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The International Measurement Evaluation Programme

IMEP-20
Trace Elements in Tuna Fish
Report to Participants

Y. Aregbe, C. Harper, I. Verbist, L. Van Nevel,
P. Smeyers, C. Quétel and P.D.P. Taylor

IMEP®

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The Mission of IRMM is to promote a common European measurement system in support of EU policies, especially health and consumer protection, environment, agriculture, internal market and industrial standards.

European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements

Contact information
Yetunde Aregbe & Lutgart Van Nevel
European Commission
Directorate-General Joint Research Centre
Institute for Reference Materials and Measurements
Retieseweg 111
B-2440 Geel • Belgium

Email: jrc-irmm-imep@cec.eu.int

Tel.: +32 (0)14 571 673
Fax: +32 (0)14 571 865

http://www.irmm.jrc.be
http://www.jrc.cec.eu.int

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IMEP®

provides certified reference values with demonstrated traceability and demonstrated uncertainty, independent of the participants' results

invites participants to supply a best estimate of the expanded measurement uncertainty of their results

enables result-oriented rather than procedure oriented evaluation of performance

demonstrates a degree of equivalence in measurement results at the global scale

Contents

Summary

The International Measurement Evaluation Programme (IMEP®) is an Interlaboratory Comparison scheme in support of EU policies (e.g. Consumer Protection, Public Health, Single Market, Environment, Research and Technology, External Trade and Economic Policy). It was founded and still continues to be co-ordinated by the IRMM, the European Commission's Joint Research Centre for Reference Materials and Measurements. Currently the IMEP® programme is used in a collaboration agreement with the European Co-operation for Accreditation (EA) to enable assessment of comparability of measurements from laboratories.

Contrary to most other external quality assessment schemes, participating laboratories in IMEP® can compare their measurement results within their reported uncertainties with external reference values, completely independent from the participants' result. Participants in IMEP® use their routine analytical procedures to measure the IMEP certified test sample (CTS). The certified test sample (CTS) has undisclosed certified reference values as measured by reference laboratories. Certified reference values are required to demonstrate traceability, and they should have demonstrated an adequately small uncertainty, as evaluated according to international guidelines. Participants in IMEP® can assess the quality of their results on an international forum by comparing their values to the IMEP certified reference values.

The European Commission (EC) has identified food safety as one of its top priorities. The White Paper on Food Safety of January 12th 2000, sets out the plans for a proactive new food policy. Measurements of contaminants in foodstuff play a key role in modernising legislation into a coherent and transparent set of rules. Maximum levels for certain metals in foodstuffs are set in the EC Regulation (466/2001). The European Commission (EC) has also requested the Scientific Committee on Food (SCF) to review the upper level of daily intake of certain metals.
Participants in IMEP-20 "Trace Elements in Tuna Fish" were offered to measure the total amount content of As, Hg, Pb, Se and methylmercury (CH_3Hg) in tuna fish. IMEP-20 is organised in collaboration with the Community Reference Laboratory for Residues - Istituto Superiore di Sanità, Rome (CRL-ISS) in support to the European network of National Reference Laboratories (NRLs). IMEP-20 is also organised particularly in view to support the acceding and candidate countries. Measurement results were reported by 235 participants from 14 EU member states, 10 acceding countries and 3 candidate countries. Amongst those there were 23 NRLs and 38 NRL nominated laboratories. In the frame of the European Co-operation for Accreditation (EA), EA-IRMM collaboration agreement, 61 laboratories, that were nominated via their National Accreditation Bodies (NABs), reported measurement results in IMEP-20.

This report presents in a graphical form the results of all participants, sorted according to different criteria. The assessment of measurement performance in IMEP-20 is based on the E_n-number evaluation. The measurement performance was only evaluated for participants who stated that they estimated their measurement uncertainty according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).

IMEP®

The forces of consumer protection, international trade and competition are driving chemical laboratories to improve the quality of their measurements. About one third of EU regulations and directives depend on measurements. Therefore measurement quality is important to enable an equivalent implementation of these regulations across an enlarged European Union (EU). To disseminate measurement traceability IRMM, the European Commission's Joint Research Centre for Reference Materials and Measurements, provides a tool to enable the benchmarking of laboratory performance.

Since 1988 the International Evaluation Programme (IMEP®) sheds light on the actual state of practice in chemical measurement performance. In early days IMEP® became internationally known because it was one of the few interlaboratory comparison schemes that was not based on consensus values derived from participants' results. Contrary to the common belief, the results of the various IMEP® comparisons showed an unexpected large spread of participants' results even for simple measurement problems, far from laboratories own quoted standards of accuracy. IMEP® aims to build up confidence where trade or border crossing problems exist. IMEP® provides support to EU policies and the chemical measurement infrastructure of the enlarged EU assisting in the development of the national measurement infrastructure. The common goal is to prove the reliability of measurement results.

IMEP® is a publicly accessible metrological Interlaboratory Comparison scheme. It guarantees the confidentiality to the identity of its participants. Participating laboratories receive the IMEP CTS with undisclosed certified reference values as measured by reference laboratories. These reference laboratories prove their claims of measurement capabilities by means of participation in internationally mutually recognised key comparisons [1]. Certified reference values are based on primary or other internationally recognised measurement procedures [2]. The underlying philosophy is that the best possible values will serve as reference and these are obtained from well-understood measurement processes rather than via a mere consensus approach. Another unique feature of IMEP® is that participants in IMEP® have always been invited to apply their routine analytical procedures but to state uncertainty estimates for their reported results. A large number of laboratories participating in IMEP® have to comply with the ISO/IEC 17025 standard [3]. They need to meet the requirement of providing reliable measurement results within uncertainties.

The need for training is generated by the requirement set by the ISO/IEC 17025 standard regarding the competence of laboratories. As laboratories are accredited against this standard, many of them need training to enable them to demonstrate measurement traceability, estimate uncertainty and perform validation. IRMM could offer training activities to participants who request additional support after the completion of the respective IMEP® comparison.

All the reports of previous IMEP® interlaboratory comparisons on amount contents of minor and trace elements in various matrices such as water, polyethylene, serum, sediments, car catalysts, wine and rice can be found on the IMEP web-site [4].

IMEP-20

The EC has identified food safety as one of its top priorities. The White Paper on Food Safety of January 12th 2000, sets out the plans for a proactive new food policy. Measurements of contaminants in foodstuff play a key role in modernising legislation into a coherent and transparent set of rules. This reinforces controls from the farm to the table and increases the capability of the scientific advice system, so as to guarantee a high level of human health and consumer protection [5]. In order to protect public health it is essential to keep contaminants at levels which are toxicologically acceptable, thus surveillance measures have been taken regarding the presence of contaminants in foodstuff.

Mercury is a potential environmental toxin. The main source of human intake of Hg contaminants originates from methylmercury in fish and fishery products. Methylmercury is particularly interesting due to its high toxicity compared to inorganic Hg and its high proportion among organomercury species in the environment. Mercury species, may induce alterations in the normal development of the brain of infants and may induce neurological changes in adults. Lead may induce reduced cognitive development in children and increased blood pressure and cardiovascular diseases in adults. To protect public health, maximum levels of Hg and Pb in fishery products are laid down in relevant regulations. The EC Directive 2001/22 describes the community methods for the sampling, the sample preparation and the analysis of Hg and Pb in fish [6]. The EC Regulation (466/2001) endorses officially the threshold value of 1 mg Hg·Kg^{-1} and 0.2 mg Pb·Kg^{-1} in tuna fish [7]. Selenium is an essential trace element for human beings. Seafood is an important source of Se intake for people in some regions. Certain forms of cancer and cardiovascular diseases have also been associated with Se deficiency. Se is also counted among the most important elements in terms of food-chain contamination. Se has the narrowest plateau between concentrations that show deficiency and toxic effects, respectively. Recently the EC has requested the SCF to review the upper level of daily intake of individual vitamins and minerals, amongst them Se, and to provide the basis for the establishment of safety factors [8]. Arsenic is a toxic element and rules for measurements of As are set in the commission decision on implementing council directive 96/23/EC concerning the performance of analytical methods and the interpretation of results [9]

Participants in IMEP-20 "Trace Elements in Tuna Fish" were offered to measure the content of As, Hg, Pb, Se and methylmercury. This report presents all results (in graphical form) from participants in IMEP-20. In addition, the applied water content determination and dry-mass correction in IMEP-20 are summarised in Annex 2 of this report.

Over the past few years, the International Committee for Weights and Measures (CIPM), the guardian of the International Measurement System (the SI), has taken several initiatives to improve the equivalence of chemical measurements worldwide. In 1999 a new international protocol was signed called the Mutual Recognition Arrangement (MRA), which IRMM signed on behalf of the EC [10]. The MRA enables National Metrology Institutes (NMIs) to demonstrate their measurement capability by participating in key comparisons and pilot studies. The same CTS as used in IMEP-20 was also offered for a pilot study to the Consultative Committee of Amount of Substance of the CIPM, (CCQM-39). 13 NMIs, signatories to the MRA, and 8 expert laboratories for methlymercury measurements participated in CCQM-P39. Results of this comparison will be accessible via the Bureau International des Poids et Mesures (BIPM) web-site [11]. Ultimately, the IMEP-20 participants can compare their results with the results of laboratories that represent their country at the international measurement structure level and vice versa.

Collaboration with the CRL-ISS

The CRLs have been designated in 1991 by the Council of the European Union [12]. Their updated powers and operating conditions are laid down in Council Directive 96/23/EC [13]. Their task is the improvement and implementation of analytical methodology and the scientific basis of residue control. In cases where the result of an analysis gives rise to a disagreement between member states the CRL has to carry out the identification and determination of residues. It can act as a referee between member states. The CRLs give scientific/technical advice to NRLs to ensure good laboratory practice. They also conduct initial and further training courses for NRLs.

One of the main tasks of a CRL is to organise proficiency testing schemes (PTs), and to evaluate the results of participating NRLs. The CRL-ISS, constantly monitors by means of PTs the performance of the NRLs for analysis of trace elements. IMEP-20 was organised in collaboration with the CRL-ISS as support to the network of NRLs in the member states and the acceding countries. Participation of NRLs in IMEP-20 was part of the mandatory activities of the NRLs with the CRL-ISS. Furthermore each NRL was invited to nominate 5 laboratories from their country, laboratories that would be regularly used as contracting laboratories when performing monitoring activities. Finally, 23 NRLs and 38 NRL nominated food control laboratories reported measurement results in IMEP-20.

Collaboration with EA

Accreditation is a very useful tool for laboratories to demonstrate technical competence to their customers. The accreditation infrastructure is an important component of the European Acquis Communautaire regarding technical infrastructure. In order to further improve the efficiency of accreditation in chemistry with respect to the evaluation and demonstration of the performance of laboratories, the EA and IRMM agreed to intensify their ongoing co-operation. A formal "letter of intent for co-operation" was signed by the Chairman of the EA, Dr. D. Pièrre and the director of IRMM at that time, Prof. M. Grasserbauer in the beginning of 2001[14]. By supporting EA, IRMM also supports the EU member states by ensuring confidence in their national measurement system. IMEP® therefore enables to assess whether national measurement systems are in place to provide a level playing field and enabling an equivalent implementation of directives across an enlarged EU.

The EA-IRMM co-operation focuses on the chemical measurements and aims to improve the metrological basis of accreditation in chemistry. This will be mainly achieved by the organisation of interlaboratory comparisons using traceable reference values obtained in terms of high quality measurements applying the principles of metrology.

Accredited laboratories need to meet the requirements, according to the ISO/IEC 17025 standard, of providing reliable measurement results within uncertainties. Recently this became a very important aspect in the collaboration agreement between IRMM and EA, because regular PT providers do not ask participants to report a measurement result within uncertainty. Therefore IMEP® serves as a unique tool for the NABs to ensure compliance of their accredited laboratories with ISO/IEC 17025. They may nominate laboratories to participate in IMEP®, to evaluate their performance against independent reliable reference values and request the laboratories to take appropriate corrective actions if needed. In the framework of this collaboration IRMM offered a number of IMEP-20 CTS to the NABs in Europe.

IMEP-20 was also organised particularly in view of support to food laboratories in acceding and candidate countries.

The Certified Test Sample

Tuna Fish

The IMEP-20 CTS is a freeze dried and ground tuna muscle powder bottled in amber glass vials each one containing about 4 grams. Within and between bottle homogeneity tests for Hg and Pb were carried out on 10 sub-samples of 10 bottles using solid sample Zeemann Atomic Absorption Spectrometry (SS-ZAAS) and on 3 sub-samples from 3 bottles applying Isotope Dilution Mass Spectrometry (IDMS). For As and Se the homogeneity was assessed by analysing 3 sub-samples from 5 bottles applying k_0-Neutron Activation Analysis (k_0-NAA). Results from these measurements were evaluated accordingly and compared to the procedures established in ISO 35, for the certification of reference materials based on analysis of variance ANOVA [15, 16].

The tuna fish originates from the Mediterranean Sea close to Messina and was taken off the market due to its elevated amount content of Hg. The range of metal amount contents was just slightly exceeding the upper limits as stated in the EC Regulation (466/2001). This tuna fish material was perfectly appropriate for the purpose of an interlaboratory comparison, because of its homogeneous distribution of contaminants. It represents a "real-life" sample that each laboratory involved in food testing or food control could have been offered by a regular client.

IMEP-20 Certified reference values

In the past IRMM has already successfully proven the measurement capabilities to measure trace elements in various matrices [1]. As a reference laboratory IRMM had to demonstrate its measurement capability for the specific measurand in the matrix to be certified. IRMM participated previous to the establishment of the certified IMEP-20 reference values to the CCQM-P39 comparison where the same CTS was used. IRMM had excellent results in CCQM-P39 and thus IRMM's measurement capability, to measure Trace Elements in Tuna Fish has been successfully confirmed by comparison to other NMIs and expert laboratories worldwide. NMIs support routine laboratories in their country with expert advice and calibration services, and may have a stated responsibility to assure that measurements are traceable. The results of CCQM-P39 will be published in the Metrologia Technical Supplement and will be accessible via the BIPM web-site [11].

Methodology

The IMEP-20 certified reference values were established by means of Primary Method of Measurements (PMM) [2]. The reference measurements for Hg and Pb were carried out using Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [17]. The reference measurements for As and Se were done by k_0-NAA. Methylmercury was measured by species-specific Gas Chromatography Isotope Dilution Inductively Coupled Plasma Mass Spectrometry (GC-ICP-MS). The IMEP-20 certified reference values were reported with a complete uncertainty budget according to the Guide to the Expression of Uncertainty in Measurement (GUM) [18].

The following institutes and departments within IRMM collaborated in the production or certification of the IMEP-20 tuna fish CTS (Table 1).

Table 1. IMEP-20 Reference laboratories

Institution
European Commission JRC
IRMM
Isotope Measurement unit Reference Materials unit Food Safety and Quality unit
Institute for Reference Materials and Measurements
Geel BELGIUM
SCK-CEN
Centre d'étude de l'énergie nucléaire
MOL BELGIUM

Certified values were established with demonstrated traceability and adequately demonstrated uncertainty for As, Hg, Pb, Se and methylmercury. The IMEP-20 certified reference value certificate was issued (see Annex 4) and distributed to all participants. The certified values for the dry-mass corrected amount contents are summarised in Table 2. The stated uncertainties are expanded uncertainties ($U = k \cdot u_c$) with a coverage factor k equal to 2.

Participant Coordination

Due to the limited number of samples IMEP-20 was restricted to participants from the EU member states and from acceding and candidate countries. International expert laboratories for methylmercury measurements were also invited for participation in IMEP-20.

In April 2003 IMEP-20 was announced to the NRLs and EA. The NRL representatives were also contacted for participation in IMEP-20 by Prof. S. Caroli, the director of the CRL-ISS. Mrs. Nicole Meuree-Vanlaethem from the Belgium Accreditation (BELAC) co-ordinated the nomination of laboratories with the NABs.

Regional Co-ordinators (RCs)

The Regional co-ordinators (RCs) are very valuable partners for IMEP®. RCs are typically people or institutions directly involved in chemical measurements and preferably experienced and competent in metrological matters, with profound knowledge of the measurement systems of their country or region. The tasks of the RCs are to act on behalf of IRMM in order to liase with participants and administer locally in each comparison, while bridging linguistic, cultural differences and taking into account any local particularities. The RCs in IMEP-20 are given in Table 3.

Timing & deadlines

The planning of the comparison was performed in spring 2003. The announcement for IMEP-20 was sent to the RCs in May 2003. After the collection of the registration forms the CTS were distributed with accompanying documents to the participants during July 2003. The initial deadline for the participants to report their results was the 31st October 2003. Subsequently result reporting was extended to the 14th November 2003. Each participant received a personal key-code in order to report their results and questionnaire information electronically through the IMEP web-site [4]. All announcements and guideline information were accessible from the IMEP web-site. The participants received by e-mail the IMEP-20 certified reference value certificate in November 2003. The IMEP-20 certified reference value certificate is also accessible via the IMEP web-site. In addition an individual certificate was distributed by post to each IMEP-20 participant in December 2003 (see Annex 4).

Table 2. Certified reference values for IMEP-20

Analyte	Certified value mg·kg^{-1} (dry-mass)	Expanded uncertainty U, k=2 mg·kg^{-1} (dry-mass)
Arsenic	**4.93**	**0.21**
Lead	**0.498 0**	**0.008 5**
Mercury	**4.32**	**0.16**
Methylmercury (CH_3Hg)	**4.24**	**0.27**
Selenium	**6.38**	**0.28**

Table 3. List of Regional Co-ordinators for IMEP-20

Country	Institution / Organisation
AUSTRIA	IFA, Interuniversitäres Forschungsinstitut für Agrarbiotechnology
BULGARIA	National Center of Metrology
CYPRUS	State General Laboratory
CZECH REPUBLIC	Czech Metrology Institute
ESTONIA	University of Tartu
FRANCE	Bureau National de Métrologie - LNE
GREECE	Aristotle University of Thessaloniki
HUNGARY	National Office of Measures (OMH)
LATVIA	Latvian National Accreditation Bureau (LATAK)
LITHUANIA	Semiconductor Physics Institute
NORWAY	National Veterinary Institute
POLAND	University of Warsaw
PORTUGAL	RELACRE – Associação dos Laboratórios Acreditados de Portugal
ROMANIA	National Institute of Metrology
SLOVAKIA	Slovak Institute of Metrology (SMU)
SLOVENIA	Metrology Institute of the Republic of Slovenia (MIRS)
SPAIN	Centro Español de Metrologia (CEM)
SWEDEN	SP Sveriges Provnings- och Forskningsinstitut
SWITZERLAND	Eidgenössische Materialprüfungs- und Forschungsanstalt (EMPA)
THE NETHERLANDS	NMi – Van Swinden Laboratorium
TURKEY	Turkish Accreditation Agency

Tuna Fish CTS mailing

The CTS were sent using express mail to all participants. Enclosed were a few accompanying documents (see Annex 4)

- An accompanying letter to the participants giving information relevant to the comparison, pointing out the deadlines and giving instructions on how to report their results via the IMEP web-site
- Online reporting guidelines were issued to show how to report results and complete the Questionnaire information electronically through the IMEP web-site
- A Sample receipt form was provided to acknowledge that the CTS arrived at its destination in good order
- An instruction letter to the participants giving information on how to report their results using their Laboratory Identification number (Lab-ID) and Key-code number
- The online questionnaire form, collects further information relating to the IMEP-20 participants. This information is used for statistical purposes and helps group the results more efficiently for the graphical presentation

Data collection

The IMEP-20 participants reported their measurement results through the IMEP web-site. After submission of their results and questionnaire information, the participants received an e-mail as a confirmation of their reported data. Any discrepancies were then corrected, no more amendments could be accepted once the certified reference value certificate was accessible via the IMEP web-site. From this point on all reported data was transferred to the IMEP-20 database.

Evaluation of performance

E_n-numbers [19] have been calculated for those participants in IMEP-20 who reported measurement results with uncertainties which were calculated according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000) [18, 20]. To enable the measurement evaluation for those participants, the same approach was applied to calculate E_n-numbers as described in [21, 22, 23]. Maximum levels of metals in foodstuff are set in the EC Regulation (466/2001). In the absence of performance characteristics for the uncertainty of the measured value for measurements of metals in tuna fish in this regulation, IRMM selected as performance characteristic an extended uncertainty from the certified reference value. $X_{ref} \pm u_{ext} = X_{ref} \pm 0.1 \cdot X_{ref}$ for the calculation of the E_n-numbers:

$$E_n = \frac{x - X_{ref}}{\sqrt{u_x^2 + \left(0.1 \cdot X_{ref}\right)^2}}$$

X_{ref}: IMEP-20 certified reference value
x: participant's reported value
u_x: participant's combined uncertainty
$0.1 \cdot X_{ref}$: selected performance criterion

It can be assumed to represent an uncertainty range that is "fit for purpose" for measurements of trace metals in fish. The evaluation of measurement performance in IMEP-20 is as follows:

$|E_n| \leq 2$ satisfactory
$2 < |E_n| \leq 3$ questionable
$|E_n| > 3$ not satisfactory

The E_n-numbers issued to the IMEP-20 participants are based on a single performance statistic, taking into account u_{ext} of the certified reference value as well as the reported uncertainty of the participant's measurement result.

IMEP-20 individual certificate

IRMM has issued individual certificates to each participant in IMEP-20. This certificate includes the reported measurement value for the IMEP-20 CTS, the IMEP-20 certified reference values and the deviation of the reported value from the certified value by percentage, and E_n-numbers for those participants who reported measurement results with uncertainties estimated according to ISO, 1995 or EURACHEM/CITAC, 2000, guides [18, 20]. For participants who did not state that they calculated the reported uncertainty according to the ISO, 1995 and/or EURACHEM/CITAC 2000 guides [18, 20] no E_n-numbers were issued. The IMEP-20 certified reference value certificate together with the individual IMEP-20 certificate were distributed to the relevant IMEP-20 participant in December 2003 (see Annex 4).

Participation in IMEP-20

Samples were distributed to 258 laboratories. Measurement results were reported by 235 participants, from 32 countries. About 50% of the 235 participants who reported results in IMEP-20 registered through the 21 RCs as listed in Table 3. 25% of the participants were nominated by their NABs and another 25% where either NRLs or NRL nominated laboratories.

Table 4: IMEP-20 participants per country

Country	Samples sent	Results received	Country	Samples sent	Results received
Argentina	1	1	**Latvia**	4	4
Australia	1	1	**Lithuania**	5	5
Austria	11	11	**Malta**	1	1
Belgium	8	6	**Norway**	4	3
Bulgaria	6	6	**Poland**	48	45
Cyprus	3	1	**Portugal**	5	4
Czech Republic	13	12	**Romania**	10	6
Denmark	5	5	**Slovakia**	32	30
Estonia	4	4	**Slovenia**	5	5
Finland	5	5	**Spain**	8	8
France	12	10	**Sweden**	4	4
Germany	14	14	**Switzerland**	3	3
Greece	3	3	**The Netherlands**	3	3
Hungary	14	11	**Turkey**	15	13
Ireland	1	1	**United Kingdom**	2	2
Italy	7	7	**U S A**	1	1
Total				258	235

Figure 1 - Figure 4 Number of tuna fish samples analysed per year

Figure 1

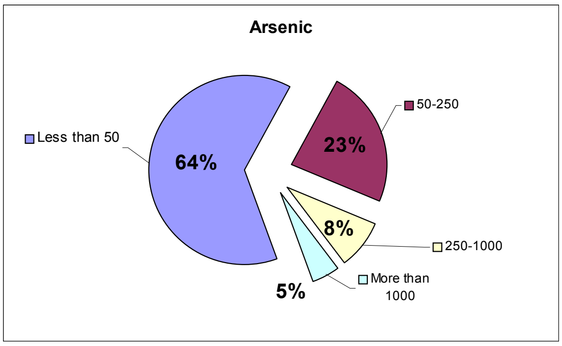


Figure 2

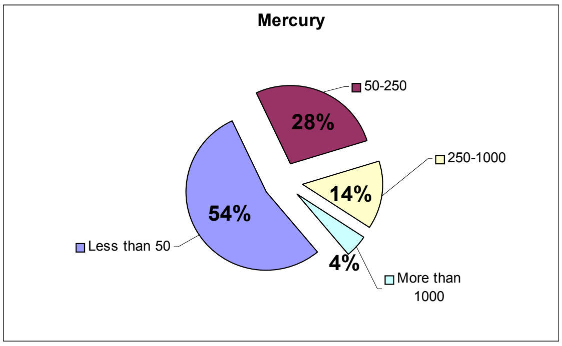


Figure 3

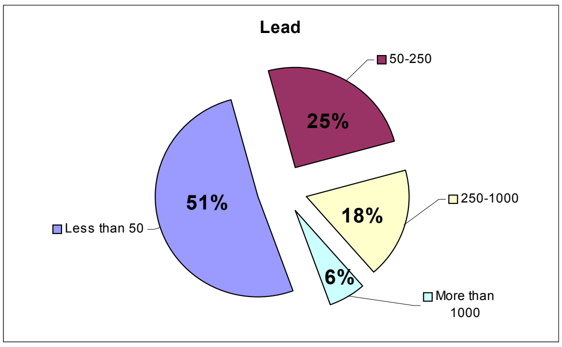
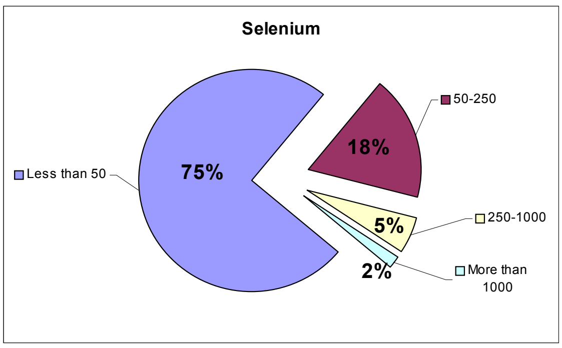


Figure 4



Data evaluation

Participants had to complete the IMEP-20 result report form and questionnaire in order to be able to submit their results via our on-line reporting system. Several conclusions can be drawn from the information provided via the questionnaires, without quoting the identity of the laboratories. For participants measuring methylmercury there was a separate questionnaire.

For all analytes under investigation in this interlaboratory comparison, the participants were free to measure the amount content of those that were of interest to their laboratory. The most popular element was Pb measured by 94% of the participants. Hg was measured by 87%, As by 72% and Se by 49% of the participants. 42% of the participants reported results for all of these 4 analytes. Methylmercury was measured by 3% of the participants. Thus, only 2.6% of the IMEP-20 participants measured all 5 analytes under investigation.

Figure 1 - Figure 4 shows by percentage how many samples were analysed per year by element.

Figure 5 Routine procedure and standards

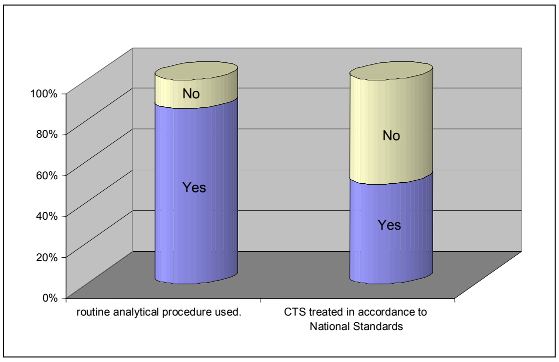


Figure 6 Time spent on measurment

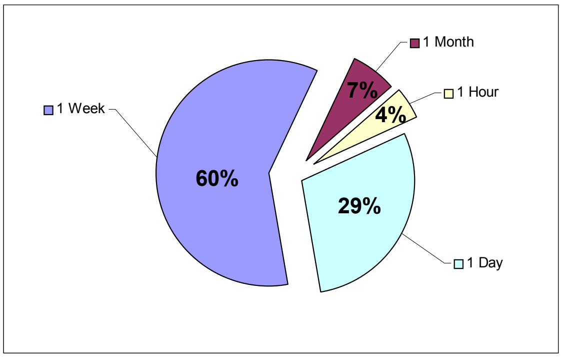


Figure 7 - Figure 10 Calibration strategy

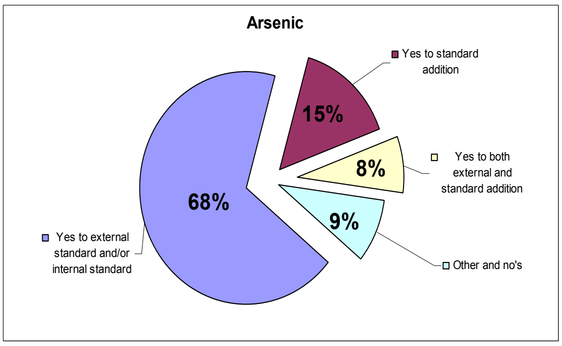


Figure 8

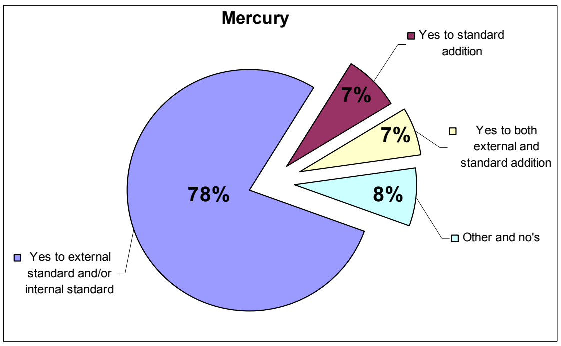


Figure 5 shows by percentage whether the CTS was analysed under routine conditions and according to (national) standards.

Figure 6 illustrates how much time was spent on average by the participants to carry out the measurements on the IMEP-20 CTS.

Figure 7 - Figure 10 shows which calibration strategy was used by the IMEP-20 participants.

67% of the laboratories participate regularly in PTs in order to assess performance for this type of analyses, but only 14% routinely use tuna fish Certified Reference Materials (CRMs) for quality assurance.
Measurement results with uncertainties were reported by 93% of the IMEP-20 participants. 46% of laboratories participating in IMEP-20 routinely report uncertainties on chemical measurements to their customers. In addition 58% of IMEP-20 participants reported their measurement uncertainties calculated according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/ CITAC (2000) [18, 20].

Table 5 gives the number of participants per element and by analytical techniques used.

Table 6 the analytical techniques are listed as applied by the 8 participants who measured the methylmercury in the tuna fish. For the graphical presentation, all analytical techniques have been grouped as shown in Table 7.

Figure 9

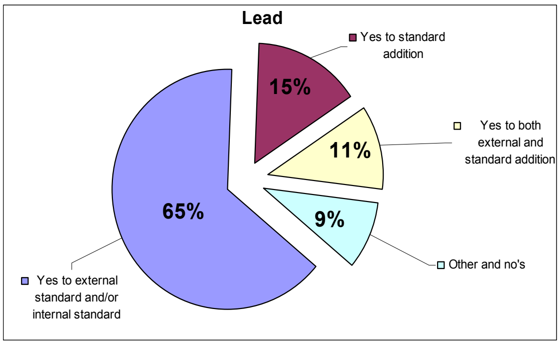


Figure 10

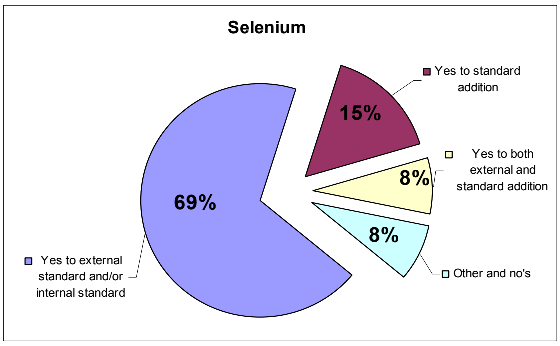


Table 5. Number of IMEP-20 participants reported results per analytical technique used

Analytical techniques	As	Hg	Pb	Se	MeHg (CH_3Hg)
ETAAS & GF-AAS	37	1	122	26	0
FIAS-AAS, FAAS & AAS	39	58	42	20	0
H-AAS, HG & CV-AAS	39	88	0	25	1
ICP-OES, ICP-AES & ICP	19	8	19	16	0
ICP-MS & HR-ICP-MS	24	16	25	23	3
OTHER	11	33	14	6	4

Table 6. Number of reported results for methylmercury per analytical technique used

Analytical techniques	MeHg (CH_3Hg)
CV-AAS	1
GC-AED & GC-ECD	2
GC-ICP-MS	1
HPLC-ICP-MS	3
None given	1

Table 7. Grouping of the analytical techniques

Analytical technique	Acronym	Group
Anodic stripping voltammetry	ASV	Other
Atomic absorption spectroscopy	AAS	FIAS-AAS, FAAS & AAS
Cathodic-stripping voltammetry	CSV	Other
Cold Vapour-atomic absorption spectroscopy	CV-AAS	H-AAS, HG & CV-AAS
Direct current plasma	DCP	Other
Electrothermal atomic absorption spectroscopy	ETAAS	ETAAS & GF-AAS
Flame atomic absorption spectroscopy	FAAS	FIAS-AAS, FAAS & AAS
Flame atomic emission spectroscopy	FAES	Other
Flame atomic fluorescence spectroscopy	FAFS	Other
Flow injection analysis system-atomic absorption spectroscopy	FIAS-AAS	FIAS-AAS, FAAS & AAS
Graphite furnace atomic absorption spectroscopy	GF-AAS	ETAAS & GF-AAS
High resolution-inductively coupled plasma-mass spectrometry	HR-ICP-MS	ICP-MS & HR-ICP-MS
Hydride generation	HG	H-AAS, HG & CV-AAS
Hydride generation-atomic absorption spectroscopy	HG-AAS	Other
Hydride-atomic absorption spectroscopy	H-AAS	H-AAS, HG & CV-AAS
Inductively coupled plasma	ICP	ICP-OES, ICP-AES & ICP
Inductively coupled plasma-atomic emission spectrometry	ICP-AES	ICP-OES, ICP-AES & ICP
Inductively coupled plasma-mass spectrometry	ICP-MS	ICP-MS & HR-ICP-MS
Inductively coupled plasma-optical emission spectrometry	ICP-OES	ICP-OES, ICP-AES & ICP
Infrared spectrometry	IR	Other
Ion chromatography	IC	Other
Metal hydride system	MHS	Other
No statement	NONE GIVEN	Other
Other	OTHER	Other
Potentiometric stripping analysis	PSA	Other
Spectrophotometry	SPECTROPH	Other
Xray flourescence	XRF	Other

Water content determination

Via the IMEP-20 questionnaire the IMEP-20 participants provided more detailed information concerning determination of the water content and the correction for dry-mass of the tuna fish CTS. The majority of IMEP-20 participants applied the drying-oven method. 7 out of the 233 IMEP-20 participants used Karl-Fischer titration to determine the water content in the CTS. A survey on the water content determination and the correction for dry-mass is summarised in Annex 2 of this report.

Graphical presentation of results

The IMEP graphs

The IMEP results are traditionally presented graphically. Based on general information of the laboratory (e.g. country of origin) and the answers given in the questionnaire, the results obtained for each element are grouped in sets of data. For each set of data, the results are plotted in ascending order against the certified reference value. The scale of the graphs, in most cases are ± 50% deviation from the certified reference value, this is chosen for convenience. No results are excluded. Participants' reported results that are off-scale are shown in text-boxes on the graphs. The IMEP-20 graphs are presented by element and can be found in Annex 1 and Annex 2 of this report.

Table 8 summarises all the IMEP-20 graphs. The "All Participants" graphs show all the results that are plotted without any grouping. The other graphs are grouped according to the analytical technique used.
The Regional graphs show all the results from the EU and EU candidate countries participants. Graphs have been prepared grouping the participants' results according to the different criteria from specific questionnaire information.
The measurement performance graphs show the results from participants who estimated their uncertainties according to ISO, 1995 and/or EURACHEM/CITAC 2000 [18, 20]. These results are sorted according to the E_n-numbers.
Located at the end of Annex 1 is a selection of methylmercury graphs.
Graphs concerning the water content determination and the correction for dry-mass can be found in Annex 2 of this report.

Acknowledgements

We acknowledge very much the efforts of S. Caroli from CRL-ISS and P. van Houwelingen from DG Enlargement to establish the contact between the IRMM and the network of NRLs from member states and acceding countries. Furthermore we thank N. Meuree-Vanlaethem for the excellent co-operation in nominating EA laboratories.
Special thanks also to B. Gawlik from the JRC-IES for his support in finding the suitable tuna fish sample for this IMEP® interlaboratory comparison and to all the scientists who contributed to the reprocessing of the sample and the establishment of the IMEP-20 certified reference values: -
J. Snell, P. Robouch, K.-H. Grobecker, M. Bickel, F. Ulberth, S. Yazgan, P. Conneely, G. Kramer from IRMM, P. Vermaercke from the SCK. The authors would also like to express their gratitude to J. Norgaard and R. Kessel for their support to the online reporting system.

Table 8: IMEP-20 graphs

General Graphs	**Prepared for all elements As, Hg, Pb and Se**
All participants	✓
Analytical techniques	✓
Regional Graphs	**Prepared for all elements As, Hg, Pb and Se**
EU Countries	✓
EU Candidate Countries	✓
EU Countries Vs. EU Candidate Countries	✓
Quality Management System Graphs	**Prepared for all elements As, Hg, Pb and Se**
ISO 17025 Vs. other	✓
Questionnaire Graphs	**Prepared for all elements As, Hg, Pb and Se**
According to experience	✓
Number of samples analysed	✓
Time spent on measurement	✓
Calibration Strategy	✓
Use of CRMs	✓
Participation in PTs	✓
Accredited - Authorised	✓
Report uncertainties to customers	✓
Calculate uncertainties to guidelines	✓
Measurement Performance Graphs	**Prepared for all elements As, Hg, Pb and Se**
Estimated uncertainty according to ISO 1995	✓
Methylmercury Graphs	**MeHg (CH_3Hg)**
All participants	✓
Analytical techniques	✓
According to experience	✓
Number of samples analysed	✓
Time spent on measurement	✓
Calibration Strategy	✓
Use of CRMs	✓
Participation in PTs	✓
Accredited - Authorised	✓
Report uncertainties to customers	✓
Calculate uncertainties to guidelines	✓
Estimated uncertainty according to ISO 1995	✓

List of abbreviations

BELAC	Belgium Accreditation
BIPM	Bureau International des Poids et Mesures (Paris, France)
CCQM	Comité Consultatif pour la Quantité de Matière
CIPM	International Committee for Weights and Measure
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRL-ISS	Istituto Superiore di Sanità, (Rome)
CRMs	Certified Reference Materials
CTS	Certified Test Samples
EA	European Co-operation for Accreditation
EC	European Commission
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
GC-ICP-MS	Gas Chromatography Isotope Dilution Inductively Coupled Plasma Mass Spectrometry
GUM	Guide for expression for Uncertainty in Measurement
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
IDMS	Isotope Dilution Mass Spectrometry
IMEP®	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements (EC, Geel, Belgium)
ISO	International Organisation for Standardisation
JRC	Joint Research Centre
MRA	Mutual Recognition Agreement
NAA	Neutron Activation Analysis
NABs	National Accreditation Bodies
NMIs	National Metrology Institutes
NRLs	National Reference Laboratories
PMM	Primary Method of Measurement
PTs	Proficiency Testing Schemes
RCs	Regional Co-ordinators
SCF	Scientific Committee on Food
SS-ZAAS	Solid Sample Zeemann Atomic Absorption Spectrometry

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Annex 1 – Graphical presentation

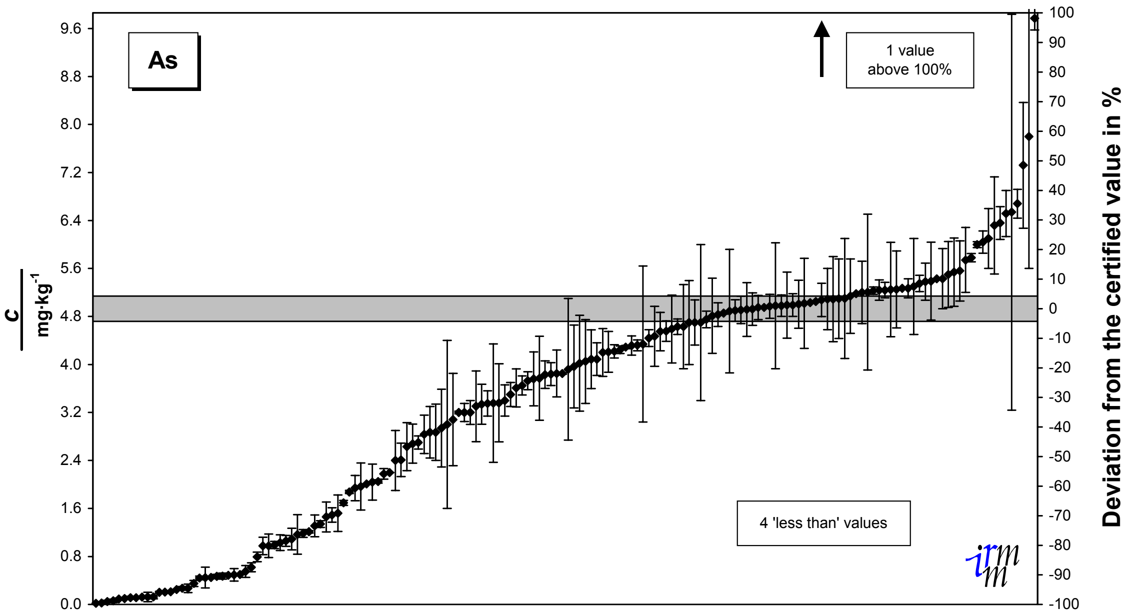
Contents

IMEP-20: Trace Elements in Tuna Fish

Annex 1 – Participants results – General Graphs

Figure 1

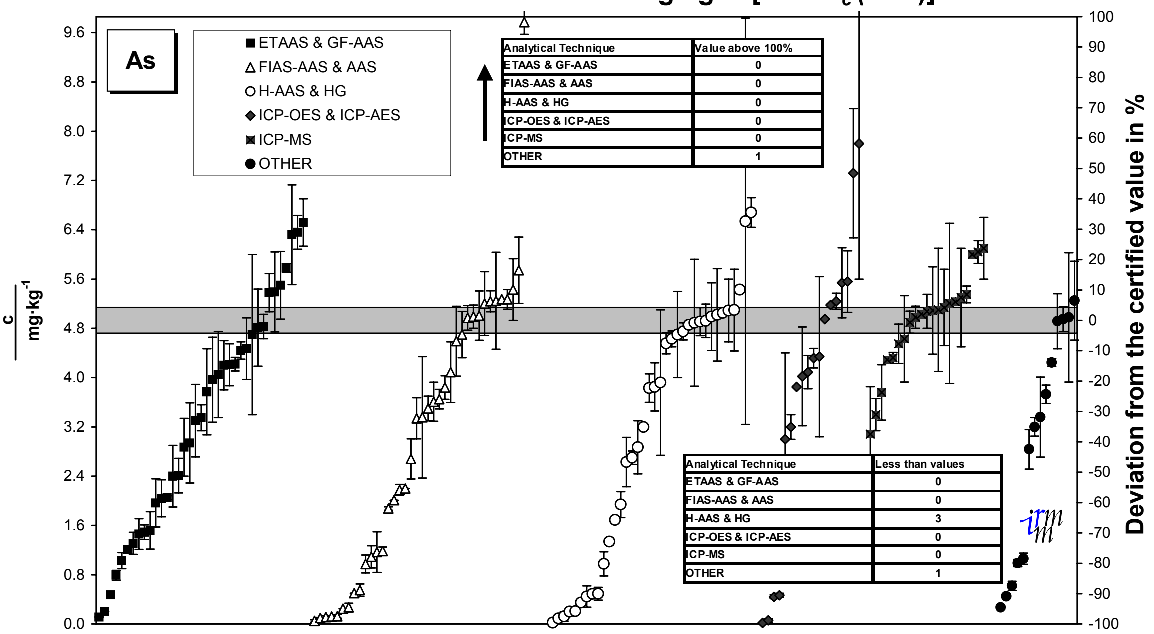
IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.93 ± 0.21 mg·kg^{-1} [U=k·u_c (k=2)]



Results from all participants

Figure 2

IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.93 ± 0.21 mg·kg^{-1} [U=k·u_c (k=2)]



Results from all participants according to analytical techniques used.

