Final Report

EUROMET.QM-S2

“Determination of Hg[*], Cd, Pb and Ni in pure and natural water at concentration levels required by the European Water Framework Directive”

Organizers:

PTB	Physikalisch-Technische Bundesanstalt, Germany
BAM	Bundesanstalt für Materialforschung und -prüfung, Germany
EC-JRC-IRMM	Institute for Reference Materials and Measurements, European Commission
LNE	Laboratoire National de Métrologie et d'Essais, France

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[*] Hg was subject of parallel Euramet and CCQM pilot studies

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1. Summary

In the framework of the Euramet (former Euromet) project 924 a comparison measurement was performed for national metrology institutes (NMI) and expert laboratories (here called potential calibration laboratories, PCL) mostly from Europe. For the NMIs the part of this project on Ni, Cd and Pb measurements was registered as the supplementary comparison Euromet.QM-S2, while the part of this project on Hg was registered as the CCQM-P100.1/2 pilot study. This comparison was related with the implementation of the EU Water Framework Directive 2000/60/EC (WFD) [1] and served as an opportunity for the participants to verify the performance of their measurement procedures for the heavy metals Hg, Ni, Cd, Pb in water at concentration levels close to the environmental quality standards (EQS). The EQS were defined in the WFD for hazardous chemical substances of priority [2].

The comparison consisted of two parts using the following samples: An ultrapure water which was gravimetrically spiked with the elements mentioned above to a concentration level close to the EQS values and a natural water fortified with the elements to slightly higher concentrations than the EQS values. The measurement results confirmed the good measurement capability of the NMIs and expert laboratories as well even for the most challenging measurement of Hg. The standard deviation of the mean of all results did not exceed 9%.

2. Introduction

According to the WFD, compliance with the environmental quality standards has to be demonstrated for surface, ground and coastal/transitional waters of the EU member states by 2015. Furthermore, the WFD requires the use of comparable measurement results for the assessment of these waters.

The comparison described here was the first step of the Euramet (former Euromet) project 924 which is aiming at demonstrating that the globally recognised "International System of Units" (SI) and the well-established metrological infrastructure of the “Meter Convention” provides an appropriate metrological basis for realizing the required comparability of the measurement results. For this purpose a three level traceability system has been proposed. It consists of the national metrology institutes which provide the link with the SI, expert laboratories (PCL) on the intermediate level which act as multipliers in the dissemination, and on the third level routine laboratories which perform the surveillance measurements under the WFD. The link between these levels shall be realized by comparison measurements. The present comparison served to link the PCLs with the NMIs and to enable the PCLs to disseminate traceability to the routine laboratories. A second comparison which is currently in progress should realize the link of the PCLs with the routine laboratories. Furthermore the integration of national quality control structures into the proposed traceability system guaranties comprehensive involvement of concerned laboratories in the EU and sustainability of the proposed system at reasonable efforts and costs.

The Euramet project has been initiated on the Euramet meeting in Vilnius in February 2006. The comparison Euromet.QM-S2 was part of this project and was registered in the Key Comparison Data Base (KCDB) of the International Bureau of Weights and Measures (BIPM) in December 2006. It was a supplementary comparison and concerned with the measurement of the elements Ni, Cd and Pb. The measurement of

Hg was subject of a parallel pilot study also organized within the framework of the Euramet project 924. On the Euramet meeting 2007 in Lisbon the Inorganic Working Group of the Technical Committee “Metrology in Chemistry” (TCMC) of Euramet adopted the project including the comparison measurements after detailed discussions.

Parallel to that the pilot studies CCQM-P100.1 (pure water) and CCQM-P100.2 (natural water) of the Consultative Committee for Amount of Substance of the Meter Convention were performed. Subject of these comparisons was only the measurement of Hg. The same samples were used for the Euromet and CCQM pilot studies, as well. For completeness the results of both pilot studies are shown and discussed in this report.

In October 2008 the inorganic working group of CCQM was informed about the results of Euromet.QM-S2. The “Draft A Report” was distributed among the participating NMIs in January 2009 and discussed at the TCMC Euramet meeting in Bucharest in February 2009.

3. Comparison measurements and samples

Due to the analytical difficulties and in consideration of numerous inexperienced participants the comparison measurement was divided into two parts of increasing analytical demands:

Part 1 (pure water): Measurement of Hg, Ni, Cd and Pb in ultra pure water at concentration levels close to the EQS values (Hg: 0.05 µg/L, Ni: 20 µg/L, Cd: 0.08 µg/L, Pb: 7.2 µg/L). The elemental concentrations were adjusted by gravimetric addition of solutions of known elemental concentrations to an ultrapure water. For all elements gravimetric reference values were available. The Hg samples were provided in 500 ml glass bottles and the Ni, Cd and Pb samples in 100 ml PFA bottles. The stability of the samples was tested by Atomic Fluorescence Spectrometry (AFS) for Hg and by ICP-MS for the other elements. The samples were dispatched in May 2007. The deadline for the submission of the results was 31 July 2007. The samples were prepared by BAM and dispatched by PTB. Before starting part 2 of the comparison the participants were informed about the reference values of the pure water samples. This should allow them to optimize their measurement procedures prior to the beginning of the second part.

Part 2 (natural water): Measurement of Hg, Ni, Cd and Pb in natural water at concentration levels higher (2 - 10 times) than the EQS values. The higher concentrations were chosen in order to balance approximately the larger difficulties due to the more complex matrix of the natural water compared to that of the pure water. The natural water was filtered and gravimetrically fortified. Because of relatively high elemental concentrations in the unfortified natural water only for Hg a gravimetric reference value was available. The Hg samples were provided in 100 ml glass bottles. For the other elements 100 ml PFA bottles were used. Stability tests were performed by means of Isotope Dilution Mass Spectrometry (IDMS). The samples were dispatched in September 2007. Deadline for submission of the results was 30 November 2007. The sample preparation and dispatch were performed by LNE.

Both, natural and pure water Hg samples were stabilized with a BrCl-solution as described in the “EPA Method 1631” guideline [3]. The other samples were acidified by means of HNO_3 for stabilization. The stability of the elemental concentrations was ensured for the duration of two months. The homogeneity of the samples was tested by comparing several aliquots. There were no indications of inhomogeneities.

4. Participants

8 NMIs participated in Euromet.QM-S2 (table 2). Among them was a national metrology institute from outside the EU, the CMQ from Chile. Additionally 20 expert laboratories (PCLs) from 9 Euramet member states attended the comparison. There were 7 expert laboratories from Germany, 4 from France, 2 from Portugal and Israel and 1 from Hungary, Norway, Finland, Austria and Italy.

Table 1a: List of NMIs which participated in Euromet.QM-S2

National Metrology Institutes	Country	Contact
BAM Bundesanstalt für Materialforschung und -prüfung	Germany	Ralf Matschat, Holger Scharf
EC-JRC-IRMM Institute for reference materials and measurements	Europe	Christophe Quetel
LNE Laboratoire national de métrologie et d'essais	France	Guillaume Labarraque, Paola Fisicaro
PTB Physikalisch-Technische Bundesanstalt	Germany	Detlef Schiel
SP Technical Research Institute of Sweden	Sweden	Bertil Magnusson
INM National Institute of Metrology	Romania	Mirella Buzoianu
NCM National Center of Metrology	Bulgaria	Boryana Koleva
CMQ Chemical Metrology Center for Water and Foodstuffs	Chile	Gabriela Massiff

Table 1b: Number of NMIs and PCLs which measured the four elements in pure and natural water respectively.

Analyte	Pure water		Natural water	
	NMIs	**PCLs**	**NMIs**	**PCLs**
Hg	5	15	5	16
Ni	6	20	6	20
Cd	7	20	7	20
Pb	8	20	7	20

5. Instructions for the participants

Technical protocols were sent to all participants of Euromet.QM-S2 prior to sample distribution providing information about the samples, sample storage and the measurement method and instrumentation. A form for reporting the results and a list of additionally requested information of the participants was added.

For CCQM-P100.1 and CCQM-P100.2 the same protocols were attached (Appendix B).

6. 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 in order to separate the Hg from the matrix and to achieve sufficient sensitivity which was particularly important for the pure water samples. The methods and the instrumentation used by the NMIs were summarized in table 2. Among the expert laboratories ICP-MS and GFAAS were most commonly applied for the measurement of Ni, Cd and Pb. For Hg almost half of the participants used AFS.

Table 2: Methods and instrumentation used by the NMIs for the measurements; CV: cold vapour; ID: isotope dilution; ICP-MS: inductively coupled plasma mass spectrometry; AFS: atomic fluorescence spectrometry; ICP OES: inductively coupled plasma optical emission spectrometry; GFAAS: graphite furnace atomic absorption spectrometry

Participant	Hg	Ni	Cd	Pb
BAM	AFS	ICP-MS	ICP-MS	ICP-MS
IRMM	ID-CV-ICP-MS	-	ID-ICP-MS	ID-ICP-MS
LNE	ID-ICP-MS ID-CV-ICP-MS	ID-ICP-MS	ID-ICP-MS	ID-ICP-MS
PTB	ID-CV-ICP-MS	ID-ICP-MS	ID-ICP-MS	ID-ICP-MS
SP	ICP-MS	ICP OES	-	ICP OES
INM	-	GF AAS	GF AAS	GF AAS
NCM	-	ICP-MS	ICP-MS	ICP-MS
CMQ	-	-	ICP-MS	ICP-MS

7. Gravimetric reference values

The gravimetric reference values β_{grav} were calculated from the gravimetrically added amount of the elements β_{add} and the amount of the element in the non-spiked pure and natural water matrix β_{matrix}, respectively, according to the following equation:

$$\beta_{\text{grav}} = \beta_{\text{add}} + \beta_{\text{matrix}} \qquad (1)$$

The uncertainty associated with the gravimetric reference values resulted from the uncertainty contributions of the added amount u_{add}, of the measurement of the elemental content of the non-spiked pure and natural water u_{matrix}, and of the repeatability of the measurements performed for the determination of the stability and homogeneity $u_{\text{stability}}$ of the samples according to:

$$U(\beta_{\text{grav}}) = 2 \cdot \sqrt{u_{\text{add}}^2 + u_{\text{matrix}}^2 + u_{\text{stability}}^2} \qquad (2)$$

The standard uncertainties u_{add} and u_{matrix} include the contributions of the density of the solutions which had to be measured in order to convert mass fractions in mass concentrations. The gravimetric reference values are given e.g. in Table 3.

