

ADVANCED ANALYTICAL METHODS FOR MERCURY DETERMINATION IN SLIGHTLY CONTAMINATED WATER SAMPLES

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Abstract. This paper presents a comparative study of mercury determination in water samples at low concentrations by 2 different techniques (cold vapour atomic absorption spectrometry, and flow injection analyses system coupled at ICP-EOS). Mono-, divalent mercury and organo-mercury compounds are converted to divalent mercury by oxidation with KBrO_3 – KBr or mixture of potassium permanganate and potassium peroxodisulphate. The solution is then reduced to the elemental form using tin chloride or natrium borohydride in acid medium. For detection of mercury using FIAS ICP-OES technique were applied 2 different pretreatment steps for calibration standards and water samples: a pre-treatment step using a mixture of acids and oxidants (such as sulphuric acid, nitric acid, potassium permanganate, potassium dichromate and potassium peroxodisulphate), heated in an ultrasonic bath (method A), and a pre-treatment step using only hydrochloric acid and potassium bromide/bromate (method B). For reducing step was used 0.3% of NaBH_4 in 0.5% NaOH solution. For cold vapour technique coupled with AAS was used a pre-treatment step with hydrochloric acid and oxidation with potassium bromide/bromate (method C). In this case, reducing agent was 10% tin chloride. The analytical performance of both methods have been investigated (detection limit, quantification limit, working range, precision, recovery). The methods are suitable for determination of low mercury content from drinking and mineral water samples.

Keywords: water, mercury, flow injection hydride generation, ICP-EOS, CV-AAS.

AIMS AND BACKGROUND

Mercury is one of the most toxic elements for human health and ecosystem and, therefore, is one of the most studied environmental pollutants. All mercury species are toxic, with organic mercury compounds generally being more toxic than inorganic species. The United States Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) lists mercury and its compounds in the third place on the ‘Priority List of Hazardous Substances’ and the European Water Framework Directive (2000/60/EG) classifies mercury as one of the 30 ‘precarious dangerous pollutants’¹. Mercury has no beneficial biological function, and its presence in living organisms is associated with cancer, birth defects. One of the routes

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of incorporation of mercury into the human body is drinking water. Hence, control of mercury is becoming increasingly important, especially in water sources². Since mercury concentrations in waters are expected to be very low, powerful techniques are required and only few of them show enough sensitivity³.

Mercury is present in the earth crust and we are all exposed to some form of mercury through the air we inhale⁴, the water we drink and the food we eat. Adding to that, mercury has been used in a wide range of products ranging through seed treatment, consumer applications, dental fillings⁵ and preservatives in vaccines. Thus, we are all exposed to mercury in some form and at different concentration⁶. Acute inhalation exposure, at high concentrations, may induce respiratory distress, including dyspnea.

Chronic exposure may induce symptoms from the central nervous system (CNS) including tremors, delusions, memory loss and neurocognitive disorders. The World Health Organisation (WHO) recommends a maximum intake of methyl mercury of $1.6 \mu\text{g kg}^{-1}$ per week⁷ and the United States Environmental Protection Agency (EPA) and National Research Council (NRC) (Ref. 8) developed a reference dose of $0.1 \mu\text{g/kg}$ body weight per day for adults. The European Drinking Water Directive (98/83/EC), transposed in Romanian Legislation as Law 458(R1)/2002, imposes limits of concentration for metallic elements in water intended for human consumption. For mercury this limit is $1 \mu\text{g/l}$. For mineral water, Romanian norm HG 1020/2005 imposes the same limit ($1 \mu\text{g/l}$).

Different analytical techniques have been used for mercury determination at low concentrations including, cold vapour atomic absorption spectrometry (CV-AAS), cold vapour atomic fluorescence spectrometry (CV-AFS) (Ref. 9), flow injection-inductively coupled plasma optical emission spectrometry (FI-ICP-OES) (Ref. 10) and inductively coupled plasma mass spectrometry (ICP-MS). FI-ICP-OES is used for the determination of mercury due to its high sensitivity and high selectivity. However, the cost of such instrumentation may still be prohibitive to many laboratories.

