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IMEP-25a: Determination of bromate in drinking water

A Collaborative Trial Report

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IMEP-25a: Determination of Bromate in Drinking Water

A Collaborative Trial Report

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1 Abstract

A collaborative study, IMEP-25a, was conducted in accordance with international protocols to determine the performance characteristics of an analytical method for the determination of dissolved bromate in drinking water. The method should fulfil the analytical requirements of the Council Directive 98/83/EC (referred in this report as the Drinking Water Directive, DWD). The method is based on ion chromatography followed by post column reaction and ultraviolet detection. This method follows a draft method from the International Organization for Standardization (Draft ISO/DIS 11206).

The existing standard method (ISO 15061:2001) is based on ion chromatography using suppressed conductivity detection for the determination of bromate concentrations ≥ 0.5 µg L^{-1} whereby a pre-concentration step may be required for the determination of bromate concentrations below as 3 µg L^{-1} to 5 µg L^{-1}. The new method includes a dilution step allowing the determination of bromate concentrations ≥ 0.5 µg L^{-1}. Furthermore, the method aims to minimize any potential interference of chlorite ions.

The collaborative study investigated different types of drinking water such as soft drinking water, hard drinking water and mineral water. Other types of water such as raw water (untreated), swimming pool water, a blank (named river water) and a bromate standard solution were also included as test samples.

All test matrices, except the swimming pool water, were spiked with high purity potassium bromate to obtain bromate concentrations ranging from 1.67 to 10.0 µg L^{-1}. Swimming pool water was not spiked as this water was incurred with bromate.

Test samples were dispatched to 17 laboratories in 9 different countries. Sixteen participants reported results.

The repeatability relative standard deviation (RSD_r) ranged from 1.2 to 4.1 % while the reproducibility relative standard deviation (RSD_R) ranged from 2.3 to 5.9 %.

These precision characteristics are in good agreement, if not better, than those of the ISO 15061. A thorough comparison of the performance characteristics is presented in this report.

All method performance characteristics obtained in the frame of this collaborative trial indicates that the draft ISO/DIS 11206 standard method meets the requirements set down by the DWD. The draft ISO/DIS 11206 standard method can be therefore considered to fit its intended analytical purpose.

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 (JRC-IRMM). 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 participating in proficiency tests (PTs) 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 interlaboratory comparison exercises (ILC) in the frame of specific EU Directives, or on request of a specific Directorate-General.

This collaborative trial was organized in collaboration with the Technical Committee 147, "*Water quality"*, Subcommittee SC 2, *"Physical, chemical and biochemical methods"* of the International Organization for Standardization (ISO), ISO TC 147 SC 2 WG 33.

IMEP is accredited according to ISO Guide 43-1. The designation of this ILC is IMEP-25a.

3 Introduction

The Council Directive 98/83/EC (DWD) [1] 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 10 µg L^{-1}. DWD specifies under Annex III, 2.1:

> "*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"*

Both the trueness and precision criteria were set at ± 25 % of the parametric value.
Bromate is identified as a by-product, originated from the reaction of the disinfectant ozone, 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 typically reaches 50 % [2].
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.
The need for reliable analytical methods at such low concentration levels as set by the European legislation was the driving motive for the International Organization for Standardization having called for the ISO 15061:2001 [6] method update, and ultimately for the conduction of IMEP-25a whereby the draft standard method ISO/DIS 11206 [7] was followed.

4 Scope and aim

The scope of this interlaboratory validation study (collaborative trial) is to establish the performance characteristics of a method to be used in the determination of bromate in the frame of the water monitoring activities carried out in support to the Drinking Water Directive 98/83/EC. This exercise was organized following ISO Guide 43-1 [8] and IUPAC guidelines [9].
The assessment of the measurement results is undertaken on the basis of requirements laid down in the ISO Standards (ISO 5725-2 [10] and ISO 13528 [11]). Furthermore, the administrative and logistic procedures of IMEP were respected.

5 Time frame

The exercise was announced via the IMEP website and by the ISO Technical Committee 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 in May - July 2009. Characterization of the content of bromate in the swimming pool water took place in July 2009.

6 Material

6.1 Preparation

Three types of drinking water have been included as test items for this exercise:

- soft drinking water,
- hard drinking water,
- mineral water

Other types of water 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 (spiked with ethylenediamine for stabilization purposes and called river water).

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 ultra pure water blank sample was prepared at IRMM.
While the test sample called river water, swimming pool and raw water are not normally intended for human consumption (hence not covered by the DWD) it can not be excluded that

these types of water might be ingested during swimming. Moreover the international draft standard under scrutiny in this collaborative trial includes drinking water, raw, surface water, partially treated and swimming pool water [7], therefore the need to include them in the exercise. All test matrices were submitted to analysis regarding the disinfection agent and the trace element content by the LHD (Landesbetrieb Hessisches Landeslabor, Wiesbaden, Germany) following standard analytical methods as described in Annex 1.

6.2 Preparation of the test samples

Potassium bromate, $KBrO_3$ of ACS ISO Reagent grade > 99.8 % purity provided by Merck (KGaA, Darmstadt, Germany) was used for the spiking of the different materials. 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 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 minutes 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 it with Milli-Q water up to 535.62 g.

When spiking the test materials, aliquots of the intermediate stock solution were accurately weighed and diluted to obtain the final bromate concentrations. These concentrations were set as the assigned (reference) values to calculate the analytical recovery.

All solutions, including the blank solution, contained ethylenediamine up to a concentration of 50 mg L^{-1} which is added as stabilizer to avoid the formation of bromate (after preparation of the solution) from bromine in the presence of ozone. The blank 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 quantification (LOQ = 0.5 µg L^{-1}, personal communication) 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, filled into 60 mL polyethylene bottles and 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 water samples using a method based on high performance liquid chromatography, coupled with an inductively coupled plasma - mass spectrometry instrument (HPLC-ICP-MS). The blank solution was not tested for homogeneity. The HPLC-ICP-MS system consisted of a Perkin Elmer quaternary pump with vacuum degasser. The analytical column was a Dionex® anion exchange column IonPac AS16 250x4 mm I.D. A sample volume of 250 µL was injected. Isocratic elution was applied using 35 mM NaOH as eluent with a flow rate of 0.3 mL min^{-1} [12].

The experimental design used for the assessment of the homogeneity of the test samples complied with the requirements set by the ISO 13528 [11] and by the IUPAC Harmonized Protocol [9].
ISO 13528 [11] describes the tests to determine if the samples are to be considered adequately homogeneous to be used in a proficiency testing exercise. These tests compare the between bottle standard deviation with the target standard deviation of an exercise. In this particular exercise we wish to check whether the material should be considered sufficiently homogeneous while using an analytical method whose precision is set from legislation. Therefore, the target standard deviation was set to 25 % of each assigned value (for each water test sample), which is the precision accepted by the DWD. Both tests indicate that all the water test samples were sufficiently homogeneous for the bromate analysis (Annex 2).
The between bottle relative standard uncertainty (u_{bb}, expressed as a percentage) ranged from 1.0 % to 6.0 %. u_{bb} was estimated using SoftCRM software [13].

6.4 Stability

An isochronous stability study [14, 15] was carried out by IRMM at three temperatures (4, 18 and 60 °C) with the aim to:

- Measure all samples under repeatability conditions (thus avoiding the need to combine the repeatability with long term reproducibility conditions).
- 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 decided to dispatch all samples under cooled conditions (4° C).
- Quantify the potential degradation during the entire interlaboratory comparison study (approximately two months).

All measurements for the stability studies were carried out by the Rheinisch-Westfälisches Institut für Wasser (IWW, Germany).
No significant degradation for any of the test samples was foreseen.
The evaluation of the stability of the test materials was made using the SoftCRM 2.0 software [13]. The materials proved to be stable at 18 °C for a length covering the whole time frame of the exercise.
The relative standard uncertainty due to the stability ranged from 2.5 % to 7.3 %.
Annex 3 shows the standard uncertainty (u_{st}) obtained from stability studies carried out at 18 °C when considering a shelf life of nine weeks. The participants were instructed to store the material at 4° C after receipt.

6.5 Distribution

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

1) Fourteen bottles, each containing ~ 60 mL of the test material (two bottles for each type of water).
2) A letter accompanying the sample (Annex 4).

3) A confirmation of receipt form (Annex 5) and

4) A copy of the standard operational procedure (SOP DRAFT: ISO/DIS 11206) to be followed strictly.

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

7 Participant invitation, registration and information

A call for participation was published on the IRMM/IMEP website (Annex 6) and via the ISO/TC 147 representative.

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

Seventeen laboratories from 9 different countries took part in this exercise (6 from European countries, 1 from the USA, 1 from The Republic of Korea and 1 from India). Results were reported by 16 participants.

The measurand was defined as bromate in six different types of water and in one synthetic standard solution. The following instructions were sent to the participants;

> *"Please perform two independent measurements per bottle on two different days (one bottle/day) following DRAFT: ISO/DIS 11206. Report the values obtained on the first day in "Measurement 1" and "Measurement 2" and the values obtained on the second day in "Measurement 3" and "Measurement 4" on the reporting website. Express the results in µg L^{-1}. The results should be reported with two decimals (or more if necessary to avoid a series of identical values)"*

Furthermore the following message was given:

> "*This is a study of the method not of the laboratory. The method must be strictly followed as described. Any deviation from the method should be reported to the organizers"*

Participants used an online form to report their measurement results and to complete the related questionnaire (Annex 7). The questionnaire was used to obtain additional information related to measurements and laboratories.

They also received an individual code to access the online reporting interface.

8 Experimental

The maximum tolerable concentration of bromate in drinking water according to the Council Directive 98/83/EC is 10 µg L^{-1}. The bromate concentrations in the IMEP-25a water samples were prepared accordingly, i.e. test water samples were spiked up to a level not exceeding

this value. Water samples with the exception of the swimming pool water and the blank solution were spiked with high purity $KBrO_3$ to achieve the levels of concentration given in Table 1. Swimming pool water, having an incurred bromate level, was not spiked. The bromate concentration level in swimming pool water was estimated from the homogeneity study performed by IWW.

No bromate could be detected in the blank sample (called river water). This sample was used to detect false positives.

The bromate concentrations in the samples used in IMEP-25a, X_{ref}, are presented in Table 1. X_{ref} was used for the assessment of the analytical recovery on the bromate determination in the different test samples.

The standard uncertainties (u_{ref}) associated with those concentrations 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 [15]:

$$u_{ref} = \sqrt{\left(u_{char}^2 + u_{bb}^2 + u_{st}^2\right)} \qquad \text{Eq. 1}$$

Where:

u_{char} is the standard uncertainty on the characterisation

u_{bb} is the standard uncertainty arising from the homogeneity studies (between-bottle)

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

The standard uncertainties for characterisation (u_{char}) were estimated for the spiked materials following the Guide to the expression of uncertainty in measurement (GUM) [16] 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 U_{ref} 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 [12].

