

Flow-Through Coulometric Determination of Mercury in Soils and Soil Extracts

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Received 24 May 1999

Trace concentrations of mercury were determined by flow-through stripping coulometry in soils and soil extracts. The method is based on the electrochemical collection of Hg in a gold-plated porous electrode followed by the galvanostatic stripping of the deposit while the stripping time is measured. Organic substances such as humic acids exert no interfering effect. The interference due to Fe(III) species can be eliminated by adding a diphosphate solution to the sample. The limit of quantification of the method is $0.5 \mu\text{g dm}^{-3}$ and the upper concentration range is about 10 mg dm^{-3} .

Mercury is one of the most dangerous contaminants in the environment and there is an increasing demand for its reliable determination. There are various analytical methods for its determination, most of them utilize the easy evaporation of elemental mercury and its measurement through atomic absorption. Electrochemical methods offer a simple alternative to spectroscopic techniques. Aqueous samples, especially those with high salt and/or acid contents can be directly analyzed electrochemically [1–5].

Automated flow-through stripping coulometry has been found suitable in the determination of mercury in water samples [6] and in monitoring of waste water [7]. We have found that the method can also be applied for complex soil samples, however, after proper sample pretreatment. Determination of forms of binding (speciation) of heavy metals in the soils is currently more important than the determination of their total content. Various soil extracts are used in speciation analysis of metals in soils. The method of flow-through stripping coulometry is very suitable for analysis of many metals including mercury in soil extracts.

The mentioned atomic absorption spectrophotometry (AAS) with the so-called cold vapour technique is currently the most commonly used method for the determination of total mercury in soil samples.

The conditions for the analysis of mercury in soils and soil extracts by flow-through stripping coulometry will be discussed in the following sections. The results

will be compared with results obtained using the AAS method.

EXPERIMENTAL

Two soil samples from Slovakia, calcalit Aplic Chernozem (1996) from surroundings of Trnava town from horizon 5–15 cm (TT-1) and soil from surroundings of Krompachy town from horizon 5–15 cm (P-65), were chosen.

Reagents of anal. grade purity were used. The solutions were prepared in freshly boiled deionized water. Hydrochloric acid and aqueous ammonia were purified by isopiestic distillation. Nitric acid was purified by subboiling distillation in a quartz apparatus (Hans Kuerner, Rosenheim, Germany). Carrier electrolyte: 0.1 mol dm^{-3} in H_2SO_4 and $0.004 \text{ mol dm}^{-3}$ in HCl and plating solution: $0.0002 \text{ mol dm}^{-3}$ in HAuCl_4 and 0.02 mol dm^{-3} in HCl. Standard solutions of Hg were prepared fresh from a reference material (Slovak Institute of Metrology, Bratislava, Slovakia) by diluting them with the carrier electrolyte.

The measurements were performed on a fully automatic electrochemical analyzer EcaFlow, Model 110 with peristaltic pumping (ISTRAN Ltd., Bratislava, Slovakia). The software delivered with the instrument was used for signal processing and evaluation. The operation principle of the instrument has been recently described [6].

The flow-through cells used were of the type EcaCell 353, equipped with compact and exchangeable porous working electrodes E53 (ISTRAN Ltd., Bratislava, Slovakia). The active electrode material was glassy carbon powder pressed to a cylindrical volume of 5 mm and 3 mm in diameter and width, respectively. Its active-surface area was about 25 cm². The flow rate both at deposition and stripping was set constant in the range of 2.0 to 3.0 cm³ min⁻¹.

The built-in reference electrode in the cell was an Ag/AgCl one in 4.16 mol dm⁻³ KCl solution. The counter electrode was a Pt wire. The potentials throughout this paper are expressed relative to the Ag/AgCl reference electrode used in the cells.

The high-pressure sample digester was a DAB II type device (Berghof Maassen, Eningen, Germany) with 50 cm³ PTFE vessels. The microwave-assisted digestion was performed in a two-vessel digester Microwave Digestion BM1S (Plazmatronika, Wrocław, Poland).

