

DISSOLVED INORGANIC ANTIMONY, SELENIUM AND TIN SPECIES IN WATER SAMPLES FROM VARIOUS SAMPLING SITES OF RIVER VARDAR IN MACEDONIA AND GREECE

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A highly effective liquid phase semi-microextraction procedure was applied for determination of ultra trace levels of dissolved inorganic species of antimony, tin and selenium in river Vardar (from the 2nd up to 420th km of the river) and its tributaries Crna Reka, Treska, Bregalnica, Pchinja and Lepenec using electrothermal atomic absorption spectrometry (ETAAS) for quantification. The concentrations for total dissolved inorganic antimony were between 6 and 242 ng/l Sb, for Sn(II, IV) – in the range of 2.7–61 ng/l Sn and for Se(IV, VI) – in the range of 15–75 ng/l Se. The higher oxidation states of antimony and selenium were found as the predominant form in the studied surface waters.

Keywords: speciation; antimony; selenium, tin; water; electrothermal atomic absorption spectrometry

РАСТВОРЕНИ НЕОРГАНСКИ ФОРМИ НА АНТИМОН, СЕЛЕН И КАЛАЈ ВО ПРИМЕРОЦИ ВОДА ОД РАЗЛИЧНИ МЕРНИ МЕСТА НА РЕКАТА ВАРДАР ВО МАКЕДОНИЈА И ГРЦИЈА

Применета е високо осетлива течно-фазна семимикроекстракција за определување ултратраги од растворените неоргански хемиски форми на антимон, калај и селен во водите од реката Вардар (од вториот до 420-ти km на реката) и нејзините притоки Црна Река, Треска, Брегалница, Пчиња и Лепенец и нивно квантифицирање со електротермичка атомска апсорпциона спектрометрија (ЕТААС). Концентрациите на вкупниот растворен антимон се движат од 6 до 242 ng/l Sb, за Sn(II, IV) во областа од 2,7 до 61 ng/l Sn и за Se(IV, VI) од 15 до 75 ng/l Se. Утврдено е дека во испитуваните примероци од површинските води повисоките оксидациони форми на антимон и селен се доминантни хемиски форми.

Клучни зборови: специјација; антимон; селен; калај; вода; електротермичка атомска апсорпциона спектрометрија

1. INTRODUCTION

Speciation of trace metals involves the determination of the chemical forms of the metal. This includes the evaluation of free metal ions, inorganic and organic complexes and organometallic compounds. Because the bioavailability of metals depends on chemical form or speciation it is necessary that analytical methods are available to determine or predict the bioavailable fraction of a metal. Biological effects have most commonly been related to the free metal ion activity.

Antimony and selenium were considered as pollutants of priority interest. The European Union established maximum allowed concentrations of 5 µg/l Sb and of 10 µg/l Se in drinking and surface waters [1–3]. In view of its low toxicity, the presence of tin in drinking and surface waters does not represent a hazard to human health. For this reason, inorganic tin is not included in the European list of water pollutants [4]. The permissible concentration of inorganic tin in surface waters according to Macedonian national regulations is 100 µg/l Sn for first and second class and 500 µg/l Sn for third class surface waters [5].

In the environment antimony is present in forms of Sb(III), Sb(V) and methyl derivatives: monomethyloantimonic and dimethyloantimonic acid. Selenium occurs in the environment as Se(IV), Se(VI), di- and trimethylselenium, selenoaminoacids (selenocystein, selenometionin), and in many organic compounds. Tin occurs as Sn(II), Sn(IV), butyl-, phenyltin and a lot of other organic tin compounds. The inorganic species of Sb and Se are more toxic than their organic forms. In contrary, tributyltin is considered as one of the most toxic tin containing substances [6, 7].

The concentrations of Sb, Se and Sn in nonpolluted waters are less than 1 µg/l. It requires application of highly sensitive hyphenated analytical procedures for accurate and reliable speciation analysis. The developed in our laboratory highly effective liquid-liquid semi-microextraction procedure for determination of Sb(III) and Sb(V) in waters [8] can be success-

fully applied for determination of Se(IV), Se(VI) and total Sn(II) + Sn(IV).

