



Quantification of uncertainty in mercury wastewater analysis at different concentration levels and using information from proficiency test with a limited number of participants

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ABSTRACT

Measurement uncertainty is one of the most required parameters of analytical quality in environmental decision-making. Several approaches have been reported for estimating uncertainty in analytical measurements. The use of proficiency test (PT) is an alternative, not only for assessing the performance of individual analytical laboratories, but also for estimating the concordance of an analytical method and their measurement uncertainties. Here we develop a PT scheme for a limited number of analytical laboratories that took part in the analysis of total mercury in samples with complex matrix (chlor-alkali process wastewater effluent) in absence of references of the highest metrological hierarchy (e.g. primary method, primary CRM). Two in-house reference materials (IHRMs) were prepared at different levels of analyte concentration and the homogeneity required was verified for the intended use. A set of parametric and robust statistical tests were applied to evaluate the assigned values of each IHRM. Metrological compatibility assessment of PT results, evaluation of individual and global performance of the laboratories, and determination of uncertainty of the analytical measurements were evaluated in this restricted study scenario. Between-laboratory differences were found not significant ($\alpha=0.05$). For both concentration levels we computed a relative standard uncertainty of 30% for the total Hg content.

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1. Introduction

Most environmental management decisions are the result of analysis of information obtained from measurements made in both internal and external monitoring of the control routines. The correct interpretation of the analytical results of such measurements requires knowledge about their quality, especially with regard to measurement uncertainty [1]. Therefore, in order to achieve the required quality on these results, it is necessary to apply principles of quality assurance (QA) and quality control (QC) in the monitoring process to eliminate causes of unsatisfactory performance [2,3]. These quality control systems should include, among other requirements, verification of the results of traceability, or at least a quantitative assessment of bias and sustained in order to ensure comparability of results over time. In practice it is difficult to demonstrate the traceability of the environmental measurements in complex matrices, like soils, sediments, wastes water, sludges. A common practice in the analytical laboratories is the use of certified reference materials (CRM), pure substances or by using other documented standards to verify the traceability or

at least the assessment of trueness [4]. However, when CRM are not available (absence on the market, difficulty in acquiring) and the use of pure calibrating substance is not appropriate because the matrix sample is complex, it is possible to evaluate the performance of analytical laboratories and calculate measurement uncertainties by using test schemes data [5]. There are not available in the market CRM of mercury in a complex matrix sample, such as the wastewater effluent of the chlor-alkali process. It should be noted that mercury is one of the heavy metals most currently found in the international, national and regional list of regulated pollutants [6–8], and is one of the pollutants discharged in the estuary of Bahía Blanca, more subject to official controls. Therefore, it is necessary to demonstrate the quality of the results of the determination of total mercury in the wastewater industrial chlor-alkali process and is useful to know the value of the measurement uncertainty of these analytical results to improve the scientific basis for management decisions. In this study, we carried out a PT scheme in order to investigate the technical competence of participating laboratories and the metrological comparability of their results. For this purpose, two in-house reference materials (IHRM) of industrial wastewater containing mercury were prepared by the Accredited Laboratory of Executive Technical Committee (CTE), government office for environmental protection in the area of the Bahía Blanca Petrochemical

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complex [9]. The homogeneity of these IHRM was checked following the procedure described by Fearn and Thompson [10] and the International Harmonized Protocol [11]. Stability of these IHRM was also tested in spite of the fact that the analyses performed by the participants were started immediately after the sample preparation. The small number of test participants was other limiting condition [12,13]. Only six laboratories located in the region of Bahía Blanca, Argentina, are in conditions to carry out this determination as a routine task. There are not reported studies in the literature for such a restrictive scenario and evaluating more than one level of the analyte concentration in the samples. Based on these limited conditions, both materials were used as test samples in the PT scheme with five of the six existing laboratories, applying the same analytical method in experimental conditions of repeatability.

The objectives of this study included: evaluation of metrological compatibility of the assay results, evaluation of individual and global performance of the participating laboratories, and the determination of the measurement uncertainty using the information obtained from a PT scheme with the following scenario: (a) appropriate reference materials are not available, (b) the limited number of participants, (c) the analytical determination is not simple and, (d) materials with different level of concentration (split-level).