The measurement of the Hg concentration of the non-spiked pure water was performed at BAM by AFS and at PTB by ID-CV-ICP-MS. The unfortified natural water was measured at LNE by ID-CV-ICP-MS and at BAM by AFS and additionally at PTB and NRC by ID-CV-ICP-MS. For the other elements ICP-MS was used by both BAM and LNE. The results for Hg of the unfortified natural water matrix showed an unexplainable spread and made further measurements of retained samples necessary. Therefore the gravimetric reference value for the natural water samples reported here differs slightly from that presented at the IAWG meeting of the CCQM in Paris 2008. Furthermore its uncertainty got larger.

8. Results

The results of the participants as reported to the coordinating laboratory are shown in tables 4 to 7 and figures 1 to 4, respectively. The results of the NMIs are given in tables and an extra graph in order to make the discussion on mean and reference values easier. All uncertainties are expanded uncertainties (k = 2). In the figures black dots represent expert laboratories and red dots NMIs.

A supplementary comparison requires reference values of the measured quantity. For the pure water samples gravimetric values from the preparation of the samples were available for this purpose. For the natural water samples the arithmetic means of the NMIs and the associated expanded uncertainties calculated according to the GUM supplement 1 for type A evaluation [4] were used:

$$U(x_i) = \frac{\sqrt{n-1}}{\sqrt{n-3}} \cdot \frac{s(q_j)}{\sqrt{n}} \cdot k \qquad (1)$$

$s(q_j)$ is the standard deviation, n the number of results, and k the coverage factor.

The reference values are summarized in the following table.

Table 3: Summary of the reference values (* based on gravimetric values). The Hg reference values are included for the sake of completeness. Coverage factor $k = 2$.

Reference values	Pure water			Natural water		
	β µg L^{-1}	U µg L^{-1}	U_{rel} %	β µg L^{-1}	U µg L^{-1}	U_{rel} %
Ni	20.40*	0.43	2.1	40.33	0.63	1.6
Cd	0.2024*	0.0051	2.5	0.902	0.061	6.8
Pb	7.95*	0.17	2.1	23.6	1.8	7.7
Hg	0.0470*	0.0028	5.9	0.570*	0.028	5.0

For the discussion the degrees of equivalence D_i with respect to the reference values, their uncertainties $U_{i,}$ and the normalized errors $E_{n,j}$ were calculated (e.g. [6,7]):

$$D_i = x_i - x_{RV}$$

$$U_i(D_i) = 2 \cdot \sqrt{u^2(x_i) + u^2(x_{RV})}$$

$$E_{n,i} = \left| \frac{D_i}{U_i} \right|$$

The following assessment criteria were applied:

$E_n \leq 1$	no significant deviation
$E_n = 1 - 1.5$	intersection
$E_n > 1.5$	significant deviation

Two NMIs made statements to the organizers explaining some unusual deviations of their results from the reference values. The SP mentioned that its ICP-MS was not functional for the measurements of Ni and Pb and therefore the less sensitive ICPOES had to be used. Furthermore the INM informed the organizers prior to the comparison to be less experienced in the measurement of the elements regarded here. Both NMIs agreed to exclude their results from the calculation of the reference and mean values if they didn't meet the above mentioned assessment criteria.

8.1 Mercury

For completion the results of the Euramet and CCQM pilot studies of Hg were added here and discussed in section 9.1 although they were not subject of Euromet.QM-S2. Participants' names were replaced by the acronym NMI-1 to NMI-5.

8.1a Mercury in pure water

The gravimetric reference value for Hg in pure water was
β_{grav}= (0.0470 ± 0.0028) µg L^{-1}.

Table 4a: Results of the NMIs which participated in Euramet 924

Hg in pure water			
Participant	Result	Uncertainty	Coverage factor
	β(Hg) in µg L^{-1}	$U(\beta(Hg))$ in µg L^{-1}	*k* 1
NMI-1	0.0432	0.0032	2.0
NMI-2	0.0471	0.0020	2.0
NMI-3	0.0482	0.0016	2.0
NMI-4	0.04825	0.0024	2.0
NMI-5	0.0537	0.0027	2.0

Fig. 1a-1: Results of NMIs of CCQM-P100.1 (unlabelled data points) and Euramet 924 for Hg in pure water.

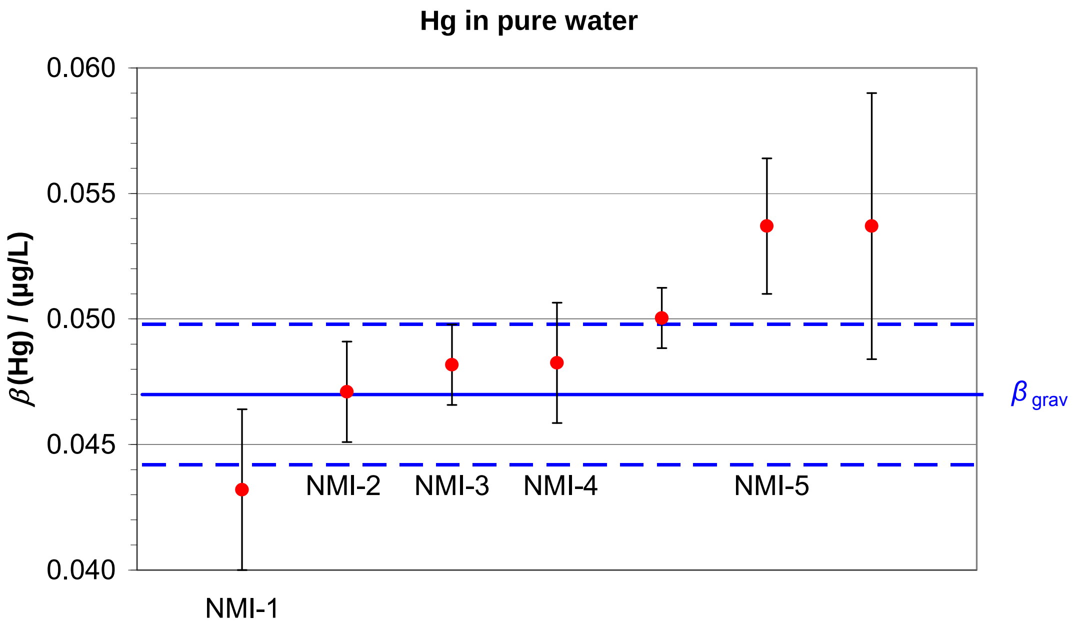
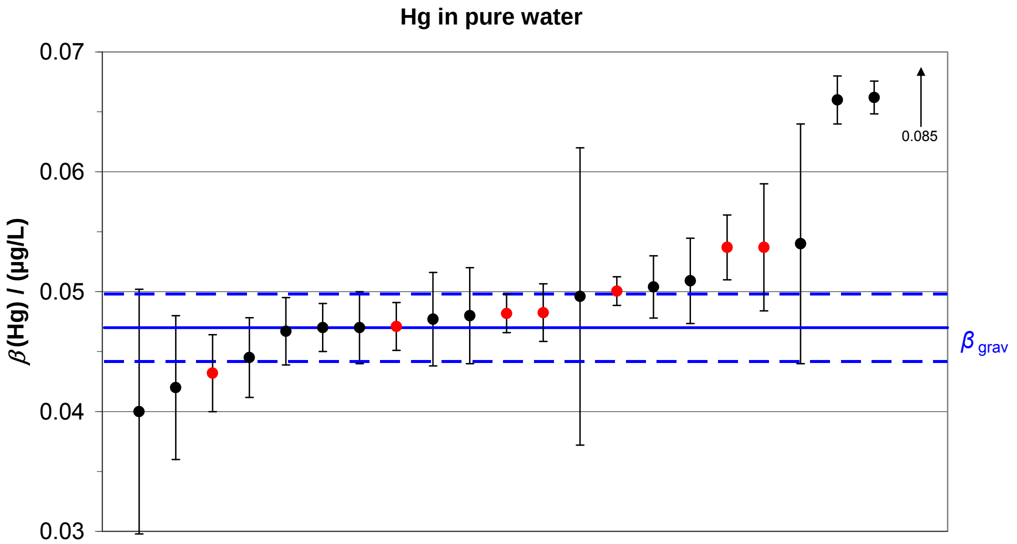


Fig. 1a-2: Results of all participants of CCQM-P100.1 and Euramet 924 for Hg in pure water.



8.1b Mercury in natural water

The gravimetric reference value for Hg in natural water was
$\beta_{\text{grav}} = (0.570 \pm 0.028)\ \mu\text{g L}^{-1}$.

Table 4b: Results of the NMIs which participated in Euramet 924.