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

Sample	Gravimetric (spike)		Homogeneity	Stability (18 °C)	Combined	u_{ref}	U_{ref}
	X_{ref} (µg L^{-1})	u_{char} (µg L^{-1})	u_{bb} (µg L^{-1})	u_{st} (µg L^{-1})	u_{ref} (µg L^{-1})	(%)	(%)
Soft Drinking Water	2.68	0.01	0.15	0.12	0.19	7.2	14.4
Hard Drinking Water	10.00	0.02	0.15	0.51	0.53	5.3	10.5
Mineral Water	3.00	0.01	0.09	0.16	0.19	6.3	12.7
Swimming Pool Water	8.44 *	0.60	0.17	0.21	0.66	7.8	15.6
Raw Water	7.95	0.02	0.17	0.29	0.33	4.2	8.4
Standard Solution	1.67	0.01	0.06	0.15	0.17	9.9	19.8

* The assigned value for swimming pool water was not gravimetrically established but derived from the homogeneity study

9 Statistical analysis

Statistical evaluation of the data was performed following international standard recommendations (ISO 5725-2 [10], ISO 13528 [11]). Additionally, the AOAC harmonized guidelines for collaborative studies were also followed as a cross validation for the data evaluation [17, 18]. The following tests were performed;

i) Analysis of variance, ANOVA, to confirm that no statistically significant difference existed, for any of the water test samples, between the two individual bottles provided to the participants, i.e. no statistical significant between-day effect (reproducibility). Since this was the case, all four measurements were pooled for further calculations

ii) Check for laboratory outliers within the series of independent replicates applying the Grubbs-internal test (repeatability)

iii) Check for outliers in the laboratory precision (variance) applying the Cochran test. This test compares the highest laboratory internal repeatability variance with the sum of reported variances from all the participants

iv) Check for outliers in the laboratory mean applying the Grubbs test. This test checks for laboratory means deviating significantly from the total mean calculated from all data reported from all participants.

10 Information on the method under validation

In the present method, the detection of bromate is performed by applying an acidic solution of potassium iodide containing a catalytic amount of molybdenum(VI). The bromate reacts with iodide to form the tri-iodide ion in a post column reaction step (PCR) which is measured by its UV at 352 nm. The proposed method can be applied to bromate concentrations higher than ≥ 0.5 µg L^{-1} without any pre-concentration step. Moreover, the present method aims to minimize any potential interference of chloride ions.

All reagents should be of recognized analytical grade as recommended in the Draft ISO/DIS 11206 document. All reagents for the preparation of the standard and calibration solutions, including the PCR reagents were comprehensively described in the standard operational procedure (SOP) distributed to participants. Quality assurance criteria were established for;

i) The minimum chromatographic resolution (resolution ≥ 1.3) and

ii) Separation conditions shall be such that possible interfering anions will not interfere with bromate

When matrix interferences were observed, it was recommended to use the standard additions method to confirm the results.

Ion chromatography (IC) coupled with post column reaction (PCR) was used by all participants as recommended in the Draft ISO 11206 standard protocol.

11 Results

11.1 Method performance assessment

Sixteen out of the seventeen laboratories reported results. Two independent measurements were reported for each bottle and for each of the five water test samples plus the blank and the synthetic bromate standard solution.

After the elimination of outliers (identified following the procedures described in Chapter 9) the precision data was calculated. Erroneous data were investigated.

Annex 8 to 13 shows all the results provided by the 16 participants. For each water sample, all four measurements and the estimated observed variability (expressed as one standard deviation) are plotted.

As it can be observed, the overall mean is not differing from the reference value for all test samples except for hard drinking water. Hence, no bias has been found for all water samples except for hard drinking water.

The distribution of the results is symmetric around the reference value for the majority of the test samples, except for swimming pool water. This sample could present some problems during analysis as experienced by IWW during the homogeneity and stability studies, although it should be kept in mind that the method used by IWW is not the same (and it is not based on the same measurement principles) as the method under investigation.

The Kernel density plots displayed in Annex 14 illustrate 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 [19].

Following the statistical approach described in chapter 9, two laboratories (L05 and L16) were identified as outliers for the synthetic standard (from the Cochran test) as they reported a within-laboratory variability which was significantly larger than those of other laboratories. Since the contribution for the observed variability arising from homogeneity and/or from the stability of the test samples was not statistically significant, the reported variability from these two laboratories can not be explained by those two contributions. Hence, these two laboratories were excluded from further statistical data evaluation related to the assessment of the method performance characteristics for all investigated water test samples (accordingly with ISO 5725-2, [10]).

After applying the Grubbs test to scrutinize the data for potential outliers within each series of independent measurements and for each laboratory, one independent measurement for raw water for L01 was found. This independent measurement was excluded from data evaluation. Table 2 provides an overview of the outliers found for all samples.

Table 2: Statistical data evaluation (scrutinizing data for outlier identification)

Sample	Laboratory	N° of outliers	Outlier type*
Soft Drinking Water	L08	4	Grubbs
Hard Drinking Water	L04 L06	4 4	Cochran
Mineral Water	L04 L08 L09	4 4 4	Cochran Grubbs Cochran
Swimming Pool Water	L06 L09	4 4	Cochran
Raw Water	L01	1	Grubbs (internal)
Standard Solution	L05 L16	4 4	Cochran

* Grubbs internal outlier refers to a single replicate being statistically significantly different from the other replicates (within a laboratory).

All the remaining measurements were used to evaluate all relevant performance characteristics related to the trueness and to the precision of the method under validation shown in Table 3, on which, the following information and method performance characteristics are given:

- The assigned value, X_{ref} and its associated combined standard uncertainty, u_{ref}
- The overall mean, X_{obs} (of all values after outlier elimination) and associated observed variability (expressed as one standard deviation, u_{obs}),
- The standard deviation S_r and the relative standard deviation RSD_r obtained under repeatability conditions (within-laboratory observed variability),
- The standard deviation S_R and relative standard deviation RSD_R, obtained under reproducibility conditions (between-laboratory observed variability),
- The repeatability r_L (as 2.8 S_r) and reproducibility limits R_L (as 2.8 S_R) [20, 17],
- The percentage of identified and excluded outliers and
- The analytical recovery R, expressed as a ratio between the observed and the assigned value according to [21]:

$$R = X_{obs} / X_{ref} .100 \qquad \text{Eq. 2}$$

Where:

X_{obs} is the overall mean of all values after outlier elimination, for each test sample

X_{ref} is the assigned value of each test sample

None of the participants reported a quantitative value for the blank sample, thus no statistical evaluation has been carried out for this sample. It can be concluded that no false positives were reported.

Table 3: Method performance characteristics from the collaborative trial on the determination of bromate in drinking water (following ISO 5725-2)

Matrix	Units	Soft drinking water	Hard drinking water	Mineral water	Swimming pool water	Raw water	Standard solution
N° of participating laboratories		13	12	11	12	14	14
Remaining data after outlier elimination		52	48	44	48	55	56
Outliers	%	7.1	14.3	21.4	14.3	1.8	0
Assigned value $X_{ref} \pm u_{ref}$	µg L^{-1}	2.68 ± 0.19	10.00 ± 0.53	3.00 ± 0.19	8.44 ± 0.66	7.95 ± 0.33	1.67 ± 0.17
Overall mean $X_{obs} \pm u_{obs}$	µg L^{-1}	2.61 ± 0.13	8.93 ± 0.46	2.94 ± 0.10	7.67 ± 0.17	7.86 ± 0.24	1.65 ± 0.10
Recovery $R \pm u_R$	%	97.4 ± 8.5	89.3 ± 6.6	98.1 ± 7.0	-	98.9 ± 5.1	99.0 ± 11.3
S_R	µg L^{-1}	0.132	0.476	0.107	0.171	0.243	0.097
RSD_R	%	5.1	5.3	3.6	2.3	3.1	5.9
R_L	µg L^{-1}	0.37	1.33	0.30	0.48	0.68	0.27
S_r	µg L^{-1}	0.084	0.112	0.067	0.095	0.125	0.068
RSD_r	%	3.2	1.3	2.3	1.2	1.6	4.1
r_L	µg L^{-1}	0.24	0.31	0.19	0.27	0.35	0.19

The analytical recovery rate ranges from 89.3 % (hard drinking water) to 99.0 % (bromate standard solution). No recovery was calculated for swimming pool water because the sample was incurred with bromate and X_{ref} was not derived from a gravimetric value. Furthermore, there was a discrepancy between the mean value extracted from the results provided by the participants and the X_{ref} obtained from the homogeneity study. IWW applied standard addition for the determination of bromate for this water due to the fact that, the result obtained after standard addition was higher than when directly interpolating the measurement result in an external calibration curve. Thus, the presence of interferences in the sample might be considered.
The uncertainty on the recovery values (u_R) was estimated as [21]:

$$u_R = R \cdot \sqrt{\left(\frac{u_{obs}}{X_{obs}}\right)^2 + \left(\frac{u_{ref}}{X_{ref}}\right)^2} \qquad \text{Eq. 3}$$

Where:
R is the analytical recovery (Eq. 2)
u_{obs} is the observed standard deviation taking into account the within- and between-laboratory variability (the overall standard deviation as provided in Table 3)
u_{ref} is the uncertainty on the assigned value
X_{obs} and X_{ref} have the same meaning as in Eq. 2

When considering the estimated uncertainty values on the recovery as a confidence interval for this method performance characteristic, one can see that for all samples except the hard drinking water, no statistically significant difference can be detected between the overall mean and the reference value. It could be concluded that for all water samples except hard drinking water no significant bias has been detected. However, if one takes into account the maximum allowable difference between the mean value of a large number of repeated measurements and the reference value, which, accordingly to the DWD, is ± 25 %, this particular sample, is still fulfilling this criterion.
Furthermore, a significance test can be performed, to test whether the analytical recovery differs significantly from the unity (or from 100 % when in percentage) according to the following equation [21]:

$$|R - 1| / u_R \qquad \text{Eq. 4}$$

The following conditions do apply:

$|R - 1| / u_R > t$: R differs significantly from the unity
$|R - 1| / u_R \leq t$: R does not differ significantly from the unity

Where:

t is a critical value

The harmonized guidelines for the use of recovery information [21] sets the critical t-value based either on a coverage factor (commonly a value of 2 is used) or on the Student's t-test value for a confidence level of 95 % and for N-1 degrees of freedom (N equals to all the measurements used to estimate the recovery). Taking the hard drinking water recovery value of 89.3 % and its associated calculated standard uncertainty of 6.6 % (N = 48) and applying Eq. 4 one gets a value of 1.62, hence < 2. Therefore there is no statistical evidence to proof that the estimated recovery differs from the unity even when taking the Student's t-critical value of 2.01, hence the observed bias for hard drinking water should not be considered statistically significant at the 95 % level.

Comparing the precision obtained with the present method and that obtained with the standard analytical method used so far (ISO 15061:2001 [6]) it can be concluded that the present method provides a significant reduction in the RSD_R and the RSD_r, particularly for the soft and hard drinking water samples, considering that these samples were spiked at rather low bromate concentration levels (e.g. soft drinking water spiked at 8.6 µg L^{-1} for ISO 15061 and at 2.68 µg L^{-1} in IMEP-25a).

The synthetic bromate standard solution gave a RSD_R of 5.9 % (corresponding to a bromate concentration level of 1.67 µg L^{-1}) while a value of 4.1 % was obtained following the ISO 15061 but for a bromate concentration of 5.7 µg L^{-1}.

