ЖАРАТЫЛЫСТАНУ ЖӘНЕ АУЫЛ ШАРУАШЫЛЫҚ ҒЫЛЫМДАР / ЕСТЕСТВЕННЫЕ И СЕЛЬСКОХОЗЯЙСТВЕННЫЕ НАУКИ / NATURAL AND AGRICULTURAL SCIENCES

UDC 628.16
SCSTI 70.27.11

ANION COMPOSITION DETERMINATION OF NATURAL WATERS BY THE METHOD OF ION CHROMATOGRAPHIC

V. Ivanova[1]
[1]*Bulgarian Institute of Metrology, National Center of Metrology, Sofia, Bulgaria*
A. Surleva[2]
[2]*University of Chemical Technology and Metallurgy, Sofia, Bulgaria*

Abstract

An ion chromatographic method for determination of anion composition of natural waters was described. An automated 850 IC Professional, Metrohm system equipped with conductivity detector after chemical and carbon dioxide suppression was used. The main analytical characteristics were estimated for each of studied analytes. The trueness of the method was estimated by analysis of certified reference material for soft drinking water. Recovery test was performed on spiked drinking water samples. The method was applied for analysis of drinking water before and after chlorination, as well as high mountain lakes.

The selected methods were successfully applied for the analysis of water samples from high mountain lakes, as well as drinking water before and after chlorination. The results obtained in this study show that there is no indication of contamination with elements or anions in the lake water. There were no deviations found from the legally acceptable values for priority substances, which could present a risk to the aquatic environment.

Key words: natural waters, мonitoring, anions, ion chromatography, drinking waters, method.

ОПРЕДЕЛЕНИЕ АНИОННОГО СОСТАВА ПРИРОДНЫХ ВОД МЕТОДОМ ИОНО–ХРОМАТОГРАФИИ

Иванова В.[1]
[1]*Болгарский институт метрологии, национальный центр метрологии, София, Болгария*
Сурлева А.[2]
[2]*Университет химических технологии и металлургии, София, Болгария*

Аннотация

Описан ионо – хроматографический метод определения анионного состава природных вод. Была использована автоматизированная система Metrohm 850 IC Professional, оснащенная детектором проводимости после химического и углекислотного подавления. Основные аналитические характеристики были оценены для каждого из исследуемых аналитов. Достоверность метода была оценена путем анализа сертифицированного эталонного материала для мягкой питьевой воды. Испытание на восстановление проводилось на образцах питьевой воды с шипами. Метод применен для анализа питьевой воды до и после хлорирования, а также высокогорных озер.

Выбранные методы были успешно применены для анализа проб воды из высокогорных озер, а также питьевой воды до и после хлорирования. Результаты, полученные в этом исследовании, показывают, что нет никаких признаков загрязнения элементами или анионами в воде озера. Не обнаружено никаких отклонений от юридически приемлемых значений для приоритетных веществ, которые могли бы представлять опасность для водной среды.

Ключевые слова: природные воды, мониторинг, анионы, ионная хроматография, питьевая вода, метод.

ИОНДЫҚ ХРОМАТОГРАФИЯЛЫҚ ӘДІСІМЕН ТАБИҒИ СУДЫҢ АНИОН ҚҰРАМЫНЫҢ АНЫҚТАУ

В. Иванова[1]
[1]*Метрология институты, метрология ұлттық орталығы, София, Болгария*
А. Сурлева[2]
[2]*Химиялық технологиялар және металлургия университеті, София, Болгария*

Андатпа

Табиғи сулардың анионның құрамын анықтау үшін иондық хроматографиялық әдіс сипатталған. Metrohm 850 IC Professional автоматтандырылған жүйесі пайдаланылды, ол химиялық және көміртегі диоксидінің сөнуінен кейін өткізгіш детектормен жабдықталған. Негізгі аналитикалық сипаттамалар зерттелген аналитиктердің әрқайсысы үшін бағаланды. Әдістің сенімділігі жұмсақ ауыз суға сертификатталған анықтамалық материалдарды талдау арқылы бағаланды. Ашық ауыз су үлгілері бойынша қалпына келтіру сынағы өткізілді. Бұл әдіс хлорлауға дейін және одан кейінгі ауыз суды, сондай – ақ альпі көлдерін талдау үшін қолданылады.

