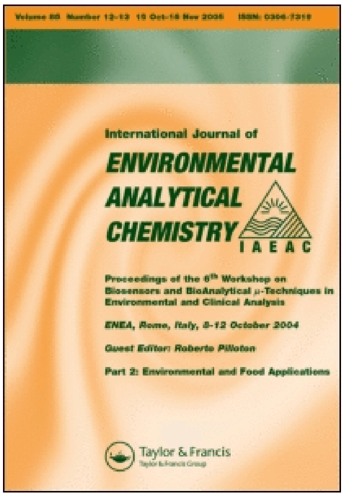

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SPECTROPHOTOMETRIC DETERMINATION OF MERCURY(II) BY FLOW INJECTION ANALYSIS*

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A new spectrophotometric FIA method for total mercury determination in water is proposed for the 5–40 ng/ml range. The method is based on the inhibitory effect of Hg(II) in the catalytic action of iodides on the As(III)–Ce(IV) reaction. By means of preconcentration techniques using $KMnO_4$ traps, ppt levels of mercury in water can be detected.

INTRODUCTION

The determination of mercury by flow injection analysis has been carried out using different techniques: atomic fluorescence detection[1] and atomic absorption spectrophotometry,[2] both based on the use of the cold vapour technique and electrochemical detection.[3–5] In the last reference, the possibility of S^{2-}, Ag(I), Hg(II) and I^- determination in the 0.5–10 ng/ml range is mentioned.

Lawrence and Rice[6] described a FIA procedure for direct sample introduction in an inductively coupled argon plasma. Lazaro *et al.*[7] proposed a catalytic–fluorimetric method for simultaneous determination of Cu(II) and Hg(II), with a sampling rate of 45 samples/hour and errors of less than 10%. Finally, Pérez Ruiz *et al.*[8] described a spectrophotometric determination based on the reaction between 4,6-diphenyl-1-thiopyran-2-thione and Hg(II) for the 1–12 μg/ml range with a sampling rate of 80 samples/hour.

In this paper a new spectrophotometric method is proposed for Hg(II) determination, which—if being used together with an appropriate preconcentration technique and adequate treatment to destroy organomercury compounds[9]—allows to achieve ng/l detection levels for total mercury in natural waters.

Although mercury levels found in industrial areas may be relatively high,[10,11] the levels in unpolluted waters are extremely low, i.e. less than 1 ng/ml in sea water and 0.05 ng/ml in rivers and lakes. For this reason, preconcentration techniques are normally applied, which simultaneously offer the advantage of mercury isolation from its matrix, decreasing the number of interferences.

In this paper we propose a spectrophotometric method based on the inhibitory effect of Hg(II) in the well known Kolthoff–Sandell reaction (catalytic action of I^- on the As(III)–Ce(IV) reaction), which we used to establish a new thermometric–kinetic method for mercury determination in the 2–8 ng/ml range in a previous

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*Dedicated to Prof. Dr. R. W. Frei.

study.[12] To achieve very low concentration levels, the preconcentration reduction–aeration technique,[13] based on the use of $KMnO_4$ traps, has been adapted to fit in with the new FIA procedure.

EXPERIMENTAL

Reagents and Solutions

—Sulphuric acid, Merck, G.R., special for Hg determination, max. 0.0000005% Hg(II), tin(II) chloride dihydrate, Merck G.R., max 0.000001% Hg(II), potassium permanganate, Merck G.R., max 0.000005% Hg(II) and hydrochloric acid, Merck, G.R.

—0.04 M Ce(IV) solution, prepared by dissolving cerium ammonium nitrate in 1.75 M H_2SO_4.

—As(III)-I^- solution, prepared by dissolving sodium arsenite (Panreac, R.A., Spain) and potassium iodide (Panreac, R.A., Spain) in 1.75 M H_2SO_4 to obtain a final concentration of 0.1 M in arsenite and 150 ng/ml of iodide.

—Mercuric chloride solution (1 g Hg(II)/l) standardized with EDTA;[14] standards were prepared daily by diluting in 0.04 M Ce(IV)–1.75 M H_2SO_4 solution.

—Ascorbic acid (Panreac, R.A., Spain) 25% (W/V) in water.

—Tin(II) chloride solution prepared from 250 g $SnCl_2 \cdot 2H_2O$ dissolved in 1 l 1:1 HCl; this solution was purified by boiling for 1 h.

—0.4 mM potassium permanganate solution.

