

Final Report

**EURAMET Project 924 part 3**

**“Determination of Hg<sup>\*</sup>, Cd, Ni and Pb in natural water at concentration levels required by the European Water Framework Directive”**

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\* Hg was also subject of the CCQM comparisons CCQM-K70 and CCQM-P100.3

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## 1. Summary

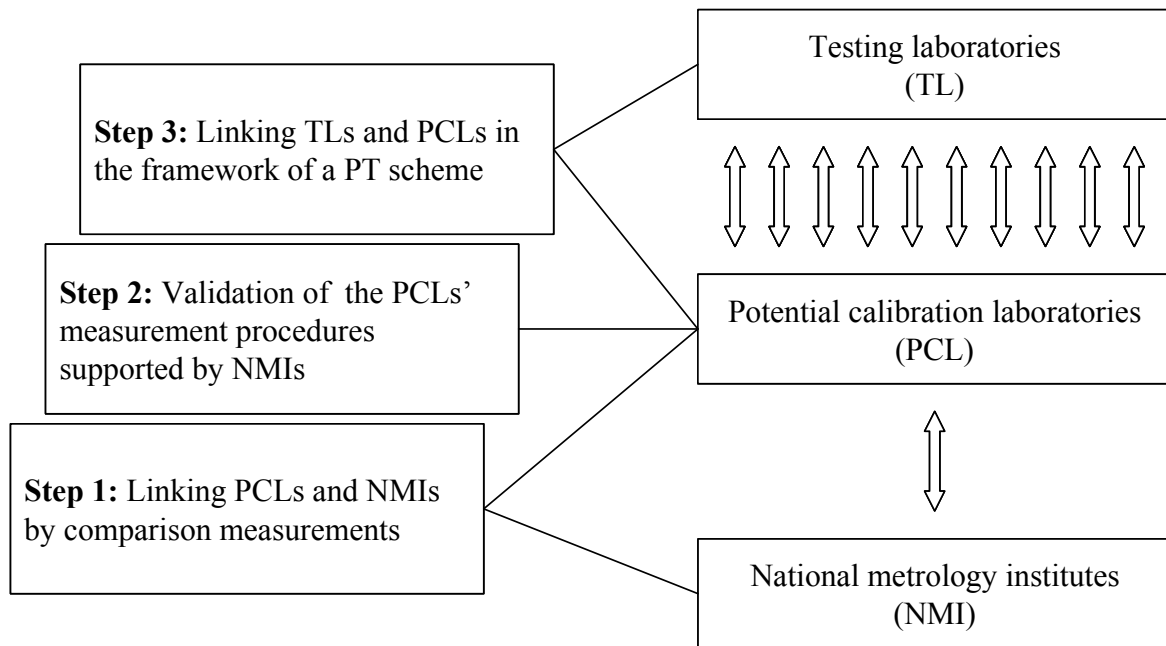
The comparison Euramet 924 part 3 addressed in particular testing laboratories which intend to perform measurements under the European Water Framework Directive (WFD) [1]. The comparison covered the measurement of the inorganic priority substances Hg, Cd, Ni and Pb in ground water at concentration levels close to the environmental quality standards (EQS) [2]. The samples were prepared gravimetrically and volumetrically, resp., and therefore, independent reference values for verification of the participant results were available. 127 laboratories from 18 countries registered to participate.

Euramet 924 part 3 completes the measurement activities of the Euramet project 924 which aimed at supporting the implementation of the European Water Framework Directive 2000/60/EC (WFD) [1]. The results of part 1 and 2 were covered in the “Final report on EUROMET-QM-S2” [7], while this report focuses on the results of part 3. Nevertheless, this report finalises the Euramet 924 project. Within the scope of this project it could be demonstrated how to provide traceability to the testing laboratories (TL) in order to enable them to achieve EU-wide comparable measurement results as required by the WFD. For that purpose, a dissemination system was tested consisting of national metrology institutes (NMI), expert laboratories and testing laboratories which were metrologically linked by comparison measurements.

## 2. Introduction

According to the WFD the EU member states have to demonstrate compliance with the environmental quality standards for their surface, ground and coastal/transitional waters by 2015. Additionally, the WFD requires that comparable measurement results have to be used for the assessments of these waters. The main objective of the Euramet project 924 is to demonstrate that the traceability to the "International System of Units" (SI) and the well-established metrological infrastructure of the “Meter Convention” form an appropriate basis for realizing the required comparability. For that purpose, a three level dissemination system has been proposed providing matrix reference materials for method validation. The system consists of national metrology institutes which provide the link to the SI, expert laboratories (here called potential calibration laboratories (PCL)) on the intermediate level which act as multipliers in the dissemination system, and on the third level routine laboratories which perform the surveillance measurements under the WFD. The link between these levels was realized in the framework of comparison measurements by sample materials featuring SI-traceable reference values for the elemental concentrations. The present comparison served to link the PCLs with the routine laboratories (figure 1, step 3). While it was hosted by a PCL, the reference values were assigned to the sample materials in cooperation with the PTB. The previous comparison Euramet.QM-S2 [7] (figure 1, step 1) which was finished in 2009 served to link PCLs to the NMIs and was organized by NMIs. In that case the reference values were assigned to the sample materials by the NMIs. Figure 1 shows the dissemination system and the actions of Euramet 924 to link their different levels.

The project has been adopted by the Inorganic Sub-Committee of the Technical Committee “Metrology in Chemistry” (TC-MC) of Euramet in 2007. Parallel to the Euramet comparison an international key comparison (CCQM-K70) and a pilot study (CCQM-P100.3) of the “Consultative Committee for Amount of Substance – Metrology in Chemistry” (CCQM) were performed. These comparisons focussed exclusively on the measurement of Hg. The same Hg samples were used for the Euramet and CCQM comparisons. For the sake of completeness, this report includes also the results of the CCQM comparisons.



*Figure 1:* Dissemination system developed within the project Euramet 924. The corresponding actions were performed in three steps. Step 1 was realized by the comparisons Euramet 924 part 1 and part 2. Step 2 served to educate the PCLs in metrological estimation of uncertainties according to GUM [6]. This was performed in the framework of a workshop at PTB. The comparison Euramet 924 part 3 intended to implement step 3.

### 3. Organization

According to the concept of the project, a PCL was intended to perform the comparison Euramet 924 part 3. Therefore the commitment of the IWW which prepared and dispatched the samples was much appreciated. The PTB provided metrological support.

IWW was invited for the comparison in July 2008. The samples were dispatched in January 2009 and the deadline for submission of the results was 27 March 2009. Unfortunately, after the dispatch of the samples a technical issue concerning the Hg samples was observed. Measurements of numerous samples showed a recovery of about 60 % along with a poor homogeneity. The participants were informed about the problems two weeks after the dispatch and were asked to stop their measurements. Several submitted results of the participants confirmed the problems observed. Probably a lot of different reasons contributed to that. Therefore, the organizers decided to repeat the Hg measurement applying the procedure that was successfully established during the first and second part of the Hg comparison in the framework of Euramet project 924. Following an EPA guideline [3], a change in the procedure was the use of BrCl for stabilization purposes instead of  $K_2Cr_2O_7$ . In October 2009, the revised Hg samples were dispatched and the deadline for the submission of the results was 16 November 2009.

In February 2009 and 2010 the organizers reported on the results at the annual meetings of the Technical Committee “Metrology in Chemistry” (TC-MC).

Each participant received a certificate together with this report.

#### 4. Measurement requirements

The target uncertainty  $U$  associated with the mass concentration  $\gamma(E)$  of the respective element  $E$  follows the Commission Directive 2009/90/EC [4], which requires “Minimum performance criteria for methods of analysis” such as an expanded uncertainty of less than 50 % of the EQS accompanied by a limit of quantification (LOQ) of 30 % of the EQS:

$$U_{\text{target}}(\gamma(E)) \leq 0.5 \cdot \text{EQS} \quad (1)$$

$$\gamma_{\text{LOQ}}(E) \leq 0.3 \cdot \text{EQS} \quad (2)$$

These minimum performance criteria along with the underlying EQS values are compiled in table 1 for all four elements  $E$  addressed in this comparison.

*Table 1:* Minimum performance criteria limit of detection  $\gamma_{\text{LOQ}}(E)$  and maximum uncertainty  $U_{\text{max}}(\gamma(E))$  for methods of analysis under the WFD [2, 4]. The Cd EQS depends upon the hardness of the water as specified in five class categories. The Euramet 924 part 3 samples fall into category “Class 3” ( $50 \text{ mg/L} \leq \gamma(\text{CaCO}_3) < 100 \text{ mg/L}$ ) according to [2] (see appendix B).

<b>E</b>	<b>EQS</b>	$\gamma_{\text{LOQ}}(E)$	$U_{\text{max}}(\gamma(E))$
	<b>µg/L</b>	<b>µg/L</b>	<b>µg/L</b>
<b>Hg</b>	0.050	0.015	0.025
<b>Cd</b>	0.090	0.027	0.045
<b>Pb</b>	7.2	2.2	3.6
<b>Ni</b>	20	6.0	10

#### 5. Samples

The approximate composition of the natural ground water used for the preparation of the samples is given in the technical protocol (appendix B and C, respectively). It was chosen due to its low concentration of heavy metals which was important to enable a gravimetric adjustment of the elemental concentrations and the provision of reference values.

Every participant was provided with two bottles containing the water samples: a glass bottle (250 ml water acidified with hydrochloric acid and adjusted with respect to its Hg content) and a PE bottle (100 ml water acidified with nitric acid and adjusted with respect to its Cd, Ni and Pb content). The participants were asked to stabilize their Hg samples immediately after receipt using a BrCl solution prepared according to [3] and to correct for the dilution caused by the addition of the stabilizer gravimetrically.

Primary elemental solutions provided by the PTB were used to adjust the desired elemental concentrations in the samples on a gravimetric basis. The target concentrations were close to the EQS values:  $\gamma(\text{Hg}) \approx (30 \dots 70) \text{ ng/L}$ ,  $\gamma(\text{Cd}) \approx (50 \dots 100) \text{ ng/L}$ ,  $\gamma(\text{Ni}) \approx (10 \dots 30) \text{ µg/L}$ ,  $\gamma(\text{Pb}) \approx (4 \dots 20) \text{ µg/L}$ . The concentrations of Hg and Cd samples were slightly higher than the EQS values.

To calculate and provide reference values, an accurate determination of the concentration of the analytes already present in the original water sample prior to the gravimetric addition (matrix content) was crucial. This was a complex task especially concerning Hg due to its low concentration. Therefore, the determination of the matrix contents was performed by the organizers. In order to check for consistency, the organizers asked the participants to measure three additional samples containing Hg in higher concentrations. These additional samples were shipped to each participant together with the samples of the comparison. The results for the additional samples were used to calculate an independent value for the Hg concentration in the original water sample prior to the Hg addition (section 9).

The stability of the elemental concentration of the samples was guaranteed for the duration of two months. The homogeneity of the samples was tested by comparing several aliquots. Stability and homogeneity surveys were performed by PTB using IDMS covering a period from the dispatch of the samples until well after the reporting deadline (see table 2). Neither stability nor homogeneity issues were visible within a relative standard uncertainty depending on the particular element of  $u_{\text{rel}}(k_{\text{exp}}) = 0.11 \dots 1.6 \%$  addressing both effects (figure 2 shows mercury as an example). The uncertainties associated with this “experimental factor”  $k_{\text{exp}}$  addressing the limits of determining homogeneity or stability issues concerning Hg, Cd, Ni and Pb are summarized in table 2.

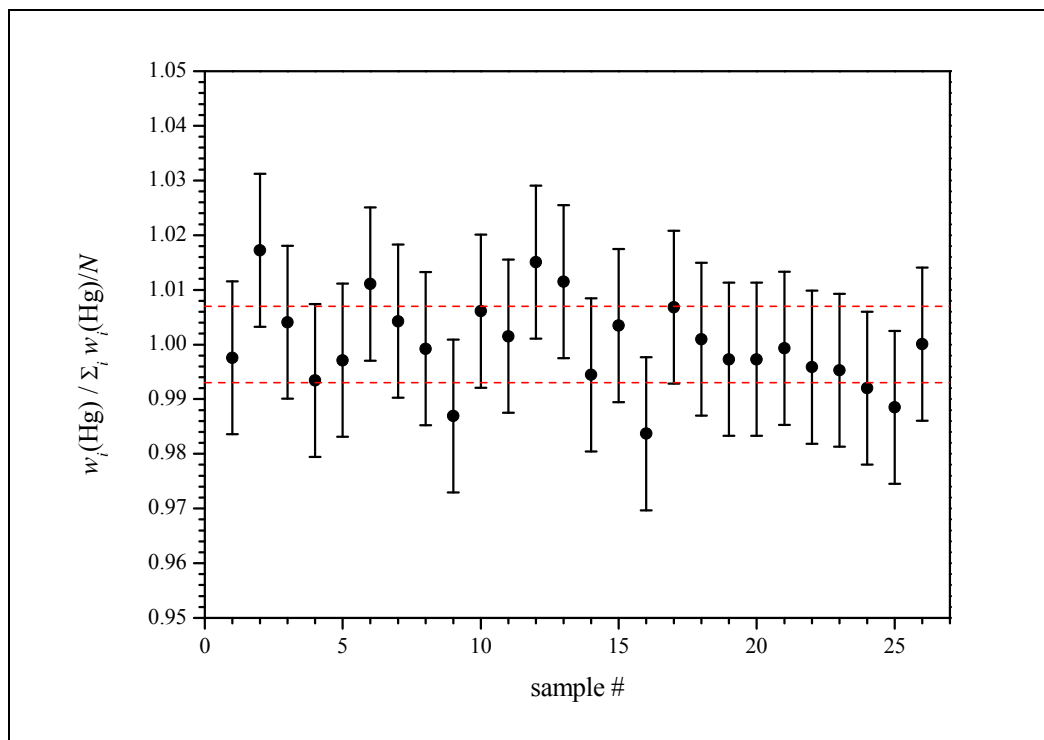


Figure 2: Normalized results of the stability and homogeneity of the mercury sample Hg-I ( $w(\text{Hg}) \approx 70 \text{ pg/g}$ ) over the duration of the comparison. Dashed red lines indicate the twofold standard uncertainty of the normalized Hg mass fractions.

*Table 2:* Relative standard uncertainties associated with the factor  $k_{\text{exp}} = 1$ , used to account for any homogeneity and stability issues (for more details refer to section 9.1).

Element	$u(k_{\text{exp}}) / k_{\text{exp}} \cdot 10^{-2}$
Hg	0.35
Cd	0.85
Ni	1.6
Pb	0.11

## 6. Participants

In total, 116 laboratories from 18 countries (114 laboratories from 17 European countries and another 2 from Israel) registered to participate in the EURAMET Project 924 (table 3).

Among them were 13 expert laboratories from 6 countries which acted as PCLs. Their predominant task was to inform testing laboratories of their region and ask them to participate.

Additionally 4 NMIs attended the comparison. These 4 NMIs and another 7 NMIs measured the Hg samples in the parallel CCQM comparisons, CCQM-K70 and CCQM-P100.3.

All participants were asked to fill in a questionnaire (appendix A) and to send it back together with their registration. 70 out of the registered 116 were so kind to answer the questions (see table 4).

*Table 3:* Number of registered Euramet 924 part 3 participants from different countries in alphabetical order without the 11 NMIs.

Country	Number of participants
Austria	11
Bosnia and Herzegovina	1
Bulgaria	7
Croatia	4
Czech Republic	1
Finland	1
France	18
Germany	33
Hungary	12
Israel	2
Italy	9
Norway	1
Portugal	4
Romania	1
Slovakia	1
Slovenia	1
Spain	5
Sweden	4

Table 4: Summarized answers, asked for in the questionnaire, provided by 70 laboratories.

Question	Answer	
	Yes	No
Do you measure samples from chemical monitoring activities related to the Water Framework Directive?	69 %	31 %
Do you measure the elements regarded here routinely?	99 %	1 %
Is your laboratory accredited according to ISO 17025 for the measurement of the elements considered here?	80 %	20 %
Do you use traceable calibration material (provided with an uncertainty statement)?	90 %	10 %
Do you use matrix-matched calibration material?	46 %	54 %
Do you use internal standards?	71 %	29 %
Do you use certified matrix reference materials for verification?	81 %	19 %
Do you use standard addition for verification?	46 %	54 %
	<b>Average</b>	
How many measurements of these four elements are you performing the year? (Please enter the number)	2000	
In how many PT schemes for these elements do you participate the year? (Please enter the number)	3	
How do you estimate measurement uncertainties? According to...		
GUM	62 %	
Nordtest	29 %	
ISO 21748	9 %	



## **7. Instructions to the participants**

Together with the samples, a technical protocol was distributed to all participants providing information about the samples, sample storage as well as the measurement method and instrumentation. A form for reporting additionally requested information of the participants was added and appended to this report in appendix A. To report their results the participants were asked to use the dedicated Excel file distributed via E-mail. The technical protocol for the rerun of the Hg measurements can be found in appendix C.

## **8. Methods and instrumentation**

Participants were free to use a method of their choice.

All participants measured the samples without digestion. For Hg almost all participants used the cold vapour technique (CV) in order to separate the Hg from the matrix and to achieve sufficient sensitivity. Among the testing laboratories inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) were most commonly applied for the measurement of Ni, Cd and Pb. For Hg almost half of the participants used atomic fluorescence spectrometry (AFS).

Eight of the participants of the CCQM comparisons used isotope dilution mass spectrometry (IDMS) in combination with a cold vapour technique. One NMI additionally applied CV-AAS. One NMI used CV-AAS exclusively, while another applied AFS. ICP-MS in combination with standard addition was used by one NMI.

No significant correlation between the method(s) used and the result(s) or a possible bias of a particular method was observed.

## 9. Reference values

### 9.1 Cadmium, nickel and lead

The Cd, Ni and Pb mass concentration reference values  $\gamma_{RV}(E)$  were calculated as the sum of the added element mass concentration  $\gamma_{add}(E)$  plus the element mass concentration  $\gamma_0(E)$  already present in the original water sample prior to the addition of the according amounts of the primary solutions (in the following called *matrix content*):

$$\gamma_{RV}(E) = \gamma_{add}(E) + \gamma_0(E) \quad (3)$$

The added element mass concentration  $\gamma_{add}(E)$  was calculated according to an equation published in [5], which was modified slightly in order to account for minor changes in the preparation described in [5]. The equation reflects the volumetric preparation of the samples, even incorporating temperature effects and residual water in the volumetric flasks. The use of gravimetrically prepared primary reference solutions of the elements E, which were applied to adjust the added concentrations  $\gamma_{add}(E)$ , ensured the traceability. The element concentration  $\gamma_0(E)$  was determined by the PTB using IDMS and one-point-calibration. Equation (4), which defines  $\gamma_{RV}(E)$ , served also as the model equation used to calculate the uncertainties associated with the reference mass concentrations (meaning of the symbols used see table 5). No significant homogeneity or stability issues were observed within the reproducibility of the IDMS method applied. The factor  $k_{exp}$  featuring a value of one accounts for this limitation with its associated uncertainty equal to the reproducibility of the IDMS method (see table 2).

$$\gamma_{RV}(E) = k_{exp} \cdot \left[ \frac{(V_{pip} + \delta V) \cdot w_z \cdot \rho_z}{k_{res} \cdot (4 \cdot V_{10} + V_5) + 5 \cdot \delta V_t} + \gamma_0(E) \right] \quad (4)$$

Table 5: Meaning of symbols used in equation (4). For more details refer to [5].

Symbol	Unit	Quantity
$\gamma_{RV}(E)$	$\mu\text{g/L}$	Mass concentration (reference value) of element E
$w_z$	$\mu\text{g/g}$	Mass fraction of element E in the primary reference solution z
$\rho_z$	$\text{g/L}$	Mass density of the primary reference solution of element E
$V_{pip}$	$\text{mL}$	Nominal volume delivered by the pipette used to dispense z
$\delta V$	$\text{mL}$	Bias of the above pipette
$V_{10}$	$\text{mL}$	Nominal volume of the 10 L volumetric flask used to dispense the original water sample (matrix)
$V_5$	$\text{mL}$	Nominal volume of the 5 L volumetric flask used to dispense the original water sample (matrix)
$k_{res}$	1	Correction for residual water in the volumetric flasks after imperfect draining
$k_{exp}$	1	Experimental factor to introduce the uncertainty contribution due to homogeneity and stability of the samples over the duration of the comparison

$\delta V_t$	mL	Bias of the flask volume due to the temperature of the original water (matrix)
$\gamma_0(E)$	$\mu\text{g/L}$	Mass concentration of the element E already present in the original water (matrix) prior the addition of the appropriate amount of primary standard solution z

## 9.2 Mercury

The Hg mass concentration reference values  $\gamma_{RV}(\text{Hg})$  were calculated as the sum of the added mass concentration  $\gamma_{add}(\text{Hg})$  plus the matrix concentration  $\gamma_0(\text{Hg})$  similar to equation (3):

$$\gamma_{RV}(\text{Hg}) = \gamma_{add}(\text{Hg}) + \gamma_0(\text{Hg}) \quad (5)$$

The added Hg mass concentration  $\gamma_{add}(\text{Hg})$  was calculated from the preparation of the samples. A 20 L-borosilicate bottle was thoroughly cleaned, checked for Hg and dried. After weighing ( $m_{1r}$ ), an approximate volume of 12 L matrix water was added. Again, after weighing ( $m_{2r}$ ), approximately 320 g hydrochloric acid ( $w(\text{HCl}) = 0.30 \text{ g/g}$ ) were added ( $m_{3r}$ ), followed by 1 kg of the primary reference solution ( $w_z = w(\text{Hg}) \approx 1.5 \text{ ng/g}$ ). After weighing ( $m_{4r}$ ), another 8 L matrix water were added ( $m_{5r}$ ) to adjust an added Hg mass concentration of  $\gamma_{add}(\text{Hg}) = 70 \text{ ng/L}$ . Since all weighing steps had to be corrected for air buoyancy using correction factors ( $K_{ij}$ ) taking into account the air density (air temperature, pressure and humidity) as well as the density of the sample ( $j$ ) at any particular step ( $i$ ) of the preparation procedure, the equation below was used to calculate the Hg mass concentration reference values  $\gamma_{RV}(\text{Hg})$ :

$$\gamma_{RV}(\text{Hg}) = k_{\text{exp}} \left[ \rho_x \frac{w_z \left[ K_{4\text{HCl}} \left( m_{4r} - \frac{K_{1\text{BSG}} \cdot m_{1r}}{K_{4\text{BSG}}} \right) - K_{3\text{HCl}} \left( m_{3r} - \frac{K_{1\text{BSG}} \cdot m_{1r}}{K_{3\text{BSG}}} \right) \right]}{K_{5\text{HCl}} \left( m_{5r} - \frac{K_{1\text{BSG}} \cdot m_{1r}}{K_{5\text{BSG}}} \right)} + \gamma_0(\text{Hg}) \right] \quad (6)$$

The mercury concentration  $\gamma_0(\text{Hg})$  in the matrix prior to the addition of mercury was determined by the PTB using IDMS combined with a standard addition technique. Since the CCQM participants were provided with three additional samples featuring gravimetrically added Hg mass concentrations ranging from approximately  $\gamma_{add,II}(\text{Hg}) = 140 \text{ ng/L}$  to  $\gamma_{add,IV}(\text{Hg}) = 280 \text{ ng/L}$ , it was possible to determine the matrix concentration  $\gamma_0(\text{Hg})$  from the participants' results in a standard addition-like evaluation [5] (see figure 3). These results were used to verify the PTB's standard addition-IDMS result of  $\gamma_0(\text{Hg}) = (2.4 \pm 1.2) \text{ ng/L}$ . Equation (6) served also as the model equation used to calculate the uncertainties associated with the Hg reference mass concentration (meaning of the symbols used see table 6). As with Cd, Ni and Pb, no significant homogeneity or stability issues were determined within the reproducibility of the IDMS method applied. The factor  $k_{\text{exp}}$  featuring a value of one accounts for this limitation with its associated uncertainty equal to the reproducibility of the IDMS method (see table 2 and figure 2).

