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IMEP-24: Analysis of eight heavy metals in toys according to EN 71-3:1994

Interlaboratory Comparison Report

Ines Baer, Johannes van de Kreeke, Inge Verbist, Danny Vendelbo, Thomas Linsinger, Piotr Robouch, Philip Taylor, Beatriz de la Calle

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Interlaboratory Comparison Report

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Contents

1 Summary

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme (IMEP). It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of soluble antimony, arsenic, barium, cadmium, chromium, lead, mercury, and selenium according to European Standard EN 71-3:1994.

The principle of the procedure in EN 71-3:1994 [1] consists in the extraction of soluble elements from toy material under the conditions simulating the material remaining in contact with stomach acid for a period of time after swallowing.

Forty participants from eighteen countries registered to the exercise, of which 33 reported results for As, 35 for Ba and Se, 37 for Cr, Pb, and Sb, 38 for Hg, and 39 for Cd. For seven measurands the test material had already been certified in the past. The validity of the certificate was reconfirmed and the certified values were taken as the reference values for this ILC. As no certified value was available for Hg, the mean value of the results provided by four expert laboratories was used together with the corresponding uncertainty. Participants were invited to report the uncertainty on their measurements. This was done by 35 of the 39 laboratories having submitted results in this exercise.

Laboratory results were rated with z and zeta scores in accordance with ISO 13528 [2]. The standard deviations for proficiency assessment were based on the analytical correction laid down in EN 71-3:1994.

2 IMEP support to EU policy

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

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

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

IMEP **supports EU policies** by organising intercomparisons in the frame of specific EU Directives, or on request of a specific Directorate-General. In the case of the IMEP-24, it was realised in the context of the Toy Safety Directive [3] applying the European Standard EN 71-3:1994.

IMEP-24 provided specific **support to the European Co-operation for Accreditation (EA)** in the frame of a Memorandum of Understanding (MoU) on a number of metrological issues, including the organisation of intercomparisons. National accreditation bodies were invited to nominate a limited number of laboratories for free participation in IMEP-24. The Swedish Board for Accreditation and Conformity Assessment (SWEDAC) liaised between EA and IMEP for this intercomparison.

3 Introduction

The requirements set up in EN 71-3:1994 are for the migration of heavy metals from the following toy materials: coatings, polymeric and similar materials, paper and paper board, textiles, glass/ceramic/metallic materials, materials intended to leave a trace, pliable modelling materials, paints and other materials [1]. The material of interest for this interlaboratory comparison is "*coating*", which is defined in the standard as:

> "*All layers of material formed or deposited on the base material or toy and includes material which includes paints, varnishes, lacquers, inks, polymers or other substances of a similar nature, whether they contain metallic particles or not, no matter how it has been applied to the toy and which can be removed by scrapping with a sharp blade.*"

Concerned heavy metals are antimony, arsenic, barium, cadmium, chromium, lead, mercury, and selenium. Their migration from toys should comply with the limits listed in Table 1 when tested according to the procedure given in the standard. An analytical correction is allowed for each element and is listed in the same table. Concretely, it means that the analytical result can be reduced by the given percentage when the analytical result equals or exceeds the set limit.

Table 1 – The eight heavy metals and their maximum limits set in EN 71-3:1994

Element	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
Limit migrated element (X_{EN}) [mg/kg]	60	25	1000	75	60	90	60	500
Analytical correction (AC) [%]	60	60	30	30	30	30	50	60

4 Scope and aim

The aim of this proficiency test is to enable laboratories performing tests on toy products to monitor their performance and to compare with other laboratories from Europe and abroad. Another aim is to identify problems related to technique and methodology. This was particularly interesting in this exercise, since the sample preparation procedure to be applied is known to cause great spread of results. The observation of this spread in former interlaboratory trials actually led to the introduction of the analytical correction into the EN 71-3:1994 [1].

5 Time frame

The project started on 18 March 2009. The EA coordinator Annika Norling then informed the national accreditation bodies. Four expert laboratories contributing to the establishment of the reference value were invited to register on the 26 March 2009 and were sent the samples on 27 April 2009. The exercise was publicly announced on the IMEP webpage[1] in the beginning of May 2009. In parallel, laboratories specialised in toy safety related analyses were contacted.

Interested laboratories could register until Friday 22 May 2009. Samples were sent out to the laboratories on 28 May 2009. For all laboratories the deadline for reporting results was on 3 July 2009.

6 Invitation, registration and distribution

Invitations for participation were sent to the EA coordinator (Annex 1) for distribution to nominated laboratories. An invitation letter was also sent to four expert laboratories to ask them to register for the establishment of the reference value (Annex 2). Notified bodies

[1] http://irmm.jrc.ec.europa.eu/html/interlaboratory_comparisons/

from the NANDO list were sent an email (Annex 3) inviting them to take part in the exercise, after having retrieved their contact information from the NANDO webpage[2]. NANDO lists notified bodies fulfilling the relevant requirements and which can be designated to carry out conformity assessment according to a directive, which in this case is the Toy Safety Directive. Finally, a call for participation was also released on the IRMM website (Annex 4).

Instructions on measurands, sample storage, reconstitution and measurement were sent to the participants in an accompanying letter together with the samples. The letter also contained the individual "code for access" to the result reporting website and the deadline for reporting (Annex 5). The reporting website included a questionnaire to collect additional information related to the experimental work (Annex 6).

The participants who submitted their result received the reference values two weeks after the reporting deadline. Forty laboratories registered out of which thirty-nine submitted results. Fig 1 represents the participating countries.

6.1 Confidentiality

EA was invited to nominate laboratories for participation. The following confidentiality statement was made to EA: "Confidentiality of the participants and their results towards third parties is guaranteed. However, IMEP will disclose details of the participants that have been nominated by EA to the EA working group for ILCs in Testing. The EA accreditation bodies may wish to inform the nominees of this disclosure."

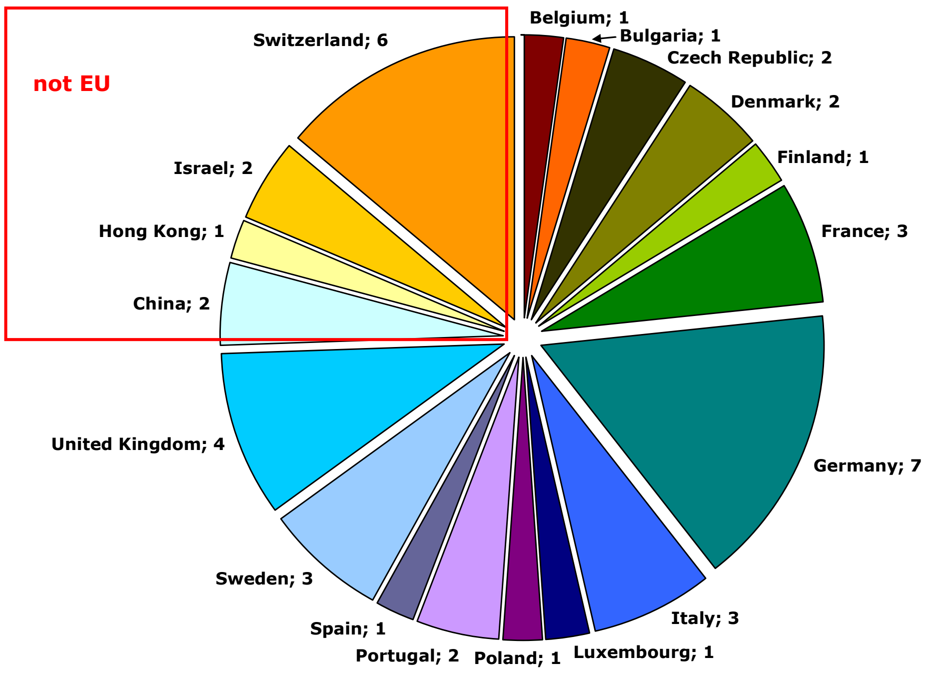
6.2 Distribution

ILC samples were dispatched by IRMM on 27 April 2009 to the certifying laboratories and on 28 May 2009 to participants. Each laboratory received one package containing a coated mild steel plate, the 'Confirmation of receipt' form (Annex 7) and an accompanying letter with instructions on sample handling, procedure and timelines (Annex 5).

The dispatch was followed by the courier's parcel tracking system on internet and in most of the cases the sample was delivered within a couple of days. In one case, the dispatch took 2 weeks. It was however assumed that the parcel was not submitted to high enough temperatures or long enough time to have an impact on the samples' stability.

[2] http://ec.europa.eu/enterprise/newapproach/nando/

Fig 1– Participating countries, number of laboratories



6.3 Procedure to apply

As this exercise was run to verify the performance of the laboratories when applying the EN 71-3:1994 [1], they were recommended to apply the corresponding procedure. Concerning the quantitative analysis of migrated elements, the standard recommends the use of methods having a detection limit of a maximum of 1/10 of the values to be determined.

7 Test material

The test material used for this exercise is the certified reference material BCR 620 and consists of alkyd resin paint on a mild steel plate. This material was certified in 1998 for levels of toxic element migration using the method specified in the EN 71-3:1994 [1]. All elements except mercury were certified. The BCR 620 was taken out of sales because of doubts of stability observed during monitoring analysis. Four expert laboratories analysed the test material again for confirmation. Their reported values would be taken as reference values (X_{ref}) in case the assumed degradation would be confirmed and the original certified values could not be used.

7.1 BCR 620

The certification report is not available for the public since the material is not commercialised anymore. However, details about the certification can be found in publications [4, 5] and are summarised hereafter. The paint was ordered at a specialised paint manufacturing company Trimite Ltd (UK). It was adulterated with 8 toxic elements at concentrations sufficient to yield soluble element concentrations at or around the maximum permissible levels. The paint was produced using dark grey "base" paint and adding a series of "tinters" each containing one of the eight toxic elements. A large single batch was produced, thoroughly mixed and dispensed into a number of 5 L tins before passing to the paint spraying contractor, Auto Imagination Ltd (UK). Before the spraying each tin was thoroughly re-mixed and as part of the spraying process the paint was passed through a turbulent mixing chamber in front of the spray jet. The amount sprayed on each panel was such that it was possible to scrape off at least 1 g of paint. The used mild steel plates were of size 150 x 100 mm and were degreased and abraded by sand blasting before application of the paint.

The certification measurements were carried out by 10 expert laboratories following the sample preparation procedure given in EN 71-3:1994 but using different instrumental techniques to analyse the sample extracts. The mean of the laboratory means was adopted as the certified value for each element in BCR 620 (Table 3).

7.2 Homogeneity and stability study

Since the material has been withdrawn from the market it was decided to carry out a homogeneity and a short-term stability study before starting the ILC. The study was performed by the Istituto Italiano Sicurezza dei Giocattoli S.r.l., Cabiate – Co (IT). Homogeneity and stability were done on the soluble elements as listed in EN 71-3:1994 (hence including Hg). Samples stored at 18 °C were used for the homogeneity study, and samples stored at 4 °C for six years were used as reference samples for the stability study.

7.2.1 Homogeneity

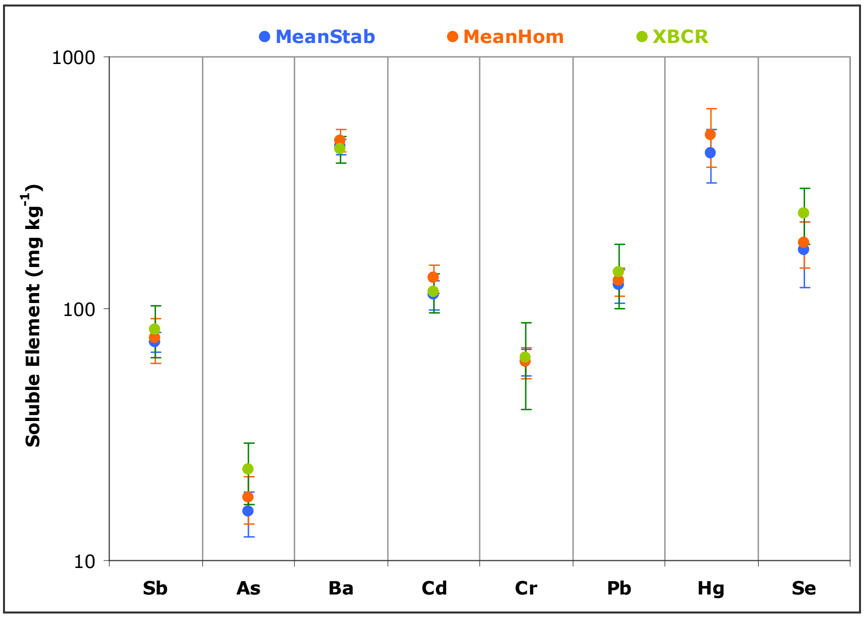
The laboratory performing the homogeneity study received 10 randomly chosen plates from the sample set stored at 18 °C and analyses were performed in duplicate following the procedure given in EN 71-3:1994 [1]. Results were evaluated according to ISO 13528 [2] and the IUPAC Harmonised Protocol guidelines [6] which describe tests to determine whether an ILC material is sufficiently homogeneous for its purpose.

The results of the homogeneity study can be found in Annex 8. The material passed the test with all elements according to the IUPAC calculations. This was considered sufficient to carry out this ILC, although ISO 13528 criteria were not met for all elements.

7.2.2 Stability

Stability was checked with the samples stored at 4 °C for six years. The results were compared to the results obtained with the samples analysed in the homogeneity study, stored at 18 °C, as well as to the certified reference values established ten years ago (cf. Ch 8). The various results were overlapping within their uncertainties (Fig 2) despite being analysed at such long time interval. Taking furthermore into account the sample preparation inherent variation, no stability issues were expected for the duration of the trial.

Fig 2 – Results of the stability & homogeneity study, shown together with the BCR values. (Concentrations and expanded uncertainties in logarithmic scale)



8 Reference values and their uncertainties

8.1 Target values

By target values is meant the concentration of heavy metals aimed at when producing the material. In this exercise they were set by the elements' concentrations of the material available. This material has been specifically produced for the toy safety norm for which the limits are set in EN 71-3:1994 [1] and target values were aimed at being close to these limits. Thus, the material was perfectly fit-for-purpose.

8.2 Establishing reference values and uncertainties (X_{ref}, U_{ref})

Four expert laboratories were contacted to perform accurate analysis so that their values could be used to either confirm the reference values from the certificate, or for the establishment of new reference values. Additionally, a reference value had to be determined for mercury, where no certified value was available. The four expert laboratories are:

- Istituto di Ricerche e Collaudi, M. Masini S.r.l., Milano (IT)
- Istituto Italiano Sicurezza dei Giocattoli S.r.l., Cabiate – Co (IT)
- LGC Ltd, Teddington (UK)
- Swedish National Testing and Research Institute, Borås (SE)

8.2.1 Comparison with BCR-620 certification

Concerning the reference values of antimony, arsenic, barium, cadmium, chromium, lead and selenium, the results of the four expert laboratories were compared with each other and then with the certified values. If the four laboratories reported results which agreed within their expanded uncertainties, the mass fraction of the different measurands was calculated as the mean of the four independent reported results, X_{exp}. The associated uncertainty is calculated by propagating contributions from characterisation (u_{char}) and homogeneity (u_{bb}) as follows [7]:

$$u_{exp} = \sqrt{\left(u_{char}^2 + u_{bb}^2\right)} \qquad \textit{(all standard uncertainties)} \qquad \text{Eq.1}$$

where the uncertainty of characterisation u_{char} is calculated from the uncertainties reported by the four laboratories [8]:

$$u_{char} = \sqrt{\left(u_1^2 + u_2^2 + u_3^2 + u_4^2\right)} \Big/ 4 \qquad \textit{(all standard uncertainties)} \qquad \text{Eq.2}$$

To evaluate the significance of the difference between the values from the expert laboratories (X_{exp}, U_{exp}) on one side, and the certified values (X_{BCR}, U_{BCR}) on the other side, the E_n number is established according to:

$$E_n = \frac{\left|X_{exp} - X_{BCR}\right|}{\sqrt{U_{exp}^2 + U_{BCR}^2}} \qquad \text{Eq.3}$$

If $E_n < 1$, then there is no significant difference between the measurement result and the certified value and X_{exp} and X_{BCR} are in agreement within their associated expanded uncertainties (U_{exp} and U_{BCR}) calculated with a coverage factor k=2 [2, 9].

The results obtained by the four expert laboratories and their expanded uncertainties are represented graphically in Annex 9 together with the BCR values. The numerical values and the calculated E_n numbers for each element can be found in Table 3. The results show that experimental values and certified values are in agreement and thus, the original certified values could be used as reference values for all measurands in this exercise (except Hg).

8.2.2 Reference value for mercury

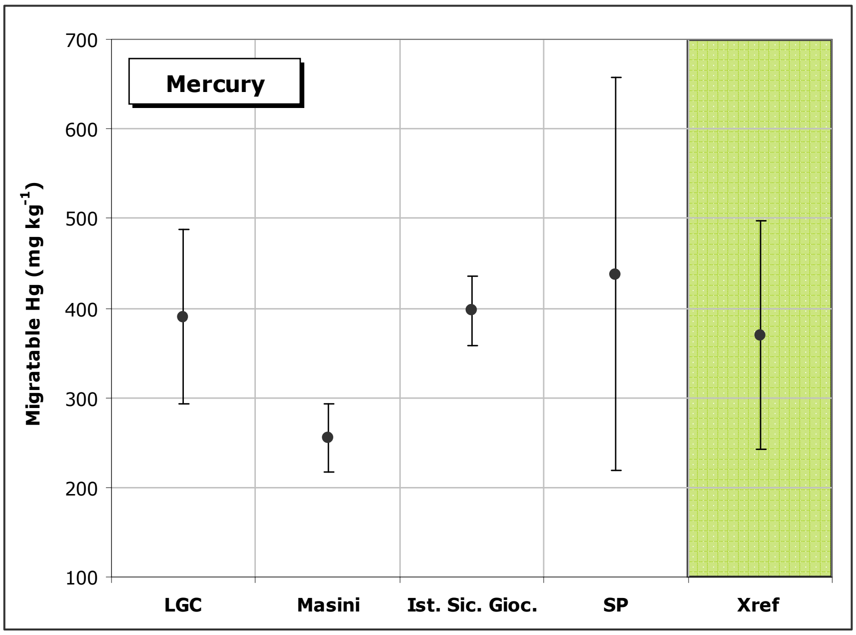
The mass fraction of mercury had not been certified for BCR 620. Thus, the results of the four expert laboratories were used for the establishment of the assigned value. As shown in Fig 3 the four reported values are within the range covered by the expanded uncertainties. The assigned value X_{ref} is thus calculated as the mean of these values and its associated uncertainty U_{ref} by using the calculations in Eq. 1 and Eq. 2. The numerical results and corresponding calculations are summarised in Table 2 below.

Table 2 – Determination of the reference value for mercury. Values from measurements and calculations. All values in (mg kg^{-1}).

Laboratory	LGC	Masini	Ist. Sic. Gioc.	SP	X_{ref}	u_{char}	u_{bb}	u_{ref}	U_{ref}*
X_{lab}	390	255	397	438	**370**				
u_{lab}	56	19	9	110		31	56	**64**	**127**

* Expanded uncertainty with a coverage factor k=2 which corresponds to a level of confidence of about 95%[10]

Fig 3 - The results of the four laboratories for mercury together with the determined reference value and their uncertainties



8.2.3 The standard deviation for proficiency assessment $\hat{\sigma}$

The standard deviation for proficiency testing $\hat{\sigma}$ is an estimate of the expected / required variability of the trial. It has to be determined for each ILC individually. In this exercise, it was established based on the analytical corrections (AC) given in EN 71-3:1994. These were interpreted as expanded uncertainties. Thus, $\hat{\sigma}$ was set as half the AC, assuming a confidence interval of 95% (Table 3).

Values highlighted in green in Table 3 below were used for the evaluation of the analytical performance of the laboratories. Consequently, the terms X_{BCR} and U_{BCR} will be replaced by X_{ref} and U_{ref} from this point on.

Table 3 – Establishment of reference values, their uncertainties and $\hat{\sigma}$. X_{BCR}, U_{BCR}, X_{exp}, U_{exp} in (mg kg^{-1}).

