The SR-XFA Method Used to Determine the Multi-Element Composition of Arctic Aerosols

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Abstract. Studying aerosols in the Arctic zone is not only valid due to climate changes that are most pronounced at high latitudes but plays an important role in the investigation of radiative transfer and mass exchange by chemical compounds in the system «continent — atmosphere — ocean». To study the multi-element composition of aerosols in high-latitude areas is a major issue for identifying the regional and global sources of pollution. The studies were performed by the method of modern high-precision X-ray fluorescence analysis using synchrotron radiation (SR XFA). The selection campaign was conducted in the village of Barentsburg in the Svalbard archipelago from 17.12.2018 to 11.04.2019 using AFA-KhA-20 filters. The SR XFA method using synchrotron radiation, developed in the Budker Institute of Nuclear Physics, SB RAS, made it possible to determine the concentrations of 22 elements: K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Pb. In addition, it was combined with the data on air mass trajectories in order to determine both the regions from which these elements were transported and the origin of these sources.

1. Introduction
The problem of exploring the Arctic environment is a priority and is included in the strategic directions of the scientific and technical development of the Russian Federation. Atmospheric aerosol, which plays an important role in the processes of radiative transfer and mass exchange in the system “continent-atmosphere-ocean”, is one of the components of the natural environment. The ambiguity of aerosol characteristics in various regions, particularly in the hard-to-reach polar ones with severe climate, is preserved due to the high variability and diversity of aerosol composition. The study of the chemical composition of aerosols in the high-latitude regions is an important problem when identifying the regional and global sources of pollution. The measurements of multi-element composition are used as the specific markers of anthropogenic and natural sources of elements in the atmospheric aerosol. It is worth noting that a modern period of aerosol investigation at high latitudes can be characterized as a gradual accumulation and identification of data on specific regions and aerosol characteristics.

The element composition of atmospheric aerosol is determined by various methods, e.g., mass-spectrometry with inductively coupled plasma, atomic adsorption analysis, etc. [1-3]. In this work, we have utilized the SR XFA method using synchrotron radiation, which is a modern nuclear-physical...
method of element analysis which makes it possible to determine the content of chemical elements in a sample to within high accuracy. The undoubted advantage of the method is its non-destructiveness and panoramas. The high SR intensity reduces analysis time, sample size and mass requirements, and detection limit. In this case, the method sensitivity reaches $10^{-9} - 10^{-7}$ g/g [4-6]. Besides, in the samples of atmospheric aerosol, the content of elements varies within a wide range and most of the methods imply either a chemical or a thermal effect on a sample which may cause either the loss of elements or reagent pollution [7].

The goal of this work is to study the mass concentrations of the element composition of atmospheric aerosols sampled by the SR XFA method in the Svalbard archipelago in the village of Barentsburg, and to estimate the effect of natural and/or anthropogenic sources on the pollution of Arctic aerosols by analyzing air mass trajectories.

2. Materials and methods

The village of Barentsburg (78.04°N, 14.13°E) is the second largest settlement in the Svalbard archipelago, located in the Arctic ocean. Atmospheric aerosols were collected using acetate filters (AFA-KhA-20) and a BUSH Type SB 0050 OHO blower. Air was pumped through the filters (8.4 m³/h) for 2-3 days. The sampling campaign was conducted from 17.12.2018 to 11.04.2019. The HYSPLIT (https://www.ready.noaa.gov/HYSPLIT.php) program was used to analyze the air mass trajectories in the Svalbard archipelago in Barentsburg.

The elements were determined by the SR XFA method at the station of element analysis (VEPP-3 store-ring) of the Siberian Center of Synchrotron and Terahertz radiation of BINP SB RAS with an energy of excitation radiation of 23 keV. For the main characteristics of the experimental station and the methodical aspects of the work see [5,6,8]. The spectra recorded were processed by the AXIL program, intended for the dispersive spectrometric energy analysis using non-linear least-squares method. The concentrations of elements were determined by external standard method [9]. The content of the following elements was estimated in aerosol samples: K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Pb. Figure 1 demonstrates the sample spectrum.

![Figure 1. Spectra of Arctic aerosol samples.](image)

3. Results and discussion

Figure 2 shows the mean element concentrations in aerosol particles from the village of Barentsburg in winter of 2018-2019. Note that according to the concentration value, the elements can be divided into the following ranges: $>100$ ng/m³: Ca, K, Fe amounted to 88% of the total; 10 – 100 ng/m³: Ti, Sr, Zn, Br amounted to 9%; 1 – 10 ng/m³: Mn, V, Cr, Cu, Pb, Co, Ni, Zr – 2.5% and As, Ga, Se, Rb,
Y, Mo, Ni with a concentration of 0.1 to 1 ng/m³, which was 0.5% of the total composition of the elements measured.

![Figure 2](image)

**Figure 2.** Element mass concentration (Avg±SD) in aerosol particles from the village of Barentsburg of 17.12.2018 to 11.04.2019.

![Figure 3](image)

**Figure 3.** Enrichment factor of aerosol elements in the village of Barentsburg.

The enrichment factor (EF =X/Xclark, where X is the element concentration) can be used to determine the source of elements in the atmospheric aerosol. The elements, whose content corresponds to the Clark content (content in the earth’s crust), are attributed to the sources of the soil-erosion type. Figure 3 shows that the particles, containing Ca, K, Fe, Ti, Mn, V, Cr, Ni, Zr, Ga, Rb, Y, Nb, are formed by natural processes. When the element EF value exceeds the Clark one more than ten times, this element is of anthropogenic origin. EF for Sr, Zn, Br, Cu, Pb, Co, As, Se, Mo exceeds ten. Thus, these elements are from a technogenic source. [10].

The contribution of the distant sources of Arctic pollution can be estimated from the daily variations of element composition. The sharp variations (3-10 times) in the concentration of elements during the period under study were recorded almost for all elements (Fig. 4). For example, a drastic increase in concentrations as compared with the mean value, was observed from 22.01 to 24.01.2019. The method of backward air mass trajectories was used to demonstrate that the aerosol is transported from industrial territories: from Norilsk, Khanty-Mansi autonomous okrug (Figs. 5 and 6).
**Figure 4.** Comparison of element content during the periods of mean (background) and high concentrations (event).

**Figure 5.** Plot of backward air trajectories of 22.01.2019.

**Figure 6.** Plot of backward air trajectories of 23.01.2019.

In other periods under study, when the element concentrations were not exceeded, predominant was the air transfer from the water area of the Arctic ocean, Greenland, and the northern part of Canada (the Province of Nunavut), where the aerosol composition depends on the natural processes for these regions, reflecting their background state.

### 4. Conclusions

It has been established that:
- the SR XRF method is optimal for studying the aerosols of chemical elements deposited on filters because of the simultaneous determination of a great number of elements (more than 20) with high sensitivity and to within fair accuracy, the sample non-destructiveness, and the absence of complex sample preparation.

- The analysis of air mass trajectories in the Svalbard archipelago in the village of Barentsburg has confirmed that during the periods in which the concentrations of all elements were exceeded, the air aerosol was transported from residential and industrial territories from Norilsk, Khanty-Mansi autonomous okrug (22.01-24.01.2019). In other periods studied, predominant was the air transport from the water area of the Arctic ocean, Greenland, and the northern part of Canada (the Province of Nunavut) where the composition of aerosols was determined by the natural processes for these regions, reflecting their background state.

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