Talanta 99 (2012) 363–368

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Development and validation of a simple thermo-desorption technique for mercury speciation in soils and sediments

A.T. Reis [a,*], J.P. Coelho [a], S.M. Rodrigues [a], R. Rocha [b], C.M. Davidson [c], A.C. Duarte [a], E. Pereira [a]

[a] CESAM/Chemistry Department, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal
[b] LECO® Instrumentos, SA, Spain
[c] WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, UK

ARTICLE INFO

Article history:
Received 13 February 2012
Received in revised form
24 May 2012
Accepted 29 May 2012
Available online 7 June 2012

Keywords:
Mercury
Speciation
Soils
Sediments
Thermo-desorption

ABSTRACT

An innovative technique for rapid identification and quantification of mercury (Hg) species in soils and sediments was developed using a direct mercury analyser. Speciation was performed by the continuous thermal-desorption of mercury species (temperature range 76–770 °C), in combination with atomic absorption spectrophotometry detection. Standard materials $HgCl_2$, Hg bound to humic acids and HgS were characterized; thermo-desorption curves of each material showed a well-resolved peak at specific temperature intervals: 125–225 °C, 100–250 °C and 225–325 °C, respectively. Certified reference materials (CRM) BCR® 142R, RTC® CRM 021, NRC® MESS-3 and PACS-2 were tested. Although the CRM were not certified for Hg species, the sum of Hg species obtained was compared to the certified value for total Hg; recoveries were 92%, 100%, 97%, and 95%, respectively. One sediment and three soil samples from mercury contaminated areas (total Hg concentrations 0.067–126 mg kg^{-1}) were analysed as well. It was possible to compare peaks of thermo-desorption curves from the samples with those from standard materials and thereby distinguish different Hg species in solid samples. Generally, Hg was present as bound to chloride or humic substances. The precision was satisfactory, as reflected by the relative standard deviations determined for standards and certified reference materials ($<11\%$; $n=10$).

1. Introduction

Mercury (Hg) is recognized as one of the most toxic metals. Its ecological and toxicological effects are however highly dependent on Hg speciation [1], as different species interact differently with the solid matrix, exhibiting different behaviour, solubility, mobility, and bioavailability [2,3]. Therefore, measurements of total Hg in soils and sediments do not provide enough information on its potential toxicity [3,4].

The behaviour of Hg in soils and sediments is very complex and is mainly controlled by adsorption and desorption processes, while the most important ligands are OH^-, Cl^-, and S-containing functional groups. Since the solubility of $HgCl_2$ and $Hg(OH)_2$ is rather high, the affinity of Hg to these ligands leads to an increased mobility [5]. This is especially true for $HgCl_2$, although if hydrolysis of Hg^{2+} occurs, it may result in the adsorption of Hg onto mineral colloids. In the presence of organic matter, the main forms of ionic mercury, Hg^{2+} and CH_3Hg^+, are strongly complexed by humic acids, fulvic acids and other organic molecules present in natural ecosystems [6]. The high affinity of Hg to sulphur explains the strong binding of Hg to soft organic matter and also the high stability of HgS [7]. In turn, the organo-mercury complexes can be adsorbed onto the surface of clays and iron, aluminium and manganese oxides. According to Han et al. [5], alkyl Hg species (such as methylmercury ($MeHg^+$) and ethylmercury ($EtHg^+$), and inorganic soluble species (such as $HgCl_2$)) are more mobile and contribute to the major portion of potential Hg toxicity in soil. On the other hand, chemically stable species, such as mercuric sulphide (HgS) are considerably less mobile and, therefore, less toxic to organisms [5].

The analysis of Hg species in soil or sediment can be accomplished by the application of sequential extraction methods [5,8–11]. These extractions are used to subdivide the Hg content of solid samples into several operational defined groups of more or less soluble species [12]. Issaro et al. [13] provided a comprehensive review of the different procedures available for Hg speciation in literature. Typical techniques for Hg speciation comprise numerous steps with one or more reagents as extractants, resulting in complex, time consuming processes with poor reproducibility, lack of selectivity, and non-specificity. Re-adsorption, background contamination or procedural losses of the volatile mercury species have also been regarded as problems associated with Hg sequential

---

[*] Corresponding author. Tel.: +351 234 370 737; fax: +351 234 370 084.
E-mail address: teresareis@ua.pt (A.T. Reis).

0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.05.065

extraction procedures [14,15]. Another limitation to these procedures is the lack of validation and reference materials for checking the performance both of method and the laboratory [14]. As an alternative, X-ray adsorption fine structure spectroscopy (EXAFS) [16,17] and X-ray absorption near edge structure (XANES) [18] can be applied to identify Hg species in soils and sediments. These techniques are however expensive and require samples with high Hg concentration (>100 mg kg^{-1}) [16].

