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APPLICATION OF FLOW INJECTION HYDRIDE GENERATION COUPLED WITH ICP-OES FOR MERCURY DETECTION IN WATERS

Luisa Roxana MANDOC (POPESCU)[1], Cristina DINU[2], Mihaela IORDACHE[3], George-Octavian BUICĂ[4], Eleonora-Mihaela UNGUREANU[5], Luoana Florentina PASCU[6]

Studies to apply flow injection-hydride generation with inductively coupled plasma atomic emission spectrometry (FIAS-ICP-OES) have been performed for mercury detection from drinking water. The results obtained by FIAS-ICP-OES method were compared to those obtained using atomic absorption spectroscopy.

Keywords: flow injection-hydride generation with inductively coupled plasma atomic emission spectrometry, mercury detection, water, atomic absorption spectroscopy

1. Introduction

Mercury is one of the most dangerous pollutants. Its presence in living organisms is associated with cancer, birth defects, and other undesirable outcomes [1]. The toxic effects of divalent mercury can be prevented to some extent either by chelating or enhancing antioxidant defense mechanisms. Vitamin E is a lipid soluble antioxidant, which plays an important role in stabilizing the cell membranes by scavenging free radicals [2]. One of the routes of incorporation mercury into the human body is drinking water. Hence, control of mercury is becoming increasingly important, especially in water sources [3]. Mercury is also one of the most poisonous elements for humans and animals [4, 5].

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[1] PosPhD, Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, National Research and Development Institute for Industrial Ecology – Ramnicu Valcea Subsidiary Romania, e-mail: mandoc_lui@yahoo.com

[2] PhD student, Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, National Research and Development Institute for Industrial Ecology – Ramnicu Valcea Subsidiary ROMANIA, e-mail: cristinadinu_2006@yahoo.com

[3] Chemist, National Research and Development Institute for Industrial Ecology – Ramnicu Valcea Subsidiary, Romania, e-mail: mihaelaz1976@yahoo.co.uk

[4] Lecturer, Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: buica_george@yahoo.com

[5] Prof., Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: em_ungureanu2000@yahoo.com

[6] Chemist, National Research and Development Institute for Industrial Ecology, Bucharest, Romania, e-mail: luoanapascu@yahoo.com

Determination of traces from this element in the environment is an urgent necessity, yet posing analytical problems because he can be found in several chemical forms. For accurate determination of mercury at trace and ultra-trace levels analytical methods are needed with high sensitivity selectivity and low detection limit. The European Drinking Water Directive (98/83/EC), transposed in Romanian Legislation as Low 458/2002, amended by Low 311/2004, imposes the limits of concentration for metallic elements in water intended for human consumption. The limit value for the toxic metal mercury is 1 µg/L.

Different analytical techniques [6 - 9] have been used for mercury determination at low concentrations including, cold vapor atomic absorption spectrometry (CV-AAS), cold vapor atomic fluorescence spectrometry (CV-AFS) [10], flow injection-inductively coupled plasma optical emission spectrometry [11] (FI-ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS), and also electrochemical methods based on modified electrodes [12].In this paper the mercury content was determined in water samples by FIAS-ICP-OES [13, 14] and the results were compared with those obtained by classical AAS method.

2. 2. Experimental

A. Materials

All the reagents were of analytical grade and used as received without further purification. All aqueous solutions were prepared in ultra pure water.

For Flow Injection Hydride Generation System FIAS 400 with Inductively Coupled Plasma Optical Emission Spectrometer (FIAS-ICP-OES) the solution used were: Merck solution for calibration (1000 mg Hg/L; ICP standards), hydrochloric acid (37%, from Merck), sodium borohydride (>96%, Merck), sodium hydroxide (pellets, for analysis, from Merck), potassium dichromate (from Merck), nitric acid (65% from Merck), sulphuric acid (98% from Merck), potassium permanganate (from Merck), potassium persulphate, hydroxylamine hydrochloride, argon 99.996% and nitrogen 99.999% from Linde-Gas.

For Atomic Absorption Spectroscopy (AAS) measurements 10% SnCl2 solution and concentrated nitric acid, from Merck, have been used. The samples were analyzed by AAS according to the procedure described in Romanian Standard SR EN 1483: 2008.

B. Apparatus

The studies were performed with a Flow Injection Hydride Generation System FIAS 400 with Inductively Coupled Plasma Optical Emission Spectrometer ICP-OES type Optima 5300 DV Perkin Elmer. The mass weight was performed using Analytical Balance Kern ABT 220-50M, and the sample incubation was done using Bandelin Sonorex Water Bath. AAS Unicam atomic spectrometer was used to analyze the mercury as alternative method.

C. Procedure

The water samples (drinking water, groundwater, surface water) and standard solutions for Hg determinations were fixed prior the analysis with 0.5 mL of stabilizing agent solution (5% $K_2Cr_2O_7$ solution in 500 mL HNO_3 to 1000 mL volumetric flask); 0.5 mL H_2SO_4 98%; 0.5 mL HNO_3 65%; 0.5 mL $KMnO_4$ (5%); 1 mL $K_2S_2O_8$ (4%) and heated on a ultrasonic bath at 50ºC for one hour (SR EN 1483/2008). This mixture was boiled at 50° C for one hour in an ultrasonic bath. Next step was the adding of 10% hydroxylamine hydrochloride solution in the sample until it became colorless and then the volumetric flask was brought to volume (50 mL) with ultra pure water. For each set of standards a blank sample was prepared using the same procedure. For the hydride vapor generation two types of solutions were used: 3% (v/v) HCl as carrier solution, and 0.3 % $NaBH_4$ (w/v) in 0.5 % NaOH (w/v) solution (freshly prepared) as reducing agent according to the procedure described in Romanian Standard SR EN ISO 11885/2009. The working conditions for determination of Hg from drinking water using the modern technique based on FIAS-ICP-OES were established [13, 14]. This method has a detection limit of xxx (Hg – 0.1 µg L^{-1}), situated under the limit values imposed by legislation. Plasma generation of the ICP-OES spectrometer requires argon gas as fuel. Nitrogen gas was used only for the cooling system of the equipment. The purity of all reagents used is critical when determining low levels of hydride elements. The operational parameters for FIAS-ICP-OES method and data processing are presented in Table 1.

