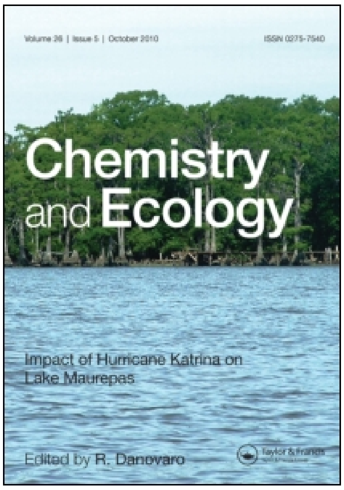

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Niedzielski, P. and Siepak, M.(2005) 'The occurrence and speciation of arsenic, antimony, and selenium in ground water of Poznań city (Poland)', Chemistry and Ecology, 21: 4, 241 — 253

To link to this Article: DOI: 10.1080/02757540500213174

URL: http://dx.doi.org/10.1080/02757540500213174

Chemistry and Ecology
Vol. 21, No. 4, August 2005, 241–253

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The occurrence and speciation of arsenic, antimony, and selenium in ground water of Poznań city (Poland)

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(Received 21 February 2005; in final form 24 May 2005)

This paper presents results of determination of total arsenic, antimony, and selenium contents as well as their species in ground water from the region of Poznań. Determinations were carried by means of atomic absorption spectrometry hyphenated with generation of hydrides and *in situ* preconcentration in a graphite tube (HG-GFAAS). In order to obtain the best efficiency of an analyte concentration process on the walls of the tube, palladium was used as a modifying agent. The concentration of total arsenic was up to 2.04 ng ml^{-1}, that of antimony up to 0.71 ng ml^{-1}, and that of selenium up to 0.44 ng ml^{-1}. The lowest concentrations of the investigated elements in ground water and the predominance of As(III), Sb(III), and Se(IV) speciation forms over As(V), Sb(V), and Se(VI) forms were found in the region, where the thickest aquitards (glacial tills of the Vistulian Glaciation) overlay an aquifer. Moreover, the geological and hydrogeological conditions of the study area are presented.

Keywords: Arsenic; Antimony; Selenium; Speciation analysis; Ground water

1. Introduction

Arsenic occurs in the geological environment in form of arsenates (e.g. scorodite, $Fe^{3+}(AsO_4)\cdot 2H_2O$). The other mineral forms are: sulphides (e.g. common arsenopyrite, FeAsS) and arsenide (e.g. trippkeite, $CuAs_2O_4$). Migration of the arsenic compounds can be limited by clay minerals, iron and aluminium hydroxides, and organic matter. Besides, some minerals e.g. iron and aluminium (hydr)oxides are particularly inclined to bound arsenic and can therefore influence its distribution in the geological environment. Depending on this environment, ground water as well as surface water may contain tenths of ng ml^{-1} to μg ml^{-1}. The main arsenic species in water are arsenites (III), arsenates (V), methyl- (monomethylarsenic acid MMAA) and dimethyl-arsenates (dimethylarsenic acid DMAA) [1–5].

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Chemistry and Ecology
ISSN 0275-7540 print/ISSN 1029-0370 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02757540500213174

Antimony is a mobile and widespread element in the environment. The content of antimony in rocks is small and does not exceed 1 $\mu g\,g^{-1}$, except in clay rocks, which contain up to 2 $\mu g\,g^{-1}$ of this element. It occurs in sulphide deposits mostly in form of antimonite (Sb_2S_3). From the high chemical similarity between antimony and arsenic, one would expect their behaviour in natural water, especially distribution and speciation, to be similar. Antimony penetrates into ground water in the form of complexes with humic acids. Depending on the geological environment and potential contamination, water can contain up to several $ng\,ml^{-1}$ of antimony. Some mineral waters, particularly hot springs, may contain even a few $\mu g\,ml^{-1}$ of this element. In the case of water pollution (municipal wastes and effluents from waste disposal sites), antimony concentrations increase to a few $ng\,ml^{-1}$ and can be like arsenic and selenium as a monitoring parameter. Its concentration in surface water and rainfall is usually less than 1 $ng\,ml^{-1}$ (in urban areas up to several $ng\,ml^{-1}$). In the environment, antimony occurs in the form of inorganic antimonates (III) and (V) and methyl derivatives: monomethylantimonic acid (MMSbA) and demthylantimonic acid (DMSbA) [3].

In view of its multivalency and complicated geochemical properties, selenium shows variable environmental behaviours. It can be adsorbed by iron oxides, clay minerals, and organic matter. The content of selenium in magmatic and sedimentary rocks rarely exceeds 0.5 $\mu g\,g^{-1}$. It occurs in approximately 50 minerals, which are mostly connected with deposits of metal sulphides (e.g. CuSe-klockmannite, $FeSe_2$-ferroselite, PbSe-clausthalite). Increased concentrations of selenium can be found in the sediment enriched with iron compounds, organic matter, as well as in salinized deposits. Depending on the geochemical environment and potential contamination, water may contain hundredths to thousandths of $ng\,ml^{-1}$ of selenium. It can be leached into ground water (like arsenic and antimony) from waste-disposal sites, especially of coal combustion ashes or from the industrial areas. In the aquatic environment, selenium occurs in the form of selenites (IV) and selenates (VI), dimethyl (volatile dimethyloselenium—DMSe and dimethylodiselenium—DMDSe) and trimethyl (trimethyloselenium—TMSe) derivatives, selenium amino acids (selenocysteine—SeC and selenometionine—SeM), and in a number of organic compounds [1–3].

Arsenic, antimony, and selenium can be easily separated from the matrix by converting them into volatile hydrides. Besides, it is possible to concentrate them on the inner surface of a graphite tube in the presence of an earlier introduced modifier. The *in situ* concentration of the analyte in a graphite tube was proposed for the first time by Drasch in 1980 [6]. In this method, the generated hydride is introduced by a carrier gas (Ar or He) into a graphite tube heated to the proper temperature. As a result of thermal decomposition, the element under determination is adsorbed on the inner walls of the graphite tube. In order to enhance the effectiveness of the concentration, the walls of the graphite tube are covered with a modifier, which is either introduced during the analysis or electrothermally deposited [7]. The modifiers used for a modification are the compounds of palladium [8–14], magnesium [10,15,16], zirconium [17], iridium [12,17–20], rhodium [21], nickel [10,22], as well as permanent modifiers like Zr, Ir, W, and Nb [9,23,24]. Palladium and other metals are able to bind arsenic, antimony, and selenium in the form of intermetallic compounds, which evaporate at temperatures higher than the evaporation temperature of the element under determination [25,26]. Other authors, however, have criticized this mechanism [27].

