Report of the 14th proficiency testing on meat, milk and fish of the European Union Reference Laboratory for chemical elements in food of animal origin

Edited by
R. Giordano, A. Sorbo,
V. Patriarca and L. Ciaralli
Report of the 14th proficiency testing on meat, milk and fish of the European Union Reference Laboratory for chemical elements in food of animal origin

Edited by
Rosa Giordano, Angela Sorbo, Valeria Patriarca and Laura Ciaralli

European Union Reference Laboratory for Chemical Elements in Food of Animal Origin - Department of Veterinary Public Health and Food Safety, Istituto Superiore di Sanità, Italy
The European Union Reference Laboratory for Chemical Elements in Food of Animal Origin (EURL-CEFAO), in the range of the duties provided in article 32 of Regulation (EC) 882/2004, yearly organizes Proficiency Tests (PTs) addressed to the National Reference Laboratories of the European Union Member States. The scheme is intended as a long-term programme to evaluate the performance of the participants. Therefore, until 2011 the activity had been planned in order to guarantee 2-3 rounds for each PT so as to periodically repeat the same combination matrix/analytes. The 14th PT consisted of three rounds on fresh matrices containing cadmium, lead, mercury and total arsenic at levels of interest. In particular, milk was prepared in liquid form, and meat and fish were proposed, for the first time, in a frozen state instead of freeze-dried. Although the performance (z-score) was assessed by means of a standard deviation for proficiency assessment generally more restrictive than that derived from Thompson/Horwitz equation, the results obtained by almost all participants were satisfactory for each round.

**Key words:** European Union Reference Laboratory; National Reference Laboratories; Chemical elements; Proficiency testings; Maximum level; Compliance assessment

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**Rapporto del 14° circuito interlaboratorio su carne, latte e pesce del Laboratorio di riferimento dell’Unione Europea per gli elementi chimici per gli alimenti di origine animale.**

A cura di Rosa Giordano, Angela Sorbo, Valeria Patriarca e Laura Ciaralli

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L’EURL-CEFAO (European Union Reference Laboratory for Chemical Elements in Food of Animal Origin: Laboratorio di riferimento dell’Unione Europea per gli elementi chimici per gli alimenti di origine animale), nell’ambito dei compiti definiti nell’articolo 32 del Regolamento (CE) 882/2004, organizza annualmente circuiti interlaboratorio rivolti ai Laboratori Nazionali di Riferimento degli Stati Membri dell’Unione Europea. Lo schema è pensato come un programma a lungo termine per valutare le prestazioni dei partecipanti; a questo fine l’attività dal 2006 al 2011 è stata pianificata anche ripetendo periodicamente la stessa combinazione matrice/analiti. Il 14° circuito si è articolato in tre diversi esercizi su matrici fresche con livelli di interesse di cadmio, piombo, mercurio e arsenico totale. Nello specifico sono stati preparati campioni di latte liquido e per la prima volta sono stati prodotti campioni di carne e pesce congelati invece che liofilizzati. Nonostante la valutazione delle prestazioni (z-score) sia stata basata su una deviazione standard in genere più restrittiva di quella calcolata con l’equazione di Thompson/Horwitz, i risultati ottenuti da quasi tutti i partecipanti sono stati soddisfacenti per ognuno degli esercizi proposti.

**Parole chiave:** Laboratorio Europeo di Riferimento; Laboratori Nazionali di Riferimento; Elementi chimici; Circuiti interlaboratorio; Tenore massimo; Dichiarazione di conformità

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ABBREVIATIONS

AAS  Atomic Absorption Spectrometry
AMC  Analytical Methods Committee
CEFAO Chemical Elements in Food of Animal Origin
CRL  Community Reference Laboratory
CV-AAS Cold Vapor Atomic Absorption Spectrometry
EC  European Commission
ETA-AAS Electrothermal Atomisation Atomic Absorption Spectrometry
EURL European Union Reference Laboratory
FAAS Flame Atomic Absorption Spectrometry
FI-FU Flow Injection analysis system – FUrnae coupling technique
GF-AAS Graphite Furnace Atomic Absorption Spectrometry
HG-AAS Hydride Generation Atomic Absorption Spectrometry
ICP-MS Inductively Coupled Plasma Mass Spectrometry
IEC International Electrotechnical Commission
IHP International Harmonized Protocol
IQR Interquartile Range
ISO International Organization for Standardization
LoD Limit of Detection
LoQ Limit of Quantification
ML Maximum Level
NRCP National Residues Control Plan
NRL National Reference Laboratory
PT Proficiency Testing
Q-ICP-MS Quadruple Inductively Coupled Plasma Mass Spectrometry
SD Standard Deviation
Z-ETA-AAS Zeeman Electrothermal Atomisation Atomic Absorption Spectrometry

Symbols

\( \alpha \) Level of significance
\( \sigma_{\text{rob}} = \text{SD}_{\text{robust}} \) Robust Standard Deviation
\( u_x \) Standard uncertainty of the assigned value
\( \sigma_{pCRL} = \sigma_{pEURL} \) Standard deviation for proficiency assessment
\( \sigma_{\text{Horwitz}} \) Standard deviation from Horwitz equation
\( U \) Expanded uncertainty
PREFACE

The European Union Reference Laboratory for Chemical Elements in Food of Animal Origin (EURL-CEFAO), formerly Community Reference Laboratory (CRL), is one of the European Union Reference Laboratories (EUR Ls) designated by Council Directive 96/23/EC (1) “on measures to monitor certain substances and residues thereof in live animals and animal products”. EURL-CEFAO is responsible for chemical elements in food of animal origin and it is hosted by the Istituto Superiore di Sanità of Rome in the Department of Veterinary Public Health and Food Safety. This assignment has been confirmed in Regulation (EC) 882/2004 (2) and following Regulations.

The Directive 96/23/EC lays down measures to monitor residues of substances listed in Annex I, namely substances having anabolic effect and unauthorized substances (Group A), residues of veterinary drugs (Group B1 and B2), other substances and environmental contaminants (Group B3). Chemical elements were included (Annex I, Group B3c) since some of them already had fixed legal limits due to their toxicity. These limits were not established as a consequence of an intentional use of substances in the treatment of animals, but as the consequence of the presence of contaminants in feed and dietary supplements and/or in the environment.

Council Directive 96/23/EC requires that each Member State yearly submit a National Reference Control Plan (NRCP) to the approval of the European Commission (EC). This plan shall contain information such as the species to be controlled; the analytes to be determined; the number of samples; the sampling procedures; the requirements for laboratories performing the analyses; the actions to be carried out in case samples are not compliant and eventually the communication of the results to the Commission.

The tasks of EUR Ls are listed in the art. 32 of Regulation (EC) 882/2004. The activity of EURL-CEFAO is mainly focused on method validation based on the most widely used techniques in its field of competence; preparation of ad hoc materials for Proficiency Testing (PT) addressed to the relevant National Reference Laboratories (NRLs); assistance to NRLs in the field of EURL activities and organization of training courses for NRLs and third Countries.

In the last 6 years a lot of resources and efforts have been lavished on the organisation of inter-laboratory comparisons. The EURL-CEFAO network consists of NRLs from the 27 Member States, that may either directly perform the analysis foreseen in the NRCP or may oversee the competence of the routine laboratories that carry out such analysis.

Each Proficiency Test is planned giving priority to the matrices of food of animal origin and elements for which Maximum Levels (MLs) are set in Commission Regulation (EC) 1881/2006 (3) and following amendments, and to those mainly considered in the NRCPs of the European Member States. Samples are prepared starting from materials purchased on the market and often adjusting the concentration levels of the analytes near their MLs.

As for the physical state of the matrix, a great effort has been accomplished during the years in order to distribute “fresh” samples, i.e. in the same way as MLs are set in the legislation. For this purpose, throughout the PTs, lyophilized samples have been substituted with liquid (milk) and frozen samples (meat, fish, liver).

As NRLs are often appointed as third parties in legal controversies, the exercises proposed by EURL-CEFAO are to be considered the most useful and proficient tests available, considering that the other available schemes on the market often do not cover matrices of interest and/or provide suitable concentration levels. The preparation of such materials has
involved the development of proper internal procedures and the Laboratory has developed a high competence in this field.

The annual PT consists of more than one round, dealing with different matrices.

The matrices and the number of rounds of the PTs are set in the annual work-programme submitted by the laboratory to the EC. In this planning, both the outcome of the previous rounds and the needs of NRLs are carefully evaluated.

In order to meet the requirements of a Reference Laboratory, the EURL-CEFAO was accredited according to ISO/IEC 17025:2005 (4). In order to face the needs arising from the updating of laws and/or regulations relevant to Maximum Levels for food of animal origin, the laboratory successfully applied for the Flexible Scope of Accreditation. As PT Provider, the EURL-CEFAO has been accredited to ISO/IEC Guide 43-1:1997 (5) and, later on, to ISO/IEC 17043:2010 (6) so as to be able to provide NRLs with exercises equivalent to the highest quality level.

Laura Ciaralli

Director of the European Union Reference Laboratory for Chemical Elements in Food of Animal Origin
Department of Veterinary Public Health and Food Safety
RATIONALE OF THE 14th PROFICIENCY TESTING

Rosa Giordano
European Union Reference Laboratory for Chemical Elements in Food of Animal Origin, Department of Veterinary Public Health and Food Safety, Istituto Superiore di Sanità, Rome

Introduction

Proficiency Tests (PTs) on the determination of total arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) in food of animal origin are yearly organized by the European Union Reference Laboratory for Chemical Elements in Food of Animal Origin (EURL-CEFAO). The PTs are addressed to the National Reference Laboratories (NRLs) of the European Union and they are carried out in the framework of the annual work programme. The participation is free of charge and each laboratory can choose one or more among the elements proposed in the PT.

The PT scheme is managed according to ISO/IEC 17043:2010 (6), replacing ISO Guide 43-1:1997 (5), the International Harmonized Protocol (IHP) (7), and the ISO 13528:2005 (8).

A detailed report, containing information about the PT scheme, the homogeneity of the test items, the list of participating laboratories and the analytical results, is drawn up for each round.

General outline

The 14th PT consisted of 3 rounds of which the last one started at the end of 2010 to be continued at the beginning of 2011. Three different matrices were prepared according to the following scheme: meat, milk and fish. This sequence was established in order to enhance NRLs in the control of the methods used for the most important matrices on a regular basis.

Cadmium, mercury, and lead were selected as analytes since Maximum Levels (MLs) are set for these elements; besides, arsenic was also considered for the toxicity of its inorganic form and its inclusion in the NRCPs.

The exercise was carefully scheduled and a short report was made available on the EURL-CEFAO website after 40 days from the deadline of the round in order to provide NRLs with information on their performance as fast as possible. As the graphs, tables and details of the statistical evaluation were completed, the final report was available only in the restricted area of the EURL-CEFAO website.

Objectives

During the five-year period 2006-2011, PTs had been planned as a long-term programme pursuing the general objective of providing the NRLs with a PT scheme that gave them the possibility:
 – to check and to improve the performance of the analytical methods used for the most important chemical elements and matrices of animal origin by preparing samples at a concentration around the MLs of the analytes;

* Former Director of the EURL-CEFAO, currently an external expert in the team.
to verify the effectiveness of the corrective actions undertaken (when necessary) through the repetition of the same matrix;
- to have a long term follow-up of their performance;
- to promote the improvement of Quality Control System.

Taking into account the general objective of the program, each annual PT was planned considering the outcome of the previous ones, the suggestions of the NRLs and the discussion during the annual workshop. Moreover, starting from 2008, the “interpretation of results” and the “acceptance/rejection of a sample” were requested as exercise in most of the rounds for matrices and analytes for which an ML exists.

The milk samples were prepared in liquid form, whereas the meat and fish samples were in frozen form to provide the samples in a physical state like the one of incurred samples. As for milk, since the certified reference materials available on the market are in freeze-dried state, the EURL considered very important to study and prepare liquid samples at suitable concentration levels as reference material and to provide the NRLs with extra-material to be used to maintain/improve the performance of the applied methods.

Test materials

The preparation of the samples was performed in the EURL-CEFAO laboratory according to its internal procedures. Only the sterilization for milk was carried out by a qualified supplier. The detailed description of each preparation is quoted in the report of the relevant round.

Homogeneity and statistical evaluation

Homogeneity was tested according to the IHP and all materials resulted to have sufficient homogeneity as discussed in the report of each round. Statistical evaluation was performed following the EURL-CEFAO internal procedure according to ISO 13528:2005 and the IHP.

The assigned value was determined using the “Consensus of Participants” approach based on data produced only by NRLs and submitted before the deadline.

The statistical evaluation of results and the rationale for the choice of the central tendency index as assigned value is detailed in each report.

Confidentiality

All information sent by participants is treated as confidential by the EURL staff. A different code number is assigned to each NRL at every round as to preserve confidentiality of data; the laboratories participating with more than one analytical method are coded with different numbers. Moreover an internal fixed code is given to each laboratory to preserve confidentiality inside the EURL staff when handling data from different PTs. When reporting results to the European Commission (EC) or during the annual Workshop, each NRL is always identified with the code relevant to the round; however the EC can request a decoded list of NRLs or the results of a specific NRL. The participants are informed on this.
PART A

First round on frozen meat

Cadmium, lead, total arsenic and mercury

Angela Sorbo (a), Andrea Colabucci (a), Maria Ciprotti (a), Laura Ciaralli (a), Alessio Pitidis (b), Marco Di Gregorio (a), Daniela Pino (a)

(a) Department of Veterinary Public Health and Food Safety
(b) Department of Environment and Primary Prevention
Specific objectives

All the NRLs (28 laboratories) subscribed to participate in this round on frozen meat for which a ML value is set both for cadmium and lead in the Commission Regulations (EC) 1881/2006 (3) and (EC) 629/2008 (9), (0.050 and 0.10 mg/kg, respectively).

As for cadmium, being this element generally analysed in previous PTs at good level, no particular problems occur and both SD and SD\textsubscript{robust} of the consensus values are lower or close to the $\sigma_{pCRL}$. A concentration of ~0.04 mg/kg – a value of ~0.01 mg/kg lower than the ML – was planned to verify whether all laboratories would consider the sample as “compliant”. Moreover, it was considered that it could be interesting to make a comparison between the performance of laboratories on this concentration, already used in 2007 on a lyophilised sample, and the present one repeated now on a frozen sample.

Lead is usually a quite difficult element to be analysed; even if a general improvement was noticed for all matrices during the PTs some important overestimates/underestimates still occur. A concentration close to 0.14 mg/kg was proposed to evaluate the degree of accordance among the NRLs when they have to state the compliance on a sample having a concentration 40% higher than the ML (0.100 mg/kg).

No MLs are set for arsenic in food, but since the element is taken into account in many NRCPs, it was considered to be of interest for NRLs. As for its determination, the worst performance among the matrices proposed, was the one relevant to the fish matrix probably because of the presence of this element as arsenobetaine. On the other hand SD and SD\textsubscript{robust} of the consensus value of the meat samples in previous PTs resulted increased when new laboratories entered the circuit. A concentration of ~0.4 mg/kg was chosen to verify the performance at a concentration similar to the one used in 2006 for meat.

Mercury on meat was proposed since some NRLs asked to include this element also in matrices different from fish. Since this element has not been announced during the workshop, just to give the NRLs the opportunity to set their methods at low concentration without the assignment of the $z$-scores, it was decided to prepare a level of 0.04 mg/kg.

Test material

Turkey meat was chosen since poultry had never been proposed before; moreover this kind of meat, having a good capability to retain water, is more appropriate than other species (e.g. bovine) when the state of the material is frozen. This material was prepared in the EURL-CEFAO laboratory.

Preparation

20 kg of slices of turkey breast was purchased at a supplier who was asked to consider some precautions in the meat choice and preparation; the meat was frozen to facilitate a water loss through thawing.

After removing water, the meat was roughly minced, blended, spiked, blended again and finally mixed using a planetary mixer, according to an internal procedure.

The material was distributed in the jars and the test items were stored at -80°C until shipment. As for contamination, the jars (n) were decontaminated and checked according to internal procedures. Briefly, after decontamination, both p-jars ($p=\sqrt{n}$-1), randomly chosen, and
the containers of the mixers were filled with water (at about half their volume) and left 30’ under shaking. The solutions were then immediately checked for metals by using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS); the results showed that the contamination was under control being all values of arsenic and cadmium lower than LoQs (Limit of Quantification) (0.040 and 0.004 μg/L, respectively) and for lead <0.030 μg/L (LoQ = 0.014 μg/L). As for the spiking of the elements, stock solutions containing the elements were gravimetrically prepared and quantitatively added to the meat previously weighed.

**Homogeneity of test items**

Homogeneity was tested according to the IHP (7). 101 test items were prepared, numbered with progressive numbers and finally divided in 10 sub-lots. One jar was randomly taken from each sub-lot in order to check homogeneity. Therefore the ten test items were analysed in duplicate by applying an accredited method based on microwave acid assisted digestion. The concentration of arsenic, cadmium and lead was obtained by using ICP-MS whereas the mercury content was determined by means of Cold Vapor-Atomic Absorption Spectrometry (CV-AAS). The results are shown in Table A1.

<table>
<thead>
<tr>
<th>Item</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Hg</th>
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<td>a</td>
<td>b</td>
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<td>66</td>
<td>316</td>
<td>326</td>
<td>40</td>
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</tr>
</tbody>
</table>

| Grand Mean | 333 | 40 | 149 | 41 |
| σ_p | 580 | 5.9 | 22.3 | 4.1 |
| S^2_an | 121 | 0.30 | 4.84 | 0.27 |
| S^2_sam | 24.8 | -0.027 | -0.292 | 0.18 |
| S_{sam}/σ_p | 0.220 | 0.093 | 0.0990 | 0.13 |
| Critical | 545 | 6.2 | 89.0 | 3.1 |
| S_{sam}^2 < Critical | Yes | Yes | Yes | Yes |

a, b = replicates of the same test item
σ_p = σ_{calc} based on grand mean
S^2_an = Analytical variance
S^2_sam = Sampling variance
S_{sam}/σ_p <0.5
Critical = Critical value based on allowable and analytical variance:
S_{sam}^2 < Critical = if S_{sam}^2 < Critical, the material has sufficient homogeneity.

The Cochran’s test did not evidence outliers. The standard deviations calculated on results were consistent, for all the elements, with the repeatability of the analytical methods. As for the
evaluation of homogeneity, the $\sigma_{pCRL}$, calculated using the mean value of the homogeneity results, was used for arsenic, cadmium and lead; as for mercury, for which no $z$-score would be assigned, the 10% of mean was used.

For all elements, analytical variances also suited the $\sigma_{pCRL}$ ($\sigma_{an}/\sigma_{pCRL} < 0.5$).

**Quality assurance in sample preparation**

All the instruments used are well maintained and calibrated. The analytical methods used are accredited. The reliability of both methods and personnel is regularly checked by means of participation in PTs, certified reference materials and control charts based on internal reference materials at concentrations of interest.

**Distribution of samples and instructions to participants**

A jar, containing about 100 g of sample, was sent to the participating laboratories. All samples were frozen, packed in polystyrene boxes and, with the exception of few NRLs, surrounded with dry-ice; gel ice packs were, instead, used for the Member States where dry-ice dispatch is not accepted.

