air buoyancy correction along with the chance of having to deal with a certified reference material that occurs as a salt. A relative expanded uncertainty U_{rel} was calculated in the range of 0.10–0.35 % associated with added lead mass concentrations $\beta_{\text{add}}(\text{Pb})$ of 5–50 $\mu\text{g L}^{-1}$.

$$\beta_{\text{add}}(\text{Pb}) = \frac{w_{\text{pur}} \cdot m(E_{\text{vE}}A_{\text{vA}})}{K \cdot m_1} \cdot \frac{v_E \cdot M(E)}{M(E_{\text{vE}} \cdot A_{\text{vA}})} \cdot \frac{m_2}{m_3} \cdot \frac{m_4}{m_5} \cdot \rho_5 \quad (2)$$

IDMS measurements

Technique

The IDMS measurements were designed as *double IDMS* experiments using the *exact matching technique* [6]. To obtain the most reliable results, the measurements were carried out on a multi collector inductively coupled plasma mass spectrometer (MC-ICP-MS) allowing for highly precise isotope ratio measurements. Therefore the obtained measurement uncertainties ($U_{\text{rel}}(\beta_{\text{IDMS}}(\text{Pb})) < 0.5 \%$) are no longer limited by the measurement itself ($u_{\text{rel}}(R(^{206}\text{Pb}/^{208}\text{Pb})) < 0.03 \%$) but by the uncertainty associated with the lead content of the standard solution used.

Table 2 Symbols used in the gravimetric sample preparation section

$\beta_{\text{add}}(\text{Pb})$	Added mass concentration of Pb in the sample ($\mu\text{g L}^{-1}$)	m_1	Mass of stock solution after preparation (g)
w_{pur}	Certified purity of the reference material (g g^{-1})	m_2	Mass of stock solution used to prepare intermediate solution (g)
$m(E_{\text{vE}}A_{\text{vA}})$	Mass of reference material used to prepare stock solution (g)	m_3	Mass of intermediate solution after preparation (g)
K	Air buoyancy correction factor (g g^{-1})	m_4	Mass of intermediate solution used to prepare sample solution (g)
ρ_5	Density of the final sample (g L^{-1})	m_5	Mass of sample solution after preparation
$E_{\text{vE}}A_{\text{vA}}$	Formula of reference material, E: cation, A: Anion, v stoichiometric number (1)	M	Molar mass (g mol^{-1})

Instrumentation

Thermo Scientific Finnigan Neptune Multicollector ICP-MS, ESI Stable Introduction System (Quartz Dual Spray Chamber and MicroFlow PFA-50 nebulizer), Neptune software Ver. 3.1.0.27, Cetac ASX-100 Autosampler.

Analytical balances

Mettler H 315, Sartorius 1702MP8 and BP220S. To reduce measurement uncertainties, all weighings, including dilution steps, were performed gravimetrically. The masses were corrected for air buoyancy. Air pressure, temperature, and humidity measurements: Testo 650.

Chemicals

Water purification system: Millipore ELIX 3 and Milli-Q Gradient ($\sigma \approx 0.055 \mu\text{S cm}^{-1}$, $w(\text{TOC}) < 5 \text{ ng g}^{-1}$). Merck nitric acid, p.a., purified by sub-boiling. NIST SRM 981 Natural lead, NIST SRM 991 Lead-206 spike.

Storage of standard solutions and samples

Standard solutions and samples are stored at room temperature. All bottles are weighed prior to and after each

sampling to keep track of changes in concentration due to evaporation losses and to be able to correct these losses.

Measurement procedure

In total, two samples of 50 g were withdrawn at a 2-month interval from each of the 12 bottles containing the different lead concentration levels in drinking water. The samples were weighed directly into acid-cleaned 100-mL LD-PE bottles. A measure of 0.7 g of subboiled nitric acid was added. Depending on the lead concentration, 1–10 g of a 7 ng g^{-1} ^{206}Pb spike solution (prepared from NIST SRM 991) was added to adjust the $^{206}\text{Pb}/^{208}\text{Pb}$ ratio to unity. The resulting nitric acid concentration was 0.15 mol L^{-1} . To match these sample blends according to their total lead amount and $^{206}\text{Pb}/^{208}\text{Pb}$ ratio, 12 calibration blends were prepared using exactly the same type of bottle, the same amounts of spike solution, and 1–10 g of a 250 ng g^{-1} standard solution (prepared from NIST SRM 981). The calibration blends were diluted using 0.15 mol L^{-1} nitric acid to match the corresponding sample blends according to their lead and acid concentration. Additionally, three sample and three calibration solutions, covering the whole concentration range, were prepared without adding the ^{206}Pb spike. They were used to determine the isotopic abundances of lead in the samples and to determine the mass bias correction factors, respectively. All sample spike