This paper presents the results of the determination of inorganic speciation forms of arsenic, antimony, and selenium and their total concentrations in water samples from a Quaternary aquifer in the area of Poznań city. Investigation sites are located in the quarters of Piątkowo and Winogrady. The aim of this research is to determine these elements in ground water samples using atomic absorptions spectrometry with hydride generation and *in situ* concentration on the inner walls of the graphite tube (HG-GFAAS). Also, attempts are made to determine if the level of total contents and speciation forms of the investigated elements depends on the thickness of an unsaturated zone and aquitards overlying the aquifer.

2. Materials and methods

2.1 *Geology of the study area*

The occurrence and lithology of Quaternary deposits are connected with an accumulative activity of the successive Scandinavian glaciers in the region of Great Poland, erosive and accumulative activity of water within a glacier and on its foreland, as well as rivers during the interglacial periods. The thickness of Quaternary deposits depends on the morphology of the Tertiary bedrock and on the present relief. In the region of the till plains, their average thickness is 50 m, and in the local hollows it is up to 80 m. The basic Quaternary sediments are represented by glacial tills, which occur in several levels. The oldest tills occur in the regions where the Tertiary surface lowers (tills of the Elsterian Glaciation). The youngest tills of the Vistulian Glaciation form till plains cut by the valley of the Warta River with tributary valleys in Poznań region. Postglacial sands and gravels as well as alluvial sandy deposits of present valleys occur locally and build the aquifers of small meaning for ground water exploitation. The aquifers within till plains are composed of fluvioglacial sands and gravels, which are covered by a layer of glacial tills, a few metres thick. These sediments are determined as buried glacial outwash. Their thickness is up to 15 m. They occur in most of the till plain regions, particularly on the west side of the town in the surroundings of Jeżyce, Winogrady, and Piątkowo.

2.2 *Hydrogeological conditions of the study area*

The location of the drilled wells in the northern districts of Poznań (Piątkowo and Winogrady) is shown on figure 1. Presented wells were sampled in order to carry chemical analyses.

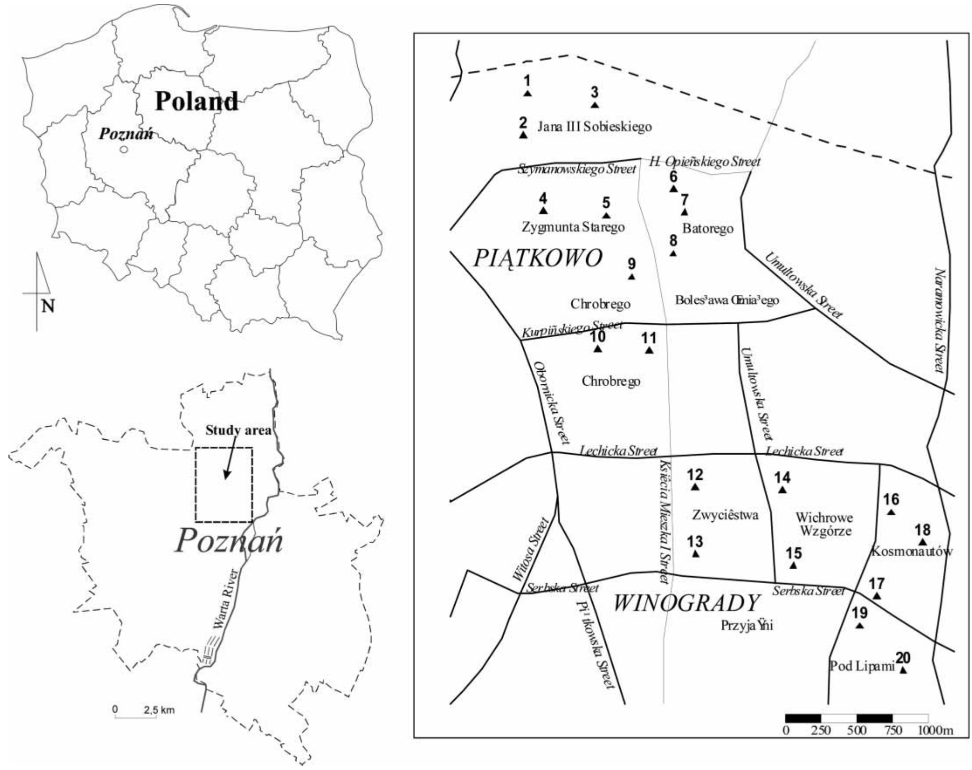

Figure 1. Location of the public wells sampled in the region of Piątkowo and Winogrady.

They were tapping the Quaternary aquifer at a depth of up to 50 m mostly at 10–40 m depending on a distribution of water-bearing sediments within glacial tills.

Hydrogeological profiles of the investigated wells in Piątkowo and Winogrady regions are presented on figure 2 (well nos 1–11) and figure 3 (well nos 12–18) in order to explain the geology and hydrogeology of this area. These profiles show that the inter-till aquifer (fluvial and fluvioglacial sands and gravels) is tapped in the northern districts of Poznań. It is also the main Quaternary aquifer within the boundaries of Poznań. According to the detailed geological map of Poland [28], this aquifer occurs between the glacial tills of the Vistulian Glaciation (symbol GzB on profiles 3 and 4—figure 2) and the Saale Glaciation (symbol GzS on profiles 8 and 9—figure 2). A confined ground water table occurs in the region of Piątkowo (figure 2). This rises in wells above the bottom of overlaying tills. An unconfined ground water table occurs on the border of Piątkowo and Winogrady regions (well nos 10 and 11—figure 2). The ground water table in Winogrady region is unconfined, despite overlaying glacial tills, and stabilizes below the till bottom (a vadose zone which is a few metres thick). This is a result of the Warta River valley proximity, which cuts water-bearing sediments.

