ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Roentgen Fluorescent Control of Heavy Metals in Precipitation of Snow Cover.

U.V. Ondar[1]*, I.V. Chambal[1], S.O. Ondar[1], A.O. Ochul-ool [1], U.V. Dordghu[1], Ch.O. Khertek[1], A.N. Smagunova[2], Ye. N. Korzhova[2], and T.V. Stepanova[2].

[1]Tuva State University, 36, Lenin Str., Kyzyl;
[2] Irkutsk State University, 1, K. Marx Str., Irkutsk

ABSTRACT

The method of roentgen-fluorescent identification of heavy metals in the samples of insoluble precipitates of snow mantle of the restrained weight has been developed. Estimates of the precision and accuracy have been established with the help of state standard samples of soils and ground sediments. The methods have been used in controlling the degree of pollution of the territory of Kyzyl with Pb, Zn and Ni, it is shown that the content of the studied heavy metals in insoluble precipitates of snow cover exceeds admissible concentration limit for soils. Recommendations for the selection of the snow samples by using the method of X-ray fluorescence for environmental monitoring consisting in the necessity to increase the area of selection of snow samples in terms of the dust load in snow have been given.

Keywords: X-ray fluorescence analysis, heavy metals, method preparation, snow cover, method of analysis, snow contamination

Corresponding author

INTRODUCTION

The snow cover like a natural pad accumulator gives the real amount of dry and wet atmospheric fallout in the cold season. During this period of the year in the areas of the continuous expansion of the snow cover, when the transfer of substances from the soil to the surface is excluded, the material and chemical composition of the solid residue becomes a function of atmospheric fallout [1, 2]. With its high absorptive capacity, snow during snowfall captures a significant portion of contaminants from the atmosphere and precipitates them on the surface. The pollution of snow cover occurs in two stages. Firstly, the contaminating of snowflakes during their formation in the cloud and precipitating onto the ground is a wet fallout of the contaminants with snow. Secondly, the pollution of the snow that has already fallen as a result of dry fallout of a matter from the atmosphere and its possible absorption from the underlying soil and rocks [1, 3]. Therefore, the chemical composition of insoluble precipitates of the snow cover (IPSC) is an integral characteristic of the transfer of atmospheric pollutants, more informative than the atmospheric aerosol [2, 4].

One detects high-density metals, sulfates, nitrates, polyaromatic hydrocarbons, protein compounds and other substances of natural and man-made formation in the snow samples [1-3, 5-7]. They consist of mineral and biogenic particles, the sources of which are soils, plants, forest fires, volcanoes, cosmic dust and gas and gas-dust outburst from the enterprises. Among the particles there are found the hollow pale-gray and white microspherules with a glassy luster and black ones with metallic appearance [8, 9]. The authors of the paper [8] claim that they are formed by pulverized-coal burning of coals at the thermal power station. There exists a space-based hypothesis of the origin [5].

V. Ye. Pavlov in collaboration with the authors [6] indicate that the pollution of snow cover is affected not only by the TPS, but also by stove heating from private buildings. In the work by V. F. Raputa and co-authors [5] it is studied the effect of transport on the level of contamination of snow in Novosibirsk, and the authors [2] show that the zone of influence of industrial emissions from non-ferrous metallurgy enterprises into the snow cover in the Arctic stretches for hundreds of kilometers.

Studying the snow composition makes it possible to determine the dust load, and information about its material composition allows to determine the source of contamination and a zone of its influence. In 2008-2010 such studies were held in the territory of Kyzyl and its surroundings, which showed considerable excess of metal content in the samples of IPSC compared to the background, which is associated with the work of Kyzyl HES, houses heating of the private sector and the presence of the primary roads [10]. Previously, the authors [11] conducted the studies on the contamination of snow cover with heavy metals by atomic absorption method. These data indicate the feasibility of systematic monitoring of the content of metals in the samples of snow, and, for this purpose, it is essential to prepare economical methods of their determining. In this respect, prospective is the use of non-destructive X-ray fluorescence method of analysis (XRFA) [12]. Therefore, the aim of the work consisted in choosing the optimal conditions of organization for monitoring the pollution of the territory of Kyzyl with metals according to the results of XRFA of the samples of IPSC.

EXPERIMENTAL PART

As consistent with the guidelines [13], at the end of February 2012, the group (~ 50) of snow samples was selected in various areas of Kyzyl. The selection was made from the site of 1×1 m^2, entire-depth of the snow pit, without affecting its ground layer. The selected material was put into the plastic bags.