Due to the abovementioned disadvantages of "conventional" sequential extractions, it was critical to develop an approach to address the issue of Hg speciation in a more efficient and less expensive manner. Methods based on species release from the matrix according to their desorption temperature have been tested [19–22]. So far, such measurements have been carried out with self-constructed apparatus consisting of a sample vessel located within an electric furnace that is directly connected to a heated quartz cell. The pyrolysis unit with the measuring cell was placed inside the detection unit of an atomic absorption spectrometer [20–22]. Since measurements were carried out under varied operational conditions (for example different heating rates and gas flow) and little is reported about accuracy and reproducibility of the results [20], it is difficult to compare data from the literature. Recently, Shuvaeva et al. [23] used a mercury analyser (RA-915+ of Lumex Ltd) for Hg speciation with some "in-house" modifications, in order to perform speciation using this equipment.

In this study we aimed to develop and test a simple procedure for Hg speciation by thermo-desorption, using a direct Hg analyser. Even though thermo-desorption techniques are not new, the use of a direct Hg analyser to do so is a significant improvement, as operational conditions can be easily standardized, allowing the intercomparison of results. For this particular work, the Advanced Mercury Analyser (AMA-254), from LECO® was used. To date, this kind of equipments have been used only in the determination of total Hg contents or in the quantification of previously chemical extracted Hg species [24]. In-house prepared standard materials were tested in order to characterize Hg compounds. Certified reference materials as well as sediment and soil samples were subsequently analysed. The results obtained by the thermo-desorption method for soil samples were later compared with those obtained by a sequential extraction method [15].

2. Materials and methods

2.1. Total mercury measurements

Total Hg concentrations were determined by thermal decomposition atomic absorption spectroscopy (AAS) with gold amalgamation (LECO®, model AMA-254) [25]. Briefly, the system consists of a nickel boat carrying the sample into a quartz combustion tube in which the solid sample is initially dried (30 s) prior to the combustion in an oxygen atmosphere, which for total Hg determination occurs at 750 °C (150 s). The mercury vapour produced is then trapped on the surface of a gold amalgamator. After a pre-determined time interval (45 s), the amalgamator is heated to 900 °C to quantitatively release the Hg which is transported to a heated cuvette (120 °C) prior to analysis by AAS using a silicon diode detector, at $\lambda = 253.6$ nm. The AMA-254 has two defined work ranges (0–30 ng and 100–500 ng).

2.2. Mercury speciation by thermo-desorption: development and validation of the technique

This technique of thermo-desorption speciation was developed using a LECO® model AMA-254, a common equipment used for Hg analysis. The main change introduced was the variation of the temperature of sample combustion (at the quartz combustion tube) and thereby controlling the release of the different Hg species from the solid matrix. While the temperature cannot be directly controlled, it can be increased by successively increasing the number of active furnaces. LECO® provided a set of 10 points, where temperature is given according to the number of active furnaces. After plotting the number of active furnaces (F) as a function of temperature (T), the equation that best described the dataset was determined ($T(°\mathrm{C}) = -0.096F^2 + 5.2F + 71$; $r^2 = 0.9993$). Using this equation, temperature was determined according to the number of furnaces that were active at each time.

2.2.1. Standard materials

Four standard materials were used in this work. Synthetic red cinnabar was purchased from Riedel-de-Haën and $HgCl_2$ from Panreac (both pure analytical quality grade). Natural cinnabar was scraped off from a natural mineral specimen, while humic acid–Hg complex was obtained by extraction from a soil sample, according to a procedure adapted from the International Humic Substance Society [26]. Since Hg concentrations in these materials were too high to be measured directly, they were diluted by thoroughly mixing with aluminium oxide in an end-over-end shaker, for a period of 10–12 h. Each material was analysed at least 10 times. Hg species were characterized by the temperature range they were released at, which consists of the temperature at which thermal-release starts, reaches the maximum and returns to the baseline.

2.2.2. Limit of detection and limit of quantification

To determine the limits of detection (Eq. (1)) and quantification (Eq. (2)), ten replicates of aluminium oxide were analysed. A limit of detection of 0.02 mg kg^{-1} and a limit of quantification of 0.03 mg kg^{-1} were established.

$$LOD = \bar{x} + (3.3 \times \sigma) \tag{1}$$

$$LOQ = \bar{x} + (10 \times \sigma) \tag{2}$$

where x is the mean ($n=10$), σ is the standard deviation ($n=10$).

