JRC Technical Notes

Sixth Workshop of the EU-RL Heavy Metals in Feed and Food

Brussels, 22 September 2011

Edited by B. de la Calle and B. Kortsen

European Union Reference Laboratory
Heavy Metals in Feed and Food

JRC 67522 - 2011

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Institute for Reference Materials and Measurements

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Institute for Reference Materials and Measurements

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Minutes of the 6th Workshop of the European Union Reference Laboratory for Heavy Metals in Feed and Food.

Brussels 22/09/2011

Welcome and opening of the event

The participants were welcome by Beatriz de la Calle, operating manager of the European Union Reference Laboratory for Heavy Metals in Feed and Food (EU-RL-HM). B. de la Calle informed that the meeting would be chaired by Piotr Robouch and that the presentations of the outcome of the proficiency tests (PTs) would be made by Fernando Cordeiro, who is a project coordinator working for the EU-RL-HM.

Professor Michael Thompson who would do a presentation later in the morning on "New light on dark uncertainty" was introduced.

Presentation of the 2010/2011 activities of the EU-RL-HM

P. Robouch made a presentation of the activities carried out by the EU-RL-HM since the 5th workshop of this network:

- Three PTs, IMEP-111, -112 and -113, were organised. IMEP-111 dealt with the determination of total Cd, Pb, As, Hg and Cu and extractable Cd and Pb in mineral feed. IMEP-112 dealt with the determination of total and inorganic As in wheat, vegetable food an algae. IMEP-113 dealt with the determination of total Cd and Pb in baby food.
- This workshop is organised for the network of National Reference Laboratories (NRLs) in which a training on "New light on dark uncertainty" is offered.

On top of the mentioned activities, the EU-RL-HM takes part as observer in the following working groups:

- Working Group of National Experts in Industrial and Environmental Contaminants: On the bases of the outcome of IMEP-107, a PT for the determination of total and inorganic As in rice, this working group has started the discussions to introduce a maximum level in the European legislation for contaminants for inorganic As in that particular food commodity. IMEP-112 will serve this working group in the discussions on the feasibility to introduce in legislation maximum limits for inorganic As in several food commodities. The outcome of IMEP-113 and IMEP-33 (the later PT for control labs) will support the discussions on maximum limits for total Cd and Pb in baby food.
- CEN/TC WG 4 Contaminants, Minerals and Trace Elements in Feed: The EU-RL-HM collaborated with this working group providing support in the organisation of a collaborative trial for the determination of inorganic As in feed, IMEP-32. The report on this exercise is now available at the EU-RL-HM webpage. A draft CEN standard is under final voting.

- CEN/TC WG 10 Elements and their chemical species: The EU-RL-HM supported this working group in the drafting of a document dealing with sample treatment for trace element determination and in the discussions on standardisation of a method in the area of metal speciation, mainly on inorganic arsenic and on methylmercury.

The attendants were informed about the last NRL who has joined the EU-RL-HM network: National Institute of Nutrition and Seafood Research (NIFES) from Norway. A representative attended for the first time the present annual workshop of the network. Although not belonging to the EU, Norway has signed an agreement according to which they commit themselves to implement the European legislation in the area of food. NIFES will take part for free in the PTs organised by the EU-RL-HM and will attend the workshops organised by the EU-RL-HM, on their own costs.

NRLs were updated about the outcome of the audit of EU-RLs organised by DG SANCO. The EU-RL-HM obtained an A overall assessment and in particular:

- Adequacy of assistance to NRLs [B]
- Appropriateness of analytical methods and techniques [B]
- Coordination and training activities carried out by the EURL [A]
- Activities carried out to support the Commission's action [A]
- Fulfilment of the requirements laid down in Article 32 (4) of Regulation 882/2004 and other relevant EU legislation [A]

The points in which the EU-RL-HM obtained a B assessment include:

- Development/validation/assessment of analytical methods
- Distribution of Standard Operating Procedures (SOPs)
- Distribution of standard materials
- Contribution of Proficiency Tests (PTs) to improvement and harmonisation of analytical methods/quality of analytical data
- Contribution of training activities to the improvement and harmonisation of analytical methods/quality of analytical data
- Contribution of other activities to the improvement and harmonisation of analytical methods/quality of analytical data

Regarding personnel, the NRLs were informed that Bibi Kortsen is the new secretary of the EU-RL-HM, replacing I. Verbist and that the EU-RL-HM is looking for a colleague to coordinate PTs. The contract offered is for a maximum duration of three years. Scientific formation and excellent writing capabilities in English are required.

Discussion of the work programme for 2012

P. Robouch presented the interlaboratory comparisons (ILCs) which will be carried out in 2012:

- A PT on heavy metals in feed premixes. NRLs have requested in previous workshops to have a proficiency test of feed premixes because this type of matrix could present some difficulties from an analytical point of view.
- A collaborative trial for the validation of a method to determine methylmercury in fish. As requested by DG SANCO this collaborative trial was introduced in the work program (WP) for 2012. This activity would complement the mandate to CEN TC 275 WG 10, to produce a standard for the determination of methylmercury in food. The method that will be standardised by CEN, is based on the use of hyphenated techniques. That method would fit the purpose of laboratories running a large number of methylmercury determinations per year but not of those laboratories that carry out methylmercury analysis on an occasional basis. For this reason the EU-RL-HM will validate a method which has been largely used in the past and which does not require the use of expensive instrumentation. The method is based on extraction of methylmercury into toluene and further complexation with L-cysteine. The method has been successfully used in some PTs organised by the EU-RL-HM. IPIMAR (Portuguese NRL for fish samples) will collaborate with the EU-RL-HM in the drafting of a standard operational procedure (SOP). B. de la Calle asked the NRLs interested in taking part in this exercise to send an e-mail to the EU-RL-HM, and to inform control laboratories in their respective countries which may have experience with the method, about this activity.
- Regarding the 7th workshop which will be organised by the EU-RL-HM, only two topics have been indicated by the NRLs as preference for the training that will take place on the occasion of that workshop, both of them dealing with methods for the determination of inorganic arsenic and methylmercury in fish/fish products. B. de la Calle reminded the NRLs that such trainings have already been organised by the EU-RL-HM in previous workshops and that several PTs have already been organised for the determination of inorganic As and methylmercury in several food commodities, including fish. For that reason it would be redundant to organise again training on those subjects. Detailed information about methods of analysis is included in the reports to participants of several PTs such as IMEP-107, -109 and -112.

Discussion on the work program for 2013

The work program for 2013 has to be submitted to DG SANCO before 30th August 2012, just before the next workshop will take place. For this reason the new items to be included in the WP for 2013 had to be decided upon during this workshop.

Some NRLs have indicated their interest in PTs dealing with inorganic As and methylmercury in seafood and on total content of heavy metals in crustaceans and cephalopods. However, these topics have already been covered in several occasions by the EU-RL-HM. The same applies to the request for PTs with matrices with Cd contents close to the maximum limits currently under negotiation at the European Commission. IMEP-113 was recently organised on total Cd and Pb determination in baby food after request by DG SANCO, to support the discussion on updates of the European Legislation on contaminants.

On request by DG SANCO, a PT will be organised in 2013 for the determination of heavy metals in mushrooms to support the discussion that will take place on the second half of 2013 to update the European legislation on contaminants.

Since the EU-RL-HM organises two PTs every year, it would be important to agree on a PT covering a feed matrix. One NRL requested a PT for the determination of heavy metals in feed matrices of vegetable origin and compound feed. Compound feed was covered in the first PT organised by the EU-RL-HM in feed, and since then most of the relevant feed matrices have been covered. For this reason it was agreed to organise a PT on compound feed again in 2013.

One NRL asked to include tin at concentrations close to the maximum limits in future PTs. Another NRL asked whether it would be possible to include also organotin compounds in the same PT. However, since organotin compounds are not in the legislation for food, most likely NRLs would not have methods in place for that type of analysis and they would not be able to report results.

An NRL requested a PT for inorganic As in rice. Such a PT was recently organised by the EU-RL-HM, IMEP-107, and therefore organising another one does no seem reasonable.

Important matters on heavy metals in feed and food according to legislation.

A. Bitterhof made a presentation on the current and forthcoming issues on heavy metals in food, which covers cadmium, lead, arsenic and mercury. A revision of Regulation 1881/2006 is on going, with an expected finalisation of 2011 for Cd and of 2012 for Pb and As. A request has been made by the European Commission to EFSA for a scientific opinion for mercury and methylmercury, opinion which is expected by mid 2012.

The revision of Regulation 1881/2006 for Cd includes a proposal for:

- Reduction of the maximum levels for Cd in some cereals, stem/root and tuber vegetables, soybeans and leaf vegetables
- Introduction of maximum levels for new food commodities such as: oilseeds, chocolate, milk and soy based formula, processed cereal based and other baby food and raw milk.
- Adjustment of classes of maximum levels for some fish species and specific vegetables

The aim of these changes is to reduce exposure, following the EFSA opinion, focusing on the main contributors for adults and/or children, such as cereals, vegetables starchy roots and potatoes. Special focus is given to food of particular importance for children such as chocolate and baby food.

Measurements at source are needed to reduce Cd in soil and in marine environment, to help to reduce Cd concentrations in crops and fish, respectively. DG SANCO participates in the discussion with DG ENTR on reduction of the levels of Cd in fertilisers.

Regarding Pb, the EFSA opinion indicated that with the current exposure there are concerns over possible neuro-developmental effects in young children, with unborn children, infants and children being the main population groups at risk. The main contributors to Pb exposure are cereals and vegetables and in the case of children also mild and milk products, baby foods, fruits, fruit juices, cocoa and chocolate products are important.

Regarding As, after the EFSA opinion adopted in 2009, there are plans for the introduction of maximum limits in rice and infant food on rice basis. There is no specific proposal for maximum limits yet, because the data collection is still on-going. Introduction of maximum limits for other cereals, algae and food supplements is also under discussion. Supporting this activities, the EU-RL-HM has organised two PTs for the determination of total and inorganic As in rice, IMEP-107, and in other food commodities, IMEP-112.

A request for a method for the determination of inorganic As and of methylmercury in food and feed has been included in the COM mandate to CEN.

Regarding mercury a revision of the existing scientific opinion has been requested to EFSA. At the moment a collection of occurrence data is on-going. In support to those activities the EU-RL-HM will organise a collaborative trial for the validation of a method to determine methylmercury in fish. Risk management discussion will start after availability of the EFSA opinion.

A. Bitterhof also presented some information on the updates to Directive 2002/32/EC. No changes in the maximum levels have been introduced. The annex has been restructured and harmonised terminology is now used. The reference to the extraction method to be used for the analysis of As, Cd, Pb and Hg has been deleted. Nevertheless, there is a pending issue on the determination of Pb in kaolinitic clay, in which there seems to be a significant difference between the concentration find after total digestion as opposed to the one found after partial extraction. The EU-RL-HM has been asked to perform a study to clarify this matter. The study has been finalised and a report will be sent to DG SANCO before the end of the year. In the future, a possible change of Directive 2002/32/EC is the establishment of maximum levels for inorganic As instead of total As.

A. Bitterhof acknowledged the sound support that the network of the EU-RL-HM has provided to DG SANCO on scientific matters related to legislative issues.

Training on *New light on dark uncertainty*

Professor Michael Thompson made a presentation on uncertainty and analytical results. He focussed on different ways of estimating uncertainty, namely building a model of the analytical process and the statistical approach. Positive and negative sides of the two approaches were discussed. Special attention was paid to the variation of uncertainty with concentration as well as to the concept of fitness-for-purpose and its implications from the cost point of view.

Presentations and discussions on the outcome of IMEP-111, -112 and -113.

Fernando Cordeiro presented the outcome of the three PTs organised by the EU-RL-HM since the last workshop. The following issues were highlighted:

- The use of a direct mercury analysis could lead to underestimation of the total content of mercury when applied to inorganic matrices, as shown by IMEP-111.

- The determination of inorganic As in wheat, vegetable food and algae (IMEP-112) is possible. The validation of the method to be used to determine inorganic As in algae has to be carried out with special care, due to the coexistence of inorganic As with many other organic species which could interfere in the determination of the, comparatively speaking, low fraction of inorganic As.
- It is possible to determine total Cd in infant formula based on soya, at a low level, such as 0.010 mg kg^{-1}, and that with the present state-of-the-art, it is not advisable to introduce a maximum limit of 0.005 mg kg^{-1} for Pb in the same matrix. Some laboratories are not able to detect Pb at that concentration and other NRLs have problems of overestimation due to contamination. A similar outcome was extracted from IMEP-33, a PT organised with the same test material for control labs. In IMEP-33 it was observed that only laboratories analysing more than 1000 of this type of samples/year, could report satisfactory results for total Pb.

One NRL indicated that the problem behind the poor results reported for total Pb in IMEP-113 and -33 could be that the methods in place at the moment have been validated for the current maximum limit in legislation for Pb in this food commodity (0.050 mg kg^{-1}) and so they are not fit-for-the purpose. When duly optimised the picture could look different. Some other NRLs, said that due to high blanks they would not be able to perform measurements of Pb at such low levels, not even after optimisation.

B. de la Calle indicated that the two National Metrology Institutes that provided the reference values for IMEP-113 and -33, stated that to determine total Pb at that low concentration, a clean room is needed and cannot be performed on a routine basis.