Судан ауыз суды хлорлау дейінгі және одан кейінгі биік таулы көлдер, сондай – ақ сынамаларды талдау үшін таңдалған әдістер тиімді қолданылды. Бұл зерттеуден алынған нәтижелер көрсетіп отырғандай, көл суында ластану элементтерінің ешқандай белгілері жоқ көрсетеді. Сулы ортаға қауіп төндіретін заттар үшін заңды қолданатын мәндерден ешқандай ауытқулар табылмады.

Түйінді сөздер: табиғи су, мониторинг, аниондар, иондық хроматография, ауыз су, әдіс.

Introduction

The environmental monitoring of pollutants in waste, surface, drinking or natural water is a requirement for achieving a good ecological and chemical status of the water, for protection of human health, the water supply system and natural ecosystems [1, 2]. Particular attention is paid to natural water as a medium for the migration of chemical elements and compounds with natural and anthropogenic origin. Many factors can have an influence – climate, relief, geological structure and rock formation, soil and vegetation cover and anthropogenic factors.

Up to now chemical monitoring of the high mountain lakes in Bulgaria has been carried out in the period 1993 – 1996 in the Rila Mountains. There was no indication for contamination with heavy metals in the considered mountain lakes, the results are below the limit of quantification of the used methods for analysis [3, 4].

Nowadays due to intense development of chemical and biochemical technologies new substances appeared in the environment, which imposes determination of new analytes in common matrices or standard anions in new matrices. The environmental and health authorities, as well as modern industrial technologies impose stringer demands to the water quality and methods for determination at trace levels are highly demanded [5 – 9]. Ion chromatography appears to be widely studied method for anion determination in different matrices in very precise and accurate manner offering low detection limits, low sample and reagent consumption, as well as short analysis time [7 – 14]. A line of studies on optimization and validation of ion chromatographic methods for anions determination aimed at ensuring quality of the results and their fit for purpose according to the demands of customers have been recently published [7 – 15].

This paper presents the results from determination of anion composition of treated and untreated drinking water, as well as high mountains lakes by ion chromatographic method with conductivity detection after chemical and carbon dioxide suppression.

Experimental

Instruments and operating conditions

An ion chromatographic, metal – free system (IC – 850 Professional model, Metrohm AG, Switzerland) controlled by Metrodata MagIC Net™ software and equipped with 858 Professional Sample Processor, sample filtration system with a 0.2 µm regenerated cellulose membrane, six channel injection valve, low pulsation high – pressure pump, chemical suppression and CO2 suppression, eluent degasser and conductivity detector was used. The separation was performed on a Metrosep A Supp 7 – 250 column (250 x 4 mm, polyvinyl alcohol with quaternary ammonium groups, 5 µm particale size), Metrosep RP 2 Guard/3.5 (polymer with pore size 0.2 µm). In order to keep the baseline signal as low as 0.99 µS/cm, 0.1 M sulphuric acid solution was used for regenerated chemical suppression. The optimized chromatographic parameters are presented in Table 1. Eluent solution was prepared by sodium carbonate suprapure Na_2CO_3 (CertiPUR®, Merck, Darmstadt, Germany). Multi ion standard solutions of fluoride, chloride, nitrate and sulphate were prepared by appropriate dilution of their anion standard stock solution (Fluka 1000 mg/L for IC, TraceCERT®, Sigma – Aldrich, Buchs, Switzerland). All solutions were prepared gravimetrically in Milli – Q water, (Mill – Q Direct 8, Merck Millipore; resistivity > 18.2 MΩcm, equipped with a Millipack 0.22µm filter). Certified Reference Material for soft drinking water UK – Anions № ERM® – CA016a, LGC, Teddington, Middlesex was used to confirm the trueness of the method. Sulphuric acid (96% Suprapur®, Merck KGaA, Darmstadt, Germany) was used in conductivity suppression regeneration system after appropriate dilution. Before measurements the solutions were filtered by MF – Millipore™ membrane filter with pore size of 0.45 µm (Merck KGaA, Darmstadt, Germany).