2.2.3. Repeatability and accuracy

The thermal-desorption method was applied to four CRM: light sandy soil BCR® 142R and sandy loam RTC® CRM 021 for soil, and marine sediments NRC® MESS-3 and PACS-2 (total Hg concentrations are indicated in Table 1). Although these CRM are not certified for Hg species, to determine the accuracy of the procedure the sum of Hg species obtained was compared to the certified value for total Hg using a t-test. The experimental t (t_{exp}) was calculated using Eq. (3). No significant difference between t_{exp} and critical t for $n-1$ was observed.

The repeatability was determined through the relative standard deviation (RSD)

$$t_{exp} = \frac{(X_{exp} - X_{certified}) \times \sqrt{n}}{SD_{exp}}, \tag{3}$$

where X_{exp} is the mean sum of Hg concentration after the thermal-release analysis; SD_{exp} is the standard deviation associated to X_{exp}; n is the number of replicates analysed.

Total Hg concentrations of the four CRMs were also tested daily to check the equipment's accuracy. At least, three replicates of each material were analysed. Total Hg concentration was found within the confidence interval for certified values with recoveries in the range 81–113% and the relative standard deviation (RSD) among replicates was $<10\%$.

2.3. Mercury speciation by thermo-desorption: application to soil and sediment samples

The proposed thermo-desorption procedure was applied to three soils and one sediment samples collected in areas of Portugal where Hg contamination was previously identified [27–29]. Sample Industrial1 is from an agricultural soil collected in the vicinity of an industrial complex located in Estarreja, North-Western coast of Portugal. Samples Mine2 and Mine3 were collected in the Caveira sulphide mine, which is located in Grândola, in the North-West region of the Iberian Pyrite Belt. Sample Sediment4 is an estuarine sediment collected at Ria de Aveiro. Mercury contamination at these sites is known to occur due to the presence of a chlor-alkali plant (in Estarreja and Ria de Aveiro) and to mining activities (Caveira) [15,30]. Superficial (0–15 cm), air-dried soils and sediments were used in this study. The dried samples were sieved to <2 mm (soils) and <1 mm (sediment) using a nylon sieve.

Total carbon (TotC) percentages were measured on an Elemental Analysis instrument (LECO CNH-2000), according to ISO 10694:1995. For the determination of organic carbon content (OrgC), an excess of solution of 4 M of hydrochloric acid (HCl) was added to a crucible containing a weighed quantity of soil. The crucibles were left to stand for 4 hours and then were dried for 16 h at 60–70 °C. The analysis of carbon content after the removal of carbonates (organic carbon) was performed using the same procedure of total carbon determinations.

The particle size distribution and clay contents of the soil samples were determined using a Coulter LS230 laser diffraction particle size analyser. The classification of soils followed the USDA Texture Classes: sand fraction ($0.050 < \% < 2$ mm), silt fraction ($0.002 < \% < 0.050$ mm), and clay fraction ($\% < 0.002$ mm). Classification of samples was achieved by using the *Talwin 42*® classification software program.

Results of thermo-desorption were compared to results from a sequential extraction procedure previously applied to the soil samples [15]. In the latter, the mobile fraction was extracted with a solution of 2% HCl + 10% ethanol, while semi-mobile and non-mobile fractions were extracted with solutions of 1:2 (v/v) HNO_3:DDI water and 1:6:7 (v/v/v) HCl:HNO_3:DDI water, respectively. A more detailed description can be found in Reis et al. [15].

Table 1
Sum of Hg fractions obtained at each desorption temperature and recovery compared to the certified value and to total Hg, as determined daily.

CRM	Mean sum of Hg fractions (mg kg^{-1})[*]	Certified value for total Hg (mg kg^{-1})	Recovery[a] (%)	Total Hg (mg kg^{-1}), as determined daily[*]	Recovery[b] (%)
BCR 142R	0.058 ± 0.002	0.067 ± 0.011	87	0.063 ± 0.003	92
CRM 021	4.9 ± 0.3	4.7 ± 0.4	104	4.9 ± 0.2	100
MESS-3	0.095 ± 0.005	0.091 ± 0.009	104	0.098 ± 0.002	97
PACS-2	2.76 ± 0.21	3.04 ± 0.20	91	2.90 ± 0.12	95

[a] Recovery = (mean sum Hg fractions/certified value) × 100.
[b] Recovery = (mean sum Hg fractions/total Hg daily determination) × 100.
[*] mean ± standard deviation (n = 10).