Reference values for Hg contents were obtained by making use of the Trace Mercury Analyser TMA-254 (Institute of Chemical Technology, Prague, Czech Republic) enabling the direct analysis of the soil samples. The conditions used for the mercury determination in solid samples were as follows: radiation source low-pressure mercury vapour lamp (wavelength 253.6 nm), time of drying 60 s, drying temperature 110°C, time of decomposition 120 s, decomposition temperature 850°C, carrier gas oxygen (flow rate 160 cm³ min⁻¹).

High-Pressure Digestion

Soil samples (0.5 to 1.0 g) were digested with a mixture of 2 cm³ of concentrated nitric acid and 6 cm³ of concentrated hydrofluoric acid in closed PTFE vessels at 180°C for 3 h. The nitrous gases in the solution were evaporated under an IR lamp. 30 cm³ of saturated boric acid was added and the solution was transferred to a 50 cm³ volumetric flask and the volume was adjusted to 50 cm³ by distilled water. To sample solutions with high Fe(III) contents (solutions coloured to yellow or brownish-yellow) solid sodium diphosphate was added prior to the analysis (1–2 g of Na₄P₂O₇ to 50 cm³ sample solution).

Microwave-Assisted Digestion

0.3 g of soil sample was digested with a mixture of 5 cm³ of concentrated nitric acid and 2 cm³ of concentrated hydrofluoric acid in a closed PTFE vessel. The digestion was provided at a pressure of 2.5 MPa for 40 min. The resulting solution was treated as above.

Extraction

To 2 g of soil sample in a 100 cm³ plastic vessel 25 cm³ of 2.0 mol dm⁻³ HNO₃ was added and after

sealing the vessel the content was shaken at laboratory temperature for 6 h. The mixture was then filtered and after adding 2 g of Na₄P₂O₇ the volume was adjusted to 50 cm³ by distilled water.

Measurement Procedure

The electrodes were plated with gold at the beginning of the analyses and the same coating was used during the measurements. The plating was performed from the flowing plating solution at a potential scanned linearly from -1500 mV to +500 mV. In most experiments 40 cm³ of the plating solution was used. The built-in program of the instrument was used for plating.

The parameters of the analysis were put in the computer of the instrument. The most decisive parameters were as follows: deposition potential 200 mV, quiescence potential 0 mV, quiescence time 10 s, stripping current 200 μA, sample volume 0.1 to 10 cm³ (depending on the expected Hg content), peristaltic pump at stripping on.

The sampling tube of the instrument was immersed to the sample solution and measurement was started. After this point the analysis proceeded fully automatically: The given volume of the sample solution was allowed to flow through the cell with the working electrode set to the deposition potential. After washing the cell with the carrier electrolyte at the same potential the potential was shifted to the quiescence value. Then the deposit was stripped with constant current to the carrier electrolyte, whereas the change of the potential of the working electrode was monitored and evaluated by the memory mapping technique [8, 9]. This technique enables to directly convert the *E vs. t* dependence to a more convenient *dt/dE vs. E* dependence. In the next step the background signal resulting from the carrier electrolyte was measured and was subtracted from the sample signal to give the background-corrected stripping potentiogram.

The concentration of metals in the sample solution was obtained after integrating the corresponding stripping peak which gives the chronopotentiometric transition time [10]. The concentration was calculated from the following expression

$$c = it / (zFV) \quad (1)$$

where *c* denotes the metal ion concentration in mol dm⁻³, *i* the dissolution current in A, *t* the chronopotentiometric transition time in s, *z* the charge number of the electrochemical stripping process (*z* = 2 for Hg), *F* the Faraday constant, and *V* the sample volume in dm³.

