

Comparative Measurements and their Compliance with Standards of Total Mercury Analysis in Soil by Cold Vapour and Thermal Decomposition, Amalgamation and Atomic Absorption Spectrometry

Manuel A. Leiva G. · Sandra Morales ·
Rodrigo Segura

Received: 18 June 2012 / Accepted: 7 November 2012 / Published online: 5 January 2013
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Abstract Two methods to measure mercury concentration in soil are compared, and their compliance with international standards is determined: cold vapour atomic absorption spectrometry and thermal decomposition, amalgamation and atomic absorption spectrophotometry. The detection limit, quantification limit and uncertainty of these two analytical methods were evaluated and compared. The results indicated that thermal decomposition, amalgamation and atomic absorption spectrophotometry had a lower quantification limit and uncertainty than cold vapour atomic absorption spectrometry (quantification limit, 0.27 vs. 0.63 mgkg⁻¹; expanded uncertainty, 9.30 % vs. 10.8 %, respectively). Thermal decomposition, amalgamation and atomic

absorption spectrophotometry allowed the determination of the base values for the concentration of mercury in soil recommended by international standards, achieving a lower detection limit than cold vapour atomic absorption spectrometry under the study conditions. In addition, thermal decomposition, amalgamation and atomic absorption spectrophotometry represent a more environmentally friendly alternative for mercury determination because this method uses fewer reagents and therefore generates less waste.

Keywords Mercury in soil · Atomic absorption spectrometry · Uncertainty · Standards compliance

M. A. Leiva G. (✉)
Centro de Ciencias Ambientales and Departamento de
Química, Facultad de Ciencias, Universidad de Chile,
Casilla 653,
Santiago, Chile
e-mail: manleiva@me.com

M. A. Leiva G.
e-mail: manleiva@uchile.cl

M. A. Leiva G. · S. Morales
Centro Nacional del Medio Ambiente,
Avenida Larraín 9975,
La Reina, Santiago, Chile

R. Segura
Departamento de Química de los Materiales, Facultad de
Química y Biología, Universidad de Santiago de Chile,
Santiago-33, Chile

1 Introduction

Mercury (Hg) is widely known for its toxicity, causing teratogenic and neurotoxic effects (IPCS 2003; WHO 2007; Zheng et al. 2007). The health of miners and other workers, as well as ecosystems, is seriously compromised by exposure to mercury or mercury derivatives (UNIDO 2004; Zheng et al. 2007; Tsuda and Yorifuji 2011). Minamata, Japan, suffered one of the most dramatic mercury contaminations in history (Tsuda and Yorifuji 2011).

Mercury sources include mining and industrial activity, particularly gold mining (Serfor-Armah et al. 2004; Strode et al. 2009; Hagan et al. 2011), and electricity generation from coal in thermoelectric power plants (Ali et al. 2011). Mercury is present in combustion gases,

sediments, soils, water and food chains. Organic mercury compounds are generally more toxic than those of other heavy metals (Corbitt et al. 2011).

Mercury is a unique metal that exists as a monoatomic vapour at room temperature. This property of mercury has allowed the development of analytical methods to determine the total Hg concentration in samples. These techniques are based on the reduction of all mercury-containing compounds to elemental mercury and the quantification of the resulting mercury vapour (Magalhaes et al. 1997; Moskalova and Zemberyova 1997; Claire et al. 2000; Raposo et al. 2003; Resano et al. 2005; Evans et al. 2008). One of these techniques is based on cold vapour atomic absorption spectrometry (CVAAS; Bulska et al. 1995; da Silva et al. 1998; SW-846 2007a). CVAAS samples must be pre-treated, in most cases with oxidant or acid mixtures (e.g. aqua regia or sulphuric-nitric acids) and oxidizing agents (e.g. potassium persulfate, potassium permanganate and bromine monochloride), and the mercury in the resulting solution must then be reduced (with stannous chloride or sodium chloride and potassium borohydride). CVAAS can be used to determine total mercury content in a wide range of environmental matrices, including soil, sediment, mud, aqueous waste, surface water and groundwater (Moskalova and Zemberyova 1997; Geng et al. 2008; Konieczka et al. 2010). However, sample preparation may affect the accuracy of the mercury concentration, which is calculated based on the absorption of Hg at 253.7 nm using a method developed in the 1930s.

The errors introduced during sample treatment have led to the development of techniques that eliminate the sample preparation step and analyze the mercury content directly using an integrated measurement system (Senila et al. 2011). The development of mercury determination techniques based on thermal decomposition, amalgamation and atomic absorption spectrometry (TDAAS) began in the 1960s (Butala et al. 2006). TDAAS involves sample combustion at high temperatures (thermal decomposition). The combustion products, including elemental mercury, first pass through a dryer and then through a gold amalgam trap, where all of the elemental mercury is captured. The amalgam is then heated, and the released mercury is analyzed using atomic absorption spectrometry.

Metrological traceability is formally defined as the “property of a measurement whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement

uncertainty” (JCGM 200, 2008). The traceability of a measurement is one of the most important issues that must be considered when building up a measurement system from which reliable, internationally recognized results are expected. In this sense, one way to ensure the traceability to the SI in chemical measurements is through the use of a traceable certified reference material.

The validation of methods is crucial for analytical development (da Silva et al. 1998; Feinberg and Laurentie 2006; Guevara-Riba et al. 2006). Validation and other activities included in quality assurance demonstrate whether an analytical method is suitable for the proposed objectives, which, in the present study, are the determination of mercury levels in soil samples and the evaluation of existing mercury-level standards.