All solutions were prepared using distilled–demineralized water, purified with a Millipore system.

Apparatus and Manifold

A Gilson Minipuls 2 peristaltic pump (8 channels), provided with normal Technicon pump tubing, a Rheodyne 5020 valve and a Beckman Acta CIII spectrophotometer provided with a quartz flow-through cell with a light path of 10 mm and a volume of 18 μl were used. Measurements were performed at a recording chart speed of 0.12 inch/min. All reactor coils and sample loops were made of PTFE tubing (i.d. 0.5 mm). Figure 1 shows the set-up of the manifold. This system allows application of this method to samples from preconcentration by mercury(II) reduction to metal mercury with $SnCl_2$, by cycling air through the sample and collecting it in a double permanganate solution trap.

Procedures

FIA procedure

Mercury solution (125 μl) is injected into a 0.04 M Ce(IV) in 1.75 M H_2SO_4 flow (0.70 ml/min) and then mixed with a second flow (0.70 ml/min) constituted by the As(III)-I^- solution in a T-type mixing joint. The reactor (6 m long) is immersed in

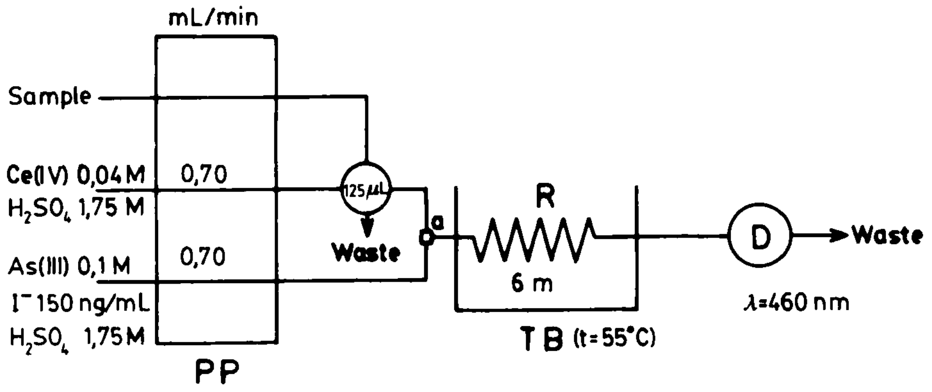

Figure 1 Schematic diagram of the flow injection system for the photometric determination of mercury. a: T-shaped junction point; R: reaction coil; PP: peristaltic pump; TB: thermostatic bath; S: sample injection; D: detector.

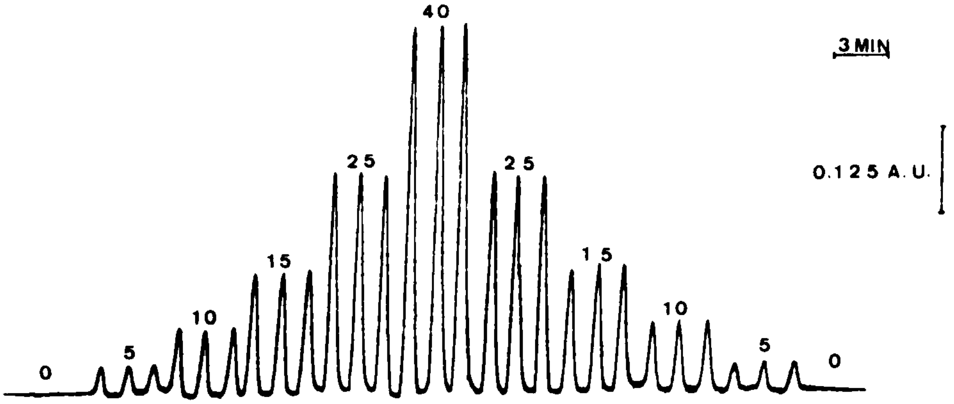

Figure 2 Calibration plot for triplicate injections of 125 μl of Hg(II) standard solution. Values assigned to the peaks are in ng/ml of Hg. $[Ce(IV)] = 4 \times 10^{-2}$ M; $[I^-] = 150$ ng/ml; $[As(III)] = 0.1$ M; $[H_2SO_4] = 1.75$ M.

a water bath controlled at 55 °C. An increase in absorbance (460 nm) is observed since the unreacted Ce(IV) is monitored. Figure 2 shows the peaks obtained when successive solutions of Hg(II) at ppb levels are injected. All samples injected should be of identical Ce(IV) and H_2SO_4 concentration as the carrier in order to avoid a negative peak when only water is injected.

