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An international proficiency test as a tool to evaluate mercury determination in environmental matrices



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ABSTRACT

We report on an international proficiency test (PT) scheme for mercury (Hg) determination in soil, sediment, fish and human-hair samples (ILAE-Hg-02). For total-Hg determination, 74% of participants had a satisfactory performance ($|z\text{-score}| \leq 2$), 8% had a questionable performance and 18% required action ($|z\text{-score}| > 3$). The best results were obtained for soil, while fish yielded the most-biased results, reflecting the analytical problems of quantifying Hg at low concentrations. Proficiency in the extraction of organometallic and available metal fractions was an important goal of the ILAE-Hg-02 and it was concluded that most laboratories are still not acquainted with the procedures for Hg fractionation; we therefore discuss their importance and highlight the need for more PT schemes dedicated to this matter, as they are an important tools in the standardization of procedures and for the development of adequate quality control/quality analysis protocols and certified reference materials.

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1. Introduction

1.1. Mercury in the environment (soil, sediment, fish and humans)

Mercury (Hg) is one of the most critical contaminants in the environment [1] and is present in water, soils, sediments and air usually at trace levels. However, several human activities (e.g., mining, industry, and sludge dumping) have increased the natural concentration of Hg and led to severely contaminated environments [2–5]. Despite efforts to reduce Hg emissions, a 2010 study by Pirrone et al. [6] estimated that global Hg emission was still nearly 7527 tons per year, which affects the atmospheric, terrestrial, aquatic, and biotic compartments. This situation is enhanced by some Hg species being particularly reactive in the environment, shifting rapidly between the four interconnected compartments in the Hg biogeochemical cycle [7]. Soils and sediments, in particular, play an important role in the Hg biogeochemical cycle, acting as a sink and a source of the element for biota and humans [8]. Also, Hg can bioaccumulate and biomagnify in biota [9–11]. It can also affect humans by direct exposure or through food consumption [12,13].

Monitoring and identification of Hg hotspots in the environment is therefore essential to maintain the health and the proper functioning of natural ecosystems, and to assure the integrity of the food chain, sustainable agricultural and piscatorial practices, and the health of humans and animals that directly or indirectly benefit from these systems. However, determining the total content of Hg is not always the most suitable approach to estimate the hazard of Hg in the environment, since the toxicological effects depend on the chemical form of the metal [14]. All data for total concentrations, without proper information about the Hg species existing, are at best insufficient for adequate risk assessment, and, in many cases, misleading due to overestimation. In addition, the chemical form of an element determines its transport in and among the environmental compartments. Consequently, the importance of analytical methods for fractionation analysis increased in recent years, enhancing the need for validated methods for identification and quantification of Hg fractions. However, difficulties have been encountered due to the complexity of Hg chemistry, particularly in complex matrices, such as soil and sediment [15]. Establishing easy-to-use protocols is key to successful assessment of risk and interaction between Hg contaminating soil or sediment.

1.2. Mercury speciation and fractionation in environmental samples

Interest in Hg speciation and fractionation has been increasing in recent years due to recognition that toxicity, bioavailability, health hazard, risk assessment, and remediation of contaminated sites must be based on the levels of specific chemical forms of Hg, rather than on total-Hg concentration [16]. This creates an analytical challenge due to:

- difficulties in isolating the compounds of interest from complex matrices, such as soil and sediment;
- changes caused in the distribution of the various chemical species during extraction [17]; and,
- lack of appropriate certified reference materials (CRMs) and quality-control (QC) procedures [16,17].

Quantification of low-concentration analytes in extracts can represent another drawback, although the development of more sensitive analytical techniques has somewhat overcome this problem (as we discuss in the next section).

A common misconception falls within the distinction of speciation and fractionation, as the two are different approaches. Speciation is defined as “measurement of the amount of one or more individual

chemical species in a sample” [18]. Currently, various methods are available for assessing Hg speciation in environmental samples, such as thermal desorption [19–21], and X-ray adsorption [22–24]. However, often speciation analysis is not attainable, because species are not stable enough to be individually determined. Instead, a common practice consists of fractionation, which should be understood as the process of classification of “an analyte or a group of analytes from a certain sample according to properties – physical (e.g., size or solubility) or chemical (e.g., bonding or reactivity) [18,25]. Single and sequential chemical-extraction procedures are used most for Hg fractionation [10,11,26–31]. Single extractions mainly aim at the determination of only one fraction of interest, such as the available fraction [32–34] or the organometallic fraction [26,35–38]. Usually, a single extracting agent is used to treat the sample and measurement is made of the amount of Hg released from the matrix into the solution [39].

The organometallic fraction is one of the main focuses of interest in Hg fractionation, due to its extreme toxicity. It is interesting to note that the percentage of total Hg it represents varies considerably among matrices. For example, in most fish samples, organometallic Hg accounts for more than 80% of total Hg [40,41], but, in soils and sediments, it usually represents less than 3% of total Hg [42–46]; still, the risk incurred by Hg in soils and sediments must not be neglected. In general, analytical methods for the determination of the organometallic fraction are performed following one of these techniques:

- distillation;
- a combination of acid leaching with solvent extraction, such as the method present in Válega et al. [26], where H₂SO₄ and toluene are used;
- the Westöo method that combines HCl and toluene [47]; or,
- alkaline dissolution, with potassium hydroxide or tetramethylammonium hydroxide [48,49].

For organometallic speciation, such as determination of methylmercury or ethylmercury, the following are commonly used:

- supercritical fluid extraction (SFE) [50,51];
- microwave digestion [37,48,52];
- derivatization [53,54];
- high-performance liquid chromatography (HPLC) [55,56]; or,
- gas chromatography (GC) [53,57]

Because of the toxicity of organometallic species, the performance of the methodologies used on their quantification has been extensively studied and an excellent review of the methods tested in collaborative trials, and the certification of reference materials, can be found in Quevauviller et al. [58].

The extraction of the so-called available fraction in soils has also been receiving some attention, mostly because it contains the species that can be taken up by plants and crops and ultimately enter the food chain. A large number of extractants have been used to assess the available fraction. Issaro et al. [59] reviewed the procedures that have been used for Hg fractionation in soil and reported more than 30 different single and sequential extraction schemes, with an equally large number of reagents used in the extractions. Other issues include temperature, soil-to-extractant ratio, and time of extraction. However, for the study of the available fraction, the most common used extractants include:

- chelating solutions, e.g., EDTA [60];
- salt solutions, e.g., 1 mol L⁻¹ CH₃COONH₄, 1 mol L⁻¹ MgCl₂, or 0.1 mol L⁻¹ CaCl₂, due to their capacity to release Hg by ion exchange [61–63]; or,
- diluted solution of acid, e.g., 0.1 mol L⁻¹ HCl [64].

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