

Preconcentration of Hg(II) and Total Hg in Waters for Flame AAS in a Flow-through Electrochemical Cell*

A. MANOVÁ**, E. BEINROHR, and L. JURICA

*Department of Analytical Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology,
SK-812 37 Bratislava
e-mail: manova@chtf.stuba.sk*

Received 16 October 2002

Mercury in water samples is determined by flame atomic absorption spectrometry after the preconcentration of Hg(II) on gold working electrode in a flow system coupled on-line to the AAS instrument. The porous electrode is made of glassy carbon particles coated with gold. Tap, river, and wastewater samples were analyzed using this method. The method enables to determine Hg in the concentration range of 0.01–30 mg dm⁻³.

Wastewaters, *e.g.* from chloro-alkali electrolytic plants may contain mercury and mercury compounds and therefore it is important to have reliable and simple methods to determine their content. There are few methods enabling the determination of traces of mercury. Most of them are based on atomic absorption spectrometry and make use of the easy reduction and evaporation of mercury to its atomic form. These analyzers chemically convert the different mercury species present in the sample solutions to elementary mercury that is then stripped by a gas to the absorption tube for measurements. The measurement step is simple but the sample preparation procedure may be rather tedious. For complex compounds the sample preparation may include a digestion of the sample to convert all mercury compounds into Hg(II), which is then reduced to elementary mercury and is transported by a gas to the absorption cuvette. Mercury can be easily preconcentrated on gold electrode, which is successfully used for its electrochemical determination [1–4]. This principle may significantly simplify the procedure owing to the fact that the reduction of Hg species and the determination can be done with the same electrode. The chemical reduction step can be omitted. The main advantages of the use of flow-through cell are simplicity, high speed, and low costs. However, like other methods, this method is also vulnerable to matrix interferences and electrode fouling. The aim of this paper is to show the utility of preconcentration determinations of Hg in waters by making use of a flow system coupled on-line to the AAS as measurement principle.

EXPERIMENTAL

Anal. grade reagents and deionized boiled cooled water were used throughout the experiments. The carrier electrolyte solution contained 0.1 mg dm⁻³ of H₂SO₄ and 0.001 mg dm⁻³ of HCl. Standard solution of 1.000 mg dm⁻³ of Hg(II) was used. Wastewater samples were obtained from the plant Grafia and from a chloro-alkali electrolytic plant. The flow-through cell for preconcentration was prepared from perspex body. The working electrode of diameter and length of 8 mm and 4 mm, respectively, was prepared from reticulated vitreous carbon "RVC of 100 pores per inch porosity" (Electrosynthesis Co., East Amherst, NY, USA) crushed to particles of 10 to 100 μm size. The surface of the working electrode was plated with a thin layer of gold. The cell was filled with 0.0002 mg dm⁻³ H[AuCl₄] in 0.02 mg dm⁻³ HCl and voltage of –2000 mV was applied to the electrodes. The flow system (Fig. 1) was constructed of PTFE tubing. The sampling valve was a 6-way one (Latek, Eppelheim, Germany). A peristaltic pump drove the liquids. For the detection of Hg a flame AAS instrument AA-6800 (Shimadzu, Kyoto, Japan) coupled on-line to the flow system was used. Acetylene–air flame was used operating under reducing conditions. The signal sensitivity was about 0.005 absorbance unit/(mg dm⁻³) (see Table 1).

Procedure

The flow system and cell were purged with 1 mg dm⁻³ HCl solution for a few min to remove possible

*Presented at the XVIth Slovak Spectroscopic Conference, Košice, 23–27 June 2002.