Presentation on the use of Advanced Mercury Analyser (AMA) for the analysis of an untypical inorganic matrix

Eva Niedobová from the Czech NRL for heavy metals in feed made a presentation on the problems encountered in her laboratory when analysing mercury in the mineral feed test material used in IMEP-111, using AMA, a patented system based in direct mercury analysis (DMA). Underestimation occurred and a more classical approach using wet digestion with nitric acid had to be used to obtain unbiased results. B. de la Calle indicated that this type of problems have been encountered and mentioned in a note of a DMA-based method validated by the Environmental Protection Agency (EPA) for the determination of mercury in sediments.

At the end of the presentation questions were made by several NRLs on how to decide which method to apply when an unknown sample is to be analysed, about the number of measurements that can be performed with the same catalyst and about experience in the application of this technique for the determination of mercury in oil.

AOB

Peter Farnel from the UK NRL for heavy metals in feed asked if it would be possible to distribute the proceedings of the EU-RL-HM workshop to control labs in the different member states for instance by placing it in the webpage of the different NRLs. The information on analytical methods and the discussions held at the workshops are frequently interesting and control labs should be able to benefit of this information.

B. de la Calle said that there could be some confidentiality issues which should be discussed. For instance, it happened in previous workshops that not all the invited speakers gave permission to distribute openly their presentations, but only to the NRL network, via the "restricted corner" of the EU-RL-HM webpage, where access is restricted via the use of password.

The Italian NRL for food was in favour of full openness, respecting of course the confidentiality of the PT scores, which is, anyhow, covered by the accreditation according to ISO Guide 43 of the EU-RL-HM as PT provider.

The report of the EU-RL-HM workshops will become a public document for distribution to European control laboratories. Discussions related to internal matters of the network and presentations for which no authorisation for open distribution is obtained from the author, will excluded from the public report.

B. de la Calle reminded NRLs that in case a laboratory receives an unsatisfactory score, or several consecutive questionable scores, in PTs organised by the EU-RL-HM, corrective actions should be taken and the laboratory should inform the EU-RL-HM how the problem has been solved.

The workshop was closed by B. de la Calle who wished the participants a good trip back home.

The list of comments/feedback collected from the evaluation form that was distributed among the participants is presented hereafter.

Minutes written by B. de la Calle

Geel, 20/10/2010

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EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements

6th EU-RL Heavy Metals Workshop
CCAB – AB-3C Brussels – 2011.09.22
29 evaluations form received out of **37** participants

1. How would you rate the following information provided to you before the event?

	Excellent	Good	Fair	Poor	N/A*
Logistical information about the event (date, place, activities, program)	**10**	**17**	**1**	**0**	**0**
Information about the objectives and theme of the event	**7**	**20**	**1**	**1**	**0**
Information about the contents of sessions / presentations	**8**	**14**	**6**	**0**	**0**

* Not applicable

If poor indicate why:

- Program changed slightly and slides were different than the handouts.
- Participants require more information in the agenda regarding presentation in order to be more prepared and to do their maximum benefit from the workshop.
- The date of the workshop should be told earlier.

2. How would you rate the ...?

	Excellent	Good	Fair	Poor	N/A*
venue / facilities	**9**	**19**	**1**	**0**	**0**
catering / meals	**2**	**15**	**5**	**0**	**5**
hotel	**See "Comments on hotels" below**				
transport arrangements	**3**	**5**	**7**	**0**	**13**
registration procedure for the event	**9**	**19**	**1**	**0**	**0**
information provided during the event	**7**	**21**	**0**	**0**	**0**
assistance provided by JRC staff	**15**	**13**	**1**	**0**	**0**
social activities organised (dinner)	**-**	**-**	**-**	**-**	**-**

* Not applicable

If poor indicate why:

- Some registration info is difficult to fill at the time of registration such as flight details.

Comments on hotels:

- FLORIS Hotel ARELQUIN Grand-Place: yes, cheap: € 110.00 (including breakfast).
- PLAZA CROWNE Hotel Europe: the hotel is OK, not great.
- N/A
- SABLON EUROSTARS ***: OK for a one-night stay! Reasonably central between station and venue.

- BEDFORD Hotel: fair, recommended: yes, it's central, has the normal things but it's not a 4*!!!

- CROWNE PLAZA Europe, rue de la Loi: expensive but comfortable and convenient for access to the conference centre. NOT recommended: it is closing down at the end of 2011.

- MOZART: small but good, in the city. NOT recommended: hotel is too small for this group.

- LE PLAZA: very nice hotel with good location: Recommended because of it's good location in the centre of the city.

- NEW HOTEL CHARLEMAGNE: good location, not expensive.

- NH Grance Place Arenberg: is OK, recommended, close to the central station and close to the Centre Albert Borschette.

- Hotel DU PARLEMENT: excellent location however rooms very very small + not quite clean. Recommended if looking for a good location – NOT recommended if personal space matters.

- Hotel METROPOLE: very good, recommended.

- NH Brussels City Centre (8/10): recommended, it's cosy and in a nice area, near metro.

- SILKEN BERLAYMONT Hotel: was good but it was too expensive (€ 172.00) because commission pays the hotel up to only € 140.00.

- CROWNE PLAZA Brussels Europa: OK but expensive.

- IBIS Centre Gare Midi Brussels: not recommended, located far from CCAB.

- Hotel BLOOM: excellent, smiling service, located near Botanique Garden, spacious room – cost maybe slightly above what is expected.

- FIRST EUROFLOT Hotel: good, good location, too expensive for reimbursement.

- Residence MARIE-THERESE: good, I would recommend it for position, services, cleanness and kindness.

3. How would you rate the ...?

	Excellent	**Good**	**Fair**	**Poor**	**N/A***
length of the event	**7**	**21**	**1**	**0**	**0**
division of time between presentations and discussions	**4**	**22**	**3**	**0**	**0**

* Not applicable

If poor indicate why: /

4. Do you have any comments concerning the <u>organisation</u> of the event, or suggestions for improvement?

- No
- None at present.
- Please send lab code before.
- The room not designed for this kind of lectures. I prefer Geel!
- Use latin letters for names of countries/Use english names as the meeting is held using english as a common language. PT results should be the first topic of the meeting as they require most attention and discussion.

5. Do you have any comments concerning the <u>content</u> of the event, or suggestions to improve events in the future?

- Maybe try to facilitate that the participants can network some more.
- No
- None at present.
- 1. Discussion on the possibility to visit an expert laboratory e.g. in order to see how particular analyses are carried out (specification: As, Hg …) inside the lab. 2. Discussion on validation data provided by expert lab to establish the assigned values especially IMEP 112 (inorganic As: rice, vegetable food, algae ...).
- Some of the material was not fully understandable, e.g. info on coloured, dotted lines or other symbols was not given.
- More about practical work.

Action: none or indicate if one should be done according the complains

Distibution: F. Ulberth – B. Kortsen – D. Florian/S. Lehto – D. Anderson

Participation list for the sixth workshop of the EU-RL Heavy Metals in Feed and Food, Brussels, 22 September 2010

Name	Organisation	Country
Gerhard LIFTINGER	Austrian Agency for Health and Food Safety	Austria
Khalid BOUTAKHRIT	Scientific Institute of Public Health	Belgium
Jean-Christophe PIZZOLON	CODA-CERVA	Belgium
Maria CHRISTOFIDOU	State General Laboratory	Cyprus
Marina KARAVIA	Department of Agriculture	Cyprus
Eva NIEDOBOVA	CISTA	Czech Republic
Rie Romme RASMUSSEN	Technical University of Denmark, National Food Ins	Denmark
Søren Roed SØRENSEN	the Danish Plant Directorate	Denmark
Roman LILLEORG	Veterinary and Food Laboratory	Estonia
Terhi ANDERSSON	Finnish Customs Laboratory	Finland
François AUGER	Laboratoire SCL de Bordeaux	France
Laurent NOEL	ANSES	France
Timo KAPP	Federal Office of Consumer Protection and Food safety	Germany
Erasmia KATSAROU	Institute of Food Hygiene of Athens	Greece
Geza MURANSZKY	CAO, FFSD, Feed Investigation NRL	Hungary
Frederick DAVIDSON	Cork Public Analyst's Laboratory	Ireland
Paola BRIZIO	IZSPLV-TORINO	Italy
Laura CIARALLI	Istituto Superiore di Sanità	Italy
Marina PATRIARCA	Istituto Superiore di Sanità	Italy
Irena JERMAKA	Research institute BIOR	Latvia
Birute MILIAUSKAITE	NFVRAI	Lithuania
Audrey CARUANA MIFSUD	Public health laboratory	Malta
Walther KLERX	Food and Consumer Product Safety Authority	Netherlands
Martijn VAN DER LEE	RIKILT	Netherlands
Kåre JULSHAMN	NIFES	Norway
Agnieszka NAWROCKA	National Veterinary Research Institute	Poland
Krystyna STARSKA	National Institute of Public Health	Poland
Susana GONÇALVES	Instituto Nacional de Recursos Biológico - IPIMAR	Portugal
Helena Maria LOURENÇO	INRB, I.P./L-IPIMAR	Portugal
Geanina VLASE	Hygiene and Veterinary Public Health Institute	Romania
Lívia FARKAŠOVA	State veterinary and food institute - Košice	Slovakia
Katarina PAVŠIČ VRTAČ	National Veterinary Institute	Slovenia
Manuela MIRAT	Laboratorio Arbitral Agroalimentario	Spain
Joakim ENGMAN	National Food Administration	Sweden
Malcolm BAXTER	FERA	United Kingdom
Peter FARNELL	LGC	United Kingdom
Invited speakers/Observers/EC staff		
Almut BITTERHOF	EC-DG SANCO	Belgium
Fernando CORDEIRO RAPOSO	EC-JRC-IRMM	Belgium
Maria Beatriz DE LA CALLE GUNTINAS	EC-JRC-IRMM	Belgium
Bibi KORTSEN	EC-JRC-IRMM	Belgium
Piotr ROBOUCH	EC-JRC-IRMM	Belgium
Michael THOMPSON	Birkbeck University of London	United Kingdom

6th EU-RL Heavy Metals Workshop

CCAB – AB-3C, Brussels, 22/09/2011
AGENDA

Thursday 22/09/2011

09:00-09:30	Welcome and opening of the event	M.B. de la Calle
09:30-10:00	Important matters on heavy metals in feed and food according to legislation	A. Bitterhof
10:00-10:45	• Presentation of the 2010/11 activities • Presentation of the WP 2012 • Outcome of the EU-RL survey • Update on the activities of the EU-RL CEFAO	F. Cordeiro/ P. Robouch L. Ciaralli
10:45-11:15	Coffee break	
11:15-12:15	New light on dark uncertainty	M. Thompson
12:15-12:45	Discussion on WP 2013	M.B. de la Calle
12:45-14:00	Lunch	
14:00-14:20	Mercury analyzer (AMA) and untypical inorganic matrix	Eva Niedobová
14.20-14.50	Visit the IMEP Gallery and Coffee break	
14.50-15:50	Presentation and discussion on the outcome of IMEP-111, IMEP-112 and IMEP-113	F. Cordeiro, P. Robouch,
15:50-16:00	Closing of the event	M.B. de la Calle

Health & Consumer Protection
Directorate-General

Health & Consumers

Directorate General

Update on current and future legislative work in the area of heavy metals in food and feed

Workshop of the EU RL Heavy Metals 22 September 2011

Almut Bitterhof

Health & Consumer Protection
Directorate-General

Current or forthcoming issues Heavy metals in food

- Cadmium
- Lead
- Arsenic
- Mercury

This presentation expresses exclusively the author's personal opinions and does not, in any case, bind the European Commission

Health & Consumer Protection
Directorate-General

Current status – Heavy metals in food

- Cadmium
  - EFSA opinion adopted January 2009
  - Review of Reg. 1881/2006 ongoing, expected finalisation: end 2011
- Lead:
  - EFSA opinion adopted: March 2010
  - Review of Reg. 1881/2006 ongoing, expected finalisation: 2012
- Arsenic:
  - EFSA opinion adopted in October 2009
  - Review of Reg. 1881/2006 ongoing, expected finalisation: 2012
- Mercury:
  - New question to EFSA on mercury and methyl mercury (July 2011): Scientific opinion expected mid 2012
  - Need for risk management measures to be discussed after availability of opinion

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Health & Consumer Protection
Directorate-General

Review of 1881/2006 - cadmium

- First proposal has been submitted for stakeholder consultation in June 2011
- Evaluation of stakeholder comments in autumn 2011
- Finalisation of technical discussions expected by end of 2011
- Expected for adoption: first half 2012

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Health & Consumer Protection
Directorate-General

Review of 1881/2006 - cadmium

- Lower maximum levels proposed for
  - Some cereals, stem/root & tuber vegetables, soybeans, leaf vegetables (excl. spinach)
- New maximum levels proposed for
  - Oilseeds, chocolate, milk and soy based formula, processed cereal based and other baby food, raw milk
- Adjustment of classes of maximum levels for some fish species and specific vegetables

Health & Consumer Protection
Directorate-General

Rationale for review

- Reduce exposure, in particular for sub population groups but also general population following EFSA opinion
- Focus on main contributors to exposure for adults and/or children: cereals and cereal products, vegetables nuts and pulses, starchy roots or potatoes
- Special focus on foods of particular importance for children (chocolate, baby food)
- New occurrence data show that adjustments are needed following the ALARA principle

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Health & Consumer Protection
Directorate-General

Cadmium – other measures

- Measures at source are needed to reduce cadmium in
  - soil→crops→ foods
  - marine environment→fish→food
- Discussion on cadmium levels in fertilisers (DG ENTR)
- Other environmental legislation is already in largely in place. SANCO involvement in all discussions related to Cadmium.

