‘Calibration and Traceability applied strategies in IMEP Interlaboratory Comparisons’ on measurements close to legal limits

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http://www.irmm.jrc.be
http://www.jrc.cec.eu.int
The promotion of a common European measurement system in support of EU policies, especially internal market, environment, health and consumer protection standards
IMEP objectives

- to enable assessment of measurement capability linked to EU policies
  - independent of private or national interest
- to enable assessment of equivalence of measurements
  - regional, national, international
- to link some key ILCs to internationally recognised measurement capabilities
  - transparency - same IMEP sample used in ILCs on all "metrological" levels
  - comparability/reliability of chemical measurement results
- to encourage participation in training activities after PTs
IMEP = ILC scheme with...

- Independent reference value
  - certification campaign, reference laboratories with demonstrated measurement capability
- “invite” participants to report measurement uncertainties
- Result-oriented evaluation of measurement performance
  - performance criteria as set relative to the reported value, but also to the reported measurement uncertainty
- Participants nominated via European/International Organisations AND regular field laboratories
IMEP reference value

• Independent from participants results

• Network of reference institutes with demonstrated measurement capabilities
  • National Metrology Institutes (NMIs)
  • Reference laboratories, expert laboratories

• Demonstrate measurement capability
  • demonstrated traceability and uncertainty
  • participation in internationally mutually recognized key comparisons and pilot studies, international recognised claims of measurement capabilities (CMCs)
  • BIPM KCDB database publicly available on the web
IMEP scope and IMEP analytes

- Environment
  - polyethylene, water, sediment, sewage sludge, fuel
- Health
  - Human serum
- Industry
  - car catalysts, isotopes in CO₂
- Food
  - water, wine, rice, tuna fish
- Trace Elements
  - Toxic, essential metals
- Organic components
  - PCBs, PAHs
- Organic components (clinical)
  - cholesterol, creatinine, amylase…..
- Organo-metal species
  - methylmercury
Demonstrate measurement capability

apply routine measurement procedure –
for
measurements close to upper limits as endorsed
in
Commission Regulation (EC) No 466/2001
and
IMEP-12: As, B, Cd, Cr, Cu, Fe, Mg, Mn, Ni and Pb in water

Synthetic water sample prepared by gravimetric addition of concentrated mono-elemental solutions in purified water

EC Directive 98/83/EC

⇒ threshold value of $44.5 \cdot 10^{-9}$ mol Cd /L

⇒ 348 participants from 46 countries !!!
IMEP-12: Trace Elements in Water

Certified value: $40.78 \times 10^{-9} \pm 0.82 \times 10^{-9} \text{mol}\cdot\text{L}^{-1}$

$[U = k \cdot u_c (k=2)]$

$E_n = \frac{x_{lab} - X_{ref}}{\sqrt{u_{lab}^2 + 0.05 X_{ref}^2}}$

Results from all participants according to analytical techniques used.

"Trueness % of parametric value" from EC Directive 98/83/EC
IMEP-12: Trace elements in Water

Certified value: \(40.78 \times 10^{-9} \pm 0.82 \times 10^{-9} \text{mol·L}^{-1}\) \([U = k \cdot u_c (k=2)]\)

Results from all participants according to the number of samples analysed per year.
IMEP-12: Trace Elements in Water

Certified value: \(40.78 \times 10^{-9} \pm 0.82 \times 10^{-9} \text{mol} \cdot \text{L}^{-1} \ [U=k \cdot u_c (k=2)]\)

Results from all participants by Calibration strategy.

- External aqueous standards
- External matrix matched standards
- Internal standard
- Standard addition

Values below -50%:
- External aqueous standards: 15
- External matrix matched standard: 1
- Internal standard: 1
- Standard addition: 0

Values above 50%:
- External aqueous standards: 26
- External matrix matched standard: 4
- Internal standard: 2
- Standard addition: 4

'Less than' value:
- External aqueous standards: 14
- External matrix matched standard: 0
- Internal standard: 2
- Standard addition: 0
IMEP-20: As, Hg, Pb, Se, MeHg in tuna fish

Real life sample taken off the market due to elevated Hg content

EC Regulation 466/2001
EC Directive 2001/22/EC

⇒ threshold value of 1 mg Hg /Kg

235 participants from 32 countries
IMEP- 20: Trace elements in Tuna Fish

Certified value : 4.32 ± 0.16 mg·kg⁻¹ \[ U = k \cdot u_c \ (k=2) \]

Results from all participants on the use of Certified Reference Materials. (CRMs)
IMEP-20: Trace elements in Tuna Fish
Certified value: $4.32 \pm 0.16 \text{ mg} \cdot \text{kg}^{-1}$ \[U=k \cdot u_c \ (k=2)\]

Results from all participants according to the Quality Management System.
IMEP- 20: Trace elements in Tuna Fish
Certified value: 4.32 ± 0.16 mg·kg⁻¹ \[U=k·u_c (k=2)\]