The estimation of uncertainty is also crucial for the validation of a measurement technique (Weckenmann et al. 2006; EURACHEM/CITAC 2007, 2012). One of the most detailed protocols is described in the Guide to the Expression of Uncertainty in Measurement (GUM) (JCGM 104 2009). This document establishes general rules with which to evaluate and express uncertainty in measurements. Many other protocols have been proposed (Guevara-Riba et al. 2006; Wallace 2010), some of which emphasize the use of routine methods from which the uncertainty can be calculated based on quality assurance or validation data (Feinberg and Laurentie 2006).

In the present study, the analytical parameters: method detection limit (MDL), method quantification limit (MQL), working range, repeatability and recovery, are evaluated and compared, using CVAAS and TDAAS techniques for measuring mercury levels in soil. The application of both techniques for soil sample analysis evaluated the effect on human's health and ecosystems based on existing international standards for mercury content in soil. The MQL and MDL results for both methods were compared with the recommendations of the USEPA, (USEPA 2004), Canada (CA-SQG 2010) and Netherlands (NL-RIVM 2001) for residential areas (23, 6.6 and 0.3 mgkg⁻¹, respectively) in order to verify the applicability of those methods.

2 Experimental Methods

2.1 Materials, Reagents and Standards

All reagents were analytical grade commercial products (Merck or Aldrich). Solutions were prepared with

ultra-pure Milli-Q water. The calibration standard was prepared using appropriate dilutions of a concentrated stock solution ($1,000 \pm 4 \text{ mg L}^{-1}$), and nominal mercury concentrations were those of certified commercial solutions (Fluka Analytical, TraceCERT® Product No.: 16482 Lot 1420021). A blank solution was used to measure the baseline.

All glass and volumetric materials were decontaminated by washing with a common detergent and rinsing three times with Milli-Q water. The materials were then soaked for 24 h in a 20 % (v/v) HNO_3 solution, and they were subsequently washed with Milli-Q water and dried in a clean environment. In both analytical methods, an analytical balance was used (Sartorius model TE124S, Sartorius Weighing Technology GmbH, Goettingen, Germany). The Certified Calibration Weights ANSI/ASTM Class 1 (Troemner, ASTM Class 1, Serial number: 63314, Troemner, Thorofare, West Deptford, NJ, USA) was used to verify and calibrate the analytical balance.

2.2 Instruments

For CVAAS mercury analysis (Unicam model 919), cold vapour was generated using an FI90 Segmented Flow Injection Vapour System (Basingstoke, UK). This system consists of an air circulation pump, a reaction vessel, an SnCl_2 dispenser, an acid gas trap and a four-way stopcock connected to a ball valve with Tygon tubing. The mercury vapour was drawn into the absorption cell in which the detection was performed with an atomic absorption spectrophotometer (ATI Unicam 939 SOLAR System, $\lambda=253.7 \text{ nm}$, 0.5-nm bandwidth with a deuterium lamp for background correction). All measurements were conducted using a hollow cathode lamp with argon as the buffer gas.

TDAAS measurements were recorded with a Milestone DMA 80 Direct Mercury Analyzer (Milestone Inc., Sorisole, Italy). After inserting the sample, the equipment was sealed, and oxygen was passed through the sample at a speed of 200 mL min^{-1} . The sample was then dried for 10 s and combusted for 100 s after the temperature had increased to approximately $550 \text{ }^\circ\text{C}$. Subsequently, the gaseous combustion products were passed through an $\text{Mn}_3\text{O}_4/\text{CaO}$ catalyst (maintained at $750 \text{ }^\circ\text{C}$) for complete oxidation; the chemical forms of Hg were converted to elemental mercury (Hg^0) vapour, and the sulphur oxides, nitrogen oxides and halogens

were trapped. The Hg^0 and other decomposition products were transferred to a tube containing gold coated with sand. Hg^0 was selectively trapped in this tube, and all other products were eliminated from the system. The trap was then heated rapidly to approximately $700 \text{ }^\circ\text{C}$, and the Hg vapour entered the spectrophotometer, where it remained for 40 s until the subsequent analysis cycle. The instrument included two measurement cells and could thus be calibrated in two ranges. The Hg concentration was calculated based on the absorbance measured at 253.7 nm and the sample weight.

2.3 Experimental Design and Uncertainty Estimation

The procedure used to evaluate the uncertainty associated with the determination of the total mercury content in soil can be divided into the following steps (JCGM 104 2009):

- Step 1 Description of the measurement procedures
- Step 2 Specification of the measurand and relation between the measurand and the variables
- Step 3 Identification of uncertainty sources
- Step 4 Effect diagram and quantification of individual uncertainties
- Step 5 Calculation of the combined uncertainty
- Step 6 Expanded uncertainty
- Step 7 Expression of results.

2.3.1 Step 1: Description of the Measurement Procedures

The measurement procedure of mercury in soils by each technique (CVAAS and TDAAS) is as follows:

CVAAS was conducted according to EPA Method 7471B (SW-846 2007a), in which 5 mL of aqua regia and 15 mL of 5 % potassium permanganate were added to 0.5 g of the soil sample, the resulting mixture was shaken for 15 min, and then heated in a temperature-controlled water bath at $95 \text{ }^\circ\text{C}$ for 30 min. The mixture was then cooled to room temperature, and 6 mL of a solution containing hydroxylamine sulphate and sodium chloride was added. All solutions and dilutions were performed with double-deionized water (resistivity, $18.2 \text{ M}\Omega\text{cm}^{-1}$). The calibration curves were prepared and treated using the procedure described for the soil sample in a concentration range of 1 to $20 \text{ }\mu\text{g L}^{-1}$.