Table 3 Symbols used in the IDMS measurements section

$\beta_{\text{IDMS}}(\text{Pb})$	Mass concentration of Pb in the sample ($\mu\text{g L}^{-1}$)	R_y	Certified isotope ratio $^{206}\text{Pb}/^{208}\text{Pb}$ in the spike (1)
ρ_x	Density of the sample (g L^{-1})	R_x	Measured and corrected isotope ratio $^{206}\text{Pb}/^{208}\text{Pb}$ in the sample (1)
K_{evap}	Evaporation correction (g g^{-1})	R_z	Certified isotope ratio $^{206}\text{Pb}/^{208}\text{Pb}$ in the standard (1)
w_z	Mass fraction of Pb in the standard solution ($\mu\text{g g}^{-1}$)	$K_{z,i}$	Mass bias correction factor used to correct the ratio $^i\text{Pb}/^{208}\text{Pb}$ (1)
m_{yx}	Mass of spike solution y in the blend bx of sample + spike (g)	$R_{x,i}$	Measured and corrected isotope ratio $^i\text{Pb}/^{208}\text{Pb}$ in the sample (1)
m_x	Mass of sample x in the blend bx of sample + spike (g)	$R_{z,i}$	Certified isotope ratio $^i\text{Pb}/^{208}\text{Pb}$ in the standard (1)
m_z	Mass of standard solution z in the blend bz of standard + spike (g)	meas	Superscript indicating measured raw data
m_{yz}	Mass of spike solution y in the blend bz of standard + spike (g)	R_{iso}	Isotope ratio $^{206}\text{Pb}/^{208}\text{Pb}$ in the standard measured with the spiked samples (1)
M_x	Molar mass of lead in the sample (g mol^{-1})	K_b	Mass bias correction factor used to correct $^{206}\text{Pb}/^{208}\text{Pb}$ in the blends (1)
M_z	Molar mass of lead in the standard (g mol^{-1})	$x_{z,i}$	Certified isotopic abundance of ^iPb in the standard (mol mol^{-1})
R_{bx}	Measured and corrected isotope ratio $^{206}\text{Pb}/^{208}\text{Pb}$ in the blend bx (1)	$x_{x,i}$	Measured isotopic abundance of ^iPb in the sample (mol mol^{-1})
R_{bz}	Measured and corrected isotope ratio $^{206}\text{Pb}/^{208}\text{Pb}$ in the blend bz (1)		

blends were measured in the order of increasing lead concentration, in turn with their matching calibration blends, together with the unspiked calibration solutions, in one sequence, overnight, within 10 h. The calibration solutions were measured at the beginning, in the middle, and at the end of the sequence. The measurement of each blend was repeated three times. Every measurement started with a 90 s take-up period and a 30 s baseline measurement. It was followed by a 120 s nitric acid rinse. Every measurement consisted of seven blocks having ten cycles/block (4.2 s integration time/cycle). The amplifiers were rotated after every block. A radio frequency power of 1 200 W was applied. The selected mass resolution was $M/\Delta M = 450$. The following cup configuration was applied: L3 = ^{202}Hg , L2 = ^{203}Tl , L1 = ^{204}Pb , C = ^{205}Tl , H1 = ^{206}Pb , H2 = ^{207}Pb , H3 = ^{208}Pb . The ^{204}Pb signal was corrected for Hg. Tl was not detectable. The resulting ratios $^{204}\text{Pb}/^{208}\text{Pb}$, $^{206}\text{Pb}/^{208}\text{Pb}$ and $^{207}\text{Pb}/^{208}\text{Pb}$ were corrected for mass bias and averaged. No outliers were found. The average standard uncertainty of the most important ratio $^{206}\text{Pb}/^{208}\text{Pb}$ was $u_{\text{rel}}(R) = 0.003\%$. Furthermore, the unspiked samples and calibration solutions were measured in a separate sequence (4 h) having exactly the same experimental design, except that each measurement was repeated four times.