The present paper shows the results of determination of total concentration and the results of speciation analysis of antimony, selenium and tin in water from 34 sampling points of river Vardar (V) and its tributaries: Crna Reka (CR), Treska (TR), Bregalnica (BR), Pchinja (PC) and Lepenec (LE). Vardar is the longest and major river of Macedonia and also major river of Greece. Lead, cadmium, zinc and chromium(VI) were analyzed in samples of river Vardar [9]. But there are no data about the content of Sb, Se and Sn in Vardar river and its tributaries. The aim of this research was to investigate the distribution of these elements from 2 km (V–1) up to 420 km (V–18) of the river to estimate the anthropological factors on the species distribution, species mobility, accumulation, transformation, to elucidate the processes in which elements take part in the environment.

2. EXPERIMENTAL

2.1. Instrumentation

The electrothermal atomic absorption spectrometry (ETAAS) measurements were carried out using a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace. The light sources were electrodeless discharge lamps for Sb, Se and Sn. The selected wavelengths were 217.6 nm for Sb, 196.0 nm for Se and 233.5 nm for Sn. The spectral bandpass was 0.2 nm for Sb, Sn and 0.7 nm for Se. Standard uncoated graphite tubes were used as atomizer. The injection of 20 µl organic phase was performed manually. Only peak areas were used for quantification. The graphite furnace operating parameters for ETAAS measurements are presented in Table 1. The extractant ammonium pyrrolidine dithiocarbamate (APDC) used for preconcentration/speciation of Sb acts as a matrix modifier for the determination of this element [10]. Palladium (5 µl 1000 ppm Pd) was used as matrix modifier for ETAAS determination of Se and Sn.

Table 1

Electrothermal atomization programme for determination of antimony, selenium and tin as dithiocarbamate complexes in xylene by ETAAS with Zeeman background correction
 Modifier for Se and Sn – 5 µl 1000 ppm Pd

Step	Temperature			Internal gas (Ar) flow rate ml/min
	Sb	Se	Sn	
Drying	120 (10, 10)	120 (10, 10)	120 (10, 10)	300
Pretreatment	1100 (10, 10)	1200 (12, 10)	1400 (15, 10)	300
Atomization	1700 (0, 3)	2200 (0, 3)	2300 (0, 3)	0
Cleaning	2300 (2, 3)	2500 (0, 3)	2500 (0, 3)	300

