

SPECIATION ANALYSIS FOR DETERMINATIONS OF ARSENIC,
ANTIMONY AND SELENIUM IN WATER SAMPLES
FROM THE LEDNICKIE LAKE

PRZEMYSŁAW NIEDZIELSKI, JERZY SIEPAK,
ZENON KOWALCZUK

Department of Water and Soil Analysis Adam Mickiewicz University, 24 Drzymały Sreet, 60-613 Poznań

Keywords: speciation, arsenic, antimony, selenium, atomic absorption, lakes.

ANALIZA SPECJACYJNA W OZNACZENIACH ARSENU,
ANTYMONU I SELENU W PRÓBKACH WODY
Z JEZIORA LEDNICKIEGO

W pracy przedstawiono wyniki oznaczeń arsenu, antymonu i selenu w wodzie jeziora Lednickiego. W badaniach skoncentrowano się na rozróżnieniu za pomocą procedur analitycznych form specjacyjnych (As, Sb(III)/(V), Se(IV)/(VI) oraz form związanych z materią organiczną) oznaczanych pierwiastków. Do oznaczeń analitycznych zastosowano opracowaną i zoptymalizowaną metodę techniki generowania wodorków absorpcyjnej spektrometrii atomowej. Uzyskano granice wykrywalności odpowiednio 0,14 ng/mL dla As(III), 0,16 ng/mL dla As ogólnego; 0,17 $\mu\text{g}/\text{dm}^3$ dla Sb(III); 0,18 $\mu\text{g}/\text{dm}^3$ dla Sb ogólnego oraz 0,15 $\mu\text{g}/\text{dm}^3$ dla selenu. W badanych próbkach wody arsen ogólny oznaczono na poziomie 1,20 $\mu\text{g}/\text{dm}^3$, antymon 0,40 $\mu\text{g}/\text{dm}^3$ i selen 0,20 $\mu\text{g}/\text{dm}^3$.

Summary

The paper presents the results of arsenic, antimony and selenium analyses in the Lednickie lake water. The study concentrates on the discrimination of speciation forms (As, Sb(III)/(V), Se(IV)/(VI) and their organic forms) of the determined elements by means of analytical procedures. A specially designed and optimised methodology of hydride generation atomic absorption spectrometry (HGAAS) was employed in the analyses. The limits of detection were established as 0.14 $\mu\text{g}/\text{dm}^3$ for As(III), 0.16 $\mu\text{g}/\text{dm}^3$ for total As; 0.17 $\mu\text{g}/\text{dm}^3$ for Sb(III); 0.18 $\mu\text{g}/\text{dm}^3$ for total Sb and 0.15 $\mu\text{g}/\text{dm}^3$ for selenium. In water samples total arsenic was present at the level of 1.20 $\mu\text{g}/\text{dm}^3$, antimony 0.40 $\mu\text{g}/\text{dm}^3$ and selenium 0.20 $\mu\text{g}/\text{dm}^3$.

INTRODUCTION

Determination of trace elements in water can provide information on their

natural content implied by the geochemical environment (geochemical background) as well as give an idea on the size of anthropopressure effect. The total content (general content) cannot give the information on the processes the elements are involved in, so on their actual toxicity, migration, bioavailability or accumulation. Speciation analysis determines the forms of elements occurrence in the environment (speciation) either as certain chemical compounds (individual speciation) or groups or classes of compounds (operational speciation) [1, 16, 30]. The aim of the study reported was to perform speciation determination of arsenic, antimony and selenium in water of the Lednickie Lake.

CHARACTERISTICS OF THE HYDROECOSYSTEM OF THE LEDNICKIE LAKE

The lake lies within the area of the Lednicki Landscape Park, localised on the grounds related to the historical origins of the Polish nation. Its area is 350 ha (according to [17] 339.1 ha), the maximum depth 15.0 m and the mean depth 7.2 m. It has a much elongated shape of 22.3 km in length and 0.8 km in width. The catchment of the lake built of boulder clays and gravel-sand formations is almost completely of agricultural use. A characteristic feature of the lake is the small vertical exchange of water. The main potential sources of pollution are the outflows from arable fields. The water from the lake has been classified as of the 3rd class of purity [34].