	Sb	As	Ba	Cd	Cr	Pb	Hg	Se
$X_{BCR} \pm U_{BCR}$*	**83 ± 19**	**23.0 ± 6.3**	**430 ± 50**	**117 ± 21**	**64 ± 24**	**140 ± 40**		**240 ± 60**
$X_{exp} \pm U_{exp}$*	66 ± 14	17.9 ± 4.4	429 ± 88	138 ± 33	58 ± 18	139 ± 20	**370 ± 127**	181 ± 46
E_n number	0.7	0.7	0.0	-0.5	0.2	0.0		0.8
AC	60%	60%	30%	30%	30%	30%	50%	60%
$\hat{\sigma}$	**30%**	**30%**	**15%**	**15%**	**15%**	**15%**	**25%**	**30%**

* Expanded uncertainty with a coverage factor k=2 which corresponds to a level of confidence of about 95%[10]

9 Reported results

9.1 General observations

From the 40 laboratories that registered, 39 submitted results and completed the associated questionnaire; 1 cancelled its participation. One laboratory reported for each element "less than" values and thus was not given any scores. A few other laboratories reported this as well, but only for 1, 2 or 5 elements. However, most of participants reported measurement results for all eight elements.

No obvious wrong result reporting was observed, although there are sometimes very low or high values. However, these were either punctually appearing for one or two elements, or they were confirmed by the participants (when re-contacting them for the analytical correction, see §9.2).

Two laboratories complained about the insufficient amount of paint and one about the insufficient amount of metal in the plate. For a reminder, the test material was conceived in view of the standard EN 71-3:1994 and the there stated amounts. One laboratory observed difficulties in sampling due to the thin lacquer, and also electrostatic loading.

9.2 Measurement results

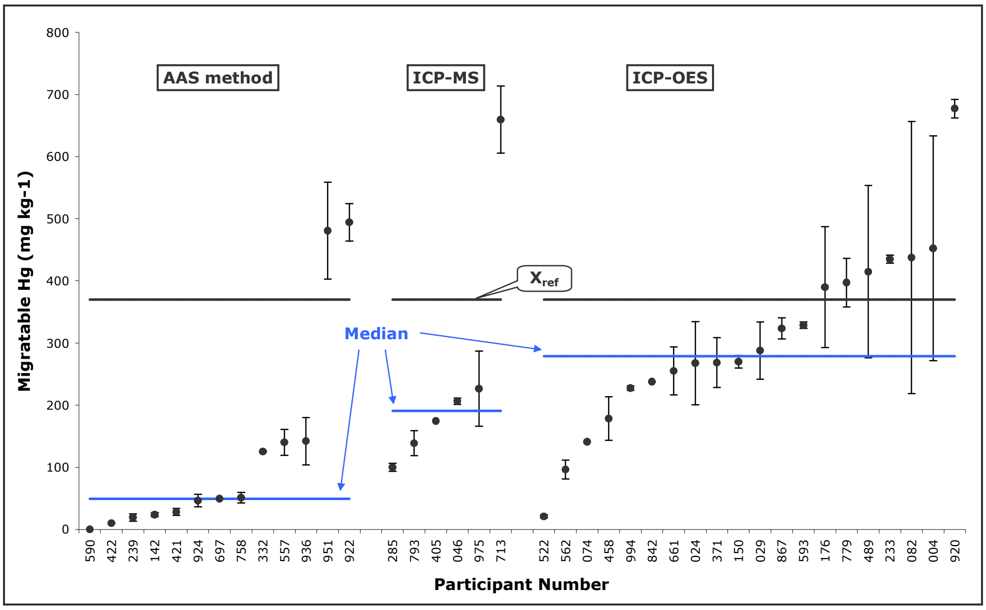
It was observed that the reported results were spread following a bi-modal distribution. This was mostly due to the application or not of the analytical correction (AC) given in the standard EN 71-3:1994. Only a few laboratories mentioned whether or not they used the AC (8 out of 39). The situation was so unclear, that it was necessary to contact all participants again in order to request specifications.

Considering this particular situation, all calculations were done on the raw non-corrected data. For each element, the results are shown in a table including the scorings and in a graph (Annex 10 to 17). The corresponding Kernel density plots can be found in Annex 18. An overview of all scorings can be found in Annex 19.

The results are generally normally distributed around the assigned value, or at least not much deviating from it (see results' graphs and Kernel plots, Annex 10 to 18). Some subpopulations can be observed in the Kernel plots mainly due to punctual very high or very low results. It is also suspected that some sub-populations are still due to the effects of the application of the analytical correction. When requesting details about the results, five laboratories did not answer (laboratories 029, 150, 239, 285, and 422). No answer was taken as non-application of analytical correction.

For selenium, mercury and, to a lesser degree, for arsenic there was a general tendency to underestimate the mass fraction. When using robust statistics and calculating the median from the results for the respective elements, those for mercury and selenium are lower than the corresponding X_{ref} value. Indeed, these elements are known to be volatile and difficult to analyse, but this should not result in such a bias. The instrumental detection appeared to have some influence on the results. About 85% of the laboratories used Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) or –Optical Emission Spectrometry (OES) and the remaining 15% atomic absorption spectroscopy (AAS), except in the case of mercury where about one third of the participant choose AAS. When the results for Hg were verified for any differences due to the methods, results obtained with AAS appeared to be lower than those obtained with ICP techniques. However, even the latter are characterised by a lower median than X_{ref}. For illustration see Fig 4. The lower results for ICP-OES could be partly explained by difficult detection, but no explanation could be found for the other two.

Fig 4 – Mercury values shown in function of the analytical method applied.



The results for selenium and arsenic were also checked for an eventual influence of the techniques used and it appears that a similar influence on the results could be observed with selenium, however not as pronounced. No influence was observed for arsenic. Considering that low results have been observed with all three techniques, the main error contributor seems to be the sample preparation.

For the remaining measurands no influence of the analytical method used was observed, with most of the participants having used ICP-OES, some ICP-MS. Other eventual factors of influence were verified according to the questionnaire's answers, but no other tendencies could be detected.

The software used to calculate robust statistics and kernel densities was provided by the Statistical Subcommittee of the Analytical Methods Committee (AMC) of the Royal Society of Chemistry [11, 12].

9.3 Scoring of results

9.3.1 Scores and evaluation criteria

Individual laboratory performance is expressed in terms of z- and zeta scores in accordance with ISO 13528 [2] and the IUPAC International Harmonised Protocol [6]:

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{and} \qquad zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

Where

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

Both scores can be interpreted as: satisfactory result for $|score| \leq 2$, questionable result for $2 < |score| \leq 3$ and unsatisfactory result for $|score| > 3$.

z score

The z score indicates whether a laboratory is able to perform the measurement in accordance with what can be considered as good practice within the EU. The standard deviation for proficiency assessment $\hat{\sigma}$ is accordingly based on experience described in the standard EN 71-3:1994. The $\hat{\sigma}$ applied in this ILC can be found in Table 3.

The IUPAC International Harmonised Protocol [6] suggests that participants can apply their own $\hat{\sigma}$ and recalculate the scores if the purpose of their measurements is different.

zeta score

The zeta score provides an indication of whether the estimate of uncertainty is consistent with the laboratory's deviation from the reference value [6]. It is calculated only for those results that were accompanied by an uncertainty statement. The interpretation is similar to the interpretation of the z score. An unsatisfactory zeta score may be caused by an underestimated uncertainty or by a large deviation from the reference value.

The standard uncertainty of the laboratory (u_{lab}) was calculated as follows. If an expanded uncertainty was reported, it was divided by the coverage factor *k*. If no coverage factor was provided, the reported uncertainty was considered as the half-width of a rectangular distribution. The reported uncertainty was then divided by $\sqrt{3}$, in accordance with recommendations issued by Eurachem and CITAC [13].

9.3.2 Scoring the reported measurement results

Scores were calculated with the raw data for all participants (not corrected for AC) except for those who reported no value or a "less than" value. These results were not used in any statistical calculation. A zeta score was calculated for results that were accompanied by an uncertainty statement. Annexes 10-17 list the scores per element and laboratory in detail, and Annex 19 summarises the scores per participant.

Table 4 summarises the distribution of scores per element. A large share of participants reported satisfactory measurement results, a small share unsatisfactory results. This is visible in good z scores, except for cadmium, lead and mercury, where satisfactory scores are below 50 % and over 35% of the laboratories got unsatisfactory results. Thus, generally the participants performed well. It should however be kept in mind that the results were evaluated with a large $\hat{\sigma}$.

The situation is slightly different for the zeta scores. Here, only two elements (barium and chromium) had over 50% of the participants getting satisfactory scores. That means that although the results reflected by the z scores are generally good, there is an obvious problem with the estimation of the uncertainty for some elements, resulting in a high number of unsatisfactory zeta scores. For all elements, except chromium, the share of satisfactory scores dropped from z score to zeta score or stayed at a similarly low level. This is particularly visible in the case of selenium, where also the number of participants having reached satisfactory scores for both, z and zeta, is the lowest for all elements.

Table 4 – Overview of scores with S(atisfactory), Q(uestionable) and U(nsatisfactory)

	z scores								zeta scores							z & zeta
	n*	S (#*)	S(%)	Q(#*)	Q(%)	U(#*)	U(%)		n*	S (#*)	S(%)	Q(#*)	Q(%)	U(#*)	U(%)	S(#*)
Sb	37	29	78%	5	14%	3	8%	Sb	33	15	45%	6	18%	12	36%	15
As	33	26	79%	6	18%	1	3%	As	30	13	43%	9	30%	8	27%	13
Ba	35	29	83%	2	6%	4	11%	Ba	32	17	53%	5	16%	10	31%	16
Cd	39	17	44%	5	13%	17	44%	Cd	35	13	37%	4	11%	18	51%	13
Cr	37	26	70%	5	14%	6	16%	Cr	33	28	85%	0	0%	5	15%	24
Pb	37	16	43%	6	16%	15	41%	Pb	34	16	47%	5	15%	13	38%	14
Hg	38	15	39%	9	24%	14	37%	Hg	35	12	34%	4	11%	19	54%	12
Se	35	25	71%	8	23%	2	6%	Se	32	9	28%	10	31%	13	41%	9

* n is the number of results for which a score was given. The total number of participants is 39.
(#) – number of laboratories

Most of the participants provided an uncertainty estimate, and most of these estimates were accompanied by a coverage factor. Only four participants did not report any uncertainty at all. This is encouraging, but contrasts with the modest share of results with a satisfactory zeta score. Considering that more than half of the participants stated in the questionnaire that they do not usually report the uncertainty to their customers, one might think that this is the reason for the lack of experience in uncertainty estimation. However, when plotting the scores in function of the reporting / non-reporting to customers, there is no tendency that those reporting uncertainties to their customers do better. As conclusion, participants are advised to verify their zeta scores, and review the principles of uncertainty estimation described in the GUM [10] and in related guidance for the field of analytical chemistry, e.g. the EURACHEM / CITAC Guide [13]. As guideline, values adopted for $\hat{\sigma}$ seem to give a realistic estimate for the average measurement uncertainty.

9.4 Results interpretation by participants

The standard EN 71-3:1994 appears to be insufficient when it comes to the question of how to deal with the analytical results and how to submit them to end-users. In §4.2 it says :

"*The analytical results of materials established in clauses 7, 8 and 9 <u>shall</u> be adjusted by subtracting the analytical correction in Table 2 to obtain an adjusted analytical result. Materials are deemed to comply with this standard if the adjusted analytical result is less than or equal to the limits in Table1 (See Annex D).*"

while Annex D.4 states :

"*To achieve consistent interpretation of results, a correction factor for each element has been introduced into the standard applicable to all instrumental techniques. These are taken from the precision data in the 1988 standard and are used when an analytical result equals or exceeds the maximum limit.*"

Although the AC "shall be applied" according to the standard, it is not as clear whether such correction should be applied by the laboratory performing the analysis or i.e. by control authorities, or customers. This led to problems in the reporting and thus the evaluation of this exercise. For this reason, it was decided to separate the evaluation in two parts – one "classical" ILC evaluation and one evaluation about the reporting and interpretation of results. The former considers mainly the analytical performance of the laboratories and has been treated in the precedent chapters. The latter will be treated hereafter.

9.4.1 Reporting of results

When setting-up this exercise it was decided not to give any specification concerning the application of the AC, the reason being that reporting is part of the proficiency test and as such should be taken into account in the evaluation. Thus, participants were asked to submit results as they would do to customers. The way of reporting a result appears to be particularly important and this was clearly an issue in this exercise. Four different behaviours were observed:

- Application of the analytical correction 'by default' (to all elements) (13 labs): defendable for practical reasons but not always necessary; e.g. in the case of arsenic, barium and selenium, where most or even all of the laboratories had results below the legislative limit, there was no need to apply it.
- No application at all (21 labs): justified, if low results (5 labs). Otherwise not (16 labs), since the results for some elements are close or above the limit. Here the question is: "How real cases are dealt with?".
- Application only to the means (while reporting the uncorrected measurements): unclear, requires specification. (3 labs)
- Application to a part of the analysed elements: justified, but requires specification. (4 labs)

Considering that the participants were to follow the standard EN 71-3:1994, and thus were aware of the presence of the clause concerning the AC, it would be desirable if reporting of results could be improved as to include specifications about its application or non-application. This making the reporting more transparent and comprehensive.

9.4.2 Assessment of compliance with EN 71-3:1994

The different ways of reporting led us to the question of how participants dealt with the overall interpretation of their results, and thus, they were asked in the questionnaire whether they '*would accept or reject the entrance of the material on the market*' (cf. Annex 6). Their assessment should be based on a simple test for each of the eight heavy metals: does the mean of my reported values X_{lab} fall below or exceed the maximum tolerable values X_{max}:

$X_{lab} < X_{max}$: compliant $X_{lab} > X_{max}$: non compliant

The parameter X_{max} was calculated for the purpose of this ILC and follows logically the concept of the AC laid down in EN 71-3:1994. X_{max} values are always larger than the official legal limits X_{EN} listed in EN 71-3:1994 as they compensate for the analytical correction AC as follows:

$$X_{max} = X_{EN} * 100/(100\text{-}AC) \quad AC \text{ in } [\%]$$

The resulting X_{max} values are listed in Table 5 together with the values for X_{EN}, X_{ref} and AC. The table also shows that the material is compliant for Sb, As, Ba, Cr and Se because $X_{ref} < X_{max}$ but not compliant for Cd, Pb and Hg because $X_{ref} > X_{max}$. This renders the test material overall not compliant (cf. EN 71-3:1994).

Table 5 – Relevant values for results interpretation. X_{EN}, X_{max}, X_{ref} in (mg kg^{-1}).

	Sb	**As**	**Ba**	**Cd**	**Cr**	**Pb**	**Hg**	**Se**
X_{EN}	60	25	1000	75	60	90	60	500
X_{max}	150	62.5	1429	107	86	129	120	1250
X_{ref}	83	23.0	430	117	64	140	370	240
AC	60%	60%	30%	30%	30%	30%	50%	60%

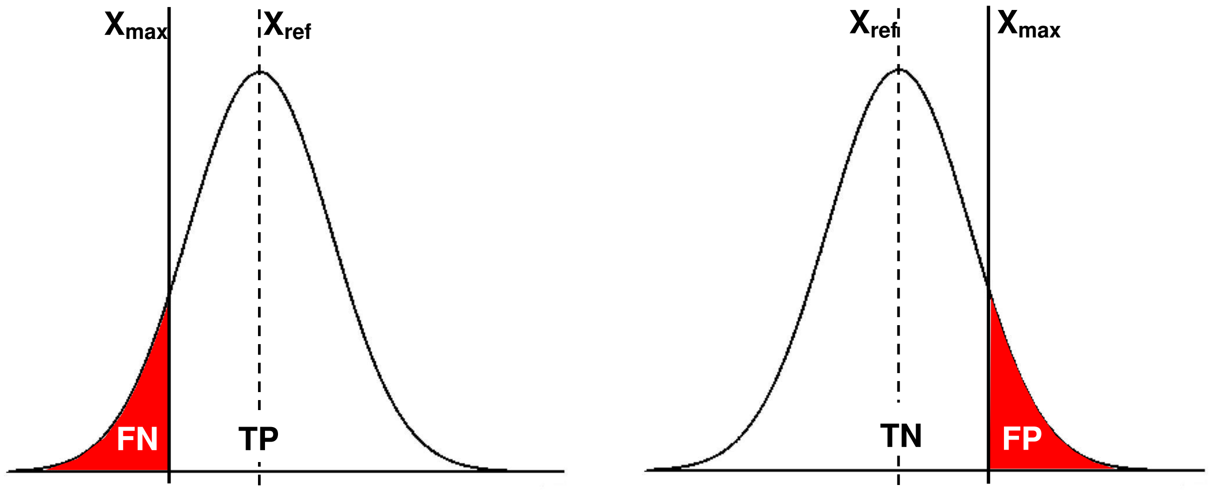
Knowing the established reference values X_{ref} of the test material this leads to four potential situations represented in the following contingency table :

		'*to be accepted*' Xref < Xmax	'*to be rejected*' Xref > Xmax
Compliant	Xlab < Xmax	TN*	FN*
Non-compliant	Xlab > Xmax	FP*	TP*

*TN – True Negative, FN – False Negative, FP – False Positive, TP – True Positive

The concept of this extended analysis is graphically displayed in Fig 5 for clarity. The analysis is very worthwhile, because it shows where wrong decisions were taken on the basis of a correct interpretation of wrong measurement results. An FN result may lead to the acceptance of a material which contains in reality unacceptable concentration of heavy metals, whereas an FP result may lead to financial losses because of undue material rejection.

Fig 5 – Graphical presentation of true positives(TP) / negatives(TN) and false positives(FP) / negatives(FN)



Annex 19 shows the scorings (z and zeta) of the participants for each element and their overall assessment of material compliance. It also shows the TN/FN/TP/FP labels that have been added by the ILC organiser (Int). As overall result, most laboratories have correctly assessed the material as being non compliant. However, nine laboratories were found to give an incorrect interpretation of their results: (i) either because they wrongly *'accepted the test material on the market'*, or (ii) because their decision was inconsistent with the results, meaning they *'reject the material'* although their results do not give reason for rejection. These participants are highlighted in bold red in Annex 19.

Another critical observation was that two laboratories correctly provided a sound overall assessment, although their measurement results were very high or very low (lab 058 and 298). This implies that their overall decision might be correct, but their results are not reliable. This was also readily visible in their large z- and zeta scores.

9.5 Further information extracted from the questionnaire

In addition to submission of the results, the participants were asked to answer a number of questions relating to the measurements. All participants completed the questionnaire, although a few participants skipped a big part of it. Since this exercise was carried out using the EN 71-3:1994, many questions were related to the sample preparation described in it. All except one laboratory indeed used the EN 71-3:1994 for the required analysis, and six participants used the standard but modified it. A sum-up of the answers to the method related questions can be found in Annex 20.

Participants were asked about the confidence level reflected by the coverage factor (k) reported. Nineteen laboratories reported a level of 95% and fourteen laboratories did not reply to this question. Two laboratories did not understand the question and six put the coverage factor k. One participant gave a level of 65% and two reported -1%. For the uncertainty estimate, several participants gave various combinations of the given choices. Twenty-three use the uncertainty of the method as determined during in-house validation. Twenty-two laboratories estimated the uncertainty using data from measurements of replicates (i.e. precision). Seven laboratories applied the ISO-GUM. Five used the known uncertainty of the standard method. It has to be emphasised that the latter should not be used on its own - the reproducibility of a standard method should always be verified by the laboratory applying it. Four laboratories made use of intercomparison data. Three made an estimation based on judgement [13] (expert guesstimate). Fifteen laboratories provide an uncertainty estimate to their customer and twenty-six do not.

Forty laboratories carry out this type of analysis regularly. However, the number of samples analysed by the forty laboratories varies a lot as can be seen in Table 6 where the number of samples per year is reported.

Table 6 – Reported number of samples analysed per year

Number of samples per year	<50	50 - 250	250 - 1000	>1000
Number of laboratories	14	6	7	13

All participants have a quality system in place. Thirty-eight laboratories have a quality system based on ISO 17025, three have a quality system based on both ISO 17025 and ISO 9000 series, one based on ISO 9000 series, and the remaining laboratories use either a combination of the above with another system or another system altogether. Thirty-seven laboratories are accredited and six laboratories are not. Twenty-one laboratories take part in an interlaboratory comparison on a regular basis.