Table 6: Meaning of symbols used in equation (6).

Symbol	Unit	Quantity
$\gamma_{rv}(\text{Hg})$	ng/L	Mass concentration (reference value) of mercury
$w_z$	ng/g	Mass fraction of mercury in the primary reference solution z
$\rho_x$	g/L	Mass density of the final sample shipped to the participants
$m_{1r}$	kg	Apparent mass of the empty 20 L glass container
$m_{3r}$	kg	Apparent mass of the empty 20 L glass container plus 12 L matrix water plus 320 g HCl (30 %)
$m_{4r}$	kg	Apparent mass of the empty 20 L glass container plus 12 L matrix water plus 320 g HCl (30 %) plus 1 kg primary reference solution ( $w(\text{Hg}) = 1.5 \text{ ng/g}$ )
$m_{5r}$	kg	Apparent mass of the empty 20 L glass container plus final sample
$K_{1BSG}$	kg/kg	Air buoyancy correction factor of borosilicate glass under the conditions when weighing the empty bottle ( $m_{1r}$ )
$K_{3BSG}$	kg/kg	see $K_{1BSG}$ , but when weighing $m_{3r}$
$K_{4BSG}$	kg/kg	see $K_{1BSG}$ , but when weighing $m_{4r}$
$K_{5BSG}$	kg/kg	see $K_{1BSG}$ , but when weighing $m_{5r}$
$K_{3HCl}$	kg/kg	Air buoyancy correction factor of approximately 2.7 % HCl under the conditions when weighing $m_{3r}$
$K_{4HCl}$	kg/kg	Air buoyancy correction factor of approximately 2.7 % HCl under the conditions when weighing $m_{4r}$
$K_{5HCl}$	kg/kg	Air buoyancy correction factor of approximately 1.5 % HCl under the conditions when weighing $m_{5r}$
$k_{exp}$	1	Experimental factor to introduce the uncertainty contribution due to homogeneity and stability of the samples over the duration of the comparison
$\gamma_0(\text{Hg})$	ng/L	Mass concentration of mercury already present in the original water (matrix) prior the addition of the appropriate amount of primary standard solution z

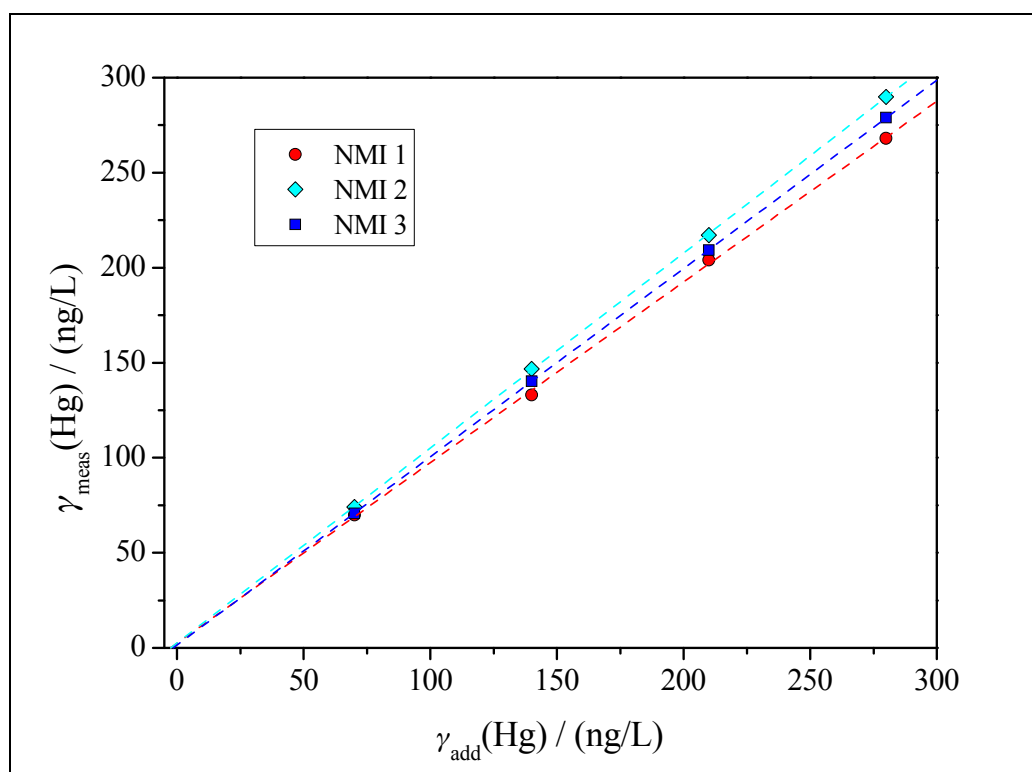


Figure 3: Matrix content  $\gamma_0(\text{Hg})$  determined from a standard addition-like evaluation according to [5] using the CCQM participants' results. To illustrate the principle the results of three national metrology institutes (NMI) were chosen.

### 9.3 Mass concentration reference values

The mass concentration reference values  $\gamma_{\text{RV}}(\text{E})$  as well as their associated uncertainties according to GUM [6] were calculated using equation (4) and (6), respectively. Table 7 shows a compilation of these reference values along with the matrix contents  $\gamma_0(\text{E})$  and their associated uncertainties.

Table 7: Mass concentration reference values  $\gamma_{\text{RV}}(\text{E})$  and matrix contents  $\gamma_0(\text{E})$  of the particular element E. The uncertainties are either standard uncertainties  $u$  valid for a coverage factor of  $k = 1$  or expanded uncertainties  $U$  with a coverage factor of  $k = 2$ .

E	Level	$\gamma_0(\text{E})$	$u(\gamma_0(\text{E}))$	$\gamma_{\text{RV}}(\text{E})$	$U(\gamma_{\text{RV}}(\text{E}))$
		$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$	$\mu\text{g/L}$
Cd	not applicable	0.0189	0.0010	0.1266	0.0030
Ni		1.43	0.072	27.15	0.94
Pb		0.086	0.004	12.313	0.069
Hg	I	0.0024	0.0012	0.0724	0.0025
Hg	II	0.0024	0.0012	0.1424	0.0028
Hg	III	0.0024	0.0012	0.2124	0.0032
Hg	IV	0.0024	0.0012	0.2824	0.0037

## 10. Results

The mass concentration results  $\gamma_{\text{meas}}(\text{E})$  reported by the participants were divided into several groups: national metrology institutes (NMI), potential calibration laboratories (PCL) and testing laboratories (TL). The arithmetic mean  $\bar{x}$  of every group, its relative standard deviation  $s/\bar{x}$ , its standard uncertainty  $u(\bar{x})$  and expanded uncertainty  $U(\bar{x})$  were calculated. Additionally, these parameters were also calculated for the complete group of participants and the Euramet group (the latter without the NMIs). Results for example stated as “< 200 ng/L” were excluded from the evaluation. To be able to compare the individual results  $\gamma_i$  to the mass concentration reference values  $\gamma_{\text{RV}}(\text{E})$  the degrees of equivalence  $d_i$  were determined also. The degree of equivalence of every result is given in the particular diagrams along with the result itself. The equations used follow [8] and [9]:

$$\bar{x} = \frac{1}{N} \cdot \sum_{i=1}^N \gamma_i \quad (7)$$

$$s^2 = \frac{1}{N-1} \cdot \sum_{i=1}^N (\gamma_i - \bar{x})^2 \quad (8)$$

$$u^2(\bar{x}) = \frac{1}{N} \cdot s^2 \quad (9)$$

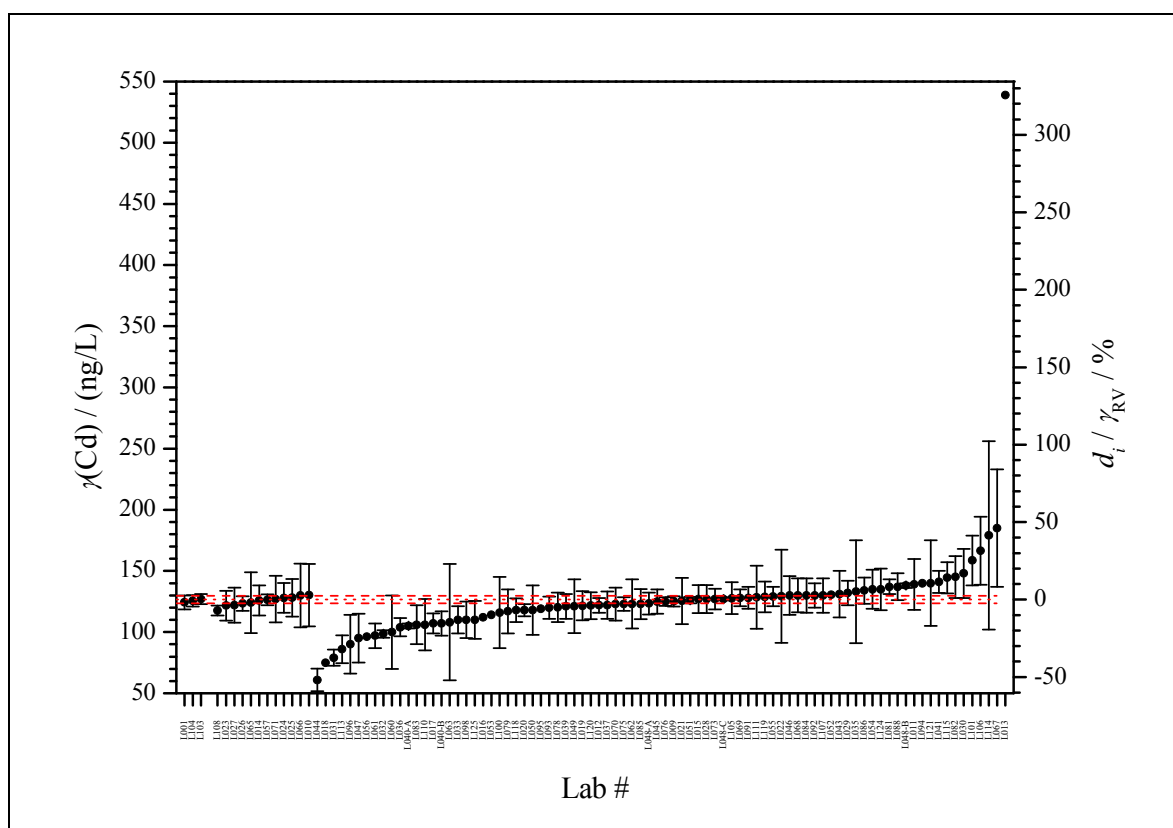
$$U(\bar{x}) = k \cdot u(\bar{x}) \quad \text{with} \quad k = 2 \quad (10)$$

$$d_i = \gamma_i - \gamma_{\text{RV}} \quad (11)$$

### 10.1 Cadmium

*Table 8:* Comparison of the mass concentration reference value  $\gamma_{RV}(\text{Cd})$  to selected arithmetic means  $\bar{x}$ .  $N$  denotes the number of results within the particular group, while  $\Delta_{\max}\gamma$  denotes the difference between the smallest reported mass concentration  $\gamma_{\min}$  and the largest  $\gamma_{\max}$ . The relative deviation  $\Delta_{\text{ref}}$  of every mean  $\bar{x}$  from the reference value  $\gamma_{RV}(\text{Cd})$  is given in the last column. Refer to section 10 and equations (7) – (10) for more details on the symbols and group names.

<b>Cadmium</b>						
	$\bar{x}$	$N$	$s/\bar{x}$	$U$	$\Delta_{\max}\gamma$	$\Delta_{\text{ref}}$
	ng/L	1	%	ng/L	ng/L	%
reference value	126.6			3.0		
all participants	127.3	99	36	9.2	478	+0.53
Euramet	127.3	96	36	9.4	478	+0.58
NMI	125.6	3	1.1	1.6	2.7	-0.79
PCL	125.3	12	15	10.5	13	-1.0
TL	127.6	84	39	11.0	478	+0.80



*Figure 4:* Reported Cd mass concentrations  $\gamma(\text{Cd})$  of all participants grouped (from left to right) into national metrology institutes (NMI), potential calibration laboratories (PCL) and testing laboratories (TL). Error bars indicate reported expanded uncertainties. Laboratories L013, L016, L018, L052, L053, L056, L094 and L095 did not report an uncertainty. Abscissa

denotes the individual laboratory code number. Right y-axis shows the individual degree of equivalence  $d_i$  related to the reference value  $\gamma_{RV}(\text{Cd})$ . The reference value and its associated expanded uncertainty  $U(\gamma_{RV}(\text{Cd}))$  is represented by the dotted red line and the dashed red lines, respectively.

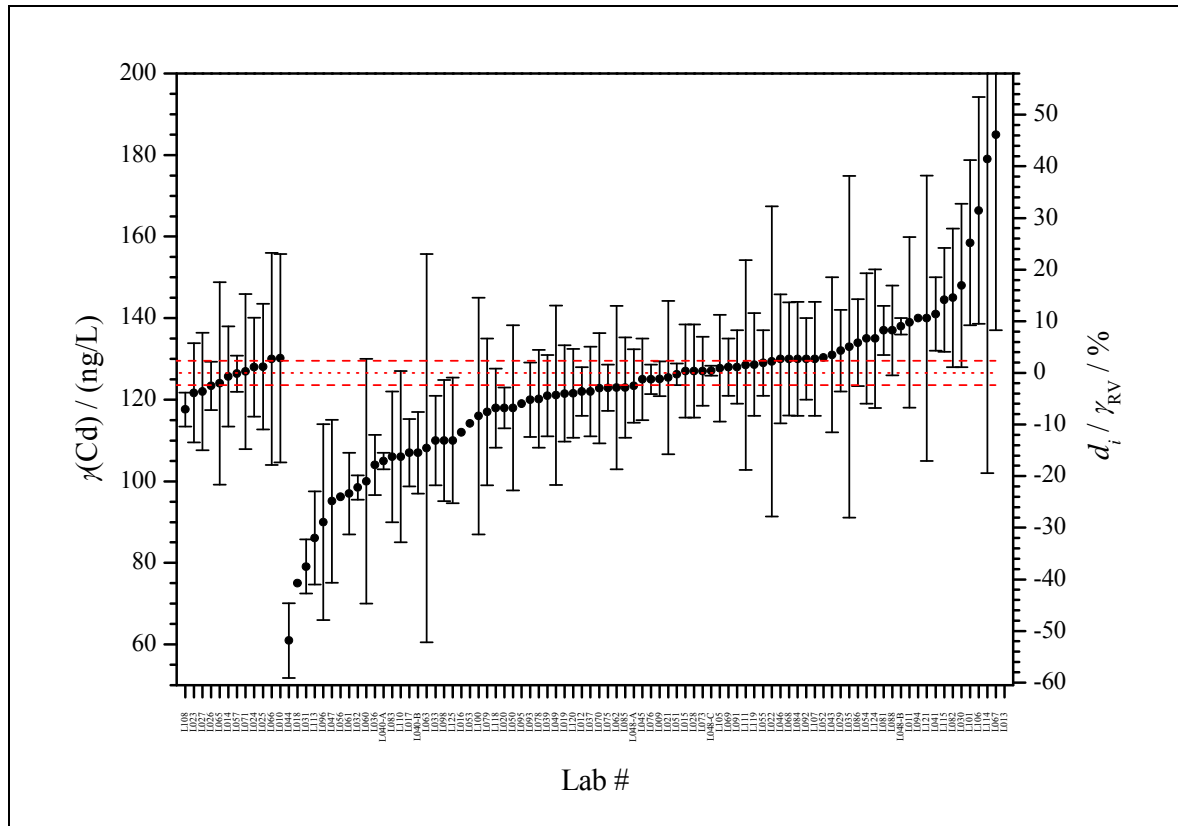


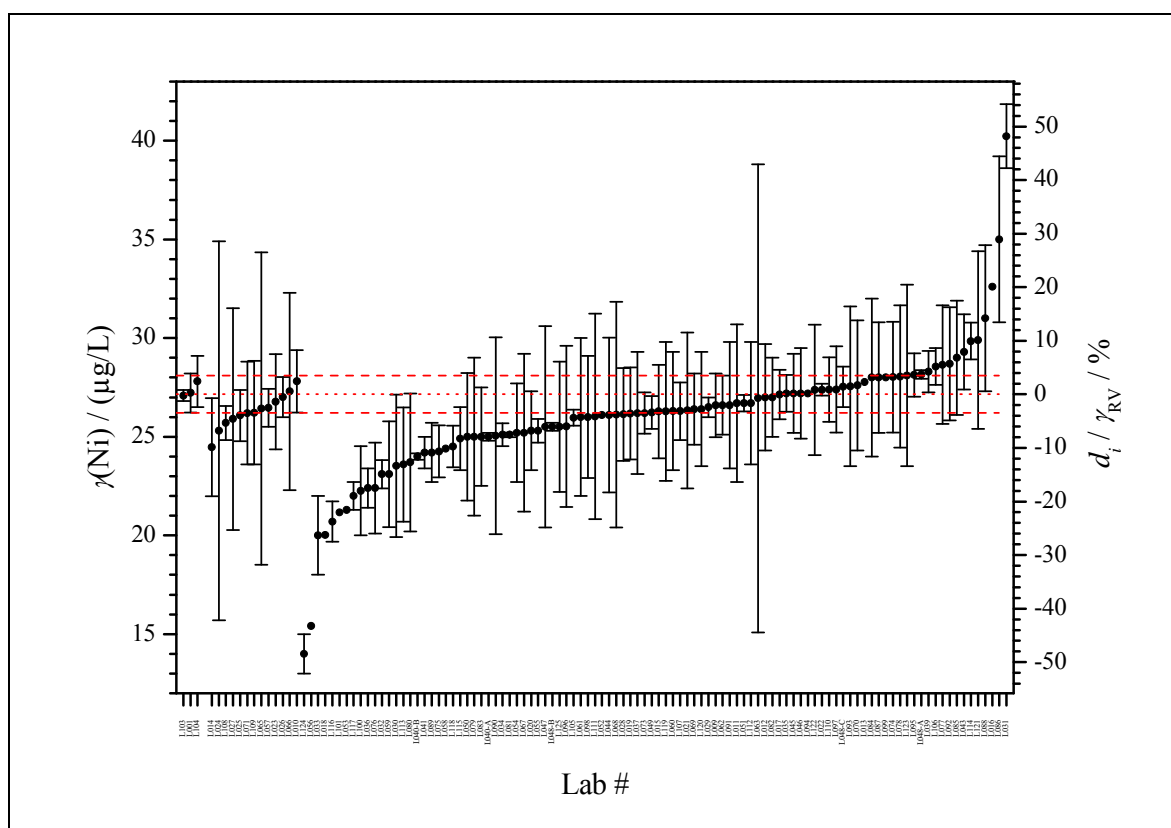
Figure 5: Reported Cd mass concentrations  $\gamma(\text{Cd})$  of PCLs and TLs. Enlarged y-axis. Result of laboratory L013 is missing because of the limited range of the y-axis. For more details refer to caption of figure 4.



## 10.2 Nickel

*Table 9:* Comparison of the mass concentration reference value  $\gamma_{RV}(\text{Ni})$  to selected arithmetic means  $\bar{x}$ .  $N$  denotes the number of results within the particular group, while  $\Delta_{\max}\gamma$  denotes the difference between the smallest reported mass concentration  $\gamma_{\min}$  and the largest  $\gamma_{\max}$ . The relative deviation  $\Delta_{\text{ref}}$  of every mean  $\bar{x}$  from the reference value  $\gamma_{RV}(\text{Ni})$  is given in the last column. Refer to section 10 and equations (7) – (10) for more details on the symbols and group names.

Nickel						
	$\bar{x}$	$N$	$s/\bar{x}$	$U$	$\Delta_{\max}\gamma$	$\Delta_{\text{ref}}$
	$\mu\text{g/L}$	1	%	$\mu\text{g/L}$	$\mu\text{g/L}$	%
reference value	27.15			0.94		
all participants	26.10	116	11.5	0.56	26	-3.9
Euramet	26.07	113	11.6	0.57	26	-4.0
NMI	27.37	3	1.4	0.44	0.7	+0.8
PCL	26.28	13	3.3	0.48	3.3	-3.2
TL	26.04	100	12.3	0.64	26	-4.1



*Figure 6:* Reported Ni mass concentrations  $\gamma(\text{Ni})$  of all participants grouped (from left to right) into national metrology institutes (NMI), potential calibration laboratories (PCL) and testing laboratories (TL). Error bars indicate reported expanded uncertainties. Laboratories L013, L016, L018, L052, L053, L056, L058, L094, L099 and L101 did not report an uncer-

tainty. Abscissa denotes the individual laboratory code number. Right y-axis shows the individual degree of equivalence  $d_i$  related to the reference value  $\gamma_{RV}(\text{Ni})$ . The reference value and its associated expanded uncertainty  $U(\gamma_{RV}(\text{Ni}))$  is represented by the dotted red line and the dashed red lines, respectively.

