

# Total Content of Arsenic, Antimony and Selenium in Groundwater Samples from Western Poland

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## Abstract

This paper presents statistical analysis of results of determination of the total content of arsenic, antimony, selenium and microcomponents in 49 samples of groundwater from an area of western Poland (Wielkopolska). The total content of arsenic reached up to 3.00 ng/ml, antimony 1.25 ng/ml, selenium < 0.15 ng/ml, at detection limits of 0.16 ng/ml for As, 0.18 ng/ml for Sb and 0.15 ng/ml for Se. The samples showed low values of the content of the elements considered relative to the values obtained for water samples from other regions. As the groundwater samples were collected from isolated water bearing horizons, the values determined for them could be treated as geogenic.

**Keywords:** arsenic, antimony, selenium, hydride generation, atomic absorption spectrometry

## Introduction

Arsenic is an element commonly found in water. It originates from geological surroundings and pollution of the environment. Therefore, the geogenic content of arsenic can vary from a few tenths of ng/ml to tens of µg/ml (in certain underground waters in California, Chile, India even a few hundred ng/ml [1, 2]). For drinking water the upper limit of arsenic is 50 ng/ml in Japan, Russia, Austria, the Czech Republic, Hungary, 10 ng/ml in Poland and Germany, 50 ng/ml in the USA. According to WHO recommendations the maximum content of arsenic in drinking water (which is the main source of inorganic arsenic for humans) should be 10 ng/ml - 1993 r. [3], before 50 ng/ml - 1984 r. [4]. With the development of

analytical chemistry and knowledge of the processes taking place in the environment and organisms, the standards concerning the content of arsenic in drinking water have changed. At present in European Union countries the admissible level of arsenic is 50 ng/ml [5], and recently a change to 10 ng/ml [6] has been proposed, similarly as in Poland (which was changed in 2000) [7, 8].

Antimony enters into the groundwaters in the form of complexes with humic acids. Depending on the geological environment and possible pollution, groundwaters may contain up to a few ng/ml of antimony. Some mineral waters, in particular hot springs, may contain even a few µg/ml of antimony. In EU countries, the admissible concentration of antimony in drinking water is 10 ng/ml [5], and a reduction of this limit to 3 ng/ml [6] has been proposed. In Poland the concentration of antimony in drinking water has been standardised at 5 ng/ml, which is recommended by WHO [4].

Table 1. Conditions of determination and parameters of the analytical method for determination of arsenic, antimony and selenium by atomic absorption spectrometry with generation of hydrides.

		As	Sb	Se
Wavelength	nm	193.7	217.6	196.0
Slit width	nm	0.5	0.2	1
Lamp current	mA	10	10	10
Limit of detection ( $3\sigma$ )	ng/ml	0.16	0.18	0.15
Sensitivity	ng/ml	0.08	0.11	0.08
Repeatability (for 10 ng/ml)	%	1.1	0.9	1.2

Depending on the geochemical surroundings and possible pollution, the content of selenium in water can vary from a few hundredth to thousands ng/ml. In Poland the mean content of selenium in water is below 0.5 ng/ml. Selenium, along with antimony and arsenic, is washed into the ground waters from dumping grounds, especially from ashes left after coal combustion. However, a comparison of selenium content in waters subjected to strong and weak anthropopressure has not revealed significant differences, which proves that urbanisation and development of industry have little effect on the content of selenium in water [3, 9]. The admissible concentration of selenium in surface waters varies from 1 ng/ml in Russia, through 8 ng/ml in Germany, 10 ng/ml in Egypt, the USA, Australia, to 50 ng/ml in the Czech Republic [9]. According to WHO recommendations the maximum concentration of selenium in drinking water should be 20 ng/ml - 1993 r. [3], (10 ng/ml - 1984 r. [4]) or, assuming that drinking water is a source of about 10% of the daily dose of selenium [4]. In EU countries the maximum concentration of selenium in drinking water is 10 ng/ml [5], and the same limit is proposed for the future [6]. In Poland the same standards as in EU countries are in force [7,8].