Fourteen laboratories use a reference material for this type of analysis. Thirteen laboratories use the reference material for the validation and nine for calibration. Five laboratories did not specify which reference material they use. Table 7 summarises the reference materials used for the validation of the methods as reported by the participants. Considering the answers with regard to the type of reference material used, care should be taken when using a standard solution delivered in connection with an instrument as reference material. A standard solution does not allow the assessment of the overall accuracy, only a matrix (certified) reference material does.

Table 7 – Reference materials used by the participants as reported in the questionnaire

Part Nr	Use of reference material?	Used for validation?	Used for calibration?	Which reference material?
058	yes	yes	yes	
082	yes	yes	no	IQC-026 Combined Quality Control Standard for checking the leach solution
150	yes	yes	yes	Perkin Elmer ICP
176	yes	yes	no	
233	yes	yes	yes	Merck 1000 ppm Standards
285	yes	yes	yes	CA011A
298	yes	no	yes	
332	yes	yes	no	
405	yes	yes	no	In house material
489	yes	yes	yes	CRM solution
522	yes	yes	yes	CRM solution
590	yes	yes	yes	Atomic Absorption Standard
661	yes	yes	no	
951	yes	yes	yes	Reference solutions from Baker for AAS

10 Conclusion

In the recent years many cases were brought to the attention of the public in relation to heavy metals in toys. However, the European standard dealing with this issue from an analytic point of view, the EN 71-3:1994, is known to give a high variation in results. This standard is currently in the process of being modified. It was however judged important to see how laboratories currently perform in the analysis of heavy metals in toys.

A former CRM consisting in a mild steel plate covered with alkyd paint was used and could be distributed to 39 participants from all over Europe and outside the EU. As expected the scatter of the results was large, but showed a close to normal distribution around the reference values for five out of eight heavy metals – antimony, barium, cadmium, chromium, lead. The participants' results tended to be lower than X_{ref} in the case of arsenic, mercury and selenium, elements known to be difficult to analyse. The lower results were mainly attributed to the sample preparation, these elements being very volatile and easy to loose.

One main issue of this exercise was the reporting of results with or without the analytical correction. The latter was introduced in EN 71-3:1994 as a mean to '*achieve consistent interpretation of results*' and is recommended to be applied when values are equal to or above the maximum limits set in the standard. The correction was applied by a number of participants, but only few of them reported that they have done so and it was very unclear which results were corrected and which not. It is recommended that more care is taken to the reporting of results, specifying clearly whether a correction was applied or not.

Participants were also evaluated on how they interpreted their own results with regard to the acceptance of the test material on the market. The majority rejected the material correctly. However, almost one third made a wrong assessment:
- accepted the material,
- rejected but it is not justified by results,
- rejected it correctly but with very unreliable results.

This alarming situation should be improved.

Finally, it should be pointed out that the reported uncertainties were often very small. This is especially noticeable when taking into account the known variation of results for this type of analysis. The questionnaire shows that half of the laboratories estimate their uncertainty using data from measurements replicates (precision only). A reliable uncertainty estimate must take into account all significant sources of uncertainty.

11 Acknowledgements

The authors thank the Istituto di Ricerche e Collaudi, M. Masini S.r.l., the Istituto Italiano Sicurezza dei Giocattoli S.r.l., the LGC Ltd, and the Swedish National Testing and Research Institute for performing high precision analyses on the test material for the establishment of the assigned values. Anne-Mette Jensen is thanked for revising the manuscript.

The laboratories participating in this exercise, listed below are kindly acknowledged.

Organisation	Country
CTIB-TCHN	BELGIUM
Testing centre ALMI TEST	BULGARIA
SGS CSTC Standards Technical Services Co. Ltd Shanghai Branch Testing Centre	CHINA
TÜV Rheinland (Shanghai) Co., Ltd	CHINA
Vyzkumny ustav organickych syntez a.s.	CZECH REPUBLIC
LABTECH s.r.o.	CZECH REPUBLIC
Eurofins Miljø A/S	DENMARK
FORCE Technology	DENMARK
Finnish Customs Laboratory	FINLAND
INTERTEK	FRANCE
SGS CTS	FRANCE
Bureau Veritas Consumer Products Services France	FRANCE
Hansecontrol Testing Institute	GERMANY
TÜV Rheinland Produkt und Umwelt GmbH	GERMANY

Organisation	**Country**
LGA QualiTest GmbH	GERMANY
Eurofins AUA GmbH	GERMANY
INDIKATOR GmbH	GERMANY
Orga Lab GmbH	GERMANY
Ostthüringische Materialprüfgesellschaft für Textil und Kunststoffe mbH	GERMANY
SGS Hong Kong Ltd.	HONG KONG
The Standards Institution of Israel – Chemistry Section	ISRAEL
The Standards Institution of Israel – Metal Section	ISRAEL
ECO Certificazioni Spa	ITALY
Istituto di Ricerche e Collaudi M. Masini S.R.L.	ITALY
Nuovo Istituto Italiano Sicurezza dei Giocattoli SRL	ITALY
Luxcontrol S.A.	LUXEMBOURG
Textile Research Institute	POLAND
CATIM	PORTUGAL
CITEVE-Centro Tecnologico das Industrias têxteis e Vestuário de Portugal	PORTUGAL
Centro de Investigación y Control de la Calidad	SPAIN
STFI-Packforsk (Innventia)	SWEDEN
ALS Scandinavia AB	SWEDEN
SP Technical Research Institute of Sweden	SWEDEN
Laboratorium der Urkantone	SWITZERLAND
Kantonale Lebensmittelkontrolle	SWITZERLAND
Laboratorio cantonale	SWITZERLAND
Harlan Laboratories Ltd	SWITZERLAND
SQTS	SWITZERLAND
Kantonales Labor Zürich	SWITZERLAND
LGC Limited	UNITED KINGDOM
Intertek	UNITED KINGDOM
SATRA Technology Centre	UNITED KINGDOM
Bureau Veritas Consumer Products Services UK Ltd	UNITED KINGDOM

Abbreviations

AAS	Atomic Absorption Spectroscopy
AC	Analytical Correction
AMC	Analytical Methods Committee of the Royal Society of Chemistry
BCR	Community Bureau of Reference
CEN	European Committee for Standardization
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRM	Certified Reference Material
EA	European Co-operation for Accreditation
EC	European Commission
EN	European Standard
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
FN / FP	False Negative / False Positive
GUM	Guide to the Expression of Uncertainty in Measurement
ICP-MS	Inductively-Coupled Plasma Mass Spectrometry
ICP-OES	Inductively-Coupled Plasma Optical Emission Spectrometry
ILC	Interlaboratory Comparison
IMEP	International Measurement Evaluation Programme
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
NANDO	New Approach Notified and Designated Organisations
MoU	Memorandum of Understanding
RSD	Relative Standard Deviation
SP	Swedish National Testing and Research Institute
SWEDAC	Swedish Board for Accreditation and Conformity Assessment
TN / TP	True Negative / True Positive

References

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Annexes

Annex 1 : Invitation to EA to nominate laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements

IMEP

Geel, 6 April 2009
JRC.D04/IBa/ive/ARES(2009)/62600

SWEDAC
Annika Norling
Box 2231
10315 Stockholm
SWEDEN

Dear Annika,

Intercomparison for heavy metals in toys according to EN71-3:1994

The Institute for Reference Materials and Measurements (IRMM) organises an interlaboratory comparison for the determination of the eight heavy metals whose safety limits are set out by the EU Toy Safety Directive (88/378/EEC) and specified in the harmonised European Standard EN71-3:1994. The concerned elements are lead, arsenic, antimony, barium, selenium, mercury, chromium and cadmium. The sample matrix is a mild steel plate coated with alkyd resin paint.

In the frame of the EA-IRMM collaboration agreement, IRMM kindly invites EA to nominate laboratories for free participation. These laboratories must be involved in toy safety evaluation and be familiar with the above mentioned standard, since it will be the method to be applied to the sample. They also should hold (or be in the process of obtaining) an accreditation for this type of measurement.

I suggest that you forward this invitation to the national EA accreditation bodies for their consideration. There is a maximum number of 65 samples at your disposal, i.e. ca. 2-3 nominees per country.

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

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.

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

Registration of participants is open until **22 May 2009**. Distribution of the samples is foreseen for the end of May-early June 2009. The deadline for the reporting of results is then scheduled for 30 June 2009. In order to register, laboratories must:

1. **Enter** their details online:

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=239

When accessing this page you might be confronted with a Certificate Error page, please press the continue button to proceed with the registration.

2. **Print** the completed form when the system asks to do so.
   Do not forget to clearly indicate on the printed form that you have been appointed by the European Cooperation for Accreditation to take part in this exercise.

3. **Send** the printout to both the IMEP-24 and the EA-IMEP-24 coordinators:

IMEP-24 coordinator	**EA-IMEP-24 coordinator**
Ms. Ines Baer	Mrs. Annika Norling
Fax +32 14 571865	Fax +46 0 791 89 29
E-mail jrc-irmm-imep@ec.europa.eu	E-mail Annika.norling@swedac.se

Please contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Ines Baer
IMEP-24 Coordinator

2

Annex 2 : Invitation to expert laboratories

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements

IMEP

Geel, 25 March 2009
JRC.D04/IBa/ive/ARES(2009)/

[Name]
[Institution]
[Address]
[Address]
[Postal Code]
[Country]

Dear [Name],

Intercomparison for heavy metals in toys according to EN71-3:1994

You have been contacted by Johannes van de Kreeke concerning the above mentioned intercomparison project. Please take note that because his leaving our institute, the project was taken over by me, Ines Baer. You have agreed to participate in the proficiency test and that your results could be used for the establishment of the reference value. Please be reminded that in that case a high precision analysis is expected of you and not a routine analysis. It goes without saying that your participation would be free of charge.

As a reminder, the interlaboratory comparison concerns the determination of the eight heavy metals whose safety limits are set out by the EU Toy Safety Directive (88/378/EEC) and specified in the harmonised European Standard EN71-3:1994. The elements are lead, arsenic, antimony, barium, selenium, mercury, chromium and cadmium. The sample matrix is a mild steel plate coated with alkyd resin paint.

I would like to inform you that the homogeneity and stability study has been realised and the results were of the quality that it was decided to proceed with the project. The exercise was launched a few days ago and the registration interface is open now. I therefore kindly invite you to register using the following link :

https://irmm.jrc.ec.europa.eu/ilc/ilcRegistration.do?selComparison=239

When accessing this page you might be confronted with a Certificate Error page, please press the continue button to proceed with the registration.

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.

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

- **Print** the completed form when the system asks to do so.
- **Send** the printout to the IMEP-24 coordinator:

IMEP-24 coordinator
Ms. Ines Baer
Fax +32 14 571865
E-mail jrc-irmm-imep@ec.europa.eu

Distribution of the samples is foreseen for the end of April 2009.

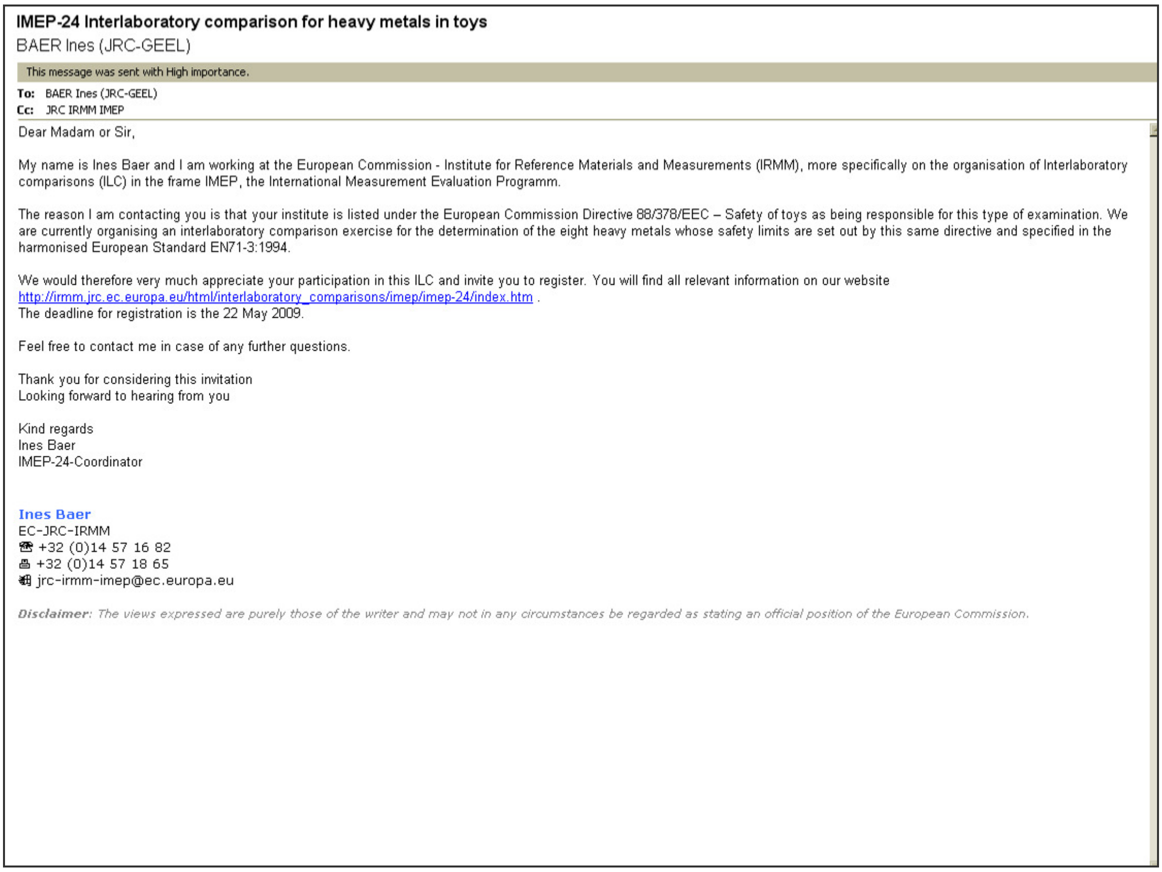
Don't hesitate to contact me if you have any questions or comments. We are looking forward to our cooperation!

With kind regards

Ines Baer
IMEP-24 Coordinator

2

Annex 3 : Invitation to notified bodies from NANDO list



IMEP-24 Interlaboratory comparison for heavy metals in toys
BAER Ines (JRC-GEEL)

This message was sent with High importance.

To: BAER Ines (JRC-GEEL)
Cc: JRC IRMM IMEP

Dear Madam or Sir,

My name is Ines Baer and I am working at the European Commission - Institute for Reference Materials and Measurements (IRMM), more specifically on the organisation of Interlaboratory comparisons (ILC) in the frame IMEP, the International Measurement Evaluation Programm.

The reason I am contacting you is that your institute is listed under the European Commission Directive 88/378/EEC – Safety of toys as being responsible for this type of examination. We are currently organising an interlaboratory comparison exercise for the determination of the eight heavy metals whose safety limits are set out by this same directive and specified in the harmonised European Standard EN71-3:1994.

We would therefore very much appreciate your participation in this ILC and invite you to register. You will find all relevant information on our website
http://irmm.jrc.ec.europa.eu/html/interlaboratory_comparisons/imep/imep-24/index.htm .
The deadline for registration is the 22 May 2009.

Feel free to contact me in case of any further questions.

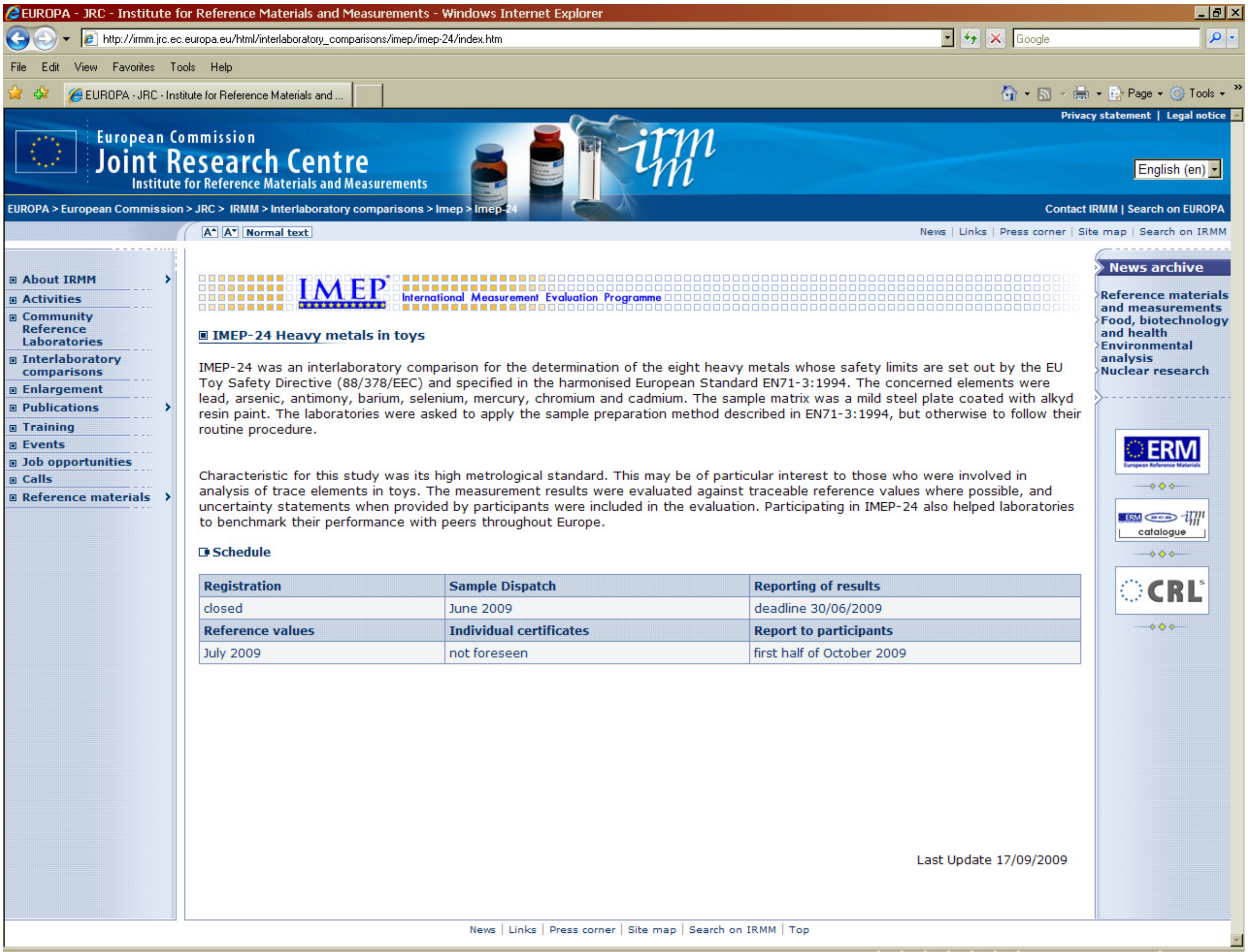
Thank you for considering this invitation
Looking forward to hearing from you

Kind regards
Ines Baer
IMEP-24-Coordinator

Ines Baer
EC-JRC-IRMM
+32 (0)14 57 16 82
+32 (0)14 57 18 65
jrc-irmm-imep@ec.europa.eu

Disclaimer: *The views expressed are purely those of the writer and may not in any circumstances be regarded as stating an official position of the European Commission.*

Annex 4 : Publication on IRMM website



EUROPA - JRC - Institute for Reference Materials and Measurements - Windows Internet Explorer

http://irmm.jrc.ec.europa.eu/html/interlaboratory_comparisons/imep/imep-24/index.htm

European Commission
Joint Research Centre
Institute for Reference Materials and Measurements

EUROPA > European Commission > JRC > IRMM > Interlaboratory comparisons > Imep > Imep-24

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IMEP International Measurement Evaluation Programme

IMEP-24 Heavy metals in toys

IMEP-24 was an interlaboratory comparison for the determination of the eight heavy metals whose safety limits are set out by the EU Toy Safety Directive (88/378/EEC) and specified in the harmonised European Standard EN71-3:1994. The concerned elements were lead, arsenic, antimony, barium, selenium, mercury, chromium and cadmium. The sample matrix was a mild steel plate coated with alkyd resin paint. The laboratories were asked to apply the sample preparation method described in EN71-3:1994, but otherwise to follow their routine procedure.

