WORLD METEOROLOGICAL ORGANIZATION
GLOBAL ATMOSPHERE WATCH

No. 154

WMO/IMEP-15 TRACE ELEMENTS IN WATER LABORATORY INTERCOMPARISON

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WMO TD No. 1195
FOREWORD

The collection/processing/analysis of trace metals in atmospheric precipitation and in aerosols still presents an enormous challenge for the Global Atmosphere Watch programme (GAW). It demands continuous quality assurance efforts by the GAW Scientific Advisory Group for Precipitation Chemistry and the Quality Assurance/Scientific Activity Centre-Americas. Laboratory intercomparisons as well as harmonisation among networks (GAW, EMEP, etc) are an essential element of quality assurance as are the provision of suitable standard reference materials. The latter is of utmost importance as it warrants comparable results within and across networks. The “ideal” standard reference material should provide concentration levels relevant to the concentrations found in ambient air, in particular, the uncertainty of the reference values should be close to the detection limit for the trace elements under consideration. However, this challenge has by and large not been met in the IMEP-15 quality assurance experiments. Nevertheless, the IMEP-15 results clearly demonstrate the difficulty in measuring “accurately” even high concentrations of trace elements under the stringent data quality objectives set by IMEP. IMEP-15 is intended as a first of a series of quality assurance experiments that will and must be continued and continuously refined, particularly with emphasis on levels of trace elements in precipitation.

Prof. Volker Mohnen
(Head of QA/SAC Americas)
ABSTRACT

The aim of IMEP® (International Measurement Evaluation Programme) is to present objectively the quality of chemical measurements. Participants in an IMEP® interlaboratory comparison compare their reported measurement results with independent external certified reference values with demonstrated traceability and uncertainty, as evaluated according to international guidelines. IMEP-15 was offered by IRMM to the World Meteorological Organization (WMO) of the United Nations. This interlaboratory comparison focused on measurements of Trace Elements in Water aiming to support the European Commission directive 98/83/EC on quality of water intended for human consumption. 25 laboratories were nominated via the Quality Assurance / Science Activity Centre (QA/SAC) for the Americas, which is part of the Global Atmosphere Watch (GAW) programme of the WMO to report measurements results on 10 trace elements in a synthetic water sample. In this paper suggestions for the evaluation of measurement performance of these laboratories are made for measurements of Cd, Cu, Ni and Pb using new simple graphical tools, the ‘Naji-plots’. The performance criteria applied are in accordance with the performance characteristics as stated in the European Commission directive 98/83/EC.
1. **INTRODUCTION**

The International Measurement Evaluation Programme (IMEP®) was established in order to shed light on the current state of practice in chemical amount measurements. Since 1988 IMEP® has been providing assistance to European Union member states and candidate countries to encourage the development of their national measurement systems. The overarching goal of this assistance is the creation of a common measurement system in support of EU policies (e.g. Consumer Protection and Public Health, Single Market, Environment, Research and Technology, External Trade and Economic Policies). Field laboratories participating in an IMEP® interlaboratory comparison carry out chemical measurements using their routine analytical set-up on the IMEP®-certified test sample (CTS) with undisclosed certified reference values. This CTS is well characterised with certified reference values, completely independent from the participants’ results. By comparing the individual measurement results of the participants with these certified reference values, field laboratories can demonstrate the quality of their measurement results. This makes IMEP® a unique interlaboratory comparison programme compared to general Proficiency Testing schemes (PTs) where in most cases the PT-reference values are derived from statistical data evaluation of participants’ results. A practice that has also been innovative with the IMEP® programme right from the beginning is that participants in IMEP® have always been invited to state uncertainty estimates for their reported results. For several years now, a rising awareness has been created throughout the “analytical measurement community” that realistic uncertainty statements are an indispensable part of all reliable measurement results. This includes chemical measurements. Particularly, laboratories that have to comply with ISO 17025, the standard for the competence of testing and calibration laboratories, are obliged to provide measurement results with uncertainties. The IMEP® approach is therefore a ‘best practice’ from a metrological point of view.