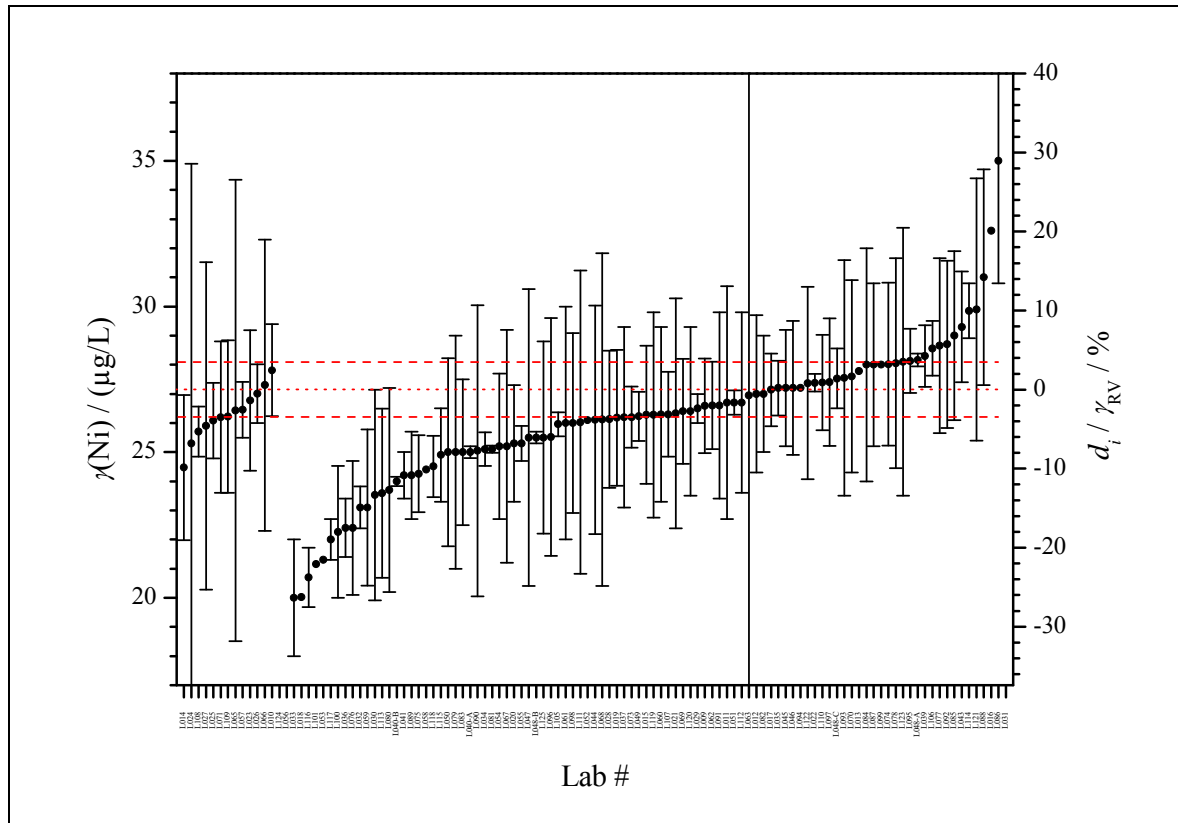
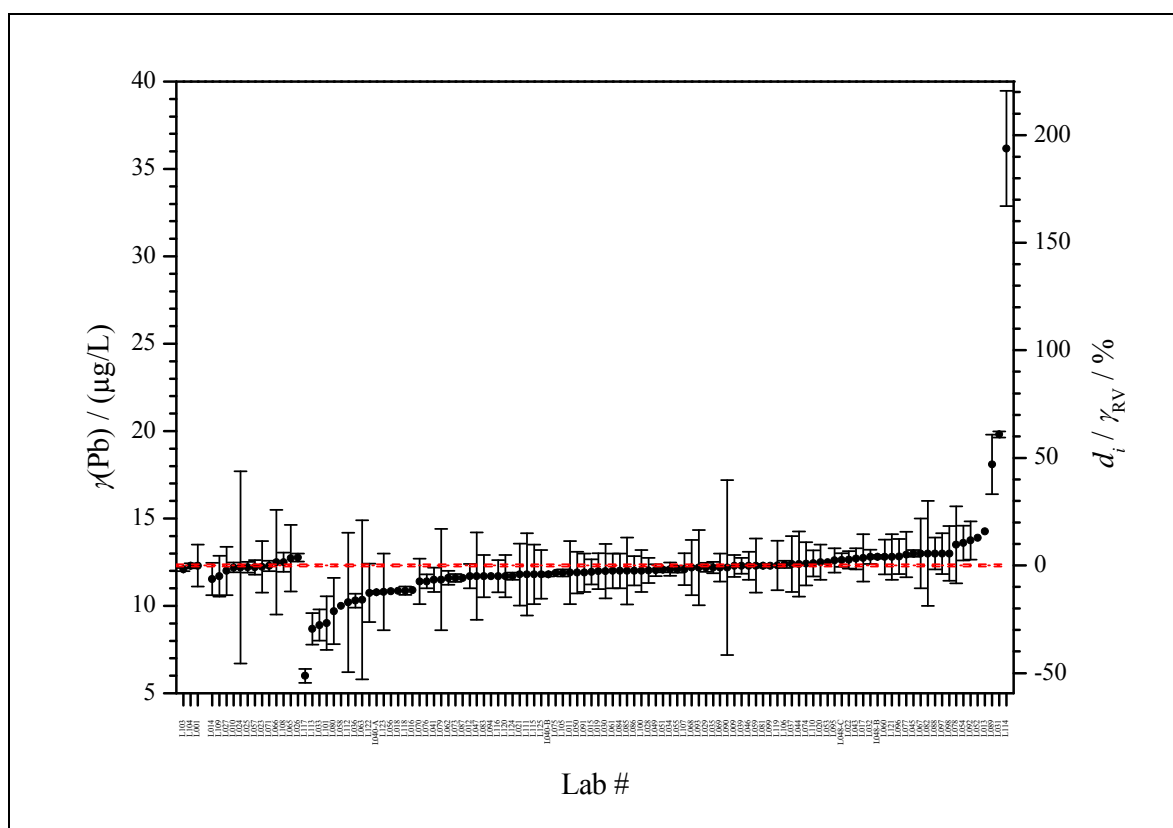


Figure 7: Reported Ni mass concentrations  $\gamma(\text{Ni})$  of PCLs and TLs. Enlarged y-axis. Results of laboratories L031, L056 and L124 are missing because of the limited range of the y-axis. For more details refer to caption of figure 6.

### 10.3 Lead

*Table 10:* Comparison of the mass concentration reference value  $\gamma_{RV}(\text{Pb})$  to selected arithmetic means  $\bar{x}$ .  $N$  denotes the number of results within the particular group, while  $\Delta_{\max}\gamma$  denotes the difference between the smallest reported mass concentration  $\gamma_{\min}$  and the largest  $\gamma_{\max}$ . The relative deviation  $\Delta_{\text{ref}}$  of every mean  $\bar{x}$  from the reference value  $\gamma_{RV}(\text{Pb})$  is given in the last column. Refer to section 10 and equations (7) – (10) for more details on the symbols and group names.

Lead						
	$\bar{x}$	$N$	$s/\bar{x}$	$U$	$\Delta_{\max}\gamma$	$\Delta_{\text{ref}}$
	$\mu\text{g/L}$	1	%	$\mu\text{g/L}$	$\mu\text{g/L}$	%
reference value	12.313			0.069		
all participants	12.28	115	21.6	0.49	30	-0.30
Euramet	12.28	112	21.9	0.51	30	-0.29
NMI	12.23	3	1.0	0.14	0.2	-0.71
PCL	12.24	13	2.9	0.20	1.2	-0.62
TL	12.28	99	23.3	0.57	30	-0.25



*Figure 8:* Reported Pb mass concentrations  $\gamma(\text{Pb})$  of all participants grouped (from left to right) into national metrology institutes (NMI), potential calibration laboratories (PCL) and test laboratories (TL). Error bars indicate reported expanded uncertainties. Laboratories L013, L016, L018, L052, L053, L056, L058, L087, L094 and L099 did not report an uncertainty.

Abscissa denotes the individual laboratory code number. Right y-axis shows the individual degree of equivalence  $d_i$  related to the reference value  $\gamma_{RV}(\text{Pb})$ . The reference value and its associated expanded uncertainty  $U(\gamma_{RV}(\text{Pb}))$  is represented by the dotted red line and the dashed red lines, respectively.

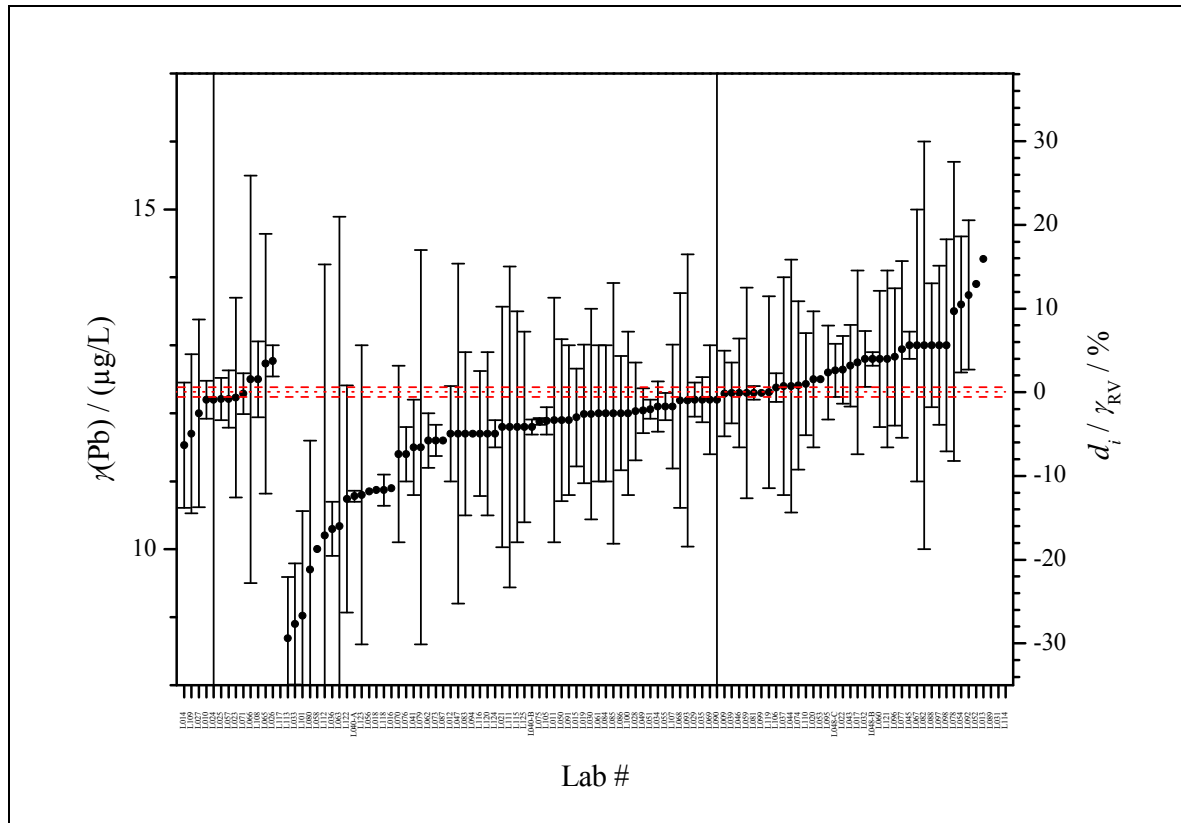
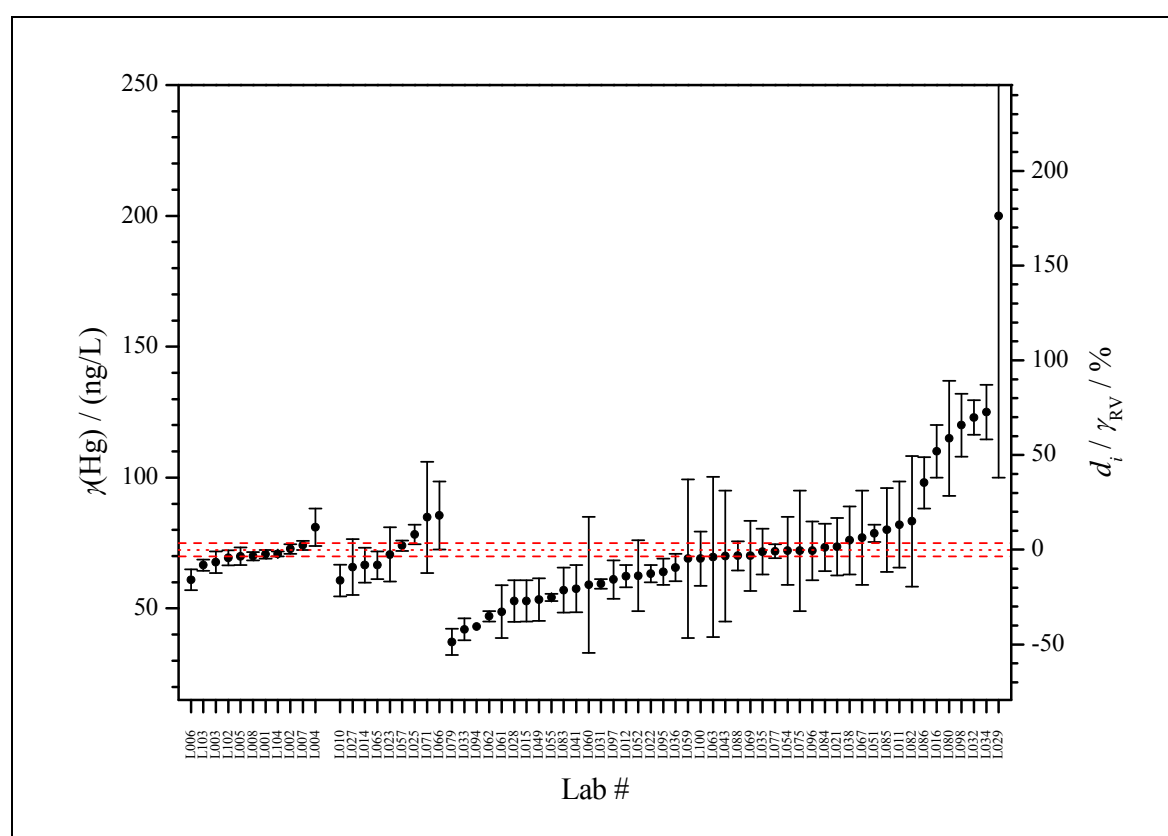


Figure 9: Reported Pb mass concentrations  $\gamma(\text{Pb})$  of PCLs and TLs. Enlarged y-axis. Results of laboratories L031, L089, L114 and L117 are missing because of the limited range of the y-axis. For more details refer to caption of figure 8.

### 10.4 Mercury

*Table 11:* Comparison of the mass concentration reference value  $\gamma_{RV}(\text{Hg})$  to selected arithmetic means  $\bar{x}$ .  $N$  denotes the number of results within the particular group, while  $\Delta_{\max}\gamma$  denotes the difference between the smallest reported mass concentration  $\gamma_{\min}$  and the largest  $\gamma_{\max}$ . The relative deviation  $\Delta_{\text{ref}}$  of every mean  $\bar{x}$  from the reference value  $\gamma_{RV}(\text{Hg})$  is given in the last column. Refer to section 10 and equations (7) – (10) for more details on the symbols and group names.

Mercury						
	$\bar{x}$	$N$	$s/\bar{x}$	$U$	$\Delta_{\max}\gamma$	$\Delta_{\text{ref}}$
	ng/L	1	%	ng/L	ng/L	%
reference value	72.4			2.5		
all participants	73.2	65	32	5.9	163	+1.1
Euramet	73.8	54	35	7.1	163	+1.9
NMI	70.3	11	7	3.0	20	-2.9
PCL	72.5	9	12	5.8	25	+0.10
TL	74.1	45	38	8.4	163	+2.3



*Figure 10:* Reported Hg mass concentrations  $\gamma(\text{Hg})$  of all participants grouped (from left to right) into national metrology institutes (NMI), potential calibration laboratories (PCL) and testing laboratories (TL). Error bars indicate reported expanded uncertainties. Laboratory

L094 did not report an uncertainty. Abscissa denotes the individual laboratory code number. Right y-axis shows the individual degree of equivalence  $d_i$  related to the reference value  $\gamma_{RV}(\text{Hg})$ . The reference value and its associated expanded uncertainty  $U(\gamma_{RV}(\text{Hg}))$  is represented by the dotted red line and the dashed red lines, respectively.

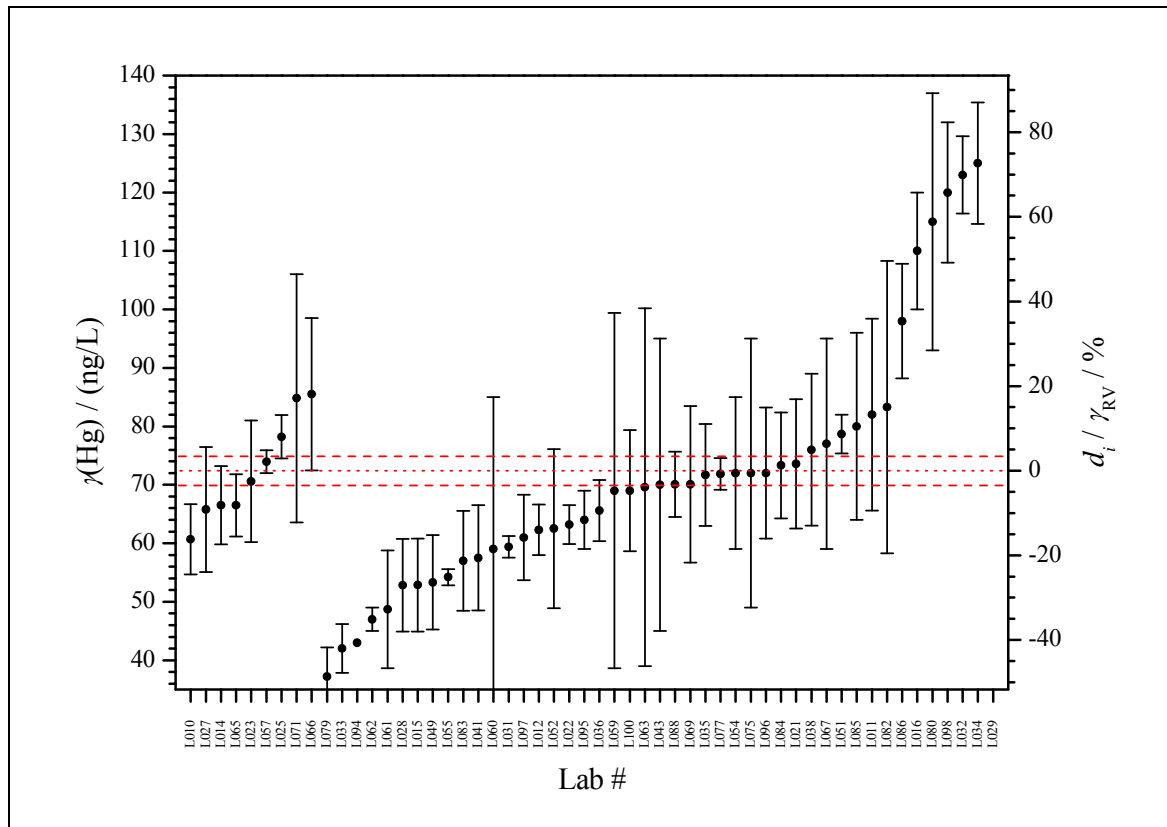


Figure 11: Reported Hg mass concentrations  $\gamma(\text{Hg})$  of PCLs and TLs. Enlarged y-axis. Result of laboratory L029 is missing because of the limited range of the y-axis. For more details refer to caption of figure 10.

## 10.5 Mercury – additional, voluntary samples

The CCQM participants were provided with three additional samples, while the Euramet participants got one additional sample (randomly drawn from the three prepared concentration levels). The intention was to calculate the matrix content  $\gamma_0(\text{Hg})$  from the results of the additional samples. For more details refer to sections 5 and 9.2.

### 10.5.1 Mercury Hg-II

*Table 12:* Comparison of the mass concentration reference value  $\gamma_{\text{RV}}(\text{Hg})$  to selected arithmetic means  $\bar{x}$ . Since the group of PCL had not enough members, the particular means of the TL and PCL group were omitted from the table.  $N$  denotes the number of results within the particular group, while  $\Delta_{\text{max}}\gamma$  denotes the difference between the smallest reported mass concentration  $\gamma_{\text{min}}$  and the largest  $\gamma_{\text{max}}$ . The relative deviation  $\Delta_{\text{ref}}$  of every mean  $\bar{x}$  from the reference value  $\gamma_{\text{RV}}(\text{Hg})$  is given in the last column. Refer to section 10 and equations (7) – (10) for more details on the symbols and group names.

Mercury – Hg-II						
	$\bar{x}$	$N$	$s/\bar{x}$	$U$	$\Delta_{\text{max}}\gamma$	$\Delta_{\text{ref}}$
	ng/L	1	%	ng/L	ng/L	%
reference value	142.4			2.8		
all participants	140.7	26	19	10.6	159	-1.2
Euramet	140.0	17	24	16.0	159	-1.6
NMI	142.0	9	7	6.4	32	-0.3

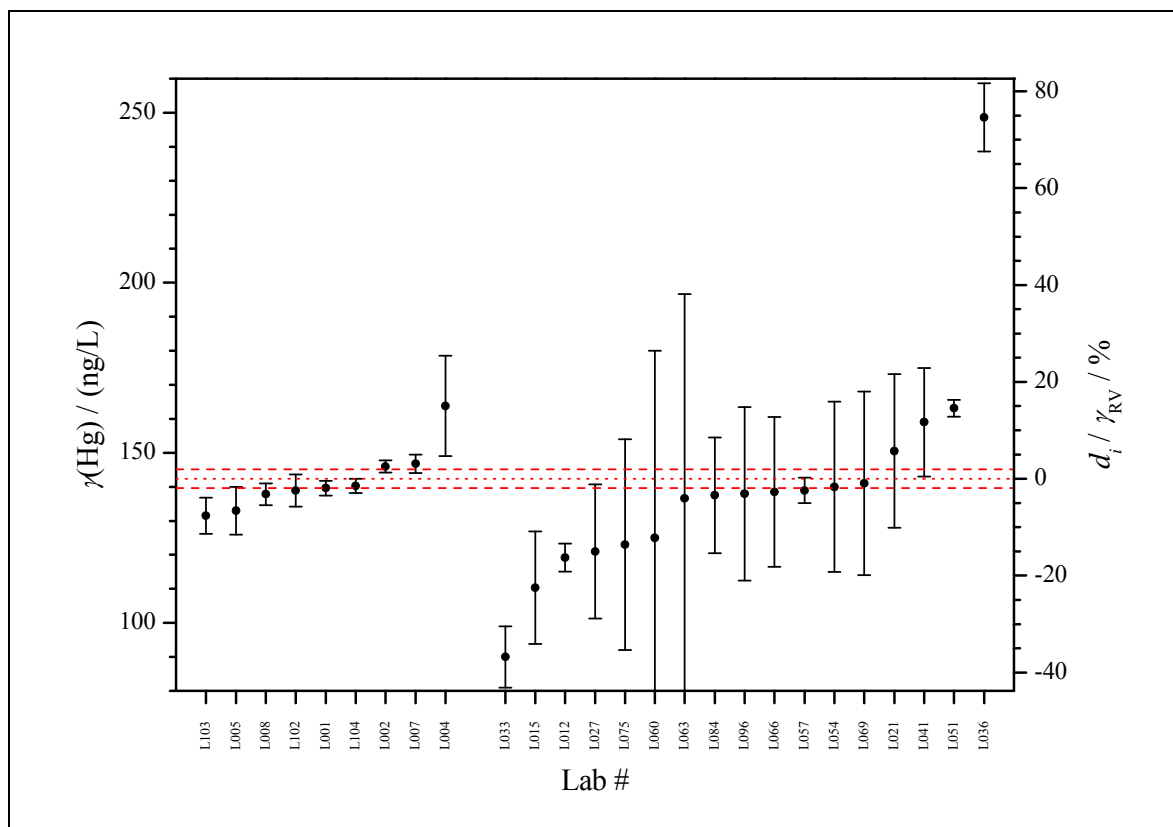


Figure 12: Reported Hg mass concentrations  $\gamma(\text{Hg})$  in the additional voluntary sample Hg-II. Participants grouped (from left to right) into CCQM participants (NMI) and Euramet participants (PCL and TL). Error bars indicate reported expanded uncertainties. Abscissa denotes the individual laboratory code number. Right y-axis shows the individual degree of equivalence  $d_i$  related to the reference value  $\gamma_{RV}(\text{Hg})$ . The reference value and its associated expanded uncertainty  $U(\gamma_{RV}(\text{Hg}))$  is represented by the dotted red line and the dashed red lines, respectively.