Characteristic for this study was its high metrological standard. This may be of particular interest to those who were involved in analysis of trace elements in toys. The measurement results were evaluated against traceable reference values where possible, and uncertainty statements when provided by participants were included in the evaluation. Participating in IMEP-24 also helped laboratories to benchmark their performance with peers throughout Europe.

Schedule

Registration	Sample Dispatch	Reporting of results
closed	June 2009	deadline 30/06/2009
Reference values	**Individual certificates**	**Report to participants**
July 2009	not foreseen	first half of October 2009

Last Update 17/09/2009

News archive
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Food, biotechnology and health
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Nuclear research

Annex 5 : Sample accompanying letter

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE
Institute for Reference Materials and Measurements
Isotope measurements

Geel, 27 May 2009
JRC.D04/IBa/ive/ARES(2009)/110360

«Title» «Firstname» «Surname»
«Organisation»
«Department»
«Address»
«Address2»
«Address3»
«Zip» «Town»
«Country»

Subject: **IMEP-24 - Intercomparison for eight heavy metals in toys**

Dear «Title» «Surname»,

Thank you very much for participating in IMEP-24, an interlaboratory comparison for the determination of the eight heavy metals whose safety limits are set out by the EU Toy Safety Directive (88/378/EEC) and specified in the harmonised European Standard EN71-3:1994. Please find further relevant information regarding your participation below.

Packages and content
This parcel contains:

a) the test material consisting of a 10 x 15 cm coated steel plate,
b) "Confirmation of receipt" form,
c) this accompanying letter.

Please check whether the sample has remained undamaged during transport, and confirm undamaged receipt with the "Confirmation of receipt" form, and please send it back by fax to +32 14 57 1865 or email to the project coordinator.
Please store the sample in the dark at ≤18 ºC until analysis.

Measurands and matrix
Measurands are the migrated concentrations of lead, arsenic, antimony, barium, selenium, mercury, chromium and cadmium to be determined as described in EN71-3:1994. The sample matrix is an alkyd resin paint deposed on a mild steel plate.

Preparing the samples for analysis
The procedures you follow for this exercise should resemble as close as possible those that you use in routine sample analysis. The amount of paint deposed on the plate is sufficient so that one gram of paint can be scrapped off for analysis. It is recommended that

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

all paint is scrapped off the plate and carefully homogenised by mixing before sieving through a 500 micron mesh, taking care not to lose the finer particles due to effects of static electricity.

Result reporting
Please report your results online at https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do . Your personal code for access is: **«Part_key»**. The website will guide you through the reporting procedure. Please enter for each parameter:

- In the spaces allocated for "measurement 1" to "measurement 3": the measurement results and the technique you used, but not the uncertainty for each individual measurement
- In the space allocated for "**measurement 4**": the **mean** of the results, the technique you used, and the **uncertainty** of the mean, including the expansion factor.

The results should be reported in the same form (e.g. number of significant figures) as those normally reported to the customer. After reporting your results, please complete the subsequent questionnaire. Do not forget to submit and confirm when required. Directly after completing the measurement results and questionnaire parts, you will be prompted to print the completed report form. Please do so, sign this paper version, put the stamp of your institute and return it to IRMM by fax or e-mail. Check your results carefully for any errors before submission, since this is your definitive confirmation.

Deadline for reporting the results is 3 July 2009.

Result assessment
Your results will be assessed against certified reference values and their uncertainties where available. The scores applied by IMEP are z and zeta scores cf. ISO 13528 [1]. They will be used for each of the eight heavy metals.

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

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

With kind regards

Dr. Ines Baer
IMEP-24 Coordinator

[1] ISO 13528:2005; Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons

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Annex 6 : Questionnaire

1. **Method related questions**

1.1. Have you used the standard method EN 71-3:1994 for the analysis ?
- ○ No
- ○ Yes

1.1.1. If yes, have you deviated from that method :
- ○ No
- ○ Yes

1.1.1.1. If yes, please specify :

1.1.2. If not, please describe briefly the method used :

1.2. If you have applied EN 71-3:1994, please answer the following questions.

1.2.1. State the sample amount used:

1.2.2. What pore size have you used for sieving ?

1.2.3. What type of shaking device have you used ?

1.2.4. Have you pre-heated the labware to 37 C ?
- ○ No
- ○ Yes

1.2.5. Did you need to adjust the pH ?
- ○ No
- ○ Yes

1.2.6. What was the final pH ?

1.2.7. Specify the type and porosity of the membrane filter :

1.2.8. Was a centrifugation step necessary ?
- ○ No
- ○ Yes

1.2.9. Did the ratio of solid to acid extractant exceed 1:50 ?

1.2.10. Did you analyse the samples on the day of processing ?
- ○ No
- ○ Yes

1.2.10.1. If not, did you adjust the acid concentration to 1 mol/l HCl ?
- ○ No
- ○ Yes

1.2.11. Have you included base material in the analysis ?
- ○ No
- ○ Yes

1.3. What are your detection limits for :

1.3.1. Arsenic

1.3.2. Barium

1.3.3. Cadmium

1.3.4. Chromium

1.3.5. Mercury

1.3.6. Lead

1.3.7. Antimony

1.3.8. Selenium

2. **Uncertainty related questions**

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

2.2. What is the basis of your uncertainty estimate (multiple answers are possible)
- ☐ a) uncertainty budget according to ISO-GUM
- ☐ b) known uncertainty of the standard method
- ☐ c) uncertainty of the method as determined during in-house validation
- ☐ d) measurement of replicates (i.e. precision)
- ☐ e) expert guesstimate
- ☐ f) use of intercomparison data
- ☐ g) other

2.2.1. If other, please specify.

2.3. Do you usually provide an uncertainty statement to your custumers for this type of analysis?
- ○ no
- ○ yes

3. **Quality related questions**

3.1. Does your laboratory have a quality system in place?
- ○ no
- ○ yes

3.1.1. If Yes, which:
- ☐ a) ISO 17025
- ☐ b) ISO 9000 series
- ☐ c) Other

3.1.1.1. If other, please specify.

3.1.2. If yes, are you accredited?
- ○ No
- ○ Yes

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

3.2. Does your laboratory carry out this type of analysis (as regards the parameters, matrix and methods
- ○ no
- ○ yes

3.2.1. If Yes, please estimate the number of samples :
- ☐ a) 0-50 samples per year
- ☐ b) 50-250 samples per year
- ☐ c) 250-1000 samples per year
- ☐ d) more than 1000 samples per year

3.3. Does your laboratory take part in an interlaboratory comparison for this type of analysis on a regular basis ?
- ○ no
- ○ yes

3.3.1. If yes, which one(s):

3.4. Does your laboratory use a reference material for this type of analysis?
- ○ no
- ○ yes

3.4.1. If yes, is the material used for the validation of procedures ?
- ○ no
- ○ yes

3.4.2. If yes, is the material used for calibration of instruments ?
- ○ no
- ○ yes

3.4.3. If yes, which one(s):

4. **In view of your results would you accept or reject the entrance of the material on the market ?**
- ☐ Accept
- ☐ Reject

4.1. Why ?

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

Annex 7 : 'Confirmation of receipt' form

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Isotope measurements

Annex to JRC.D04/IBa/ive/ARES(2009)/110360

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

IMEP-24

Migrated concentrations of Pb, As, Sn, Ba, Se, Hg, Cr and Cd in toys

Confirmation of receipt of the samples

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

ANY REMARKS ……………………………
……………………………

Date of package arrival ……………………………

Signature ……………………………

Please return this form to:
Dr Ines Baer

IMEP-24 Coordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium

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

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line (32-14) 571 682. Fax: (32-14) 571 865.

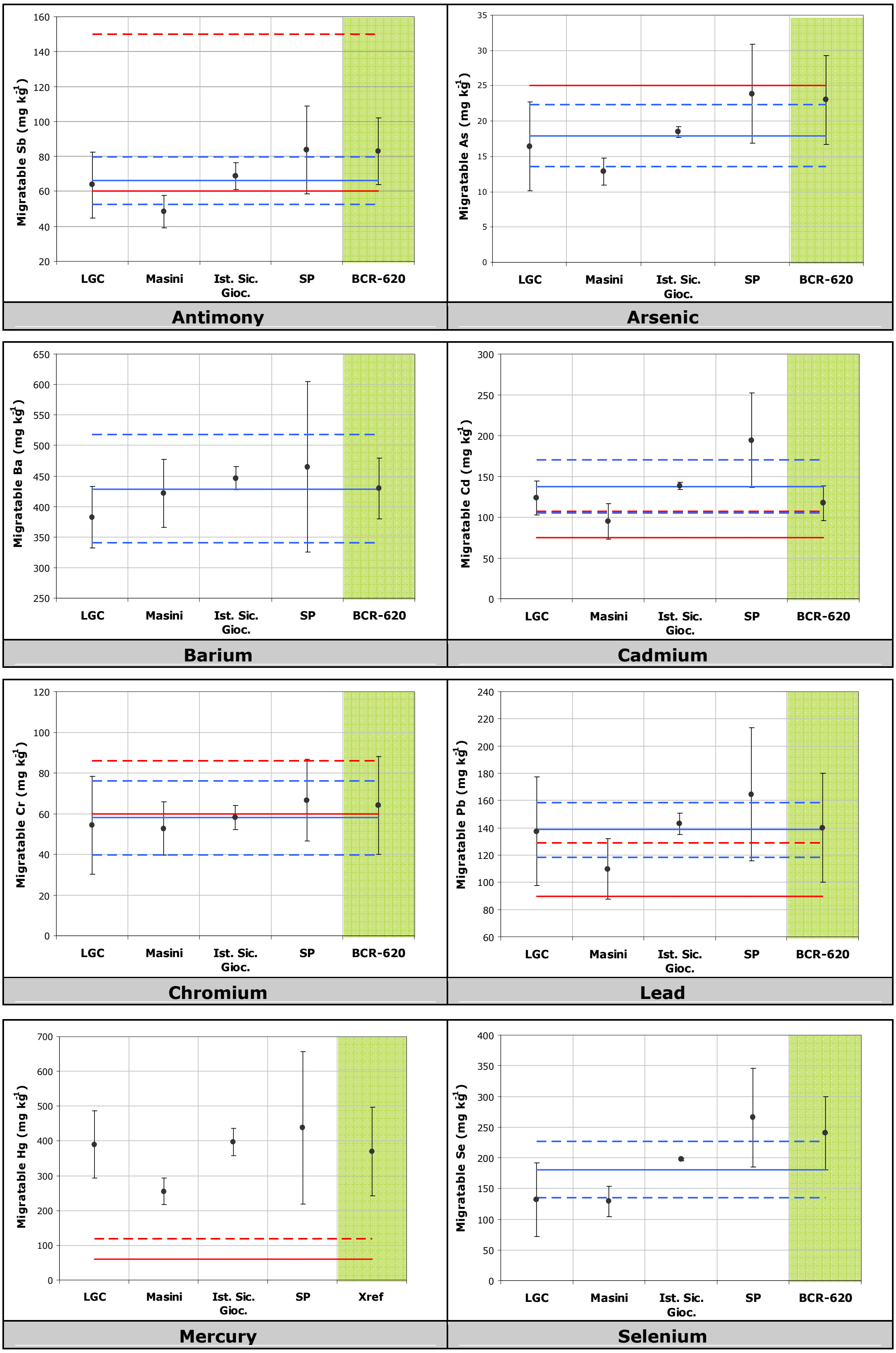
E-mail: jrc-irmm-imep@ec.europa.eu

IMEP®

Annex 8 : Homogeneity study

	Sb		As		Ba		Cd		Cr		Pb		Hg		Se	
Sample	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2	R1	R2
1801	75.1	71.6	19.9	19.0	436.3	468.8	137.5	136.6	55.3	55.2	120.8	120.3	523.6	545.7	219.8	220.7
1578	71.2	87.5	20.8	18.6	422.2	459.0	137.5	139.5	54.2	60.3	118.8	131.6	467.7	527.0	208.8	212.8
1478	62.0	63.2	13.9	13.9	447.6	438.6	130.5	137.9	60.4	58.8	124.9	130.8	497.7	594.6	161.5	173.6
1140	72.1	80.2	15.7	16.9	485.6	474.7	131.6	134.7	57.9	59.4	137.5	140.7	450.9	531.0	180.0	180.0
1138	69.3	69.1	17.2	16.7	475.4	455.7	134.1	132.6	59.0	58.4	142.4	141.1	478.7	497.8	183.8	184.3
0733	73.4	73.7	15.5	16.7	456.8	483.7	109.6	136.0	59.2	68.6	120.8	126.1	380.0	408.0	169.3	169.2
0652	74.9	80.1	18.3	18.2	506.2	483.1	124.6	147.3	62.6	65.2	125.9	138.2	483.5	514.3	171.2	168.5
0508	84.7	84.2	17.5	19.3	503.9	497.5	125.4	139.5	64.1	66.6	119.5	131.6	552.8	608.2	188.2	190.3
0164	88.2	71.2	18.3	18.2	430.6	449.2	123.2	118.2	64.0	68.9	127.4	115.5	382.5	389.8	175.3	162.5
0163	83.1	85.8	19.8	20.0	468.8	470.5	139.8	131.0	61.9	64.7	123.2	137.2	485.8	505.4	166.1	166.4
Mean	76.0		17.7		465.7		132.4		61.2		128.7		491.3		182.6	
$\hat{\sigma}$ [%]	30		30		15		15		15		15		25		30	
$\hat{\sigma}$ [mg kg^{-1}]	22.8		5.3		69.9		19.9		9.2		19.3		122.8		54.8	
Homogeneity test according to the IUPAC International Harmonised Protocol (mg^2 kg^{-2})																
s^2_{an}	33.44		0.604		232.3		79.25		8.780		43.71		1271		16.96	
s^2_{sam}	28.71		3.311		360.3		0		10.06		29.41		3086		356.9	
σ^2_{all}	46.82		2.543		439.2		35.47		7.593		33.55		1357		270.1	
Crit value c	121.8		5.392		1060		146.7		23.144		107.2		3835		525.0	
$s^2_{sam} \leq c$?	Passed		Passed		Passed		Passed		Passed		Passed		Passed		Passed	
Homogeneity test according to ISO 13528 (mg kg^{-1})																
0.3 $\hat{\sigma}$	6.843		1.595		20.96		5.956		2.756		5.792		36.844		16.435	
s_x	6.740		1.901		21.83		5.908		3.802		7.160		61.00		19.11	
s_w	5.782		0.777		15.24		8.902		2.963		6.611		35.65		4.118	
s_s	5.358		1.820		18.98		0		3.172		5.423		55.55		18.89	
$s_s \leq 0.3\hat{\sigma}$	Yes		No		Yes		Yes		No		Yes		No		No	
Test	Passed		Failed		Passed		Passed		Failed		Passed		Failed		Failed	

Annex 9 : Reference values and their associated uncertainties



X_{exp} — Legal limit from EN 71-3:1994 (LL)

$X_{exp} \pm U_{exp}$ — Max experimental value giving LL after applying analytical correction from EN 71-3:1994

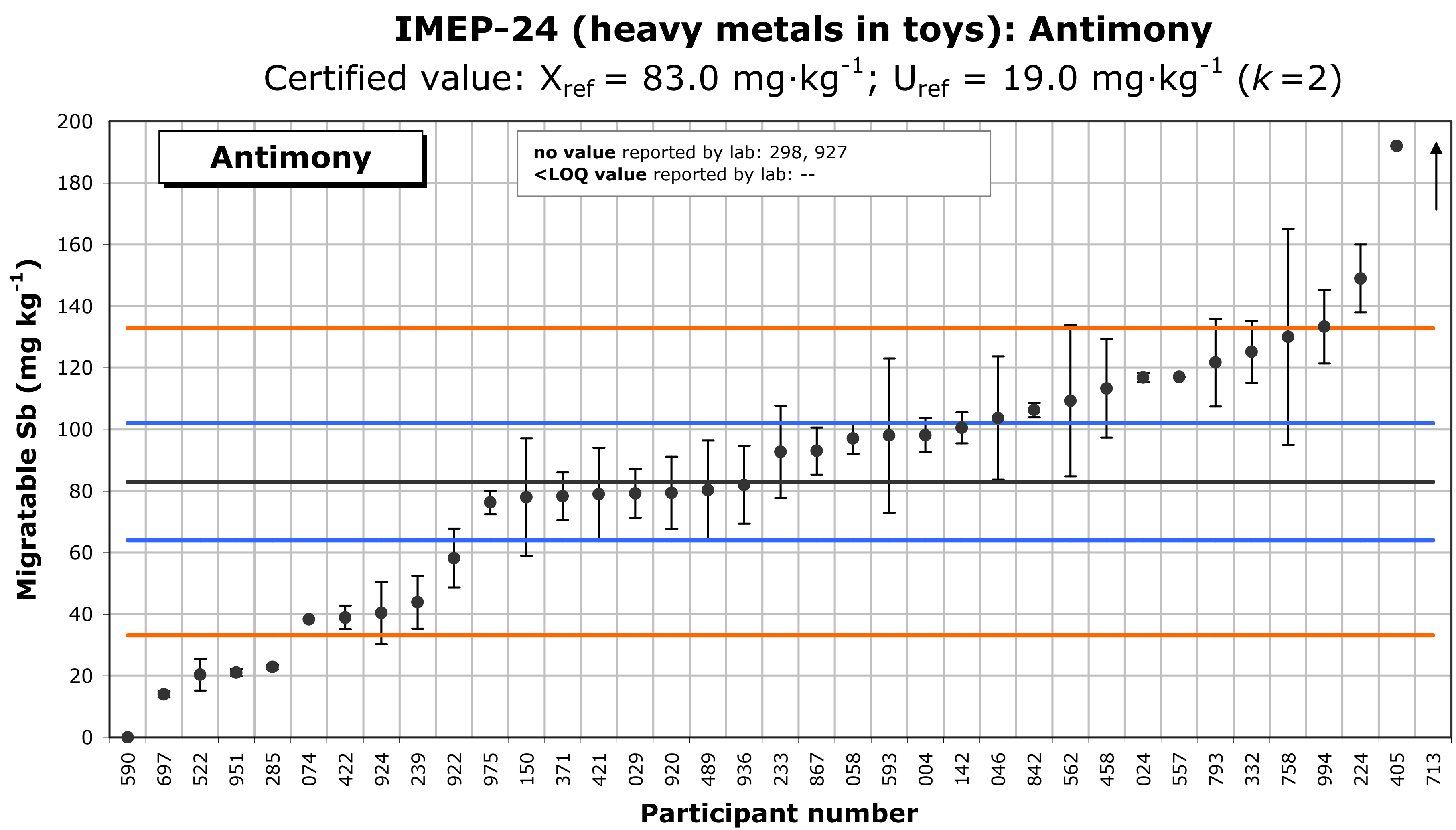
If not present, the respective value is above the presented range.