**The author to whom the correspondence should be addressed.

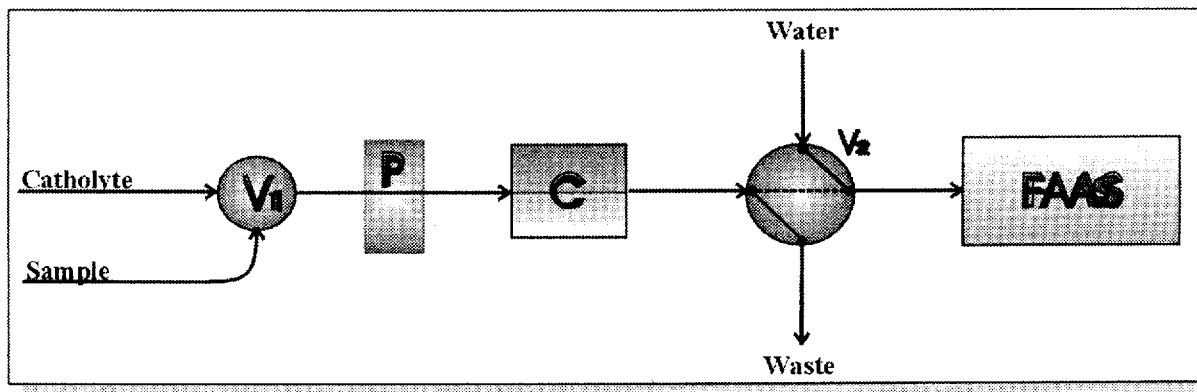


Fig. 1. Diagram of the flow system. P – peristaltic pump, C – electrochemical cell, V_1 , V_2 – valves, FAAS – flame atomic absorption spectrometry.

Table 1. Figures of Merit

Preconcentrated volume cm^3	Detection limit mg dm^{-3}
1	0.35
10	0.035
25	0.014
50	0.007

contamination. The working electrode was brought at the deposition potential. A given volume of the sample solution filtered through a $0.45 \mu\text{m}$ membrane filter was pumped through the system at the flow rate $8 \text{ cm}^3 \text{ min}^{-1}$ and was mixed with the carrier electrolyte. This solution passed through the cell where mercury in the sample was preconcentrated. The system was subsequently rinsed with the carrier electrolyte, the flow was stopped and the deposit was stripped at constant current. After this step the system was rinsed again with the carrier electrolyte. The next step included the ignited flame of the AAS instrument and the preconcentrated Hg was eluted to the instrument by making use of the valve. The integrated signal was measured and the corresponding Hg concentration was calculated by means of a calibration plot. The cell was washed again with $1 \text{ mol dm}^{-3} \text{ HCl}$ to prepare the system for the next run.

DISCUSSION

Mercury can easily be determined in various samples by FAAS after the preconcentration of Hg(II) species on gold working electrode. However, the porous working electrode used in this technique may rapidly be clogged when analyzing wastewater with high content of colloidal particles. Moreover, dissolved gases may be liberated from waters, which tend to

form bubbles in the pores of the working electrode, decreasing its active surface and efficiency. Hence, for direct analysis of such samples an oxygen scavenger is desirable. Preliminary measurements have demonstrated the utility of a cell with a gold working electrode. To minimize the clogging of the electrode, a membrane filter was used for the samples inlet to the target cell. Most waters, especially wastewaters, contain organic matter, which may reduce mercury to its elementary form. However, elementary mercury cannot be preconcentrated electrochemically. To determine the total Hg content, the sample should be treated first to transform all Hg species into an electrochemically active, ionic form. For most water samples, which do not contain reducing species, acidification with a mineral acid proved to be sufficient to liberate mercury from complex compounds. In the presence of reducing substances the acidification caused poor recoveries, probably as the result of a rapid reduction of Hg species to elementary mercury. On the other hand, excellent results were obtained with the addition of an acidified potassium permanganate solution.

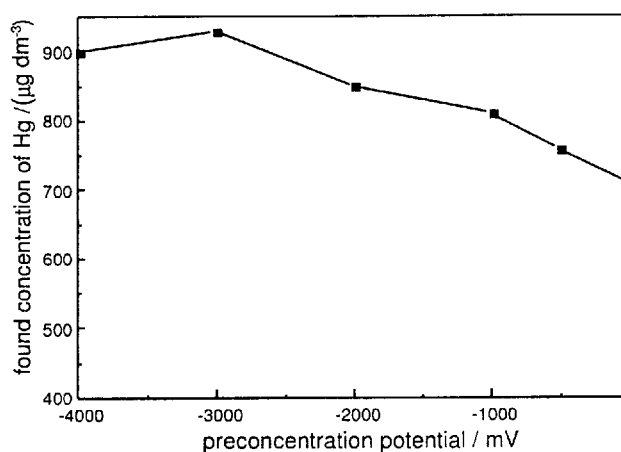


Fig. 2. Influence of the preconcentration potential on the signal of Hg.