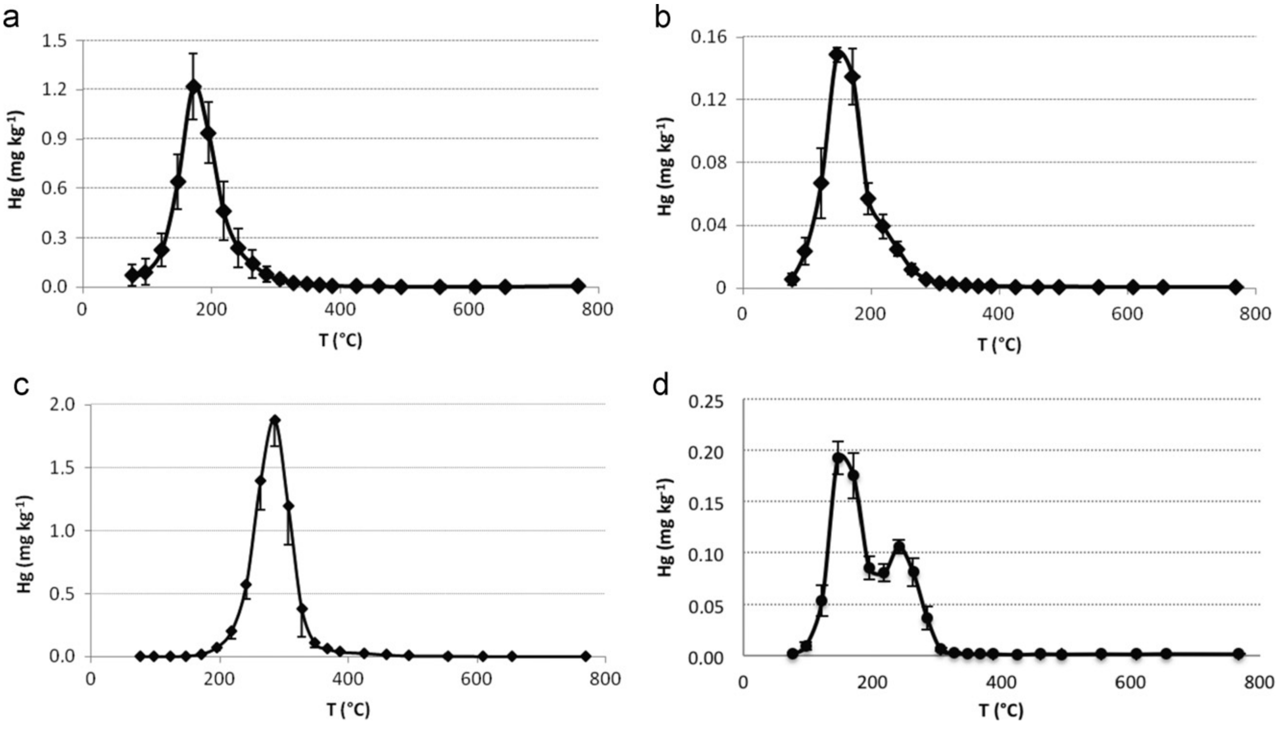

Fig. 1. Thermo-desorption curves of standard Hg materials. (a) $HgCl_2$, (b) Hg-humic acids, (c) HgS synthetic and (d) $HgCl_2$, Hg-HA and HgS mixture.

3. Results and discussion

3.1. Analytical performance and validation

3.1.1. Standard materials

The thermo-desorption curves (TDC) obtained for the standard materials are shown in Fig. 1 (mean and standard deviation). Synthetic HgS is released in the range of 225–325 °C (Fig. 1c). However, as natural cinnabar was prepared from the scraping of a natural mineral specimen, a pure substance was not achieved and additional peaks could be observed (TDC not shown); hence, this standard was not further used. Temperatures of release of $HgCl_2$ and Hg bound to humic acids are similar. Results of solid-phase thermal-desorption indicate that $HgCl_2$ is released in the range of 125–225 °C (Fig. 1a), while Hg bound to humic acids is released between 100 °C and 240 °C (Fig. 1b); therefore, it was not possible to differentiate the two species. The $HgCl_2$, Hg bound to humic acids and synthetic HgS standards were mixed (1:1:10) and analysed. The results (Fig. 1d) confirm this observation, as only two peaks can be identified: $HgCl_2$ and Hg bound to humic acids overlap. However, the differentiation of these species from cinnabar is attainable, giving a good indication of how reactive Hg present in a sample can be.

The RSD of $HgCl_2$, Hg bound to humic acids, and HgS was 10.8%, 5.9%, and 10.9%, respectively; which were considered acceptable precision values.