2. **THE WORLD METEOROLOGICAL ORGANIZATION (WMO)**

In 1951 the WMO was established as a specialized agency of the United Nations. Today there are 185 Members, comprising 179 Member States and six Member Territories to the WMO. Within the United Nations, the WMO provides the authoritative scientific voice on the state and behaviour of the Earth’s atmosphere and climate. To this end, the Atmospheric Research and Environment Programme (AREP) co-ordinates and stimulates research on the composition of the atmosphere, the physics and chemistry of clouds, weather modification techniques, tropical meteorology processes and weather forecasting, focusing on extreme weather events and socio-economic impacts [1]. The Global Atmosphere Watch (GAW) programme of the WMO provides reliable long-term observations of the chemical composition of the atmosphere and related parameters in order to improve the understanding of atmospheric chemistry, and to organize assessments in support of formulating environmental policy [2]. The Quality Assurance / Science Activity Centre for the Americas (QA/SAC) is part of the GAW programme [3].

3. **IMEP®-15 “TRACE ELEMENTS IN WATER”**

Water is the most essential and precious resource for the wellbeing of all living species on the planet. Water availability in nature depends on climate, geographical and regional/seasonal influences. Anthropogenic increase of pollutants in water has become a serious threat to the preservation of water supply and water quality for generations to come. Nowhere is this need more accurate than for the water used in domestic and industrial food production processes.

**Keywords**: measurement performance evaluation, interlaboratory comparison, water analysis, trace elements, Naji-plots, uncertainty, World Meteorological Organization

Awareness throughout the international community has been raised that legislative measures are required to ensure that water intended for human consumption is wholesome and clean in order to protect human health from the adverse effects of any contamination. Within the EU this objective is met in the relevant EC directive 98/83/EC [4]. It is stated in article 7 of this directive that it is obligatory to monitor the water quality by means of frequent measurements. Hence, measurements of metals in water play a key role in complying with this directive. IMEP-15 “Trace Elements in Water” was offered by IRMM to the Scientific Advisory Group for Precipitation Chemistry (SAG-PC) for laboratories nominated via the QA/SAC Americas. The SAGs are scientific bodies nominated by the EC Panel of the WMO that assist in management and implementation of the various sections of the GAW programme. Specifically, the SAG-PC oversees the collection of precipitation chemistry data and provides policy direction to the QA/SAC Americas, which is tasked with implementing the GAW precipitation programme. In the past, the QA/SAC Americas (or its predecessors) had organised on regular basis comparisons on trace metal analysis in rainwater for WMO/GAW laboratories to participate. Recently, the SAG-PC decided to discontinue this activity. Therefore the WMO/GAW were pleased to offer their nominated laboratories the opportunity to participate in IMEP-15. Furthermore, participation in IMEP-15 was of great interest to the QA/SAC in view of the intended collaboration between the WMO and the CIPM (International Committee for Weights and Measures) [5] focusing on the standardisation, accuracy and reliability of data obtained in the course of its work.

Participants in IMEP-15 were offered to measure the amount content of As, B, Cd, Cr, Cu, Fe, Mg, Mn, Ni and Pb in a water Certified Test Sample (CTS). The same CTS was also offered to participants in IMEP-12 [6] and to EUROMET (project 528 [7]). In such a way, the WMO/GAW nominated laboratories could compare their results with the results of laboratories that represent their country at EUROMET level and with other field laboratories from all over the world.

