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Interlaboratory Comparison Report

Fernando Cordeiro, Franz Schmitz, Inge Verbist, Håkan Emteborg, Jean Charoud-Got, Maria C. Contreras Lopez, Philip Taylor, Beatriz de la Calle

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IMEP-25b: Determination of Bromate in Drinking Water

Interlaboratory Comparison Report

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Contents

1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme® (IMEP). IMEP organises interlaboratory comparisons (ILC's) in support to EU policies. This ILC exercise reports the performance of the laboratories on the determination of bromate in drinking water in support to the Council Directive 98/83/EC (Drinking Water Directive, DWD).

Seven test materials were included in this study: soft drinking water, hard drinking water, mineral water, swimming pool water, raw water (untreated), a bromate standard solution and a blank solution consisting of non-spiked ultra pure water. The bottles containing the blank solution were labelled as river water.

The 25 participating laboratories were invited via the IRMM website and the European Co-operation for Accreditation.

z scores were calculated with a target standard deviation of 25 % of the reference value. The scores were satisfactory for a high share of the participants (75 % for soft drinking water, 90 % for hard drinking water, 73 % for mineral water, 100 % for swimming pool water, 86 % for raw water and bromate standard solution, respectively). In addition, zeta scores were calculated for participants having reported a measurement uncertainty. These were however, less satisfactory on average.

In summary, the measurement capabilities of laboratories involved in the determination of bromate measurements in the frame of the DWD is satisfactory considering that the concentration levels in almost all matrices were lower or equal to the maximum permitted level of bromate in these types of matrices.

2 IMEP support to EU policy

The International Measurement Evaluation Programme® IMEP is owned by the Joint Research Centre - Institute for Reference Materials and Measurements. IMEP provides support to the European measurement infrastructure in the following ways:

IMEP promotes metrology from the highest level down to the field laboratories. These laboratories can benchmark their measurement results against the IMEP certified reference value. This value is established according to metrological best practice.

IMEP helps laboratories to assess their estimate of measurement uncertainty. The participants are invited to report the uncertainty on their measurement result. IMEP integrates the estimate into the scoring, and provides assistance for the interpretation.

IMEP supports EU policies by organising intercomparisons in the frame of specific EU Directives, or on request of a specific Directorate-General. IMEP-25b provided specific support to the following stakeholders:

- The European Co-operation for Accreditation (EA) in the frame of a formal collaboration on a number of metrological issues, including the organisation of intercomparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-25b. Mr. Boyan Ivanichkov from the Bulgarian Accreditation Service (BAS) liaised between EA and IMEP for this intercomparison. This report does not discern the EA nominees from the other participants. Their results are however summarised in a separate report to EA.

- This exercise was run in collaboration with the ISO TC 147 SC 2 WG 33 and carried out in parallel with an ILC (IMEP-25a) conducted to validate a new method for the determination of bromate in several types of water matrices (project ISO 11206 [1]).

IMEP is accredited according to ISO Guide 43. The designation of this ILC is IMEP-25b.

3 Introduction

The Council Directive 98/83/EC of the 3rd November 1998 [2] (referred as the Drinking Water Directive, DWD) on the quality of water intended for human consumption, provides the legislative framework to protect human health from adverse effects of any contamination of water intended for human consumption by ensuring that it is wholesome and clean. Bromate is one of the chemical parameters included in that Directive with a maximum allowed limit of bromate in water for human consumption of 10 µg L^{-1}. It is also specified in the DWD that:

> "*performance characteristics are that the method of analysis used must, as a minimum, be capable of measuring concentrations equal to the parametric value with a trueness, precision and limit of detection specified of ± 25 % of the parametric value*".

Bromate is identified as an unwanted disinfection by-product, originated from the reaction of ozone, used as disinfectant with some natural constituents of water. The bromide concentration and the ozone dose can be used to predict the bromate formation during ozonation, knowing that the conversion of bromide to bromate reaches about 50 %.
The ingestion of large amounts of bromate appears to cause gastrointestinal symptoms such as nausea, vomiting, diarrhea and abdominal pains [3]. Bromate is also an active oxidant in

biological systems and has been shown to cause an increase in renal tumours and thyroid follicular cell tumours in rats.
Bromate is an undesirable constituent of drinking water because it has been suspected to act as a human carcinogen [4, 5].

This evidence leads to the conclusion that, without compromising the microbiological quality of drinking-water, appropriate steps should be taken to minimize the concentration of any disinfection by-product.
Furthermore, the performance of laboratories in analysing this analyte should be regularly assessed which constitutes the aim of the present intercomparison exercise.

4 Scope and aim

The scope of this ILC is to test the competence of the laboratories with water monitoring activities in the frame of the Directive 98/83/EC. The assessment of the measurement results is undertaken on the basis of requirements laid down in legislation (DWD) and follows the administrative and logistic procedures of IMEP.

5 Time frames

On 29th April 2009 EA was invited to nominate laboratories in the frame of the collaboration agreement between IRMM and EA. Other laboratories were publicly invited via the IMEP website in April 2009. Registration was opened till 15th June 2009. The samples were dispatched on 23rd June 2009. The deadline for submission of results was 25th August 2009.
The homogeneity and stability studies were carried out between May and July 2009. Characterization of the natural content of bromate in the swimming pool water took place in July 2009.

6 Test material

6.1 Preparation

Three types of drinking water have been included as test materials for this exercise:
- soft drinking water,
- hard drinking water,
- mineral water

Other types of water which were included in the exercise were:
- swimming pool water,
- raw water (untreated),
- a synthetic bromate standard solution,
- ultra pure water (Milli-Q type) used as blank.

Soft, hard, raw and swimming pool water were provided by the Landesbetrieb Hessisches Landeslabor (Wiesbaden, Germany). Mineral water was purchased at a local supermarket. The blank sample is ultra pure water prepared at IRMM.

6.2 Preparation of the test water samples

For the spiking of the different materials, potassium bromate, $KBrO_3$ of ACS ISO Reagent grade > 99.8 % purity provided by Merck (KGaA, Darmstadt, Germany) was used. Milli-Q ultra pure type water (Millipore S.A. N.V., Belgium) was used for preparation and dilution of the bromate stock solutions.

A 1005.5 mg L^{-1} bromate stock solution was prepared by weighing 0.6388 g of $KBrO_3$ (the mole fraction of 76.58 % BrO_3 in $KBrO_3$ was used) and dissolving it in 486.50 g of Milli-Q water and carefully mixing for 30 min using a magnetic stirrer.

A 100.27 mg L^{-1} intermediate stock solution was prepared by taking 253.41 g of the stock solution and diluting them with Milli-Q water up to 535.62 g.

For the spiking of the test materials, aliquots of the intermediate stock solution were accurately weighed and diluted to obtain the final bromate concentrations presented in Table 1.

A solution of 50 mg L^{-1} of ethylene diamine in Milli-Q water was used as blank solution. This solution was measured by SGS, Institut Fresenius GmbH (Taunusstein, Germany) using liquid chromatography followed by inductively coupled plasma mass spectrometry (LC-ICP-MS) to check for the presence of bromate. The concentration of bromate was below the limit of detection (LOD = 0.5 µg L^{-1}) thus the material could be used as a blank for the purpose of this exercise.

All water samples were filtered through a 0.45 µm membrane filter and filled into 60 mL polyethylene bottles. These bottles were then stored at 4 °C until dispatch.

6.3 Homogeneity

Homogeneity studies were carried out by the Rheinisch-Westfälisches Institut für Wasser (IWW, Germany) for all six water samples. The blank solution was not tested for homogeneity. The experimental design used complied with the requirements set by the ISO 13528 [6] and by the IUPAC Harmonized Protocol [7].

The between bottle relative standard uncertainty (u_{bb}) for the samples ranged from 1.0 to 6.0 %. The relative standard uncertainty (u_{st}) due to the stability test ranged from 2.5 to 7.3 %. These uncertainties contribute to the combined standard uncertainty for the reference value.

Both ISO 13528 and the IUPAC Harmonized Protocol [6, 7] describe the requirements for tests to determine sufficient homogeneity of test samples. These tests compare the between bottle homogeneity with the standard deviation for proficiency assessment ($\hat{\sigma}$). Both tests indicate that all the water test samples are sufficiently homogeneous for the bromate analysis (Annex 1).

6.4 Stability

An isochronous stability study [8] was carried out by IRMM at three temperatures (4, 18 and 60 °C) with the aim to:

- Find suitable temperature conditions for sample dispatch. Linear regression of the stability data indicated sufficient stability at all temperatures for the investigated time (Annex 2). Nevertheless, due to a delay in the stability measurements it was thus decided to dispatch all samples under cooled conditions (4° C).

- Quantify the potential degradation during the entire interlaboratory comparison study (approximately one month).

The participants were instructed to store the material at 4° C after receipt.
No significant degradation for any of the test samples is foreseen.

The evaluation of the stability of the test materials was made using the SoftCRM software [9]. The materials proved to be stable at 18 °C for a length covering the whole time frame of the ILC exercise.

Table 1 and Annex 2 shows the standard uncertainty (u_{st}) obtained from stability studies carried out at 18 °C after a period of time of 7 weeks.

6.5 Distribution

The ILC samples were dispatched to the participants by IRMM on 23rd of June 2009. Each participant received one package containing:

1) seven bottles containing each ~ 60 mL of the test material (one bottle for each type of water). The samples were dispatched at 4 °C.
2) confirmation of receipt form (Annex 5) and
3) letter accompanying the sample (Annex 4).

The dispatch was followed by the messenger's parcel tracking system on internet.

7 Participant invitation, registration and information

Invitations for participation were sent to the EA contact person for distribution to nominated laboratories (Annex 3). A call for participation was also released on the IRMM website. The measurand was defined as bromate in water.

The letter accompanying the samples provided the general instructions for participants, i.e. the measurand, type of samples, analytical method to use, etc (Annex 4).

Laboratories were instructed to perform two or three independent analyses per measurand. They were asked to report their measurement values, the mean, its associated uncertainty and the coverage factor. Participants were requested to report their results as they usually report to their customers (e.g. number of significant figures). A sample receipt confirmation form was also included (Annex 5).

Participants used an online form to report their measurement results and to complete the related questionnaire (Annex 6). They received an individual code to access this online form. The reporting unit was µg L^{-1}.

7.1 Confidentiality

EA was invited to nominate laboratories for participation. Instructions were provided to all participants on the confidentiality of their results. The following confidentiality statement was made to EA:

"Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA Working Group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure."

8 Reference values and their uncertainties

8.1 Assigned values

The maximum tolerable concentration of bromate in drinking water according to the Council Directive 98/83/EC is 10 µg L^{-1}. The bromate concentration in IMEP-25b water samples was prepared accordingly. Water samples with the exception of the swimming pool water and the blank solution were spiked with high purity $KBrO_3$ to achieve the level of concentration given in Table 1. Nominal (gravimetric) values were used as assigned values.
Swimming pool water, having a naturally occurring bromate level was not spiked. The average value obtained from the homogeneity studies provided by IWW, was used as the assigned

value. The blank sample (called river water) gave a value < 0.5 µg L^{-1}. No scoring was therefore provided for this sample.

IMEP-25b assigned values X_{ref} are presented in Table 1. Uncertainties listed in the table are standard uncertainties.

