DETERMINATION OF POLLUTANTS IN HIGH MOUNTAIN LAKES BY ION CHROMATOGRAPHY AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

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Abstract: The ecological monitoring of pollutants in high mountain lakes is a requirement for achieving a good ecological and chemical quality of water in order to protect the human health and natural ecosystems. The study and evaluation of high mountain lakes is of important significance since they are sensitive to global, regional and local ecological changes. The usage of reliable analytical methods for the determination of pollutants will allow to make a modern assessment of the ecological status of the waters in Bulgaria. The current requirements for determination of controlled pollutants require the application of methods with lower detection limits, good repeatability and accuracy of measurement. This article summarizes the results of a study of six high mountain lakes in Pirin, Bulgaria. For this purpose, the elements were determined by Inductively Coupled Plasma Mass Spectrometry and the anions by Ion Chromatography.

Keywords: High Mountain Lakes, Natural Water, Ecology, Monitoring, Element Analysis, Anions, Mass Spectrometry, Ion Chromatograph

1. 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.

More and more scientists are interested in monitoring, studying and assessing the natural water because they are extremely sensitive to global, regional and local environmental changes. Each water source has a unique identity or have a set of physical and chemical characteristics that can change over time and takes its own place among the aquatic ecosystems.

Up to now chemical monitoring of the high mountain lakes in Bulgaria has been carried out for the determination of inorganic compounds by X-ray fluorescence analysis and atomic absorption spectrometry and for cation by flame photometry in the period 1993-1996 in the Rila Mountain. There was no indication for contamination with heavy metals in the considered mountain lakes, the results are below the limit of quantification [3,4]. The natural chemical composition of the water, the hydrochemical parameters, the geochemical and anionic composition of the rainfall and snow were also studied in this period. [3]. An Ion chromatography was used to determine the major components such as chloride, nitrate, sulphate and carbonate [4].

To obtain more accurate and reliable information about the ecological status of the studied lakes, it is necessary to make a more detailed analysis using more sensitive and modern methods with a low detection limit, such as ICP MS (Inductively Coupled Plasma Mass Spectrometry). The contemporary Ion Chromatography (IC) is a sufficiently sensitive and reliable method for determination of low concentrations of anions in natural water.

2. Methods, samples and reagents

2.1. Sampling

The studied samples were taken in August 2017 from 6 high mountain lakes in Pirin Mountain – Frog Lake, Eye Lake (Ravnishko Lake), Muratovo (Juniper Lake), Fish (Fish Banderishko Lake), Long (Upper Banderishko Lake), Lake under the Long. The Banderishki lakes are a large group of lakes in Central North Pirin, located in the Banderitsa Cirque and giving rise to the Banderitsa River. They are glacial lakes formed on granite basis.

The sampling was done for a short period of time, avoiding seasonal climatic changes (precipitation). The samples were stored into sterile sample tubes and those intended for element analysis were preserved by addition of nitric acid.

2.2 Instruments and operating conditions

ICP MS is a modern analytical method characterized by the possibility of simultaneous multielement determination, high sensitivity, wide dynamic range and rapidity of analysis [9].

At the same time, the Ion chromatography is a unique, high performance analytical method for determination of ions in water samples [10]. Both methods complement very well each other and give more complete information on the quality of the water.

The more important parameters of the ICP mass spectrometer and Ion chromatograph during the analysis are presented in Table 1.

2.3. Reagents and Certified Reference Materials

All solutions were prepared with deionized water Milli-Q (18.2 MΩcm, Millipore, Merck). Certified Reference Material for ICP MS (ULTRA SCIENTIFIC, North Kingstown, USA) was used to determine the elements. All standard solutions were prepared to appropriate concentration by dilution with deionized water and 2% nitric acid (HNO3 Suprapur®, Merck, Darmstadt, Germany).

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).

The developed and validated methods allow the determination of low concentrations of elements and anions which are below the established limits for natural water.

The limits of detection (DL) and limits of quantification (QL) obtained by ICP MS are presented in Table 2. The values are in the order of ng/L - μg/L.

The concentration of Cr, Ag, In, Bi is below the DL or between the DL and QL. The results for the element Ni ranged from 0.24 to 0.35 μg/L, Cd - from 0.006 to 0.023 μg/L, Pb - from 0.11 to 0.16 μg/L and are below the recommended limit values, set out in the Directive 2013/39/EC [6]. The results for the elements Mn (ranged from 0.41 to 6.1 μg/L), Cu (ranged 0.12 to 0.40 μg/L) and U (ranged from 0.02 to 2.92 μg/L) are also below the regulation limits on inland surface waters, stated in Ordinance № H-4 of 14.09.2012 [7]. The measurement uncertainty was below 5% for each element.