Estimation of measurement uncertainty

An uncertainty budget was set up describing the double IDMS measurement based on Eq. 3 as the mathematical model (symbols Table 3). A relative expanded uncertainty U_{rel} in the range of 0.44–0.35 % was calculated associated with lead mass concentrations $\beta(\text{Pb})$ of 5–50 $\mu\text{g L}^{-1}$. The calculations were carried out using the GUM Workbench 1.2 (Metrodata).

$$\begin{aligned}
 K_{z,204} &= \frac{x_{z,204}}{x_{z,208}} \cdot \frac{1}{R_{z,204}^{\text{meas}}}, & K_{z,206} &= \frac{x_{z,206}}{x_{z,208}} \cdot \frac{1}{R_{z,206}^{\text{meas}}}, \\
 K_{z,207} &= \frac{x_{z,207}}{x_{z,208}} \cdot \frac{1}{R_{z,207}^{\text{meas}}} \\
 R_{x,204} &= K_{z,204} \cdot R_{x,204}^{\text{meas}}, & R_{x,206} &= K_{z,206} \cdot R_{x,206}^{\text{meas}}, \\
 R_{x,207} &= K_{z,207} \cdot R_{x,207}^{\text{meas}} \\
 \sum_i R_{x,i} &= R_{x,204} + R_{x,206} + R_{x,207} + 1, \\
 \sum_i R_{z,i} &= \frac{x_{z,204}}{x_{z,208}} + \frac{x_{z,206}}{x_{z,208}} + \frac{x_{z,207}}{x_{z,208}} + 1 \\
 x_{x,204} &= \frac{R_{x,204}}{\sum_i R_{x,i}}, & x_{x,206} &= \frac{R_{x,206}}{\sum_i R_{x,i}}, & x_{x,207} &= \frac{R_{x,207}}{\sum_i R_{x,i}}, \\
 x_{x,208} &= \frac{1}{\sum_i R_{x,i}}
 \end{aligned}$$

$$\begin{aligned}
 M_x &= x_{x,204} \cdot M_{204} + x_{x,206} \cdot M_{206} + x_{x,207} \cdot M_{207} \\
 &\quad + x_{x,208} \cdot M_{208} \\
 M_z &= x_{z,204} \cdot M_{204} + x_{z,206} \cdot M_{206} + x_{z,207} \cdot M_{207} \\
 &\quad + x_{z,208} \cdot M_{208} \\
 R_y &= \frac{x_{y,206}}{x_{y,208}}, & R_z &= \frac{x_{z,206}}{x_{z,208}}, & R_x &= R_{x,206}, & K_b &= \frac{R_z}{R_{\text{iso}}} \\
 R_{\text{bx}} &= K_b \cdot R_{\text{bx}}^{\text{meas}}, & R_{\text{bz}} &= K_b \cdot R_{\text{bz}}^{\text{meas}} \\
 \beta_{\text{IDMS}}(\text{Pb}) &= \frac{\rho_x}{K_{\text{evap}}} \cdot w_z \cdot \frac{m_{yx}}{m_x} \cdot \frac{m_z}{m_yz} \cdot \frac{M_x}{M_z} \cdot \frac{R_y - R_{\text{bx}}}{R_{\text{bx}} - R_x} \cdot \frac{R_{\text{bz}} - R_z}{R_y - R_{\text{bz}}} \cdot \frac{\sum_i R_{x,i}}{\sum_i R_{z,i}} \quad (3)
 \end{aligned}$$

Results and discussion

Matrix content

As already mentioned above, the content arising from the matrix was determined similar to a standard addition experiment. This requires the analyte already present in the matrix and the added analyte to behave in the same way, which is a reasonable assumption considering the analyte element(s) and the drinking water matrix. Due to the addition of acid and standard solutions, strictly speaking the original matrix content is slightly higher than the determined analyte content arising from the matrix. However, within the limits of uncertainty, this difference is negligible. Therefore, in the following, the “analyte content arising from the matrix” β_0 is called matrix content, to simplify matters. The results of the participants of the interlaboratory comparisons 3/2004 TW A2, and 1/2006 TW A2 were used to calculate the robust consensus means β_{rcm} of all samples [7, 8] along with their uncertainties. These means should be the sum of the matrix content and the concentration arising from the added amount of the analyte (added mass concentration β_{add}). Equation 4 shows the corresponding relation with lead as an example.