Hg in natural water			
Participant	Result	Uncertainty	Coverage factor
	β (Hg) in µg L^{-1}	$U(\beta$ (Hg)) in µg L^{-1}	*k* 1
NMI-4	0.5551	0.038	2.0
NMI-3	0.5565	0.0073	2.0
NMI-2	0.573	0.006	2.0
NMI-1	0.597	0.041	2.0
NMI-5	0.657	0.076	2.0

Fig. 1b-1: Results of the NMIs of CCQM-P100.2 (unlabelled data points) and Euramet 924 part 2 for Hg in natural water.

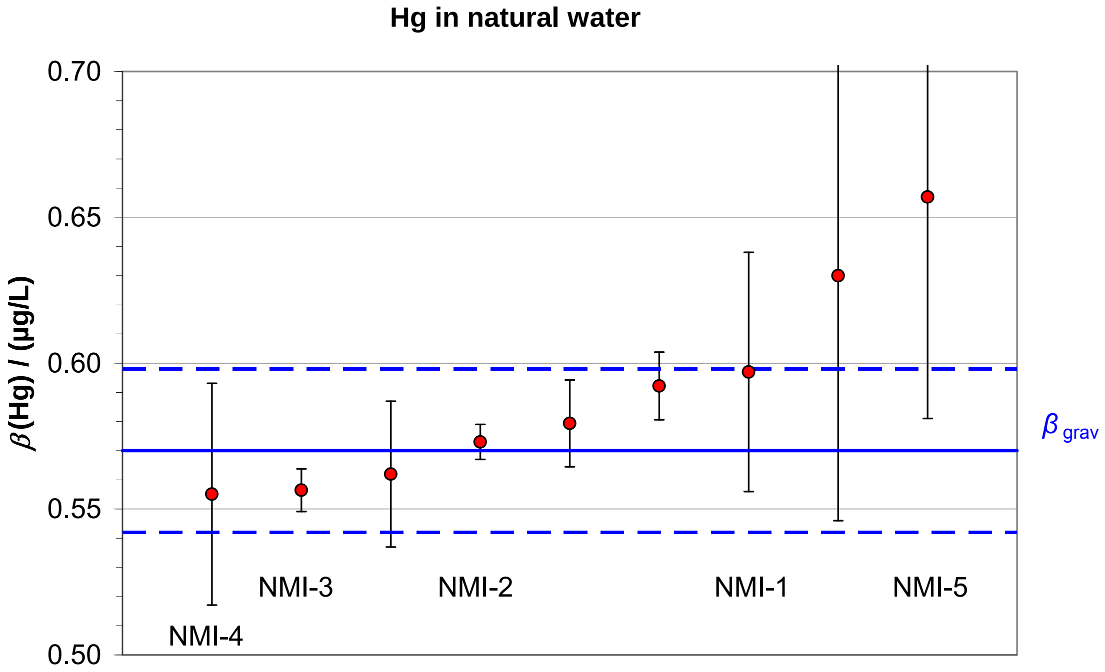
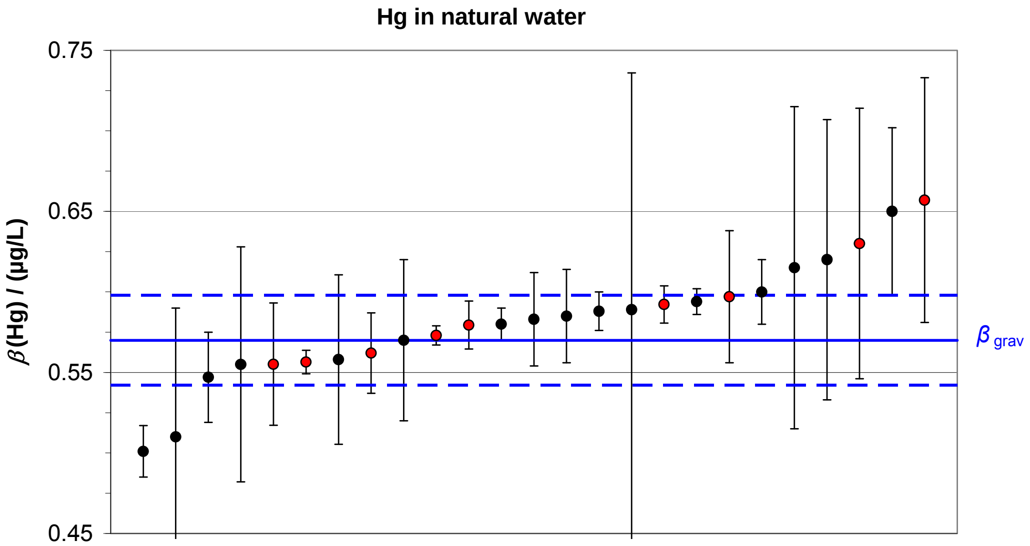


Fig. 1b-2: Results of all participants of CCQM-P100.2 and Euramet 924 for Hg in natural water.



8.2 Nickel

8.2a Nickel in pure water

The gravimetric reference value for the elemental concentration of Ni was $\beta_{\text{grav}} = \beta_{\text{RV}}$ = (20.40 ± 0.43) µg L^{-1}.

Table 5a: Results of the NMIs for the measurement of Ni in pure water

NMIs	Result	Uncertainty	Coverage factor	Degree of equi-valance	Uncertainty of D	Normalized error
	β (Ni) µg L^{-1}	$U(\beta$ (Ni)) µg L^{-1}	k 1	D_i µg L^{-1}	U_i µg L^{-1}	E_i
INM	17.165	1.205	2.0	3.24	1.28	2.53
SP	20.17	0.40	2.0	0.23	0.59	0.39
NCM	20.26	0.28	2.0	0.14	0.51	0.27
BAM	20.40	0.44	2.0	0.00	0.62	0.00
LNE	20.52	0.14	2.0	0.12	0.45	0.27
PTB	20.77	0.21	2.0	0.37	0.48	0.77

Fig. 2a-1: Results of the NMIs for the measurement of Ni in pure water.

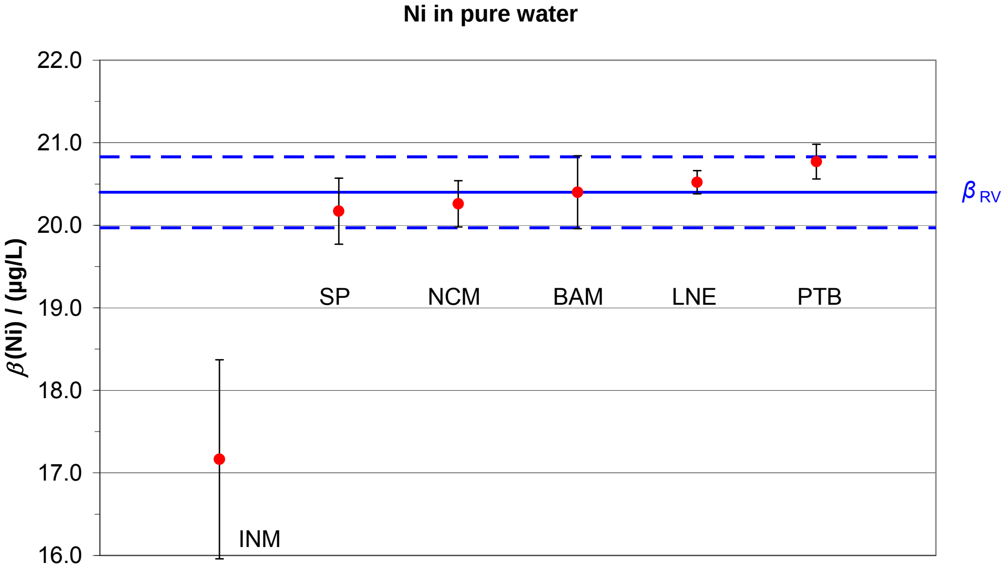
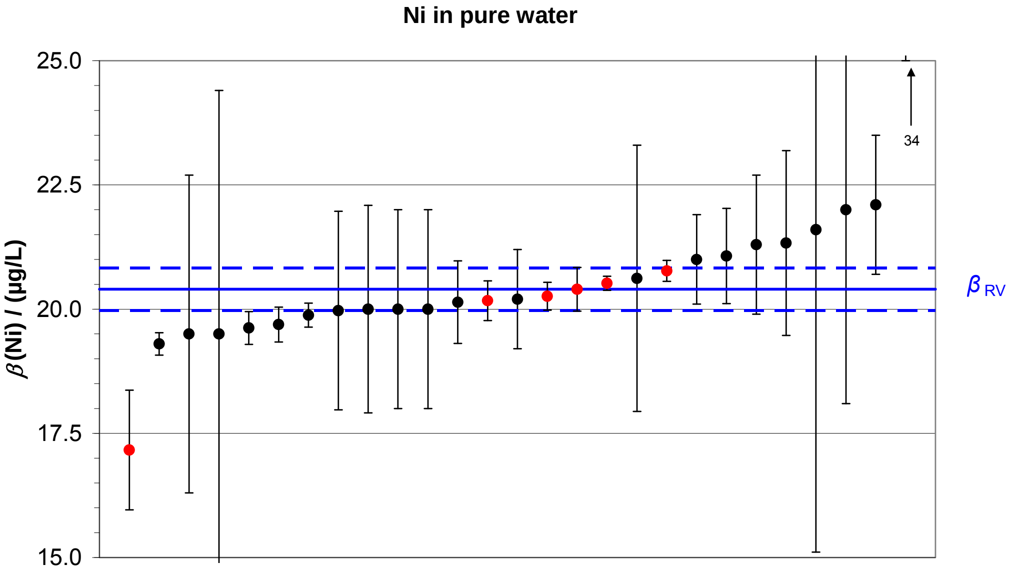


Fig. 2a-2: Results of all participants for the measurement of Ni in pure water.