The uncertainties associated with the reference values (u_{ref}) were calculated by propagating contributions for characterisation, i.e. from the spiking procedures (u_{char}), homogeneity (u_{bb}) and stability studies (u_{st}) as follows:

$$u_{ref} = \sqrt{(u_{char}^2 + u_{bb}^2 + u_{st}^2)}$$

(all standard uncertainties)

Where;

u_{char} is the standard uncertainty on the characterisation

u_{bb} is the standard uncertainty on the homogeneity (between-bottle)

u_{st} is the standard uncertainty arising from the stability studies

Table 1: Assigned (reference) values and their associated standard uncertainties

Sample	Gravimetric (spike) X_{ref} (µg L^{-1})		u_{char} (µg L^{-1})	Homogeneity u_{bb} (µg L^{-1})	Stability (18 °C) u_{st} (µg L^{-1})	Combined u_{ref} (µg L^{-1})
Soft Drinking Water	2.68	±	0.01	0.15	0.12	0.19
Hard Drinking Water	10.00	±	0.02	0.15	0.51	0.53
Mineral Water	3.00	±	0.01	0.09	0.16	0.18
Swimming Pool Water	8.44	±	0.60	0.17	0.21	0.66
Raw Water	7.95	±	0.02	0.17	0.29	0.33
Bromate Std. Sol.	1.67	±	0.01	0.06	0.15	0.17

8.2 Uncertainty estimations

The standard uncertainties (u_{char}) were estimated for the spiked materials following the GUM approach [10] combining the uncertainty derived from the preparation of the stock solutions, from spiking with pipettes, from the weighed mass of sample and from the purity of the $KBrO_3$ standard material. The expanded uncertainty was calculated applying a coverage factor of 2, representing a confidence level of approximately 95 %. For the swimming pool water u_{char} was provided by IWW.

9 Reported results

9.1 General observations

From the 25 laboratories that registered for participation, 24 submitted their results and completed the questionnaire (1 laboratory cancelled its participation due to technical problems). Some laboratories did not report values for all samples, or reported "less than" values. These results were not assessed.

Annexes 7 to 12 list the individual measurement results. The various techniques used such as: ion chromatography or liquid chromatography (IC or LC) coupled with post column reaction (PCR) and the instrumental detection system, such as conductivity, ultraviolet detection or mass spectrometry (CD, UV, MS) are presented.

It appears that the distribution of the results is quite symmetric around the reference value, although a sub-population can be distinguished for two water samples due to two very high results. The Kernel density plots displayed in Annex 13 illustrates these findings.

The Kernel densities were calculated using the software of the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry [11].

9.2 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z and zeta scores in accordance with ISO 13528 [6]:

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{and}$$

$$zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

Where

x_{lab} is the measurement result reported by a participant
X_{ref} is the certified reference value (assigned value)
u_{ref} is the standard uncertainty of the reference value
u_{lab} is the standard uncertainty reported by a participant
$\hat{\sigma}$ is the standard deviation for proficiency assessment

Both scores can be interpreted as:
- satisfactory result for |score| ≤ 2,
- questionable result for 2 < |score| ≤ 3 and
- unsatisfactory result for |score| > 3

z score indicates whether a laboratory is able to perform the measurement in accordance with European legislation. The standard deviation for proficiency assessment $\hat{\sigma}$ is derived from the Council Directive recommended limits for the method trueness as ± 25 % of the assigned value. Should participants feel that the $\hat{\sigma}$ values are not fit for their purpose they can recalculate their scorings with a standard deviation matching their requirements, as recommended in the IUPAC Harmonized Protocol [7].

Zeta score states if the laboratory result agrees with the assigned value within the respective uncertainties. An unsatisfactory zeta-score might be due either to an underestimated uncertainty, or to a large error causing a large deviation from the reference value, or to a combination of the two factors. A laboratory with an unsatisfactory zeta-score has an estimation of the uncertainty of its measurements which is not consistent with the laboratory deviation from the reference value.

The standard uncertainty of the laboratory (u_{lab}) was calculated dividing the reported expanded uncertainty by the reported coverage factor (*k*). When *k* was not specified, the reported expanded uncertainty was considered as the half-width of a rectangular distribution; u_{lab} was then calculated by dividing this half-width by √3, as recommended by EURACHEM / CITAC [12]. When no uncertainty was reported no zeta score was provided.

The reported standard uncertainty u_{lab} should fall in a range between a minimal required (u_{min}), and a maximal allowed (u_{max}). u_{min} is set to the standard uncertainty of the assigned value. u_{max} is set to the standard deviation accepted for the proficiency test assessment, $\hat{\sigma}$.

If the standard uncertainty from the laboratory $u_{lab} < u_{min}$ it is likely that the laboratory has underestimated its uncertainty. Indeed, it is unlikely that a laboratory carrying the analysis on a routine basis is able to measure the measurand with an uncertainty smaller than the uncertainty associated to the gravimetric process.

If $u_{lab} > u_{max}$, some effort should be made to reduce it because it is not in compliance with the European legislation requirements. Annex 7 to 12 presents the evaluation for the reported standard uncertainties.

9.3 Laboratory results and scorings

A z score was calculated for all participants except for those who reported no value or who have reported a "lower than" value. These results were not used in any statistical calculation. A zeta score was calculated for results that were accompanied by an uncertainty statement. Annex 14 lists the overall scores for each laboratory and for all water samples included in this exercise. Table 2 provides an overview of the satisfactory, questionable and unsatisfactory scores obtained in this exercise. All participants except two have reported a "lower than" value for the blank (river water).

Reported values for the blank solution ranged from < 0.2 to < 14 µg L^{-1}, which indicates that analytical methods with different performance characteristics have been used in this exercise. Due to the reduced number of participants reporting values for the blank sample no scoring has been estimated for this sample.

Table 2: Overview of scores: S (satisfactory), Q (questionable), U (unsatisfactory)

	z score				zeta score				both z and zeta scores
	S	Q	U	n (*)	S	Q	U	n (*)	S
Soft drinking water	75 %	8 %	17 %	12	80 %	10 %	10 %	10	58
Hard drinking water	90 %	10 %	0 %	20	65 %	12 %	24 %	17	50
Mineral water	73 %	13 %	13 %	15	77 %	0 %	23 %	13	53
Swimming pool water	100 %	0 %	0 %	20	76 %	18 %	6 %	17	87
Raw water	86 %	10 %	5 %	21	76 %	12 %	12 %	17	52
Bromate Std. solution	86 %	0 %	14 %	14	73 %	27 %	0 %	11	57
River water (blank)	no scoring				no scoring				no scoring

(*) n is the number of results for which a score was given.
The total number of participants (with and without a score) is 24.

Most of the participants provided an uncertainty estimate, and most of these estimates were accompanied by a coverage factor. On average 81 % of the laboratories have reported their estimated uncertainty (10 laboratories out of the 12 for soft drinking water, 17 out of 20 for hard drinking water and for the swimming pool water, 13 out of 15 for mineral water, 17 out of 21 for river water and 11 out of the 14 laboratories for the bromate standard solution).
The basis of the reported uncertainty estimation (more than one reply possible) was as follows: In-house method validation was mentioned 15 times, measurement of replicates (i.e. precision) was mentioned 13 times, use of interlaboratory comparison data was mentioned 3 times and the ISO Guide to the Expression of Measurement Uncertainty was mentioned 4 times.
Only three out of the 13 laboratories who based their uncertainty on replicate measurements use this as the only source of their estimation. These three laboratories are likely to underestimate their uncertainty by excluding other sources of uncertainty.

Many participants (13 out of 24) do not usually report the uncertainty to their customers.
The low share of results with a satisfactory zeta score for some samples shows that many laboratories still encounter difficulties to provide a reasonable uncertainty estimate. These laboratories are well advised to become familiar with the principles of uncertainty estimation as described by the GUM [10] and in related guidance for the field of analytical chemistry, e.g. the EURACHEM / CITAC Guide [12]. Also, the ISO/TS 21748 [13] or ISO 5725-3 [14] could be followed, whereby the single-laboratory reproducibility standard deviation (also called intermediate precision) can be used as a reasonable estimation of their own uncertainty (pro-

vided several sources of uncertainty are covered in their experimental design and no significant laboratory bias is observed).

In addition to submission of the results, the participants were asked to answer a number of questions relating to the measurements. The majority of the participants completed the questionnaire. Issues that may be relevant to the outcome of the intercomparison are discussed below.

Most participants appeared to be experienced or very experienced: 87 % indicated to carry out this type of analysis (as regards to the measurand, matrix and method of analysis) on a routine basis. Among these, 26 % of the laboratories do analyse up to 50 samples per year (0-50), 26 % do analyse between 50 and 250 (50-250), 9 % between 250 and 1000 (250-1000) and 22 % more than 1000 samples a year (> 1000). These figures suggest that IMEP-25b has been indeed a representative study for the current capabilities of European laboratories for routine control measurements of bromate in drinking water.

Four laboratories out of the 24 stated that they are not participating in any interlaboratory comparison. The same number of participants (not necessarily the same) declared they do not use a reference material for this type of analysis. Three out of which declared that they use a reference material for validation purposes but not for calibration purposes.

10 Multivariate data analysis

Multivariate analysis (chemometric approach) of the data was done by interpreting the multivariate relationship between bromate (normalized and expressed as a z-score) and the set of responses gathered from the questionnaire, once transformed into numerical variables. The statistical data treatment was performed using The Unscrambler 9.8 (CAMO Software AS, Norway).

A multivariate linear relationship between the measurement result (z score for bromate as the Y-variable) and the set of variables obtained by the questionnaire (X-variables) was obtained by means of a partial least square regression model (PLS-R). It enables the assessment of the relationship between the quality of the measurement results and the reasons why they might be different, depending on the responses to the questionnaire.

A model has been established for each of the water samples. The majority of the models were successful in explaining most of the total variance in the data, while using the first 2-3 principal components.

Each measurement result is projected onto the model (PLS score plot) which enables the identification of any clustering among results. An example is presented for mineral water

(Figure 1). The two laboratories for which an unsatisfactory z-score has been calculated could be easily identified.

As a general conclusion it appears that laboratories analysing more than 250 samples per year under routine conditions are reporting acceptable results for all investigated samples, i.e. with $|z| \leq 2$. Most of the laboratories reporting values outside acceptance limits (questionable or unsatisfactory, $|z| > 2$) have less experience in analysing these type of test materials (0-50 samples per year).

Furthermore, the detection system (either conductivity (CD) or ultraviolet detection, UV) was identified for 18 out of the 24 participants. Among those, 10 used conductivity, 7 used UV and 1 used mass spectrometry as their detection system. For all test samples under investigation in this exercise and for all laboratory results for which a questionable or a non satisfactory z value was calculated ($|z| > 2$) the overall performance due to the detection system used was as follows; for questionable results ($2 < |z| \leq 3$) four laboratories used conductivity while only one used UV detection, for unsatisfactory results ($|z| > 3$) four laboratories used conductivity and three used UV as their detection system.

For the remaining laboratories the detection system has not been reported. One could conclude the detection system used is not as relevant as the number of analysis carried out per year, although the number of unsatisfactory z score is slightly higher for laboratories using conductivity detection.