RESULTS AND DISCUSSION

Trace concentrations of Hg were determined in a

flow-system by constant current stripping chronopotentiometry in coulometric mode. Mercury was electrodeposited from the flowing sample solution in an electrochemical flow-through cell on a large porous electrode plated with a thin layer of gold. The deposited mercury was then stripped with constant current and the potential change of the working electrode was recorded and evaluated. Since complete electrochemical yields were achieved at both the deposition and dissolution steps, the mercury concentration in the sample solution could be calculated from Faraday's law without calibration process. The utility of the method named flow-through stripping coulometry was demonstrated with the analysis of two types of soil samples: one with a high mercury content and the other with a low one. The mobile fraction of mercury was determined by extraction with diluted nitric acid. The determination of total mercury in soil required the digestion of the samples. The sample solutions from both procedures are complex and the sample matrix interfered in the determination by stripping coulometry.

Concentrations of Fe(III) above 10 mg dm^{-3} in the sample deteriorated the signals and caused lower recoveries (Fig. 1). This interference is probably due to the reduction of Fe(III) to Fe(II) in the deposition step increasing significantly the currents and the corresponding potential drop inside the bulk of the porous electrode. Owing to this potential drop the active-surface area might be too low to ensure a complete deposition of Hg(II) ions from the flowing sample solution.

Various procedures have been tested to eliminate the adverse effect of Fe(III) species. The addition of ascorbic acid to reduce Fe(III) to Fe(II) has not solved the problem, as the residues of the ascorbic acid in the cell gave rise to high signals obscuring the Hg signal. The use of complexing agents such as potassium fluoride, citric acid or tartaric acid was also unsuccessful. On the other hand, the addition of sodium diphosphate to the sample solution significantly improved the recoveries (Fig. 1) and therefore it was used in further measurements.

Copper does not interfere since its stripping peak is far from that of Hg (Fig. 2). Moreover, the deposition of Cu(II) can easily be minimized by setting the deposition potential to 300 mV where Cu(II) is not deposited.

Organic substances such as humic acids adsorbed to the electrode surface may interfere since they can be oxidized at potentials near to the stripping peak of Hg. Fortunately, no significant adsorption was observed in the treated acidic solutions. However, the base line for soil samples at potentials above 600 mV was higher than that for standard solutions (see the insert in Fig. 2) but it did not interfere in the evaluation of the signals.

The parameters for the determination of Hg by

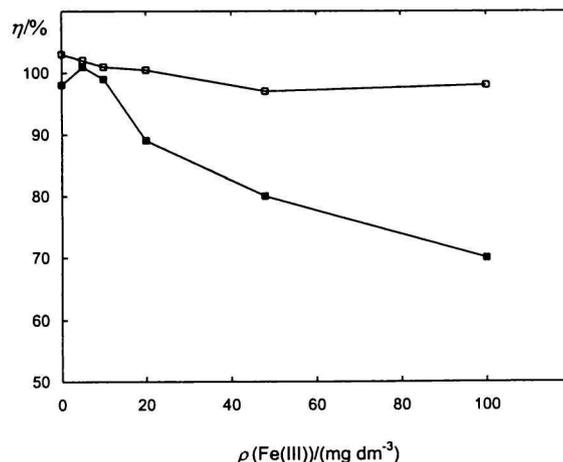


Fig. 1. Influence of the Fe(III) concentration in the sample on the recovery of Hg without (■) and with the addition of 1 g of $\text{Na}_4\text{P}_2\text{O}_7$ (□) to 50 cm^3 of sample solution. Hg added $10 \mu\text{g dm}^{-3}$, sample volume 2 cm^3 , deposition potential 300 mV, dissolution current $200 \mu\text{A}$.

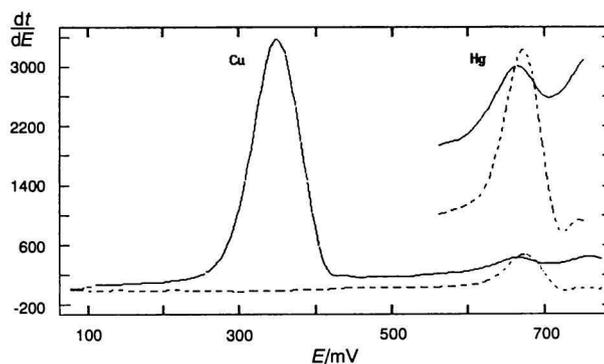


Fig. 2. The converted chronopotentiograms (dt/dE vs. E) of the soil extract (full line) and that of a standard solution (dashed line) containing $10 \mu\text{g dm}^{-3}$ of Hg. Sample volume 2 cm^3 , deposition potential 200 mV, dissolution current $200 \mu\text{A}$. Insert: the zoomed Hg signals.

