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A COMPARATIVE STUDY OF A KINETIC–THERMOMETRIC METHOD AND THE ATOMIC ABSORPTION COLD VAPOUR TECHNIQUE FOR DETERMINATION OF MERCURY TRACES AND ULTRATRACES

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ABSTRACT

A comparative study of the results obtained on determining traces and ultratraces of mercury by means of a thermometric–kinetic method and the cold vapour AA technique is carried out. Whereas the latter technique is more convenient and quicker, the thermometric technique is cheaper and has lower maintenance costs.

Treatment of the sample with metallic zinc allows the mercury content to be determined and free and combined iodide to be differentiated.

The use of the reduction–aeration preconcentration technique permits mercury determination in sea and potable waters at ng l^{-1} levels.

INTRODUCTION

Mercury is one of the most toxic metals known [1,2]; consequently almost all countries in the world have very strict legislation aimed at controlling the mercury content of water and food.

Levels of mercury found in non-polluted waters are very low, less than 1 ng ml^{-1} in sea water and 0.05 ng ml^{-1} in rivers and lakes. Such concentrations usually decrease with water depth, yet they may greatly increase in industrial coastal areas [3,4]. Theoretical models show that Hg(II) is in the form of chloro complexes in sea water and mainly in hydroxo complexes in rivers [4].

Spanish legislation permits a maximum content of 1 ng ml^{-1} of mercury in potable waters. Hence, environmental mercury controls and determinations are of great importance. Preconcentration techniques may sometimes be required due to low mercury concentrations, simultaneously facilitating isolation from its matrix.

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Following new research in our Department, directed towards comparative studies for heavy metal trace determination in water samples, a kinetic-thermometric method, based on the inhibitory effect of mercury in the Kolthoff–Sandell reaction, is compared in this paper with the cold vapour AA technique.

EXPERIMENTAL

Apparatus

Kinetic–thermometric method

Temperature measurements were carried out using a thermometric titrator designed by Lumbiarres et al. [5], constituted by a 100 kΩ thermistor and a Wheatstone bridge fed with 11.91 V provided by a stabilized source. Its sensitivity was 66.6 mV °C^{-1}, corresponding to 0.006 °C cm^{-1} in the 5 mV scale of the register (OmniScribe, Houston). The adiabatic cell is shown in Fig. 1.

AA cold vapour technique

The following equipment was required: a Perkin Elmer 703 AA spectrophotometer; a mercury hollow cathode lamp (Perkin Elmer Intensitrom TM Lamp 2317); an absorption cell made in the laboratory from PVC tube 1.2 cm in diameter and 10 cm in length, provided with two quartz windows; a fishtank air pump of adjustable flow (1 l min^{-1}); and a Houston OmniScribe recorder (0.5 V scale range, speed 0.5 cm min^{-1}).

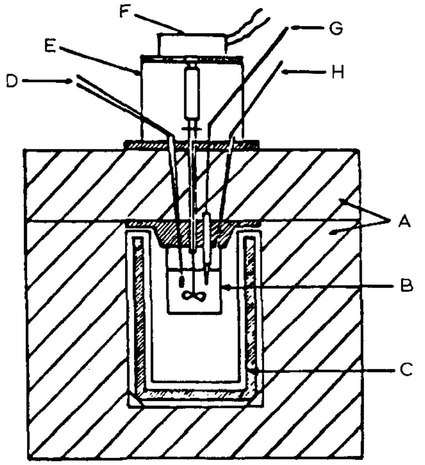

Fig. 1. Thermometric cell: A, porespan block; B, polystyrene beaker; C, Dewar; D, 100 Ω resistor; E, plexiglass; F, 500 rev min^{-1} synchronous motor; G, thermistor; H, syringe guide for sample addition.

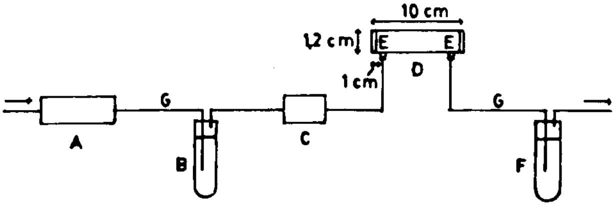

Fig. 2. Reduction–aeration system scheme: A, fish-tank air pump; B, reduction–aeration reactor; C, desiccant tube; D, absorptiometric cell with silica windows; F, $KMnO_4$ trap; G, PVC tubes.

Throughout determinations, measurements were carried out both by recording the absorption peak and simultaneously using the spectrophotometer area integrator.