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Health & Consumer Protection
Directorate-General

Review of 1881/2006 - lead

- EFSA identified a need to reduce exposure – concern over possible neuro-developmental effects in young children
- Population group mainly at risk: unborn child, infants, children
- Codex review of levels also planned

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Health & Consumer Protection
Directorate-General

Review of 1881/2006 - lead

- Main contributors to exposure very similar as in case of cadmium
- Mainly: Cereals, vegetables (in particular potatoes), to a lesser extent also meat/fish
- Important for infants/children also:
  - Milk and milk products
  - Baby foods (all kinds incl. formulae)
  - Fruit and fruit products, fruit juices
  - Cocoa and chocolate products

Health & Consumer Protection
Directorate-General

Arsenic

- EFSA opinion adopted in October 2009
- Review of 1881/2006 ongoing
- Planned introduction of MLs for inorganic arsenic in rice and infant food on rice basis: no proposal for specific MLs yet, data collection still ongoing
- Under discussion also: other cereals, algae, food supplements

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Health & Consumer Protection
Directorate-General

Arsenic – analytical issues

- EU RL heavy metals proficiency test on total and inorganic arsenic
  - in rice (second half 2009)
  - in vegetable, cereals and algae matrix (2011)
- Method for the determination of inorganic arsenic in food and feed - included in COM mandate for CEN (deadline 31.12.2011)

Health & Consumer Protection
Directorate-General

Mercury

- New question to EFSA for a review of their 2004 scientific opinion on mercury and methyl mercury in food – Deadline June 2012
- Data collection ongoing for occurrence data
- WP EU RL Heavy metals 2012: Collaborative trial for the validation of a method for methyl mercury in fish
- Risk management discussion to start after availability of EFSA opinion
  - Review of maximum levels needed?
  - Review of consumption advice needed?
  - Other measures?

This presentation expresses exclusively the author's personal opinions and does not, in any case, bind the European Commission

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Directorate-General

Heavy metals in feed

- Commission Regulation (EU) No 574/2011 of 16 June 2011 amending Annex I to Directive 2002/32/EC
  - Annex restructured and harmonised terminology used
  - No changes in the maximum levels
  - Reference to extraction method to be used for the analysis on arsenic, cadmium, lead and mercury deleted

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Heavy metals in feed

- However equivalent extraction efficiency for heavy metals in minerals and feed with high mineral content of major importance (cf. lead in kaolinitic clay).
  - Based on work performed in EURL → issue needs to be addressed in legislation.
- Possible changes as regards heavy metals:
  - Establishment of maximum levels for inorganic arsenic instead of total arsenic.
  - No other major changes envisaged.
  - Minor changes in maximum levels possible following evidence of need (increase or decrease).

This presentation expresses exclusively the author's personal opinions and does not, in any case, bind the European Commission

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Contact

Almut.Bitterhof@ec.europa.eu

Thank you for your attention!

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Joint Research Centre (JRC)

EU-RL-HM workshop 2011

Beatriz de la Calle

Information

2010/2011 Activities

EURL-HM activities in 2010/11

- ✓ 5th WS of the EU-RL-HM network (24/09/10)
- ✓ 11th PT on total Cd, Pb, As, Hg and Cu and extractable Cd and Pb in mineral feed (IMEP-111 EUR 24758 EN - 2011)
- ✓ 12th PT on total and inorganic As in wheat, vegetable food and algae (IMEP-112 EUR 24937 EN - 2011)
- ✓ 13th PT on total Cd and Pb in baby food (IMEP-113 EUR ----- EN – 2011)
- ✓ 6th workshop of the EU-RL-HM network (*now*)

Participation in:

- WG National Experts in Industrial & Environmental Contaminants

  * IMEP-112 - to support the discussions on the feasibility to introduce in legislation **maximum levels for iAs** in several food commoditites.

  * IMEP-113 (and IMEP-33) - to support discussions on **max. levels for total Cd & Pb** in baby food.

- CEN/TC WG Contaminants, Minerals and Trace Elements in Feed

  collaboration = organisation of a **collaborative trial** for the determination of iAs in feed (IMEP-32) "link to webpage"

- CEN/TC 275 WG 10 Trace Elements in Food

  contributed in drafting document dealing with **sample treatment** for trace elements determination

The EU-RL-HM website

EURL Heavy Metals in Feed and Food

About us | Legislation | Network laboratories | Interlaboratory comparisons | What's new? | Contacts | Network pages

European Union Reference Laboratory for Heavy Metals in Feed and Food

The European Union Reference Laboratory for Heavy Metals in Feed and Food was created to implement Regulation (EC) No 882/2004 on official controls performed to ensure the verification of compliance with the feed and food law, animal health and animal welfare rules. Regulation (EC) No 776/2006 nominates the Joint Research Centre as the European Union Reference Laboratory (EU-RL) for Heavy Metals in Feed and Food. It is established at the JRC Institute for Reference Materials and Measurements (IRMM) and works together with appointed national reference laboratories (NRLs) of the EU Member States.

Heavy metals are present in all foodstuffs. Their amount in food and feed depends on the natural content and on the conditions under which food and feed are produced and processed. Some heavy metals have nutritional functions and are essential to the health. But others such as lead, cadmium and mercury have no nutritional relevance and can cause serious illnesses.

To reduce the risk to human health associated with a high heavy metal content in food and feed, maximum allowed limits in several commodities have been laid down in the European legislation. The CRL acts in this frame of legislation dealing with controls of heavy metal content in food and feed as a result of environmental or industrial contamination.

Tasks of the EU-RL for Heavy Metals in Feed and Food

The task of the EU-RL for Heavy Metals in Feed and Food is to facilitate the implementation of Regulation (EC) No 18812006 and Directive 2001/22/EC establishing the maximum levels of heavy metals such as lead, mercury and cadmium in different foods.

One of the core tasks of the CRL is to organise interlaboratory comparisons where the appointed national reference laboratories can participate. Furthermore it supports and gives advice to the European authorities and the NRLs on scientific matters. Development and validation of standardised analytical methods can also be carried out if the national reference laboratories ask for it, as well as training on the relevant European legislation.

The three types of matrices covered by the CRL are: wild caught fish, food of plant origin and animal feed.

http://irmm.jrc.ec.europa.eu/EURLs/EURL_heavy_metals/legislation/Pages/index.aspx

News …

- Bibi Kortsen Konrad joined the EURL-HM group
- EURL-HM is looking for a new PT coordinator

http://irmm.jrc.ec.europa.eu/job_opportunities/fellowships_at_irmm/Pages/index.aspx

Information

Audit of the EURL-HM

Overall Assessment A-

Assessment by evaluation theme

1. Adequacy of assistance to NRLs [B]
2. Appropriateness of analytical methods and techniques [B]
3. Coordination and training activities carried out by the EURL [A]
4. Activities carried out to support the Commission's action [A]
5. Fulfillment of the requirements laid down in Article 32 (4) of Regulation 882/2004 and other relevant EU legislation [A]

No weaknesses identified ☺

B mark = (simply) adequate

Adequacy of assistance to NRLs

1.1. Development/validation/assessment of analytical methods

1.2. Distribution of Standard Operating Procedures (SOPs)

1.3. Distribution of standard materials

1.4. Contribution of Proficiency Tests (PTs) to improvement and harmonisation of analytical methods/quality of analytical data

1.5. Contribution of training activities to the improvement and harmonisation of analytical methods/quality of analytical data

1.6. Contribution of other activities to the improvement and harmonisation of analytical methods/quality of analytical data

Discussion

WP 2012

Work program 2012

- PT on heavy metals in feed premixes.
- Collaborative trial for the validation of a method to determine methylmercury in fish.

  Method based on extraction into toluene and complexation with cysteine. No hypenation needed.
- 7th workshop (& training) = September 2012
- Process a mushroom material @ IRMM for a 2013 ILC

SOP from the literature

- Weigh about **200 mg** of freeze-dried sample to a centrifuge tube (FEP with screw cap of ETFE, Nalgene).
- Add **10 ml of hydrobromic acid** (47 % m/m, Merck) + **20 ml of toluene** (≥ 99 % m/m, Merck).
- Stir the mixture in a vortex **for about 5 minutes and centrifuge for 20 minutes at 3000 rpm**.
- Remove 15 ml of organic phase and placed into another tube which was previously added **6 ml of cysteine solution (1 % L-cysteine hydrochloride, monohydrate in 12.5 % of sodium sulphate and 0.8 % of sodium acetate**, all Merck).
- Add 15 ml of toluene to the tube containing the initial hydrobromic acid and repeat the process.
- Shake (manually and vortex) the tube containing the solution of cysteine and toluene (30 ml) and
- centrifuge for 20 minutes at 3000 rpm.
- **Transfer to another centrifuge tube 3 ml of cysteine for subsequent analysis.**
- From this solution withdraw between **100 a 500 µl** for the small boat.
- Put the small boat on mercury analyzer and read according to the instructions of the mercury analyser **(LECO, AMA 254)**.

C. Alfonso et al., *J Sci Food Agric,* 88:2543–2550 (2008)
R. Scerbo et al., *EnvironTechnol,* 19:339–342 (1998)

- EU-RL-HM needs support from NRLs (familiar with the method) to draft the SOP.
- Looking for laboratories with experience in the field and that would like to take part in this exercise.

Discussion

Discussion

WP 2013 ?

Discussion work program 2013

A must: ILC – Mushrooms (As, Cd, Pb, Hg?)

Wishes you expressed:

- ☑ *Metals in seafood, crustaceans, cephalopodes*
- ☑ *Cd @ ML levels in foodstuffs*
- ❑ Feed matrices of vegetable origin & compound feed

what else?

Discussion

Update on the activities of the EU-RL CEFAO

Laura Ciaralli
European Union - Reference Laboratory
for
Chemical Elements
in Food of Animal Origin

Materials and analytes

Analytes: Cd, Pb, total Hg and As

2006	**Meat** 2 Samples freeze-dried	**Milk** 2 Samples freeze-dried	
2007	**Meat** 1 Sample freeze-dried	**Milk** 2 Samples liquid	**Fish** matrix 1 Sample freeze-dried
2008	**Liver** 1 Sample freeze-dried	**Milk** 2 Samples liquid	**Meat** 1 Sample freeze-dried
2009	**Fish** matrix 1 Sample freeze-dried	**Milk** 2 Samples liquid	
2010	**Meat** 1 Sample frozen	**Milk** 1 Sample liquid	**Fish** matrix 1 Sample frozen
2011	**Liver** 1 Sample frozen	**Meat** 1 Sample freeze-dried	

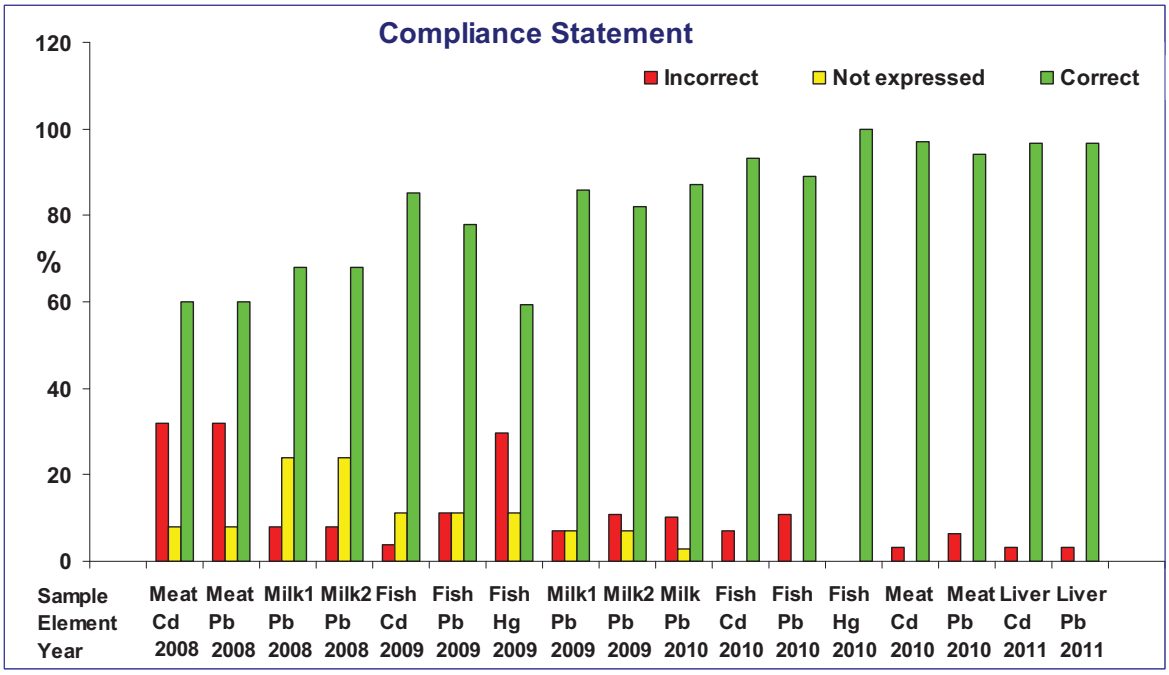
SWEDAC ACKREDITERING 1856 ISO/IEC Guide 43-1

ISO/IEC 17043:2010 !!