A comparison between the performance characteristics of ISO 15061:2001 and those of the new method under validation is provided in Table 4.

Table 4: Method performance characteristics - Comparative results for ISO 15061:2001 Vs Draft ISO/DIS 11206:2010

	Method	n	x_{ref} µg L^{-1}	R %	RSD_R %	RSD_r %
Standard Solution	ISO 15061:2001	20	5.70	95.4	4.1	3.1
	ISO 11206:2010	*14*	*1.67*	*99.0*	*5.9*	*4.1*
Hard Drinking Water	ISO 15061:2001	19	2.70	92.4	19.9	8.5
	ISO 11206:2010	*12*	*10.00*	*89.3*	*5.3*	*1.3*
Soft Drinking Water	ISO 15061:2001	19	8.60	96.1	17.1	6.0
	ISO 11206:2010	*13*	*2.68*	*97.4*	*5.1*	*3.2*

Method performance characteristics were validated following the AOAC International guidelines for collaborative studies [17, 18]. AOAC guidelines establish a maximum outlier rate of 2/9, i.e. 2 laboratory failures in a 9-laboratory study. Applying this criterion to our case a maximum number of laboratories which can be identified and accepted as true outliers are 3 (rate 2/9 ~ 3/14). Since the total number of participant laboratories in this study is 14 (after excluding the two laboratories which reported false data for the synthetic standard solution) the

maximum number of laboratories being identified as outliers (see Table 3) is never over the AOAC maximum limit, thus no differences in the estimated method performance characteristics were attained when following these two protocols.

11.2 Information extracted from the questionnaire

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

As an attempt to have a holistic interpretation from the data a multivariate approach was carried out by establishing a multivariate linear relationship between the measurand (bromate) and the set of responses gathered from the questionnaire, once transformed into numerical variables. Partial least square regression models (PLS-R) were used. The statistical data treatment was performed using The Unscrambler 9.8 (CAMO Software AS, Norway).

The multivariate approach provides a graphical interpretation of the results obtained by interlaboratory comparison exercises, allowing the differentiation of laboratories according to their different procedures and enables the assessment of the relationship between the measurement result and the reasons why it might be different, depending on the responses to the questionnaire. Laboratories L08 and L16 were both easily discriminated from the others.

For most of the investigated water samples, there is a direct correlation between the reported bromate concentrations and the injection volume used, so that those using lower injection volumes reported lower bromate concentrations (compared to the overall average) and vice versa (63 % of the participants injected a sample volume of 1000 µL, 13 % injected 250 µL, 19 % injected 225 µL and 6 % used 100 µL as injection volume).

Also the type of eluent used, i.e. sulphuric acid or carbonated eluents, seems to be an important parameter. There was a trend for laboratories which used carbonated eluents to report low bromate concentrations.

The third influencing parameter is the experience of the laboratory in bromate analysis.

Most participants have a large experience in the analysis of bromate in water: 75 % indicated that they carry out this type of analysis (as regards to the measurand, matrix and method of analysis) on a routine basis. The distribution of this 75 % in terms of analysis/year is shown in Figure 1.

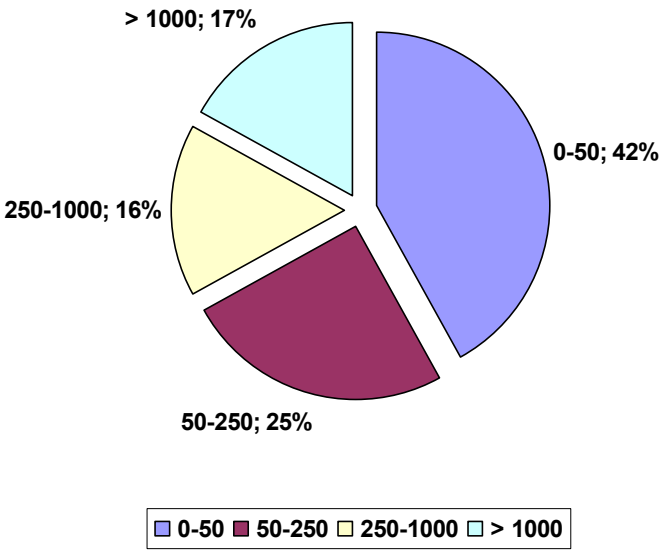

Fig. 1 Distribution of the number of analysis/year among the most experienced laboratories

The number of measurements carried out per year is negatively correlated with the observed results, i.e. laboratories analysing a high number of samples per year (> 1000), have reported, on average, bromate concentrations lower than those laboratories which analysed a lower number of samples per year.

As observable from the plots provided in Annex 8 to 13, there was a rather high consistency among all the participants, hence none of the effects previously mentioned had a significant impact on the precision characteristics of the analytical method under scrutiny.

Among all the sixteen participants fourteen laboratories declared to have a laboratory quality system in place. Seven participants are accredited for this type of analysis. This parameter does not seem to have any influence in the reported results.

Four participants declared to have modified the SOP. Table 5 shows all the modifications as reported by the participants.

Table 5: Modifications to the Draft ISO/DIS 11206 SOP as reported by the participants

Laboratory	ISO/DIS 11206 SOP modification
L01	I have used different conditions at the PCR reaction coil. With our system (eluent flow 1.0 mL min^{-1} and PCR flow 0.25 mL min^{-1}) we achieve 54 mmol L^{-1} potassium iodide and 40 µmol L^{-1} ammonium heptamolybdate. The explanation why we used this is in the following article: *"Trace-level determination of bromate in water by ion chromatography"* [22]
L04	The amount of ammonium molybdate in the PCR reagent was reduced to 0.43 µmol L^{-1}. Vacuum degassing was used instead of helium sparging. Dissolve 22.5 g of KI in approximately 250 ml of water in a 500 mL volumetric flask. Dilute to volume with water. Degas the solution by vacuum filtration through a 0.2 µm nylon filter and maintain vacuum for ~ 10 min. or until bubbles are not released from the solution. Add 112 µL of the ammonium heptamolybdate tetrahydrate solution that was prepared as per section 5.14, place the solution in the PCR module and pressurize with ultra high purity nitrogen. Wrap the container in foil to prevent light exposure. The above procedure was used when it was found that the background UV absorbance was increasing ~ 40 mAU from the beginning to the end of the sequence by using the amounts of ammonium molybdate and the helium sparging described in 5.15
L08 *	Calibration standards and PCR as detailed above
L16 *	Calibration standards and PCR as detailed above

* Those two participants used a quadratic calibration curve instead of a linear one (see text for more details)

L08 and L16, which were discriminated from the multivariate data analysis, have changed the PCR reagents used: ammonium molybdate tetrahydrate instead of ammonium heptamolybdate tetrahydrate as recommended by the Draft ISO 11206 SOP, however these names refer to the same analytical reagent commercialized by different chemical reagent providers and so it was not considered as a SOP modification. These two participants, as indicated in Table 5, have also changed the method protocol regarding calibration by recurring to a quadratic calibration curve. All the remaining participants used a linear calibration curve.
Four participants have identified interferences. The interference was identified as chlorite.
Only one participant used the method of standard addition.

12 Conclusion

IMEP-25a assessed the method performance characteristics of a draft international standard ISO/DIS 11206 aimed to measure the total concentration of bromate in water.
Based on the statistical evaluation of the results from this collaborative trial it could be concluded that the proposed method is suitable for the quantitative determination of bromate in drinking water as requested by the European legislation and in other types of water, such as swimming pool, raw and in a synthetic bromate solution. The levels of concentration in bromate used for this exercise were low (in accordance to European legislation) which made this exercise particularly challenging. Indeed, all except one water sample were spiked at levels below the so called legislative parametric value of 10 µg L^{-1} in bromate.
The trueness and precision of the method are far below the maximum allowed percent deviation (± 25 %) from the parametric value, which allows the conclusion that the present method fits its intended analytical purpose.
Furthermore, the present method compares favourably with the former standard method, achieving higher precision and lower deviation to the reference values, for identical test matrices.

Acknowledgments

K.H. Röhrig (SGS, Institut Fresenius GmbH, Taunusstein, Germany) is acknowledged for the bromate determination on the blank solution. D. Schwesig (IWW, Rheinisch-Westfälisches Institut für Wasser, Germany) is acknowledged for the bromate determination carried out for the homogeneity and stability studies.
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Abbreviations

AMC	Analytical Methods Committee of the Royal Society of Chemistry
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
UV	Ultraviolet detection
IC	Ion chromatography
PCR	Post column reaction

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Annex 1: Description of sample matrices (analysed before spiking with bromate and ethylenediamine)

Sample matrix		Drinking water, soft	Drinking water, hard	Mineral water	Swimming pool water	Raw water
Disinfection agent		ClO_2	ClO_2	none	ClO_2	unknown
Parameter		Mass concentration (mg L^{-1}, if not stated otherwise)				
Ions						
Ammonium (NH_4^+-N)	EN ISO 11732 (CFA)	≤ 0,07	≤ 0,07	≤ 0,07	≤ 0,07	≤ 0,07
Bromide (Br^-)	EN ISO 10304-1 (IC)	0,06	0,06	≤ 0,05	0,03	0,1
Chloride (Cl^-)	EN ISO 10304-1 (IC)	9,5	34	2,9	140	63
Chlorite (ClO_2^-)	EN ISO 10304-3 (IC)	0,06	≤ 0,01	≤ 0,01	≤ 0,01	≤ 0,01
Fluoride (F^-)	EN ISO 10304-1 (IC)	0,1	0,17	0,02	0,19	0,17
Nitrate (NO_3^--N)	EN ISO 10304-1 (IC)	2,3	0,52	1,5	1,9	1,7
Nitrite (NO_2^--N)	EN ISO 10304-1 (IC)	< 0,02	< 0,02	≤ 0,02	< 0,02	< 0,02
o-Phosphate (PO_4^{3-}-P)	EN ISO 15681-2 (CFA)	0,008	0,012	≤ 0,005	0,02	0,039
total-phosphorous (P)	EN ISO 15681-2 (CFA)	0,17	0,17	0,1	0,1	0,11
Sulfate (SO_4^{2-})	ISO 10304-1 (IC)	19	67	18	140	48
Elements						
Aluminium (Al)	EN ISO 11885 (ICP-OES)	0,01	0,02	≤ 0,01	0,16	0,02
Antimony (Sb)	EN ISO 17294-2 (ICP-MS)	≤ 0,0005	≤ 0,0005	≤ 0,0005	≤ 0,0005	≤ 0,0005
Arsenic (As)	EN ISO 17294-2 (ICP-MS)	≤ 0,0005	≤ 0,0005	≤ 0,0005	0,001	0,002
Barium (Ba)	EN ISO 11885 (ICP-OES)	0,02	0,12	≤ 0,01	0,06	0,05
Boron (B)	EN ISO 11885 (ICP-OES)	0,02	0,05	0,03	0,05	0,05
Cadmium (Cd)	EN ISO 17294-2 (ICP-MS)	≤ 0,0005	≤ 0,0005	≤ 0,0005	≤ 0,0005	≤ 0,0005
Calcium (Ca)	EN ISO 11885 (ICP-OES)	20	110	80	88	85
Chromium (Cr)	EN ISO 17294-2 (ICP-MS)	≤ 0,002	≤ 0,002	≤ 0,002	0,002	≤ 0,002
Copper (Cu)	EN ISO 17294-2 (ICP-MS)	0,004	0,17	0,002	0,004	0,003
Iron (Fe)	EN ISO 11885 (ICP-OES)	0,009	0,088	≤ 0,01	0,001	0,002
Lead (Pb)	EN ISO 17294-2 (ICP-MS)	≤ 0,0005	0,003	≤ 0,0005	≤ 0,0005	≤ 0,0005
Magnesium (Mg)	EN ISO 11885 (ICP-OES)	4,8	17	0,74	13	13

