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COOPERATION BETWEEN NMIs AND PROFICIENCY TESTING PROVIDERS CAN IMPROVE THE QUALITY OF ANALYSES

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Abstract: Certified Reference Materials and Proficiency Testing Schemes are essential tools to ensure the quality of analyses of "field" chemical laboratories. LNE, the French National Metrology Institute has participated in a proficiency test, organized by BIPEA, on the determination of mercury and selenium in drinking water to guarantee the traceability of laboratory measurement to the SI unit. This new cooperation between NMI and PT providers allows to establish new traceability schemes for chemical analyses.

Keywords: Proficiency testing, traceability, chemical metrology.

1. INTRODUCTION

Accreditation of laboratories for chemical analyses is an essential quality management tool and a means to obtain confidence and comparability of results. Due to the recent introduction of the international standard ISO/CEI 17025 [1], field laboratories have expressed their need of specific traceability schemes to ensure the reliability of chemical measurements. These traceability schemes are mainly based on the use of Certified Reference Materials (CRMs). The way to establish the traceability in chemical analysis is different from the physical measurements [2-3]. In chemical metrology, it is essential to use different kinds of "etalons" to ensure the traceability of measurements to the SI:

- Pure solutions for the calibration of analytical instruments
- Matrix reference materials similar to "real" samples in order to validate the analytical protocol.

The high number of reference materials currently available, around 20 000, is far from covering the needs of laboratories, particularly in some fields such as environment, where matrix effect play a very important role on the analytical procedure. Considering the overall cost to produce certified reference materials, it will never exist enough matrix reference materials for covering all parameters routinely analysed.

Interlaboratory comparisons and especially proficiency testing schemes (PTS) are common tools proposed to field laboratories to evaluate their competency [4]. In Europe, more than 800 PTS are regularly organised in various scientific sectors, particularly in chemistry. In the field of environment, the number of analytical parameters proposed in the different PTS is much higher than the number of CRMs available. For instance, in water analysis, 250 parameters are covered by PTS while only 30 are offered by CRMs to laboratories for methods validation. In a sense, PTS can be considered as an efficient tool to compensate the lack of CRMs and for ensuring the quality of analyses. However, the metrological traceability of the consensus value of a PTS is rarely established since assigned values are usually determined through statistical calculations taking into account the results of all the participant laboratories [5].

2. TRACEABILITY OF CONSENSUS VALUES

2.1. Role and use of PTS

Proficiency testing schemes are one important means for the assessment of the quality of routine measurements performed by laboratories, they consist of interlaboratory comparison. They also represent an objective assessment of the quality of analyses through the comparison of results with other laboratories, known as external quality assessment. The PT provider will carry out the following steps:

-1 Determination of the assigned vale (for instance: X: robust average, ISO 5725-5 algo A)

-2 Determination of the standard uncertainty for proficiency assessment (for instance: robust standard deviation S*, ISO 5725-5 algo A)

-3 Calculation of performance statistics (for instance: z score z=(xi – X)/S* lower than 2)

According to the type of assigned value chosen, the traceability increases from low to high level of traceability:

- Consensus values based on the results of all participating laboratories
- Consensus values based on selected laboratories
- Reference values
- Certified reference values
- "Calculated values"

2.2. Assigned values evaluated from PTS results

The evaluation of the assigned value and of its uncertainty can be obtained using ISO/FDIS 13528 standard (§5.5 and 5.6) according to the following formula:

When using the consensus value from expert laboratories, the assigned value X is the robust mean and its uncertainty is given by equation 1.

$$u_X = \frac{1,23}{p'} \times \sqrt{\sum_{i=1}^{i=p} u_i^2}$$

In that case, a possible unknown bias in the results of expert laboratories may exist; the traceability is not proved.

When the consensus value X is obtained from all participants, the assigned value is also the robust mean and its uncertainty is expressed as, equation 2:

$$u_X = 1,23 \times s^* / \sqrt{p}$$

This is the usual method carried out by PT providers, the traceability is also not demonstrated.