Figure 3

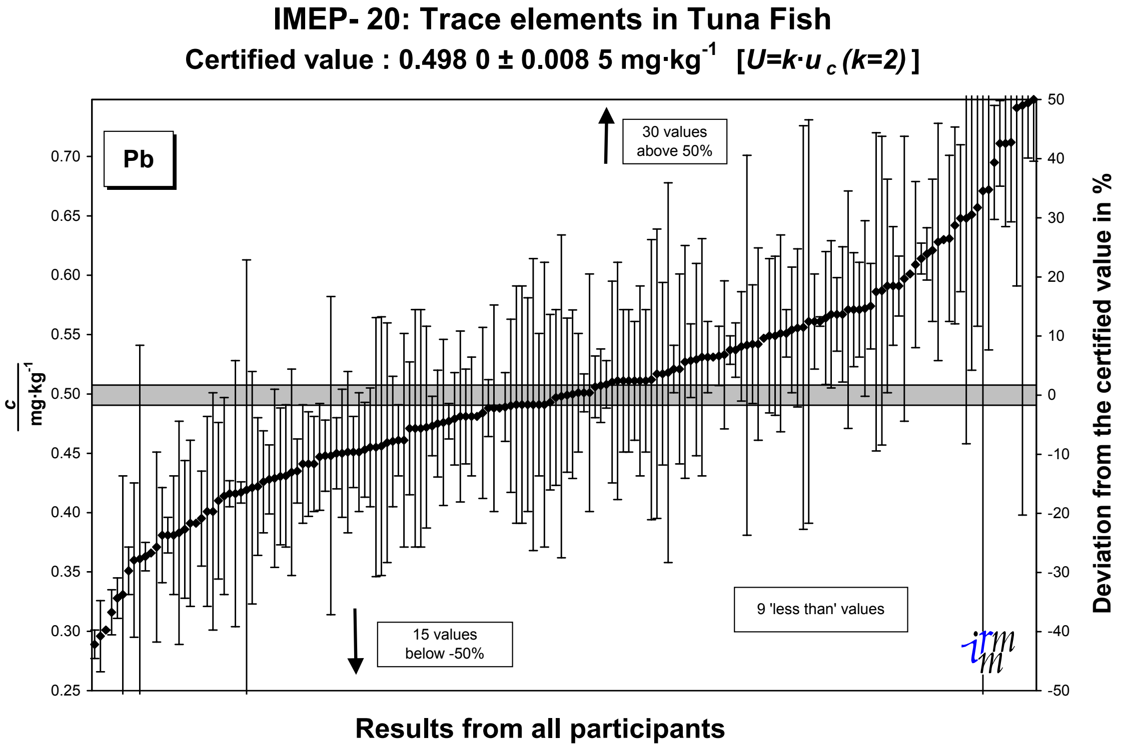


Figure 4

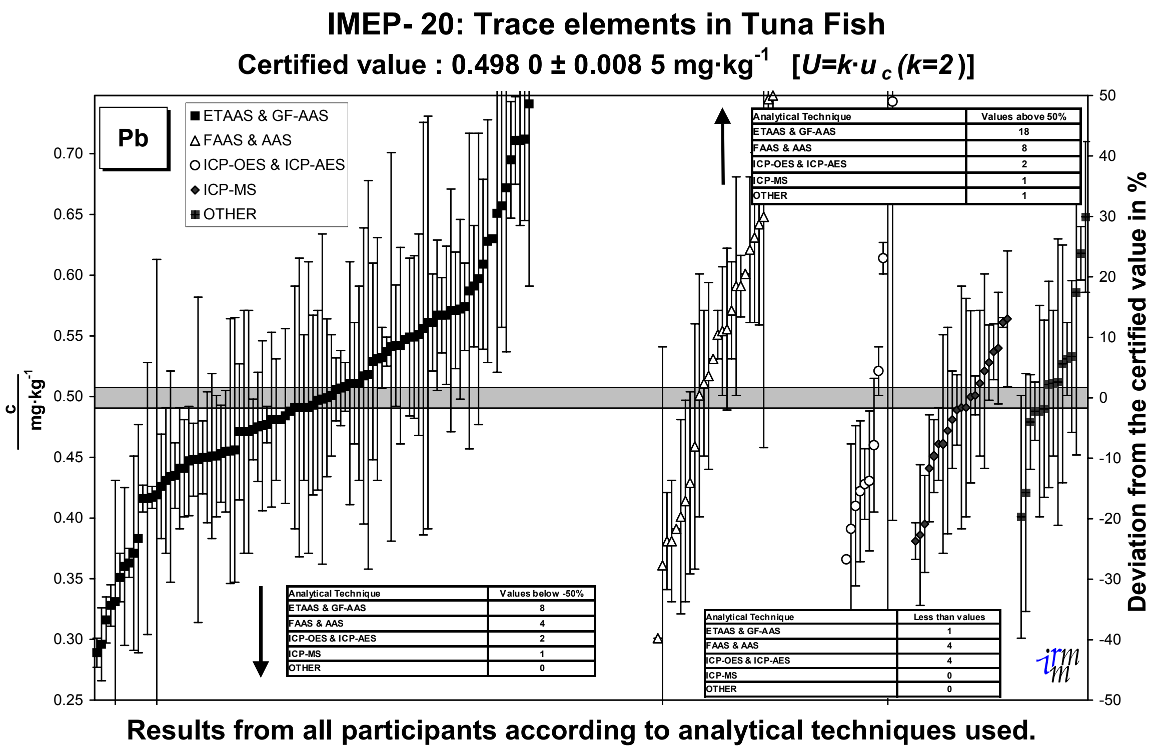
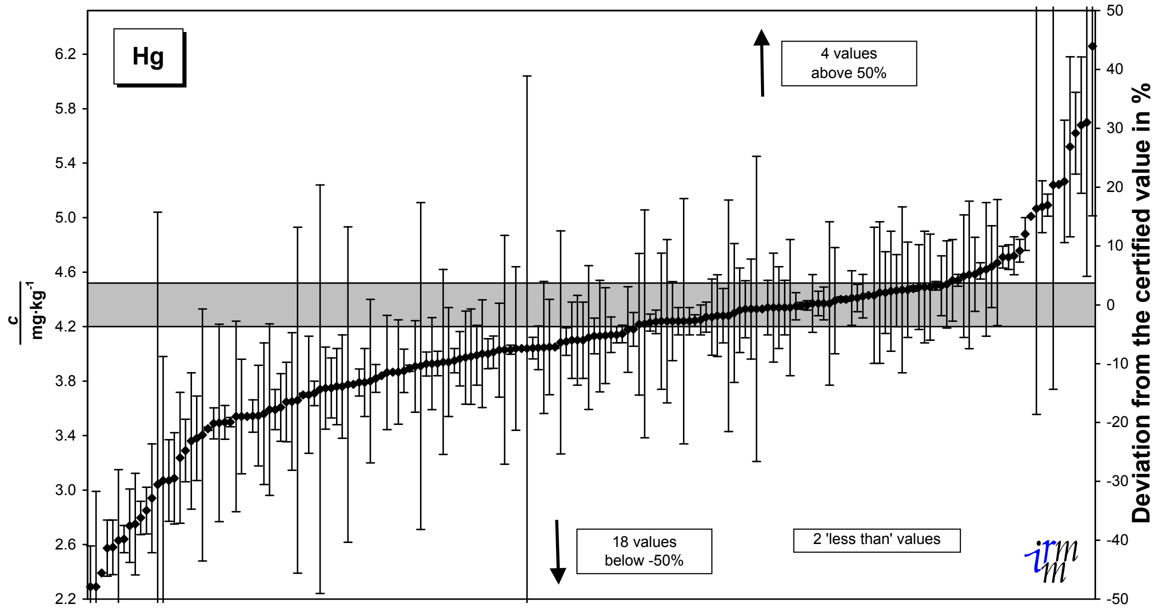


Figure 5

IMEP- 20: Trace elements in Tuna Fish

Certified value : 4.32 ± 0.16 mg·kg^{-1} [$U=k \cdot u_c$ (k=2)]

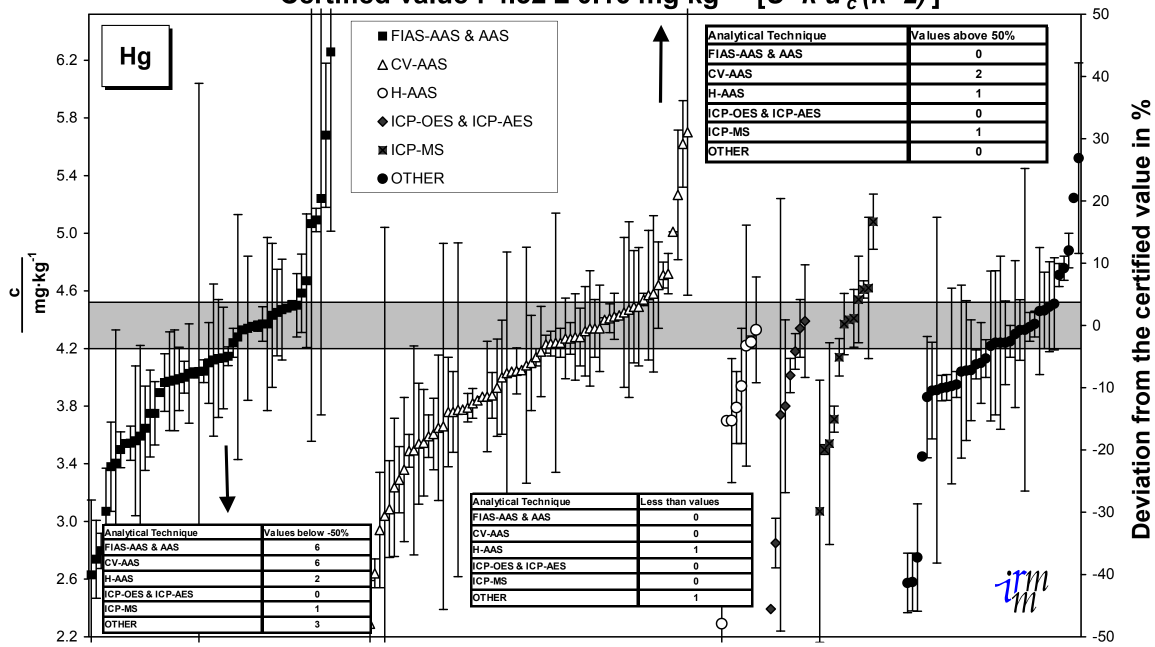


Results from all participants

Figure 6

IMEP- 20: Trace elements in Tuna Fish

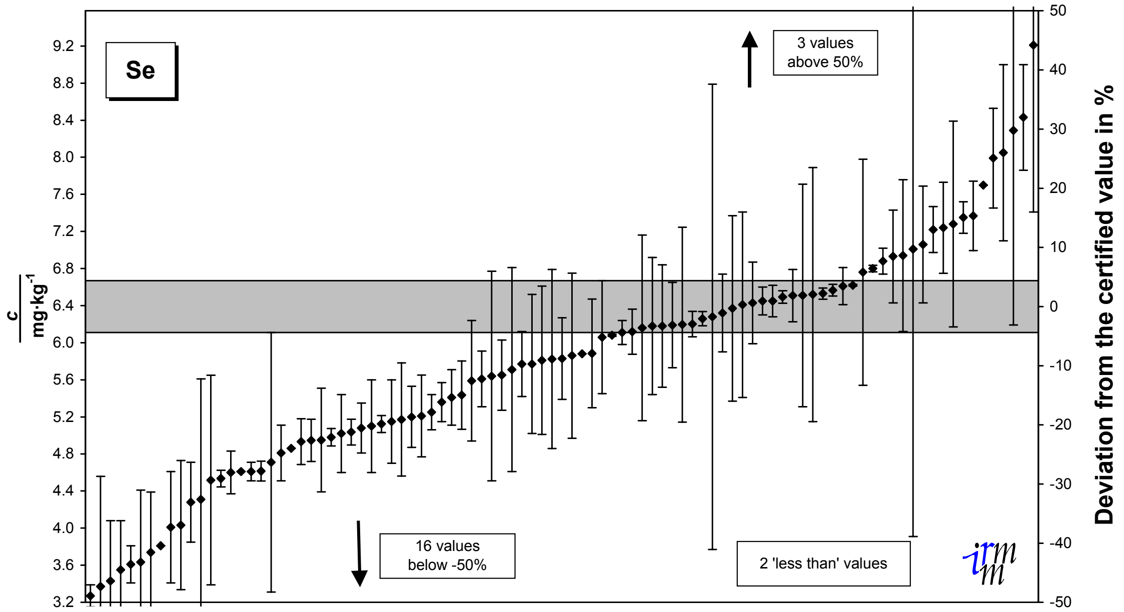
Certified value : 4.32 ± 0.16 mg·kg^{-1} [$U=k \cdot u_c$ (k=2)]



Results from all participants according to analytical techniques used.

Figure 7

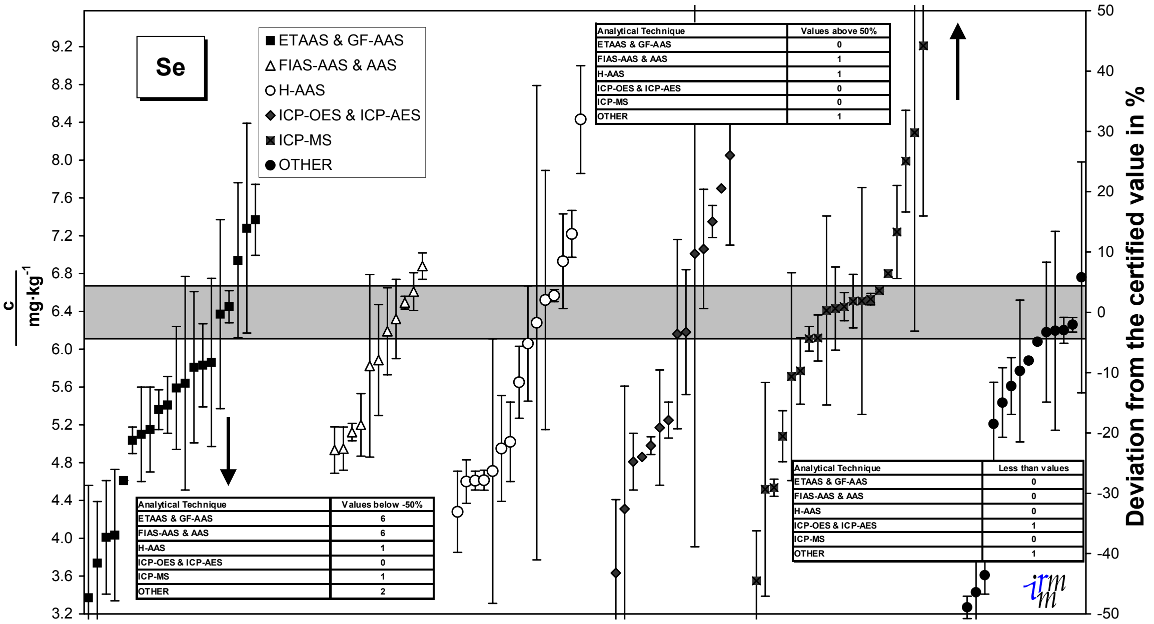
IMEP- 20: Trace elements in Tuna Fish
Certified value : 6.38 ± 0.28 mg·kg^{-1} [$U=k \cdot u_c$ (k=2)]



Results from all participants

Figure 8

IMEP- 20: Trace elements in Tuna Fish
Certified value : 6.38 ± 0.28 mg·kg^{-1} [$U=k \cdot u_c$ (k=2)]

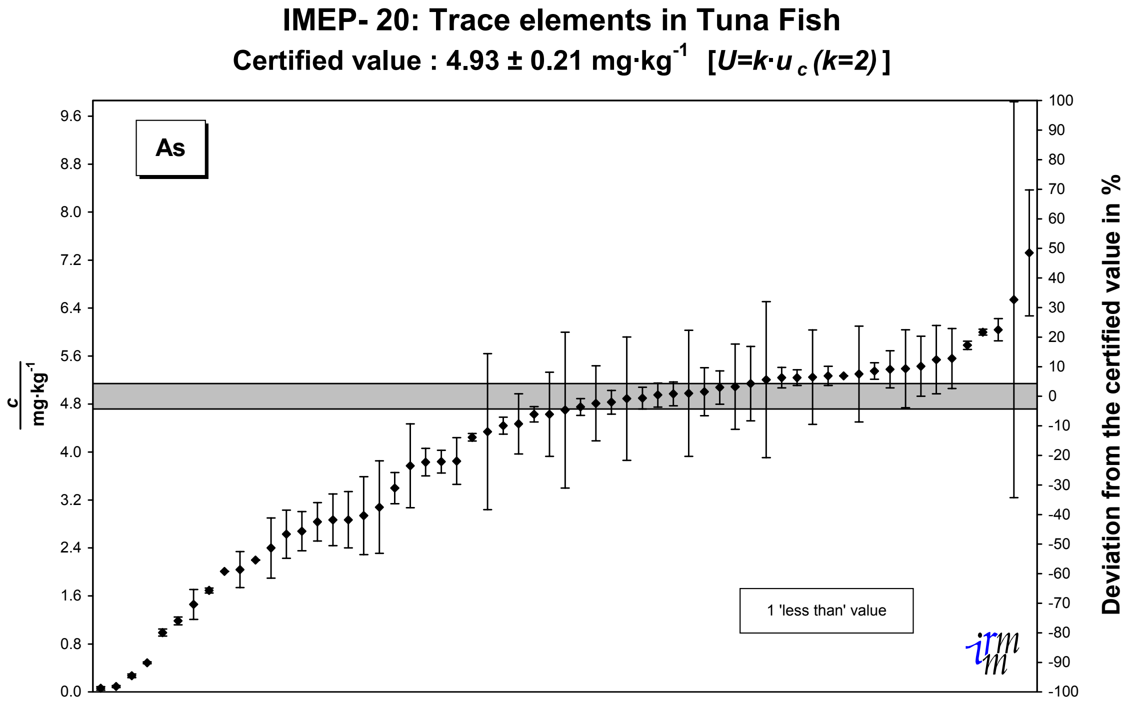


Results from all participants according to analytical techniques used.

IMEP-20: Trace Elements in Tuna Fish

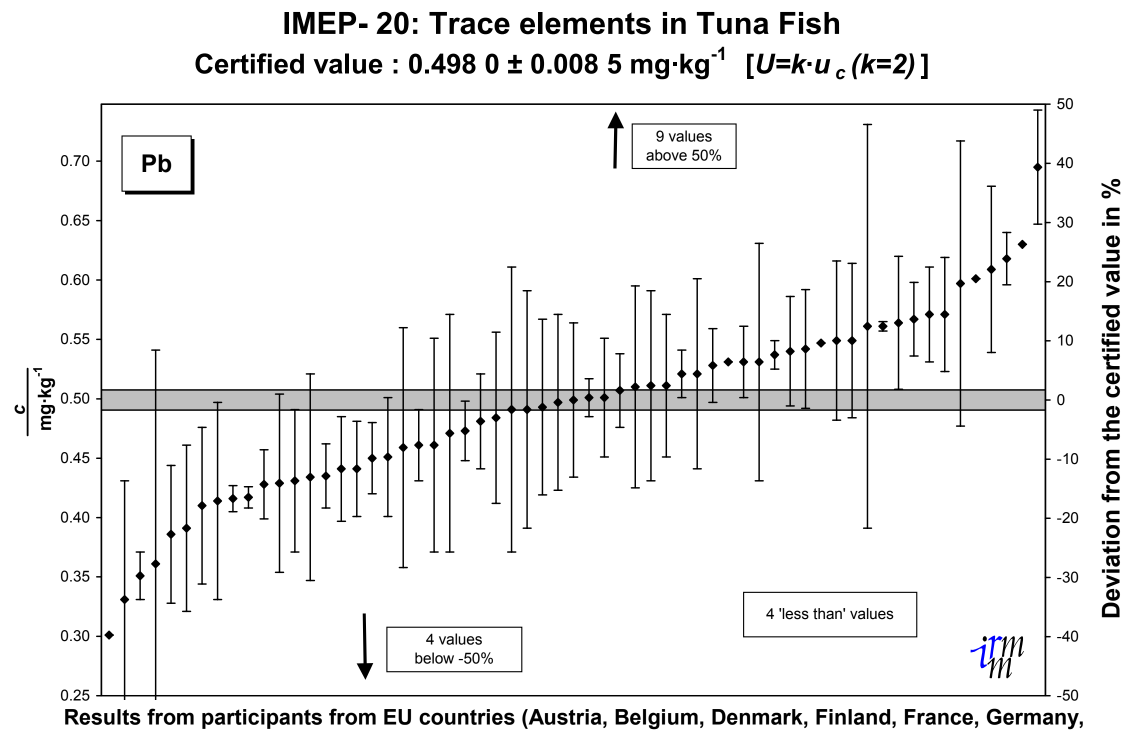
Annex 1 – Participants results – Regional Graphs

Figure 9



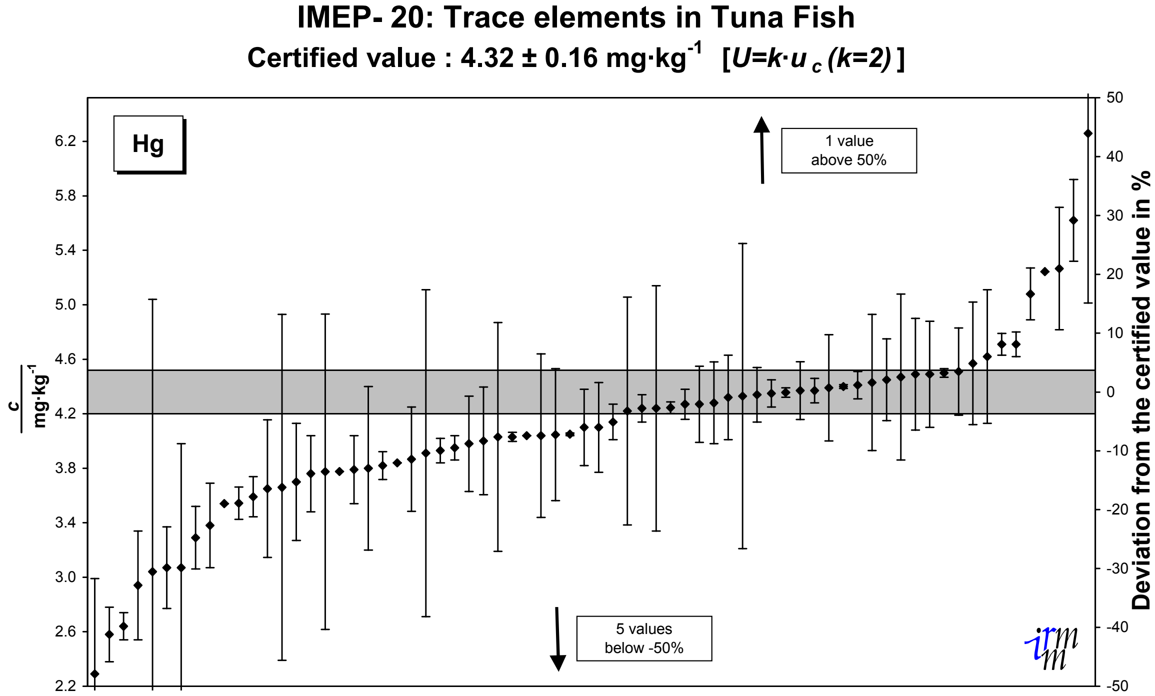
Results from participants from EU countries (Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Portugal, Spain, Sweden, The Netherlands and United Kingdom).

Figure 10



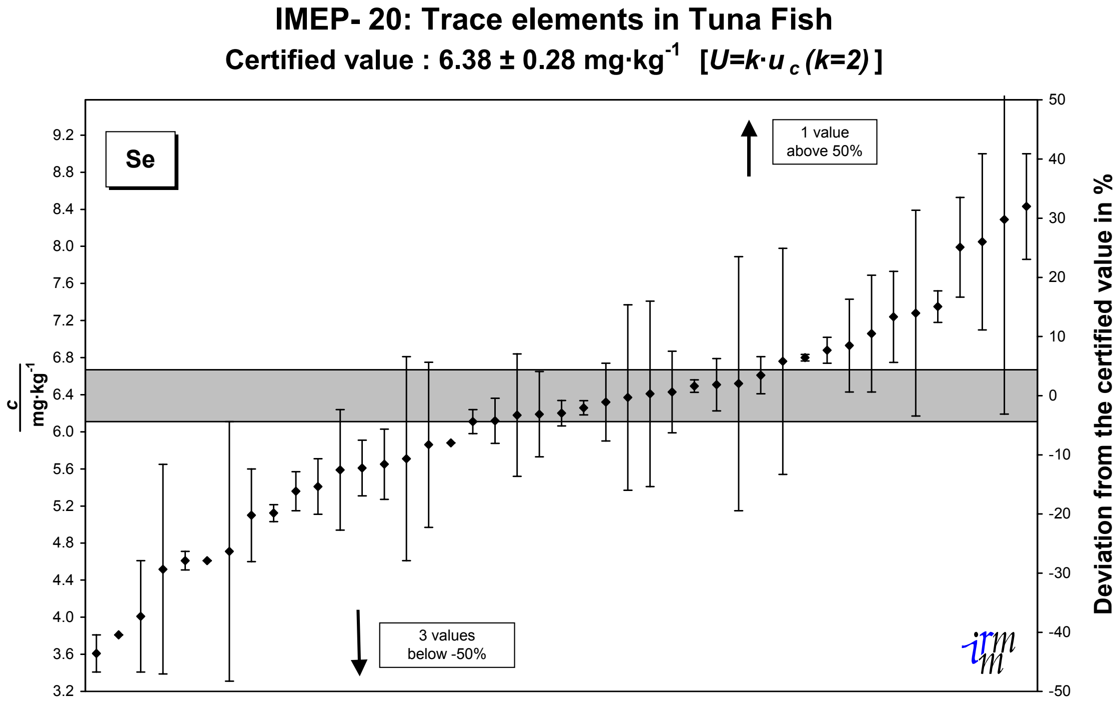
Results from participants from EU countries (Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Portugal, Spain, Sweden, The Netherlands and United Kingdom).

Figure 11



Results from participants from EU countries (Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Portugal, Spain, Sweden, The Netherlands and United Kingdom).

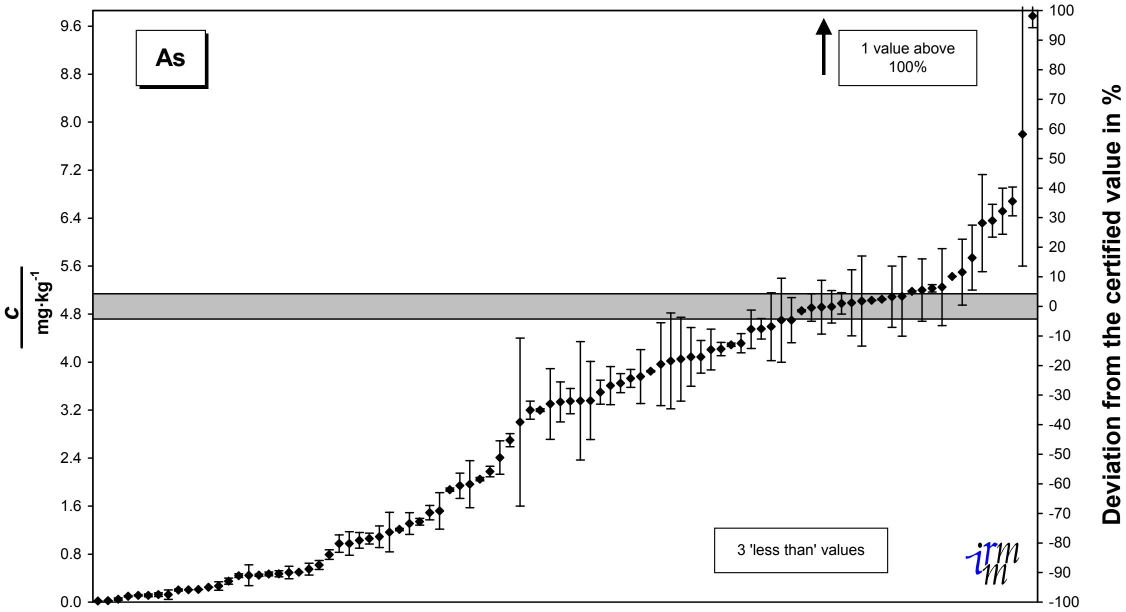
Figure 12



Results from participants from EU countries (Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, Portugal, Spain, Sweden, The Netherlands and United Kingdom).

Figure 13

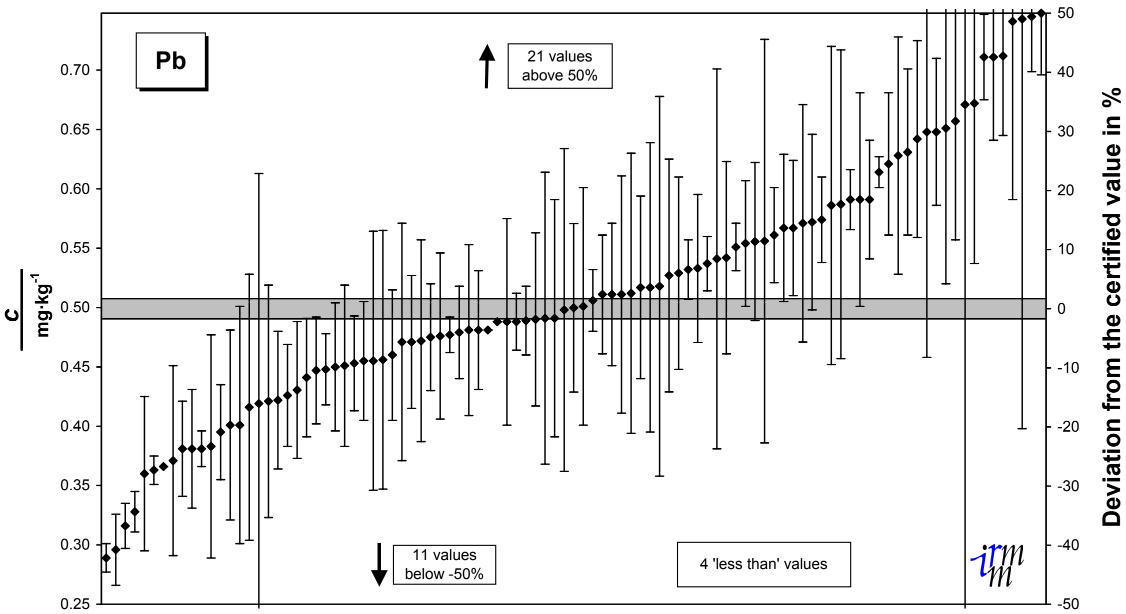
IMEP- 20: Trace elements in Tuna Fish
Certified value 4.93 ± 0.21 mg·kg^{-1} [$U=k \cdot u_c$ $(k=2)$]



Results from EU candidate countries (Bulgaria, Cyprus, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Romania, Slovakia, Slovenia and Turkey).

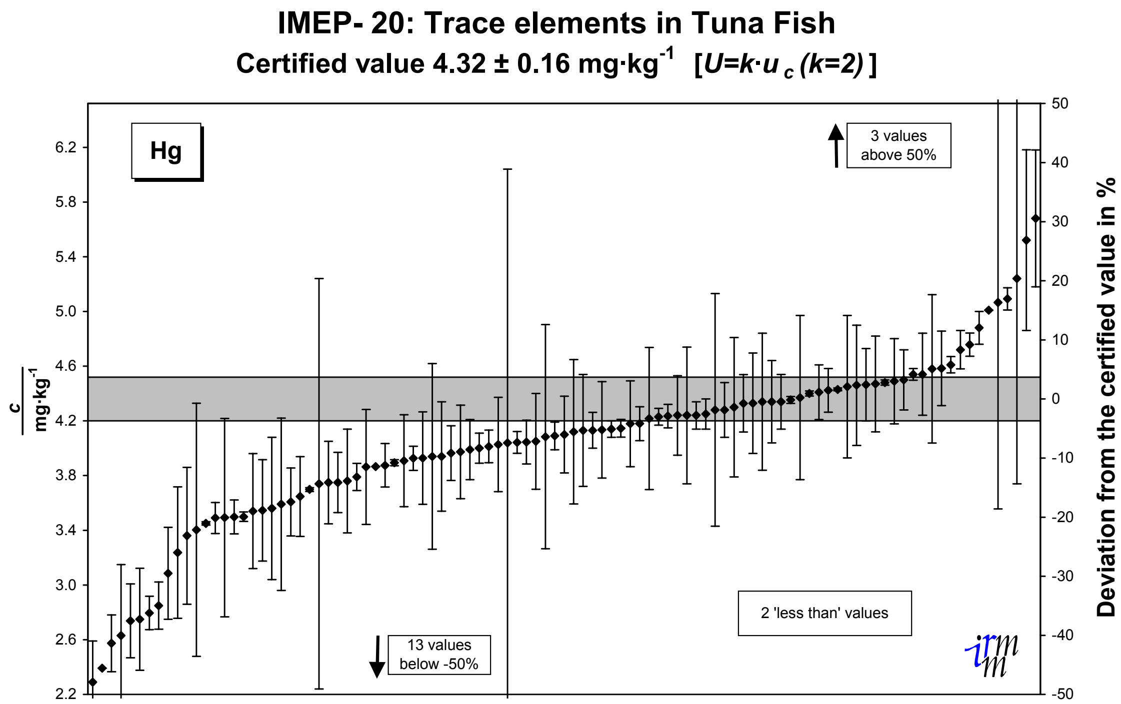
Figure 14

IMEP- 20: Trace elements in Tuna Fish
Certified value 0.498 0 ± 0.008 5 mg·kg^{-1} [$U=k \cdot u_c$ $(k=2)$]



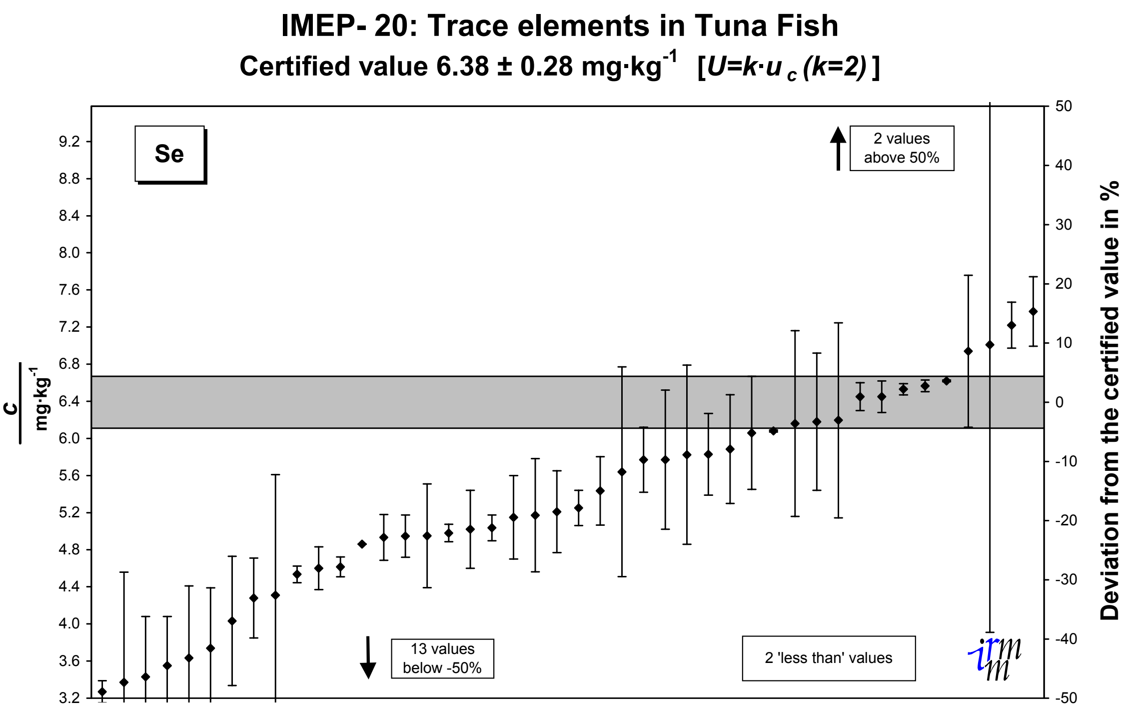
Results from EU candidate countries (Bulgaria, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Romania, Slovakia, Slovenia and Turkey).

Figure 15



Results from EU candidate countries (Bulgaria, Cyprus, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Romania, Slovakia, Slovenia and Turkey).

Figure 16



Results from EU candidate countries (Bulgaria, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Poland, Romania, Slovakia, Slovenia and Turkey).

Figure 17

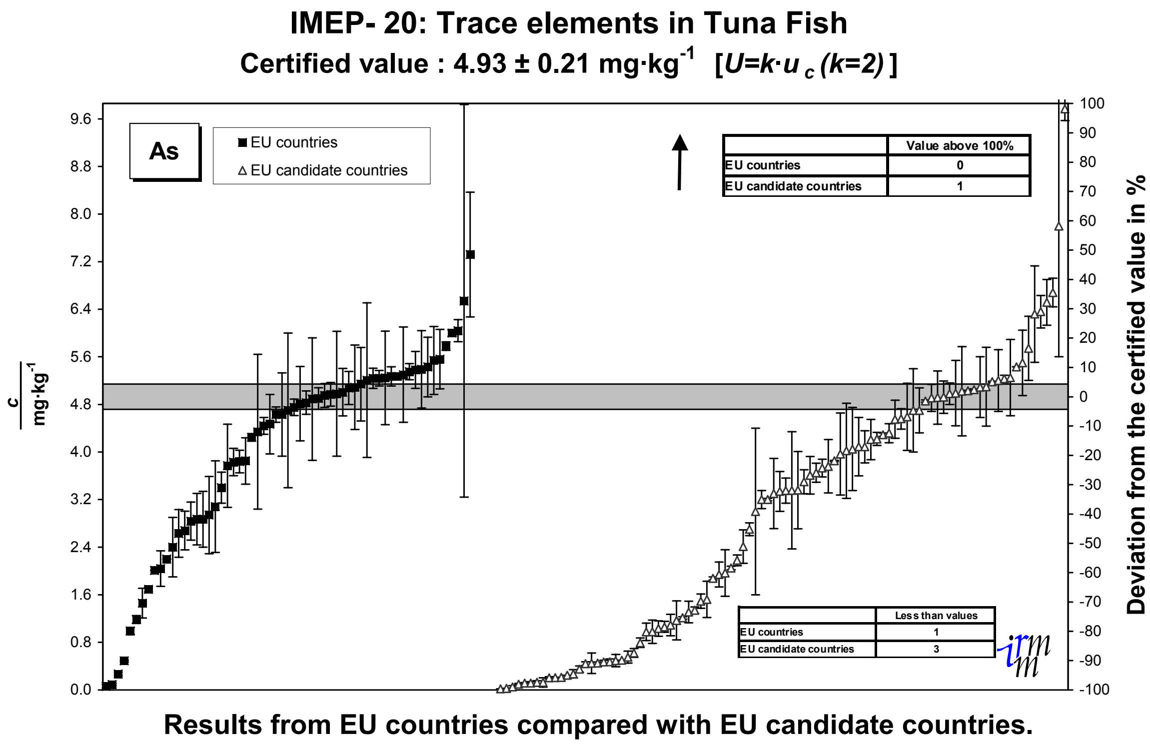


Figure 18

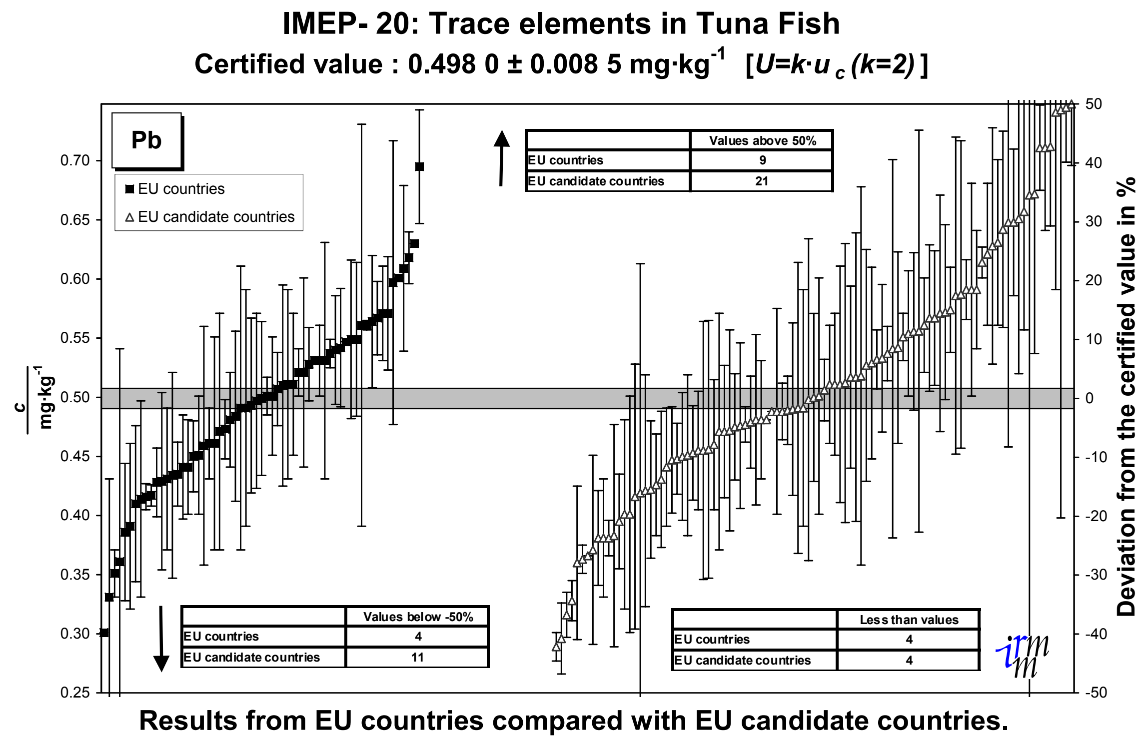
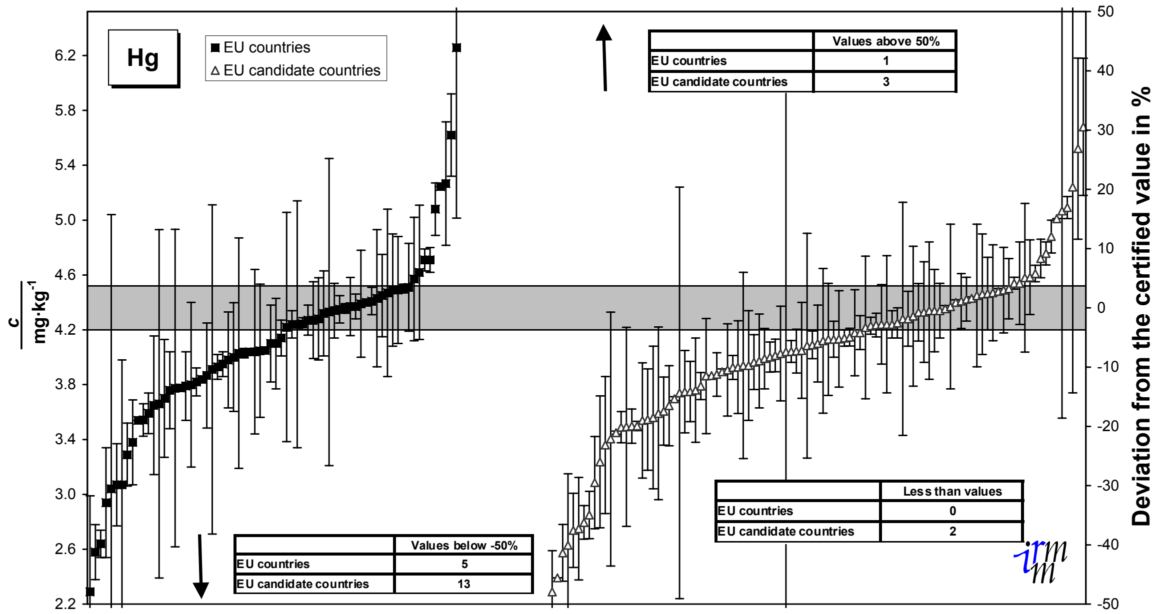


Figure 19

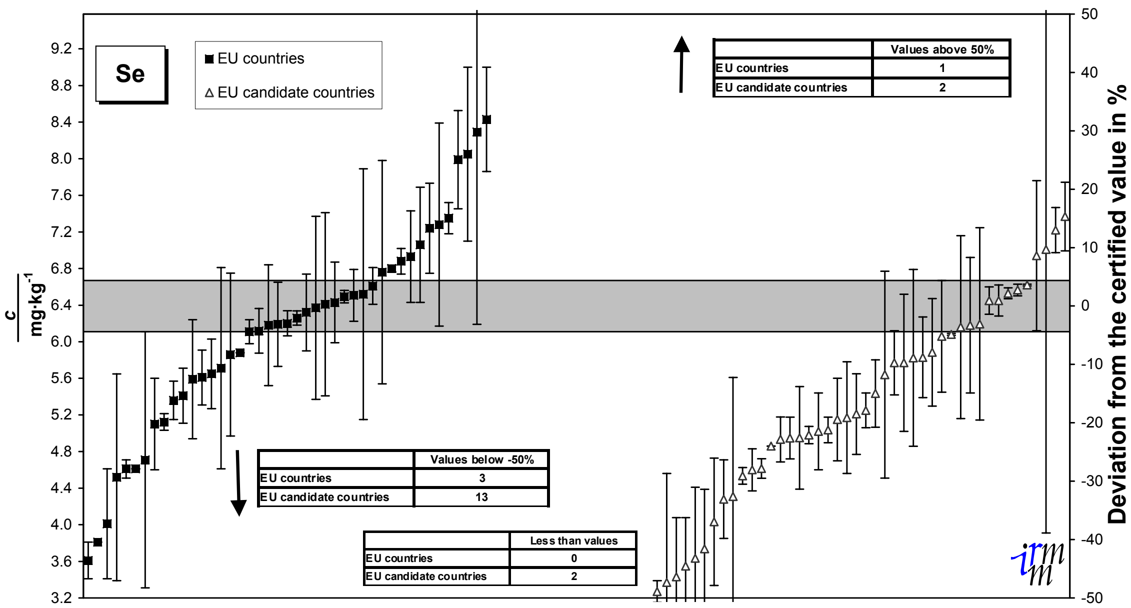
IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.32 ± 0.16 mg·kg^{-1} [$U=k \cdot u_c\,(k=2)$]



Results from EU countries compared with EU candidate countries.