$$\beta_{\text{rcm}}(\text{Pb}) = \beta_{\text{add}}(\text{Pb}) + \beta_0(\text{Pb}). \quad (4)$$

This equation can be regarded as a linear equation with a slope of 1 and a y-intercept equal to $\beta_0(\text{Pb})$. Therefore, plotting these means $\beta_{\text{rcm}}(\text{Pb})$ against the added mass concentrations $\beta_{\text{add}}(\text{Pb})$ has to yield the matrix mass concentration $\beta_0(\text{Pb})$ as the y-intercept. In most cases, the slopes were not very close to 1. For lead, for example, a slope of approximately 0.95 was found. Therefore it was necessary to rearrange Eq. 4 to yield a more general form (Eq. 5). Providing that the means recover a certain fraction a_1 of the true lead concentration $\beta(\text{Pb})$ leads to:

$$\beta_{\text{rcm}}(\text{Pb}) = a_1 \cdot \beta(\text{Pb}) = a_1 \cdot \beta_{\text{add}}(\text{Pb}) + \underbrace{a_1 \cdot \beta_0(\text{Pb})}_{=a_0} \quad (5)$$

$$\beta_{\text{rcm}}(\text{Pb}) = a_1 \cdot \beta_{\text{add}}(\text{Pb}) + a_0$$

$$\beta_0(\text{Pb}) = \frac{a_0}{a_1}$$

This linear function shows that the matrix content $\beta_0(\text{Pb})$ is equal to the x -intercept of the plot of $\beta_{\text{rcm}}(\text{Pb})$ versus $\beta_{\text{add}}(\text{Pb})$. Given that the relative uncertainties of the means (3.5–7.5 %) are more than ten times larger than the uncertainties of the added mass concentration it seemed reasonable to calculate the parameters a_0 and a_1 of the linear fit function by minimizing the sum of the y -residuals. This was done using the built-in Excel-function `rgp()`. The resulting parameters of this linear regression were $a_0 = (0.51 \pm 0.50) \mu\text{g L}^{-1}$ and $a_1 = 0.949 \pm 0.017$. The uncertainty associated with the matrix content was calculated according to an equation published in Ref. [9]. A new approach for the calculation of the matrix content using a generalized least-squares regression and therefore taking into account uncertainties in the x and y -directions will shortly be published (M. Koch, in preparation). The matrix mass concentration of lead calculated using the added mass concentration and the consensus means was $\beta_0(\text{Pb}) = (0.54 \pm 0.53) \mu\text{g L}^{-1}$ (Fig. 2). To check the consistency of the added mass concentrations and the IDMS reference values, the same calculations were carried out using the IDMS results: $a_0 = (0.303 \pm 0.025) \mu\text{g L}^{-1}$, $a_1 = 1.00036 \pm 0.00083$ and $\beta_0(\text{Pb}) = (0.303 \pm 0.025) \mu\text{g L}^{-1}$. These parameters and their associated uncertainties demonstrated both the validity of added mass concentrations calculated from

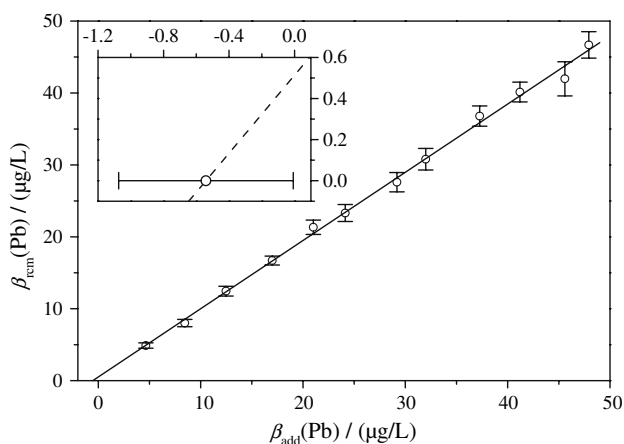


Fig. 2 The x -intercept of the linear fit of the consensus means $\beta_{\text{rcm}}(\text{Pb})$ versus the added mass concentration of lead $\beta_{\text{add}}(\text{Pb})$ is equal to the concentration $\beta_0(\text{Pb})$ arising from the matrix. The variances of slope and y -intercept along with their covariance were used to estimate the uncertainty of $\beta_0(\text{Pb})$; enlarged plot for details