## Materials and Methods

### Instruments and Reagents

A two-beam spectrometer SpectrAA 20 Plus (Varian) was used, with HCL lamps (Varian). Hydrides were generated in a VGA-77 connected with electrothermally heated quartz cell ETC-60. Argon was used as a carrier gas.

The samples were mineralised in a Merck MW 500 microwave mineraliser. The fundamental physical and chemical parameters were determined on an ion-chromatograph Dionex DX-120 (anions) and a Perkin Elmer Analyst 300 atomic absorption spectrometer (cations). All the reagents used were of analytical grade and the redistilled water was additionally purified in a MilliQ device. The reference standards were from the commercial standard for AAS analysis (Promochem) of a concentration of 1 mg/ml. A solution of 1  $\mu$ g/ml, stable for 3 months, was prepared by dilution and stored

in a polyethylene cell (Nalgene). Standards of lower concentrations were prepared daily using the polyethylene cells. All standard solutions were stabilised by hydrochloric acid ( $p=1.19$  g/ml) in the amount of 1 ml/l. Solutions of sodium borohydride were made by dissolving this compound in a 1% (w/v) solution of sodium hydrochloride. The solutions were not filtered and prepared daily. Hydrochloric acid solutions were used for generation of hydrides  $p=1.19$  g/ml, while nitric (V) acid was used for mineralisation  $p=1.64$  g/ml.

### Samples

Samples were collected from groundwaters from southern Wielkopolska (near Kalisz) and eastern Wielkopolska (near Gniezno), a few sources of mineral water and tap water from Poznani, Gniezno, Konin and Plock. Samples of underground water were collected from piezometers after a short period of pumping. Routine methods of environmental sample collection were used [9]. The samples were transported in polyethylene bottles (Nalgene) for trace analysis. The determinations were performed immediately after transportation to the laboratory. When it was necessary to keep a sample in store it was frozen and kept in a freezer. The samples treated with HCl or HCl and HNO<sub>3</sub> (V) after heating in a microwave were stored at a temperature of about 4°C. It was established that sample storage for a few days did not cause a loss of the elements determined. For the majority of samples elemental analysis was performed according to the international standards (ISO) and using standard methods. For each sample two independent determinations were made and the measurements were 6 or 10 times repeated.

### Methodology

The environmental samples had to be treated prior to determinations of arsenic, antimony and selenium [10]:

1. mineralisation of the organic compounds present in the sample,
2. reduction to As(III), Sb(III) and Se(IV).

The procedures were performed in a microwave mineraliser in sealed teflon cells. Samples were mineralised by nitric acid (V) and then reduced by HCl.

Table 2. Parameters of statistical analysis of the samples of groundwaters.

	c*	NO <sub>3</sub>	Cl	PO <sub>4</sub>	SO <sub>4</sub>	Na	K	Ca	Mg	Fe	Mn
Number of samples	49	46	46	46	49	46	46	46	46	46	46
Mean content	565	0.66	23	0.24	40	31.2	4.3	58.0	15.2	2.39	0.15
The lowest content	129	ud	2	ud	ud	3.5	1.0	8.6	1.8	0.01	ud
The highest content	1778	10	77	1.60	290	180	25.5	218	39.9	12.90	0.77
Median µg/ml	487	ud	15	0.90	14	17.3	4.0	55.5	11.3	1.39	0.07
The lower quartile	381	ud	10	0.06	6	8.0	2.0	30	6.9	0.52	0.04
The upper quartile	645	0.20	36	0.35	52	42.5	5.5	73	19.9	3.26	0.17
Standard deviation	350	1.86	18	0.32	58	34.3	3.9	38.5	10.1	2.92	0.19

\* – conductivity in µS/cm      ud – undetected

## Results and Discussion

Results of determination of basic physical and chemical parameters as well as total content of arsenic, selenium and antimony in the samples of groundwaters were subjected to statistical analysis. For the purpose of analysis the samples were divided according to the area of collection. Results of the statistical analysis are presented in the Tables given below.