Figure 20

IMEP- 20: Trace elements in Tuna Fish
Certified value : 6.38 ± 0.28 mg·kg^{-1} [$U=k \cdot u_c\,(k=2)$]



Results from EU countries compared with EU candidate countries.

IMEP-20: Trace Elements in Tuna Fish

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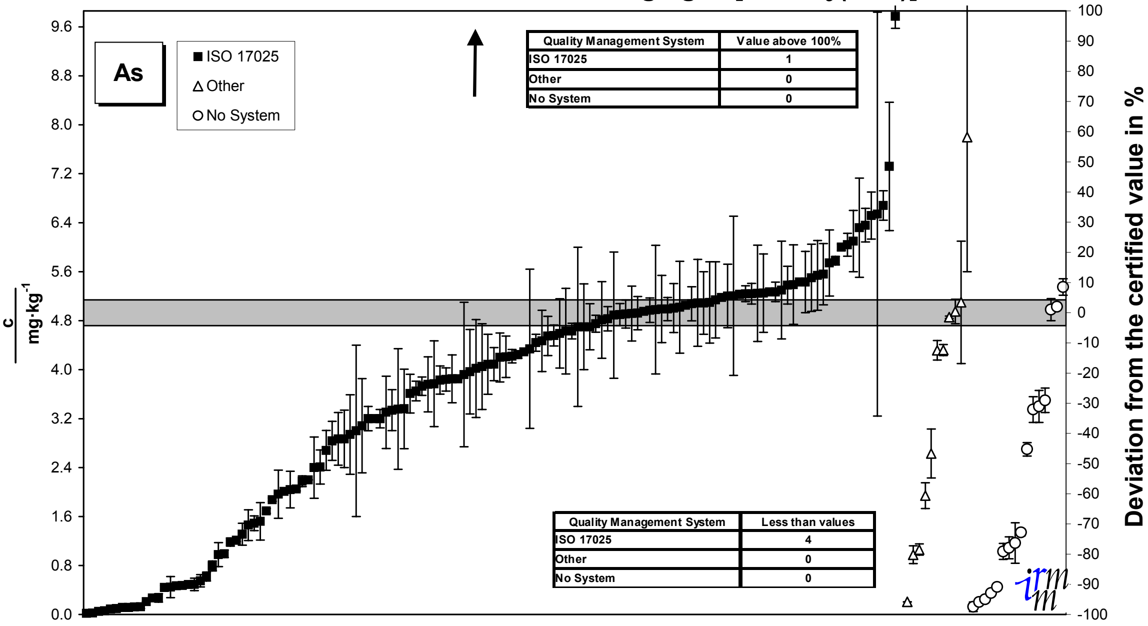
Figure 21

IMEP- 20: Trace elements in Tuna Fish

Certified value : 4.93 ± 0.21 mg·kg^{-1} [*U=k·u$_c$(k=2)*]

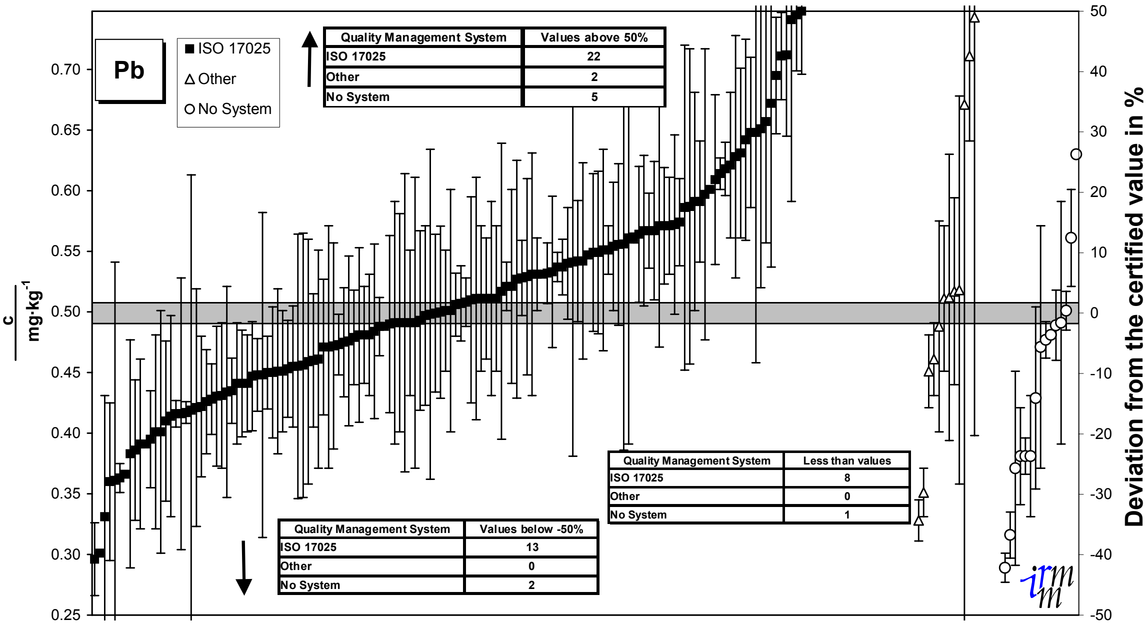


Results from all participants according to the Quality Management System.

Figure 22

IMEP- 20: Trace elements in Tuna Fish

Certified value : 0.498 0 ± 0.008 5 mg·kg^{-1} [*U=k·u$_c$(k=2)*]

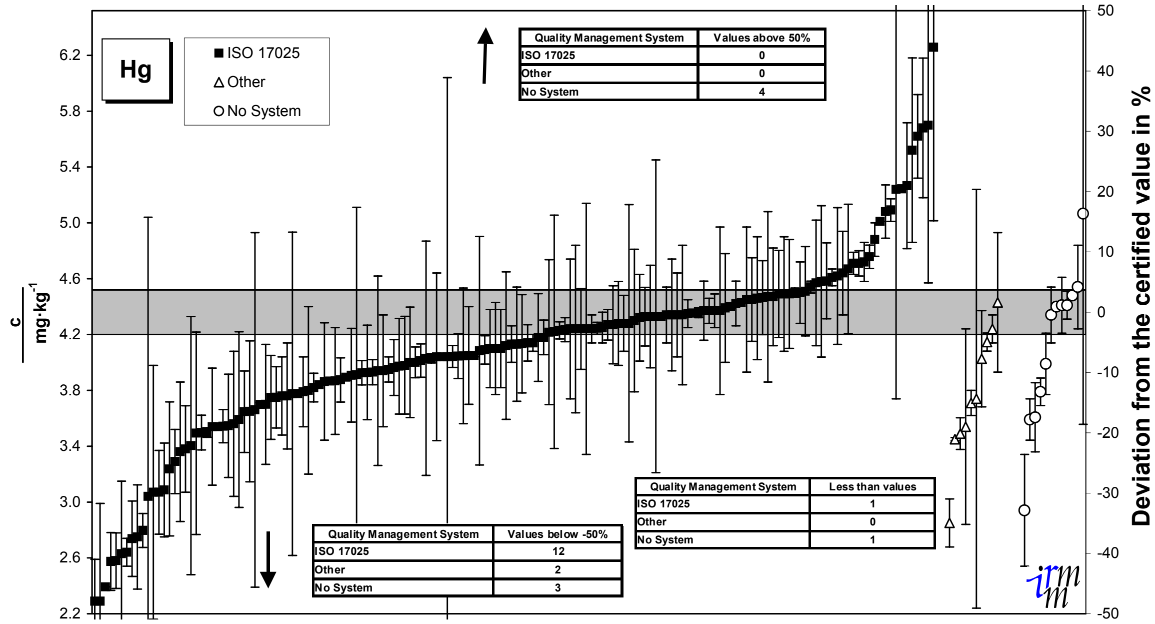


Results from all participants according to the Quality Management System.

Figure 23

IMEP- 20: Trace elements in Tuna Fish

Certified value : 4.32 ± 0.16 mg·kg^{-1} [$U=k\cdot u_c\,(k=2)$]

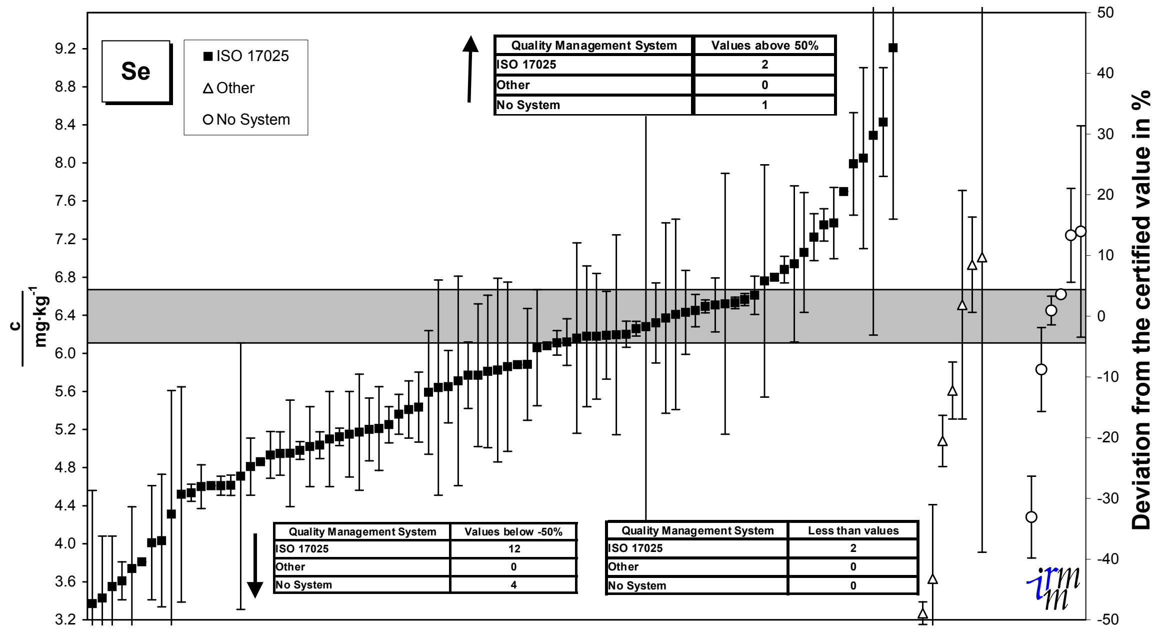


Results from all participants according to the Quality Management System.

Figure 24

IMEP- 20: Trace elements in Tuna Fish

Certified value : 6.38 ± 0.28 mg·kg^{-1} [$U=k\cdot u_c\,(k=2)$]



Results from all participants according to the Quality Management System.

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Figure 25

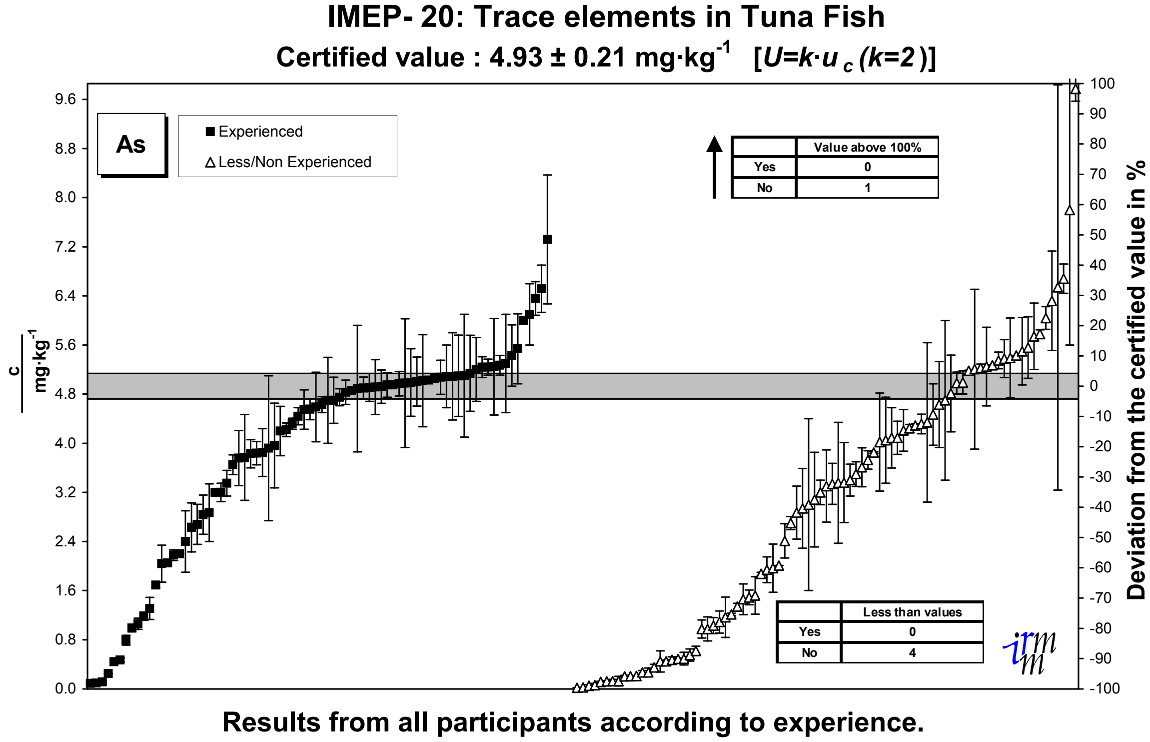


Figure 26

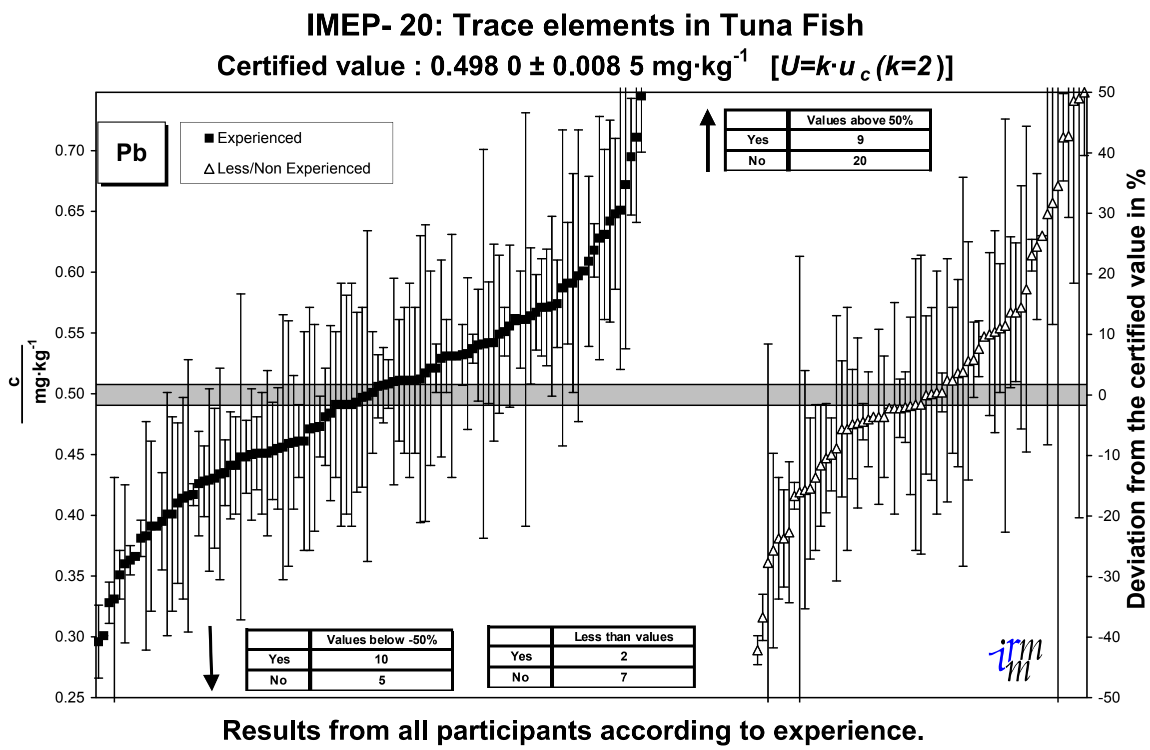
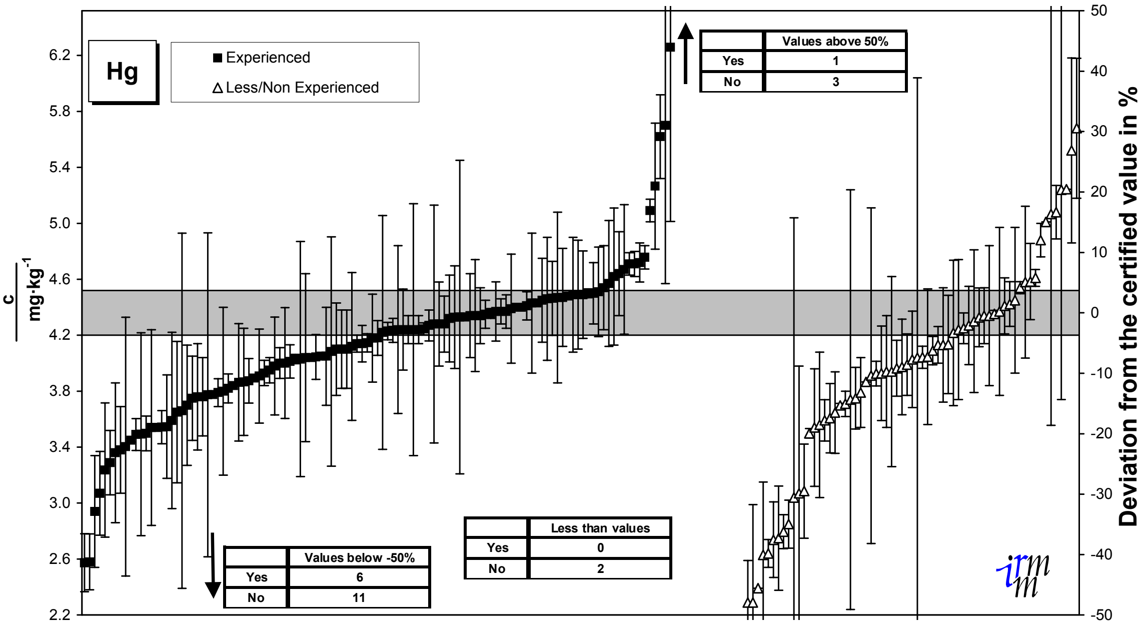


Figure 27

IMEP- 20: Trace elements in Tuna Fish

Certified value : 4.32 ± 0.16 mg·kg^{-1} [$U=k \cdot u_c (k=2)$]

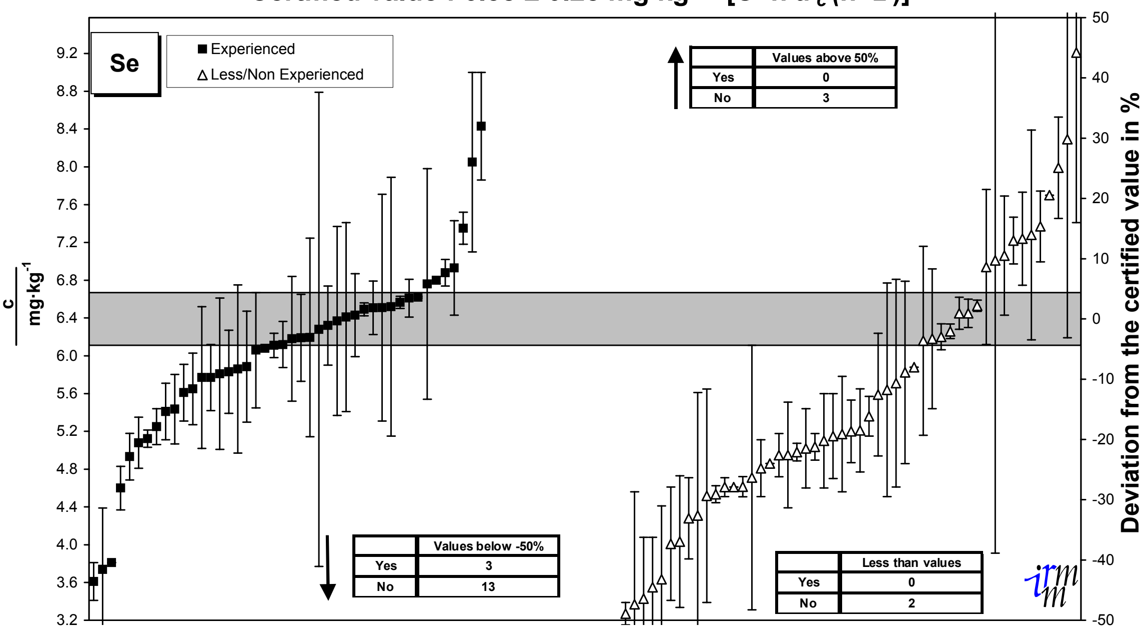


Results from all participants according to experience.

Figure 28

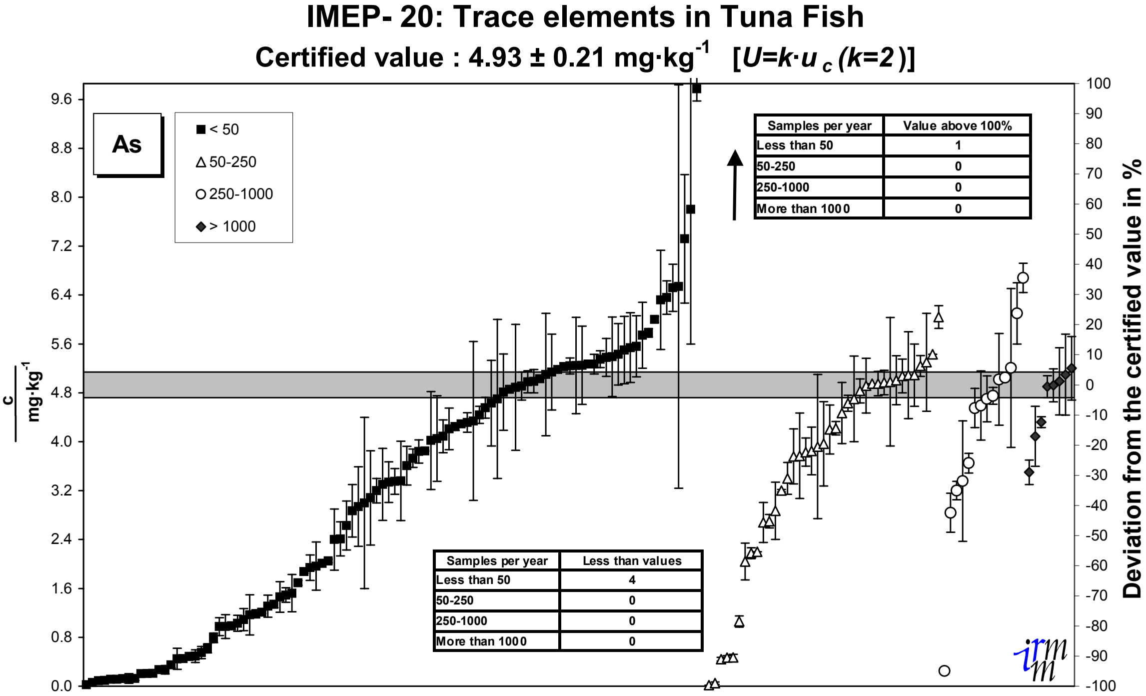
IMEP- 20: Trace elements in Tuna Fish

Certified value : 6.38 ± 0.28 mg·kg^{-1} [$U=k \cdot u_c (k=2)$]



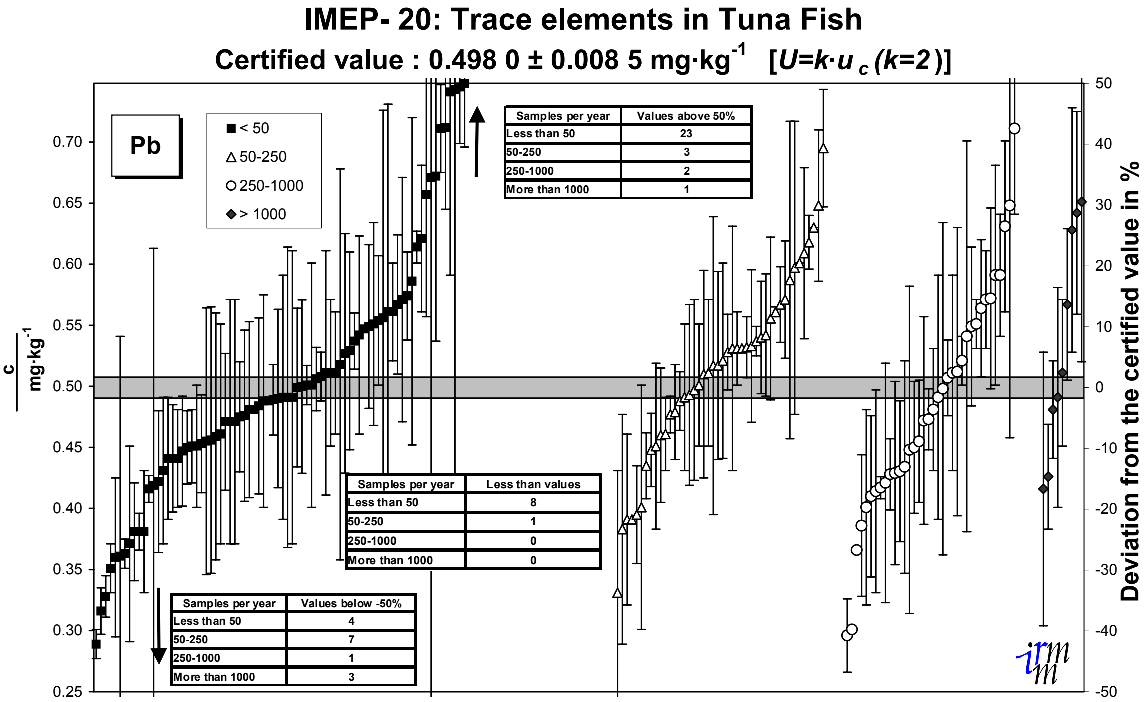
Results from all participants according to experience.

Figure 29



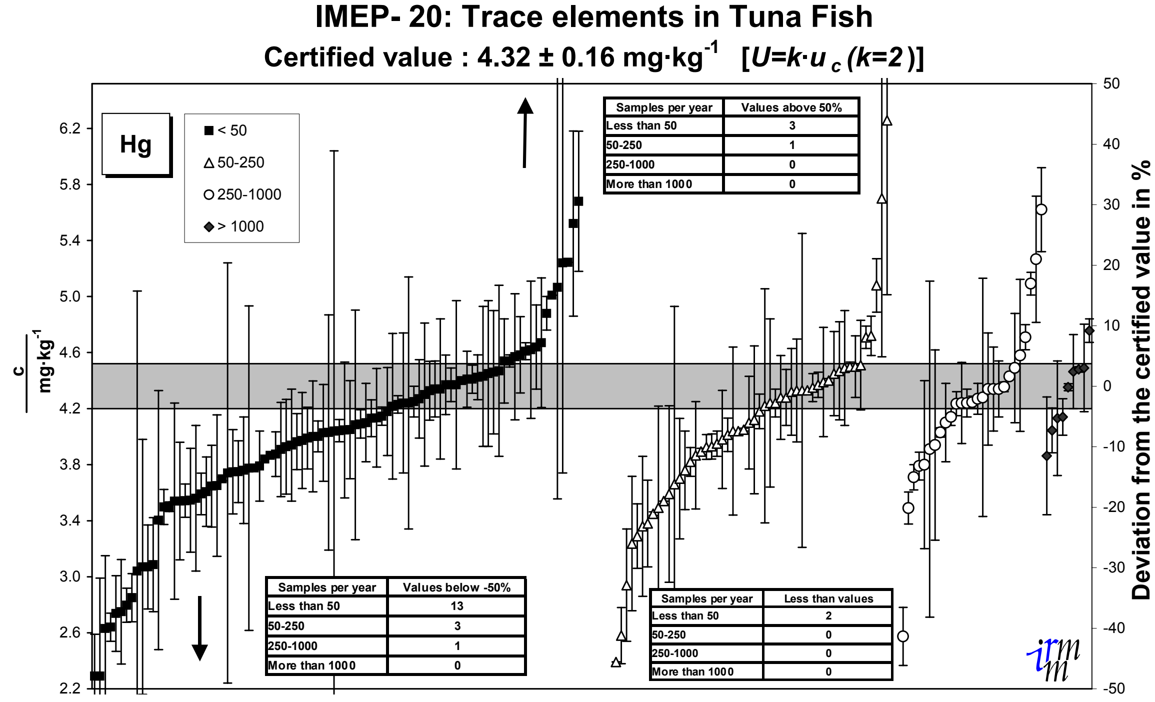
Results from all participants according to how many samples analysed per year.

Figure 30



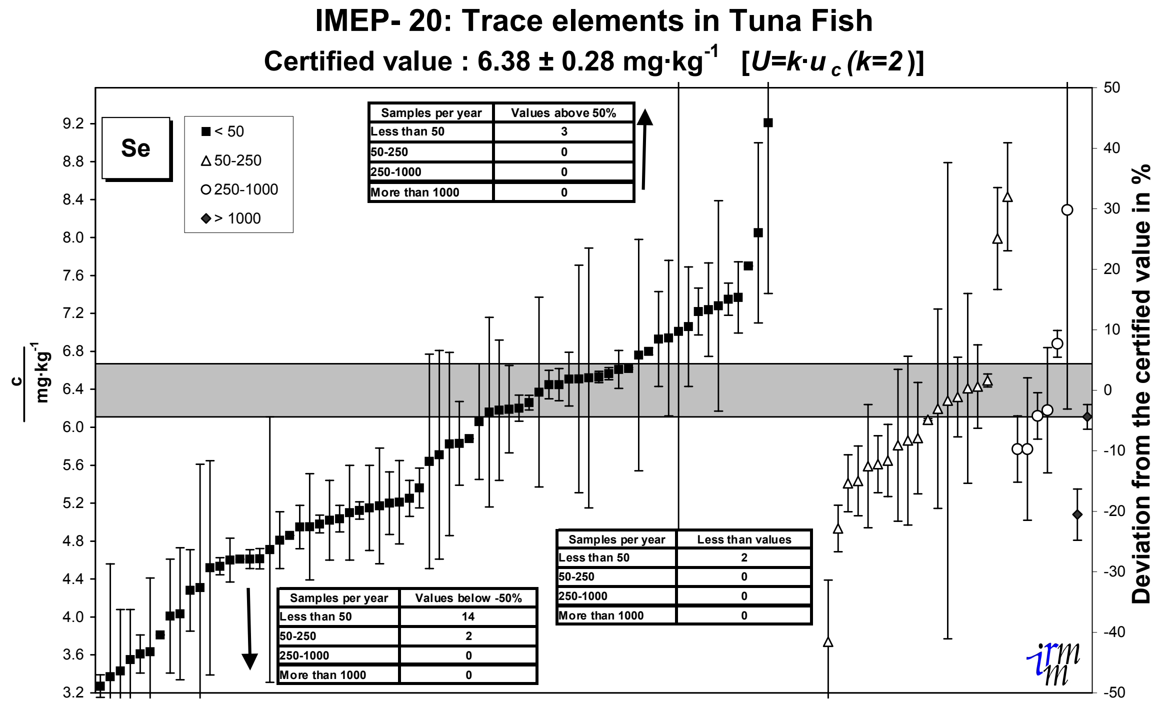
Results from all participants according to how many samples analysed per year.

Figure 31



Results from all participants according to how many samples analysed per year.

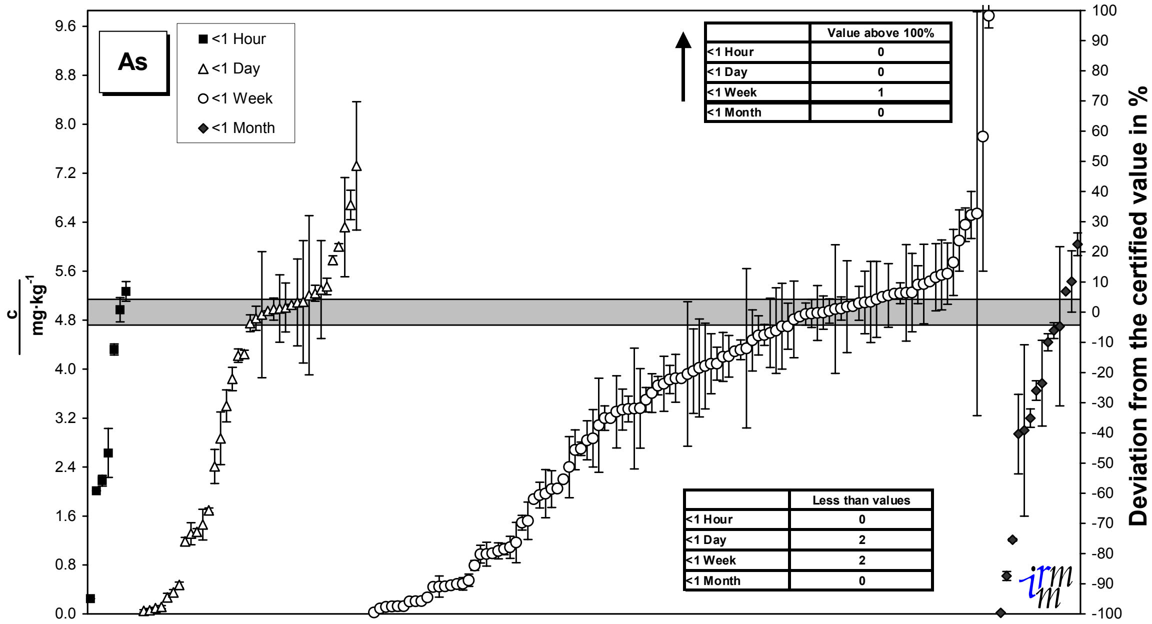
Figure 32



Results from all participants according to how many samples analysed per year.

Figure 33

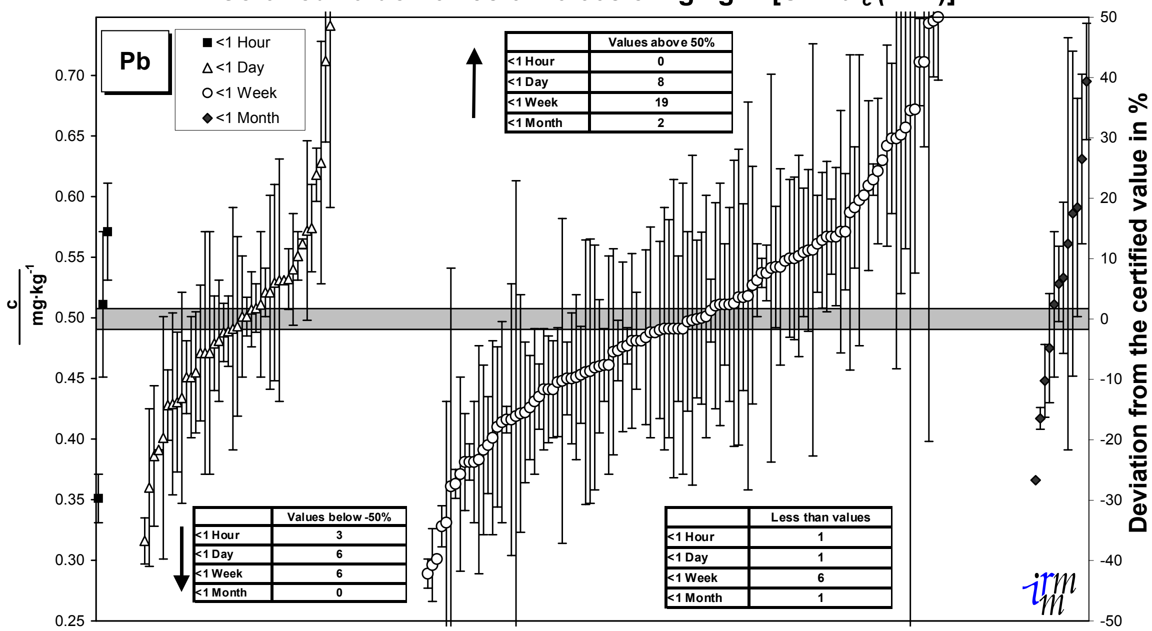
IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.93 ± 0.21 mg·kg-1 [U=k·u c (k=2)]



Results from all participants according to the time spent on the measurement.

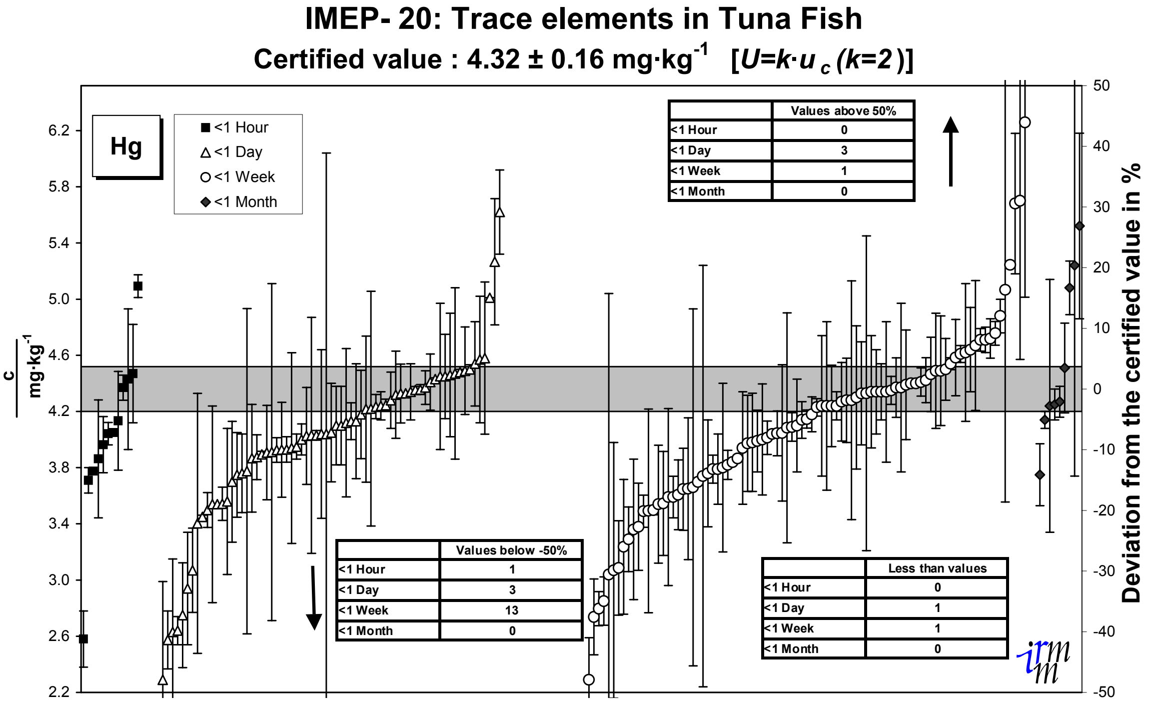
Figure 34

IMEP- 20: Trace elements in Tuna Fish
Certified value : 0.498 0 ± 0.008 5 mg·kg-1 [U=k·u c (k=2)]



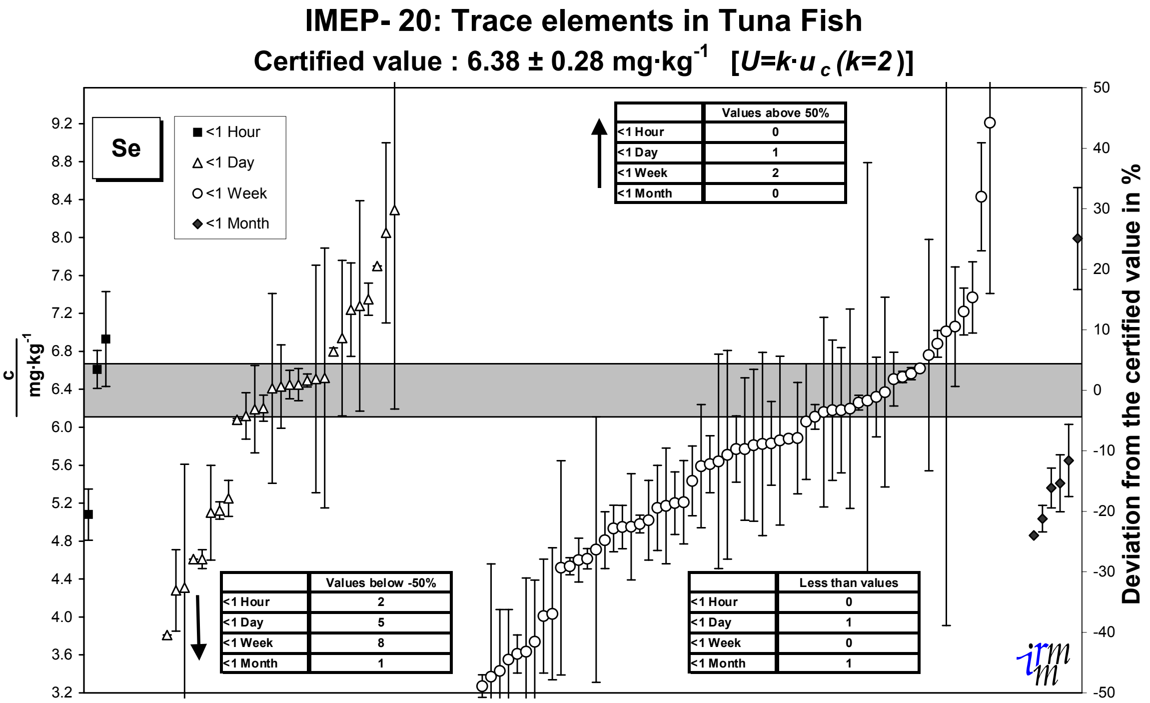
Results from all participants according to the time spent on the measurement.