The mechanisms of the lake succession and evolution are different from those of other lakes in the Wielkopolska region. The gully of the lake was formed in the last glaciation period. The lake's level of trophy was relatively high, higher than those of other lakes, and stable for thousands years. In the last 50 years rapid changes in the trophy towards hypertrophy have been observed at a systematic decrease of the water table. The lake status is affected by the agricultural areas and the Poznań-Gniezno highway [3].

ARSENIC, ANTIMONY AND SELENIUM IN NATURAL WATERS

Arsenic is commonly found in natural waters, and its content depends on the geological environment and pollution. As it forms complexes with low-molecular organic compounds it adsorbs on a suspension [9]. In general it occurs at two degrees of oxidation (III) and (V), and forms many inorganic compounds (arsenates (III) and (V) which transform into one another depending on the environmental conditions) and organic compounds [19]. Direct products of microbiological transformations of inorganic arsenic compounds are the methyl derivatives: monomethyl arsenic acid (MMAA) and dimethylarsenic acid (DMAA). The toxicity of the arsenic compounds decreases in the following sequence: arsenates (III), 60-times less toxic arsenates (V) and 100-times less toxic methylated forms: monomethyl-, dimethyl derivatives, and organic compounds (e.g. arsenobetaine AsB, arsenocholine AsC, arsenosugars

AsS, arsenolipides AsL [4, 6]. The admissible concentration of arsenic in surface waters in Poland is $50 \mu\text{g}/\text{dm}^3$ for water of 1st and 2nd class of purity, and $200 \mu\text{g}/\text{dm}^3$ for 3rd class of purity, whereas in the USA the admissible concentration is $100 \mu\text{g}/\text{dm}^3$. The maximum concentration of arsenic in drinking water in Poland is $50 \mu\text{g}/\text{dm}^3$, and recently a decrease of this value to $10 \mu\text{g}/\text{dm}^3$ has been proposed [24].

The concentration of antimony in surface waters and precipitation is usually below 1 ppb, in the cities up to a few ppb. In water antimony behaves similarly to arsenic, it occurs in the form of antimonates (III) and (V), methyl derivatives: monomethyloantimonic acid (MMSbA) and dimethyloantimonic acid (DMSbA), which (of 3000 known antimony compounds) are detectable in natural waters [19, 29]. The compounds of Sb(III) as well as Sb(V) undergo hydrolysis as $\text{Sb}(\text{OH})_3$ and $\text{Sb}(\text{OH})^{-6}$, respectively. In Poland the concentration of antimony in water is not standardised at present, however it has been recommended to introduce the highest admissible level as $5 \mu\text{g}/\text{dm}^3$ [33], the same as recommended by WHO [14].

The risk of pollution with selenium is not high, and the problem of the geochemical equilibrium between its excess and deficit is related to natural factors rather than anthropopressure. Depending on the geochemical background, and general pollution water can contain from a few hundred to a few thousand $\mu\text{g}/\text{dm}^3$ (drained waters), and the concentration of selenium is greater in fresh waters. In Poland the mean concentration of selenium is about $0.05 \mu\text{g}/\text{dm}^3$. A comparison of the selenium content in non-polluted waters and in those subjected to strong anthropopressure does not show significant differences, apart from some specific cases, which means that industry and urban developments have little effect on the contents of selenium in water [9, 13]. In waters of pH close to neutral, the dominant ions SeO_3^{-2} and SeO_4^{-2} are adsorbed by iron minerals, iron hydroxides and organic matter, and are deposited on the bottom. Selen naturally occurs in the form of selenides, selenates (IV) and (VI), di-(dimethylselenium Dme and dimethylidiseelenium DMDSe) and trimethyl derivatives (trimethylselenium TMSe), selenaminoacids (selenocysteine SeC and selenemethionine SeM) and in many organic compounds [19, 25, 26]. In microbiological processes taking place in bottom deposits, labile selenium-organic compounds are formed and released to the bulk water [20]. According to WHO recommendations, the maximum concentration of selenium in drinking water is $10 \mu\text{g}/\text{dm}^3$ (1984 [13]) or $20 \mu\text{g}/\text{dm}^3$ [14], assuming that drinking water covers 10% of daily intake of selenium. In Poland the maximum concentration of selenium in drinking water is $10 \mu\text{g}/\text{dm}^3$ [27] and the same threshold is proposed to hold in future [33].

SAMPLING

Samples to be studied were taken at the sites marked on the map in Fig. 1 (after [3]).