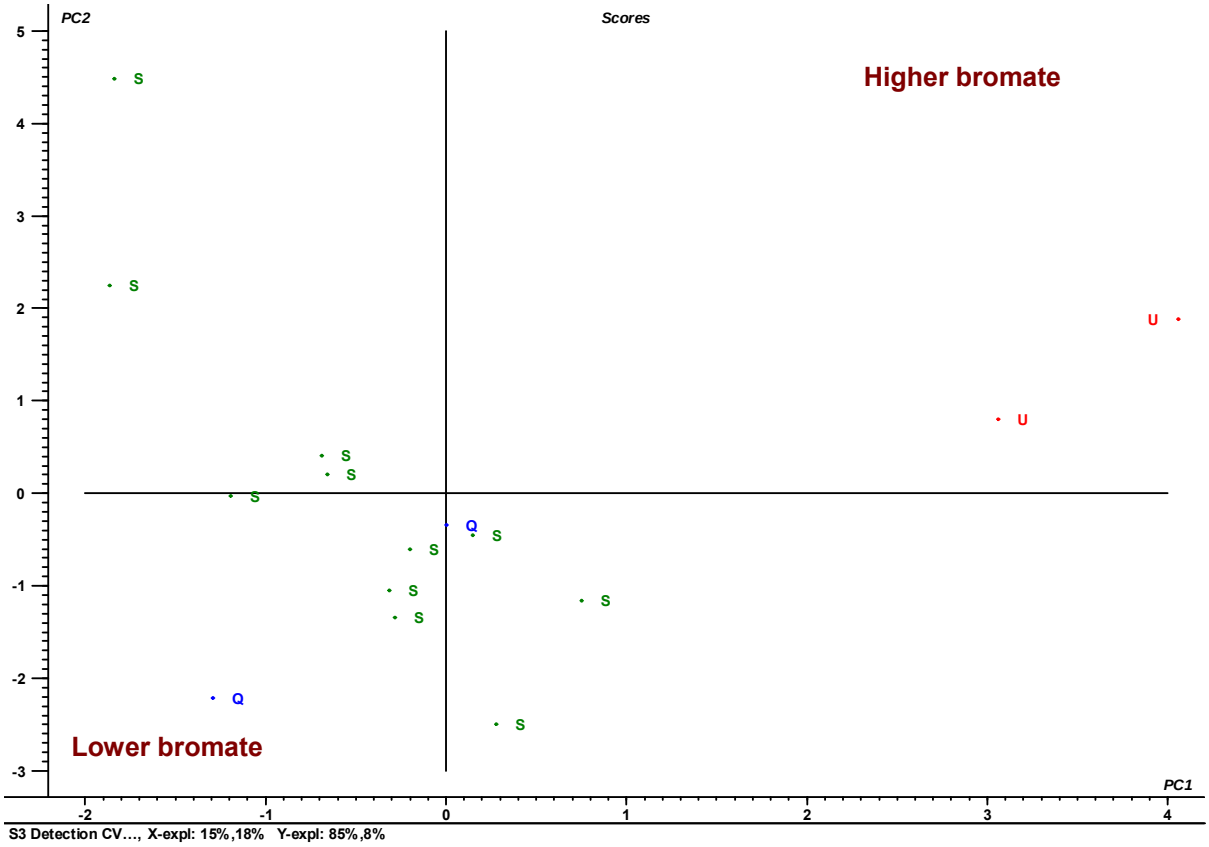

Fig.1. PLS-R score plot for mineral water: projected laboratory z-scores showing their respective score evaluation; U refers to unsatisfactory, Q to questionable and S to satisfactory

11 Conclusion

IMEP-25b studied the capability of analytical laboratories to measure total concentration of bromate in three types of drinking water plus three other water matrices.
Considering the percentage of satisfactory z-scores, which ranged from 75 to 100 % depending on the matrix, the measurement capabilities of laboratories involved in routine bromate measurements in the frame of the Drinking Water Directive appear positive, despite the low bromate concentrations, which made this exercise particularly challenging.

Zeta scores were calculated when an uncertainty estimate was reported. These were less satisfactory than the z-scores for four samples showing that many laboratories encounter difficulties to provide a reasonable uncertainty estimate.

It was noted that 79 % of the participants used an appropriate reference material for the validation of their measurement procedures.

Best performance tended to be observed in laboratories that carried out a large number of analysis each year and in matrices where the bromate level was relatively high.

The use of a multivariate data analysis approach for data interpretation for interlaboratory comparisons provided an easy graphical tool to identify laboratories which provided measurement results significantly different from the others (unsatisfactory z scores).

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Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
EA	European Co-operation for Accreditation
EC	European Commission
EURACHEM	A focus for Analytical Chemistry in Europe
GUM	Guide to the Expression of Uncertainty in Measurement
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
MS	Mass Spectrometry
CD	Conductivity detection
UV	Ultraviolet detection
IC	Ion chromatography
LC	Liquid chromatography
PCR	Post column reaction

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Annexes

Annex 1: Homogeneity tests

	Soft		Hard		Mineral		Swimming		Raw		BrO_3 Std Sol.	
Measurement results (µg L^{-1})												
Bottle N°	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**	**R_1**	**R_2**
22	3.00	2.82	10.39	9.97	3.77	3.68	8.62	8.08	7.71	7.49	2.09	2.19
63	2.66	2.64	9.71	10.42	3.52	3.27	8.37	8.52	7.40	6.90	2.24	2.31
119	3.12	2.76	10.01	9.74	3.78	3.59	8.04	8.13	7.33	7.48	2.02	2.21
135	2.55	2.37	10.18	9.85	3.41	3.59	9.42	8.52	7.74	7.77	2.12	2.11
167	2.41	2.86	9.68	9.62	3.25	3.36	8.61	7.84	7.18	7.74	2.12	2.01
240	2.83	2.99	10.42	10.32	2.96	3.41	7.99	7.97	7.26	7.61	2.05	1.99
251	2.51	2.44	10.22	10.43	3.25	3.82	8.24	8.56	8.37	7.70	2.02	2.13
299	2.62	2.52	10.22	10.25	3.08	3.57	9.10	8.59	7.39	7.58	2.15	2.07
325	2.85	2.52	10.15	10.04	3.52	3.66	8.24	9.10	7.79	7.70	2.03	2.02
370	3.32	2.79	10.21	10.06	3.28	3.34	8.46	8.33	7.50	7.25	2.14	2.22
Mean	2.73		10.09		3.46		8.44		7.54		2.11	
σ (25 %)	0.682		2.524		0.864		2.109		1.886		0.528	
Homogeneity test according to the ISO 13528 (values in µg L^{-1})												
0.3 σ	0.205		0.757		0.259		0.633		0.566		0.158	
S_x	0.210		0.214		0.179		0.315		0.248		0.076	
S_w	0.203		0.218		0.217		0.377		0.256		0.068	
S_S	0.152		0.147		0.090		0.168		0.170		0.059	
$S_S \leq \sigma$?	Yes		Yes		Yes		Yes		Yes		Yes	
Test result	**Passed**		**Passed**		**Passed**		**Passed**		**Passed**		**Passed**	
Homogeneity test according to IUPAC International Harmonised Protocol (values in µg L^{-1})												
S_{an}^2	0.041		0.048		0.047		0.142		0.066		0.005	
S_{Sam}^2	0.023		0.022		0.009		0.028		0.029		0.003	
σ_{All}^2	0.051		0.573		0.067		0.400		0.320		0.025	
Critical value	0.137		1.126		0.174		0.896		0.668		0.052	
$S_{Sam}^2 \leq$ critical?	Yes		Yes		Yes		Yes		Yes		Yes	
Test result	**Passed**		**Passed**		**Passed**		**Passed**		**Passed**		**Passed**	

Notes:

R_1 denote replicate 1, R_2 denote replicate 2. For all other abbreviations, see the respective references. The standard deviation for proficiency assessment ($\hat{\sigma}$) that is used in this table was calculated as a fraction of the mean calculated from the homogeneity studies, not as a fraction of the reference value.

Annex 2: Stability tests

	Soft drinking water			
	Results in µg L^{-1}			
	Weeks			
Bottle	0	3	5	7
1	3,11	2,69	3,18	2,88
2	3,03	2,94	3,19	2,83
Slope =	-0,014			
SE Slope =	0,026			
Intercept =	3,032			
SE Intercept =	0,117		u_{St} µg L^{-1}	0.12
Correlation Coefficient =	0,045		u_{St} (%)	4.1
Slope of the linear regression significantly <> 0 (95%) :	No			
Slope of the linear regression significantly <> 0 (99%) :	No			
Test results	Stable			

	Hard drinking water			
	Results in µg L^{-1}			
	Weeks			
Bottle	0	3	5	7
1	9,86	10,83	9,67	9,57
2	10,31	10,38	10,08	10,13
Slope =	-0.053			
SE Slope =	0.057			
Intercept =	10.302			
SE Intercept =	0.258		u_{St} µg L^{-1}	0.51
Correlation Coefficient	0.127		u_{St} (%)	5.0
Slope of the linear regression significantly <> 0 (95%) :	No			
Slope of the linear regression significantly <> 0 (99%) :	No			
Test results	Stable			

	Mineral water			
	Results in µg L^{-1}			
	Weeks			
Bottle	0	3	5	7
1	3,43	3,5	3,31	3,33
2	3,67	3,64	3,41	3,45
Slope =	-0.029			
SE Slope =	0.015			
Intercept =	3.576			
SE Intercept =	0.070		u_{St} µg L^{-1}	0.16
Correlation Coefficient =	0.370		u_{St} (%)	4.7
Slope of the linear regression significantly <> 0 (95%) :	No			
Slope of the linear regression significantly <> 0 (99%) :	No			
Test results	Stable			

	Swimming pool water			
	Results in µg L^{-1}			
	Weeks			
Bottle	0	3	5	7
1	8,37	8,76	8,29	8,43
2	8,31	8,42	8,63	8,29
Slope =	0.001			
SE Slope =	0.025			
Intercept =	8			
SE Intercept =	0.115		u_{St} µg L^{-1}	0.21
Correlation Coefficient =	0		u_{St} (%)	2.5
Slope of the linear regression significantly <> 0 (95%) :	No			
Slope of the linear regression significantly <> 0 (99%) :	No			
Test results	Stable			

	Raw water			
	Results in µg L^{-1}			
	Weeks			
Bottle	0	3	5	7
1	7,82	7,53	7,82	7,7
2	7,41	7,84	7,32	7,29
Slope =	-0.019			
SE Slope =	0.034			
Intercept =	7.661			
SE Intercept =	0.153		u_{St} µg L^{-1}	0.29
Correlation Coefficient	0.049		u_{St} (%)	3.8
Slope of the linear regression significantly <> 0 (95%) :	No			
Slope of the linear regression significantly <> 0 (99%) :	No			
Test results	Stable			

	Bromate Standard Solution			
	Results in µg L^{-1}			
	Weeks			
Bottle	0	3	5	7
1	2,14	2,21	2,04	2,35
2	2,06	2,05	1,94	2,14
Slope =	0.012			
SE Slope =	0.018			
Intercept =	2.073			
SE Intercept =	0.081		u_{St} µg L^{-1}	0.15
Correlation Coefficient =	0.066		u_{St} (%)	7.3
Slope of the linear regression significantly <> 0 (95%) :	No			
Slope of the linear regression significantly <> 0 (99%) :	No			
Test results	Stable			

Annex 3: Invitation to EA to nominate laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements

IMEP

Geel, 29 April 2009
JRC.D04/FCo/ive/ARES(2009)/82694

Mr Boyan Ivanichkov
Bulgarian Accreditation Service (BAS)
Executive Agency at the Ministry of Economy and Energy
52 A "Dr. G. M. Dimitrov" Blvd.
BG-1797 Sofia
BULGARIA

Dear Mr Ivanichkov,

Intercomparison for bromate in drinking water

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison for the determination of bromate in drinking water. Seven sample matrices will be considered in this exercise; hard drinking water, soft drinking water, mineral water, raw water, swimming pool water, river water and a bromate standard solution.