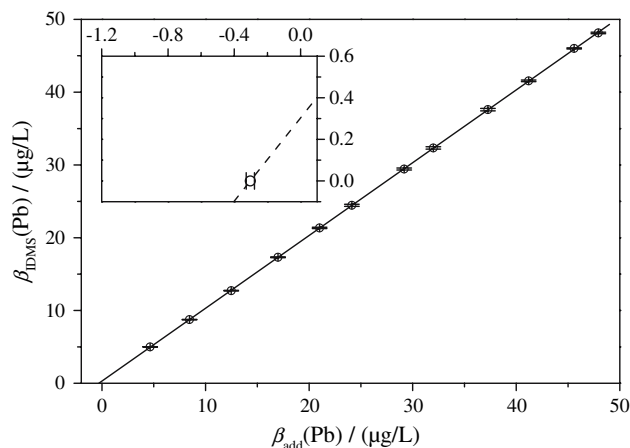


Fig. 3 The x -intercept of the linear fit of the IDMS values $\beta_{\text{IDMS}}(\text{Pb})$ versus the added mass concentration of lead $\beta_{\text{add}}(\text{Pb})$ is equal to the concentration $\beta_0(\text{Pb})$ arising from the matrix. The variances of slope and y -intercept along with their covariance were used to estimate the uncertainty of $\beta_0(\text{Pb})$; enlarged plot for details. The slope is equal to 1 within the limits of uncertainty. The consistency of the added mass concentrations $\beta_{\text{add}}(\text{Pb})$ was demonstrated by the primary IDMS measurements

the gravimetric preparation and the reference values obtained by the described IDMS measurements (Fig. 3).

Reference values

The reference values were calculated as the sum of the added mass concentration and the matrix content obtained by the described standard addition-like method:

$$\beta(\text{Pb}) = \beta_{\text{add}}(\text{Pb}) + \beta_0(\text{Pb}). \quad (6)$$

Despite the different relative expanded uncertainties associated with the gravimetric and volumetric sample preparation (< 0.4 % and < 1 %, respectively), Eq. 6 as the mathematical model yielded relative expanded uncertainties of 2–20 % associated with reference lead concentrations of 5–50 $\mu\text{g L}^{-1}$ regardless of the preparation procedure. These calculated reference values were compared to the reference values determined by the IDMS measurements (Fig. 4). Unlike the consensus values (Fig. 5), they were in very good agreement with the IDMS values. Their uncertainties and deviations from the IDMS values increased all the more, the closer the reference values got to the matrix concentration. This behavior is reasonable because larger concentrations should be measurable with smaller uncertainties. Therefore, the added mass concentrations completed by the matrix concentration derived from the consensus values were suited for use as the reference values. By contrast, the deviations and the uncertainties of the consensus values themselves showed no dependency on the concentration

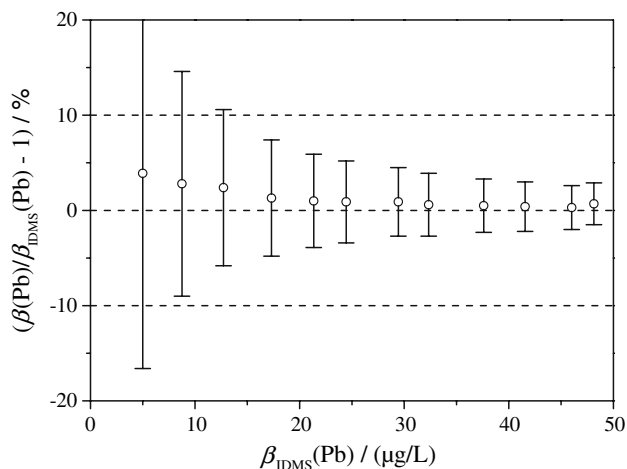


Fig. 4 Relative deviations of the reference values $\beta(\text{Pb})$ calculated as the sum of the added mass concentration $\beta_{\text{add}}(\text{Pb})$ and the content $\beta_0(\text{Pb})$ arising from the matrix obtained using the consensus values $\beta_{\text{rcm}}(\text{Pb})$ in the described standard addition-like method compared to the IDMS values $\beta_{\text{IDMS}}(\text{Pb})$. The deviations are small (<4%) and, within their uncertainties, in very good agreement with the reference values determined by the IDMS measurements