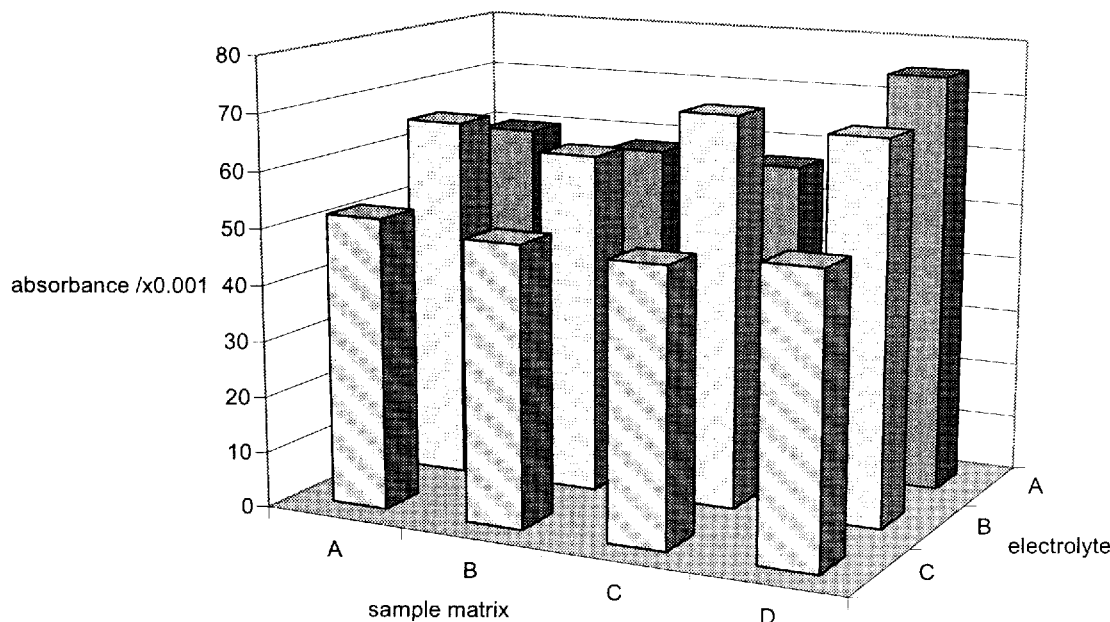


Fig. 3. Influence of the sample matrix and electrolyte on the signal of Hg. A - $0.1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4 + 0.001 \text{ mol dm}^{-3} \text{ HCl}$, B - $1 \text{ mol dm}^{-3} \text{ HCl}$, C - $1 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, D - $1 \text{ mol dm}^{-3} \text{ HNO}_3$.

This is probably due to the oxidation of various Hg species to Hg(II), which can be preconcentrated on the electrode. Flow-through systems enable a simple and elegant on-line sample pretreatment just by mixing a suitable modifier solution to the flowing sample. The flow system used in this work enabled to mix the sample solution with a carrier electrolyte just through segmenting the sample and carrier electrolyte flows by switching the valve periodically once to the sample and then to the electrolyte. The carrier electrolyte contained diluted sulfuric acid with a small amount of hydrochloric acid and potassium permanganate. The role of the hydrochloric acid was to facilitate the stripping of mercury and to shift its stripping peak to a potential range with minimum interferences arising from an oxidation of the gold electrode and a signal produced by stripping of frequently present Cu. The presence of potassium permanganate in the carrier electrolyte ensured the oxidation of reducing species as well as various mercury species in the sample solution before they entered the cell. Experiments were carried out with various concentration of the potassium permanganate in the carrier electrolyte. The main problem was its interference during the stripping step as a result of the rapid chemical oxidation of the deposit competing with the electrochemical stripping. Fortunately, the system made it possible to stop the flow before the stripping started and the permanganate in the diffusion layer could be reduced electrochemically. Then, the applied current could perform the stripping of the deposit to the permanganate-free diffusion layer. Though Hg(II) can already be deposited at potentials below +600 mV, much more negative potentials should be used when potassium permanganate is