In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. They should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. The maximum number of participants in this exercise is limited by the number of samples to 300.

Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 715. Fax: (32-14) 571 865.

E-mail: jrc-irmm-imep@ec.europa.eu

Annex 4: Letter accompanying the sample

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for reference materials and measurements
Isotope measurements

IMEP

Geel, 23 June 2009
JRC.D04/FCo/ive/ARES(2009)/141563

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«ADDRESS4»
«ZIP» «TOWN»
«COUNTRY»

Participation to IMEP-25b, a proficiency test exercise for the determination of bromate in water

Dear «TITLE» «SURNAME»,

Thank you for participating in the IMEP-25b intercomparison for the determination of **bromate** in water.

This parcel contains:
a) Seven bottles containing each ~ 60 mL of the test material (one bottle for each type of water)
b) A "Confirmation of Receipt" form
c) This accompanying letter

Please check whether the bottles containing the test material remained undamaged during transport. Then, please send the "Confirmation of receipt" form back (fax: +32-14-571865, e-mail: jrc-irmm-imep@ec.europa.eu). You should store the samples in a dark and cold place (at 4 °C) until analysis.

The measurand is: Bromate in six different types of water plus one bromate standard solution. The procedure used for the analyses should resemble as closely as possible the one that you use in routine sample analysis.

Please perform two or three independent measurements per measurand. Correct the measurement results for recovery, and report the corrected values (if applicable) plus their mean on the reporting website. The results should be reported in the same form (e.g., number of significant figures) as those normally reported to the customer.

You can find the reporting website at https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do
To access this webpage you need a personal password key, which is: «PARTKEY». The system will guide you through the reporting procedure. Please enter for each parameter

the two or three measurement results plus the technique you used, but do not report the uncertainty for each individual measurement. In addition, please report the mean of the results with technique and with uncertainty information in the allocated space for "measurement 4". After entering all results, please also complete the relating questionnaire. Do not forget to save, submit and confirm always when required.

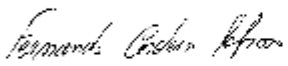
Directly after submitting your results and the questionnaire information online, you will be prompted to print the completed report form. Please do so, sign the paper version and return it to IRMM by fax or by e-mail. Check your results carefully for any errors before submission, since this is your definitive confirmation.

The deadline for submission of results is 25/08/2009.

Please keep in mind that collusion is contrary to professional scientific conduct and serves only to nullify the benefits of proficiency tests to customers, accreditation bodies and analysts alike.

Your participation in this project is greatly appreciated. If you have any remaining questions, please contact me by e-mail:
JRC-IRMM-IMEP@ec.europa.eu

With kind regards



Dr. Fernando Cordeiro
IMEP-25b Co-ordinator

Enclosures: 1) Seven bottles containing each ~ 60 mL of the test material (one bottle for each type of water); 2) confirmation of receipt form.

Cc: P. Taylor

«PARTKEY»

Annex 5: Sample receipt confirmation form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Isotope measurements

Annex to JRC.D04/FCo/ive/ARES(2009)/141563

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«ZIP» «TOWN»
«COUNTRY»

IMEP-25b

determination of **bromate** in water

Confirmation of receipt of the samples

Please return this form at your earliest convenience.
This confirms that the sample package arrived.
In case the package is damaged,
please state this on the form and contact us immediately.

ANY REMARKS .....
.....

Date of package arrival .....

Signature .....

Please return this form to:
Dr Fernando Cordeiro

IMEP-25 a Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

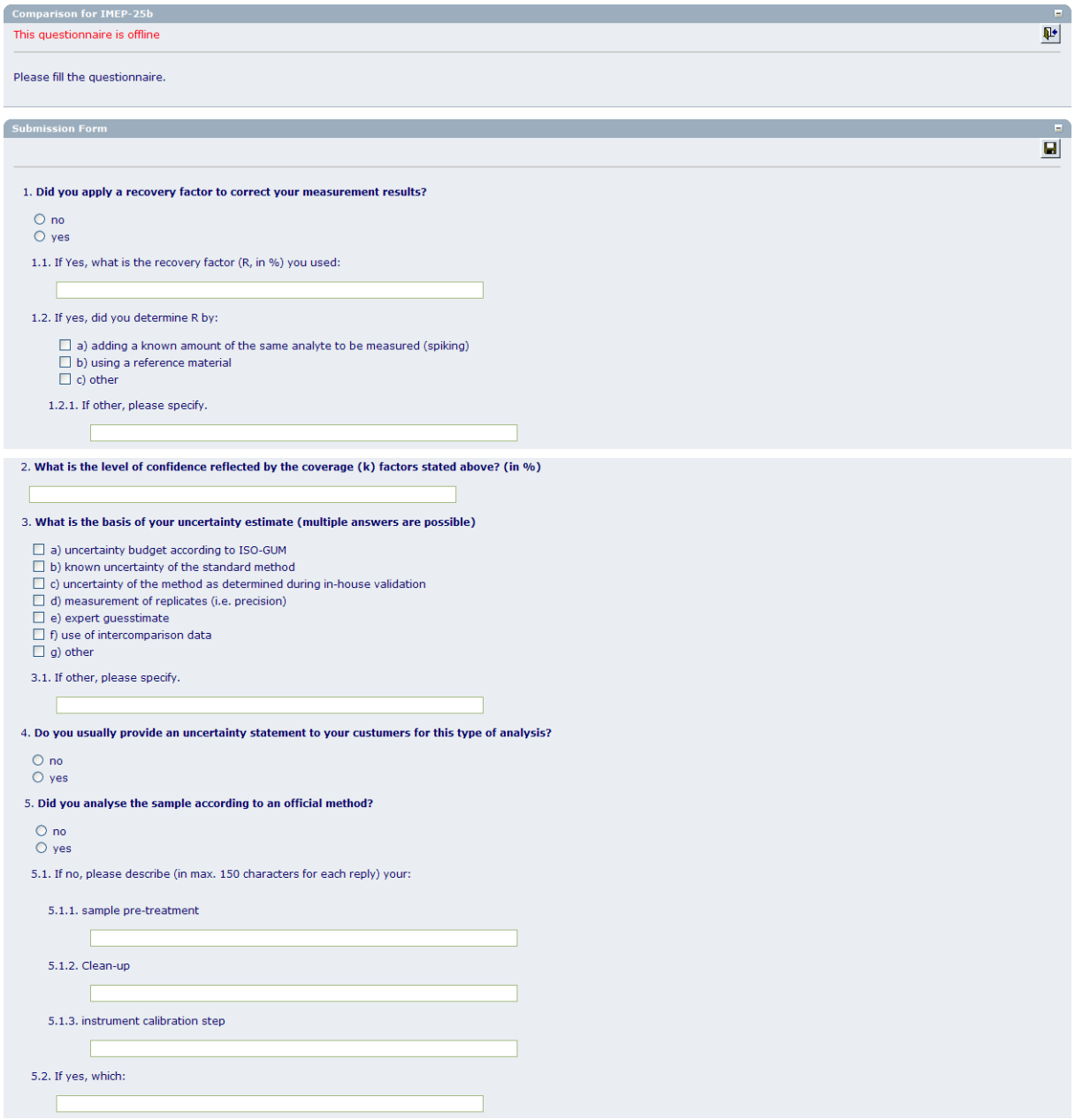
Fax : +32-14-571865
e-mail : jrc-irmm-imep@ec.europa.eu

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 715. Fax: (32-14) 571 865.

E-mail: jrc-irmm-imep@ec.europa.eu

IMEP

Annex 6: Questionnaire



Comparison for IMEP-25b

This questionnaire is offline

Please fill the questionnaire.

Submission Form

1. **Did you apply a recovery factor to correct your measurement results?**

- ○ no
- ○ yes

1.1. If Yes, what is the recovery factor (R, in %) you used:

1.2. If yes, did you determine R by:

- ☐ a) adding a known amount of the same analyte to be measured (spiking)
- ☐ b) using a reference material
- ☐ c) other

1.2.1. If other, please specify.

2. **What is the level of confidence reflected by the coverage (k) factors stated above? (in %)**

3. **What is the basis of your uncertainty estimate (multiple answers are possible)**

- ☐ a) uncertainty budget according to ISO-GUM
- ☐ b) known uncertainty of the standard method
- ☐ c) uncertainty of the method as determined during in-house validation
- ☐ d) measurement of replicates (i.e. precision)
- ☐ e) expert guesstimate
- ☐ f) use of intercomparison data
- ☐ g) other

3.1. If other, please specify.

4. **Do you usually provide an uncertainty statement to your custumers for this type of analysis?**

- ○ no
- ○ yes

5. **Did you analyse the sample according to an official method?**

- ○ no
- ○ yes

5.1. If no, please describe (in max. 150 characters for each reply) your:

5.1.1. sample pre-treatment

5.1.2. Clean-up

5.1.3. instrument calibration step

5.2. If yes, which:

6. **Does your laboratory carry out this type of analysis (as regards the parameters, matrix and methods)?**

- ○ no
- ○ yes

6.1. If yes, please estimate the number of samples:

- ☐ a) 0-50 samples per year
- ☐ b) 50-250 samples per year
- ☐ c) 250-1000 samples per year
- ☐ d) more than 1000 samples per year

7. **Does your laboratory have a quality system in place?**

- ○ no
- ○ yes

7.1. If yes, which:

- ☐ a) ISO 17025
- ☐ b) ISO 9000 series
- ☐ c) Other

7.1.1. If other, please specify.

7.2. If yes, are you accredited?

- ○ No
- ○ Yes

7.2.1. If yes, by which Accreditation Body have you been accredited?

8. **Does your laboratory take part in an interlaboratory comparison for this type of analysis on a regular basis?**