Figure 35



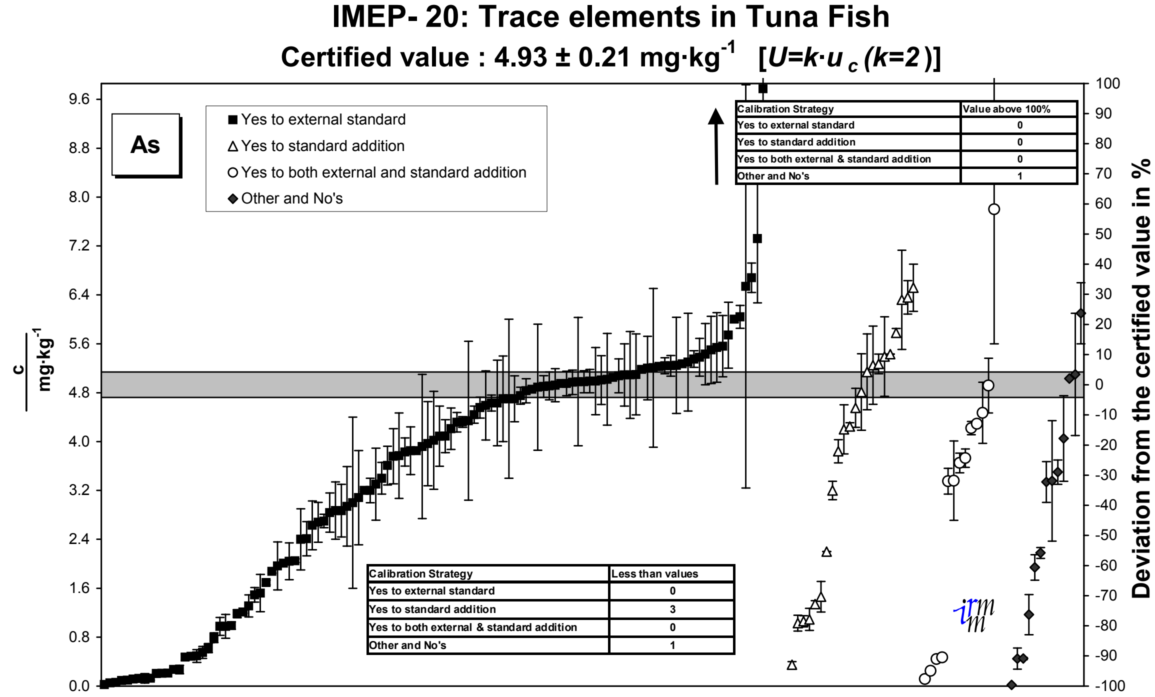
Results from all participants according to the time spent on the measurement.

Figure 36



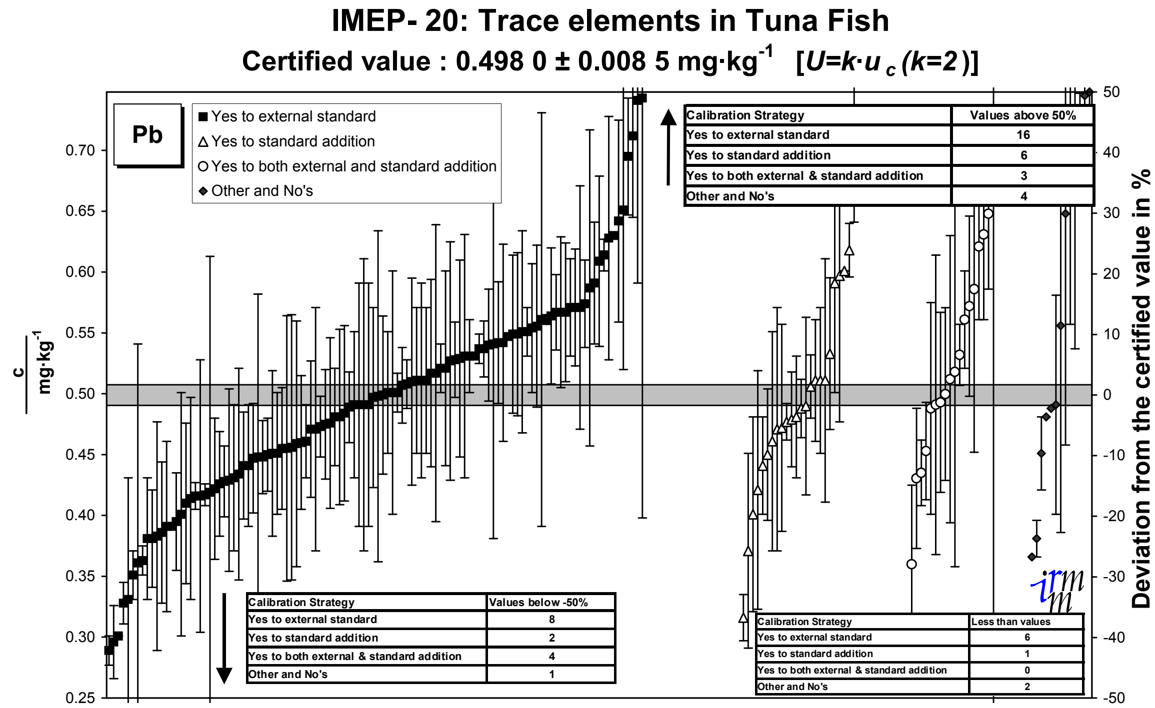
Results from all participants according to the time spent on the measurement.

Figure 37



Results from all participants according to Calibration Strategy.

Figure 38

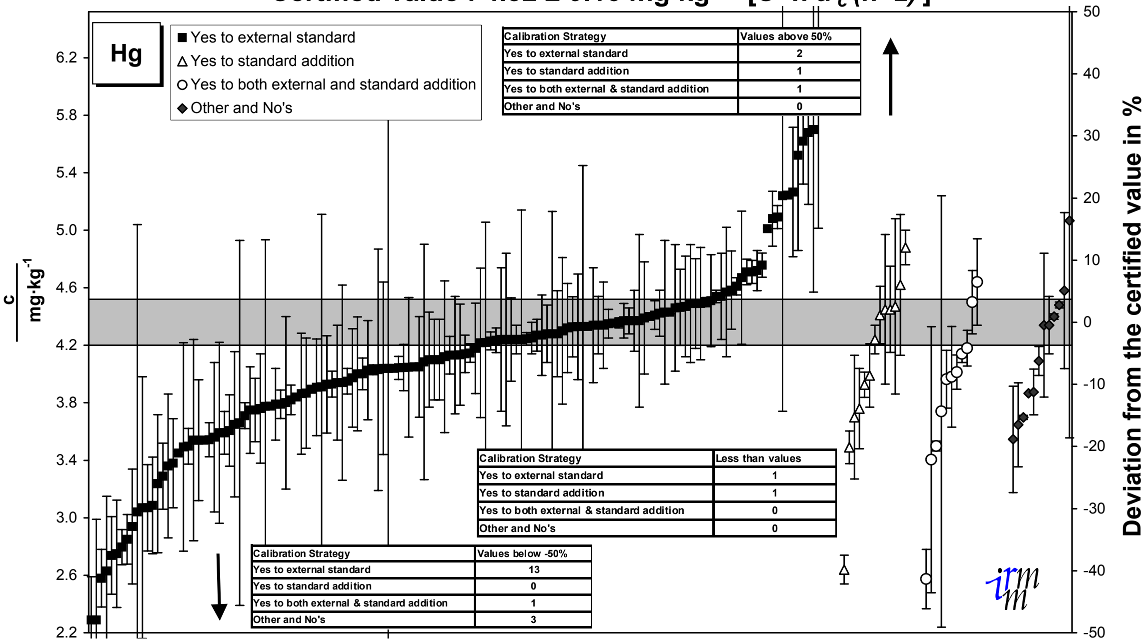


Results from all participants according to Calibration Strategy.

Figure 39

IMEP- 20: Trace elements in Tuna Fish

Certified value : 4.32 ± 0.16 mg·kg^{-1} [U=k·u_c (k=2)]

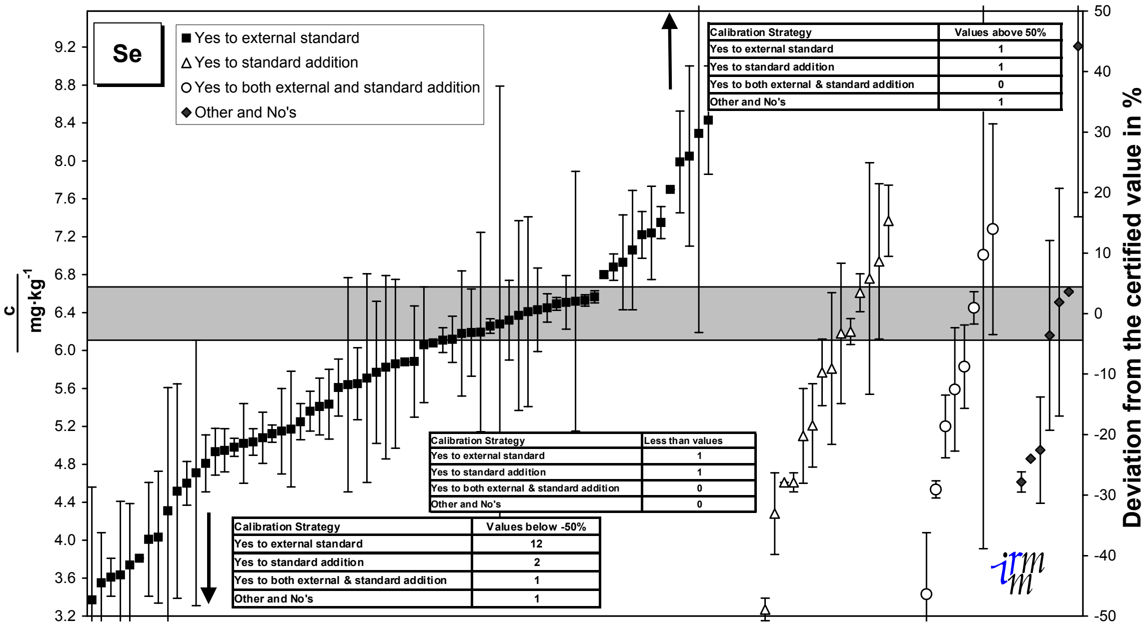


Results from all participants according to Calibration Strategy.

Figure 40

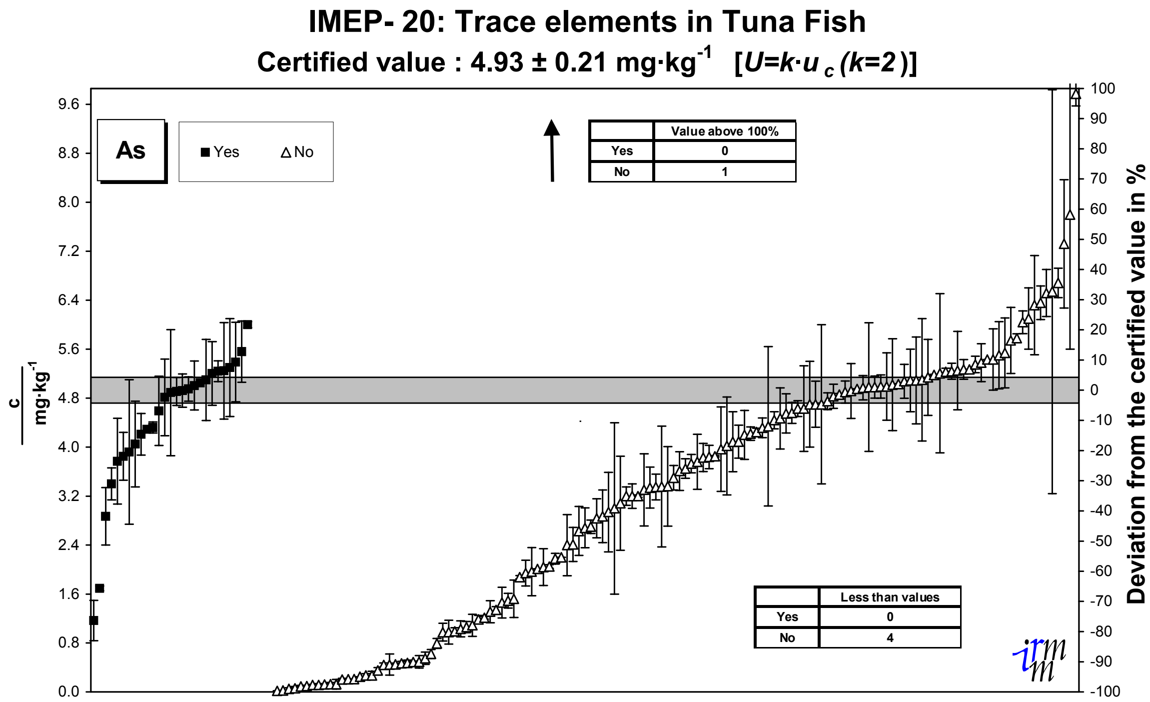
IMEP- 20: Trace elements in Tuna Fish

Certified value : 6.38 ± 0.28 mg·kg^{-1} [U=k·u_c (k=2)]



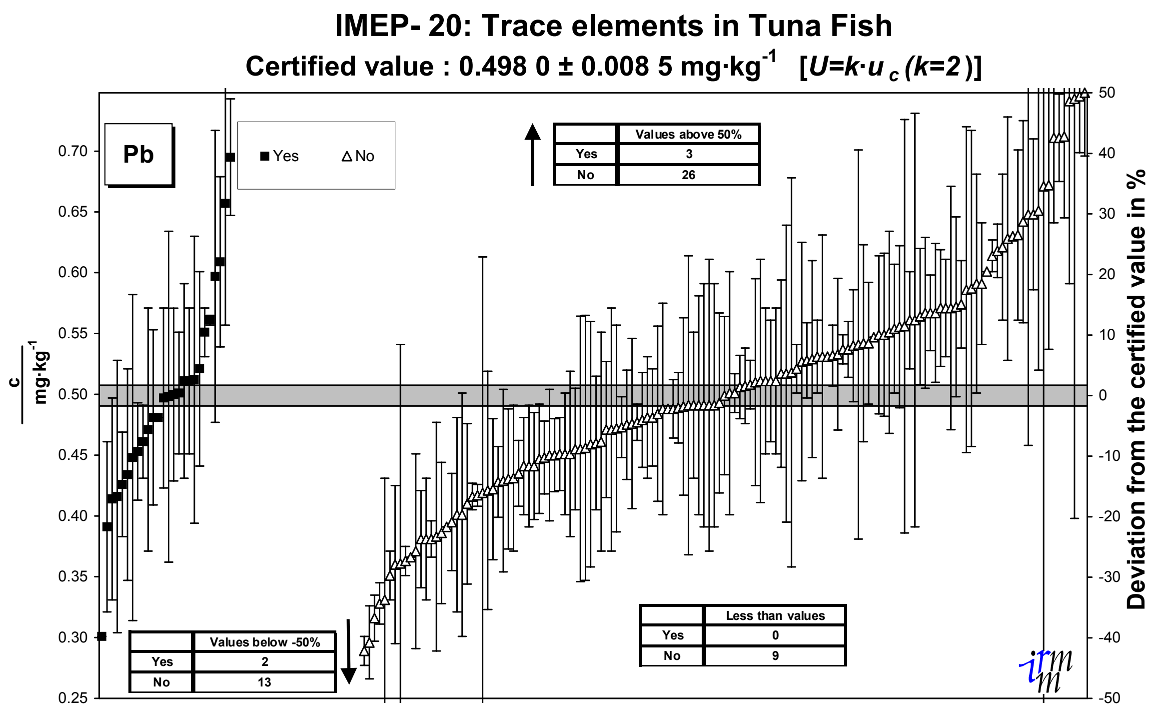
Results from all participants according to Calibration Strategy.

Figure 41



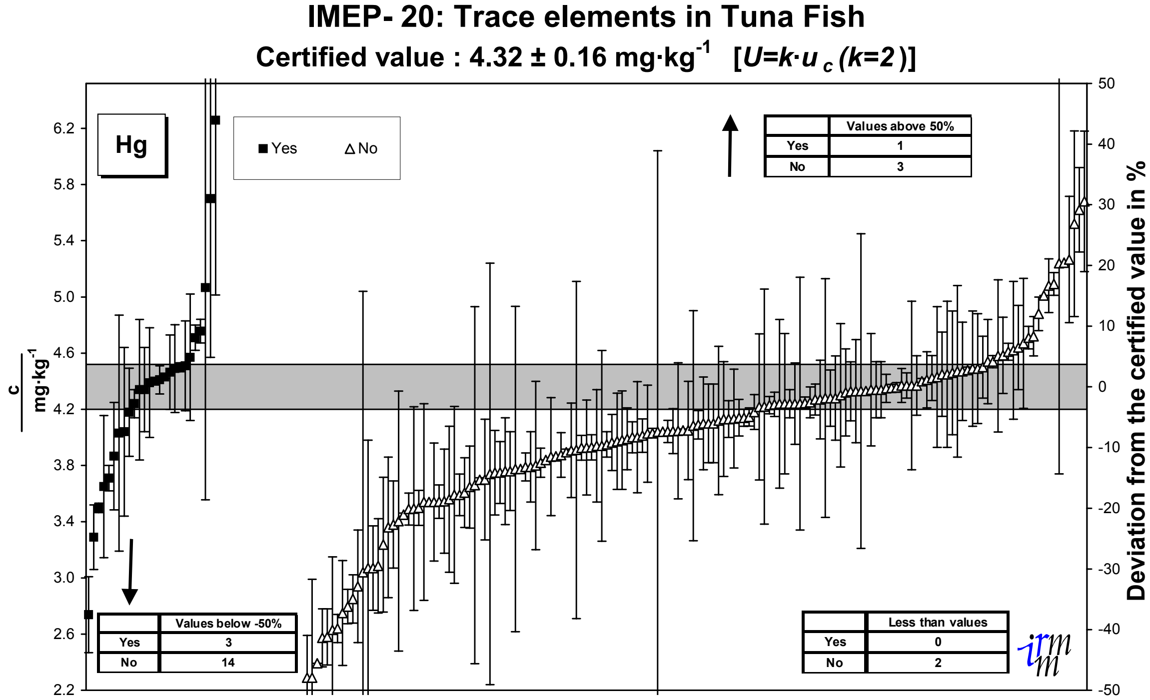
Results from all participants on the use of Certified Reference Materials. (CRMs)

Figure 42



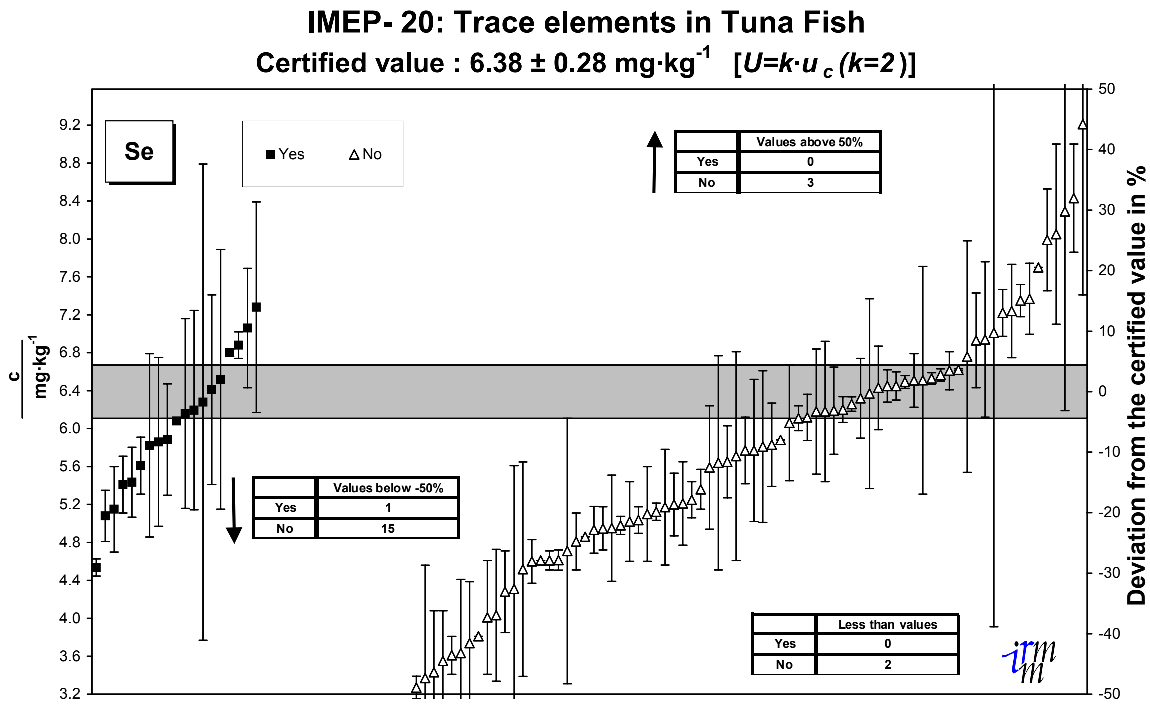
Results from all participants on the use of Certified Reference Materials. (CRMs)

Figure 43



Results from all participants on the use of Certified Reference Materials. (CRMs)

Figure 44



Results from all participants on the use of Certified Reference Materials. (CRMs)

Figure 45

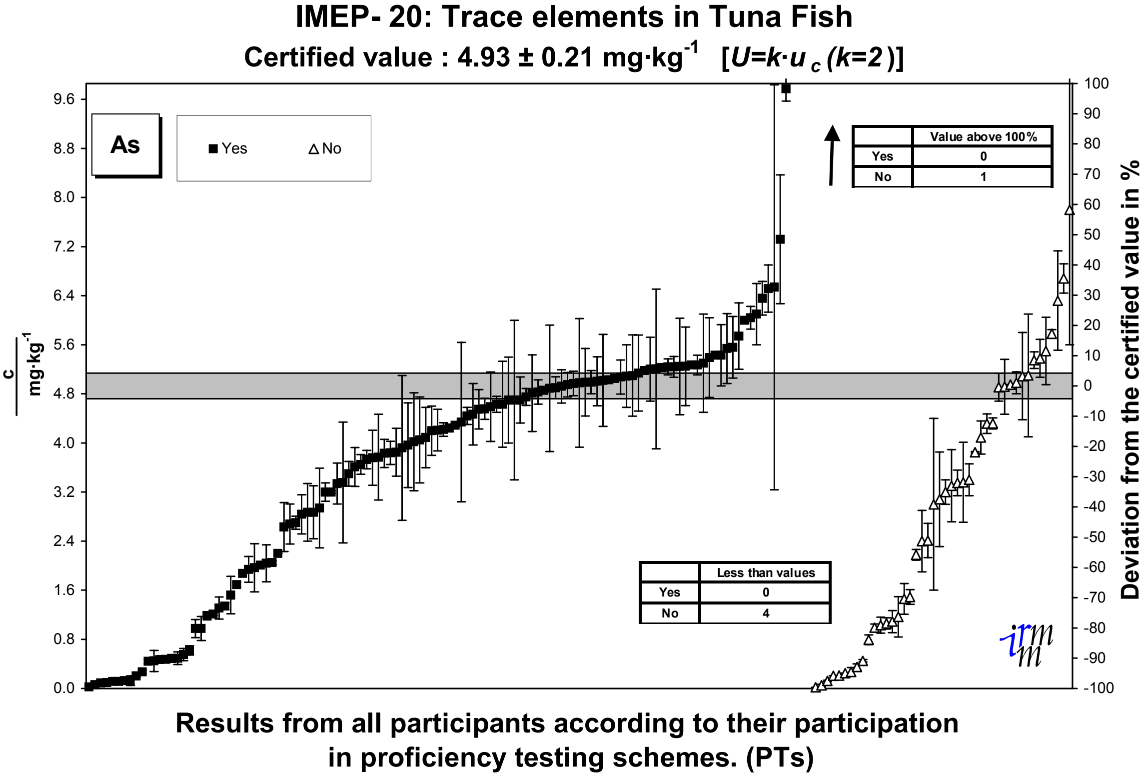


Figure 46

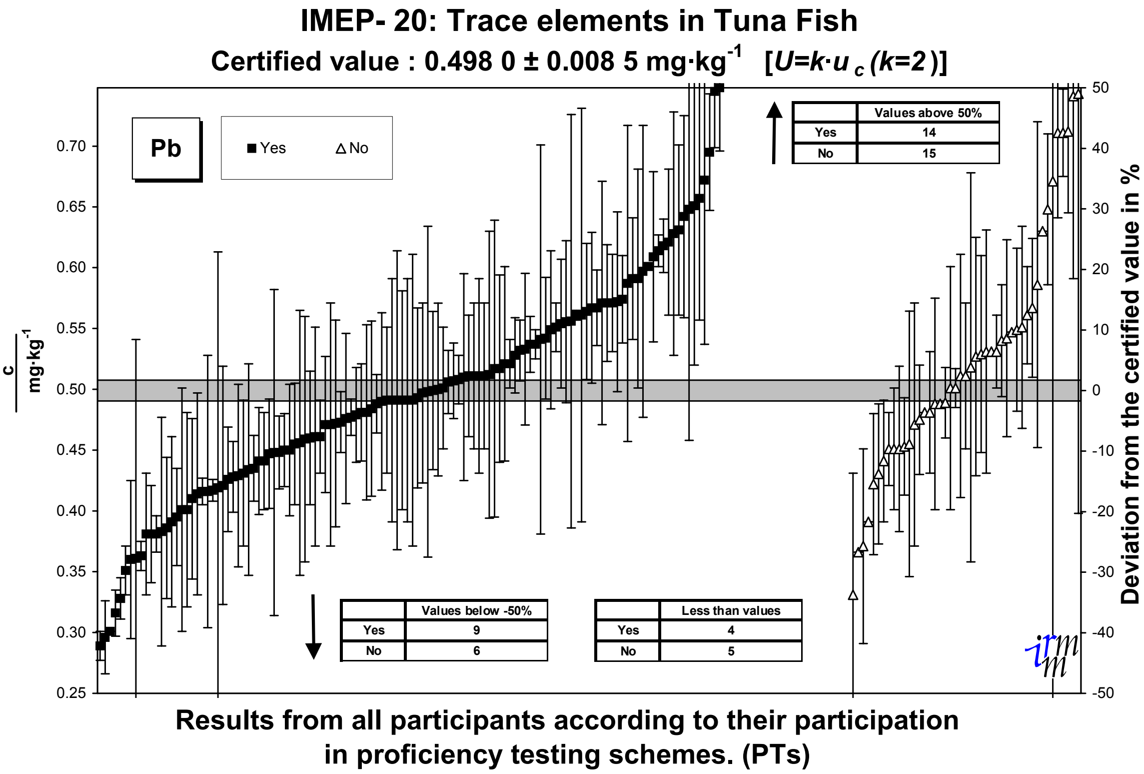
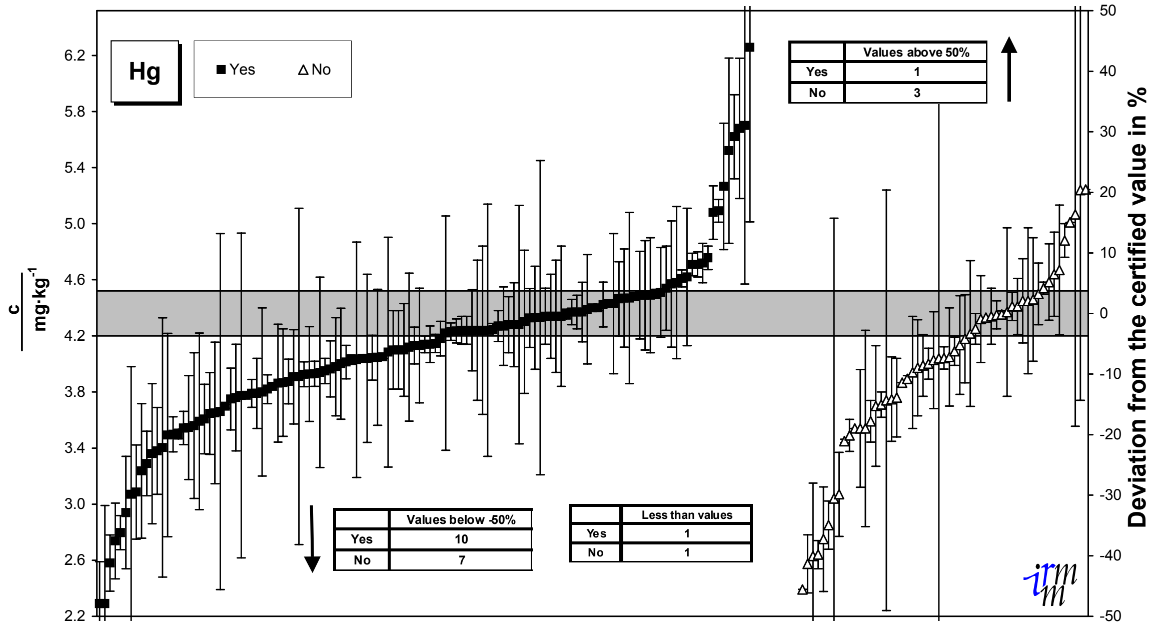


Figure 47

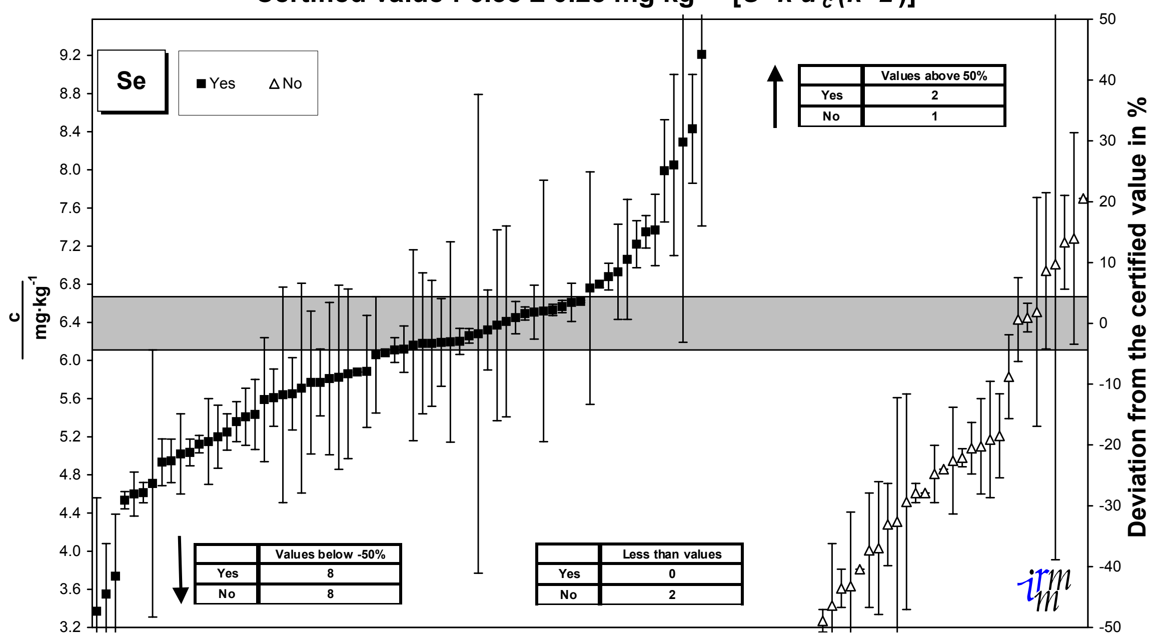
IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.32 ± 0.16 mg·kg^{-1} [$U=k \cdot u_c (k=2)$]



Results from all participants according to their participation in proficiency testing schemes. (PTs)

Figure 48

IMEP- 20: Trace elements in Tuna Fish
Certified value : 6.38 ± 0.28 mg·kg^{-1} [$U=k \cdot u_c (k=2)$]



Results from all participants according to their participation in proficiency testing schemes. (PTs)

Figure 49

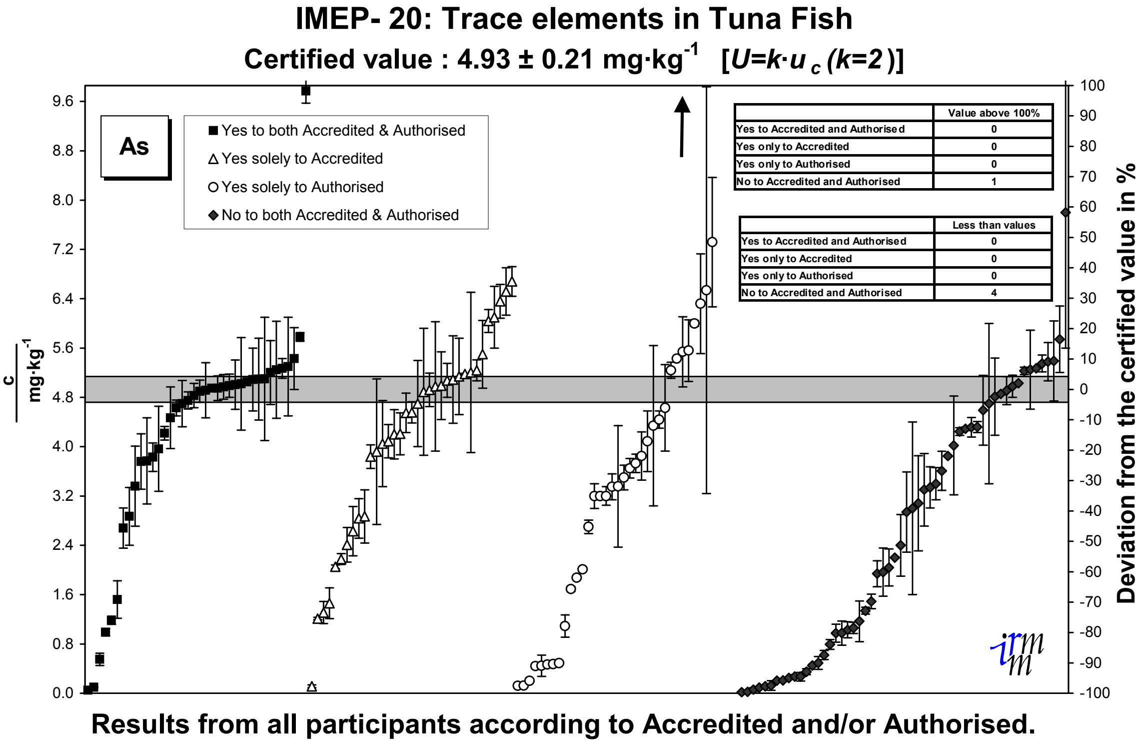


Figure 50

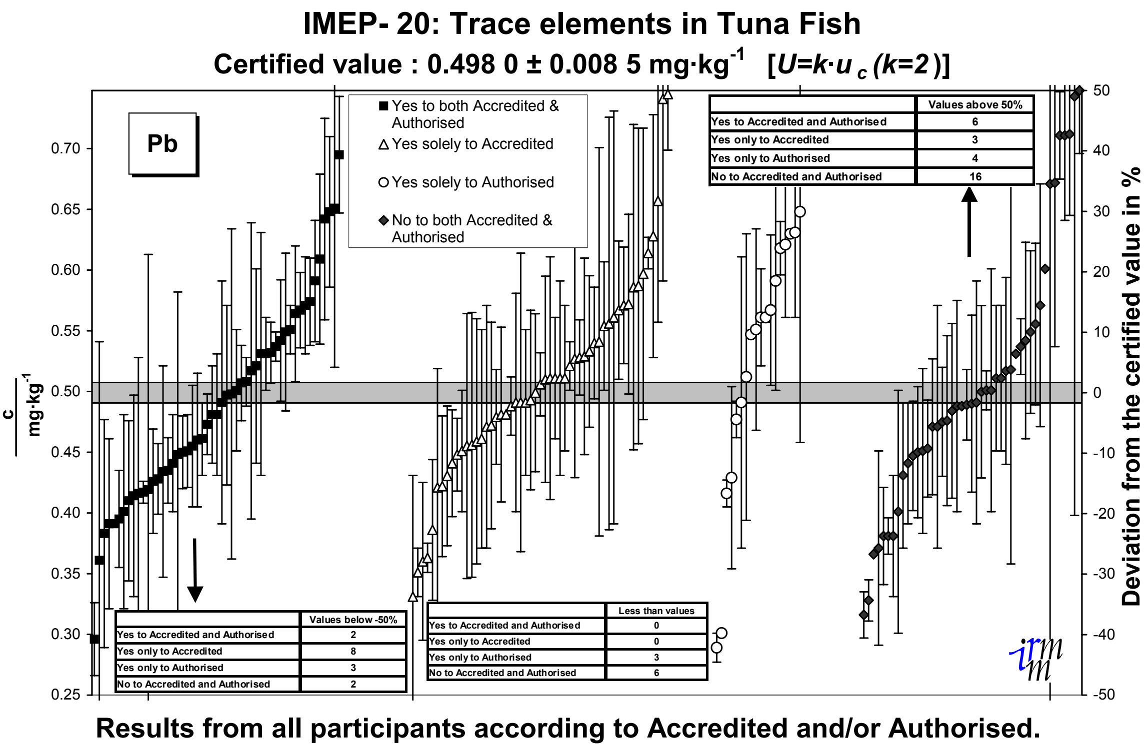
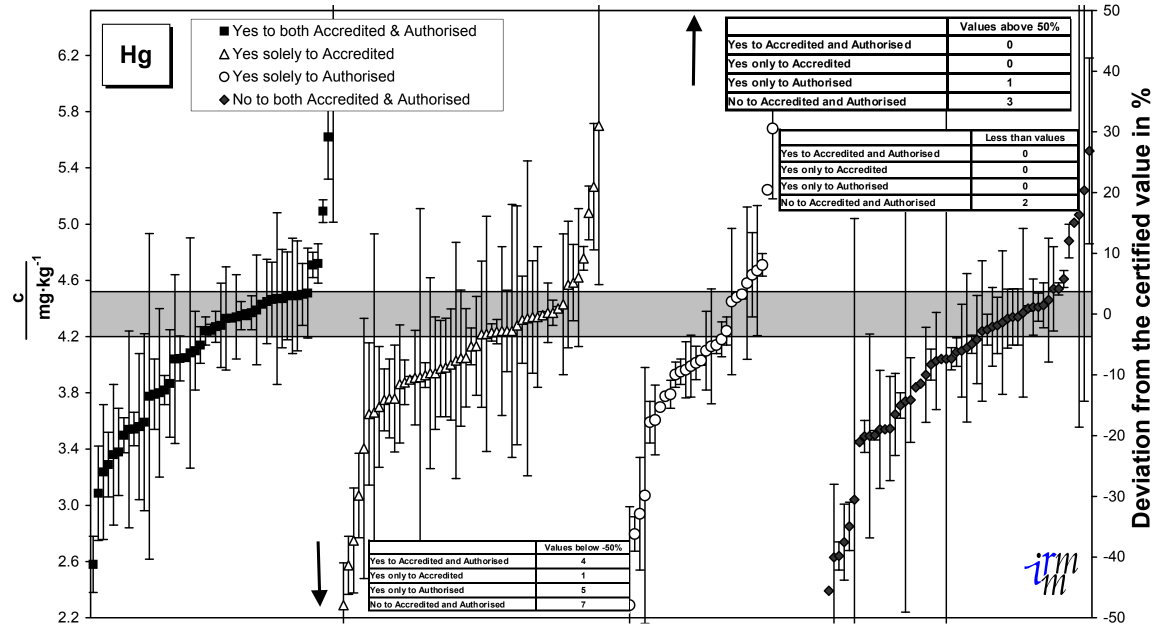


Figure 51

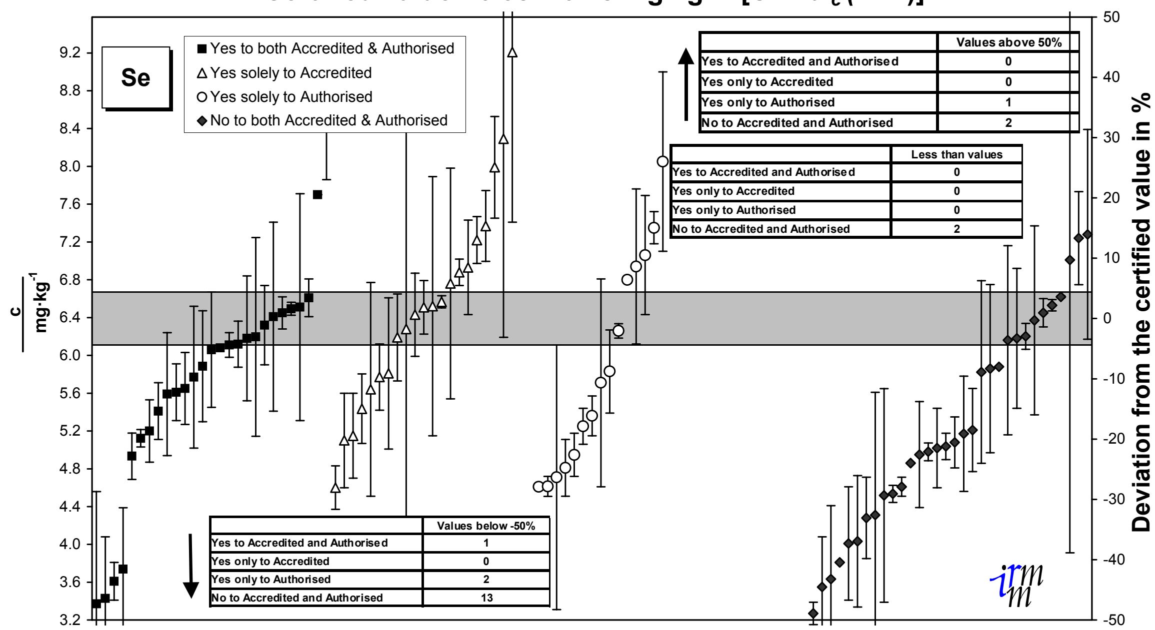
IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.32 ± 0.16 mg·kg-1 [U=k·u c (k=2)]



Results from all participants according to Accredited and/or Authorised.