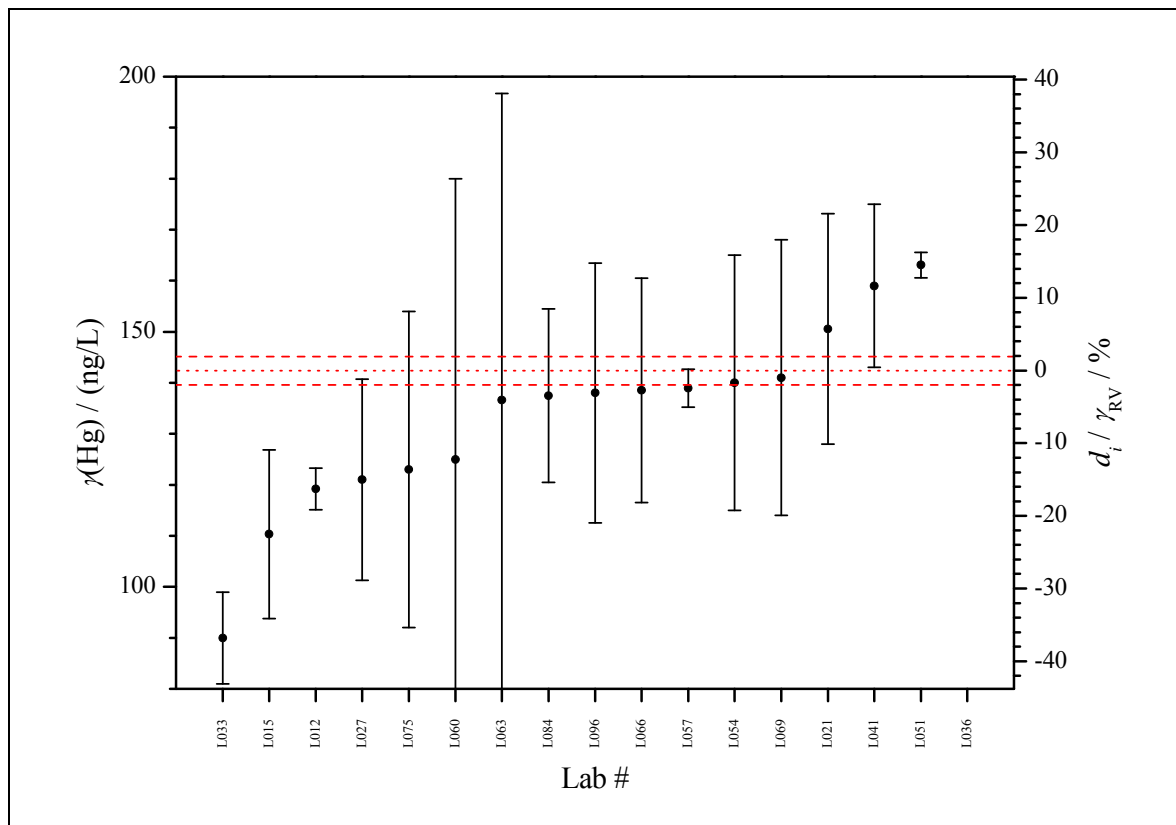
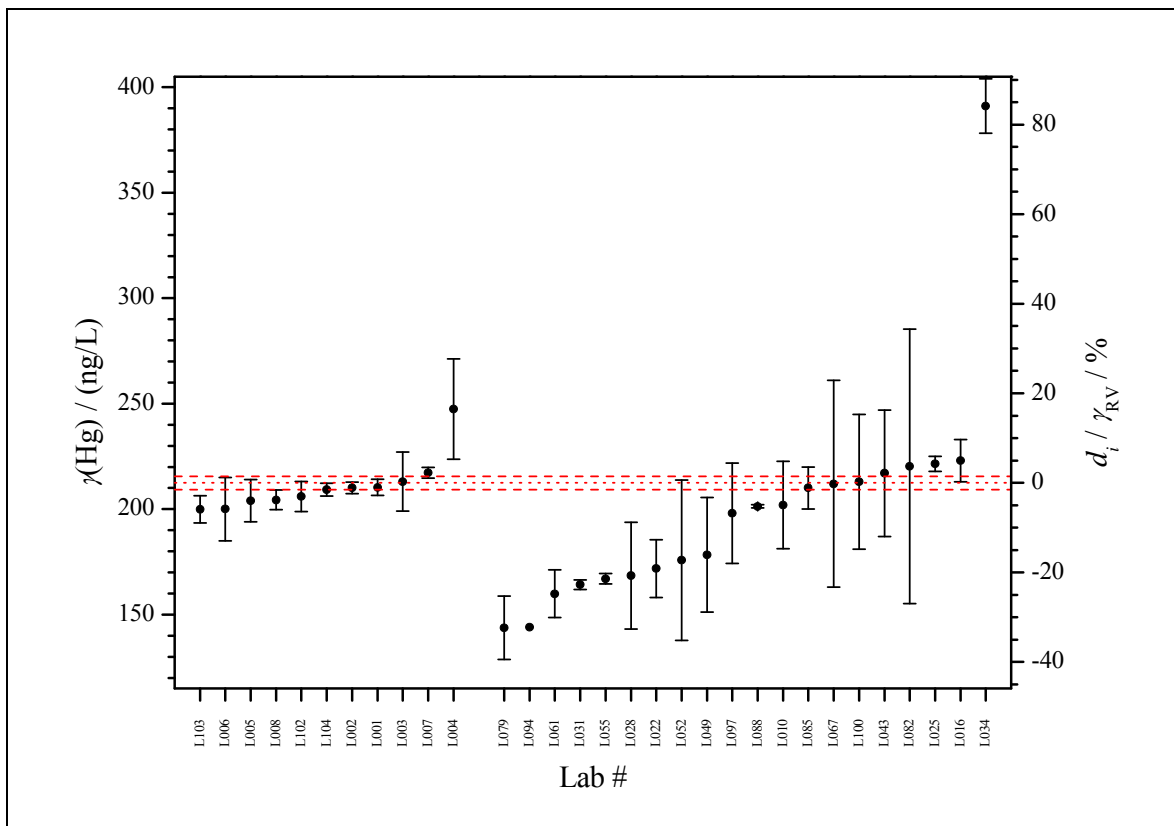


Figure 13: Reported Hg mass concentrations  $\gamma(\text{Hg})$  in the additional voluntary sample Hg-II. Only PCLs and TLs shown. Enlarged y-axis. Result of laboratory L036 is missing because of the limited range of the y-axis. For more details refer to caption of figure 12.

### 10.5.2 Mercury Hg-III

*Table 13:* Comparison of the mass concentration reference value  $\gamma_{RV}(\text{Hg})$  to selected arithmetic means  $\bar{x}$ . Since the group of PCL had not enough members, the particular means of the TL and PCL group were omitted from the table.  $N$  denotes the number of results within the particular group, while  $\Delta_{\max}\gamma$  denotes the difference between the smallest reported mass concentration  $\gamma_{\min}$  and the largest  $\gamma_{\max}$ . The relative deviation  $\Delta_{\text{ref}}$  of every mean  $\bar{x}$  from the reference value  $\gamma_{RV}(\text{Hg})$  is given in the last column. Refer to section 10 and equations (7) – (10) for more details on the symbols and group names.

Mercury – Hg-III						
	$\bar{x}$	$N$	$s/\bar{x}$	$U$	$\Delta_{\max}\gamma$	$\Delta_{\text{ref}}$
	ng/L	1	%	ng/L	ng/L	%
reference value	212.4			3.2		
all participants	203.3	31	21	15.3	247	-4.2
Euramet	199.1	20	26	23.3	247	-6.2
NMI	211.0	11	6	7.9	48	-0.6



*Figure 14:* Reported Hg mass concentrations  $\gamma(\text{Hg})$  in the additional voluntary sample Hg-III. Participants grouped (from left to right) into CCQM participants (NMI) and Euramet participants (PCL and TL). Error bars indicate reported expanded uncertainties. Laboratory L094 did not report an uncertainty. Abscissa denotes the individual laboratory code number. Right

y-axis shows the individual degree of equivalence  $d_i$  related to the reference value  $\gamma_{RV}(\text{Hg})$ . The reference value and its associated expanded uncertainty  $U(\gamma_{RV}(\text{Hg}))$  is represented by the dotted red line and the dashed red lines, respectively.

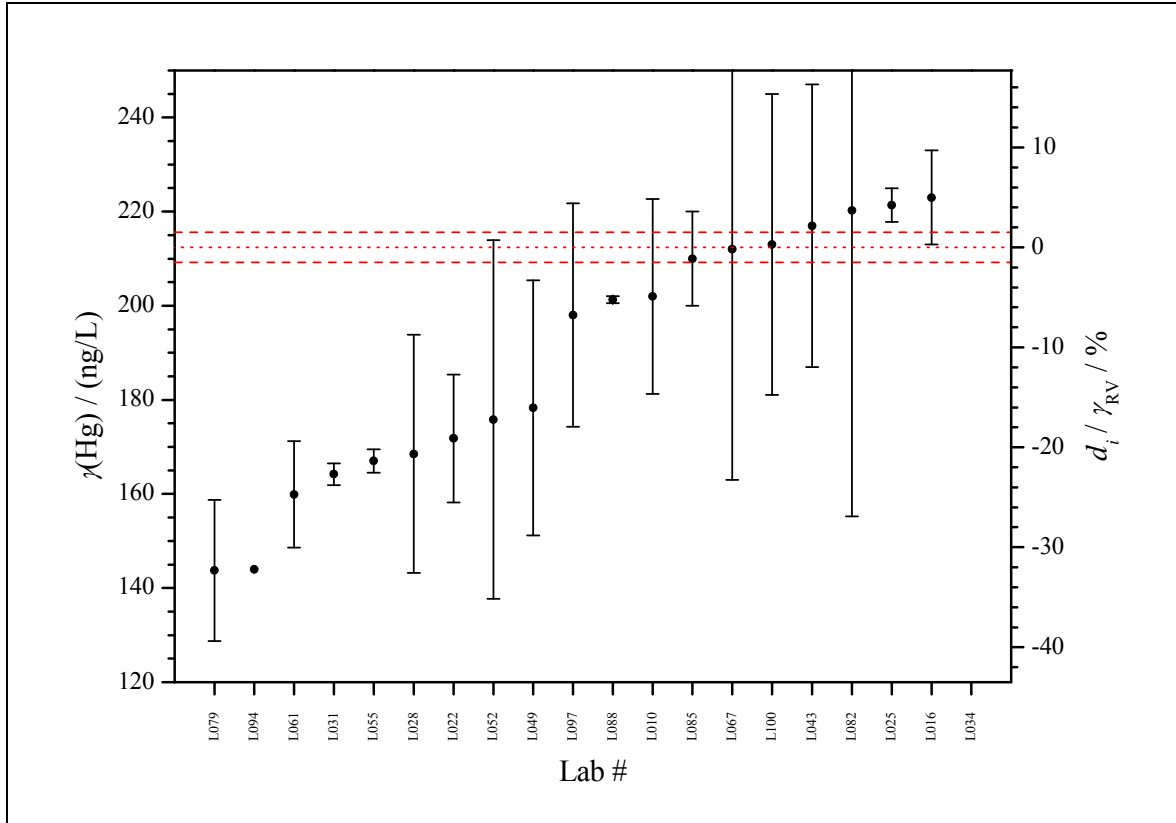
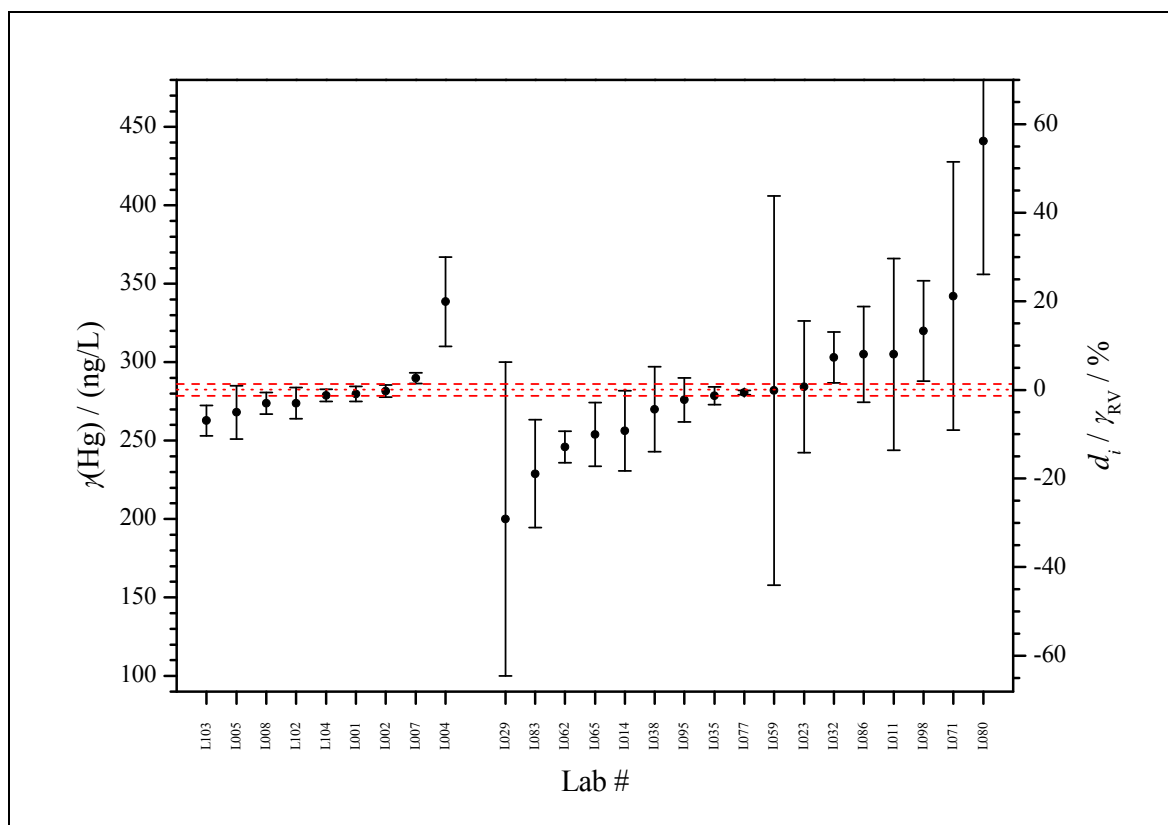


Figure 15: Reported Hg mass concentrations  $\gamma(\text{Hg})$  in the additional voluntary sample Hg-III. Only PCLs and TLs shown. Enlarged y-axis. Result of laboratory L034 is missing because of the limited range of the y-axis. For more details refer to caption of figure 14.

### 10.5.3 Mercury Hg-IV

*Table 14:* Comparison of the mass concentration reference value  $\gamma_{RV}(\text{Hg})$  to selected arithmetic means  $\bar{x}$ . Since the group of PCL had not enough members, the particular means of the TL and PCL group were omitted from the table.  $N$  denotes the number of results within the particular group, while  $\Delta_{\max}\gamma$  denotes the difference between the smallest reported mass concentration  $\gamma_{\min}$  and the largest  $\gamma_{\max}$ . The relative deviation  $\Delta_{\text{ref}}$  of every mean  $\bar{x}$  from the reference value  $\gamma_{RV}(\text{Hg})$  is given in the last column. Refer to section 10 and equations (7) – (10) for more details on the symbols and group names.

Mercury – Hg-IV						
	$\bar{x}$	$N$	$s/\bar{x}$	$U$	$\Delta_{\max}\gamma$	$\Delta_{\text{ref}}$
	ng/L	1	%	ng/L	ng/L	%
reference value	282.4			3.7		
all participants	285.4	26	15	17.2	241	+1.1
Euramet	286.6	17	18	25.4	241	+1.5
NMI	283.0	9	8	14.8	76	+0.2



*Figure 16:* Reported Hg mass concentrations  $\gamma(\text{Hg})$  in the additional voluntary sample Hg-IV. Participants grouped (from left to right) into CCQM participants (NMI) and Euramet participants (PCL and TL). Error bars indicate reported expanded uncertainties. Abscissa denotes the individual laboratory code number. Right y-axis shows the individual degree of equivalence  $d_i$  related to the reference value  $\gamma_{RV}(\text{Hg})$ . The reference value and its associated ex-

panded uncertainty  $U(\gamma_{RV}(\text{Hg}))$  is represented by the dotted red line and the dashed red lines, respectively.

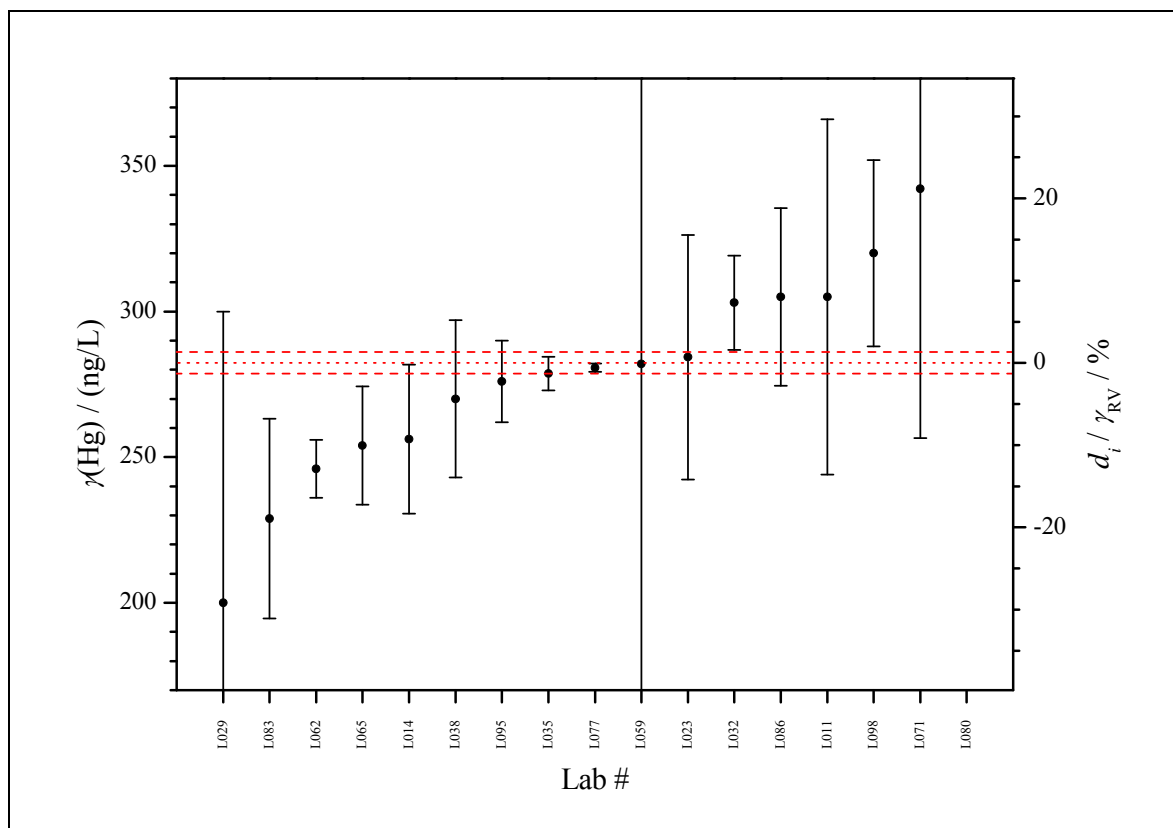


Figure 17: Reported Hg mass concentrations  $\gamma(\text{Hg})$  in the additional voluntary sample Hg-IV. Only PCLs and TLs shown. Enlarged y-axis. Result of laboratory L080 is missing because of the limited range of the y-axis. For more details refer to caption of figure 16.

## 10.6 Scoring

In order to assess the participants' performance two parameters were calculated: the En-score as well as the z-score [10]:

$$E_n = \frac{d_i}{u(d_i)} = \frac{\gamma_i - \gamma_{RV}}{\sqrt{u^2(\gamma_i) + u^2(\gamma_{RV})}} \quad (12)$$

$$z = \frac{d_i}{s} = \frac{\gamma_i - \gamma_{RV}}{s} \quad (13)$$

The En-score takes into account the uncertainty  $u(d_i)$  of the degree of equivalence  $d_i$ , which is calculated from the according uncertainties associated with the individual result  $\gamma_i$  and with the reference value  $\gamma_{RV}$ . This way, the En-score assesses not only the ability of a certain participant to measure as close as possible to the reference value, but also how reasonable the participant has estimated the uncertainty associated with the result reported. In contrast, the z-score relates the degree of equivalence to a standard uncertainty that can be either estimated from the results of the participants or that bases on an agreement or a certain requirement announced beforehand. In the case of Euramet 924 part 3 a standard deviation  $s$ , which equals 10 % of the according reference value, was used following the recommendations in the "Technical Agreement of the Self-committed Network of PT Providers" [11]:

$$s = 0.1 \cdot \gamma_{RV} \quad (14)$$

The En- as well as the z-score are interpreted in the same commonly accepted way (see table 15 for details). Therefore, participants which reported an uncertainty larger than the 10 % standard deviation agreement from [11] benefit from the assessment based on  $E_n$ , while participants who underestimated their uncertainty with respect to the degree of equivalence are favoured by the use of z-scores. Therefore, participants who reported no uncertainty at all (assumed to be zero by the providers) benefit particularly from the use of z-scores.

*Table 15:* Ranges of the scoring parameters  $E_n$  and  $z$  along with their interpretation. Since both parameters are interpreted in the same way (criteria boundaries 2 and 3 are equal), only  $E_n$  is shown as an example.

Result	Score
Satisfactory	$ E_n  \leq 2$
Questionable	$2 <  E_n  < 3$
Unsatisfactory	$ E_n  \geq 3$

In the Commission Directive 2009/90/EC an upper uncertainty limit was defined [4], which was already described in section 4. The compliance with this uncertainty requirement was therefore used in addition to the En- and z-score, respectively, to assess the participants' results.