An information message was sent out by e-mail before shipment so that laboratories could make their own arrangements for the reception of the package. The instructions on sample handling and storage were also supplied.

The participants were asked to treat the test material as if it were a sample for their routine analysis; they were also asked to analyse the same number of replicates that they normally use. The results were reported in the appropriate form and then sent to the EURL-CEFAO, either by e-mail or fax along with the required additional information (e.g. method used and its details, instrumentation, etc.). As for cadmium and lead, the laboratories were asked to state the compliance of the sample.

The samples were sent on 9 March 2010. The deadline for results was 17 April 2010.

The table of $z$-scores was made available at the website within about 40 days from the deadline; NRLs were informed on this.

**Statistical evaluation of results**

The procedure reported in the IHP (7) was followed. The first stage of this procedure consists in screening and rejecting the data that are obviously not valid. Measurement results reported as “smaller than” are not usually considered in any calculation and no scores are given; the results arriving long after the deadline are not included in the data set used to calculate the assigned value, but only the $z$-score is assigned.

**Arsenic, cadmium and lead**

**Assigned value ($\hat{X}$)**

The assigned value of each analyte was determined as a consensus value based on the results of the participants using robust statistics. Briefly, clearly aberrant results and/or extreme outliers ($\pm 50\%$ of the median) were removed from the data set and the robust statistics was applied to the remaining data; the robust average, calculated using Algorithm A, was adopted as assigned
value; a visual presentation of the results in the remaining data set, outliers aside, showed a roughly symmetric distribution for all elements. As for the uncertainty of the assigned value, the conservative expression \( u_X = 1.25 \times \sigma_{rob} / \sqrt{n} \), reported in the ISO 13528:2005 (8), was used.

The kernel density estimates of the distribution of the results (extreme outliers excluded), using a bandwidth \( (h) \) of 0.75 \( \sigma_{pCRL} \), always showed unimodal and symmetric densities. The robust statistics and kernel plots were obtained using a software tool developed by Analytical Methods Committee (AMC) (available from: http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/RobustStatistics.asp10).

Taking into account that the assigned values are based on the participant results, the possible difference between the two main techniques used by NRLs was also evaluated.

**Standard deviation for proficiency assessment**

The standard deviation for proficiency assessment \( (\sigma_p) \) is usually derived from the Horwitz equation. Nevertheless, considering that the level of performance required from the NRLs should be higher than that of routine control laboratories, adequate lower values of standard deviation were set for the proficiency assessment \( (\sigma_{pCRL}) \). The equations are reported in Table A2.

**Scores and evaluation criteria**

The laboratory performance was expressed in terms of \( z \)-scores \( (z=(X_{lab} - \bar{X}) / \sigma_p) \) in accordance with ISO 13528:2005 and the IHP. The interpretation of the \( z \)-scores was the one adopted at international level: \( |z| \leq 2 \): satisfactory result; \( 2 < |z| < 3 \): questionable result; \( |z| \geq 3 \): unsatisfactory result.

In order to allow an easy comparison among the performances obtained in the EURL-PTs and those of other programmes, the \( z \)-scores calculated using a \( \sigma_{pHorwitz} \) are reported as well.

**Acceptance of a sample**

Considering the ML established by Commission Regulations (EC) 1881/2006 (3) and (EC) 629/2008 (9), for cadmium and lead in meat, \( 0.050 \) mg/kg and \( 0.10 \) mg/kg, respectively, the acceptance of the sample, as indicated in Commission Regulation (EC) 333/2007 (point D.2.1) (10), must be assessed “taking into account the expanded measurement uncertainty”.

In order to express acceptability, details were given in the “Technical Information”. However, the correct procedure is the following:
a) express the results in the same units and with the same number of significant figures as the relevant ML;

b) subtract the value of uncertainty from the result; (taking care of rounding the result of the computation to the same number of significant figures as the ML);

c) compare this value with the ML;

d) accept the sample if this value is lower or equal to the ML.

The interpretation of NRLs is reported in Table A3; the text in the box means a wrong interpretation of the acceptance.

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**Mercury**

Although z-scores were not assigned the usual statistical procedure was applied.

**Results and comments**

All NRLs analysed cadmium and lead; 23 NRLs submitted results for arsenic and mercury; three NRLs participated using two methods based on different techniques for cadmium, lead and arsenic; a laboratory used two methods for mercury.

The results, as reported by the participants, are shown in Table A4, together with the z-scores that were calculated considering both the $\sigma_{pCRL}$ and the $\sigma_{pHorwitz}$.

The data for each element (Annexes A1.1 to A1.4) are also presented in two different graphs.

The first one shows the distribution of the results (arrived within deadline) according to the technique used, whereas the distribution of z-scores, shown in the second one, refers to all results. The distribution of results and the corresponding expanded uncertainties are reported in Annex A1.5.
Table A4. Assigned values (\(\bar{X}\)), standard deviations, results (mg/kg) and z-scores

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<th>Lead</th>
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<td>(\sigma_{\text{Horwitz}})</td>
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Results and z-scores

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<th>(\sigma_{\text{CRL}})</th>
<th>z-score</th>
<th>(\sigma_{\text{Horwitz}})</th>
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- data not submitted; * data arrived after the deadline

From a statistical point of view, the results can be considered satisfactory, since the data set used for the assigned value produced mean, median and robust mean that are practically the same for each analyte. No outlier was found for either cadmium or lead.

Since the analytical methods (Annexes A2.1 to A2.5) used in the network of the NRLs (Annex A2.6) are mainly based on two techniques, the effect of the techniques on the assigned value was evaluated. The comparison done for cadmium and lead between the two main analytical techniques, namely ICP-MS and GF-AAS (Z-ETA-AAS+ETA-AAS), showed that the difference between the means of the two sub-datasets is not statistically different (Cd: 0.043±0.0034; 0.043±0.0044; Pb: 0.146±0.011; 0.140±0.022). As for arsenic just an extreme
outlier (±50% of the median) occurred and it was removed. The prevailing techniques are ICP-MS (n. 12) and HG-AAS (n. 8) whereas a lower number of methods are based on GF-AAS (n. 4). A difference (p=0.05) between the means of the ICP-MS and HG-AAS results was observed (0.420 mg/kg; 0.368 mg/kg, respectively; difference 0.052 mg/kg).

This statistical difference is due to the fact that the lowest value (0.272 mg/kg) in the data set belongs to the HG-AAS sub-dataset, while the highest one (0.523 mg/kg) to the ICP-MS. When the two results are removed from each sub-dataset, the difference became poorly significant (p=0.2); moreover they do not affect the assigned value, being this the same with and without these values. All this considered, it is possible to be confident that, also for arsenic, the assigned value is not biased.

From an analytical point of view it is worth noticing that the dispersion of the results for cadmium is not statistically different between the sub-datasets (ICP-MS and GF-AAS), whereas SDs for lead (F-test=0.2) were statistically different; by observing previous PTs, the lower is the concentration in the sample, the more evident is the difference.

As for arsenic, there seems to be a trend towards underestimating for the methods using the HG-AAS technique; this might be caused by the principle of the method, based on redox reaction, and by the sample preparation. Both steps can be critical and these issues will be dealt in detail during the annual workshop. It is not casual that the lowest result comes from a laboratory that has participated for arsenic only recently. On the other hand, ICP-MS technique requires more training for the analysis of this element compared with the one necessary for the analysis of cadmium or lead. This last remark is confirmed by laboratory 111 that is new in the use of ICP-MS: its performance is very good for cadmium and lead, but not as good for arsenic.

All considered, the objectives of the PT have been quite satisfactory. As for the improvement of the performance of NRLs, it was noticed that the number of laboratories that analyse arsenic is increasing: 19 results in the previous sample of meat (12th PT, 3rd round) versus 27 results of the present round; moreover, the outcome in terms of z-score has improved for all the analytes.

As it is reported in the following tables (Tables A5 and A6), all z-scores were <2 for Cd; two questionable results (1:Pb; 1:As) and one unsatisfactory z-score for As were noticed; the percentage of z-scores < 1 was high for all the elements.

The general improvement, when the distribution of z-scores ($\sigma_{pCRL}$) is compared with the ones of previous PTs, is evident for cadmium and lead.

Table A5. Comparison between the distribution of z-scores according both to $\sigma_{pCRL}$ and $\sigma_{pHorwitz}$

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<th>$\sigma_{pHorwitz}$</th>
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<td>$</td>
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<tr>
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<td>1/27 (4%)</td>
</tr>
<tr>
<td>Cadmium</td>
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</tr>
<tr>
<td>Lead</td>
<td>31/32 (97%)</td>
<td>1/32 (3%)</td>
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Table A6. Distribution of z-scores in five years period 2005-2010

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<td>10th PT (A)</td>
<td>14th PT</td>
<td>11th PT</td>
</tr>
<tr>
<td>≤ 2</td>
<td>94.5%</td>
<td>92.0%</td>
<td>91.3%</td>
</tr>
<tr>
<td>2 &lt; z &lt; 3</td>
<td>0</td>
<td>4.0%</td>
<td>0</td>
</tr>
<tr>
<td>≥ 3</td>
<td>5.5%</td>
<td>4.0%</td>
<td>8.7%</td>
</tr>
</tbody>
</table>
As for arsenic the results are quite similar in terms of z-scores but a better agreement has been achieved among the laboratories since the SD and SD_{robust} shifted from 18% to 12% and from 15% to 10%, respectively.

The positive outcome for all the elements is certainly the consequence of the good work done by the NRLs in improving their methods, but also of the regular repetition of the same matrices throughout the years; this enabled NRLs to check the suitability of their corrective actions.

As far as the acceptability of the sample is concerned, several problems were noticed in the previous PTs due to an incorrect application of the rules for the compliance statement of the sample. In the present PT, instead, it is possible to see in the histogram (Figure A1), only 5% of the NRLs (considering both Cd and Pb) have made a mistake in the computation of the compliance.

Moreover, an opinion was expressed by 100% of the laboratories and this also represents an achievement. In the 13th PT in fact, ~10% (mean of 2 rounds) of laboratories did not express any opinion on the acceptability of the sample and ~10% stated a wrong acceptance in terms of simple computation. Nevertheless three wrong answers are still present in this round (2 for Pb; 1 for Cd; see Table A3) and it is necessary to quickly fill this gap.

As for the specific objective of the round, that was to test the consensus degree in the compliance assessment of a sample having a target concentration, the results are reported in the following graphs (Figure A2).
As for cadmium, the consensus in stating the sample as compliant is almost unanimous also considering that the unique statement of non-compliance came from one NRL that made a computational mistake. This demonstrates the outstanding analytical performance achieved for this element in a sample having a concentration of 0.007 mg/kg lower than the ML.

The analysis of lead produced an agreement of 72% in stating the sample as “noncompliant” for a concentration 0.041 mg/kg higher than the ML. The percentage increases up to ~78%, if the computation errors (2 results) are excluded. It is worth noticing that among the seven compliant results only two were obtained by ICP-MS technique, whereas five by GF-AAS as a consequence of the limit of this last technique at low levels of concentration.

As for the performance criteria of analytical methods, set out in Table 5 point C. 3.3.1 of Commission Regulation (EC) 333/2007, some improvements are still necessary from NRLs. Briefly, LoD (Limit of Detection) and LoQ shall be, respectively, less than one tenth and one fifth of the ML for cadmium and less than one fifth and two fifths for lead, being the ML of the latter less than 100 µg/kg.

Not all the labs submitted LoD and LoQ values, some only LoD, others only LoQ. Other NRLs did not specify measurement units and, for this reason, were not taken into account.

Since considerations on LoQ and LoD are similar, only some comments on LoQ will be made. As for cadmium (ML = 0.050 mg/kg), the table reported in Annex A2.3, shows that ten LoQs are higher or equal to 0.010 mg/kg, that is one fifth of the ML, whereas according to the criteria of Commission Regulation (EC) 333/2007 they should be lower. As for the techniques employed, five were obtained by using GF-AAS, four by ICP-MS and one by FAAS (total 10).

As far as lead (ML = 0.10 mg/kg) a total of 9 LoQs are higher than what stated in Commission Regulation (EC) 333/2007, all using AAS techniques; eight GF-AAS and one FAAS (Annex A2.4).

However, to be exhaustive, it is necessary to point out that two laboratories, using two different techniques, reported two different LoQs for cadmium and lead. One of them fulfilled the requirements of Commission Regulation (EC) 333/2007. Therefore, NRLs that avail themselves of methods not fulfilling this performance are realistically 8 and 7 for cadmium and lead, respectively.

As for mercury, 24 results were submitted and no clearly aberrant or qualitative data were produced. Both basic statistics and robust statistics were performed in order to compare the tendency central indicators including their standard deviations (mean: 0.042 ± 0.0044, median: 0.041 and robust mean: 0.042 ± 0.0047). It is possible to point out that the indicators of the central tendency are practically the same and that there is no difference between the SD of mean and the SD of robust mean.

Data were well spread around the mean value; the maximum and minimum result submitted was 0.052 mg/kg and 0.036 mg/kg, respectively.

The data set was normally distributed according to Kolmogorov-Smirnov probability plot (p-value = 0.053) and the distribution was unimodal. The two main techniques used by NRLs (CV-AAS and HG-AAS) were also compared in terms of mean and standard deviation obtaining the following results: 0.042 ± 0.0044 mg/kg for CV-AAS and 0.042 ± 0.0048 mg/kg for HG-AAS. The absence of a statistical difference between 13 standard deviation and mean was confirmed by applying the F-test (p = 0.838) and t-test (p = 0.899), respectively.

Even though the performance of NRLs for mercury has not been considered in terms of z-scores, it is easily deducible that the results obtained are extremely satisfactory.

Results are reported in Table A7 and in Figures A3-4.
Table A7. Assigned value (\( \bar{x} \)) and results (mg/kg)

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<th>Parameter</th>
<th>Mercury</th>
</tr>
</thead>
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<td>( \bar{x} )</td>
<td>0.042</td>
</tr>
<tr>
<td>( \sigma_x )</td>
<td>0.001</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Results</th>
</tr>
</thead>
<tbody>
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<td><strong>Lab. code</strong></td>
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<td>103</td>
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</tr>
<tr>
<td>116</td>
</tr>
<tr>
<td>117</td>
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</tbody>
</table>

* data arrived after the deadline

Figure A3. Estimate kernel density for mercury
Figure A4. Probability plot for mercury
Annex A1 • FIRST ROUND

Statistics, distribution of results and z-scores

A1.1. Arsenic in frozen meat

Parameters for statistical evaluation

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<th>Parameter</th>
<th>All results</th>
<th>Without outliers</th>
</tr>
</thead>
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<td>H15 SD</td>
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Distribution of results

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<th>Q-ICP-MS</th>
<th>Z-ETA-AAS</th>
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</thead>
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</table>

z-score ($\sigma_{pCRL}$)

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<th>HG-AAS</th>
<th>ICP-MS</th>
<th>Q-ICP-MS</th>
<th>Z-ETA-AAS</th>
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A1.2. Cadmium in frozen meat

Parameters for statistical evaluation

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Distribution of results

z-score (σpCRL)

Lab. code Arrived after deadline
A1.3. Lead in frozen meat

Parameters for statistical evaluation

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Distribution of results

z-score ($\sigma_{CRL}$)

Lab. code

| Arrived after deadline |
## A1.4. Mercury in frozen meat

### Parameters for statistical evaluation

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### Distribution of results

![Distribution of results graph]

The graph shows the distribution of mercury measurements in frozen meat across different analytical methods. The x-axis represents the measurement numbers (102 to 123), and the y-axis represents the concentration in mg/kg. Different methods are color-coded: CV-AAS (green), Direct Analyzer (purple), HG-AAS (yellow), ICP-MS (cyan), and Q-ICP-MS (blue).
A1.5. Distribution of results and corresponding expanded uncertainties (U)

**Cadmium results ± U**

**Lead results ± U**
Annex A2 • FIRST ROUND
Technical information, analytical methods and participants

A2.1. Technical information accompanying the samples

CRL-ISS 14th PT, 1st Round on Frozen Meat

Your Lab. Code is:................
Bottle No. :

Technical information
The round is based on total As, Cd and Pb; nevertheless the material was also spiked with mercury (total Hg <100 µg/kg) to offer the NRLs the opportunity to apply the Hg method on this matrix. Therefore the Hg elaboration will be carried out with the only indicative purposes and the z-scores will not be calculated. Each NRL is free to choose the elements to be analysed among the proposed ones.

Test material
- One sample of frozen ground turkey meat about 100 g
- The bottle must be stored in the freezer until analysis is carried out
- When defrosted, the bottle shall be identified by applying the label you will find in the envelope.

Instructions
○ Handling of the PT item
  Treat the test material as a routine sample; the number of replicates must be the same ones used in routine procedures. However, for the preparation:
  - thaw when ready to analyse (e.g. at room temperature or in refrigerator);
  - after thawing, mix the material to ensure that the sample is homogeneous before starting the analysis;
  - the separation of some liquid can occur: in this case, care must be taken to avoid loss of liquid;
  - the sample can be stored in a refrigerator (~ 4°C) for a period of 4 days, at the most; the sample can be refrozen, if necessary; the surplus can be eliminated as usual as routine sample.

○ Analysis
  Determine the total content of the selected elements according to your analytical methods.
  Please note: when the sample digestion is performed by microwave and the method is based on oxidation-reduction reactions, such as the determination of As by HG-AAS and of Hg by CV-AAS, we suggest to follow the procedure described in the EN 13805:2002. The Standard recommends to degas the digested solution in an ultrasonic bath to minimize the influence of nitrous gases on the determination; if it is not possible, we recommend to leave the test solution loosely covered for at least 12 h (overnight) after digestion.
  Describe your procedure in the section “Further Information or Brief Description of the Analytical Method” of the Results Form.
Reporting the results
- Please, fill the form in all its sections, including the number of the bottle
- Express the concentration in mg/kg
- Express the results with 3 significant figures (ex.: 0.245; 0.240; 0.0245) please note that these figures are different from the ones at point 4
- Report the “mean value” and the “standard deviation” of the replicates in the proper column of the Results form. If the laboratory performs only one replicate, the result should be reported in the “Mean value” column as well
- Results reported as “<” will not be included in the calculation of assigned value and z-score
- As for the expanded uncertainty, please note that the “coverage factor” is = 2 [Commission Regulation (EC) 333/2007]

Interpretation of results
As for Cd and Pb, the acceptability of the sample is required.
- Please, follow what is stated in the Commission Regulation (EC) 333/2007, Part D “Reporting and Interpretation of Results”

Deadline
- Data should be submitted not later than 17 April 2010 via e-mail, by fax (+39 06 49902721) or by post.
- For further information please contact the CRL-ISS, e-mail (crl@iss.it)
### A2.2. ARSENIC: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected.

#### SAMPLE TREATMENT

<table>
<thead>
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<th>Laboratory code</th>
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## MEASUREMENT

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A2.3. CADMIUM: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected.

### SAMPLE TREATMENT

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### A2.4. LEAD: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected.