Annex 10 : Results for Antimony

X_{ref} = 83.0 and U_{ref} = 19.0; all values are given in (mg kg^{-1})

Part Nr	x1	x2	x3	x4	Ulab	*k**	Mean	ulab	Technique	z	zeta
004	102	97.3	95.0		24.5	2	98.1	12.3	ICP-OES	0.6	1.0
024	117	116.8			35.1	1	116.9	35.1	ICP-OES	1.4	0.9
029	77.5	80.2	80		12.7	2	79.2	6.4	ICP-OES	-0.2	-0.3
046	100	105	106		1.4	√3	104	0.8	ICP-MS	0.8	2.2
058					20	2	97	10	XRF- Indicative Quantity Test	0.6	1.0
074						2	38.3075		ICP-OES	-1.8	
142	110	95.1	96.3		16	2	100.5	8	ICP-OES	0.7	1.4
150	74	82	78		8	√3	78	4.6	ICP-OES	-0.2	-0.5
224	146	152			29.8	√3	149	17.2	HG-AAS	2.7	3.4
233					5.59	√3	92.7	3.23	ICP-OES	0.4	1.0
239	48.507	40.340	42.877		8.575	2	43.908	4.288	ICP-OES	-1.6	-3.8
285	22.67	21.9	23.9		0.82	1	22.82	0.82	ICP-MS	-2.4	-6.3
332	133.0	123.5	119.0		0.22	2	125.2	0.11	FAAS	1.7	4.4
371	77.60	80.12	77.17		11.74	60	78.30	0.20	ICP-OES	-0.2	-0.4
405	194	190					192		ICP-MS	4.4	
421					16	√3	79	9	ICP-MS	-0.2	-0.3
422	39.2	40.1	37.5		3.89	2	38.9	1.95	ICP-MS	-1.8	-4.5
458	111	119	110		10	2	113	5	ICP-OES	1.2	2.8
489	83	82	76		7.6	2	80	3.8	ICP-OES	-0.1	-0.3
522	20	23	18		5.1	2	20	2.6	ICP-OES	-2.5	-6.4
557	119	117	115		12	2	117	6	ICP-OES	1.4	3.0
562	132.5	93.9	101.6		14.2	2	109.3	7.1	ICP-OES	1.1	2.2
590							0.0021		FAAS	-3.3	
593	92	95	107		2.4	0.4	98	6.0	ICP-OES	0.6	1.3
697	14	14	14		1	√3	14	1	ICP-MS	-2.8	-7.2
713	223	228	240		6.8	2	230	3.4	ICP-MS	5.9	14.6
758	128.0	136.0	126.0		10.583	2	130.0	5.292	ICP-OES	1.9	4.3
793	128	115	122		11.0	2	122	5.5	ICP-MS	1.6	3.5
842	114.32	104.02	100.50		0.038	2	106.28	0.019	ICP-OES	0.9	2.5
867	90	93	96		5	√3	93	3	ICP-OES	0.4	1.0
920	79.4	79.4	79.4		15	2	79.4	8	ICP-OES	-0.1	-0.3
922	60.9	57.5	55	59.5	3.8	2	58.2	1.9	FAAS	-1.0	-2.6
924	40.7	40.9	39.5		10.1	2	40.4	5.1	ICP-OES	-1.7	-4.0
936	81	83			5	2	82	3	ETAAS	0.0	-0.1
951	21.28	20.10	21.78		1.22	√3	21.05	0.70	Graphite Furnace AAS	-2.5	-6.5
975	75.2	77.4			15	2	76.3	8	ICP-MS	-0.3	-0.6
994	135	137	128			2	133		ICP-OES	2.0	

* √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3.1



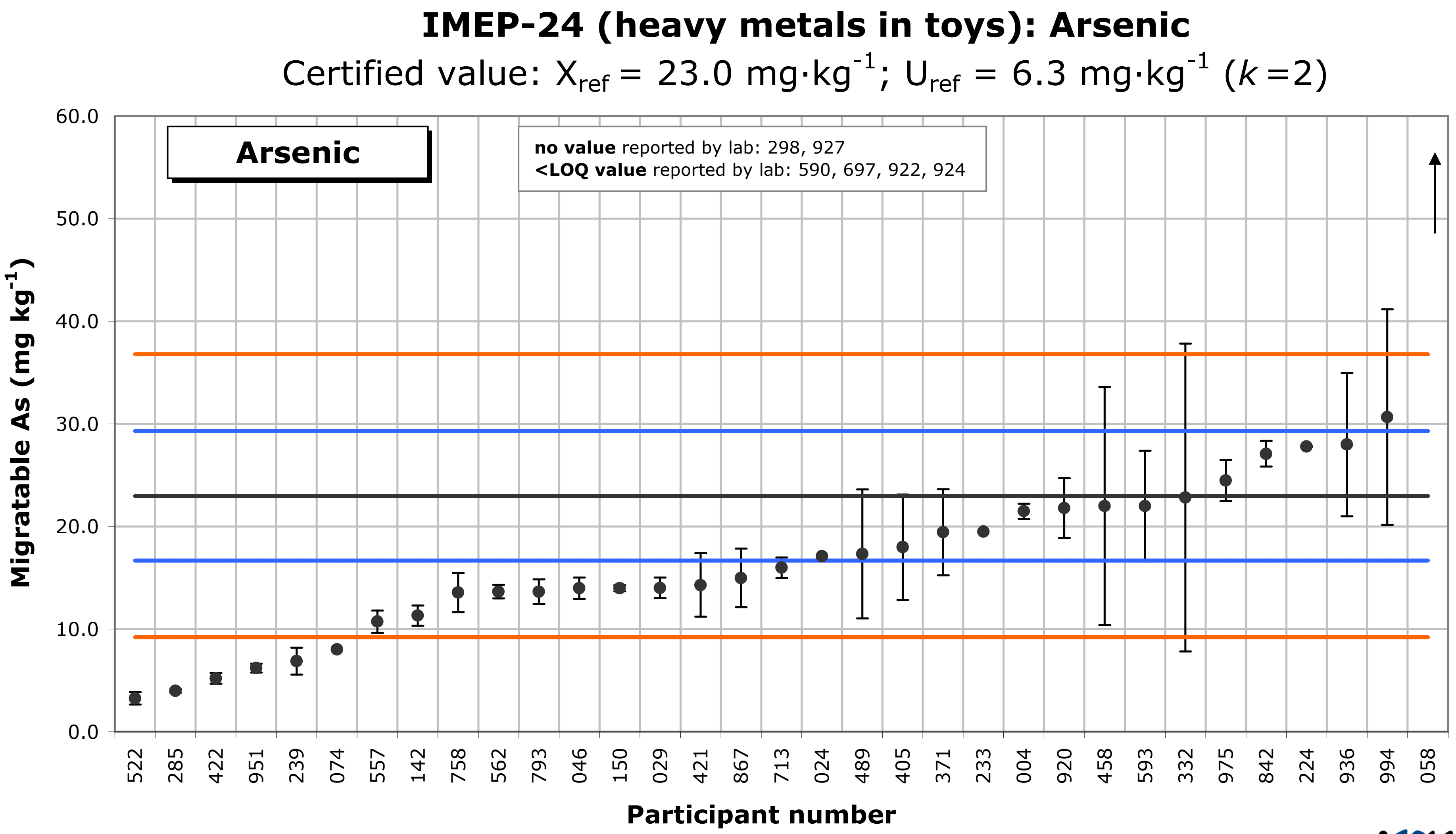
This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to **Xref**, the blue lines mark the boundary of the reference interval (**Xref ± 2uref**), and the orange lines that of the target interval (**Xref ± 2σ**).

Annex 11 : Results for Arsenic

X_{ref} = 23.0 and U_{ref} = 6.3; all values are given in (mg kg^{-1})

Part Nr	x1	x2	x3	Ulab	*k**	Mean	ulab	Technique	z	zeta
004	21.7	21.2	21.6	5.4	2	21.5	3.1	ICP-OES	-0.2	-0.3
024	16.65	17.56		5.13	1	17.11	5.13	ICP-OES	-0.9	-1.0
029	13.9	14.4	13.8	3.10	2	14.0	1.55	ICP-OES	-1.3	-2.6
046	13	14	15	0.3	√3	14	0.2	ICP-MS	-1.3	-2.9
058				20	2	156	10	XRF- Indicative Quantity Test	19.3	12.7
074						8.01305		ICP-OES	-2.2	
142	11.8	10.7	11.5	1.0	2	11.3	0.5	ICP-OES	-1.7	-3.7
150	13	14	15	1	√3	14	1	ICP-OES	-1.3	-2.8
224	27.1	28.5		5.56	√3	27.8	3.21	HG-AAS	0.7	1.1
233				11.61	√3	19.5	6.70	ICP-OES	-0.5	-0.5
239	8.340	5.819	6.522	1.3044	2	6.894	0.6522	ICP-OES	-2.3	-5.0
285	4.07	3.77	4.14	0.16	1	3.99	0.16	ICP-MS	-2.8	-6.0
332	18.0	21.0	29.5	0.04	2	22.8	0.02	FAAS	0.0	-0.1
371	19.27	19.13	19.98	2.92	60	19.46	0.05	ICP-OES	-0.5	-1.1
405	18	18				18		ICP-MS	-0.7	
421				2.86	√3	14.3	1.65	ICP-MS	-1.3	-2.4
422	5.38	5.20	5.06	0.521	2	5.21	0.261	ICP-MS	-2.6	-5.6
458	22	23	21	2	√3	22	1	ICP-OES	-0.1	-0.3
489	18	19	15	4.2	2	17	2.1	ICP-OES	-0.8	-1.5
522	3.2	3.6	3	0.6	2	3.3	0.3	ICP-OES	-2.9	-6.2
557	11.2	10.9	10.1	1.1	2	10.7	0.6	ICP-OES	-1.8	-3.8
562	14.5	12	14.5	1.04	√3	13.7	0.60	ICP-OES	-1.4	-2.9
590	<1							FAAS		
593	23	22	21	1.25	√3	22	0.72	ICP-OES	-0.1	-0.3
697	<5	<5	<5					ICP-OES		
713						16		ICP-MS	-1.0	
758	13.24	13.61	13.90	0.662	2	13.58	0.331	HG-AAS	-1.4	-3.0
793	16.0	11.0	14.0	1.2	2	13.7	0.6	ICP-MS	-1.4	-2.9
842	26.92	26.91	27.44	0.038	√3	27.09	0.022	ICP-OES	0.6	1.3
867	14	15	16	1	√3	15	1	ICP-OES	-1.2	-2.5
920	21.8	21.8	21.8	15	2	21.8	8	ICP-OES	-0.2	-0.1
922	<22	<22	<22					FAAS		
924	<5	<5	<5					ICP-OES		
936	28	28		6	2	28	3	ETAAS	0.7	1.1
951	5.91	6.48	6.24	0.43	√3	6.21	0.25	Graphite Furnace AAS	-2.4	-5.3
975	24	25		10.5	√3	25	6.1	ICP-MS	0.2	0.2
994	30	32	30	0.4	2	31	0.2	ICP-OES	1.1	2.4

* √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3.1



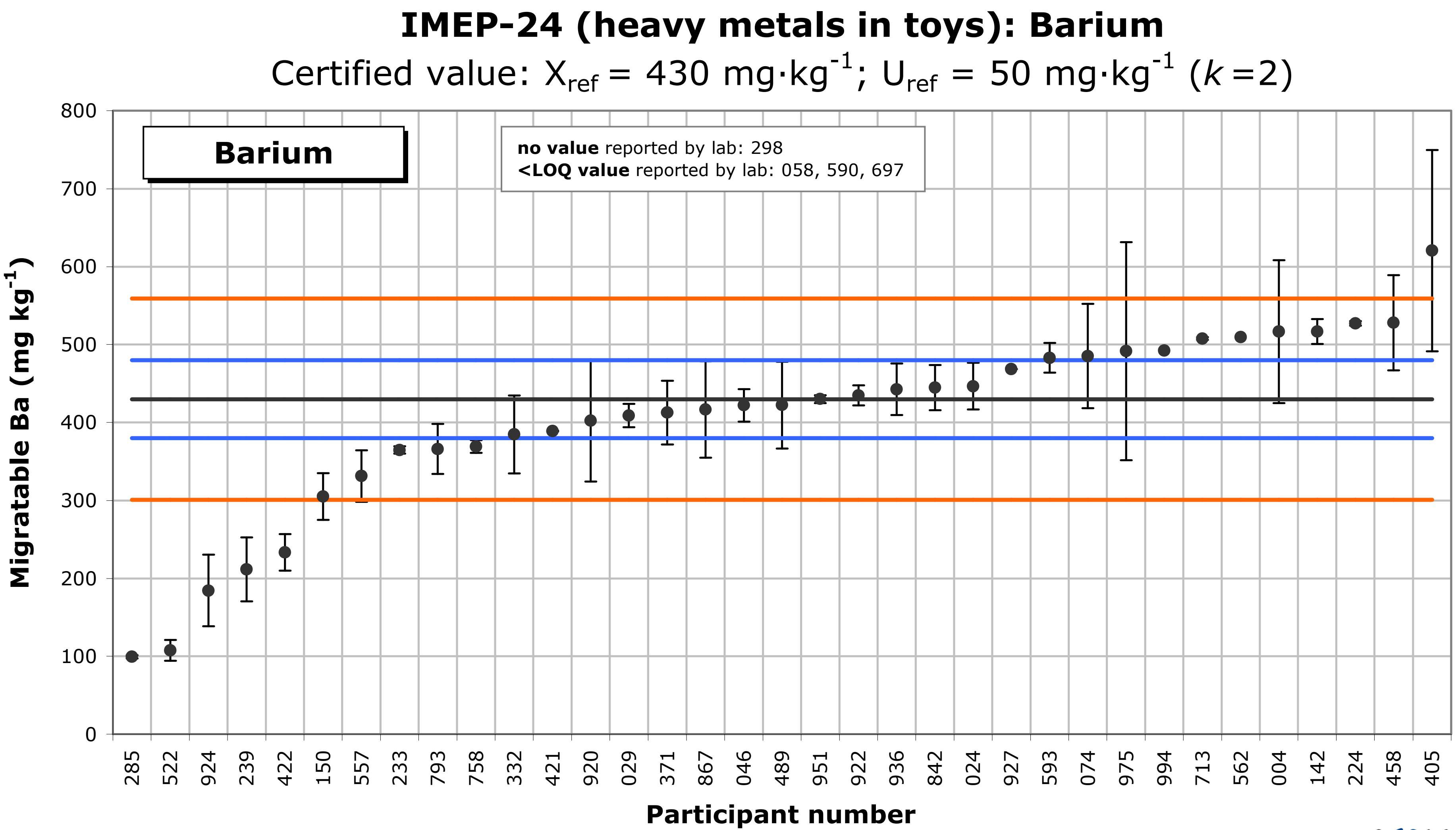
This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to **Xref**, the blue lines mark the boundary of the reference interval (**Xref ± 2uref**), and the orange lines that of the target interval (**Xref ± 2σ**).

Annex 12 : Results for Barium

X_{ref} = 430 and U_{ref} = 50; all values are given in (mg kg^{-1})

Part Nr	x1	x2	x3	x4	Ulab	k*	Mean	ulab	Technique	z	zeta
004	518	519	513		129	2	517	65	ICP-OES	1.3	1.3
024	407.2	485.9			67	1	446.6	67	ICP-OES	0.3	0.2
029	403.0	411.3	411.9		40.9	2	408.7	20.5	ICP-OES	-0.3	-0.7
046	429	422	415		4.9	√3	422	2.8	ICP-MS	-0.1	-0.3
058	<66								XRF- Indicative Quantity Test		
074						2	485.2105		ICP-OES	0.9	
142	528	517	505		23	2	517	12	ICP-OES	1.3	3.1
150	295	305	315		30	√3	305	17	ICP-OES	-1.9	-4.1
224	526.63	527.42			105.4	√3	527.03	60.9	ICP-OES	1.5	1.5
233					4.66	√3	364.7	2.69	ICP-OES	-1.0	-2.6
239	244.205	185.984	204.748		40.950	2	211.646	20.475	ICP-OES	-3.4	-6.8
285	97.99	97.44	102.4		2.22	1	99.28	2.22	ICP-MS	-5.1	-13.2
332	375.5	392	386.5		0.72	2	384.7	0.36	FAAS	-0.7	-1.8
371	414.85	412.85	410.0		61.9	30	412.57	2.1	ICP-OES	-0.3	-0.7
405	639	602					621		ICP-MS	3.0	
421					78	√3	389	45	ICP-MS	-0.6	-0.8
422	233	237	230		23.3	2	233	11.7	ICP-MS	-3.0	-7.1
458	530	525	529		5	2	528	3	ICP-OES	1.5	3.9
489	416	422	429		13	2	422	7	ICP-OES	-0.1	-0.3
522	112	111	100	107	13.3	2	108	6.7	ICP-OES	-5.0	-12.5
557	331	333	330		33	2	331	17	ICP-OES	-1.5	-3.3
562	492.6	474.2	561.5		61.1	2	509.4	30.6	ICP-OES	1.2	2.0
590	<1								FAAS		
593	481	463	505		1.85	√3	483	1.07	ICP-OES	0.8	2.1
697	<100	<100	<100	<100					ICP-OES		
713	507	506	510		3	2	508	2	ICP-MS	1.2	3.1
758	371.0	372.0	364.5		8.145	2	369.2	4.073	ICP-OES	-0.9	-2.4
793	388	341	369		32	2	366	16	ICP-MS	-1.0	-2.2
842	443.59	452.56	437.95		0.038	2	444.70	0.019	ICP-OES	0.2	0.6
867	410	410	430		21	√3	417	12	ICP-OES	-0.2	-0.5
920	400.8	404.8	400.8		15	2	402.1	8	ICP-OES	-0.4	-1.1
922	376.5	480.6	421.1	460.8	29	2	434.8	15	FAAS	0.1	0.2
924	181	187	185		46	2	184	23	ICP-OES	-3.8	-7.2
927	448	489					469		ICP-OES	0.6	
936	454	431			30	2	443	15	ETAAS	0.2	0.4
951	422.63	449.23	418.37		33.19	√3	430.08	19.16	Graphite Furnace AAS	0.0	0.0
975	495	488			91.5	2	492	45.8	ICP-MS	1.0	1.2
994	508	490	479		15.8	2	492	7.9	ICP-OES	1.0	2.4

* √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3.1



This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to **Xref**, the blue lines mark the boundary of the reference interval (**Xref ± 2uref**), and the orange lines that of the target interval (**Xref ± 2σ**).

Annex 13 : Results for Cadmium

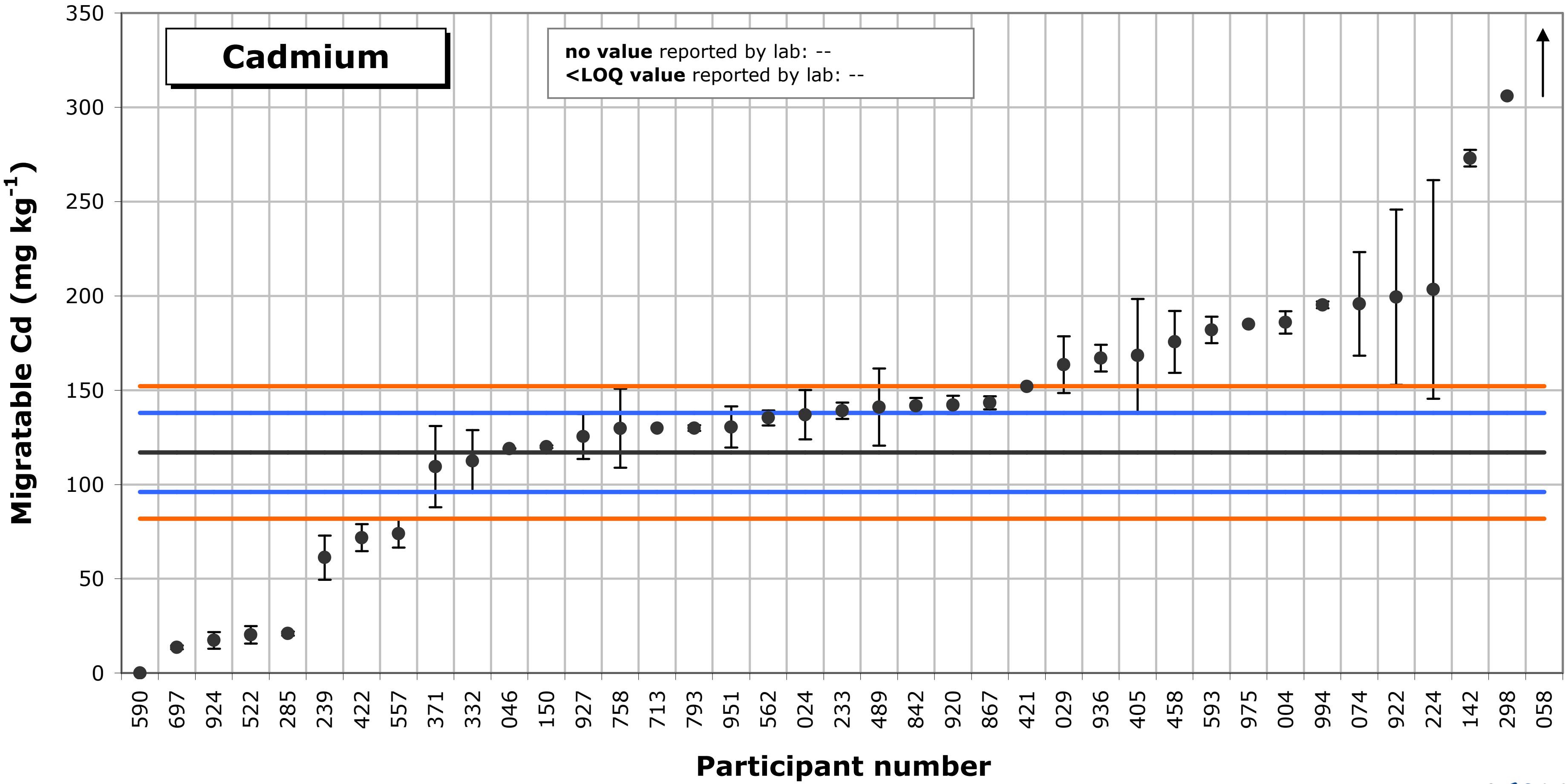
X_{ref} = 117 and U_{ref} = 21; all values are given in (mg kg^{-1})