a – ramp time; b – hold time

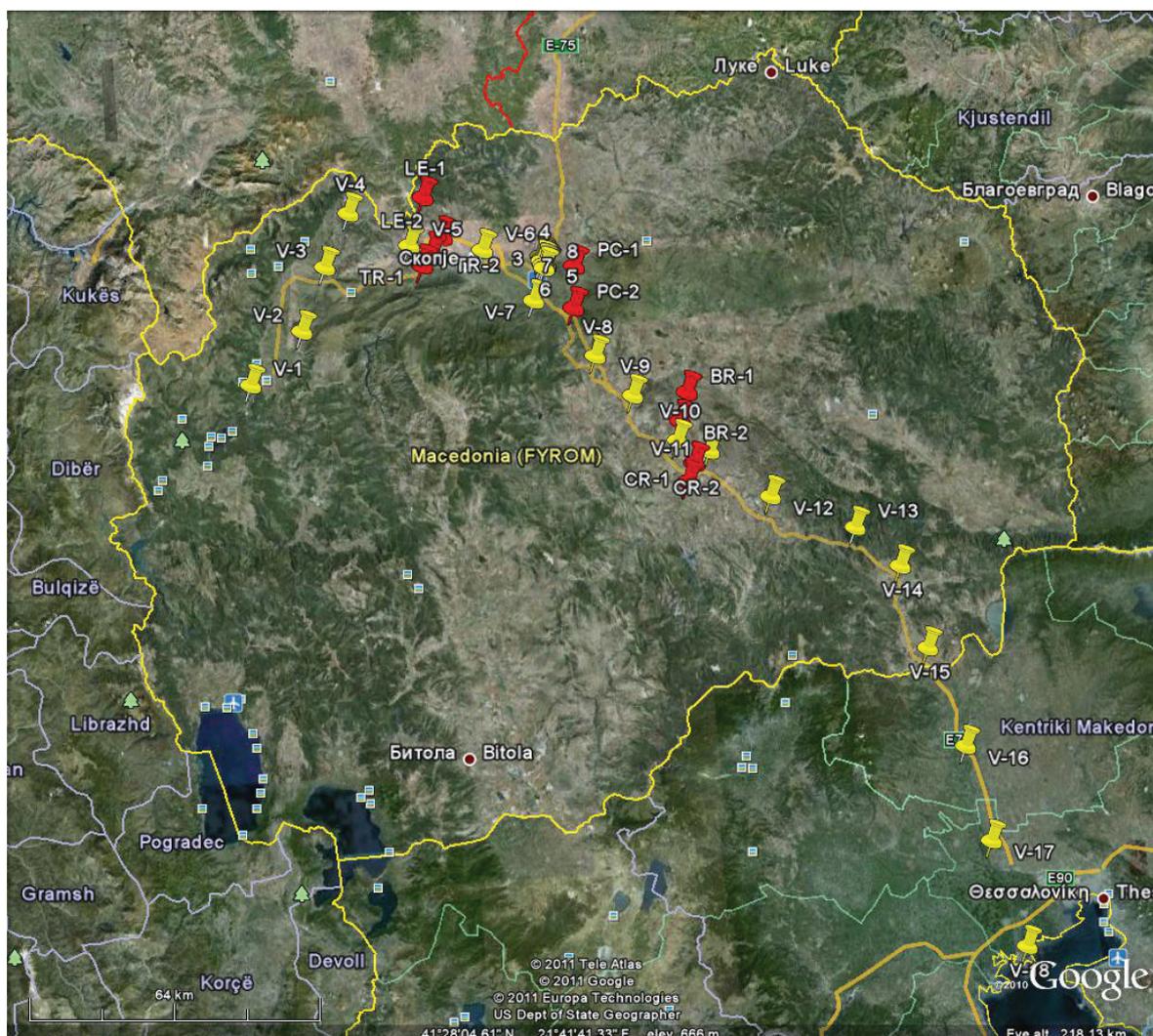


Fig. 1. Sampling sites

2.2. Reagents and materials

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout the study. A ready for use stock standard solutions for AAS (Merck, Darmstadt, Germany) with concentration of 1 g/l Sb(III), Se(IV) and Sn(IV) were used. Intermediate standard solutions with concentration 10 µg ml⁻¹ were prepared weekly by appropriate dilution with 0.5 mol/l HCl. The standard solutions at ng/mL level were prepared daily.

River water reference material for trace metals SLRS-5 (National Research Council Canada) with information value for antimony of 0.3 µg/l was used after fivefold dilution for checking the accuracy of the developed method.

2.3. Sample collection and preparation

The samples were collected in high density polyethylene (PE) bottles and filtered through 0.45 µm membrane filters. Then to the filtrates solid EDTA (1 g/l EDTA) was added and mixed. The filtrates were transferred to

the laboratory and stored in a refrigerator at 4 °C. The separation/preconcentration procedure was finished within 5 days of sample collection. Sampling points are presented in Figure 1. Characteristic parameters of the waters of river Vardar are summarized in Table 2.

2.4. Procedure

The sample was placed in a 100 ml volumetric flask up to the mark. One milliliter conc. HCl (37 %, *m/V*) was added and the sample was homogenized by shaking. Then 0.5 ml 2% ammonium pyrrolidine dithiocarbamate (APDC) and 250 µl xylene were added. The extraction was performed shaking the flask for 8 min. The organic phase remains as upper layer above the aqueous phase. Without any separation this xylene phase containing the dithiocarbamate complexes of the both Sb(III) and Sb(V), Sn(II) + Sn(IV) and of Se(IV) species was directly introduced into the graphite furnace and the temperature program (Table 1) was started. The obtained absorbance signals correspond to the concentration of i) total inorganic antimony + organic no charged antimony species; ii) total inorganic tin + organic no charged tin species; iii) Se(IV) + organic no charged selenium species. To a second aliquot of the sample placed in a 100 ml volumetric flask 1 ml of 1 mol/l acetate buffer solution (pH 5), 0.5 ml 2 % APDC and 250 µl xylene were added. After 8 min extraction the concentration of Sb(III) was measured in the xylene phase by ETAAS. To a third aliquot of the sample placed in a 100.0 ml volumetric flask 250 µl xylene were added. After 8 min extraction the concentration of no charged organic species of Sb, Sn and Se were measured in the xylene phase by ETAAS. For determination of total selenium, Se(VI) species were preliminary reduced to Se(IV) with ascorbic acid (0.5 g ascorbic acid dissolved in 100 ml sample, acidified with 1 ml conc. HCl).