Taking into regard the values of the physical and chemical parameters, the waters satisfy the requirements specified for drinking water and water for household use. Only a high content of iron, characteristic of low-oxidised underground water suggests a need for water treatment. The samples coming from one of the sites in Gniezno are characterised by very high electrolytic conductivity and high content of the ions analysed, which can indicate either a specific geochemical surrounding or pollution from earlier years (e.g. it could have been a dumping ground). The samples of groundwaters make a highly diverse set as illustrated by their spatial and depth distribution obtained in statistical analysis.

Table 3. Parameters of statistical analysis of the groundwater samples.

	As	Sb	Se
Number of samples	49	49	49
Mean content	0.88	0.53	< 0.15
The lowest content	< 0.15	0.20	–
The highest content	3.00	1.25	–
Median ng/ml	0.85	0.45	–
The lower quartile	0.40	0.40	–
The upper quartile	1.15	0.65	–
Standard deviation	0.62	0.20	–

The content of selenium in the samples studied was below the limits of detectability. The results of determinations of arsenic and antimony vary in a wide range of

concentrations. However, a rather small distance between the quartiles indicates that the results surround the mean values. The results of arsenic determination are around the mean value, while those of antimony determination are focused on the right to the mean value, which means that the values higher than the mean dominate.

Different authors have reported results of determination of arsenic in natural waters. Drinking waters contain a few (110) ng/ml [11], only mineral waters about 1 ng/ml As (V) [12, 13], 0.006 ng/ml As (III) and tap water - 3.88 ng/ml As (V) [14]. Groundwaters from India contain high levels of arsenic 58-164 ng/ml As (III) and 181-275 ng/ml As (V) [16]. As far as antimony is concerned, drinking water was reported to contain from 0.13 ng/ml [18] to 0.19 ng/ml Sb (III) and 0.39 ng/ml Sb (V) [19]. The content of selenium in drinking water varies from 0.02-0.03 ng/ml [17, 20], through 0.1 ng/ml [21, 22], 0.2 ng/ml [23, 24] up to 0.6 ng/ml [21], and the compounds of Se (VI) dominate [21, 24]. The values are similar to the results of determination of arsenic, antimony and selenium in surface waters being of a few ng/ml for arsenic, about 1 and below 1 ng/ml for antimony and at the limit of detectability (0.15 ng/ml) for selenium [25-27]. Taking into regard the specific character of each biotope (described by the geochemical surrounding, hydrogeochemical conditions and anthropopressures) we decided not to compare our results with those of other authors referring to other areas. Such a comparison, in particular for water samples coming from different geochemical environments, determining the levels of the elements analysed, could lead to incorrect conclusions as to the natural and anthropogenic contents of the elements analysed.

## References

1. CHATTERJEE A., DAS D., MANDAL B.K., CHOWDHURY T.R., SAMANTA G., CHAKRABORTI D., *Analyst* 120, 3, 1995.
2. MERIAN E., *Metals and their compounds in the Environment*, VCH, 1991.
3. *Guidelines for drinking water quality. Second edition. Volume 1. Recommendations.* WHO, Geneva 1993.
4. *Guidelines for drinking-water quality*, WHO, Geneva 1984.