Part Nr	x1	x2	x3	x4	Ulab	k*	Mean	ulab	Technique	z	zeta
004	179	186	193		46.5	2	186	23.3	ICP-OES	3.9	2.7
024	137.4	136.6			20.5	1	137.0	20.5	ICP-OES	1.1	0.9
029	163.0	165.2	162.2		16.4	2	163.5	8.2	ICP-OES	2.6	3.5
046	120	118	119		0.7	√3	119	0.4	ICP-MS	0.1	0.2
058					61	2	4392	31	XRF- Indicative Quantity Test	243.6	132.5
074							195.7942		ICP-OES	4.5	
142	235	298	286		66	2	273	33	ICP-OES	8.9	4.5
150	120	110	130		12	√3	120	7	ICP-OES	0.2	0.2
224	207.49	199.53			40.8	√3	203.51	23.6	ICP-OES	4.9	3.4
233					4.81	√3	139.2	2.78	ICP-OES	1.3	2.0
239	74.374	50.770	58.558		11.712	2	61.234	5.856	ICP-OES	-3.2	-4.6
285	21.21	19.63	22.24		1.07	1	21.03	1.07	ICP-MS	-5.5	-9.1
298	305	307			2	2	306	1	FAAS	10.8	17.9
332	124.0	111.5	102.0		0.22	2	112.5	0.11	FAAS	-0.3	-0.4
371	109.65	109.3	109.6		16.43	30	109.5	0.55	ICP-OES	-0.4	-0.5
405	174	163					169		ICP-MS	2.9	
421					30	2	152	15	ICP-MS	2.0	1.9
422	72.9	68.4	74.3		7.19	2	71.9	3.60	ICP-MS	-2.6	-4.1
458	179	173	175		6	2	176	3	ICP-OES	3.3	5.4
489	143	140	140		3.5	2	141	1.8	ICP-OES	1.4	2.3
522	23	20	18		4.6	2	20	2.3	ICP-OES	-5.5	-9.0
557	74.4	74.3	73.4		7.4	2	74.0	3.7	ICP-OES	-2.4	-3.9
562	143.9	125.8	136.4		4.33	2	135.4	2.17	ICP-OES	1.0	1.7
590							0.00238		FAAS	-6.7	
593	182	173	191		1.85	0.7	182	2.64	ICP-OES	3.7	6.0
697	14	13	14		1	√3	14	1	ICP-OES	-5.9	-9.8
713	127	130	133		4	2	130	2	ICP-MS	0.7	1.2
758	130.0	129.0	130.5		1.528	2	129.8	0.764	ICP-OES	0.7	1.2
793	130	118	142		11	2	130	6	ICP-MS	0.7	1.1
842	131.91	143.88	149.35		0.038	2	141.71	0.019	ICP-OES	1.4	2.4
867	140	140	150		7	√3	143	4	ICP-OES	1.5	2.3
920	142.9	140.9	142.9		15	2	142.2	8	ICP-OES	1.4	2.0
922	188.3	208.1	208.1	193.2	11.6	2	199.4	5.8	FAAS	4.7	6.9
924	17.4	17.7	17.2		4.4	2	17.4	2.2	ICP-OES	-5.7	-9.3
927	139	112					126		ICP-OES	0.5	
936	171	163			7.1	2	167	3.6	ETAAS	2.8	4.5
951	117.57	130.13	143.90		13.19	√3	130.53	7.62	Graphite Furnace AAS	0.8	1.0
975	193	177			27.5	2	185	13.8	ICP-MS	3.9	3.9
994	202	193	191		4.4	2	195	2.2	ICP-OES	4.5	7.3

* √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3.1

IMEP-24 (heavy metals in toys): Cadmium

Certified value: X_{ref} = 117 mg·kg^{-1}; U_{ref} = 21 mg·kg^{-1} (k =2)



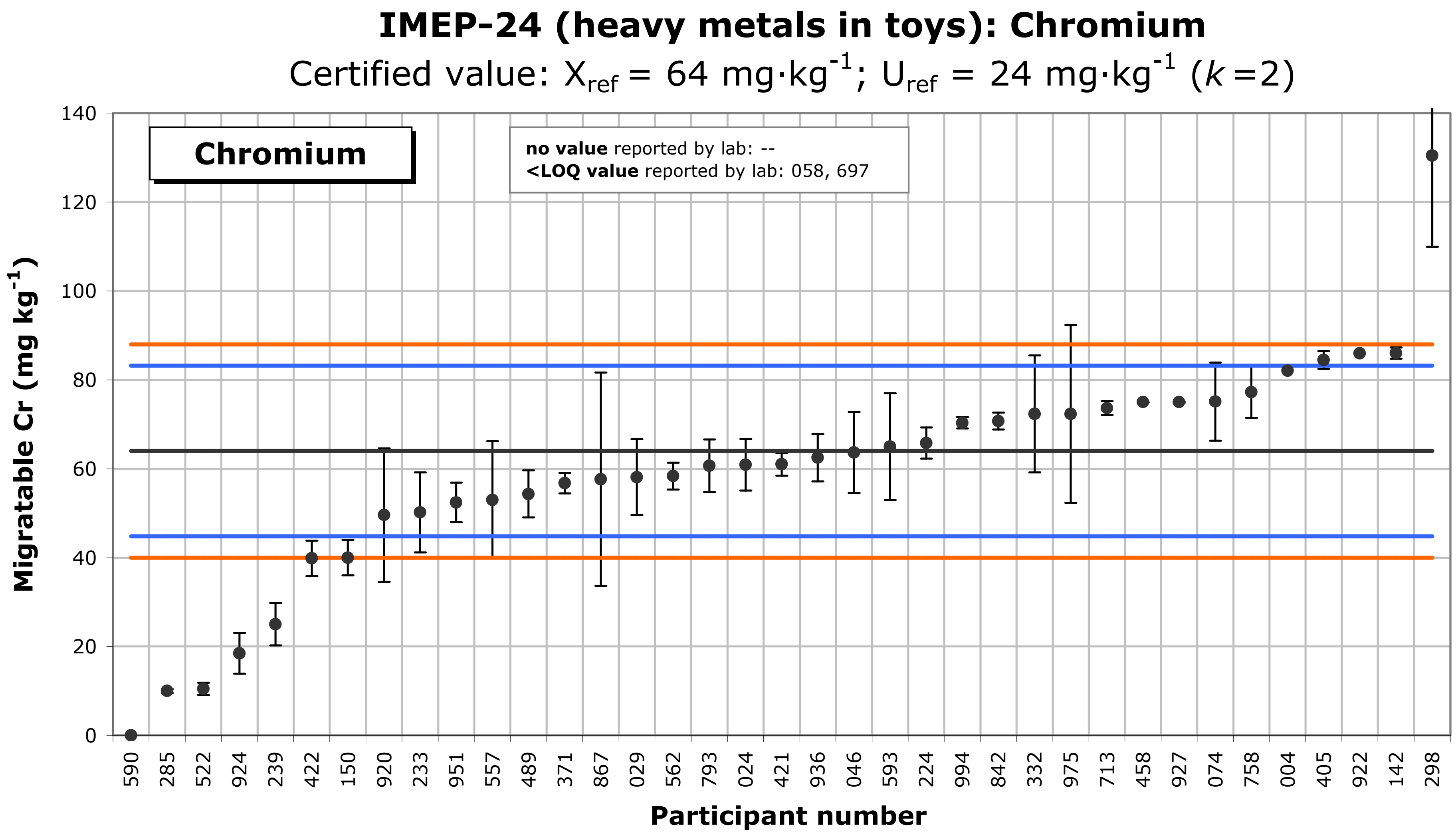
This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to **Xref**, the blue lines mark the boundary of the reference interval (**Xref ± 2uref**), and the orange lines that of the target interval (**Xref ± 2σ**).

Annex 14 : Results for Chromium

X_{ref} = 64 and U_{ref} = 24; all values are given in (mg kg^{-1})

Part Nr	x1	x2	x3	x4	Ulab	k*	Mean	ulab	Technique	z	zeta
004	82.3	83.2	80.8		20.5	2	82.1	10.3	ICP-OES	1.9	1.1
024	60.29	61.5			9.13	1	60.90	9.13	ICP-OES	-0.3	-0.2
029	57.6	58.5	58.2		5.8	2	58.1	2.9	ICP-OES	-0.6	-0.5
046	62	66	63		1.3	√3	64	0.8	ICP-MS	0.0	0.0
058	<31								XRF- Indicative Quantity Test		
074							75.1126		ICP-OES	1.2	
142	86.6	87.4	84.1		3.5	2	86.0	1.8	ICP-OES	2.3	1.8
150	40	37	43		4	√3	40	2	ICP-OES	-2.5	-2.0
224	66.11	65.42			13.16	√3	65.77	7.60	ICP-OES	0.2	0.1
233					9.0	√3	50.2	5.2	ICP-OES	-1.4	-1.1
239	29.772	21.262	24.045		4.809	2	25.026	2.405	ICP-OES	-4.1	-3.2
285	9.99	9.53	10.57		0.43	1	10.03	0.43	ICP-MS	-5.6	-4.5
298	128	133			8	2	131	4	ETAAS	6.9	5.3
332	66.5	79.0	71.5		0.14	2	72.3	0.07	FAAS	0.9	0.7
371	56.32	57.11	56.95		8.52	30	56.79	0.28	ICP-OES	-0.8	-0.6
405	86	83					85		ICP-MS	2.1	
421					12	√3	61	7	ICP-MS	-0.3	-0.2
422	42.1	39.4	38.0		3.98	2	39.8	1.99	ICP-MS	-2.5	-2.0
458	75	74	76		2	2	75	1	ICP-OES	1.1	0.9
489	55	53	55		2.3	2	54	1.2	ICP-OES	-1.0	-0.8
522	11	11	10	10	1.4	2	11	0.7	ICP-OES	-5.6	-4.5
557	52.2	53.3	53.5		5.3	2	53.0	2.7	ICP-OES	-1.1	-0.9
562	64.9	49.4	60.8		2.6	2	58.4	1.3	ICP-OES	-0.6	-0.5
590							0.00049		FAAS	-6.7	
593	65	62	68		1.9	0.7	65	2.7	ICP-OES	0.1	0.1
697	<10								ICP-OES		
713	71	71	79		5.8	2	74	2.9	ICP-MS	1.0	0.8
758	77.0	76.8	78.0		1.286	2	77.3	0.643	ICP-OES	1.4	1.1
793	69.2	54.2	58.7		5.3	2	60.7	2.7	ICP-MS	-0.3	-0.3
842	70.34	70.91	70.92		0.038	2	70.72	0.019	ICP-OES	0.7	0.6
867	57	58	58		3	√3	58	2	ICP-OES	-0.7	-0.5
920	49.6	49.6	49.6		15	2	49.6	8	ICP-OES	-1.5	-1.0
922	85.7	85.2	87.2	85.7	5.1	2	86.0	2.6	FAAS	2.3	1.8
924	18.7	18.6	18.1		4.6	2	18.5	2.3	ICP-OES	-4.7	-3.7
927	69	81					75		ICP-OES	1.1	
936	65.6	62.2	59.7		3.5	2	62.5	1.8	FAAS	-0.2	-0.1
951	50.23	51.86	55.20		4.46	√3	52.43	2.57	Graphite Furnace AAS	-1.2	-0.9
975	71.0	73.7			8.8	2	72.4	4.4	ICP-MS	0.9	0.7
994	72	69	70		1.6	2	70	0.8	ICP-OES	0.7	0.5

* √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3.1



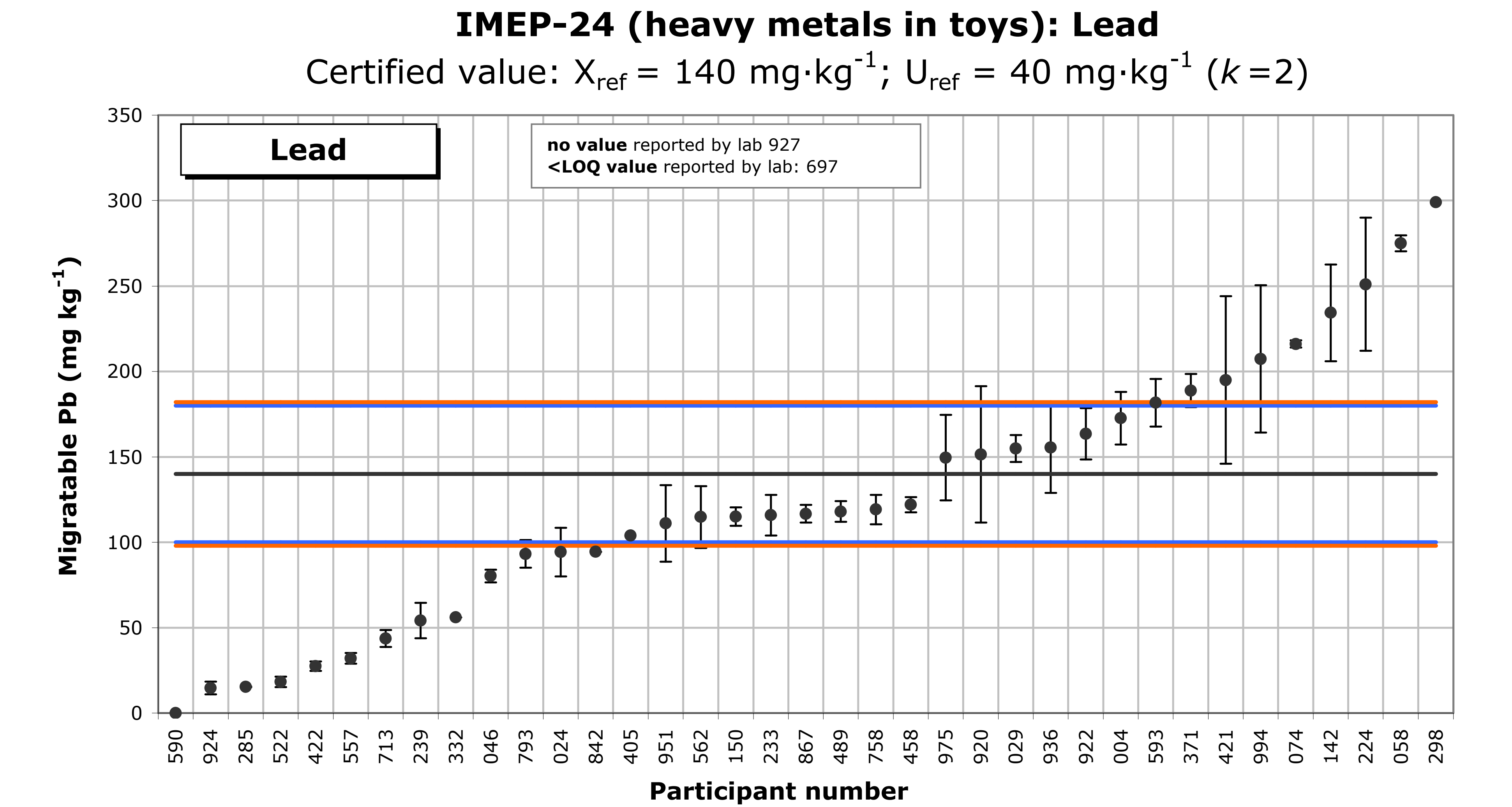
This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to **Xref**, the blue lines mark the boundary of the reference interval (**Xref ± 2uref**), and the orange lines that of the target interval (**Xref ± 2σ**).

Annex 15 : Results for Lead

X_{ref} = 140 and U_{ref} = 40; all values are given in (mg kg^{-1})

Part Nr	x1	x2	x3	Ulab	*k**	Mean	ulab	Technique	z	zeta
004	163	173	182	43	2	173	22	ICP-OES	1.6	1.1
024	101.1	87.47		14.14	1	94.29	14.14	ICP-OES	-2.2	-1.9
029	155.6	155.3	153.8	15.5	2	154.9	7.8	ICP-OES	0.7	0.7
046	81	75	85	3.7	√3	80	2.1	ICP-MS	-2.8	-3.0
058				30	2	275	15	XRF- Indicative Quantity Test	6.4	5.4
074						216.0752		ICP-OES	3.6	
142	223	243	237	20	2	234	10	ICP-OES	4.5	4.2
150	115	120	110	12	√3	115	7	ICP-OES	-1.2	-1.2
224	244.30	257.81		50.2	√3	251	29.0	ICP-OES	5.3	3.2
233				5.13	√3	115.9	2.96	ICP-OES	-1.1	-1.2
239	66.999	43.918	51.573	10.315	2	54.163	5.158	ICP-OES	-4.1	-4.2
285	15.43	15	15.78	0.32	1	15.40	0.32	ICP-MS	-5.9	-6.2
298	276	322		46	2	299	23	FAAS	7.6	5.2
332	66.5	52.5	49.0	0.1	2	56.0	0.1	FAAS	-4.0	-4.2
371	188.6	184.3	193.6	28.32	30	188.8	0.94	ICP-OES	2.3	2.4
405	113	95				104		ICP-MS	-1.7	
421				39	√3	195	23	FAAS	2.6	1.8
422	22.8	37.8	22	2.75	2	27.5	1.38	ICP-MS	-5.4	-5.6
458	134	123	109	25	2	122	13	ICP-OES	-0.9	-0.8
489	113	120	121	8.7	2	118	4.4	ICP-OES	-1.0	-1.1
522	20	18	17	3.1	2	18	1.6	ICP-OES	-5.8	-6.1
557	32.8	30.5	33.0	3.2	2	32.1	1.6	ICP-OES	-5.1	-5.4
562	134.1	77.6	132.7	5.4	2	114.8	2.7	ICP-OES	-1.2	-1.2
590						0.00495		FAAS	-6.7	
593	189	182	174	2.1	0.70	182	3.0	ICP-OES	2.0	2.1
697	<20							ICP-OES		
713	49	41	41	5.0	2	44	2.5	ICP-MS	-4.6	-4.8
758	117.0	119.0	121.5	4.509	2	119.2	2.255	ICP-OES	-1.0	-1.0
793	72.3	79.3	128	8.1	2	93.2	4.1	ICP-MS	-2.2	-2.3
842	73.70	94.76	114.82	0.038	2	94.43	0.019	ICP-OES	-2.2	-2.3
867	110	120	120	6	√3	117	3	ICP-OES	-1.1	-1.1
920	150.8	150.8	152.8	15	2	151.5	8	ICP-OES	0.5	0.5
922	173.4	153.6	163.5	9.8	2	163.5	4.9	FAAS	1.1	1.1
924	14.6	14.7	14.9	3.7	2	14.7	1.9	ICP-OES	-6.0	-6.2
936	151	160		14	2	156	7	ETAAS	0.7	0.7
951	91.14	120.73	121.30	18.10	√3	111.06	10.45	Graphite Furnace AAS	-1.4	-1.3
975	153	146		26.5	2	150	13.3	ICP-MS	0.5	0.4
994	214	205	203	4.7	2	207	2.4	ICP-OES	3.2	3.3

