Quality Monitoring of Natural Water from Southwest District of Moscow Using Total Reflection X-ray Fluorescence Analysis

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Abstract. Pollution of drinking and natural waters is the fundamental environmental problem. Due to the rapid development of human economic and industrial activity, monitoring of the environmental situation is necessary. Total Reflection X-ray Fluorescence Analysis makes it possible to determine the elemental composition of water quickly and accurately for a large number of elements simultaneously. The work is devoted to the study of water sources in the southwest district of Moscow: Ramenka and Rogachevka rivers and the drinking water source in the park of the 50th anniversary of the October. During the work, suitable conditions were found that make it possible to perform the analysis quickly (the analysis time does not exceed 10 min. for one sample) and to determine a number of elements at the macro-, micro- and trace levels. The obtained results are compared with the current Russian sanitary standards.

Keywords: water, quality monitoring, elemental composition, Total Reflection X-ray Fluorescence

1 Introduction

The human impact on the environment leads to a change in the chemical composition of water used in everyday life, compared with its natural composition. Water is used by humankind everywhere, including cooking and drinking, so attention should be paid to water analysis. One of the most effective modern methods for determining the elemental composition of water is Total Reflection X-ray Fluorescence Analysis (TXRF). The method allows to determine small amounts of substance (less pg in absolute values) with low detection limits (down to ng/l for liquid samples) (Alov, 2011). This method allows investigating a wide variety of objects: water, soils, geological, mineralogical, technological, archaeological and food samples, it is suitable in medical industry, art and forensic. TXRF method has a number of advantages: a small amount of analyzed sample, a simplified procedure for quantitative analysis due to the use of the internal standard and the elimination of matrix effects. The TXRF method is characterized by a small amount of reagents and hence a low cost of analysis (Klockenkämper, von Bohlen, 2013). The method is

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widely used for the analysis of liquid objects, which is facilitated by a very simple and fast sample preparation procedure. In most papers the sample preparation procedure consists of the following steps: 1) getting an aliquot, 2) introduction of an internal standard into aliquot, 3) transfer of a sample drop onto a reflector substrate, 4) drying the droplet in a vacuum desiccator or on a hot plate, 5) measuring the TXRF spectrum and calculation of concentrations by the internal standard technique (De La Calle et al., 2013). Similar approach was used for determination of heavy metals in Mexican Lerma river (Zarazua et al., 2006) and monitoring of water quality of Toledo river in Brazil (Espinoza-Quinones et al., 2010) by TXRF with synchrotron radiation excitation.

The purpose of this work is to determine the elemental composition of the natural waters of the southwest district of Moscow: Ramenka and Rogachevka rivers and the drinking water source in the park of the 50th anniversary of the October using the TXRF method, as well as comparing the data obtained with the Russian sanitary standards.

2 Samples

Several samples from water system of Moscow southwest district were taken for the analysis. The pond in the flow of Ramenka river (sample 1), Ramenka river itself (sample 2), Rogachevka river (sample 3), which is a confluent of Ramenka, Ramenka river after the confluence of both rivers (sample 4), the artesian source of drinking water (sample 5) and also sample of the snow from a slope of Ramenka river. The sampling scheme is shown on Fig. 1.

3 Experimental

Water samples were acquired in plastic bottles. The measurements were carried out on the TXRF spectrometer S2 PICOFOX (Bruker Nano GmbH, Germany) using quartz reflectors. The excitation was performed by Mo Kα (17.5 keV) radiation. The time of the spectrum acquisition is 250 s. Gallium solution with the concentration 1000 mg/l is used as an internal standard. This element is easily detected by TXRF. It does not present in sample and does not cause spectral interference with elements in sample. The volume of the aliquots was chosen to be 0.5 ml, the volume of the internal standard solution was 5 µl. The volume of the analyzed solution deposited on the reflector is 1-2 µl.

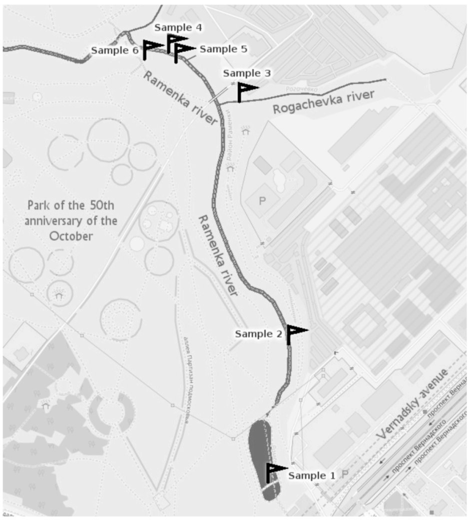

Fig. 1. Scheme of water sampling from the park of the 50th anniversary of the October located in southwest district of Moscow.

4 Results and discussion

In water samples S, Cl, K, Ca macroelements, Fe, Cu, Zn, Br, Sr microelements and trace elements Ti, Mn, Ba, Pb were detected. Analysis results are listed in Table 1.