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<td>SnCl₂</td>
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<td>Final volume (mL or g)</td>
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</tr>
<tr>
<td>4 ≤ x ≤ 5</td>
<td>102, 108, 134</td>
</tr>
<tr>
<td>8 ≤ x ≤ 10</td>
<td>101, 104, 110, 112, 114, 116, 118, 120, 124, 126</td>
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<td>20</td>
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<tr>
<td>50</td>
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<tr>
<td>100</td>
<td>111, 133</td>
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### MEASUREMENT

<table>
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<tr>
<td>FAAS</td>
<td>102, 110, 120</td>
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<tr>
<td>ETA-AAS</td>
<td>109, 112, 114, 123, 125, 129, 131, 134</td>
</tr>
<tr>
<td>Q-ICP-MS</td>
<td>101, 105, 111, 113, 115, 117, 119, 121, 122, 126, 127, 130, 133</td>
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<tr>
<td>SF-ICP-MS</td>
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<td>Z-ETA-AAS</td>
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#### Determination technique

<table>
<thead>
<tr>
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<tr>
<td>1:2</td>
<td>114</td>
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<td>1:4</td>
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<td>1:10</td>
<td>101, 105, 122, 126</td>
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<td>1:50</td>
<td>108, 119</td>
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<td>1:100</td>
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<td>no</td>
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#### Calibration

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<td>External linear</td>
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<tr>
<td>Method of Addition</td>
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<tr>
<td>Method of Addition Calibrate</td>
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<td>Calibration Algorithm</td>
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#### Matrix modifier

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<tr>
<td>NH₄H₂PO₄</td>
<td>106, 108, 112, 129</td>
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<tr>
<td>NH₄H₂PO₄ + Mg(NO₃)₂</td>
<td>114, 116, 118</td>
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<tr>
<td>Pd(NO₃)₂</td>
<td>103, 123, 131</td>
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<tr>
<td>Pd + Mg(NO₃)₂</td>
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<td>Other</td>
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#### Internal Standard

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<tr>
<td>Bi</td>
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<tr>
<td>In</td>
<td>126</td>
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<tr>
<td>In + Y + Bi</td>
<td>117</td>
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<tr>
<td>Re</td>
<td>127</td>
</tr>
<tr>
<td>Rh</td>
<td>105, 111, 115, 119, 121, 128</td>
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#### Wavelength

<table>
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<th>Laboratory code</th>
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<tr>
<td>213.0</td>
<td>120</td>
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<tr>
<td>217.0</td>
<td>102, 110</td>
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<td>253.7</td>
<td>125</td>
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#### Isotopic mass (amu)

<table>
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<tbody>
<tr>
<td>202</td>
<td>117</td>
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<tr>
<td>206, 207, 208</td>
<td>121, 122</td>
</tr>
<tr>
<td>207</td>
<td>111</td>
</tr>
<tr>
<td>208</td>
<td>101, 105, 113, 119, 126, 127, 128, 130, 133</td>
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<tr>
<td>208 (206 + 207)</td>
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#### LoD of the method (mg/kg)

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<th>LoD of the method (mg/kg)</th>
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<td>≤ 0.001</td>
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<tr>
<td>&gt; 0.001 - &lt; 0.005</td>
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<td>≥ 0.005 - ≤ 0.006</td>
<td>106, 111, 122</td>
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<td>≥ 0.010 - ≤ 0.015</td>
<td>105, 124, 129</td>
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<td>0.020</td>
<td>103, 114, 120, 131, 134</td>
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<tr>
<td>0.023</td>
<td>112</td>
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<td>0.040</td>
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<td>0.050</td>
<td>109</td>
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*to be continued*
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<tr>
<td>≤ 0.001</td>
<td>113, 116</td>
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<tr>
<td>&gt; 0.001 - ≤ 0.005</td>
<td>118, 126, 128, 130</td>
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</tr>
<tr>
<td>0.020</td>
<td>105, 106, 129</td>
</tr>
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<td>0.033</td>
<td>117</td>
</tr>
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<td>0.040</td>
<td>114, 120, 131</td>
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<td>0.048</td>
<td>124</td>
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<td>0.060</td>
<td>103, 134</td>
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<tr>
<td>0.069</td>
<td>112</td>
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<tr>
<td>0.080</td>
<td>125</td>
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<td>0.10</td>
<td>109</td>
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<table>
<thead>
<tr>
<th>Quality control sample</th>
<th>Laboratory code</th>
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<tbody>
<tr>
<td>BCR 184 bovine muscle</td>
<td>124</td>
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<tr>
<td>BCR 185r Bovine Liver</td>
<td>101, 111, 126, 133</td>
</tr>
<tr>
<td>BCR 186 Pig Kidney</td>
<td>122, 123</td>
</tr>
<tr>
<td>NIST 1577c Bovine Liver</td>
<td>130</td>
</tr>
<tr>
<td>NIST 1566b Oyster Tissue</td>
<td>109, 119</td>
</tr>
<tr>
<td>NIST 1548a Total Diet</td>
<td>119</td>
</tr>
<tr>
<td>NIST 1547 peach leaves</td>
<td>119</td>
</tr>
<tr>
<td>NRCC DORM-3 Fish Protein</td>
<td>134</td>
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<td>CRM</td>
<td>110, 125</td>
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<tr>
<td>CRL RM 12th PT</td>
<td>123</td>
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<tr>
<td>CRL RM 12th PT, 3 freeze-dried bovine meat</td>
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<tr>
<td>CRL RM 13th PT 1st Milk B</td>
<td>128</td>
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<tr>
<td>CRL RM 13th PT</td>
<td>116</td>
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<tr>
<td>Certified Custom Solution (HM29)</td>
<td>108</td>
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<tr>
<td>blanks, standard, CRM</td>
<td>117</td>
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<tr>
<td>QC Standards</td>
<td>112</td>
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<td>Recovery</td>
<td>102</td>
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<td>Spiked Samples</td>
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<td>Standard Addition</td>
<td>120</td>
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<td>Yes</td>
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### A2.5. MERCURY: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected.

#### SAMPLE TREATMENT

<table>
<thead>
<tr>
<th>Sample treatment</th>
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<tbody>
<tr>
<td>Sample amount (g)</td>
<td>&lt;0.1 123 0.1 101, 113, 114, 127, 130 0.5 ≤ x &lt;1 102, 104, 105, 106, 116, 126, 128, 133 1 103, 108, 119, 120, 129 1.7 ≤ x ≤ 2 109, 115</td>
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<tr>
<td>Digestion</td>
<td>Dry ashing 113, 118 High pressure 105, 106, 117, 119 Microwave assisted 102, 103, 104, 108, 109, 115, 116, 121, 123, 126, 133 Open wet 120, 129, 131 EN 13805 128 Other 101, 110, 114, 127, 130</td>
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<tr>
<td>Acids and H₂O₂</td>
<td>HNO₃ 104, 105, 108, 109, 110, 117, 119, 123, 131, 133 HNO₃ + H₂O₂ 103, 115, 116, 121, 126, 128 HNO₃ + HCl + H₂O₂ 102, 106 HNO₃ + H₂SO₄ 120, 129</td>
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<tr>
<td>Chemicals</td>
<td>Au 128 NaBH₄ + NaOH 106, 115, 116 SnCl₂ 102, 104, 105, 109, 120 V₂O₅ 120</td>
</tr>
<tr>
<td>Final volume (mL or g)</td>
<td>5 108, 110 10 126 15 116 20 104, 106, 115, 131 25 102, 121, 123 50 105, 109, 117, 119, 128 100 103, 120, 129, 133</td>
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## MEASUREMENT

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<tr>
<td><strong>Determination technique</strong></td>
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<td>CV-AAS</td>
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<td>Direct Analyzer</td>
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<tr>
<td>HG-AAS</td>
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<td>Q-ICP-MS</td>
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<td>Other</td>
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<tr>
<td><strong>Dilution for determination</strong></td>
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<td>1:2</td>
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<td>108, 119</td>
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<td>1:100</td>
<td>128</td>
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<tr>
<td>no</td>
<td>117</td>
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<td><strong>Calibration</strong></td>
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<td>Other</td>
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<td><strong>Internal Standard</strong></td>
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<td>In</td>
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<tr>
<td>In+Y+Bi</td>
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<td>Rh</td>
<td>119, 128, 133</td>
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<td><strong>Wavelength</strong></td>
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<td>253.6</td>
<td>102, 118</td>
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<td>253.65</td>
<td>130</td>
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<tr>
<td>254</td>
<td>101</td>
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<td><strong>Isotopic mass (amu)</strong></td>
<td></td>
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<tr>
<td>201</td>
<td>133</td>
</tr>
<tr>
<td>202</td>
<td>113, 119, 126, 128</td>
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<tr>
<td>206, 207, 208</td>
<td>117</td>
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<tr>
<td><strong>LoD of the method (mg/kg)</strong></td>
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<tr>
<td>≤ 0.0006</td>
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<td>≥ 0.001 - ≤ 0.002</td>
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<td>≥ 0.005 - ≤ 0.006</td>
<td>109, 116</td>
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<td>0.010</td>
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<td>0.015</td>
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<tr>
<td><strong>LoQ of the method (mg/kg)</strong></td>
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<tr>
<td>≤ 0.001</td>
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<td>≥ 0.002 - ≤ 0.007</td>
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<td>0.025</td>
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<td><strong>Quality control sample</strong></td>
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<tr>
<td>BCR 185r Bovine Liver</td>
<td>101</td>
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<td>BCR 186 Pig Kidney</td>
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<td>BCR 151Skm Milk Powder</td>
<td>130</td>
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<td>ERM-CE 278 Mussel Tissue</td>
<td>106</td>
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<td>NIST 1566b Oyster Tissue</td>
<td>109, 119</td>
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<tr>
<td>NIST 1548a Total Diet</td>
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<tr>
<td>NIST 1547 Peach Leaves</td>
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### A2.6. List of participants

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<thead>
<tr>
<th>Name of the Organisation of the European Union National Reference Laboratories and address</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austrian Agency for Health and Food Safety, Competence Centre for Elements Spargelfeldstrasse 191A, 1220 Wien</td>
<td>Austria</td>
</tr>
<tr>
<td>CODA-CERVA, Veterinary and Agrochemical Research Centre OD Chemical Safety of the Food Chain, Operational Unit Trace Element Leuvensesteenweg 17, B-3080 Tervuren</td>
<td>Belgium</td>
</tr>
<tr>
<td>Central Laboratory of Veterinary Control and Ecology (CLVCE) 5 Iskarko Shousse, Str., BG-1528 Sofia</td>
<td>Bulgaria</td>
</tr>
<tr>
<td>State General Laboratory, Ministry of Health 44 Kimonos Street, 1451 Nicosia</td>
<td>Cyprus</td>
</tr>
<tr>
<td>State Veterinary Institute Olomuc, Department of Residues and National Reference Laboratory for Chemical Elements, Laboratory in Kromeritz Hulinska 228, 767 60 Kromeritz</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>Technical University of Denmark, National Food Institute Mørkhøj Bygade 19 Buiding B , DK- 2860 Søborg</td>
<td>Denmark</td>
</tr>
<tr>
<td>Estonian Veterinary and Food Laboratory Kreutzwaldi 30, 51006 Tartu</td>
<td>Estonia</td>
</tr>
<tr>
<td>Finnish Food Safety Authority Evira, Chemistry and Toxicology Unit Mustialankatu 3, FI-00790 Helsinki</td>
<td>Finland</td>
</tr>
<tr>
<td>AFSSA LERQAP, French Food Safety Agency Laboratory for Studies and Research on Food Quality and Processing, Unité CIME 23, Avenue du Général de Gaulle, F-94706 Maisons- Alfort Cedex</td>
<td>France</td>
</tr>
<tr>
<td>Federal Office of Consumer Protection and Food Safety (BVL) Referat 501, Mauerstr. 39-42, D-10117 Berlin</td>
<td>Germany</td>
</tr>
<tr>
<td>Institute of Food Hygiene of Athens, Ministry of Rural Development and Food 25 Neapoleos st., 15310 Agia Paraskevi</td>
<td>Greece</td>
</tr>
<tr>
<td>Laboratory Central Agricultural Office Food and Feed Safety Directorate, Mester utca 81, H-1095 Budapest</td>
<td>Hungary</td>
</tr>
<tr>
<td>Istituto Superiore di Sanità, Department of Veterinary Public Health and Food Safety Viale Regina Elena 299, 000161 Roma</td>
<td>Italy</td>
</tr>
<tr>
<td>Department of Agriculture, Fisheries and Food Backweston Laboratory campus, Young’s Cross, Celbridge, Co. Kildare</td>
<td>Ireland</td>
</tr>
<tr>
<td>National Diagnostic Centre of Food and Veterinary Service of Latvia, Food and Environmental Investigation Laboratory, Instrumental Analysis Division Lejupes Street 3, Riga LV-1076</td>
<td>Latvia</td>
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<tr>
<td>Name of the Organisation of the European Union National Reference Laboratories and address</td>
<td>Country</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>National Food and Veterinary Risk Assessment Institute, Laboratory department, Chemistry section J. Kairiukscio str. 10, LT- 08409 Vilnius</td>
<td>Lithuania</td>
</tr>
<tr>
<td>Institut Scientifique de Santé Publique, Produits de consommation Rue Juliette Wytsman Straat 14 1050 Brussels</td>
<td>Luxemburg</td>
</tr>
<tr>
<td>Public Health Laboratory, Department for Environmental Health Evans Buildings, Merchant Street, Valletta VLT 1179</td>
<td>Malta</td>
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<tr>
<td>Rikilt – Institute of Food Safety Akkermaalsbos 2, 6708 Wageningen, Building No 123</td>
<td>The Netherlands</td>
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<tr>
<td>Agri-Food and Biosciences Institute, Food Chemistry Newforge Lane, Belfast, BT6 9FY</td>
<td>Northern Ireland</td>
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<tr>
<td>National Veterinary Research Institute, Department of Pharmacology and Toxicology Al. Partyzantow 57, 24-100 Pulawy</td>
<td>Poland</td>
</tr>
<tr>
<td>INRB – IP, Laboratorio Nacional de Investigação Veterinária Estrada de Benfica 701, 1549-011 Lisboa</td>
<td>Portugal</td>
</tr>
<tr>
<td>Hygiene Institute of Public Sanitary Veterinary Health, NRL of Heavy Metals in Food of Animal Origin and Feed Street Campul Mosilor 5, Sector 2, 021201 Bucharest</td>
<td>Romania</td>
</tr>
<tr>
<td>State Veterinary and Food Institute Hlinkova 1 , 040 01 Kosice</td>
<td>Slovakia</td>
</tr>
<tr>
<td>National Veterinary Institute, Laboratory for Residue Analyses, University of Ljubljana Veterinary Faculty Gerbiceva 60, 1000 Ljubljana</td>
<td>Slovenia</td>
</tr>
<tr>
<td>Institute of Public Health, Ljubljana of the Republic of Slovenia (only Hg) Grablovičeva 44, 1000 Ljubljana</td>
<td>Slovenia</td>
</tr>
<tr>
<td>Ministerio de Agricultura, Pesca y Alimentación, Grupo Arbitral Agroalimentario Carretera de la Coruna Km 10700 ,28023 Madrid</td>
<td>Spain</td>
</tr>
<tr>
<td>National Food Administration Box 622 SE-751 26 Uppsala</td>
<td>Sweden</td>
</tr>
<tr>
<td>The Food and Environment Research Agency, Environmental Contaminants Team Sand Hutton, York, Y041 1LZ</td>
<td>United Kingdom</td>
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<table>
<thead>
<tr>
<th>CRL for Chemical Elements in Food of Animal Origin</th>
<th>Italy</th>
</tr>
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<tbody>
<tr>
<td>Istituto Superiore di Sanità</td>
<td></td>
</tr>
<tr>
<td>Viale Regina Elena 299, 000161 Roma</td>
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</table>
PART B
Second round on milk
Cadmium, lead and total arsenic

Angela Sorbo (a), Laura Ciaralli (a), Andrea Colabucci (a), Maria Ciprotti (a), Alessio Pitidis (b), Marco Di Gregorio (a), Daniela Pino (a)

(a) Department of Veterinary Public Health and Food Safety
(b) Department of Environment and Primary Prevention
Specific objectives

Analytes, matrices and the general objectives of the 14th PT were described in the report of the first round on frozen meat that was sent to the NRLs participating and not participating to the exercise. It is available on the website as well.

Specific objectives were pursued in the second round on milk taking into account the outcome of the previous PTs on this matrix. Moreover considering that milk samples could be useful for NRLs to maintain/improve the performance of their methods, the shipment of several bottles was also planned.

As for arsenic a concentration level of \( \sim 0.035 \) mg/kg was considered suitable to verify NRLs performances. The choice of this level was based on the following remarks:

- rice milk is considered contaminated if it contains tens µg/kg;
- the lowest value in the EURL PTs was \( \sim 0.040 \) mg/kg and the general performance in the exercise was satisfactory;
- some problems were noticed in the 12th PT being SD and SDsub quite different. This difference, caused by some outliers, was considerably reduced in the following exercise (13th PT) meaning that several difficulties in the determination of arsenic in milk had been overcome and the level of the 14th PT was planned in order to confirm this evidence.

A concentration level of \( \sim 0.006 \) mg/kg was planned for cadmium, taking into account that:

- no ML for cadmium in milk is set but several Member States consider this element in their Monitoring Plans with action levels that fall between 0.005 mg/kg and 0.01 mg/kg;
- some problems were seen in the 12th PT when the level of concentration for cadmium in both samples was \( \sim 0.006 \) mg/kg. A general improvement in the analysis of this element on milk had been reached in the 13th PT, therefore, in order to confirm the overcoming of possible difficulties, it was deemed useful to use a level similar to the one of the 12th PT.

As for lead, important goals for EURL-CEFAO are to harmonise the performance of NRLs methods around the limit and to verify that the compliance statement is correctly considered by the NRLs. A ML value equal to 0.020 mg/kg is set for lead in the Commission Regulation (EC) 1881/2006 (3), so a concentration level of \( \sim 0.024 \) mg/kg was planned for the 14th PT.

Test material

Commercial long-life partially skimmed milk was chosen as test material and was spiked in the EURL-CEFAO laboratory. It was considered convenient to use the same brand of milk and the same test item bottles of the previous PTs.

Preparation

The bottles \( (n) \) were decontaminated and checked according to internal procedures. After decontamination, both p-bottles \( (p = \sqrt{n} - 1) \), randomly chosen, and the containers of the mixers were filled with water (at about half of their volume) and left 30’ under shaking. The solutions were then immediately checked for arsenic, cadmium and lead by using ICP-MS. The results showed that the contamination was under control being all values of arsenic and cadmium lower than LoQs (0.092 and 0.013 µg/L, respectively). As for lead, values obtained were lower than LoQ for all the bottles and lower than 0.035 µg/L for the glassware used (LoQ = 0.018 µg/L).

As for milk preparation, twenty litres of materials were necessary in order to supply each laboratory with 10 bottles. Ten litres of partially skimmed milk were spiked with a chemical
elements certified standard solution in order to obtain the expected concentration of arsenic, cadmium and lead. The sample was properly stirred for about 30 minutes. This procedure was performed on two portions of 10 litres each and the two resulting spiked samples were collected together. The final material was stirred for about 10 minutes. Both stock solutions for the spiking and milk to be spiked were gravimetrically measured.