2. Experimental

2.1. Organisation of PT

The scheme was organised by the CTE of the government of Bahía Blanca, Argentina, in cooperation with private laboratories, research laboratories and researchers from the Universidad Nacional del Sur. The PT coordinator was responsible for: (a) designing the scheme, (b) sampling the test materials, (c) preparation and validation of the IHRM, (d) development and simultaneous distribution of instructions and IHRM to participating laboratories, and (e) collection and statistical analysis of the data obtained from the PT. The materials investigated were identical to those used in compliance with external and internal tests in order to be sure that the representativeness of each IHRM was enough.

This PT scheme was performed using the combination of criteria and guidelines proposed by the IUPAC/CITAC Guide [6], ISO Standard 5725 [14], AOAC Guidelines [15], ASTM Standard E 691 [16], taking into account lack of CRM (primary and secondary standard), the limited number of participants and the different levels of Hg in the test items.

Participating laboratories had to use the analytical official method consistent with their normal routine practice, i.e., methods were not adjusted for participate in this PT.

2.2. Description and collection of IHRMs

All participating laboratories in the PT had to analyse each of the IHRMs. Candidates IHRM were collected directly from two different chlor-alkali process effluents, containing Hg residues and they were divided into two groups; samples with low level concentration of Hg, and samples with high level concentration of Hg. All procedures for sampling and bottling were established according to international standards [17]. The PT coordinator established that all analyzes had to be carried out within 24 h because the stability in these types of samples is very important. Physicochemical characteristics of this complex material matrix are shown in Table 1.

Table 1
Wastewater characteristics.

| Parameter | Units | Range | Number of analysis |
|------------------------------|----------------------|---------------|--------------------|
| pH | | 6–12 | 162 |
| Conductivity | μScm^{-1} | 5000–60,000 | 139 |
| Turbidity | NTU | 13–500 | 109 |
| Temperature | $^{\circ}\text{C}$ | 20–43 | 137 |
| Total solids | mg L^{-1} | 1600–30,000 | 109 |
| Settable solids (10 min.) | ml L^{-1} | 0.1–200 | 157 |
| Settable solids (2 h) | ml L^{-1} | 0.1–100 | 153 |
| Chemical oxygen demand | mg L^{-1} | 20–900 | 115 |
| Total petroleum hydrocarbons | mg L^{-1} | 0.1–30 | 36 |
| Chloride | mg L^{-1} | 1300 | 53 |
| Total lead | mg L^{-1} | 0.003–0.007 | 45 |
| Total cadmium | mg L^{-1} | 0.0006–0.007 | 47 |
| Total mercury | mg L^{-1} | 0.0001–0.0374 | 118 |

2.2.1. Sample 1 (LL)–IHRM

This sample is an industrial effluent discharge into the Bahía Blanca estuary. This effluent is subjected to continuous monitoring and audits to verify compliance with the maximum allowable limit of total mercury in 0.0050 mg L^{-1} ; typical value is around 0.0015 mg L^{-1} . About 10 L of this material was collected in a suitable preconditioned polyethylene tank and immediately transported to the laboratory. The precondition step included an acid wash [filling the tank with 2% (v/v) nitric acid solution] and subsequent washings with the sample itself.

2.2.2. Sample 2 (HL)–IHRM

This material corresponds to an intermediate effluent of the same industrial process, with concentrations of total mercury in the level of 0.005 mg L^{-1} . The coordinator of PT collected a similar volume of this sample (10 L) applying the same Sample 1 preparation protocol, but now applied to Sample 2.

2.3. Preparation of the IHRMs

Preparation of samples for the participating laboratories is a fundamental and critical step of the PT scheme [18]. Thus, the homogenization and sub-sampling of Sample 1 and Sample 2 were treated strictly in order to ensure that all participating laboratories analyzed identical subsamples of these test samples. Five portions of 200 mL of Sample 1, with thorough mixing, were sequentially added to the bottles preconditioned, thus obtaining each final subsamples which were immediately sealed. Subsequently, Sample 2 was subsampled in the same way of Sample 1. Finally, these bottles of both IHRM were immediately labeled and randomly distributed among the participating laboratories, emphasizing the importance of the complete homogenization of each IHRM prior to the execution of the determination of total mercury. Each laboratory analyzed one sample of each level of analyte concentration.

2.4. Homogeneity of samples

To test for sufficient homogeneity of the IHRM, respect to total mercury content, a high analytical precision of 0.0001 mg L^{-1} (LL) and 0.0002 mg L^{-1} (HL) were necessary. For this purpose, three random subsamples of each IHRM were sent to an external laboratory after sealing the samples. The analyses were performed following the approach proposed by Fearn and Thompson [10] by triplicate instead of duplicate, applying the SM 3112B method [17].

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