Results from all participants according to uncertainties calculated within the Guidelines of Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000).
Fit for purpose criteria in IMEP-20

- setting external specifications for required measurement quality

- IMEP-20: fit for purpose” performance criteria: 20% of $X_{ref}$ (corresponds to $\sigma = 0.1X_{ref}$ for z-scores)

$$E_n = \frac{x_{lab} - X_{ref}}{\sqrt{u_{lab}^2 + (0.1X_{ref})^2}}$$

with

$$|E_n| \leq 2 = \text{satisfactory}$$

$$2 < |E_n| < 3 = \text{questionable}$$

$$|E_n| \geq 3 = \text{unsatisfactory}$$

$$z = \frac{x_{lab} - X_{ref}}{0.1X_{ref}}$$

with

$$|z| \leq 2 = \text{satisfactory}$$

$$2 < |z| < 3 = \text{questionable}$$

$$|z| \geq 3 = \text{unsatisfactory}$$

- Setting criteria for minimum and maximum acceptable uncertainty

$$u_{ref} \leq u_{lab} \leq 0.1X_{ref}$$
Scoring: $E_n$-numbers

IMEP- 20: Trace elements in Tuna Fish

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

Results from all participants

Deviation from the certified value in %

±100%

±20%

±10%

±5%
IMEP-20: As in Tuna Fish
Results per instrumental technique

Percentage of participants per technique:
- ETAAS & GF-AAS: 37 part.
- FIAS-AAS, FAAS & AAS: 35 part.
- ICP-OES, ICP-AES: 17 part.
- ICP-MS & HR-ICP-MS: 24 part.
- OTHER: 10 part.
Using the same sample material in the interlaboratory comparisons at the various metrological levels

Measurement capabilities can be compared
Demonstration of competence, CMC claims: statements of the measurement capabilities of each NMI in a BIPM database publicly available on the Web.
Traceability to SI

Certified values (from isotopic CRM)
Expressed in SI units and/or traceable to SI

Calibrated ICP-MS measurements
traceable to SI

Calibrated weighing measurements
traceable to SI

## Uncertainty budget

Table 9: Main contributors to the total uncertainty

<table>
<thead>
<tr>
<th>Contributory factor</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Within bottle homogeneity</td>
<td>42.4</td>
</tr>
<tr>
<td>Water content (kf)</td>
<td>35.6</td>
</tr>
<tr>
<td>Deadtime blends</td>
<td>5.5</td>
</tr>
<tr>
<td>Between bottle homogeneity</td>
<td>4.9</td>
</tr>
<tr>
<td>Ratio measurement (207/206) K-factor for isotope composition</td>
<td>4.5</td>
</tr>
<tr>
<td>Ratio measurement (208/206) K-factor for blends</td>
<td>3.6</td>
</tr>
<tr>
<td>Hg isobaric overlap on isotopic composition</td>
<td>1.1</td>
</tr>
<tr>
<td>Ratio measurement for isotopic composition</td>
<td>0.7</td>
</tr>
<tr>
<td>Spike concentration</td>
<td>0.4</td>
</tr>
<tr>
<td>Others</td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Total expanded uncertainty (k=2)</strong></td>
<td><strong>1.7</strong></td>
</tr>
</tbody>
</table>
EU Food measurement infrastructure

- Annual report to the EC
- Promote advances in research to NRLs
- "Referee" for NRLs in case of disagreement
- Training courses for NRLs
- NRL PT result evaluation

91/664/EEC

Designation of CRLs

NRLs

Compulsory Participation in PTs

EU-legislation

EU council decision

Member states
Accreditation infrastructure


Demonstrate meas. capability

Compliance with ISO/IEC 17025 “uncertainty”

Measurement evaluation “scores”

Participation in PTs

Corrective actions

ILAC-MRA

EA-MLA

EA

Accredited laboratories

Nominated by ABs for participation in IMEP

44 accreditation bodies (international)

20 accreditation bodies (Europe)

34 accreditation bodies (Europe)

CIPM

Nominated by ABs

Accredited laboratories

Corrective actions

Participation in PTs

Measurement evaluation “scores”

Compliance with ISO/IEC 17025 “uncertainty”

Demonstrate meas. capability

memorandum of understanding
Trace elements in Tuna Fish with IMEP-20 certified value: 4.32 ± 0.16 mg·kg⁻¹ \[U=k\cdot u_c (k=2)\]

Results from CCQM-P39
IMEP-20

Trace elements in Tuna Fish

with IMEP-20 certified value: $4.32 \pm 0.16 \text{mg}\cdot\text{kg}^{-1}$ $[U=k\cdot u_c (k=2)]$

Results from CCQM-P39, NRLs

Results from CCQM-P39, NRLs

2 values NRL
below -50%
Trace elements in Tuna Fish
with IMEP-20 certified value: $4.32 \pm 0.16 \text{ mg} \cdot \text{kg}^{-1}$  
$[U=k \cdot u_c (k=2)]$