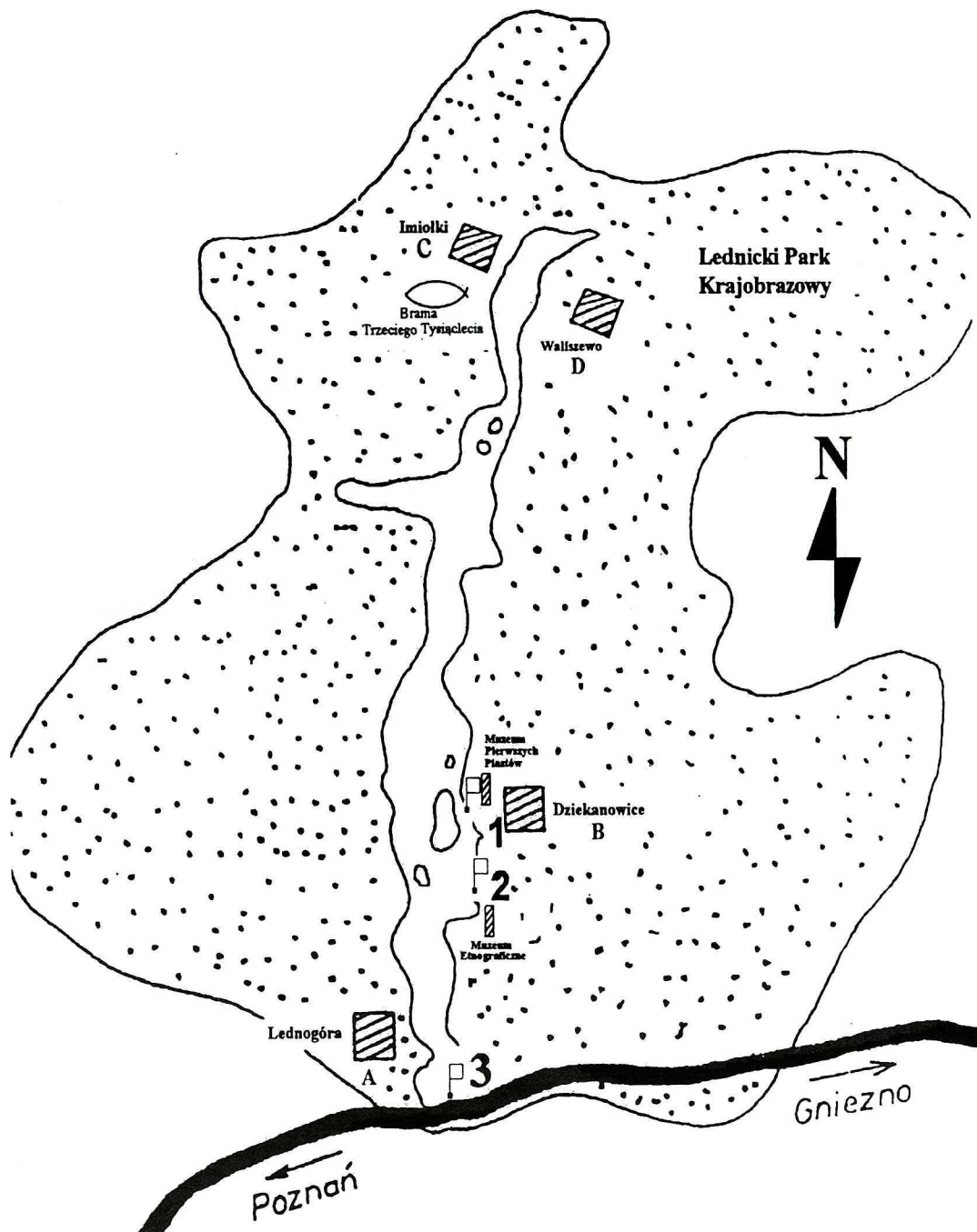


Fig. 1. A map of the Lednickie Lake with the sites of water sample collection (1, 2, 3) and places subjected to considerable anthropopressure (A, B, C, D)

The samples were taken from the bulk water. The methods of sampling were the same as recommended for routine use in determinations of environmental samples. The samples were not fixed so as not to disturb the speciation equilibrium. For speciation determination the samples were collected and transported in anaerobic conditions and determinations were made immediately after delivery to the lab. The samples were transported in polyethylene bottles used for trace analyses (Nalgene).