Preparation of IPSC samples

In the laboratory, the samples of snow were thawed out in a clean container and IPSC were separated from snow water by filtration on a pre-weighed filters of «a blue ribbon» type. To do this, the entire volume of the produced water was filtered through a plaited filter. Note that the filtered water must be clear, otherwise, it is re-filtered through the same filter. The sludge mass is used for assessing the dust load of snow, which is also one of the indicators of contamination of the snow cover.

To determine the heavy metals in the material of IPSC, the filters with precipitates were incinerated at 450 ° C [14]. For this purpose, the filter with the precipitate was placed first into the crucible that was preliminarily weighted and brought to constant mass and then in a cold muffle furnace, next, after having held the temperature at 250 ° C, it was raised every 30 minutes by 50 ° C until 450 ° C and then the sample was being kept in the furnace within two hours. With such method of ashing of the material, the losses of microelements owing to their volatility can be neglected [14]. The ashed material with ethanol added was crushed to a particle size of less than 60 microns in an agate mortar. The content of Pb, Zn and Ni in the samples was determined, but the methodological research was carried out only by using Pb and Ni, the wavelengths of analytical lines of which are extreme for the considered band.

It was discovered that the IPSC mass for the most samples was insufficient for their XRFA under standard conditions: the cuvettes added to the used spectrometer had a diameter of 4 cm. Therefore, by the development of methods of XRFA of the IPSC samples, it was necessary to solve the following problems:

- to make the cuvette off smaller diameter ~2 cm;
- to select the optimum sample of the material of IPSC being placed in the cuvette;
- to choose a method of analysis;
- to estimate the precision and accuracy of the results of analysis.

The conditions of registration of X-ray spectra

The research was carried out on the X-ray fluorescence spectrometer VRA-30 of Carl Zeiss (Germany). The fluorescence was excited by radiation of the X-ray tube with a Rh-anode working in the mode: voltage of 40 kV, current strength of 40 mA. The emission was expanded into spectrum according to the Soller method using the crystal-analyzer LiF [200] and recorded with a scintillation detector with an exposure of 60 seconds (or 100 seconds). The intensities of Ni, Zn Kα- lines, Pb Lβ-line and scattered radiation were measured in the conditions given in Table 1. To account the apparatus drift, the identified intensities were registered in relative units (I_{rel}).

Table 1. The conditions of registering the intensity of the fluorescent and scattered radiations

Analytic lines	Wavelengths of, nm	
	Line	Background
PbLβ	0,0982	0,1015
ZnKα	0,1435	0,1466
NiKα	0,1658	0,1599

Methodological developments

The content of particulate pollutant selected in the territory in the depth of the continent is close to the content of soils [1-4], thus in solving the assigned tasks the group of SSS of soils and bottom sediments was used, it included the following 24 samples: СГХМ-1, СГХМ-3, СГХ-5, СКР-2, СДО-5, СДО-7, СГХМ-2, СГХМ-4, СП-1, СП-2, СП-3, СГХ-1, СГХ-3, СКР-1, СКР-3, СДПС-3, ССК-1, СЧТ-2, СЧТ-3, СДО-1, СДО-3, СДО-4, СДО-8, СДО-9. The content of Ni, Pb and Zn in them altered within (%): 0,001-1,37; 0,0008-0,105; 0,001-0,12, respectively.

For the production of the cuvettes from a metal tube, the external diameter of which was 20 mm, the internal one was 18 mm, 8 rings of 4.5 mm were cut. The radiographic film of RM-B mark being washed from the emulsion was stuck to the one end of the ring. The idea to use a thin Mylar film as a window failed because it could not be fixed onto the ring. They were used for the method preparation and analysis of the IPSC samples.

When planning an experiment according to the scheme of two-factor analysis of variance, we estimated the errors characterizing quality of cuvette workmanship (coefficient of variation V_{cuv}) and instability of conditions of their input into the spectrometer ($V_{уст}$). The experiment was carried out by measuring an intensity (I_{σ}) of scattered radiation at the site of the lines NiKα and PbLβ, when the samples were empty cuvettes. The results of analysis of variance showed insignificance of error V_{cuv} for the two lines against the background of error of reproducibility (V_r) of measurement Iσ being equal to 1,54 and 0,7% correspondingly for the lines indicated above; the error (V_{cuv}) is meaningful only for PbLβ-line and is equal to 1.04%. Taking into account the requirements for accuracy ($V_{доп}$) analysis of environmental samples [15], one can draw a conclusion about the suitability of using the created cuvettes for further research.