Although the maximum integration time of the apparatus was 1 min which was insufficient for the signal to return to the baseline, there was a linear relationship between the integrated area and the mercury content.

The block diagram of the system employed is presented in Fig. 2.

Mercury preconcentration

The system used, which is shown in Fig. 3, consisted of a fishtank air pump (1 l min^{-1}), a 6 l sample vessel, a tube packed with glass wool, a double trap with $KMnO_4$ and a hot air convector.

Reagents and solutions

The reagents used were: concentrated hydrochloric acid (Merck); concentrated sulphuric acid (Merck); 2 N H_2SO_4; 0.1 M ceric ammonium nitrate in 2 N H_2SO_4; 0.1 M sodium arsenite dissolved in 2 N H_2SO_4; potassium iodide, 1 g l^{-1} stock solution (standards were prepared daily by diluting with 2 N H_2SO_4; Hg(II), 1 g l^{-1} stock solution prepared by dissolving $Hg(NO_3)_2$ in 0.5% HNO_3 (standards were prepared daily by diluting with 2 N H_2SO_4; Sn(II) solution prepared from 50 g $SnCl_2 \cdot 2H_2O$ dissolved in 250 ml 1 : 1 HCl; 0.4 mM $KMnO_4$.

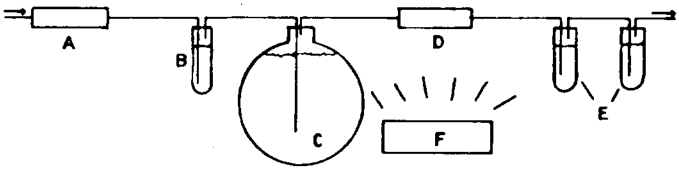

Fig. 3. Preconcentration system for Hg(II) determination: A, Fishtank air pump; B, $KMnO_4$ trap with H_2SO_4; C, reduction–aeration reactor vessel; D, glass-wool desiccator; E, double $KMnO_4$ trap for mercury; F, convector.

Procedures

Kinetic–thermometric method for iodide determination

10 ml of 0.1 M Ce(IV), 10 ml of 0.1 M sodium arsenite and 29 ml of 2 N H_2SO_4 were placed in the thermometric cell. The stirrer and the recorder (2.5 cm min^{-1}) were turned on. When the baseline was perfectly horizontal, 1 ml sample solution (250–1000 ng of iodide) was injected as quickly as possible.

The initial reaction rate was measured by the initial rate method applied to the thermometric curve.

Kinetic–thermometric method for mercury determination

The method described for iodide determination was used for mercury determination, with the addition of 800 ng iodide to the initial mixture. The mercury content in the injected sample had to be between 75 and 500 ng.

AA cold vapour technique for mercury determination

10 ml sample (0.01–0.1 μg Hg(II)) and 1 ml conc. H_2SO_4 were made up to 25 ml total volume with distilled water. The mixture was placed in a screw cap tube and 1 ml Sn(II) solution was then added. The tube was quickly connected to the air-flow system (Fig. 2), and the spectrophotometer integrator was turned on; the absorption peak was simultaneously recorded.

Mercury preconcentration

The desired volume of sample was placed in a 6-l vessel and then 5 ml conc. H_2SO_4 and 5 ml Sn(II) solution were added. The air pump was quickly connected in order to drag the reduced mercury to the traps. The vessel output 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 dragged aerosol. The tubes were heated with an air convector to prevent water condensation. Metallic mercury vapour was collected in the double trap, each containing 2.5 ml of 0.4 mM $KMnO_4$, 0.5 ml conc. H_2SO_4 and 9.5 ml H_2O.

RESULTS

Mercury(II) kinetic–thermometric determination

Different kinetic–thermometric methods for the determination of inorganic species have already been developed in our Department [6–12]. Among these methods those which were based on the Ce(IV)–As(III) Kolthoff–Sandell reaction gave the best results, allowing determination of 250–1000 ng of I^-, 75–500 ng of Hg(II) and 100–500 ng of Ag(I). Mercury levels were only determined in pharmaceutical products [6].

Since our purpose was to apply this method for mercury determination in natural waters having very low mercury content, we were compelled to modify the experimental conditions to increase the sensitivity.

Several analytical parameters were revised (concentration ranges of applicability, reproducibility, etc.) and also the determination of mercury traces in the presence of iodide was studied; iodide concentration in water can be greater than the metal content, and therefore it could seriously interfere with metal determination.