NRCPs are targeted to detect illegal treatment or to control compliance with the MRLs for veterinary medicinal products, the MLs for pesticides or the MLs laid down in relevant legislation on contaminants .

For this reason

the concentration of the samples used in EU-RL CEFAO PTs were always adjusted to this aim.



Materials and analytes

Analytes: Cd, Pb, total Hg and As

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2007	**Meat** 1 Sample freeze-dried	**Milk** 2 Samples liquid	**Fish** matrix 1 Sample freeze-dried
2008	**Liver** 1 Sample freeze-dried	**Milk** 2 Samples liquid	**Meat** 1 Sample freeze-dried
2009	**Fish** matrix 1 Sample freeze-dried	**Milk** 2 Samples liquid	
2010	**Meat** 1 Sample frozen	**Milk** 1 Sample liquid	**Fish** matrix 1 Sample frozen
2011	**Liver** 1 sample frozen	**Meat** 1 Samples freeze-dried	

Materials and analytes

Analytes: Cd, Pb, and Total As

.....			
2010	**Meat** 1 Sample frozen	**Milk** 1 Sample liquid	**Fish** matrix 1 Sample frozen
2011	**Liver** 1 sample frozen	**Meat** 1 Samples freeze-dried	
2012	**Milk** 1 Sample liquid	Interlaboratory Method Validation on Cheese	

THANK YOU FOR YOUR ATTENTION !!!!!!!!!!!!

New light on dark uncertainty

Michael Thompson

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New light on dark uncertainty

- Dark uncertainty—metrology and statistics.
- A metrological mystery.
- How uncertainty varies with concentration.
- What *exactly* is fitness for purpose?
- Balancing the costs of analysis and sampling.

What is uncertainty?

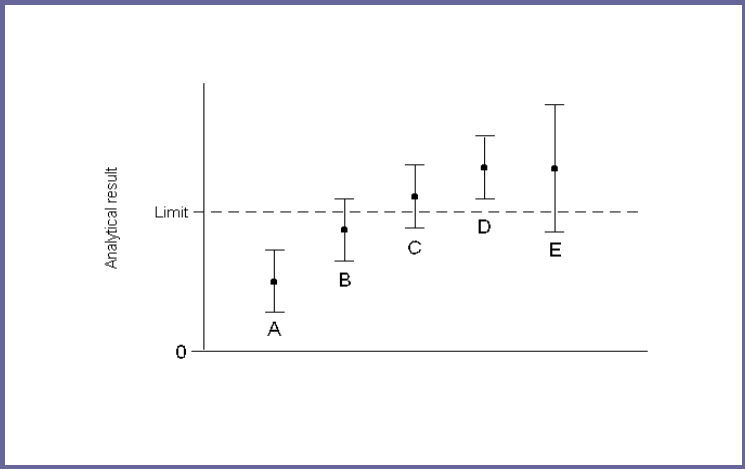
- *Measurement uncertainty*: non-negative parameter characterising the dispersion of the quantity values being attributed to a measurand, based on the information used.

VIM—International vocabulary of metrology, 3rd Edition, 1998.

Why is uncertainty important?

- Analysis is conducted to help us make decisions.
- Logically we cannot make a valid decision without knowing the uncertainty on the result.

Does this batch of material contain less than the maximum allowed concentration of an impurity?



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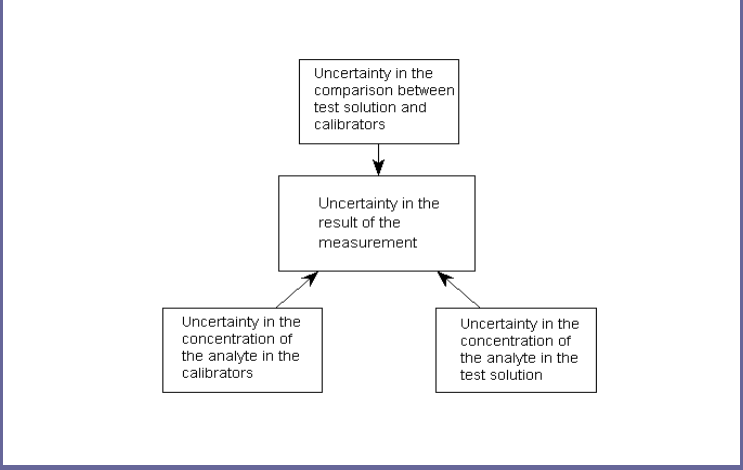
Estimation of uncertainty: the metrological approach

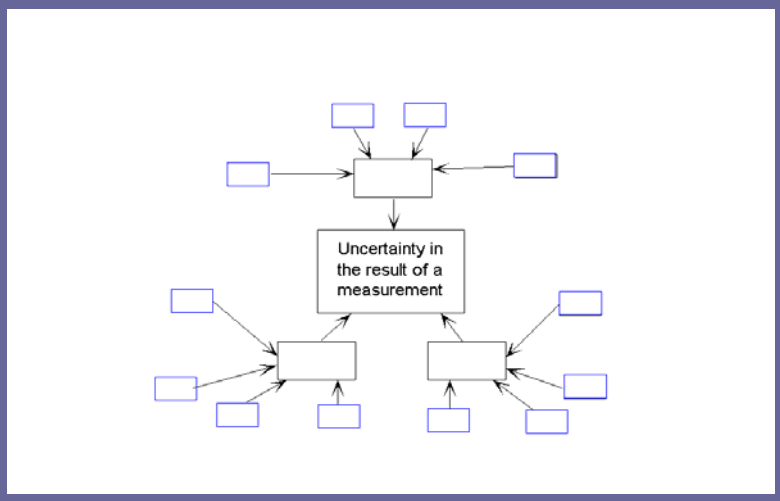
ISO/IEC Guide 98:1995 Guide to the expression of uncertainty in measurement (GUM). ISO, Geneva (1995)

Eurachem/CITAC Guide (2000) "Quantifying uncertainty in analytical measurement", 2nd edition.

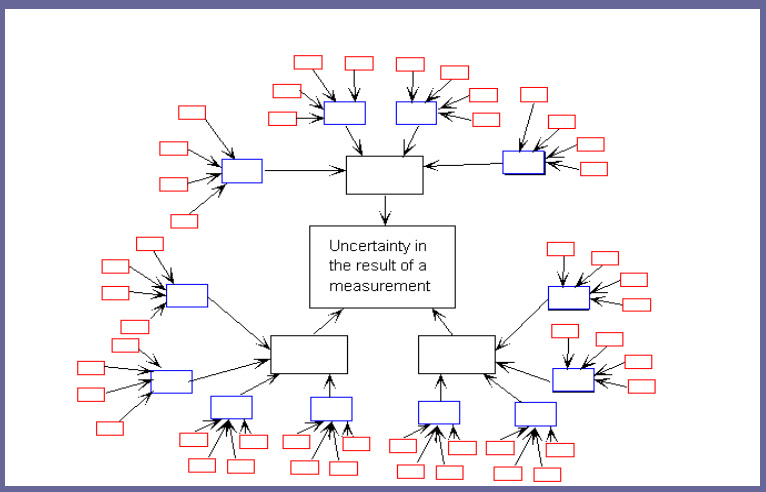
Build a model of the analytical process



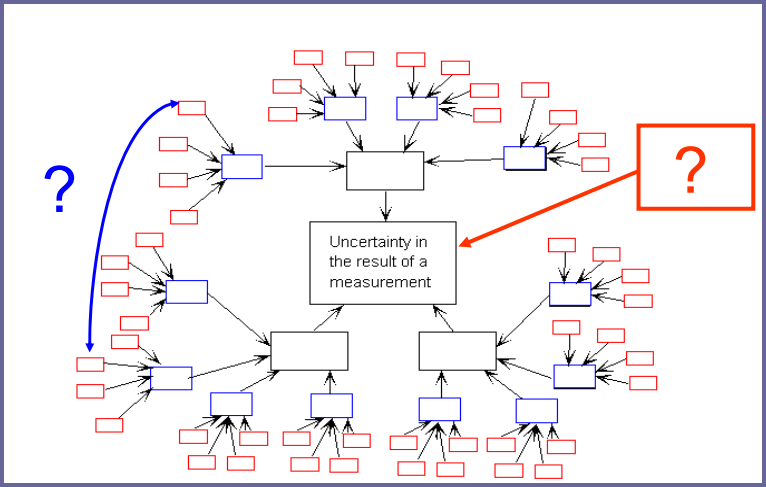
Next stage



…and again…



Potential problems with a model



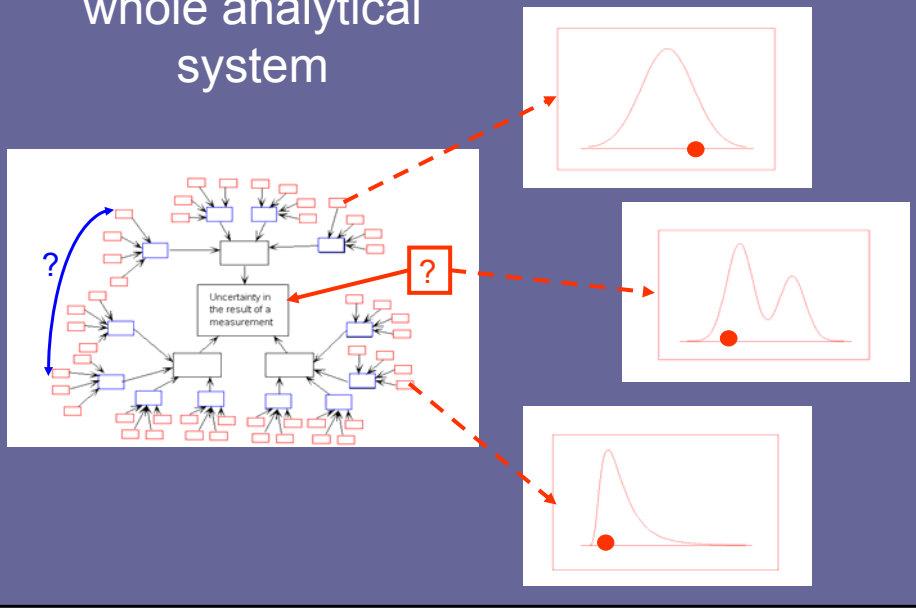
The statistical approach

- Replicate the measurement process under appropriate conditions.
- Equate the standard deviation with the standard uncertainty.
- Quick and simple (but not always cheap).
- Not necessary to identify causes of variation.
- Unknown causes accounted for.

Problems with the statistical approach (based on replication)

- Valid only if
- the analytical method is unbiased,
- the replication is random and independent, and can visit all parts of the potential variation with equal probability.

Random replication of whole analytical system



Some conditions of measurement

- Calibration precision— does not include day-to-day variations, laboratory bias or method bias.
- Repeatability precision —does not include bias or method bias.
- Reproducibility precision (single method) —does not account for method bias.
- Reproducibility precision (multiple method)—??

Conditions for estimating precision, zinc in food

Conditions		RSD %
Calibration		1.9
Repeatability	σ_r	2.9
Reproducibility (single method)	σ_R	5.8
Reproducibility (various methods)		7.4

Comparison of metrological and statistical approaches to estimating uncertainty

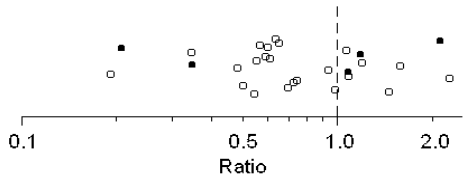
M Thompson, SLR Ellison (2011) *Accred Qual Assur (submitted, 2011)*

σ_R as an estimator of u

- Strict metrologists believe that σ_R is too small, because it does not sample the whole variable space,
- and does not provide traceability.
- Others believe that the 'cause-and-effect' approach cannot model a complex operation like chemical analysis, and provides an estimate that is too small.
- Why not eliminate belief—do an experiment!