Water analysis

Natural water samples were collected in polyethylene vessels of 25 l capacity. These vessels had previously been treated for 24 h with 10% HNO_3 and rinsed three times with the water sample; to the final collected sample were added 25 ml of 10% HNO_3 and 1.18 g of $K_2Cr_2O_7$ (Panreac, R.A., Spain). This procedure preserved the samples for one week.[15] To analyse these samples, the reduction–aeration technique was applied using the following procedure: Mercury was preconcentrated from 5 litres; the sample was placed in a 6 l vessel and then 5 ml of conc. H_2SO_4 and 3.5 g of potassium permanganate were added. The samples were kept for several hours to ensure complete oxidation of organic mercury compounds. The required quantity of 25% (W/V) ascorbic acid to eliminate the excess of $KMnO_4$ and, finally, 30 ml of the Sn(II) solution were added. The air pump was quickly connected in order to transport the reduced mercury to the traps. The vessel outlet was attached to a tube packed with glass wool in order to avoid $KMnO_4$ reduction in the traps by the Sn(II) contained in the transporting aerosol. The tubes were heated with an air convector to prevent water condensation. Metallic mercury vapour was collected in the traps, each containing 2.5 ml of 0.4 mM $KMnO_4$ and enough H_2SO_4 to reach a final concentration of 1.75 M. The volume of each solution trap was 12.5 ml. The mercury recovery was always approx. 100%. This procedure was successfully applied for the determination of mercury in various sea and tap water samples.

RESULTS AND DISCUSSION

Influence of Flow Injection Variables

The influence of the reaction coil length on the resulting peak heights showed an increase with the length of the tube up to 6 m; then a decrease occurred due to the dispersion of the injected sample, counteracting the former effect.

Figure 3 shows the peak height variation with the carrier flow at several bath temperatures. In general, peaks become higher with temperature; however, the reproducibility of the peak height decreases with the increase of this variable. Two maxima can be seen in Figure 3, one at 45 °C and a total flow of 0.7 ml/min and another at 55 °C and a total flow of 1.4 ml/min. These last experimental conditions were chosen, as the residence time was considerably lower, viz., 49 sec at 1.4 ml/min versus 100 sec at 0.7 ml/min. The separate flow rates of the carrier and the reagent solution were always kept the same. In Figure 4 the peak heights are plotted as a function of the injected sample volume. A volume of 125 μl was chosen, which is near the limit of the linear dependence of the response on the injection volume. The dispersion coefficient for the proposed FIA system was $D = 5.0$.

Effect of Variables of the Chemical Reaction

In Figure 5 the dependence of the peak height on the As(III), Ce(IV), I^- and H_2SO_4 concentrations is shown. The following were chosen as the best analytical concentrations: 0.04 M of Ce(IV) in 1.75 M H_2SO_4 as a carrier, and a solution of 0.1 M sodium arsenite, 150 ng/ml of iodide and 1.75 M H_2SO_4 in the second channel. The sample solutions were injected in the Ce(IV) channel and had to be

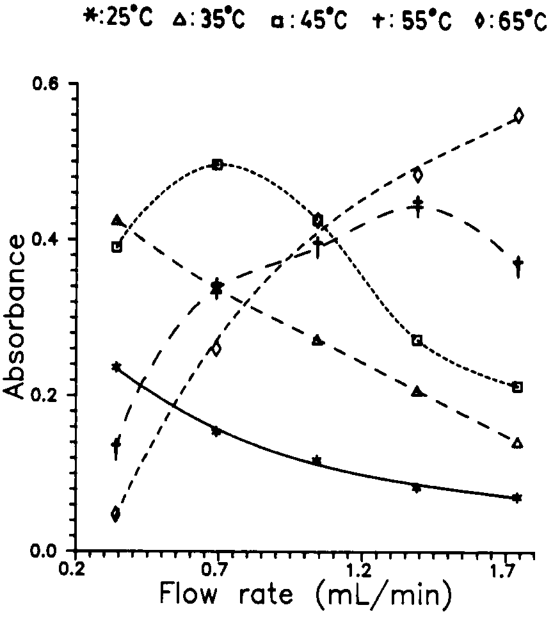

Figure 3 Influence of the total flow rate and the temperature on the peak height. [Hg(II)] = 40 ng/ml; $[I^-]$ = 100 ng/ml; [Ce(IV)] = 5×10^{-3} M; [As(III)] = 0.1 M; $[H_2SO_4]$ = 1.75 M.