4. THE CERTIFIED TEST SAMPLE

The water samples were synthetically prepared at the Institute for Agrobiotechnology (IFA, Tulln, Austria). The whole water batch was prepared by gravimetric addition of concentrated mono-elemental solutions in purified water in order to keep the concentration of the elements close to the relevant limits as stated in the water directive. Stability and homogeneity were assessed and to be found fit for purposes. Certified reference values in IMEP® are required to demonstrate traceability and they should have a demonstrated an adequately small uncertainty, as evaluated according to international guidelines. Four renowned reference laboratories were selected:

- BAM (Bundesanstalt für Materialforschung und –prüfung – Berlin, Germany)
- BOKU (University of Agricultural Sciences – Wien, Austria)
- LGC (Laboratory of the Government Chemist – Teddington, United Kingdom)
- NMIJ (National Measurement Institute of Japan – Tsukuba, Japan)

Along with the IRMM, these laboratories established the reference values of the water CTS. These laboratories have a proven record to fulfil the terms required for reference laboratories in IMEP®[8]. A certificate with the IMEP-15 reference values as listed in Table 1 was issued and distributed to all IMEP-15 participants. The complete information on the characterisation of the CTS and the establishment of the IMEP-15 reference values can be found in the IMEP-12 certification report [9].

Table 1: Certified amount concentrations of trace elements in the IMEP-15 CTS

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference Value with expanded uncertainty ($U_{ref} = k \cdot u_{ref}$, coverage factor $k = 2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>(0.121 ± 0.012) µmol/L</td>
</tr>
<tr>
<td>Boron</td>
<td>(12.11 ± 0.24) µmol/L</td>
</tr>
<tr>
<td>Cadmium</td>
<td>(40.78 ± 0.82) nmol/L</td>
</tr>
<tr>
<td>Chromium</td>
<td>(1.010 ± 0.029) µmol/L</td>
</tr>
<tr>
<td>Copper</td>
<td>(3.412 ± 0.068) µmol/L</td>
</tr>
<tr>
<td>Iron</td>
<td>(3.805 ± 0.091) µmol/L</td>
</tr>
<tr>
<td>Lead</td>
<td>(42.27 ± 0.85) nmol/L</td>
</tr>
<tr>
<td>Magnesium</td>
<td>(1.590 ± 0.032) mmol/L</td>
</tr>
<tr>
<td>Manganese</td>
<td>(1.30 ± 0.13) µmol/L</td>
</tr>
<tr>
<td>Nickel</td>
<td>(0.3951 ± 0.0079) µmol/L</td>
</tr>
</tbody>
</table>

5. PARTICIPANTS IN IMEP-15

IMEP-15 was offered by IRMM free of charge as support of the EU to the WMO. The nomination of laboratories for IMEP-15 was co-ordinated by the QA/SAC Data Manager responsible for quality assurance of the WMO/GAW precipitation chemistry data. 34 laboratories in 29 countries were nominated for participation in IMEP-15. Eventually, 25 participants, from 23 countries and 4 continents, reported measurement results. The list of participating countries is given in Table 2. The participants reported their measurement results and the questionnaire information online via the IMEP® web-site [10]. The large majority of the participants used the analytical techniques they routinely apply for measurements of element content in similar type of samples. The toxic elements such as cadmium, nickel and lead have been measured by the majority (> 90%) of IMEP-15 participants, while copper was measured by all participants. Chromium, arsenic, iron, magnesium, and manganese were in a second category (measured by 60-90% of participants) and the least popular element was boron, which was measured by half of the participants. Table 3 summarises the response of the IMEP-15 participants to the questions concerning their regular participation in PT schemes, their uncertainty estimation/reporting and their use of water CRMs. More information about the logistics and the data evaluation in IMEP-15 are given in the IMEP-15 participants’ report [11]. Furthermore all the reported measurement results are presented graphically in this report. The results are grouped according to different criteria from specific questionnaire information. The IMEP-15 report to participants was distributed to all IMEP-15 participants and can also be downloaded from the IMEP® web-site [10].