To select an optimal mass (m_j) of the sample by having placed the material of SSS СДО-4 in the cuvette, we estimated the dependence of intensity of NiKα- and PbLβ-lines measured simultaneously with the background (I_{l+b}), intensity ($I_{фр}$) of background registered with the line (see Table 1), and intensity (I_l) of fluorescence without background of value m_j. At that, the value m_j (g) were altered: 0.05; 0.07; 0.12; 0.20; 0.30; 0.70 and 1.0. To manufacture radiators, the material, placed in the cuvette, after its uniform distribution with spatula manually, was manually compacted with a punch, the diameter of which corresponded to the internal cuvette size. The built dependences $I_{l+b} = f(m)$, $I_{фр} = f(m)$ and $I_l = f(m)$ have shown that even when m is equal to 0.3 g, the values I_l approximate saturation (93%) even for PbLβ- line.

To study the dependence of error (coefficient of variation V_{rad}) of preparing radiators of the weight of the material being placed in the cuvette, the experiment described above had been repeated 8 times, measuring in terms of repeatability of the intensity I_{l+b} and I_{fr}. Dispersions V^2_{rad} for the masses of the range 0.3-1.0 g turned out to be homogeneous: the values V_{rad} amounted to 2%. For radiators of weight from 0,2-0,05 g, the values V_{rad} raised by 2 and 6 times, respectively.

Researches on the selection of the analysis method were performed by using the samples of 0.3 and 1.0 grams, placing the material of the state standard sample (SSS) of soils and sediments in the cuvettes. At the same time, we measured the intensity of the lines PbLβ- and NiKα- and background, and the specified lines (see Table 1). The group was divided into two groups: the first 6 SSS from the listed above were used as calibration samples (CS), and the other - as the test samples. At the same time, we tested the application of methods of the direct external standard (DES) and standard-background (SB). The intensity of the background I'_b under the analytical lines was taken into account with the help of the value I_{fr}, measured simultaneously with the line (see Table 1), with subsequent correction of the dependence of the intensity of the background on the wavelength: $I'_b = I_{fr}K$. Coefficient K was determined by means of the background sample made from boric acid.

RESULTS AND DISCUSSION

For both compared methods, calibration diagrams were curvilinear. For the method of DES, it is connected with the effects of absorption of primary and secondary radiations(μ_m), as in the SSS, the content of Fe_2O_3 ranges from 0.99% (UDPS -3) to 24.87% (JDO -6). At the same time, the upper range values Fe_2O_3 are characteristic for high contents of Pb and Ni. The background-standard method was to eliminate this effect, but in terms of our analysis, it has not occurred. It is likely to be conditioned due to the fact that the relative contribution of the radiation scattered by a thick organic window of the cuvette, in the intensity I_b grows with the increase μ_m of the material of samples, which reduces the value of the analytical parameter I_l / I_b of the method of standard-background.

With the help of the built calibration curves, we analyzed the second group of the SSS, according to their results, we assessed the precision (repeatability and internal precision) and accuracy (V_a), which characterizes the deviation of the results of the analysis of the certified contents C_{cert} (Table 2).

Table 2. Assessment of precision and accuracy, obtained according to the results of the analysis of SSS

Metrological performance	Constant of variation in determining							
	Pb for mass				Ni for mass			
	m = 1,0 g		m = 0,3 g		m = 1,0 g		m = 0,3 g	
	PVS	FSC	PVS	FSC	PVS	FSC	ПВС	FSC
Repeatability (V_r)	2,8	3,0	3,0	3,2	2,5	3,1	3,5	3,6
Laboratory precision ($V_{Rл}$)	3,9	5,2	4,2	4,4	4,2	4,8	5,4	5,2
Accuracy (V_a)	30	21	35	32	21	21	29	25

As one can see, the results of evaluation of precision (C_i) XRFanalysis of IPSC meet the requirements for accuracy $V_{доп}$ [15]. Low accuracies V_a characterizing the difference between the obtained C_i and certified C_{cert} contents of the elements i in the SSS should be connected with the specific conditions of analysis, due to the limited mass of the material under study. For this reason, the material being analyzed was placed in the cuvettes the organic window of which was about 0.1 mm thick instead of 6 mm, used in the standard cuvettes attached to the spectrometer. As it has been noted above, larger values of V_a are connected with the fact that under these conditions, the standard- background method takes into poor consideration the effects of absorption. Furthermore, in some SSS the content of Pb and Ni was less than the detection limit C_{min}, and in the others - they were at the level of C_{min}, which also led to the increase of values V_a. The obtained values of V_a do not provide a basis for conclusions about the inaplicability of the XRF method for controlling the content of the inorganic components in the material of IPSC.