Manganese (Mn)	EN ISO 17294-2 (ICP-MS)	0,003	0,002	≤ 0,0005	≤ 0,0005	≤ 0,0005
Nickel (Ni)	EN ISO 17294-2 (ICP-MS)	0,001	0,003	≤ 0,001	0,002	0,004
Potassium (K)	EN ISO 11885 (ICP-OES)	1,0	2,6	0,2	3,6	3,1
Selenium (Se)	EN ISO 17294-2 (ICP-MS)	≤ 0,005	≤ 0,005	≤ 0,005	≤ 0,005	≤ 0,005
Silicon (Si)	EN ISO 11885 (ICP-OES)	8,8	7,7	2,4	3,3	3,1
Sodium (Na)	EN ISO 11885 (ICP-OES)	7,4	17	1,8	77	28
Tin (Sn)	EN ISO 17294-2 (ICP-MS)	0,0005	0,016	≤ 0,0005	≤ 0,0005	≤ 0,0005
Zinc (Zn)	EN ISO 11885 (ICP-OES)	0,01	0,05	≤ 0,01	0,008	0,003
Sum parameter						
Acid capacity (pH 4,3/mmol L^{-1})	DIN 38409-7	1,1	5,1	3,7	2	3,6
Base capacity (pH 8,2/mmol L^{-1})	DIN 38409-7	≤ 0,02	0,06	0,12	0,04	0,08
Hardness $\Sigma(Ca^{2+}+Mg^{2+})$ (mmol L^{-1})		0,7	3,4	2,0	2,7	2,7
Total bound nitrogen (TN_b)	EN 12260	2,7	1,1	2,0	2,4	2,1
Total inorganic carbon (TIC)	EN 1484	13	61	47	24	44
Total organic carbon (TOC)	EN 1484	1	2,7	≤ 1	2,2	1,4

All measurements carried out at the LHL, Landesbetrieb Hessisches Landeslabor (Wiesbaden, Germany)

Annex 2: Homogeneity tests

	Soft		Hard		Mineral		Swimming		Raw		Standard 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^2_{an}	**0.041**		**0.048**		**0.047**		**0.142**		**0.066**		**0.005**	
S^2_{Sam}	**0.023**		**0.022**		**0.009**		**0.028**		**0.029**		**0.003**	
σ^2_{All}	**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**	
$S^2_{Sam} \leq$ critical?	**Yes**		**Yes**		**Yes**		**Yes**		**Yes**		**Yes**	
Test result	**Passed**		**Passed**		**Passed**		**Passed**		**Passed**		**Passed**	

R_1 denotes replicate 1, R_2 denotes replicate 2. The standard deviation for the ILC assessment (σ) that is used in this table was calculated as a fraction (25 %) of the mean calculated from the homogeneity studies, not as a fraction of the reference value.

Following the ISO 13528: 2005 [11];

S_x is the standard deviation of the samples average,

S_w is the within-samples/bottle standard deviation,

S_S is the between-sample/bottle standard deviation

Following the IUPAC Harmonized protocol [9];

S^2_{an} is estimated analytical variance (within-sample/bottle)

S^2_{Sam} is the estimated sample variance (between-sample/bottle)

σ^2_{All} is the maximum allowed variance ($0.09\sigma^2$)

Critical value $C = F_1 \sigma^2_{All} + F_2 S^2_{an}$, with F_1, F_2 being constants derived from F-test tables corresponding to the number of bottles used to the homogeneity study.

Annex 3: 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**			

Note: Standard uncertainty u_{st} obtained from stability studies, was computed using the SoftCRM 2.0 carried out at 18 °C and considering a shelf life of nine weeks.

	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**			

Note: Standard uncertainty u_{st} obtained from stability studies, was computed using the SoftCRM 2.0 carried out at 18 °C and considering a shelf life of nine weeks.

Annex 4: Letter accompanying the sample

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Isotope measurements

Geel, 04 June 2009
JRC.D04/IBa/ive/ARES(2009)/115822

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

Participation to IMEP-25a, a collaborative trial for the determination of bromate in water

Dear «TITLE» «SURNAME»,

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

This parcel contains:
a) Fourteen bottles containing each ~ 60 mL of the test material (two bottles for each type of water)
b) A copy of the standard operational procedure (DRAFT: ISO/DIS 11206) which **must** be followed strictly
c) A "Confirmation of Receipt" form
d) 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 ºC) until analysis.

The measurand is: Bromate in six different types of water plus one bromate standard solution.

Please perform two independent measurements per bottle on two different days (one bottle/day) following DRAFT: ISO/DIS 11206. Report the values obtained on the first day in "Measurement 1" and "Measurement 2" and the values obtained on the second day in "Measurement 3" and "Measurement 4" on the reporting website. Express the results in µg L^{-1}. The results should be reported with two decimals (or more if necessary to avoid a series of identical values). A chroma-

togram representative of every one of the different samples analysed must be faxed to F. Cordeiro.

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. 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.

Please note that

THIS IS A STUDY OF THE METHOD NOT OF THE LABORATORY. THE METHOD MUST BE STRICTLY FOLLOWED AS DESCRIBED.

Report any deviation from the method.

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-25a Co-ordinator

Enclosures:
1) Fourteen bottles containing each ~ 60 mL of the test material (two bottles for each type of water)
2) DRAFT: ISO/DIS 11206
3) Confirmation of receipt form
4) Accompanying letter

Cc: P. Taylor

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)/141290

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

IMEP-25a

a collaborative trial for the 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 …….
…….

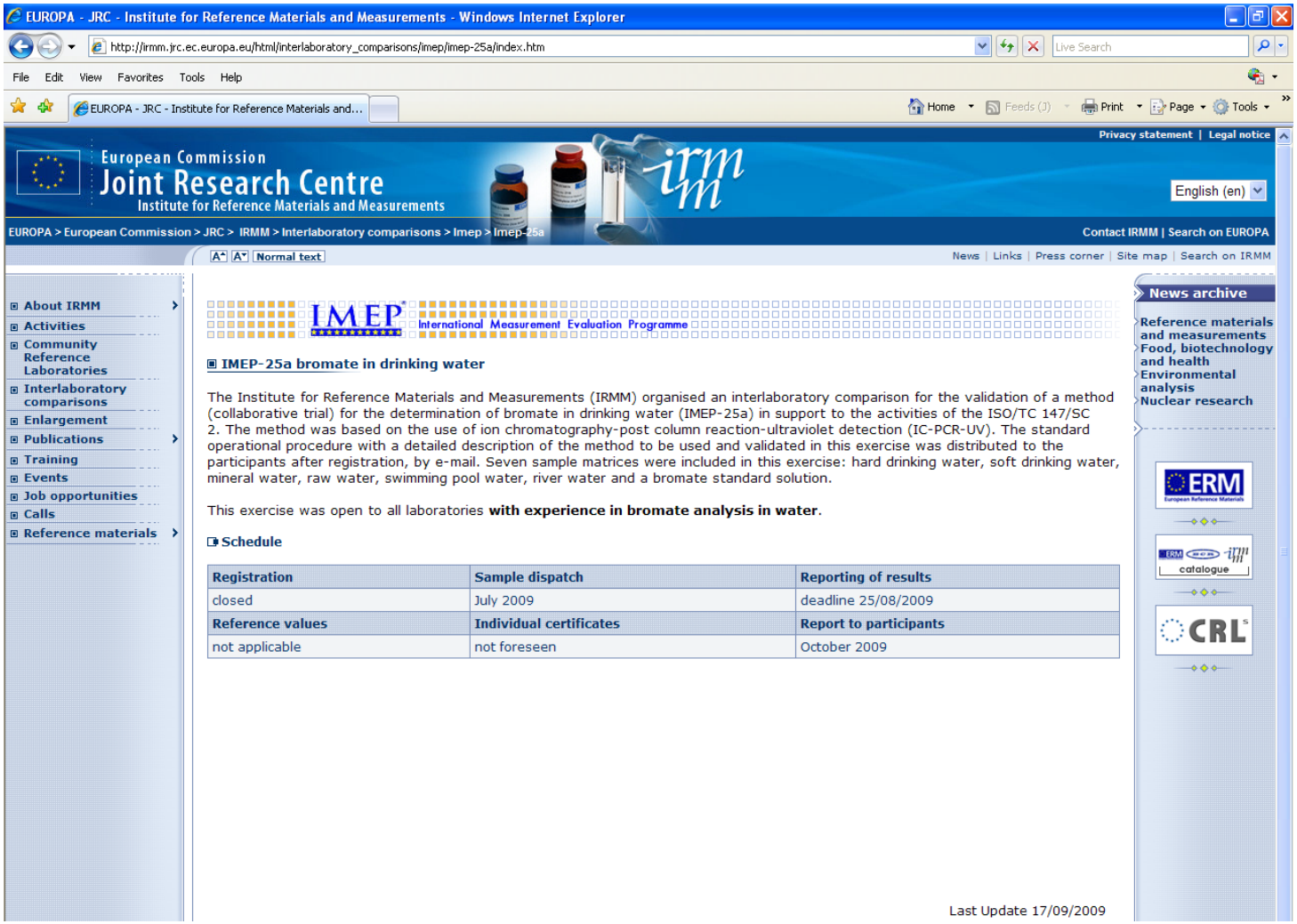
Date of package arrival …….

Signature …….