3.1.2. Certified reference materials

The TDC obtained for the CRM are displayed in Fig. 2 (mean curve and standard deviation). For BCR® 142R (Fig. 2a), one major peak was identified in the temperature range 220–260 °C, which is consistent with $HgCl_2$ and/or Hg bound to humic acids. A second smaller peak was identified at 600–650 °C, which could not be assigned to any Hg compound analysed in this study. In CRM 021 (Fig. 2b), the main percentage of Hg is released at 150–170 °C, which suggests that, again, chloride and/or humic acids species are present in this soil. A second peak can be seen at temperatures above 500 °C, which, according to Biester et al. [19] may correspond to HgO. For MESS-3 (Fig. 2c), one single and well-resolved peak was identified at 220–240 °C, which partially overlaps the $HgCl_2$/Hg bound to humic acids region. As can be seen in Fig. 2d, PACS-2 only has one peak, in the range of 140–220 °C, which is equivalent to $HgCl_2$ and/or Hg bound to humic acids.

Recovery was within the range of 87–104% (Table 1) and Hg concentration was within the certified confidence interval. In Table 1 the recovery comparing the thermo-desorption of the different CRM against the mean of total Hg determined daily is also presented. This approach is important considering that the response of the equipment is dependent on the condition of the catalytic tube. It is a fact that the equipment's accuracy decreases with time due to deterioration of this component. However, the frequent replacement of the catalytic tube would be extremely expensive and time consuming. Therefore, it continues to be used while the value determined for a CRM is within the certified confidence interval. When recovery was re-calculated considering the concentration obtained daily for each CRM, it improved to 92–100%. The values of t_{exp} for the four CRM analysed were lower than the respective critical value ($p=0.01$), which indicates that there are no significant differences between the certified and measured values; therefore, the accuracy of the method is considered satisfactory.

The low %RSD (3.4%, 6.1%, 5.3%, 7.6% for BCR 142R, CRM 021, MESS-3 and PACS-2, respectively) denotes a good repeatability of the method.

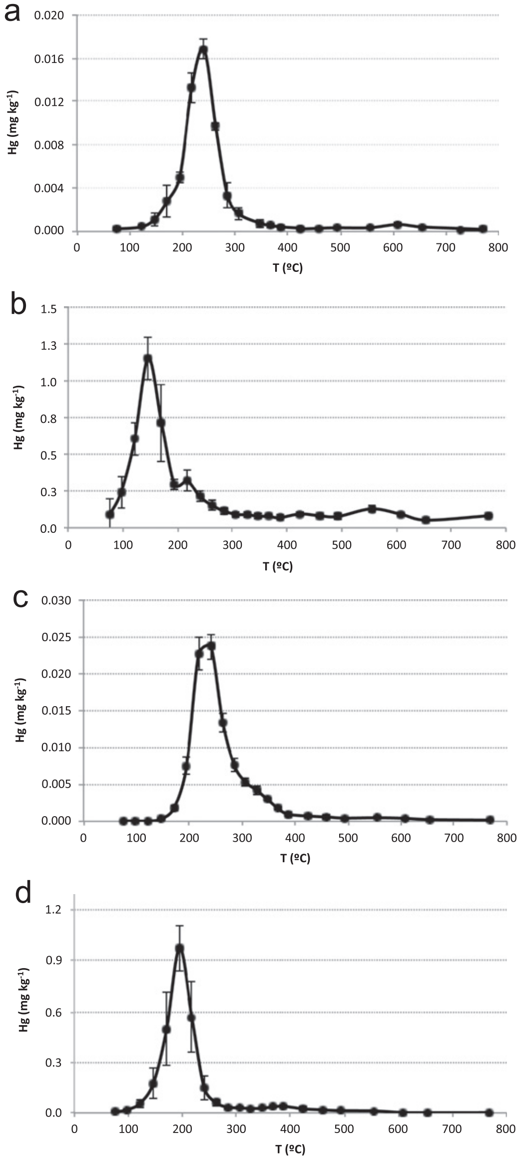

Fig. 2. Thermo-desorption curves for standard reference materials: (a) BCR 142R, (b) CRM 021, (c) MESS-3, and (d) PACS-2.

3.2. Soil and sediment samples

The TDC of the four samples analysed are shown in Fig. 3 (mean curve and standard deviation). Sample Industrial1 (Fig. 3a) shows a peak, consistent with $HgCl_2$ and/or Hg bound to humic acids and it represents 10.7 ± 0.4 mg kg^{-1} (91% of total Hg). The species have a homogenous distribution, indicated by the low RSD (3.4%, $n=7$). Hg°, which is known to be the main species emitted from chlor-alkali plants, was not detected in sample Industrial1. According to Biester and Scholz. [22], this species should be released at temperatures between 70 and 120 °C, which was not verified in any sample. Lack of Hg° may result from re-emission to atmosphere or oxidation to Hg^{2+}.