Four hundred and forty test items were obtained dispensing about 30 mL of spiked milk into the proper bottles by using a pump and each bottle was singly numbered.

In order to ensure milk stability, the samples were sterilized in autoclave for 3 minutes at 120°C. The bottles were then quenched in chilled water to avoid the browning process of sugars naturally present in milk. This process was subcontracted to a qualified supplier: the Standard Laboratory of Milk of the Associazione Italiana Allevatori (Italian Breeders Association) (www.aia.it/lsl/index.htm). The material preparation and the sterilization were performed on the same day.

### Homogeneity of test items

Homogeneity was tested according to the IHP (7). The 440 test items were divided in 20 sub-lots. One bottle was randomly taken from each sub-lot in order to check homogeneity. Therefore the twenty test items were analysed in duplicate by applying a method based on microwave acid assisted digestion and ICP-MS as measurement technique. The results are shown in Table B1.

### Table B1. Homogeneity data: results of homogeneity test (μg/kg)

<table>
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<th>Cadmium</th>
<th>Lead</th>
</tr>
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<td>a</td>
<td>b</td>
<td>a</td>
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<td>37.9</td>
<td>6.4</td>
</tr>
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<td>37.7</td>
<td>6.4</td>
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<tr>
<td>508</td>
<td>38.1</td>
<td>38.6</td>
<td>6.3</td>
</tr>
<tr>
<td>532</td>
<td>37.8</td>
<td>37.9</td>
<td>6.4</td>
</tr>
</tbody>
</table>

| Grand Mean | 37.59 | 6.4 | 27.0 |
| σ₂ | 6.20 | 0.99 | 5.03 |
| S₂<sub>an</sub> | 0.374 | 0.111 | 2.391 |
| S₂<sub>sam</sub> | 0.237 | -0.004 | -0.519 |
| S₂<sub>an</sub>/σ<sub>p</sub> | 0.099 | 0.106 | 0.307 |
| Critical | 5.714 | 0.147 | 4.983 |
| S₂<sub>an</sub> < Critical | Yes | Yes | Yes |

a, b = replicates of the same test item; σ<sub>p</sub> = σ<sub>CRL</sub> based on grand mean; S₂<sub>an</sub> = Analytical variance; S₂<sub>sam</sub> = Sampling variance; S₂<sub>an</sub>/σ<sub>p</sub> < 0.5. Critical = Critical value based on allowable and analytical variance; S₂<sub>an</sub> < Critical = if S₂<sub>an</sub> < Critical, the material has sufficient homogeneity.
Considering the test for significant inhomogeneity, the material resulted to have sufficient homogeneity for all the elements.

The standard deviations calculated on results were consistent, for all the elements, with the repeatability of the analytical methods.

As for the evaluation of homogeneity, the $\sigma_p$, calculated using the mean value of the homogeneity results, was used for arsenic, cadmium and lead; for all elements, analytical variances suited the $\sigma_p$ ($\sigma_{an}/\sigma_p < 0.5$).

**Quality assurance in sample preparation**

All the instruments used were well maintained and calibrated.

The analytical method used for the homogeneity test was a method accredited within the “flexible scope”; more specifically the accredited method included in the “fixed scope” of accreditation was improved in terms of both precision and accuracy.

The reliability of both methods and personnel of the EURL is regularly checked by means of participation in PTs, certified reference materials and control charts based on internal reference materials at concentrations of interest.

**Distribution of samples and instructions to participants**

Ten bottles, each containing 30 mL of milk, were sent to the NRLs which had been informed by mail about the sample shipment. The participants were required to analyse one sample and to save the surplus of bottles for their internal scope storing these last samples in the freezer.

The instructions on sample handling and storage and a “Results form” were supplied; in this latter additional information (e.g. method used and its details, instrumentation, etc.) was required together with the compliance statement of the sample in the case of lead.

The participants were asked to treat the test material as if it were a sample for their routine analysis; they were also asked to analyse the same number of replicates that they normally use. The NRLs sent the “Results form” to the EURL-CEFAO, either by e-mail or fax.

The samples were sent on 15 June 2010. The deadline for the submission of results was fixed on 10 September 2010. The table of $z$-scores was made available on the web site within about 40 days from the deadline; NRLs were informed on this.

**Statistical evaluation of results**

The procedure reported in the IHP (7) was followed.

The first stage of this procedure consists of screening and rejecting the data that are obviously not valid.

Measurement results reported as “smaller than” are not usually considered in any calculation and no scores are given; the results arriving long after the deadline are not included in the data set used to calculate the assigned value, but only the $z$-score is assigned.
Arsenic, cadmium and lead

Assigned value (\( \hat{X} \))

The assigned value of each analyte was determined as a consensus value based on the results of the participants using robust statistics. According to the EURL procedure, results clearly aberrant and outside the range \( \pm 50\% \) of the median were removed from the data set and the robust statistics was applied to the remaining data; the robust mean, calculated using Algorithm A, was adopted as assigned value for cadmium and lead; regarding arsenic, the median was chosen as the most suitable estimate of the assigned value.

As for its uncertainty, the conservative expression:

\[
u_X = 1.25 \times \frac{\sigma_{\text{rob}}}{\sqrt{n}}\]

reported in ISO 13528:2005 (8) was used for cadmium and lead while for arsenic the Adjusted Median Absolute Deviation (sMAD) was used instead of the robust standard deviation (\( \sigma_{\text{rob}} \)).

The kernel density estimates of the distribution of the results (extreme outliers excluded), using a bandwidth (h) of \( 0.75\sigma_{\text{pEURL}} \), always showed unimodal and symmetric densities. The robust statistics and kernel plots were obtained using a software tool developed by AMC (available from: http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/RobustStatistics.asp10).

Taking into account that the assigned values were based on the participants’ results, the possible difference between the two main techniques used by NRLs was also evaluated and reported at point 6.

Standard deviation for proficiency assessment

The standard deviation for proficiency assessment (\( \sigma_p \)) is usually derived from the Horwitz equation. Nevertheless, considering that the level of performance required from the NRLs should be higher than that of routine control laboratories, adequate lower values of standard deviation were set for the proficiency assessment (\( \sigma_{pEURL} \)).

The equations are reported in Table B2.

<p>| Table B2. Standard deviation for proficiency assessment based on EURL-CEFAO algorithm |
|---------------------------------|----------------------------------|---------------------------------|</p>
<table>
<thead>
<tr>
<th>Element</th>
<th>Range of concentration (C) (µg/kg)</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>( \leq 50 )</td>
<td>( \sigma_{\text{PCRL}} = (20+0.013C^2)^{0.5} )</td>
</tr>
<tr>
<td></td>
<td>( \geq 51 )</td>
<td>( \sigma_{\text{PCRL}} = 0.15C )</td>
</tr>
<tr>
<td>Cadmium</td>
<td>( \leq 10 )</td>
<td>( \sigma_{\text{PCRL}} = (0.07+0.022C^2)^{0.5} )</td>
</tr>
<tr>
<td></td>
<td>( \geq 11 )</td>
<td>( \sigma_{\text{PCRL}} = 0.15C )</td>
</tr>
<tr>
<td>Lead</td>
<td>( \leq 10 )</td>
<td>( \sigma_{\text{PCRL}} = 0.30C )</td>
</tr>
<tr>
<td></td>
<td>11-50</td>
<td>( \sigma_{\text{PCRL}} = (2+0.032C^2)^0.5 )</td>
</tr>
<tr>
<td></td>
<td>( \geq 51 )</td>
<td>( \sigma_{\text{PCRL}} = 0.18C )</td>
</tr>
</tbody>
</table>

Scores and evaluation criteria

The laboratory performance was expressed in terms of z-scores (\( z=(X_{\text{lab}}-\hat{X})/\sigma_p \)) in accordance with ISO 13528:2005 and the International Harmonised Protocol. The interpretation of the z-scores was the one adopted at international level: \( |z| \leq 2 \): satisfactory result; \( 2<|z|<3 \): questionable result; \( |z| \geq 3 \): unsatisfactory result.

In order to allow an easy comparison among the performances obtained in the EURL PTs and those of other programmes, the z-scores calculated using a \( \sigma_{\text{pHorwitz}} \) are reported as well.
Acceptance of a sample

Considering the ML established by Commission Regulation (EC) No 1881/2006 (3), for lead in milk (0.020 mg/kg), the acceptance of the sample, as indicated in Commission Regulation (EC) 333/2007 (point D.2.1) (10), must be assessed “taking into account the expanded measurement uncertainty”.

The correct procedure to consider the sample as compliant or not compliant is the following:

a) express the results in the same units and with the same number of significant figures as the relevant ML;
b) subtract the value of uncertainty from the result; (taking care of rounding the result of the computation to the same number of significant figures as the ML);
c) compare this value with the ML;
d) accept the sample if this value is lower or equal to the ML.

Results and comments

Arsenic was analysed by 23 NRLs; 26 NRLs submitted results for cadmium and lead. Four Laboratories participated in the exercise using two methods based on different techniques therefore the number of results for some elements was greater than the number of participants. The results of arsenic, cadmium and lead, as reported by the participants, are shown in Table B3, together with the $z$-scores calculated using both the $\sigma_{pEURL}$ and the $\sigma_{pHorwitz}$.

The main items of the statistical evaluation are summarized in the Annexes B1.1 to B1.3. The relevant tables contain a column reporting the evaluation with all results (clearly aberrant data and qualitative data excluded) and without outliers (beyond the range $\pm$ 50% median). Two bar graphs are also reported for each element representing the distribution of results by technique and the distribution of $z$-scores by Laboratory code.

The distribution of the Pb results and the relevant expanded uncertainties are reported in Annex B1.4. As far as cadmium is concerned, two results arrived on time were aberrant (ten times the expected value) and were removed from the dataset used for the statistical evaluation. The NRL submitting these results, informed the EURL that there was a mistake in their reporting the data and sent again the correct ones to the EURL.

This amendment arrived after the deadline, but before the preparation of the short report, so the corrected data were not considered in the statistical evaluation and were only included in the final table of $z$-scores with an asterisk indicating their late submission.

As far as the instrumental techniques are concerned, ICP-MS was the prevalent technique used in the present round and there was an increase in the number of participants that had employed methods based on this technique. The percentage increase in the use of this technique was As: +15.8%, Cd: +11.7%, Pb: +18.2%.

Figure B1 shows the variation in the ICP-MS usage compared with the previous PT on milk. It is valuable that some NRLs have tested this more sensitive technique.

The other technique mainly used was the AAS coupled with the Graphite furnace for cadmium and lead, and with a Hydride Generation System for arsenic. The difference between the sub-datasets produced using these different techniques were evaluated during the process of the estimate of the assigned values.

The outcome is reported in Table B3 for each analyte, together with some considerations on the overall results.
Table B3. Assigned values ($\hat{X}$), standard deviations, results (mg/kg) and z-scores

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Arsenic</th>
<th>Cadmium</th>
<th>Lead</th>
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<td>0.0252</td>
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<tr>
<td>$\mu_E$</td>
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<td>0.0002</td>
<td>0.0005</td>
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<td>$\sigma_{EURL}$</td>
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<tr>
<td>$\sigma_{Horwitz}$</td>
<td>0.00818</td>
<td>0.0013</td>
<td>0.00554</td>
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</table>

Results and z-scores

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<th>z-score</th>
<th>z-score</th>
<th>Result</th>
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<td></td>
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<td>$\sigma_{Horwitz}$</td>
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<td>$\sigma_EURL$</td>
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<td>-0.2</td>
<td>-0.2</td>
<td>0.0247</td>
<td>-0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>27</td>
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<td>0.0</td>
<td>0.0</td>
<td>0.0061</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0239</td>
<td>-0.3</td>
<td>-0.2</td>
</tr>
<tr>
<td>28</td>
<td>0.043</td>
<td>0.9</td>
<td>0.7</td>
<td>0.006</td>
<td>0.0</td>
<td>0.0</td>
<td>0.024</td>
<td>-0.3</td>
<td>-0.2</td>
</tr>
<tr>
<td>29</td>
<td>0.0491</td>
<td>1.9</td>
<td>1.5</td>
<td>0.0068</td>
<td>0.9</td>
<td>0.6</td>
<td>0.0264</td>
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<td>30</td>
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<td>-0.3</td>
<td>0.0276</td>
<td>0.5</td>
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<td>31</td>
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<td>-0.2</td>
<td>-0.1</td>
<td>0.006</td>
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<td>0.025</td>
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<td>32</td>
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<td>-0.2</td>
<td>-0.1</td>
<td>0.0062</td>
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<td>0.2</td>
<td>0.025</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>33</td>
<td>0.0393</td>
<td>0.3</td>
<td>0.3</td>
<td>0.0051*</td>
<td>-1.0</td>
<td>-0.7</td>
<td>0.0256</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>3*</td>
<td></td>
<td></td>
<td></td>
<td>0.0058</td>
<td>-0.2</td>
<td>-0.2</td>
<td>0.024</td>
<td>-0.3</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

– data not submitted.
* data arrived after the deadline.
Concerning arsenic, only one datum higher than median ± 50% was removed from data set. The probability plot of the results, performed by Ryan-Joiner test, showed a not normal distribution (p < 0.01, α = 0.05). This test was chosen as reference being the most suitable one for checking the normality of small datasets. However, Anderson-Darling and Kolmogorov-Smirnov tests were also applied and they confirmed that the dataset was not normal. According to the International Harmonized Protocol, the distribution of results was checked again after removing the outliers, found by means of proper statistical tests. The data, outliers aside, were still not normally distributed (Ryan-Joiner: p = 0.036, α = 0.05) and the application of robust statistics was carefully considered. The dataset was divided in two sub-datasets taking into account the main analytical techniques used by the NRLs (HG-AAS and ICP-MS). It resulted that data from ICP-MS were normally distributed (Ryan-Joyner: α = 0.05, p > 0.100) but the ones produced by HG-AAS were at normality limit (Ryan-Joyner: α = 0.05, p = 0.052). This outcome was confirmed by Kolmogorov-Smirnov and Anderson-Darling tests. F-test, t-test and non parametric Mann-Whitney test were applied in order to compare standard deviations, means and medians of the two techniques. The difference between the means (HG-AAS: 0.0404 mg/kg; ICP-MS: 0.0378 mg/kg) and the medians (HG-AAS: 0.0370 mg/kg; ICP-MS: 0.0372 mg/kg) were not statistically significant (t-test: p = 0.24; Mann-Whitney: p = 0.43). As for standard deviations, the results from ICP-MS were less spread than those produced by HG-AAS (Mean±SD: 0.0378±0.0031 and 0.0404±0.0059, respectively) with an Interquartile range (IQR) that was 3.3 times lower than the IQR range of HG-AAS.

The indicators of central tendency are summarized in the boxplot of Figure B2. Comparing mean and median from all data with the values from each sub-dataset, it was found that the higher differences came from HG-AAS. In particular, means and medians differed for 0.002 mg/kg and 0.0002 mg/kg, respectively. The difference between the means was ten times higher than the one between the medians caused by several high values in the HG-AAS sub-dataset.

As for ICP-MS, the median was the same as that from all results and the mean differed for only 0.001 mg/kg.
This evaluation was made possible by both the improvement in the performance of the results produced by ICP-MS and their increased number. In fact, this outcome was not so clear in the previous rounds when the ICP-MS was present with a lower number of results. An overall overview of all dataset of arsenic confirmed that HG-AAS, based on redox reaction and dry ashing for the sample preparation, has more than one critical step and can produce spread results especially in a small dataset. This analytical point of view therefore led to consider the median of all data as the best estimate of assigned value because this indicator is less sensitive to extreme values than mean and robust mean.

As for cadmium, Ryan-Joiner test produced a not normal distribution \((p < 0.01, \alpha = 0.05)\) in the dataset from which two aberrant results had been deleted. Nevertheless, after removing two outliers data resulted normally distributed \((p >0.1, \alpha = 0.05)\); therefore the robust statistic was applied to the dataset (two outliers included) without any close examination. From a statistical point of view, the results can be considered satisfactory, since the data set used for the assigned value produced mean, median and robust mean that are practically the same (0.0061 mg/kg, 0.0060 mg/kg and 0.0060 mg/kg, respectively). The kernel density plot \((h=0.0007\text{mg/kg})\) showed an unimodal distribution.

The two main techniques, namely ICP-MS and GF-AAS, had means and medians that were not statistically different \((t\text{-test: } p=0.43; \text{ Mann-Whitney: } p=0.86)\). It was noticed that standard deviations were statistically different between the sub-datasets \((F\text{-test: } p=0.010)\) due to the fact that the lower and higher values belonged to the dataset from GF-AAS producing a dispersion higher.

For lead, two data beyond the range \(\pm 50\%\) of the median were removed from dataset. Ryan-Joiner test produced a not normal distribution \((p = 0.033, \alpha = 0.05)\) but after removing two outliers the data resulted normally distributed \((p >0.100, \alpha = 0.05)\). Therefore, the robust
A statistic was applied to the dataset including the two outliers. The statistical evaluation showed that mean, median and robust mean were quite coincident (0.0254 mg/kg, 0.0254 mg/kg and 0.0252 mg/kg, respectively); the kernel density plot (h=0.0035 mg/kg) confirmed the unimodality of the results.

The main techniques, namely GF-AAS and ICP-MS, were evaluated. F-test, t-test and non-parametric Mann-Whitney test were applied in order to compare standard deviations, means and medians of the two techniques. In each sub-dataset mean, median and robust mean were quite coincident (ICP-MS: 0.0247, 0.0249, 0.0247; GF-AAS: 0.0268, 0.0263, 0.0264). The difference between the means was equal to 0.0021 (t-test: p = 0.034 and Mann-Whitney test: p=0.032) and they differed from the robust mean (dataset of all data) of 0.0016 and -0.0005, respectively; similarly the medians. Unlike the outcome of arsenic, the difference between the means was statistically significant because of the general good performance reached by the NRLs. Although the ICP-MS sub-dataset showed a standard deviation (0.0016 mg/kg) significantly (F-test: p=0.08) lower compared to the one of GF-AAS (0.0027 mg/kg), however the spread of the GF-AAS can be considered satisfactory (CV 10%); therefore the two sub-datasets were regarded as equivalent and the robust mean of the dataset was used as assigned value.

The technical information, details of the analytical methods applied by participants and the list of NRLs are reported in Annex B2.