Table 1

Optimized parameters for Hg detection by FIAS-ICP-OES [13, 14]

Spectrometer parameters					
Hg Wavelength: 194.168 nm			Replicates 3 times		
Integration time: 0.05 s			Transient Read Delay 0.0 s		
			Transient Read Time 15.0 s		
Plasma parameters					
Plasma flow rate 15 L/min			Power RF 1300 W		
Auxiliary flow rate 0.2 L/min			PlasmaView Axial		
Nebulizer flow rate 0.6 L/min			View distance 15.0 mm		
Flow Injection Programme					
Step	Time (s)	Pump 1 (U/min)	Pump 2 (U/min)	Valve	Read
Prefil	15	80	100	Fill	-
1	10	80	100	Fill	-
2	15	80	100	Inject	On
Spectral Peak Processing			Time Processing		
Peak Algoritm : Peak Height			Peak Algoritm : Peak Height		
Points per peak : 3 points			Smooting points : 19 points		
Spectral corrections : None					

Hg was detected by ICP-OES at specific wavelength (194.168 nm) and the method applied with the used equipment was perfectly able to measure it accurately even in presence of interferents.

3. Results and Discussion

The method for determining mercury (FIAS-ICP-OES) was tested on real samples of water which were initially analysed according to a traditional method: Atomic Absorption Spectroscopy (AAS).

The working range for Hg determination using FIAS-ICP-OES is linear between 1 μg L^{-1} ÷ 18 μg L^{-1} Hg for the wavelengths tested. The linear equation (correlation coefficient $R \geq 0.997$) of the curve was: $y = 13818x$ (μg L^{-1}) - 2179.8. The slope of the calibration curve b = 13818 μg^{-1} L represents method sensitivity. The residual standard deviation was S_{Y1} = 1066μg L^{-1}, and the standard deviation of the method was S_{x01} = 0.077μg L^{-1}.

The detection limit (LOD) was of 0.10 μg L^{-1} and quantification limit (LOQ) of 0.38 μg L^{-1}; they allow the detection of Hg from drinking water samples at the allowed level of concentration ($\overline{x}$ = 0.160μg L^{-1}, σ_{blind} = 0.057 μg L^{-1}). In figure 1 is presented the peak height for Hg. The Bias limit value is 2.82% for 99% confidence level and 9 freedom degrees. For the level of concentration of 6 μg/L, the recovery percentage must be situated in the 60 to 115 % range. The experimental results were situated in this range. In the tables 3 and 4, all the obtained values of recovery percentage for different types of standard solutions respect this requirement.

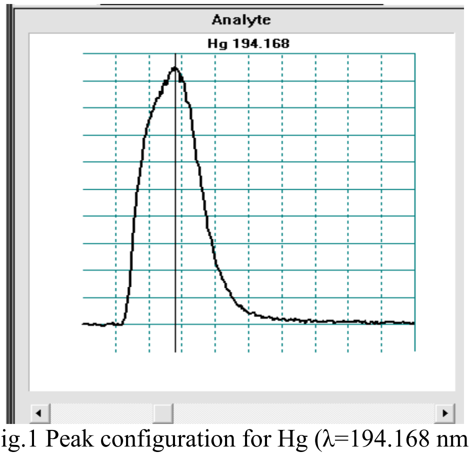

Fig.1 Peak configuration for Hg (λ=194.168 nm).

For detection of mercury in real samples, in the laboratories of environmental analysis from Romania, Atomic Absorption Spectroscopy (AAS) is currently used. The method of analysis for the detection of mercury (FIAS-ICP-

OES) in environmental analysis laboratories proposed by [13, 14] was used in order to meet the requirements of national environmental legislation. The detection limit of the method is 0.1 μg L^{-1} to FIAS-ICP-OES and AAS has a detection limit of mercury in drinking water of 1 μg L^{-1}.

The FIAS-ICP-OES modern method was applied to real samples of used water for the determination of mercury (table 2.) with satisfactory results. In the study were included the used water samples collected from the same point, but in different data, from industrial platform Ramnicu Valcea. The obtained results are presented in Table 2. Following experimental results on real samples (P_1 – P_6) a margin of error of the method less than that obtained by AAS method was achieved which indicates that the method can be used in analytical determinations of real samples for concentrations over 0.1 μg L^{-1}.

Table 2

Determinations of mercury (in μg/L) in real samples by AAS and FIAS-ICP-OES

Real samples	***Method***	
	FIAS-ICP-EOS	***AAS***
P_1	3.46	2.98
P_2	4.38	4.35
P_3	6.25	5.62
P_4	3.60	2.89
P_5	24.00	22.50
P_6	22.96	28.00

4. Conclusions

The modern FIAS-ICP-OES method provides a useful tool to analyze these waters, giving results in agreement with those furnished by the traditional method (Atomic Absorption Spectroscopy).

This method can be applied for the analytical control of mercury from different types of water drinking water, groundwater and surface water.

This value is lower that given by AAS, for which the detection limit was of 1 μg L^{-1}. The FIAS-ICP-OES method meet the criteria for determination of mercury in agreement with the national environmental legislation. This method used for the determination of mercury has high sensitivity and selectivity. However, the cost of such instrumentation may still be prohibitive to many laboratories.

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