THE METHODS OF SPECIATION ANALYSIS

Determinations were performed by the absorption atomic spectrometry with generation of hydrides [4] at the operational distinction of speciation forms. Measurements were performed on a double-beam spectrometer SpectrAA 20 Plus, made by Varian, using HCl lamps made by Varian, As – 193.7 nm, Sb – 217.6 nm, Se – 196.0 nm). Generation of hydrides was conducted in continuous operation system on an attachment VGA-77 with multichannel peristaltic pump, glass u-separator of gas phase and quartz cell electrothermally heated in the range from room temperature to 1000°C. Argon was used as a carrier gas. For sample preparation we used a microwave mineraliser made by Merck MW 500, with a set of closed teflon vessels (microwave power 530 W, the maximum pressure 2.5 – 3.0 MPa).

All reagents were analytically pure, water was redistilled and purified in a Milli-Q instrument made by Milipore. The standard solutions were prepared from commercial standards for AAS analysis, of a concentration of 1 g/dm³. By dissolving it a solution of 1 mg/dm³ was made, stable for about 3 months and stored in a polyethylene cell (Nalgene). Lower-concentration standards were prepared on the day of determination, in polyethylene cells. Sodium borohydride solutions were made by dissolving sodium borohydride in a 1% solution of sodium hydroxide. The solutions were clear and did not require filtration, they were made on the day of determination. Solutions of hydrochloric acid were made by dilution of the acid of $r = 1.19$ g/cm³. The methods were verified by using the certified reference material SRM 1643d, in 50-times dilution to the level of environmental concentrations of the elements determined.

The cycle of operations of the speciation analysis by the AAS method with generation of hydrides can be illustrated by the following scheme – Fig. 2. It should be noted that both dissolved and suspended fractions were jointly subjected to reduction and mineralisation, and the error in determinations was assumed as constant.

1. Determinations of as-collected samples, without any preliminary procedures, determination of the contents of As(III), Sb(III) and Se(IV).
2. Determinations of samples after reduction with different reagents, determinations of the total content of antimony and selenium in inorganic compounds, determinations of the sum of arsenic content in inorganic compounds, in MMAA and DMAA.

3. Determinations of samples after mineralisation of organic compounds and reduction, determination of the total content of arsenic, antimony and selenium.

4. Calculations of the total contents of As(V), Sb(V) and Se(VI) and their contents in organic compounds.

The above scheme of speciation analysis shows the group character of determinations of particular fractions, and illustrates the operational character of the application of mineralisation and reduction.

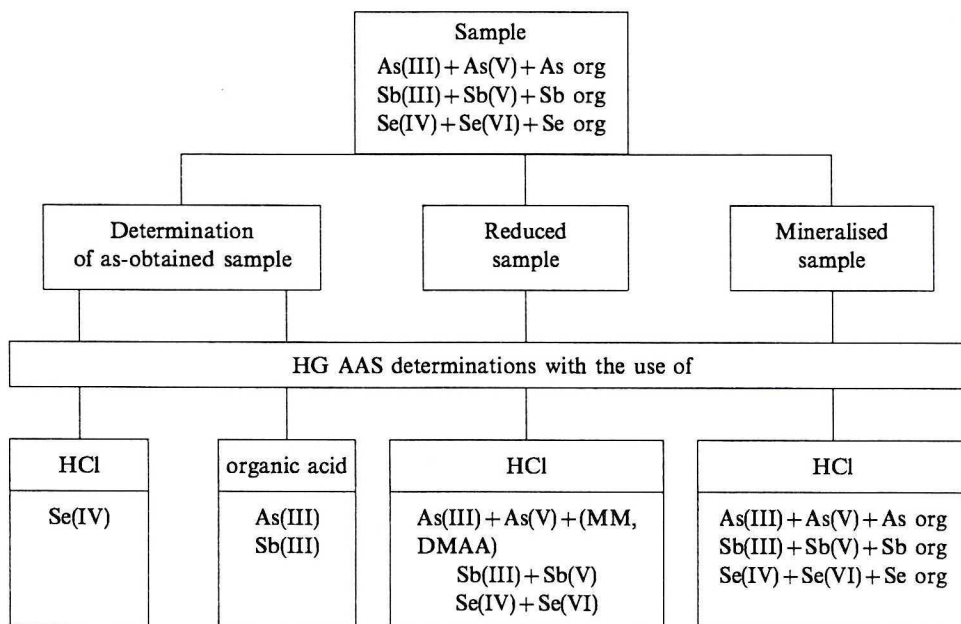


Fig. 2. A scheme of the speciation analysis procedure by HG AAS

RESULTS AND DISCUSSION

The analytical method applied was validated. Its basic parameters were determined: detectability $2s$, determinability $3s$, sensitivity and precision [2, 15, 21], and the data are given in Table 1.