Bridge potential optimisation

With the aim of obtaining greater slopes and less background, the bridge potential was changed to correspond to different recorder scales (2.5 and 10 mV). For potentials of the Wheatstone bridge between 10 and 12 V, the background baseline was at a minimum. It strongly increased for greater potentials, probably due to excessive power dissipation in the thermistor. For this reason and in order to work at maximum sensitivity, the instrument was adjusted to potential of 11.91 V and thus the scale of the recorder corresponded to 0.006 °C cm^{-1} (0.15 °C full scale).

Calibration curves

Using the procedure described and injecting 1 ml of solutions of different I^- concentrations, two calibration straight lines were plotted at two different

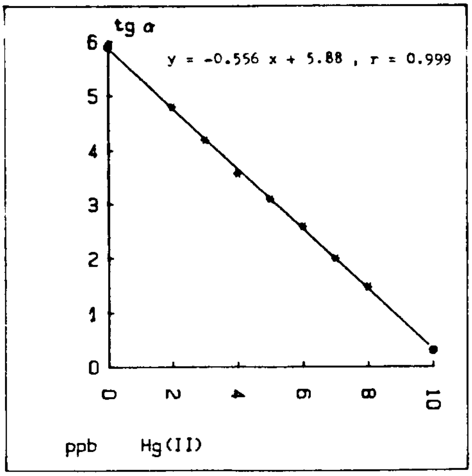

Fig. 4. Calibration curve for kinetic–thermometric Hg(II) determination: $[I^-] = 16$ ppb; recorder sensitivity, 5 mV; bridge potential, 11.91 V.

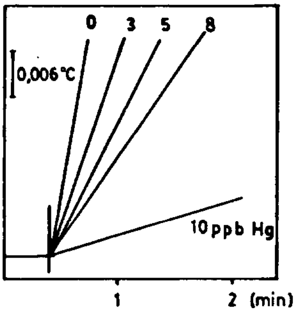

Fig. 5. Temperature–time curves obtained in Hg(II) kinetic–thermometric determinations: 800 ng I^- were injected into samples of different mercury content; recorder speed, 0.5 cm min^{-1}.

recorder scales (5 and 20 mV)

$\mathrm{tg}\alpha = 0.549\ [I^-]\ \mathrm{ng\ ml^{-1}} - 0.886,$

$r = 0.999$, 5 mV, range 2–10 ng ml^{-1} I^-

$\mathrm{tg}\alpha = 0.123\ [I^-]\ \mathrm{ng\ ml^{-1}} + 0.056,$

$r = 0.999$, 20 mV, range 10–40 ng ml^{-1} I^-

With the aim of determining Hg(II), two straight lines were obtained by applying the same procedure and injecting 1 ml I^- solution containing either 500 or 800 ng into samples in the cell containing 2–8 ng ml^{-1} of Hg(II). The resulting lines were

$\mathrm{tg}\alpha = -0.475\ [Hg^{2+}]\ \mathrm{ng\ ml^{-1}} + 3.84,\ r = 0.999$, 500 ng I^-

$\mathrm{tg}\alpha = -0.556\ [Hg^{2+}]\ \mathrm{ng\ ml^{-1}} + 5.88,\ r = 0.999$, 800 ng I^-

For later determinations it was found to be preferable to inject 1 ml I^- solution containing 800 ng (Figs. 4 and 5), since the application range (2–10 ng per ml^{-1} Hg(II) in the cell) and sensitivity were greater.

Reproducibility

Reproducibility of the results was calculated by applying the proposed method to independent Hg(II) samples of 8 ng ml^{-1}. The relative standard deviation was 0.49%.

Hg(II) determination by AA

In order to investigate the applicability of the proposed thermometric method, the cold vapour AA technique was used [14] for comparison, since it has been recognised as a quick, safe and precise method.

In this method organomercurial compounds are converted to inorganic mercury salts, which are reduced to metallic mercury by means of Sn(II),

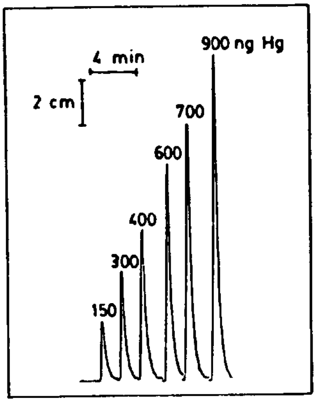

Fig. 6. Calibration curve peaks for mercury determination by CVAAS: record sensitivity, 500 mV; recorder speed, 0.5 cm min^{-1}.

whose vapour is dragged to spectrophotometric absorption cell by an air or inert gas flow. Absorbances are measured at 253.7 nm.