Barwick and Ellison (1998)

Anal Commun **35**: 377-383

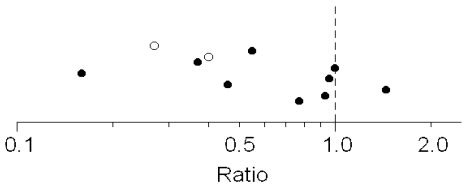


u/σ_R

Median = 0.65

Thompson et al (2002)

Analyst **127**: 1669-1675

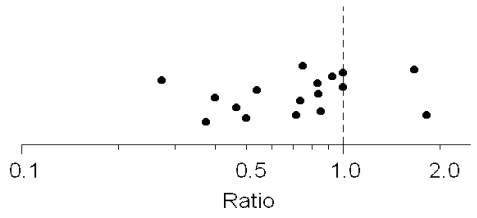


u/σ_R

Median = 0.55

Populaire and Giménez (2006)

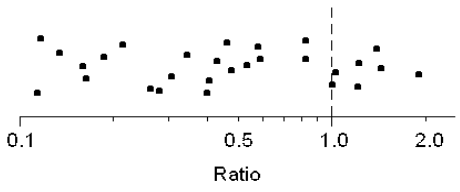
Accred Qual Assur **10**: 485-493



u/σ_R

Median = 0.75

BIPM International Key Comparisons
Thompson and Ellison (2011?)



u/σ_R

Median = 0.45

New light on dark uncertainty

- Dark uncertainty—metrology and statistics.
- A metrological mystery.
- How uncertainty varies with concentration.
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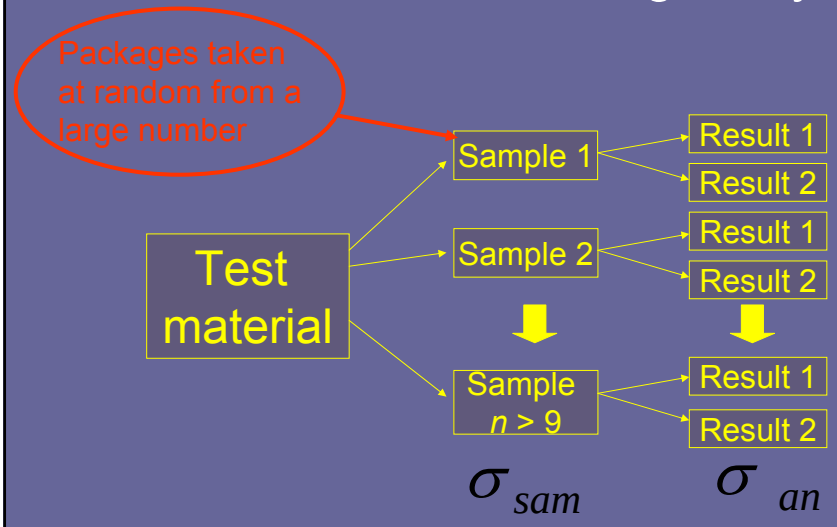
The analyst's dilemma

- To check whether an influence is significant and add the appropriate uncertainty contribution to the budget; or
- To assume from the outset that there is zero effect and, as a corollary, zero uncertainty contribution.

Real-life example—testing a reference material for homogeneity



Analysis of variance when $\sigma_{sam} = 0$

- About half of the estimates of the between-sample standard deviation s_{sam} will be zero.
- The upper 95% confidence limit of s_{sam} will be $0.82\sigma_{an}$.
- Should you add this contribution to the uncertainty budget when it is almost certain that $\sigma_{sam} = 0$?

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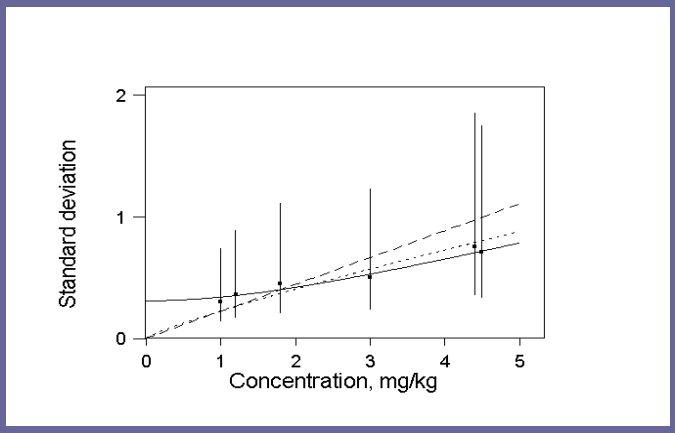
M Thompson (2011) *Trends Anal. Chem.* (in press)
http://dx.doi.org/10.1016/j.trac.2011.03.012

Validation cannot tell you!

Collaborative trial, σ_R
(interlaboratory study)

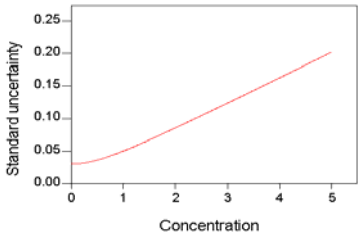


Requirements for a useful function

- Parsimonious—few empirical parameters.
- Theoretically correct.
- Rigorously tested by experiment.

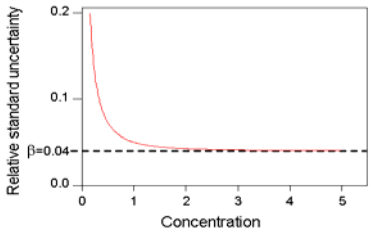
A plausible functional dependence

- Postulate 1: a baseline uncertainty. α
- An independent uncertainty proportional to concentration. βc
- The correct combination of these two uncertainties. $\sigma_c = \sqrt{\alpha^2 + (\beta c)^2}$

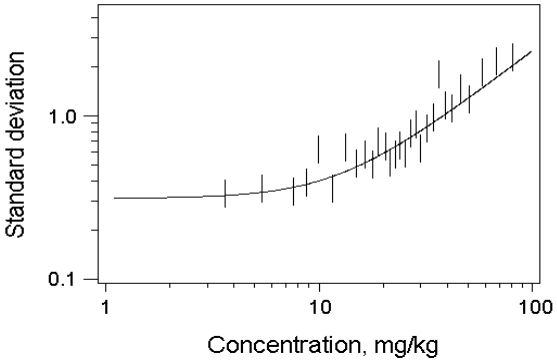


$$\sigma = \sqrt{0.03^2 + (0.04c)^2}$$

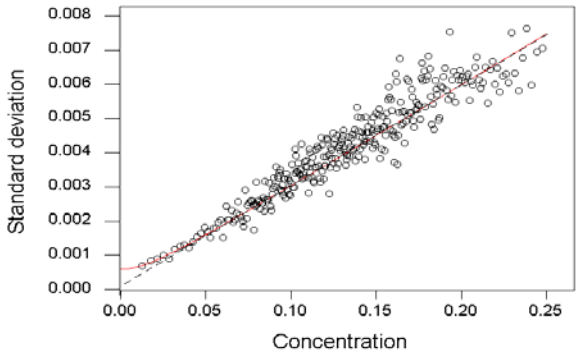
$$\frac{\sigma}{c} = \sqrt{\frac{0.03^2}{c^2} + 0.04^2}$$



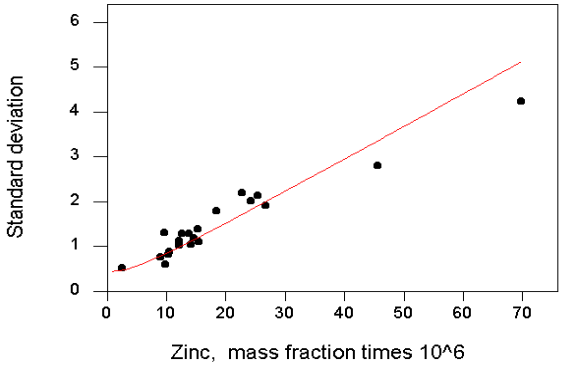
Repeatability (within laboratory)—Ni in soils, ~6000 results



Repeatability (within laboratory)—ethanol in breath, ~30 000 results



Reproducibility (between laboratory) zinc in foodstuffs, ~2200 results



New light on dark uncertainty

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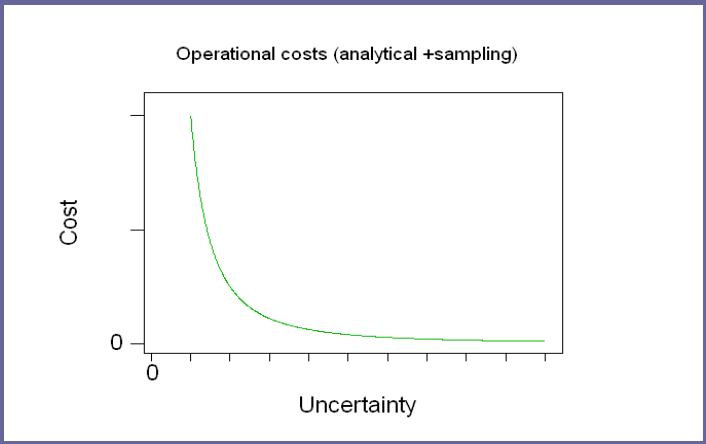
M Thompson, T Fearn (1996) Analyst 121: 275-278.

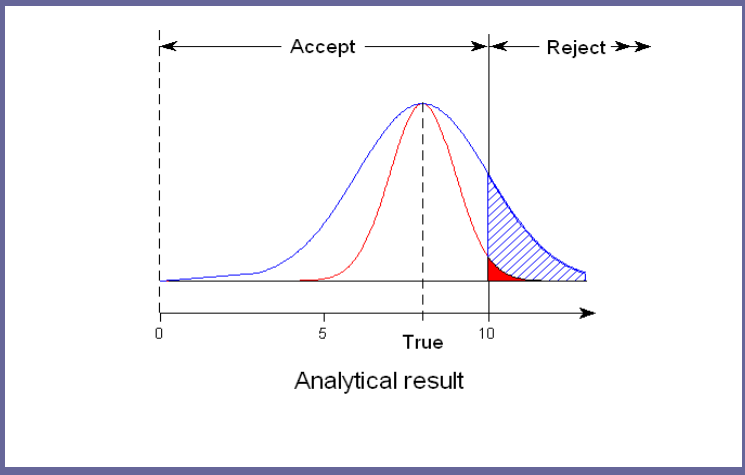
What *exactly* is fitness for purpose?

- When the uncertainty is optimal for the application.
- When the total cost is least for the end-user.

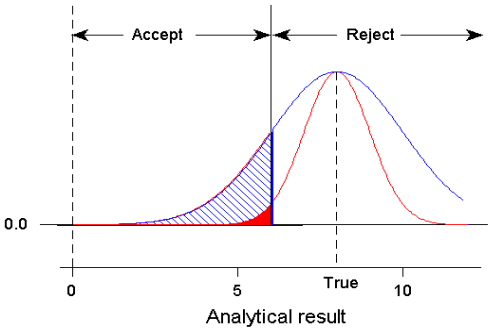
Operational costs of sampling and analysis



Cost of incorrect decisions—probabilities of false rejection

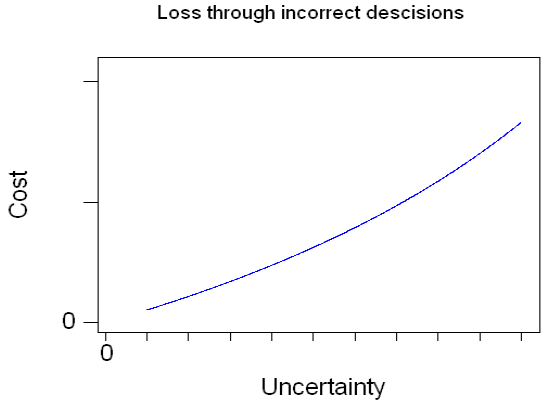


Probabilities of false acceptance

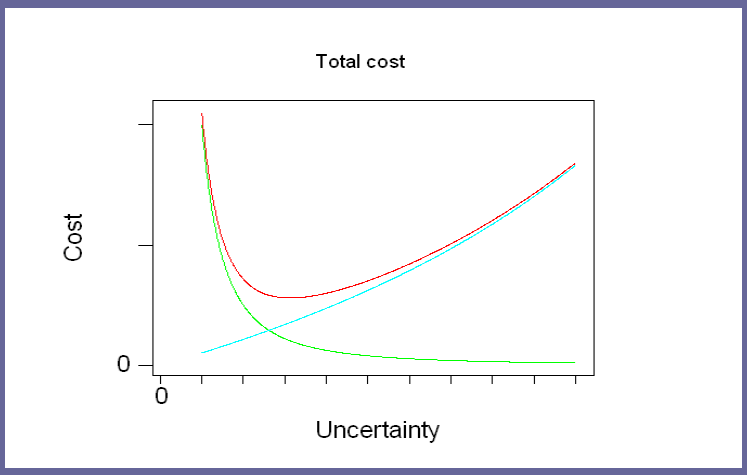


There are potential costs resulting from incorrect decisions based on the result.

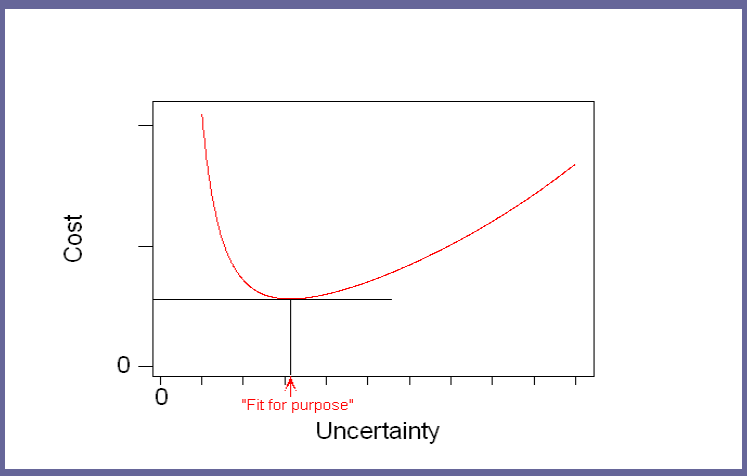
Average loss = Cost of incident × probability of incident



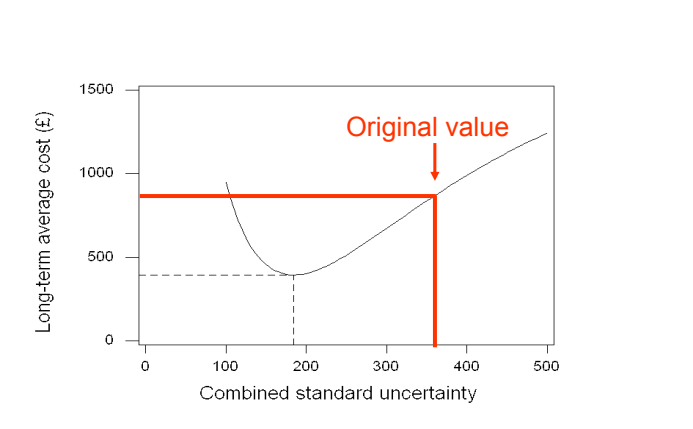
Long-term loss



Fit-for-purpose uncertainty



Example—nitrate in lettuce



Lyn et al. (2007) Accred Qual Assur 12: 67-74.