Table 2: Geographical distribution of the laboratories from 23 countries reporting measurement results in IMEP-15

<table>
<thead>
<tr>
<th>Continent</th>
<th>Countries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Africa</td>
<td>Tunisia</td>
</tr>
<tr>
<td>Americas</td>
<td>Chile</td>
</tr>
<tr>
<td>Asia</td>
<td>Mongolia; Thailand; United Arab Emirates.</td>
</tr>
<tr>
<td>Europe</td>
<td>Czech Republic; Finland; France; Germany; Iceland; Italy; Latvia; Norway; Poland; Portugal; Republic of Cyprus; Russia; Slovak Republic; Spain; Switzerland; The Netherlands; United Kingdom; Yugoslavia</td>
</tr>
</tbody>
</table>

Table 3: Summary of replies to the IMEP-15 questionnaire

<table>
<thead>
<tr>
<th>Question</th>
<th>Yes</th>
<th>No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regular participation in PT schemes for this type of analysis?</td>
<td>74%</td>
<td>26%</td>
</tr>
<tr>
<td>Routinely use of water CRMs for quality assurance?</td>
<td>70%</td>
<td>30%</td>
</tr>
<tr>
<td>Routinely report uncertainty on chemical measurements to their customers?</td>
<td>35%</td>
<td>65%</td>
</tr>
<tr>
<td>Report measurement uncertainty in IMEP-15?</td>
<td>78%</td>
<td>22%</td>
</tr>
<tr>
<td>Reported measurement uncertainty according to GUM?</td>
<td>61%</td>
<td>39%</td>
</tr>
</tbody>
</table>

6. SUGGESTION FOR PERFORMANCE EVALUATION OF NOMINATED LABORATORIES IN IMEP-15

One of the main characteristics of IMEP® interlaboratory comparisons is that reference values are independent from the participants' results and are established using as far as possible primary methods of measurements [12]. The comparison of the participants' reported measurement results with the reference values and the consequent evaluation of performance is therefore straightforward. However, IRMM has never commented on the quality of the measurement results. For the first time IRMM issued in the frame of the recent IMEP-19 comparison individual certificates to each participant that included the reported measurement value for the CTS, the certified reference values and the deviation of the reported value from the certified value by percentage [13]. Furthermore normalised errors, 'E_r-numbers' [14], were calculated for those participants who declared that they reported measurement results with uncertainties calculated according to the Guides for Quantifying Measurement Uncertainty (GUM) issued by the

International Organization for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000) [15, 16].

Not only are maximum levels of metals are set in the directive 98/83/EC on the quality of water intended for human consumption, but also performance characteristics are specified in this directive. Furthermore, the directive specifically requires laboratories to [...] be capable of measuring concentrations equal to the parametric value with a trueness, precision and limit of detection specified [...]. For the metals under investigation in IMEP-15 the “trueness of parametric value” is stated to be 10% (\(U = k \cdot u_c\), coverage factor \(k = 2\)). This performance criterion set in the relevant directive was consequently used when evaluating the measurement results of the IMEP-15 participants. As in all IMEP® interlaboratory comparisons full confidentiality was guaranteed with respect to the link between result and identity of the participant.

The evaluation of results reported for IMEP-15 was performed using the \(z\)-scores and \(E_n\)-numbers calculated according to [17].

The following equations were used:

\[
z\text{-score} = \frac{x_{lab} - X_{ref}}{0.05 X_{ref}} \quad (1)
\]
\[
E_n\text{-number} = \frac{x_{lab} - X_{ref}}{\sqrt{u_{lab}^2 + (0.05 X_{ref})^2}} \quad (2)
\]

\(x_{lab}\) is the reported value of an IMEP-15 participant
\(u_{lab}\) is the combined measurement uncertainty of an IMEP-15 participant
\(X_{ref}\) is the reference value.

The “trueness of parametric value” criterion as stated in the water directive \(X_{ref} \pm 0.05 \cdot X_{ref}\) (combined uncertainty) was used as performance evaluation reference value.