Caveira soils (Mine2 and Mine3 Fig. 3(b) and (c)) appeared to contain the same species, because one peak was identified between 125 and 275 °C in the two samples. In both cases, these species represent a significant percentage of total Hg concentration (84% and 85%, respectively), corresponding to concentrations of 106 ± 6 mg kg^{-1} and 56.2 ± 4.2 mg kg^{-1}. As found for sample Industrial1, $HgCl_2$ and/or Hg bound to humic acids in Caveira soils

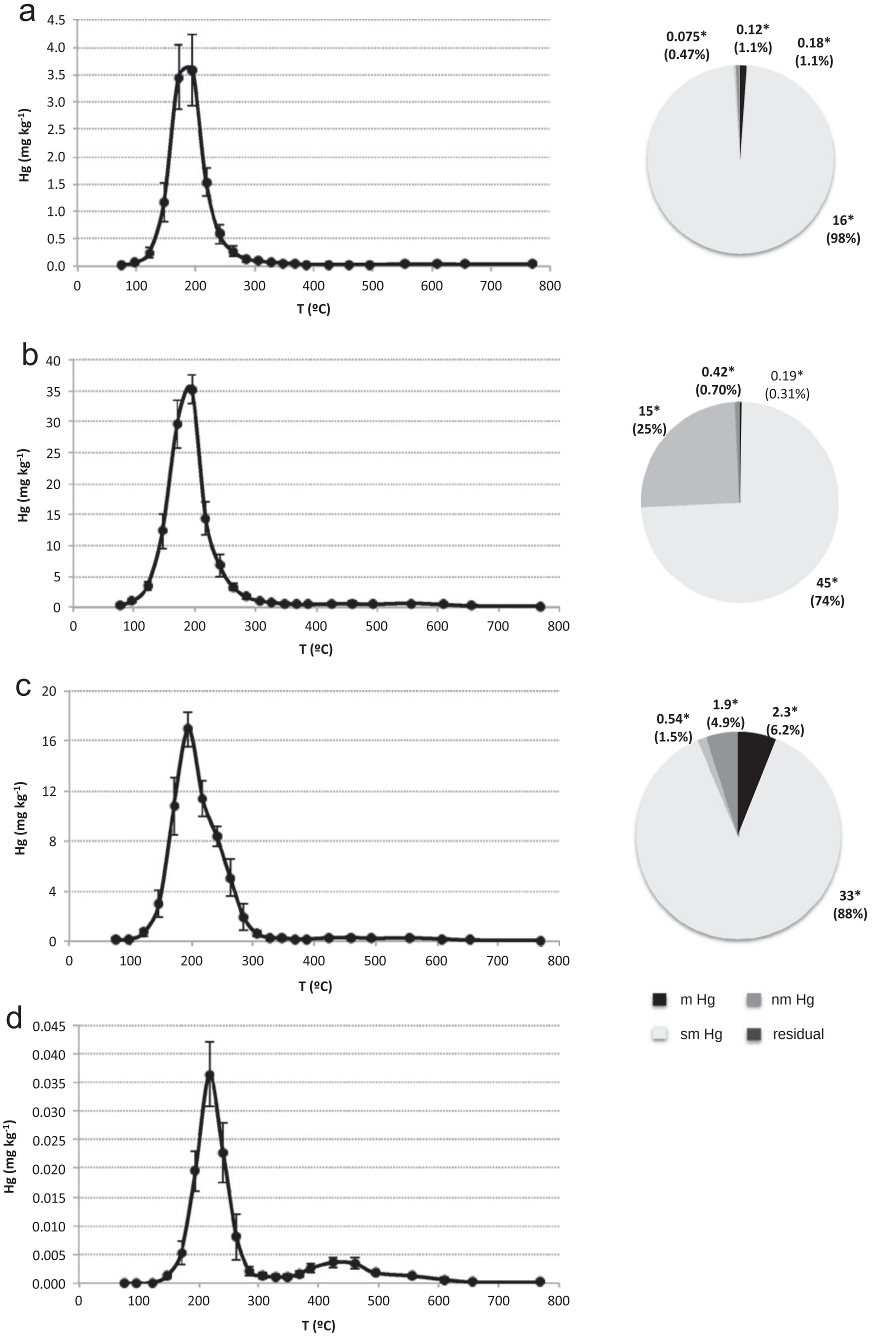

Fig. 3. Left: Thermo-desorption curves for samples 1–4 (n=7). Right: Hg distribution according to its extractability for samples 1–3 (results previously published in [15]); *mg kg^{-1}; m — mobile; sm— semi-mobile; nm — non-mobile. (a) Soil1, (b) Mine2, (c) Mine3 and (d) Sediment4.

also shows a homogeneous distribution, as indicated by the low RSD (< 8%). Mine2 also exhibits a second smaller peak at 450–650 °C, consistent with HgO. This species represents 1.8% of total Hg and has a RSD of 20.3%, indicating that the distribution of this compound in the sample is comparatively more heterogeneous.