flow-through stripping coulometry have been recently optimized [6]. Using the operational parameters given in Experimental, a limit of quantification of about $0.5 \mu\text{g dm}^{-3}$ Hg in both the soil extracts and digested soil sample solutions can be achieved for 2 cm^3 sample solution. The limit of quantification (LOQ) was checked with the analysis of model synthetic samples over a wide range of analyte concentrations. Determined amounts of mercury in synthetic samples were compared with the added mercury. The results were evaluated using the linear regression analysis. The LOQ for flow-through stripping coulometry was computed from the confidence band according to Ref. [11] by the program Adstat ver. 1.2 (TriloByte Ltd., Pardubice, Czech Republic). The upper concentration level found by addition of Hg standard to the sample solutions was about 10 mg dm^{-3} . In the paper [12] total

Table 1. Comparison of the Results of Hg Determination Obtained with the Microwave-Assisted and High-Pressure Digesters

Soil sample	$w(\text{Hg})/(\text{mg kg}^{-1})$		
	Microwave	High-Pressure	Reference value ^a
P-65	0.52 ± 0.01	0.49 ± 0.04	0.49 ± 0.05
TT-1	0.076 ± 0.003	0.080 ± 0.003	0.077 ± 0.001

a) TMA analyzer.

Table 2. Mercury Contents in the Soil Samples and Extracts

Soil sample	Soil	Extract	Extractable
	$w(\text{Hg})/(\text{mg kg}^{-1})$	$w(\text{Hg})/(\text{mg kg}^{-1})$	$\eta/\%$
P-65	0.52 ± 0.01	0.30 ± 0.01	57.9
TT-1	0.076 ± 0.003	0.049 ± 0.009	64.4

mercury was determined in various soil samples by the method AAS using TMA-254. Detection limit (LOD) described in paper [12] was 0.15 ng of Hg.

In this paper the limit of quantification of Hg was calculated using the method named flow-through stripping coulometry. Its value is 1 ng of Hg. LOQ is usually higher than LOD. The value of LOQ achieved in this paper is satisfactory for reliable determination of mercury in soil samples.

Soil samples were treated by digestion with a mixture of nitric and hydrofluoric acids in closed vessels (see Experimental). The results of total mercury contents in two soils determined by flow-through stripping coulometry and using TMA-254 instrument are compared in Table 1. The confidence interval of mass fraction $w(\text{Hg})$ obtained by TMA-254 was calculated according to [13] from the results obtained on six measurements from solid samples. The confidence intervals of $w(\text{Hg})$ for flow-through stripping coulometry were calculated from the results obtained on six parallel decomposed samples [13]. All confidence intervals were calculated on the significance level $\alpha = 0.05$. There was no significant difference between the results obtained from samples digested in the microwave-assisted digester and the high-pressure device (Table 1).

Mercury in the soil samples was extracted with 2.0 mol dm⁻³ nitric acid for determination of its indication value. The results are collected in Table 2. About 60 % of the total mercury can be extracted with diluted nitric acid. Since the extraction is simpler than the digestion, the extraction procedure may provide an indicator value for screening procedures for possible mercury contamination of soils. These values are the maximally bioavailable forms for plants.

The determination step by flow-through stripping coulometry is simple and reliable. A complete measurement can be performed within 3–5 min depend-

ing on the sample volume taken for analysis. The method is suitable mainly for analysis of various soil extracts.

Acknowledgements. This work was supported by Grant provided by the Slovak Grant Agency for Science under No. 1/4198/97. One of the authors (E. Beinrohr) thanks for the financial support provided by the Volkswagen Foundation, Germany through the Collaborative Research Grant I/F1 023 and by the Slovak Grant Agency VEGA, project No. 1/6103/99.

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