2.4. Assigned values evaluated from "external" results

The evaluation of the assigned value and of its uncertainty can be obtained using ISO/FDIS 13528 standard (§5.2, §5.3 and 5.4):

- Formulation: ISO/FDIS 13528 §5.2 : X is obtained by calculation and u(X) is evaluated according to GM. This is the case, for instance for the gravimetric preparation of pure substances.
- ~~Certified reference value ISO/FDIS 13528 §5.3: X~~ and u(X) are given in the certificate. Its obviously

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depends on the availability of CRMs and could be expensive.

- Reference value ISO/FDIS 13528 §5.4, equations 3 and 4:

$$X = X_{CRM} + \overline{D} \qquad (3)$$

$$u_X = \sqrt{u_{CRM}^2 + u_D^2} \qquad (4)$$

X_{CRM} is the value of the CRM; D is the difference between the value of the PT sample and the CRM. This is the recommended method by ISO 13528.

3. COOPERATION WITH PT PROVIDERS

3.1. Context of the cooperation with PT provider

LNE, the French Metrological Institute has recently been more active helping improving the quality of measurements of field laboratories. The objective is to obtain traceable reference values for PT schemes. This is derived from ISO/FDIS 13528 §5.4, presented above; but the PTS sample is not compared to a CRM but is actually analysed with a primary method.

In France 27 PT providers are registered in the EPTIS database and are routinely carrying out 160 schemes. A collaboration was initiated with BIPEA (Bureau InterProfessionnel d'Etudes Analytiques) which is accredited since 2004. It has around 1000 members in 40 countries. The cooperation was performed on analyses of heavy metals in dinking water.

Another collaboration has been initiated with EMD (Ecole des Mines de Douai, an Engineer School at the University level), member of the Central Laboratory of Air
(1) Quality Survey. It concerned analysis of heavy metals in air particles.

3.2. Methods

A close collaboration with Proficiency Testing providers has been put in place by supplying a reference value to samples used during a PTS. To achieve this goal, a primary method, the isotope dilution (ID), is carried out for the
(2) analysis of trace elements in various matrices [6-7]. The result obtained using the ID on a PTS sample is compared to the consensus value assigned by the provider. This allows to underline a possible bias, for instance due to the analytical method, between the consensus value and the reference value.

A drinking water sample was spiked with metal salt in order to obtain final concentrations of about 40 µg/l for selenium and 4 µg/l for mercury. 54 laboratories have participated in the mercury scheme and 57 in the selenium scheme, using the following methods:

- AAS (Atomic Absorption Spectroscopy) with cold vapour for mercury analysis following NF EN 1483 standard method [8].
- AAS with graphite furnace and ICP/OES (Inductively Coupled Plasma / Optical Emission Spectroscopy) for selenium analysis, following NF EN ISO 15586 and NF EN ISO 11885 standard methods respectively [9-10].

In ambient air particles, As and Cd have been analysed. 10 laboratories have participated in the schemes.
Robust statistical protocols have been used to determine the assigned values by both PT providers [11].

For the primary method carried out by LNE, two ICP/MS (Inductively Coupled Plasma / Mass Spectrometry) instruments have been used: a quadrupole system with a collision cell for the selenium analysis and a high resolution system for mercury analysis. The uncertainty of measurement has been evaluated using the GUM approach [12].

3. RESULTS

Results are presented in the following figures (Fig. 1, 2, 3 and 4).
For water analyses, the regular distribution curves indicate that a good coherence has been obtained within the laboratories. One value higher than 10 µg/l for mercury and two values higher than 90 µg/l for selenium have not been represented on the graphs but these values have been taken into account for the assigned values calculations.

For mercury analysis (Fig. 1), results have shown a very good consistency between the assigned value and the reference value.
- Assigned value: 3.76 µg/l, robust standard deviation: 0.09 µg/l.
- Reference value: 3.76 µg/l , standard uncertainty 0.10 µg/l (due to the relatively high level of the uncertainty of isotopic value).