Table 1. Parameters of the analytical method

	As(III)	As	Sb(III)	Sb	Se
	$\mu\text{g}/\text{dm}^3$				
detectability 2σ	0.09	0.11	0.11	0.12	0.10
determinability 3σ	0.14	0.16	0.17	0.18	0.15
sensitivity	0.08	0.09	0.11	0.11	0.08
precision	5–25% (depending on the level of the concentrations determined)				

The parameters of the method allow determinations of the speciation forms of the elements studied As(III), As (general), Sb(III), Sb (general), Se(IV), and Se (general) in samples of natural waters.

The total content of these elements in the samples studied were determined by making use of the reference material SRM 1643d and the results are collected in Table 2. The recovery of the elements studied was very good – from 95 to 101%, which testifies to a high accuracy of the method [21].

Table 2. Determinations in the reference material SRM 1643d

	As	Sb	Se
theoretically predicted content $\mu\text{g}/\text{dm}^3$	1.11 ± 0.03	1.1 ± 0.1	0.23 ± 0.01
content determined $\mu\text{g}/\text{dm}^3$	1.12 ± 0.05	1.05 ± 0.06	0.22 ± 0.03
recovery %	101 ± 5	95 ± 6	96 ± 13

The method proposed was resistant to small (10%) changes in the reagents concentration, which did not affect significantly its parameters. As the limits of determinability of the method are comparable to the concentrations of the elements studied in natural waters [20], the methods are suitable for determinations of their contents in environmental samples. The samples chosen for speciation analysis were the same for which determinations of pH, electrolytic conductivity, and concentrations of nitrates, chlorates, phosphates and sulphates had been made earlier.

Table 3. Physical and chemical parameters of water samples from Lednickie Lake (May 1998)

Sample	cond $\mu\text{S}/\text{cm}$	pH –	NO_3	Cl	PO_4	SO_4	Na	K	Ca	Mg	Fe	Mn
			$\mu\text{g}/\text{dm}^3$									
sampling place*: 1	833	8.12	1.08	84	#	223	17	6.5	115	26.7	#	#
2	832	8.20	1.19	80	#	215	16.5	6.7	114	27.0	#	#
3	826	7.70	0.86	83	#	207	17	6.2	114	26.3	#	#

* according to the map (Fig. 1) # – below the limit of detectability

Anions were determined by ionic chromatography, while cations by flame absorption/emission spectrometry. The samples were collected from the surface layer of the lake water near the shore in the period of the spring water mixing (May 4th, 1998), and determinations were performed directly after sample collection. The values of the 12 parameters obtained are given in Table 3. The determinability limit of $0.15 \mu\text{g}/\text{dm}^3$ (3s) at the minimum standard deviation of $0.05 \mu\text{g}/\text{dm}^3$ was assumed in all determinations. In Table 4 we gave the determinability limits at the particular values determined, and zero at the calculated values. The values below $0.15 \mu\text{g}/\text{dm}^3$ (3s) are only estimates and can be charged with a significant error, even higher than 30% [8].

Table 4. Results of the speciation analysis of arsenic, antimony and selenium in water from the Lednickie Lake (May 1998)

Sample	As				Sb				Se				
	III	V	org	total	III	V	org	total	IV	VI	org	total	
	$\mu\text{g}/\text{dm}^3$												
sampling place*:	1	0.85	0.35	< 0.15	1.20	0.30	< 0.15	< 0.15	0.30	< 0.15	< 0.15	0.20	0.20
	2	0.95	0.15	< 0.15	1.10	0.30	< 0.15	0.10	0.40	< 0.15	< 0.15	0.15	0.15
	3	1.00	0.20	< 0.15	1.20	0.40	< 0.15	0.10	0.50	< 0.15	0.15	< 0.15	0.15

* according to the map (Fig. 1)

The contents of the metals determined in the lake water are lower than those admissible for drinking water equal to 50 and 10 $\mu\text{g}/\text{dm}^3$ for As and Se [27] or, according to WHO recommendations: 10, 5 and 20 $\mu\text{g}/\text{dm}^3$ for As, Sb and Se, respectively [14]. Unfortunately, the lack of earlier data and thus impossibility of making comparisons does not allow us to conclude to which degree the contents of the metals and their speciation have been established by natural processes or anthropopressure. The data reported in this work are the first determinations of speciation forms of arsenic, antimony and selenium in the water from the Lednickie lake.