Table 1 Ion chromatographoperating conditions

IC–850 Professional, Metrohm AG	
Column	Metrosep A Supp 7– 250/4.0
Precolumn	Metrosep RP 2 Guard/3.5
Eluent	Na_2CO_3 (3.6 mmol/L)
Eluent flow rate	0.7 mL/min
Elution mode	Isocratic
Sample volume	20 µL
Column temperature	45 ^{o}C
Detection	Suppressed conductivity
Determination mode	Peak area

Reagents and Certified Reference Materials

All solutions were prepared gravimetrically with deionized water Milli–Q(18.2MΩcm, Millipore, Merck). Multiion standard solutions were prepared by appropriate dilution of their anion standard stock solution 1000 mg/L, TraceCERT®, (Sigma–Aldrich, Buchs, Switzerland). Before measurements, the samples were filtered through MF–Millipore™ membrane filter with pore size of 0.45 µm (Merck KGaA, Darmstadt, Germany).

Results and discussion

A previously developed and validated ion chromatographic method was used [16]. The studied anions are separated by 3.6 mmol/L Na_2CO_3 eluent under the optimized parameters presented in the Table 1. All anions were completely separated in a run with total analysis time of 30 min. The developed and validated methods allowed the determination of low concentrations of anions which werebelow the established limits for natural water [17].

Analysis of water from high mountain lakes

The anionic composition is an important indicator of the water quality and ecological lakes status. Different types of minerals, rock mass, acid rain, human and animal activity are major sources of increased concentrations of anions in the water [8]. The results are presented in Table 2 and 3. The measurement uncertainty varies between 7–10% for different anions. Samples were also tested for bromide (Br^-), bromate (BrO_3^-), nitrite (NO_2^-) and phosphate (PO_4^{3-}).The results are below the detection limits and no contamination of the water was found.

Table 2 Anion composition of waters of high mountain lakes from Pirin mountain, Bulgaria

lakes	F^- mg/L	BrO_3^- mg/L	Cl^- mg/L	NO_2^- mg/L	Br^- mg/L	NO_3^- mg/L	PO_4^{3-} mg/L	SO_4^{2-} mg/L
Frog lake	0.017	<DL	0.20	<DL	<DL	0.064	<DL	1.5
Eye lake	0.026	<DL	0.31	<DL	<DL	0.054	<DL	1.3
Muratovo lake	0.057	<DL	0.28	<DL	<DL	0.16	<DL	2.0
Fish lake	0.027	<DL	0.26	<DL	<DL	0.26	<DL	1.7
Long lake	0.020	<DL	0.25	<DL	<DL	0.081	<DL	1.8
Lake under the Long	0.043	<DL	0.23	<DL	<DL	0.047	<DL	2.8

Analysis of drinking water

The validated method was applied for analysis of treated and untreated drinking water [17]. The recovery for standard anions obtained in spiked certified reference material for soft drinking water (UK – Anions № ERM® – CA016a) were between 98 and 106%. The results are presented in Figure 1. The obtained concentrations are far below the recommended chemical and indicator values in drinking water [5].