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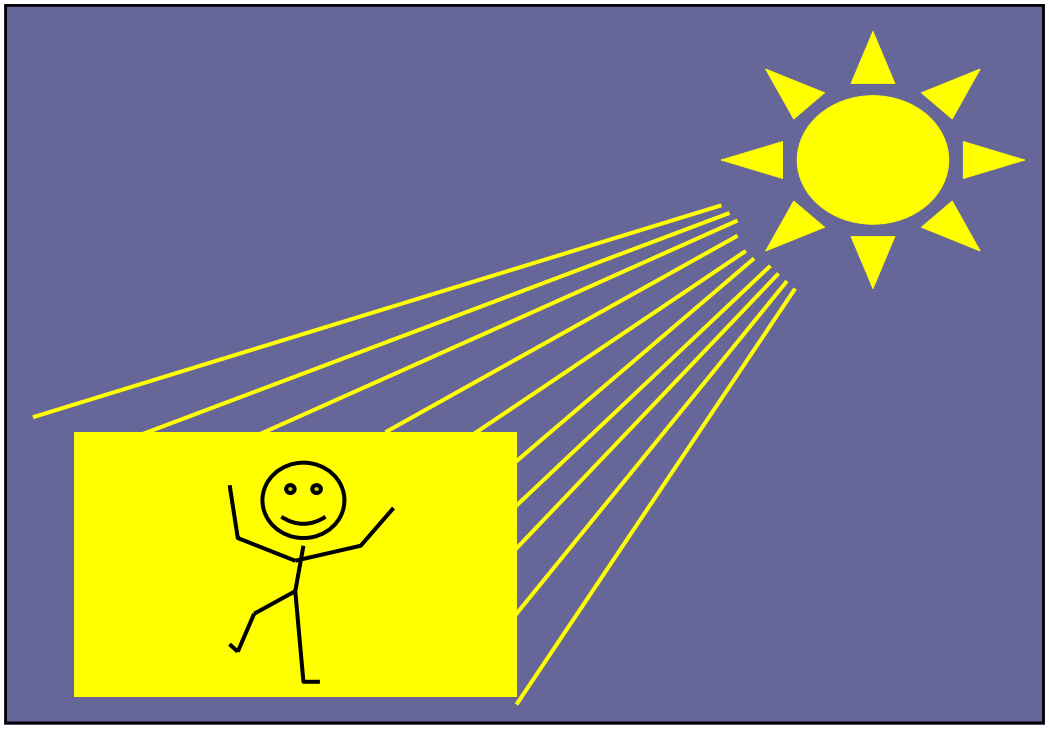
Sampling and analysis—optimal use of money

- Total cost: $L_{tot} = L_{sam} + L_{an}$
- Combined uncertainty: $u_{tot} = \sqrt{u_{sam}^2 + u_{an}^2}$
- But: $L_{sam} \approx \frac{Q_{sam}}{u_{sam}^2}, \quad L_{an} \approx \frac{Q_{an}}{u_{an}^2}$

Optimised outcome

- Minimum cost: $L_{tot}^* = \frac{\left(\sqrt{Q_{sam}} + \sqrt{Q_{an}}\right)^2}{u_{tot}^2}$

When: $\frac{u_{sam}}{u_{an}} = \left(\frac{Q_{sam}}{Q_{an}}\right)^{1/4}$



Joint Research Centre (JRC)

Discussion work program 2013

Beatriz de la Calle

… Your wishes for PTs

- My wish would be metals, including inorganic arsenic and methylmercury in an appropriate seafood sample

- For future ILCs: to look into the new proposed MLs for cadmium in a range of foodstuffs (currently under negotiation in the Commission). Maybe conduct ILCs on the new ML levels in some of these foodstuffs.
- Feed matrices of vegetable origin and compound feed

- Determination of Cd, Pb, Hg, As (total) in crustaceans (e.g. shrimbs, lobsters) or in cephalopods (e.g. octopuses, squids, etc)

… Your wishes for PTs

- Feed to analyse for the typical elements and inorganic arsenic
- Proficiency tests with seafood matrices (crustacean or bivalve/ cephalopod molluscs

… Your wishes for training

- Training in methods of determination of inorganic As and/or Methyl-Hg in fish/fish products
- Training on technical procedures for arsenic determination

Mercury analyzer (AMA) and untypical inorganic matrix

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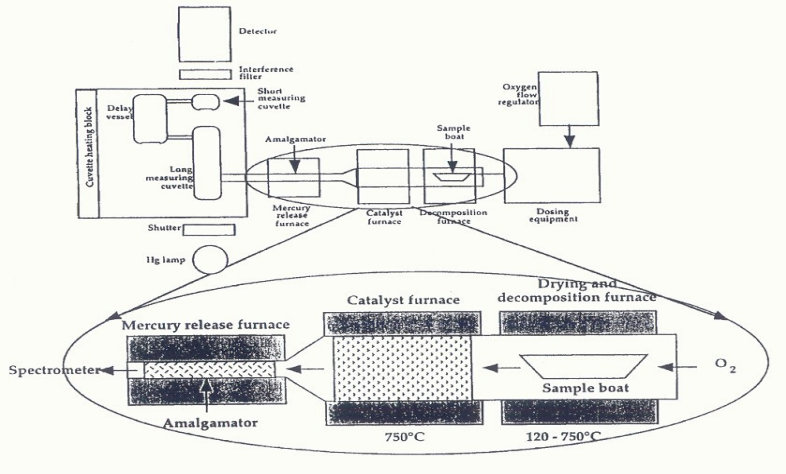
Mercury analyzer (AMA-254)

- Widely used in analysis of environmental samples (soils, waters, sediments), geological materials, biological materials, food, feedingstuf etc.
- Fast, cheap, precise, user friendly, solid or liquid samples etc.

Principle of Mercury analyzer



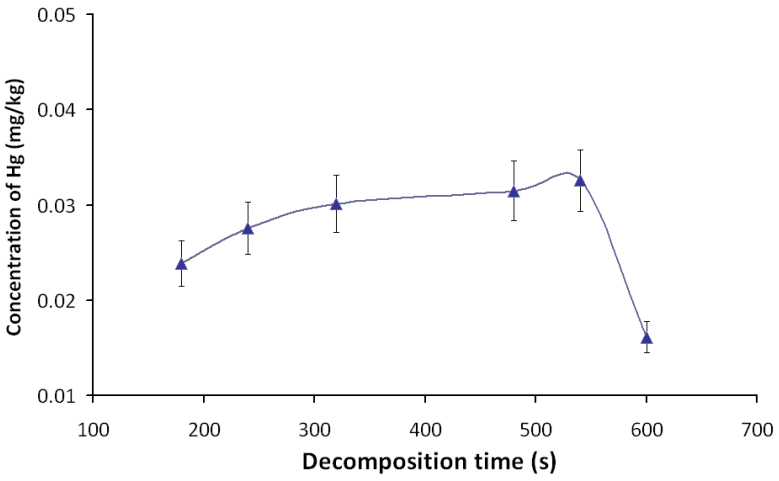
Analysis of solid samples

- 100 mg of sample (LOQ 0.0005 mg/kg)
- Drying (30 s)
- Decomposition (180 s)
- Waiting (60 s)

Analysis of BCR-032 Moroccan phosphate rock

- 0.0239 mg/kg instead of 0.044 mg/kg.

Effect of increasing time of decomposition



Sample preparation

- 3 g of sample
- 7 ml HCl + 21 ml HNO_3
- 1 h at 250 °C
- 100 ml volumetric flask

Analysis of liquid samples

- 100 µl of sample (LOQ 0.017 mg/kg)
- Drying (70 s)
- Decomposition (120 s)
- Waiting (60 s)

Analysis of BCR-032 Moroccan phosphate rock - 0.043 mg/kg,
certified value - 0.044 mg/kg

Conclusion

- Analysis of liquid extracts is possible solution for analysis of „untypical“ inorganic matrix.
- Short life of catalyst and sample boat.
- Higher limit of detection/quantification and uncertainty.

Joint Research Centre (JRC)

EU-RL-HM ILCs for 2010 / 2011

F. Cordeiro, I. Baer, P. Robouch, B. De la Calle

IRMM - Institute for Reference Materials and Measurements
Geel - Belgium

http://irmm.jrc.ec.europa.eu/
http://www.jrc.ec.europa.eu/

- **IMEP-111: Total Cd, Pb, As, Hg and Cu, Extractable Cd and Pb in Mineral Feed**
- **IMEP-112: Total & iAs in Wheat, Vegetables and Algae**
- **IMEP-113 / 33: Total Cd and Pb in Baby Food**

IMEP-111

- **CRM BCR-032** (Moroccan phosphate rock)
- **Stability and homogeneity studies not performed.** Information from CRM certificate
- **Scoring** (z- & ζ-score)
- **Report available**

IMEP-111: Reference values

Assigned values and their associated uncertainties

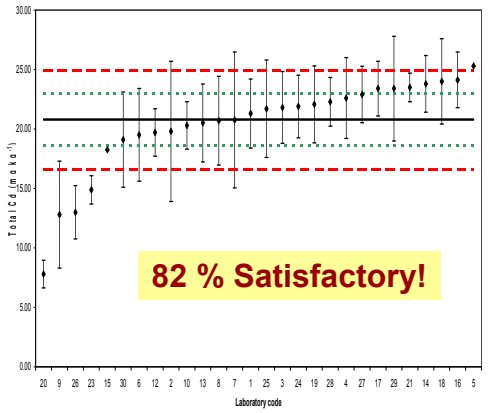
Measurand	X_{ref} (mg kg^{-1})	u_{ref} (mg kg^{-1})	U_{ref} (mg kg^{-1})	σ (mg kg^{-1})
Total Cd	20.8	1.1	2.2	2.1
Extractable Cd				
Total Pb	3.8	0.3	0.5	1.0
Extractable Pb				
Total As	9.5	0.6	1.1	1.0
Total Hg	0.044	0.003	0.006	0.007
Total Cu	33.7	1.9	3.7	3.0

X_{ref} is the reference value and $U_{ref} = k\ u_{ref}$ is the estimated associated expanded uncertainty; with a coverage factor k= 2 corresponding to a level of confidence of about 95 %.

Assigned values for :
- total contents of **Cd**, **As**, and **Cu** taken from **CRM** certification
- **total Hg** and **Pb** determined at **IRMM** by ID-ICP-MS
- **extractable Cd** and **Pb** determined at **IRMM**

IMEP-111: Total & Ext. Cd

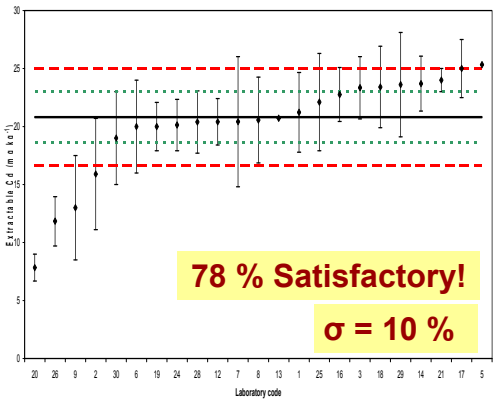
IMEP-111: Results for total Cd
Certified range: 20,8 ± 2,2 mg kg^{-1} (k=2)



82 % Satisfactory!

This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval ($X_{ref} \pm 2u_{ref}$: 20,8 ± 2,2 mg kg^{-1}), the red dashed lines delimit the target interval ($X_{ref} \pm 2\sigma$: 20,8 ± 4,2 mg kg^{-1})

IMEP-111: Results for Extractable Cd
Certified range: 20,8 ± 2,2 mg kg^{-1} (k=2)



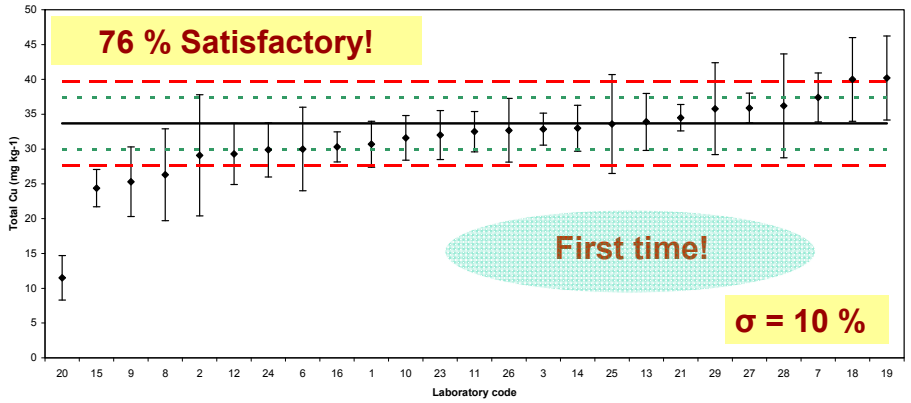
78 % Satisfactory!