Figure 52

IMEP- 20: Trace elements in Tuna Fish
Certified value : 6.38 ± 0.28 mg·kg-1 [U=k·u c (k=2)]

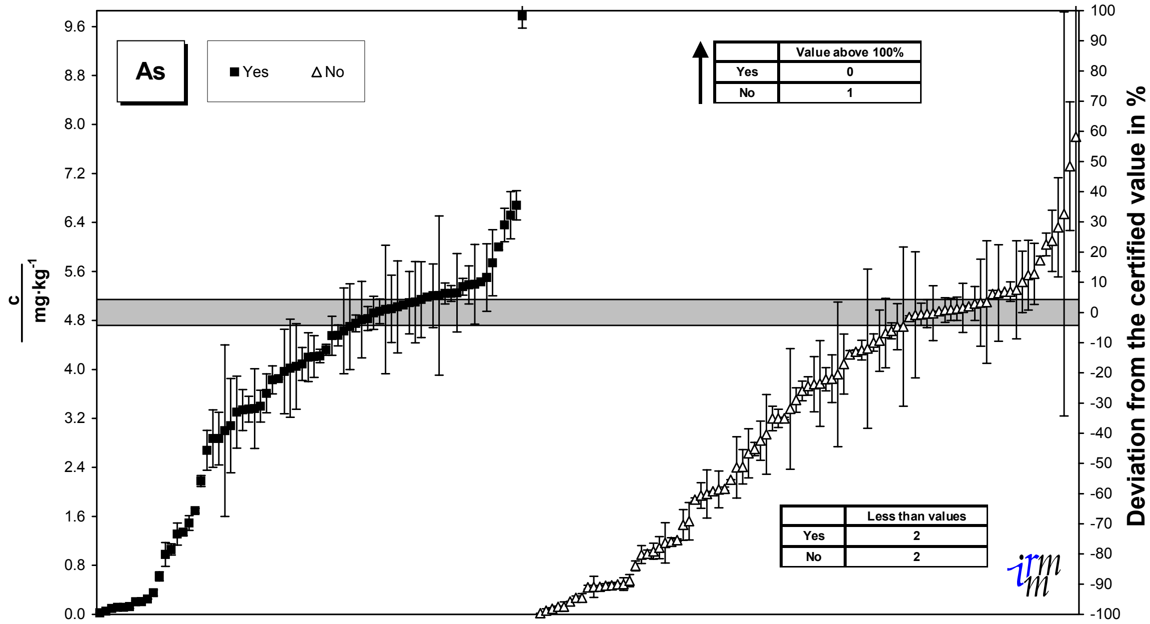


Results from all participants according to Accredited and/or Authorised.

Figure 53

IMEP- 20: Trace elements in Tuna Fish

Certified value : 4.93 ± 0.21 mg·kg^{-1} [$U=k \cdot u_c (k=2)$]

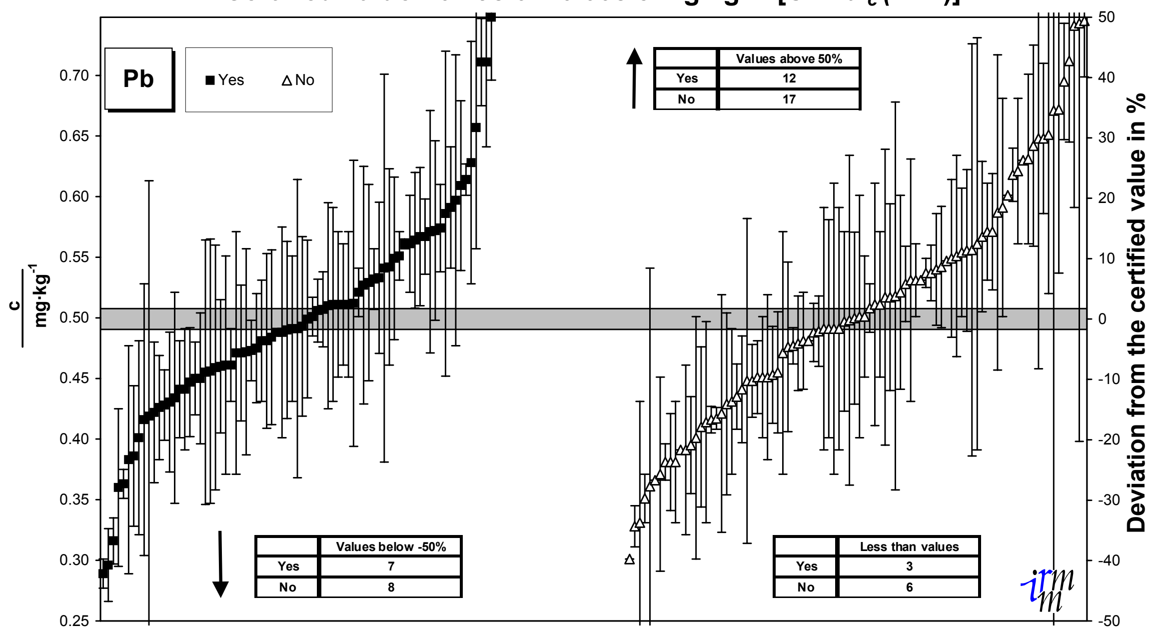


Results from all participants according to uncertainties being reported on their chemical measurements to customers.

Figure 54

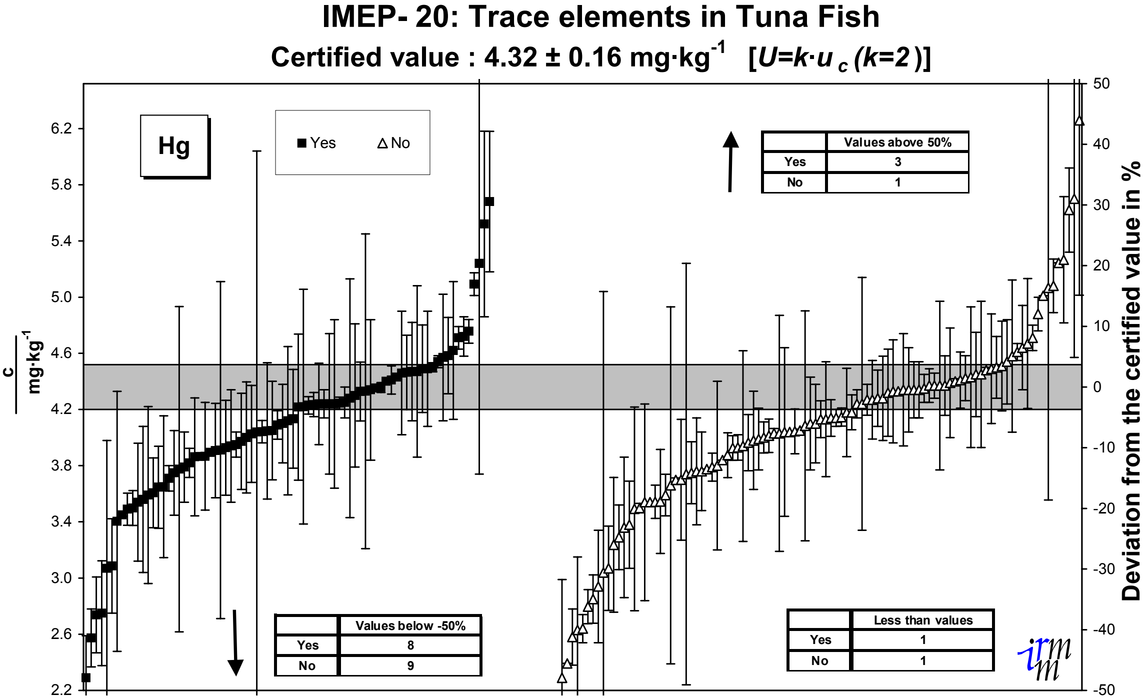
IMEP- 20: Trace elements in Tuna Fish

Certified value : 0.498 0 ± 0.008 5 mg·kg^{-1} [$U=k \cdot u_c (k=2)$]



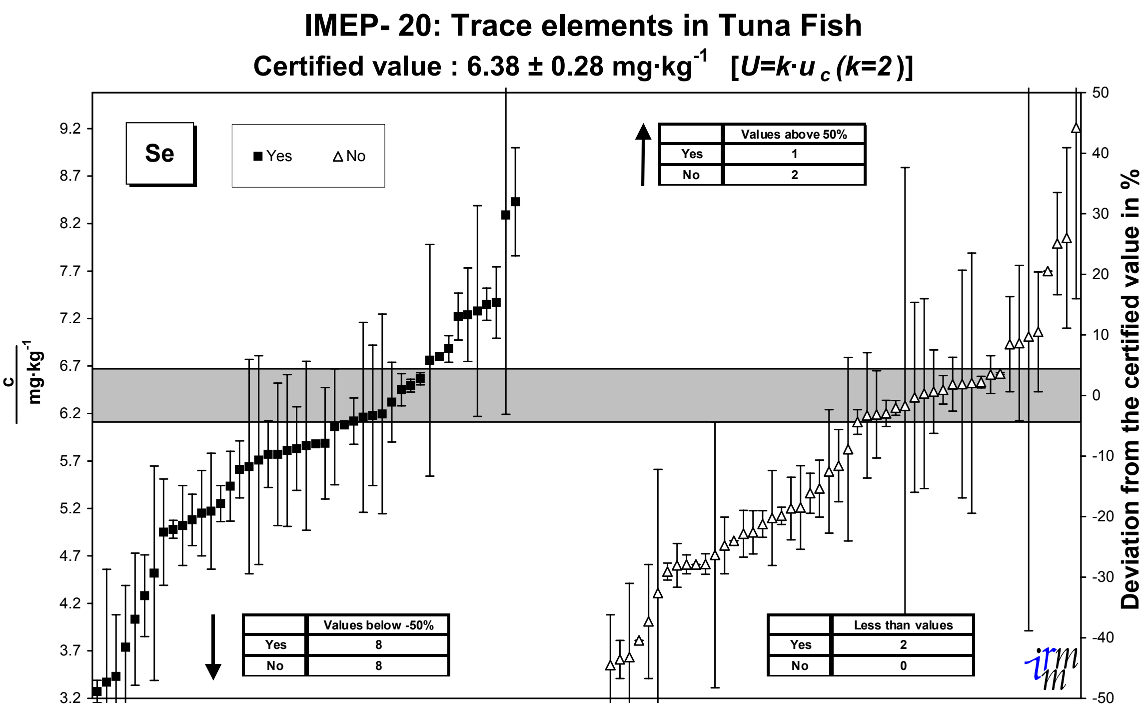
Results from all participants according to uncertainties being reported on their chemical measurements to customers.

Figure 55



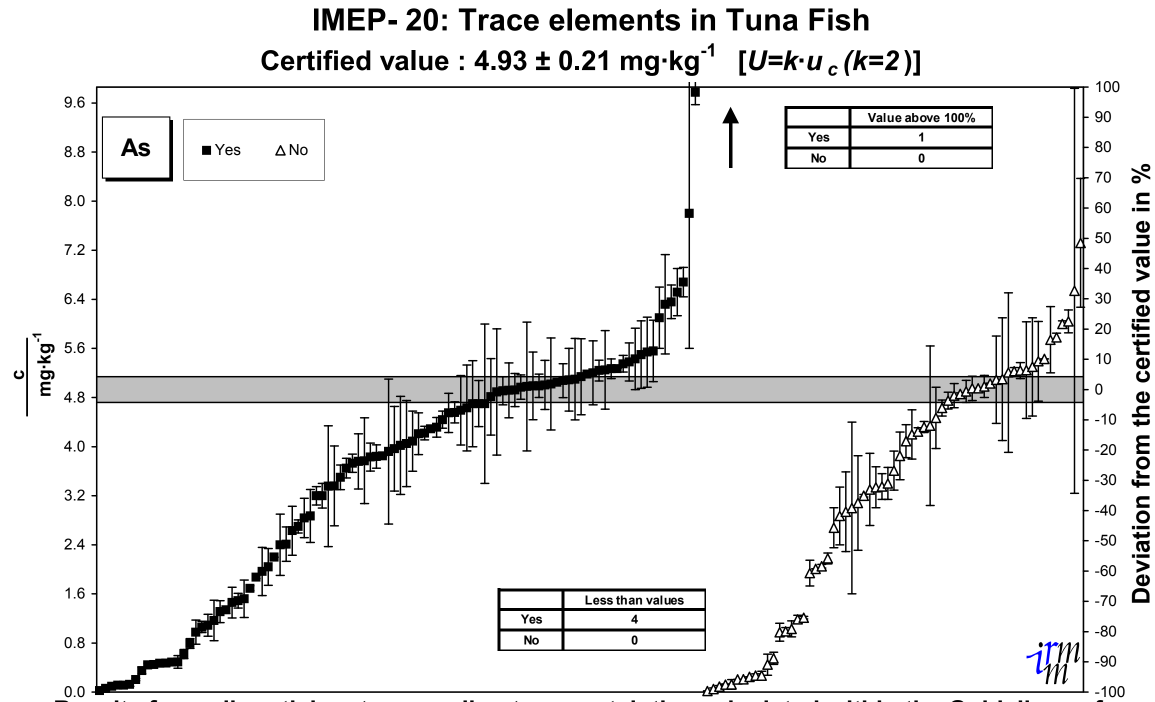
Results from all participants according to uncertainties being reported on their chemical measurements to customers.

Figure 56



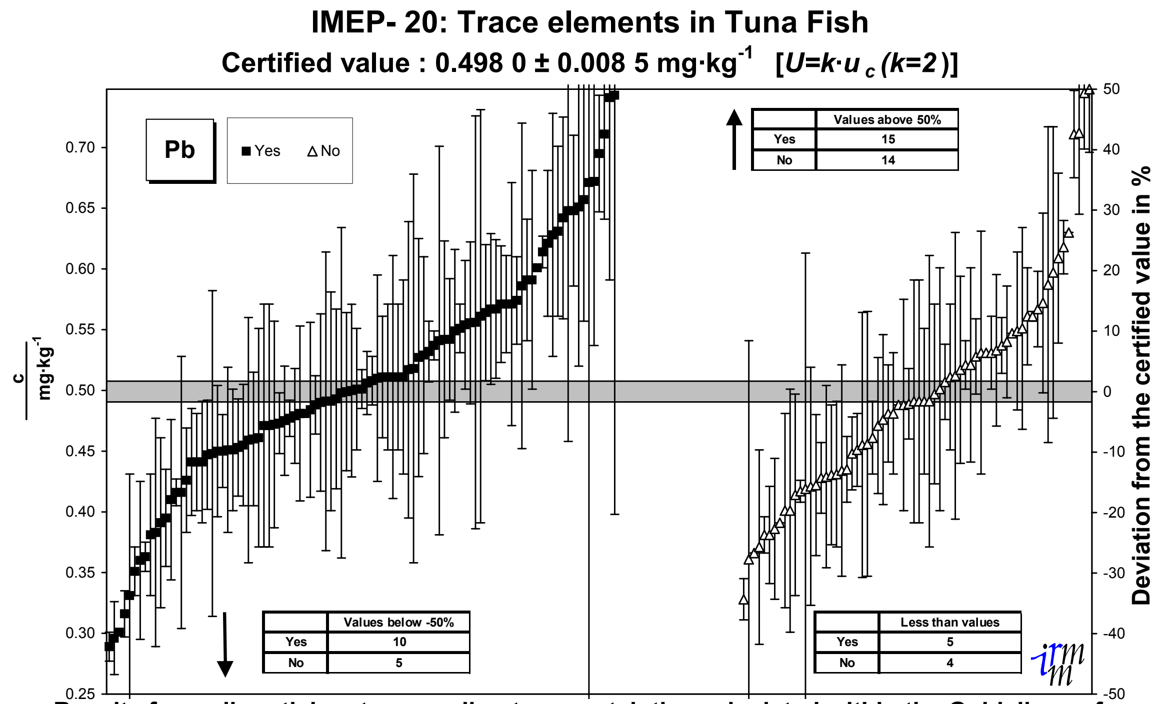
Results from all participants according to uncertainties being reported on their chemical measurements to customers.

Figure 57



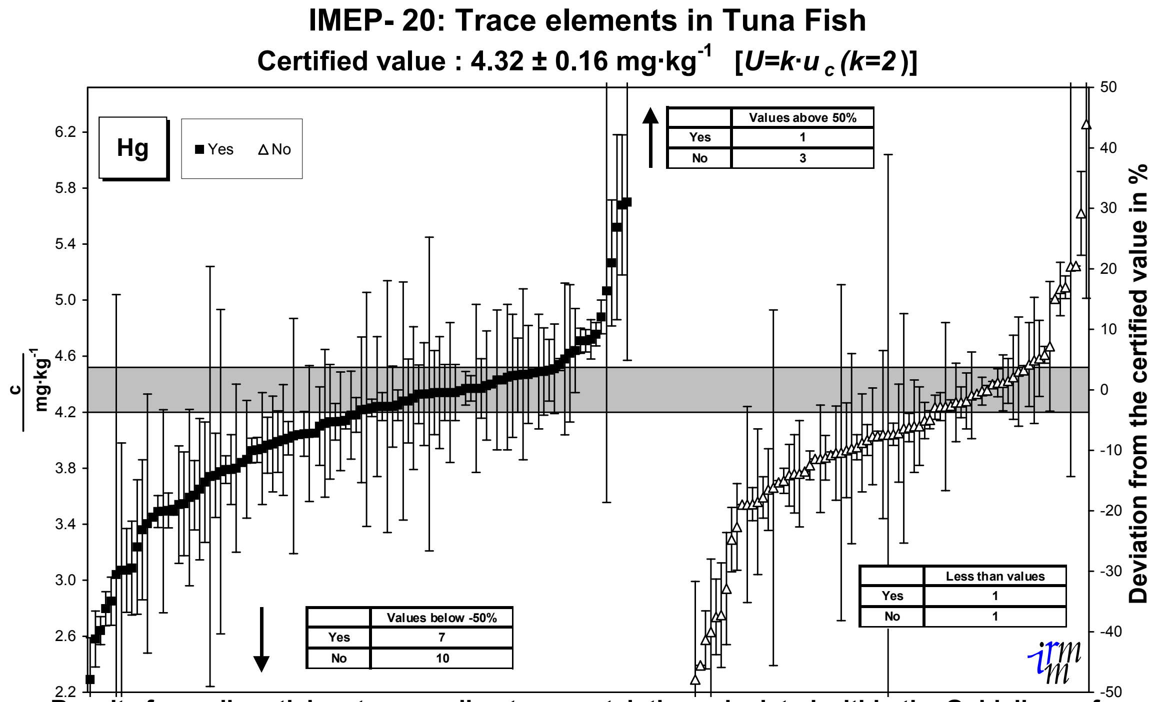
Results from all participants according to uncertainties calculated within the Guidelines of Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).

Figure 58



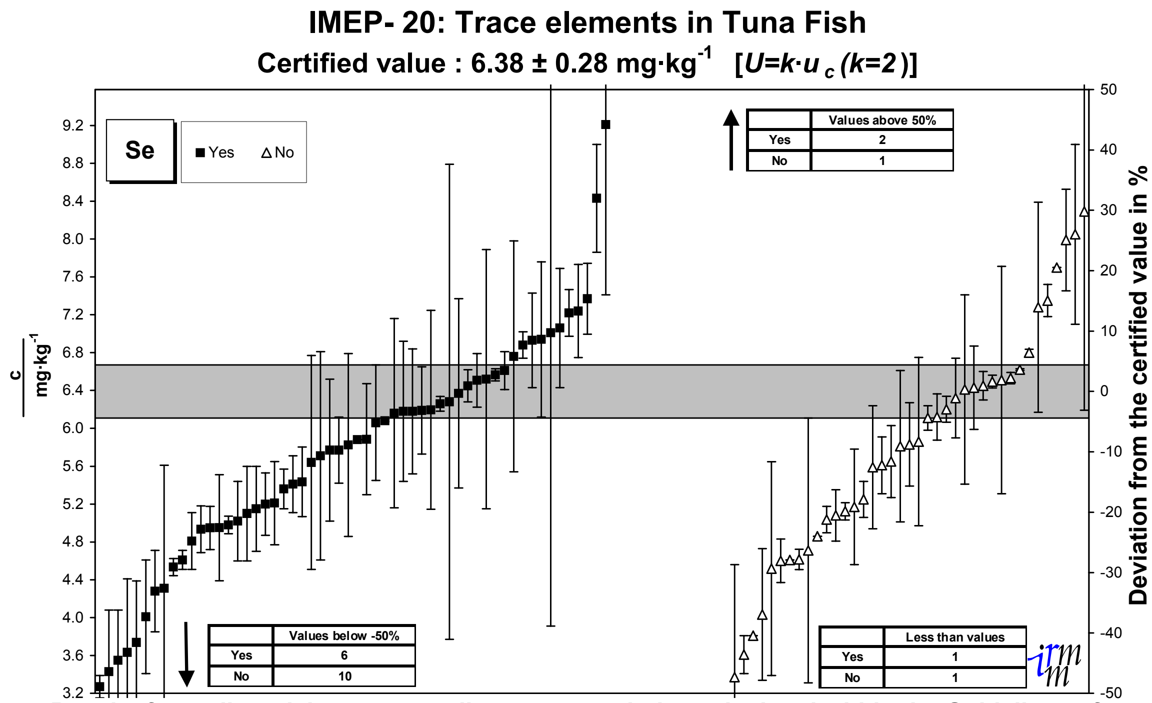
Results from all participants according to uncertainties calculated within the Guidelines of Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).

Figure 59



Results from all participants according to uncertainties calculated within the Guidelines of Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).

Figure 60



Results from all participants according to uncertainties calculated within the Guidelines of Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).

IMEP-20: Trace Elements in Tuna Fish

Annex 1 – Participants results – Performance Graphs

Figure 61

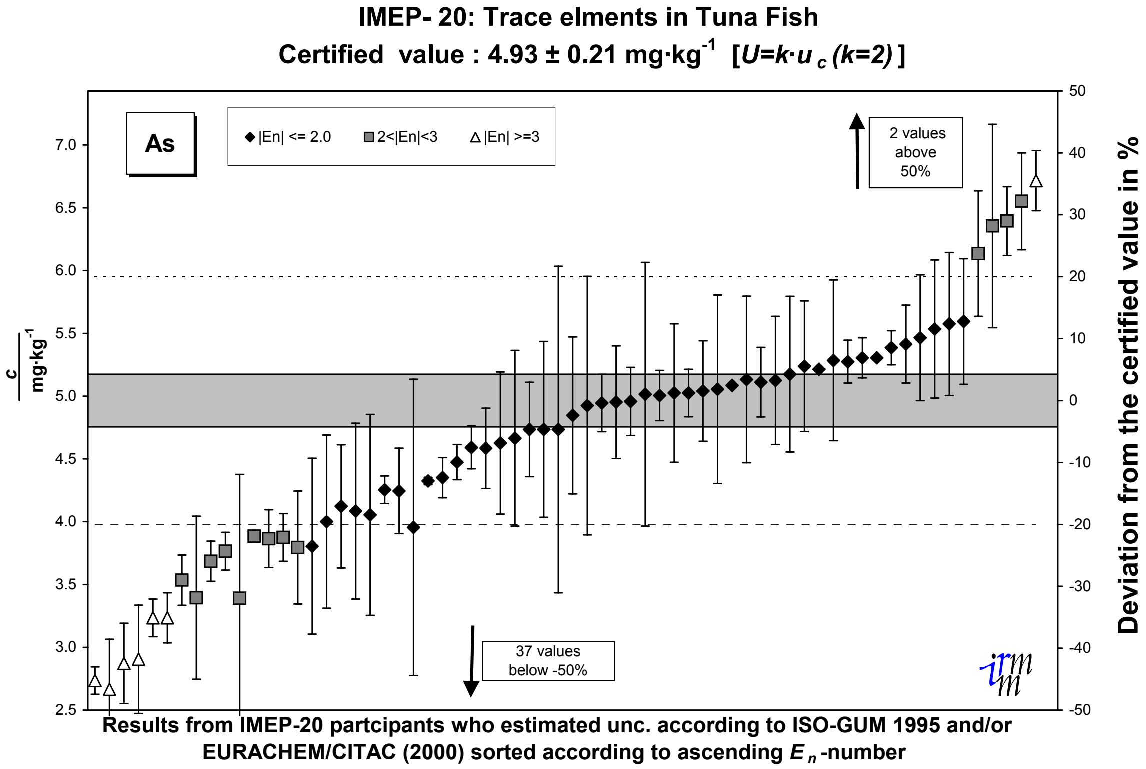


Figure 62

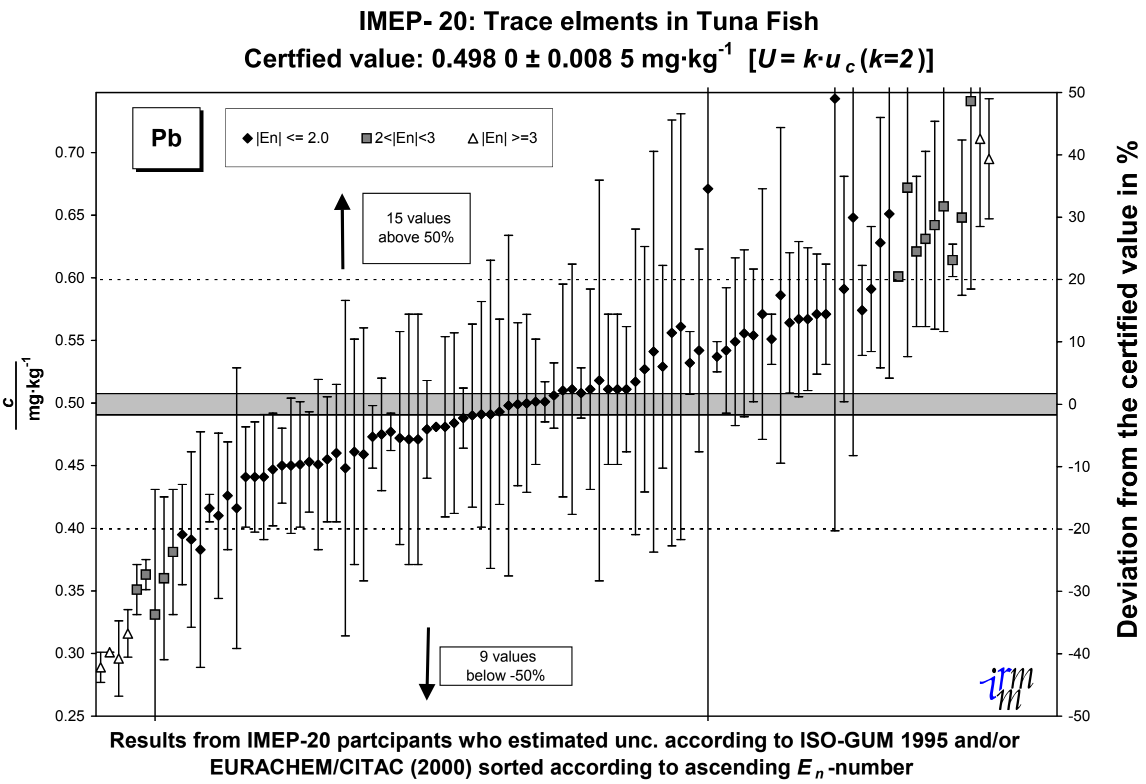
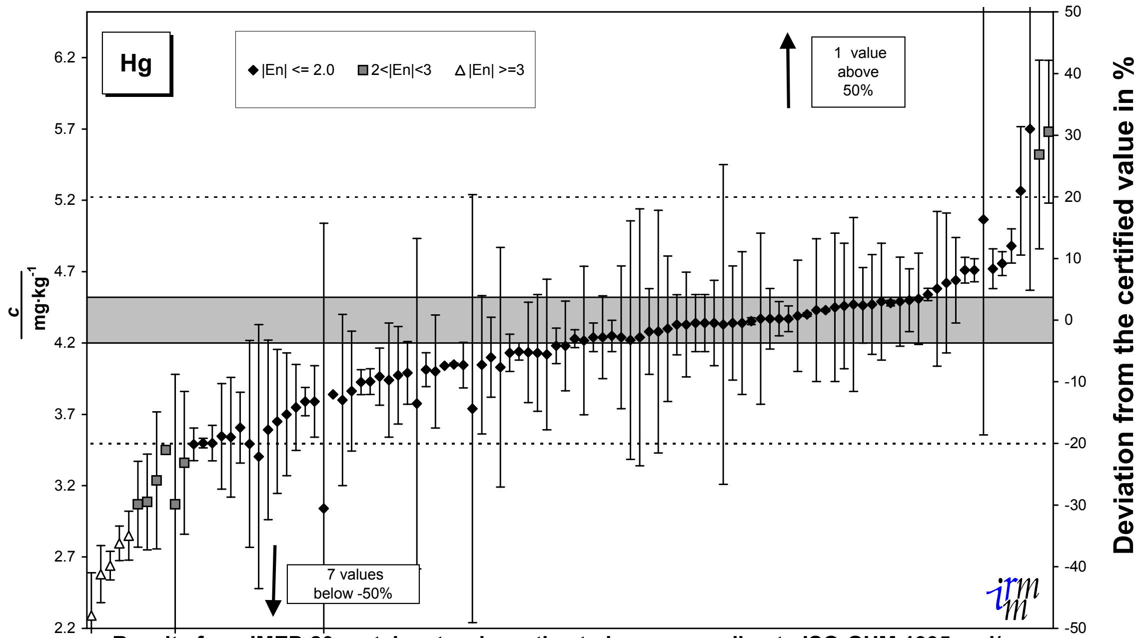


Figure 63

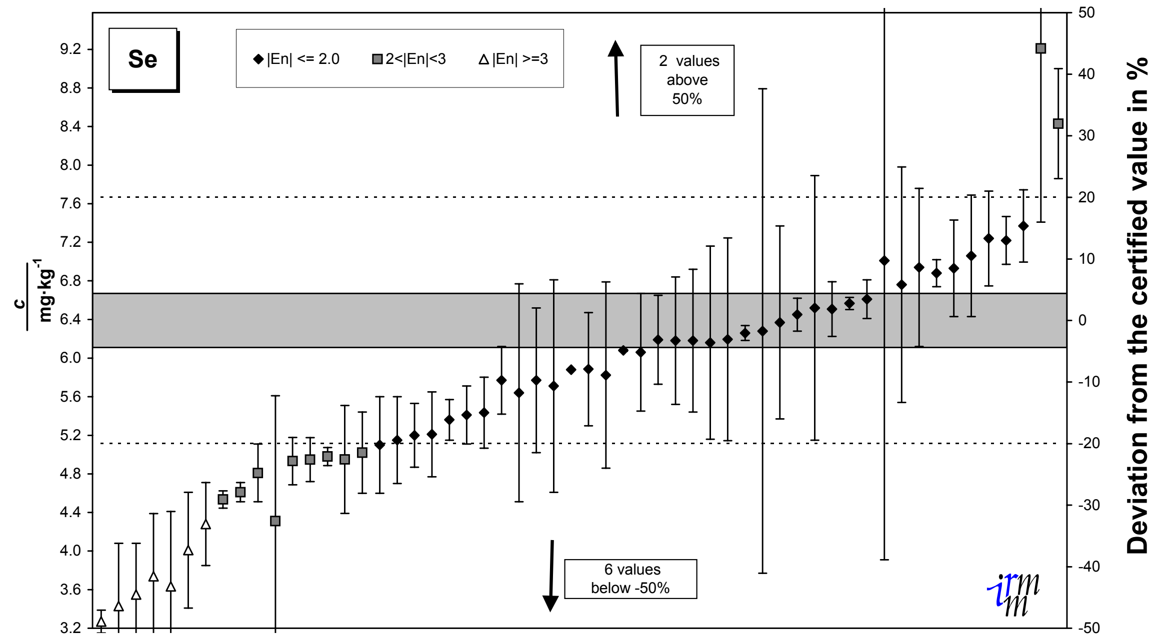
IMEP- 20: Trace elments in Tuna Fish
Certified value : 4.32 ± 0.16 mg·kg^{-1} [$U = k \cdot u_c$ (k=2)]



Results from IMEP-20 partcipants who estimated unc. according to ISO-GUM 1995 and/or EURACHEM/CITAC (2000) sorted according to ascending E_n-number

Figure 64

IMEP- 20: Trace elments in Tuna Fish
Certified value : 6.38 ± 0.28 mg·kg^{-1} [$U = k \cdot u_c$ (k=2)]



Results from IMEP-20 partcipants who estimated unc. according to ISO-GUM 1995 and/or EURACHEM/CITAC (2000) sorted according to ascending E_n-number

IMEP-20: Trace Elements in Tuna Fish

Annex 1 – Participants results – Methylmercury Graphs

Figure 65

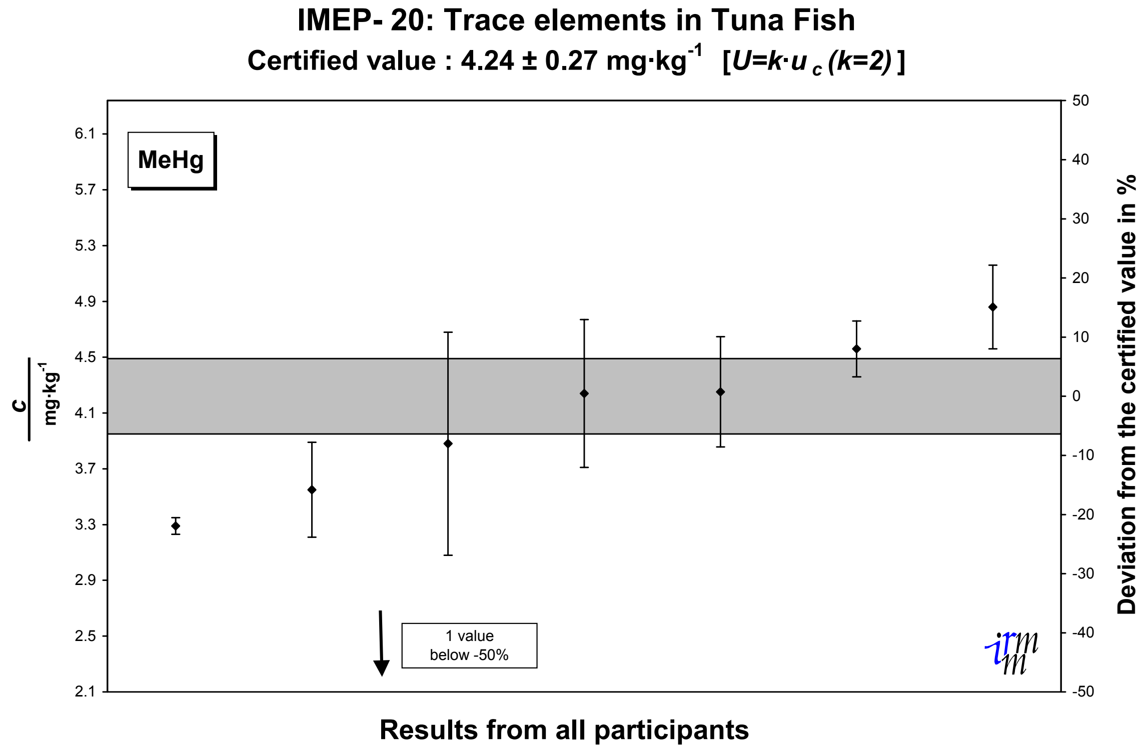


Figure 66

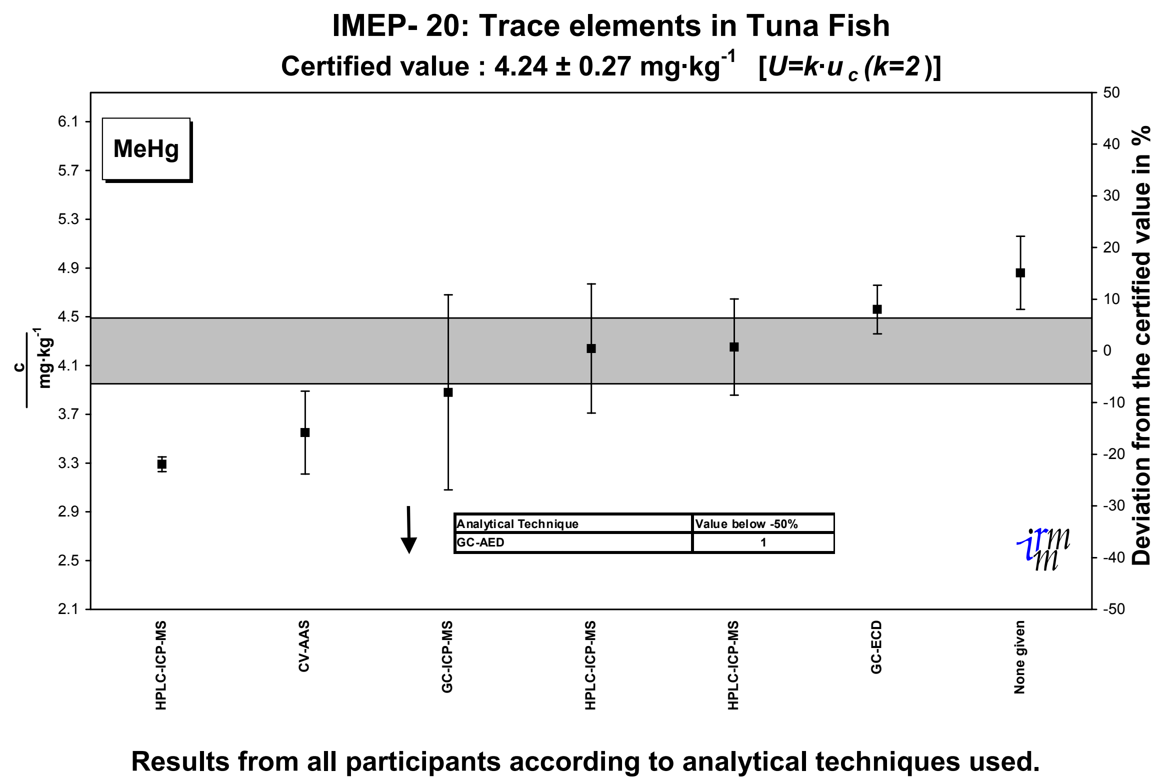
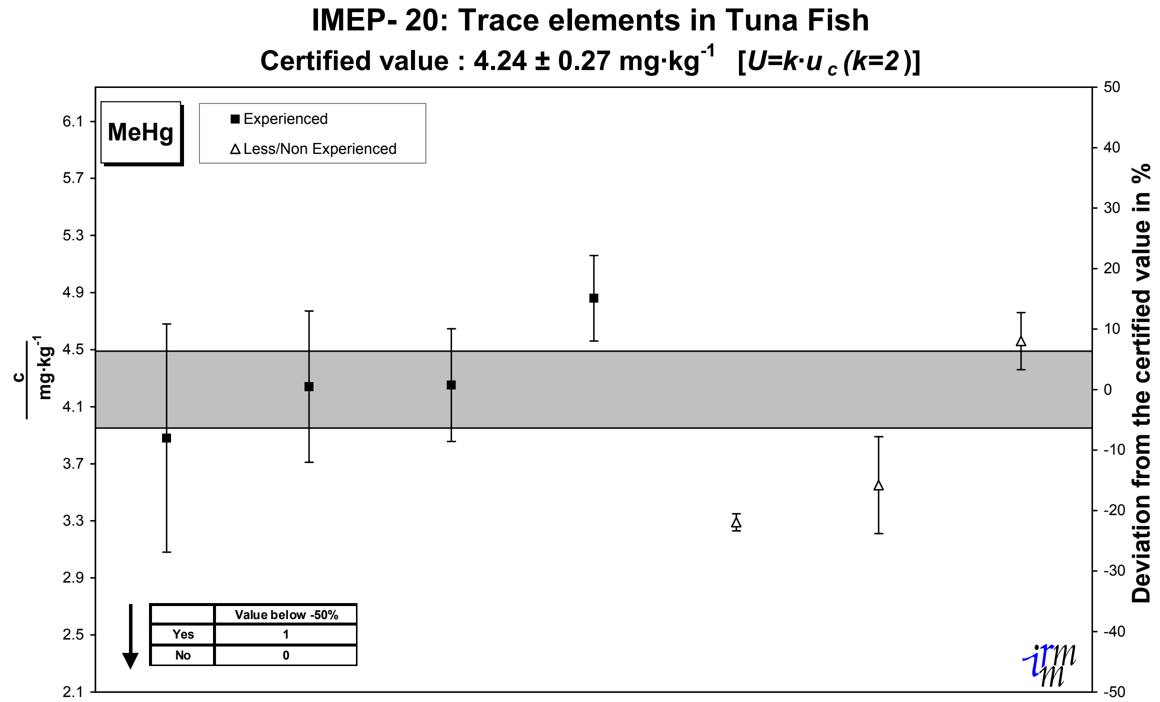
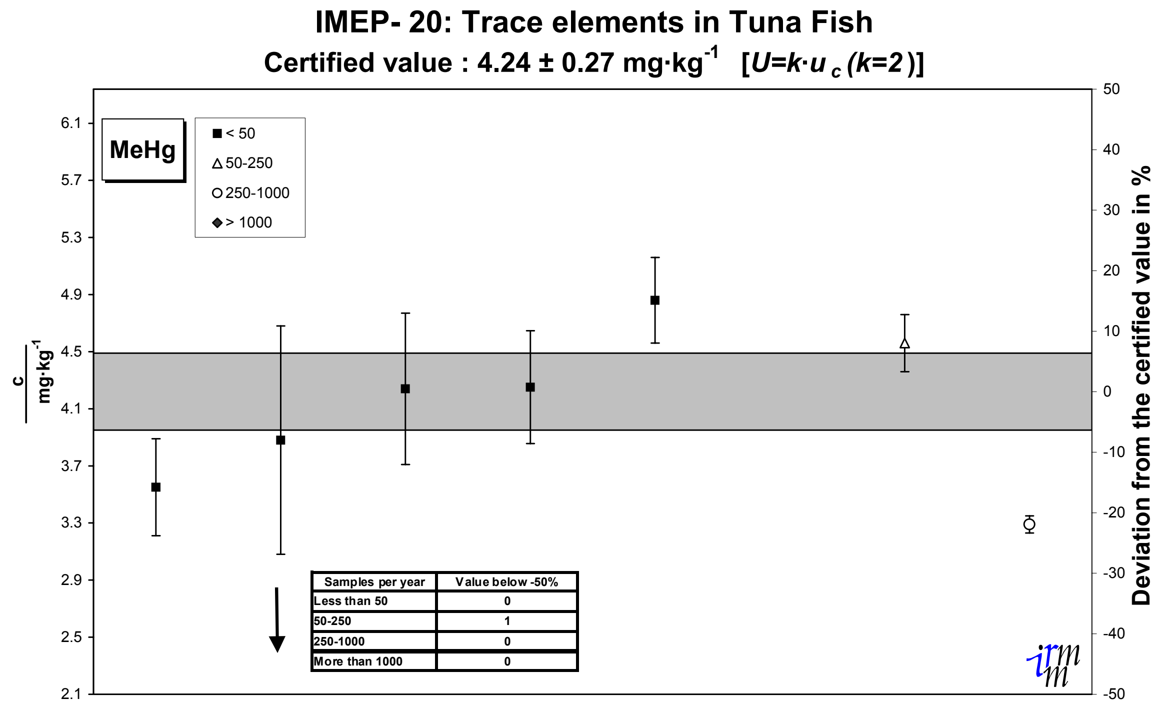


Figure 67



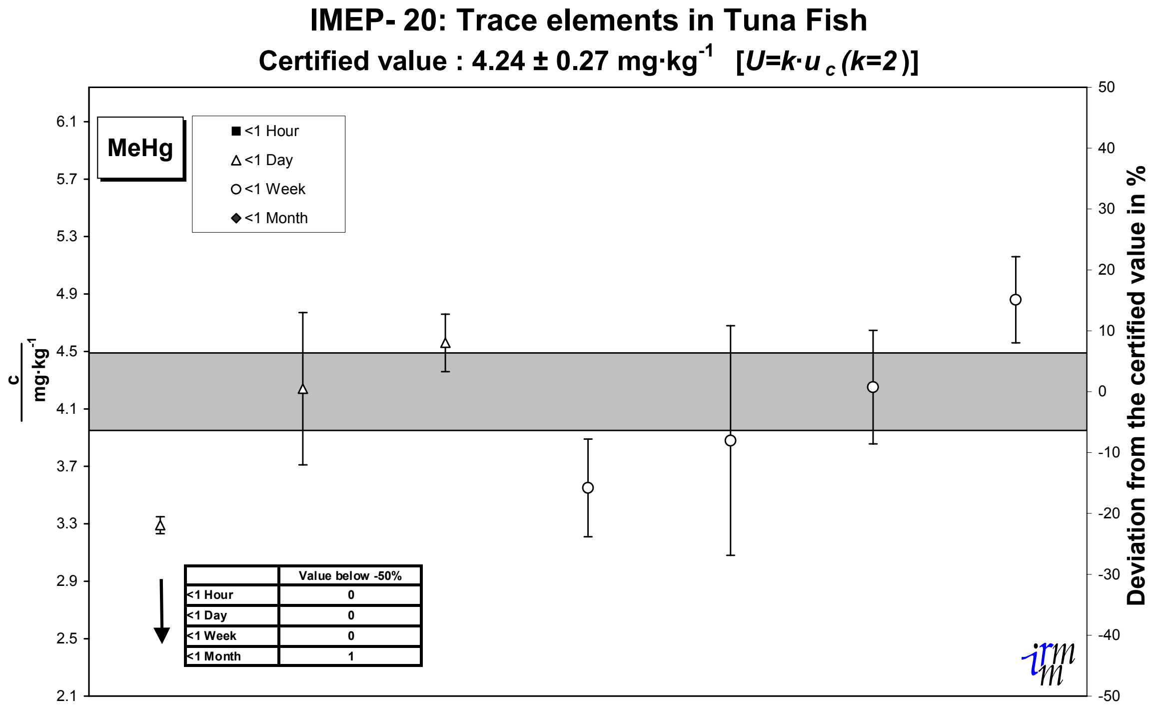
Results from all participants according to experience.