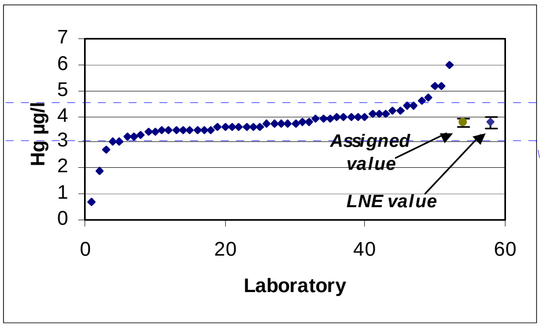

Fig. 1. Distribution curve of results, analysis of mercury

For selenium analysis (Fig. 2), a lesser level of consistency is observed between the assigned and the reference value.

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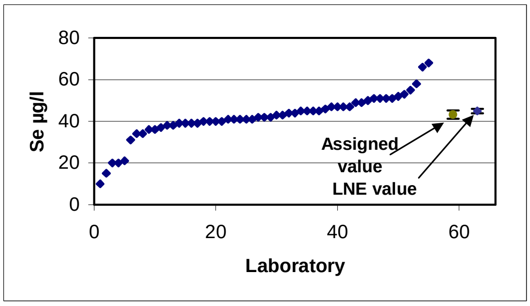

Fig. 2. Distribution curve of results, analysis of selenium

- Assigned value: 43.2 µg/l, robust standard deviation: 1.0 µg/l.
- Reference value: 44.9 µg/l, standard uncertainty: 0.54 µg/l. But the two values are not significantly different (at risk 5%).

For As analysis in air particles (Fig 3) a very good consistency between the assigned value and the reference value, but it should be noted that the uncertainty of the assigned value is very large.

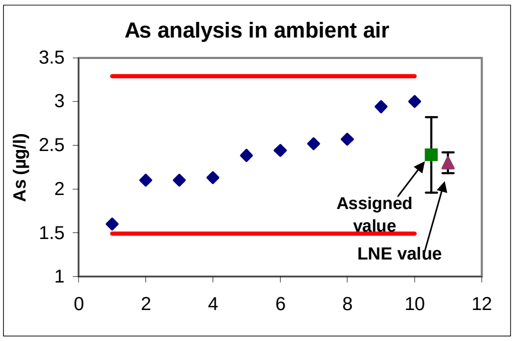

Fig. 4 Distribution curve of results, analysis of Arsenic

- Assigned value: 2.39 µg/l, robust standard deviation: 0.21 µg/l.
- Reference value: 2.301 µg/l , standard uncertainty 0.064 µg/l

For Cadmium analysis a lesser consistency was obtained (Fig. 4).

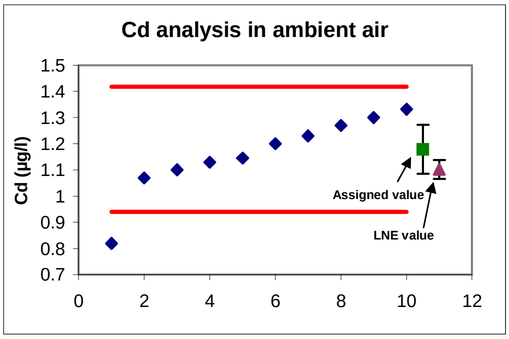

Fig. 4 Distribution curve of results, analysis of cadmium

- Assigned value: 1.179 µg/l, robust standard deviation: 0.093 µg/l.
- Reference value: 1.102 µg/l , standard uncertainty 0.018 µg/l

For these the parameters in water, the traceability of the assigned value has been demonstrated. It has also been concluded that the analysis of mercury and selenium in water following the standard methods don't present an analytical bias, at these concentration levels. The same conclusion can be drawn for the parameters in air particles but the demonstration is less consistent due to the relatively low number of laboratories participants in PT schemes.

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4. CONCLUSION

The development of traceability chains for chemical analyses strongly depends on the development of new certified reference materials with matrices presenting a high level of commutability. Due to the shortage of CRMs, a possible way is to integrate Proficiency Testing Schemes in traceability chains. But the results of PTS suffer from a lack of metrological traceability. A cooperative study between LNE and BIPEA (and at a lower extent with EMD) has demonstrated that it is possible to use a primary method to provide a reference value and therefore to clarify the doubt regarding the traceability of the consensus value of the PTS. LNE has initiated cooperation with other French PT providers to cover different sectors and focus studies on organic compounds, particularly when analytical problems have been identified.

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