- ○ no
- ○ yes

8.1. If yes, which one(s)

9. **Does your laboratory use a reference material for this type of analysis?**

- ○ no
- ○ yes

9.1. If yes, is the material used for the validation of procedures?

- ○ no
- ○ yes

9.2. If yes, is the material used for calibration of instruments?

- ○ no
- ○ yes

9.3. If yes, which one(s)

10. **Do you have any comments? Please let us know: ...**

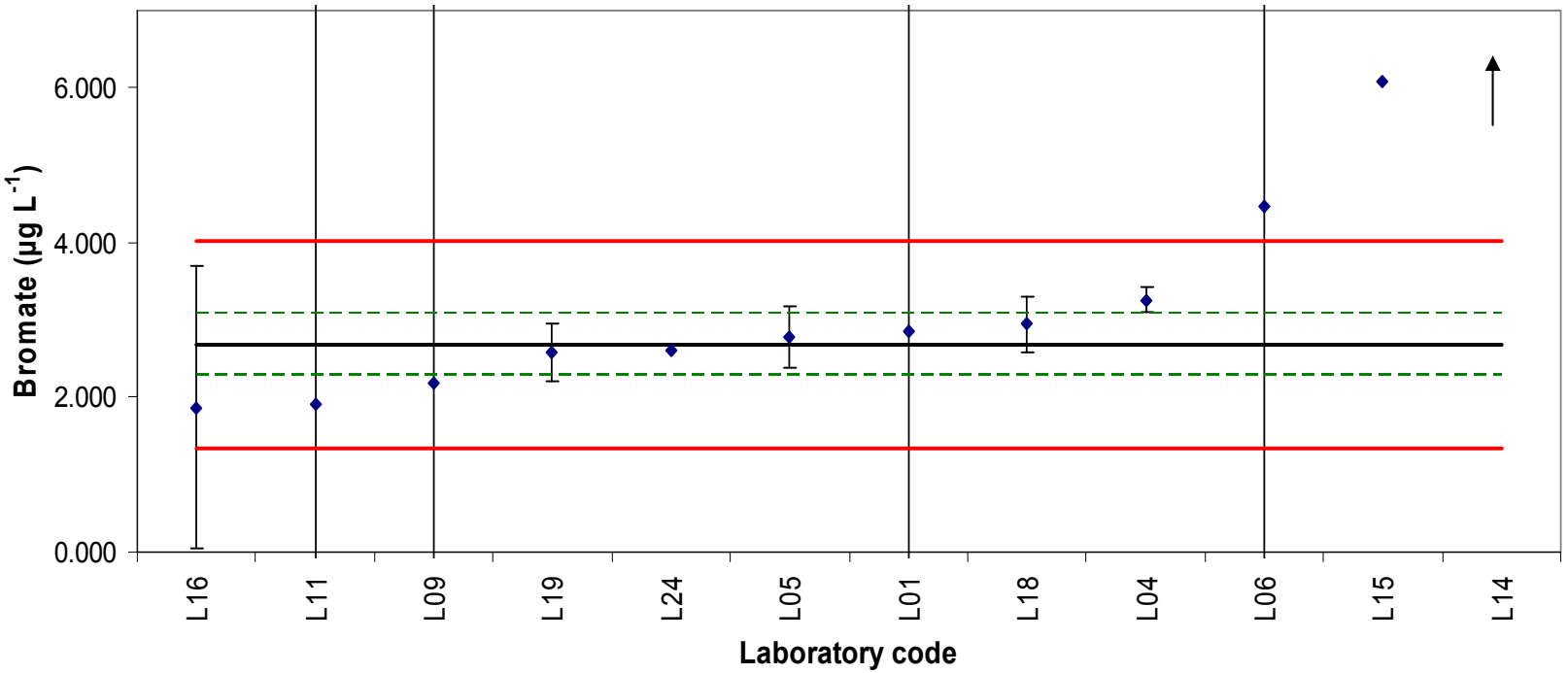
Annex 7: Bromate in Soft Drinking Water; X_{ref} = 2.68 ± 0.39 µg L^{-1} (k=2)

	x_1	x_2	x_3	x_4	U_{Lab}	k	Mean calc.	Z-score	Zeta	u_{lab}	Technique
L16	2	1.7	1.9		1.82	√3	1.867	-1.2	-0.7	c	IC
L11	1.86	1.74	1.89	2.14	15	√3	1.908	-1.2	-0.1	c	LC
L09	2.28	1.87	2.4	< 2.5	10	√3	2.183	-0.7	-0.1	c	LC
L19	2.73	2.71	2.31	2.58	0.367	√3	2.583	-0.1	-0.3	a	IC-PCR-UV
L24	2.4	2.8					2.600	-0.1			IC-CD
L05	3.1	2.5	2.7	2.8	0.4	2	2.775	0.1	0.3	a	IC-PCR-UV
L01	3	2.7			50	1	2.850	0.3	0.0	c	IC-CD
L18	3.18		2.7	2.95	0.369	2	2.943	0.4	1.0	a	IC-PCR-UV
L04	3.36	3.15		3.26	0.16	2	3.257	0.9	2.8	b	IC-MS
L06	10.6	2.8	0	4.5	9.3	2.92	4.475	2.7	0.6	c	IC-UV
L15	6.2	6.01	6				6.070	5.1			IC-CD
L14	52.6	52.2	52.2	52.3	0.42	√3	52.325	74.1	158.4	a	IC-CD
L02	< 2	< 2	< 2	< 2							IC-CD
L03	< 5	< 5	< 5	< 5							LC
L07	< 3	< 3	< 3								IC-CD
L08	< 5	< 5				2					IC-CD
L10	< 5	< 5	< 5	< 5							IC-PCR-UV
L12	< 4	< 4	< 4	< 4		2					IC-CD
L13	< 5	< 5	< 5	< 5							IC-UV
L17	< 10	< 10	< 10	< 10							LC
L20	< 5										IC
L21	< 1	< 1	< 1	< 1							IC-CD
L22	< 14	< 14	< 14	< 14							IC-CD
L23	< 6	< 6	< 6								LC-UV

Where: a = acceptable u_{lab} ($u_{min} \leq u_{lab} \leq u_{max}$), b = not acceptable u_{lab} ($u_{lab} < u_{min}$) and c = not acceptable u_{lab} ($u_{lab} > u_{max}$)

IMEP 25b (Bromate in Soft Drinking Water)

Reference value; X_{ref} = 2.68 ± 0.39 µg L^{-1} (k = 2)



This plot shows all measurement results and their associated uncertainties.
These uncertainties are shown as reported with various coverage factors or levels of confidence.
12 laboratories reported values "lower than". The green band refers to the reference interval ($X_{ref} \pm 2u_{ref}$)
the red band refers to the target interval ($X_{ref} \pm 2\sigma$)

Institute for Reference Materials and Measurements

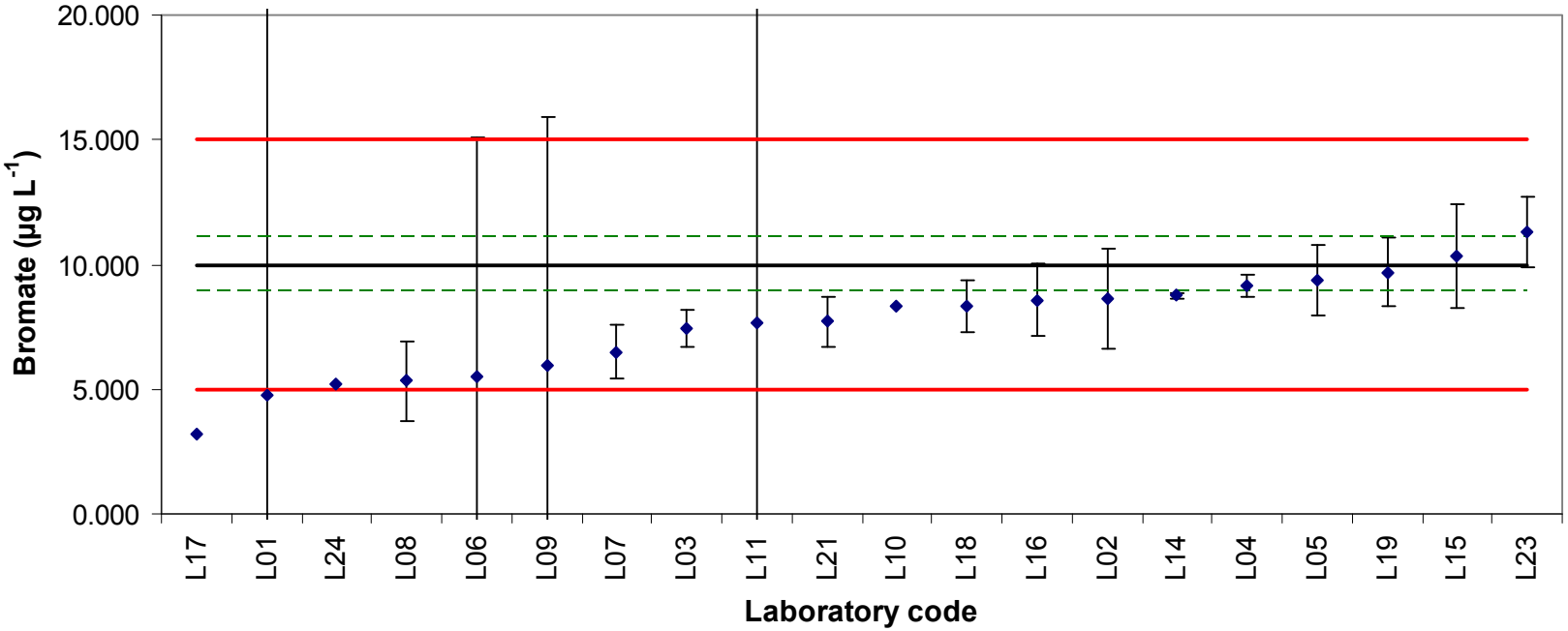
Annex 8: Bromate in Hard Drinking Water; X_{ref} = 10.00 ± 1.05 µg L^{-1} (k=2)

	x_1	x_2	x_3	x_4	U_{Lab}	k	Mean Calc.	Z-score	Zeta	u_{lab}	Technique
L17	3.2	3.5	2.8	3.2			3.175	-2.7			LC
L01	4.8	4.7			50	1	4.750	-2.1	-0.1	c	IC-CD
L24	5	5.4					5.200	-1.9			IC-CD
L08	5.7	5			1.6	2	5.350	-1.9	-4.9	a	IC-CD
L06	11.4	5.2	0	5.5	9.6	2.92	5.525	-1.8	-1.3	c	IC-UV
L09	5.96	5.9	5.94	5.93	10	√3	5.933	-1.6	-0.7	c	LC
L07	6.3	6.7	6.5		1.1	√3	6.500	-1.4	-4.2	a	IC-CD
L03	7.61	7.24	7.36		0.74	2	7.403	-1.0	-4.0	b	LC
L11	7.4	7.45	7.51	8.32	15	√3	7.670	-0.9	-0.3	c	LC
L21	7.8	8	7.8	7.3	1	2	7.725	-0.9	-3.1	a	IC-CD
L10	8.3						8.300	-0.7			IC-PCR-UV
L18	8.5	8.1		8.3	1.04	2	8.300	-0.7	-2.3	a	IC-PCR-UV
L16	8.5	8.6	8.6		1.45	√3	8.567	-0.6	-1.4	a	IC
L02	8.3	8.7	8.9	8.63	2	2	8.633	-0.5	-1.2	a	IC-CD
L14	8.72	8.7	8.79	8.74	0.087	√3	8.738	-0.5	-2.4	b	IC-CD
L04	9.12	9.18	9.15		0.46	2	9.150	-0.3	-1.5	b	IC-MS
L05	9.3	10.2	8.6	9.4	1.4	2	9.375	-0.3	-0.7	a	IC-PCR-UV
L19	9.09	10.1	9.85	9.68	1.38	√3	9.680	-0.1	-0.3	a	IC-PCR-UV
L15	11	9.9	10.1		2.1	2	10.333	0.1	0.3	a	IC-CD
L23	11.6	11.2	11.1		1.4	√3	11.300	0.5	1.3	a	LC-UV
L12	< 4	< 4	< 4	< 4		2					IC-CD
L13	< 5	< 5	< 5	< 5							IC-UV
L20	< 5										IC
L22	< 14	< 14	< 14	< 14							IC-CD