Small resources and low renewal rates characterize the discussed aquifer [29]. This is exploited by some industrial plants for the purposes of individual water supply. Most of the public wells marked as an emergency water supply for the town tap this aquifer. In the region of Piątkowo and Podolany, a local aquifer occurs under the tills of the Saale Glaciation (GzS). The wells, which tap this aquifer, are showed on figure 3 (the public well no. 3; depth of water bearing horizon 35.5 m).

2.3 *Equipment and solutions*

An atomic absorption spectrometer SpectrAA 20 Plus (Varian) was used to measure arsenic, antimony, and selenium in ground water sampled from the wells in the region of Piątkowo and

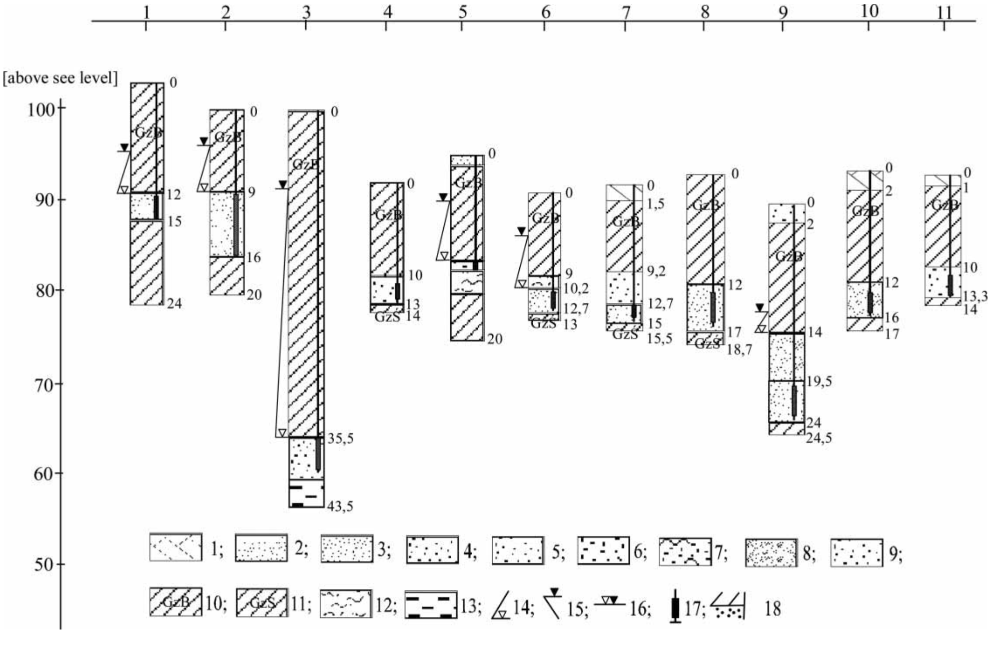

Figure 2. Geological profiles of the public wells in the Piątkowo region (for explanations see figure 3).

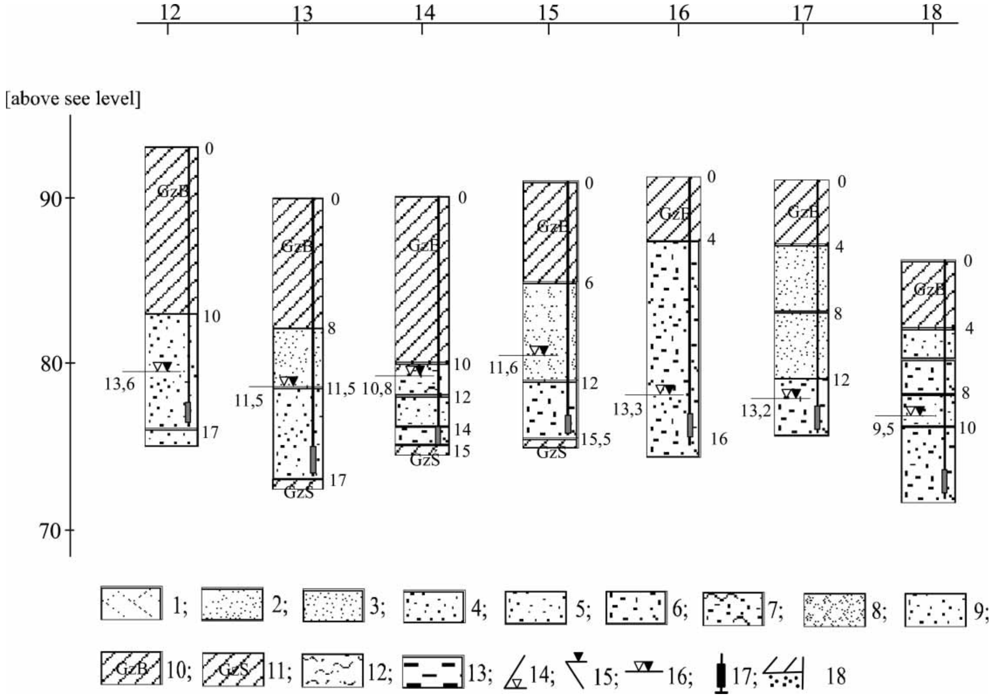

Figure 3. Geological profiles of the public wells in the Winogrady region. 1: banks; 2: fine sands; 3: medium-grained sands; 4: coarse-grained sands; 5: gravels and sands; 6: gravels; 7: clayey gravels; 8: silty sands; 9: vari-grained sands; 10: glacial tills of the Vistulian glaciation; 11: glacial tills of the Saale Glaciation; 12: silts; 13: clays; 14: confined ground water table encountered during drilling; 15: stabilized ground water table; 16: unconfined ground water table; 17: well screen; 18: depths of layers occurrence [m].

Winogrady by the HG-GFAAS method (atomic absorption spectrometry with hydride generation and *in situ* concentration in a graphite tube). The concentration and electrothermal atomization were carried out on an atomizer GTA-96 (Varian), temperature-programmable in the range 40–3000 °C with an accuracy of 1 °C and rate of up to 2000 °C s^{-1}. The gas (argon) flow rate ranged from 0 to 3 L min^{-1} and was stopped during measurements of absorbency (table 1). Moreover, the atomizer was co-working with an autosampler, which is able to host 45

Table 1. Conditions of arsenic, antimony, and selenium determination by the HG-GFAAS method.