Common application for \(z\)-scores:
- “satisfactory” results are obtained when \(|z| \leq 2\)
- “preventive” actions may be considered when \(2 < |z| \leq 3\)
- “corrective” actions must be implemented when \(|z| > 3\)

Similar conclusions are drawn from \(E_n\)-numbers:
\(|E_n| \leq 2 \Leftrightarrow \text{“satisfactory” results;}
\(|E_n| > 3 \Leftrightarrow \text{“corrective” action.}

Applying (1) and (2), a laboratory reporting a result \((x_{lab})\) that deviates by 10% from the reference value will have a \(z\)-score equal to 2 and \(|E_n| \leq 2\), depending on the combined uncertainty \((u_{lab})\). Only 61% of the IMEP-15 participants quantified their measurement uncertainty according to GUM and/or EURACHEM/CITAC [15, 16]. Other participants used measurement repeatability (2s) or method validation data obtained from quality control charts to estimate their uncertainties.

Laboratories that reported no uncertainty value \((u_{lab} = 0)\) obtain an \(E_n\)-number equal to the \(z\)-score.

IMEP® graphs sorted by ascending \(E_n\)-numbers including all reported IMEP-15 measurement results are presented for Cd, Cu, Ni and Pb, the four elements measured by a large majority of IMEP-15 participants (Figures 1a, 2a, 3a, and 4a). Unlike traditional IMEP® graphs, the grey range is not the “certification-range” (Table 1) \(X_{ref} \pm U_{ref}\) with \(U_{ref} = k \cdot u_{cref}\), coverage factor

$k = 2$, but represents the “performance evaluation reference range”, $X_{ref} \pm 0.05 \cdot X_{ref}$ used as “target” performance criterion in this article. The maximum scale of the graphs is set for convenience to $\pm 50\%$ from the reference value. The results outside this scale are not presented graphically but the total number of these results is provided in the corresponding textboxes. The general IMEP-15 graphs presenting the participants’ measurement results with the reference values within its uncertainty can be found in the IMEP-15 participants’ report [11].

7. GRAPHICAL EVALUATION OF IMEP-15 PARTICIPANTS RESULTS, THE ‘NAJI PLOTS’

P. Robouch, Naji Younes and Peter Vermaercke recently described a simple graphical approach [17] to present the laboratory performance in an interlaboratory comparison (ILC). This approach is designed for ILC schemes with independently determined reference values, such as IMEP<sup>®</sup>. The “Naji Plot” provides information about $E_n$-numbers while comparing on the abscissa the laboratory results with the reference value (cf. z-score) and on the ordinate the ratio of reported uncertainties to the target/nominal uncertainty (i.e. $0.05 \cdot X_{ref}$). Assuming that the $E_n$-number is smaller than a certain criteria $C$ ($E_n \leq C$), one derives the following relation described in [17].

$$E_n = \frac{x_{lab} - X_{ref}}{u_{lab}^2 + (0.05 \cdot X_{ref})^2} \leq C \quad \Leftrightarrow \quad \left[ \frac{1}{C^2} \left( \frac{x_{lab} - X_{ref}}{0.05 \cdot X_{ref}} \right)^2 \right] - 1 \leq \left( \frac{u_{lab}}{0.05 \cdot X_{ref}} \right)^2$$

$$\Leftrightarrow \frac{z^2}{C^2} - 1 \leq \left( \frac{u_{lab}}{0.05 \cdot X_{ref}} \right)^2$$

(3)

When plotting z-scores on the abscissa versus the squared ratio of the reported laboratories’ uncertainties to the target uncertainty on the ordinate, one obtains three sets of parabolas for $C = 1$, 2 or 3, respectively. These parabolas delimit the different $E_n$-number performance criteria domains mentioned earlier:

a) $|E_n| \leq 1$;
b) $1 < |E_n| \leq 2$;
c) $2 < |E_n| \leq 3$
d) $|E_n| > 3$.