σ = 10 %

This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval ($X_{ref} \pm 2u_{ref}$: 20,8 ± 2,2 mg kg^{-1}), the red dashed lines delimit the target interval ($X_{ref} \pm 2\sigma$: 20,8 ± 4,2 mg kg^{-1})

IMEP-111: Total Cu

IMEP-111: Results for total Cu
Certified range: 33,7 ± 3,7 mg kg^{-1} (k=2)



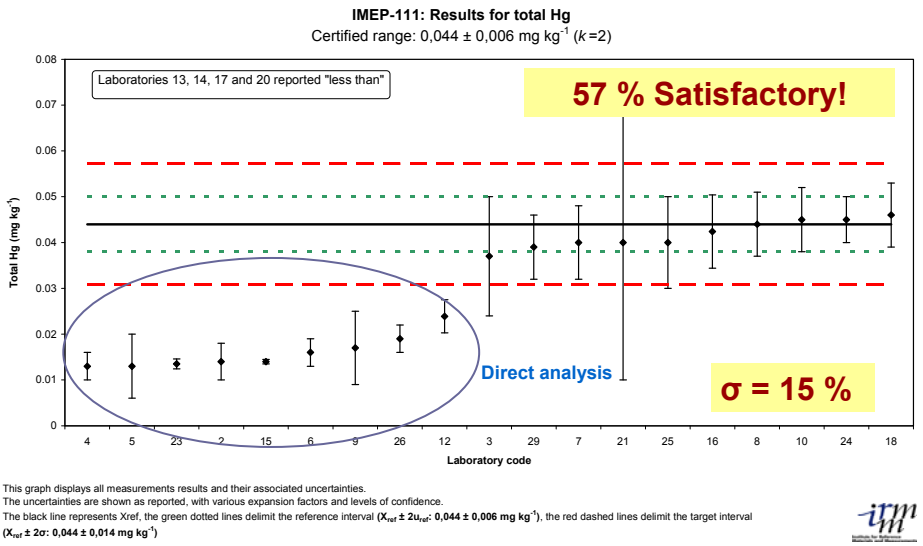
76 % Satisfactory!

First time!

σ = 10 %

This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval ($X_{ref} \pm 2u_{ref}$: 33,7 ± 3,7 mg kg^{-1}), the red dashed lines delimit the target interval ($X_{ref} \pm 2\sigma$: 33,7 ± 6,0 mg kg^{-1})

IMEP-111: Total Hg



This graph displays all measurements results and their associated uncertainties.
The uncertainties are shown as reported, with various expansion factors and levels of confidence.
The black line represents Xref, the green dotted lines delimit the reference interval ($X_{ref} \pm 2u_{ref}$: 0,044 ± 0,006 mg kg^{-1}), the red dashed lines delimit the target interval ($X_{ref} \pm 2\sigma$: 0,044 ± 0,014 mg kg^{-1})

Scoring

- Participants **invited** to report uncertainty
- Reported uncertainty **rated**

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

states if the laboratory result agrees with the assigned value within the respective uncertainties

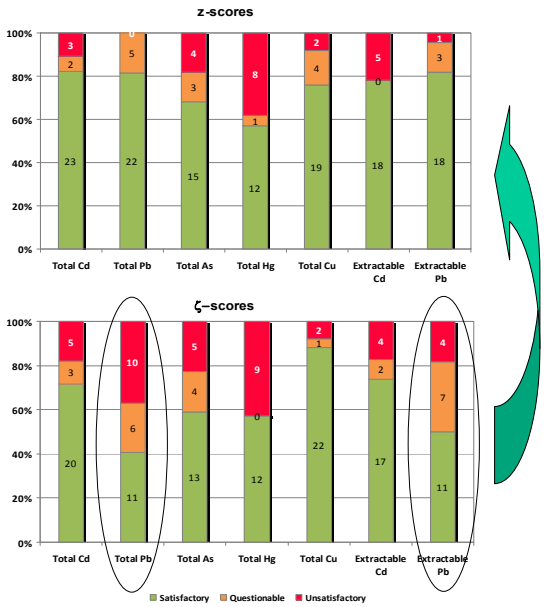
$$z = \frac{x_{lab} - x_{ref}}{\sigma}$$

indicates degree of compliance with peers, legislation, ...

$$u_{min} \leq u_{lab} \leq u_{max}$$

indication of the plausibility of uncertainty estimate

IMEP-111: Scoring



Less satisfactory ζ-scores

IMEP-111: Conclusions

- **Clustered results for total Hg (by technique)**,
  Results by thermal decomposition-amalgamation are negatively biased
  Not observed for CV-AAS, CV-AFS and ICP-MS

- **1st EU-RL-HM PT with total Cu** as measurand.
  No significant problems

- **Extra efforts** required for the **evaluation of measurement uncertainties**
  (unsatisfactory ζ-scores higher than those of z-scores)

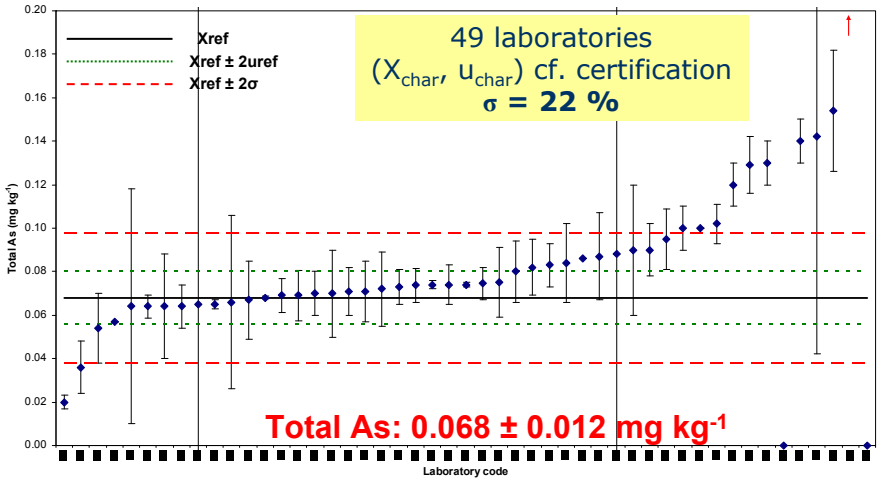
IMEP-112

- Wheat: ISS provide 20 Kg of wheat from an area with high As content.
- Vegetable food (spinach): *SRM 1570a* (NIST)
- Algae: *Candidate CRM* material (IRMM)

Stability and homogeneity studies performed (FERA, UK) for wheat and obtained from the RM certificate for vegetable food and algae.
Assigned values by 7 expert laboratories
(all iAs & total As in wheat)

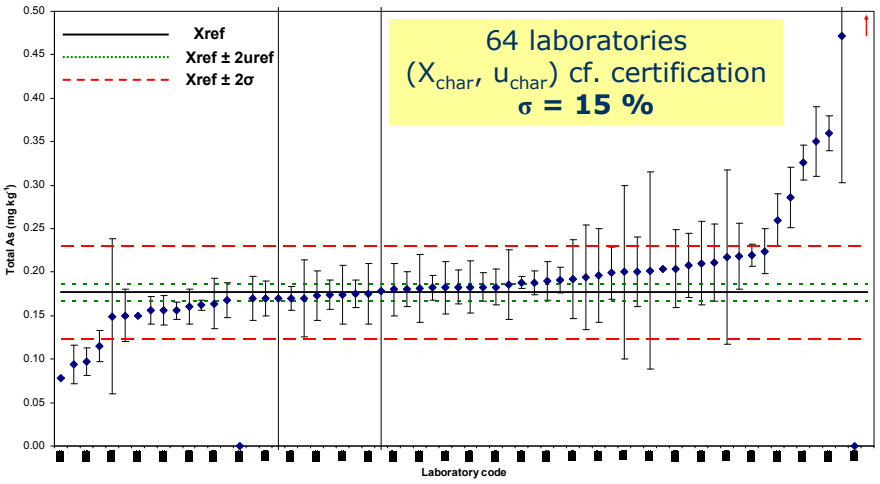
Scoring (z- & ζ-score)
Report finalised (available soon)

IMEP-112: Total As in Vegetables



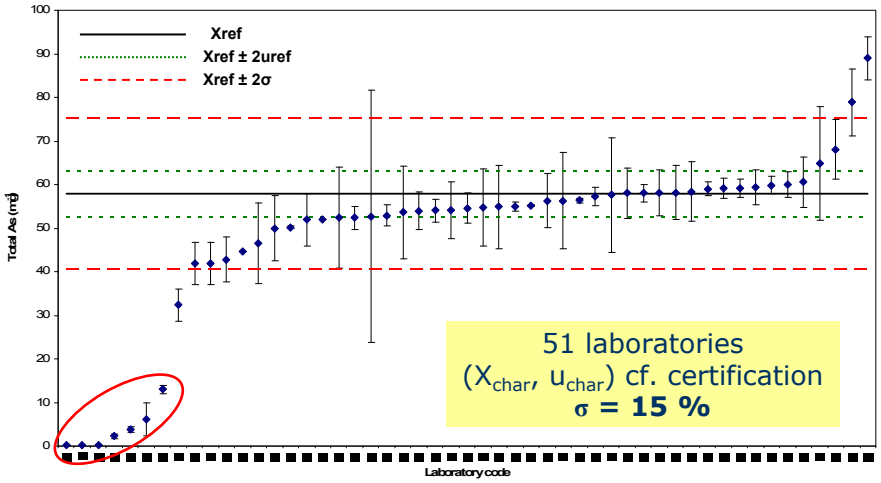
74 % Satisfactory!

IMEP-112: Total As in Wheat



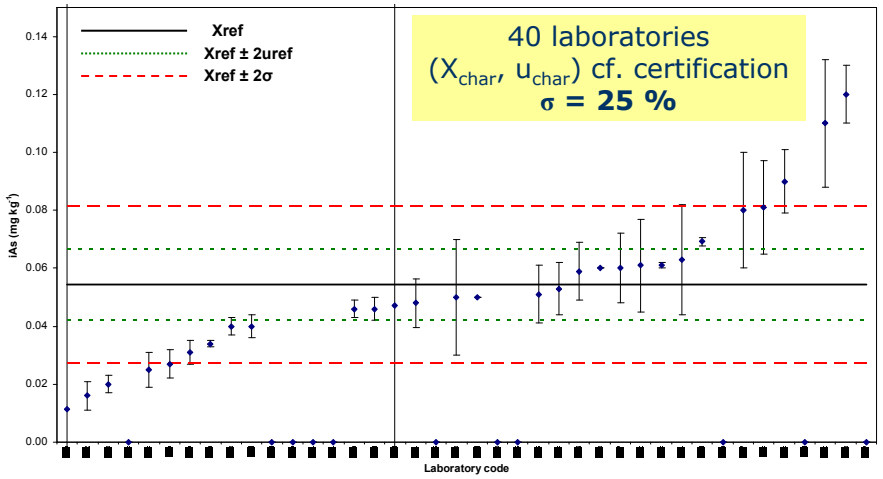
84 % Satisfactory!

IMEP-112: Total As in Algae



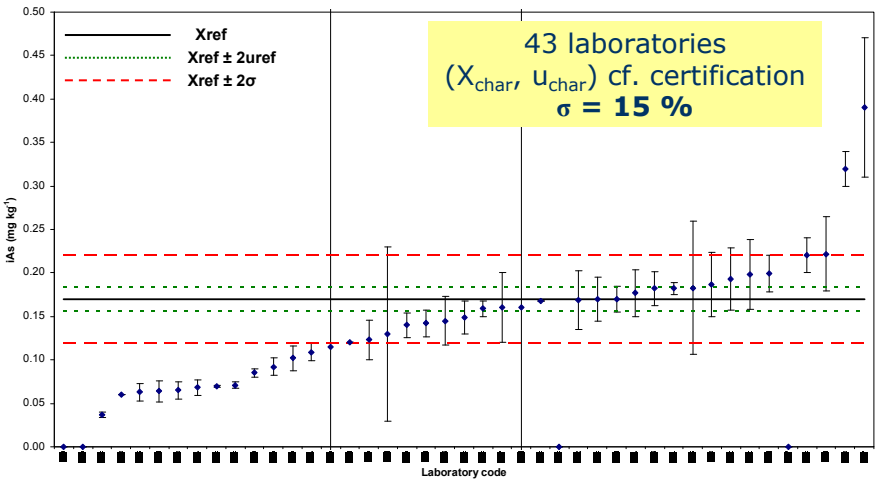
82 % Satisfactory!

IMEP-112: iAs in Vegetables



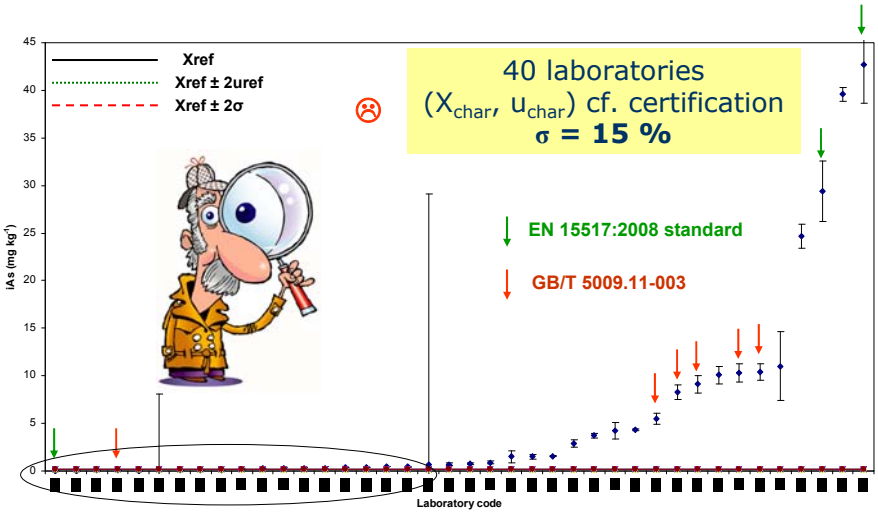
77 % Satisfactory!