A comparison of results of Hg speciation with those from sequential extraction is shown in Fig. 3. A previously performed sequential extraction procedure [15] revealed that Hg was mainly present (74–98%) as semi-mobile species in the soil samples (mostly Hg° and Hg^{2+} complexes —[5]), with a significant amount of non-mobile Hg (HgS, HgSe— [5]) being detected in Mine2 as well (25%). The results of both procedures (thermo-desorption and sequential extraction) are in agreement, considering that $HgCl_2$ or Hg bound to humic matter were the main species identified in all samples, and a stable species (released only at higher temperature) was also identified in Mine2.

Sediment4 showed two peaks: a major peak is visible at 150–300 °C; that represents a concentration of 0.096 ± 0.005 mg kg^{-1} (78% of total Hg); it also has low RSD (5.0%, n=7). The identification of this compound is not clear, as it partially overlaps the $HgCl_2$ and humic matter peaks; however, the release of mercury at a slight higher temperature suggests that Hg may be chemically bound to the matrix instead of physically adsorbed [3]. Sediments from this area have higher content in organic matter (about 10%) [31] than the studied soils (2–3%) [27], which may justify the stronger bound to the matrix. A second smaller peak was released in the temperature range of 375–500 °C and it does not correspond to any of the standards analysed in this study. However, Biester et al. [19] found that $HgSO_4$

and HgO were the only compounds to be released above 400 °C. As $HgSO_4$ is not stable under environmental conditions [19], it is unlikely that it is present in Sediment4; therefore, HgO is the most reasonable justification for the second peak observed. This species is responsible for 8.7% of total Hg in the sample and exhibits a higher RSD (19.5%), which can indicate that HgO is heterogeneously distributed. The same was observed in sample Mine2.

4. Conclusion

The thermo-desorption technique provides an attractive alternative in Hg speciation, as it allows a fast and relatively easy identification and quantification of Hg species within soil and sediment samples. In this study it was possible to obtain thermo-desorption curves for standard materials such as $HgCl_2$, Hg–humic acids and HgS using an automatic Hg analyser, since each material showed a well-resolved peak at specific temperature intervals: 125–225 °C for $HgCl_2$, 100–250 °C for Hg–humic acids and 225–325 °C for HgS.

The results obtained by the two methods (thermo-desorption and sequential extraction) are consistent, but the thermo-desorption technique offers many advantages over conventional methods for mercury speciation: is selective, sensitive, allows the prompt identification of several Hg species, is free of cross contamination, can be applied to a vast range of total Hg concentrations, requires none or little sample preparation which also prevents the loss of volatile Hg compounds, since the analysis is performed directly on the solid sample. No residues are produced because no reagents are used, and a small quantity (<1 g) of sample is required. The low limit of quantification is another advantage of this technique, as even low concentrations of a species can be quantified. It was found that the RSD depends on the occurring Hg compound, but, overall, the repeatability of the method is good. Since the equipment used is commercially available, operational conditions can be standardized and results obtained by different laboratories can be easily compared.

The developed technique can be an important contribution for the preliminary screening of the potential risk associated to Hg contamination at a given locale. Even though the complete separation, identification and quantification of all Hg species is still not possible, indication on how they interact with the matrix is attainable, providing relevant information on the potential mobility and availability of the samples Hg species. In the future, several aspects will be studied, mainly targeting the separation of $HgCl_2$ from Hg bound to humic acids and identification of the new Hg species.

Acknowledgements

The authors would like to thank the Portuguese Foundation for Science and Technology for supporting this study via a PhD Grant (SFRH/BD/43681/2008; A.T. Reis) and Project SEPMERCURY—Sequential extraction methods for assessing the origin, mobility and toxicity of mercury from contaminated solid matrices and preparation of new sediment and soil reference materials (PTDC/AAC-AMB/105157/2008).