A comprehensive and convenient way to get a graphical overview of the participants' performance is the Naji-plot proposed in [10]. To understand that the Naji-plot shows all the information contained in the En-score, its definition has to be rearranged while a slightly modi-

fied Z-score (using the standard uncertainty  $u(\gamma_{RV})$  associated with the reference value as the denominator instead of the standard deviation  $s$ ) is introduced. The quantity  $C$  denotes the criteria boundaries of the scoring ranges according to table 15. Therefore,  $C$  is either 2 or 3. According to equation 19, when plotting the square of the uncertainty ratio  $[u(\gamma_i)/u(\gamma_{RV})]^2$  versus the Z-score, the criteria boundaries ( $C = 2$  and  $C = 3$ , resp.) are parabolas passing through  $(0,-1)$  and  $(Z = C, 0)$  [10]. This way the parabolas separate three regions that are directly related to the scoring ranges shown in table 15. Additionally, the maximum uncertainty  $U_{max}$  required by [4] (see table 1) confines the regions at the top and prevents results with large Z-scores from being satisfactory or questionable merely by reporting inappropriately large uncertainties. A detailed description can be found in the caption of figure 18.

$$E_n = \frac{\gamma_i - \gamma_{RV}}{\sqrt{u^2(\gamma_i) + u^2(\gamma_{RV})}} < C \quad (15)$$

$$Z = \frac{\gamma_i - \gamma_{RV}}{u(\gamma_{RV})} \quad (16)$$

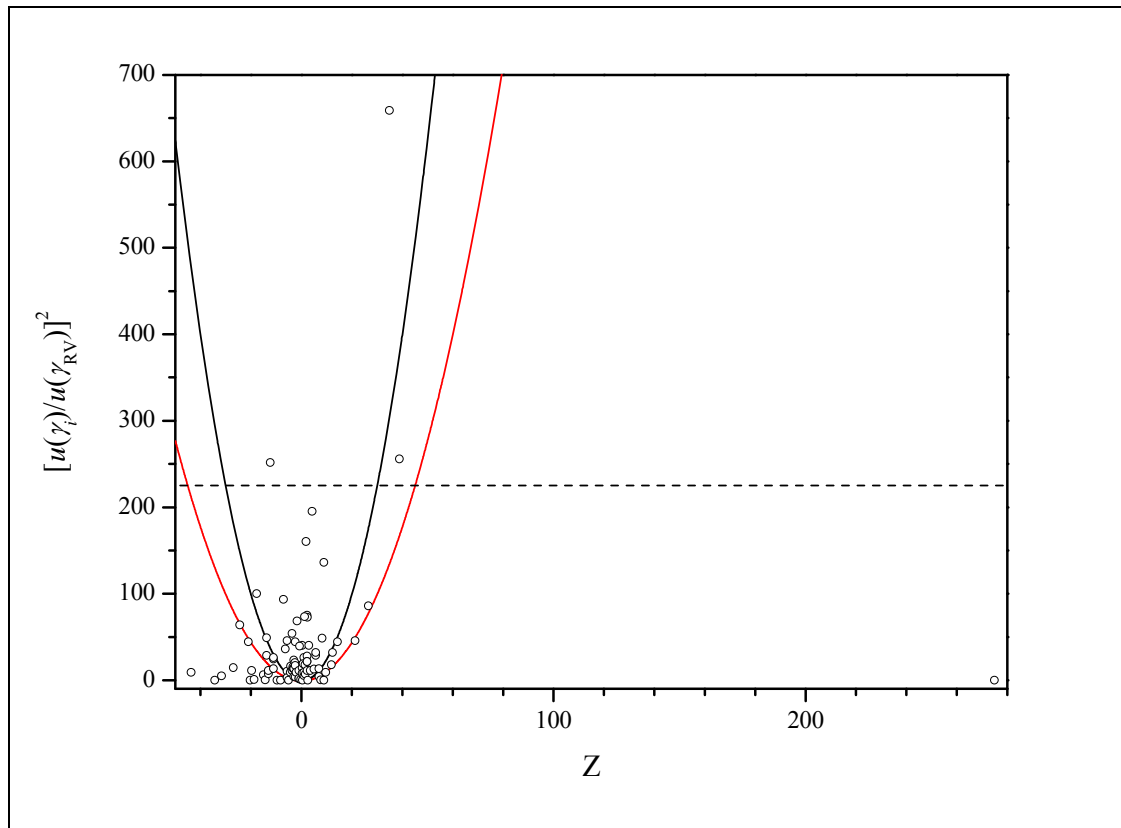
$$\frac{(\gamma_i - \gamma_{RV})^2}{u^2(\gamma_i) + u^2(\gamma_{RV})} < C^2 \quad (17)$$

$$\frac{1}{C^2} \underbrace{\frac{(\gamma_i - \gamma_{RV})^2}{u^2(\gamma_{RV})}}_{=Z^2} - 1 < \left( \frac{u(\gamma_i)}{u(\gamma_{RV})} \right)^2 \quad (18)$$

$$\frac{Z^2}{C^2} - 1 < \left( \frac{u(\gamma_i)}{u(\gamma_{RV})} \right)^2 \quad (19)$$

### 10.6.1 Naji-plots and pie-charts

In order to visualize all the performance data and the compliance with the minimum performance criteria – namely the maximum measurement uncertainty – at least one Naji-plot per element (and in some cases additionally a “zoomed-in” version) was drawn. For a more detailed description refer to the last section and [10]. To reduce the large amount of information to the simple decision whether the participation was successful or not, pie-charts were plotted showing the fractions of satisfactory, questionable and unsatisfactory results in case the  $E_n$ - or the z-score would have been applied in conjunction with the maximum uncertainty requirement.



*Figure 18:* Naji-plot of all Cd mass concentration results and associated uncertainties as reported by the participants. Dotted line denotes the maximum uncertainty boundary. Data points below this line meet therefore the uncertainty requirements. Inside the black parabola the satisfactory results are located. Between the black and red parabola results are interpreted as questionable, while outside the red parabola results are unsatisfactory. For more details and the axis labels refer to section 10.6 and equations 15-19.



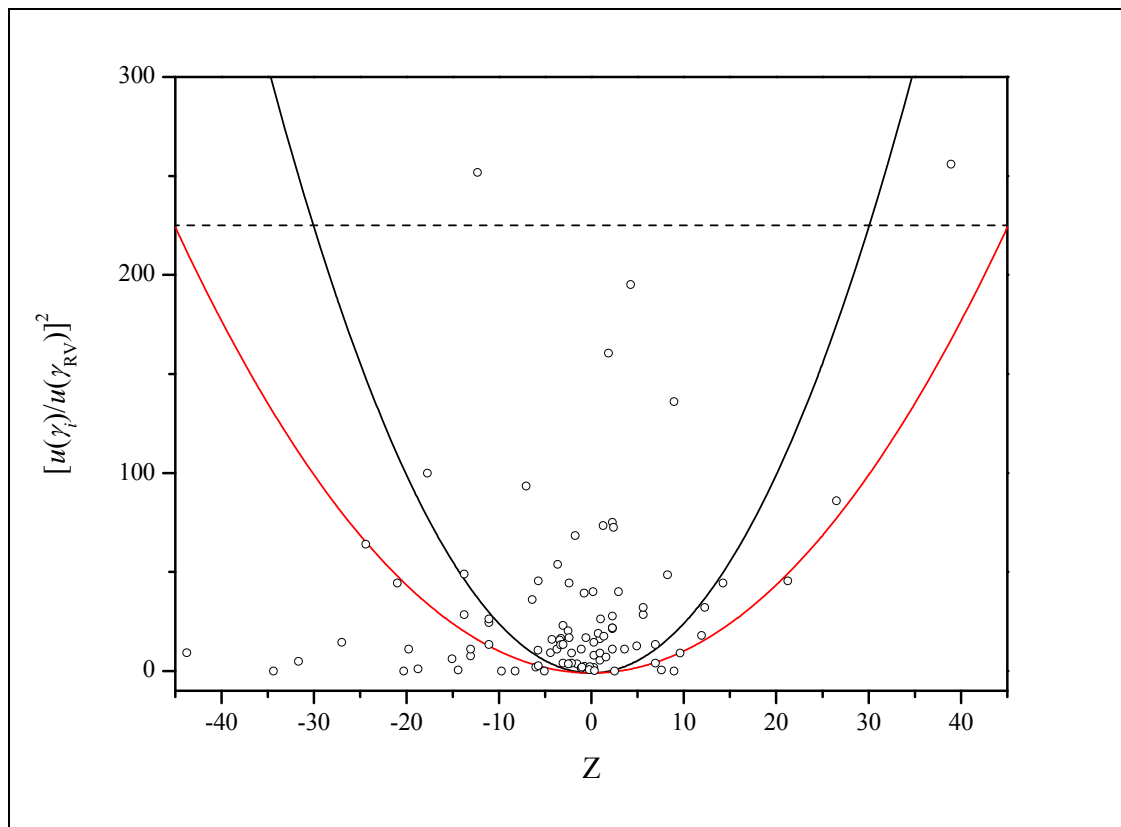


Figure 19: Detailed enlargement from figure 18.

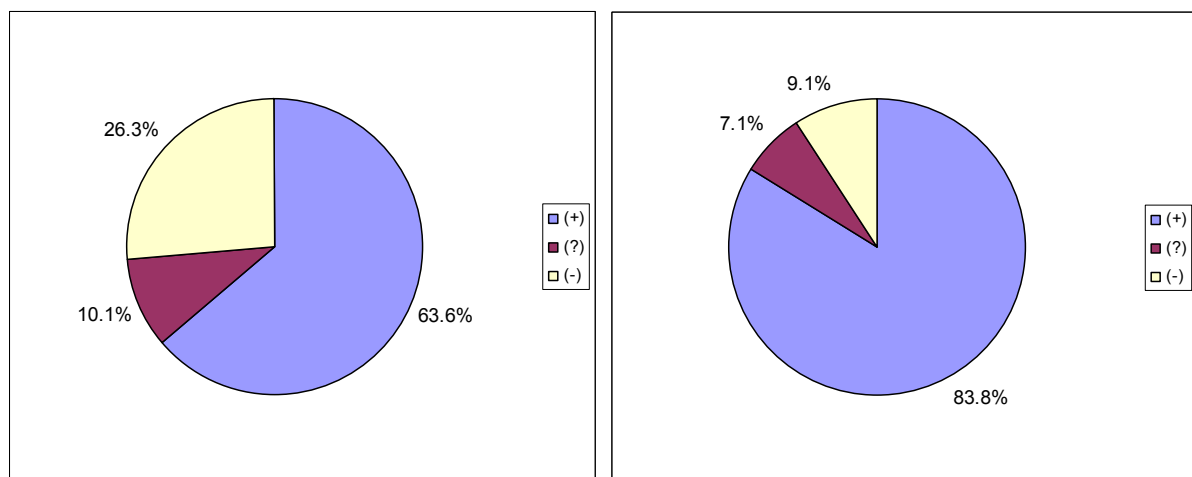


Figure 20: Cd mass concentration. Fractions of satisfactory (blue), questionable (magenta) and unsatisfactory (light yellow) results. Left: based on En-scores according to equation 12. Right: based on z-scores according to equations 13 and 14. Fractions may not add up to 100 % because of rounding errors.

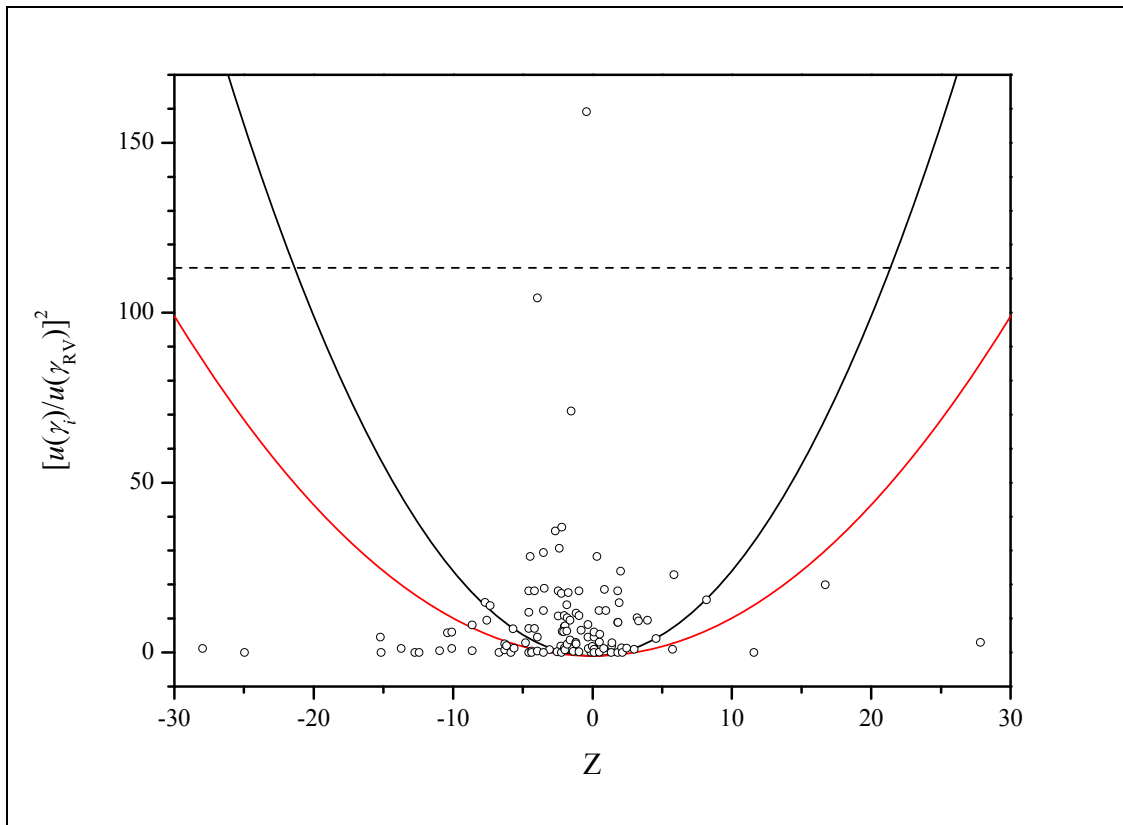


Figure 21: Naji-plot of all Ni mass concentration results and associated uncertainties as reported by the participants. Dotted line denotes the maximum uncertainty boundary. Data points below this line meet therefore the uncertainty requirements. Inside the black parabola the satisfactory results are located. Between the black and red parabola results are interpreted as questionable, while outside the red parabola results are unsatisfactory. For more details and the axis labels refer to section 10.6 and equations 15-19.

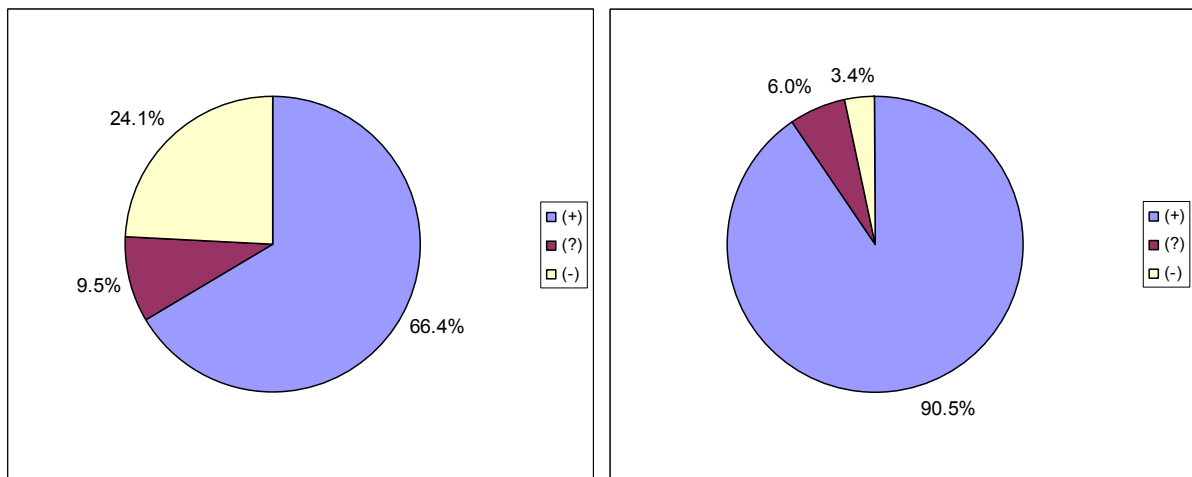
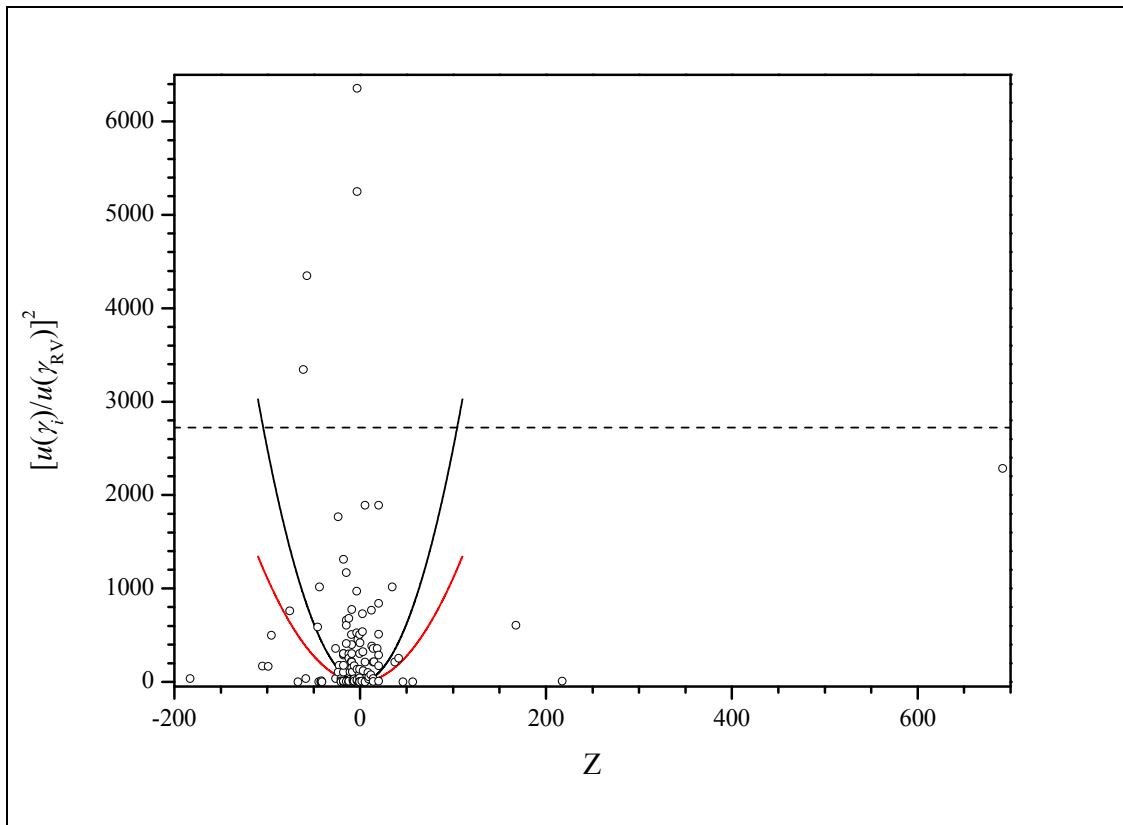


Figure 22: Ni mass concentration. Fractions of satisfactory (blue), questionable (magenta) and unsatisfactory (light yellow) results. Left: based on En-scores according to equation 12. Right: based on z-scores according to equations 13 and 14. Fractions may not add up to 100 % because of rounding errors.



*Figure 23:* Naji-plot of all Pb mass concentration results and associated uncertainties as reported by the participants. Dotted line denotes the maximum uncertainty boundary. Data points below this line meet therefore the uncertainty requirements. Inside the black parabola the satisfactory results are located. Between the black and red parabola results are interpreted as questionable, while outside the red parabola results are unsatisfactory. For more details and the axis labels refer to section 10.6 and equations 15-19.

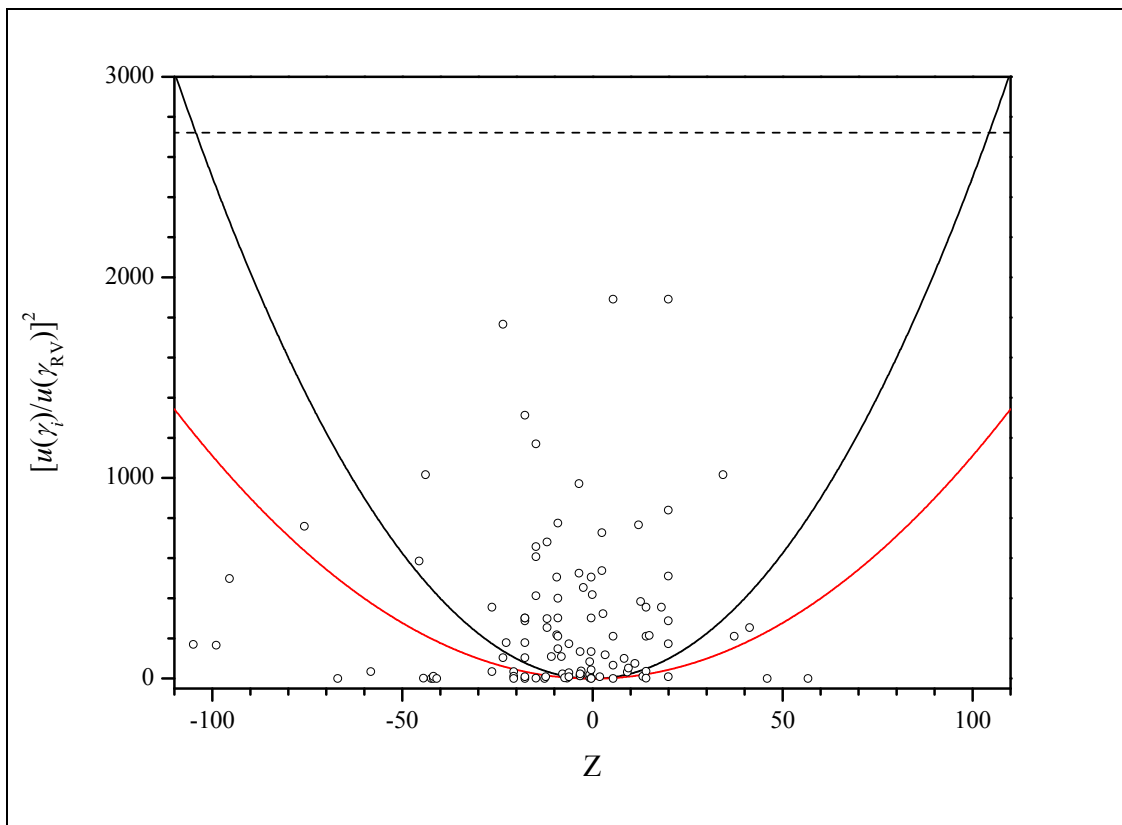


Figure 24: Detailed enlargement from figure 23.

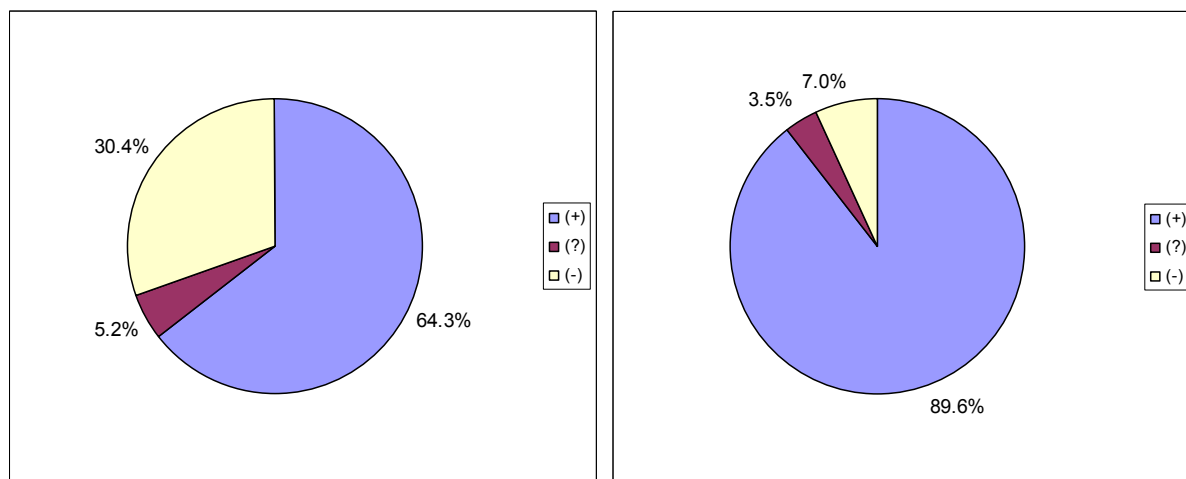
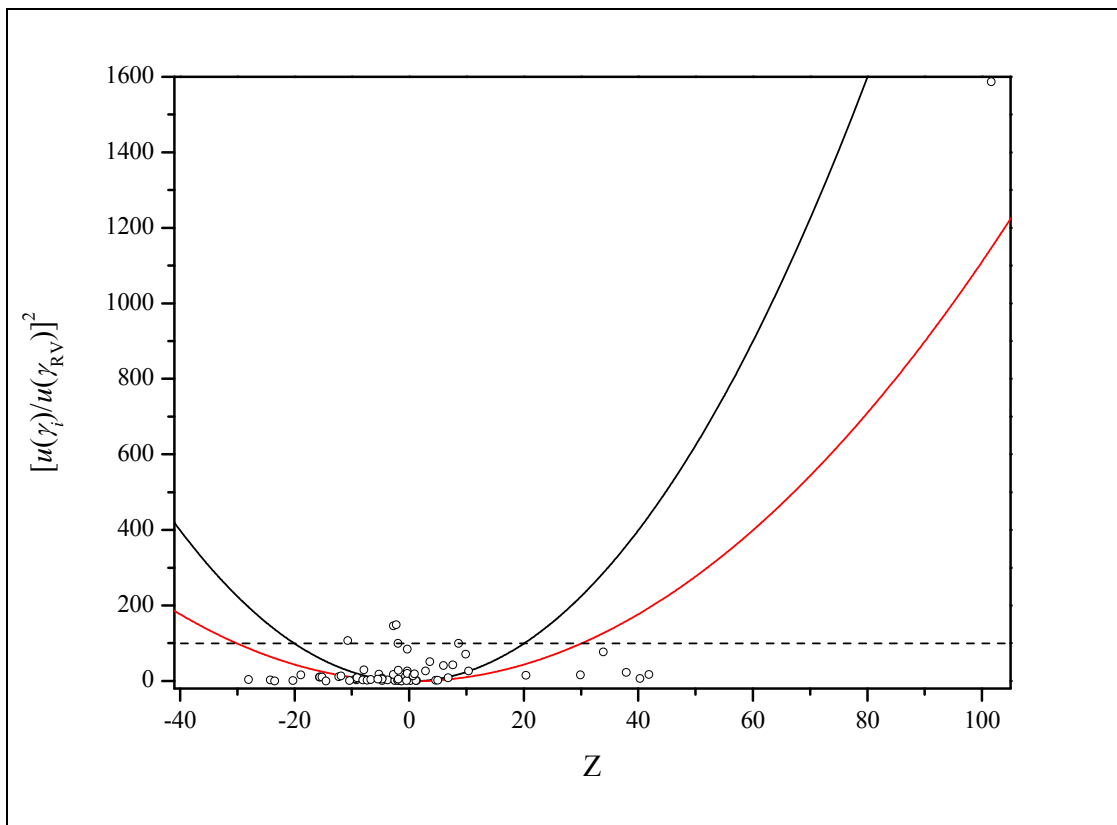


Figure 25: Pb mass concentration. Fractions of satisfactory (blue), questionable (magenta) and unsatisfactory (light yellow) results. Left: based on En-scores according to equation 12. Right: based on z-scores according to equations 13 and 14. Fractions may not add up to 100 % because of rounding errors.