As far as arsenic is concerned, its form at the 3rd degree of oxidation was dominant making over 70% of its total content [18, 28, 31], however, the presence of compounds with arsenic at the 5th degree of oxidation was also noted [5, 7, 10, 11, 18]. In one sample (3) a small amount of arsenic bound with organic matter was found.

Antimony occurred at the 3rd oxidation degree, which is characteristic of waters of poor oxygenation [12, 32], in sample (3) a considerable amount of antimony at the 5th degree of oxidation was detected, which indicates different red-ox conditions in this part of the lake [32], in sample (2) a small amount of antimony (V) bound with organic matter was found.

Selenium occurred almost exclusively in organic compounds [22, 23, 25, 26], in sample (3) they were mineralised to significant degree to Se(VI), which testifies to good oxygenation in this part of the lake.

The samples taken at the same time have very similar chemical composition, i.e. the contents of macroelements and general content of trace elements (Table 4). Only identification of the speciation forms gives an idea on differences between different parts of the lake caused by specific hydrochemical conditions and hydrobiological processes.

CONCLUSION

Speciation determinations of arsenic, antimony and selenium in the waters of the Lednickie lake were performed for the first time and may be used as reference for further studies. The proposed new method for speciation determinations of

arsenic, antimony and selenium, along with the optimisation of the method of hydride generation in atomic absorption spectroscopy (HGAAS) for investigation of surface water samples make it possible to trace the concentrations of these elements on the trace level below $\mu\text{g}/\text{dm}^3$. Therefore, the method as well as the analytical procedure can be recommended for routine analyses of surface water samples.

ACKNOWLEDGEMENTS

Financial assistance from the State Committee for Scientific Research within Grant no. 3 T09C 111 14, is gratefully acknowledged.

REFERENCES

- [1] Bernhard M. (red.): *The importance of Chemical "Speciation" in Environmental Processes*, Springer-Verlag, Berlin 1986.
- [2] Bulska E., J.R. Dojlido: *Wybrane aspekty walidacji metod analitycznych*, Sympozjum „Jakość pracy w laboratorium badania wody”, Warszawa 1998.
- [3] Burhardt L.: *Problemy zanieczyszczenia i ochrony wód powierzchniowych – dziś i jutro*, Wyd. UAM, 25–34 (1992).
- [4] Burguera M., J.L. Burguera: *Analytical methodology for speciation of arsenic in environmental and biological samples*, *Talanta*, **44**, 1581–1604 (1997).
- [5] Chakraborti D., W. de Jonghe, F. Adams: *The determination of arsenic by electrothermal atomic absorption spectrometry with a graphite furnace*, *Anal. Chim. Acta*, **120**, 121–127 (1980).
- [6] Chatterjee A., D. Das, B.K. Mandal, T.R. Chowdhury, G. Samanta, D. Chakraborti: *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)**, 643–650 (1995).
- [7] Chwastowski J., E. Sterlińska, W. Żmijewska, J. Dudek: *Application of a Chelating Resin Loaded with Thionalide to Speciation Analysis of As III, V in Natural Waters*, *Chem. Anal. (Warsaw)*, **41**, 45–53 (1996).
- [8] Czarniecka I.: *Walidacja metod analitycznych*, Polfa, Warszawa 1995.
- [9] Dojlido J.R.: *Chemia wód powierzchniowych*, Wyd. Ekonomia i Środowisko, Białystok 1995.
- [10] Driehaus W., M. Jekel: *Determination of As(III) and total inorganic arsenic by on-line pretreatment in hydride generation atomic absorption spectrometry*, *"Fresenius" J. Anal. Chem.*, **343**, 343–352 (1992).
- [11] Elteren J.T., N.G. Haselager, H.A. Das: *Determination of arsenate in aqueous samples by precipitation of the arsenic (V) – molybdate complex with tetraphenylphosphonium chloride and neutron activation analysis or hydride generation atomic absorption spectrometry*, *Anal. Chim. Acta*, **252**, 89–95 (1991).
- [12] Gaboś S., E. Bulska, A. Hulanicki, N.I. Shcherbinina, E.M. Sedykh: *Proconcentration of inorganic species of antimony by sorption on Polyorgs 31 followed by atomic absorption spectrometry determination*, *Anal. Chim. Acta*, **342**, 167–174 (1997).
- [13] *Guidelines for drinking-water quality*, WHO, Geneva 1984.
- [14] *Guidelines for drinking water quality. Second edition. Volume 1. Recommendations*, WHO, Geneva 1993.
- [15] *Guide to Analytical Quality Control for Water Analysis*, CEN/TC 230 "Water analysis", 1995.
- [16] Hulanicki A.: *Analiza specjacyjna metali*, Wyd. UAM, Poznań, 7–18 (1998).
- [17] Jańczak J. (red.): *Atlas jezior Polski*, Bogucki Wydawnictwo Naukowe, Poznań 1996.