The overall performance, expressed in terms of z-scores, is summarized in Table B4.

| Element   | \( \sigma_{pCRL} \) | \( z \leq 2 \) | \( 2 < |z| < 3 \) | \( z \geq 3 \) | \( \sigma_{pHorwitz} \) | \( z \leq 2 \) | \( 2 < |z| < 3 \) | \( z \geq 3 \) |
|-----------|---------------------|----------------|----------------|----------------|---------------------|----------------|----------------|----------------|
| Arsenic   | 26/27 (96%)         | 1/27 (4%)      | 1/27 (4%)      | 26/27 (96%)    | 1/27 (4%)          | 26/27 (96%)    | 1/27 (4%)      | 26/27 (96%)    |
| Cadmium   | 29/31 (94%)         | 1/31 (3%)      | 1/31 (3%)      | 30/31 (97%)    | 1/31 (3%)          | 30/31 (97%)    | 1/31 (3%)      | 30/31 (97%)    |
| Lead      | 29/31 (94%)         | 2/31 (6%)      | 2/31 (6%)      | 29/31 (94%)    | 1/31 (3%)          | 29/31 (94%)    | 1/31 (3%)      | 29/31 (94%)    |

As shown above and also reported in Figure B3, the number of z-scores \( \leq 2 \) is satisfactory for all the elements; but the performance can actually be considered even better by looking at Table B3 where the individual z-scores are reported and where it is possible to see that the number of z-scores <1 is high (As: 81%; Cd: 94%; Pb: 87%).

As for unsatisfactory results, the EURL tried to investigate the causes of the underperformance. By examining the information reported in the “Results Form” a possible cause was found for the z-score=3 for cadmium. The results belong to a laboratory that used the “bracketing calibration” for the first time, but this bracketing was applied in a concentration range where the analytical response could not be linear: more precisely, the highest standard was too high and as a consequence the concentration of the sample was overestimated. The same laboratory obtained results rather satisfactory for arsenic and lead even if the range used for the bracketing calibration was not quite appropriate; nevertheless being the linearity range of the technique applied for lead (GF-AAS) and arsenic (HG-AAS) wider than the one for cadmium (GF-AAS), the overestimate for these elements was less important. Anyway the laboratory, verifying the linearity of the analytical signal in the range used for the “bracketing calibration”, can better set the two standards used for the bracketing and consequently can improve the performance for all the elements.
Another NRL (code 24) obtained an unsatisfactory $z$-score for lead and a questionable result for cadmium (Figure B4). The “Results Form” is not supportive in the analyses of the possible causes of the underperformance due to the scarce information given; nevertheless the EURL control chart, in which the Lab $z$-scores on milk are plotted, shows that the performance of the methods used by the Lab is not steady yet. A trend to an overestimate is noticeable for both the elements.
The other unsatisfactory result for lead was obtained using a method based on FAAS; in spite of the low sensitivity of the technique the \( z \)-score of the previous PTs fell always in the satisfactory area. Nevertheless, it is to be reported that this NRL participates in the PTs using another method based on ICP-MS that gave always good results.

Concerning the unsatisfactory result for arsenic, it was produced by a Lab whose control chart shows that its methods achieved a good performance for cadmium and lead, but not yet for arsenic.

As for the general improvement, this is not so evident if only the comparison between \( z \)-scores distribution and the one in previous PTs is used. In fact, a progress in the degree of spread for the same concentration was noticed comparing the standard deviations along the PTs for all elements. Focusing on lead, for which a ML is set, the statement is supported by the decrease of the Interquartile range of the distribution of the results. As it is possible to see (Figure B5), an interquartile range of 2.5 \( \mu \)g/kg was achieved in 2010: this represents a high level of agreement of the middle 50% of the results.

![Figure B5. Interquartile ranges of lead results in milk during a period of three-years (2007-2010)](image)

As far as the acceptability of the sample is concerned, the interpretation of NRLs is reported in Table B5: the text in the box means a wrong computation for the compliance assessment based on the expanded uncertainty reported by the relevant NRL. Unlike the round on meat for which a judgment was expressed for all results, there were 3 “not expressed” opinions for milk as evidenced in the table. One of them belongs to a Lab that informed that their method was being developed; nevertheless this Lab expressed the compliance correctly by using another method. Regarding the other two Labs, both of them used validated methods and reported the uncertainty value; one of them reported that the method (already accredited for other matrices) is not accredited for milk yet, whereas no comments were found from the other Lab; both had stated the compliance for meat.
Table B5. Interpretation of results for lead

<table>
<thead>
<tr>
<th>Lab. code</th>
<th>Acceptance (Pb)</th>
<th>Lab. code</th>
<th>Acceptance (Pb)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>19</td>
<td>no</td>
</tr>
<tr>
<td>2</td>
<td>yes</td>
<td>20</td>
<td>yes</td>
</tr>
<tr>
<td>3</td>
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<td>5</td>
<td>yes</td>
<td>23</td>
<td>yes</td>
</tr>
<tr>
<td>6</td>
<td>no</td>
<td>24</td>
<td>not expressed</td>
</tr>
<tr>
<td>7</td>
<td>no</td>
<td>25</td>
<td>yes</td>
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<td>10</td>
<td>yes</td>
<td>28</td>
<td>not expressed</td>
</tr>
<tr>
<td>11</td>
<td>no</td>
<td>29</td>
<td>yes</td>
</tr>
<tr>
<td>12</td>
<td>yes</td>
<td>30</td>
<td>no</td>
</tr>
<tr>
<td>13</td>
<td>no</td>
<td>31</td>
<td>no</td>
</tr>
<tr>
<td>15</td>
<td>not expressed</td>
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</tr>
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<td>33</td>
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</tr>
<tr>
<td>18</td>
<td>no</td>
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</tr>
</tbody>
</table>

As for the 3 wrong interpretations, a common error occurred: when the uncertainty was subtracted from the result, the obtained value was equal to the ML (0.020 mg/kg), but according to the Commission Regulation (EC) 333/2007: “... sample does not exceed the respective maximum level as laid down in Commission Regulation (EC) No. 1881/2006 taking into account the expanded measurement uncertainty…” (10). For this reason a sample where the concentration, subtracted of its uncertainty, is equal to the ML is acceptable. Of course, in such a situation, additional analyses and investigations are appropriate for incurred samples. None of the Labs made comments on their statement. The expanded uncertainties for lead are reported in Figure D.

The tables of LoDs and LoQs are reported in Annexes B2.1 to B2.3; for lead (ML = 0.020 mg/kg) a total of four laboratories reported a LoQ value not compliant with the relevant regulation; however, it is necessary to point out that one of these NRLs that had used a different technique reported a value for LoQ that fulfilled the requirements of Commission Regulation (EC) 333/2007.

Moreover, very low values of LoQ that seemed unrealistic were reported as well. The topic was discussed during the latest meeting of the network. In order to harmonize the procedure of estimate of these parameters it was decided to prepare a common draft procedure that will be sent to NRLs for comments and suggestions in the first months of 2011.
Annex B1 • SECOND ROUND

Statistics, distribution of results and z-scores

B1.1. Arsenic in milk

Parameters for statistical evaluation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>All results</th>
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<tbody>
<tr>
<td>n</td>
<td>27</td>
<td>26</td>
</tr>
<tr>
<td>mean</td>
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<td>0.0388</td>
</tr>
<tr>
<td>SD</td>
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<td>0.00429</td>
</tr>
<tr>
<td>min</td>
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<td>0.0333</td>
</tr>
<tr>
<td>max</td>
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<tr>
<td>H15 robust mean</td>
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<tr>
<td>H15 SD</td>
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<tr>
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</tr>
<tr>
<td>sMAD</td>
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<td>0.00245</td>
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</table>

Distribution of results

![Graph showing distribution of results](image)

z-score (σpCRL)

![Graph showing z-score distribution](image)
B1.2. Cadmium in milk

Parameters for statistical evaluation

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>Without outliers</th>
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</thead>
<tbody>
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<td>28</td>
</tr>
<tr>
<td>mean</td>
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<td>0.0061</td>
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<tr>
<td>SD</td>
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<td>median</td>
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<td>0.0060</td>
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<td>H15 robust mean</td>
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<td>H15 SD</td>
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</table>

Distribution of results

z-score ($\sigma_pCRL$)

Lab. code

Arrived after deadline
B1.3. Lead in milk

Parameters for statistical evaluation

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<th>Without outliers</th>
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</tr>
<tr>
<td>mean</td>
<td>0.0265</td>
<td>0.0254</td>
</tr>
<tr>
<td>SD</td>
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<td>0.00244</td>
</tr>
<tr>
<td>median</td>
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<td>0.0254</td>
</tr>
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<td>min</td>
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</tr>
<tr>
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<td>0.0321</td>
</tr>
<tr>
<td>H15 robust mean</td>
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<td>0.0252</td>
</tr>
<tr>
<td>H15 SD</td>
<td>0.00226</td>
<td>0.00192</td>
</tr>
</tbody>
</table>

Distribution of results

![Graph showing distribution of results]

z-score ($\sigma_{CRL}$)

![Graph showing z-score distribution]

Lab code - Arrived after deadline
B1.4. Distribution of results and corresponding expanded uncertainties (U)

Lead results ± U

mg/kg
Annex B2 • SECOND ROUND

Technical information, analytical methods and participants

B2.1. Technical information accompanying the samples

CRL-ISS 14\textsuperscript{th} PT 2\textsuperscript{nd} Round

\textit{Determination of Total As, Cd and Pb in Liquid Milk}

Your Lab. Code is: .................

Technical information

1) Test material
   - One sample of sterilized partially skimmed milk.
   - You will receive 10 equivalent bottles.
   - The analysis can be carried out on either of them, indistinctly.
   - Each bottle contains about 30 g of milk.
   - NRLs that use Flame AAS for milk analysis will receive 2 boxes of vials.
   - The surplus of vials for your internal scope shall be stored in the freezer; in this way they are stable for two years.

2) Analysis
   - Each NRL is free to choose the elements to be analysed among As, Cd and Pb.
   - The bottles that will be analysed for the PT participation, can be stored at room temperature till their opening, then they must be kept in fridge (+4 °C) for a maximum period of 5 days.
   - Before analysis, bottles must be softly shaken (to dissolve the possible fat present in milk) without giving rise to foam.
   - The participants should treat the test material as if it were a sample for their routine analysis; the number of replicates must be the same ones used in routine procedures.

3) Reporting the results
   - Please, fill the form in all its sections.
   - Report the number of the bottle used for the analysis (page 1).
   - When more than one bottle has been used, indicate the numbers of all the bottles in the Notes (page 2 or 3).
   - Express the results in mg/kg.
   - Express the results as follows:
     - 2 significant figures for Cd (ex. 0.24; 0.024; 0.0024)
     - 3 significant figures for As (ex. 0.245; 0.240; 0.0245)
     - 3 significant figures for Pb (ex. 0.245; 0.240; 0.0245)
   - Report the “mean value” and the “standard deviation” of the replicates in the proper column of the Results form. If the laboratory performs only one replicate, the result should be reported in the “Mean value” column as well.
   - Results reported as “<” will not be included in the calculation of assigned value and z-score.
   - As for the expanded uncertainty, please note that the “coverage factor” is = 2 [Commission Regulation (EC) 333/2007].
4) Interpretation of results for Pb

Report the acceptability of the sample taking into account:
- the maximum level fixed by Commission Regulation (EC) 1881/2006
- units and significant figures set in the Commission Regulation (EC) 333/2007 Annex part D1.1 (please note that these figures are different from the ones at the point 3)

5) Assigned value and evaluation of performance

- As Assigned Value the Algorithm A is used.
- The Laboratory performance will be expressed as z-score.
- The value of Sigma for Proficiency Assessment (σp) is set for each element and it is calculated using the equations reported below:

<table>
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<th>MILK</th>
<th>Concentration (C) µg/kg</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
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<td>≤ 50</td>
<td>σp_CRL = (20+0.013C^0.5)</td>
</tr>
<tr>
<td></td>
<td>&gt;51</td>
<td>σp_CRL = 0.15C</td>
</tr>
<tr>
<td>Cd</td>
<td>≤ 10</td>
<td>σp_CRL = (0.07+0.022C^0.5)</td>
</tr>
<tr>
<td></td>
<td>&gt;11</td>
<td>σp_CRL = 0.15C</td>
</tr>
<tr>
<td></td>
<td>≤ 10</td>
<td>σp_CRL = 0.30C</td>
</tr>
<tr>
<td>Pb</td>
<td>&gt;11 – ≤ 50</td>
<td>σp_CRL = (2+0.032C^0.5)</td>
</tr>
<tr>
<td></td>
<td>&gt;51</td>
<td>σp_CRL = 0.18C</td>
</tr>
</tbody>
</table>

- In order to allow an easy comparison among the performances obtained in the CRL-ISS PTs and those obtained in other programmes, the CRL-ISS also provides the Horwitz σp.

6) Deadline

- Data should be submitted not later than 10 September via e-mail to crl@iss.it or by fax (+39 06 49902721).
- Once results will be submitted, you will receive a confirmatory e-mail to your relevant e-mail within 24 working hours.
### B2.2. ARSENIC: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected. Only the codes of the laboratories that provided LoD and LoQ together with measurement unit have been reported.

#### SAMPLE TREATMENT

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<th>Sample treatment</th>
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</tr>
<tr>
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## MEASUREMENT

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*to be continued*
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**LoQ of the method**

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<td>Pig Kidney BCR 186</td>
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<tr>
<td>RM CRL-ISS 13\textsuperscript{th} PT Milk B</td>
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<tr>
<td>RM CRL-ISS 13\textsuperscript{th} PT Milk A and B</td>
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<tr>
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<td>RM CRL-ISS 12\textsuperscript{th} PT Bovine meat</td>
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<tr>
<td>Recovery values</td>
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<tr>
<td>Spiked milk</td>
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**Quality control sample**

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<tr>
<td>Recovery values</td>
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<tr>
<td>Spiked Sample @ 20µg/kg * 3</td>
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### B2.3. CADMIUM: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected. Only the codes of the laboratories that provided LoD and LoQ together with measurement unit have been reported.

#### SAMPLE TREATMENT

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### MEASUREMENT

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<td><strong>LoD of the method</strong></td>
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</tr>
<tr>
<td>0.0001 mg/l</td>
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<tr>
<td>0.0001 mg/kg</td>
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</tr>
<tr>
<td>0.0004 mg/kg</td>
<td>4, 23</td>
</tr>
<tr>
<td>&gt;0.0005 mg/kg ≤ 0.008 mg/kg</td>
<td>7, 15, 16</td>
</tr>
<tr>
<td>0.001 mg/kg</td>
<td>1, 5, 25</td>
</tr>
<tr>
<td>0.002 mg/kg</td>
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</tr>
<tr>
<td>&gt;0.004 mg/kg ≤ 0.05 mg/kg</td>
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</tr>
<tr>
<td>0.0112 µg/kg</td>
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<td>0.02 µg/kg</td>
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<tr>
<td>0.059 µg/kg</td>
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<tr>
<td>0.8 µg/kg</td>
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<tr>
<td>1.5 µg/kg</td>
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<tr>
<td>2.5 µg/kg</td>
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*to be continued*
continues

<table>
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<tbody>
<tr>
<td>&gt;0.0002 mg/kg &lt; 0.0003</td>
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<tr>
<td>0.0008 mg/kg</td>
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<td>&gt;0.0089 mg/kg &lt; 0.001 mg/kg</td>
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<tr>
<td>&gt;0.0016 mg/kg &lt; 0.002 mg/kg</td>
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<td>0.006 mg/kg</td>
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<tr>
<td>0.008 mg/kg</td>
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</tr>
<tr>
<td>0.01 mg/kg</td>
<td>2</td>
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<td>&gt;0.004 µg/kg</td>
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<td>0.0373 µg/kg</td>
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<td>0.03 µg/kg</td>
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<td>1 µg/kg</td>
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<td>3 µg/kg</td>
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<tr>
<td>5 µg/kg</td>
<td>14</td>
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| LoQ of the method                                |                  |
| BCR 150                                          | 28               |
| BCR 150, BCR 151, NIST 1549                      | 19               |
| BCR 151                                          | 4, 20            |
| BCR 151 and fortified blank milk                 | 30               |
| NIST 1547, NIST 1568, DORM 3                     | 25               |
| Bovine Muscle Powder NIST 8414                   | 5                |
| MRC                                              | 31               |
| RM CRL-ISS 13th PT Milk B                        | 1, 15, 32        |
| RM CRL-ISS 13th PT Milk A and B                  | 2, 8             |
| RM CRL-ISS 12th, 13th PT Milk A and B            | 12               |
| RM CRL-ISS 13th PT 1st Milk                      | 16, 33           |
| Blanks, standard, MRC                            | 22               |
| Recovery values                                  | 26               |
| Spiked milk                                      | 6                |
| Spiked Sample @ 20 µg/kg * 3                      | 27               |
| Yes                                              | 14, 18, 23       |
## B2.4. LEAD: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected. Only the codes of the laboratories that provided LoD and LoQ together with measurement unit have been reported.