*Figure 26:* Naji-plot of all Hg mass concentration results (sample Hg-I) and associated uncertainties as reported by the participants. Dotted line denotes the maximum uncertainty boundary. Data points below this line meet therefore the uncertainty requirements. Inside the black parabola the satisfactory results are located. Between the black and red parabola results are interpreted as questionable, while outside the red parabola results are unsatisfactory. For more details and the axis labels refer to section 10.6 and equations 15-19.

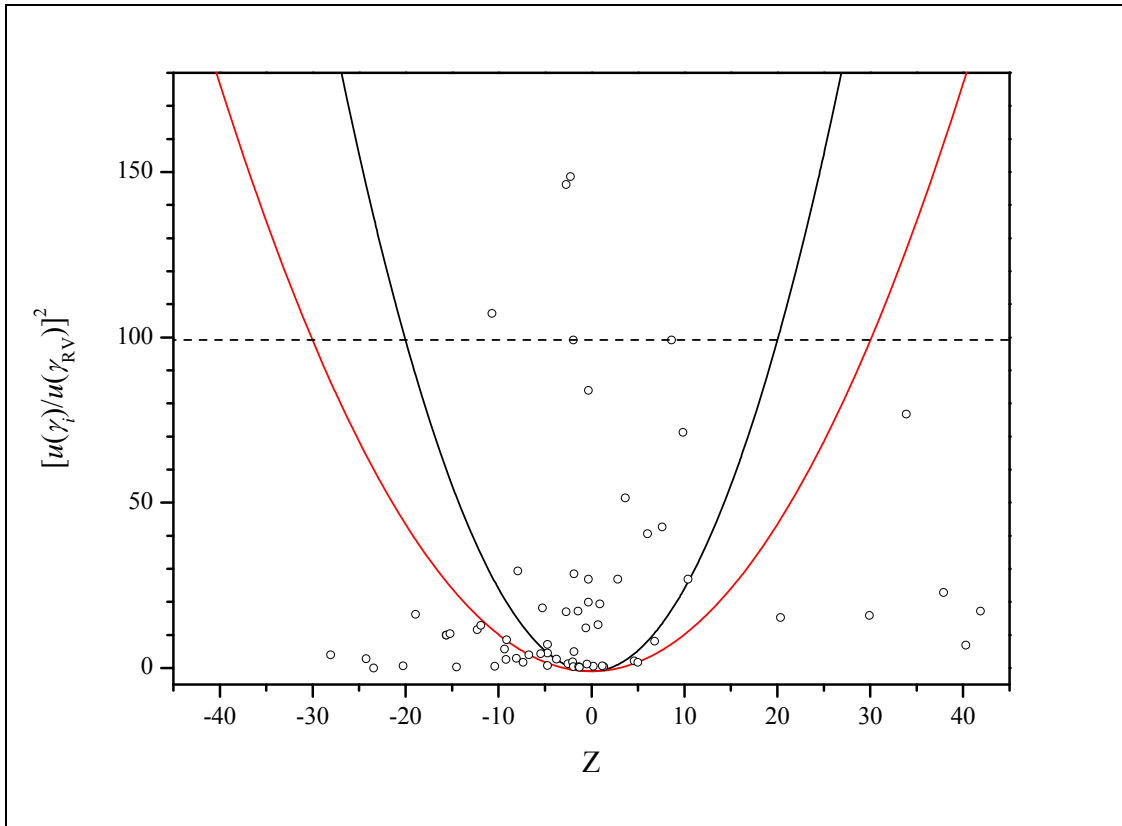


Figure 27: Detailed enlargement from figure 26.

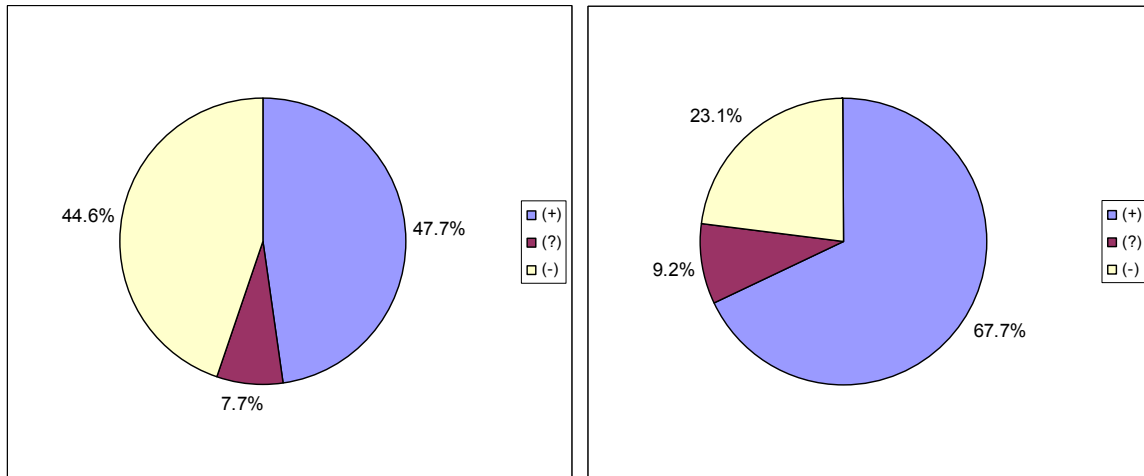


Figure 28: Hg mass concentration in sample Hg-I. Fractions of satisfactory (blue), questionable (magenta) and unsatisfactory (light yellow) results. Left: based on En-scores according to equation 12. Right: based on z-scores according to equations 13 and 14. Fractions may not add up to 100 % because of rounding errors.

### 10.6.2 Individual results and laboratory performance – cadmium

*Table 16:* En- and z-scores calculated from the Cd mass concentrations  $\gamma_i$  and their associated expanded uncertainties  $U(\gamma_i)$  as reported by the participants in the order of their laboratory code numbers. Interpretation of scores see table 15. Additionally, last column shows compliance with the “minimum performance criteria”, for more details refer to section 4. All quantities rounded to the same number of digits for the sake of clarity. Calculations were carried out with all digits reported. (n.r. = not reported).

<b>Cadmium</b>					
<b>Lab</b>	$\gamma(\text{Cd})$	$U(\gamma)$	$E_n$	$z$	$U(\gamma)$
<b>Code</b>	<b>ng/L</b>	<b>ng/L</b>	<b>1</b>	<b>1</b>	$\leq U_{\max}$
L001	124.3	5.7	-0.7	-0.2	yes
L009	125.1	4.3	-0.6	-0.1	yes
L010	130.2	25.6	0.3	0.3	yes
L011	139.0	20.9	1.2	1.0	yes
L012	122.0	6.0	-1.4	-0.4	yes
L013	539.0	n.r.	274.9	32.6	yes
L014	125.7	12.3	-0.1	-0.1	yes
L015	127.0	11.4	0.1	0.0	yes
L016	112.0	n.r.	-9.7	-1.2	yes
L017	107.0	8.2	-4.5	-1.5	yes
L018	75.0	n.r.	-34.4	-4.1	yes
L019	121.5	11.8	-0.8	-0.4	yes
L020	118.0	5.0	-2.9	-0.7	yes
L021	125.4	18.8	-0.1	-0.1	yes
L022	129.4	38.0	0.1	0.2	yes
L023	121.7	12.2	-0.8	-0.4	yes
L024	128.0	12.1	0.2	0.1	yes
L025	128.1	15.4	0.2	0.1	yes
L026	123.4	5.9	-1.0	-0.3	yes
L027	122.0	14.4	-0.6	-0.4	yes
L028	127.0	11.4	0.1	0.0	yes
L029	132.0	10.0	1.0	0.4	yes
L030	148.0	20.0	2.1	1.7	yes
L031	79.1	6.6	-13.1	-3.8	yes
L032	98.5	3.0	-13.2	-2.2	yes
L033	110.0	11.0	-2.9	-1.3	yes
L035	133.0	41.9	0.3	0.5	yes
L036	104.0	7.4	-5.7	-1.8	yes
L037	122.0	11.0	-0.8	-0.4	yes

<b>Cadmium</b>					
<b>Lab</b>	$\gamma(\text{Cd})$	$U(\gamma)$	$E_n$	$z$	$U(\gamma)$
<b>Code</b>	<b>ng/L</b>	<b>ng/L</b>	<b>1</b>	<b>1</b>	$\leq U_{\max}$
L039	121.0	10.0	-1.1	-0.4	yes
L040-A	105.0	2.0	-12.0	-1.7	yes
L040-B	107.0	10.0	-3.8	-1.5	yes
L041	141.0	9.0	3.0	1.1	yes
L043	131.0	19.0	0.5	0.3	yes
L044	60.9	9.1	-13.7	-5.2	yes
L045	125.0	10.0	-0.3	-0.1	yes
L046	130.0	15.8	0.4	0.3	yes
L047	95.1	20.0	-3.1	-2.5	yes
L048-A	123.4	9.0	-0.7	-0.3	yes
L048-B	138.0	2.0	6.3	0.9	yes
L048-C	127.1	1.2	0.3	0.0	yes
L049	121.1	22.0	-0.5	-0.4	yes
L050	118.0	20.2	-0.8	-0.7	yes
L051	126.2	2.7	-0.2	0.0	yes
L052	130.4	n.r.	2.5	0.3	yes
L053	114.2	n.r.	-8.3	-1.0	yes
L054	135.0	16.0	1.0	0.7	yes
L055	129.0	8.0	0.6	0.2	yes
L056	96.2	n.r.	-20.3	-2.4	yes
L057	126.4	4.4	-0.1	0.0	yes
L060	100.0	30.0	-1.8	-2.1	yes
L061	97.0	10.0	-5.7	-2.3	yes
L062	123.0	20.0	-0.4	-0.3	yes
L063	108.1	47.6	-0.8	-1.5	no
L065	124.0	24.8	-0.2	-0.2	yes
L066	130.0	26.0	0.3	0.3	yes
L067	185.0	48.0	2.4	4.6	no
L068	130.0	13.9	0.5	0.3	yes
L069	128.0	7.0	0.4	0.1	yes
L070	122.8	13.5	-0.5	-0.3	yes
L071	126.9	19.0	0.0	0.0	yes
L073	127.0	8.5	0.1	0.0	yes
L075	122.9	5.7	-1.2	-0.3	yes
L076	125.0	3.6	-0.7	-0.1	yes
L078	120.2	12.0	-1.0	-0.5	yes



<b>Cadmium</b>					
<b>Lab</b>	$\gamma(\text{Cd})$	$U(\gamma)$	$E_n$	$z$	$U(\gamma)$
<b>Code</b>	<b>ng/L</b>	<b>ng/L</b>	<b>1</b>	<b>1</b>	$\leq U_{\max}$
L079	117.0	18.0	-1.1	-0.8	yes
L081	137.0	6.0	3.1	0.8	yes
L082	145.0	17.0	2.1	1.5	yes
L083	106.0	16.0	-2.5	-1.6	yes
L084	130.0	14.0	0.5	0.3	yes
L085	123.0	12.3	-0.6	-0.3	yes
L086	134.0	10.7	1.3	0.6	yes
L088	137.0	11.0	1.8	0.8	yes
L091	128.0	9.0	0.3	0.1	yes
L092	130.0	10.0	0.7	0.3	yes
L093	120.0	9.1	-1.4	-0.5	yes
L094	140.0	n.r.	8.9	1.1	yes
L095	119.0	n.r.	-5.1	-0.6	yes
L096	90.0	24.0	-3.0	-2.9	yes
L098	110.0	14.8	-2.2	-1.3	yes
L100	116.0	29.0	-0.7	-0.8	yes
L101	158.5	20.2	3.1	2.5	yes
L103	127.0	4.0	0.2	0.0	yes
L104	125.5	4.6	-0.4	-0.1	yes
L105	127.7	13.1	0.2	0.1	yes
L106	166.4	27.8	2.8	3.1	yes
L107	130.0	14.0	0.5	0.3	yes
L108	117.6	4.2	-3.5	-0.7	yes
L110	106.0	21.0	-1.9	-1.6	yes
L111	128.5	25.7	0.1	0.2	yes
L113	86.1	11.4	-6.9	-3.2	yes
L114	179.0	77.0	1.4	4.1	no
L115	144.5	12.7	2.7	1.4	yes
L118	118.0	9.7	-1.7	-0.7	yes
L119	128.6	12.6	0.3	0.2	yes
L120	121.6	10.9	-0.9	-0.4	yes
L121	140.0	35.0	0.8	1.1	yes
L124	135.0	17.0	1.0	0.7	yes
L125	110.0	15.4	-2.1	-1.3	yes

### 10.6.3 Individual results and laboratory performance – nickel

*Table 17:* En- and z-scores calculated from the Ni mass concentrations  $\gamma_i$  and their associated expanded uncertainties  $U(\gamma_i)$  as reported by the participants in the order of their laboratory code numbers. Interpretation of scores see table 15. Additionally, last column shows compliance with the “minimum performance criteria”, for more details refer to section 4. All quantities rounded to the same number of digits for the sake of clarity. Calculations were carried out with all digits reported. (n.r. = not reported).

<b>Nickel</b>					
<b>Lab Code</b>	<b><math>\gamma(\text{Ni})</math> <math>\mu\text{g/L}</math></b>	<b><math>U(\gamma)</math> <math>\mu\text{g/L}</math></b>	<b><math>E_n</math> 1</b>	<b><math>z</math> 1</b>	<b><math>U(\gamma)</math> <math>\leq U_{\max}</math></b>
L001	27.22	0.99	0.1	0.0	yes
L009	26.59	1.62	-0.6	-0.2	yes
L010	27.81	1.58	0.7	0.2	yes
L011	26.70	4.00	-0.2	-0.2	yes
L012	27.00	2.70	-0.1	-0.1	yes
L013	27.78	n.r.	1.3	0.2	yes
L014	24.47	2.49	-2.0	-1.0	yes
L015	26.28	2.37	-0.7	-0.3	yes
L016	32.60	n.r.	11.6	2.0	yes
L017	27.14	1.25	0.0	0.0	yes
L018	20.02	n.r.	-15.2	-2.6	yes
L019	26.18	2.33	-0.8	-0.4	yes
L020	25.30	2.00	-1.7	-0.7	yes
L021	26.33	3.95	-0.4	-0.3	yes
L022	27.38	0.30	0.5	0.1	yes
L023	26.77	2.41	-0.3	-0.1	yes
L024	25.30	9.60	-0.4	-0.7	yes
L025	26.08	1.30	-1.3	-0.4	yes
L026	27.01	1.01	-0.2	-0.1	yes
L027	25.90	5.62	-0.4	-0.5	yes
L028	26.13	2.35	-0.8	-0.4	yes
L029	26.50	0.50	-1.2	-0.2	yes
L030	23.53	3.61	-1.9	-1.3	yes
L031	40.23	1.63	13.9	4.8	yes
L032	23.10	0.72	-6.8	-1.5	yes
L033	20.00	2.00	-6.5	-2.6	yes
L034	25.10	0.58	-3.7	-0.8	yes
L035	27.20	0.94	0.1	0.0	yes
L036	22.40	1.00	-6.9	-1.7	yes

<b>Nickel</b>					
<b>Lab</b>	$\gamma(\text{Ni})$	$U(\gamma)$	$E_n$	$z$	$U(\gamma)$
<b>Code</b>	$\mu\text{g/L}$	$\mu\text{g/L}$	<b>1</b>	<b>1</b>	$\leq U_{\text{max}}$
L037	26.20	3.10	-0.6	-0.3	yes
L039	28.30	1.06	1.6	0.4	yes
L040-A	25.00	0.20	-4.5	-0.8	yes
L040-B	24.00	0.16	-6.6	-1.2	yes
L041	24.20	0.80	-4.8	-1.1	yes
L043	29.30	1.90	2.0	0.8	yes
L044	26.11	3.92	-0.5	-0.4	yes
L045	27.20	2.00	0.0	0.0	yes
L046	27.20	2.30	0.0	0.0	yes
L047	25.50	5.10	-0.6	-0.6	yes
L048-A	28.16	0.22	2.1	0.4	yes
L048-B	25.50	0.20	-3.4	-0.6	yes
L048-C	27.53	1.03	0.5	0.1	yes
L049	26.23	0.84	-1.5	-0.3	yes
L050	25.00	3.23	-1.3	-0.8	yes
L051	26.70	0.42	-0.9	-0.2	yes
L052	26.10	n.r.	-2.2	-0.4	yes
L053	21.30	n.r.	-12.4	-2.2	yes
L054	25.20	2.50	-1.5	-0.7	yes
L055	25.30	0.60	-3.3	-0.7	yes
L056	15.42	n.r.	-25.0	-4.3	yes
L057	26.46	0.96	-1.0	-0.3	yes
L058	24.40	n.r.	-5.9	-1.0	yes
L059	23.10	2.68	-2.9	-1.5	yes
L060	26.30	3.00	-0.5	-0.3	yes
L061	26.00	4.00	-0.6	-0.4	yes
L062	26.60	1.50	-0.6	-0.2	yes
L063	26.95	11.86	0.0	-0.1	no
L065	26.43	7.92	-0.2	-0.3	yes
L066	27.30	5.00	0.1	0.1	yes
L067	25.20	4.00	-0.9	-0.7	yes
L068	26.12	5.71	-0.4	-0.4	yes
L069	26.40	1.80	-0.7	-0.3	yes
L070	27.60	3.30	0.3	0.2	yes
L071	26.20	2.60	-0.7	-0.3	yes
L073	26.20	1.05	-1.3	-0.3	yes

<b>Nickel</b>					
<b>Lab</b>	<b><math>\gamma(\text{Ni})</math></b>	<b><math>U(\gamma)</math></b>	<b><math>E_n</math></b>	<b><math>z</math></b>	<b><math>U(\gamma)</math></b>
<b>Code</b>	<b><math>\mu\text{g/L}</math></b>	<b><math>\mu\text{g/L}</math></b>	<b>1</b>	<b>1</b>	<b><math>\leq U_{\text{max}}</math></b>
L074	28.02	2.80	0.6	0.3	yes
L075	24.26	1.32	-3.6	-1.1	yes
L076	22.40	2.30	-3.8	-1.7	yes
L077	28.65	3.00	1.0	0.6	yes
L078	28.05	3.60	0.5	0.3	yes
L079	25.00	4.00	-1.0	-0.8	yes
L080	23.70	3.50	-1.9	-1.3	yes
L081	25.10	0.12	-4.3	-0.8	yes
L082	27.00	2.00	-0.1	-0.1	yes
L083	25.00	2.50	-1.6	-0.8	yes
L084	28.00	4.00	0.4	0.3	yes
L085	29.00	2.90	1.2	0.7	yes
L086	35.00	4.20	3.6	2.9	yes
L087	28.00	2.80	0.6	0.3	yes
L088	31.00	3.70	2.0	1.4	yes
L089	24.20	1.50	-3.3	-1.1	yes
L090	25.05	5.00	-0.8	-0.8	yes
L091	26.60	3.20	-0.3	-0.2	yes
L092	28.70	2.87	1.0	0.6	yes
L093	27.55	4.05	0.2	0.1	yes
L094	27.20	n.r.	0.1	0.0	yes
L095	28.13	1.10	1.4	0.4	yes
L096	25.52	4.08	-0.8	-0.6	yes
L097	27.40	2.19	0.2	0.1	yes
L098	26.00	3.09	-0.7	-0.4	yes
L099	28.00	n.r.	1.8	0.3	yes
L100	22.26	2.26	-4.0	-1.8	yes
L101	21.16	n.r.	-12.7	-2.2	yes
L103	27.09	0.28	-0.1	0.0	yes
L104	27.80	1.30	0.8	0.2	yes
L105	25.96	0.41	-2.3	-0.4	yes
L106	28.56	0.94	2.1	0.5	yes
L107	26.30	1.46	-1.0	-0.3	yes
L108	25.70	0.86	-2.3	-0.5	yes
L109	26.22	2.62	-0.7	-0.3	yes
L110	27.39	1.64	0.3	0.1	yes

<b>Nickel</b>					
<b>Lab Code</b>	$\gamma(\text{Ni})$ <b><math>\mu\text{g/L}</math></b>	$U(\gamma)$ <b><math>\mu\text{g/L}</math></b>	$E_n$ <b>1</b>	$z$ <b>1</b>	$U(\gamma) \leq U_{\max}$
L111	26.03	5.21	-0.4	-0.4	yes
L112	26.70	3.10	-0.3	-0.2	yes
L113	23.59	2.90	-2.3	-1.3	yes
L114	29.85	0.94	4.1	1.0	yes
L115	24.90	1.60	-2.4	-0.8	yes
L116	20.70	1.02	-9.3	-2.4	yes
L117	22.00	0.70	-8.8	-1.9	yes
L118	24.51	1.05	-3.7	-1.0	yes
L119	26.28	3.52	-0.5	-0.3	yes
L120	26.40	2.90	-0.5	-0.3	yes
L121	29.90	4.50	1.2	1.0	yes
L122	27.37	3.30	0.1	0.1	yes
L123	28.10	4.60	0.4	0.3	yes
L124	14.00	1.00	-19.2	-4.8	yes
L125	25.50	3.30	-1.0	-0.6	yes

#### 10.6.4 Individual results and laboratory performance – lead

Table 18: En- and z-scores calculated from the Pb mass concentrations  $\gamma_i$  and their associated expanded uncertainties  $U(\gamma)$  as reported by the participants in the order of their laboratory code numbers. Interpretation of scores see table 15. Additionally, last column shows compliance with the “minimum performance criteria”, for more details refer to section 4. All quantities rounded to the same number of digits for the sake of clarity. Calculations were carried out with all digits reported. (n.r. = not reported).