	As	Sb	Se
Wavelength (nm)	193.7	217.6	196.0
Slit (nm)	0.5	0.2	1
Lamp current (mA)	10	10	10
Concentration of hydrochloric acid used for total concentration determinations (M)	10	1	1
Concentration of hydrochloric acid used for species determinations of Sb and Se and citric acid for As determinations (M)	5	1	1
Reductor concentration (%)	1	0.3	0.3
Modificator mass (Pd) (μg)	4	2	2
Atomization temperature (°C)	2000		
Concentration temperature (°C)	200		
Sample flow rate (mL min^{-1})	5		
Reducer flow rate (mL min^{-1})	1		
Acid flow rate (mL min^{-1})	1		
Concentration time (s)	60		

samples. Hydrides were generated in a device VGA-77 (Varian) connected with a graphite tube through an elastomer cable ended with a quartz capillary removed from the atomizer during atomization. A Teflon-coated liner was applied in order to place a capillary in a graphite furnace. Only the end of the capillary was placed in a graphite cuvette. When the *in situ* concentration was applied, the graphite tube was covered with pyrolytic graphite and was used without the platform. The carrier gas was argon of N-50 purity (99.999%) obtained from BOC GAZY (Poznań, Poland).

All the reagents used were analytically pure, and redistilled water was subjected to ionic exchange in a Milli-Q (Milipore, Bedford, MA). Standard solutions were prepared from commercial standards for AAS analysis with a concentration of $1\,\mathrm{mg\,ml^{-1}}$ concentration. They were diluted to a concentration of $1\,\mu\mathrm{g\,ml^{-1}}$, which was stable for about 3 months, and stored in polyethylene vessels (Nalgene). A solution of sodium borohydride was made on the day of analysis by dissolving $NaBH_4$ in a 1% (w/v) solution of sodium hydroxide (Sigma Aldrich, Milwaukee, WI). A modifier solution (Pd) was prepared by diluting a commercial solution of palladium nitrate at a concentration of 10 g/L. The solution of HCl ($\rho = 1.19\,\mathrm{g\,ml^{-1}}$) was made by dilution. A solution of thiourea was prepared by dissolving 15.2 g of thiourea in 200 mL of water. The certified reference material used was SLRS-3 (Promochem, Poland); see table 2.

2.4 *Analytical method*

Determinations were carried out by the HG-GFAAS method with the operational species distinction and the application of a developed methodology [10,13,14].

During analytical work, the temperature program used consisted of five stages: drying, thermal reduction in the modifier, hydride concentration (trapping), atomization, and cell cleaning. For each stage, the temperature, duration and gas flow rate were adjusted. The program automatically activated the feeding device, which introduced a certain volume of the modifier into the graphite tube. After drying and reduction, when the temperature decreased to that of the trapping, the quartz capillary tube was placed inside the tube. From that moment, concentration of the hydrides generated was begun. After removing the capillary tube, the atomization took place, and then the analytical signal was measured. After analysis, the graphite tube was cleaned (table 3).

The temperature for arsenic, antimony, and selenium concentration was chosen on the basis of absorbency measurements in the temperature range of 50–400 °C in the presence of palladium as a modifier (figure 4).

Table 2. Temperature programme followed by the determination of arsenic, antimony, and selenium using the atomic absorption spectrometry method with hydride generation and *in situ* preconcentration in a graphite tube [10,13].

Step of analysis	Temperature (°C)	Time (s)	Gas flow	Procedure	Reading
Drying	85–120	20.0	+	Introduction of modifier	–
Reduction	1200	2.0	+	Thermal reduction in modifier	–
Concentration	200	60.0	–	Introduction of quartz capillary	–
Atomisation	2000	2.0	–	Removing of capillary	+
Cleaning	2500	2.0	+	Cleaning of graphite tube	–

Table 3. Results of arsenic, antimony, and selenium determinations in the certified reference standard material SLRS-3 by HG-GFAAS.

		Results of determination		
Elements	Certified value (ng mL^{-1})	By standard addition (ng mL^{-1})	Calibration curve (ng mL^{-1})	Recovery (%)
As	0.72 ± 0.05	0.78 ± 0.04	0.78 ± 0.05	108 ± 5
Sb	0.12 ± 0.01	0.11 ± 0.01	0.10 ± 0.01	$92 \pm 8/83 \pm 8$
Se	Non-certified	–	–	–

For the determinations of arsenic, antimony, and selenium, the highest analytical signal was obtained at a temperature of 200 °C (figure 4). Determinations of the speciation forms by the HG-GFAAS method were carried out according to the following scheme:

1. Direct determination of the samples without the preliminary treatment—determinations of As(III); (in a citric acid environment), Sb(III), Se(IV).
2. Determination of total arsenic, antimony, and selenium in the environment of HCl acid in the samples after reduction with thiourea.
3. Calculations of As(V), Sb(V), and Se(VI) contents from the subtraction of results obtained in points 1 and 2.

The basic parameters of the analytical method of arsenic, antimony, and selenium determinations using the HG-GFAAS method are shown in table 4.

2.5 *Sample collection*

Ground water sampling from the public wells involved pumping water at least three times by means of a hand pump. Water samples, in which As, Sb, and Se were determined, were stored in polyethylene vessels for trace analyses (Nalgene). Samples were not preserved and filtered in order to avoid a disruption of the speciation balance. After collection, the sample

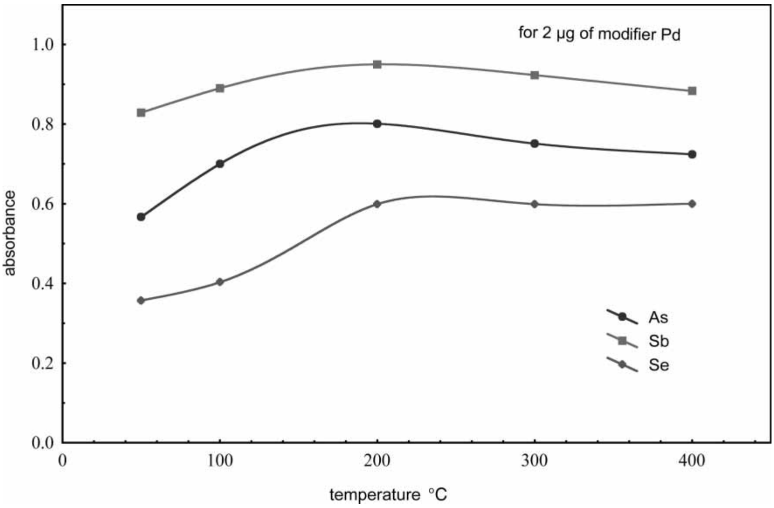

Figure 4. Temperature dependence of the analytical signal corresponding to arsenic, antimony, and selenium (1 ng/mL).