Table 2

Characteristic parameters of water samples from river Vardar

Parameter	Minimum value	Maximum value
pH	7.40	8.45
Dissolved oxygen (mg/l)	10.6	12.3
Hydrogen carbonates (mg/l)	85	156
Carbonates (mg/l)	3.4	8.4
Chlorides (mg/l)	10.6	13.2
Sulphates (mg/l)	10.1	27.2
Calcium (mg/l)	26	49
Magnesium (mg/l)	9	11

3. RESULTS AND DISCUSSION

In our previous work a highly effective liquid phase semi-microextraction procedure was developed for 400 fold preconcentration/speciation of inorganic antimony species in environmental waters [8]. It was established from further laboratory experiments with tap, river and lake waters that at the optimal conditions for quantitative extraction of inorganic Sb(III) and Sb(V) (pH 1.0 ± 0.2 ; extraction time 8 min) the following species of Se and Sn can be completely transferred from 100 ml water to 250 μ l xylene:

- inorganic Se(IV);
- inorganic Sn(II, IV);
- organic no charged complexes of Sb, Se and Sn.

In order to differentiate the organic from inorganic antimony, selenium and tin species, the liquid phase semi-microextraction has to be performed in absence of APDC. It could be expected that xylene as organic solvent with low polarity will extract only the nonpolar uncharged organic species of antimony, selenium and tin. The concentration of inorganic species can be calculated from the difference between the total content and the concentration of organic species. In this way the semi-microextraction procedure summarized in Figure 2 allows preconcentration/speciation of antimony, selenium and tin species in natural waters.

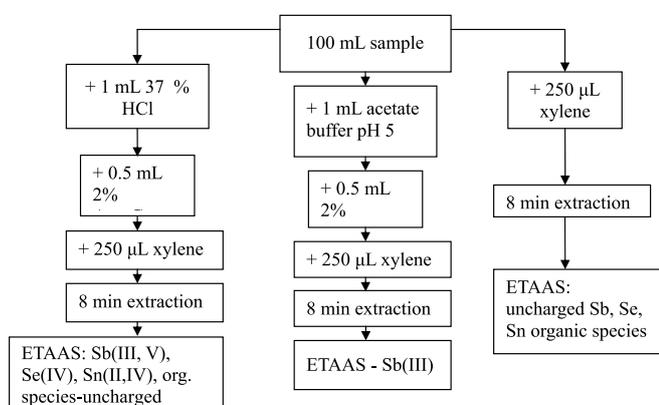


Fig. 2. Schematic presentation of liquid phase semi-microextraction for preconcentration/speciation of Sb, Se and Sn

3.1 Analytical performance of procedure

Quantification has been performed based on calibration using 0.1 mol/l HCl spiked with 100 ng/ml Sb(III), Se(IV), Sn(IV). The detection limit (evaluated as the concentration corresponding to three times the standard deviation of seven replicate measurements of a blank sample) of this method with an enrichment factor of 400 was 2 ng/l of Sb Sn, and 5 ng/l of Se. The relative standard deviations for spiked samples were lower than 9 %. But for samples and species fractions with analyte species content around the detection limit relative standard deviations up to 25 % were registered. The accuracy of Sb determination was routinely checked with each run using fivefold diluted certified river water reference material SLRS-5 (National Water Research Institute, Canada). Recovery studies of Sn and Se were performed sequentially after spiking river water samples with these analytes. Mean recoveries were between 93 and 106 % which is in the accepted range for recovery (90–110 %) [11].

3.2. Application to analysis of samples from river Vardar

The semi-microextraction procedure, described in Section 2.4 and presented in Figure 2 were applied for analysis of river waters from 25 sites of Vardar, Macedonia, 3 sites of Vardar, Greece (3) and 8 sites of rivers flowing into Vardar, Macedonia. The results from the analysis of the total content of inorganic Sb, Se and Sn are presented in Table 3. The results from speciation analysis performed for six samples are given in Table 4. From the results the following conclusions can be done:

- The concentrations of Sb, Se and Sn in river Vardar are far below the permissible levels.
- Inorganic antimony(V) is the predominant form.
- No charged organic antimony species were not detected.