The conducted studies show that if the XRF method is to be planned for estimating the contamination of the territory, it is necessary to change the selection criteria of snow samples. Sample site of 1 m^2 in size is not enough, its size should be considerably increased. In the controlled area it should be organized several sites of 1 m^2 and selected the snow from each of them. The number of sites depends on the snow cover depth and indicative information about the dust load of snow on the controlled territory.

The developed methods of X-ray fluorescence analysis of the samples of limited mass was used for detection of the metals in the samples of IPSC, selected in the city of Kyzyl. To analyze greater number of the samples from the selected, we decided to put the material of IPSC of 0.3 and 0.1 g into civettes. The latter mass is allowed to use, based on the inaccuracies of preparation of radiators V_{rad} from the material of less than 0.3 g and the obtained values of V_a.

The content of Pb, Zn and Ni was assessed in the samples. Calibration curves were built by means of the SSS of soils and sediments using the method of direct external standard, but the measured intensities of analytical lines corrected background intensity $I_{фр}$ according to the method mentioned above.

Each sample in the laboratory precision conditions has been analyzed twice, and, from the results, the point estimate (coefficient of variation $V_{Rл}$) of laboratory precision for Pb, Zn and Ni has been calculated (Table. 3)

Table 3. Estimates of metrological performance (MP) for the samples of IPSC

The estimated elements	Estimates of MP for the mass of radiator			
	m = 0,3 g		m = 0,1 g	
	$V_{Rл}$, %	C_{min}, %	$V_{Rл}$, %	C_{min}, %
Pb	8,4	0,008	17	0,01
Zn	3,1	0,005	9,9	0,007
Ni	6,1	0,007	9,6	0,009

On the basis of the obtained results of estimation of Pb, Zn and Ni, we have evaluated the degree of contamination (H_c) of the controlled territory with these elements by the formula $H_c = C_i/C_{mpa}$, where C_i, $C_{mpa\ i}$ – the content of element *i* in the sample and its maximum prohibitive amount (MPA) in mg/kg, respectively (Table 4). Since the standards of MPA for heavy metals in IPSC are absent, the values of the obtained concentration have been compared with the JDC for the soils, which for Pb, Zn and Ni are equal to 0,0032, 0,0055 and 0,0020%, respectively [16].

As one can see from Table 4, pollution index ranges from 1.7 to 12.2 for Pb; from 2.2 to 54.5 for Zn; from 5.5 to 9.5 for Ni. The obtained information indicates a high level of contamination of the snow cover of the territory of Kyzyl by high density metals, which indicates the need for organization of close monitoring of their content in order to identify sources of pollution and work out measures on reduction o emissions.

Table 4. Pollution rate of the snow cover with heavy metals for the territory of Kyzyl

Samples	Values of H_C for the elements		
	Pb	Zn	Ni
1	1,9	10,4	7,0
2	3,4	8,1	9,0
3	3,7	16,0	9,5
4	5,1	16,2	7,5
5	12,2	10,0	7,5
6	0,6	14.4	8,0
7	3,1	7,3	7,5
8	7,5	14,7	7,5
9	4,1	8,0	8,5
10	5,3	54,5	7,5
11	1,9	6.4	6,7
12	12,2	5,8	8,5
13	2,5	27,3	6,0
14	6,9	7,6	7,5
15	2,5	14,1	8,5
16	2,5	2,2	7,5
17	0,5	5,5	6,3
18	1,7	4,5	6,0
19	4,1	9,3	8,0
20	5,3	10,0	7,5
21	3,4	8,1	7,0
22	4,1	10,1	7,5
23	4,4	11,1	7,5
24	3,4	10,7	5,5
25	3,4	10,5	5,5
Note: The remaining 25 samples have not been analyzed due to their limited material			

SUMMARY

Thus, the researches on the development of X-ray fluorescence analysis of insoluble precipitation of snow cover were conducted. The samples of snow were first thawed out, then filtered to separate IPSC out. It is recommended to pre-determine the dust load, and then choose the area of snow selection in order to obtain a sufficient mass of material for XRF analysis of IPSC. It was estimated metrological characteristics of the developed method of XRF analysis of IPSC: the coefficients of variations and defining minima; their values proved to be satisfactory. By means of the elaborated methods, the degree of pollution of snow cover in Kyzyl was evaluated. As to the concentration of Pb, Zn and Ni, the IPSC samples turned out to be contaminated.