Figure 68



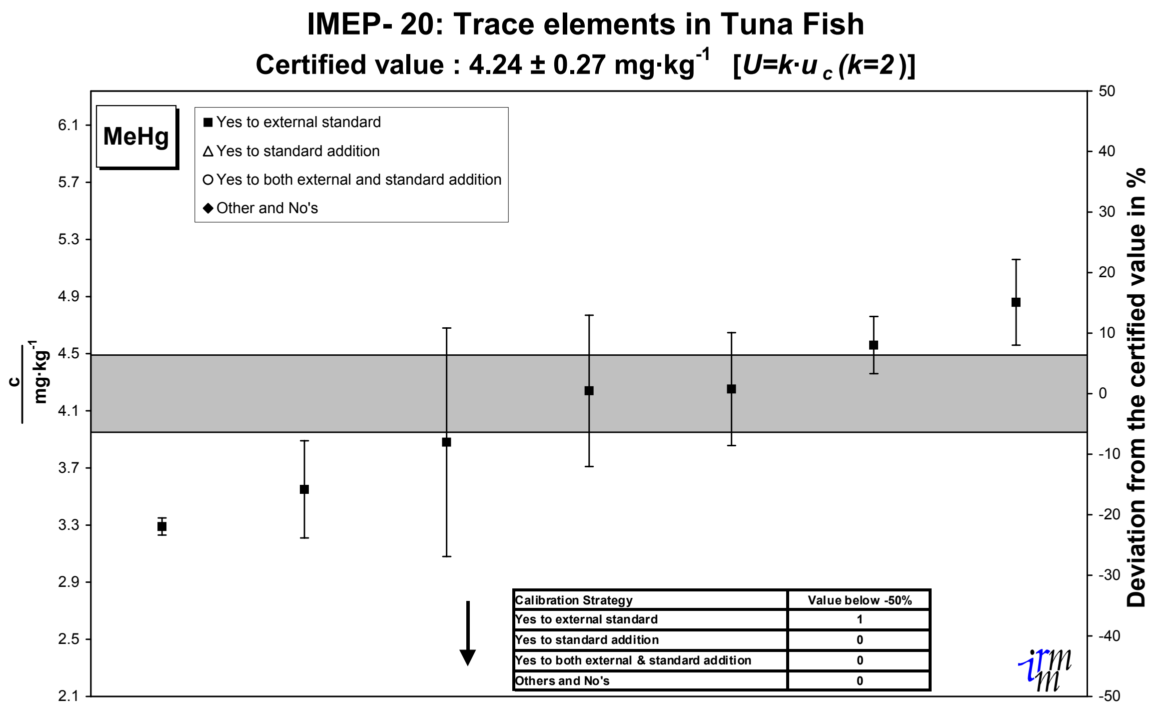
Results from all participants according to how many samples analysed per year.

Figure 69



Results from all participants according to the time spent on the measurement.

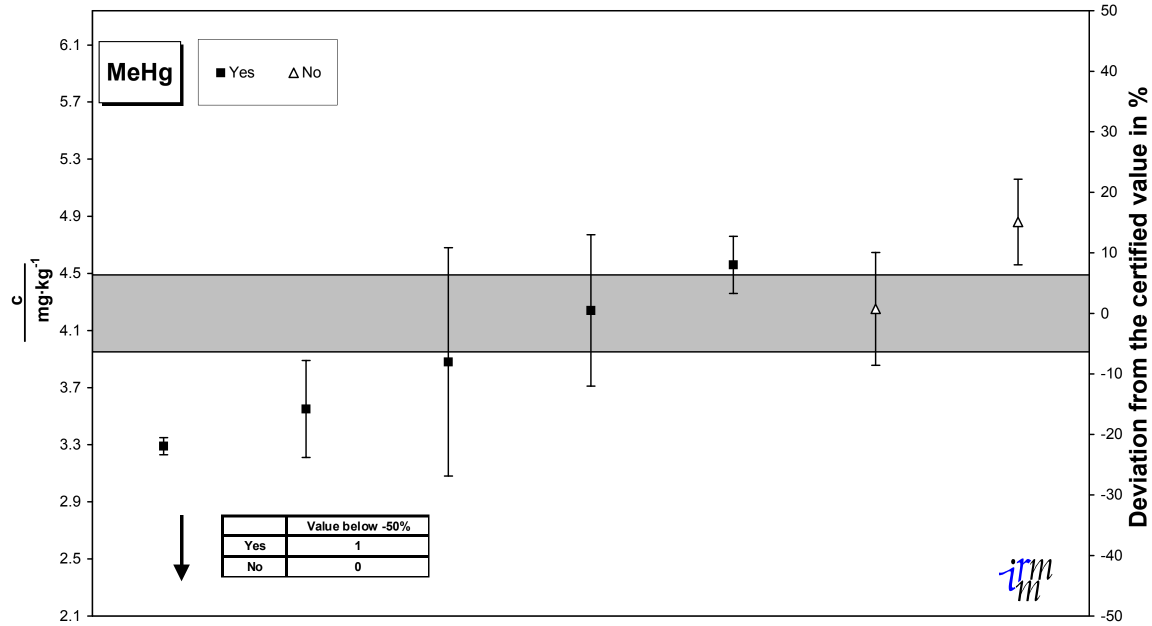
Figure 70



Results from all participants according to Calibration Strategy.

Figure 71

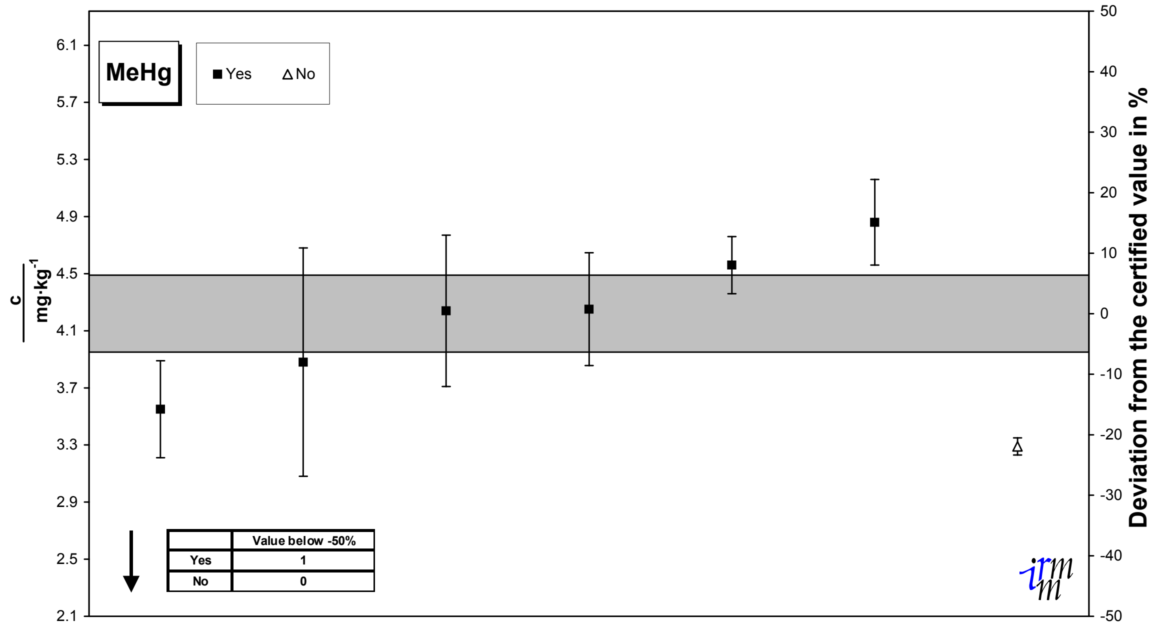
IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.24 ± 0.27 mg·kg⁻¹ [*U=k·u c (k=2)*]



Results from all participants on the use of Certified Reference Materials. (CRMs)

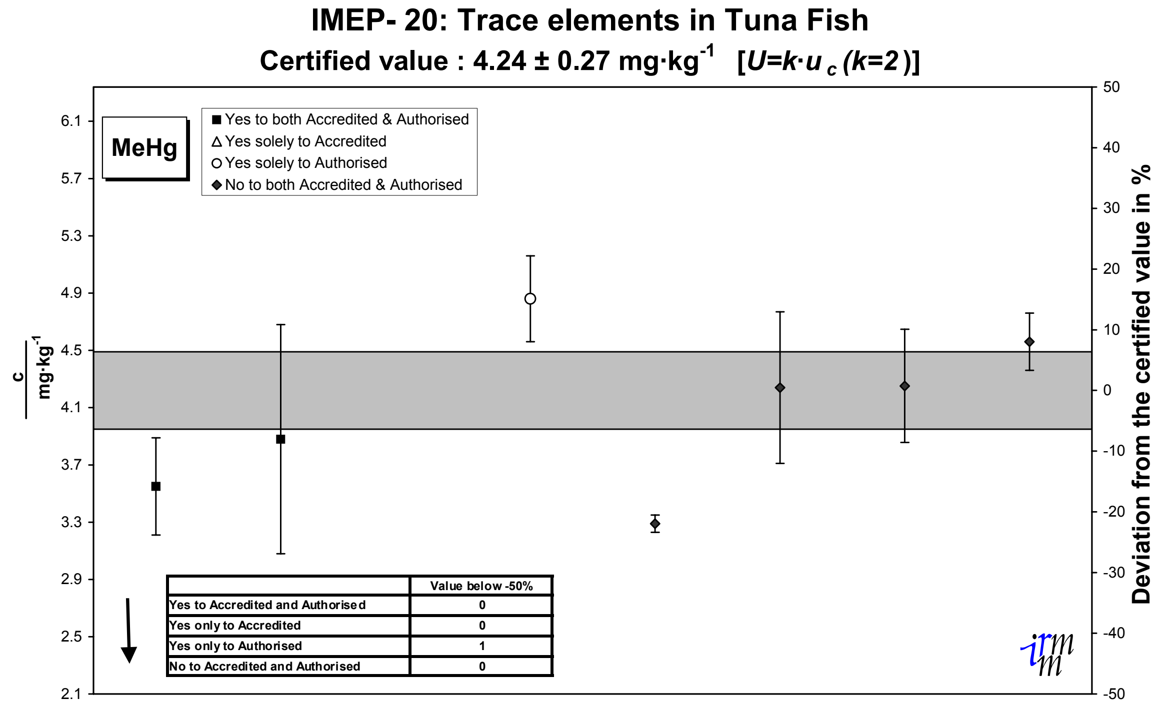
Figure 72

IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.24 ± 0.27 mg·kg⁻¹ [*U=k·u c (k=2)*]



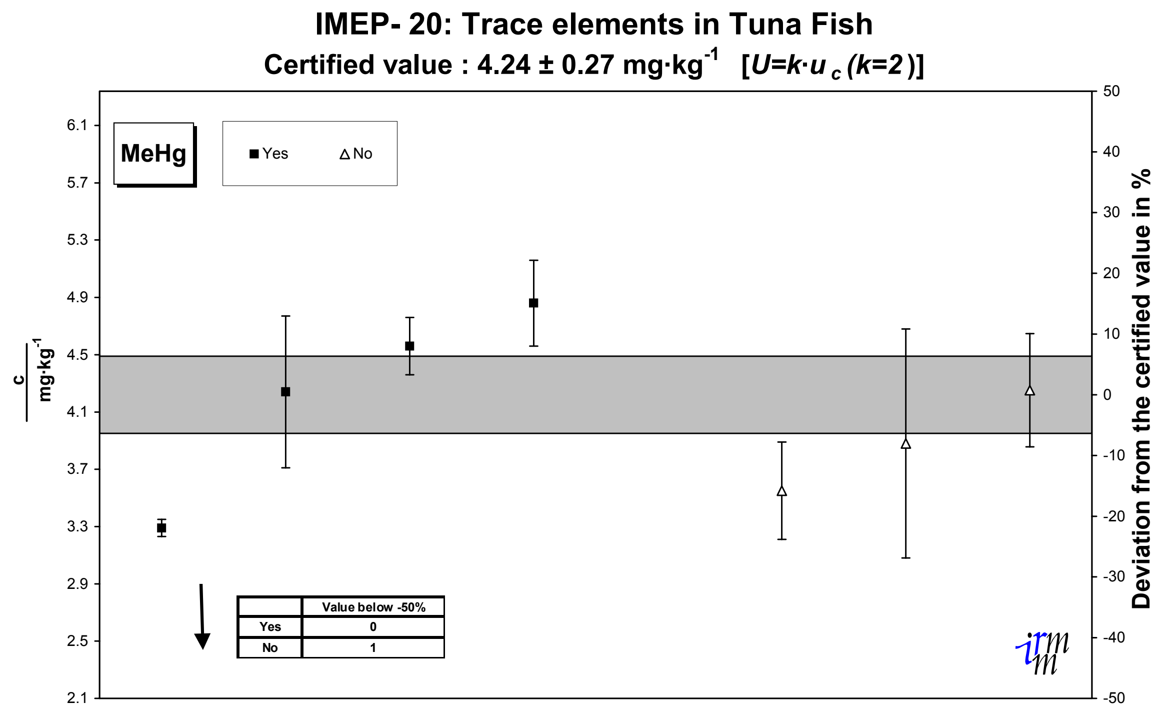
Results from all participants according to their participation in proficiency testing schemes. (PTs)

Figure 73



Results from all participants according to Accredited and/or Authorised.

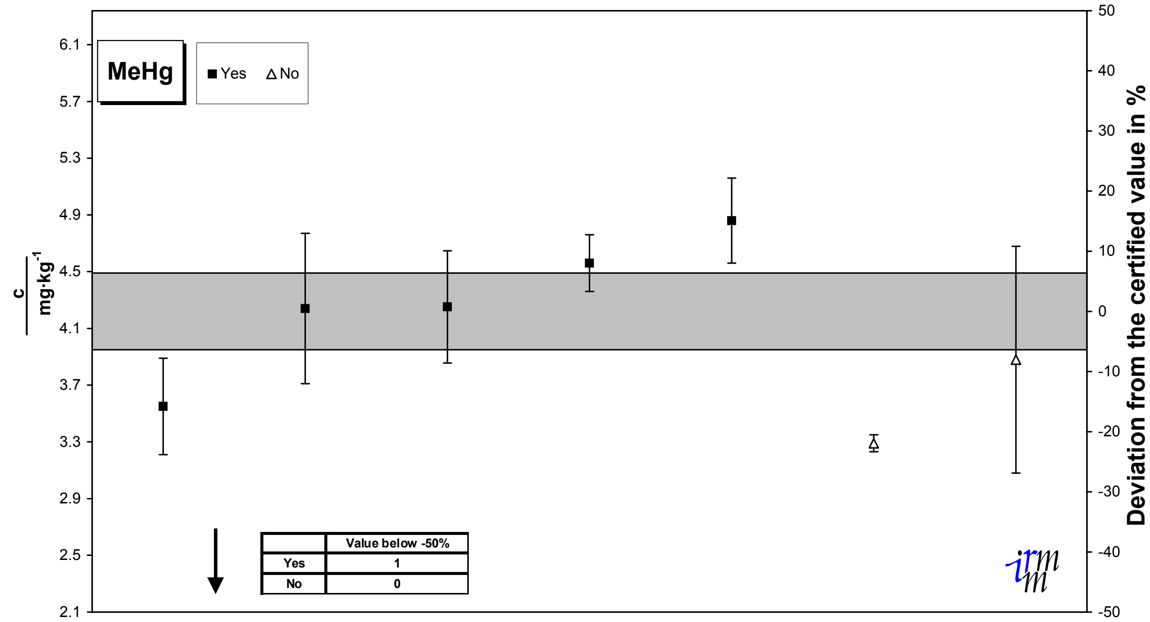
Figure 74



Results from all participants according to uncertainties being reported on their chemical measurements to customers.

Figure 75

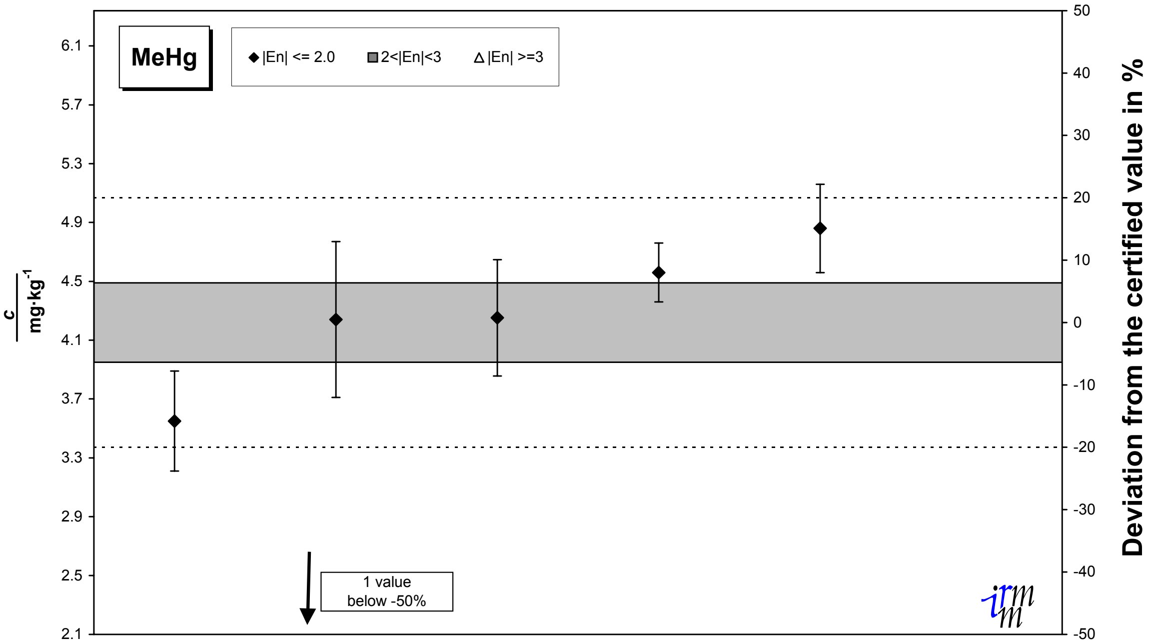
IMEP- 20: Trace elements in Tuna Fish
Certified value : 4.24 ± 0.27 mg·kg^{-1} [$U=k \cdot u_c$ ($k=2$)]



Results from all participants according to uncertainties calculated within the Guidelines of Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).

Figure 76

IMEP- 20: Trace elments in Tuna Fish
Certified value : 4.24 ± 0.27 mg·kg^{-1} [$U=k \cdot u_c$ ($k=2$)]



Results from IMEP-20 partcipants who estimated unc. according to ISO-GUM 1995 and/or EURACHEM/CITAC (2000) sorted according to the E_n-number

Annex 2 – Water Content Determination

Contents

Water content determination

The determination of the water content in food matrices is a challenging task and to some extent "operationally defined" [1, 2]. Therefore IRMM has been approached several times in the past by laboratories from the food sector to organise an IMEP® interlaboratory comparison on the water content determination in a food matrix. Although the tuna fish CTS used in IMEP-20 had not been certified for its water content, IRMM took the opportunity to provide a survey on the water content determination and correction for dry-mass using the information received from the IMEP-20 participants. A similar survey has been done in IMEP-19 "Trace Elements in Rice". The results can be found in the IMEP-19 participants' report, which is accessible via the IMEP web site [3].

The results of the water content determination and correction for dry-mass in IMEP-20 are summarised in this Annex. In view of the importance of the water content determination in food analysis, IRMM asked the laboratories to provide information on the analytical method used. From the IMEP-20 questionnaire, participants were asked the average sample mass used for the water content determination, the determined water content in percentage, the applied dry-mass correction factor used in the measurement equation to calculate the total amount content of the trace elements present in the CTS, and whether the CTS was equilibrated with ambient humidity conditions prior to the water content determination.

Figure 1 shows the IMEP-20 participants' response to the questions relating to the water content determination and correction for "dry-mass". 70% of IMEP-20 participants reported a value for the water content determination. 62% of IMEP-20 participants reported a value for the dry-mass correction. 72% of IMEP-20 participants reported the average sample mass in grams used for the water content determination and 31% of IMEP-20 participants equilibrated the CTS with ambient humidity conditions prior to water content determination. 28% of IMEP-20 participants did not determine the water content in the CTS at all.

Figure 1 Participants' responses to questions 6, 7, 8, 9 and 10 shown by %

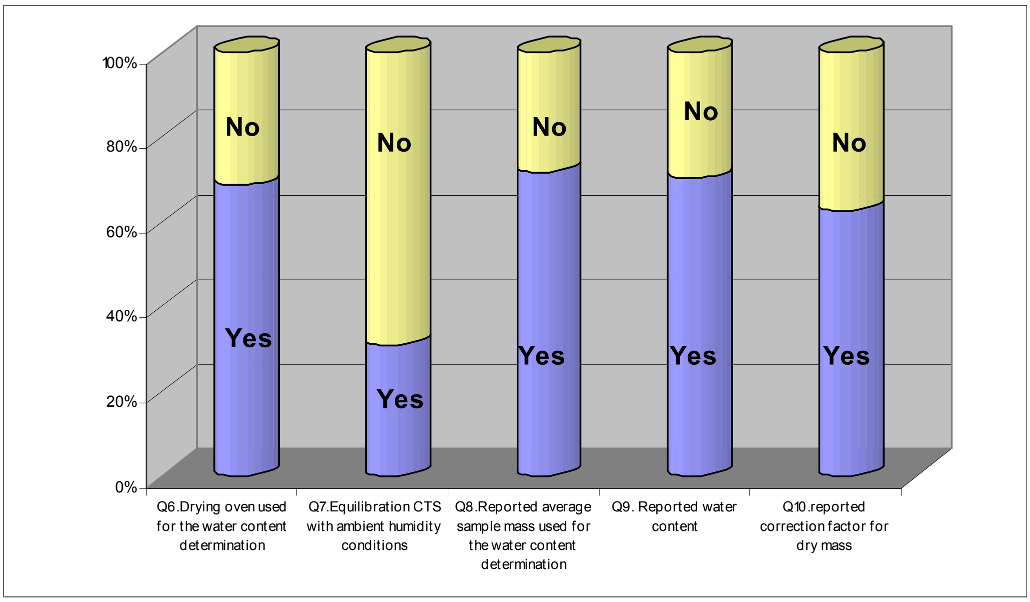


Figure 2 Methods used for the water content determination

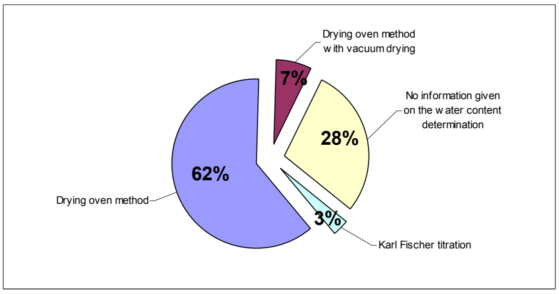


Figure 3 Drying temperatures used for the water content determination of the non-equilibrated CTS

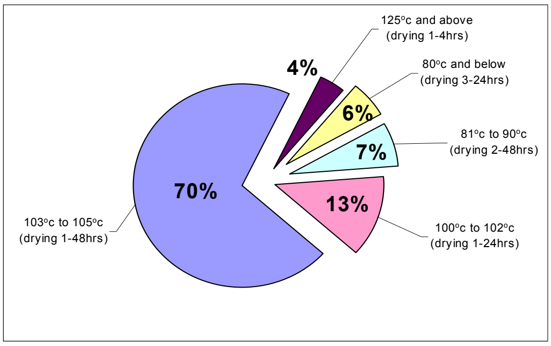


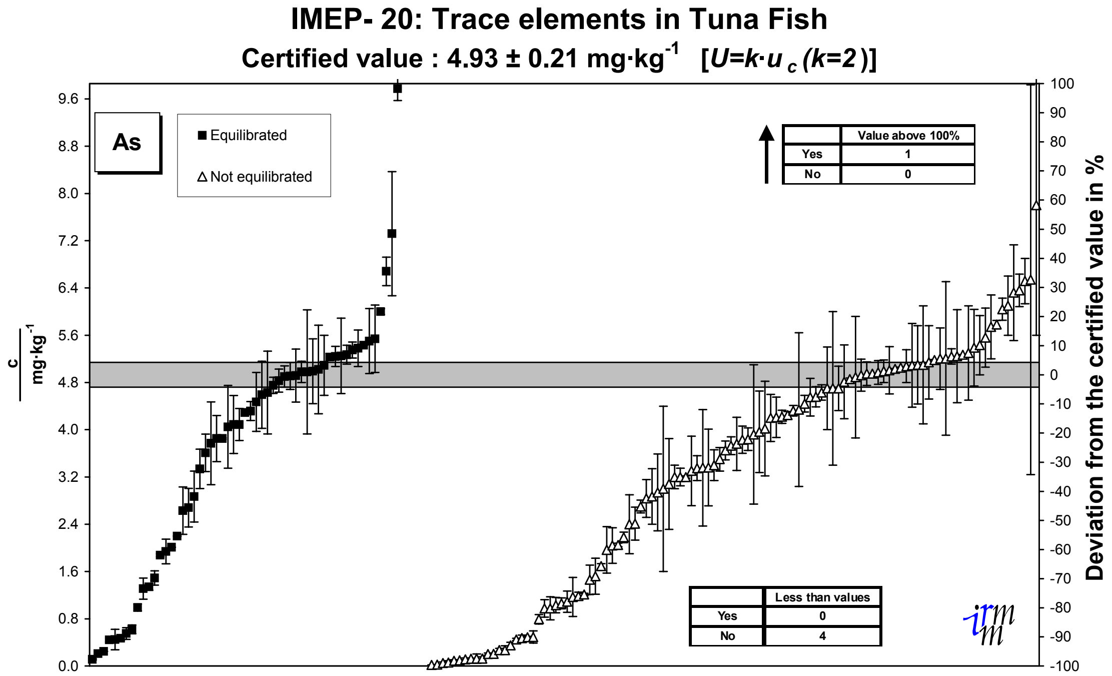
Figure 2 shows by percentage the methods used for the water content determination, 69% of IMEP-20 participants applied the drying-oven method to determine the water content in the CTS. 16 participants out of those 69% used vacuum drying. 3% used Karl-Fischer titration to determine the water content. 1 participant corrected for dry-mass using the Mettler LP16 infrared dryer. 1 participant dried the sample in a dessicator with P_2O_5 and another participant freeze-dried the sample prior to measurements. 3 participants reported values for the water content without specifying the method used. 29% of the IMEP-20 participants applied the drying oven method on the non-equilibrated sample and reported also a correction factor for the water content. These participants applied different drying times and temperatures. Almost half of these participants applied the drying-oven method at 105°C, mostly using a drying time between 1 to 6 hours. 12 participants applied the drying-oven method at 105°C, using a drying time between 10 hours and 1 day. In Figure 3 the drying temperatures for oven-drying on the non-equilibrated CTS are shown. Drying times are given in parenthesis.

Water content of the IMEP-20 CTS

To establish the certified reference values in IMEP-20 a thorough study was carried out at IRMM on the determination of the water content and the hygroscopic behaviour of the CTS. The correction factor for dry-mass was deduced from the water content measurements of the non-equilibrated CTS. The water content of the non-equilibrated CTS was measured with two independent methods, Karl-Fischer titration and drying-oven. There were no significant differences to the results of the water content in the non-equilibrated CTS, for the two methods applied.

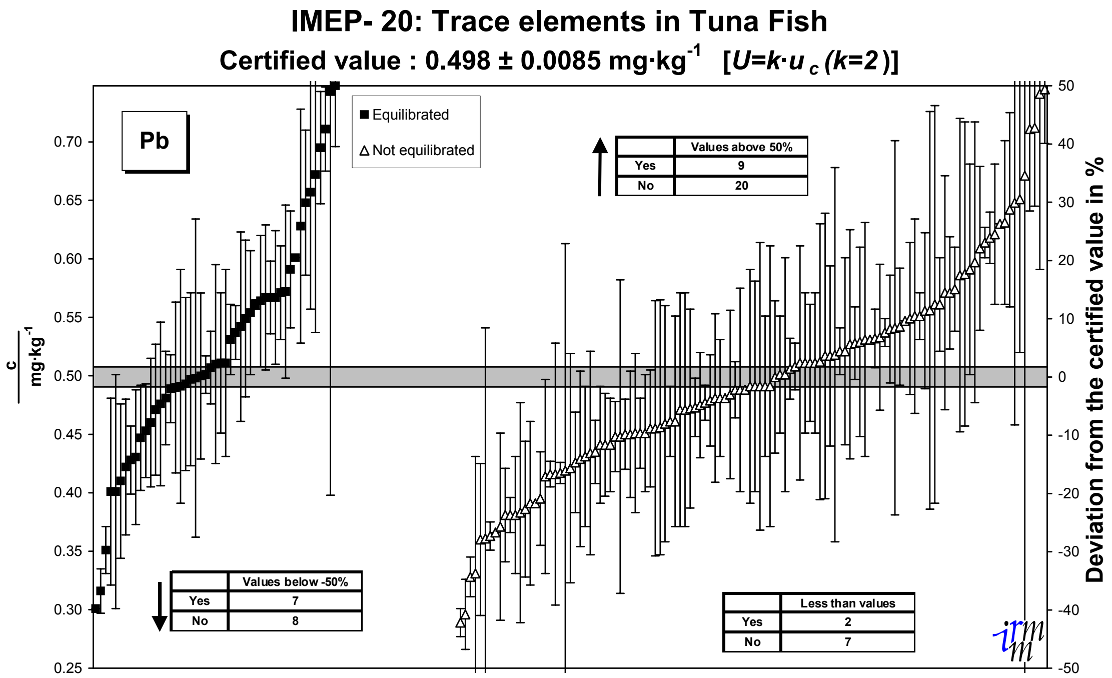
In Figure 4 - Figure 7 are the results for As, Hg, Pb and Se, which are sorted according to the measurements performed on the equilibrated or non-equilibrated CTS prior to the measurements.

Figure 4



Results from all participants according to the sample equilibration with ambient humidity conditions, prior to the determination of the water content.

Figure 5

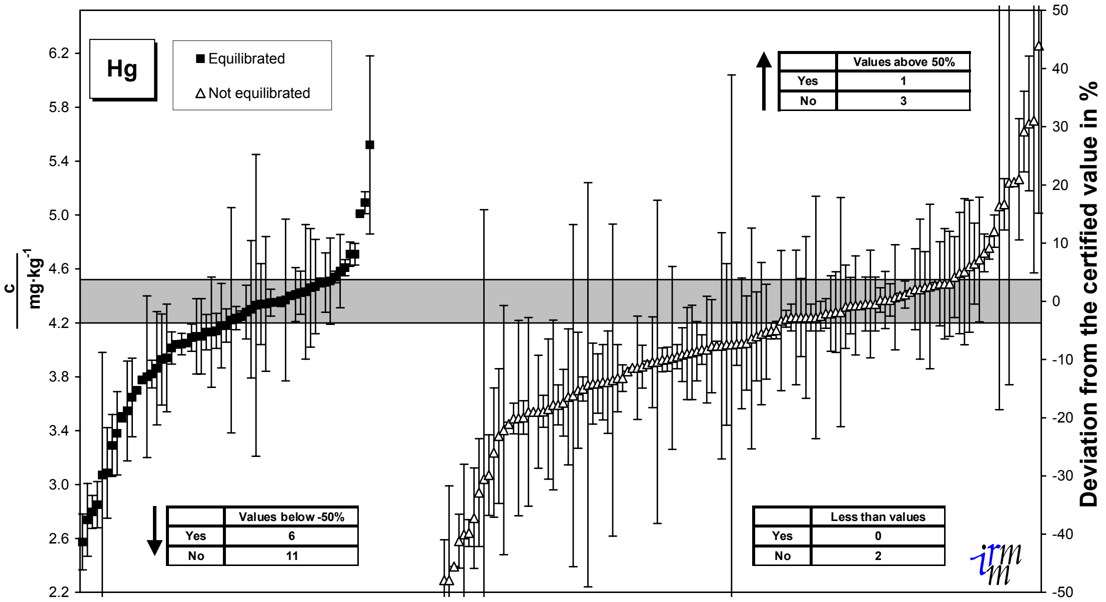


Results from all participants according to the sample equilibration with ambient humidity conditions, prior to the determination of the water content.

Figure 6

IMEP- 20: Trace elements in Tuna Fish

Certified value : 4.32 ± 0.16 mg·kg^{-1} [U=k·u_c (k=2)]

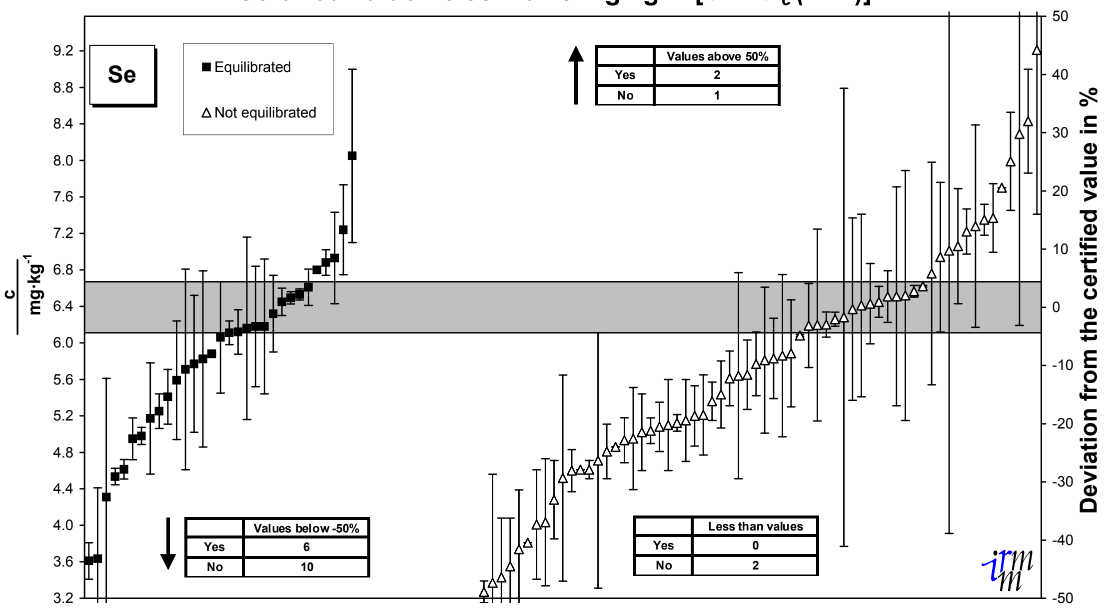


Results from all participants according to the sample equilibration with ambient humidity conditions, prior to the determination of the water content.

Figure 7

IMEP- 20: Trace elements in Tuna Fish

Certified value : 6.38 ± 0.28 mg·kg^{-1} [U=k·u_c (k=2)]



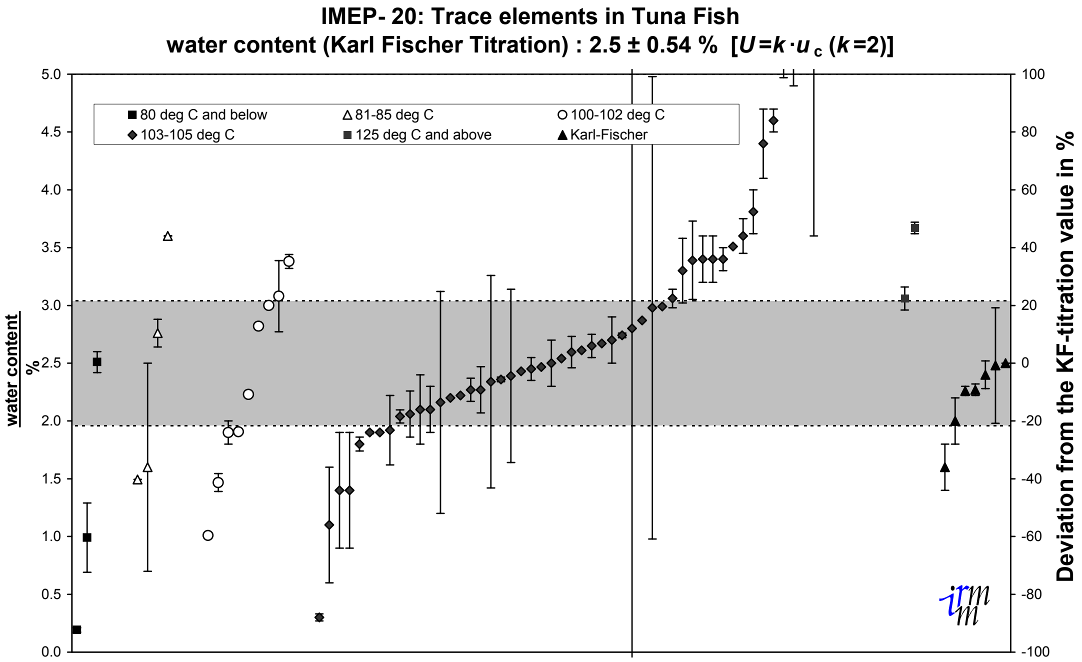
Results from all participants according to the sample equilibration with ambient humidity conditions, prior to the determination of the water content.

In Figure 8 the reported values for the water content of the 29% of IMEP-20 participants using the drying oven method are graphically displayed according to the applied drying temperatures. Furthermore the results for the water content as reported by the participants using Karl-Fischer titration are also included in this graph. The water content of the CTS was measured by IRMM using the drying oven method and Karl-Fischer titration on 10 non-equilibrated CTS.

There was no significant difference of the water content observed applying these two independent methods.

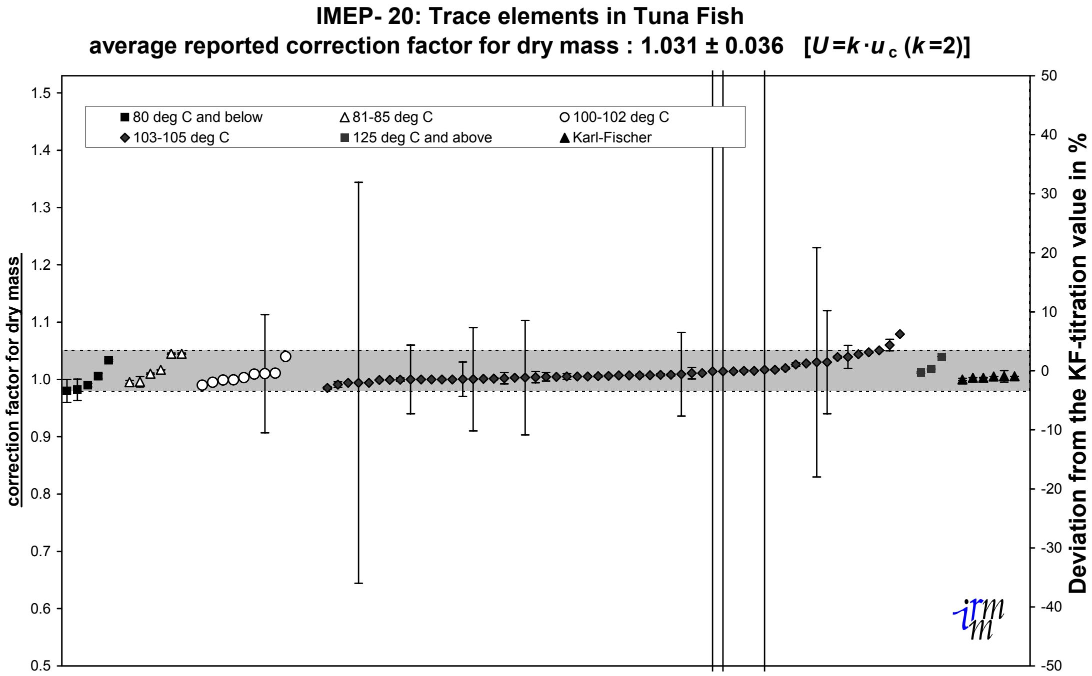
The Karl-Fischer value within its expanded uncertainty is given by the grey range between the broken lines in Figure 8. IRMM has to emphasise again that this is NOT a certified value for the water content in the CTS. This additional information is merely for the IMEP-20 participants.

Figure 8



Results for water content on the non-equilibrated CTS as reported by IMEP-20 participants using drying-oven method according to applied drying temperature or Karl-Fischer Titration

Figure 9



Results for the correction factor for dry-mass on the non-equilibrated CTS as reported by IMEP-20 participants using drying-oven method according to applied drying temperature or Karl-Fischer Titration

In Figure 9 the reported values for the dry-mass correction factor are from the same participants as in Figure 8 according to the applied drying temperature. The average reported value (excluding the value above 50% deviation) is given in the grey range between the broken lines. The reported dry-mass correction factors had been reported by the participants either as values below or above 1. To enable the calculation of an average value the reported dry-mass correction factors were all transferred to correction factors larger than 1. The displayed correction factors in Figure 9 correspond to the ratio of the sample mass before drying, to the sample mass after drying, also including a possible correction for moisture uptake while sample handling. The participants applied this “dry-mass correction” to the mass of the sample used for the measurements to correct for the mass loss due to drying in combination with a correction for possible hygroscopicity.

The importance of the water content determination was clearly identified, from the information given by the participants in IMEP-20 and IMEP-19, which was the previously organised IMEP® interlaboratory comparison on a food matrix. It was confirmed that the drying-oven method is the most common method used for water content determination in this kind of matrix. This is obviously due to the fact that for a lot of food matrices the drying-oven method is obligatory stated as reference method in the CODEX Alimentarius [4]. The positive response to this survey encourages IRMM to investigate the feasibility of an IMEP® comparison on water content determination in food matrices in the future.