In the paper are presented the working conditions for determination of Hg from water samples using flow injection-hydride generation with inductively coupled plasma atomic emission spectrometry (FIAS-ICP-EOS) and cold vapour atomic absorption spectrometry (CV-AAS).

The hydride technique involves the reaction of acidified aqueous samples with a reducing agent, such as sodium borohydride. This reaction generates a volatile hydride which is transported to a quartz cell by means of an argon carrier gas. In the quartz cell, the hydrides are converted to gaseous metal atoms, which are then transported in plasma by argon gas. ICP-EOS use specific wavelengths to detect metallic elements and the methods applied with this equipment are perfectly able to measure accurately an analyte in the presence of interferences¹¹.

EXPERIMENTAL

Apparatus. Flow Injection Hydride Generation System FIAS 400 with Inductively Coupled Plasma Optical Emission Spectrometer ICP-EOS type Optima 5300 DV Perkin Elmer, Analytical Balance Kern ABT 220-50M, Bandelin Sonorex Water Bath, Atomic absorption spectrometer ATI UNICAM type 929 with hollow cathode lamp for Hg determination.

Reagents. Reagents and water can contain mercury as an impurity. For high sensitivity were used only ultra-pure reagents with a very low mercury content compared to the lowest analyte concentration. Merck solution for calibration (1000 mg Hg/l; ICP standards), hydrochloric acid (37%, Merck quality), sodium borohydride (>96%, Fluka quality), sodium hydroxide (pellets, Gr for analysis, Merck quality), potassium dichromate (Merck quality), nitric acid (65% Merck quality), sulphuric acid (98% Merck quality), potassium permanganate (Merck quality), potassium persulphate, hydroxylamine hydrochloride, potassium bromated (Merck quality), potassium bromide (Merck quality), argon 99.996% purity, nitrogen 99.99% purity (Linde-Gas quality), ultra-pure water with a resistivity of ≥ 18.2 M Ω is used for all aqueous solutions and cleaning procedures.

Sample collection and conditioning. Mercury vapour can diffuse through various plastics, for this reason glass or special plastics tubing like FEP (fluorinated ethylene-propylene) should be used.

Tap waters and spring waters were collected in borosilicate glasses, and mineral water was a commercial products. All materials used for sampling activities were previously washed overnight with a 10% HNO₃ and rinsed with ultra-pure water. Sample may be preserved with dichromate/HNO₃ (method A) and with HCl and potassium bromide/bromated (methods B and C) for at least 24 h before determination. If preserved samples must to be stored, they should be analysed in maximum 4 weeks after collection.

Sample digestion and standard calibration preparation. Mono-, divalent mercury and organo-mercury compounds are converted to divalent mercury by oxidation with KBrO₃-KBr (methods B and C) or mixture of potassium permanganate and potassium peroxodisulphate (method A). The solution is then reduced to the elemental form using tin chloride (method C) or sodium borohydride in acid medium (methods A and B).

Sample preparation is a key step for the accurate determination of mercury in different water samples. For total mercury determination, sample digestion prior to analysis is usually needed for the decomposition of organic matrix.

Digestion of water samples (after they have been preserved) is as follows:

– 0.5 ml H₂SO₄ 98%; 0.5 ml HNO₃ 65%; 0.5 ml KMnO₄ (5%); 1 ml K₂S₂O₈ (4%) (Ref. 12). This mixture is boiled at 50°C for 1 h in an ultrasonic bath. Next

step is adding 0.5 ml of 10% hydroxylamine hydrochloride solution until the sample became colourless and then the volumetric flask is brought to volume (50 ml) with ultra-pure water (method A);

– with 0.5 ml 10% hydroxylamine hydrochloride solution until the sample became colourless and then the volumetric flask is brought to volume (50 ml) with ultra-pure water (methods B and C) (Ref. 13).

Calibration standards (50 ml) were freshly prepared with 0.5ml of dichromate/HNO₃ for method A and for the methods B and C with 0.5 ml HCl and 1 ml potassium bromide/bromated then following the same treatment described above as water samples.