Table 4. Parameters of the analytical method (HG-GFAAS) used for determinations of arsenic, antimony, and selenium ($n = 10$).

	As	Sb	Se
Detection limit (3σ) (ng mL^{-1})	0.019	0.014	0.018
Determination limit (6σ) (ng mL^{-1})	0.033	0.024	0.036
Sensitivity (ng mL^{-1})	0.007	0.006	0.007
Reproducibility (for 10 ng mL^{-1}) (%)	3.8 (12.7*)	2.9 (10.1*)	4.2 (12.8*)

*For 0.1 ng mL^{-1}.

Table 5. Location of the sampling sites (wells) in the region of Piątkowo and Winogrady.

Well	Housing estate	Geographical coordinates	
Piątkowo			
1	Jana III Sobieskiego 18	52° 27′ 51.2″ N	16° 54′ 25.3″ E
2	Jana III Sobieskiego 2	52° 27′ 42.4″ N	16° 54′ 23.6″ E
3	Jana III Sobieskiego 24	52° 27′ 48.8″ N	16° 54′ 48.6″ E
4	Chrobrego 11	52° 27′ 25.2″ N	16° 54′ 52.7″ E
5	Chrobrego 5	52° 27′ 26.6″ N	16° 54′ 30.6″ E
6	Batorego 13	52° 27′ 31.3″ N	16° 55′ 15.9″ E
7	Batorego 17	52° 27′ 26.2″ N	16° 55′ 19.7″ E
8	Śmiałego 4	52° 27′ 17.2″ N	16° 55′ 15.9″ E
9	Chrobrego 19	52° 27′ 12.4″ N	16° 55′ 01.2″ E
10	Chrobrego 41	52° 26′ 57.2″ N	16° 54′ 49.3″ E
11	Chrobrego 29	52° 26′ 56.8″ N	16° 55′ 07.5″ E
Winogrady			
12	Zwycięstwa 22	52° 26′ 27.9″ N	16° 55′ 23.4″ E
13	Zwycięstwa 19	52° 26′ 13.5″ N	16° 55′ 23.8″ E
14	Wichrowe Wzgórze 27	52° 26′ 27.4″ N	16° 55′ 53.9″ E
15	Wichrowe Wzgórze 23	52° 26′ 11.4″ N	16° 55′ 57.5″ E
16	Kosmonautów 13	52° 26′ 22.4″ N	16° 56′ 31.9″ E
17	Kosmonautów 4	52° 26′ 04.6″ N	16° 56′ 26.3″ E
18	Kosmonautów 17	52° 26′ 16.2″ N	16° 56′ 42.6″ E
19	Pod Lipami 4	52° 25′ 49.0″ N	16° 56′ 35.5″ E
20	Pod Lipami 14	52° 25′ 58.7″ N	16° 56′ 20.4″ E

was cooled down to 4 °C and transported to the laboratory. When it was impossible to carry out determinations right after the samples were delivered to the laboratory, the samples were frozen and stored at −30 °C. A total of 20 water samples were collected in order to carry chemical analyses (the region of Piątkowo and Winogrady—figure 1). A sampling position was determined with the help of a Global Positioning System (table 5).

3. Results and discussion

The total content of arsenic in ground water samples ranges from 0.58 to 2.04 ng ml^{-1}, for antimony from 0.25 to 0.71 ng ml^{-1}, and for selenium from 0.17 to 0.44 ng ml^{-1} (table 6). The lowest concentrations of total arsenic and antimony contents as well as one of the lowest of selenium concentrations in the set of 20 samples occur in well no. 3 (Jana III Sobieskiego housing estate in Piątkowo; 0.40 ng ml^{-1} As; 0.24 ng ml^{-1} Sb; 0.19 ng ml^{-1} Se—table 6). This concentration level for these microelements can be associated with the fact that the aquitards overlying the aquifer in this well are the thickest of all the wells (figure 4, well no. 3, 35 m

Table 6. Total content of arsenic, antimony, and selenium (ng mL^{-1}) and ratio of their speciation forms in ground water samples from the region of Piątkowo and Winogrady.

Well	Housing estate	As (III)/(V)	As (total) (ng mL^{-1})	Sb (III)/(V)	Sb (total) (ng mL^{-1})	Se (IV)/(VI)	Se (total) (ng mL^{-1})
Piątkowo							
1	Jana III Sobieskiego 18	0.26	1.44	0.60	0.40	2.11	0.28
2	Jana III Sobieskiego 2	0.39	1.06	0.92	0.25	1.80	0.28
3	Jana III Sobieskiego 24	1.11	0.40	3.00	0.24	1.11	0.19
4	Chrobrego 11	0.36	1.10	0.22	0.71	1.22	0.20
5	Chrobrego 5	0.61	1.24	1.00	0.48	1.56	0.23
6	Batorego 13	1.11	0.76	0.40	0.35	3.33	0.26
7	Batorego 17	0.81	0.85	0.31	0.38	1.00	0.20
8	Śmiałego 4	0.76	0.58	0.40	0.35	1.09	0.44
9	Chrobrego 19	0.69	0.98	0.67	0.30	2.56	0.32
10	Chrobrego 41	0.68	0.84	0.68	0.57	3.00	0.20
11	Chrobrego 29	1.47	0.79	0.75	0.28	1.50	0.20
Winogrady							
12	Zwycięstwa 22	0.72	0.62	0.66	0.48	2.22	0.29
13	Zwycięstwa 19	0.88	0.75	1.62	0.34	1.50	0.20
14	Wichrowe Wzgórze 27	0.70	0.75	0.56	0.42	1.73	0.30
15	Wichrowe Wzgórze 23	0.97	1.52	0.59	0.43	2.25	0.26
16	Kosmonautów 13	0.83	0.75	0.91	0.42	1.80	0.28
17	Kosmonautów 4	0.64	0.59	0.79	0.52	2.50	0.35
18	Kosmonautów 17	0.65	2.04	0.58	0.41	2.00	0.30
19	Pod Lipami 4	0.65	0.81	0.56	0.39	2.40	0.17
20	Pod Lipami 14	2.44	1.55	0.63	0.39	3.11	0.37

of glacial tills of the Vistulian Glaciation). The concentrations do not exceed drinking-water standards [30, 31].