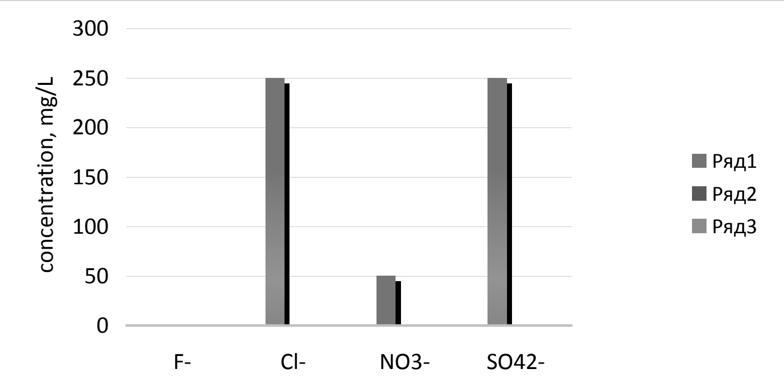
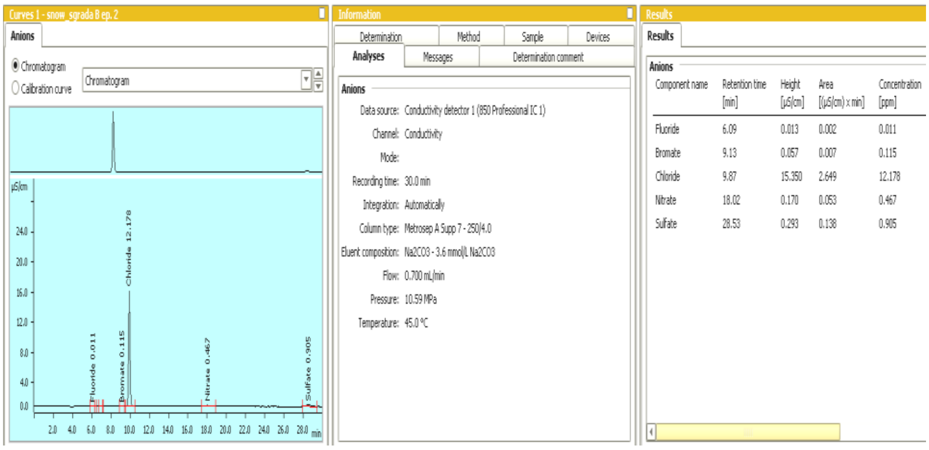


Figure 1 Results from analysis of drinking water by validated ion chromatographic method. Series 1 - recommended concentrations [5]; series 2 - untreated drinking water; series 3 - chlorinated drinking water

Analysis of wet deposits

Wet deposit from region of Sofia, Bulgaria were analyzed by the validated method. The chromatogram is presented on Figure 2. No matrix interference was observed. The retention times of studied anionscoincided with the standards within 2%. The studied wet deposits contained fluoride, chloride, nitrate and sulfate ions at different concentrations depending of the sampling site. Bromate, nitrite and phosphate anions were found occasionally.



Anions

Data source: Conductivity detector 1 (850 Professional IC 1)
Channel: Conductivity
Mode:
Recording time: 30.0 min
Integration: Automatically
Column type: Metrosep A Supp 7 - 250/4.0
Eluent composition: Na2CO3 - 3.6 mmol/L Na2CO3
Flow: 0.700 mL/min
Pressure: 10.59 MPa
Temperature: 45.0 °C

Anions

Component name	Retention time [min]	Height [µS/cm]	Area [(µS/cm) x min]	Concentration [ppm]
Fluoride	6.09	0.013	0.002	0.011
Bromate	9.13	0.057	0.007	0.115
Chloride	9.87	15.350	2.649	12.178
Nitrate	18.02	0.170	0.053	0.467
Sulfate	28.53	0.293	0.138	0.905

Figure 2 Chromatogram of wet deposit sample obtained at the optimized chromatographic conditions with Na_2CO_3 eluent. Sample composition: F^- – 0.011 mg/L; BrO_3^- – 0.115 mg/L; Cl^- – 12.78 mg/L; NO_3^- – 0.467 mg/L and SO_4^{2-} – 0.905 mg/L

Conclusion

The selected methods were successfully applied for the analysis of water samples from high mountain lakes, as well as drinking water before and after chlorination. The results obtained in this study show that there is no indication of contamination with elements or anions in the lake water. There were no deviations found from the legally acceptable values for priority substances, which could present a risk to the aquatic environment.