Calibrations curves

These were obtained according to the prodecures described herein. The peaks obtained are shown in Fig. 6. The resulting straight lines when areas or peaks were represented vs. mercury content are

area (spec. unities) $= 8.3 \times 10^{-3}\,[\text{Hg}^{2+}]$ ng $\text{ml}^{-1} - 3.6 \times 10^{-3}$, $r = 1.000$;

height (cm) $= 0.015\,[\text{Hg}^{2+}] + 1.75 \times 10^{-2}$, $r = 0.999$;

both valid in the 5–1000 ng range of Hg(II).

Reproducibility

The proposed method was applied to ten independent samples with 500 ng Hg. R.s.d. was 2.5% when the areas were used, and 3.2% for heights.

Hg(II) determination in natural waters

Preconcentration

Preconcentration techniques were indispensable due to the very low Hg concentration in natural waters.

From the proposed methods we opted for the reduction–aeration technique using a $KMnO_4$ trap [15], since it requires neither additional equipment, nor special reagents (polyurethane foams) loaded with ammonium diethyldithiocarbamate [16], or silica gel with 2-mercaptobenzothiazol [17]. Nevertheless, amalgamation with gold collectors needs a special heating system to liberate mercury [18].

The initial tests indicated that the use of a single $KMnO_4$ trap allowed only a 87% recovery, whereas with a double trap this recovery was 100%.

TABLE 1

Hg content found by AA

Sample	Sampling date	Peak area (a.u.)	x (ng Hg)	Ppt in water [a]
Sea water, Cala Mayor	6/vi/85	1.585	201	54 ± 1
		1.595	202	
		1.627	206	
			$\bar{x} = 203 \pm 2.6$	
Sea water, Soller beach	9/vi/85	1.110	139	33 ± 4
		0.921	114	
		1.050	131	
			$\bar{x} = 128 \pm 12.7$	
Potable water, Faculty of Sciences	11/vi/85	0.686	84	16 ± 4
		0.512	61	
		0.542	65	
			$\bar{x} = 70 \pm 12.3$	
Drinkable water, Palma de Mallorca water works	12/vi/85	0.540	65	17 ± 3
		0.599	72	
		0.679	83	
			$\bar{x} = 73.3 \pm 9.1$	

[a] Ppt in water = (ng of Hg in sample − 14 ng in blank) per 3.5 l; calibration line, $y(\text{area}) = 0.045 + (7.66 \times 10^{-3})x$ (ng Hg).

TABLE 2

Hg content found by thermometry

Samples	Sampling date	tgα	x (ng Hg)	Ppt in water [a]
Sea water, Cala Mayor	6/vi/85	2.08	158	41 ± 1
		2.08	158	
		2.10	154	
			$\bar{x} = 157 \pm 2.31$	
Sea water, Soller beach	9/vi/85	2.50	85	20 ± 2
		2.55	76	
		2.47	90	
			$\bar{x} = 84 \pm 7.1$	
Potable water, Faculty of Sciences	11/vi/85	2.65	58	11 ± 1
		2.70	50	
		2.70	50	
			$\bar{x} = 53 \pm 4.6$	
Drinkable water, Palma de Mallorca water works	12/vi/85	2.70	50	13 ± 2
		2.60	67	
		2.65	58	
			$\bar{x} = 58.3 \pm 8.5$	

[a] Ppt in water = (ng of Hg in sample − 14 ng in blank) per 3.5 l; calibration line, $y(\text{tg}\alpha) = 2.99 - (5.77 \times 10^{-3})x$ (ng Hg).

Analysis of natural water samples

Samples were collected in polyethylene vessels of 25 l capacity. These vessels had previoulsy been treated for 24 h with 10% HNO_3 and rinsed three times with the water sample; to the final collected sample were added 250 ml of 1% HNO_3 and 1.18 g $K_2Cr_2O_7$ (0.005%). This procedure preserved samples for 1 week [19].

Reagents blanks

Mercury was determined in five independent blanks, resulting in an average value of 14 ng.

Results

Determination of the mercury content in the traps was carried out by both thermometric and AA techniques, as previously described. Results obtained when mercury was determined in Mallorca sea water, and in potable water, are shown in Tables 1 and 2.

Given the extremely low mercury levels, it can be accepted that the results obtained by the two techniques do not differ significantly.

CONCLUSION

It can be concluded that the cold vapour AA technique is more convenient than the thermometric one, due to its ease and speed of operation. Thermometry can however compete favourably with AA owing to its lower cost. Both techniques are more favourable than the previously established kinetic–spectrophotometric method [13].

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