For each set of standards was prepared a blank sample using the same procedure.

Instrumental set-up. Plasma generation of the ICP-EOS spectrometer requires argon gas as fuel. Nitrogen gas is used only for the cooling system of the equipment. The purity of all reagents used is critical when determining low levels of hydride elements. All the glasswear used in this method were cleaned by soaking them in 10% HNO₃ for 24 h and rinsed with ultra-pure water 3 times before using.

For the hydride vapour generation were used 2 types of solutions: 3% (v/v) HCl as carrier solution and 0.3% NaBH₄ (w/v) in 0.5% NaOH (w/v) solution, as reducing agent, which should be freshly prepared¹⁴.

Chemical vapour generation remains the most popular and successful sample introduction approach for trace mercury determination. For the CV-AAS technique reducing agent was tin chloride 10%.

The operational parameters for the spectrometer, plasma, FIAS and data processing are presented in Table 1. Parameters for CV-AAS are shown in Table 2.

Table 1. Parameters for FIAS-ICP-EOS

Spectrometer parameters			
Hg wavelenghts	194.168 nm	purge gas flow	normal
Integration time	0.05 s	transient read delay	0.0 s
Replicates	3 times	transient read time	15.0 s
Plasma parameters			
Plasma flow rate	15 l/min	power RF	1300 W
Auxiliar flow rate	0.2 l/min	plasma view	axial
Nebuliser flow rate	0.6 l/min	view distance	15.0 mm

to be continued

Continuation of Table 1

Flow injection programme					
Step	Time (s)	Pump 1 (U/min)	Pump 2 (U/min)	Valve	Read
Prefill	15	80	100	fill	–
1	10	80	100	fill	–
2	15	80	100	inject	on
Spectral peak processing			Time processing		
Peak algorithm: peak height			peak algorithm: peak height		
Points per peak: 3 points			smoothing points: 19 points		
Spectral corrections: none					

Table 2. Parameters for CV-AAS

CV-AAS parameters	
Hg wavelengths: 253.7 nm	Signal: continue
Bandpass: 0.5nm	Resamples: 2

Internal validation of the method. To establish the performance parameters of the methods (linearity, working range, detection limit, quantification limit, repeatability, recovery), different tests¹⁵ were performed for each method (Table 3).

Table 3. Tests used for determination of performance parameters of the methods

Performance parameters	Method A	Method B	Method C
Linearity, working range	standard solutions between 1–18 µg Hg/l	standard solutions between 2–10 µg Hg/l	standard solutions between 2–10 µg Hg/l
LOD and LOQ	10 independent fortified blank solutions measured each of them one time	10 independent blank solutions measured each of them one time	10 independent fortified blank solutions measured each of them one time
Repeatability	10 independent standard solutions of 9 µg Hg/l concentration	10 independent standard solutions of 6 µg Hg/l concentration	10 independent standard solutions of 6 µg Hg/l concentration
Recovery	5 independent water samples of 6 µg Hg/l	5 independent water samples of 5 µg Hg/l	5 independent water samples of 5 µg Hg/l

LOD – limits of detection; LOQ – limits of quantification.

RESULTS AND DISCUSSION

From internal validation results that the working range for Hg determination using FIAS-ICP-EOS is linear between 1–18 µg Hg/l (method A) and between 2–10 µg Hg/l (methods B and C). The methods A and B measure the height of the peaks for each standard solution and process the data in order to obtain a calibration

curve. In Figs 1–3 are presented the calibration curve for Hg – methods A, B and C, respectively. In the tests for the homogeneity of the variance, PG values are lower than the Fischer–Snedecor F value.