Results from CCQM-P39, NRLs and NRLs nominated participants
NMIs – NRLs – NRL nominated – regular food control laboratories

- CCQM-P39 and IMEP-20: Perfect demonstration of the measurement capabilities across the international measurement infrastructure for a measurement close to upper limit

National Metrology Institutes
National Reference Laboratories
Monitoring laboratories
Accredited field laboratories
Invited expert laboratories

Expert laboratories demonstrate capabilities on national level beyond the “closed walls” of NMIs

CCQM group meetings with NMIs, CODEX/AOAC, national food representatives and PT providers
Tuna Fish batch

CCQM-P39
NMIs

IMEP-20
Support to CRL-ISS
NRLs
(NRL nominated labs)

IMEP-20
EA nominated labs
Support to new member states
food field laboratories
expert labs MeHg

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

Results from all participants

IMEP-20 reference value

Deviation from the certified value in %

Hg

Results from all participants

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

Results from all NRL participants

IMEP-20 reference value

Deviation from the certified value in %

Hg

Results from all participants
water batch

EUROMET 528
RMOs

IMEP-15
WMO/GAW nominated laboratories

IMEP-12
EA nominated labs
Support to new member states
European and International field laboratories

Results from all participants
including "Trueness % of parametric value" from water directive 98/83/EC

IMEP-12: Trace elements in Water
Certified value: 40.78·10^-9 ± 0.82·10^-9 mol·L^-1 \[ U = k · u_c (k=2) \]

IMEP-15: Trace elements in Water
Certified value: 40.78·10^-9 ± 0.82·10^-9 mol·L^-1 \[ U = k · u_c (k=2) \]

Deviation from the certified value in %

20 25 30 35 40 45 50 55 60

Cd

1 'less than' value
4 values above 50%
2 values below -50%

EUROMET project 528 (Cd)

Vituki
ITM LGC
IRMM BAM
NMi
VUV WRI

CD

20.39 25.39 30.39 35.39 40.39 45.39 50.39 55.39 60.39

amount content (10^-12 mol/g)

IMEP-12 reference value

Results from all participants
including "Trueness % of parametric value" from water directive 98/83/EC
Step 1: select a few laboratories with non-satisfactory results for different typical experimental approaches (e.g. diff. techniques)

Step 2: identify labs who want to improve

Step 3: ‘on the spot’ investigation with educator under total non-disclosure (questionnaire)

Step 4: present results to all IMEP participants in anonymous way via the internet http://www.imep.ws
IMPROVING AFTER IMEP

ICP-MS

<table>
<thead>
<tr>
<th>GENERAL</th>
<th>As</th>
<th>Cd</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Ni</th>
<th>B</th>
<th>Pb</th>
<th>Cr</th>
</tr>
</thead>
</table>

- use of internal standards: multiple internal standards, check if $I_x/I_y = \text{const}$
  
  It was recommended that multiple internal standards should be used for evaluation. In case that the ratio of internal standards is 1, the result is OK. In case of different results, cross checks with respect to blank levels of the internal standards have to be performed. Moreover, an independent sample should be selected as QC standard.

- external calibration
  
  Take care that concentration of the sample is within the calibration range

- IDMS
  
  - select isotopes carefully (interference) check method for optimum RSD
  - select signal intensities ~200,000 to avoid uncertainty caused by deadtime => select blend ratio accordingly
  - choose carefully between optimum ratio due to error magnification factor and optimum ratio for ICP-MS (1:1)
IMPROVING AFTER IMEP

Nickel

value µg/L

IMEP 12 cert.  Lab X  follow up cert  Lab X follow-up

Lab X follow-up
Method validation and calibration

- CRMs used for method development and validation
- Minority of participants used CRMs regularly for quality assurance; CRMs in the field of food and feed only 10% of total CRMs but with increasing trend
- Standard solutions are used for instrumental calibration
- Matrix match of CRMs

Conclusion on measurement performance can only be drawn when information on recovery is taken into account !!!
Traceability

• Property of result of a measurement related to stated references (national, international standards, SI) through an unbroken chain of comparisons all having stated uncertainties

• Traceability can be established by the use of CRMs and assessment of measurement uncertainty

Why demonstration is needed….

• Traceability enables to demonstrate equivalence of measurement results

• International acceptance of measurement services/standards from different laboratories in view of mutual recognition agreements of national metrology, reference or accredited laboratories (CIP-MRA, EA-MLA)

• Required in view of compliance with ISO17025 (traceability to internationally accepted stated references together with their stated measurement uncertainties)
Reports and publications

- http://www.imep.ws
  - IMEP reports to participants (downloads)
  - IMEP certification reports (downloads)
  - References to all relevant publications (certification, scoring etc..)
  - Link to IMEP-EDUC web-site

  - Final reports on CCQM key comparisons and pilot studies

- http://www.bipm.org
  - BIPM KCDB: Calibration and Measurement Capabilities (CMC claims)
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• M. Lauwaars + team (FSQ-unit)
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• E. Garlick + team (INFunit, MILC system)