8.2b Nickel in natural water

The arithmetic mean of the results of the NMIs served as the reference value $\beta_{\text{mean,NMIs}} = \beta_{\text{RV}}$ = (40.33 ± 0.63) µg L^{-1} (SP result not included in $\beta_{\text{mean,NMIs}}$).

Table 5b: Results of the NMIs for the measurement of Ni in natural water

NMIs	Result	Uncertainty	Coverage factor	Degree of equi-valance	Uncertainty of D	Normalized error
	β (Ni) µg L^{-1}	$U(\beta$ (Ni)) µg L^{-1}	k 1	D_i µg L^{-1}	U_i µg L^{-1}	E_i
SP	34.8	1.5	2.0	5.53	1.62	3.40
BAM	39.8	2.6	2.0	0.53	2.67	0.20
NCM	40.0	1.4	2.0	0.33	1.53	0.21
PTB	40.1	0.6	2.0	0.19	0.87	0.22
LNE	40.79	0.32	2.0	0.46	0.70	0.66
INM	40.91	3.04	2.0	0.58	3.10	0.19

Fig. 2b-1: Results of the NMIs for the measurement of Ni in natural water.

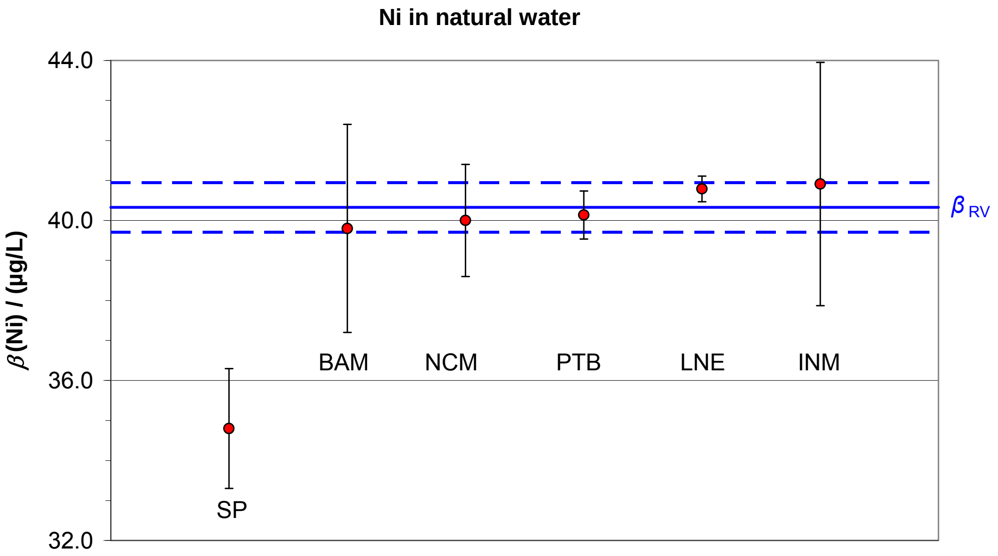
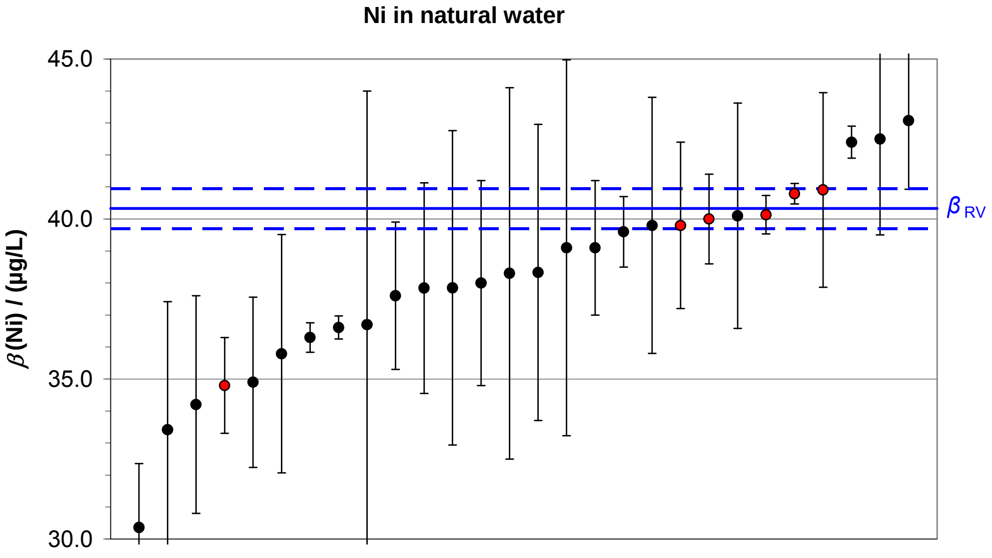


Fig. 2b-2: Results of all participants for the measurement of Ni in natural water.



8.3 Cadmium

8.3a Cadmium in pure water

The gravimetric value β_{grav} = (0.2024 ± 0.0051) µg L^{-1} for the elemental concentration of Cd served as the reference value β_{RV}.

Table 6a: Results of the NMIs for the measurement of Cd in pure water

NMIs	Result	Uncer-tainty	Coverage factor	Degree of equiva-lance	Uncer-tainty of D	Normali-zed error
	β (Cd) µg L^{-1}	$U(\beta$ (Cd)) µg L^{-1}	k 1	D_i µg L^{-1}	U_i µg L^{-1}	E_i
NCM	0.194	0.004	2.0	0.0084	0.0065	1.30
LNE	0.1948	0.0039	2.0	0.0076	0.0064	1.18
CMQ	0.201	0.004	2.2	0.0014	0.0065	0.22
EC-JRC-IRMM	0.2059	0.0048	2.0	0.0035	0.0070	0.50
BAM	0.2078	0.0062	2.0	0.0054	0.0080	0.67
PTB	0.208	0.004	2.1	0.0056	0.0065	0.86
INM	0.2129	0.0162	2.0	0.0105	0.0170	0.62

Fig. 3a-1: Results of the NMIs for the measurement of Cd in pure water

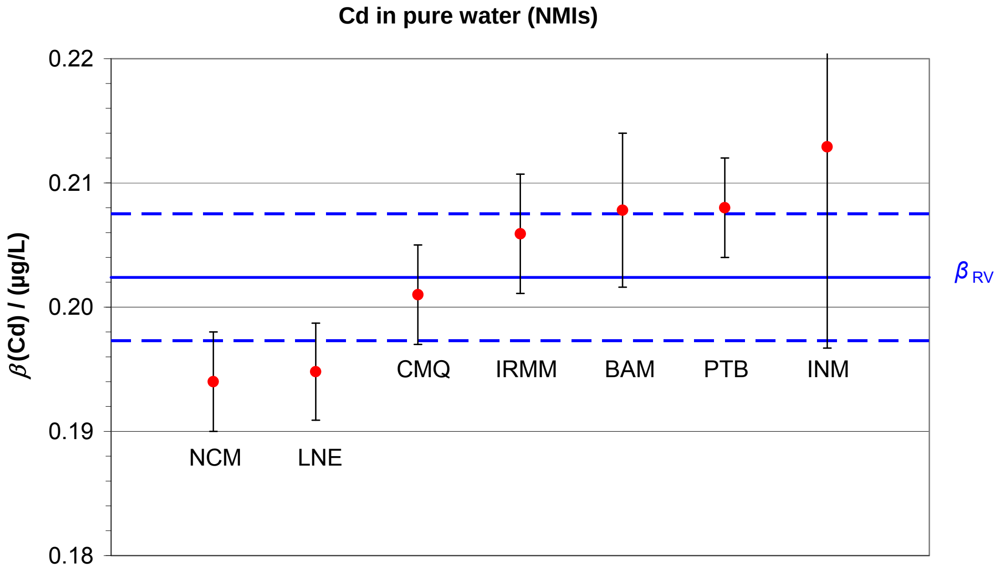
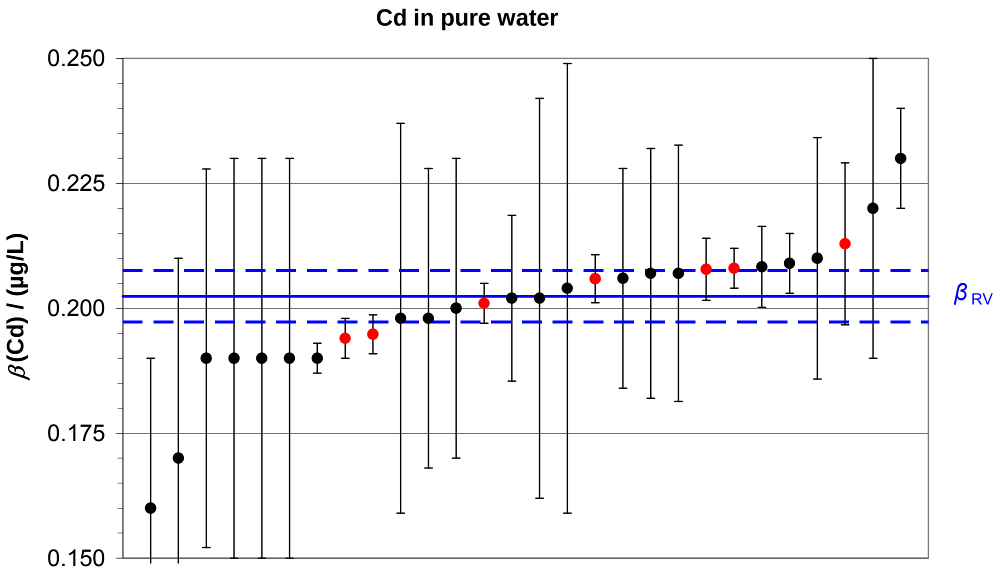


Fig. 3a-2: Results of all participants for the measurement of Cd in pure water



8.3b Cadmium in natural water

The arithmetic mean of the NMI results $\beta_{\mathrm{mean,NMIs}}$ was used as the reference value β_{RV} = (0.902 ±0.061) µg L^{-1}.