- [18] Lopez A., R. Torralba, M.A. Palacios, C. Camara: *Generation of AsH₃ from As(V) in the absence of KI As prereducing agent: speciation of inorganic arsenic*, *Talanta*, **39**, 1343–1348 (1992).
- [19] Łobiński R., F.C. Adams: *Speciation analysis by gas chromatography with plasma source spectrometric detection*, *Spectrochim. Acta*, **52B**, 1865–1903 (1997).
- [20] Merian E.: *Metals and their compounds in the Environment*, VCH, Weinheim 1991.
- [21] Niedzielski P., J. Siepak: *Analiza specjacyjna metali*, Wyd. UAM, Poznań, 47–66 (1998).
- [22] Ornemark U., A. Olin: *Preconcentration and separation of inorganic selenium on Dowex IX8 prior to hydride generation-atomic absorption spectrometry*, *Talanta*, **41**, 67–74 (1994).
- [23] Pedersen G.A., E.H. Larsen: *Speciation of four selenium compounds using high performance liquid chromatography with on-line detection by inductively coupled plasma mass spectrometry or flame atomic absorption spectrometry*, *Fresenius J. Anal. Chem.*, **358**, 591–598 (1997).
- [24] Proposal for a Council Directive concerning the quality of water intended for human consumption [95/0010 (SYN)]. Preparation of the “Environment” council meeting, 19 and 20 June; 1995.
- [25] Pyrzyńska K.: *Speciation analysis of selenium*, IV International Symposium, Warszawa 1998.
- [26] Pyrzyńska K.: *Speciation analysis of some organic selenium compounds. A review*, *Analyst*, **121**, 77R–83R (1996).
- [27] Rozporządzenie Ministra Zdrowia i Opieki Społecznej z dnia 4 maja 1990 r. zmieniające rozporządzenie w sprawie warunków, jakim powinna odpowiadać woda do picia i na potrzeby gospodarcze (Dz.U. Nr 35, poz. 205).
- [28] Schaumlöffel D., B. Neidhart: *A FIA-system for As(III)/As(V)-determination with electrochemical hydride generation and AAS-detection*, “Fresenius” *J. Anal. Chem.*, **354**, 866–869 (1996).
- [29] Smichowski P., Y. Madrid, C. Camara: *Analytical methods for antimony speciation in waters at trace and ultratrace levels. A review*, “Fresenius” *J. Anal. Chem.*, **360**, 623–629 (1998).
- [30] Sobczyński T., J. Siepak: *Analiza specjacyjna metali*, Wyd. UAM, Poznań, 67–78 (1998).
- [31] Stummeyer J., B. Harazim, T. Wippermann: *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**, 344–351 (1996).
- [32] Sun Y.C., J.Y. Yang, Y.F. Lin, M.H. Yang: *Determination of antimony (III, V) in natural waters by coprecipitation and neutron activation analysis*, *Anal. Chim. Acta*, **276**, 33–37 (1993).
- [33] Wichrowska B.: *Aktualne normatywy jakości wody do picia*, *Rocznik PZH*, nr 2, 1997.
- [34] Zerbe J.: *Prawne i ekonomiczne aspekty ochrony środowiska*, Wyd. UAM, Poznań 1992.

Received: March 29, 1999, accepted: August 5, 1999.