TDAAS was conducted according to EPA Method 7473 (SW-846 2007b), in which 0.5 g of the soil sample is transferred to a nickel vessel. The sample was automatically transferred from this to the quartz combustion tube in the spectrophotometer. Calibration curves were constructed for two standard solution concentration ranges: 0.5–20 and 20–1,000 ng, each of which 0.5 g was added to the quartz tube.

The method detection limit (MDL) and method quantification limit (MQL) estimations were determined from the standard deviation of ten independent measurements in which mercury was detected in a real sample. Therefore, the standard deviations of measurements that detected any level of mercury concentration in the first third of the calibration curve were calculated. Thus, the MDL and MQL were defined as three and ten times, respectively (Shrivastava and Gupta 2011).

2.3.2 Step 2: Specification of the Measurand and Relation Between the Measurand and the Variables

The following mathematical model can express the mercury concentration in soil:

$$c_{ss} = c_{cc} f_{rp} \frac{1}{f_{re}} f_{co} \quad (1)$$

where c_{ss} is the concentration in the soil sample (milligrams per kilogram); c_{cc} is the mercury concentration or content determined from the calibration curve, the unit depending on the method; f_{co} is a conversion factor for the concentration obtained from calibration curve to sample; f_{rp} is the reproducibility factor; and f_{re} is the recovery factor.

2.3.3 Steps 3 and 4: Identification of Uncertainty Sources, Building Cause and Effect Diagrams and Quantification of Individual Uncertainties

According to Eq. 1, the cause and effect diagram can be drawn from the sources of uncertainty for this method (see Fig. 1).

Calibration curve Two calibration methods are considered: the linear regression model and the polynomial regression model, for CVAAS and TDAAS, respectively. The calibration curve was constructed

from three successive measurements of each calibration standard concentration.

The linear regression model, shown in Eq. 2, is used for calibration in CVAAS.

$$y = b_1 c_{cc} \quad (2)$$

where y is the absorbance value read in the CVAAS measurement, and c is the concentration obtained from the calibration curve in micrograms per litre. The predicted value in the lineal regression model (c_{pred}) was calculated from the observed response (y_{obs}) according to:

$$c_{pred} = \frac{y_{obs}}{b_1}, \quad (3)$$

and the following equation is used to calculate the uncertainty from the linear calibration curve:

$$s_1(y_{obs}) = s \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_{pred} - \bar{c})^2}{\sum_{j=1}^n (c_j - \bar{c})^2}} \quad (4)$$

$$u_1(c_{pred}) = \frac{s_1(y_{obs})}{b_1} \quad (5)$$

where s is a residual standard deviation, p is the number of measurements made to determine a particular value, n is the total number of data points used for the calculation, \bar{c} is the mean concentration value of the different standard stock solutions and c_j is the concentration of each calibration standard observed at each calibration point.

A polynomial regression model, shown in Eq. 5, was used for the TDAAS method.

$$y_{obs} = d_1 c_{pred} + d_2 c_{pred}^2 \quad (6)$$

where y_{obs} is the absorbance reading values in the TDAAS measurement, and c_{pred} is the mercury amount obtained from calibration curve (nanograms). The predicted value (c_{pred}) is calculated from the observed response (y_{obs}) as follows:

$$c_{pred} = -\frac{d_1}{2d_2} \sqrt{\frac{d_1^2}{4d_2^2} + \frac{y_{obs}}{d_2}} \quad (7)$$