Table 6b: Results of the NMIs for the measurement of Cd in natural water

NMIs	Result	Uncertainty	Coverage factor	Degree of equiva-lance	Uncertainty of D	Normalized error
	β(Cd) µg L^{-1}	$U(\beta$ (Cd)) µg L^{-1}	k 1	D_i µg L^{-1}	U_i µg L^{-1}	E_i
INM	0.806	0.080	2.0	0.096	0.101	0.95
NCM	0.841	0.024	2.0	0.061	0.066	0.93
LNE	0.860	0.007	2.0	0.042	0.061	0.68
PTB	0.932	0.013	2.2	0.030	0.062	0.48
CMQ	0.945	0.018	2.2	0.043	0.064	0.68
EC-JRC-IRMM	0.946	0.017	2.0	0.044	0.063	0.69
BAM	0.984	0.057	2.0	0.082	0.084	0.98

Fig. 3b-1: Results of the NMIs for the measurement of Cd in natural water

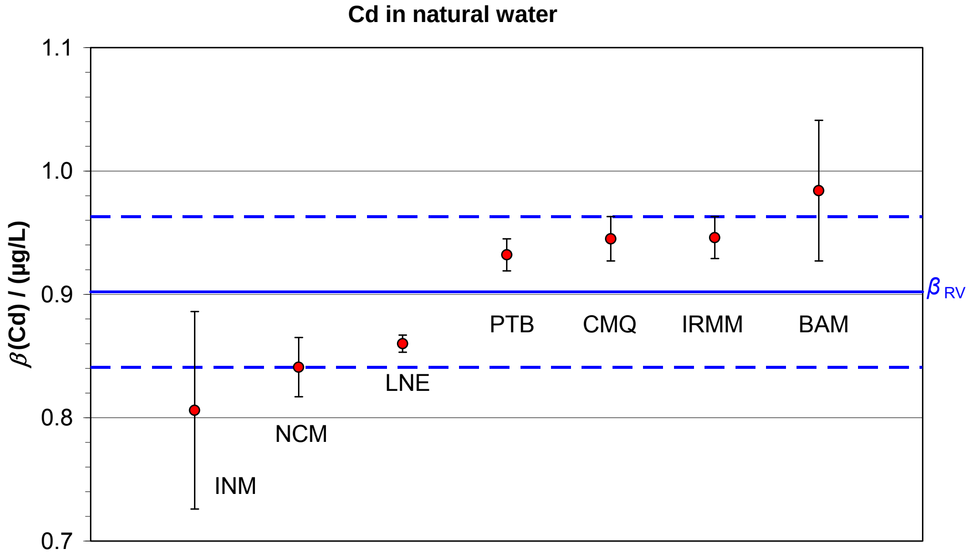
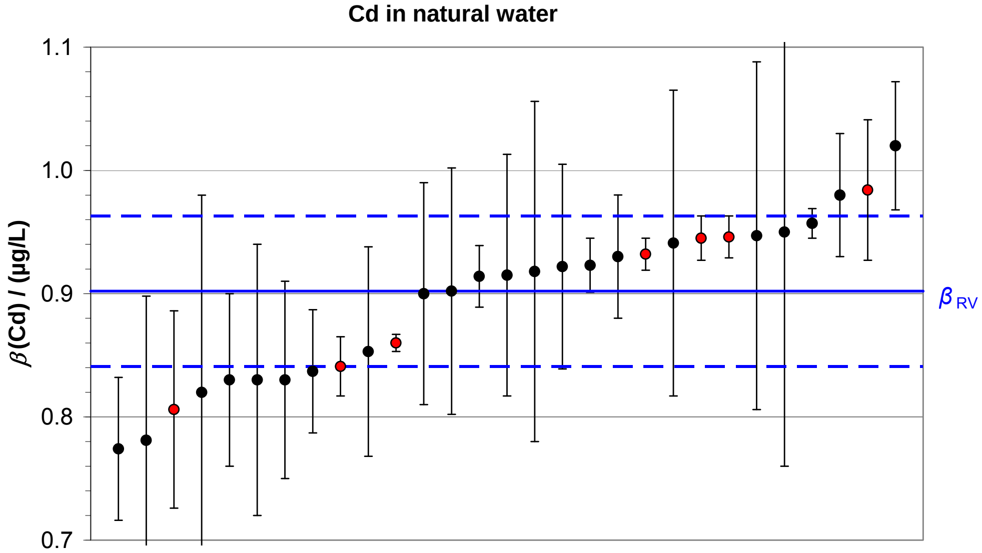


Fig. 3b-2: Results of all participants for the measurement of Cd in natural water.



8.4 Lead

8.4a Lead in pure water

A gravimetrically determined elemental concentration was available and taken as the reference value $\beta_{grav} = \beta_{RV}$ = (7.95 ± 0.17) µg L^{-1}.

Table 7a: Results of the NMIs for the measurement of Pb in pure water.

NMIs	Result	Uncertainty	Coverage factor	Degree of equi-valance	Uncertainty of D	Normalized error
	β (Pb) µg L^{-1}	$U(\beta$ (Pb)) µg L^{-1}	k 1	D_i µg L^{-1}	U_i µg L^{-1}	E_i
CMQ	7.80	0.11	2.2	0.150	0.20	0.74
NCM	7.87	0.08	2.0	0.080	0.19	0.43
LNE	8.006	0.091	2.0	0.056	0.19	0.29
SP	8.02	0.40	2.0	0.070	0.43	0.16
EC-JRC-IRMM	8.028	0.043	2.0	0.078	0.18	0.44
PTB	8.03	0.06	2.1	0.080	0.18	0.44
BAM	8.087	0.190	2.0	0.137	0.25	0.54
INM	8.840	0.620	2.0	0.890	0.64	1.38

Fig. 4a-1: Results of the NMIs for the measurement of Pb in pure water

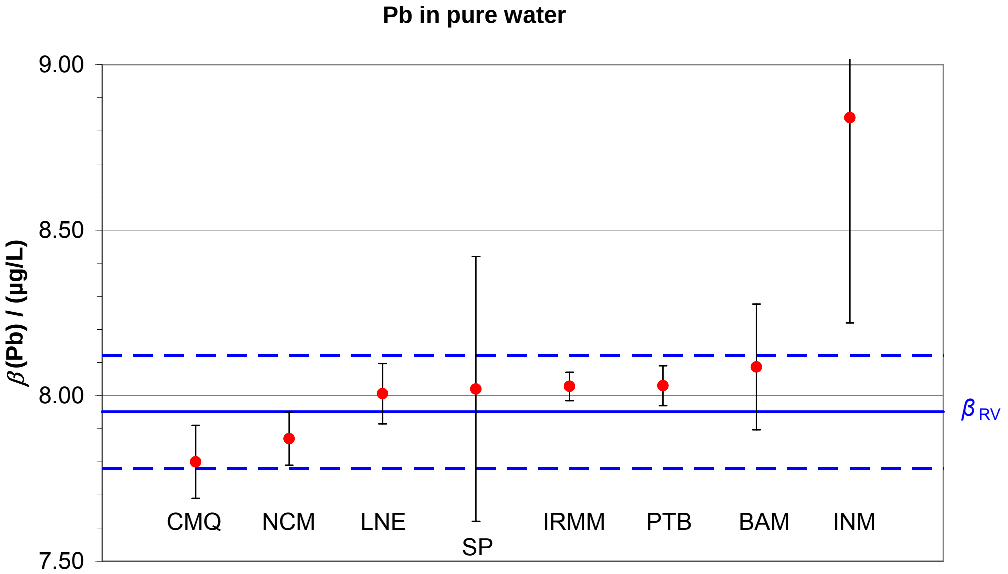
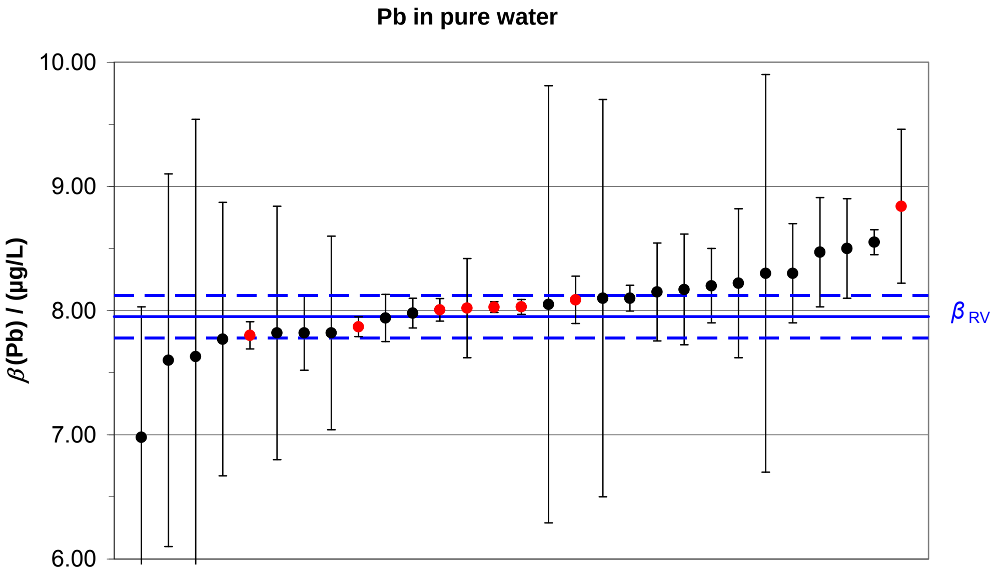


Fig. 4a-2: Results of all participants for the measurement of Pb in pure water



8.4b Lead in natural water

The mean value of the NMIs $\beta_{\text{mean,NMIs}}$ was used as the reference value β_{RV} = (23.6 ± 1.8) µg L^{-1} (SP result not included in $\beta_{\text{mean,NMIs}}$)

Table 7b: Results of the NMIs for the measurement of Pb in natural water.