References

1. S. Rückhold et al. *Fresenius J. Anal. Chem* (2000) 368: 522-527
2. S. Rückhold et al . *Fresenius J. Anal. Chem* (2000) 370: 189-193
3 http://www.imep.ws
4. CODEX Alimentarius, Standard and Standard Methods, Volume 13, codexstan-234, 1999

Annex 3 – Additional Information presentation

Contents

IMEP-20: Trace Elements in Tuna Fish

Annex 3 – Additional Information – Tables & Pie Charts

Table 1. Laboratories who participate regularly in Proficiency Testing Schemes (PTs)

Country	Proficiency Testing Schemes (PTs)	No. of Labs
AUSTRIA	CHEK-Netherlands, LVU-Germany, FAPAS Series 7, IAEA, IMEP, ALVA	7
BELGIUM	FAPAS, Quasimeme, EU-CRL, ISS	4
BULGARIA	AMOS-1998, IMEP-19, FAPAS series 7, Round 43, WEPAL- IPE	4
CYPRUS	FAPAS	1
CZECH REPUBLIC	Body Fluids, University Erlangen-Germany, tissue IAEA, Ekocentrum Ostrava-Czech Republic, FAPAS, APLAC, CALITAX-Spain, NFA-Sweden, We organise test of determination of having metals	10
DENMARK	EUROFINS, BIPEA, FAPAS series 07, 47, 48, 40, 41	4
ESTONIA	Estonian Environmental Researcher Centre, FAPAS, NFA-Sweden	4
FINLAND	FAPAS, CHEK, ISS, VTT-Finland, Finnish Environment Institute	5
FRANCE	AFSSA, BIPEA, IAG, FAPAS, CRL-ISS-ROMA-Italy	8
GERMANY	BgVV, FAPAS, IAEA, LVU, BVL, LVL, IMEP, NIST, QUASIMEME, Federal Office for Consumer Protection and Food Safety	13
GREECE	Elements in synthetic solutions of animal origin	1
HUNGARY	FAPAS, BSI Mertcontrol Rt-Hungary, National Food Investigation Institute (OÉVI)-Hungary, OKK-OKI, VITUKI	6
IRELAND	FAPAS	1
ITALY	CRL programme, FAPAS	3
LATVIA	IMEP-19, FAPAS, LIVSMEDELS VERKET-Sweden, NFA-Sweden	3
LITHUANIA	FAPAS, NFA-Sweden, IMEP, LIVSMEDELS VERKET, MUVA	4
NORWAY	FAPAS, Quasimeme, LIVSMEDELS VERKET-Sweden, NRL-ISS	3

Table 1. Laboratories who participate regularly in Proficiency Testing Schemes (PTs)

Country	Proficiency Testing Schemes (PTs)	No. of Labs
POLAND	Inst. of Technology Cracow, EUROMET 563, 548, IMEP, FAPAS, APLAC, PZH, IChTJ-Poland, EI JRC Ispra, CEN/TCU PRAQ-III project QI16, National Institute of Hygiene-Poland, National Veterinary Institut -Pulawy, OZNACZANIE ZAWARTO, Samples of animal origin prepared by PIWET-Pulawy	20
PORTUGAL	CRL-ISS, FAPAS, Inter 2000	3
ROMANIA	INFRAS, IMEP	3
SLOVAKIA	NRC-Liptovsky Mikulas, VUVH Bratislava, CZPI Brno-Czech Republic, FAPAS, IAEA-Austria, IMEP, National Reference Centre for Proficiency Testing, SZU Praha	18
SLOVENIA	FAPAS - Series 7, Round 46, IMEP	5
SPAIN	FAPAS, NFA, NRL	8
SWEDEN	NFA, FAPAS	4
SWITZERLAND	IMEP, FAPAS	1
THE NETHERLANDS	ISS-CRL-Italy, KDLL	2
TURKEY	FAPAS, IMEP, UME	9
UNITED KINGDOM	FAPAS, ISS	2

Table 2. Summary of the self-declared status, Accredited – Authorised for As

Country	Yes to both Accredited/ Authorised for As	Yes only to Accredited for As	Yes only to Authorised for As	No to both Accredited/ Authorised for As	No. of Labs
ARGENTINA	0	0	1	0	1
AUSTRALIA	0	0	0	1	1
AUSTRIA	1	2	1	3	7
BELGIUM	0	0	3	1	4
BULGARIA	0	2	0	4	6
CZECH REPUBLIC	4	5	0	1	10
DENMARK	2	1	0	2	5
ESTONIA	0	1	1	0	2
FINLAND	0	1	0	2	3
FRANCE	2	0	4	2	8
GERMANY	10	2	0	1	13
GREECE	0	0	0	1	1
HUNGARY	2	2	3	4	11
IRELAND	0	0	0	1	1
ITALY	0	3	1	0	4
LATVIA	1	1	0	2	4
LITHUANIA	0	0	0	4	4
MALTA	0	0	0	1	1
NORWAY	0	3	0	0	3
POLAND	0	3	7	16	26
PORTUGAL	0	0	1	1	2
ROMANIA	1	0	1	3	5
SLOVAKIA	6	5	0	2	13
SLOVENIA	1	0	1	0	2
SPAIN	2	1	1	2	6
SWEDEN	0	2	2	0	4
SWITZERLAND	2	0	1	0	3
THE NETHERLANDS	2	0	0	1	3
TURKEY	1	0	6	6	13
UNITED KINGDOM	0	1	0	0	1
U S A	1	0	0	0	1
TOTALS	38	35	34	61	168

Figure 1 Summary of the self-declared status, Accredited – Authorised for As

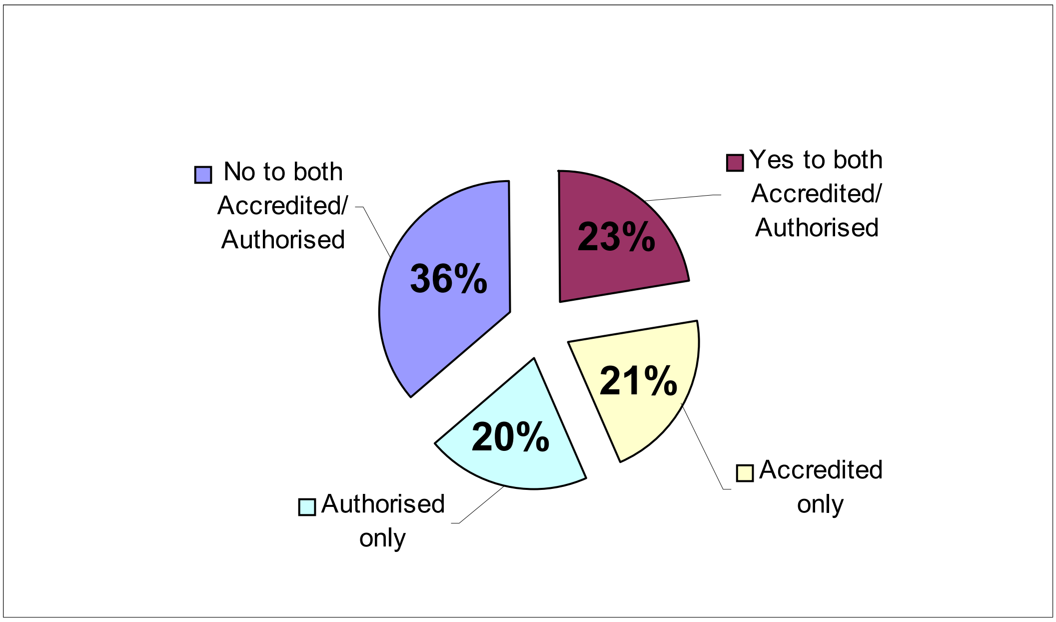


Table 3. Summary of the self-declared status, Accredited – Authorised for Pb

Country	Yes to both Accredited/ Authorised for Pb	Yes only to Accredited for Pb	Yes only to Authorised for Pb	No to both Accredited/ Authorised for Pb	No. of Labs
ARGENTINA	0	0	1	0	1
AUSTRALIA	0	0	0	1	1
AUSTRIA	4	3	0	4	12
BELGIUM	1	0	2	2	5
BULGARIA	0	2	0	4	6
CZECH REPUBLIC	4	6	0	2	12
DENMARK	2	2	0	1	5
ESTONIA	2	2	0	0	4
FINLAND	0	2	0	2	4
FRANCE	5	2	2	1	10
GERMANY	12	2	0	0	14
GREECE	0	0	2	0	2
HUNGARY	4	3	1	3	11
IRELAND	0	1	0	0	1
ITALY	0	5	1	1	7
LATVIA	0	1	0	2	3
LITHUANIA	1	0	0	4	5
MALTA	0	0	0	1	1
NORWAY	1	2	0	0	3
POLAND	1	9	7	23	40
PORTUGAL	0	1	3	0	4
ROMANIA	1	0	1	3	5
SLOVAKIA	7	15	1	5	27
SLOVENIA	2	0	0	3	5
SPAIN	4	2	0	1	7
SWEDEN	2	2	0	0	4
SWITZERLAND	2	0	1	0	3
THE NETHERLANDS	2	0	0	1	3
TURKEY	1	1	6	5	13
UNITED KINGDOM	0	1	0	0	1
U S A	1	0	0	0	1
TOTALS	59	64	28	69	220

Figure 2 Summary of the self-declared status, Accredited – Authorised for Pb

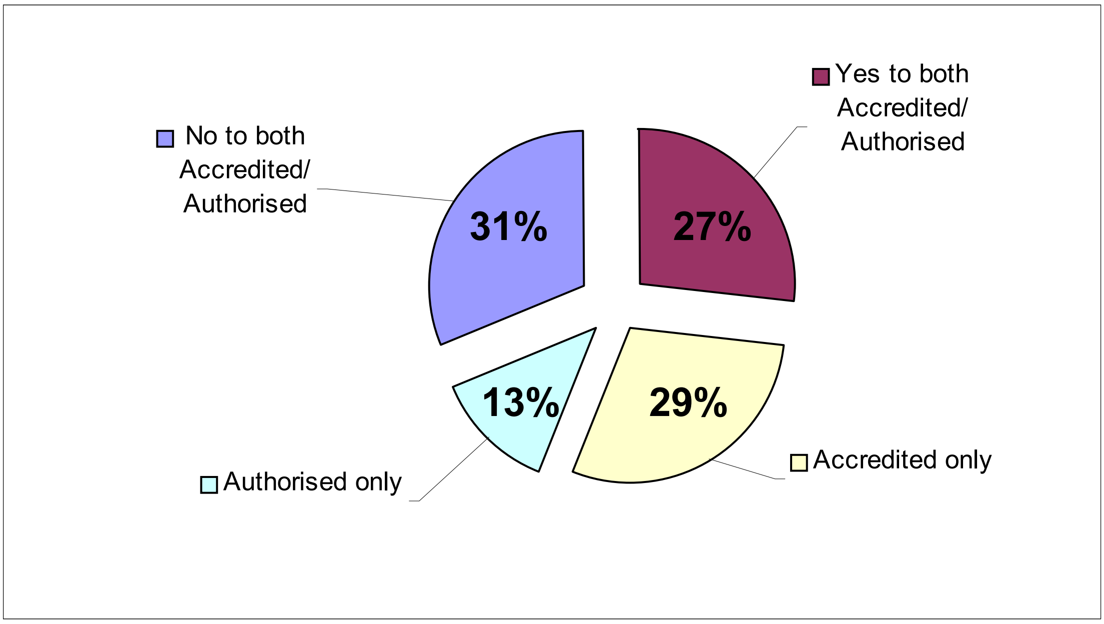


Table 4. Summary of the self-declared status, Accredited – Authorised for Hg

Country	Yes to both Accredited/ Authorised for Hg	Yes only to Accredited for Hg	Yes only to Authorised for Hg	No to both Accredited/ Authorised for Hg	No. of Labs
ARGENTINA	0	0	1	0	1
AUSTRALIA	0	0	0	1	1
AUSTRIA	4	3	0	1	8
BELGIUM	0	0	4	2	6
BULGARIA	0	0	0	2	2
CYPRUS	1	0	0	0	1
CZECH REPUBLIC	4	6	0	2	12
DENMARK	2	2	0	1	5
ESTONIA	1	1	0	0	2
FINLAND	1	4	0	0	5
FRANCE	4	0	4	2	10
GERMANY	12	2	0	0	14
GREECE	0	0	3	0	3
HUNGARY	1	1	3	4	9
IRELAND	0	1	0	0	1
ITALY	0	5	1	1	7
LATVIA	1	1	0	2	4
LITHUANIA	1	0	0	2	3
MALTA	0	0	0	1	1
NORWAY	0	3	0	0	3
POLAND	2	6	7	23	38
PORTUGAL	1	0	1	1	3
ROMANIA	1	0	1	2	4
SLOVAKIA	7	12	1	5	25
SLOVENIA	1	0	0	3	4
SPAIN	1	2	1	2	6
SWEDEN	1	2	1	0	4
SWITZERLAND	2	0	1	0	3
THE NETHERLANDS	2	0	0	1	3
TURKEY	1	0	6	6	13
UNITED KINGDOM	0	1	0	0	1
U S A	1	0	0	0	1
TOTALS	52	52	35	64	203

Figure 3 Summary of the self-declared status, Accredited – Authorised for Hg

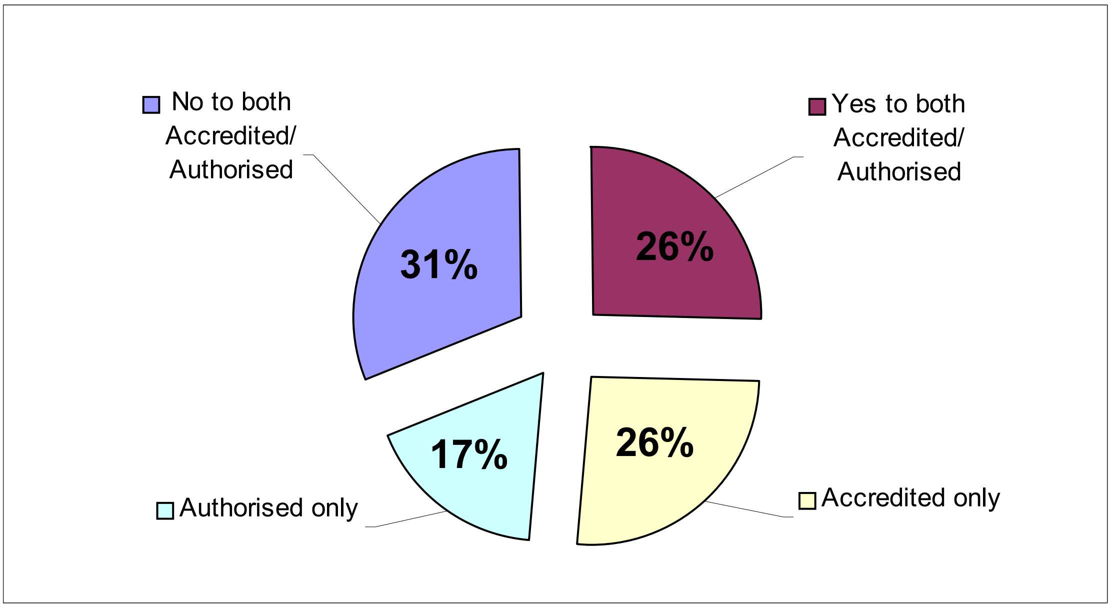


Table 5. Summary of the self-declared status, Accredited – Authorised for Se

Country	Yes to both Accredited/ Authorised for Se	Yes only to Accredited for Se	Yes only to Authorised for Se	No to both Accredited/ Authorised for Se	No. of Labs
ARGENTINA	0	0	1	0	1
AUSTRALIA	0	0	0	1	1
AUSTRIA	0	2	1	1	4
BELGIUM	0	0	3	2	5
BULGARIA	0	2	0	3	5
CZECH REPUBLIC	4	4	0	1	9
DENMARK	1	1	0	2	4
ESTONIA	0	1	1	0	2
FINLAND	0	1	0	0	1
FRANCE	1	0	2	3	6
GERMANY	10	2	0	1	13
GREECE	0	0	0	1	1
HUNGARY	1	1	3	5	10
ITALY	0	2	1	1	4
LATVIA	0	0	0	1	1
LITHUANIA	0	0	0	2	2
NORWAY	0	3	0	0	3
POLAND	0	0	1	13	14
PORTUGAL	0	0	1	0	1
ROMANIA	1	0	1	3	5
SLOVAKIA	5	0	0	2	7
SLOVENIA	0	0	0	1	1
SWEDEN	1	1	1	1	4
SWITZERLAND	2	0	0	0	2
THE NETHERLANDS	1	0	1	1	3
TURKEY	0	0	1	4	5
UNITED KINGDOM	0	1	0	0	1
U S A	1	0	0	0	1
TOTALS	28	21	18	49	116

Figure 4 Summary of the self-declared status, Accredited – Authorised for Se

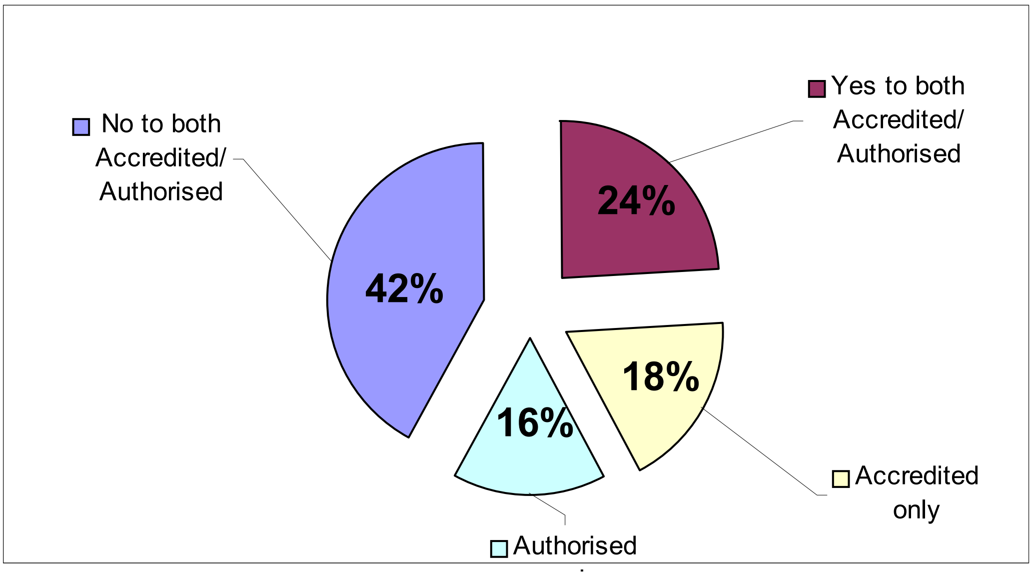


Table 6. Summary of the self-declared status, Accredited – Authorised for MeHg

Country	Yes to both Accredited/ Authorised for MeHg	Yes only to Accredited for MeHg	Yes only to Authorised for MeHg	No to both Accredited/ Authorised for MeHg	No. of Labs
ARGENTINA	0	0	0	1	1
BELGIUM	0	0	1	0	1
CZECH REPUBLIC	0	0	0	1	1
FRANCE	0	0	1	0	1
GERMANY	0	0	0	1	1
POLAND	1	0	0	0	1
THE NETHERLANDS	1	0	0	0	1
UNITED KINGDOM	0	0	0	1	1
TOTALS	2	0	2	4	8

Figure 5 Summary of the self-declared status, Accredited – Authorised for MeHg

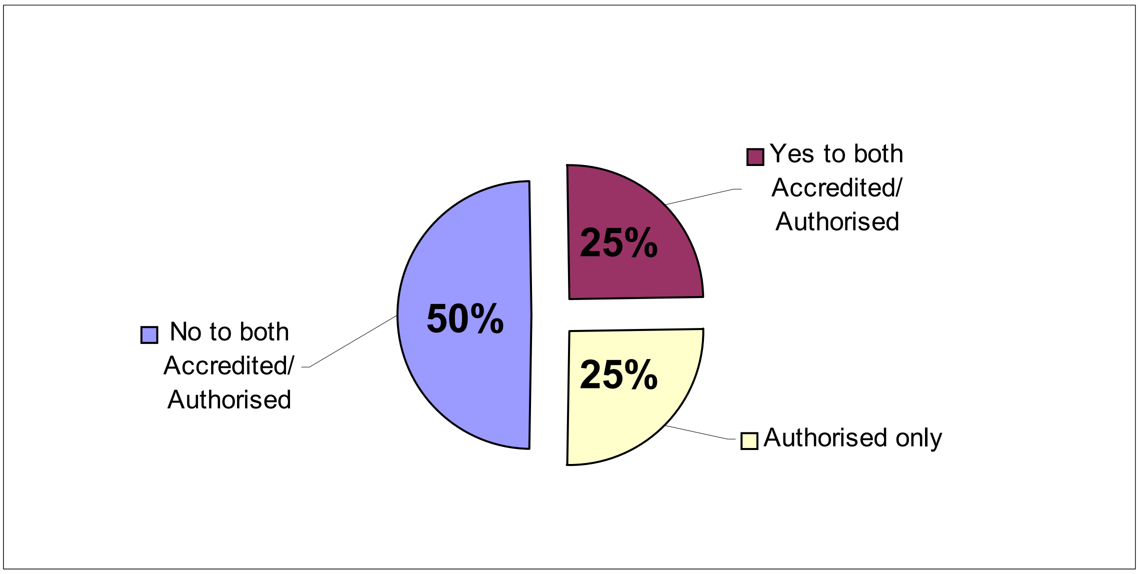


Table 7. Positive responses to Question 4, digestion step for As

Country	Yes to both Separation/pre-concentration for As	Yes only to Separation for As	Yes only to Pre-concentration for As	No to both Separation/pre-concentration for As	No. of Labs
ARGENTINA	0	0	0	1	1
AUSTRALIA	0	0	0	1	1
AUSTRIA	0	1	0	6	7
BELGIUM	0	0	0	4	4
BULGARIA	0	1	0	5	6
CZECH REPUBLIC	0	1	0	8	9
DENMARK	0	1	0	4	5
ESTONIA	0	0	0	2	2
FINLAND	0	0	0	3	3
FRANCE	0	0	1	7	8
GERMANY	1	0	1	11	13
GREECE	0	0	0	1	1
HUNGARY	0	0	0	11	11
IRELAND	0	0	0	1	1
ITALY	0	0	0	4	4
LATVIA	0	0	0	4	4
LITHUANIA	0	0	0	4	4
MALTA	0	0	0	1	1
NORWAY	0	1	0	2	3
POLAND	0	4	1	20	25
PORTUGAL	0	0	0	2	2
ROMANIA	0	0	0	5	5
SLOVAKIA	0	1	0	12	13
SLOVENIA	0	1	0	1	2
SPAIN	0	0	0	5	5
SWEDEN	0	1	0	3	4
SWITZERLAND	0	0	0	3	3
THE NETHERLANDS	0	0	0	3	3
TURKEY	0	1	2	10	13
UNITED KINGDOM	0	0	0	1	1
U S A	0	0	0	1	1
TOTALS	1	13	5	146	165

Table 8. Negative responses to Question 4, digestion step for As

Country	Yes to both Separation/pre-concentration for As	Yes only to Separation for As	Yes only to Pre-concentration for As	No to both Separation/pre-concentration for As	No. of Labs
CZECH REPUBLIC	0	0	0	1	1
POLAND	0	1	0	0	1
SPAIN	0	0	0	1	1
TOTALS	0	1	0	2	3

Figure 6 Positive responses to Question 4, digestion step for As

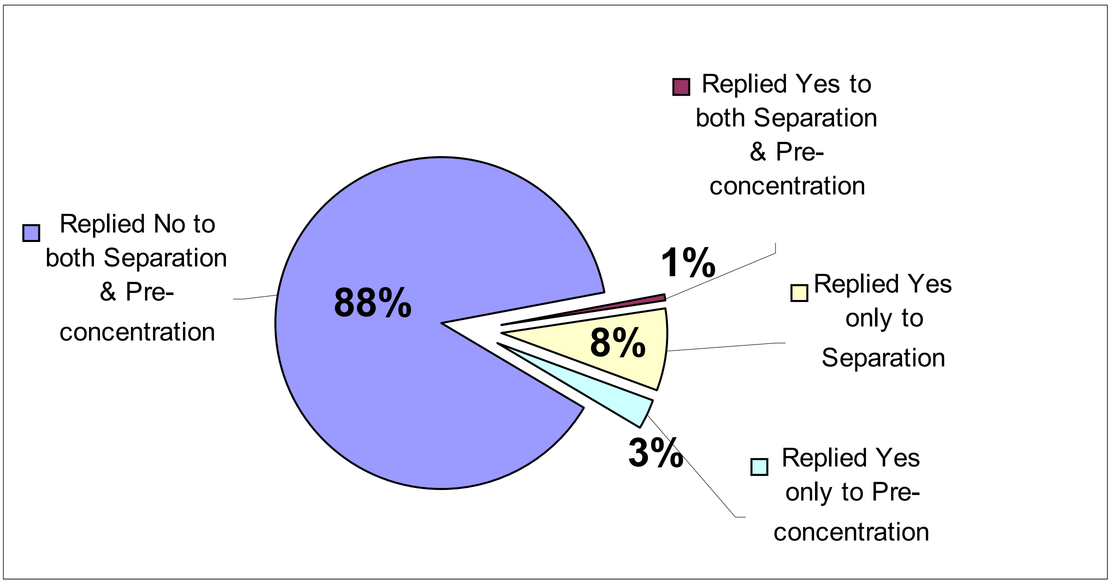


Table 9. Positive responses to Question 4, digestion step for Pb

Country	Yes to both Separation/pre-concentration for Pb	Yes only to Separation for Pb	Yes only to Pre-concentration for Pb	No to both Separation/pre-concentration for Pb	No. of Labs
ARGENTINA	0	0	0	1	1
AUSTRALIA	0	0	0	1	1
AUSTRIA	0	0	0	11	11
BELGIUM	0	0	0	5	5
BULGARIA	0	0	0	6	6
CZECH REPUBLIC	0	0	0	10	10
DENMARK	0	1	0	4	5
ESTONIA	0	0	0	4	4
FINLAND	0	0	0	4	4
FRANCE	0	0	1	9	10
GERMANY	0	0	0	14	14
GREECE	0	0	0	2	2
HUNGARY	0	0	0	11	11
IRELAND	0	0	0	1	1
ITALY	0	0	0	7	7
LATVIA	0	0	0	3	3
LITHUANIA	0	0	0	5	5
MALTA	0	0	0	1	1
NORWAY	0	0	0	3	3
POLAND	2	4	1	32	39
PORTUGAL	0	0	0	4	4
ROMANIA	0	0	0	5	5
SLOVAKIA	0	1	1	25	27
SLOVENIA	0	1	0	3	4
SPAIN	0	0	0	6	6
SWEDEN	0	0	0	4	4
SWITZERLAND	0	0	0	3	3
THE NETHERLANDS	0	0	0	3	3
TURKEY	0	1	2	10	13
UNITED KINGDOM	0	0	0	1	1
U S A	0	0	0	1	1
TOTALS	2	8	5	199	214

Table 10. Negative responses to Question 4, digestion step for Pb

Country	Yes to both Separation/pre-concentration for Pb	Yes only to Separation for Pb	Yes only to Pre-concentration for Pb	No to both Separation/pre-concentration for Pb	No. of Labs
CZECH REPUBLIC	0	0	0	2	2
POLAND	0	1	0	0	1
SLOVAKIA	0	0	0	2	2
SPAIN	0	0	0	1	1
TOTALS	0	1	0	5	6

Figure 7 Positive responses to Question 4, digestion step for Pb

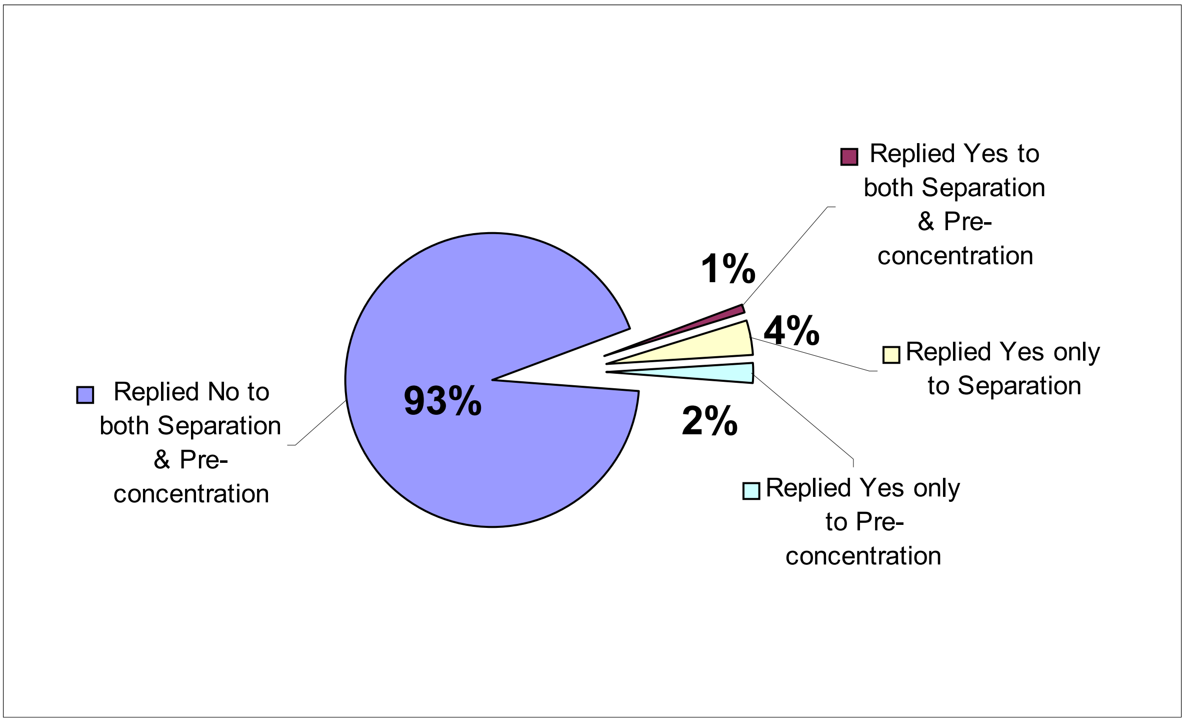


Table 11. Positive responses to Question 4, digestion step for Hg

Country	Yes to both Separation/pre-concentration for Hg	Yes only to Separation for Hg	Yes only to Pre-concentration for Hg	No to both Separation/pre-concentration for Hg	No. of Labs
ARGENTINA	0	0	0	1	1
AUSTRALIA	0	0	0	1	1
AUSTRIA	0	1	0	7	8
BELGIUM	0	0	0	6	6
BULGARIA	0	0	0	2	2
CYPRUS	0	0	0	1	1
CZECH REPUBLIC	0	0	0	10	10
DENMARK	0	1	0	4	5
ESTONIA	0	0	0	2	2
FINLAND	0	0	0	5	5
FRANCE	0	0	2	8	10
GERMANY	0	1	0	13	14
GREECE	0	1	0	2	3
HUNGARY	0	0	1	8	9
IRELAND	0	0	0	1	1
ITALY	0	0	0	7	7
LATVIA	0	0	0	4	4
LITHUANIA	0	0	0	3	3
MALTA	0	0	0	1	1
NORWAY	0	1	1	1	3
POLAND	0	5	1	30	36
PORTUGAL	0	0	0	3	3
ROMANIA	0	0	0	4	4
SLOVAKIA	0	1	0	21	22
SLOVENIA	0	1	0	3	4
SPAIN	0	0	0	6	6
SWEDEN	0	1	0	3	4
SWITZERLAND	0	0	0	3	3
THE NETHERLANDS	0	0	0	3	3
TURKEY	0	1	2	10	13
UNITED KINGDOM	0	0	0	1	1
U S A	0	0	0	1	1
TOTALS	0	14	7	175	196

Table 12. Negative responses to Question 4, digestion step for Hg

Country	Yes to both Separation/pre-concentration for Hg	Yes only to Separation for Hg	Yes only to Pre-concentration for Hg	No to both Separation/pre-concentration for Hg	No. of Labs
CZECH REPUBLIC	0	0	0	2	2
POLAND	0	1	0	1	2
SLOVAKIA	0	0	0	3	3
TOTALS	0	1	0	6	7

Figure 8 Positive responses to Question 4, digestion step for Hg

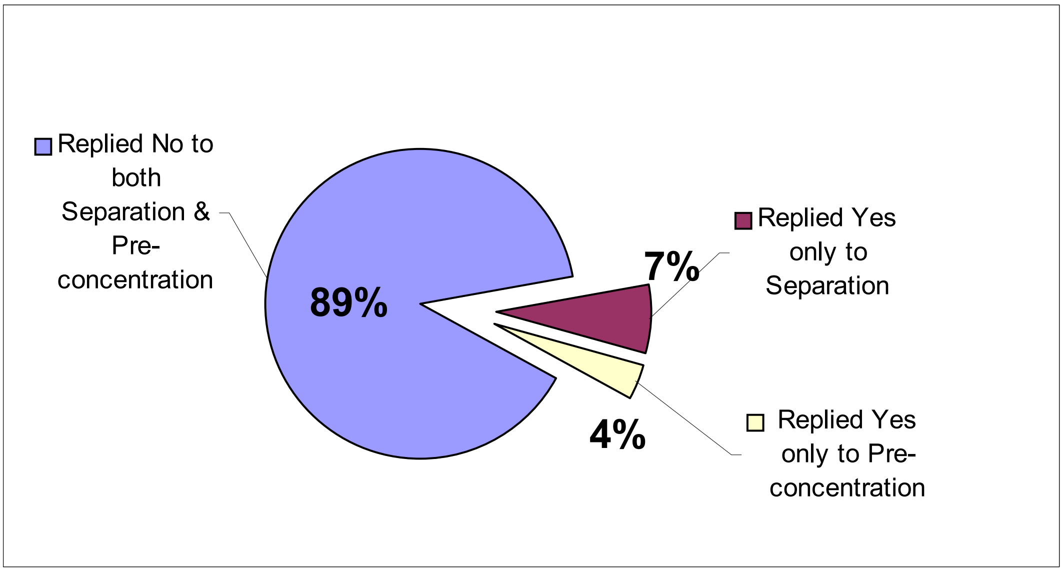


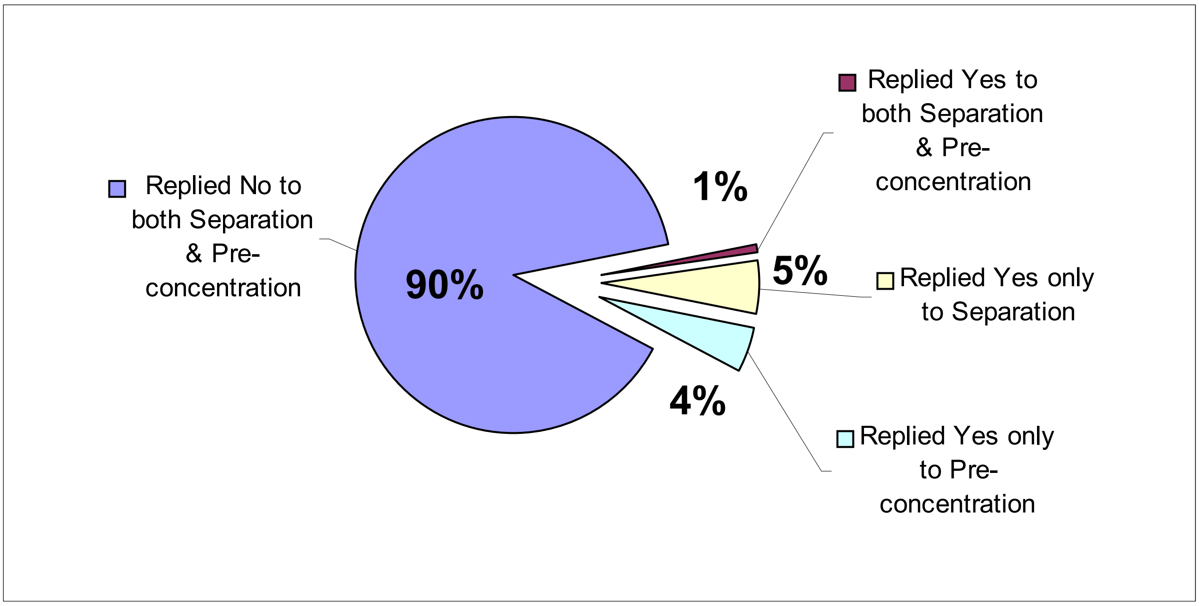
Table 13. Positive responses to Question 4, digestion step for Se

Country	Yes to both Separation/pre-concentration for Se	Yes only to Separation for Se	Yes only to Pre-concentration for Se	No to both Separation/pre-concentration for Se	No. of Labs
ARGENTINA	0	0	0	1	1
AUSTRALIA	0	0	0	1	1
AUSTRIA	0	0	0	4	4
BELGIUM	0	0	0	5	5
BULGARIA	0	1	0	4	5
CZECH REPUBLIC	0	0	0	8	8
DENMARK	0	1	0	3	4
ESTONIA	0	0	0	2	2
FINLAND	0	0	0	1	1
FRANCE	1	0	1	4	6
GERMANY	0	0	1	12	13
GREECE	0	0	0	1	1
HUNGARY	0	0	0	10	10
ITALY	0	0	0	4	4
LATVIA	0	0	0	1	1
LITHUANIA	0	0	0	2	2
NORWAY	0	1	0	2	3
POLAND	0	1	1	12	14
PORTUGAL	0	0	0	1	1
ROMANIA	0	0	0	5	5
SLOVAKIA	0	1	0	7	8
SWEDEN	0	1	0	3	4
SWITZERLAND	0	0	1	1	2
THE NETHERLANDS	0	0	0	3	3
TURKEY	0	0	1	4	5
UNITED KINGDOM	0	0	0	1	1
U S A	0	0	0	1	1
TOTALS	1	6	5	103	115

Table 14. Negative responses to Question 4, digestion step for Se

Country	Yes to both Separation/pre-concentration for Se	Yes only to Separation for Se	Yes only to Pre-concentration for Se	No to both Separation/pre-concentration for Se	No. of Labs
CZECH REPUBLIC	0	0	0	1	1
TOTALS	0	0	0	1	1

Figure 9 Positive responses to Question 4, digestion step for Se



Annex 4 – Documentation

Contents

IMEP-20: Trace Elements in Tuna Fish

Annex 4 – Documentation

Figure 1

EUROPEAN COMMISSION
DIRECTORATE GENERAL JRC
JOINT RESEARCH CENTRE
IRMM
Institute for Reference Materials and Measurements

IMEP®

Geel, 17 March 2003
IM/L/26/03

International Measurement Evaluation Programme

IMEP-20 Trace Elements in Tuna Fish

The International Measurement Evaluation Programme (IMEP®) was established and is operated by the Institute for Reference Materials and Measurements (IRMM) in order to picture objectively the degree of equivalence of chemical measurements by comparing them with external reference values (not derived from participant's results). Previous IMEP® interlaboratory comparisons have focused on different elements in various matrices such as water, sediment, serum, wine, rice and others. Information about these activities can be found on the IMEP website http://www.imep.ws.

Participating laboratories receive a Certified Test Sample (CTS) (with undisclosed amount content values), which is to be measured using routine analytical procedures. The measurement results of participants will be evaluated against metrological reference values obtained using a primary method of measurement (Isotope Dilution Mass Specrometry). Full confidentiality is guaranteed with respect to the link between measurement results and the participants' identity.

IRMM is now launching the IMEP-20 interlaboratory comparison that focuses on the analysis of total amount contents of Hg, Pb, As, Se and methylmercury in tuna fish. The CTS is available in glass vials containing 4 g of tuna fish.

IRMM is a Joint Research Centre of the European Commission (JRC). The mission of the JRC is to support the development and implementation of EU policies. IRMM organises this comparison for European laboratories involved in food analysis. These laboratories are either nominated by the National Accreditation Body or by the National Reference Laboratories. Furthermore, IMEP-20 is also particularly addressed to food laboratories from the European Union and candidate countries.

The samples will be available around June/July 2003. You can express your interest to participate until 13th June 2003 and the deadline for reporting results would be 31st October 2003. As a first feedback, participating laboratories will receive the reference values in December 2003. The full participants' report will be distributed in April 2004.

If you would be interested in joining this IMEP-20 interlaboratory comparison, please fill in the registration sheet and return it to your Regional Coordinator. A general list with IMEP regional co-ordinators is available on the IMEP website http://www.imep.ws.

Yours sincerely

Dr.Y. Aregbe
IMEP-20 Co-ordinator
IM Unit - IRMM

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 •Fax: +32-(0)14-571 865 • imep@irmm.jrc.be • yetunde.aregbe@irmm.jrc.be •
www.imep.ws • http://www.irmm.jrc.be

Figure 2

IMEP-20 : TRACE ELEMENTS IN TUNA FISH

REGISTRATION SHEET

We would like to participate in the IMEP-20 interlaboratory comparison.

In the framework of the support of IRMM to the Candidate Countries participation to laboratories nominated by the Regional Co-ordinators is free of charge.

Please complete the form in capital letters

NAME: ……………………………………………………………….
FIRM/INSTITUTE: ……………………………………………………………….
DEPARTMENT: ……………………………………………………………….
ADDRESS: ……………………………………………………………….
……………………………………………………………….
……………………………………………………………….
COUNTRY: ……………………………………………………………….

TELE.: ……………………………………………………………….
FAX.: …………………………………………………………………..
E-MAIL: ……………………………………………………………….

Would you please indicate with "YES" or "NO" in the list below your analytes of interest.

Hg (tot. amount cont.)	**Pb (tot. amount cont.)**	**Se (tot. amount cont.)**	**As (tot. amount cont.)**	**Methylmercury (Hg-organo species)**

(*)Please return this sheet to the IMEP regional co-ordinator in your country **before 13th June 2003** (the list of IMEP regional co-ordinators can be found on http://www.imep.ws)

* The IMEP® programme works in close co-operation with regional co-ordinators. Hence it is possible that you receive this registration sheet via different communication channels. You can register via IRMM or via your regional co-ordinator. All registrations are centralised at IRMM. In case more than one registration rom your laboratory is received, the name of the person who registers will be important. Different names will count as multiple registrations.

Figure 3

EUROPEAN COMMISSION
DIRECTORATE GENERAL JRC

JOINT RESEARCH CENTRE
IRMM
Institute for Reference Materials and Measurements

IMEP®

Geel, 30th June 2003
IM/L/58/03

IMEP-20: Trace Elements in Tuna Fish

Dear «title» «surname»,

Please find enclosed the sample together with the following documentation: 1) Instruction letter on how to report your results and questionnaire information.
2) IMEP-20 sample confirmation form, which must be returned immediately to IRMM.

The IMEP-20 interlaboratory comparison involves the determination of total amount contents of Hg, Pb, As, Se and methylmercury. Participants may select to analyse the elements relevant for their application. The Certified Test Sample (CTS) is in glass bottles containing 4g of Tuna Fish. The deadline for reporting the results and returning the completed questionnaire is 31st October 2003. A first feedback, concerning the IMEP-20 reference values, is foreseen for December 2003. The report for the participants containing the graphical display of all laboratory results as well as the reference values will be distributed by April 2004.

The results should be reported electronically via the Internet to IRMM. Instructions for reporting your results can be found at http://www.instruction20.imep.ws Therefore you have been allocated a laboratory identification number (Lab-ID) and a Key-code number, please use these numbers when reporting online.

The login page on the IMEP web site is located at: http://www.data20.imep.ws

Your LAB-ID No:- «Person_id»

Your KEY-CODE No:- «KeyCode»

When you have submitted your results and questionnaire information you will receive an e-mail as a confirmation of your reported results within the next days. On receipt of this e-mail please check your reported results carefully for any errors. In case you need to adjust any of your results, you will need to send an e-mail (imep@irmm.jrc.be) or fax (+32 14 571 865), with the amended details as soon as possible. If we don't receive a reply we assume that your reported results are correct and your results will then be transferred to our database. Once the results have been entered into our database there will be no further possibility for any changes. If you have any questions or problems, please do not hesitate to contact us.