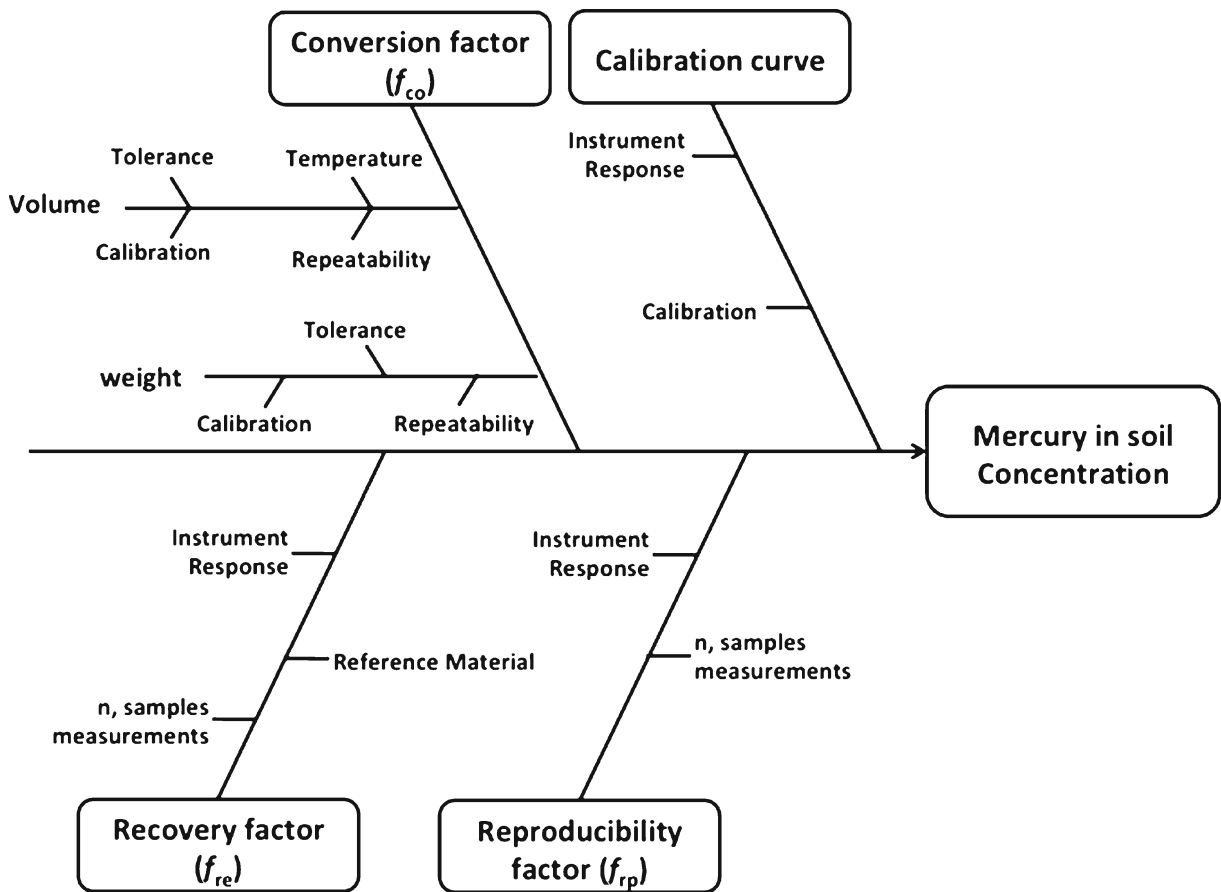


Fig. 1 Cause–effect diagram for estimation of the measurement uncertainty of mercury concentrations in soils

From the definition of uncertainty:

$$u(c_{pred}) = \frac{\delta c}{\delta y} u(y_{obs}) \tag{8}$$

$$u(c_{pred}) = \frac{1}{2d_2} \frac{u(y_{obs})}{\sqrt{\frac{d_1^2}{4d_2^2} + \frac{y_{obs}}{d_2}}} \tag{9}$$

where $u(y_{obs})$ can be calculated from Eq. 5, and the relative uncertainty can be calculated according to:

$$u_{r-cc} = \frac{u(c_{pred})}{c_{pred}} \tag{10}$$

A rigorous explanation of the uncertainty calculation can be found in the literature (Bruggemann and Wenrich 2002; Heydorn and Anglov 2002; Lu and Chen 2007).

Repeatability factor (f_{rp}) The uncertainty resulting from variations in concentration can be estimated with a repeatability condition, i.e. closeness of the agreement between the results of successive measurements of the same measurand carried out under the same measurement conditions (Ref GUM). A series of ten independent samples were measured on the same day and ten on different days, by CVAAS and TDAAS, respectively, in order to get the standard deviation, which can then be used directly as standard uncertainty (a normal distribution is assumed).

The relative uncertainty of repeatability can be estimated from Eq. 11.

$$u_{r-rp} = \sqrt{\left(\frac{s_{rp-same\ day}}{c_{same\ day} \sqrt{n_{same\ day}}}\right)^2 + \left(\frac{s_{rp-diff\ day}}{c_{diff\ day} \sqrt{n_{diff\ day}}}\right)^2} \tag{11}$$

where s_{rp-i} is the standard deviation obtained from the

repeatability study, and n_i is the number of measurements, on the same or different days. The reproducibility factor is considered with a value equal to 1, and their uncertainty is obtained according to Eq. 11.

Recovery factor (f_{re}) To determine the recovery, a commercial certified reference material of soil (CRM, number: SQC001, lot: 13214) provided by RTC Corporation (RTC Corp, Laramie, WY, USA). The mercury content of this CRM is traceable to the Mercury Standard Reference Material from the National Institute of Standards and Technology (NIST SRM 3133) as reported in the certificate from CRM. Selection of the reference material was made considering its traceability, price and market availability for routine analysis.

The relative standard uncertainty of the recovery (u_{re}) was calculated based on the uncertainty of the CRM (u_{CRM}) with a known concentration c_{CRM} as well as from the standard deviation (s_{re}) obtained from a number of measurements (n_{re}) and the average measured concentration (c_{re}) according to Eq. 12:

$$u_{r-re} = \frac{1}{f_{re}} \sqrt{\left(\frac{s_{re}}{c_{re}\sqrt{n_{re}}}\right)^2 + \left(\frac{u_{CRM}}{c_{CRM}}\right)^2} \quad (12)$$

where f_{rec} corresponds to the recovery factor calculated according to Eq. 13:

$$f_{re} = \frac{c_{rp}}{c_{CRM}} \quad (13)$$

A significance test was conducted to prove whether f_{re} differs significantly from 1. The statistical t test was calculated from Eq. 14:

$$t = \frac{1 - f_{re}}{f_{re}u_{r-re}} \quad (14)$$

The t test value was compared with the two-tailed critical t test value for $n-1$ degrees of freedom with 95 % confidence. If the t test value was greater than or equal to the critical t test value, the recovery deviated significantly from 1.0, and the concentration values were then corrected according to the recovery factor, calculated from Eq. 13; otherwise, f_{re} will be set equal to 1.0 (Bruggemann and Wenrich 2002).