* √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3.1



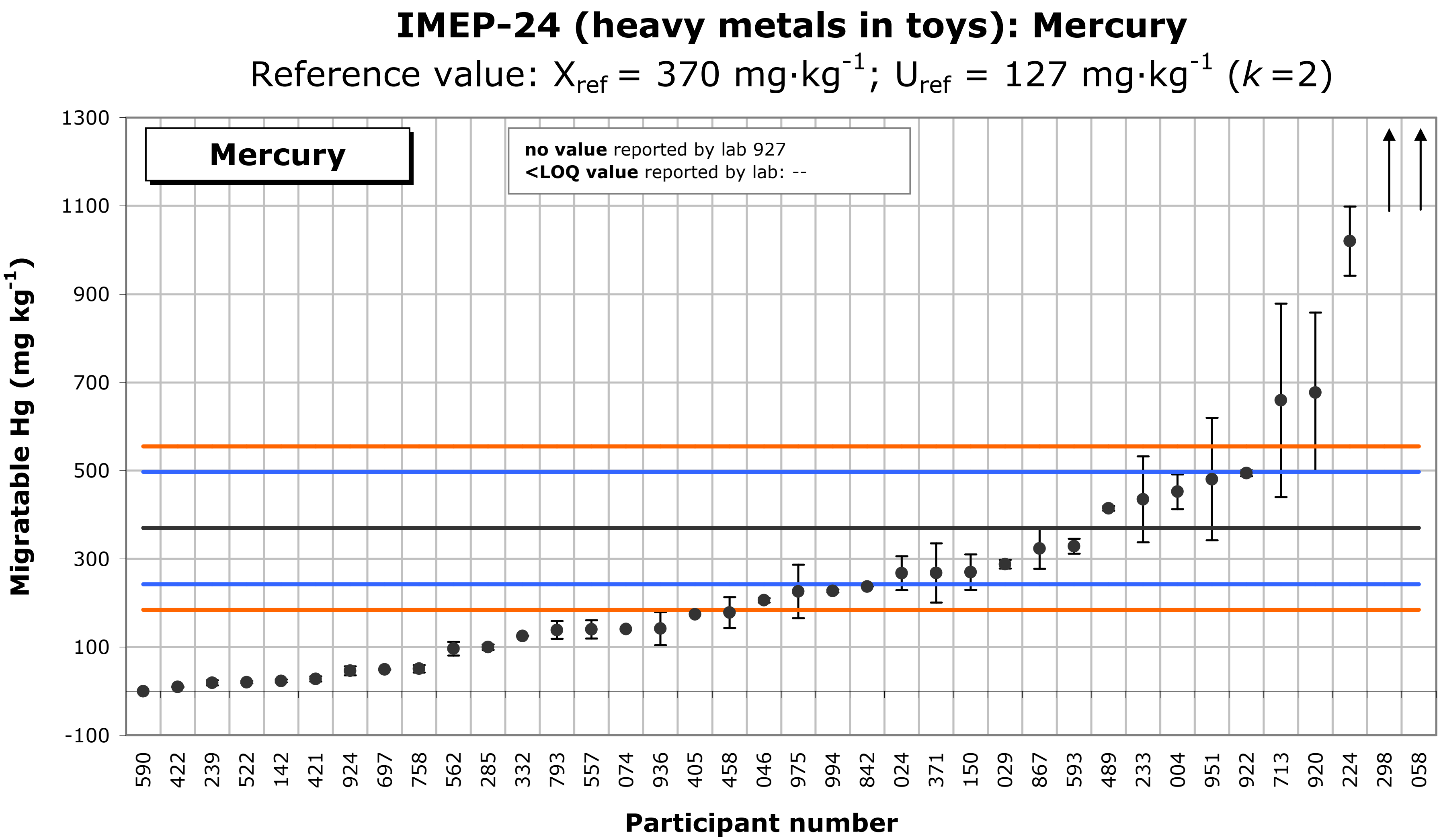
This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to **Xref**, the blue lines mark the boundary of the reference interval (**Xref ± 2uref**), and the orange lines that of the target interval (**Xref ± 2σ**).

Annex 16 : Results for Mercury

X_{ref} = 370 and U_{ref} = 127; all values are given in (mg kg^{-1})

Part Nr	x1	x2	x3	x4	Ulab	*k**	Mean	ulab	Technique	z	zeta
004	469	435	453		181	2	452	90	ICP-OES	0.9	0.7
024	278.9	256.3			66.9	1	267.6	66.9	ICP-OES	-1.1	-1.1
029	278.9	291.2	293.4		46.0	2	287.8	23.0	ICP-OES	-0.9	-1.2
046	215	208	196		5.1	√3	206	2.9	ICP-MS	-1.8	-2.6
058					95	2	4623	48	XRF- Indicative Quantity Test	46.0	53.5
074							140.7179		ICP-OES	-2.5	
142	25.2	23.2	22.0		3.3	2	23.5	1.7	CV-AFS	-3.7	-5.4
150	290	270	250		10	√3	270	6	ICP-OES	-1.1	-1.6
224	970	1070	1020		204	√3	1020	118	AMA analyzer	7.0	4.9
233					6.45	√3	434.9	3.72	ICP-OES	0.7	1.0
239	18.046	20.293			5.751	2	19.170	2.876	CV-AAS	-3.8	-5.5
285	92.63	108	99		6.31	1	99.88	6.31	ICP-MS	-2.9	-4.2
298	2564	2612			68	2	2588	34	Hg-Analyzer (AAS by Combustion)	24.0	30.7
332	126.9	130.5	118.5		0.22	2	125.3	0.11	CV-AAS	-2.6	-3.8
371	270.3	265.25	269.45		40.25	50	268.33	0.81	ICP-OES	-1.1	-1.6
405	164	185					175		ICP-MS	-2.1	
421					5.6	√3	28	3.2	CV-AAS	-3.7	-5.4
422	10.8	5.50	13.9		1.01	2	10.1	0.51	CV-AAS	-3.9	-5.6
458	188	158	189		35	2	178	18	ICP-OES	-2.1	-2.9
489	480	422	342		138.6	2	415	69.3	ICP-OES	0.5	0.5
522	19	22	21		2.6	2	21	1.3	ICP-OES	-3.8	-5.5
557	150	130	140		21	2	140	11	CV-AAS	-2.5	-3.6
562	98.7	88	102.3		15.4	2	96.3	7.7	ICP-OES	-3.0	-4.3
590							0.00086		FAAS	-4.0	
593	312	349	325		5.05	0.5	329	10.10	ICP-OES	-0.4	-0.6
697	55	50	43		1	√3	49	1	HG-AAS	-3.5	-5.0
713	708	668	602		54	2	659	27	ICP-MS	3.1	4.2
758	50.0	47.3	55.67		8.569	2	51.0	4.285	CV-AAS	-3.4	-5.0
793	105	135	176.0		20	2	139	10	ICP-MS	-2.5	-3.6
842	194.62	229.74	288.52		0.038	2	237.63	0.019	ICP-OES	-1.4	-2.1
867	330	320	320		17	√3	323	10	ICP-OES	-0.5	-0.7
920	666.7	682.5	682.5		15	2	677.2	8	ICP-OES	3.3	4.8
922	530.1	485.5	465.7	495.4	30.2	2	494.2	15.1	FAAS	1.3	1.9
924	46.9	46.3	45.9		10.2	2	46.4	5.1	FIMS	-3.5	-5.1
936	150	134			38	2	142	19	CV-AAS	-2.5	-3.4
951	444.37	485.40	512.50		78.03	√3	480.76	45.05	FIAS MHS	1.2	1.4
975	222	231			60.5	2	227	30.3	ICP-MS	-1.6	-2.0
994	206	226	250		3.6	2	227	1.8	ICP-OES	-1.5	-2.2

* √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3.1



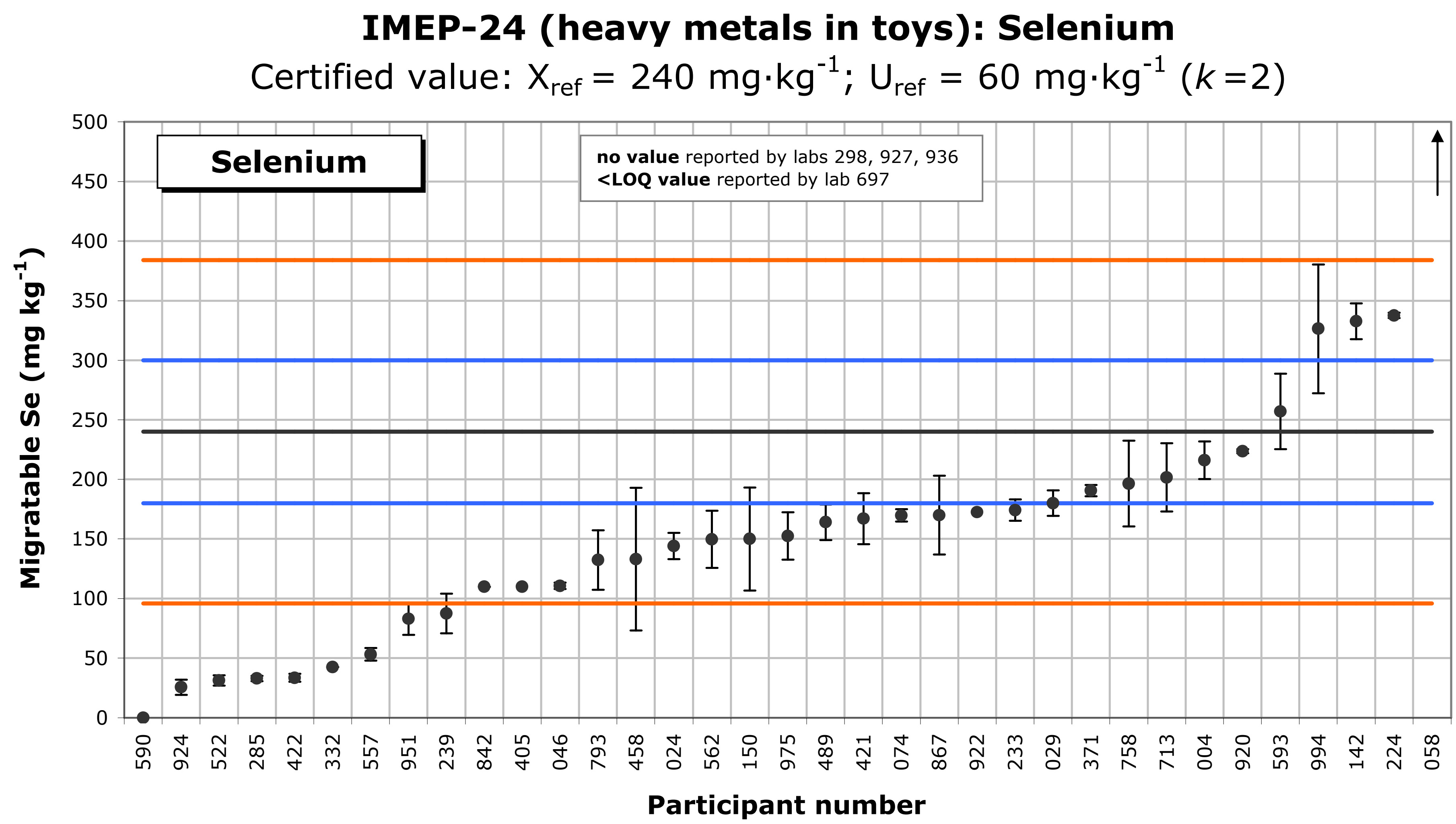
This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to **Xref**, the blue lines mark the boundary of the reference interval (**Xref ± 2uref**), and the orange lines that of the target interval (**Xref ± 2σ**).

Annex 17 : Results for Selenium

X_{ref} = 240 and U_{ref} = 60; all values are given in (mg kg^{-1})

Part Nr	x1	x2	x3	x4	Ulab	k*	Mean	ulab	Technique	z	zeta
004	206	216	226		54	2	216	27	ICP-OES	-0.3	-0.6
024	150.9	137.2			43.2	1	144.1	43.2	ICP-OES	-1.3	-1.8
029	181.6	182.1	176.4		36.0	2	180.0	18.0	ICP-OES	-0.8	-1.7
046	115	103	114		2.7	√3	111	1.6	ICP-MS	-1.8	-4.3
058					34	2	1416	17	XRF- Indicative Quantity Test	16.3	34.1
074							169.7634		ICP-OES	-1.0	
142	296	344	358		65	2	333	33	ICP-OES	1.3	2.1
150	160	140	150		15	√3	150	9	ICP-OES	-1.3	-2.9
224	338	337			67.6	√3	338	39.0	HG-AAS	1.4	2.0
233					4.78	√3	174.2	2.76	ICP-OES	-0.9	-2.2
239	108.370	70.574	83.517		16.703	2	87.487	8.352	ICP-OES	-2.1	-4.9
285	31.69	31	36		2.21	1	32.9	2.21	ICP-MS	-2.9	-6.9
332	37.0	48.0	42.5		0.08	2	42.5	0.04	FAAS	-2.7	-6.6
371	190.38	187.55	193.92		28.59	60	190.62	0.48	ICP-OES	-0.7	-1.6
405	103	117					110		ICP-MS	-1.8	
421					33	√3	167	19	ICP-MS	-1.0	-2.1
422	35.7	34.1	30.5		3.34	2	33.4	1.67	ICP-MS	-2.9	-6.9
458	144	135	120		24	2	133	12	ICP-OES	-1.5	-3.3
489	165	161	166		5.3	2	164	2.7	ICP-OES	-1.1	-2.5
522	34	29	31		4.3	2	31	2.2	ICP-OES	-2.9	-6.9
557	55.5	53.0	50.9		5.3	2	53.1	2.7	ICP-OES	-2.6	-6.2
562	161	123.5	164.7		19.9	2	149.7	10.0	ICP-OES	-1.3	-2.9
590							0.00033		FAAS	-3.3	
593	262	268	241		2.2	√3	257	1.3	ICP-OES	0.2	0.6
697	<100								ICP-MS		
713	245	180	180		31.6	2	202	15.8	ICP-MS	-0.5	-1.1
758	191.0	193.0	205.5		15.716	2	196.5	7.858	ICP-OES	-0.6	-1.4
793	126	109	162		11	2	132	6	ICP-MS	-1.5	-3.5
842	90.42	110.43	128.78		0.038	2	109.88	0.019	ICP-OES	-1.8	-4.3
867	160	180	170		9	√3	170	5	ICP-OES	-1.0	-2.3
920	222.2	224.2	224.2		15	2	223.5	8	ICP-OES	-0.2	-0.5
922	172.9	155.6	187.8	173.4	10.8	2	172.4	5.4	FAAS	-0.9	-2.2
924	25.6	25.9	25.2		6.4	2	25.6	3.2	ICP-OES	-3.0	-7.1
951	67.69	88.48	92.61		13.56	√3	82.93	7.83	Graphite Furnace AAS	-2.2	-5.1
975	160	145			21.5	2	153	10.8	ICP-MS	-1.2	-2.7
994	336	318	325		10.4	2	326	5.2	ICP-OES	1.2	2.8

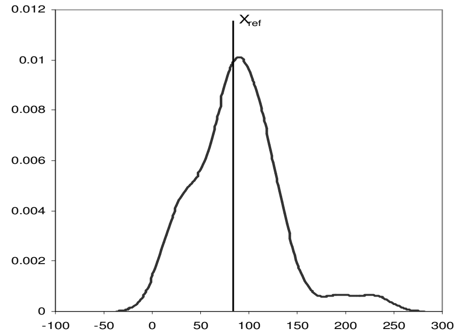
* √3 is set by the ILC coordinator when no expansion factor *k* is reported. The reported uncertainty was assumed to have a rectangular distribution with *k*=√3. For explanation see Ch 9.3.1



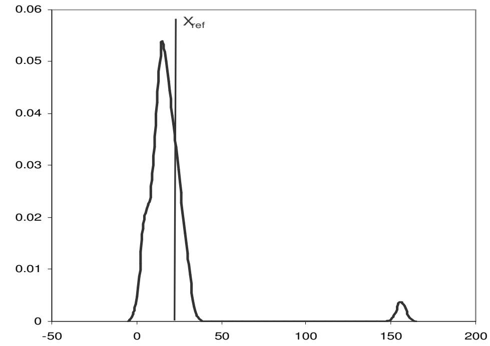
This graph displays all revised measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to **Xref**, the blue lines mark the boundary of the reference interval (**Xref ± 2uref**), and the orange lines that of the target interval (**Xref ± 2σ**).

Annex 18 : Kernel densities

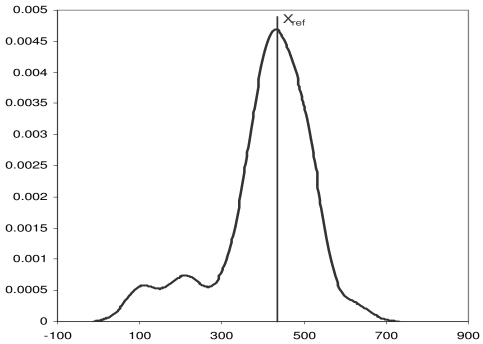
Kernel densities [mg kg^{-1}]



