- ORAL PRESENTATION -

DETERMINATION OF VOLATILE METALLIC ELEMENTS IN WATER USING FLOW INJECTION HYDRIDE GENERATION COUPLED WITH ICP-EOS

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Abstract

In the study were developed two methods for quantification of mercury and tin in water samples. The methods were performed with Perkin Elmer 5300 DV Optima ICP-EOS spectrometer by continuous hydride generation using flow injection analysis system.

For detection of mercury, a pre-treatment step was applied using an ultrasonic bath and a mixture of acids and oxidants (such as sulphuric acid, nitric acid, potassium permanganate, potassium dichromate).

Mercury was detected at 194.168 nm wavelength, using as reducing agent 0.3% of $NaBH_4$ in 0.5% NaOH solution. The detection limit of the method is 0.1 µg/L, precision is 3.2% and uncertainty of measurement is 8.5%.

Tin was detected at 189.927 nm wavelength. To generate tin gas, sample solutions in 4% boric acid and 0.5 M HCl were mixed in line with a solution of 1% $NaBH_4$ and 2% NaOH. The detection limit of the method is 0.2 µg/L, sufficient for tin levels commonly found in water samples. Precision of the method is 3.1% and uncertainty of measurement is 9.3%.

Keywords: water, tin, mercury, ICP-EOS, hydride generation

1. Introduction

Mercury is one of the most harmful pollutants and it has become widespread into the environment mainly because of anthropogenic activities. Mercury has no beneficial biological function, and 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 of mercury into the human body is drinking water. Hence, control of mercury is becoming increasingly important, especially in water sources. Since mercury concentrations in waters are expected to be very low, powerful techniques are required and only few of them show enough sensitivity. 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 have been used for mercury determination at low concentrations including, cold vapor atomic absorption spectrometry (CV-AAS), cold vapor atomic fluorescence spectrometry (CV-AFS) [3], flow injection-inductively coupled plasma optical emission spectrometry [4] (FI-ICP-OES) ,and inductively coupled plasma mass spectrometry (ICP-MS). FI-ICP-OES is used for the determination of mercury due to its high sensitivity, high selectivity, and However, the cost of such instrumentation may still be prohibitive to many laboratories.

Inorganic tin salts are poorly absorbed and rapidly excreted in the faeces; as a result they have a low toxicity. Only about 5% is absorbed from the gastrointestinal tract, widely distributed in the body and then excreted by the kidney. Some tin is deposited in lung and bone. Some tin salts can cause renal necrosis after parenteral doses [5]. The WHO 1973 permissible limit for tin in tinned food is 250 micrograms per kg. This level is well below the level of 5-7 mg per kg body weight shown to give rise to toxic symptoms [6]. Amounts in excess of 130 mg per day have been shown to accumulate in liver and kidneys. Many of the organotin compounds are toxic; the most toxic being trimethyltin and triethyltin, which are well absorbed from the gastrointestinal tract [7]. The main results of toxicity are skin and eye irritation; cholangitis of the lower biliary tract [8] and later hepatotoxicity; and neurotoxicity, which has been shown to be due to intramyelin oedema induced by triethyltin, and neuronal necrosis caused by trimethyltin. Experimental studies have failed to reveal any evidence of carcinogenicity, mutagenicity, or teratogenicity [9,10]. Recent studies suggest that tin compounds exhibit some antitumour activity and may have a future role in cancer diagnosis and chemotherapy, and in controlling hyperbilirubinaemia [11,12].

EXPERIMENTAL SECTION

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.

Reagents: Merck solution for calibration (1000 mg Sn/L; 1000 mg Hg/L; ICP standards), hydrochloric acid (37%, Merck quality), sodium borohydride (>96%, Merck 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 argon 99,996% purity, nitrogen 99,999% purity (Linde-Gas quality), ultra pure water.