Where: a = acceptable u_{lab} ($u_{min} \leq u_{lab} \leq u_{max}$), b = not acceptable u_{lab} ($u_{lab} < u_{min}$) and c = not acceptable u_{lab} ($u_{lab} > u_{max}$)

IMEP 25b (Bromate in Hard Drinking Water)

Reference value: X_{ref} = 10.0 ± 1.05 µg L^{-1} (k = 2)



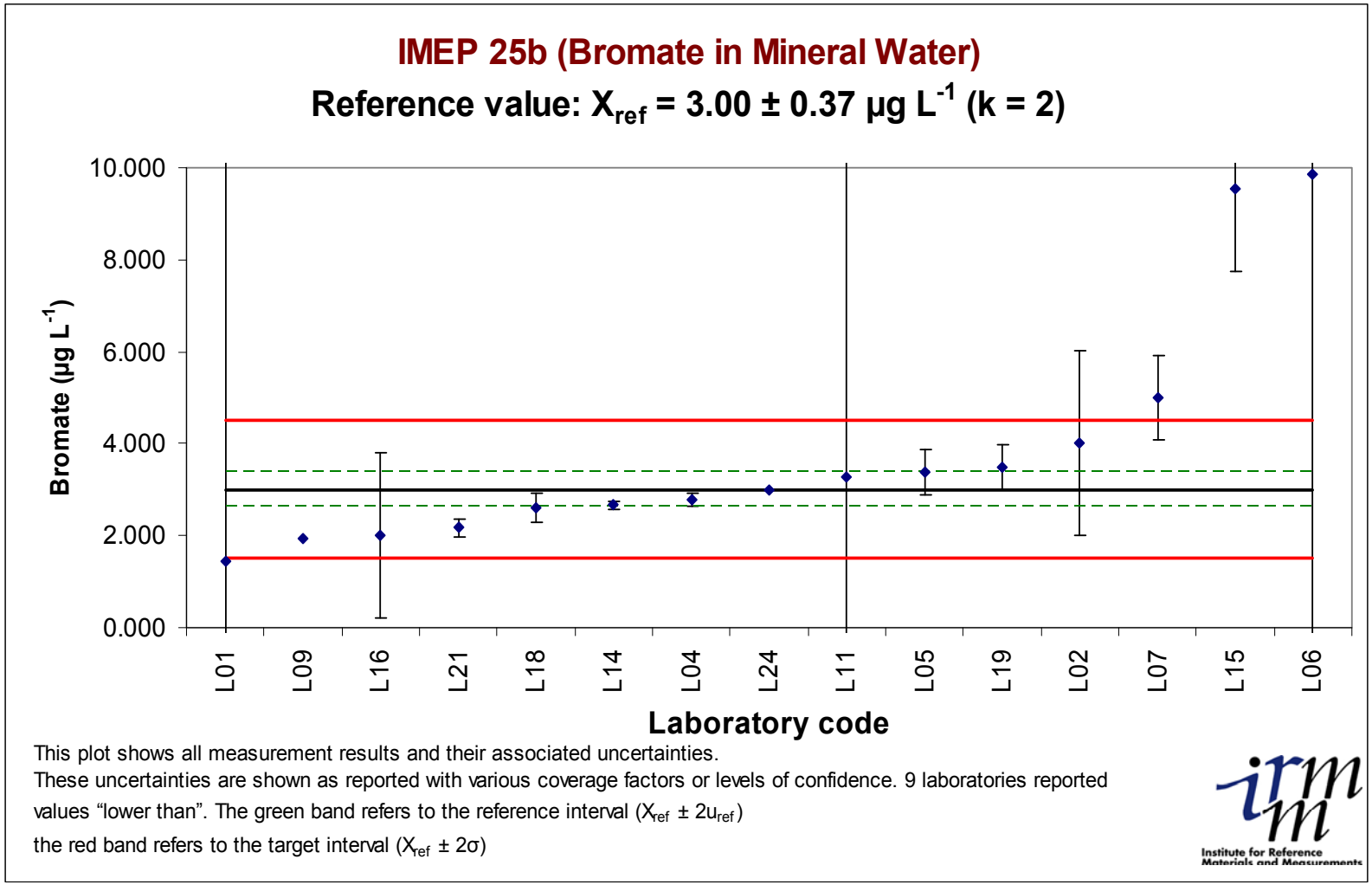
This plot shows all measurement results and their associated uncertainties.
These uncertainties are shown as reported with various coverage factors or levels of confidence. 4 laboratories reported values "lower than". The green band refers to the reference interval (X_{ref} ± $2u_{ref}$)
the red band refers to the target interval (X_{ref} ± 2σ)

Institute for Reference Materials and Measurements

Annex 9: Bromate in Mineral Water; X_{ref} = 3.00 ± 0.37 µg L^{-1} (k=2)

	x_1	x_2	x_3	x_4	U_{Lab}	k	Mean Calc.	Z-score	Zeta	u_{lab}	Technique
L01	1.3	1.6			50	1	1.450	-2.1	0.0	c	IC-CD
L09	1.95	1.95	1.87	<2.5			1.923	-1.4			LC
L16	1.9	2.1	2		1.8	√3	2.000	-1.3	-0.9	a	IC
L21	2.1	2.3	2.1	2.2	0.2	2	2.175	-1.1	-3.9	b	IC-CD
L18	2.6	2.6	2.6		0.325	2	2.600	-0.5	-1.6	b	IC-PCR-UV
L14	2.71	2.66	2.62	2.66	0.083	√3	2.663	-0.5	-1.8	b	IC-CD
L04	2.77	2.77	2.77		0.14	2	2.770	-0.3	-1.2	b	IC-MS
L24	3	3					3.000	0.0			IC-CD
L11	2.91	3.29	3.43	3.4	15	√3	3.258	0.3	0.0	c	LC
L05	3.6	3.2	3.3	3.4	0.5	2	3.375	0.5	1.2	a	IC-PCR-UV
L19	3.07	4.06	3.3	3.47	0.494	√3	3.475	0.6	1.4	a	IC-PCR-UV
L02	4.1	4.2	3.7	4.02	2	2	4.005	1.3	1.0	a	IC-CD
L07	4.8	5.2	5		0.9	√3	5.000	2.7	3.6	a	IC-CD
L15	10.5	8.6			1.8	2	9.550	8.7	7.1	a	IC-CD
L06	0	29.6	0	9.9	28.8	2.92	9.875	9.2	0.7	c	IC-UV
L03	< 5	< 5	< 5	< 5							LC
L08	< 5	< 5				2					IC-CD
L10	< 5										IC-PCR-UV
L12	< 4	< 4	< 4	< 4		2					IC-CD
L13	< 5	< 5	< 5	< 5							IC-UV
L17	< 10	< 10	< 10	< 10							LC
L20	< 5										IC
L22	< 14	< 14	< 14	< 14							IC-CD
L23	< 6	< 6	< 6								LC-UV

Where: a = acceptable u_{lab} ($u_{min} \leq u_{lab} \leq u_{max}$), b = not acceptable u_{lab} ($u_{lab} < u_{min}$) and c = not acceptable u_{lab} ($u_{lab} > u_{max}$)



This plot shows all measurement results and their associated uncertainties.
These uncertainties are shown as reported with various coverage factors or levels of confidence. 9 laboratories reported values "lower than". The green band refers to the reference interval (X_{ref} ± 2u_{ref})
the red band refers to the target interval (X_{ref} ± 2σ)

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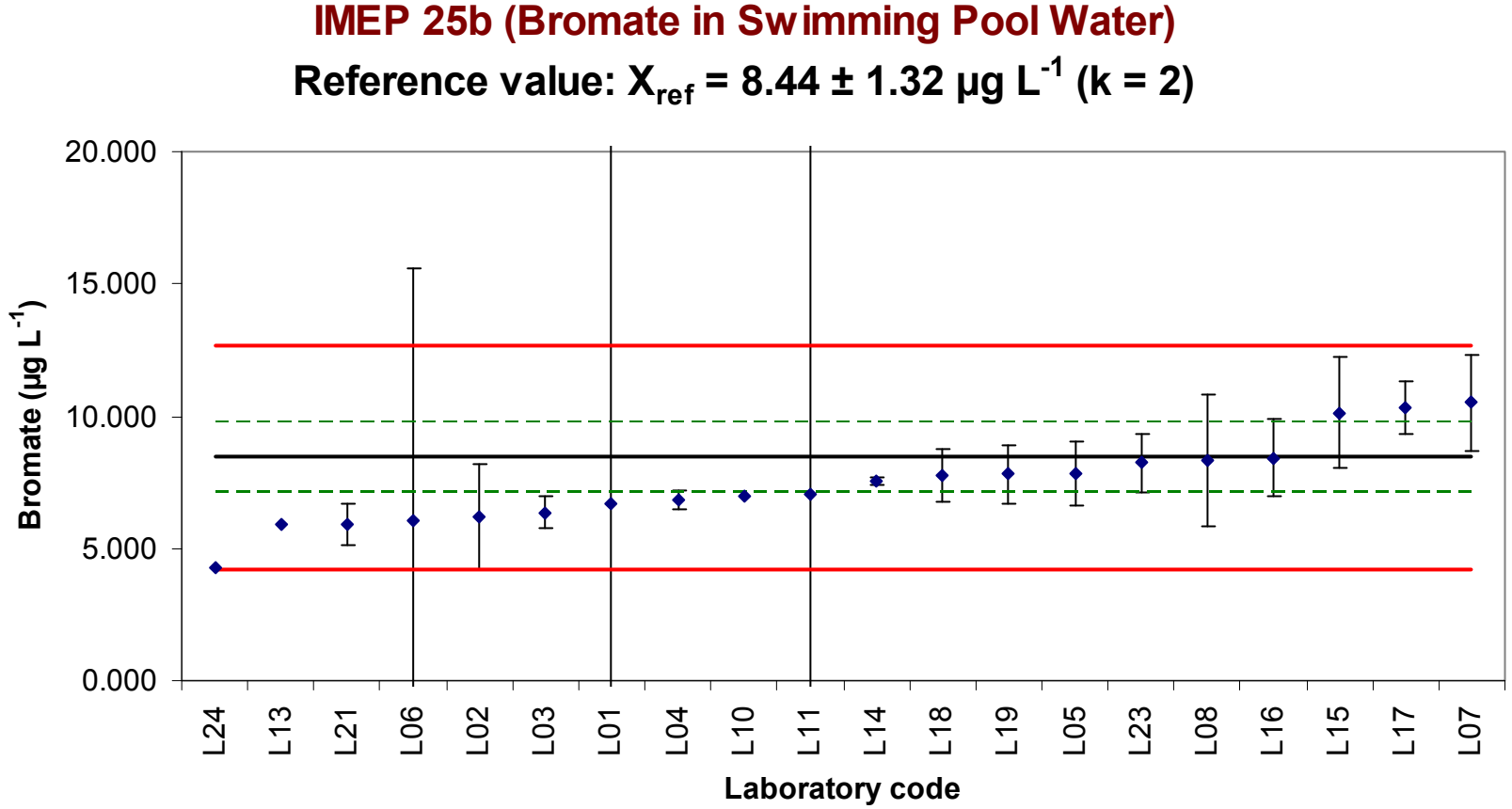
Annex 10: Bromate in Swimming Pool Water; X_{ref} = 8.44 ± 1.32 µg L^{-1} (k=2)