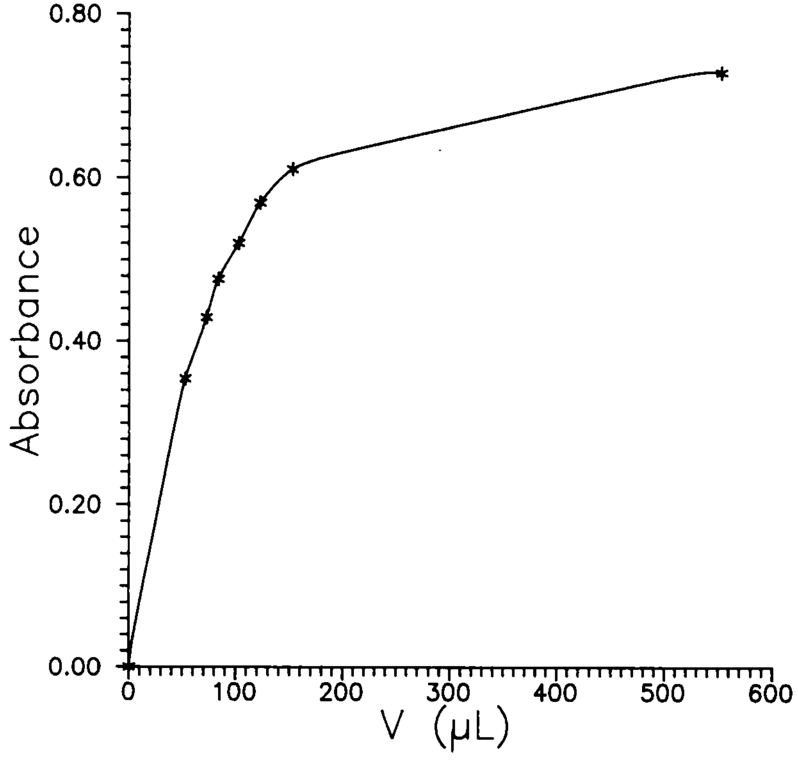

Figure 4 Influence of the sample volume injected on the peak heights. [Hg(II)] = 40 ng/ml; $[I^-]$ = 150 ng/ml; [Ce(IV)] = 4×10^{-2} M; [As(III)] = 0.1 M; $[H_2SO_4]$ = 1.75 M.