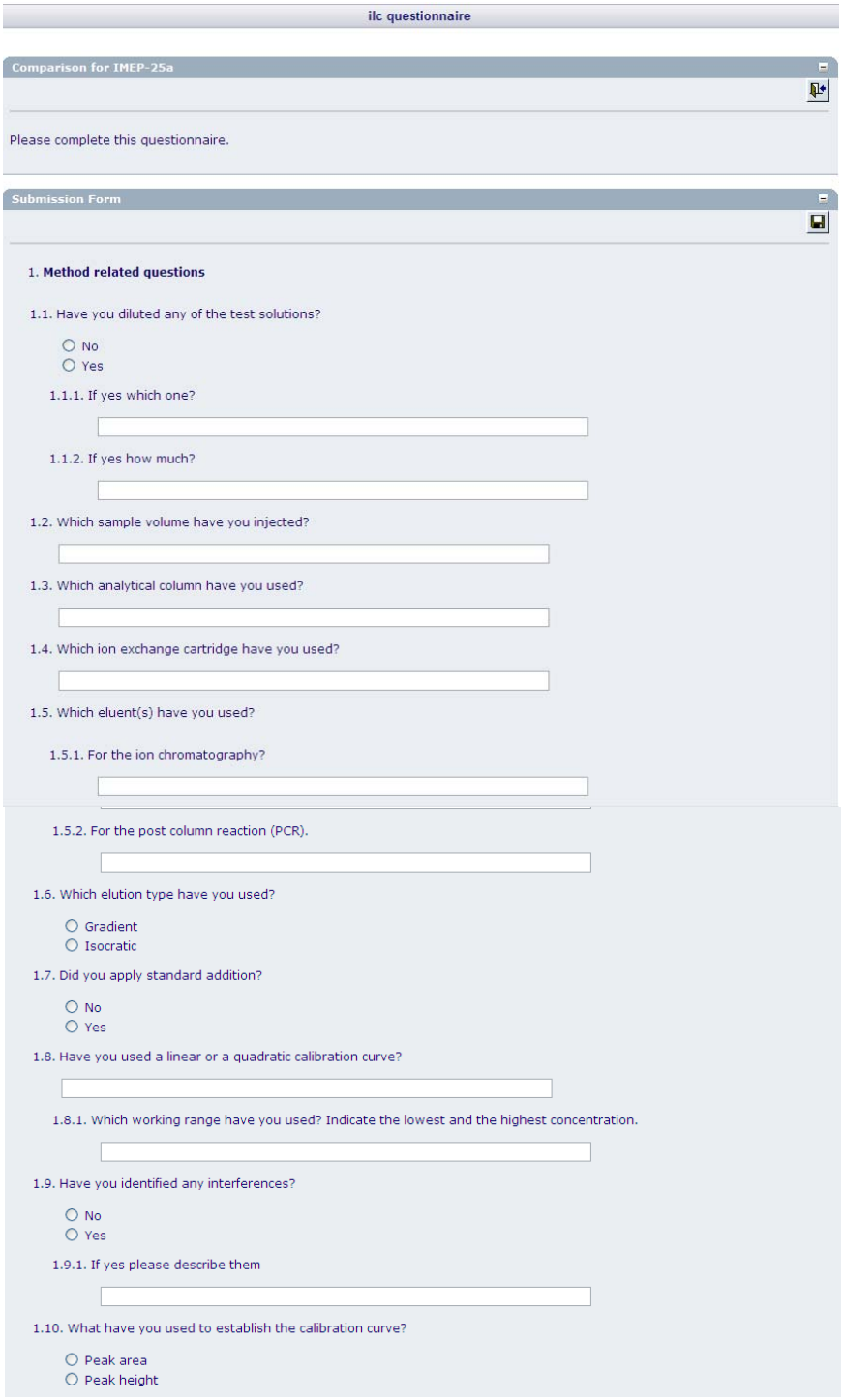
Please return this form to:
Dr. Fernando Cordeiro
IMEP-25a Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

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

Annex 6: IMEP Web announcement



Annex 7: Questionnaire



ilc questionnaire

Comparison for IMEP-25a

Please complete this questionnaire.

Submission Form

1. **Method related questions**

1.1. Have you diluted any of the test solutions?

- ○ No
- ○ Yes

1.1.1. If yes which one?

1.1.2. If yes how much?

1.2. Which sample volume have you injected?

1.3. Which analytical column have you used?

1.4. Which ion exchange cartridge have you used?

1.5. Which eluent(s) have you used?

1.5.1. For the ion chromatography?

1.5.2. For the post column reaction (PCR).

1.6. Which elution type have you used?

- ○ Gradient
- ○ Isocratic

1.7. Did you apply standard addition?

- ○ No
- ○ Yes

1.8. Have you used a linear or a quadratic calibration curve?

1.8.1. Which working range have you used? Indicate the lowest and the highest concentration.

1.9. Have you identified any interferences?

- ○ No
- ○ Yes

1.9.1. If yes please describe them

1.10. What have you used to establish the calibration curve?

- ○ Peak area
- ○ Peak height

1.11. Which bandwidth have you used for the spectrophotometric detection?

1.12. Have you found any sample for which the resolution R is lower than 1.3?

- ○ No
- ○ Yes

1.12.1. I yes which was the resoltuion found for:

1.12.1.1. Sample 1

1.12.1.2. Sample 2

1.12.1.3. Sample 3

1.12.1.4. Sample 4

1.12.1.5. Sample 5

1.12.1.6. Sample 6

1.12.1.7. Sample 7

2. **Did you modify the prescribed standard operational procedure?**

- ○ No
- ○ Yes

2.1. If yes, please specify the modifications introduced.

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

- ○ No
- ○ Yes

3.1. 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

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

- ○ No
- ○ Yes

4.1. If yes, which?

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

4.1.1. If other, please specify.

5. **Is your laboratory accredited for this type of analysis?**

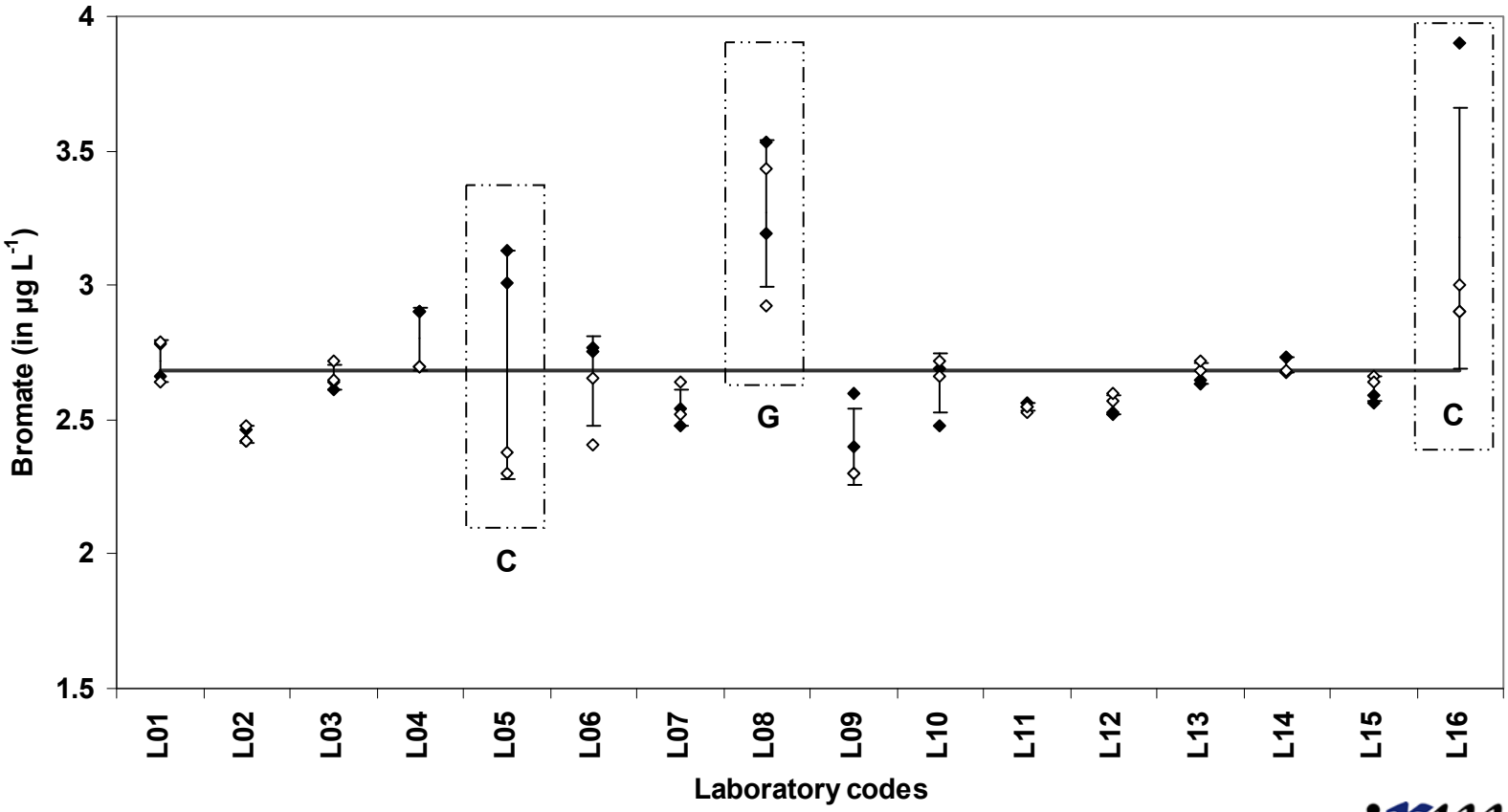
- ○ No
- ○ Yes

5.1. If yes, by which accreditation body?

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

Annex 8: Bromate in Soft Drinking Water; X_{ref} = 2.68 µg L^{-1}

	x_1	x_2	x_3	x_4	Mean Cal.
L01	2.78	2.66	2.64	2.79	2.72
L02	2.46	2.42	2.42	2.48	2.45
L03	2.64	2.61	2.65	2.72	2.66
L04	2.9	2.9	2.7	2.7	2.8
L05	3.13	3.01	2.38	2.3	2.71
L06	2.751	2.765	2.41	2.652	2.645
L07	2.54	2.48	2.52	2.64	2.55
L08	3.53	3.19	2.92	3.43	3.27
L09	2.6	2.4	2.3	2.3	2.4
L10	2.48	2.69	2.66	2.72	2.64
L11	2.55	2.56	2.53	2.55	2.55
L12	2.52	2.53	2.57	2.6	2.56
L13	2.63	2.65	2.68	2.72	2.67
L14	2.731	2.729	2.676	2.682	2.705
L15	2.56	2.59	2.66	2.64	2.61
L16	2.9	3.9	3	2.9	3.2



This plot shows all measurement results. The solid line refers to the reference value. The averaged mean value is 2.68 µg L^{-1}. Identified laboratories were considered outliers, (C = Cochran, G = Grubbs). Solid squares indicate bottle 1, open ones bottle 2.