Only two of these parabolas ($C = 2$ and 3, dashed and straight line, respectively) are presented in Figures 1b, 2b, 3b and 4b for Cd, Cu, Ni and Pb. Laboratories having reported no uncertainty are plotted on the abscissa ($u_{lab} = 0 \Rightarrow E_n = z$).

8. DISCUSSION

At first, several general observations should be mentioned. As the IMEP-15 reference values are independent of the participants’ reported measurement results no outlier tests are required; all results are to be treated alike. In general, about 55% of the IMEP-15 participants reported “satisfactory” results. (But 8% of the results were reported without any uncertainty at all). Approximately 30% outlying values ($|E_n| > 3$) were reported for which “corrective” actions need to be identified and implemented. For about 15% several “preventive” actions ($2 < |E_n| \leq 3$) may also be expected (Table 4).
The four Naji-plots presented (Figures 1b, 2b, 3b and 4b) urge for additional criteria of an acceptable uncertainty range: some IMEP-15 participants report “huge” uncertainties, other report very small or no uncertainties at all. On the one hand the water directive clearly states what should be the maximal acceptable uncertainty:

\[ u_{\text{lab}} \leq 0.05 \cdot X_{\text{ref}} \]

Laboratories reporting larger uncertainties may not have their experimental procedure under control, or may have overestimated some uncertainty components. On the other hand, it is fairly unlikely and also unnecessary that routine or field laboratories fulfil the terms required for reference laboratories in IMEP®. A reasonable estimate of the minimal acceptable uncertainty can therefore be derived from the reference uncertainty of the water CTS as determined by the IMEP-15 reference laboratories (Table 1):

\[ u_{\text{ref}} \leq u_{\text{lab}} \]

For the 4 elements under investigation the certified reference values have a relative uncertainty of 2%. They represent the state of the art of the measurement under investigation. Laboratories reporting no or smaller uncertainty are very likely to have underestimated some of the uncertainty components or did not take some sources of uncertainty into account.

These maximum and minimum acceptable uncertainty criteria are presented in the ‘Naji-plot’ as two horizontal dashed lines. The first one for \((u_{\text{lab}}/0.05 \cdot X_{\text{ref}})^2 = 1\) corresponding to \(u_{\text{lab}} = 0.05 \cdot X_{\text{ref}}\). The second one for \((u_{\text{lab}}/0.05 \cdot X_{\text{ref}})^2 \approx 0.04\) corresponding to \(u_{\text{ref}} = u_{\text{lab}}\). A detailed analysis of the compliance of IMEP-15 participants with these two uncertainty criteria is only appropriate for laboratories having reported “satisfactory” results (\(|En| \leq 2\)). From Table 4 it can be seen that to average about 30% “satisfactory” results within an “acceptable uncertainty” were reported. Best results were achieved for Cu with 44% of the IMEP-15 participants reporting satisfactory results within acceptable uncertainties.

**Table 4: Review of the participants’ performance in IMEP-15**

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>En</td>
<td>&gt; 3)</td>
<td>48%</td>
<td>20%</td>
</tr>
<tr>
<td>(2 \leq</td>
<td>En</td>
<td>\leq 3)</td>
<td>-</td>
<td>8%</td>
</tr>
<tr>
<td>(</td>
<td>En</td>
<td>\leq 2)</td>
<td>52%</td>
<td>72%</td>
</tr>
<tr>
<td>(</td>
<td>En</td>
<td>\leq 2), (u_{\text{lab}} &gt; 0.05 \cdot X_{\text{ref}})</td>
<td>17%</td>
<td>8%</td>
</tr>
<tr>
<td>(u_{\text{lab}} &lt; u_{\text{ref}})</td>
<td>-</td>
<td>4%</td>
<td>-</td>
<td>5%</td>
</tr>
<tr>
<td>(u_{\text{lab}} = u_{\text{ref}})</td>
<td>9%</td>
<td>16%</td>
<td>5%</td>
<td>5%</td>
</tr>
<tr>
<td>(u_{\text{ref}} \leq u_{\text{lab}} \leq 0.05 \cdot X_{\text{ref}})</td>
<td>26%</td>
<td>44%</td>
<td>18%</td>
<td>29%</td>
</tr>
<tr>
<td>Total number of reported measurement results (^{(i)})</td>
<td>23</td>
<td>25</td>
<td>22</td>
<td>24</td>
</tr>
</tbody>
</table>