NMIs	Result	Uncertainty	Coverage factor	Degree of equi-valance	Uncertainty of D	Normalized error
	β (Pb) µg L^{-1}	*U*(*β* (Pb)) µg L^{-1}	*k* 1	D_i µg L^{-1}	U_i µg L^{-1}	E_i
SP	19.7	1.1	2.0	3.86	2.12	1.82
INM	20.16	2.04	2.0	3.40	2.73	1.25
CMQ	23.46	0.48	2.1	0.10	1.87	0.06
LNE	24.26	0.17	2.0	0.70	1.82	0.38
NCM	24.4	0.6	2.0	0.84	1.91	0.44
BAM	24.5	1.2	2.0	0.94	2.17	0.43
PTB	24.60	0.10	2.1	1.04	1.81	0.57

Fig. 4b-1: Results of the NMIs for the measurement of Pb in natural water

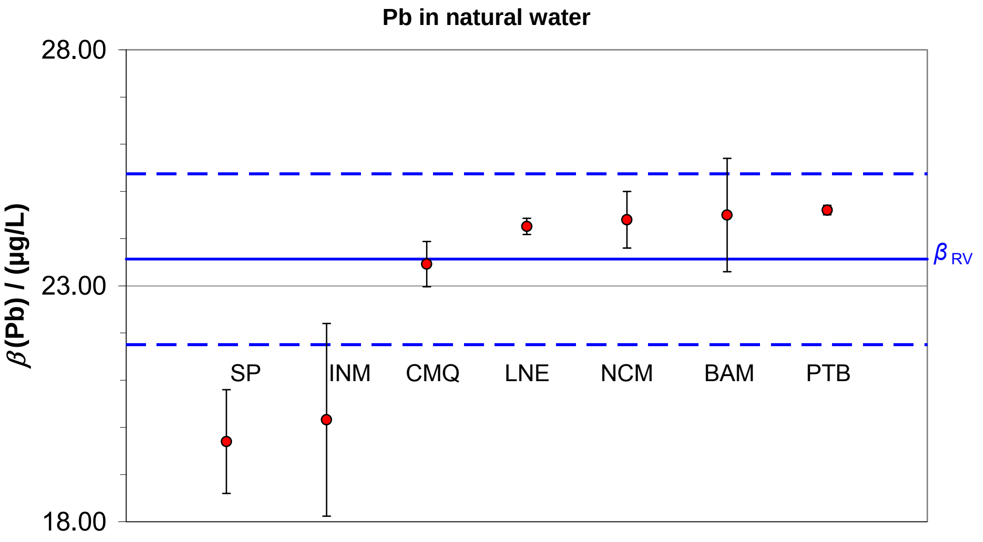
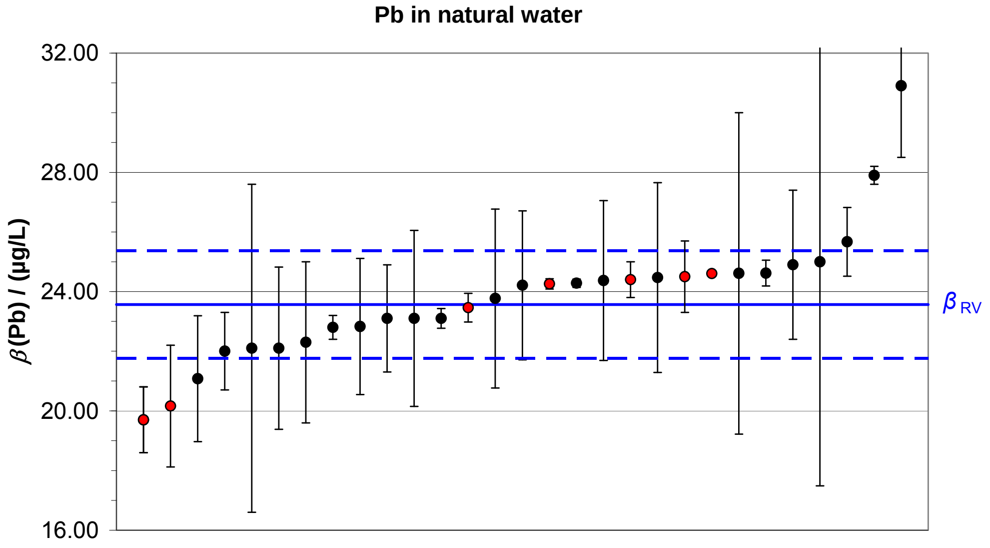


Fig. 4b-2: Results of all participants for the measurement of Pb in natural water.



9. Discussion

9.1 Mercury

The Hg results are shown in section 8.1.

The reference and the mean values of the results and their uncertainties are summarized in table 8. For the pure water measurement the three largest results of the expert laboratories were not included in the mean of all. The mean values of the results of the NMIs include results of non-European NMIs which participated in the CCQM pilot study but not in the Euramet 924 pilot study.

Table 8: Gravimetric and arithmetic mean values of the results of all participants and of the NMIs together with their associated expanded uncertainties (k = 2) and standard deviations for the measurement of Hg.

Hg	**Pure water**				**Natural water**			
	β µg L^{-1}	U µg L^{-1}	U_{rel} %	s %	β µg L^{-1}	U µg L^{-1}	U_{rel} %	s %
Grav.value	0.0470	0.0028	5.9	-	0.570	0.028	5.0	-
Mean, all	0.0480	0.0019	3.9	7.9	0.582	0.015	2.6	6.3
Mean, NMIs	0.0492	0.0035	7.0	7.6	0.589	0.027	4.5	5.9

From table 8 a general trend can be stated to measure too high values. This can certainly be explained by contaminations occurring during the sample preparation and the measurement procedure.

Figures 1a and 1b show the results ordered according to their numerical values. They exhibit S-shaped curves which indicate normal distributions. The relative standard deviation of all pure water results is less than 8% and that of the natural water even about 6%. This is remarkably small considering the low Hg concentration.

There is no significant difference between the spread of the results of the NMIs and that of the expert laboratories. But for both measurements the means of all participants are closer to the reference values than those of the NMIs (table 8). This can be explained by the predominant use of AFS by expert laboratories. The AFS provided remarkably good results and seems to be very suitable for this analytical task which can also be seen from table 9.

Table 9: Trueness and precision of the results (Euramet 924 comparison and CCQM-P100.1/2) depending on the measurement technique used; n : Number of the participants using a technique; $\Delta\beta_{rel}$ relative deviation of the arithmetic mean and the gravimetric reference value; s_{rel}: relative standard deviation of the results.

Measurement technique	Pure water			Natural water		
	n	$\Delta\beta_{rel}$ %	s_{rel} %	n	$\Delta\beta_{rel}$ %	s_{rel} %
AAS	4	15.9	15.3	5	4.7	6.9
AFS	8	3.3	5.9	7	0.9	4.8
ICP-MS	4	21.0	33.0	5	3.0	8.1
ID ICP-MS	4	5.9	5.8	5	4.0	6.3

9.2 Nickel

The results are given in section 8.2.

For the pure water measurement the result of the INM was not considered for the calculation of the mean of the NMIs and its standard deviation because it didn't meet the assessment criteria mentioned above. Furthermore one result of an expert laboratory (largest value outside the range of fig.2a-2) was not included in the calculation of the mean of all. For the natural water measurement the result of SP cannot be considered for the mean and reference values. The E_n value of the SP result was > 1.5.

Table 10: Gravimetric and mean values of the results of all participants and of the NMIs, and their associated expanded uncertainties (k = 2) and standard deviations for the measurement of Ni.

Ni	Pure water				Natural water			
	β µg L^{-1}	U µg L^{-1}	U_{rel} %	s_{rel} %	β µg L^{-1}	U µg L^{-1}	U_{rel} %	s_{rel} %
Grav. value	20.40	0.43	2.1	-	n/a	-	-	-
Mean, all	20.44	0.32	1.6	3.8	38.2	1.2	3.0	7.7
Mean, NMIs	20.42	0.30	1.5	1.2	40.33	0.63	1.6	1.2

Table 10 shows that the gravimetric value and the arithmetic mean agree very well in the case of the pure water measurement. The relative standard deviation of the mean of all is less than 4% and that of the NMIs is even about 1%.

For the natural water measurement the arithmetic mean of the NMIs was chosen as the reference value. Fig. 2b-1 shows that all the results of the NMIs are within the range of the associated uncertainty although its value is only 1.6%. Therefore there was no need for calculating mean values other than the arithmetic mean and to investigate their applicability as reference value. In contrary to the NMI results the relative standard deviation of the results of all participants was 7.7%. Furthermore there is a significant deviation between the mean of the NMIs (reference value) and the mean of all. Both effects are obviously caused by the matrix of the natural water samples although the elemental concentration was relatively large.

9.3 Cadmium

The results are given in section 8.3.