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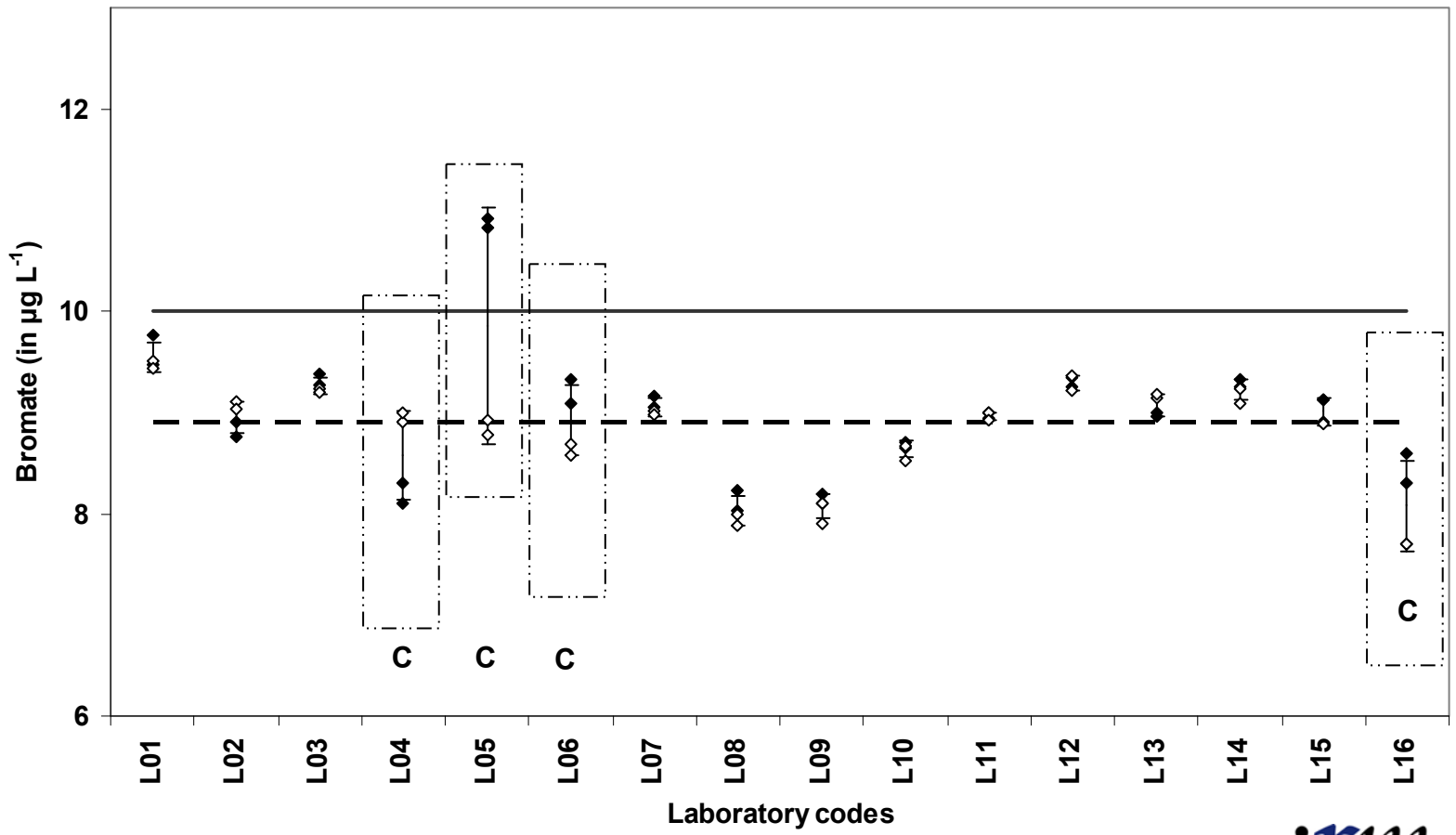
Annex 9: Bromate in Hard Drinking Water; X_{ref} = 10.00 µg L^{-1}

	x_1	x_2	x_3	x_4	Mean Cal.
L01	9.47	9.77	9.51	9.44	9.55
L02	8.76	8.9	9.1	9.04	8.95
L03	9.28	9.38	9.23	9.19	9.27
L04	8.3	8.1	8.9	9	8.6
L05	10.91	10.83	8.78	8.92	9.86
L06	9.092	9.325	8.584	8.685	8.922
L07	9.17	9.05	9.02	8.97	9.05
L08	8.23	8.02	7.88	8	8.03
L09	8.1	8.2	7.9	8.1	8.1
L10	8.71	8.65	8.67	8.52	8.64
L11	8.95	8.99	9	8.92	8.97
L12	9.26	9.34	9.21	9.37	9.30
L13	8.99	8.96	9.15	9.18	9.07
L14	9.334	9.256	9.243	9.09	9.231
L15	9.13	9.13	8.91	8.88	9.01
L16	8.6	8.3	7.7	7.7	8.1

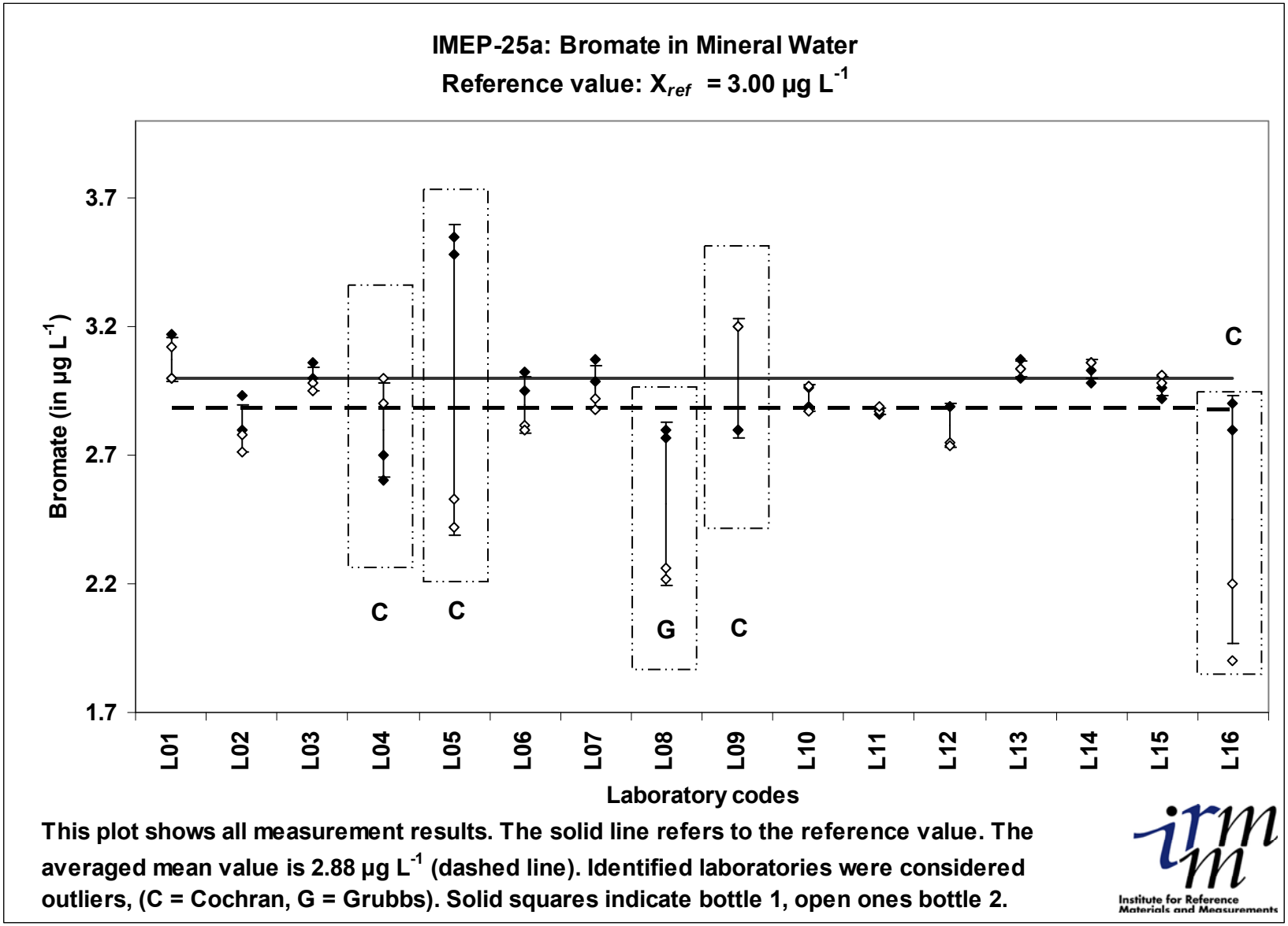


This plot shows all measurement results. The solid line refers to the reference value. The averaged mean value is 8.91 µg L^{-1} (dashed line). Identified laboratories were considered outliers, (C = Cochran). Solid squares indicate bottle 1, open ones bottle 2.

Institute for Reference Materials and Measurements

Annex 10: Bromate in Mineral Water; X_{ref} = 3.00 µg L^{-1}

	x_1	x_2	x_3	x_4	Mean Cal.
L01	3	3.17	3.12	3	3.07
L02	2.8	2.93	2.71	2.78	2.81
L03	3	3.06	2.98	2.95	3.00
L04	2.6	2.7	3	2.9	2.8
L05	3.55	3.48	2.42	2.53	3.00
L06	2.951	3.025	2.817	2.798	2.898
L07	2.99	3.07	2.88	2.92	2.97
L08	2.77	2.8	2.26	2.22	2.51
L09	2.8	2.8	3.2	3.2	3.0
L10	2.89	2.96	2.87	2.97	2.92
L11	2.86	2.87	2.87	2.89	2.87
L12	2.89	2.89	2.75	2.74	2.82
L13	3	3.07	3.036	3.039	3.036
L14	3.033	2.984	3.061	3.061	3.035
L15	2.96	2.92	3.01	2.98	2.97
L16	2.9	2.8	2.2	1.9	2.5



This plot shows all measurement results. The solid line refers to the reference value. The averaged mean value is 2.88 µg L^{-1} (dashed line). Identified laboratories were considered outliers, (C = Cochran, G = Grubbs). Solid squares indicate bottle 1, open ones bottle 2.

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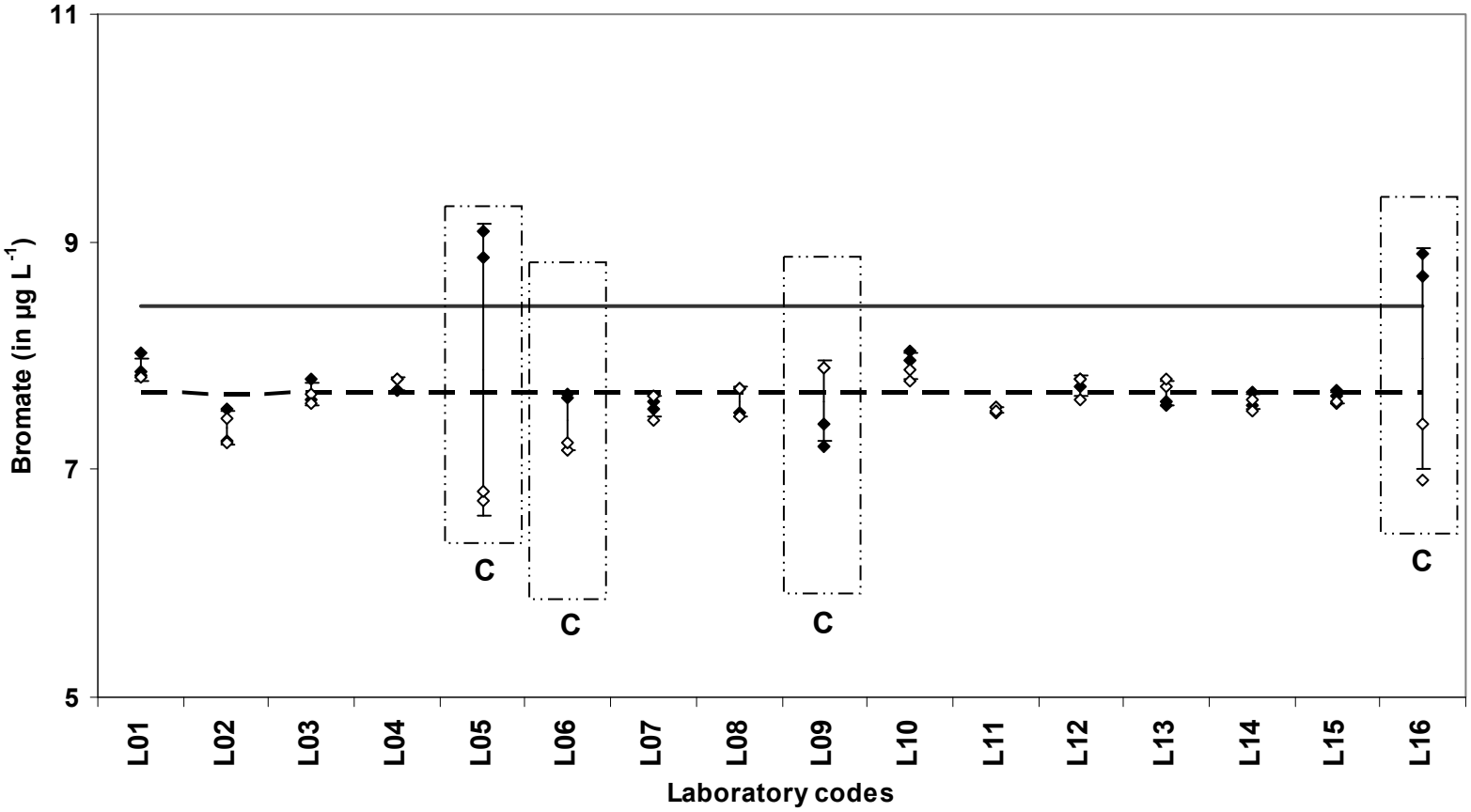
Annex 11: Bromate in Swimming Pool Water; X_{ref} = 8.44 µg L^{-1}