Yours sincerely,

Dr. Y. Aregbe
IMEP-20 Co-ordinator, IRMM – JRC – EC
Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 •Fax: +32-(0)14-571 865 • imep@irmm.jrc.be • yetunde.aregbe@irmm.jrc.be •
www.imep.ws • http://www.irmm.jrc.be

Figure 4

EUROPEAN COMMISSION
DIRECTORATE GENERAL JRC
JOINT RESEARCH CENTRE
IRMM
Institute for Reference Materials and Measurements

«title» «firstname» «surname»
«companyinstitute»
«address»
«Town»
«zip» «country»

LAB-ID No. «person_id»

IMEP-20

Trace Elements in Tuna Fish
Confirmation of safe receipt - IMEP-20 Tuna sample

Please return this form immediately to IRMM, this confirms that the sample package arrived. (in case it is damaged, please contact us immediately).

Please complete or amend the address information in case needed. (capital letters).

We have received the sample package in good order

Date of package arrival:……………………..

Signature:……………………………………

Please return the form to:

Dr. Y. Aregbe
IMEP-20 Co-ordinator
IRMM – JRC – EC
Retieseweg
B-2440 GEEL, Belgium

Tel : +32 (0) 14 571 673
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Retieseweg, B-2440 Geel, Belgium
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Figure 5

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DIRECTORATE GENERAL JRC
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IRMM
Institute for Reference Materials and Measurements

IMEP®

IMEP-20: Trace Elements in Tuna Fish
GUIDELINES to Participants on Reporting Results & completing the Questionnaire Online

The result reporting web page

Please use your allocated laboratory identification number (Lab-ID) and Key-code number when reporting online. The login page on the IMEP web site is located at: http://www.data20.imep.ws

Retieseweg, B-2440 Geel, Belgium
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Figure 6

Completing the Results Report Form

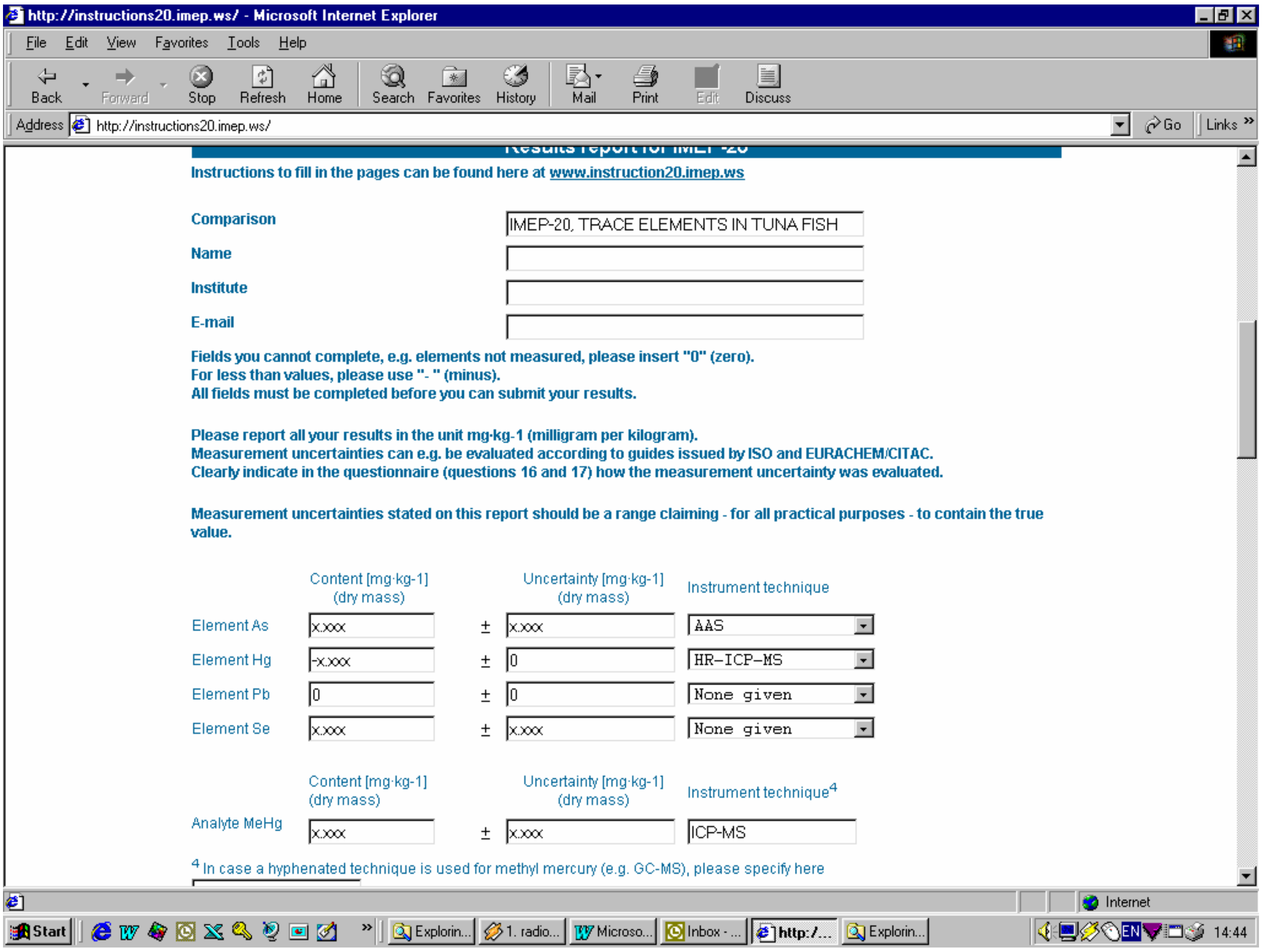
1. You have to report the element content and its uncertainty in **mg·kg^{-1}**

2. The fields in the Result Report Form are defined as **numerical decimal fields**. Data input using scientific format is not possible.

3. Due to the fact that the fields in the Result Report Form are defined as numerical fields you must enter "0" (zero) if you have not measured one element.

If you report an upper limit as a result you have to enter "–" (minus sign) instead of the "<" less than sign.

(See example below, where "x.xxx" stands for a reported numerical result).


http://instructions20.imep.ws/ - Microsoft Internet Explorer

Instructions to fill in the pages can be found here at www.instruction20.imep.ws

Comparison	IMEP-20, TRACE ELEMENTS IN TUNA FISH
Name	
Institute	
E-mail	

Fields you cannot complete, e.g. elements not measured, please insert "0" (zero).
For less than values, please use "- " (minus).
All fields must be completed before you can submit your results.

Please report all your results in the unit mg·kg-1 (milligram per kilogram).
Measurement uncertainties can e.g. be evaluated according to guides issued by ISO and EURACHEM/CITAC.
Clearly indicate in the questionnaire (questions 16 and 17) how the measurement uncertainty was evaluated.

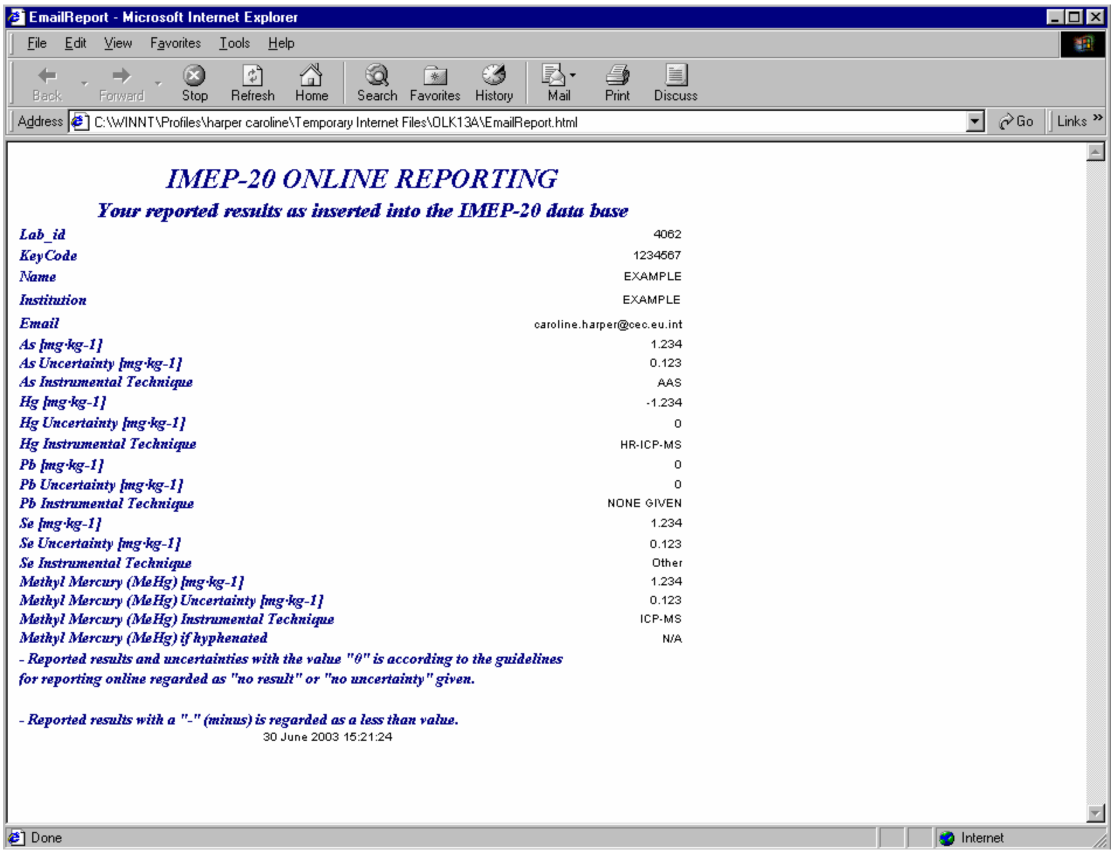
Measurement uncertainties stated on this report should be a range claiming - for all practical purposes - to contain the true value.

	Content [mg·kg-1] (dry mass)		Uncertainty [mg·kg-1] (dry mass)	Instrument technique
Element As	x.xxx	±	x.xxx	AAS
Element Hg	-x.xxx	±	0	HR-ICP-MS
Element Pb	0	±	0	None given
Element Se	x.xxx	±	x.xxx	None given

	Content [mg·kg-1] (dry mass)		Uncertainty [mg·kg-1] (dry mass)	Instrument technique[4]
Analyte MeHg	x.xxx	±	x.xxx	ICP-MS

[4] In case a hyphenated technique is used for methyl mercury (e.g. GC-MS), please specify here

Figure 7



IMEP-20 ONLINE REPORTING

Your reported results as inserted into the IMEP-20 data base

Lab_id	4062
KeyCode	1234567
Name	EXAMPLE
Institution	EXAMPLE
Email	caroline.harper@cec.eu.int
As [mg·kg-1]	1.234
As Uncertainty [mg·kg-1]	0.123
As Instrumental Technique	AAS
Hg [mg·kg-1]	-1.234
Hg Uncertainty [mg·kg-1]	0
Hg Instrumental Technique	HR-ICP-MS
Pb [mg·kg-1]	0
Pb Uncertainty [mg·kg-1]	0
Pb Instrumental Technique	NONE GIVEN
Se [mg·kg-1]	1.234
Se Uncertainty [mg·kg-1]	0.123
Se Instrumental Technique	Other
Methyl Mercury (MeHg) [mg·kg-1]	1.234
Methyl Mercury (MeHg) Uncertainty [mg·kg-1]	0.123
Methyl Mercury (MeHg) Instrumental Technique	ICP-MS
Methyl Mercury (MeHg) if hyphenated	N/A

- Reported results and uncertainties with the value "0" is according to the guidelines for reporting online regarded as "no result" or "no uncertainty" given.

- Reported results with a "-" (minus) is regarded as a less than value.

30 June 2003 15:21:24

As soon as all the participants' results are entered in the IMEP-20 database, you will receive a certificate with the IMEP-20 reference values including your reported results in a regular text format (see table below as an example):

Element	Reported Measurement Result mg·kg^{-1} (dry-mass)	Reported Uncertainty mg·kg^{-1} (dry-mass)
As	x.xxx	x.xxx
Hg	<x.xxx	No unc. reported
Pb	No value reported	No unc. reported
Se	No value reported	No unc. reported
methylmercury	No value reported	No unc. reported

Figure 8

Completing the Questionnaire Form for all participants

1. You must enter data in every field, otherwise your questionnaire information cannot be submitted. If a question cannot be answered you must enter N/A (not applicable)

2. Particularly for Questions 4) and 6) please make sure that you enter N/A in all the fields in the table that are not applicable.

3. Text fields are a maximum of 100 characters.

4. Participants NOT measuring methylmercury have to submit their results after having answered question 17; (questions 18-27 are related to methylmercury measurements only)

Instructions for Question 6

Due to requests from laboratories in the food sector, IRMM would like to provide a survey about applied water content determination and dry-mass correction in IMEP-20. A special appendix will be included in the IMEP-20 report, to emphasize the importance of this matter in food analysis.

Method A

Drying-oven-YES:

State temperature and drying time applied for oven drying. If vacuum (reduced pressure) was applied state pressure in mbar. In case vacuum-drying was NOT applied please insert N/A in this field.

Method B

Karl-Fischer titration-YES:

In case elevated temperature was used during KF-titration state extraction temperature in °C, otherwise insert N/A in this field. If delay time "t (delay)" was used as stop criterion state delay time in seconds, if "stop drift" was used as stop criterion state which value (µL/min) was set, otherwise insert N/A. State the extraction time in minutes applied for the KF-titration

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 •Fax: +32-(0)14-571 865 • imep@irmm.jrc.be • yetunde.aregbe@irmm.jrc.be
www.imep.ws • http://www.irmm.jrc.be

Figure 9

Instructions for Questions 8 to 10

Please report all values including uncertainty!

Instructions for Question 10

Factor for dry-mass correction:
Insert the applied dry mass correction factor used in the measurement equation to calculate the total amount content of the trace elements present in the Tuna fish sample. (This factor is deduced from the water content determination but also accounts for possible corrections due to the hygroscopicity of the Tuna fish material).

Completing the Questionnaire Form for participants who also measure methylmercury

1. **Questions 18-27 have to be answered only by participants measuring methylmercury**
2. **The default setting for the text fields is N/A. If you measure methlymercury please overwrite all the "N/A-fields" with your answers to the specific questions**

Figure 10

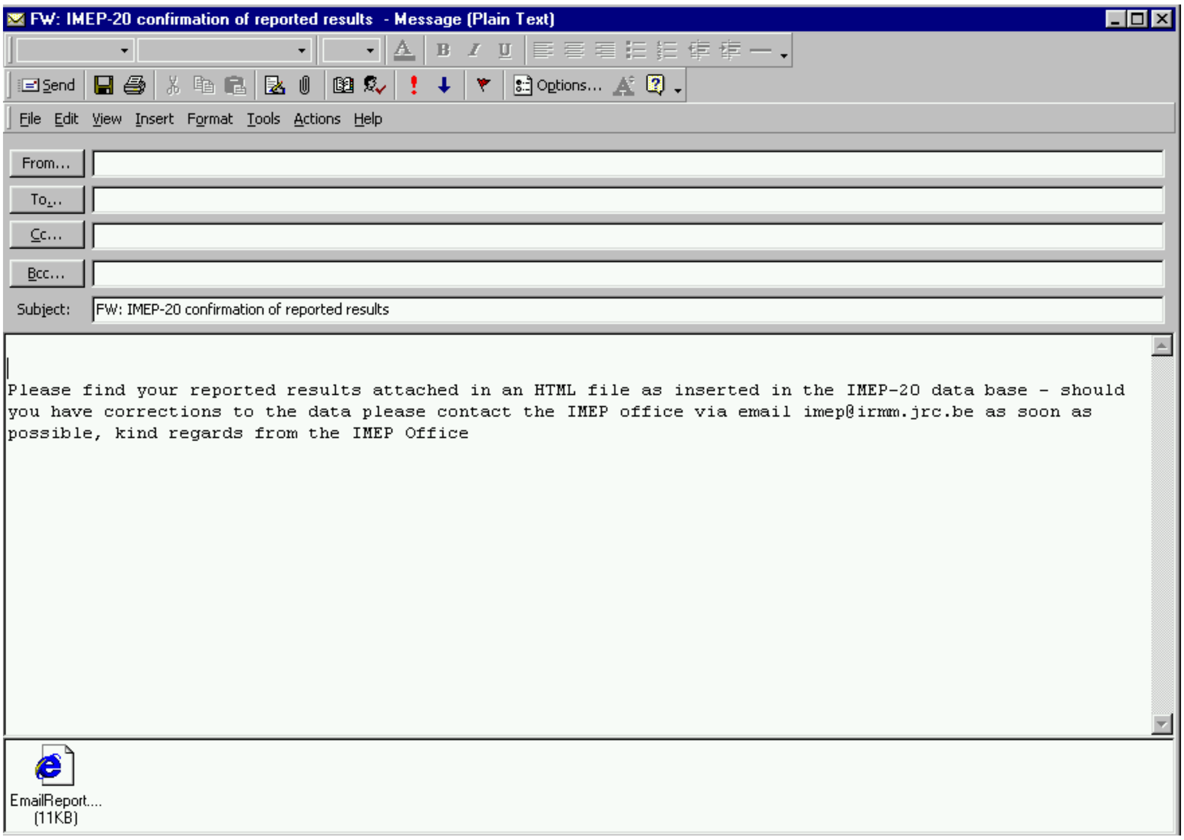

FW: IMEP-20 confirmation of reported results - Message (Plain Text)
Send
Options...
File Edit View Insert Format Tools Actions Help
From...
To...
Cc...
Bcc...
Subject:
FW: IMEP-20 confirmation of reported results
Please find your reported results attached in an HTML file as inserted in the IMEP-20 data base - should you have corrections to the data please contact the IMEP office via email imep@irmm.jrc.be as soon as possible, kind regards from the IMEP Office
EmailReport....
(11KB)

Figure 11

IMEP-20 ONLINE REPORTING

Your reported results as inserted into the IMEP-20 data base

Lab_id
KeyCode
Name
Institution
Email
As [mg·kg-1]
As Uncertainty [mg·kg-1]
As Instrumental Technique
Hg [mg·kg-1]
Hg Uncertainty [mg·kg-1]
Hg Instrumental Technique
Pb [mg·kg-1]
Pb Uncertainty [mg·kg-1]
Pb Instrumental Technique
Se [mg·kg-1]
Se Uncertainty [mg·kg-1]
Se Instrumental Technique
Methyl Mercury (CH3hg) [mg·kg-1]
Methyl Mercury (CH3Hg) Uncertainty [mg·kg-1]
Methyl Mercury (CH3Hg) Instrumental Technique
Methyl Mercury (CH3Hg) if hyphenated

- Reported results and uncertainties with the value "0" is according to the guidelines for reporting online regarded as "no result" or "no uncertainty" given.

- Reported results with a "-" (minus) is regarded as a less than value.

Figure 12

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP®

IM/L/95/03
24 November 2003

IMEP-20

Trace Elements in Tuna Fish

Certified Reference Values

analyte	certified value $mg \cdot kg^{-1}$ (dry mass)	expanded uncertainty *U*, *k*=2 $mg \cdot kg^{-1}$ (dry mass)
Arsenic	4.93	0.21
Lead	0.498 0	0.008 5
Mercury	4.32	0.16
Methylmercury	4.24	0.27
Selenium	6.38	0.28

Dr. Y. Aregbe
IMEP-20 Co-ordinator
IRMM

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 • Fax: +32-(0)14-571 865
jrc-irmm-imep@cec.eu.int • http://www.imep.ws • http://www.irmm.jrc.be

Institute for Reference Materials and Measurements

IMEP: an IRMM programme, with the aim to enable evaluation of performance in chemical measurements and to establish their degree of international equivalence

The certified reference values on this certificate were derived from reference measurements with demonstrated traceability and adequately demonstrated uncertainty.

The following institutes and units within IRMM collaborated in the production or certification of the IMEP-20 tuna fish certified test samples

Isotope Measurement unit
Reference Materials unit
Food Safety and Quality unit

Studiecentrum voor Kernenergie
Centre d'étude de l'énergie nucléaire
Boeretang 200
2400 MOL
Belgium
http://www.sck.be

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 • Fax: +32-(0)14-571 865
jrc-irmm-imep@cec.eu.int • http://www.imep.ws • http://www.irmm.jrc.be

Figure 13

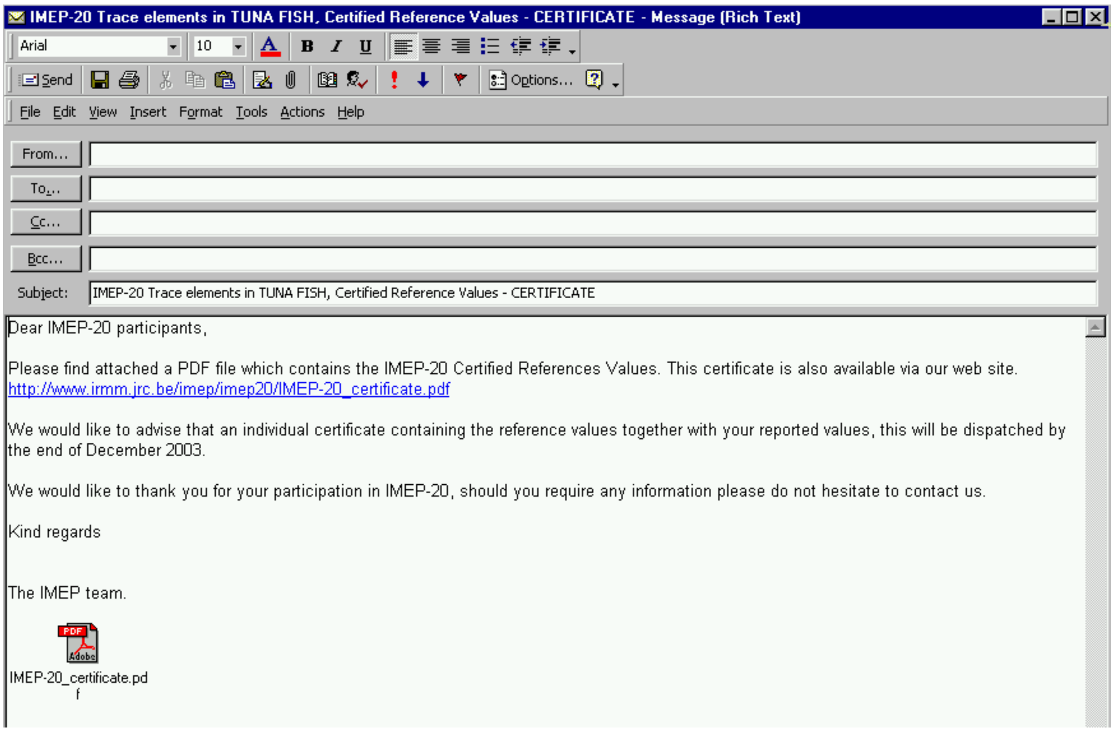

IMEP-20 Trace elements in TUNA FISH, Certified Reference Values - CERTIFICATE - Message (Rich Text)
Arial
10
Send
Options...
File Edit View Insert Format Tools Actions Help
From...
To...
Cc...
Bcc...
Subject:
IMEP-20 Trace elements in TUNA FISH, Certified Reference Values - CERTIFICATE
Dear IMEP-20 participants,
Please find attached a PDF file which contains the IMEP-20 Certified References Values. This certificate is also available via our web site.
http://www.irmm.jrc.be/imep/imep20/IMEP-20_certificate.pdf
We would like to advise that an individual certificate containing the reference values together with your reported values, this will be dispatched by the end of December 2003.
We would like to thank you for your participation in IMEP-20, should you require any information please do not hesitate to contact us.
Kind regards
The IMEP team.
PDF
Adobe
IMEP-20_certificate.pdf

Figure 14

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Geel, 16th December 2003
IM/L/101/03/«LAB_ID»

«Title» «firstname» «surname»
«companyinstitute»
«address»
«town»
«zip» «country»

Dear «Title» «surname»,

IMEP-20 Trace Elements in Tuna Fish

Please find enclosed the IMEP-20 reference value certificate together with your individual IMEP-20 certificate. IRMM has issued individual certificates to each participant in IMEP-20. This certificate includes your reported measurement value for the analytes under evaluation in the IMEP-20 Certified Test Sample, the IMEP-20 Certified Reference Values and the deviation of your reported value from the certified value in percentage.

Furthermore E_n-numbers [1] have been calculated for those participants in IMEP-20 who reported measurement results with uncertainties estimated according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000). Please note that for participants who did not state that they calculated the reported uncertainty according to the (ISO, 1995) and/or EURACHEM/CITAC (2000) guides no E_n-numbers were issued.

Maximum levels of metals in foodstuff are set in the commission regulation (EC) 466/2001. In absence of performance characteristics for a target value of uncertainty for measurements of metals in Tuna Fish in this regulation, IRMM selected as performance evaluation criterion a range of ± 10% from the reference value. It can be assumed to be "fit for purpose" for measurements of trace metals in foodstuff.

The IMEP-20 participant's report is under preparation and on its completion will be dispatched to you during the first quarter of 2004.

We would like to thank you for taking part in this comparison and hope you have found your participation useful.

Yours sincerely,

Dr. Y. Aregbe
IMEP-20 Co-ordinator

[1] The E_n-scoring is based on single performance statistics: ISO/IEC GUIDE 43-1:1997 (E)

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 • Fax: +32-(0)14-571 865
jrc-irmm-imep@cec.eu.int • http://www.imep.ws • http://www.irmm.jrc.be

Figure 15

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
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IMEP®

M/L/94/02/1870
December 2003

Certificate

IMEP-20 Trace Elements in Tuna Fish

Issued to: «Title» «firstname» «surname»
«companyinstitute»
«town»«zip» «country»

analyte	reported value mg·kg^{-1}	reported uncertainty mg·kg^{-1}	certified value mg·kg^{-1} (dry-mass)	expanded uncertainty U, k=2 mg·kg^{-1} (dry-mass)	deviation from certified value	E_n-number
Arsenic	<As>	<unc_As>	**4.93**	**0.21**	<As_Dev_Cert_Value>	<As_Enscore>
Lead	<Pb>	<unc_Pb>	**0.498 0**	**0.008 5**	<Pb_Dev_Cert_Value>	<Pb_Enscore>
Mercury	<Hg>	<unc_Hg>	**4.32**	**0.16**	<Hg_Dev_Cert_Value>	<Hg_Enscore>
Methylmercury	<MeHg>	<unc_MeHg>	**4.24**	**0.27**	<MeHg_Dev_Cert_Value>	<MeHg_Enscore>
Selenium	<Se>	<unc_Se>	**6.38**	**0.28**	<Se_Dev_Cert_Value>	<Se_Enscore>

$$E_n = \frac{x - X_{ref}}{\sqrt{u_x^2 + (0.1 \cdot X_{ref})^2}}$$

$|E_n| \leq 2$ satisfactory

$2 < |E_n| \leq 3$ questionable

$|E_n| > 3$ not satisfactory

X_{ref} certified IMEP-20 reference value
x participant's reported value
u_x participant's reported combined uncertainty
$0.1 \cdot X_{ref}$ selected performance criterion

Please note that E_n-numbers were only issued to participants who reported measurement results with uncertainties, which have been calculated according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).r.

Dr. Y. Aregbe
IMEP-20 Co-ordinator
Retieseweg, B-2440 Geel, Belgium
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The following institutes and units within IRMM collaborated in the production or certification of the IMEP-20 tuna fish certified test samples

Institute for Reference Materials and Measurements

Isotope Measurement unit
Reference Materials unit
Food Safety and Quality unit

STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ÉTUDE DE L'ÉNERGIE NUCLÉAIRE

Studiecentrum voor Kernenergie
Centre d'étude de l'énergie nucléaire
Boeretang 200
2400 MOL
Belgium
http://www.sck.be

Figure 16

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

IMEP®

M/L/94/02/1870
December 2003

Certificate

IMEP-20 Trace Elements in Tuna Fish

Issued to: «Title» «firstname» «surname»
«companyinstitute»
«town»«zip» «country»

analyte	reported value mg·kg^{-1}	reported uncertainty mg·kg^{-1}	certified value mg·kg^{-1} (dry-mass)	expanded uncertainty U, k=2 mg·kg^{-1} (dry-mass)	deviation from certified value	E_n-number
Arsenic	<As>	<unc_As>	**4.93**	**0.21**	<As_Dev_Cert_Value>	
Lead	<Pb>	<unc_Pb>	**0.498 0**	**0.008 5**	<Pb_Dev_Cert_Value>	
Mercury	<Hg>	<unc_Hg>	**4.32**	**0.16**	<Hg_Dev_Cert_Value>	
Methylmercury	<MeHg>	<unc_MeHg>	**4.24**	**0.27**	<MeHg_Dev_Cert_Value>	
Selenium	<Se>	<unc_Se>	**6.38**	**0.28**	<Se_Dev_Cert_Value>	

$$E_n = \frac{x - X_{ref}}{\sqrt{u_x^2 + (0.1 \cdot X_{ref})^2}}$$

$|E_n| \leq 2$ satisfactory
$2 < |E_n| \leq 3$ questionable
$|E_n| > 3$ not satisfactory

X_{ref} certified IMEP-20 reference value
x participant's reported value
u_x participant's reported combined uncertainty
$0.1 \cdot X_{ref}$ selected performance criterion

Please note that E_n-numbers were only issued to participants who reported measurement results with uncertainties, which have been calculated according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).r.

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Figure 17 Only available on-line

IMEP-20

Trace Elements in Tuna Fish

RESULTS REPORT FORM

(Deadline 31st October 2003)

(Please use capital letters)
Name :
Organisation :
Address :

Country :
Email address :
LAB-ID No. :

Please report all your results and uncertainties in the unit **$mg \cdot kg^{-1}$** (milligram per kilogram). Measurement uncertainty can, e.g. be evaluated according to guides issued by ISO[1] and EURACHEM/CITAC[2]. Clearly indicate in the questionnaire (questions 16 to17) how the measurement uncertainty was evaluated.

Analyte	**Content in $mg \cdot kg^{-1}$ (dry-mass)**	**Uncertainty in $mg \cdot kg^{-1}$ (dry-mass)**	**Instrumental technique[3]**
As			
Hg			
Pb			
Se			

Analyte	**Content in mg $(CH_3Hg) \cdot kg^{-1}$ (dry-mass)**	**Uncertainty in mg $(CH_3Hg) \cdot kg^{-1}$ (dry-mass)**	**Instrumental Technique [3,4]**
Methylmercury			

[4]In case a hyphenated technique is used (for example GC-MS etc.…), please specify here:______________________________

Date:

[1] International Organisation for Standardisation, "Guide to the Expression of Uncertainty in Measurement", © ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1995

[2]EURACHEM/CITAC, "Quantifying Uncertainty in Analytical Measurement", Second Edition, 2000, http://www.eurachem.bam.de/index.htm or http://www.measurementuncertainty.org/mu/guide

[3] Please use the acronyms given at the end of the questionnaire

Retieseweg, B-2440 Geel, Belgium
Tel.: +32-(0)14-571 673 • Fax: +32-(0)14-571 865
•imep@irmm.jrc.be•http://www.irmm.jrc.be• http://www.imep.ws

Figure 18 Only available on-line

IMEP-20 - Trace Elements in Tuna Fish
QUESTIONNAIRE FORM

The purpose of this questionnaire is to enable the organiser to compare measurement performance with additional factors such as analytical techniques, water content determination, quality management system in use, accreditation and present this to the participants in a graphical form.

ALL ANSWERS WILL BE TREATED CONFIDENTIALLY
(Non-disclosure of the identity of the laboratories)
PLEASE COMPLETE THIS FORM TOGETHER WITH THE RESULT FORM.

1. **a) How does your laboratory consider itself, experienced or less/non-experienced in the analysis of the following analytes in Tuna Fish? b) Also please indicate how many samples does your laboratory routinely analyse per year for these elements.**

Analytes	Experienced	Less/non-experienced	Number of tissue samples of animal origin analysed per year			
			< 50	50-250	250-1000	> 1000
As						
Hg						
Pb						
Se						

2. **Was the IMEP-20 Certified Test Sample (CTS) treated according to the same analytical procedure as routinely used for this sample type?**

   ☐ YES ☐ NO

3. **Was the CTS treated in accordance to National or other standards (e.g. EN, ISO) ?**

   ☐ YES ☐ NO

   If "YES", which one?……………………………………………………………………………….

   ……

Figure 19 Only available on-line

4. Did the analytical procedure involve the following steps: a) a digestion step?

☐ **YES (If YES please complete the table below for each analyte)**

☐ **NO (if NO please indicate in the table below which sample mass was used)**

(Enter N/A in fields that are not applicable)

Analytes	Sample mass used (g)	Acids or reagents used	Type of destruction or equipment used (Microwave, high pressure ashing, dry ashing etc)
As			
Hg			
Pb			
Se			

Did the analytical procedure involve: b) a separation step?
c) a pre-concentration step?

Analytes	b) a separation step?		c) a pre-concentration step?	
	Yes	No	Yes	No
As				
Hg				
Pb				
Se				

5. How long did you spend carrying out your measurement?

Analytes	< 1 hour	< 1 day	< 1 week	< 1 month
As				
Hg				
Pb				
Se				

6. Indicate which method was used for the "water content determination"?

(Please complete the tables below, enter N/A in fields that are not applicable)

Procedure A

Drying-oven		Temperature (°C)	Drying time (hours)	Vacuum - drying pressure (mbar)
Yes	No			

Figure 20 Only available on-line

Procedure B

Karl-Fischer titration		Temperature (°C)	Stop criteria		Extraction time (min)
Yes	No		drift (µL/min$^{-1)}$	time (s)	

Solvent used for KF-titration ……………………………………………………..……….

Comments ……………………………………………………..…………………………

7. **Was the Tuna fish sample equilibrated with ambient humidity conditions, prior to the determination of the water content?**

☐ YES ☐ NO

8. **What was the average sample mass (g) used for the "water content determination" with its uncertainty?**

………… **g** ± …………**g**

9. **What was the determined water content in the Tuna Fish sample with its uncertainty, state by percentage?**

………… **%** ± …………**%**

10. **What was the applied correction factor for dry-mass with its uncertainty?**

………… ± …………

11. **Which "calibration strategy" was used for the measurements?**

Analytes	Calibrated with external standard		Please specify internal standard used with external calibration	Method of standard addition calibration		Isotope dilution		Other
	Yes	No		Yes	No	Yes	No	
As						N/A		
Hg								
Pb								
Se								

12. **Does your laboratory routinely use Tuna fish Certified Reference Materials (CRMs) for quality assurance?** ☐ YES ☐ NO

If "YES", state which CRMs, the supplier and how the CRMs are used in your laboratory (e.g. validation of procedures, calibration of instruments, other):

………

Figure 21 Only available on-line

13. Does your laboratory participate regularly in a proficiency-testing scheme in order to assess performance for this type of analysis? ☐ YES ☐ NO

If "YES", state which proficiency-testing scheme and organiser:

....…………

14. Is your laboratory working according to the ISO 17025 standard or another quality management system standard? Please indicate the quality management system in use?

☐No quality management system in use.

☐ISO 17025

☐Other (e.g. EN45000, ISO 25, ISO 9000 series, CEN, GLP, EPA, TQM, national standards)

Please indicate:
...…………………………………………………………………..…………………

15. Is your laboratory accredited or authorised (e.g. by national law or regulatory authority) for measurements of trace element content in samples of animal origin?

Analytes	Accredited		Authorised	
	Yes	No	Yes	No
As				
Hg				
Pb				
Se				

16. Do you routinely report uncertainties on chemical measurements to your customers?

☐ YES ☐ NO

17. Are your reported uncertainties in IMEP-20 calculated according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000)?

☐ YES ☐ NO

If "NO", how was the measurement uncertainty evaluated?

....…………………………………………….

....…………………………………………….

Figure 22 Only available on-line

Acronyms for the Analytical Techniques in IMEP-20			
Anodic stripping voltammetry	ASV	Hydride generation-atomic absorption spectroscopy	HG-AAS
Atomic absorption spectroscopy	AAS	Hydride atomic absorption spectroscopy	H-AAS
Cathodic-stripping voltammetry	CSV	Inductively coupled plasma	ICP
Cold vapour-atomic absorption spectroscopy	CV-AAS	Inductively coupled plasma-atomic/optical emission spectrometry	ICP-AES/OES
Direct current plasma	DCP	Inductively coupled plasma-mass spectrometry	ICP-MS
Electrothermal atomic absorption spectroscopy	ETAAS	Infrared spectrometry	IR
Flame atomic absorption spectroscopy	FAAS	Ion chromatography	IC
Flame atomic emission spectroscopy	FAES	Metal hydride system	MHS
Flame atomic fluorescence spectroscopy	FAFS	No statement	None given
Flow injection analysis system-atomic absorption spectroscopy	FIAS-AAS	Other	OTHER
Graphite furnace-atomic absorption spectroscopy	GF-AAS	Potentiometric stripping analysis	PSA
High resolution-inductively coupled plasma-mass spectrometry	HR-ICP-MS	Spectrophotometry	Spectroph.
Hydride generation	HG	X-ray fluorescence	XRF

18. a) How does your laboratory consider itself, experienced or less/non-experienced in the analysis of methylmercury in Tuna Fish? b) please indicate how many samples does your laboratory routinely analyse per year for this element.

Analyte		Experienced	Less/non-experienced	Number of tissue samples of animal origin analysed per year			
				< 50	50-250	250-1000	> 1000
Methylmercury (CH_3Hg)	N/A						

19. How long did you spend carrying out your measurement?

Analyte		< 1 hour	< 1 day	< 1 week	< 1 month
Methylmercury (CH_3Hg)	N/A				

20. Which "calibration strategy" was used for the MeHg measurements?

Analyte		Calibrated with external standard		Please specify internal standard used with external calibration	Method of standard addition calibration		Isotope dilution		Other
	N/A	Yes	No	N/A	Yes	No	Yes	No	N/A
Methylmercury (CH_3Hg)									

Figure 23 Only available on-line

If isotope dilution was applied was the spike involved a Hg isotopically enriched CH_3Hg material?

☐ YES ☐ NO ☐ N/A

Isotope dilution was applied without using a Hg isotopically enriched CH_3Hg material?

☐ YES ☐ NO ☐ N/A

Please state brief details of the approach…………………………………………………………..

21. If a measurement strategy based on standard addition or isotope dilution was used, which of the options below most closely fits the timing of the spike addition in your method?

Analyte	Some hours prior to MeHg extraction	Immediately prior to MeHg extraction	After MeHg extraction prior to measurements	N/A
Methylmercury (CH_3Hg)				

22. If the measurement strategy applied was based on ID and used Hg isotopically enriched CH_3Hg, please complete the following questions?

a) Was the methylmercury in the spike material?

☐ in-house synthesised ☐ supplied from outside agency ☐ N/A

b) If known, which method was used for methylmercury synthesis?………………………

c) Which enriched isotope was used?………………………………………

d) How was the methylmercury concentration of the spike evaluated?

Reference to an external document ☐ YES ☐ NO ☐ N/A

Measured in-house ☐ YES ☐ NO ☐ N/A

Please give brief details of the method………………………………………

23. Please briefly describe your measurement process by listing the types of reagents and apparatus applied. If applicable, please name reagents for the extraction and derivatisation of CH_3Hg, in the samples?

a) Sample mass ………… **g**

b) Extraction reagents (e.g. HCI, TMAH etc.) ………………………………………

Figure 24 Only available on-line

c) Extraction apparatus ………………………………………

d) Derivatisation reagents (e.g. $NaB(C_2H_5)_4$, Grignard etc.) ……………………

e) Species separation apparatus (e.g. GC, LC, column type, carrier) ……………………

f) Dectector (e.g. CV-AAS, ICP-MS etc.). ………………………………………

24. Were Hg species other than methyl and oxidised inorganic Hg observed in the sample with the measurement method applied?

☐ YES ☐ NO ☐ N/A

If YES, please specify:

a) Elemental mercury ………………………………………

b) Dimethylmercury ………………………………………

c) Ethylmercury ………………………………………

d) Other ………………………………………

25. Is your laboratory accredited or authorised (e.g. by national law or regulatory authority) for measurements of trace element content in samples of animal origin?

Analyte	Accredited			Authorised		
	Yes	No	N/A	Yes	No	N/A
Methylmercury (CH_3Hg)						

26. In case your reported uncertainties for the methylmercury measurements were evaluated according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000)? (you have answered yes to question 17!) then

What was the main individual source of uncertainty? …………………………………
Which calculation method was used for the estimation of the final combined measurement uncertainty? ………………………………………………………………………...

27. In the final combined measurement uncertainty was estimated with the help of computer software, which package was used?

a) Microsoft Excel ☐ YES ☐ NO ☐ N/A

b) GUM specific software ☐ YES ☐ NO ☐ N/A

please specify……………………………………………………………………

c) Combination of software packages ☐ YES ☐ NO ☐ N/A

please specify……………………………………………………………………

European Commission

EUR 21018 EN – DG Joint Research Centre, Institute for Reference Materials and Measurements – IMEP-20 Trace Elements in Tuna Fish, Report to Participants
Y. Aregbe, C. Harper, I. Verbist, L. Van Nevel, P. Smeyers, C. Quétel and P.D.P. Taylor

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Abstract

The International Measurement Evaluation Programme (IMEP®) was established in order to shed light on the current state of the practice in chemical amount measurements. IMEP runs in support of EU policies (e.g. Consumer Protection and Public Health, Single Market, Environment, Research and Technology, External Trade and Economic Policy). The aim of this interlaboratory comparison programme was to picture objectively the degree of equivalence and the quality of chemical measurements by comparing participant's measurement results with external reference values, completely independent from the participants' result. These reference values are required to demonstrate traceability and they should have a demonstrated and adequately small uncertainty, as evaluated according to international guidelines. In IMEP® participating laboratories receive a Certified Test Sample (with undisclosed concentration values), which they can analyse using their routine analytical procedures. Participants in IMEP can compare, on an international forum, their values to the IMEP-reference values and in this way assess the quality of their results. The European Commission has identified food safety as one of its top priorities. The White Paper on Food Safety of January 12, 2000 sets out the plans for a proactive new food policy. Measurements of contaminants in foodstuff play a key role in modernising legislation into a coherent and transparent set of rules. Mercury is a potential environmental toxicant. The main source of human intake of mercury contaminants originates from methylmercury in fish and fishery products. Hg and Pb may induce dysfunctions in humans. Very recently another EC Regulation (466/2001) was introduced that endorses officially the threshold value of 1 mg Hg·Kg-1 and 0.2 mg Pb·Kg-1 in tuna fish. Certain forms of cancer and cardiovascular diseases have also been associated with Se deficiency. Se is also counted among the most important elements in terms of food-chain contamination. Recently the European Commission has requested the Scientific Committee on Food (SCF) to review the upper level of daily intake of Se SCF/CS/NUT/UPPLEV/11 Final, Nov/2000. Arsenic is a mononuclidic toxic element. Participants in IMEP-20 "trace elements in tuna fish" were offered to measure the content of As, Hg, Pb, Se and methylmercury. IMEP-20 is organised in collaboration with the Community Reference Laboratory for Residues - Istituto Superiore di Sanità, Rome (CRL-ISS) for the National Reference Laboratories (NRLs). Measurement results were reported by 235 participants, amongst those 22 NRLs, ,37 NRL nominated laboratories and 61 EA nominated laboratories. This report presents in a graphical form the results of all participants, sorted according to different criteria, together with the reference value