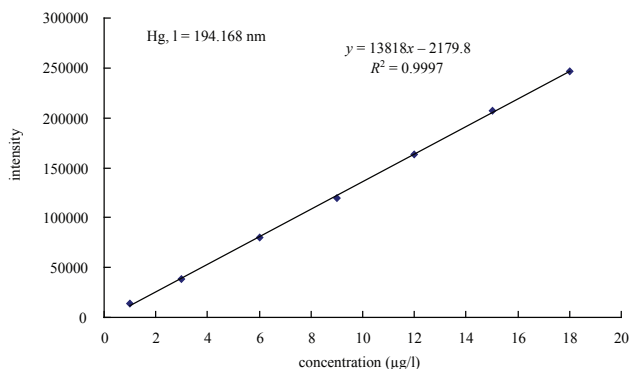


Fig. 1. Calibration curve for Hg – method A

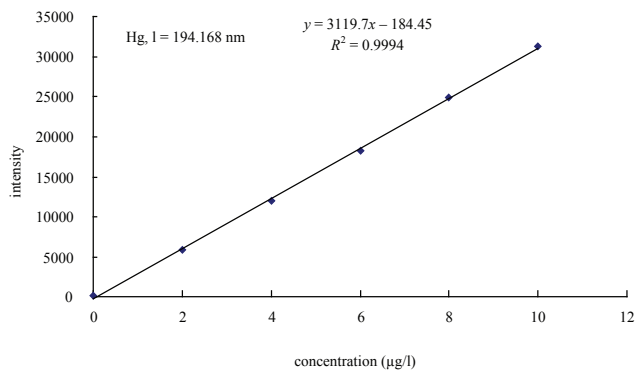


Fig. 2. Calibration curve for Hg – method B

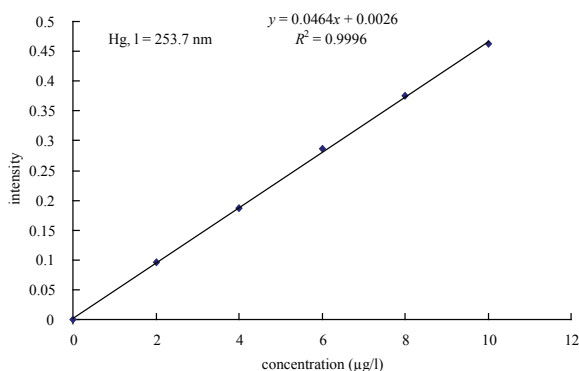


Fig. 3. Calibration curve for Hg – method C

Table 4 provides results of linearity and working range tests for all the investigated methods.

Table 4. Linearity and working range

Hg (method A)		
$y = 13818x - 2179.8$ curve linear equation	$b = 13818 \mu\text{g/l}$ sensitivity, the slope of the calibration curve	$s^2_1 = 3.2\text{E}+14$ $s^2_{10} = 1.08\text{E}+15$, $\text{PG} = s^2_{10}/s^2_1 = 3.375 < F_{9,9;0,99} = 5.35$
$S_{Y1} = 1066 \mu\text{g/l}$ residual standard deviation $R = 0.9997$	$S_{x01} = 0.077 \mu\text{g/l}$ method standard deviation	$V_{x01} = 0.84\%$ coefficient of variation
correlation coefficient, accepted values $R \geq 0.997$		
Hg (method B)		
$y = 3119x - 184.4$ curve linear equation	$b = 3119 \mu\text{g/l}$ sensitivity, the slope of the calibration curve	$s^2_1 = 331515.6$ $s^2_{10} = 1034691.8$ $\text{PG} = s^2_{10}/s^2_1 = 3.121 < F_{9,9;0,99} = 5.35$
$S_{Y1} = 226.2 \mu\text{g/l}$ residual standard deviation $R = 0.9997$	$S_{x01} = 0.073 \mu\text{g/l}$ method standard deviation	$V_{x01} = 1.45\%$ coefficient of variation
correlation coefficient, accepted values $R \geq 0.997$		
Hg (method C)		
$y = 0.046x + 0.002$ curve linear equation	$b = 0.0464 \mu\text{g/l}$ sensitivity, the slope of the calibration curve	$s^2_1 = 4.71\text{E}-06$ $s^2_{10} = 2.14\text{E}-05$, $\text{PG} = s^2_{10}/s^2_1 = 4.550 < F_{9,9;0,99} = 5.35$
$S_{Y1} = 0.0029 \mu\text{g/l}$ residual standard deviation $R = 0.9998$	$S_{x01} = 0.0624 \mu\text{g/l}$ method standard deviation	$V_{x01} = 1.25\%$ coefficient of variation
correlation coefficient, accepted values $R \geq 0.997$		