<b>Lead</b>					
<b>Lab Code</b>	$\gamma(\text{Pb})$ <b><math>\mu\text{g/L}</math></b>	$U(\gamma)$ <b><math>\mu\text{g/L}</math></b>	$E_n$ <b>1</b>	$z$ <b>1</b>	$U(\gamma) \leq U_{\max}$
L001	12.30	1.20	0.0	0.0	yes
L009	12.29	0.63	-0.1	0.0	yes
L010	12.20	0.28	-0.8	-0.1	yes
L011	11.90	1.80	-0.5	-0.3	yes
L012	11.70	0.70	-1.7	-0.5	yes
L013	14.27	n.r.	56.7	1.6	yes
L014	11.53	0.92	-1.7	-0.6	yes
L015	11.94	0.72	-1.0	-0.3	yes

<b>Lead</b>					
<b>Lab</b>	$\gamma_i(\text{Pb})$	$U(\gamma)$	$E_n$	$z$	$U(\gamma)$
<b>Code</b>	$\mu\text{g/L}$	$\mu\text{g/L}$	<b>1</b>	<b>1</b>	$\leq U_{\text{max}}$
L016	10.90	n.r.	-41.0	-1.1	yes
L017	12.75	1.35	0.6	0.4	yes
L018	10.87	n.r.	-41.8	-1.2	yes
L019	11.99	1.02	-0.6	-0.3	yes
L020	12.50	1.00	0.4	0.2	yes
L021	11.80	1.77	-0.6	-0.4	yes
L022	12.64	0.50	1.3	0.3	yes
L023	12.23	1.47	-0.1	-0.1	yes
L024	12.20	5.50	0.0	-0.1	no
L025	12.21	0.31	-0.6	-0.1	yes
L026	12.77	0.23	3.8	0.4	yes
L027	12.00	1.38	-0.5	-0.3	yes
L028	12.03	0.72	-0.8	-0.2	yes
L029	12.20	0.25	-0.9	-0.1	yes
L030	11.99	1.55	-0.4	-0.3	yes
L031	19.81	0.17	81.7	6.1	yes
L032	12.80	0.41	2.3	0.4	yes
L033	8.90	0.89	-7.6	-2.8	yes
L034	12.10	0.37	-1.1	-0.2	yes
L035	12.20	0.33	-0.7	-0.1	yes
L036	10.30	0.40	-9.9	-1.6	yes
L037	12.40	1.60	0.1	0.1	yes
L039	12.30	0.45	-0.1	0.0	yes
L040-A	10.78	0.08	-29.0	-1.2	yes
L040-B	11.80	0.11	-7.9	-0.4	yes
L041	11.50	0.70	-2.3	-0.7	yes
L043	12.70	0.60	1.3	0.3	yes
L044	12.40	1.86	0.1	0.1	yes
L045	13.00	0.20	6.5	0.6	yes
L046	12.30	0.80	0.0	0.0	yes
L047	11.70	2.50	-0.5	-0.5	yes
L048-B	12.80	0.10	8.0	0.4	yes
L048-C	12.63	0.39	1.6	0.3	yes
L049	12.04	0.33	-1.6	-0.2	yes
L050	11.90	1.19	-0.7	-0.3	yes
L051	12.06	0.14	-3.2	-0.2	yes

<b>Lead</b>					
<b>Lab</b>	$\gamma_i(\text{Pb})$	$U(\gamma)$	$E_n$	$z$	$U(\gamma)$
<b>Code</b>	$\mu\text{g/L}$	$\mu\text{g/L}$	<b>1</b>	<b>1</b>	$\leq U_{\text{max}}$
L052	13.90	n.r.	46.0	1.3	yes
L053	12.50	n.r.	5.4	0.2	yes
L054	13.60	1.00	2.6	1.0	yes
L055	12.10	0.20	-2.0	-0.2	yes
L056	10.85	n.r.	-42.4	-1.2	yes
L057	12.21	0.42	-0.5	-0.1	yes
L058	10.00	n.r.	-67.0	-1.9	yes
L059	12.30	1.55	0.0	0.0	yes
L060	12.80	1.00	1.0	0.4	yes
L061	12.00	1.00	-0.6	-0.3	yes
L062	11.60	0.40	-3.5	-0.6	yes
L063	10.34	4.55	-0.9	-1.6	no
L065	12.73	1.91	0.4	0.3	yes
L066	12.50	3.00	0.1	0.2	yes
L067	13.00	2.00	0.7	0.6	yes
L068	12.19	1.58	-0.2	-0.1	yes
L069	12.20	0.80	-0.3	-0.1	yes
L070	11.40	1.30	-1.4	-0.7	yes
L071	12.29	0.30	-0.1	0.0	yes
L073	11.60	0.23	-5.9	-0.6	yes
L074	12.41	1.24	0.2	0.1	yes
L075	11.88	0.05	-10.2	-0.4	yes
L076	11.40	0.40	-4.5	-0.7	yes
L077	12.94	1.30	1.0	0.5	yes
L078	13.50	2.20	1.1	1.0	yes
L079	11.50	2.90	-0.6	-0.7	yes
L080	9.70	1.90	-2.7	-2.1	yes
L081	12.30	0.10	-0.2	0.0	yes
L082	13.00	3.00	0.5	0.6	yes
L083	11.70	1.20	-1.0	-0.5	yes
L084	12.00	1.00	-0.6	-0.3	yes
L085	12.00	1.92	-0.3	-0.3	yes
L086	12.00	0.84	-0.7	-0.3	yes
L087	11.60	n.r.	-20.7	-0.6	yes
L088	13.00	0.91	1.5	0.6	yes
L089	18.10	1.70	6.8	4.7	yes

<b>Lead</b>					
<b>Lab</b>	$\gamma_i(\text{Pb})$	$U(\gamma_i)$	$E_n$	$z$	$U(\gamma_i)$
<b>Code</b>	$\mu\text{g/L}$	$\mu\text{g/L}$	<b>1</b>	<b>1</b>	$\leq U_{\text{max}}$
L090	12.20	5.00	0.0	-0.1	no
L091	11.90	1.10	-0.7	-0.3	yes
L092	13.74	1.10	2.6	1.2	yes
L093	12.19	2.15	-0.1	-0.1	yes
L094	11.70	n.r.	-17.8	-0.5	yes
L095	12.60	0.69	0.8	0.2	yes
L096	12.83	1.01	1.0	0.4	yes
L097	13.00	1.17	1.2	0.6	yes
L098	13.00	1.56	0.9	0.6	yes
L099	12.30	n.r.	-0.4	0.0	yes
L100	12.00	1.20	-0.5	-0.3	yes
L101	9.02	1.54	-4.3	-2.7	yes
L103	12.09	0.10	-3.9	-0.2	yes
L104	12.29	0.14	-0.3	0.0	yes
L105	11.89	0.20	-4.0	-0.3	yes
L106	12.38	0.21	0.6	0.1	yes
L107	12.10	0.91	-0.5	-0.2	yes
L108	12.50	0.56	0.7	0.2	yes
L109	11.70	1.17	-1.0	-0.5	yes
L110	12.43	0.75	0.3	0.1	yes
L111	11.80	2.36	-0.4	-0.4	yes
L112	10.20	3.99	-1.1	-1.7	no
L113	8.69	0.90	-8.0	-2.9	yes
L114	36.17	3.30	14.5	19.4	yes
L115	11.80	1.70	-0.6	-0.4	yes
L116	11.70	0.92	-1.3	-0.5	yes
L117	6.00	0.40	-31.1	-5.1	yes
L118	10.87	0.23	-12.0	-1.2	yes
L119	12.31	1.41	0.0	0.0	yes
L120	11.70	1.20	-1.0	-0.5	yes
L121	12.80	1.30	0.7	0.4	yes
L122	10.74	1.67	-1.9	-1.3	yes
L123	10.80	2.20	-1.4	-1.2	yes
L124	11.70	0.20	-5.8	-0.5	yes
L125	11.80	1.40	-0.7	-0.4	yes



### 10.6.5 Individual results and laboratory performance – mercury

In this report the individual results and performance data only in case of the obligatory mercury sample Hg-I are presented. Since the sample Hg-II through Hg-IV were voluntary and several participants reported that the measurements were carried out with less efforts and/or inferior methods the performance data would not be representative or even misleading.

*Table 19:* En- and z-scores calculated from the Hg mass concentrations  $\gamma_i$  and their associated expanded uncertainties  $U(\gamma_i)$  as reported by the participants in the order of their laboratory code numbers (only sample Hg-I is covered by the table). Interpretation of scores see table 15. Additionally, last column shows compliance with the “minimum performance criteria”, for more details refer to section 4. All quantities rounded to the same number of digits for the sake of clarity. Calculations were carried out with all digits reported. (n.r. = not reported).

<b>Mercury</b>					
<b>Lab Code</b>	<b><math>\gamma_i</math>(Hg) ng/L</b>	<b><math>U(\gamma_i)</math> ng/L</b>	<b><math>E_n</math> 1</b>	<b><math>z</math> 1</b>	<b><math>U(\gamma_i)</math> <math>\leq U_{\max}</math></b>
L001	70.7	1.6	-1.2	-0.2	yes
L002	72.7	1.9	0.2	0.0	yes
L003	67.7	4.1	-2.0	-0.7	yes
L004	81.0	7.1	2.3	1.2	yes
L005	69.9	3.4	-1.2	-0.3	yes
L006	60.9	4.0	-4.8	-1.6	yes
L007	74.1	1.7	1.1	0.2	yes
L008	70.0	1.6	-1.7	-0.3	yes
L010	60.7	6.0	-3.6	-1.6	yes
L011	82.0	16.4	1.2	1.3	yes
L012	62.3	4.3	-4.1	-1.4	yes
L014	66.5	6.7	-1.7	-0.8	yes
L015	52.9	7.9	-4.7	-2.7	yes
L016	110.0	10.0	7.3	5.2	yes
L021	73.6	11.0	0.2	0.2	yes
L022	63.2	3.3	-4.5	-1.3	yes
L023	70.6	10.4	-0.3	-0.3	yes
L025	78.2	3.7	2.6	0.8	yes
L027	65.8	10.7	-1.2	-0.9	yes
L028	52.8	7.9	-4.7	-2.7	yes
L029	200.0	100.0	2.6	17.6	no
L031	59.4	1.9	-8.4	-1.8	yes
L032	123.0	6.6	14.3	7.0	yes
L033	42.0	4.2	-12.4	-4.2	yes
L034	125.0	10.4	9.8	7.3	yes

<b>Mercury</b>					
<b>Lab</b>	$\gamma_i(\text{Hg})$	$U(\gamma)$	$E_n$	$z$	$U(\gamma)$
<b>Code</b>	<b>ng/L</b>	<b>ng/L</b>	<b>1</b>	<b>1</b>	$\leq U_{\max}$
L035	71.7	8.7	-0.2	-0.1	yes
L036	65.6	5.2	-2.4	-0.9	yes
L038	76.0	13.0	0.5	0.5	yes
L041	57.5	9.0	-3.2	-2.1	yes
L043	70.0	25.0	-0.2	-0.3	yes
L049	53.3	8.1	-4.5	-2.6	yes
L051	78.7	3.3	3.0	0.9	yes
L052	62.5	13.6	-1.4	-1.4	yes
L054	72.0	13.0	-0.1	-0.1	yes
L055	54.2	1.4	-12.7	-2.5	yes
L057	73.9	2.0	0.9	0.2	yes
L059	69.0	30.4	-0.2	-0.5	no
L060	59.0	26.0	-1.0	-1.9	no
L061	48.7	10.1	-4.6	-3.3	yes
L062	47.0	2.0	-15.8	-3.5	yes
L063	69.6	30.6	-0.2	-0.4	no
L065	66.5	5.3	-2.0	-0.8	yes
L066	85.5	13.0	2.0	1.8	yes
L067	77.0	18.0	0.5	0.6	yes
L069	70.1	13.4	-0.3	-0.3	yes
L071	84.8	21.2	1.2	1.7	yes
L075	72.0	23.0	0.0	-0.1	yes
L077	71.9	2.7	-0.3	-0.1	yes
L079	37.2	5.0	-12.6	-4.9	yes
L080	115.0	22.0	3.8	5.9	yes
L082	83.3	25.0	0.9	1.5	yes
L083	57.0	8.6	-3.5	-2.1	yes
L084	73.3	9.1	0.2	0.1	yes
L085	80.0	16.0	0.9	1.0	yes
L086	98.0	9.8	5.1	3.5	yes
L088	70.1	5.6	-0.8	-0.3	yes
L094	43.0	n.r.	-23.4	-4.1	yes
L095	64.0	5.0	-3.0	-1.2	yes
L096	72.0	11.2	-0.1	-0.1	yes
L097	61.0	7.3	-3.0	-1.6	yes
L098	120.0	12.0	7.8	6.6	yes

<b>Mercury</b>					
<b>Lab</b>	<b><math>\gamma_i(\text{Hg})</math></b>	<b><math>U(\gamma)</math></b>	<b><math>E_n</math></b>	<b><math>z</math></b>	<b><math>U(\gamma)</math></b>
<b>Code</b>	<b>ng/L</b>	<b>ng/L</b>	<b>1</b>	<b>1</b>	<b><math>\leq U_{\max}</math></b>
L100	69.0	10.4	-0.6	-0.5	yes
L102	69.3	2.9	-1.7	-0.4	yes
L103	66.5	2.1	-3.6	-0.8	yes
L104	70.8	1.0	-1.2	-0.2	yes

## 10.7 Statistics

A large number of laboratories across Europe responded positively to the invitation to participate in the Euramet 924 part 3 comparison. They were free to register for all elements or for just selected ones. Table 20 shows a compilation of the numbers.

*Table 20:* Number of registered participants  $N_{\text{reg}}$  of Euramet 924 part 3 and CCQM-K70/CCQM-P100.3 (NMI), grouped by elements E, in total and divided into national metrology institutes (NMI) and Euramet participants (PCL plus TL). Number of results submitted  $N_{\text{sub}}$  and fraction  $\phi$  of results submitted ( $\phi = N_{\text{sub}} / N_{\text{reg}}$ ).

E	$N_{\text{reg}}$			$N_{\text{sub}}$ total	$\phi$ %
	NMI	Euramet	total		
Cd	} 3	} 116	} 119	96	81
Ni				113	95
Pb				113	95
Hg	11	91	102	65	64
-----					
Hg-II				26	
Hg-III	voluntary additional samples			31	not applicable
Hg-IV				26	

Since the result of a measurement is rather meaningless without a stated uncertainty, all participants were asked to report the uncertainties associated with their results. Table 21 shows an overview of the number of laboratories which did not report their uncertainties.

*Table 21:* Number of laboratories which submitted results  $N_{\text{sub}}$  but no associated uncertainties  $N_{\text{noMU}}$ . Fraction  $\phi$  denotes the percentage of results reported without uncertainties ( $\phi = N_{\text{noMU}} / N_{\text{sub}}$ ).

E	$N_{\text{sub}}$	$N_{\text{noMU}}$	$\phi$ %
Cd	96	8	8
Ni	113	10	9
Pb	113	10	9
Hg	65	1	1.5
-----			
Hg-II	26	0	0
Hg-III	31	1	3
Hg-IV	26	0	0

Based on the En- and z-scores as defined in equations 12-14 and taking into account the criteria boundaries from table 15 as well as the maximum uncertainty requirement (section 4), all results reported were grouped into three categories: satisfactory, questionable and unsatisfactory results. Table 22 shows a summary of all elements depending on whether the En- or the z-score was used to assess the data. See also figures 20, 22, 25 and 28.

*Table 22:* Fractions  $\phi(c) = N(c)/N_{\text{sub}}$  of satisfactory ( $c = "+"$ ), questionable ( $c = "?"$ ) and unsatisfactory ( $c = "-"$ ) mass concentration results of the element E as reported by the participants. The En-score decreases the fractions of satisfactory results dramatically in case of all elements when compared to the z-score. In addition to the scores, the maximum uncertainty requirement was applied according to section 4. Fractions may not add up to 100 % because of rounding errors.

E	En-score			z-score		
	$\phi(+)$ %	$\phi(?)$ %	$\phi(-)$ %	$\phi(+)$ %	$\phi(?)$ %	$\phi(-)$ %
Cd	63.6	10.1	26.3	83.8	7.1	9.1
Ni	66.4	9.5	24.1	90.5	6.0	3.4
Pb	64.3	5.2	30.4	89.6	3.5	7.0
Hg	47.7	7.7	44.6	67.7	9.2	23.1

## 11. Discussion

Since no significant method-dependency of the results was observable, it seems that experienced laboratories applying methods known to generate biased results are well aware of this fact and correct their results accordingly. On the other hand even the most robust and bias-free method is no guarantee for accurate results.

The potential calibration laboratories (PCL) performed without any exception better than the testing laboratories (TL). This can be clearly derived from the experimental standard deviations  $s$ , characterizing the arithmetic means. The PCLs showed standard deviations significantly smaller (up to 8 times) than those calculated for the TLs. See table 23 for details.

*Table 23:* Ratio  $r$  of the performance parameter relative standard deviation  $s/\bar{x}$  of the results reported by the potential calibration laboratories (PCL) and testing laboratories (TL).

E	$s/\bar{x}$		$r$
	%		
	PCL	TL	1
Cd	15	39	2.6
Ni	3.3	12.3	3.7
Pb	2.9	23.3	8.0
Hg	12	38	3.2

The deviations of the mean values from the reference values were insignificant for PCLs and TLs as well regarding all the elements, with one exception: Ni. In the case of Ni the mean values of PCL and TL were slightly smaller than the reference value. This effect was also observed in Euramet part 2 but not in part 1. Since from part 1 to part 2 the matrix was changed from pure water to surface water, this effect could be attributed to the natural water matrix.

Although a comparison of the results of Euramet 924 part 1 and part 2 with the results of part 3 is difficult, because of the different elemental contents in the sample and their different matrices, it seems as if the measurement performance of the PCLs was slightly improved.

The performance of the guest NMIs in case of Cd, Ni and Pb and the participants of CCQM-K70/CCQM-P100.3 (exclusively NMIs) in case of Hg is even better than that of the PCLs in terms of accuracy (deviation from the reference value) and precision (standard deviation of the respective arithmetic mean). This way, the link between PCLs and NMIs established in part 1 and 2 of the Euramet 924 comparison, was again confirmed.

Table 20 suggests to some degree a decreasing percentage of results submitted by registered laboratories parallel to the decreasing mass concentration. The conclusion seems obvious that with increasing difficulties the percentage of submitted results decreases. Figure 29 tries to illustrate this interrelation. On the other hand, those laboratories capable of managing even more difficult tasks show a larger percentage of reported uncertainties (table 21).

To assess the data in a more formal way compared with part 1 and 2 of this Euramet 924 study was important, since the large number of testing laboratories used this comparison to evaluate their capabilities with respect to the requirements of the WFD.

Therefore, three different scoring schemes were applied:

First, En-scores combined with an upper uncertainty limit: From the metrological viewpoint this scoring scheme is the most reasonable, because it takes into account the reference value and its associated uncertainty as well as the uncertainties reported by the participants. Therefore, in every single case the deviation from the reference value is compared to the uncertainty associated with this deviation (consisting of the two uncertainty contributions mentioned before) in order to check whether the deviation is significant or not. A participant reporting a very large uncertainty is always on the safe side, because even large deviations from the reference value will be insignificant and the result reported will thus be satisfactory. To define an upper uncertainty limit beforehand (as done in this comparison) will avoid such a behaviour effectively. This scoring scheme produced in the case of Cd, Ni and Pb around 2/3 satisfactory and 1/4 unsatisfactory results. Therefore approximately 3/4 of the participants would have been assessed to be able to carry out the measurements under the WFD. Looking at Hg, approximately 1/2 satisfactory and unsatisfactory results were submitted. Taking into account the clearly smaller number of participants, this seems to suggest a certain need for further improvements of the measurement capabilities of the testing laboratories. With regard to all 4 elements the Naji-plots (figures 18, 21, 23 and 26) showed several participants which overestimated their uncertainties even though their deviations from the reference value (expressed in terms of  $Z$ ) are very small. These participants should consider revising their way of estimating uncertainties in order to reflect the fact that they perform actually much better than their reported uncertainties would suggest.

Second, z-scores combined with an upper uncertainty limit: As discussed in section 10.6 the deviation from the reference value was compared to a flat 10 % standard deviation disregarding the uncertainties reported by the participants as well as the uncertainty associated with the reference value (in this case insignificant with respect to the 10 %). Since obviously a certain amount of participants tends to underestimate their uncertainties, this scoring scheme produced a larger fraction of satisfactory results, namely around 90 % in the case of Cd, Ni and Pb. This fraction drops down to 68 % satisfactory results in case of Hg. The gap between the ability to measure Hg and the ability to measure Cd, Ni and Pb is retained. When considering the smaller number of participants feeling capable of measuring Hg, the smaller fraction of satisfactory results seems even more dramatic. While most testing laboratories are able to measure Cd, Ni and Pb under the WFD, in the case of Hg there is still some room left for improvements.

Third, z-scores without taking the upper uncertainty limit into account: Very similar to the second scoring scheme, this scheme used z-scores to assess the data, but the results mentioned above (small  $Z$ , large  $U$ ) were interpreted as satisfactory also. This scoring scheme was used as the basis of the individual certificates issues together with this report.

Summarizing all observations, part 3 of the Euramet 924 comparison was an important step to establish traceability of measurement results to ensure the comparability as required in the WFD. At the same time it served as an opportunity for all testing laboratories to assess their capabilities with respect to the requirements of the WFD.

The performance of the PCLs was slightly improved compared with part 1 and 2 of Euramet 924. This obviously underpins the established up-link of the PCLs and shows their ability to act as multipliers in a European traceability chain.

The results confirm the applicability of a hierarchic dissemination structure as proposed in the Euramet project 924. Obviously, the PCLs proved to be laboratories having appropriate measurement capabilities to take over the responsible task to be the intermediate level in a metrological dissemination system. Such a system provides essential advantages and could be the key to meeting the requirements of the WFD concerning comparability of the measurement results used for the assessment of water and would additionally provide sustainability as long as the testing laboratories are obliged to participate regularly in PT schemes.