	x_1	x_2	x_3	x_4	Mean Cal.
L01	8.03	7.86	7.82	7.81	7.88
L02	7.26	7.53	7.23	7.45	7.37
L03	7.61	7.79	7.67	7.58	7.66
L04	7.7	7.7	7.8	7.8	7.8
L05	9.09	8.87	6.72	6.81	7.87
L06	7.635	7.659	7.174	7.241	7.427
L07	7.6	7.53	7.44	7.65	7.56
L08	7.72	7.5	7.71	7.47	7.60
L09	7.2	7.4	7.9	7.9	7.6
L10	7.96	8.04	7.87	7.78	7.91
L11	7.5	7.54	7.55	7.52	7.53
L12	7.73	7.8	7.8	7.61	7.74
L13	7.57	7.6	7.73	7.79	7.67
L14	7.674	7.572	7.523	7.616	7.596
L15	7.64	7.7	7.58	7.6	7.63
L16	8.7	8.9	6.9	7.4	8.0



This plot shows all measurement results. The solid line refers to the reference value. The averaged mean value is 7.67 µg L^{-1} (dashed line). Identified laboratories were considered outliers, (C = Cochran). Solid squares indicate bottle 1, open ones bottle 2.

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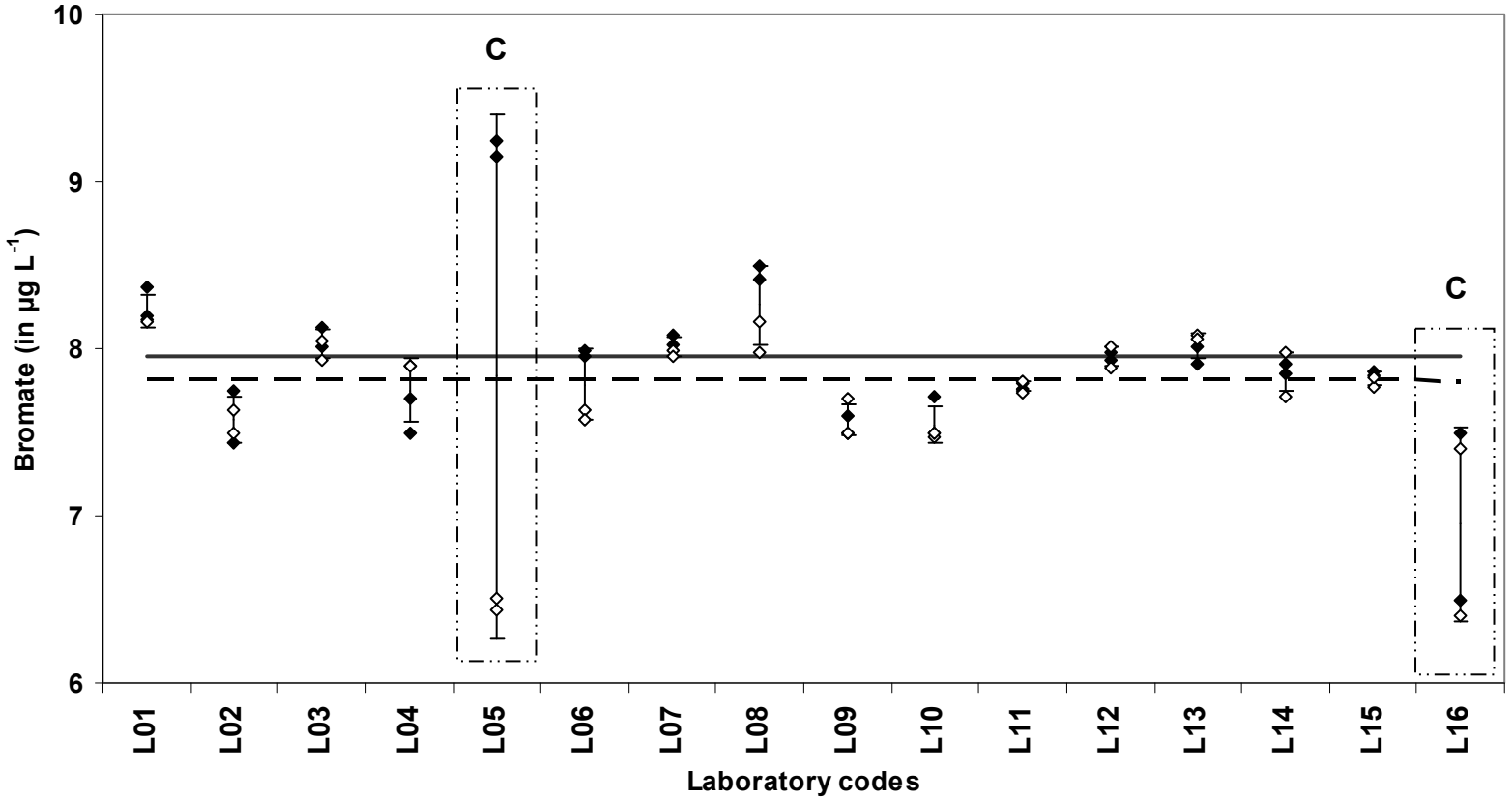
Annex 12: Bromate in Raw Water; X_{ref} = 7.95 µg L^{-1}

	x_1	x_2	x_3	x_4	Mean Cal.
L01	8.19	8.37	8.17	8.16	8.22
L02	7.44	7.75	7.63	7.49	7.58
L03	8.01	8.13	7.93	8.05	8.03
L04	7.7	7.5	7.9	7.9	7.8
L05	9.24	9.15	6.51	6.44	7.84
L06	7.952	7.984	7.629	7.58	7.786
L07	8.08	8.02	7.99	7.95	8.01
L08	8.41	8.5	7.98	8.16	8.26
L09	7.6	7.5	7.7	7.5	7.6
L10	7.71	7.5	7.47	7.5	7.55
L11	7.76	7.79	7.81	7.74	7.78
L12	7.98	7.93	7.88	8.01	7.95
L13	7.91	8.01	8.08	8.06	8.02
L14	7.91	7.845	7.977	7.715	7.862
L15	7.84	7.86	7.77	7.83	7.83
L16	7.5	6.5	7.4	6.4	7.0

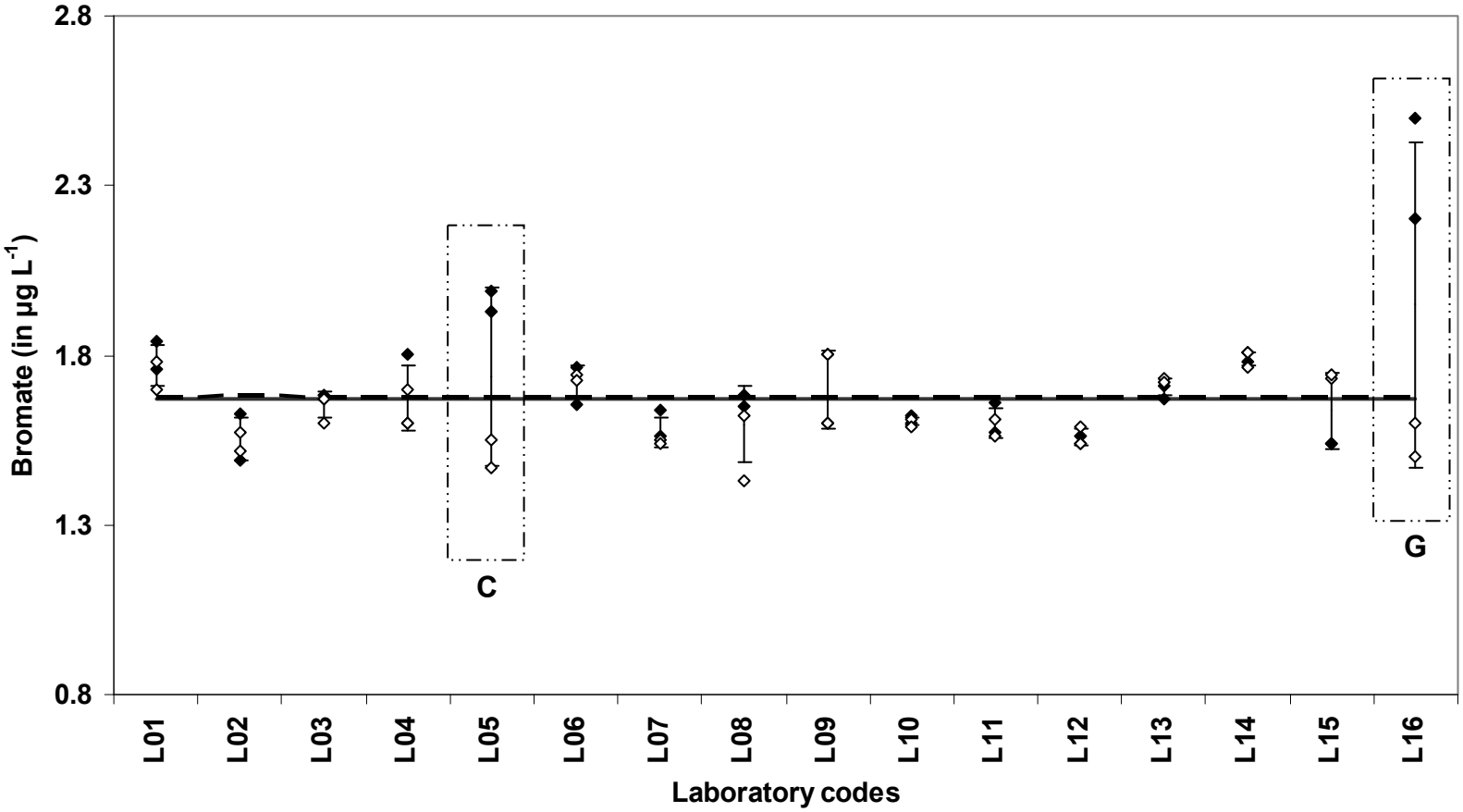


This plot shows all measurement results. The solid line refers to the reference value. The averaged mean value is 7.81 µg L^{-1} (dashed line). Identified laboratories were considered outliers, (C = Cochran). Solid squares indicate bottle 1, open ones bottle 2.