As(III), Sb(III), and Se(IV) are determined in ground water samples collected in Poznań region. Contents of As(V), Sb(V), and Se(VI) are determined according to the given methodology. Results presented in table 6 show the presence of the investigated microelements at different oxidation levels.

Different arsenic species are observed in water sampled from the wells in the region of Piątkowo and Winogrady. The form As(V) prevails in water of all wells except for well nos 3, 6, 11, and 20, where the As(III) form is dominant. During determinations of antimony species, high concentrations of Sb(V) are found in water samples except for water from well nos 3 and 13. In the case of selenium species determinations, it is found that in the water sampled from well no. 7, the speciation forms are balanced, while in other samples, the Se(IV) form prevailed (table 6).

A predominance of As(III), Sb(III) and Se(IV) concentrations over As(V), Sb(V), and Se(VI) forms is observed only in the water sampled from the well no. 3. In the case of antimony, there is three times more of the Sb(III) form than of the Sb(V) form. It is possible that this kind of species distribution is affected by a different thickness of deposits overlying the aquifer.

Figure 5 shows the dependence of pH on E_H. Each of the points on the diagram is marked with the symbol of the well number.

In the case of arsenic-species determination (figure 5), $H_2AsO_4^-$ and $HAsO_4^{2-}$ have prevailed. At lower E_H, values the H_3AsO_3 form occurs. In ground water, arsenic can migrate in form of different anions: AsO_4^{3-}, $H_2AsO_3^-$, $HAsO_4^{2-}$, $H_2AsO_4^-$, AsO_2^-, $HAsO_3^{2-}$ and neutral particles: H_2AsO_3 [1, 32]. Anion $HAsO_4^{2-}$ occurs in water at pHs above 7.2. Below this value, a dominant form is usually $H_2AsO_4^-$. The variation in As forms depends not only on pH but also on the redox conditions [33, 34] and microbiological processes [35], which cause oxidation of arsenides to

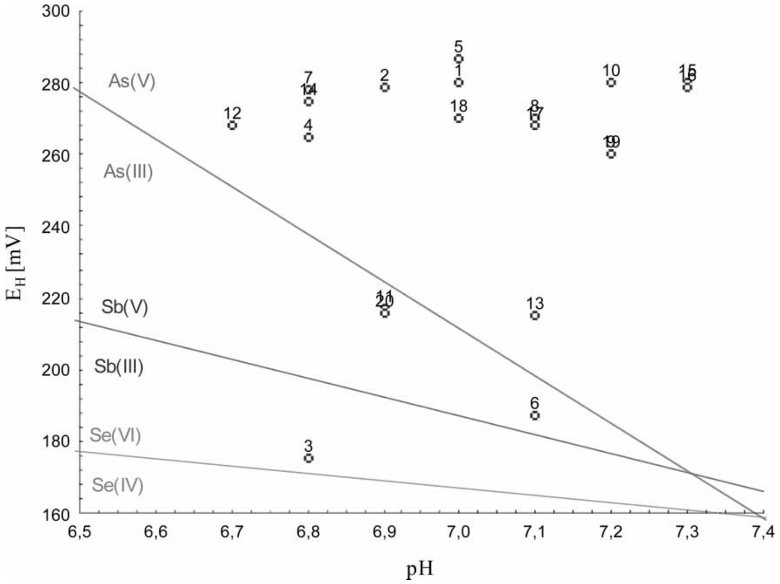

Figure 5. Diagram showing the pH and E_H dependence of arsenic, antimony, and selenium speciation forms occurring in the Quaternary aquifer in the Piątkowo and Winogrady region.

arsenates [2, 34]. In the aeration zone, the As(V) form prevails, and the As(V) form dominates in the reducing conditions [2].

In the case of antimony-species determination (figure 5), the predominance of the $Sb(OH)_6^-$ form and the occurrence of the $Sb(OH)_3$ form are observed. The form in which antimony occurs in ground water depends mostly on water pH and E_H, and on the presence of micro-organisms [36].

In the case of selenium (figure 5), only the $HSeO_3^-$ form is observed. In ground water, the form of selenium occurrence depends on the redox potential, pH, and micro-organism activity [37]. The basic form, in which selenium migrates in ground water characterized by the pH close to the neutral, is SeO_4^{2-} anion [1].

The concentration of arsenic in ground water on the territory of Poland ranges from $0.1\,ng\,ml^{-1}$ to tens of $ng\,ml^{-1}$ [3], whereas in ground water of the Warta River valley in Poznań, the concentration reached only to $2.31\,ng\,ml^{-1}$ As [38]. Concentrations of As determined in ground water of eastern and northern Wielkopolska voivodship are up to $3.00\,ng\,ml^{-1}$ [39]. The amounts of As in ground water in England are 0.5–$10\,ng\,ml^{-1}$ [40]; in Bangladesh, Nickson *et al.* found As concentrations of 10–$268\,ng\,ml^{-1}$ [41] and Ahmed *et al.* found As concentrations of 2.5–$846\,ng\,ml^{-1}$ [42]. Ground water and some mineral water in India contain 58–$164\,ng\,ml^{-1}$ of As (III) and 181–$275\,ng\,ml^{-1}$ of As (V) [43, 44]. High concentrations of arsenic in ground water (up to $50\,ng\,ml^{-1}$) have been found in the desert [45]. The mean concentration of antimony in ground water of Poland is up to $0.13\,ng\,ml^{-1}$ [3]. Ground water of the Warta River valley in Poznań city contains $0.49\,ng\,ml^{-1}$ of Sb [38]. In ground water of southern and eastern Wielkopolska voivodship, the Sb concentration of $1.25\,ng\,ml^{-1}$ has been determined [39]. Ground water from deserts can contain up to 0.1–$0.2\,ng\,ml^{-1}$ of antimony [45]. Selenium, according to the geochemical surroundings and potential pollution, occurs in concentrations of hundreds to even thousands of $ng\,ml^{-1}$. Selenium in ground water of Poland is found at concentrations starting from $0.10\,ng\,ml^{-1}$ and increases together with the pollutant inflow [3]. On the other hand, in ground water of Poznań city, the concentration of Se is up to $0.51\,ng\,ml^{-1}$ [38]. In the Niedzielski study, the concentration of selenium is found to be less than 0.15 ng ml^{-1} [39]. In ground water of Slovenia, the selenium concentration is up to 0.2 ng ml^{-1} [44], while in ground water of deserts, the concentration ranges from 0.9 to 2.8 ng ml^{-1} [45].