Conversion factor (f_{co}) The conversion factor depends on the measurement method to be used, CVAAS or TDAAS. For CVAAS, a portion of the sample is

weighed, digested and afore to 100 mL in volumetric flask. The f_{co} is calculated according to Eq. 15:

$$f_{co}^{CV} = \frac{V_{100}}{w} \quad (15)$$

where V_{100} is the volume of the volumetric flask (0.1 L), and w is the sample weight in kilograms. The uncertainty is estimated from the following equations:

$$u_{r-f_{co}^{CV}} = \frac{u_{f_{co}^{CV}}}{f_{co}^{CV}} = \sqrt{\left(\frac{u_{V_{100}}}{V_{100}}\right)^2 + \left(\frac{u_w}{w}\right)^2} \quad (16)$$

In order to estimate the uncertainty of the volume of the solution contained in the volumetric flask, three major sources of uncertainty were considered: (1) uncertainty in the certified internal volume of the flask, (2) variation in filling the flask to the mark, and (3) flask and solution temperatures differing from the temperature at which the volume of the flask was calibrated; more details are available in the literature (Jurcovan et al. 2012). The three uncertainty sources give the expanded uncertainty ($k=2$) for the 100-mL volumetric flask (Hirschmann Laborgeräte GmbH & Co., Germany) of 100 ± 0.2 mL.

For the contribution of weighing on an analytical balance (w), the manufacturer's literature identifies three uncertainty sources: (1) repeatability (ten replicate weighings were made), (2) readability (digital resolution) of the balance scale, and (3) contribution due to the uncertainty in the calibration function of the scale. This calibration function has two potential uncertainty sources, identified as the balance's sensitivity and linearity. Buoyancy correction is not considered. Detailed calculations for uncertainties in mass can be very intricate, and it is important to refer to the manufacturer's literature where mass uncertainties are dominant (EURACHEM/CITAC 2012). In this work, the detailed calculations are omitted for clarity. The relative expanded uncertainty ($k=2$) for the weighing operation at the low level (200–600 mg) was estimated at 0.7 %.

In the case of the TDAAS, a portion of the sample was weighed and automatically transferred from sample reservoir to the quartz combustion tube in the spectrophotometer, for which the f_{co} and $u_{f_{co}}$ uncertainty is estimated according to the

following equations:

$$f_{co}^{TD} = \frac{1}{w} \quad (17)$$

$$u_{r-f_{cor}}^{TDASS} = \frac{u_{i-f_{cor}}^{TDASS}}{f_{co}^{TDASS}} = \sqrt{\left(\frac{u_w}{w}\right)^2} \text{ or } u_{r-f_{co}}^{f_{co}^{TD}} = \frac{u_{f_{co}}^{f_{co}^{TD}}}{f_{co}^{f_{co}^{TD}}} = \sqrt{\left(\frac{u_w}{w}\right)^2} \quad (18)$$

The rigorous explanation of the uncertainty calculation of the volumetric and weighing operation is outside the scope of this paper, but more details can be found in the literature (NPL 2004; EURAMET 2012).

2.3.4 Steps 5, 6 and 7: Combined Uncertainty Calculation, Expanded Uncertainty, and Expression of Results

Subsequently, the relative combined uncertainty of the method (u_{rc}) was calculated as the geometric sum of the relative standard uncertainties (u_{r-i}) from uncorrelated sources of uncertainty according to the following equation:

$$u_{r-c} = \sqrt{\sum_{i=1}^n u_{r-i}^2} \quad (19)$$

The results are presented as the extended uncertainty (U) calculated using coverage factor $k=2$. This calculation provided a confidence level of approximately 95 %, and U was calculated from the following equation:

$$U_{r-e} = ku_{r-c} = 2u_{r-c} \quad (20)$$

The results of the calculations can be expressed as: $c_{Hg} \pm U_{r-e}c_{Hg}$.

3 Results and Discussion

3.1 Calibration Curve, MDL and MQL

A calibration curve was constructed to determine mercury concentration in soil using CVAAS and TDAAS. For CVAAS, the working concentrations were 0 to 20 mgL⁻¹. For TDAAS, two calibration curves were used, one for mercury concentrations between 0 and

20 mgkg⁻¹ (low range), and another one for mercury concentrations between 20 and 1,000 mgkg⁻¹ (high range). Each calibration curve was constructed based on triplicate absorbance measurements to obtain the average value and the standard deviation for each standard solution. The results are shown in Fig. 2. A high correlation coefficient was obtained for the calibration curves ($r^2 > 0.998$). Table 1 lists the equations for the calibration curves constructed using the least squares fit.

Table 1 shows that the MDL and MQL of CVAAS are 37 % and 33 % higher than the MDL and MQL of TDAAS, respectively. These results will be described below in the context of current international standards for determining total mercury concentration in soil.

3.2 Repeatability

The descriptive statistics and repeatability data for mercury concentration in soil in representative samples are given in Table 2. The repeatability was expressed as a relative standard deviation (RSD). The average value and the standard deviation were calculated from independent replicates measured on the same day and on successive days. Equation 11 was used to calculate the relative uncertainty. Within a single day, the standard relative uncertainty varied from 2.7 % to 2.3 % for CVAAS and TDAAS, respectively; on successive days, the uncertainty varied from 3.1 % to 2.2 %.

3.3 Recovery

The Hg recovery was determined based on the analysis of the CRM. A number of independent mercury measurements (n) were performed on a single day using each method. The averages, standard deviations, uncertainties (Eq. 12) and recoveries (Eq. 13) are listed in Table 3, from which we can conclude that the quantitative recovery, calculated according to Eq. 16, was 91 % and 98 % for the CVAAS and TDAAS, respectively.