Analysis of water reservoirs (samples 1-4) shows that water from Ramenka river (sample 2) has the highest mineralization of all investigated water samples (fig. 2). The highest concentration of such elements as S, Cl, K, Ca, Cu, Zn, Br was found in this sample. At the same time the content of same elements is much lower in the pond from which the river flows (sample 1). It is presumably due to the sedimentation of water followed by transition of elements to muddy sediment at the bottom of the reservoir.

In the confluent of the Ramenka river – Rogachevka river, the content of elements of S, Cl, K, Ca, Cu, Zn, Br is also lower than in Ramenka (sample 3). The mineralization of water after confluence of Rogachevka to Ramenka decreases due to dilution.

Waters investigated meet the standards set for a household water (see Table 2), with the exception of the Ramenka river (sample 2), in which chlorine content is exceeds the maximum allowed concentration (488 mg/l).

Sample 5 – drinking water sample was also compared with standards for drinking water. As can be seen from Tables 1, 2, content of (S, Cl, Ca, Fe, Cu, Zn, Ba) is within the permissible concentrations. In addition to these elements, traces of titanium and lead were found in drinking water in an amount several times lower than maximum allowed concentrations.

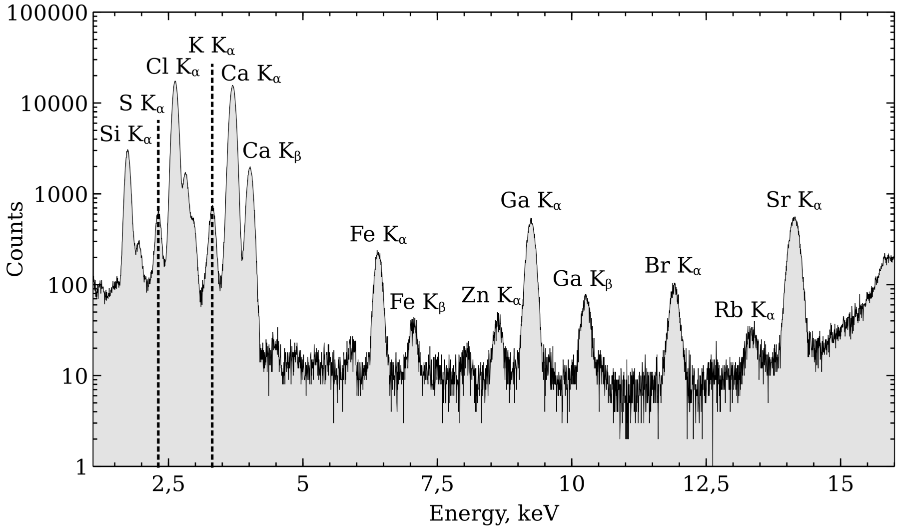

Fig. 2. TXRF spectrum of water from Ramenka river (sample 2).

The results of the analysis of the snow (sample 6) showed that it contains the minimum amounts of all the elements. This can be explained by the fact that the snow condenses in the atmosphere and absorbs only volatile and aerosol contamination. Also a sample of snow was selected in a place that is located quite far from the roadways. Consequently, the snow did not have time to become contaminated with additional substances. The melt water, formed during the melting of snow, also meets the requirements for the purity of water by the parameters studied.

Table 1. TXRF results of water elemental composition determination for rivers located in southwest district of Moscow.

	Concentraion, mg/l					
	1	2	3	4	5	6
S	9.2±1.5	15.7±5.6	15.3±4.6	21.5±4.8	16.8±3.3	0.22±0.13
Cl	42.7±3.7	488±132	56±11	154±15	20.3±3.0	1.25±0.19
K	8.8±0.6	7.5±1.2	10.7±2.3	12±1	1.2±0.3	0.34±0.03
Ca	56.8±3.9	146±54	42±10	81±40	44.1±15.1	0.66±0.05
Fe	0.14±0.07	< 0.03	< 0.03	< 0.03	< 0.03	0.04±0.02
Cu	0.012±0.003	< 0.002	not det.	not det.	< 0.002	0.0021±0.0003
Zn	0.02±0.01	0.047±0.01	0.013±0.005	0.04±0.02	0.015±0.006	0.024±0.004
Br	0.036±0.02	0.10±0.03	0.05±0.01	0.05±0.01	0.17±0.02	0.0019±0.0002
Sr	0.33±0.02	0.54±0.21	6.2±1.0	5.95±0.70	0.19±0.03	0.0011±0.0003
Mn	0.12±0.01	< 0.005	not det.	not det.	not det.	0.005±0.002
Ti	< 0.02	< 0.02	not det.	< 0.02	< 0.02	0.004±0.002
Pb	< 0.002	not det.	< 0.002	not det.	0.005±0.002	< 0.002
Ba	< 0.05	< 0.06	< 0.05	not det.	< 0.05	not det.

Table 2. Element concentration allowed by the Russian sanitary standards for household and drinking water.

Element	Cl^-	Fe	Cu	Zn	Br^-	Sr	Mn	Ti	Pb	Ba
Concentraion, mg/l	350	0.3	1	1	0.2	7	0.1	0.1	0.01	0.1

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