4. Summary

Preliminary research shows low levels of arsenic, antimony, and selenium contents in ground water that can be a result of both the geochemical environment and anthropogenic pressure. Moreover, this indicates the speciation of the studied elements, which occur in ground water in the region of Poznań. It has been found that the level of the total microelement contents in ground water and distribution of their species can depend on the thickness of the deposits overlying the aquifer. Thus, glacial tills of the Vistulian Glaciation might be a natural barrier against pollutants leaching from the land surface to the aquifer. This kind of work can become a basis for future research, which would help identify trends in ground water, especially anthropogenic influence, as well as the statistical compilation of microelement content in ground water.

Acknowledgements

Part of this study has been financially supported by the Minister of Scientific Research and Information Technology within the project no. 3 P04G 074 24. These results were partly presented in a research report for the Department of Protection of the Environment of Poznań city [46]. Dr M. Siepak is a scholar of Foundation for Polish Science.

References

[1] A. Macioszczyk. *Hydrogeochemistry* (in Polish), Geological Publishing House, Warsaw (1987).

[2] A. Kabata-Pendias. Biogeochemistry of arsenic and selenium. In *Arsenic and Selenium in Environment—Ecological and Methodical Problems* (in Polish), p. 9, DW Scan Company, Warsaw (1994).

[3] A. Kabata-Pendias, H. Pendias. Biogeochemistry of trace elements (in Polish). Scientific Publishing House, Warsaw (1999).

[4] E. Merian. Metals and Their Compounds in the Environment, VCH, Weinheim (1991).

[5] J.R. Dojlido. Chemistry of surface water (in Polish). *Wydawnictwo Ekonomia i Środowisko Bjatystok* (1995).

[6] G. Drasch, L. Meyer, G. Kauert. Application of the furnace atomic absorption method for the detection of arsenic in biological samples by means of the hydride technique. *Fresen. J. Anal. Chem.*, **304**, 141 (1980).

[7] R.M. Camero, R.E. Sturgeon. Hydride generation-electrostatic depositiongraphite furnace atomic absorption spectrometric determination of arsenic, selenium and antimony. *Spectrochim. Acta B*, **52**, 753 (1999).

[8] Z. De-qiang, S. Han-wen, Y. Li-li. Detarmination of trace inorganic selenium in organoselenium (selenosugar) oral nutrition liquids by graphite furnace atomic absorpion spectrometry with hydride generation. *Fresen. J. Anal. Chem.*, **359**, 492 (1997).

[9] F. Laborda, J. Medrano, J.I. Cortes, J.M. Mir, J.R. Castillo. Comparison of palladium and zirconium treated graphite tubes for in-atomizer trapping of hydrogen selenide in hydride generation electrothermal atomization atomic absorption spectrometry. *Spectrochim. Acta B*, **54**, 343 (1999).

[10] P. Niedzielski, M. Siepak, J. Siepak. Comparison of modifiers for determination of arsenic, antimony and selenium by absorption atomic spectrometry with atomization in a graphite tube or hydride generation and *in-situ* preconcentration in a graphite tube. *Microchem. J.*, **72**, 137 (2002).

[11] R. Kalahne, G. Henrion, A. Hulanicki, S. Garbos, M. Walcerz. Comparison of AAS with hydride concentration in a graphite furnace with other spectrometric techniques. *Spectrochim. Acta B*, **52**, 1509 (1997).

[12] H. Matusiewicz, R.E. Sturgeon. Atomic spectrometric detection of forming elements following *in-situ* trapping within a graphite furnace. *Spectrochim. Acta B*, **51**, 377 (1996).

[13] P. Niedzielski, M. Siepak, Determination of Sb (III) and Sb (V) in water samples by hydride generation atomic absorption spectrometry with *in-situ* trapping in a graphite tube. *Anal. Lett.*, **36**, 971 (2003).

[14] P. Niedzielski, M. Siepak, B. Dudzińska-Huczuk. Hydride generation atomic absorption spectrometry with *in-situ* trapping in graphite tube in determination of Se (IV) and Se (VI) in Baltic Sea water samples. *Centr. Eur. J. Chem.*, **1**, 314 (2003).

[15] H.O. Haug, Y. Liao. Investigation of the automated determination of As, Sb and Bi by flow-injection hydride generation using *in-situ* trapping on stable coatingsin graphite furnace atomic absorption spectrometry. *Fresen. J. Anal. Chem.*, **356**, 435 (1996).

[16] M. Elsayed, E. Bjorn, W. Frech. Optimisaiton of operating parameters for simultaneous multi-element determination of antimony, arsenic, bismuth and selenium by hydride generation, graphite atomiser sequestration atomic absorption spectrometry. *J. Anal. Atom Spectrom.*, **15**, 697 (2000).

[17] J. Murphy, G. Shlemmer, I.L. Shuttler, P. Jones. Simultaneous multi-element determination of hydride-forming elements by 'in-atomiser trapping' electrotermal atomic absorption spectrometry on an iridium-coated graphite tube. *J. Anal. Atom Spectrom.*, **14**, 1593 (1999).

[18] J.Y. Cabon, W. Erler. Determination of selenium species in seawater by flow injection hydride generation *in-situ* trapping followed by electrothermal atomic absorption spectrometry. *Analyst*, **123**, 1565 (1998).