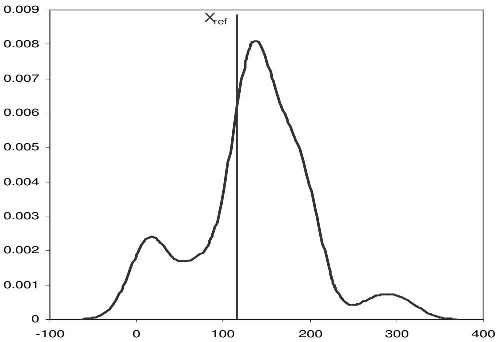
Antimony



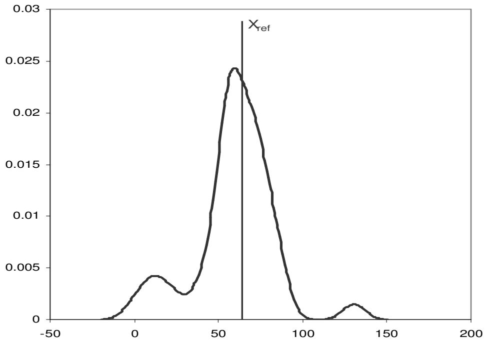
Arsenic



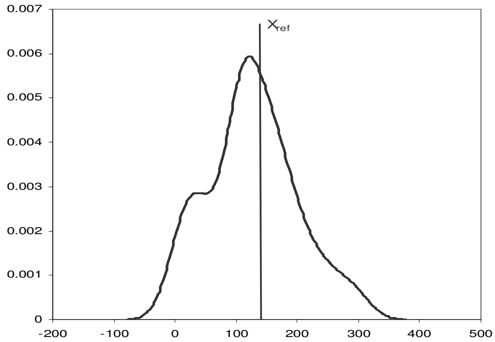
Barium



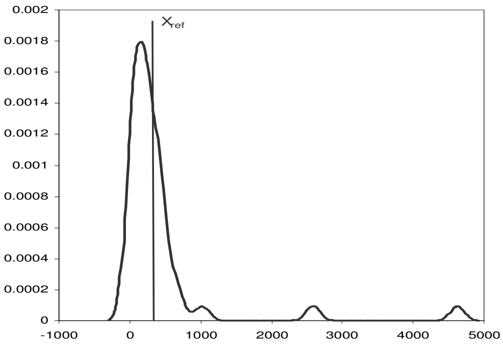
Cadmium



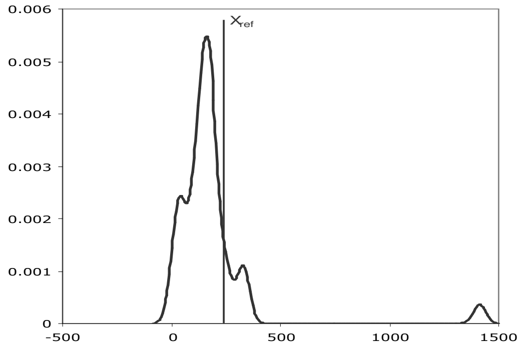
Chromium



Lead



Mercury



Selenium

Annex 19 : Summary of scorings and results interpretation

Part	Sb			As			Ba			Cd			Cr			Pb			Hg			Se			Questionnaire Q4:
Nr	z	zeta	Int*	z	zeta	Int*	z	zeta	Int*	Z	zeta	Int*	z	zeta	Int*	z	zeta	Int*	z	zeta	Int*	z	zeta	Int*	Would you accept or reject material on market?
004	0.6	1.0	TN	-0.2	-0.3	TN	1.3	1.3	TN	3.9	2.7	TP	1.9	1.1	TN	1.6	1.1	TP	0.9	0.7	TP	-0.3	-0.6	TN	Reject
024	1.4	0.9	TN	-0.9	-1.0	TN	0.3	0.2	TN	1.1	0.9	TP	-0.3	-0.2	TN	-2.2	-1.9	FN	-1.1	-1.1	TP	-1.3	-1.8	TN	Reject
029	-0.2	-0.3	TN	-1.3	-2.6	TN	-0.3	-0.7	TN	2.6	3.5	TP	-0.6	-0.5	TN	0.7	0.7	TP	-0.9	-1.2	TP	-0.8	-1.7	TN	Reject
046	0.8	2.2	TN	-1.3	-2.9	TN	-0.1	-0.3	TN	0.1	0.2	TP	0.0	0.0	TN	-2.8	-3.0	FN	-1.8	-2.6	TP	-1.8	-4.3	TN	Reject
058	0.6	1.0	TN	19.3	12.7	FP				243.6	132.5	TP				6.4	5.4	TP	46.0	53.5	TP	16.3	34.1	FP	Reject
074	-1.8		TN	-2.2		TN	0.9		TN	4.5		TP	1.2		TN	3.6		TP	-2.5		TP	-1.0		TN	Reject
142	0.7	1.4	TN	-1.7	-3.7	TN	1.3	3.1	TN	8.9	4.5	TP	2.3	1.8	FP	4.5	4.2	TP	-3.7	-5.4	FN	1.3	2.1	TN	Reject
150	-0.2	-0.5	TN	-1.3	-2.8	TN	-1.9	-4.1	TN	0.2	0.2	TP	-2.5	-2.0	TN	-1.2	-1.2	FN	-1.1	-1.6	TP	-1.3	-2.9	TN	Reject
224	2.7	3.4	TN	0.7	1.1	TN	1.5	1.5	TN	4.9	3.4	TP	0.2	0.1	TN	5.3	3.2	TP	7.0	4.9	TP	1.4	2.0	TN	Reject
233	0.4	1.0	TN	-0.5	-0.5	TN	-1.0	-2.6	TN	1.3	2.0	TP	-1.4	-1.1	TN	-1.1	-1.2	FN	0.7	1.0	TP	-0.9	-2.2	TN	Reject
239	-1.6	-3.8	TN	-2.3	-5.0	TN	-3.4	-6.8	TN	-3.2	-4.6	FN	-4.1	-3.2	TN	-4.1	-4.2	FN	-3.8	-5.5	FN	-2.1	-4.9	TN	**Accept**
285	-2.4	-6.3	TN	-2.8	-6.0	TN	-5.1	-13.2	TN	-5.5	-9.1	FN	-5.6	-4.5	TN	-5.9	-6.2	FN	-2.9	-4.2	FN	-2.9	-6.9	TN	**Reject**
298										10.8	17.9	TP	6.9	5.3	FP	7.6	5.2	TP	24.0	30.7	TP				Reject
332	1.7	4.4	TN	0.0	-0.1	TN	-0.7	-1.8	TN	-0.3	-0.4	TP	0.9	0.7	TN	-4.0	-4.2	FN	-2.6	-3.8	TP	-2.7	-6.6	TN	Reject
371	-0.2	-0.4	TN	-0.5	-1.1	TN	-0.3	-0.7	TN	-0.4	-0.5	TP	-0.8	-0.6	TN	2.3	2.4	TP	-1.1	-1.6	TP	-0.7	-1.6	TN	Reject
405	4.4		FP	-0.7		TN	3.0		TN	2.9		TP	2.1		TN	-1.7		FN	-2.1		TP	-1.8		TN	Reject
421	-0.2	-0.3	TN	-1.3	-2.4	TN	-0.6	-0.8	TN	2.0	1.9	TP	-0.3	-0.2	TN	2.6	1.8	TP	-3.7	-5.4	FN	-1.0	-2.1	TN	Reject
422	-1.8	-4.5	TN	-2.6	-5.6	TN	-3.0	-7.1	TN	-2.6	-4.1	FN	-2.5	-2.0	TN	-5.4	-5.6	FN	-3.9	-5.6	FN	-2.9	-6.9	TN	**Reject**
458	1.2	2.8	TN	-0.1	-0.3	TN	1.5	3.9	TN	3.3	5.4	TP	1.1	0.9	TN	-0.9	-0.8	FN	-2.1	-2.9	TP	-1.5	-3.3	TN	Reject
489	-0.1	-0.3	TN	-0.8	-1.5	TN	-0.1	-0.3	TN	1.4	2.3	TP	-1.0	-0.8	TN	-1.0	-1.1	FN	0.5	0.5	TP	-1.1	-2.5	TN	Reject
522	-2.5	-6.4	TN	-2.9	-6.2	TN	-5.0	-12.5	TN	-5.5	-9.0	FN	-5.6	-4.5	TN	-5.8	-6.1	FN	-3.8	-5.5	FN	-2.9	-6.9	TN	**Accept**
557	1.4	3.0	TN	-1.8	-3.8	TN	-1.5	-3.3	TN	-2.4	-3.9	FN	-1.1	-0.9	TN	-5.1	-5.4	FN	-2.5	-3.6	TP	-2.6	-6.2	TN	Reject
562	1.1	2.2	TN	-1.4	-2.9	TN	1.2	2.0	TN	1.0	1.7	TP	-0.6	-0.5	TN	-1.2	-1.2	FN	-3.0	-4.3	FN	-1.3	-2.9	TN	Reject
590	-3.3		TN							-6.7		FN	-6.7		TN	-6.7		FN	-4.0		FN	-3.3		TN	**Accept**
593	0.6	1.3	TN	-0.1	-0.3	TN	0.8	2.1	TN	3.7	6.0	TP	0.1	0.1	TN	2.0	2.1	TP	-0.4	-0.6	TP	0.2	0.6	TN	Reject
697	-2.8	-7.2	TN							-5.9	-9.8	FN							-3.5	-5.0	FN				**Accept**
713	5.9	14.6	FP	-1.0		TN	1.2	3.1	TN	0.7	1.2	TP	1.0	0.8	TN	-4.6	-4.8	FN	3.1	4.2	TP	-0.5	-1.1	TN	Reject
758	1.9	4.3	TN	-1.4	-3.0	TN	-0.9	-2.4	TN	0.7	1.2	TP	1.4	1.1	TN	-1.0	-1.0	FN	-3.4	-5.0	FN	-0.6	-1.4	TN	Reject
793	1.6	3.5	TN	-1.4	-2.9	TN	-1.0	-2.2	TN	0.7	1.1	TP	-0.3	-0.3	TN	-2.2	-2.3	FN	-2.5	-3.6	TP	-1.5	-3.5	TN	Reject
842	0.9	2.5	TN	0.6	1.3	TN	0.2	0.6	TN	1.4	2.4	TP	0.7	0.6	TN	-2.2	-2.3	FN	-1.4	-2.1	TP	-1.8	-4.3	TN	Reject
867	0.4	1.0	TN	-1.2	-2.5	TN	-0.2	-0.5	TN	1.5	2.3	TP	-0.7	-0.5	TN	-1.1	-1.1	FN	-0.5	-0.7	TP	-1.0	-2.3	TN	**Accept**
920	-0.1	-0.3	TN	-0.2	-0.1	TN	-0.4	-1.1	TN	1.4	2.0	TP	-1.5	-1.0	TN	0.5	0.5	TP	3.3	4.8	TP	-0.2	-0.5	TN	Reject
922	-1.0	-2.6	TN			TN	0.1	0.2	TN	4.7	6.9	TP	2.3	1.8	FP	1.1	1.1	TP	1.3	1.9	TP	-0.9	-2.2	TN	Reject
924	-1.7	-4.0	TN			TN	-3.8	-7.2	TN	-5.7	-9.3	FN	-4.7	-3.7	TN	-6.0	-6.2	FN	-3.5	-5.1	FN	-3.0	-7.1	TN	**Accept**
927							0.6		TN	0.5		TP	1.1		TN										Reject
936	0.0	-0.1	TN	0.7	1.1	TN	0.2	0.4	TN	2.8	4.5	TP	-0.2	-0.1	TN	0.7	0.7	TP	-2.5	-3.4	TP				Reject
951	-2.5	-6.5	TN	-2.4	-5.3	TN	0.0	0.0	TN	0.8	1.0	TP	-1.2	-0.9	TN	-1.4	-1.3	FN	1.2	1.4	TP	-2.2	-5.1	TN	**Accept**
975	-0.3	-0.6	TN	0.2	0.2	TN	1.0	1.2	TN	3.9	3.9	TP	0.9	0.7	TN	0.5	0.4	TP	-1.6	-2.0	TP	-1.2	-2.7	TN	Reject
994	2.0		TN	1.1	2.4	TN	1.0	2.4	TN	4.5	7.3	TP	0.7	0.5	TN	3.2	3.3	TP	-1.5	-2.2	TP	1.2	2.8	TN	Accept, Reject

* *Int* is the interpretation whether the reported result is a true negative (TN), true positive (TP), false negative (FN) or false positive (FP) result. Highlighted in bold red are participants whose conclusion is either *Accept* as this conclusion is considered wrong or *Reject* when the reported results do not give rise to this conclusion. See Ch 9.4.2 for further details.

Annex 20 : Experimental details derived from questionnaire

Part Nr	Official Method	Modification / Method description	Sample amount	Sieve size	Shaking device
004	EN71-3		meas 1: 300 mg, meas 2: 200 mg, meas 3: 280 mg	0.5 mm	Grant OLS 200
024	EN71-3		1 g	500 micron	None
029	EN71-3				
046	EN71-3	Paint was scraped / homogenised / sieved through 500µm mesh		500 µm	MS2 Minishaker IKA
058	No	XRF screening test for content (no migration)			
074	EN71-3	EN 71-3, paragraph 8.1.1	0.4115 g	0.5 mm	linitest
082	EN71-3		0.13-0.18 g	0.5 mm	shaking water bath
142	EN71-3		100 mg	0.5 mm	horizontal shaker
150	EN71-3 modified	No sieving; Weight to Volume 1:50, add 0.07 mol/l HCl (pH 1.4), 1 h shaked, 1 h at 37° C, filtrated, measurement with ICP	0.2 - 0.3 g	n.a.	typical lab shaker
176	EN71-3		0.31	500 micron	Horizontal shaking water bath 200 strokes/min
224	EN71-3		made-ground 0.1 g / 5 ml	pore size 0.5 mm	horizontal shaker LT2
233	EN71-3 modified	we removed 0.24 g of sample and diluted it with 25 ml of HCl 0.07N	0.24 g	whatman 1	maxi shake Heto
239	EN71-3		0.3 g, 0.4 g	0.5 mm	normal stirrer
285	EN71-3		200 mg	0.5 mm	Kreisschüttler
298	EN71-3 modified	No Sieve Filtration	0.105 g; 0.068 g	none	by hand
332	EN71-3	The test were carried out according to EN 71-3 point 8.1.2	1 g	500 micron	water bath with shaking device
371	EN71-3	We have scrap the paint ? pass through the pore size ? weight the powder obtained add a volume equal to 50x mass : skake one hour at 37°C without light rest one hour and after filter	good	500 mesh	rotation magnet stired
405	EN71-3		0.2 g	0.5 mm	Shaking water bath
421	EN71-3		0.1 g for ICP-MS 0.3 for FAAS and CVAAS (Pb & Hg)	none	magnetic stirrer
422	EN71-3				
458	EN71-3	0.15 g of sievedpaint was extracted with 7.5 ml of 0.07M hydrochloric acid in a plastic test tube. The paint was shaken at 37°C in the dark in a water bath before allowing to stand for another hour at 37°C. The solution was filtered through a 0.45 µm PVDF syringe filter and analsed using a VARIAN VISTA PRO ICP-OES with axial torch.	0.15 g	0.5 mm	grant shaking water bath
489	EN71-3		0.2 g	300 - 500 um	mechanical shaker
522	EN71-3		0.2 g	300 - 500 um	mechanical shaker

Part Nr	Official Method	Modification / Method description	Sample amount	Sieve size	Shaking device
557	EN71-3	Part 8.1 of SN EN 71-3	1 g	0.5 mm	horizontal shaking device
562	EN71-3		0.1 g	0.5 mm	
590	EN71-3			0.5 mm	Shaker with ideal swivel motion IKA KS 130 basic
593	EN71-3	the sample with 0.07 N of HCl is agited into a water bath at 37℃ during 1 hour, and without agitation during 1 hour. The sample is then filtered and analyzed into ICP-OES	0.1 g	500 µm	Water bath
661	EN71-3		600 mg	500 µm	mechanical shaking
697	EN71-3	0.5 g/25 ml; 1h shaking, 1h standing (37±2℃), 9.9 ml + 0.1 ml internal standard, Hg dilution 1:10	0.5 g	520	horizontal shaker with circular motion
713	EN71-3	EN 71-3:1994 + A1 2000 + AC 2002/ HCl Extraction 2h/ Filtration/ ICP-MS	50 mg each	non	magnetic stirrer, water bath
758	EN71-3		0.5 g	500 micron	magnetic stirring
779	EN71-3		200 mg	500 um	orbital shaker
793	EN71-3	Paint is scraped off and sieved on 0.5 mm sieve. Subsample is the weighed into extraction tube, and extraction liqiud is added (L/S=50). After extraction liqiud is analyzed on ICPMS.	0.2 g	0.5 mm	Shaking table
842	EN71-3	Sample scraped from plate using scalpel and sieved. Weighed out 0.3g in triplicate into conical flask. 0.07 HCl solution preheated to 37C. Pipetted 15ml of 0.07 HCl in to each flask. Flask shaken and pH measured. Sample placed in water bath at 37C and shaken in the dark for 1h, then left to stand for 1 h. Solution filtered and diluted to 25ml prior to analysis by ICP-OES	0.3 g	0.5 mm	Shaken by hand
867	EN71-3		0.2 g	0.5 mm	horizontal shaker
920	EN71-3 modified	5 ml extraction volume diluted 4x before analysis	0.1 g	0.5 mm	orbital
922	EN71-3	migration of heavy metals (Sb, As, Ba, Cd, Cr, Pb, Hg and Se) from the toy to the hydrochloric acid solution 0.07M, determination of the metals migrated using FAAS	1.0092	0.05	a water-bath with a shaking device
924	EN71-3	The test portion was 200mg and mixed with 10 ml of 0.07 mol/l HCl and diluted to 25 ml.	200 mg	0.5 mm	Thermostatic inkubator
927	EN71-3		1 g	500 micron	none
936	EN71-3 modified	The sample wasn't sieved because of the available amount	0.2 g	none	water bath with orbital saking
951	EN71-3 modified	Sieving was not possible, because the static electricity was to high	about 100 mg for one sample		Roller Mixer SRT 2 - Stuart Scientific, CAT No SRT2; Nr: R000 101 155
975	EN71-3		200 mg	500 micron	Waterbath with agitation
994	EN71-3		0.1033. 0.1027. 0.1005 gram	nominal aperture size 0.5 mm	water shaker bath 150rpm

Part Nr	Preheated labware	adjusted pH ?	Final pH	Membrane filter	Centri-fugation	Solid/Acid ratio > 1:50	Analysis on day of preparation?	If not, adjusted acid concentration to 1 mol/l HCl ?	Inclusion of base material
004	No	No	1.0-1.5	PALL, Bulk GHP Acrodisc with 0.45 µm GHP membrane	No	no	Yes		No
024	No	No			No	No	No	No	No
029	No	No	about 1	0.45 µm	No	no	No	Yes	No
046	No	No	1	0.45 µm Minsart (Sartorius)	No	no	Yes		No
058									
074	No	No		0.45 um, sartorius	No	no	Yes		No
082	No	No	<1.5	Acrodisc Syringe Filters, 0.45 µm	No	no	Yes		No
142	No	Yes	< 1.5	0.45 µm cellulose acetate	No	no	No	Yes	No
150	Yes	No	1.4	0.45 um	No	no	Yes		No
176	Yes	No		millipore 0.45µm aqueous syringe fllter	No	No	Yes	No	No
224	Yes	Yes	1.1	Whatman ME 25/21 St, Membrane Filtres 0.45 µm	No	the ratio of solid to acid was exactly 1:50	Yes	No	No
233	Yes	No	1.4		No	no, it was 1:104	Yes		Yes
239	Yes	No	1	0.45 um	No	No	Yes		
285	Yes	No	1.3	0.43 µm	No	No	Yes		Yes
298	No	No		0.45 um	No	no	No	Yes	No
332	Yes	No	1.22	0.45 µm	No	no	Yes	No	No
371	Yes	No	1.5	0.45 µm	No	no	Yes		No
405	No	No	1.5	0.45 um	No	No	Yes	Yes	No
421	Yes	No	1.25	0.45 um membrane filter	No	no	Yes	No	No
422									
458	No	No	1.0 to 1.5	PVDF 0.45 µm	No	No	Yes	No	No
489	Yes	No	Acidic	0.45 um	No	no	Yes		No
522	Yes	No	Acidic	0.45 um	No	No	Yes		No
557	Yes	No	< 1.5	CM 0.45 µm	No	No	Yes	No	Yes
562	Yes	No	1.0~1.3	0.45 um	No	No	Yes		No
590	No	No	1.4	membrane filter (Mixed cellulosa ester) 0.45 µm diameter 0.47 mm	No	no	Yes	No	Yes
593	Yes	No	between 1 to 1.5	acrodisc 0.45 µm	No	no	Yes	Yes	No
661	No	No	1.3	0.45 µm	No	no	Yes		No
697	No	Yes	1.1 - 1.4	cellulosemischester, 0.45 µm	No	no	Yes	No	No
713	No	No	1.3	Regenerated cellulose 0.45 µm	No	no	Yes		No

Part Nr	Preheated labware	adjusted pH ?	Final pH	Membrane filter	Centri-fugation	Solid/Acid ratio > 1:50	Analysis on day of preparation?	If not, adjusted acid concentration to 1 mol/l HCl ?	Inclusion of base material
758	Yes	No	1.5	Schleicher and Schuell, 595, 4 - 7 µm	No	no	Yes		No
779	Yes	No	1.5	0.45 um	No	no	Yes		No
793	Yes	No	below 1.5	0.45 m polycarbonate	No	no	No	No	No
842	Yes	No	1.15	0.45 um Nylon	No	No	Yes		No
867	No	No		0.45	No		No	No	No
920	No	No	1.3	millipore 0.45 µm	No	no	Yes		No
922	Yes	Yes	1.12	whatman 1001 125	No	no	Yes	No	No
924	No	No	~1.3	Glass microfibre filters GF/A	No	Yes	No	Yes	No
927	Yes	No	1.28	whatman 50	No	no, it didn't	No	No	No
936	No	No	1.3	0.45 µm; cellulose nitrate	No	no	No	Yes	No
951	Yes	No	1.3	Nylon - 0.45 µm	No	no	No		Yes
975	Yes	No	1-1.5	45 µm	No	No	Yes		No
994	Yes	No	1.3	pore size of 0.45 4m	No	no	Yes		No

European Commission

EUR 24094 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: IMEP-24: Analysis of eight heavy metals in toys according to EN 71-3:1994
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Abstract

The Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre (JRC), a Directorate-General of the European Commission, operates the International Measurement Evaluation Programme (IMEP). It organises interlaboratory comparisons (ILC's) in support to EU policies. This report presents the results of an ILC which focussed on the determination of soluble antimony, arsenic, barium, cadmium, chromium, lead, mercury, and selenium according to European Standard EN 71-3:1994.

The principle of the procedure in EN 71-3:1994 consists in the extraction of soluble elements from toy material under the conditions simulating the material remaining in contact with stomach acid for a period of time after swallowing.

Forty participants from eighteen countries registered to the exercise, of which 33 reported results for As, 35 for Ba and Se, 37 for Cr, Pb, and Sb, 38 for Hg, and 39 for Cd. For seven measurands the test material had already been certified in the past. The validity of the certificate was reconfirmed and the certified values were taken as the reference values for this ILC. As no certified value was available for Hg, the mean value of the results provided by four expert laboratories was used together with the corresponding uncertainty. Participants were invited to report the uncertainty on their measurements. This was done by 35 of the 39 laboratories having submitted results in this exercise.

Laboratory results were rated with z and zeta scores in accordance with ISO 13528. The standard deviations for proficiency assessment were based on the analytical correction laid down in EN 71-3:1994.

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