Institute for Reference Materials and Measurements

Annex 13: Bromate in Standard Solution; X_{ref} = 1.67 µg L^{-1}

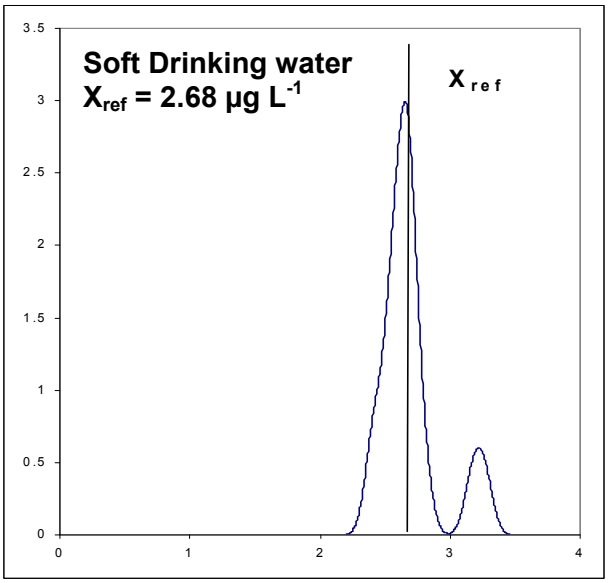
	x_1	x_2	x_3	x_4	Mean Cal.
L01	1.76	1.84	1.7	1.78	1.77
L02	1.49	1.63	1.52	1.57	1.55
L03	1.67	1.68	1.6	1.67	1.66
L04	1.6	1.8	1.6	1.7	1.7
L05	1.93	1.99	1.47	1.55	1.74
L06	1.655	1.764	1.741	1.726	1.722
L07	1.64	1.56	1.55	1.54	1.57
L08	1.68	1.65	1.62	1.43	1.60
L09	1.6	1.8	1.8	1.6	1.7
L10	1.62	1.6	1.61	1.59	1.61
L11	1.57	1.66	1.56	1.61	1.60
L12	1.56	1.54	1.59	1.54	1.56
L13	1.67	1.71	1.73	1.72	1.71
L14	1.78	1.808	1.764	1.806	1.790
L15	1.54	1.54	1.73	1.74	1.64
L16	2.2	2.5	1.6	1.5	2.0

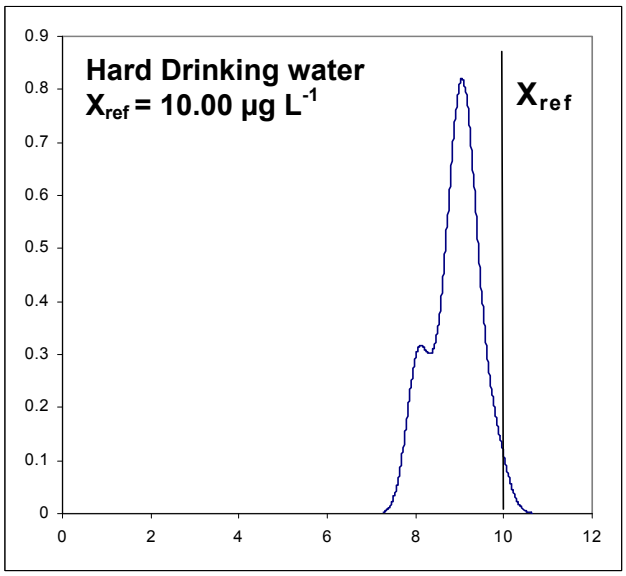


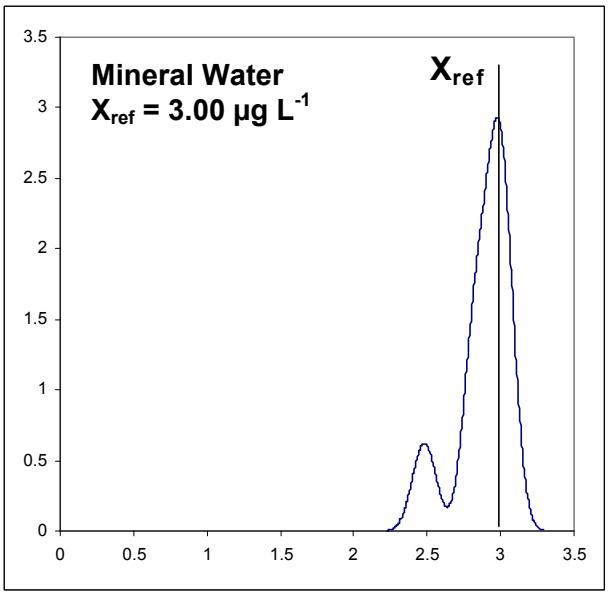
This plot shows all measurement results. The solid line refers to the reference value. The averaged mean value is 1.68 µg L^{-1} (dashed line). Identified laboratories were considered outliers, (C = Cochran, G = Grubbs). Solid squares indicate bottle 1, open ones bottle 2.

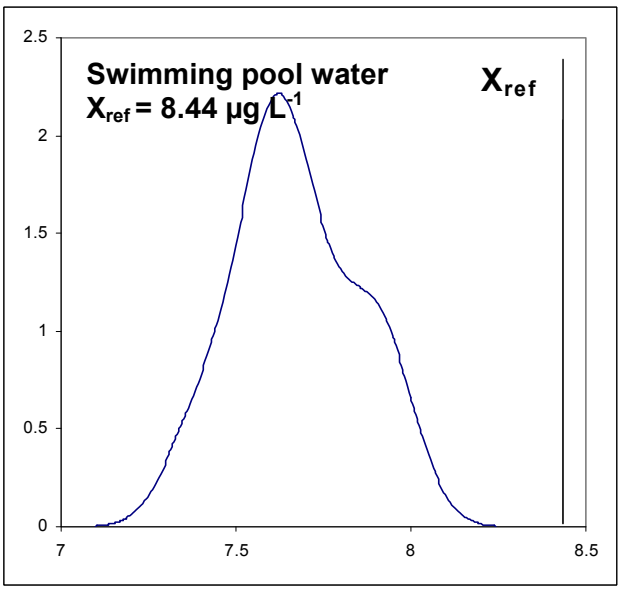
Institute for Reference Materials and Measurements

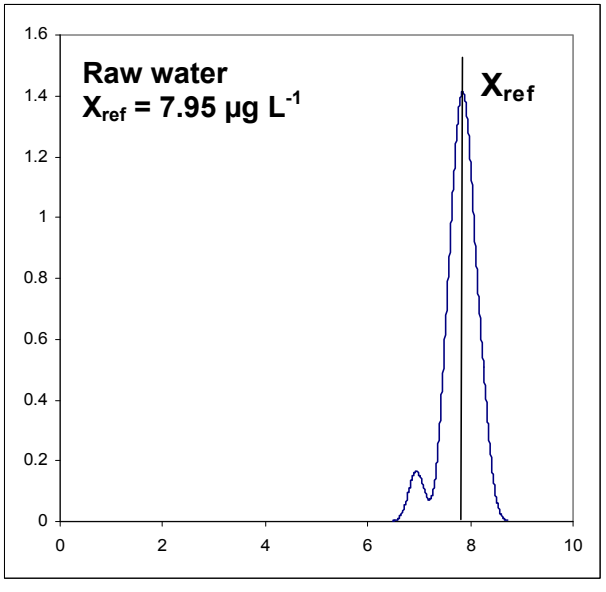
Annex 14: Kernel densities (X axes in µg L^{-1})

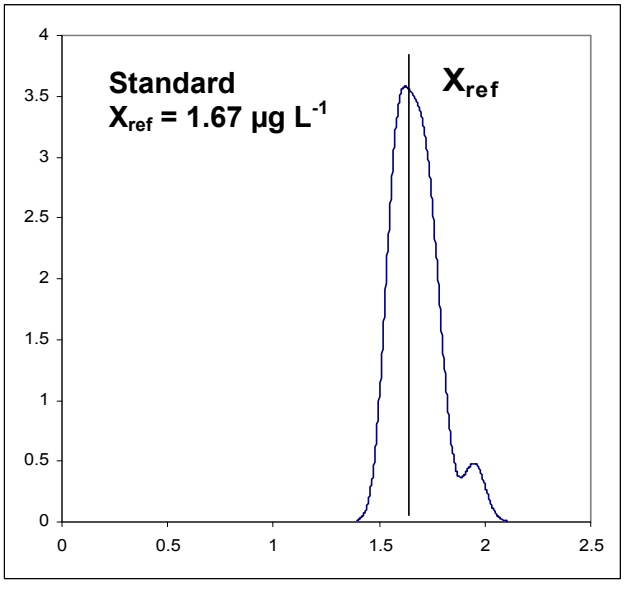












European Commission

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Author(s): F. Cordeiro, F. Schmitz, I. Verbist, H. Emteborg, J. Charoud-Got, M. C. Lopez, P. Robouch, P. Taylor, M. Beatriz de la Calle
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Abstract
A collaborative study, IMEP-25a, was conducted in accordance with international protocols to determine the performance characteristics of an analytical method for the determination of dissolved bromate in drinking water. The method should fulfil the analytical requirements of the Council Directive 98/83/EC (referred in this report as the Drinking Water Directive, DWD). The method is based on ion chromatography followed by post column reaction and ultraviolet detection. This method follows a draft method from the International Organization for Standardization (Draft ISO/DIS 11206).
The previous standard method (ISO 15061:2001) is based on ion chromatography using suppressed conductivity detection whereby a pre-concentration step may be required for the determination of bromate concentrations as low as 3 µg L-1 to 5 µg L-1. The new method includes a dilution step allowing the determination of bromate concentrations ≥ 0.5 µg L-1. Furthermore, the method aims to minimize any potential interference of chlorite ions.
The collaborative study investigated different types of drinking water such as soft drinking water, hard drinking water and mineral water. Other types of water such as raw water (untreated), swimming pool water, a blank (named river water) and a bromate standard solution were also included as test samples.
All test matrices, but the swimming pool water, were spiked with high purity potassium bromate to obtain bromate concentrations ranging from 1.67 to 10.0 µg L-1. Swimming pool water was not spiked as this water was incurred with bromate.
Test samples were dispatched to 17 laboratories in 9 different countries. Sixteen participants reported results. The repeatability relative standard deviation (RSDr) ranged from 1.2 to 4.1 % while the reproducibility relative standard deviation (RSDR) ranged from 2.3 to 5.9 %.
These precision characteristics are in good agreement, if not better, than those of the ISO 15061. A thorough comparison of the performance characteristics is presented in this report. All method performance characteristics obtained in the frame of this collaborative trial indicates that the draft ISO/DIS 11206 standard method meets the requirements set down by the DWD. The draft ISO/DIS 11206 standard method can be therefore considered to fit its intended analytical purpose.

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