- Selenium(VI) is the predominant inorganic selenium form.
- No charged organic selenium species were not detected.
- No charged organic tin species were detected in only three of investigated 34 samples at concentrations 54 ng/l (V-10), 62 ng/l (V-16) and 67 ng/l (V-17).
- For antimony a trend of enhancing of its

concentration from the second kilometer to 388 km of the river was observed. The concentrations of Sb in river Vardar and its tributaries become higher after the cities of Skopje (V-6) and Veles, the inflow of Bregalnica river (after V-7) and in the samples from Bregalnica river (Br-1 and BR-2) mainly due to the anthropogenic activities [12–16].

Table 3

*Inorganic antimony, tin and selenium in river Vardar
(Number of parallel determinations $n = 2-3$)*

Sampling site	Sb(III, V) ng/l	Sn(II, IV) ng/l	Se(IV, VI) ng/l
V-1	6 ± 1	2.8 ± 0.3	17 ± 2
V-2	7 ± 1	2.7 ± 0.3	15 ± 2
V-3	7 ± 1	2.8 ± 0.3	21 ± 2
V-4	8 ± 1	3.4 ± 0.4	23 ± 2
LE-1	10 ± 1	9.1 ± 0.6	30 ± 2
LE-2	12 ± 1	10.3 ± 0.7	31 ± 2
V-5	26 ± 2	15 ± 1	43 ± 2
TR-1	22 ± 2	34 ± 2	18 ± 2
TR-2	19 ± 1	36 ± 2	19 ± 2
3	32 ± 2	6.1 ± 0.3	27 ± 2
4	30 ± 2	5.2 ± 0.3	33 ± 2
5	48 ± 3	6.8 ± 0.4	66 ± 5
6	44 ± 3	3.9 ± 0.3	61 ± 3
7	42 ± 2	3.8 ± 0.3	59 ± 4
8	67 ± 4	46 ± 4	70 ± 4
PC-1	25 ± 2	25 ± 2	38 ± 3
V-8	57 ± 3	21 ± 2	40 ± 3
V-9	58 ± 5	12 ± 1	36 ± 3
V-11	58 ± 4	10.2 ± 0.8	36 ± 3
BR-1	242 ± 15	18 ± 1	45 ± 2
BR-2	65 ± 6	13 ± 1	42 ± 2
V-12	68 ± 5	38 ± 3	56 ± 3
V-13	65 ± 4	33 ± 3	54 ± 2
V-14	84 ± 4	41 ± 3	64 ± 3
V-15	97 ± 5	44 ± 2	66 ± 3
V-16	223 ± 22	51 ± 4	68 ± 4
V-17	226 ± 23	61 ± 5	65 ± 5
V-18	242 ± 15	43 ± 3	75 ± 6

Table 4

Inorganic antimony and selenium species in river Vardar
(number of parallel determinations $n = 2$)

Sampling site	Sb(III) ng/L	Sb(V) ng/L	Se(IV) ng/L	Se(VI) ng/L
V-6	10±1	60 ± 3	11±1	25 ± 2
V-7	13 ± 2	60 ± 2	10 ± 1	27 ± 2
V-10	12 ± 1	64 ± 4	13 ± 1	63 ± 5
CR-1	14 ± 2	55 ± 4	2.3 ± 0.3	44 ± 4
CR-2	11 ± 1	63 ± 6	5.7 ± 0.5	56 ± 4
PC-2	7 ± 1	88 ± 6	7.3 ± 0.7	34 ± 3

The higher antimony concentrations in the Greek part of Vardar (V-16, V-17, V-18) could be explained with the geological characteristics of the region [17, 18].

4. CONCLUSION

The measured concentrations of inorganic antimony, selenium and tin species were far below the allowed limits. The concentration range for total inorganic analytes was between 6 and 242 ng/l for Sb, 2.7 and 61 ng/l for Sn and 15 and 75 ng/l for Se. The higher oxidation states of antimony and selenium were found as the predominant form in all studied samples. The anthropogenic influence was expressed in higher levels of antimony.

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