The values of coefficient of variation (Hg: 0.84% for method A; 1.45% – method B and 1.25% – method C) are lower than 3%, including the test method in the category of good analytical methods (according to Horwitz the coefficient of variation must be situated in the range 22.6 to 33% (Refs 16 and 17)). For 10 $\mu\text{g/l}$ level of concentration, the recovery percentage must be situated in the 60 to 115% range¹⁸ and the experimental results were situated in this range (92.8–104.3%) for all tested methods. The detection limits (LOD) and quantification limits (LOQ) for method A and C allows the detection of Hg from drinking and mineral water samples at the level of concentration imposed by legislation.

In Table 5 are presented performance parameters (detection limit, quantification limit, repetability, precision, recovery) for the methods A, B and C.

Table 5. Performance parameters for Hg

Performance parameters	Method A	Method B	Method C
LOD and LOQ	LOD = 0.10 µg/l LOQ = 0.38 µg/l	LOD = 0.21 µg/l LOQ = 0.69 µg/l	LOD = 0.04 µg/l LOQ = 0.12 µg/l
Repeatability, precision	X = 8.821 µg/l s = 0.285 µg/l r = 0.806 µg/l RSDr= 3.23%	X = 5.36 µg/l s = 0.19 µg/l r = 0.54 µg/l RSDr= 3.57%	X = 6.01 µg/l s = 0.10 µg/l r = 0.27 µg/l RSDr = 1.62%
Recovery	6 µg/l	5 µg/l	5 µg/l
$\bar{x}_f \pm s_{x_f}$, µg/l	6.70 ± 0.130 µg/l	5.326 ± 0.094 µg/l	4.937 ± 0.218 µg/l
η_m	92.8%	104.3%	96.7%

RSDr – ???

The results show that methods A and C are suitable for Hg determination from drinking and mineral water at the level of maximum admitted concentration. Depending on the laboratory equipment, can be used either of these two methods for slightly contaminated water samples.

Analysis of mercury from real water samples. Using the developed analytical methods was performed a comparative study concerning the determination of mercury from different types of water. In the study were included 4 tap water samples collected from Bucharest, Calarasi (surface water as source for drinking water) and Pitesti, Giurgiu (ground water as source for drinking water), 3 samples of mineral waters as commercial product (Calipso, Roua, Boholt) and 3 samples of spring water collected from the Bucovina county. All the results were situated under the detection limits of the methods and in case of methods A and C were at the level of maximum admitted concentration according to Drinking Water Law 458(R1)/2002 and Mineral Water Norm HG 1020/2005. The obtained results are presented in Table 6.

Table 6. Concentration of mercury in water samples (a – tap water; b – mineral water; c – spring water)

Sample	Concentration (µg Hg/l)		
	Method A	Method B	Method C
1a	Hg < 0.1	Hg < 0.2	Hg < 0.04
2a	Hg < 0.1	Hg < 0.2	Hg < 0.04
3a	Hg < 0.1	Hg < 0.2	Hg < 0.04
4a	Hg < 0.1	Hg < 0.2	Hg < 0.04
5b	Hg < 0.1	Hg < 0.2	Hg < 0.04
6b	Hg < 0.1	Hg < 0.2	Hg < 0.04
7b	Hg < 0.1	Hg < 0.2	Hg < 0.04
8c	Hg < 0.1	Hg < 0.2	Hg < 0.04
9c	Hg < 0.1	Hg < 0.2	Hg < 0.04
10c	Hg < 0.1	Hg < 0.2	Hg < 0.04

CONCLUSIONS

The proposed FIAS-ICP-OES and CV-AAS methods provide low detection and quantification limits and good RSD. The statistical interpretation of the experimental results proved that the proposed methods (methods A and C), applied with FIAS-ICP-EOS equipment and CV-AAS, could be successfully used for the analytical control of the Hg of drinking and mineral water samples. The methods were verified on different real water samples and the results were included in the acceptable concentration limits.

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