CONCLUSION

The possibility of using X-ray fluorescence method for the determination of heavy metals in samples of the restricted mass has been estimated. It has been shown that the cuvette made for these purposes does not allow to use the radiation scattered by the sample, for accounting the absorbing characteristics of the samples. The contents of Pb, Zn and Ni in the samples of IPSC selected in Kyzyl have been determined. A substantial degree of contamination of the territory has been estimated. Recommendations on snow sampling for environmental monitoring by using X-ray fluorescence method to control heavy metals in the IPSC material have been given.

ACKNOLEDGEMENTS

The work is performed within the framework of government order № 2014/51 in the scope of scientific work as a part of basic state order of the Ministry of Education and Science of Russia (№ RSW 3838).

REFERENCES

[1] Korolyeva G. P. Geochemical research of atmospheric precipitations. Estimate of ecological state of environment (the Irkutsk region) / G.P. Korolyeva, M.S. Kholodoyeva. – The Publisher: LAP Lambert Academic Publishing, Germany, 2013. – 67 p. – ISBN 978-3-659-42549-3.

[2] Shevchenko V.P. Distribution and composition of insoluble particles in snow in the Arctic / V.P. Shevchenko, A.P. Lisitsyn, R. Stein and the others // The Problems of the Arctic and the Antarctic. – 2006. – №75. – P. 106-118.

[3] Vasilenko N.V. Monitoring of snow contamination / N.V. Vasilenko, I.M. Nazarov, Sh.M. Fridman. – L.: Hydrometeorological publishing, 1985. – 354 p.

[4] Onishchuk N.A. Elemental composition of atmospheric precipitations in the territory of Lake Baikal / Onishchuk N.A., Khodzher T.V. // Optics of Atmosphere and Ocean. – 2009. – V. 22. – № 6. – P. 579-584.

[5] Raputa V.F. Experimental investigation and numerical analysis of the processes of spread of contamination of the snow cover in the environs of superhighway / V.F. Raputa, V.V. Kokovkin, S.V. Morozov // Chemistry in the interests of sustainable development. – 2010. – V.18. – P. 63-70.

[6] Pavlov V. Ye. The study of aerosol precipitations of polyaromatic carbohydrates within sphere of influence of Barnaul / V. Ye. PavlovПавлов, S.V. Morozov, V.F. Raputa and the others // Chemistry in the interests of sustainable development. – 2011. – V. 19. – P. 287-294.

[7] Kokovkin V. V. The research of the processes of regional pollution of snow by the cities of the South of Western Siberia / V.V. Kokovkin, V.F. Raputa, A.N. Romanov and the others // The Polzunov Herald. – 2011. – № 4-2. – P. 89-93.

[8] Kizilshnein L. Ya. Silica-alumina microspheres of ash of dust coal firing / L. Ya. Kizilshnein, A.L. Shpitsgluz, V.G. Rylov // Chemistry of solid propellant. – 1987. – № 6. – P. 122-126.

[9] Ivanov A.V. The intensity of fallout of fine-dispersed cosmic matter onto the Earth / A.V. Ivanov, К.P. Florensky // Geochemistry. – 1970. – № 11. – P. 1365-1372.

[10] Kara-sal I.D. Assessment of ecological and geochemical state of the territory of Kyzyl (The Republic of Tyva): the author's abstract of dissertation …. Candidate of Geographic Science: 25.00.36. – Tomsk, 2012. – 23 p.

[11] Ondar U.V. Investigation of snow pollution of the city of Kyzyl / U.V. Ondar, Khovalyg A.A., O.Ch. Oorzhak // The materials of the 1st international theoretical and practical conference for young scientists, postgraduates and students «The pressing issues of ethnoecological and ethnocultural traditions of the peoples of Sayano-Altai», Kyzyl, June 28 - July 2, 2012. – P. 258-259.

[12] Korzhova Ye. N. Определение неорганических загрязнителей в аэрозолях воздуха / Ye.N. Korzhova, O.V. Kuznetsova, A.N. Smagunova, M.V. Stavitskaya // The Journal of Analytical Chemistry. – 2011. – V. 66, № 3. – p. 228-246.

[13] GD 52.04.186-89. Guidance document on air pollution monitoring. – M. 1991. – 409 p.

[14] SS 269229-94. Raw materials and foodstuff. Sample preparation. Mineralization for detection of toxic elements. – M.: Standardinform, 2010. – 12 p.

[15] SS 17.4.3.03-85. Protection of nature. Soils. General requirements for the methods of determination of polluting substances. – M.: Standardinform, 2008. – 2 p.

[16] Approximately acceptable concentrations (AAC) of chemical substances in soil: Hygienic regulations. – M.: Federal center for hygiene and epidemiology of Russian Consumer Federation, 2009. – 10 p.