### SAMPLE TREATMENT

<table>
<thead>
<tr>
<th>Sample treatment</th>
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<tbody>
<tr>
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<td><strong>Method</strong></td>
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<td>AOAC</td>
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<td>EN 14082:2002</td>
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<td>EN 15763</td>
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<td>AOAC 999.10 Chapter 9</td>
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<td>LST EN 14084:2003</td>
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<td><strong>Sample amount (g)</strong></td>
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<tr>
<td>&lt;1</td>
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<td>&gt;1 - &lt;2</td>
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<td>&gt;2 - &lt;3</td>
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<td>&gt;3 - &lt;5</td>
<td>2, 12, 13, 15, 16, 21, 25, 33</td>
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<td>10</td>
<td>4</td>
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<td>15</td>
<td>23</td>
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<tr>
<td>Not indicated</td>
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<tr>
<td><strong>Digestion</strong></td>
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<tr>
<td>Dry ashing</td>
<td>4, 12, 18, 23, 29</td>
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<tr>
<td>Dry ashing+ Mg(NO₃)₂</td>
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<td>Open wet</td>
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<td>High pressure</td>
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<td><strong>Acids and H₂O₂</strong></td>
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<tr>
<td>HNO₃+H₂O₂</td>
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<tr>
<td>HNO₃+HCl</td>
<td>5, 23</td>
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<tr>
<td>HNO₃+H₂SO₄</td>
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<td>HNO₃+HCl+H₂O₂</td>
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<tr>
<td><strong>Chemicals</strong></td>
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<td>HNO₃+HCl</td>
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<td>SnCl₂</td>
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<tr>
<td>1 mL H₂O</td>
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<tr>
<td><strong>Volume</strong></td>
<td></td>
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<tr>
<td>5 mL</td>
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<td>8 mL</td>
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<td>10 mL</td>
<td>7, 14, 15, 20, 23, 24, 25, 30</td>
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<td>13 mL</td>
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<td>20 mL</td>
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<td>25 mL</td>
<td>5, 11, 29, 31, 33</td>
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<tr>
<td>30 g</td>
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<td>50 mL</td>
<td>1, 2, 8, 22</td>
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<td>100 mL</td>
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## MEASUREMENT

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<tr>
<td>Determination technique</td>
<td>Q-ICP-MS 1, 3, 5, 8, 9, 11, 13, 19, 21, 22, 26, 27, 28, 32, 33</td>
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<td></td>
<td>I-CP-MS 2, 25</td>
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<td>ETA-AAS 12, 16, 18, 29, 31</td>
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<td>Z-ETA-AAS 4, 6, 15, 20, 23, 24, 30</td>
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<tr>
<td></td>
<td>FAAS 7</td>
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<tr>
<td></td>
<td>Not indicated</td>
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</tbody>
</table>

| Dilution for determination, if any | 1:2 | 21, 32 |
|                                   | 1:2.5 | 9 |
|                                   | 3 | 8 |
|                                   | 1:5 | 27 |
|                                   | 1:10 | 5, 13, 19, 25 |

| Calibration                  | External linear 1, 2, 5, 6, 7, 8, 11, 13, 15, 16, 18, 19, 20, 21, 22, 23, 25, 26, 31, 33 |
|------------------------------| External non linear 12, 28, 29 |
|                              | Method of additions calibration 3, 9, 30, 32 |
|                              | Method of additions 27 |
|                              | Linear bracketing 4 |
|                              | Not indicated 10, 24 |

| Matrix modifier               | NH₄H₂PO₄+Mg(NO₃)₂ 4, 6, 23, 29 |
|-------------------------------| NH₄H₂PO₄ 30 |
|                              | Pd 18 |
|                              | Ni(NO₃)₂ 24 |
|                              | Pd+Mg(NO₃)₂ 15, 20 |
|                              | Pd(NO₃)₂·2H₂O 12 |

| Internal standard             | Rh 3, 8, 21, 25, 27, 28, 32 |
|-------------------------------| In 13 |
|                              | Bi 9, 33 |
|                              | Lu 5 |
|                              | Re 26 |
|                              | In+Y+Bi 22 |
|                              | Not indicated 1, 2, 11, 19 |

| Wavelength (λ)                | 283.3 | 6, 12, 15, 16, 18, 20, 23, 24, 29, 30 |
|-------------------------------| 217 | 7 |
|                              | 283.2 | 4 |
|                              | 253.7 | 31 |

| Isotopic mass (amu)           | 207 | 28 |
|-------------------------------| 208 | 1, 2, 8, 11, 13, 19, 21, 25, 26, 33 |
|                              | 206,207,208 22 |
|                              | 206+207+208 3, 5, 9, 27 |
|                              | 208; (206+207) 32 |

*to be continued*
### LoD of the method

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Laboratory code</th>
</tr>
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<tbody>
<tr>
<td>0.0005 mg/kg</td>
<td>13, 33</td>
</tr>
<tr>
<td>0.001 mg/kg</td>
<td>1, 4, 23, 25</td>
</tr>
<tr>
<td>0.0013 mg/kg</td>
<td>15</td>
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<tr>
<td>0.002 mg/kg</td>
<td>16, 30</td>
</tr>
<tr>
<td>0.003 mg/kg</td>
<td>5</td>
</tr>
<tr>
<td>0.004 mg/kg</td>
<td>29</td>
</tr>
<tr>
<td>0.005 mg/kg</td>
<td>2</td>
</tr>
<tr>
<td>0.006 mg/kg</td>
<td>7</td>
</tr>
<tr>
<td>0.0155 µg/kg</td>
<td>11</td>
</tr>
<tr>
<td>0.21 µg/kg</td>
<td>21</td>
</tr>
<tr>
<td>0.26 µg/kg</td>
<td>27</td>
</tr>
<tr>
<td>2 µg/kg</td>
<td>6, 19</td>
</tr>
<tr>
<td>2.5 µg/kg</td>
<td>8</td>
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### LoQ of the method

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<tr>
<td>0.001 mg/kg</td>
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</tr>
<tr>
<td>≥0.00017 mg/kg ≤0.0002 mg/kg</td>
<td>1, 4, 23</td>
</tr>
<tr>
<td>0.003 mg/kg</td>
<td>25</td>
</tr>
<tr>
<td>≥0.004 mg/kg ≤0.005 mg/kg</td>
<td>16, 15, 5</td>
</tr>
<tr>
<td>0.006 mg/kg</td>
<td>30</td>
</tr>
<tr>
<td>0.008 mg/kg</td>
<td>29</td>
</tr>
<tr>
<td>≥0.01 mg/kg ≤0.012 mg/kg</td>
<td>2, 18, 7</td>
</tr>
<tr>
<td>0.0518 µg/kg</td>
<td>11</td>
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<tr>
<td>0.47 µg/kg</td>
<td>21</td>
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<tr>
<td>0.867 µg/kg</td>
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</tr>
<tr>
<td>2 µg/kg</td>
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</tr>
<tr>
<td>0.003 µg/kg</td>
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### Quality control

<table>
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<tbody>
<tr>
<td>BCR 150</td>
<td>9, 28</td>
</tr>
<tr>
<td>BCR 150, BCR 151, NIST 1549</td>
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<tr>
<td>BCR 151</td>
<td>4, 20</td>
</tr>
<tr>
<td>BCR 151 and fortified blank milk</td>
<td>30</td>
</tr>
<tr>
<td>NIST 1547, NIST 1568, DORM 3</td>
<td>25</td>
</tr>
<tr>
<td>Whole Milk Powder NIST 8435</td>
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</tr>
<tr>
<td>MRC</td>
<td>31</td>
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<tr>
<td>RM CRL-ISS 13th PT Milk B</td>
<td>1, 15, 32</td>
</tr>
<tr>
<td>RM CRL-ISS 13th PT Milk A and B</td>
<td>2, 8</td>
</tr>
<tr>
<td>RM CRL-ISS 12th, 13th PT Milk A and B</td>
<td>12</td>
</tr>
<tr>
<td>RM CRL-ISS 13th PT 1st Milk</td>
<td>16, 33</td>
</tr>
<tr>
<td>Blanks, standard, MRC</td>
<td>22</td>
</tr>
<tr>
<td>Recovery values</td>
<td>26</td>
</tr>
<tr>
<td>Spiked milk</td>
<td>6</td>
</tr>
<tr>
<td>Spiked Sample @ 20 µg/kg*3</td>
<td>27</td>
</tr>
<tr>
<td>Yes</td>
<td>18, 23</td>
</tr>
</tbody>
</table>
### B2.5. List of participants

<table>
<thead>
<tr>
<th>Name of the Organisation of the European Union National Reference Laboratories and address</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austrian Agency for Health and Food Safety, Competence Centre for Elements Spargelfeldstrasse 191A, 1220 Wien</td>
<td>Austria</td>
</tr>
<tr>
<td>CODA-CERVA, Veterinary and Agrochemical Research Centre OD Chemical Safety of the Food Chain, Operational Unit Trace Element Leuvensesteenweg 17, B-3080 Tervuren</td>
<td>Belgium</td>
</tr>
<tr>
<td>Central Laboratory of Veterinary Control and Ecology (CLVCE) 5 Iskarko Shousse, Str., BG-1528 Sofia</td>
<td>Bulgaria</td>
</tr>
<tr>
<td>State General Laboratory, Ministry of Health 44 Kimonos Street, 1451 Nicosia</td>
<td>Cyprus</td>
</tr>
<tr>
<td>State Veterinary Institute Olomuc, Department of Residues and National Reference Laboratory for Chemical Elements, Laboratory in Kromeritz Hulinska 2286, 767 60 Kromeritz</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>Technical University of Denmark, National Food Institute Mørkæj Bygade 19 Buiding B , DK- 2860 Søborg</td>
<td>Denmark</td>
</tr>
<tr>
<td>Estonian Veterinary and Food Laboratory Kreutzwaldi 30, 51006 Tartu</td>
<td>Estonia</td>
</tr>
<tr>
<td>Finnish Food Safety Authority Evira, Chemistry and Toxicology Unit Mustialankatu 3, FI-00790 Helsinki</td>
<td>Finland</td>
</tr>
<tr>
<td>ANSES- Laboratoire de sécurité des aliments Unité Contaminants Inorganiques et Minéraux de l’Environnement LNR Métaux lourds 23, Avenue du Général de Gaulle, F-94706 Maisons- Alfort Cedex</td>
<td>France</td>
</tr>
<tr>
<td>Federal Office of Consumer Protection and Food Safety (BVL) Referat 501, Mauerstr. 39-42, D-10117 Berlin</td>
<td>Germany</td>
</tr>
<tr>
<td>Institute of Food Hygiene of Athens, Ministry of Rural Development and Food 26 Neapoleos st., 15310 Agia Paraskevi</td>
<td>Greece</td>
</tr>
<tr>
<td>Laboratory Central Agricultural Office Food and Feed Safety Directorate, Mester utca 81, H-1095 Budapest</td>
<td>Hungary</td>
</tr>
<tr>
<td>Department of Agriculture, Fisheries and Food Backweston Laboratory campus, Young’s Cross, Celbridge, Co. Kildare</td>
<td>Ireland</td>
</tr>
<tr>
<td>Istituto Superiore di Sanità, Department of Veterinary Public Health and Food Safety Viale Regina Elena 299, 000161 Roma</td>
<td>Italy</td>
</tr>
<tr>
<td>National Diagnostic Centre of Food and Veterinary Service of Latvia, Food and Environmental Investigation Laboratory, Instrumental Analysis Division Lejupes Street 3, Riga LV-1076</td>
<td>Latvia</td>
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<table>
<thead>
<tr>
<th>Name of the Organisation of the European Union National Reference Laboratories and address</th>
<th>Country</th>
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<tbody>
<tr>
<td>National Food and Veterinary Risk Assessment Institute, Laboratory department, Chemistry section J. Kairiukscio str. 10, LT- 08409 Vilnius</td>
<td>Lithuania</td>
</tr>
<tr>
<td>Institut Scientifique de Santé Publique, Produits de consommation Rue Juliette Wytsman Straat 14 1050 Brussels</td>
<td>Luxemburg</td>
</tr>
<tr>
<td>Public Health Laboratory, Department for Environmental Health Evans Buildings, Merchant Street, Valletta VLT 1179</td>
<td>Malta</td>
</tr>
<tr>
<td>Rikilt – Institute of Food Safety Akkermaalbos 2, 6708 Wageningen, Building No 123</td>
<td>The Netherlands</td>
</tr>
<tr>
<td>National Veterinary Research Institute, Department of Pharmacology and Toxicology Al. Partyzantow 57, 24-100 Pulawy</td>
<td>Poland</td>
</tr>
<tr>
<td>INRB – IP, Laboratorio Nacional de Investigação Veterinária Estrada de Benfica 701, 1549-011 Lisboa</td>
<td>Portugal</td>
</tr>
<tr>
<td>Hygiene Institute of Public Sanitary Veterinary Health, NRL of Heavy Metals in Food of Animal Origin and Feed Street Campul Mosilor 5, Sector 2, 021201 Bucharest</td>
<td>Romania</td>
</tr>
<tr>
<td>State Veterinary and Food Institute Hlinkova 1 , 040 01 Kosice</td>
<td>Slovakia</td>
</tr>
<tr>
<td>National Veterinary Institute, Laboratory for Residue Analyses, University of Ljubljana Veterinary Faculty Gerbiceva 60, 1000 Ljubljana</td>
<td>Slovenia</td>
</tr>
<tr>
<td>Ministerio de Agricultura, Pesca y Alimentación, Grupo Arbitral Agroalimentario Carretera de la Coruna Km 10700,28023 Madrid</td>
<td>Spain</td>
</tr>
<tr>
<td>National Food Administration Box 622 SE-751 26 Uppsala</td>
<td>Sweden</td>
</tr>
<tr>
<td>The Food and Environment Research Agency, Environmental Contaminants Team Sand Hutton, York, YO41 1LZ</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>CRL for Chemical Elements in Food of Animal Origin Istituto Superiore di Sanità Viale Regina Elena 299, 000161 Roma</td>
<td>Italy</td>
</tr>
</tbody>
</table>
PART C

Third round on frozen fish

Cadmium, lead, total arsenic and mercury

Laura Ciaralli (a), Maria Ciprotti (a), Andrea Colabucci (a), Alessandra Sepe (a), Angela Sorbo (a), Alessio Pitidis (b), Sergio Costantini (a), Marco Di Gregorio (a), Daniela Pino (a)

(a) Department of Veterinary Public Health and Food Safety
(b) Department of Environment and Primary Prevention
Specific objectives

The PT scheme is in accordance with the ISO Guide 43-1:1997 (5) and the requirements of ISO/IEC 17043:2010 (6), the International Harmonized Protocol (IHP) (7) and the ISO 13528:2005 (8).

The NRLs of all EU MSs, and EURL participated in this round.

Each laboratory is represented by a code number which was randomly given to the participants at each round; the laboratories using more than one analytical method were coded with two different numbers; therefore, the number of results for some elements is greater than the number of participants. Each laboratory was free to choose one or more among these elements: arsenic, cadmium, mercury, and lead.

ML values are set for cadmium, lead and mercury in the Commission Regulations (EC) 1881/2006 (3) and (EC) 629/2008 (9).

As for cadmium, being this element generally analysed at good level, a concentration of ~0.07 mg/kg - a value of ~0.02 mg/kg higher than the lowest ML set for the element – was planned to verify whether all laboratories would consider the sample as “non-compliant”. This objective could be achieved since no high overestimations had been noticed in the second round on meat sample where the cadmium concentration had been of 0.043 mg/kg.

Lead is usually a quite difficult element to be analysed, but a general improvement was noticed for all matrices during PTs; moreover a satisfactory outcome had been noticed in the previous round on frozen meat, also for this element. Therefore, the sample concentration was planned at ~0.35 mg/kg to explore the agreement on the compliance assessment of a concentration close to the ML.

No MLs are set for arsenic in food, but the element is of interest for several NRLs. As for its determination, the worst performance among the matrices proposed was the one relevant to the fish matrix probably because of the presence of this element as arsenobetaine. A concentration (~1.0 mg/kg) close to the one of the 13th PT was chosen to see if there was an improvement in performance. In that PT, in fact, results were such as not to allow the assignment of a consensus value.

Mercury is usually analysed at very good level. Since the concentration of mercury and arsenic are adjusted by using different species of fish containing both elements, the levels in the prepared material derive from the ratio between their amounts. The ratio, then, must represent a good compromise for both the elements. All considered, the mercury level was of ~0.2 mg/kg.

Test material

The state of the materials was frozen so that the sample was really similar to incurred samples.

Preparation

Two species of frozen fish were mixed in order to obtain the foreseen concentration of arsenic and mercury. After removing the ice and water, together with the non edible parts, they were minced roughly and finally blended. The composite bulk was spiked with certified standard solutions of cadmium and lead, homogenised again and finally mixed using a planetary mixer, according to an internal procedure.
The material was distributed in the jars and the test items were stored at -80°C until shipment. As for the compliance assessment, the NRLs were asked to consider the sample as trout.

Contamination control

The jars \( n \) were decontaminated and checked according to an internal procedure. Briefly, after decontamination, both \( p \)-jars \( (p = \sqrt{n-1}) \), randomly chosen, and the containers of the mixers were filled with water (at about half their volume) and left 30’ under shaking; similarly for the container of the planetary mixer. The solutions were then immediately checked for arsenic, cadmium and lead by using ICP-MS; the results showed that contamination was under control being all values lower than LoQs (As: 0.092 µg/L; Cd: 0.013 µg/L, Pb: 0.018 µg/L).

Homogeneity of test items

Homogeneity was tested according to the IHP (7). 120 test items were prepared, identified with progressive numbers and finally divided in 11 sub-lots. One jar was randomly taken from each sub-lot in order to check homogeneity. Therefore the eleven test items were analysed in duplicate by applying an accredited method based on microwave acid assisted digestion. The concentration of arsenic, cadmium and lead was obtained by using ICP-MS whereas mercury was determined by means of CV-AAS. The results are shown in Table C1.

<table>
<thead>
<tr>
<th>Item</th>
<th>As</th>
<th>Cd</th>
<th>Pb</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>7</td>
<td>0.893</td>
<td>0.889</td>
<td>0.074</td>
<td>0.072</td>
</tr>
<tr>
<td>11</td>
<td>0.892</td>
<td>0.911</td>
<td>0.074</td>
<td>0.075</td>
</tr>
<tr>
<td>20</td>
<td>0.888</td>
<td>0.915</td>
<td>0.072</td>
<td>0.075</td>
</tr>
<tr>
<td>30</td>
<td>0.902</td>
<td>0.905</td>
<td>0.074</td>
<td>0.074</td>
</tr>
<tr>
<td>41</td>
<td>0.906</td>
<td>0.925</td>
<td>0.074</td>
<td>0.076</td>
</tr>
<tr>
<td>55</td>
<td>0.907</td>
<td>0.911</td>
<td>0.074</td>
<td>0.075</td>
</tr>
<tr>
<td>63</td>
<td>0.903</td>
<td>0.920</td>
<td>0.073</td>
<td>0.076</td>
</tr>
<tr>
<td>74</td>
<td>0.908</td>
<td>0.909</td>
<td>0.074</td>
<td>0.075</td>
</tr>
<tr>
<td>92</td>
<td>0.876</td>
<td>0.911</td>
<td>0.072</td>
<td>0.075</td>
</tr>
<tr>
<td>107</td>
<td>0.891</td>
<td>0.945</td>
<td>0.074</td>
<td>0.078</td>
</tr>
<tr>
<td>114</td>
<td>0.884</td>
<td>0.928</td>
<td>0.072</td>
<td>0.076</td>
</tr>
<tr>
<td>Grand mean</td>
<td>0.905</td>
<td>0.074</td>
<td>0.376</td>
<td>0.219</td>
</tr>
<tr>
<td>( \sigma_g )</td>
<td>0.1310</td>
<td>0.0088</td>
<td>0.050</td>
<td>0.0234</td>
</tr>
<tr>
<td>( S^2_{\text{an}} )</td>
<td>0.000357</td>
<td>0.0000032</td>
<td>0.000072</td>
<td>0.0000127</td>
</tr>
<tr>
<td>( S^2_{\text{sam}} )</td>
<td>-0.000108</td>
<td>-0.0000010</td>
<td>-0.0000190</td>
<td>-0.0000031</td>
</tr>
<tr>
<td>( S^2_{\text{sam}}/\sigma_g )</td>
<td>0.144</td>
<td>0.203</td>
<td>0.170</td>
<td>0.152</td>
</tr>
<tr>
<td>Critical</td>
<td>0.00316</td>
<td>0.00016</td>
<td>0.000479</td>
<td>0.000102</td>
</tr>
<tr>
<td>( S^2_{\text{sam}} ) &lt; Critical</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

\( a, b = \) replicates of the same test item
\( \sigma_g = \sigma_{\text{CRL based on grand mean}} \)
\( S^2_{\text{an}} = \) Analytical variance
\( S^2_{\text{sam}} = \) Sampling variance
\( S^2_{\text{sam}}/\sigma_g <0.5 \)
\( \text{Critical} = \) Critical value based on allowable and analytical variance:
\( S^2_{\text{sam}} < \text{Critical} : \) if \( S^2_{\text{sam}} < \text{Critical} \), the material has sufficient homogeneity.
The Cochran’s test did not evidence outliers. The standard deviations calculated on results were consistent, for all the elements, with the repeatability of the analytical methods. As for the evaluation of homogeneity, the $\sigma_{pEURL}$ calculated using the mean value of the homogeneity results, was used for arsenic, cadmium, lead and mercury.

For all elements, analytical variances also suited the $\sigma_{pEURL}$ ($\sigma_{an}/\sigma_{pEURL} <0.5$).