\(^{(i)}\) excluding reported upper limits

\(^(*)\) no uncertainty reported
9. CONCLUSION

IMEP-15 is another example confirming once more the benefit for participation in an interlaboratory comparison where reference values are independently determined from the participants’ results. The evaluation of the reported results was made according to performance criteria set by the water directive 98/83/EC. This directive explicitly requires: [the measurement results to be within 10% relative uncertainty encompassing the “true amount content value”]. The suggested performance evaluation of the GAW/WMO nominated laboratories in IMEP-15 was done according to best metrological practice and to the above-mentioned directive. Each of the presented “Naji-plots” clearly delimits the satisfactory performance area: \(|E_n| \leq 2\), and \(u_{\text{ref}} \leq u_{\text{lab}} \leq 0.05 \cdot x_{\text{ref}}\). A rapid overview of over- or underestimated uncertainty is directly available. These plots are a helpful tool for the SAG-PC of the GAW/WMO to evaluate the performance of their nominated laboratories in IMEP-15. It may help the QA/SAC responsible to nominate laboratories for future participation in similar exercises.

Acknowledgement

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Figure 1a: Cd-results from GAW/WMO nominated laboratories in IMEP-15 sorted by ascending $E_n$-number;
Performance evaluation reference value: $40.78 \pm 2.04 \text{ nmol} \cdot \text{L}^{-1} \ [U = 0.05 \cdot X_{ref}]

Figure 1b: “Naji-plot” of Cd-results from GAW/WMO nominated laboratories in IMEP-15

IMEP 15 - Cd

$(u_{lab}/(0.05 X_{ref})^2$ $|E_n| > 3$

$|E_n| > 3$

$|E_n| < 2$

$|u_{lab} = 0.05 X_{ref}$

$|u_{lab} = U_{ref}$

Deviation from the certified value in 

$e_{\text{nmol.L}^{-1}}$

$\Delta$ $|E_n| > 3$

$\Delta$ $|E_n| > 3$

$|E_n| < 2$

$2$ values below $-50\%$

$4$ values above $50\%$

$u_{lab} = \text{combined participant's uncertainty}$

$u_{lab} = \text{U}_{\text{ref}}$

$u_{lab} = 0.05 \cdot X_{\text{ref}}$
Figure 2a: Cu-results from GAW/WMO nominated laboratories in IMEP-15 sorted according to ascending En-number;
Performance evaluation reference value: 3.412 ± 0.171 µmol·L⁻¹ \([U=0.05\cdot X_{\text{ref}}]\)

Figure 2b: “Naji-plot” of Cu-results from GAW/WMO nominated laboratories in IMEP-15
Figure 3a: Ni-results from GAW/WMO nominated laboratories in IMEP-15 sorted according to ascending $E_n$-number; Performance evaluation reference value: $0.3951 \pm 0.0198 \, \mu\text{mol}\cdot\text{L}^{-1}$ [$U = 0.05 \cdot X_{\text{ref}}$]

Figure 3b: “Naji-plot” of Ni-results from GAW/WMO nominated laboratories in IMEP-15
Figure 4a: Pb-results from GAW/WMO nominated laboratories in IMEP-15 sorted according to ascending $E_n$-number; Performance evaluation reference value: $42.27 \pm 2.11 \text{nmol} \cdot \text{L}^{-1}$ [$U = 0.05 \cdot X_{ref}$]

Figure 4b: “Naji-plot” of Pb-results from GAW/WMO nominated laboratories in IMEP-15

\[ \left( \frac{u_{lab}}{0.05 \cdot X_{ref}} \right)^2 \]
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43. Recent progress in sunphotometry (determination of the aerosol optical depth). November 1986.


58. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at BAPMoN sites for the years 1986 and 1987 (WMO TD No. 306).


62. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at BAPMoN sites for the year 1988 (WMO TD No. 355).


69. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at Global Atmosphere Watch (GAW)-BAPMoN sites for the year 1989 (WMO TD No. 400).


72. Integrated Background Monitoring of Environmental Pollution in Mid-Latitude Eurasia by Yu.A. Izrael and F.Ya. Rovinsky, USSR (WMO TD No. 434).


75. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at Global Atmosphere Watch (GAW)-BAPMoN sites for the year 1990 (WMO TD No. 447).


77. Report of the WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques, Lake Arrowhead, California, 14-19 October 1990.


84. Provisional Daily Atmospheric Carbon Dioxide Concentrations as measured at GAW-BAPMoN sites for the year 1991 (WMO TD No. 543).

85. Chemical Analysis of Precipitation for GAW: Laboratory Analytical Methods and Sample Collection Standards by Dr Jaroslav Santroch (WMO TD No. 550).


89. 4th International Conference on CO$_2$ (Carqueiranne, France, 13-17 September 1993) (WMO TD No. 561).


91. Extended Abstracts of Papers Presented at the WMO Region VI Conference on the Measurement and Modelling of Atmospheric Composition Changes Including Pollution Transport, Sofia, 4 to 8 October 1993 (WMO TD No. 563).


97. Quality Assurance Project Plan (QAPjP) for Continuous Ground Based Ozone Measurements (WMO TD No. 634).


104. Report of the Fourth WMO Meeting of Experts on the Quality Assurance/Science Activity Centres (QA/SACs) of the Global Atmosphere Watch, jointly held with the First Meeting of the Coordinating Committees of IGAC-GLONET and IGAC-ACE, Garmisch-Partenkirchen, Germany, 13 to 17 March 1995 (WMO TD No. 689).


113. The Strategic Plan of the Global Atmosphere Watch (GAW) (WMO TD No. 802).


120. WMO-UMAP Workshop on Broad-Band UV Radiometers (Garmisch-Partenkirchen, Germany, 22 to 23 April 1996) (WMO TD No. 894).


126. Guidelines for Site Quality Control of UV Monitoring (lead author A.R. Webb) (WMO TD No. 884).


129. Guidelines for Atmospheric Trace Gas Data Management (Ken Masarie and Pieter Tans), 1998 (WMO TD No. 907).


131. WMO Workshop on Regional Transboundary Smoke and Haze in Southeast Asia (Singapore, 2 to 5 June 1998) (Gregory R. Carmichael). Two volumes.


133. Workshop on Advanced Statistical Methods and their Application to Air Quality Data Sets (Helsinki, 14-18 September 1998) (WMO TD No.956).


135. Sixth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Zurich, Switzerland, 8-11 March 1999) (WMO TD No.1002).


139. The Fifth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting (Halkidiki, Greece, September 1998) (WMO TD No. 1019).


146. Quality Assurance in monitoring solar ultraviolet radiation: the state of the art (WMO TD No. 1180).

147. Workshop on GAW in RA VI (Europe), Riga, Latvia, 27-30 May 2002.


149. Comparison of Total Ozone Measurements of Dobson and Brewer Spectrophotometers and Recommended Transfer Functions (prepared by J. Staehelin, J. Kerr, R. Evans and K. Vanicek) (WMO TD No. 1147).

150. Updated Guidelines for Atmospheric Trace Gas Data Management (Prepared by Ken Maserie and Pieter Tans (WMO TD No. 1149).