	x_1	x_2	x_3	x_4	U_{Lab}	k	Mean Calc.	Z-score	zeta	u_{lab}	Technique
L24	4.3	4.3					4.300	-2.0			IC-CD
L13	5.9	5.9	5.9	5.9			5.900	-1.2			IC-UV
L21	6.5	5.6	5.7	5.8	0.8	2	5.900	-1.2	-3.3	b	IC-CD
L06	0	7	11.2	6.1	9.5	2.92	6.075	-1.1	-0.7	c	IC-UV
L02	6.2	5.8	6.5	6.17	2	2	6.168	-1.1	-1.9	a	IC-CD
L03	6.23	6.7	6.17		0.62	2	6.367	-1.0	-2.8	b	LC
L01	6	7.4			50	1	6.700	-0.8	0.0	c	IC-CD
L04	6.87	6.76	6.82		0.34	2	6.817	-0.8	-2.4	b	IC-MS
L10	7.2	6.8					7.000	-0.7			IC-PCR-UV
L11	7.41	7.22	6.54	6.91	15	√3	7.020	-0.7	-0.2	c	LC
L14	7.46	7.62	7.57	7.55	0.15	√3	7.550	-0.4	-1.3	b	IC-CD
L18	7.7	7.8	7.75		0.969	2	7.750	-0.3	-0.8	b	IC-PCR-UV
L19	7.84	7.62	7.98	7.81	1.11	√3	7.813	-0.3	-0.7	a	IC-PCR-UV
L05	8.3	8.1	7.1	7.8	1.2	2	7.825	-0.3	-0.7	b	IC-PCR-UV
L23	8.4	7.8	8.6	8.1	1.1	√3	8.225	-0.1	-0.2	b	LC-UV
L08	8.9	7.8			2.5	2	8.350	0.0	-0.1	a	IC-CD
L16	8.3	8.6	8.4		1.45	√3	8.433	0.0	0.0	a	IC
L15	10.5	9.9	10	10.1	2.1	2	10.125	0.8	1.4	a	IC-CD
L17	10.4	10.6	10	10.3	1	2	10.325	0.9	2.3	b	LC
L07	10.5	10.5	10.5		1.8	√3	10.500	1.0	1.7	a	IC-CD
L09	0.2	0.19	0.4	< 2.5							LC
L12	< 4	< 4	< 4	< 4		2					IC-CD
L20	< 5										IC
L22	< 14	< 14	< 14	< 14							IC-CD

Where: a = acceptable u_{lab} ($u_{min} \leq u_{lab} \leq u_{max}$), b = not acceptable u_{lab} ($u_{lab} < u_{min}$) and c = not acceptable u_{lab} ($u_{lab} > u_{max}$)



This plot shows all measurement results and their associated uncertainties.
These uncertainties are shown as reported with various coverage factors or levels of confidence. 4 laboratories reported values "lower than". The green band refers to the reference interval (X_{ref} ± $2u_{ref}$)
the red band refers to the target interval (X_{ref} ± 2σ)

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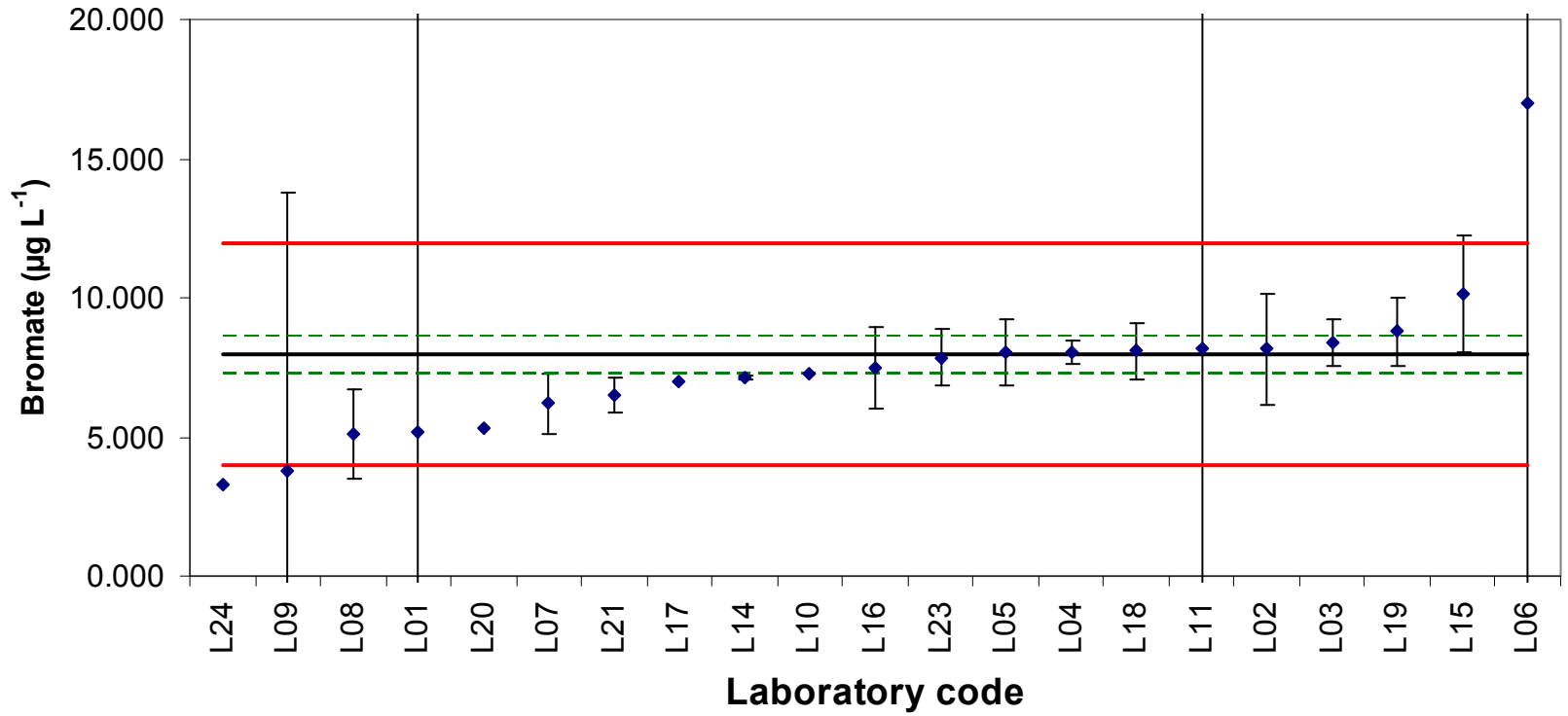
Annex 11: Bromate in Raw Water; X_{ref} = 7.95 ± 0.66 µg L^{-1} (k=2)

	x_1	x_2	x_3	x_4	U_{Lab}	k	Mean Calc.	Z-score	zeta	u_{lab}	Technique
L24	1.4	5.2					3.300	-2.3			IC-CD
L09	3.88	3.63	3.81	3.77	10	√3	3.773	-2.1	-0.7	c	LC
L08	5.1	< 5			1.6	2	5.100	-1.4	-3.3	a	IC-CD
L01	5.3	5			35	1	5.150	-1.4	-0.1	c	IC-CD
L20	5.3						5.300	-1.3			IC
L07	6.4	6	6.2		1.1	√3	6.200	-0.9	-2.4	a	IC-CD
L21	6.8	6.1	6.3	6.8	0.6	2	6.500	-0.7	-3.2	b	IC-CD
L17	7.1	7.6	6.3	7			7.000	-0.5			LC
L14	7.11	7.15	7.07	7.11	0.074	√3	7.110	-0.4	-2.5	b	IC-CD
L10	7.5	7				2	7.250	-0.4			IC-PCR-UV
L16	7.1	7.8	7.5		1.48	√3	7.467	-0.2	-0.5	a	IC
L23	7.7	8	7.9		1	√3	7.867	0.0	-0.1	a	LC-UV
L05	8.6	8	7.5	8	1.2	2	8.025	0.0	0.1	a	IC-PCR-UV
L04	8.05	8.05	8.05		0.4	2	8.050	0.1	0.3	b	IC-MS
L18	8.3	7.9	8.1		1.01	2	8.100	0.1	0.2	a	IC-PCR-UV
L11	8.04	7.94	8.43	8.2	15	√3	8.153	0.1	0.0	c	LC
L02	9	7	8.5	8.17	2	2	8.168	0.1	0.2	a	IC-CD
L03	8.07	8.72			0.84	2	8.395	0.2	0.8	a	LC
L19	8.04	9.54	8.77	8.78	1.25	√3	8.783	0.4	1.0	a	IC-PCR-UV
L15	10.8	9.5			2.1	2	10.150	1.1	2.0	a	IC-CD
L06	10.4	38.6	1.9	17	32.4	2.92	16.975	4.5	0.8	c	IC-UV
L12	< 4	< 4	< 4	< 4		2					IC-CD
L13	< 5	< 5	< 5	< 5							IC-UV
L22	< 14	< 14	< 14	< 14							IC-CD

Where: a = acceptable u_{lab} ($u_{min} \leq u_{lab} \leq u_{max}$), b = not acceptable u_{lab} ($u_{lab} < u_{min}$) and c = not acceptable u_{lab} ($u_{lab} > u_{max}$)



This plot shows all measurement results and their associated uncertainties.
These uncertainties are shown as reported with various coverage factors or levels of confidence. 3 laboratories reported values "lower than". The green band refers to the reference interval (X_{ref} ± $2u_{ref}$)
the red band refers to the target interval (X_{ref} ± 2σ)