**Quality assurance in sample preparation**

All the instruments used are well maintained and calibrated. The analytical methods used are accredited. The reliability of both methods and personnel is regularly checked by means of participation in PTs, certified reference materials and control charts based on internal reference materials at concentrations of interest.

**Distribution of samples and instructions to participants**

A jar, containing about 100g of sample, was sent to the participating laboratories. All samples were frozen, packed in polystyrene boxes and, with the exception of few NRLs, surrounded with dry-ice; gel ice packs were, instead, used for the MSs where dry-ice dispatch is not accepted.

An information message was sent out by e-mail before shipment so that laboratories could make their own arrangements for the reception of the package. The instructions on sample handling and storage were also supplied.

The participants were asked to treat the test material as if it were a sample for their routine analysis; they were also asked to analyse the same number of replicates that they normally use. The results were reported in the appropriate form and then sent to the EURL-CEFAO, either by e-mail or fax along with the required additional information (e.g. method used and its details, instrumentation, etc.). As for cadmium, lead and mercury the laboratories were asked to state the compliance of the sample considering it as trout.

The samples were sent on 29 November 2010. The deadline for results was fixed at 31 January 2011. Unfortunately, the delivery has encountered problems in the four MSs where dry-ice dispatch is not accepted; in some cases it was hampered by the weather while misunderstandings between courier and customs took place in others.

A new shipment was successfully carried out after the Christmas holidays. The deadline for results was postponed at 15 February 2011.

The table of $z$-scores was made available at the web site at 18 March 2011.

**Statistical evaluation of results**

The procedure reported in the IHP (7) was followed. The first stage of this procedure consists in screening and rejecting unsafe results and data that are obviously not valid (>10 times greater or lower than the expected value). The replicates are mediated and compared with the mean value reported by the Lab; if the values are not coherent, the result is excluded from the dataset used for deriving the Assigned Value; the $z$-score is assigned using as result the mean value submitted by the laboratory. Results reported as “smaller than” are not usually considered in any calculation and no scores are given.
Arsenic, cadmium, lead and mercury

Assigned value ($\hat{X}$)

The assigned value of each analyte was determined as a consensus value based on the results of the participants using robust statistics. Only the results produced by the NRLs of the EU were considered in the determination of the assigned value and in the evaluation of the general performance as well.

Briefly, extreme outliers ($\pm 50\%$ of the median) and unsafe results were removed from the data set and the robust statistics was applied to the remaining data; the robust average, calculated using Algorithm A, was adopted as assigned value; a visual presentation of the results in the remaining data set, outliers aside, showed a roughly symmetric distribution for all elements. As for the uncertainty of the assigned value, the conservative expression $u_X = 1.25 \times \frac{\sigma_{rob}}{\sqrt{n}}$, reported in the ISO 13528:2005 (8), was used.

The kernel density estimates of the distribution of the results (extreme outliers excluded), using a bandwidth ($h$) of $0.75 \sigma_{pEURL}$, always showed unimodal and symmetric densities. The robust statistics and kernel plots were obtained using a software tool developed by AMC (available from: http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/Software/RobustStatistics.asp10).

Taking into account that the assigned values are based on the participant results, the possible difference between the two main techniques used by NRLs was also evaluated.

Standard deviation for proficiency assessment

The standard deviation for proficiency assessment ($\sigma_p$) is usually derived from the Horwitz equation. Nevertheless, considering that the level of performance required from the NRLs should be higher than that of routine control laboratories, adequate lower values of standard deviation were set for the proficiency assessment ($\sigma_{pEURL}$). The equations are reported in Table C2.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (C) µg/kg</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>≤ 120</td>
<td>$\sigma_{pEURL} = 0.22 C$</td>
</tr>
<tr>
<td></td>
<td>121-500</td>
<td>$\sigma_{pEURL} = (321+0.020 C^2)^{0.5}$</td>
</tr>
<tr>
<td></td>
<td>≥ 501</td>
<td>$\sigma_{pEURL} = 0.145 C$</td>
</tr>
<tr>
<td>Cadmium</td>
<td>≤ 600</td>
<td>$\sigma_{pEURL} = (18+0.011 C^2)^{0.5}$</td>
</tr>
<tr>
<td></td>
<td>≥ 601</td>
<td>$\sigma_{pEURL} = 0.10 C$</td>
</tr>
<tr>
<td>Mercury</td>
<td>≤ 800</td>
<td>$\sigma_{pEURL} = (18+0.011 C^2)^{0.5}$</td>
</tr>
<tr>
<td></td>
<td>≥ 801</td>
<td>$\sigma_{pEURL} = 0.10 C$</td>
</tr>
<tr>
<td>Lead</td>
<td>≤ 150</td>
<td>$\sigma_{pEURL} = (62+0.020 C^2)^{0.5}$</td>
</tr>
<tr>
<td></td>
<td>151-350</td>
<td>$\sigma_{pEURL} = (128+0.018 C^2)^{0.5}$</td>
</tr>
<tr>
<td></td>
<td>351-800</td>
<td>$\sigma_{pEURL} = (128+0.017 C^2)^{0.5}$</td>
</tr>
<tr>
<td></td>
<td>≥ 801</td>
<td>$\sigma_{pEURL} = 0.10 C$</td>
</tr>
</tbody>
</table>

Scores and evaluation criteria

The laboratory performance was expressed in terms of $z$-scores ($z=(X_{lab}-\hat{X})/\sigma_p$) in accordance with ISO 13528:2005 and the International Harmonised Protocol. The interpretation of the $z$-scores was the one adopted at international level: $|z|\leq2$: satisfactory result; $2< |z|<3$: questionable result; $|z|\geq3$: unsatisfactory result.
In order to allow an easy comparison among the performance obtained in the EURL- PTs and those of other programmes, the $z$-scores calculated using a $\sigma_{\text{Horwitz}}$ are reported as well.

**Acceptance of a sample**

Considering the ML established by Commission Regulations (EC) 1881/2006 (3) and (EC) 629/2008 (9), the acceptance of the sample, as indicated in Commission Regulation (EC) 333/2007 (point D.2.1) (10), must be assessed “taking into account the expanded measurement uncertainty”. In order to express acceptability, details were given in the “Technical information”.

However, the correct procedure is the following:

- express the results in the same units and with the same number of significant figures as the relevant ML;
- subtract the value of uncertainty from the result; (taking care of rounding the result of the computation to the same number of significant figures as the ML);
- compare this value with the ML;
- accept the sample if this value is lower or equal to the ML.

The interpretation of NRLs is reported in Table C3; the text in the box means a wrong interpretation of the acceptance.

**Table C3. Interpretation of results for cadmium, lead and mercury**

<table>
<thead>
<tr>
<th>Lab. code</th>
<th>Acceptance (Cd)</th>
<th>Acceptance (Pb)</th>
<th>Acceptance (Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>2</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>4</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>6</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
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<tr>
<td>8</td>
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<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
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<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>11</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>12</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>13</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>14</td>
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<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>15</td>
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<td>No</td>
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</tr>
<tr>
<td>16</td>
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<td>Yes</td>
</tr>
<tr>
<td>17</td>
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<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>18</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>19</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>20</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>21</td>
<td>No</td>
<td>No</td>
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</tr>
<tr>
<td>22</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
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<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>24</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>25</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>26</td>
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<td>No</td>
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</tr>
<tr>
<td>27</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>30</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>31</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>32</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Results and comments

All NRLs analysed mercury; one of them participated using two different techniques.

Cadmium and lead were analysed by 27 and 26 NRLs, respectively; two NRLs participated using two methods based on different techniques. 22 NRLs analysed arsenic; two NRLs participated using two different technique.

The results of arsenic, cadmium and lead, as reported by the participants, are shown in Table C4, together with the z-scores that were calculated considering both the \( \sigma_{\text{pEURL}} \) and the \( \sigma_{\text{pHorowitz}} \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Arsenic</th>
<th>Cadmium</th>
<th>Mercury</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{X} )</td>
<td>0.926</td>
<td>0.075</td>
<td>0.222</td>
<td>0.370</td>
</tr>
<tr>
<td>( U_x )</td>
<td>0.0223</td>
<td>0.0012</td>
<td>0.00488</td>
<td>0.00720</td>
</tr>
<tr>
<td>( \sigma_{pEURL} )</td>
<td>0.134</td>
<td>0.0089</td>
<td>0.0237</td>
<td>0.0496</td>
</tr>
<tr>
<td>( \sigma_{pHorowitz} )</td>
<td>0.150</td>
<td>0.017</td>
<td>0.0445</td>
<td>0.0687</td>
</tr>
</tbody>
</table>

### Table C4. Assigned values (\( \bar{X} \)), standard deviations, results (mg/kg) and z-scores

<table>
<thead>
<tr>
<th>Lab. code</th>
<th>Result</th>
<th>z-score</th>
<th>( \sigma )</th>
<th>z-score</th>
<th>( \sigma )</th>
<th>z-score</th>
<th>( \sigma )</th>
<th>z-score</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sigma_{pEURL} )</td>
<td>( \sigma_{pHorowitz} )</td>
<td>( \sigma_{pEURL} )</td>
<td>( \sigma_{pHorowitz} )</td>
<td>( \sigma_{pEURL} )</td>
<td>( \sigma_{pHorowitz} )</td>
<td>( \sigma_{pEURL} )</td>
<td>( \sigma_{pHorowitz} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.899</td>
<td>-0.2</td>
<td>-0.2</td>
<td>0.0769</td>
<td>0.2</td>
<td>0.1</td>
<td>0.250</td>
<td>1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>2</td>
<td>1.1</td>
<td>1.3</td>
<td>1.2</td>
<td>0.08</td>
<td>0.6</td>
<td>0.3</td>
<td>0.23</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>0.858</td>
<td>-0.5</td>
<td>-0.5</td>
<td>0.076</td>
<td>0.3</td>
<td>0.2</td>
<td>0.179</td>
<td>-1.8</td>
<td>-1.0</td>
</tr>
<tr>
<td>4</td>
<td>0.952</td>
<td>0.2</td>
<td>0.2</td>
<td>0.074</td>
<td>-0.1</td>
<td>-0.1</td>
<td>0.231</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>5</td>
<td>0.820</td>
<td>-0.8</td>
<td>-0.7</td>
<td>0.104</td>
<td>3.3</td>
<td>1.7</td>
<td>0.216</td>
<td>-0.3</td>
<td>-0.1</td>
</tr>
<tr>
<td>6</td>
<td>1.025</td>
<td>0.7</td>
<td>0.7</td>
<td>0.0723</td>
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<td>-0.2</td>
<td>0.187</td>
<td>-1.5</td>
<td>-0.8</td>
</tr>
<tr>
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<td>–</td>
<td>–</td>
<td>–</td>
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<td>1.7</td>
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<td>0.24</td>
<td>0.8</td>
<td>0.4</td>
</tr>
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<td>8</td>
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<td>–</td>
<td>–</td>
<td>0.0771</td>
<td>0.2</td>
<td>0.1</td>
<td>0.254</td>
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</tr>
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<td>0.4</td>
<td>0.3</td>
<td>0.075</td>
<td>0.0</td>
<td>0.0</td>
<td>0.214</td>
<td>-0.3</td>
<td>-0.2</td>
</tr>
<tr>
<td>10</td>
<td>0.959</td>
<td>0.2</td>
<td>0.2</td>
<td>0.0825</td>
<td>0.8</td>
<td>0.4</td>
<td>0.218</td>
<td>-0.2</td>
<td>-0.1</td>
</tr>
<tr>
<td>11</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.0706</td>
<td>-0.5</td>
<td>-0.3</td>
<td>0.231</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>12</td>
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<td>0.1</td>
<td>0.1</td>
<td>0.0751</td>
<td>0.0</td>
<td>0.0</td>
<td>0.211</td>
<td>-0.5</td>
<td>-0.2</td>
</tr>
<tr>
<td>13</td>
<td>0.905</td>
<td>-0.2</td>
<td>-0.1</td>
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– data not submitted
The data for each element (Annexes C1.1 to C1.4) are also presented in two different graphs. The first one shows the distribution of the results according to the technique used, while in the second one the distribution of z-scores is shown.

From a statistical point of view, the results can be considered satisfactory, since the datasets were considered suitable for deriving a consensus value for all analytes.

As for arsenic two results out of 24 were outside ±50% of the median (Labo code 20 and 30), therefore they were removed from the dataset. The 22 remaining results showed a symmetric and also normal distribution, characterized by a reduced dispersion of data (SD ~10%).

The prevailing techniques were ICP-MS (n. 13) and HG-AAS (n. 6) whereas 2 results were produced using GF-AAS; one method was based on cold vapour generation coupled with atomic fluorescence. Both the distributions of the two main techniques (ICP-MS and HG-AAS) were normal; no statistical differences were observed neither in their means (t-test: p=0.26) or in their variances (F-test: p=0.96); also the mean value obtained grouping the remaining 3 results was consistent with the other two (Figure C1). Therefore the dataset (n. 22) used for deriving a consensus value was fitting to use the robust mean as assigned value.

From the analytical point of view, comparing the performance with the one of the 13th PT on fish, an improvement was noticed. It is, however, important to underline that the two outliers outside ±50% of the median were obtained using HG-AAS technique; an outlier (z-score-normalized test) with a lower weight was produced by ICP-MS.

As for cadmium one result out of 29 was outside +50% of the median (Lab code 17), while another one (Lab code 5) was close to the upper limit (+50% of the median). Also this value was removed from the data set since it was produced by FAAS; considering the low sensitivity of this technique and the low concentration of the analysed sample, the result was considered affected by high uncertainty. The elaboration on the remaining 27 results was straightforward being the data set symmetric and normal. The prevailing techniques, GF-AAS and ICP-MS, were quite balanced (n. 14 and 11, respectively). Both distributions were normal. A higher dispersion of data was
noticed in the GF-AAS sub-data set (SD 8.5%), different from the one of the ICP-MS (SD 4.7%),
but the F-test gave a p-value of 0.09; no statistical differences were noticed between the means.

The dataset (n. 27) produced mean, median and robust mean that were practically the same.
Also from an analytical point of view results were, on the whole, satisfactory since the standard
deviation of the dataset was 7.5% while the standard deviation of all results, outliers included,
was ~17.5%, value that is lower than the one derived from the Thompson equation (22%).

No extreme outliers (±50% median) were found in the dataset (n. 28) of lead: the distribution
was normal; the values of the mean, median and robust mean were comparable (mg/kg: 0.369,
0.364, 0.370); the value of SD of 9.5% indicates that the results are clustered and, on the whole,
also satisfactory from the analytical point of view.

Similarly to cadmium, the main analytical techniques, ICP-MS and GF-AAS, were quite
balanced (n. 11 and 14, respectively). The GF-AAS distribution was normal whereas it was not
so in the ICP-MS sub-dataset since one outlier (0.418) deviated the distribution from normality;
due to this departure from normality the Levene and Mann-Whitney tests were used to compare
the variances and medians, respectively. The dispersion of the results was higher in the GF-
AAS sub-dataset than in the one of ICP-MS (SD%: 9.7 vs 5.4), but a low statistical significance
(Levene’s test p=0.06); however it can be considered at a good value, from the analytical point
of view. The Mann-Whitney test pointed out a statistically significant difference (p=0.04)
between the medians of the two sub-datasets: ICP-MS vs GF-AAS 0.377 vs 0.360. Nevertheless,
considering all results (n. 28) the dataset has an acceptable variability, an unimodal distribution
(Figure C2) that significantly meets the criteria of normality (Ryan-Joiner test: p>0.100).

![Figure C2. Kernel density plot for lead (n. 28) using h based on the expected σPEURL](image)

Therefore, the robust mean (0.370 mg/kg) was considered reliable as assigned value. On the
other hand, even if one of the two sub-datasets had represented the “true” distribution, the
failing to take its average as the “true value” of the sample had, however, no significant effect
on z-scores. In fact, in the worst case, if 0.360 had been the “true value”, extreme z-scores, such
as -1.6 and +1.4, would become -1.4 and +1.6 σPEURL = 0.050).

As for mercury one result (Lab code 32) out of 28 was rejected since the submitted result was not
consistent with the reported replicates (mean=0.232; replicates: 0.2678, 0.2705, 0.2679, 0.2715,
corresponding mean= 0.269) No extreme outliers (±50% median) were found in the dataset (n. 27).
The distribution was normal (Ryan-Joiner p>0.100) and unimodal (Figure C3); the central tendency
indicators had values nearly coincident (mean 0.222, median 0.218, robust mean 0.222).
Therefore the data elaboration was straightforward. The results were clustered, being the SD% 9.3, they can also be considered satisfactory from the analytical point of view.

As for the $z$-scores, all values were $\leq 2$ for mercury and lead; two unsatisfactory $z$-scores were noticed for cadmium and arsenic (Table C5).

Table C5. Distribution of $z$-scores based on Horwitz and EURL $\sigma_p$

| Element   | $|z| \leq 2$ | $2 < |z| < 3$ | $|z| \geq 3$ | $|z| < 2$ | $2 < |z| < 3$ | $|z| \geq 3$ |
|-----------|-------------|-------------|-------------|-------------|-------------|-------------|
| Arsenic   | 22/24 (92%) | 0%          | 2/24 (8%)   | 22/24 (92%) | 0%          | 2/24 (8%)   |
| Cadmium   | 27/29 (93%) | 0%          | 2/29 (7%)   | 28/29 (96.5%) | 0%          | 1/29 (3.5)  |
| Mercury   | 28/28 (100%) | 0%          | 28/28 (100%) | 0%          | 0%          | 0%          |
| Lead      | 28/28 (100%) | 0%          | 28/28 (100%) | 0%          | 0%          | 0%          |

As for unsatisfactory $z$-score of cadmium, one was caused by a Lab that in the previous round on frozen meat had obtained a good performance whereas questionable results had been noticed for both cadmium and lead in the milk round. The Lab attributed the poor performance to a problem in the microwave apparatus. The other unsatisfactory result was produced by a lab that uses F-AAS techniques that allowed a good performance in the 13th PT on fish when the concentrations were higher than the one of the present round.

The details of the analytical methods used by participants are summarized in Annexes C2.1 to C2.5, while Annex C2.6 reports the participating NRLs.

As far as the compliance assessment of the sample is concerned, some errors still persisted. Since the issue is important, a comment is reported for each of them. The MLs are set in the Commission Regulation (EC) 1881/2006, updated by the Commission Regulation (EC) 629/2008 and Commission Regulation (EU) 420/2011 (11) that, nevertheless, do not regard the species examined. Therefore the MLs relevant to trout are set in Commission Regulation (EC) 1881/2006 as follows:

- Cd: 0.050 mg/kg (point 3.2.5)
- Pb: 0.30 mg/kg (point 3.1.5)
- Hg: 0.50 mg/kg (point 3.3.2)

while the procedure is described in Commission Regulation (EC) 333/2007 (see point 5.1.4) (10).
The distribution of the results with their expanded uncertainties is shown in Figure C4.

Figure C4. Distribution of results and corresponding expanded uncertainties (U)
Lab code 17 stated the sample as non-compliant for lead even if the result was lower than ML; these cases are simple since not even the uncertainty is to be considered.

For the same element (Pb) Lab code 15 did not accept the sample even if the result (0.35 mg/kg) subtracted of the stated uncertainty (0.094) was lower than ML (0.30 mg/kg).