Procedure: The water samples (drinking water, groundwater, surface water) and standard solutions for Hg determinations should be fixed prior the analysis with 0,5mL of stabilizing agent solution (5% $K_2Cr_2O_7$ solution in 500 mL HNO_3 to 1000 mL volumetric flask); 0,5mL H_2SO_4 98%; 0,5 mL HNO_3 65%; 0,5 mL $KMnO_4$ (5%); 1 mL $K_2S_2O_8$ (4%) [19]. This mixture is boiled at 50° C for one hour in an ultrasonic bath. Next step is adding 10% hydroxylamine hydrochloride solution until the sample became colorless and then the volumetric flask is brought to volume (50mL) with ultra pure water (table 1). For each set of standards was prepared a blank sample using the same procedure. For the hydride vapor generation were used two types of solution: 3% (v/v) HCl as carrier solution and 0.3 % $NaBH_4$ (w/v) in 0.5%NaOH (w/v) solution as reducing agent, which should be freshly prepared [18]. For tin determination the water samples (drinking water, groundwater, surface water) and standard solutions must have the same pH-value (recommended value: pH 2-3), for this reason the water samples and standard solution are prepared in 4% boric acid in 0,5m HCl. For each set of standards was prepared a blank sample using the same procedure. For the hydride vapour generation were used two types of solution: 4% boric acid in 0,5m HCl as carrier solution and 1% $NaBH_4$ (w/v) in 2%NaOH (w/v) solution as reducing agent, which should be freshly prepared[19].

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.

In the paper are presented the working conditions for determination of Hg and Sn from drinking water using the modern technique based on flow injection-hydride generation with inductively coupled plasma atomic emission spectrometry (FIAS-ICP-EOS). The methods applied with this modern technique has low detection limits (Hg – 0.1µg/L, Sn – 0.2µg/L), situated under the limit values imposed by legislation.

Table 1. Pretreatment step for Hg, Sn determination with FIAS-ICP-EOS

Element	Pretreatment procedure for each standard solution and sample
Hg	0,5mL5% $K_2Cr_2O_7$; 0,5mL H_2SO_4 98%; 0,5 mL HNO_3 65%; 0,5 mL $KMnO_4$ (5%); 1 mL $K_2S_2O_8$ (4%) heat on a ultrasonic bath at 50ºC for one hour.
Sn	5 mL 4% boric acid in 0,5m HCl (pH 2-3)

Plasma generation of the ICP-EOS spectrometer require 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.

Table 2. Parameters for FIAS-ICP-EOS

Spectrometer parameters		
Hg Wavelenghts: 194.168 nm;	Replicates	3 times
Sn Wavelenght: 189.927 nm	Purge Gas Flow	normal
Integration time: 0.0 5 s	Transient Read Delay	0.0 s
	Transient Read Time	15.0 s

<table>
<tr><th colspan="6">Plasma parameters</th></tr>
<tr><td colspan="2">Plasma flow rate</td><td>15 L/min</td><td colspan="2">Power RF</td><td>1300 W</td></tr>
<tr><td colspan="2">Auxiliar flow rate</td><td>0.2 L/min</td><td colspan="2">Plasma View</td><td>Axial</td></tr>
<tr><td colspan="2">Nebuliser flow rate</td><td>0.6 L/min</td><td colspan="2">View distance</td><td>15.0 mm</td></tr>
<tr><th colspan="6">Flow Injection Programme</th></tr>
<tr><td>Step</td><td>Time (s)</td><td>Pump 1 (U/min)</td><td>Pump 2 (U/min)</td><td>Valve</td><td>Read</td></tr>
<tr><td>Prefil</td><td>15</td><td>80</td><td>100</td><td>Fill</td><td>-</td></tr>
<tr><td>1</td><td>10</td><td>80</td><td>100</td><td>Fill</td><td>-</td></tr>
<tr><td>2</td><td>15</td><td>80</td><td>100</td><td>Inject</td><td>On</td></tr>
<tr><th colspan="3">Spectral Peak Processing</th><th colspan="3">Time Processing</th></tr>
<tr><td colspan="2">Peak Algoritm :</td><td>Peak Height</td><td colspan="2">Peak Algoritm :</td><td>Peak Height</td></tr>
<tr><td colspan="2">Points per peak :</td><td>3 points</td><td colspan="2">Smooting points :</td><td>19 points</td></tr>
<tr><td colspan="2">Spectral corrections :</td><td>None</td><td colspan="3"></td></tr>
</table>

The operational parameters for the spectrometer, plasma, FIAS and data processing are presented in table 2.

