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

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ИОНДЫҚ ХРОМАТОГРАФИЯЛЫҚ ӘДІСІМЕН ТАБИҒИ СУДЫҢ АНИОН ҚҰРАМЫНЫҢ АНЫҚТАУ

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ОПРЕДЕЛЕНИЕ АНИОННОГО СОСТАВА ПРИРОДНЫХ ВОД МЕТОДОМ ИОНО–ХРОМАТОГРАФИИ

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Annotation

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 main directions of development of the ion chromatographic method in the field of applications are summarized. Special attention is paid to high– speed and high– performance chromatography. The analytical capabilities of the ion chromatographic method are compared. It has been shown that in many cases for analytical practice there is no need to use expensive equipment. Chromatography is one of the most promising modern methods in determining product quality. The method is actively used both in production and in laboratories.

Key words: natural waters, monitoring, anions, ion chromatography, waters.

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. Обобщены основные

направления развития ионо–хроматографический метода в области применений. Особое внимание уделено высокоскоростной и высокоэффективной хроматографии. Проведено сравнение аналитических возможностей ионо–хроматографический метода. Показано, что во многих случаях для аналитической практики нет необходимости в использовании дорогой аппаратуры. Хроматография является одним из перспективных современных методов в определении качества продукции. Метод активно применяется как на производстве, так и лабораториях.

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

Аңдатпа

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. Өтініштер саласында ион хроматографиялық әдістерін дамытудың негізгі бағыттары келтірілген. Жоғары жылдамдықты және жоғары өнімді хроматографияға ерекше көңіл бөлінеді. Ионды хроматографиялық әдісінің аналитикалық мүмкіндіктері салыстырылады. Көптеген жағдайларда аналитикалық тәжірибе үшін қымбат жабдықты пайдаланудың қажеті жоқ екенін көрсетті Хроматография өнімнің сапасын анықтаудағы ең перспективалы заманауи әдістердің бірі болып табылады. Бұл әдіс өндіріс пен лабораторияларда белсенді қолданылады.

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

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 technologiesnew 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 offeringlow 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 beenrecently 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

1.1 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 ^oC
Detection	Suppressed conductivity
Determination mode	Peak area

1.2. 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 limitsfor natural water [17].

Analysis of water from high mountain lakes

The anionic composition is an important indicator of the water quality and ecological lakesstatus. 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].

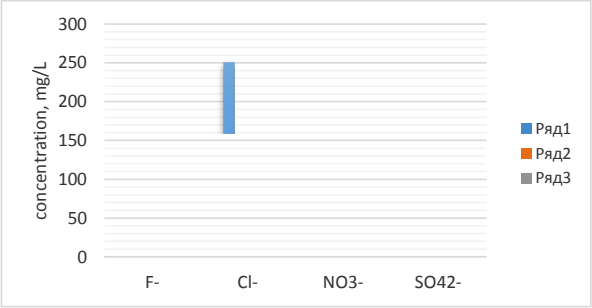

Figure 1 Results from analysis of drinking water by
validated ion chromatographic method. Series 1: recommended concentrations [5];
series 2 untreated drinking water; series 3 – chlorinated drinking water

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.

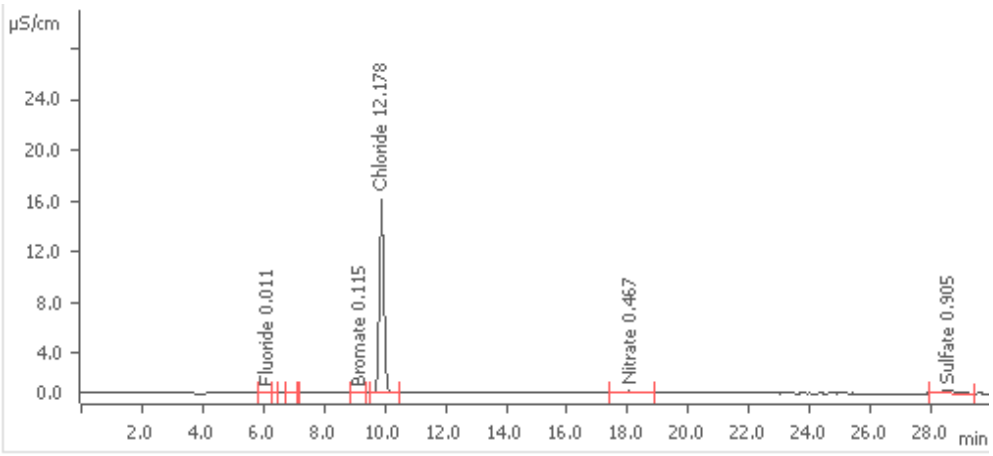

Figure 2 Chromatogram of wet deposit sample obtained at the optimized chromatographic conditions with Na_2CO_3 eluent. Sample composition: F^- – 0.011 mg/L; BrO_3^- – 0.115 mg/L; Cl^- – 12.78 mg/L; NO_3^- – 0.467 mg/L and SO_4^{2-} – 0.905 mg/L

Conclusions

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.

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