References

[1] T.W. Clarkson, Environ. Health Perspect. 110 (2002) 11–123.
[2] M. Lodenius, in: C.J. Watras, J.W. Huckabee (Eds.), Mercury Pollution—Integration and Synthesis, Lewis Publishers Boca Raton, FL (USA), 1994, pp. 343–354.
[3] H. Biester, G. Müller, H.F. Schöler, Sci. Total Environ. 284 (2002) 191–203.
[4] N. Beckvar, J. Field, S. Salazar, R. Hoff, Contaminants in Aquatic Habitats at Hazardous Waste Sites: Mercury, Department of Commerce Editor, Seattle, Washington, 1996. (p. 64).
[5] Y. Han, H.M. Kingston, H.M. Boylan, G.M.M. Rahman, S. Shah, R.C. Richter, D.D. Link, S. Bhandari, Anal. Bioanal. Chem. 375 (2003) 428–436.
[6] L.C. Oliveira, R.L. Serudo, W.G. Botero, A.G.R. Mendonça, A.D. Santos, J.C. Rocha, F.S.C. Neto, Quím. Nova 30 (2007) 274–280.
[7] E. Schuster, Water Air Soil Pollut. 56 (1991) 667–680.
[8] N.S. Bloom, E. Preus, Proceedings of the 2nd International Symposium on Contaminated Sediments, 2003, pp. 331–336.
[9] R. Fernández-Martínez, M.I. Rucandio, Anal. Bioanal. Chem. 375 (2003) 1089–1096.
[10] N.W. Revis, T.R. Osborne, D. Sedgley, A. King, Analyst 114 (1989) 823–825.
[11] H. Sakamoto, T. Tomiyasu, N. Yonehara, Anal. Sci. 8 (1992) 35–39.
[12] R. Rubio, G. Rauret, J. Radioanal. Nucl. Chem. 208 (1996) 529–540.
[13] N. Issaro, C. Abi-Ghanem, A. Bermond, Anal. Chim. Acta 631 (2009) 1–12.
[14] J.R. Bacon, C.M. Davidson, Analyst 133 (2008) 25–46.
[15] A.T. Reis, S.M. Rodrigues, C.M. Davidson, E. Pereira, A.C. Duarte, Chemosphere 81 (2010) 1369–1377.
[16] C.S. Kim, G.E. Brown, J.J. Rytuba, Sci. Total Environ. 261 (2000) 157–168.
[17] C.S. Kim, J.J. Rytuba, G.E. Brown, J. Colloid Interface Sci. 271 (2004) 1–15.
[18] C.S. Kim, N.S. Bloom, J.J. Rytuba, G.E. Brown, Environ. Sci. Technol. 37 (2003) 5102–5108.
[19] H. Biester, M. Gosar, G. Müller, J. Geochem. Explor. 65 (1999) 195–204.
[20] H. Biester, G. Nehrke, J. Fresenius, Anal. Chem. 358 (1997) 446–452.
[21] A. Bollen, A. Wenke, H. Biester, Water Res. 42 (2008) 91–100.
[22] H. Biester, C. Scholz, Environ. Sci. Technol. 31 (1997) 233–239.
[23] O.V. Shuvaeva, M.A. Gustaytis, G.N. Anoshin, Anal. Chim. Acta 621 (2008) 148–154.
[24] E. Pereira, S.M. Rodrigues, M. Otero, M. Válega, C.B. Lopes, P. Pato, J.P. Coelho, A.I. Lillebø, A.C. Duarte, M.A. Pardal, R. Rocha, TrAC—Trends. Anal. Chem. 27 (2008) 959–970.
[25] C.T. Costley, K.F. Mossop, J.R. Dean, L.M. Garden, J. Marshall, J. Carroll, Anal. Chim. Acta 405 (2000) 179–183.
[26] International Humic Substance Society. Isolation of IHSS Soil Fulvic and Humic Acids, 2008 (cited 2011 February). Available from: 〈http://www.ihss.gatech.edu/soilhafa.html〉.
[27] A.T. Reis, S.M. Rodrigues, C. Araújo, J.P. Coelho, E. Pereira, A.C. Duarte, Sci. Total Environ. 407 (2009) 2689–2700.
[28] F. Barriga, in: R.D. Dallmeyer, E. Martinez (Eds.), Pre-mesozoic Geology of Iberia, Springer-Verlag, 1990, pp. 369–379.
[29] J.P. Coelho, M.E. Pereira, A.C. Duarte, M.A. Pardal, Estuarine Coastal Shelf Sci. 65 (2005) 492–500.
[30] S.M. Rodrigues, B. Henriques, J. Coimbra, E.F.D. Silva, M.E. Pereira, A.C. Duarte, Chemosphere 78 (2010) 1301–1312.
[31] M. Válega, A.I. Lillebø, I. Caçador, M.E. Pereira, A.C. Duarte, M.A. Pardal, Chemosphere 72 (2008) 1607–1613.