[19] D.L. Tsalev, V.I. Slaveykovaa, L. Lampugnanib, A. D'Ulivob, R. Georgievac. Permanent modification in electrothermal atomic absorption spectrometry—advances, anticipations and reality. *Spectrochim. Acta B*, **55**, 473 (2000).

[20] J.F. Tyson, N.G. Sundin, Ch.P. Hanna, S.A. McIntosh. Determination of Se in urine by flow injection hydride generation electrothermal atomic absorption spectrometry with in-atomizer trapping. *Spectrochim. Acta B*, **52**, 1773 (1997).

[21] Z. Ni, Z. Rao, M. Li. Minimalization of phosphate interference in the direct determination of arsenic in urine by electrothermal atomic absorption spectrometry. *Anal. Chem. Acta*, **334**, 177 (1996).

[22] B.T. Kildahl, W. Lund. Determination of arsenic and antimony in wine by electrothermal atomic absorption spectrometry. *Fresen. J. Anal. Chem.*, **354**, 93 (1996).

[23] J. Moreda-Piñeiro, C. Moscoso-Pérez, P. López-Mahía, S. Muniategui-Lorenzo, E. Fernández-Fernández, D. Prada-Rodríguez. Comparative study of different permanently-treated graphite tubes for the determination of As, Sb, and Se in natural waters by hydride generation-electrothermal atomic absorption spectrometry. *Anal. Chim. Acta*, **431**, 157 (2001).

[24] S. Garboś, M. Wałcerz, E. Bulska, A. Hulanicki. Simultaneous determination of Se and As by hydride generation atomic absorption spectrometry with analyte concentration in a graphite furnace coated with zirconium. *Spectrochim. Acta B*, **50**, 1669 (1995).

[25] J.L. Fischer. Electrothermal atomization of palladium stabilized selenium in the presence of phosphate. *Spectrochim. Acta B*, **57**, 525 (2002).

[26] J.L. Fischer, C.J. Rademeyer. Kinetics of selenium atomization in electrothermal atomization atomic absorption spectrometry (ETA-AAS). *Spectrochim. Acta B*, **57**, 549 (1998).

[27] H.M. Ortner, E. Bulska, U. Rohr, G. Schlemmer, S. Weinbruch, B. Welz. Modifiers and coatings in GFAAS-facts and fictions. In *Proceedings of 4th European Furnace Symposium*, p. 11, Kosice (1999).

[28] R. Chmal. *Detailed Geological Map of Poland 1:50 000*, sheet: Poznań (471), Polish Geological Institute, Warsaw (1997).

[29] S. Dąbrowski. Aquifers renewal in Poznań region. In: *Proceedings* of the *Conference on Surface Water of Poznań City* (in Polish), A. Kaniecki, J. Rotnicka (Eds), p. 139, UAM, Sorus, Poznań (1995).

[30] Ordinance of Minister of Health from 19 November, According to Quality of Water Used by People to Drink (Dz.U. 02.203.1718) (in Polish); (2002).

[31] Guidelines for Drinking Water Quality Volume 1. Recommendations, 2nd ed., WHO, Geneva (1993).

[32] S. Maity, S. Chakravarty, P. Thakur, K.K. Gupta, S. Bhattacharjee, B.C. Roy. Evaluation and standarisation of a simple HG-AAS method for rapid speciation of As(III) and As(V) in some contaminated groundwater samples of West Bengal, India. *Chemosphere*, **54**, 1199 (2004).

[33] D.L. Corwin, A. David, S. Goldberg. Mobility of arsenic in soil from the Rocky Mountain Arsenal area. *J. Contam. Hydrol.*, **39**, 35 (1999).

[34] O. Sracek, P. Bhattacharya, G. Jacks, J.P. Gustafsson, M. Brömssen. Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments. *Appl. Geochem.*, **19**, 169 (2004).

[35] D. Stüben, Z. Berner, D. Chandrasekharam, J. Karmakar. Arsenic enrichment in groundwater of West Bengal, India: geochemical evidence for mobilization of As under reducing conditions. *Appl. Geochem.*, **18**, 1417 (2003).

[36] M. Filella, N. Belzile, Yu.W. Chen. Antimony in the environment: a review focused on natural waters II Relevant solution chemistry. *Earth-Sci. Rev.*, **59**, 265 (2002).

[37] J.P. Diaz, M. Navarro, H. Lopez, M.C. Lopez. Selenium (IV) and (VI) levels in potable, irrigation and waste waters from an industrial zone in southeastern Spain. *Sci. Tot. Environ.*, **186**, 231 (1996).

[38] M. Siepak, J. Przybyłek, P. Niedzielski. The application of a speciation analysis of metalloids microtrace content to the research on ground water flow in the area of, Dębina' water intake with induced infiltration in Poznań city (in Polish). *Ekol. Technika*, **12**, 22 (2004).

[39] P. Niedzielski, J. Siepak, M. Siepak. Total Content of Arsenic, Antimony and Selenium in Groundwater Samples from Western Poland. *Pol. J. Enviro. Stud.*, **5**, 347 (2001).

[40] P.L. Smedley, D.G. Kinniburgh. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.*, **17**, 517 (2002).

[41] R.T. Nickson, J.M. McArthur, P. Ravenscroft, W.G. Burgess, K.M. Ahmed. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl. Geochem.*, **15**, 403, (2000).

[42] K.M. Ahmed, P. Bhattacharya, M.A. Hasan, S.H. Akhter, S.M. Mahbub Alam, M.A. Hossain Bhuyian, M. Badrul Imama, A. Aftab Khan, O. Sracek. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. *Appl. Geochem.*, **19**, 181 (2004).

[43] G. Tao, E.H. Hansen. 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**, 333 (1994).

[44] M. Veber, K. Cujes, S. Gomiscek. Determination of selenium and arsenic in mineral waters with hydride generation atomic absorption spectrometry. *J. Anal. At. Spectrom.*, **9**, 285 (1994).

[45] P.L. Smedley, W.M. Edmunds. Redox patterns and trace-element behavior in the East Midlands Triassic sandstone aquifer. *UK Ground Water*, **40**, 44 (2002).

[46] P. Niedzielski, M. Siepak, J. Przybyłek, J. Siepak. Arsenic, antimony and selenium in Poznan city water—micropollutants or microcompounds? (in Polish). Betagraf, Poznań (2002).