The statistical significance (Eq. 14) was calculated based on these measurements. For CVAAS, the calculated t -statistic was higher than the two-tailed critical t -statistic for $n-1$ degrees of freedom with 95 % confidence, indicating that the mercury concentration measured for the CRM was significantly different from that measured in the standard solution. Therefore, a

Fig. 2 Calibration curves for mercury concentration determined by cold vapour atomic absorption spectrometry (CVAAS, **a**) and thermal decomposition, amalgamation and atomic absorption spectrophotometry (TDAAS, **b**). For TDAAS, two calibration curves were used: low level (*dashed line*) and high level (*solid line*)

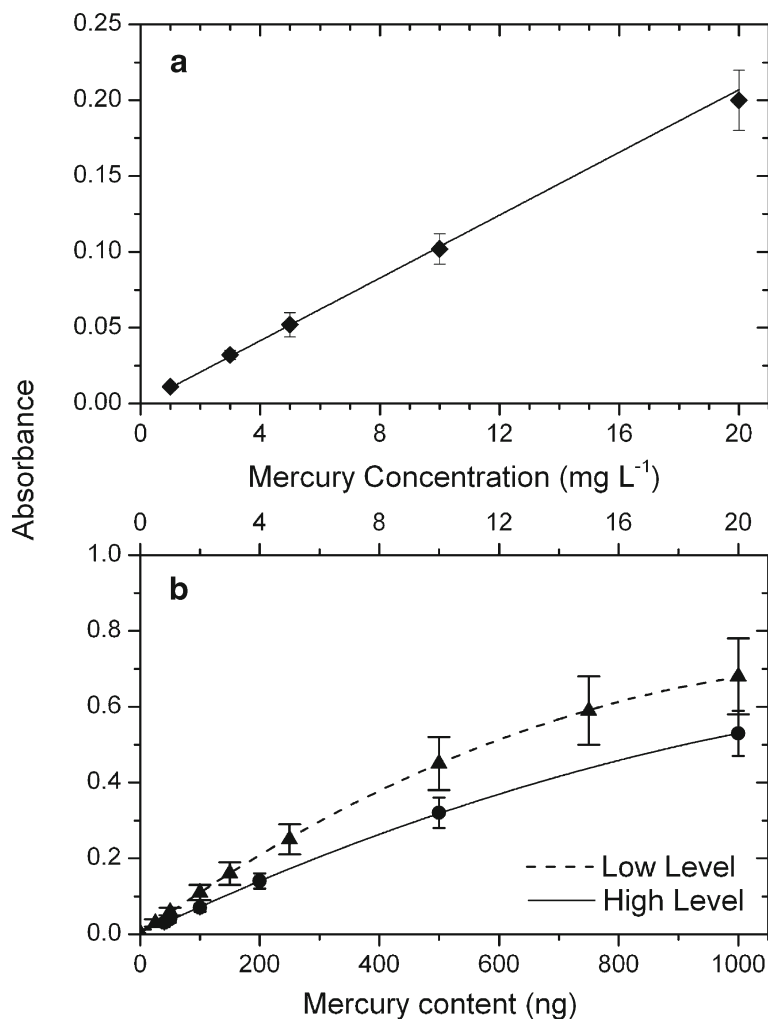


Table 1 Analytical parameters for the determination of mercury concentration in soil by cold vapour atomic absorption spectrometry (CVAAS) and thermal decomposition, amalgamation and atomic absorption spectrophotometry (TDAAS)

Description	CVAAS	TDAAS
LOD (mgkg ⁻¹)	0.19	0.08
LOQ (mgkg ⁻¹)	0.63	0.27
Calibration range	1–20 µgL ⁻¹	0.5–20 ng (low level) 20–1,000 ng (high level)
Calibration point	1.0, 3.0, 5.0, 10.0, 20.0 µgL ⁻¹	0.0, 0.5, 1.0, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0 ng (low level) 40.0, 50.0, 100, 200, 500, 1,000 ng (high level)
Number of calibration points	5	8 (low), 6 (high)
Number of replicates per calibration point	3	3 (low), 3 (high)
Calibration equation	$y=(1.04\pm 0.01) 10^{-2} x$	$y=(5.60\pm 0.01) 10^{-2} x - (1.11\pm 0.01) 10^{-3} x^2$ (low level) $y=(7.4\pm 0.1) 10^{-4} x - (2.3\pm 0.2) 10^{-7} x^2$ (high level)
Correlation coefficient, r^2	0.998	0.998 (low), 0.999 (high)
Residual standard deviation	0.0007	0.0011 (low), 0.0006 (high)

Table 2 Repeatability data for the methods used to determine mercury concentration in soil: cold vapour atomic absorption spectrometry (CVAAS) and thermal decomposition, amalgamation and atomic absorption spectrophotometry (TDAAS)

Description	CVAAS	TDAAS
Same day		
Number of replicates, n_s	10	10
Mean, c_s (mgkg ⁻¹)	0.82	0.83
Standard deviation, s_s (mgkg ⁻¹)	0.070	0.060
Standard uncertainty, u_s (mgkg ⁻¹)	0.022	0.019
Relative standard uncertainty, u_{ss}	0.027	0.023
Different days		
Days, n_d	10	9
Mean, c_d (mgkg ⁻¹)	0.82	0.85
Standard deviation, s_d (mgkg ⁻¹)	0.080	0.060
Standard uncertainty, u_d (mgkg ⁻¹)	0.025	0.019
Relative standard uncertainty, u_{dd}	0.031	0.024
Combined uncertainty same and different days	0.041	0.033

recovery factor correction of 0.91 (91 %) was required. For TDAAS, the calculated t -statistic was lower than the two-tailed critical t -statistic, indicating that it was not necessary to apply the recovery factor correction because the concentration of mercury in the CRM was not significantly different from that in the standard solution; hence, the correction factor was equal to 1.0 (100 %).