Acknowledgement The financial support of the Science and Research program of the University of Chemical Technology and Metallurgy, Bulgaria through the project 11802/2018 is gratefully acknowledged.

References:

1. B. Lopez–Ruiz. Advances in the determination of inorganic anions by ion chromatography; J. Chromatography A. 881 (2000) 607 –627
2. E. Rodriguez, S. Poynter, M. Curran, P. Haddad, R. Shellie, N. Nesterenko, B. Paull. Capillary ion chromatography with on–column focusing for ultra–trace analysis of methanesulfonate and inorganic anions in limited volume Antarctic ice core samples; Journal of Chromatography A. 1409 (2015) 182–188
3. J.N. Stamenov, B.I. Vachev. Monitoring and management of mountain environment. Journal of Environmental Radioactivity 72 (2004) 121–128
4. G. Pekov, P. Mandjukov, S. Tsakovski, V. Simeonov. Chemical and multivariate statistical analysis of waters from the Rila mountain lake. Observatoire de mounagne de Moussala, OM2, 1998 Sofia, 253–258 p.
5. European Commision 2014 Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Off. J. Eur. Commun. 2014 L221, 1–101.
6. European Commission 2002 Off. J. Eur. Commun. L221 8–36

7. D. Živojinović, L. Rajaković, Application and validation of ion chromatography for the analysis of power plants water: Analysis of corrosive anions in conditioned water–steam cycles, 2011 Desalination 275 17–25
8. M. Cengiz, A. Bilgin, Determination of major sodium iodide symporter (NIS) inhibitors in drinking waters using ion chromatography with conductivity detector,2016 J. Pharm. Biomed. Analysis 120 190–197
9. D. Verrey, M. Louyer, O. Thomas, E. Baurès, Direct determination of trace–level haloacetic acids in drinking water by two–dimensional ion chromatography with suppressed conductivity, 2013 Microchemical J. 110 608–613.
10. E. Gilchrist, D. Healy, V. Morris, J. Glennon, A review of oxyhalide disinfection by–products determination inwaterby ion chromatography and ion chromatography–mass spectrometry,2016 Anal. Chim. Acta 942 12–22
11. H. Abudiak, C. Robinson, M. Duggal, S. Strafford, K. Toumba, Effect of fluoride sustained slow–releasing device on fluoride, phosphate and calcium levels in plaque biofilms over time measured using ion chromatography, 2012 J. Dentistry 40 632–638
12. I. Bajenaru, I. Minca, C. Guran, A. Josceanu, F. Bacalum, Validation of an Ion Chromatographic Method for Determinationof Anions in Wet Depositions, 2013 Rev. Chim.(Bucharest) 64 122913
13. C. Lopez–Moreno, I. Viera, A. Urbano, Validation of an ion chromatographic method for the quantification ofanions in water, 2010 Desalination 26 111–116
14. A. Krata, V. Kontozova–Deutsch, L. Bencs, F. Deutsch, R. Van Grieken, Single–run ion chromatographic separation of inorganic and low–molecular–massorganic anions under isocratic elution: Application to environmental samples, 2009 Talanta 79 16– 21.
15. Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method.
16. V. Ivanova, A. Surleva, B. Koleva, Validation of Ion Chromatographic Method for Determination of Standard Inorganic Anions in Treated and Untreated Drinking Water, IOP Conf. Ser.: Mater. Sci. Eng. 374 (1), 2018, 012053.
17. V. Ivanova, B. Koleva, A. Surleva, Determination of pollutants in high mountain lakes by ion chromatography and inductively coupled plasma mass spectrometry, Metrology and metrological assurance 2018, 10–14 September 2018, Sozopol, Bulgaria, pp 264–267.