It is obvious that the distributions of the results of both measurements are not clearly S-shaped as shown in the figures 3a and 3b. This concerns the results of the expert laboratories and the NMIs as well. Rather two groups of results were formed, more clearly visible in the case of the natural than in the case of the pure water results. Unfortunately no concrete reason for this behaviour could be found. Possible explanations are a bias of one or both groups or a problem with the sample as well. Of course it has to be taken into account that the elemental concentration was rather low. Furthermore in the case of the measurement of the natural water samples matrix effects could influence the results. This is in particular relevant for ICP-MS which was used by two-thirds of the participants and for which mass inferences could have been occurred.

The heterogeneous distribution of the results in the case of the natural water measurement advised to try the application of the “Mixture Model” [5] for the calculation of the reference value. The resulting distribution function (fig. 5) clearly confirmed the bimodal structure caused by an upper group of four and a lower group of three results. However the calculated MMmedian (tab. 11) is about 3% larger than the arithmetic mean. Furthermore the range of its uncertainty only partially overlaps with the uncertainties of the three lower results. In contrary to that the four upper results are right in the middle (fig. 5) of the uncertainty range. However, as mentioned above there is no evidence to prefer one of the both groups. Therefore a weighting of the groups as resulting from the “Mixture Model” cannot be justified.

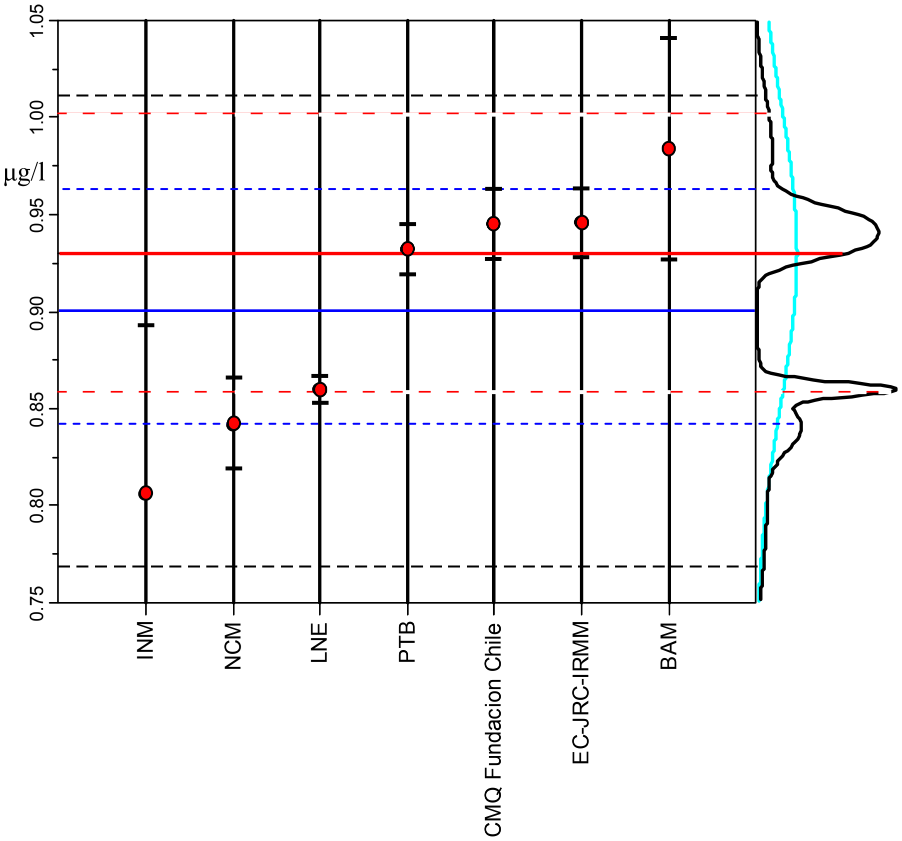
In principle there was a lack of information for the participants to calculate comprehensive uncertainty budgets which is a precondition for the application of the “Mixture Model”. The budgets couldn’t include uncertainty contributions of the observed discrepancy of the results wherever it was coming from. Therefore the distribution functions were insufficiently known. In such a case the best unbiased estimator is the arithmetic mean. Furthermore the results of the expert laboratories supported the use of the arithmetic mean. Its distribution fits well to that of the NMIs (fig 3b-2) and therefore its arithmetic mean agrees well with that of the NMIs (table 11) within the given uncertainties.

The relative standard deviations of the results of all participants for the pure and natural water measurements are in the order of 7%. Obviously the more difficult measurement of the natural water samples due to the matrix was almost compensated by the higher elemental concentration. However this compensation effect is not found for the results of the NMIs.

Table 11: Gravimetric and mean values of the results of all participants and of the NMIs, and their associated expanded uncertainties (k = 2) and standard deviations for the measurement of Cd.

Cd	Pure water				Natural water			
	β µg L^{-1}	U µg L^{-1}	U_{rel} %	s_{rel} %	β µg L^{-1}	U µg L^{-1}	U_{rel} %	s_{rel} %
Grav. value	0.2024	0.0051	2.5		n/a	-	-	
Mean, all	0.2002	0.0054	2.7	6.9	0.896	0.025	2.8	7.2
Mean, NMIs	0.2035	0.0066	3.2	3.5	0.902	0.061	6.8	7.3
MMmedian	-	-	-	-	0.930	0.072	7.7	-

Fig. 5: Results of the NMIs for the measurement of Cd in natural water including the arithmetic mean of the NMIs (blue line), its uncertainty range (dashed blue lines), and the MMmedian (red line), and its associated uncertainty (uncertainty range: dashed red lines, MMmodel distribution functions: black and turquoise lines) calculated by means of the “Mixture Model” [5].



9.4 Lead

The results are given in section 8.4.

For the pure water measurement the means of the results of the NMIs and of all participants as well are close to the reference value. The standard deviations of the results are in the order of 4%. However, for natural water the spread of the results of all participants was the largest of all measurements in the framework of this comparison although the Pb concentration was relatively high. Obviously, the natural matrix strongly influenced the measurements. That is a similar situation as for Ni.

The result of SP was not considered for the calculation of the mean of the NMIs because it did not meet the assessment criteria probably due to the known experimental difficulties. Beside the arithmetic mean also the weighted mean was discussed as the reference value ($\beta_{\text{weighted mean, NMIs}}$ = (24.5 ± 1.6) µg L^{-1}). However this value is due to the small uncertainty of one participant located just at the upper side of all results and the associated uncertainty range does not include all results. Therefore the arithmetic mean seemed to be more appropriate as the reference value.

Table 12: Gravimetric reference and mean values of the results of all participants, of the NMIs, their associated expanded uncertainties (k = 2) and their standard deviations for the measurement of Pb.

Pb	**Pure water**				**Natural water**			
	β µg L^{-1}	U µg L^{-1}	U_{rel} %	s_{rel} %	β µg L^{-1}	U µg L^{-1}	U_{rel} %	s_{rel} %
Grav. value	7.95	0.17	2.1	-	n/a	-	-	
Mean all	8.04	0.13	1.7	4.3	23.80	0.83	3.5	9.0
MeanNMIs	8.09	0.27	3.3	4.0	23.6	1.8	7.7	7.3

10. Conclusion

The comparison measurements have demonstarted that the NMIs and selected expert laboratories have the measurement capabilities to provide the metrological basis for a traceability system which supports the implementation of the WFD.

A further comparison which is just in progress will include test laboratories and intends to link them with the NMIs and expert laboratories. This comparison is the third step of the Euramet project 924. Parallel to that, the key comparison CCQM-K70 and the pilot study CCQM-P100.3 which are only concerned with the measurement of Hg will be organized by BAM, PTB and LNE.

11. References

[1] http://ec.europa.eu/environment/water/water-framework/index_en.html

[2] http://ec.europa.eu/environment/water/water-dangersub/surface_water.htm

[3] USEPA. Method 1631 Revision E: EPA-821-R-02-019. August 2002 http://www.epa.gov/waterscience/methods/1631method.html

[4] Evaluation of measurement data, Supplement 1 to the GUM, JCGM 101, 2008, chapter 6.4.9.4 http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf

[5] D. L. Duewer, Accred. Qual. Assur. 13 (2008) 193 -216

[6] R. Willink, Metrologia 40 (2003) 9 -17

[7] G. Ratel, Metrologia 42 (2005) 140 -144

Appendix A:

CCQM-P100.1 and Euromet 924

"Determination of Hg and Ni. Cd. Pb respectively in pure water at concentration levels required by the European environmental quality standards"

Technical Protocol

1. Introduction

The EU water framework directive 2000/60/EC which is aiming at providing a "good water quality" for surface. ground and coastal/transitional water within the EU by 2015 requires comparable measurement results for monitoring and assessments of the waters. Therefore national metrology institutions are addressed to develop and to provide the appropriate traceability and dissemination basis for the implementation of the directive.

The Euromet project 924 is concerned with this subject. The project intends to link the NMIs with the monitoring (routine) laboratories via calibration laboratories acting as multipliers on an intermediate level of the dissemination chain. Potential calibration laboratories (PCL) shall be enabled to provide internationally accepted and traceable measurement results themselves. These PCLs should be linked with the NMIs by means of the present comparison measurement.

Concerning hazardous chemical substances the "good water quality" has been defined by environmental quality standards (EQS) in a list of priority substances [1]. As an example the inorganic substances Hg. Pb. Cd and Ni have been selected as subject of the Euromet project 924. These elements should be measured in the framework of the present comparison in gravimetrically prepared pure and natural water samples. The element contents are on a level of the environmental quality standards (EQS).