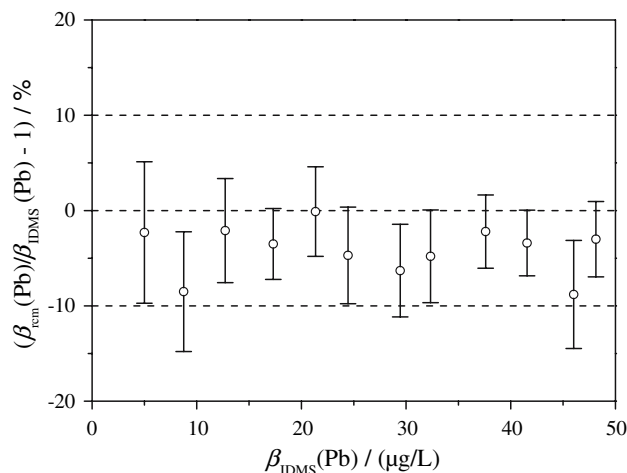


Fig. 5 Relative deviations of the consensus values $\beta_{\text{rcm}}(\text{Pb})$ compared to the IDMS values $\beta_{\text{IDMS}}(\text{Pb})$. The deviations are larger (<10%) and in several cases not in agreement, or in poor agreement, with the reference values determined by the IDMS measurements, even considering their uncertainties

(Fig. 5). While the deviations were more than twice as large, the uncertainties were smaller. A few values were in good or acceptable agreement with the IDMS measurements, but they were scattered randomly over the concentration range. Therefore, the use of consensus values as the reference values seems questionable. Furthermore, there would be no proper way to show the traceability to the SI. In Table 4, the different results of the lead mass concentrations and their associated uncertainties are compiled. Very similar results were also found for

cadmium, chromium, copper, and nickel, regardless of the preparation method (volumetric or gravimetric).

Traceability to the SI

The added mass concentration $\beta_{\text{add}}(\text{Pb})$ is traceable to the SI (Eqs. 1, 2) by linking it to the certified mass concentration of the reference solution β_{ref} and the purity of the certified reference material w_{pur} , respectively, provided

Table 4 Compilation of the different lead mass concentrations β and their associated relative expanded uncertainties U_{rel} obtained during drinking-water interlaboratory comparison 1/2006 TW A2

IDMS values		Added concentration			Added concentration + matrix content			Robust consensus means		
$\beta_{\text{IDMS}} (\mu\text{g L}^{-1})$	$U_{\text{rel}} (\%)$	$\beta_{\text{add}} (\mu\text{g L}^{-1})$	$U_{\text{rel}} (\%)$	$\Delta (\%)$	$\beta_{\text{add}} + \beta_0 (\mu\text{g L}^{-1})$	$U_{\text{rel}} (\%)$	$\Delta (\%)$	$\beta_{\text{rcm}} (\mu\text{g L}^{-1})$	$U_{\text{rel}} (\%)$	$\Delta (\%)$
5.00	0.44	4.652	0.35	-6.8	5.19	20.5	3.9	4.88	7.4	-2.3
8.75	0.39	8.455	0.34	-3.3	9.00	11.8	2.8	8.01	6.3	-8.5
12.72	0.37	12.48	0.17	-1.8	13.02	8.2	2.4	12.45	5.5	-2.1
17.31	0.36	17.00	0.16	-1.8	17.54	6.1	1.3	16.70	3.7	-3.5
21.35	0.36	21.02	0.14	-1.5	21.56	4.9	1.0	21.33	4.7	-0.1
24.46	0.36	24.13	0.13	-1.3	24.67	4.3	0.9	23.32	5.1	-4.7
29.44	0.36	29.18	0.11	-0.9	29.72	3.6	0.9	27.60	4.9	-6.3
32.34	0.36	32.00	0.11	-1.0	32.54	3.3	0.6	30.79	4.9	-4.8
37.60	0.36	37.26	0.10	-0.9	37.81	2.8	0.5	36.79	3.8	-2.2
41.56	0.36	41.20	0.10	-0.8	41.74	2.6	0.4	40.14	3.4	-3.4
46.01	0.36	45.59	0.10	-0.9	46.14	2.3	0.3	41.97	5.7	-8.8
48.14	0.35	47.93	0.10	-0.4	48.48	2.2	0.7	46.69	3.9	-3.0