Table 3 Recovery data for the methods used to determine mercury concentration in soil: cold vapour atomic absorption spectrometry (CVAAS) and thermal decomposition, amalgamation and atomic absorption spectrophotometry (TDAAS)

Description	CVAAS	TDAAS
Certified material concentration, C_M (mgkg ⁻¹)	3.41	
Standard uncertainty, u_M (mgkg ⁻¹)	0.077	
Number of replicates, n_{re}	11	11
Mean, c_r (mgkg ⁻¹)	3.09	3.34
Standard deviation, s_r (mgkg ⁻¹)	0.08	0.12
Standard uncertainty, u_r (mgkg ⁻¹)	0.024	0.036
Relative standard uncertainty, u_{rr}	0.008	0.011
Recovery factor (f_r)	0.91	0.98
Critical t test value	4.33	0.84
Two-tailed critical t test value ($n_{re}-1$)	2.23	
Factor should be applied?	Yes	No

3.4 Combined and Expanded Uncertainty

The combined and expanded uncertainties (Eqs. 19 and 20) were calculated for the uncertainty sources. The relative combined and expanded uncertainties of the two methods are listed in Table 4. The results showed that the expanded uncertainty of mercury quantification using CVAAS was 10.8 %, which was greater than the expanded uncertainty of 9.30 % using TDAAS. This outcome is consistent with the reduced number of sample preparation steps required for TDAAS than for CVAAS.

There are few reports in the literature on comparative studies of methods of analysis of mercury in soil, and almost none that consider estimation of the uncertainty. However, some papers have compared the mercury content in different reference materials, finding variation coefficients in the range of 5 % to 15 % (Moskalova and Zemberyova 1997; Kocman et al. 2005). On the other hand, in general, the results in the literature show that TDAAS is faster and generates less waste than CVAAS (Claire et al. 2000).

3.5 Determination of Total Mercury Concentration in Soil

Because of the negative effects of mercury on human health and on ecosystems, standards have been established to limit the risk of mercury exposure. Analytical methods with sufficiently low MDL and MQL values are therefore required to enforce these standards (EURACHEM/CITAC 2007).

Chile has no standards limiting metal content in soil, including standards to limit mercury. However, current law allows the enforcement of international standards from countries such as the Netherlands, Canada and the USA. Netherland standards established a base value of 0.3 mgkg⁻¹ and an intervention value of 10 mgkg⁻¹ for mercury; the former value is known as the background level, and the latter value is known as the contamination level above which environmental intervention is considered. US and Canadian standards have established baseline and intervention values of 6.6 and 23 mgkg⁻¹, respectively.

Based on the MDL and MQL of CVAAS and TDAAS determined during the methods' validation, TDAAS can be used to evaluate all the standards described above, but with caution in the case of the Dutch

Table 4 Estimated uncertainties of the methods used to determine mercury concentration in soil: cold vapour atomic absorption spectrometry (CVAAS) and thermal decomposition, amalgamation and atomic absorption spectrophotometry (TDAAS)