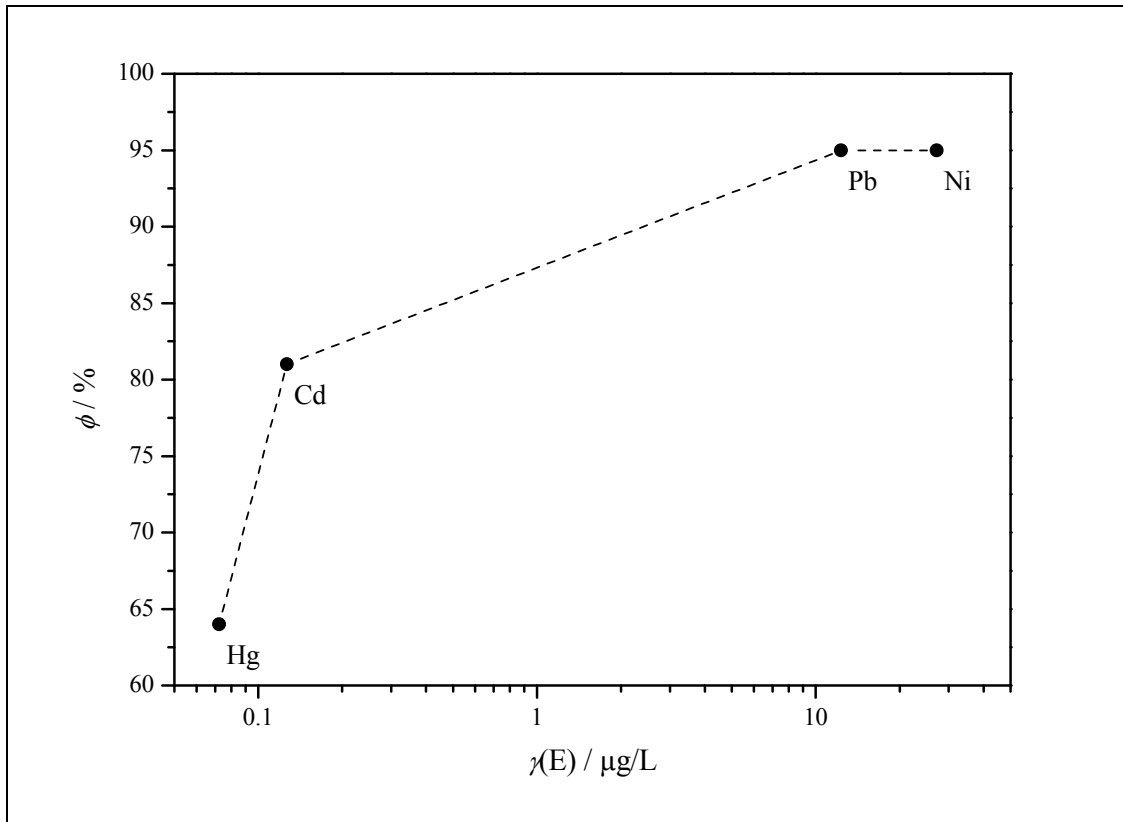


Figure 29: The percentage  $\phi$  of results submitted by registered participants decreases with increasing difficulties (decreasing mass concentration  $\gamma$  of the element E).



## 12. References

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- [2] Annex I: Environmental Quality Standards for Priority Substances and certain other Pollutants *in*: Proposal for a Directive of the European Parliament and of the Council on Environmental Quality Standards in the field of water policy and amending Directive 2000/60/EC. (COM (2006) 397 final). [http://ec.europa.eu/environment/water/water-dangersub/surface\\_water.htm](http://ec.europa.eu/environment/water/water-dangersub/surface_water.htm)
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- [5] Olaf Rienitz, Detlef Schiel, Bernd Güttler, Michael Koch and Ulrich Borchers, *A convenient and economic approach to achieve SI-traceable reference values to be used in drinking-water interlaboratory comparisons*, *Accred Qual Assur* (2007) 12:615-622
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- [9] Dieter Richter, Wolfgang Wöger, Werner Hässelbarth (eds.), *Data analysis of key comparisons*, Braunschweig and Berlin, 2003, ISBN 3-89701-933-3.
- [10] Piotr Robouch, Naji Younes, Peter Vermaercke, The „Naji Plot“, a simple graphical tool for the evaluation of inter-laboratory comparisons *in*: Dieter Richter, Wolfgang Wöger, Werner Hässelbarth (eds.), *Data analysis of key comparisons*, Braunschweig and Berlin, 2003, ISBN 3-89701-933-3.
- [11] Technical Agreement of the Self-committed Network of PT Providers “PT-WFD” to Support the Implementation of the Water Framework Directive, 2<sup>nd</sup> official version, 2010-01-10.

## Appendix A

### Invitation for participation in the EURAMET comparison measurement

#### **„Trace elements in natural water at concentration levels required by the European Water Framework Directive 2000/60/EC (WFD) “**

Dear Colleagues,

The “European Association of National Metrology Institutes” (EURAMET) established a project organized by the National Metrology Institutes of France (LNE) and Germany (PTB and BAM). It aims at ensuring the metrological traceability of the measurements of inorganic priority substances under the WFD, carried out by monitoring laboratories. The traceability will be established by the National Metrology Institutes (NMI) or by recognised reference laboratories, acting as potential calibration laboratories (PCL) in different European countries. The project intends to demonstrate the comparability of measurement results issued by laboratories of a representative number of European Countries with the aid of a comparison measurement.

We kindly invite you as testing laboratory and expert in water analysis to participate in this comparison. Subject is the determination of heavy metal concentrations in ground water at levels required by WFD.

Please find further information, a questionnaire and the registration form on the next pages. If you intend to participate, please send the filled-in registration form and the filled-in questionnaire to the address specified on the registration form.

The data treatment will be performed in an anonymous way, and the participation of laboratories will be considered with confidentiality.

After the project being completed, a workshop will be organised in order to present the main conclusions and outputs of the comparison to the participating laboratories.

Thank you for your collaboration.

Best regards.

## Additional technical information

<i>Subject:</i>	Measurement of the inorganic priority substances Hg, Cd, Ni and Pb in a natural ground water
<i>Samples:</i>	Two bottles will be provided, a glass bottle (250ml) containing Hg stabilized with BrCl and a PE bottle (100ml) for the other elements acidified with nitric acid
<i>Target concentrations:</i>	Hg (30 - 70) ng/l Cd (50 - 100) ng/l Ni (10 - 30) µg/l Pb ( 4 - 20) µg/l
<i>Target uncertainties:</i>	≤ 30 % of the EQS values
<i>Number of participants:</i>	Limited to about 20 participants per country. Therefore a selection of laboratories might be necessary. Registered laboratories will be informed about their participation by the end of October 08.
<i>Certificate</i>	Each laboratory will get a certificate about its participation after completion of the measurements
<i>Cost:</i>	Participation is free of charge

## Timeschedule

<i>Deadline for registration:</i>	<b>by 31. September 2008</b>
<i>Distribution of the samples:</i>	January 2009
<i>Deadline for submission of the results:</i>	by 31. March 2009

## Organization

EURAMET:	Physikalisch -Technische Bundesanstalt (PTB) Detlef Schiel Bundesallee 100, 38116 Braunschweig, Germany Tel: +49 531 5923110, Fax: +49 531 5923015 <a href="mailto:detlef.schiel@ptb.de">detlef.schiel@ptb.de</a> , <a href="http://www.ptb.de/">http://www.ptb.de/</a>
	Laboratoire National de Métrologie et d'essais (LNE), Paola Fiscaro LNE, 1, rue Gaston Boissier, 75724 Paris Cedex 15, France Tél: +33 1 40 43 37 59, Fax: +33 1 40 43 37 37, <a href="mailto:paola.fiscaro@lne.fr">paola.fiscaro@lne.fr</a> , <a href="http://www.lne.fr/">http://www.lne.fr/</a>
	Bundesanstalt für Materialforschung und -prüfung (BAM) Holger Scharf Richard-Willstätter Straße 11, 12489 Berlin, Germany Tel: +49 30 8104 1114, Fax:+49 3081041107, <a href="mailto:holger.scharf@bam.de">holger.scharf@bam.de</a> , <a href="http://www.bam.de/">http://www.bam.de/</a>
	EURAMET: <a href="http://www.euramet.org/index.php?id=homepage">http://www.euramet.org/index.php?id=homepage</a>
Regional:	PCL or NMI of your country

## Questionnaire

If you are interested to participate in the comparison, please fill in this questionnaire and registration form and send them together to address specified below:

	<b>Yes</b>	<b>No</b>
Do you measure samples from chemical monitoring activities related to the Water Framework Directive?	<input type="checkbox"/>	<input type="checkbox"/>
Do you measure the elements regarded here routinely?	<input type="checkbox"/>	<input type="checkbox"/>
How many measurements of these four elements are you performing the year? (Please enter the number)	<input style="width: 100px; height: 20px;" type="text"/>	
In how many PT schemes for these elements do you participate the year? (Please enter the number)	<input style="width: 100px; height: 20px;" type="text"/>	
Is your laboratory accredited according to ISO 17025 for the measurement of the elements considered here?	<input type="checkbox"/>	<input type="checkbox"/>
Do you use traceable calibration material (provided with an uncertainty statement)?	<input type="checkbox"/>	<input type="checkbox"/>
Do you use matrix-matched calibration material?	<input type="checkbox"/>	<input type="checkbox"/>
Do you use internal standards?	<input type="checkbox"/>	<input type="checkbox"/>
Do you use certified matrix reference materials for verification?	<input type="checkbox"/>	<input type="checkbox"/>
Do you use standard addition for verification?	<input type="checkbox"/>	<input type="checkbox"/>
How do you estimate measurement uncertainties?		
According to GUM	<input type="checkbox"/>	<input type="checkbox"/>
According to Nordtest	<input type="checkbox"/>	<input type="checkbox"/>
According to ISO 21748	<input type="checkbox"/>	<input type="checkbox"/>

## Registration form

for the participation in the comparison measurement of the EURAMET project 924:  
 „Trace elements in natural water at concentration levels required by the European  
 Water Framework Directive 2000/60/EC (WFD) “

Measurand		Participation		Method of measurement
Element	Mass concentration	Yes	No	
Hg	30 - 70 ng/l			
Cd	50 - 100 ng/l			
Pb	4 - 20 µg/l			
Ni	10 - 30 µg/l			

<b>Contact person</b>	
<b>Institute</b>	
<b>Address</b>	
<b>Country</b>	
<b>Email</b>	
<b>Tel. Number</b>	
<b>Fax Number</b>	
<b>Date, Signature</b>	

Please return the filled-in registration form together with the filled-in questionnaire until **31. September 2008** to:

Physikalisch -Technische Bundesanstalt (PTB)  
 Detlef Schiel  
 Bundesallee 100, 38116 Braunschweig, Germany  
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## Appendix B

### CCQM-K70, CCQM-P100.3 and Euromet 924 (part 3)

„Trace elements in natural water at concentration levels required by the European Water Framework Directive 2000/60/EC (WFD)“

#### Technical Protocol

##### 1. Introduction

The present comparison belongs to the activities of the Euromet project 924 which serves to support the implementation of the EU water framework directive 2000/60/EC. The comparison is concerned with the determination of Hg, Cd, Ni, and Pb in natural water at concentration levels close to the EQS values defined by the WFD [1]. It succeeds the previous comparisons (CCQM-P100.1 / Euromet 924 (part 1) and CCQM-P100.2 / Euromet 924 (part 2), resp.) concerned with the determination of these element contents close to the EQS values in pure water samples and in a natural water matrix at concentration levels up to ten times the EQS values. Therefore, the present comparison combines the difficulties arising from a natural water matrix with those caused by low concentration levels. In contrast to Euromet 924 (part 3), both the pilot study CCQM-P100.3 and the key comparison CCQM-K70 will focus exclusively on the determination of the Hg concentration.

##### 2. Samples

Two different samples were prepared: One for the Hg determination and the second for the determination of Cd, Ni, and Pb. Each Euromet 924 participant will be provided both with a 250 mL glass bottle (Hg determination) and a 250 mL HD-PE bottle (Cd, Ni, and Pb determination). CCQM participants will just get the 250 mL glass bottle. There is no difference between the Euromet and the CCQM samples. All participants will also be provided with an additional 250 mL glass bottle containing a sample with a different Hg concentration (up to four times higher). The participants are kindly asked to determine also the Hg concentration of this additional sample. The results will be used to determine the Hg concentration of the original water sample prior to the Hg addition. This will be done in a way similar to a standard addition experiment [2]. The Hg concentration of the original water sample will be an important component of the reference value.

The samples were prepared by the “Rheinisch-Westfaelisches Institut für Wasser” (IWW), Muelheim an der Ruhr, Germany, from a carefully selected ground water. After filtration (pore size  $< 0.45 \mu\text{m}$ ) every desired elemental concentration was adjusted by adding volumetrically the necessary amount of a gravimetrically prepared monoelemental stock solution. These monoelemental stock solutions were primary solutions [3] prepared at the PTB, and serve to ensure traceability. To stabilize the element(s) of interest, all samples contain  $\text{HNO}_3$  ( $\approx 0.005 \text{ g/g} = 0.5 \%$ ), the samples intended for the determination of Hg additionally contain  $\text{K}_2\text{Cr}_2\text{O}_7$  (50 mg/L).

Their stability was tested and can be guaranteed for the duration of two months. Therefore it is advisable to perform the Hg measurement shortly after the receipt of the samples.

**All participants are asked to report the receipt of their samples via e-mail (contact Detlef Schiel or in case of French participants contact your local provider). Please report also the condition of your samples at the time of receipt. Damaged bottles will be replaced immediately.**

Table 1: Approximate composition of the natural water matrix determined on a prior sample from the same origin (note that the stabilizers used will change particularly pH, Cr and nitrate values). In terms of hardness the sample belongs to “Class 3” according to the WFD.

Parameter	Unit	Result
Conductivity (20°C)	µS/cm	211
pH at 10.5 °C		6.31
Absorbance at 254 nm	1/m	0.62
Oxygen	mg/l	7.4
Calcium	mg/l	20.6
Magnesium	mg/l	4.9
Sodium	mg/l	12.9
Potassium	mg/l	1.2
Fluoride	mg/l	< 0.10
Chloride	mg/l	13.3
Nitrate	mg/l	28.9
Sulphate	mg/l	37.4
HCO <sub>3</sub> <sup>-</sup>	mmol/l	0.37
Nitrite	mg/l	< 0.020
Ammonium	mg/l	< 0.020
ortho-Phosphate	mg/l	< 0.10
Arsenic	mg/l	< 0.00050
Chromium	mg/l	< 0.0010
Aluminium	mg/l	< 0.010
Iron	mg/l	< 0.010
Manganese	mg/l	< 0.010
Total cyanide	mg/l	< 0.010
Dissolved Organic Carbon	mg/l	0.46

Table 2: Approximate mass concentrations of the elements of interest in the samples.

Element	Unit	Range
Hg	ng/L	30...70
Cd	ng/L	50...150
Ni	µg/l	10...30
Pb	µg/L	4...20

### 3. Analysis

All participants are encouraged to use their most sensitive and accurate methods. If available IDMS should be applied. Due to the low Hg content cold vapour techniques may be appropriate [4].

### 4. Reporting

**Deadline for the submission** of results is **27 March 2009**.

All participants will be provided with an Excel worksheet via e-mail. Please use this worksheet to report your results and additional information. If you encounter any problems using this worksheet, please contact Detlef Schiel.

Send all your results to the following address via e-mail:

Dr. Detlef Schiel  
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38116 Braunschweig  
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**CCQM only:** Please provide us additionally with information on the following items:

- Comprehensive uncertainty budget according to *GUM* [5]
- Single values of replicate samples/measurements (at least five)
- Density of the sample (result and its associated uncertainty), if needed

**French Euromet participants only:** Please send the Excel worksheet, containing your results and additional information, to your local provider.

### 5. References

- [1] Annex 1 of the Commission Proposal from 17 July 2006 (COM (2006) 397 final). [http://ec.europa.eu/environment/water/water-dangersub/surface\\_water.htm](http://ec.europa.eu/environment/water/water-dangersub/surface_water.htm)
- [2] Rienitz O, Schiel D, Güttler B, Koch M and Borchers U, *A convenient and economic approach to achieve SI-traceable reference values to be used in drinking-water interlaboratory comparisons*, *Accred Qual Assur* (2007) 12:615-622
- [3] Kipphardt H, Matschat R, Rienitz O, Schiel D, Gernand W, Oeter D, *Traceability system for elemental analysis*, *Accred Qual Assur* (2006) 10: 633-639
- [4] S J Christopher. S E Long. M S Rearick. and J D Fassett. *Development of Isotope Dilution Cold Vapor Inductively Coupled Plasma Mass Spectrometry and Its Application to the Certification of Mercury in NIST Standard Reference Materials*. *Anal Chem.* (2001) 73: 2190-2199.
- [5] *Guide to the Expression of Uncertainty in Measurement*. ISO. Geneva. 1993.



## Appendix C



### CCQM-K70, CCQM-P100.3 and Euramet 924 (part 3)

„Trace elements in natural water at concentration levels required by the European Water Framework Directive 2000/60/EC (WFD)“

## Technical Protocol for the Rerun of the Hg Trial (September 09)

### 1 Introduction

The present comparison belongs to the activities of the Euramet project 924 which serves to support the implementation of the EU water framework directive 2000/60/EC. The comparison is concerned with the determination of Hg, Cd, Ni, and Pb in natural water at concentration levels close to the EQS values defined by the WFD [1]. It succeeds the previous comparisons (CCQM-P100.1 / Euramet 924 (part 1) and CCQM-P100.2 / Euramet 924 (part 2), resp.) concerned with the determination of these elements in pure water samples close the EQS values and in a natural water matrix at concentration levels up to ten times the EQS values. Therefore, the present comparison combines the difficulties arising from a natural water matrix with those caused by the low levels close to the EQS values. In contrast to Euramet 924 (part 3), both the pilot study CCQM-P100.3 and the key comparison CCQM-K70 will focus exclusively on the determination of the Hg concentration.

Due to technical problems with the mercury samples in the first round (January 2009) the interlab trial is now repeated for mercury.

### 2. Samples

Only **one groundwater sample** is used both for the preparation of the Euramet 924 part 3 and the CCQM-K70/CCQM-P100.3 samples. All participants will be provided with a 250 mL DURAN glass bottle (Hg determination). There is no difference between the Euramet and the CCQM samples concerning the Hg content.

In addition to this, all participants will be provided with a 250 mL DURAN glass bottle containing a sample with a different Hg concentration (up to four times higher). The participants are kindly asked to determine also the Hg concentration of this additional sample. The results will be only used to determine the Hg concentration of the original water sample prior to the Hg addition. This will be done in a way similar to a standard addition experiment [2]. The Hg concentration of the original water sample will be an important component of the reference value.

The samples were prepared by the “Rheinisch-Westfaelisches Institut für Wasser” (IWW), Muelheim an der Ruhr, Germany, from a carefully selected ground water. After filtration (pore size < 0.45 µm) the desired elemental Hg concentration was adjusted by adding gravimetrically the necessary amount of a gravimetrically prepared monoelemental mercury stock solution. This monoelemental mercury stock solution is a primary solution [3] prepared at the PTB, and served to ensure traceability.

Although the stability of the samples is guaranteed until the deadline (as long as the stabilisation protocol is followed closely by the participant) it is advisable to perform the Hg measurement shortly after the receipt of the samples.

**All participants are asked to report the receipt of their samples via e-mail (contact Detlef Schiel or in case of French participants contact your local provider). Please report also the condition of your samples on the time of receipt. Damaged bottles will be replaced immediately.**

Table 1: Approximate composition of the natural water matrix determined on a prior sample from the same origin (note that the stabilizers used in the trial will change particularly pH, potassium and chloride values).

Parameter	Unit	Result
Conductivity (20°C)	µS/cm	457
pH		7.86
Oxygen	mg/l	7.3
Calcium	mg/l	44
Magnesium	mg/l	7.5
Sodium	mg/l	43
Potassium	mg/l	4.2
Fluoride	mg/l	0.12
Chloride	mg/l	49
Nitrate	mg/l	13
Sulphate	mg/l	46
HCO <sub>3</sub> <sup>-</sup>	mmol/l	2,32
Nitrite	mg/l	< 0.01
Ammonium	mg/l	< 0.01
Phosphate	mg/l	0.14
Arsenic	mg/l	0.0005
Chromium	mg/l	< 0.005
Aluminium	mg/l	0.002
Iron	mg/l	< 0.010
Manganese	mg/l	< 0.010
Total cyanide	mg/l	< 0.010
Total Organic Carbon	mg/l	0.64

Table 2: Approximate mass concentrations of the elements of interest in the samples.

Element	Unit	Range
Hg	ng/L	30...80

## 2.1 Stabilisation and pre-treatment of the samples

Due to the recent developments in the standardisation of the AAS Hg methods the sample stabilisation and pre-treatment is now adjusted to follow the new ISO/DIS 12846 “Water quality — Determination of mercury — Method using atomic absorption spectrometry (AAS) with and without enrichment”.

According to clause 7.4 of the draft standard the samples are just **acidified with 1 ml HCL ( $w(\text{HCl}) = 360 \text{ g/kg}$  ( $\rho(\text{HCl}) = 1,19 \text{ g/ml}$ ) per 100 ml** of the sample.

**This requires that on the arrival of the samples in the laboratory 2 ml potassium bromide - potassium bromate reagent (6.1.4) per 100 ml of the sample must be added.**

Allow the samples to rest for at least 24 h prior to analysis. If the yellow coloration due to free bromine does not persist during this period, add a further 1 ml of potassium bromide - potassium bromate reagent (6.1.4) and then allow another 24 h resting.

**The reagent can be prepared as follows (see ISO/DIS 12846)**

### **6.1.2 Potassium bromate solution, $c(\text{KBrO}_3) = 0,0333 \text{ mol/l}$ .**

Dissolve 1,39 g of potassium bromate in 250 ml of water (6.1.1). Potassium bromate can be purified, if necessary, by heating in a muffle furnace overnight at  $250 \text{ }^\circ\text{C} \pm 20 \text{ }^\circ\text{C}$ .

### **6.1.3 Potassium bromide solution, $c(\text{KBr}) = 0,2 \text{ mol/l}$ .**

Dissolve 5,95 g of potassium bromide in 250 ml of water (6.1.1). Potassium bromide can be purified, if necessary, by heating in a muffle furnace overnight at  $300 \text{ }^\circ\text{C} \pm 20 \text{ }^\circ\text{C}$ .

### **6.1.4 Potassium bromide - potassium bromate reagent**

Mix equal volumes of potassium bromate (6.1.2) and potassium bromide solution (6.1.3). A total volume of 200 ml will allow digestion for 100 samples.

NOTE pre mixed ampoules for potassium bromate-bromide stock solution are commercially available. This reagent has been found to contain negligible mercury concentrations.

The reagent may be stable for some days up to several weeks. This must be checked. The solution should be colourless.

## 3 Analysis

All participants are encouraged to use their most sensitive and accurate methods. If available IDMS should be applied. Due to the low Hg content cold vapour techniques may be appropriate [4].

## 4 Reporting

**Deadline for the submission of results is 16<sup>th</sup> November 2009.**

All participants will be provided with an Excel worksheet by e-mail. Please use this worksheet to report your results and additional information. If you encounter any problems using this worksheet, please contact Detlef Schiel.

Send all your results to the following address by e-mail:

Dr. Detlef Schiel  
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Bundesallee 100  
38116 Braunschweig  
Germany  
Fax: +49-531-592-3015  
e-mail: [detlef.schiel@ptb.de](mailto:detlef.schiel@ptb.de)

**CCQM only:** Please use also the attached form (Results Report) and provide us with the requested additional information (including an uncertainty budget according to the *GUM* [5]).

**French Euramet participants only:** Please send the Excel worksheet, containing your results and additional information, to your local provider.

## 5 References

- [1] Annex 1 of the Commission Proposal from 17 July 2006 (COM (2006) 397 final).  
[http://ec.europa.eu/environment/water/water-dangersub/surface\\_water.htm](http://ec.europa.eu/environment/water/water-dangersub/surface_water.htm)
- [2] Rienitz O, Schiel D, Güttler B, Koch M and Borchers U, *A convenient and economic approach to achieve SI-traceable reference values to be used in drinking-water interlaboratory comparisons*, *Accred Qual Assur* (2007) 12:615-622
- [3] Kipphardt H, Matschat R, Rienitz O, Schiel D, Gernand W, Oeter D, *Traceability system for elemental analysis*, *Accred Qual Assur* (2006) 10: 633-639
- [4] S J Christopher, S E Long, M S Rearick, and J D Fassett, *Development of Isotope Dilution Cold Vapor Inductively Coupled Plasma Mass Spectrometry and Its Application to the Certification of Mercury in NIST Standard Reference Materials*. *Anal Chem.* (2001) 73: 2190-2199.
- [5] *Guide to the Expression of Uncertainty in Measurement*. ISO. Geneva. 1993.