Values not rounded according to their uncertainties to ensure better comparability. Relative deviations Δ from IDMS reference values

that β_{ref} and w_{pur} , respectively, are traceable themselves. Unfortunately the matrix content derived from the consensus values at first does not seem to be traceable to the SI. But the uncertainty associated with the matrix content calculated using the consensus values is large enough to cover its *true* value. Furthermore, the matrix is just a small contribution to the reference value, except for those close to the matrix content. But even in these cases, the uncertainty associated with the reference value (now dominated by the contribution of the matrix content) increases sufficiently to include the *true* value (Fig. 4). This was demonstrated experimentally by IDMS measurements for cadmium, chromium, copper, lead, and nickel in the concentration ranges usually found in German drinking-water interlaboratory comparisons. At least for these elements and concentration ranges, the reference values obtained by combining the volumetrically or gravimetrically added amount and the matrix content calculated with the described standard addition-like method using the consensus values have proven to be traceable to the SI. But there are limitations that need further research, for example elements or other analytes that are volatile or not stable and therefore tend to change their concentration in an unpredictable way after the preparation, which causes the value of the added mass concentration to be useless. To re-establish the applicability of Eqs. 1 and 2 under these circumstances, contributions have to be added taking stability, adsorption and/or volatility problems into account. Another problem is caused by matrix concentrations in the order of the reference values themselves. The resulting large uncertainties associated with the reference values may limit their use as reference values.

Conclusion

It was demonstrated that SI-traceable reference values to be used in drinking-water interlaboratory comparisons can be achieved without any additional efforts. These reference values were obtained by combining already existing data coming from the sample preparation and the consensus

values. As expected, gravimetric sample preparation yielded a slightly smaller uncertainty than volumetric, but the uncertainty associated with the reference value was virtually not affected by the contribution of the sample preparation procedure. There is only one additional effort the PT provider has to face—setting up a proper uncertainty budget describing the sample preparation. This concept shows a way to provide SI-traceable reference values without the regular participation of an NMI applying primary methods being necessary. The role of the NMI is focused on the validation of the application of the described concept. This task may include guidance and support in the uncertainty calculation, but may include just as well the participation in interlaboratory comparisons, i.e. from time to time or if the concept shall be applied to problematic analytes or analytes other than the discussed ones, and to changed matrices.

References

1. Council Directive 98/83/EC on the quality of water intended for human consumption, Official Journal of the European Communities, L 330/32 (1998)
2. Kipphardt H, Matschat R, Rienitz O, Schiel D, Gernand W, Oeter D (2006) Traceability system for elemental analysis. *Accred Qual Assur* 10:633–639
3. Verordnung über die Qualität von Wasser für den menschlichen Gebrauch (Trinkwasserverordnung–TrinkwV 2001), Bundesgesetzblatt, Teil I Nr. 24 (2001)
4. Umweltbundesamt, Empfehlung für die Durchführung von Ringversuchen zur Messung chemischer Parameter und Indikatorparameter zur externen Qualitätskontrolle von Trinkwasseruntersuchungsstellen, Bundesgesundheitsbl–Gesundheitsforsch–Gesundheitsschutz (2003) 46:1094–1095
5. Guide to the Expression of Uncertainty in Measurement (1993) ISO, Geneva
6. Sargent M, Harte R, Harrington C (eds) (2002) Guidelines for achieving high accuracy in isotope dilution mass spectrometry (IDMS). Royal Society of Chemistry
7. DIN 38402-45 (2003) Ringversuche zur externen Qualitätskontrolle von Laboratorien
8. ISO 13528 (2005) Statistical methods for use in proficiency testing by interlaboratory comparisons
9. Rienitz O, Röhker K, Schiel D, Han J, Oeter D (2006) New equation for the evaluation of standard addition experiments applied to ion chromatography. *Microchim Acta* 154:21–25