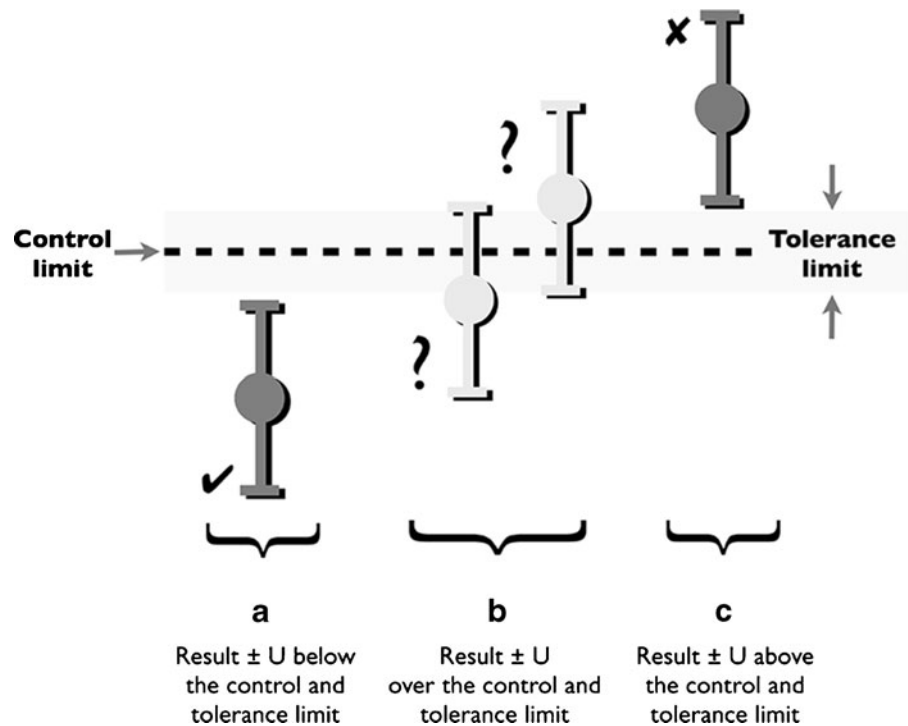
Influence magnitude	Value	Unit	Relative standard uncertainty
CVAAS			
Calibration curve (Eq./5/)	15.8	μgL^{-1}	0.018
Repeatability factor (Eq./11/)	1.000	adim	0.041
n measurements on same day ($n=11$)	0.82	mgkg^{-1}	0.027
n measurements on different days ($n=11$)	0.82	mgkg^{-1}	0.031
Recovery factor, u_{r} (Eq./12/)	0.910	adim	0.029
CRM	3.41	mgkg^{-1}	0.023
Cobs ($n=11$)	3.09	mgkg^{-1}	0.012
Conversion factor (Eq./16/)	0.196	$\text{mgL}\mu\text{g}^{-1}\text{kg}^{-1}$	0.0073
Volume	0.100	L	0.002
Weight	0.51×10^{-3}	kg	0.007
Relative combined standard uncertainty, u_c			0.054
Expanded relative uncertainty, $U_{C_{\text{Hg}}}$ ($k=2$)	3.40	mgkg^{-1}	0.108
TDAAS			
Calibration curve (Eq./10/)	702	ng	0.020
Repeatability factor (Eq./11/)	1.000	adim	0.033
n measurements on same day	0.83	mgkg^{-1}	0.023
n measurements on different days	0.85	mgkg^{-1}	0.022
Recovery factor, u_{r} (Eq./12/)	1.0	adim	0.025
CRM	3.41	mgkg^{-1}	0.023
Cobs ($n=11$)	3.34	mgkg^{-1}	0.026
Conversion factor (Eq./18/)	0.0048	$\text{mgng}^{-1}\text{kg}^{-1}$	0.007
Weight	0.20×10^{-3}	kg	0.007
Relative combined standard uncertainty, u_c			0.0458
Expanded relative uncertainty, $U_{C_{\text{Hg}}}$ ($k=2$)	3.34	mgkg^{-1}	0.0930

The result expressed with the expanded uncertainty, calculated using a coverage factor $k=2$, at a level of confidence of 95 %, is $3.40 \pm 0.37 \text{ mgkg}^{-1}$. The uncertainty corresponds to 10.8 %. The result expressed with the expanded uncertainty, calculated using a coverage factor $k=2$, at a level of confidence of 95 %, is $3.34 \pm 0.31 \text{ mgkg}^{-1}$. The uncertainty corresponds to 9.30 %

standards, according to which, the MQL of TDAAS can be from 0.24 to 0.30 mg/kg if the confidence level of the uncertainty (relative uncertainty, 9.3 %) is considered, and when the highest value of this interval is compared with the 0.3 mg/kg of the regulated value in the Dutch standard, the MQL for TDAAS are at the limit. So, it is therefore important to estimate and verify the uncertainty and consider if the uncertainty sources have been taken into account. In contrast, the MQL of CVAAS was higher than the baseline value established in the German and Dutch standards. In addition, the uncertainty of the method must be considered in order to comply with environmental standards.

The comparison of the results accounted for the uncertainty in the Hg concentration measurements in particular, but it will be applicable to any environmental measurement, using the criteria shown in Fig. 3, which shows hypothetical results of Hg concentrations in soil samples from different sites. The expanded uncertainty is superimposed over these results. These hypothetical results showed the way in which they are used to evaluate the performance of specifications that establish a control concentration limit. The results clearly show that the measurements in region a are within the specified limits and that those in c are above the limits because the difference between the results

Fig. 3 Uncertainty and standards compliance limit



and the control limit is greater than their uncertainty in both cases. However, the results in region b could be either above or below the control limit, and therefore, it is not possible to evaluate whether these results meet the specifications, and further studies are required to establish compliance with the control limit.

4 Conclusions

The two methods described in the present study can be used to determine total mercury concentration in soil. CVAAS and TDAAS were validated and compared using a CRM and replicate analysis of independent samples using an established method. The main conclusions of this work are the following:

- Mercury concentration could be measured reliably and accurately using both CVAAS and TDAAS. However, the statistical analysis showed that CVAAS required a recovery correction factor, while TDAAS did not require a correction factor.
- CVAAS had a greater uncertainty than TDAAS, at 10.8 % vs. 9.30 %, respectively.

- TDAAS represents a more environmentally friendly alternative for mercury determination because it uses fewer reagents and therefore decreases waste. In contrast, CVAAS requires sample preparation steps before the measurement can be made. CVAAS also requires reagents to generate mercury vapour, which leads to greater waste generation.
- To enforce the baseline and intervention values for mercury in soil, analytical methods must satisfy the purpose for which they are designed. Therefore, the MDL and MQL have to be determined and compared with the standard values. Under the conditions used in this study, TDAAS is acceptable for use in the compliance assessment of a wider range of standards than CVAAS.

Finally, it is important to mention that if the results of the analytical procedure applied under routine conditions are traceable to the reference used, and its corresponding uncertainty is reported, we can do everything possible to make the results of the unknown samples traceable under an assurance and quality control system.

Acknowledgements This study was conducted under an agreement between the Centro de Ciencias Ambientales, Facultad de Ciencias, Universidad de Chile and the Centro Nacional

del Medio Ambiente. The authors thank an anonymous referee of the journal for very useful comments on a previous draft.

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