IMEP-112: iAs in Wheat



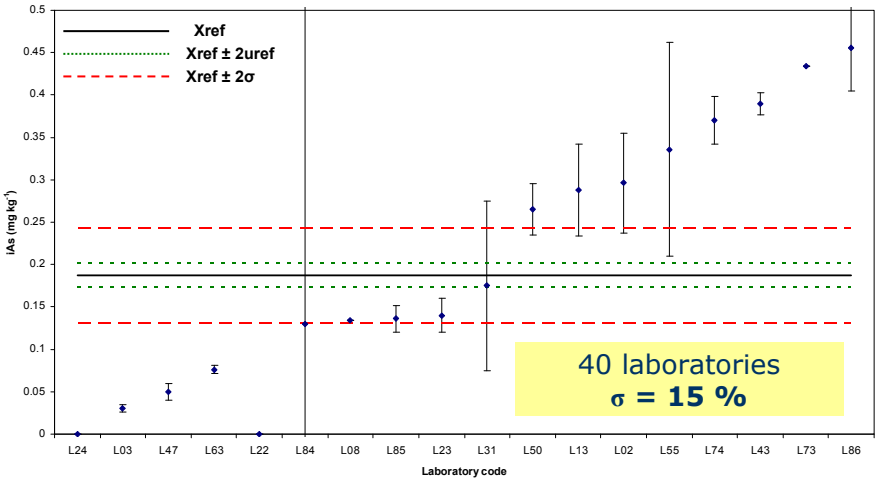
58% Satisfactory!

IMEP-112: iAs in Algae



Only 16 % Satisfactory!

IMEP-112: iAs in Algae (zoom)



IMEP-112: Conclusions

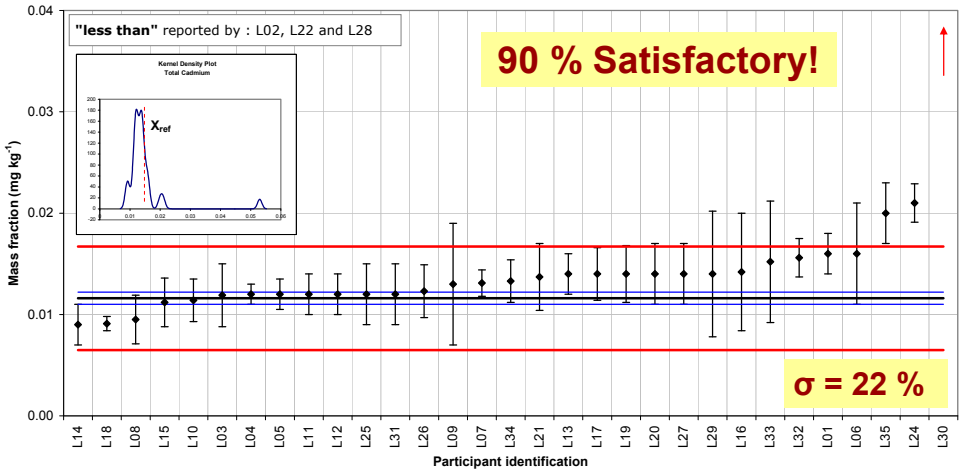
- **Yes, it is possible to measure iAs in food**
  within ± 15 % in **wheat and (rice)**
- **Results not method-dependent**
  European expert labs agree on one (X_{ref}) value with a std of 10 %,
  (except for marine samples)
- **Some methods are tedious** but do not require fancy instrumentation,
  other are user-friendly but imply the use of HPLC-ICP-MS
- Marine samples present more problems (iAs) due to a complicated distribution of species. A careful method optimisation allowed the achievement of the X_{ref}.
- Another ILC would be required for marine samples

IMEP-113 / IMEP-33

- **Commercially available milk powder**,
  Purchased in a local pharmacy
- Material prepared by the RM unit (IRMM)
  (homogenised and bottled)
- **Stability & homogeneity studies**
  Performed by ALS Scandinavia
  Evaluated (ISO 13528)
- Two expert labs for certification
  LGC Ltd (UK NMI) & IRMM, using ID-ICP-MS
  σ as 22 % of X_{ref}

IMEP-113 (Total Cd and Pb in baby food): Total Cd in powder

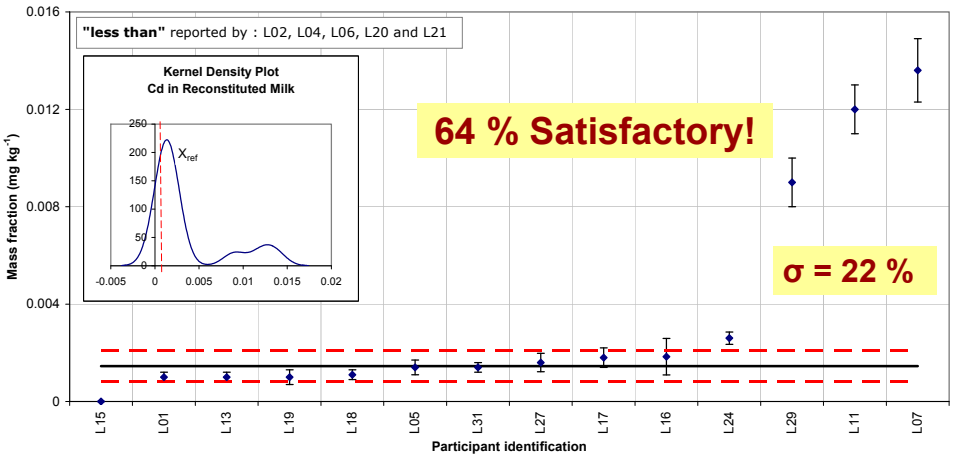
Certified value: X_{ref} = 0.0116 mg·kg^{-1}; U_{ref} = 0.0006 mg·kg^{-1} (k=2); σ = 0.0026 mg·kg^{-1}



This graph displays all measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to X_{ref}, the blue lines mark the boundary of the reference interval ($X_{ref} \pm 2u_{ref}$), and the red lines the target interval ($X_{ref} \pm 2\sigma$).

IMEP-113: Total Cd and Pb in baby food: Total Cd in reconstituted milk

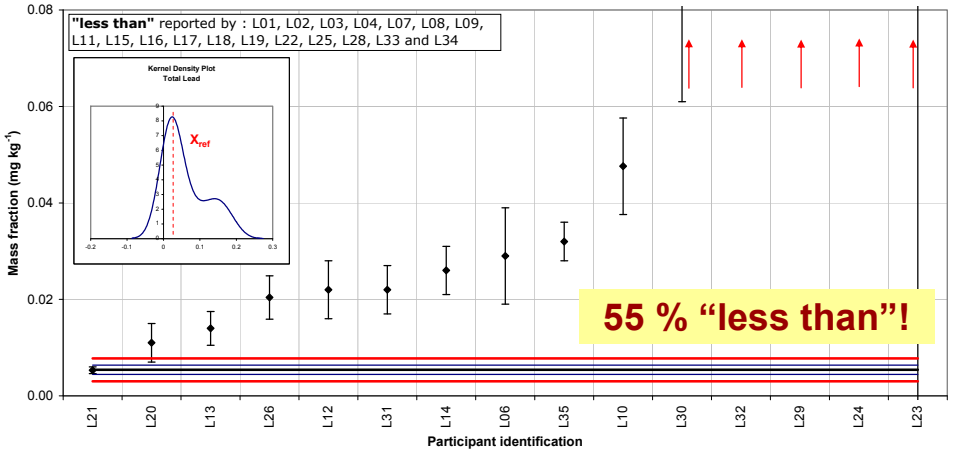
Certified value: X_{ref} = 0.00145 mg·kg^{-1}; U_{ref} = 0.0008 mg·kg^{-1} (k=2); σ = 0.00032 mg·kg^{-1}



This graph displays all measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to X_{ref}, the blue lines mark the boundary of the reference interval ($X_{ref} \pm 2u_{ref}$), and the red lines the target interval ($X_{ref} \pm 2\sigma$).

IMEP-113 (Total Cd and Pb in baby food): Total Pb in powder

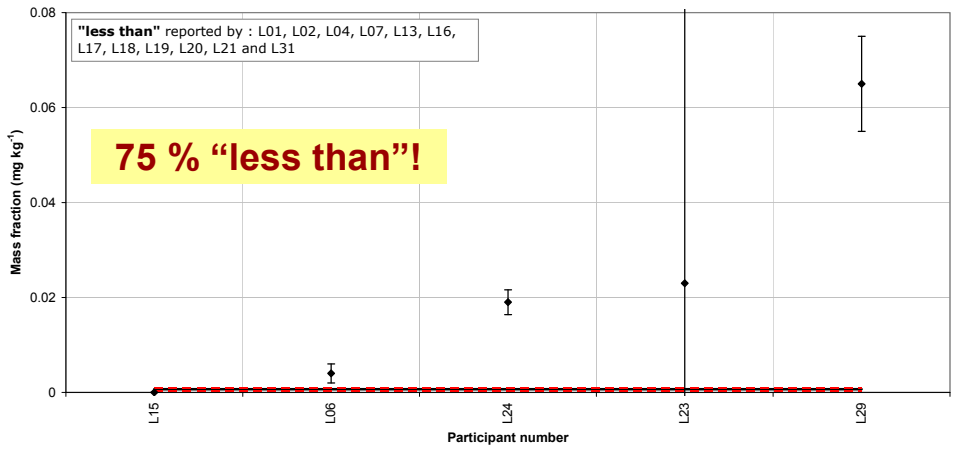
Certified value: X_{ref} = 0.0054 mg·kg^{-1}; U_{ref} = 0.001 mg·kg^{-1} (k=2); σ = 0.0012 mg·kg^{-1}



This graph displays all measurement results and their associated uncertainties. The uncertainties are shown as reported.
The thick black line corresponds to X_{ref}, the blue lines mark the boundary of the reference interval ($X_{ref} \pm 2u_{ref}$), and the red lines the target interval ($X_{ref} \pm 2\sigma$).

IMEP-113 (Cd and Pb in baby food): Total Pb in reconstituted milk

Certified value: X_{ref} = 0.00068 mg·kg^{-1}; U_{ref} = mg·kg^{-1} (k=2); σ = 0.00015 mg·kg^{-1}



IMEP-113 / IMEP-33

	IMEP-113		IMEP-33	
	% Sat (z- ≤ 2)	% Uns (z- > 3)	% Sat (z- ≤ 2)	% Uns (z- > 3)
Cd Powder	90	9	81	9
Cd reconstituted	64	36	63	34
Pb Powder	7	93	19	79
Pb reconstituted	0 (75 % "less than")	-	20	72

In IMEP-33 9 labs have reported X_{lab} < LOD (!)

IMEP-113 / IMEP-33 Conclusions (I)

- **Satisfactory results for Cd** (powder).
  Less satisfactory for reconstituted milk,
- **Higher accuracy for more experienced labs**, follow an official method (15/35 did not in IMEP-113 and 26/62 in IMEP-33!), use of RM for validation,
- **Higher % of "less than" for Pb and an overestimation** (analyte level close to the LoD + high risk of contamination)

IMEP-113 / IMEP-33 Conclusions (II)

- **Difficulties in reporting for the reconstituted milk**
  10 out of 17 for IMEP-113
  18 out of 39 for IMEP-33 gave incoherent ratios powder/reconstituted
- **ICP-MS more accurate** for total Pb in IMEP-33
  Comparing to ET-AAS
- **90 % Cd (3 NRLs out of 31) z-score > 2**
  σ = 22 % → X_{lab}-X_{ref} > 44 %

Acknowledgements

- **All NRLs and IMEP-33 participants**
- **Expert laboratories → $X_{ref} \pm U_{ref}$**
- **I. Verbist, B. Kortsen (logistic support)**

European Commission

JRC 67522 – Joint Research Centre – Institute for Reference Materials and Measurements
Title: Sixth Workshop of the EU-RL Heavy Metals in Food and Feed
Author(s): B. de la Calle, B. Kortsen
Luxembourg: Publications Office of the European Union
2011 – 79 pp. – 21 x 29.7 cm

Abstract

The task of the EU-RL for Heavy Metals in feed and Food is to facilitate the implementation of Regulation (EC) No 1881/2006 and Directive 2001/22/EC establishing the maximum levels of heavy metals such as lead, mercury and cadmium in different foods and feed.

One of the duties of the EU-RL-HM is to organise a workshop for the network of National Reference Laboratories and to report on main subjects dealt with in the mentioned workshop.

This report summarises the discussions that took place during the 6th Workshop organised by the EU-RL-HM which took place in Brussels on 22th September 2011 and the agreements reached on that occasion.

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