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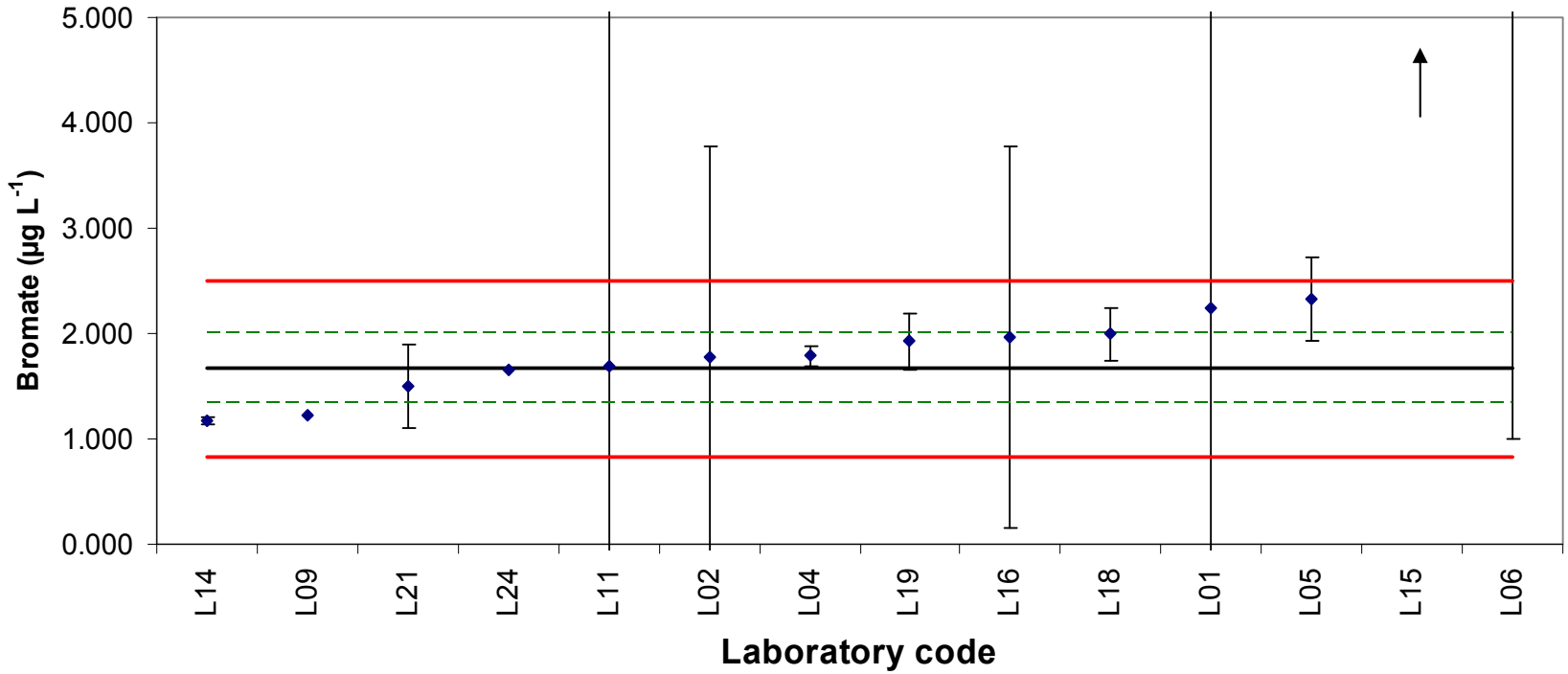
Annex 12: Bromate Std. Solution; X_{ref} = 1.67 ± 0.33 µg L^{-1} (k=2)

	x_1	x_2	x_3	x_4	U_{Lab}	k	Mean Calc.	Z-score	zeta	u_{lab}	Technique
L14	1.16	1.16	1.2	1.17	0.042	√3	1.173	-1.2	-3.0	b	IC-CD
L09	1.18	1.22	1.28	<2.5			1.227	-1.1			LC
L21	1.3	1.4	1.7	1.6	0.4	2	1.500	-0.4	-0.7	b	IC-CD
L24	1.5	1.8					1.650	0.0			IC-CD
L11	2.07	< 1	< 1	1.32	15	2	1.695	0.1	0.0	c	LC
L02	1.6	2.2	1.5	1.8	2	2	1.775	0.3	0.1	a	IC-CD
L04	1.82	1.75	1.79		0.09	2	1.787	0.3	0.7	b	IC-MS
L19	1.76	2.22	1.8	1.92	0.273	√3	1.925	0.6	1.1	b	IC-PCR-UV
L16	1.9	2	2		1.81	√3	1.967	0.7	0.3	a	IC
L18	2	2	2		0.25	2	2.000	0.8	1.6	b	IC-PCR-UV
L01	2.4	2.1			50	1	2.250	1.4	0.0	c	IC-CD
L05	2.5	2.4	2.1	2.3	0.4	2	2.325	1.6	2.5	a	IC-PCR-UV
L15	7.5	7.4					7.450	13.8			IC-CD
L06	7.3	14.9	5.7	9.3	8.3	2.92	9.300	18.3	2.7	c	IC-UV
L03	< 5	< 5	< 5	< 5							LC
L07	< 3	< 3	< 3								IC-CD
L08	< 5	< 5									IC-CD
L10	< 5										IC-PCR-UV
L12	< 4	< 4	< 4	< 4		2					IC-CD
L13	< 5	< 5	< 5	< 5							IC-UV
L17	< 10	< 10	< 10	< 10							LC
L20	< 5										IC
L22	< 14	< 14	< 14	< 14							IC-CD
L23	< 6	< 6	< 6								LC-UV

Where: a = acceptable u_{lab} ($u_{min} \leq u_{lab} \leq u_{max}$), b = not acceptable u_{lab} ($u_{lab} < u_{min}$) and c = not acceptable u_{lab} ($u_{lab} > u_{max}$)



This plot shows all measurement results and their associated uncertainties.
These uncertainties are shown as reported with various coverage factors or levels of confidence. 10 laboratories reported values "lower than". The green band refers to the reference interval (X_{ref} ± $2u_{ref}$)
the red band refers to the target interval (X_{ref} ± 2σ)

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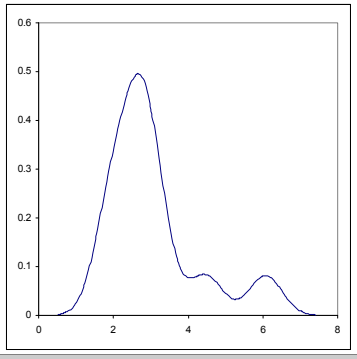
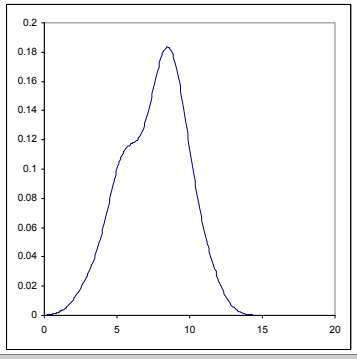
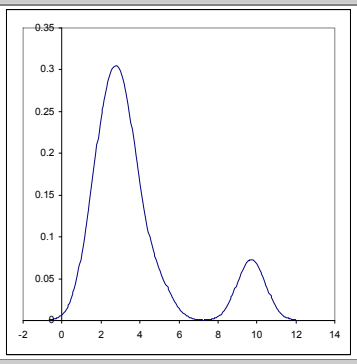
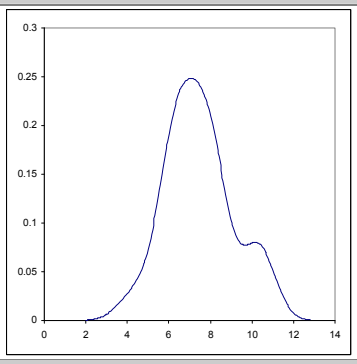
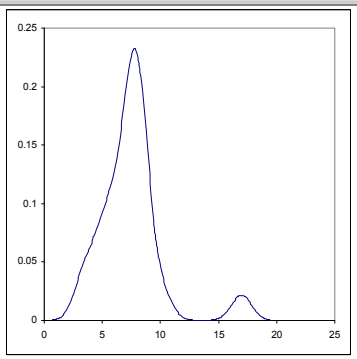
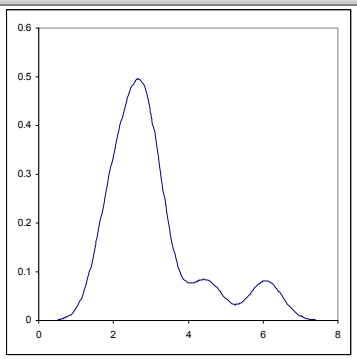
Annex 13: Kernel densities

X axes in µg L^{-1}	
	
Soft drinking water	Hard drinking water
	
Mineral water	Swimming pool water
	
Raw water	Bromate Std. solution

Annex 14: Summary of laboratory scores

	Soft Drinking Water		Hard Drinking Water		Mineral Water		Swimming pool		Raw Water		Standard Solution	
	Z-score	Zeta	Z-score	Zeta	Z-score	Zeta	Z-score	zeta	Z-score	zeta	Z-score	zeta
L01	0.3	0.0	-2.1	-0.1	-2.1	0.0	-0.8	0.0	-1.4	-0.1	1.4	0.0
L02			-0.5	-1.2	1.3	1.0	-1.1	-1.9	0.1	0.2	0.3	0.1
L03			-1.0	-4.0			-1.0	-2.8	0.2	0.8		
L04	0.9	2.8	-0.3	-1.5	-0.3	-1.2	-0.8	-2.4	0.1	0.3	0.3	0.7
L05	0.1	0.3	-0.3	-0.7	0.5	1.2	-0.3	-0.7	0.0	0.1	1.6	2.5
L06	2.7	0.6	-1.8	-1.3	9.2	0.7	-1.1	-0.7	4.5	0.8	18.3	2.7
L07			-1.4	-4.2	2.7	3.6	1.0	1.7	-0.9	-2.4		
L08			-1.9	-4.9			0.0	-0.1	-1.4	-3.3		
L09	-0.7	-0.1	-1.6	-0.7	-1.4				-2.1	-0.7	-1.1	
L10			-0.7				-0.7		-0.4			
L11	-1.2	-0.1	-0.9	-0.3	0.3	0.0	-0.7	-0.2	0.1	0.0	0.1	0.0
L13							-1.2					
L14	74.1	158.4	-0.5	-2.4	-0.5	-1.8	-0.4	-1.3	-0.4	-2.5	-1.2	-3.0
L15	5.1		0.1	0.3	8.7	7.1	0.8	1.4	1.1	2.0	13.8	
L16	-1.2	-0.7	-0.6	-1.4	-1.3	-0.9	0.0	0.0	-0.2	-0.5	0.7	0.3
L17			-2.7				0.9	2.3	-0.5			
L18	0.4	1.0	-0.7	-2.3	-0.5	-1.6	-0.3	-0.8	0.1	0.2	0.8	1.6
L19	-0.1	-0.3	-0.1	-0.3	0.6	1.4	-0.3	-0.7	0.4	1.0	0.6	1.1
L20									-1.3			
L21			-0.9	-3.1	-1.1	-3.9	-1.2	-3.3	-0.7	-3.2	-0.4	-0.7
L23			0.5	1.3			-0.1	-0.2	0.0	-0.1		
L24	-0.1		-1.9		0.0		-2.0		-2.3		0.0	

Blank cells refers to measurements for which, either a "lower than" value has been reported (no z value) or for which no uncertainty has been reported (no zeta value).

European Commission

EUR 24136 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: IMEP-25b Determination of bromate in drinking water – Interlaboratory Comparison Report
Authors: Fernando Cordeiro, Franz Schmitz, Inge Verbist, Håkan Emteborg, Jean Charoud-Got, Maria C. Contreras Lopez, Philip Taylor, Beatriz de la Calle
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Abstract

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme® (IMEP). IMEP organises interlaboratory comparisons (ILC's) in support to EU policies. This ILC exercise reports the performance of the laboratories on the determination of bromate in drinking water in support to the Council Directive 98/83/EC (Drinking Water Directive, DWD).

Seven test materials were included in this study: soft drinking water, hard drinking water, mineral water, swimming pool water, raw water (untreated), a bromate standard solution and a blank solution consisting of non-spiked ultra pure water. The bottles containing the blank solution were labelled as river water.

The 25 participating laboratories were invited via the IRMM website and the European Co-operation for Accreditation.

z scores were calculated with a target standard deviation of 25 % of the reference value. The scores were satisfactory for a high share of the participants (75 % for soft drinking water, 90 % for hard drinking water, 73 % for mineral water, 100 % for swimming pool water, 86 % for raw water and bromate standard solution, respectively). In addition, zeta scores were calculated for participants having reported a measurement uncertainty. These were however, less satisfactory on average.

In summary, the measurement capabilities of laboratories involved in the determination of bromate measurements in the frame of the DWD is satisfactory considering that the concentration levels in almost all matrices were lower or equal to the maximum permitted level of bromate in these types of matrices.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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