The case of the Lab code 13, could, instead, raise some doubt since the result (0.35) for lead subtracted of the uncertainty (0.049) produces a value equal to the ML and so the sample was compliant because it is not higher than ML. Nevertheless in this case further investigations are appropriate.

Moreover it is important to underline the criticality of rounding the figures of the result according to the ones of the ML. On this issue it also necessary to underline the error of Lab code 2 that expressed the result for cadmium with a lower number of significant figures than the one of the relevant ML (0.050 mg/kg).

As for cadmium, Lab code 5 stated the result (0.104) as compliant; this value subtracted of its uncertainty (0.006) provides a result much higher than the ML for trout (0.050).

Finally, the statement of Lab code 6 cannot be evaluated being the uncertainty the same as the result, probably a typing mistake.
Annex C1 • THIRD ROUND

Statistics, distribution of results and z-scores

C1.1. Arsenic in frozen fish

Parameters for statistical evaluation

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Distribution of results

z-score ($\sigma_{pCRL}$)

Lab code
C1.2. Cadmium in frozen fish

Parameters for statistical evaluation

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Distribution of results

z-score ($\sigma_p^{CRL}$)
C1.3. Lead in frozen fish

Parameters for statistical evaluation

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Distribution of results

![Graph showing distribution of results]

z-score ($\sigma_pCRL$)

![Graph showing z-score distribution]

Lab code
C1.4. Mercury in frozen fish

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Distribution of results

z-score (σ\(_{\text{PEURL}}\))
Annex C2 • THIRD ROUND

Technical information, analytical methods and participants

C2.1. Technical Information accompanying the samples

EURL-CEFAO 14th PT, 3rd Round on Frozen Fish

Your Lab. Code is:

Technical Information

The round is based on the determination of:
- total As, Cd, Hg and Pb in frozen fish; each NRL is free to choose the elements to be analysed among the proposed ones.
- total As in the water Arsenobetaine solution
- total As in the water solution of Inorganic Arsenic in 2% HNO3.

Samples:
- frozen fish test material (~100g) with ID number
- water solution of Arsenobetaine (~30 mL) without ID number
- water solution of Inorganic Arsenic in 2% HNO3 (~40 mL) without ID number

Storage

Frozen Fish: the sample must be stored in the freezer until analysis. Please note that even if the sample arrives partially de-frozen, store it in the freezer and carry out the analysis anyway.

Solutions: the solutions of As and Arsenobetaine can arrive in a frozen state, partially de-frozen or liquid. Please, store them in the refrigerator at 4°C and do not freeze them again. Leave Arsenobetaine in its dark bottle.

Handling of the PT items

Fish sample: treat the sample as a routine sample; the number of replicates must be the same ones used in routine procedures. However, for the preparation:
- thaw when ready to analyse (e.g. at room temperature or in refrigerator);
- after thawing, mix the material to ensure that the sample is homogeneous before starting the analysis; the separation of some liquid can occur, in this case, care must be taken to avoid loss of liquid; manually stir the sample so as to make it re-absorb its own water;
- the sample can be stored in a refrigerator (~4°C) for a period of 4 days, at most; the sample can be re-frozen, if necessary; the surplus can be eliminated as usual as routine samples.

Note: In the EN 14627:2005 (E) “Foodstuffs - Determination of trace elements - Determination of total arsenic and selenium by hydride generation atomic absorption spectrometry (HGAAS) after pressure digestion” is stated: “A digestion temperature up to 320 °C may be necessary in order to enable the hydridisation of the arsenic compounds and in order to determine all different arsenic species in the foodstuff.” Moreover when the sample digestion is performed by microwaves and the method is based on oxidation-reduction reactions, such as the determination of As by HG-AAS and of Hg by CV-AAS, we suggest to follow the procedure described in the EN 13805:2002. The Standard recommends to degas the digested solution in an ultrasonic bath to minimize the influence of nitrous gases on the determination; if it is not possible, we recommend to leave the test solution loosely covered for at least 12 h (overnight) after digestion. Describe your procedure in the section “Further Information or Brief Description of the Analytical Method” of the Results Form.
**Arsenobetaine solution:** To avoid the contamination of the instruments, consider that the As concentration is higher than 0.2 mg/l.

*Note:* for HG-AAS determination it is necessary to digest the solution as if it were a fish sample.

**Inorganic As solution:** the As concentration is higher than 0.1 mg/l; you can analyse it as a normal standard solution.

**Reporting the results**

- Please, fill out the form in all its sections, including the number of the bottle of the fish sample
- Express the concentration in:
  - mg/kg for fish sample
  - mg/l for the solutions
- Express the results with 3 significant figures (ex.: 0.245; 0.240; 0.0245).
  *Note:* these figures are different from the ones requested in the Interpretation of Results.
- Report the “mean value” and the “standard deviation” of the replicates in the proper column of the Results form. If the laboratory performs only one replicate, the result should be reported in the “Mean value” column as well
- Results reported as “<” will not be included in the calculation of assigned value and z-score.

**Interpretation of results**

As for Cd, Hg and Pb, the acceptability of the sample is required. To this end consider the fish as a Trout and follow what is stated in the Commission Regulation (EC) 333/2007, Part D “Reporting and Interpretation of Results” considering the sample as a “sample for enforcement”.

**Deadline**

- Data should be submitted not later than 31 January 2011 via e-mail, by fax (+39 06 49902721) or by post.
- For further information please contact the EURL-CEFAO, e-mail (crl@iss.it)
C2.2. ARSENIC: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected.

### SAMPLE TREATMENT

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*to be continued*
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continues

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## C2.3. CADMIUM: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected.

### SAMPLE TREATMENT

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Rapporti ISTISAN

continues

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## C2.4. LEAD: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected.

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*to be continued*
### Rapporti ISTISAN

12/56

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**Comments, Remarks**

LOQ= minimum detectable amount in real matrix

Samples were received cool but separated. 4

30
### C2.5. MERCURY: analytical methods applied by the participants

The details of methods are tabulated as reported by the participants but some obvious errors have been corrected.

#### SAMPLE TREATMENT

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<td><strong>Wavelength</strong></td>
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<tr>
<td>253.65</td>
<td>25, 31</td>
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<tr>
<td>253.7</td>
<td>1, 2, 4, 5, 6, 7, 8, 9, 10, 11, 17, 19, 20, 26, 27, 30, 32</td>
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<tr>
<td>253.8</td>
<td>16</td>
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<tr>
<td><strong>Isotopic mass (amu)</strong></td>
<td></td>
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<tr>
<td>201</td>
<td>24</td>
</tr>
<tr>
<td>202</td>
<td>28, 13, 12, 14, 21, 23</td>
</tr>
<tr>
<td><strong>LoD of the method (mg/kg)</strong></td>
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</tr>
<tr>
<td>≤ 0.001</td>
<td>2, 3, 13, 16, 17, 19, 21, 23, 25, 26, 27</td>
</tr>
<tr>
<td>≥ 0.001 - ≤ 0.002</td>
<td>5, 12</td>
</tr>
<tr>
<td>&gt;0.002 - ≤ 0.003</td>
<td>6, 10</td>
</tr>
<tr>
<td>≥0.004 - ≤ 0.005</td>
<td>7, 20, 32</td>
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<tr>
<td>0.008</td>
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<tr>
<td>0.01</td>
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<tr>
<td>0.010</td>
<td>28, 31</td>
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<tr>
<td>0.016</td>
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<tr>
<td>0.038</td>
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<tr>
<th>Measurement</th>
<th>Laboratory code</th>
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<tbody>
<tr>
<td>&lt; 0.004</td>
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<tr>
<td>0.005</td>
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<td>0.006</td>
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<td>0.007</td>
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<td>0.01</td>
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<td>0.010</td>
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<td>0.012</td>
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<td>0.014</td>
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<td>0.017</td>
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<tr>
<td>0.02</td>
<td>2, 3</td>
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<tr>
<td>0.024 (m = 0.7 g)</td>
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<tr>
<td>0.020</td>
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<tr>
<td>0.030</td>
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<tr>
<td>0.050</td>
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<tr>
<td>0.076</td>
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<tr>
<td>0.08 mg/kg for m = 0.5g</td>
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<table>
<thead>
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<th>Measurement</th>
<th>Laboratory code</th>
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<tr>
<td>NRC CNRC DORM3</td>
<td>2, 21, 25</td>
</tr>
<tr>
<td>CRM422, DORM3</td>
<td>1</td>
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<tr>
<td>CRM; CE278, 1566B, Dorm-2</td>
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<tr>
<td>standard addition</td>
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<tr>
<td>TORT-2</td>
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<tr>
<td>CRM 422, CRM 278R</td>
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<tr>
<td>MRC</td>
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<tr>
<td>14th PT 1st Round on Frozen meat</td>
<td>10</td>
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<tr>
<td>SPIKED SAMPLES</td>
<td>11</td>
</tr>
<tr>
<td>Nist 2976</td>
<td>12</td>
</tr>
<tr>
<td>BCR 424</td>
<td>13</td>
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<tr>
<td>blanks; standard, MRC</td>
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<tr>
<td>IAEA-407</td>
<td>15</td>
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<tr>
<td>CRM 2976/ PT 13th Fish muscle</td>
<td>19</td>
</tr>
<tr>
<td>Fish CRL-ISS 13th PT 2nd round</td>
<td>24, 27</td>
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<tr>
<td>DOLT-4, TORT-2, Spiking of the sample</td>
<td>28</td>
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<tr>
<td>BCR 151</td>
<td>31</td>
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<tr>
<td>Oyster tissue BCR 1566 B yes</td>
<td>32</td>
</tr>
<tr>
<td>yes</td>
<td>16, 26, 30</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Comments, remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOQ= minimum detectable amount in real matrix</td>
</tr>
<tr>
<td>Samples were received cool but separated.</td>
</tr>
</tbody>
</table>
### C2.6. List of participants

<table>
<thead>
<tr>
<th>Name of the Organisation of the European Union National Reference Laboratories and address</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austrian Agency for Health and Food Safety, Competence Centre for Elements</td>
<td>Austria</td>
</tr>
<tr>
<td>Spargelfeldstrasse 191A, 1220 Wien</td>
<td></td>
</tr>
<tr>
<td>CODA-CERVA, Veterinary and Agrochemical Research Centre</td>
<td>Belgium</td>
</tr>
<tr>
<td>OD Chemical Safety of the Food Chain, Operational Unit Trace Element</td>
<td></td>
</tr>
<tr>
<td>Leuvensesteenweg 17, B-3080 Tervuren</td>
<td></td>
</tr>
<tr>
<td>Central Laboratory of Veterinary Control and Ecology (CLVCE)</td>
<td>Bulgaria</td>
</tr>
<tr>
<td>5 Iskarko Shousse, Str., BG-1528 Sofia</td>
<td></td>
</tr>
<tr>
<td>State General Laboratory, Ministry of Health</td>
<td>Cyprus</td>
</tr>
<tr>
<td>44 Kimonos Street, 1451 Nicosia</td>
<td></td>
</tr>
<tr>
<td>State Veterinary Institute Olomuc, Department of Residues and</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>National Reference Laboratory for Chemical Elements, Laboratory in Kromeritz</td>
<td></td>
</tr>
<tr>
<td>Hulinska 2286, 767 60 Kromeritz</td>
<td></td>
</tr>
<tr>
<td>Technical University of Denmark, National Food Institute</td>
<td>Denmark</td>
</tr>
<tr>
<td>Mørkhøj Bygade 19 Building B , DK- 2860 Søborg</td>
<td></td>
</tr>
<tr>
<td>Estonian Veterinary and Food Laboratory</td>
<td>Estonia</td>
</tr>
<tr>
<td>Kreutzwaldi 30, 51006 Tartu</td>
<td></td>
</tr>
<tr>
<td>Finnish Food Safety Authority Evira, Chemistry and Toxicology Unit</td>
<td>Finland</td>
</tr>
<tr>
<td>Mustialankatu 3, FI-00790 Helsinki</td>
<td></td>
</tr>
<tr>
<td>ANSES- Agence nationale de sécurité sanitaire de l’alimentation,</td>
<td>France</td>
</tr>
<tr>
<td>de l’environnement et du travail. Laboratoire de sécurité des aliments</td>
<td></td>
</tr>
<tr>
<td>Unité Contaminants Inorganiques et Minéraux de l’Environnement</td>
<td></td>
</tr>
<tr>
<td>LNR Métaux lourds</td>
<td></td>
</tr>
<tr>
<td>23, Avenue du Général de Gaulle, F-94706 Maisons- Alfort Cedex</td>
<td></td>
</tr>
<tr>
<td>Federal Office of Consumer Protection and Food Safety (BVL)</td>
<td>Germany</td>
</tr>
<tr>
<td>Referat 501, Mauerstr. 39-42, D-10117 Berlin</td>
<td></td>
</tr>
<tr>
<td>Institute of Food Hygiene of Athens, Ministry of Rural Development and Food</td>
<td>Greece</td>
</tr>
<tr>
<td>25 Neapoleos st., 15310 Agia Paraskevi</td>
<td></td>
</tr>
<tr>
<td>Laboratory Central Agricultural Office Food and Feed Safety Directorate,</td>
<td>Hungary</td>
</tr>
<tr>
<td>Mester utca 81, H-1095 Budapest</td>
<td></td>
</tr>
<tr>
<td>Department of Agriculture, Fisheries and Food</td>
<td>Ireland</td>
</tr>
<tr>
<td>Backweston Laboratory campus, Young’s Cross, Celbridge, Co. Kildare</td>
<td></td>
</tr>
<tr>
<td>Istituto Superiore di Sanità, Department of Veterinary Public Health and Food Safety</td>
<td>Italy</td>
</tr>
<tr>
<td>Viale Regina Elena 299, 000161 Roma</td>
<td></td>
</tr>
</tbody>
</table>

To be continued
Name of the Organisation of the European Union National Reference Laboratories and address | Country
---|---
National Diagnostic Centre of Food and Veterinary Service of Latvia, Food and Environmental Investigation Laboratory, Instrumental Analysis Division Lejupes Street 3, Riga LV-1076 | Latvia
National Food and Veterinary Risk Assessment Institute, Laboratory department, Chemistry section J. Kairiukscio str. 10, LT- 08409 Vilnius | Lithuania
Institut Scientifique de Santé Publique, Produits de consommation Rue Juliette Wytmsan Straat 14 1050 Brussels | Luxemburg
Public Health Laboratory, Department for Environmental Health Evans Buildings, Merchant Street, Valletta VLT 1179 | Malta
Rikilt – Institute of Food Safety Akkermaalsbos 2, 6708 Wageningen, Building No 123 | The Netherlands
Agri-Food and Biosciences Institute, Food Chemistry Newforge Lane, Belfast, BT6 9FY | Northern Ireland
National Veterinary Research Institute, Department of Pharmacology and Toxicology Al. Partyzantow 57, 24-100 Pulawy | Poland
Instituto Nacional dos Recursos Biológicos (INRB) Fish and fishery products: INRB, IP/L- IPIMAR Instituto Português de Investigação Marinha (IPIMAR) Av. Brasilia, 1449-006 Lisboa | Portugal
Institute for Hygiene and Veterinary Public Health NRL of Heavy Metals in Food of Animal Origin and Feed Street Campul Mosilor 5, Sector 2, 021201 Bucharest | Romania
State Veterinary and Food Institute Hlinkova 1 , 040 01 Kosice | Slovakia
National Veterinary Institute, Laboratory for Residue Analyses, University of Ljubljana Veterinary Faculty Gerbiceva 60, 1000 Ljubljana | Slovenia
Ministerio de Agricultura, Pesca y Alimentaciòn, Grupo Arbitral Agroalimentario Carretera de la Coruna Km 10700 ,28023 Madrid | Spain
National Food Administration Box 622 SE-751 26 Uppsala | Sweden
The Food and Environment Research Agency, Trace Elements Unit Sand Hutton, York, Y041 1LZ | United Kingdom

EURL-CEFAO European Union Reference Laboratory for Chemical Elements in Food of Animal Origin
Istituto Superiore di Sanità
Viale Regina Elena 299, 000161 Roma | Italy
CONCLUSIONS

Rosa Giordano*  
European Union Reference Laboratory for Chemical elements in food of animal origin,  
Department of Veterinary Public Health and Food Safety, Istituto Superiore di Sanità, Rome

The outcome of the 14th PT can be considered satisfactory from several points of view. One is the participation of all NRLs confirming the high appreciation of this comparative test; the other regards the performance expressed in terms of $z$-scores that is far above the basic level expected from a laboratory, since the percentage of the $z$-scores $\leq 2$ is high. Moreover, the proportion of the $z$-scores $\leq 1$ is also high notwithstanding the $z$-scores are calculated using the more restrictive $\sigma_{EURO}$L. The comparison with the previous PTs showed a general improvement that is not only linked to the reduction of outliers and tails in the distribution of data, but also to a decreased spread in the central region of data. This last concept is evidenced by the decrease of the standard deviations of the means of the results and by the Interquartile Ranges proving the progress of the NRLs already endowed with good performance.

In the first round on meat the improvement can be seen comparing the percentage of $z$-scores belonging to the “satisfactory class” with the ones of the previous PTs at the same level of concentration. Moreover the use of frozen material, instead of the freeze-dried, was able to prove the actual performance of the NRLs. The performance of NRLs for mercury was not considered in terms of $z$-scores since this exercise was not announced during the annual workshop. Although mercury was analysed for the first time at a low concentration and in this matrix, the outcome was extremely satisfactory. This statement is supported by the good value of standard deviation, the agreement among the indicators of central tendency (arithmetical mean, robust mean and median) and the absence of clearly aberrant or qualitative data.

As for the second round on milk, the greatest improvement was found in lead, whose results were usually more spread. A positive outcome of this round was the increased number of NRLs using the ICP-MS and the improvement of their performance with this technique.

As for arsenic, the large number of accurate results together with the increased number of NRLs using ICP-MS confirmed that methods based on HG-AAS technique can produce spread results since they are affected by more than one critical step.

The third round on fish confirmed the progress achieved on the analysis of lead and arsenic: this is a noteworthy result as the analysis of these elements had presented problems since the early PTs. As for cadmium and mercury the results were satisfactory stressing the high performance of the network in analysing these elements. As far as arsenic is concerned the improvement already verified in the second round was confirmed strengthening the opinion on the poor performance of the methods based on HG-AAS technique.

As for the compliance statement, some difficulties noticed in the previous PTs were overcome. In fact, considering both cadmium and lead, only 5% of the NRLs made a mistake in the computation of the compliance. Moreover, a statement was produced by almost all laboratories and this also represents an achievement due to the high number of laboratories not expressing any judgement in the past. Nevertheless the occurrence of some sporadic mistake strengthens the importance and the need to continue the exercise in the next PTs since no doubt must remain when handling this issue.

* Former Director of the EURL-CEFAO, currently an external expert in the team.
The positive outcome for all the elements is certainly the consequence of the good work done by the NRLs for the improvement of their methods, but it is also due to the regular repetition of the same matrices throughout the years because this repetition enabled NRLs to check the suitability of their corrective actions.
REFERENCES