The link to global metrology was established by the participation of the CCQM in this comparison measurement. The pilot study CCQM-P100.1 is only concerned with the determination of the Hg content. The same samples are used for the comparison of Euromet 924 and CCQM-P100.1. Due to formal reasons some participants of Euromet 924 are also participants of CCQM-P100.1. The second comparison using samples prepared from natural water will be organized immediately after the submission deadline of this comparison.

2. Samples

In contrary to our announcement the samples are free of charge.

The samples were prepared by the "Federal Institution of Material Research and Testing" (BAM) by adding gravimetrically certain amounts of standard solutions of Cd. Ni. Pb. and Hg to ultra pure water (Millipore Milli-Q). The standard solutions were prepared gravimetrically from metals all having certified purities. The resulting stock solutions were diluted gravimetrically over several steps to the final concentration of the samples. A gravimetric reference value will be provided immediately after the submission deadline.

Euromet 924 participants are provided with a 100 mL PFA bottle containing the Cd. Ni and Pb sample and with a 500 mL glass bottle containing the Hg sample. CCQM-P100.1 participants are only provided with the Hg samples. The Cd. Ni and Pb solution (100 mL PFA bottle) was stabilized by adding 1 ml subboiled nitric acid. The Hg solution (500 mL glass bottle) was stabilized with a BrCl-solution as described in the "EPA Method 1631" guideline [2]. Their stability was tested and can be ensured for the duration of two months. Therefore it is advisable to perform the measurements within two months after receipt of the samples.

The samples were weighed directly after bottling. The corresponding plastic bags are both labelled with the tare mass of the particular bottle including its screw cap and label and with the total mass (tare mass plus sample). **All participants are asked to measure the total mass of the bottles immediately after receipt in order to check for losses during transport.**

The approximate element mass concentrations are in the following ranges: Cd 0.1 - 0.5 µg/L. Ni 5 - 30 µg/L. Pb 2 - 10 µg/L. Hg 0.02 - 0.1 µg/L.

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 [3]. In order to enable the participants to use additional enrichment steps prior to the analysis a larger amount of the Hg sample (500 mL) has been provided.

4. Reporting

Deadline for the submission of the results is July 31th 2007. Please use the attached form (Results Report) and provide us also with the requested additional information (including an uncertainty budget according to *GUM* [4]). Send all your results to the following address by e-mail or fax:

Dr. Detlef Schiel
Physikalisch-Technische Bundesanstalt
Bundesallee 100
38116 Braunschweig
Germany

Fax: +49-531-592-3015
e-mail: detlef.schiel@ptb.de

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
[2] EPA. Method 1631. Revision E: Mercury in Water by Oxidation. Purge and Trap. and Cold Vapor Atomic Fluorescence Spectrometry. 2002. available at http://www.epa.gov/waterscience/methods/1631method.html
[3] S J Christopher. S E Long. M S Rearick. and J D Fassett. Anal. Chem. 2001. 73. 2190-2199.
[4] Guide to the Expression of Uncertainty in Measurement. ISO. Geneva. 1993.

RESULTS REPORT

CCQM P100.1 / Euromet 924 (part 1)
Pure water samples

Please return together with your results report by July 31th. 2007.

NAME :
FIRM/INSTITUTE :
DEPARTMENT :
ADDRESS :

COUNTRY
TEL :
FAX :
E-mail :

Please report your results and uncertainties in mass concentration (µg·L^{-1}) along with the sample (bottle) number. Details concerning the method calculation of results and associated uncertainties should be given in your report.

Element	Bottle no.	Mass concentration in µg·L^{-1}	Expanded uncertainty in µg·L^{-1}	Coverage factor ($p \approx$ 95 %)
Ni				
Cd				
Pb				
Hg				

DATE:

SIGNATURE:

Additional information

Results of the sample replicates

Determination	β(Ni) in µg·L^{-1}	β(Cd) in µg·L^{-1}	β(Pb) in µg·L^{-1}	β(Hg) in µg·L^{-1}
1				
2				
3				
4				
5				

If more than 5 determinations were carried out please insert more lines

Further information and details can be added in pages below or in a separate report if preferred. Please provide a complete description of the method used and include the following information. An uncertainty calculation should be prepared according to the *Guide to the Expression of Uncertainty in Measurement*.

1. **Particular sample treatment. e.g. clean room preparation**
2. **Density (result. associated uncertainty and method used for determination if needed)**
3. **Measurement technique**
4. **Calibration procedure**
5. **Details of the source of your calibration standard together with the purity and associated uncertainty.**

Appendix B:

CCQM-P100.2 and Euromet 924 (part 2)

"Determination of Hg and Ni. Cd. Pb respectively in fortified natural water

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 measurement of the concentrations of Hg. Ni. Cd and Pb in natural surface water and succeeds the previous comparison (CCQM-P100.1 and Euromet 924 (part 1)) concerned with the measurement of these elements in pure water samples. The particular difficulty of the present comparison is the presence of a natural matrix. The samples are gravimetrically spiked by the elements regarded here. The element concentrations are slightly higher than that of the pure water samples. The pilot study CCQM-P100.2 is only concerned with the measurement of the Hg concentration.

Again two different samples will be prepared: One for the Hg measurement (glass bottle) and the other for the measurements of Ni. Cd and Pb (PFA bottle). The Euromet participants will be provided with both samples whereas the CCQM participants will only get the Hg sample. The Hg samples used for Euromet 924 and CCQM-P100.2 are the same. Due to formal reasons some participants of Euromet 924 are also participants of CCQM-P100.2.

2. Samples

The samples were prepared by the "Laboratoire National de métrologie et d'Essais " (LNE) by spiking gravimetrically certain amounts of standard solutions of Cd. Ni. Pb and Hg to a natural surface water. The standard solutions were prepared gravimetrically from metals all having certified purities. The resulting stock solutions were diluted gravimetrically over several steps to the final concentration of the samples.

Euromet 924 participants are provided with a 100 mL PFA bottle containing the Cd. Ni. and Pb sample and with a 100 mL glass bottle containing the Hg sample. The Cd. Ni. and Pb solution (100 mL PFA bottle) was filtered (pore size 0.45 µm) and stabilized by adding 2 % Suprapur nitric acid. The Hg solution (100 mL glass bottle) was also filtered (0.45 µm) and stabilized with a BrCl-solution as described in the "EPA Method 1631" guideline [2]. Their stability was tested and can be ensured for the duration of two months. Therefore it is advisable to perform the Hg measurement quickly after the receipt of the samples (at the best before the end of September)

The samples were weighed directly after bottling. The corresponding plastic bags are both labelled with the tare mass of the particular bottle including its screw cap and label and with the total mass (tare mass plus sample). **All participants are asked to measure the total mass of the bottles immediately after receipt in order to check for losses during transport.**

The major components of the natural surface water and their levels measured by ICP-OES are the following:

Cations	mg/l
Ca^{2+}	111
Mg^{2+}	25.8
Na^{+}	14.4
K^{+}	3.0
Fe^{2+}	0.20
Mn^{2+}	0.03

The approximate element mass concentrations are in the following ranges: Cd: 0.2 – 1 µg/L. Ni: 10 – 50 µg/L. Pb: 5 – 30 µg/L. Hg: 0.2 – 1 µg/L.

In contrary to our announcement the samples are free of charge.

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 [3].

4. Reporting

Deadline for the submission of the results is October 31th 2007. Please use the attached form (Results Report) and provide us also with the requested additional information (including an uncertainty budget according to *GUM* [4]). Send all your results to the following address by e-mail or fax:

Dr. Detlef Schiel
Physikalisch-Technische Bundesanstalt
Bundesallee 100
38116 Braunschweig
Germany
Fax: +49-531-592-3015
e-mail: detlef.schiel@ptb.de

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
[2] EPA. Method 1631. Revision E: Mercury in Water by Oxidation. Purge and Trap. and Cold Vapor Atomic Fluorescence Spectrometry. 2002. available at http://www.epa.gov/waterscience/methods/1631method.html
[3] S J Christopher. S E Long. M S Rearick. and J D Fassett. Anal. Chem.. 2001. 73. 2190-2199.
[4] Guide to the Expression of Uncertainty in Measurement. ISO. Geneva. 1993.

RESULTS REPORT

CCQM P100.2/ Euromet 924 (part 2)
Natural water samples

Please fill in this form and return it together with your results report by October 31th 2007.

NAME :
FIRM/INSTITUTE :
DEPARTMENT :
ADDRESS :

COUNTRY
TEL :
FAX :
E-mail :

Please report your results. uncertainties in mass concentration (µg·L^{-1}) and the temperature for which the mass concentration value is valid along with the sample (bottle) number. Details concerning the method. calculation of results and associated uncertainties should be given in your report.

Element	Bottle no.	Mass concentration in µg·L^{-1}	Expanded uncertainty in µg·L^{-1}	Coverage factor ($p \approx$ 95 %)	Temperature in ^{o}C
Ni					
Cd					
Pb					
Hg					

DATE:

SIGNATURE:

Additional information

Results of the sample replicates

Determination	β(Ni) in µg·L^{-1}	β(Cd) in µg·L^{-1}	β(Pb) in µg·L^{-1}	β(Hg) in µg·L^{-1}
1				
2				
3				
4				
5				

If more than 5 determinations were carried out. please insert more lines

Further information and details can be added in pages below. or in a separate report if preferred. Please provide a complete description of the method used and include the following information. An uncertainty calculation should be prepared according to the *Guide to the Expression of Uncertainty in Measurement*.

1. **Particular sample treatment. e.g. clean room preparation**
2. **Density (result. associated uncertainty and method used for determination if needed)**
3. **Measurement technique**
4. **Calibration procedure**
5. **Details of the source of your calibration standard together with the purity and associated uncertainty.**