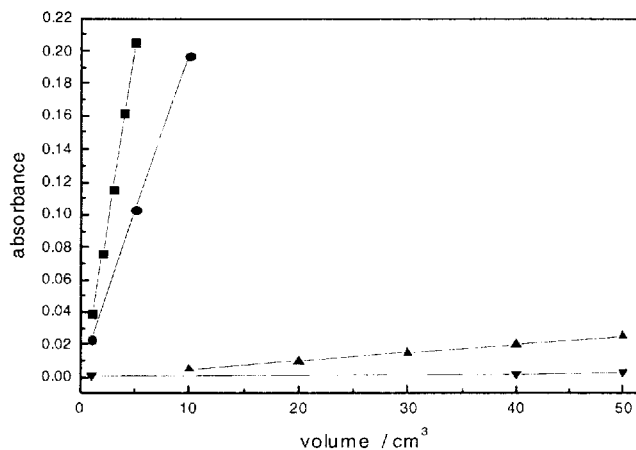


Fig. 4. Dependence of the signal on the sample volume for various concentrations of Hg. ■ 10 mg dm^{-3} , ● 5 mg dm^{-3} , ▲ 0.1 mg dm^{-3} , ▼ blank.

present. The optimum potential range for preconcentration is -1000 mV to -3000 mV . At more negative potentials high currents occur, which adversely influence the noise level as a result of bubble formation at the working electrode (Fig. 2).

The stripping current in the range of $200 \mu\text{A}$ to $500 \mu\text{A}$ has only a negligible influence on the results. However, stripping currents higher than $500 \mu\text{A}$ produced small signals with enhanced relative noise level. Hence the current of $200 \mu\text{A}$ to $500 \mu\text{A}$ was used in further experiments. The gold electrode needed little care. The electrode surface was automatically cleaned after each run by means of the carrier electrolyte with the electrode set to 1000 mV for 10 s . After a few weeks of

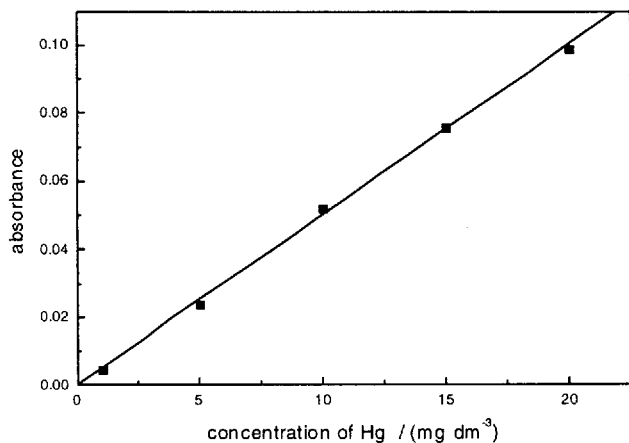


Fig. 5. Calibration curve. Linear regression $Y = 0.0002 + 0.005X$, $R = 0.99941$, $N = 5$.

use the electrode was polished and used further. The influence of various inorganic and organic substances on the determination of Hg was tested (Fig. 3). The influence of the sample volume for various concentrations of Hg on the signal is presented in Fig. 4. In Fig. 5 the calibration curve is shown.

Samples with low conductivity can also be analyzed since they are mixed in the flow system with the carrier electrolyte to form a conductive solution.

CONCLUSION

Flame atomic absorption in connection with flow-through electrochemical cell provides a useful tool for determination of mercury in water samples. The main advantage of the method lies in its simplicity and low costs.

REFERENCES

1. Vydra, F., Stulik, K., and Julakova, E., *Electrochemical Stripping Analysis*. Ellis Horwood, Chichester, 1976.
2. Jagner, D. and Aren, K., *Anal. Chim. Acta* 141, 157 (1982).
3. Rievaj, M. and Bustin, D., *Analyst* 117, 1471 (1992).
4. Gil, E. P. and Ostapczuk, P., *Anal. Chim. Acta* 293, 55 (1994).