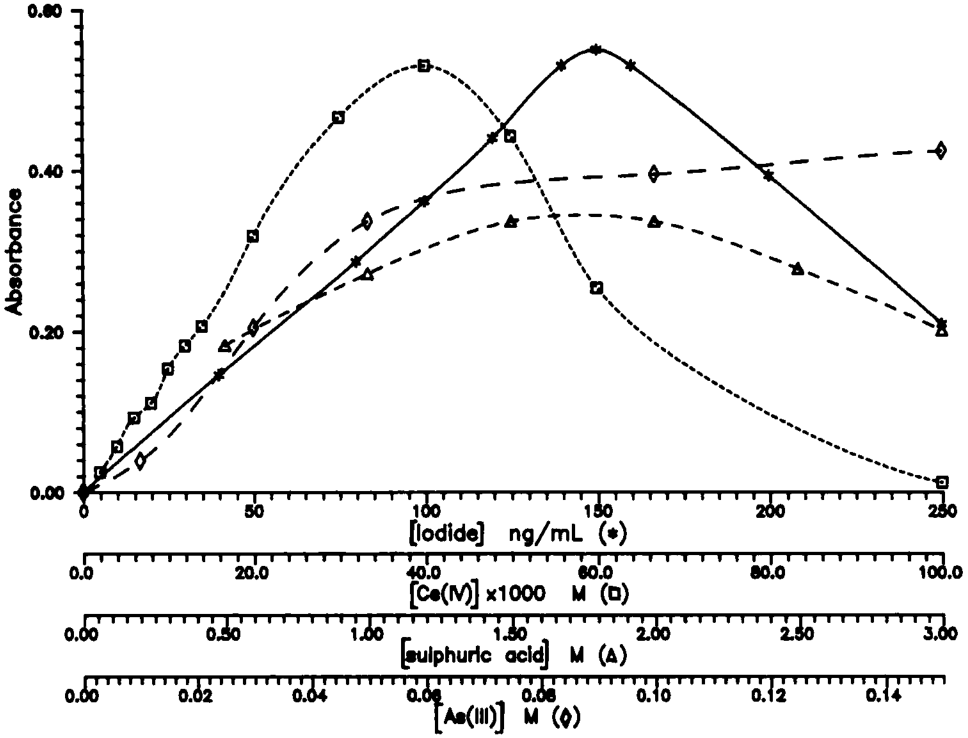

Figure 5 Influence of the reagent concentrations on the peak height. [H_2SO_4] optimization: [Hg(II)] = 40 ng/ml; [I^-] = 100 ng/ml; [Ce(IV)] = 5×10^{-3} M; [As(III)] = 0.1 M. [Ce(IV)] optimization: [Hg(II)] = 40 ng/ml; [I^-] = 100 ng/ml; [As(III)] = 0.1 M; [H_2SO_4] = 1.75 M. [As(III)] optimization: [Hg(II)] = 40 ng/ml; [I^-] = 100 ng/ml; [Ce(IV)] = 4×10^{-2} M; [H_2SO_4] = 1.75 M. [I^-] optimization: [Hg(II)] = 40 ng/ml; [As(III)] = 0.1 M; [Ce(IV)] = 4×10^{-2} M; [H_2SO_4] = 1.75 M.

of the same Ce(IV) and H_2SO_4 concentrations as in the carrier stream to avoid negative peaks.

Calibration Curves

Using the optimal conditions a linear relationship was obtained between the peak height and the mercury concentration in the 2–40 ng/ml range. The relative standard deviation for 20 ng/ml of mercury was 1.5% ($n = 10$). The analytical signal was obtained within 49 sec after sample injection. The rate of analysis is about 70 samples/hour.

Effect of Interfering Ions

Table 1 shows the tolerance to different ions in the determination of 20 ng/ml of mercury(II). An ion is considered not to interfere when its presence causes a deviation of less than 3 times the standard deviation.

As can be seen the method is strongly affected by the presence of some ions, notably Fe(III) and Pd(II).

Table 1 Tolerance level of various ions in the determination of 20 ng/ml of mercury(II)

Interfering ion	*Tolerance (ng/ml)*
Cr(III), Ni(II), Pb(II), Mn(II)	> 1000[a]
Cu(II), Co(II), Al(III)	500
Ca(II), Mg(II), Zn(II), Cd(II), Sb(III), Ba(II), Sr(II), Ti(IV), Bi(III), V(V)	100
Fe(III)	50
Pd(II)	< 1

[a] Maximum tested.

Table 2 Determination of mercury(II) in Mallorca sea water and potable water

Sample	*ng/l found by*	
	FIA	*CVAAS*
Palma bay	45 ± 1	50 ± 1
Sóller bay	35 ± 2	35 ± 3
Palma waterworks	20 ± 2	18 ± 3

Preconcentration for Mercury Determination in Natural Waters

Since normal levels of mercury in various types of water samples are generally at sub-ng/ml levels, preconcentration is often necessary. The method used is a procedure of mercury(II) reduction to metal mercury by reaction with tin(II) chloride, with subsequent passing of air through the sample and a double trap containing a potassium permanganate solution. Before injecting, this solution must be decolorized with ascorbic acid as has been indicated previously. In this way, mercury is separated from the matrix and interference by other elements is avoided. The effect of the Mn(II) originating from the permanganate trap was studied. To this end known quantities of mercury were added to solutions of identical composition to that in the traps; a slight deviation was found with respect to the calibration curve in the absence of Mn(II). Although the plot did not pass through the origin, linearity was observed over the same concentration range.

In Table 2, the results obtained when applying the FIA method and the Cold Vapour Atomic Absorption Spectrophotometry (CVASS) technique[16] (3 replicates) on samples preconcentrated by the reduction–aeration technique are shown. The results are seen to be closely analogous.

CONCLUSION

The proposed method has as its main advantage the high sensitivity for Hg(II); it is 200 times more sensitive than the conventional FIA method with spectrophotometric detection.[8] Together with an appropriate preconcentration procedure, it is applicable to the determination of mercury in natural waters which generally contain sub-ng/ml levels. It also provides a good alternative to the usual method for mercury determination, the cold vapour atomic absorption technique, which will not always be available. Moreover, the FIA method has a good precision, is easy to operate and the sampling frequency is high.

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