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 interferences. To establish the performance parameters of the methods, the tests indicated in table 3 were performed [13].

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

Linearity	**LOD and LOQ**	**Test for the homogeneity of the variance**	**Repeatability precision, recovery**
7 standard solutions between 1 µg/L ÷ 18 µg/L Hg 0.5 mL; 1.5 mL; 3 mL; 4.5 mL; 6 mL; 7.5 mL; 9 mL; from 0.1 mg/L to 50 mL	10 independent fortified blank solutions measured each of them one time.	-10 independent standard solution of 1µg/L concentration;	- 10 independent standard solution of 9 µg/L concentration.
		- 10 independent standard solution of 18 µg/L concentration.	- 5 independent standard solution of 6 µg/L
7 standard solutions between 10 µg/L ÷ 70 µg/L Sn 0.5 mL; 1.0 mL; 1.5 mL; 2.0 mL; 2.5 mL; 3.0 mL; 3.5 mL;from 1.0 mg/L to 50 mL	10 independent fortified blank solutions measured each of them one time	-10 independent standard solution of 10µg/L concentration;	- 10 independent standard solution of 35 µg/L concentration.
		- 10 independent standard solution of 70 µg/L concentration.	- 5 independent standard solution of 36 µg/L

The mathematical relations and the admissible range or value for some important parameters, such as: bias, coeficient of variation (relative standard deviation) and recovery are presented in table 4. Two aspects are important for Internal Quality Control: the analysis of "control materials", such as CRM or spiked samples, to monitor trueness (recovery) and replication of analysis to monitor precision. Both aspects form a part of statistical control, a tool for monitoring the accuracy of an analytical system. Recovery studies were performed to same matrix type (drinking water) at different levels of analytic concentration.

Table 4. Mathematical equations used for evaluation of recovery, precision and bias

Recovery, %	**Bias, %** **Bias**	**Relative standard deviation, %**
$\bar{\eta}$ (%) = $\frac{\overline{x_f} - \overline{x_b}}{\overline{x_a}}$ 100, %, $\overline{x_f}$ = mean value of fortified samples, µg/L; $\overline{x_b}$ = mean value of unfortified samples, µg/L; $\overline{x_a}$ = concentration of added standard solution, µg/L. For 10 µg/L mean recovery = 60-115% [14,16]	= $\frac{x_f - x_a}{x_a} \times 100$, % Bias value < t(99,9) =2.82 [15,16]	RSD = $\frac{S_r}{\bar{x}} \times 100$, S_r = standard deviation of concentrations, µg/L; $\bar{x}$ = mean value of concentrations, µg/L. for 10 µg/L, acceptable RSD values: Horwitz, 22.6 -33 %; AOAC Peer Verified Methods, 15 - 21% [14,16]

RESULTS AND DISCUSSION

The working range for Hg and Sn determination using FIAS-ICP-EOS is linear between 1 µg/L ÷ 18 µg/L Hg µg/L and between 10 µg/L ÷ 70 µg/L Sn for all tested wavelenghts. In the tests for the homogeneity of the variance, PG values are lower than Fischer-Snedecor F value. The values of coefficient of variation (Hg: 0.84% for λ=194.168 nm; 1.33% for Sn: λ=189.927 nm lower than 3%, situate the test methods as good analytical methods. The detection limits (LOD) and quantification limits (LOQ), allows the detection of Hg and Sn from drinking water samples at the normed level of concentration (table 5). In figures 1and 2 are presented the evolutions in time of peak height for Hg and Sn. The method measure the high of the peaks for each standard solution and process the data in order to obtain a calibration curve. The Bias values are situated under the limit value for both elements and all wavelenghts. The limit value is 2.82% for 99% confidence level and 9 freedom degrees. For 10 µg/L level of concentration, the recovery percentage must be situated in the 60 to 115 % range. In the tables 6 and 7, all the obtained values of recovery percentage for different types of standard solutions respects requirement.