5. Council Directive of 15 July 1980 relating to the quality of water intended for human consumption (80/778/EEC). Official Journal of the European Communities, 1 229/11 **1980**.
6. Proposal for a Council Directive concerning the quality of water intended for human consumption [95/0010 (SYN)] **1995**.
7. Drinking water quality in Poland by Minister of Health (Dz. U. Nr 35, poz. 205) and (dz. U. Nr 82, poz. 937).
8. WICHROWSKA B., Actual normative of drinking water quality, (in Polish) Rocznic PZH 2, **1997**.
9. DOJLIDO J.R., BEST G.A., Chemistry of water and water pollution, Ellis Horwood **1993**.
10. SIEPAK J., Speciation analysis of metals, (in Polish) Wyd. UAM, Poznan **1998**.
11. STUMMEYER J., HARAZIM B., WIPPERMANN T., Speciation of arsenic in water samples by high-performance liquid chromatography-hydride generation-atomic absorption spectrometry at trace levels using a post-column reaction system, "Fresenius" J. Anal. Chem. **354**, 344, **1996**.
12. SAVERWYNS S., ZHANG X., VANHAECKE F., CORNELIS R., MOENS L., DAMS R., Speciation of Six Arsenic Compounds Using High-performance Liquid Chromatography-Inductively Coupled Plasma Mass Spectrometry With Sample Introduction by Thermospray Nebulization, JAAS **12**, 1047, **1997**.
13. CHWASTOWSKA J., STERLINSKA E., ZMIJEWSKA W., DUDEK J., Application of a Chelating Resin Loaded with Thionalide to Speciation Analysis of As III, V in Natural Waters. Chem. Anal. **41**, 45, **1996**.
14. CHAKRABORTI D., DE JONGHE W., ADAMS F., The determination of arsenic by electrothermal atomic absorption spectrometry with a graphite furnace. Anal. Chim. Acta **120**, 121, **1980**.
15. HENZE G., WAGNER W., SANDER S., Speciation of arsenic(V) and arsenic(III) by cathodic stripping voltammetry in fresh water samples, Fresenius J Anal Chem **358**, 741, **1997**.
16. CHATTERJEE A., DAS D., MANDAL B.K., CHOWDHURY T.R., SAMANTA G., CHAKRABORTI D., Arsenic in ground water in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part I. arsenic species in drinking water and urine of the affected people, Analyst **120**, 3, **1995**.
17. VEBER M., CUJES K., GOMISCEK S., Determination of selenium and arsenic in mineral waters with hydride generation atomic absorption spectrometry, JAAS **9**, 30, **1994**.
18. POSTUPOLSKI A., GOLIMOWSKI J., Trace Determination of Antimony and Bismuth in Snow and Water Samples by Stripping Voltammetry, Electroanalysis **3**, 793, **1991**.
19. GARBOS S., BULSKA E., HULANICKI A., SHCHERBININA N.I., SEDYKH E.M., Preconcentration of inorganic species of antimony by sorption on Polyorgs 31 followed by atomic absorption spectrometry determination. Anal. Chem. Acta. **342**, 167, **1997**.
20. TAO G., HANSEN E.H., Determination of Ultra-trace Amounts of Selenium(IV) by Flow Injection Hydride Generation Atomic Absorption Spectrometry With On-line Preconcentration by Coprecipitation With Lanthanum Hydroxide, Analyst **119**, 20, **1994**.
21. ORNEMARK U., OLIN A., Determination of Dissolved Selenium(VI) in Freshwater, Talanta **41**, 1675, **1994**.
22. CARRERO P.E., TYSON J.F., Determination of selenium by atomic absorption spectrometry with simultaneous retention of selenium(IV) and tetrahydroborate(III) on an anion-exchange resin followed by flow injection hydride generation from the solid phase, Analyst **122**, 915, **1997**.
23. ORNEMARK U., PETERSSON J., OLIN A., Determination of total selenium in water by atomic-absorption spectrometry after hydride generation and preconcentration in a cold trap system, Talanta **39**, 1089, **1992**.
24. ORNEMARK U., OLIN A., Preconcentration and separation of inorganic selenium on dowex 1X8 prior to hydride generation-atomic absorption spectrometry, Talanta **41**, 67, **1994**.
25. NIEDZIELSKI P., SIEPAK J., KOWALCZUK Z., Speciation Analysis of Arsenic, Antimony and Selenium in the Surface Waters of Poznan, Polish Journal of Environmental Studies **8(3)**, 183, **1999**.
26. NIEDZIELSKI P., SIEPAK J., KOWALCZUK Z., Speciation Analysis of Arsenic, Antimony and Selenium in the Waters of Lakes Subjected to Various Levels of Anthropopressure, Chemia i inzynieria ekologiczna **4**, 1, **1999**.
27. NIEDZIELSKI P., SIEPAK J., KOWALCZUK Z., Speciation Analysis of Arsenic, Antimony and Selenium in Waters of the Lednickie Lake, Archives of Environmental Protection **1**, 73, **2000**.