Table 1. ICP MS and IC operating conditions

Varian ICP MS	
Isotopes measured	
^{53}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{65}Cu, ^{71}Ga, ^{107}Ag, ^{109}Ag, ^{111}Cd, ^{113}In, ^{115}In, ^{137}Ba, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{209}Bi, ^{238}U	
ICP source settings	
Data acquisition parameters	
Scanning mode	Peak Hopping
Detecting mode	Counting
Spray Chamber Temperature (°C)	3.00
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 °C
Detection	Suppressed conductivity
Determination mode	Peak area

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 presented in Table 5 for fluoride (F-), chloride (Cl^-), nitrate (NO_3^-) and sulphate (SO_4^{2-}) show good water quality. 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-}). 0The results are below the DLs and no contamination of the water was found.

4. Conclusion

The selected methods were successfully applied for the analysis of water samples from Banderishki lakes. 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.

This research raises the question of the lack of in-depth monitoring of the status of the high mountain lakes in Pirin, which will help to clarify the ecological

situation in the area. It is also necessary to carry out studies not only on inorganic pollutants, but to track the processes of oxidation, pH and conductivity. This type of monitoring could contribute to identify the impact of human activity and the change of water quality.

Table 2. Limit of detection (DL) and limit of quantification (QL) obtained by ICP MS

	Cr µg/L	Mn µg/L	Co µg/L	Ni µg/L	Cu µg/L	Ga µg/L	Ag µg/L	Cd µg/L	In µg/L	Ba µg/L	Tl µg/L	Pb µg/L	Bi µg/L	U µg/L
Limit of detection, (DL)	0.1	0.02	0.003	0.03	0.05	0.002	0.003	0.002	0.0009	0.007	0.0006	0.034	0.01	0.001
Limit of quantification, (QL)	0.4	0.08	0.009	0.1	0.16	0.008	0.01	0.006	0.003	0.024	0.002	0.11	0.034	0.003

Table 3. Concentration of elements obtained by ICP MS

Banderishki lakes	Altitude, m	Area, da	Depth, m	Cr µg/L	Mn µg/L	Co µg/L	Ni µg/L	Cu µg/L	Ga µg/L	Ag µg/L	Cd µg/L	In µg/L	Ba µg/L	Tl µg/L	Pb µg/L	Bi µg/L	U µg/L
Frog lake	2322	5.6	2	<DL	0.41	0.011	0.29	0.24	0.011	<DL	0.023	>DL, <QL	1.5	0.0046	0.11	<DL	0.02
Eye lake	2026	2.6	5.4	<DL	6.1	0.017	0.26	0.40	0.020	<DL	0.016	<DL	1.8	0.0070	0.11	>DL, <QL	0.24
Muratovo lake	2230	12.3	3.2	<DL	3.9	0.028	0.35	0.16	0.061	<DL	0.010	<DL	2.3	0.0058	0.16	<DL	2.92
Fish lake	2190	65	12.2	<DL	2.7	0.021	0.27	0.20	0.041	<DL	0.006	<DL	1.8	0.0066	0.11	<DL	1.45
Long lake	2310	45.5	10	<DL	2.7	0.018	0.24	>DL, >QL	0.022	<DL	0.010	<DL	1.8	0.0058	>DL, <QL	<DL	0.79
Lake under the Long	-	-	-	<DL	1.7	0.025	0.24	>DL, >QL	0.022	<DL	0.020	<DL	2.1	0.0057	0.12	<DL	1.4

Table 4. Limit of detection (DL) and limit of quantification (QL) obtained by IC

	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
Limit of detection, (DL)	0.004	0.02	0.003	0.005	0.01	0.006	0.008	0.005
Limit of quantification, (QL)	0.01	0.05	0.01	0.01	0.03	0.02	0.02	0.02

Table 5. Analytical results obtained by IC

Banderishki lakes	Altitude, m	Area, da	Depth, m	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	2322	5.6	2	0.017	<DL	0.20	<DL	<DL	0.064	<DL	1.5
Eye lake	2026	2.6	5.4	0.026	<DL	0.31	<DL	<DL	0.054	<DL	1.3
Muratovo lake	2230	12.3	3.2	0.057	<DL	0.28	<DL	<DL	0.16	<DL	2.0
Fish lake	2190	65	12.2	0.027	<DL	0.26	<DL	<DL	0.26	<DL	1.7
Long lake	2310	45.5	10	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

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