Table 5. Linearity, LOD and LOQ

Hg, λ=194.168 nm		
y = 13818x -2179.8 curve linear equation	b = 13818µg^{-1}L *sensitivity, the slope of the calibration curve*	s^2_1 = 2E+14 s^2_{10}= 1.08E+15, PG = s^2_1/ s^2_{10} = 0.185< $F_{9,9\,;0,99}$ = 5.35
S_{Y1} = 1066µg/L *residual standard deviation*	S_{x01} = 0,077µg/L *method standard deviation*	V_{x01} = 0.84% *coeficient of variation*
R = 0,9997 Correlation coefficient, accepted values R≥0.997	$\bar{x}$ = 0.160µg/L, σ_{blanc} = 0.057 µg/L **LOD** = 0.10 µg/L, **LOQ** = 0.38 µg/L	
Sn, λ=189.927 nm		
y = 2325.9x-109.43 curve linear equation	b = 2325.9µg^{-1}L *sensitivity, the slope of the calibration curve*	s^2_1 = 1.65 E+13, s^2_{10}= 7.52 E+14, PG = s^2_1/ s^2_{10} = 0.022< $F_{9,9\,;0,99}$ = 5.35
S_{Y1} = 1087 µg/L *residual standard deviation*	S_{x01} = 0.467 µg/L *method standard deviation*	V_{x01} = 1.33 %, *coeficient of variation*
R=0.9994 Correlation coefficient, accepted values R≥0.997	$\bar{x}$ = 1.357 µg/L, σ_{blanc} = 0.063 µg/L **LOD** = 0.20 µg/L, **LOQ** = 1.0 µg/L	

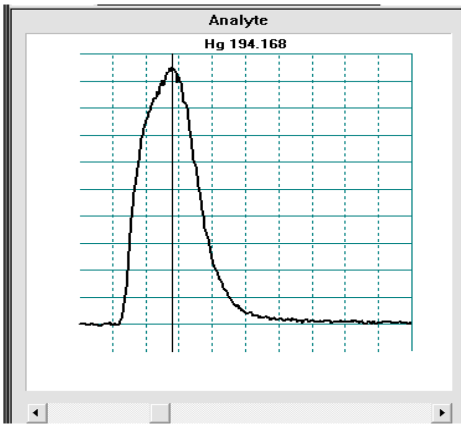

Fig. 1 Peak configuration for Hg (λ=194.168 nm)

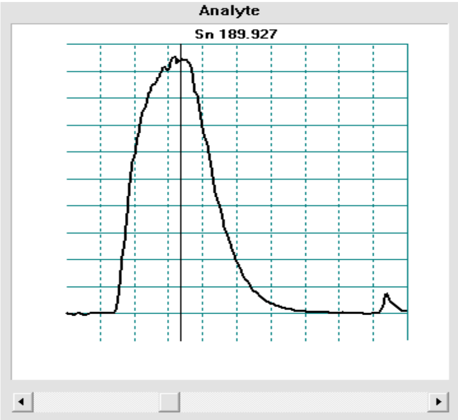

Fig. 2 Peak configuration for Sn (λ=189.927 nm)

Table 6. Precision and bias data on SRM Merck

Parameter	**Hg**	**Sn**
	λ=194.168 nm	**189.927nm**
RSD_r, %	2.72%	3.07%
Bias %	0.13%	0.10%

Table 7. Recovery data on SRM Merck

Parameter	**MERCURY**	**TIN**
	λ=194.168 nm	**189.927nm**
	6 µg/L	36 µg/L
$\overline{x}_f \pm s_{xf}$, µg/L	6.70 ± 0.13	36.08 ± 0.64
$\eta_m \pm s_\eta$, %	92.8 ± 5.07	90.2 ± 3.83

CONCLUSIONS

The proposed FIAS-ICP-OES method gives low LOD and good R.S.D. The statistical interpretation of the experimental results proved that the proposed methods applied with FIAS-ICP-EOS equipment could be successfully used for the analytical control of the Hg and Sn from drinking water, groundwater and surface water. The method was verified with real samples and applied satisfactory to the determination of tin and mercury in different samples.

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