УДК 551.52

ATMOSPHERIC AEROSOLS AND POSSIBILITIES OF THEIR ANALYSIS FOR ELEMENTAL CONTENT AT THE IBR-2 REACTOR

V.F.Peresedov

Analytical possibilities of neutron activation analysis for studying the elemental content of atmospheric aerosols at the IBR-2 reactor are discussed on the basis of the experimental results on concentrations of nearly 40 elements in the air of two, namely, a remote and an industrial Siberian regions. Methodological aspects of the use of small-pore filters, the influence of their background trace-element contents on the sensitivity of NAA, the reliability of the results, as well as preferable strategy of atmospheric aerosols sampling are discussed.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

Атмосферные аэрозоли и возможности анализа их элементного состава на реакторе ИБР-2

В.Ф.Переседов

На основе экспериментальных результатов количественного определения около 40 элементов в атмосферном воздухе двух регионов Сибири — фонового и промышленного — обсуждаются аналитические возможности использования нейтронного активационного анализа (НАА) для изучения элементного состава атмосферных аэрозолей на реакторе ИБР-2. Рассматриваются методические вопросы использования мелкопористых фильтров, влияния содержащихся в них микропримесей на чувствительность НАА, надежности получаемых результатов, а также предпочтительная стратегия отбора образцов.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

Most important goals of environmental monitoring are the estimation of the state of the environment, prognosis and elaboration of scientifically grounded recommendations for rational use of natural resources. For reliable estimates numerical data on pollutant contents in atmospheric air, soil, vegetation, water, etc., are needed. Moreover, it is necessary to known the elemental content of atmospheric aerosols, because often their contribution to contamination of the environment exceeds the allowed limit. Significant influence of atmospheric aerosols on the quality of the environment, human health, and the vegetable and animal world is caused by their characteristics, including the wide spectrum of sizes, chemical and ionic compositions, and the character of the quantitative elemental

distributions of aerosol particles of different sizes and their concentration levels in atmosphere.

Nowadays, systematic complex studies of aerosols and their influence on the environment have become an important scientific problem in connection with increasing technogenic impact on the environment. In atmosphere, aerosols of different origin experience intense intermixing and complex physical-chemical transformations. As a consequence, identification of the sources of atmospheric pollution and estimation of their emission power are difficult. Without knowing the emission power it is impossible to obtain reliable quantitative estimates of the aerosol contribution to the processes responsible for changes in the climate and the quality of the environment.

The developed mathematical methods and the measured spectra of aerosol sizes together with the obtained quantitative contents of elements in aerosols allow one to describe complex processes of their transformation and drifting, determine the sources and estimate their power, calculate the space-time fields of the concentrations of contaminating elements, and estimate the state and the quality of the environment.

Experimental

In these investigations an important stage is the accumulation of reliable and representative data on the content of trace-elements in the atmospheric air of different regions. The content of unbasic (trace) elements in atmospheric air is significantly lower than their content in such biomonitors as soil, vegetation, etc. Usually, sampling of atmospheric aerosols over a wide spectrum of sizes and masses is realized by aspiration of atmospheric air through small-pore filters using cascade impactors. As a result, the necessary amount of elements for the related analytical method can be accumulated on the corresponding filter of the impactor. Only analytical methods which provide high sensitivity, reliability, and selectivity can be successfully used for the analysis of atmospheric aerosols. This is especially important when samples of very clean atmospheric air or fractions of aerosols with low contents in the spectrum of masses are analysed.

Over the last years, a large number of aerosol samples collected by specialists from the Institute of Chemical Kinetics and Combustion (ICKC) SB RAS in different Siberian regions were analysed in the NAA department [1—3]. The obtained results confirmed the possibility of reliable determination of nearly 30-40 elements in coarse and submicronic aerosols.

Analytical possibilities of the NAA for these studies at the IBR-2 reactor are the subject of this work. The IBR-2 reactor is equipped with irradiation channels allowing the irradiation of samples with high neutron fluxes using a pneumatic facility. We apply NAA procedures for short-, medium-, and long-life nuclides. The identification of the elements is done over a wide spectrum of nuclides. The neutron spectra from the IBR-2 reactor contain thermal, epithermal, and fast neutrons [4] and allow two regimes of sample irradiation, i.e., irradiation with thermal, epithermal and fast neutrons and epithermal and fast neutrons. In the first regime, the sensitivity of the analysis is higher for Na, Al, Si, S, Cl, K, Sc, Ca, Cr, Ti, V, Mn, Co, Fe, Cu, Zn, La, Ce, Pr, Nd, Eu, Gd, Dy, Lu, Os, and Pt. In the second regime it is higher for F, Mg, Ga, Ge, Se, As, Br, Sr, Rb, Y, Zr, Nb, Ru, Mo, Tc, Rh, Cd,

Pd, Ag, In, Sn, Te, Sb, I, Ba, Cs, Pr, Sm, Tb, Ho, Tm, Er, Hf, Yb, W, Ta, Re, Ir, Hg, Au, Th, and U. The specifics of the neutron energy spectrum and the possibility of sample irradiation in two regimes (with and without Cadmium) allow one to provide the selectivity of the analysis relative to the elements interesting for aerosol studies. This is also important for the identification of the majority of their sources.

Determination of the net content of elements in atmospheric air requires that the background content of trace-elements in blank filters was subtracted. Therefore, reliable determination of the content of elements in blank filters is important. If dispersion of elements in blank filters is not high, subtraction and determination of the concentration of elements in atmospheric air will be more reliable. Often, dispersion is significantly high. For the F1 and F2 filters discussed below its mean value is ≈ 30%. The value of dispersion strongly depends on the technology of the filters production. In the studies of atmospheric aerosols the choice of a suitable filter for NAA with a low content of trace-elements is important. It is even better if a blank filter does not contain significant amounts of the elements whose nuclei are very strongly activated and can create an excessive Compton background and, as a result, significantly reduce the NAA sensitivity. The use of filters effectively adsorbing aerosols over a wide range of their sizes is most preferable in the analysis of their different fractions. Some errors of the analysis can be reduced if identical filters are used in all stages of cascade impactors.

In the general case, when the concentrations of elements in the samples are not very high, it is most desirable that the ratio of the element's amount accumulated from air to its amount in the blank filter $R_i = m_i / m_{i,0}$ (m_i is the mass of the i-th element) is high. An increase in $m_i = n_i \cdot V_{\text{air}}$ can be provided by aspiration of larger volumes of air (n_i is the concentration of the i-th element in air). However, sometimes excessive m_i amounts are undesirable because nuclides of the corresponding elements can significantly reduce the sensitivity. In practice, the accumulated m_i depends on a particular problem (study of hourly, daily, weekly, or monthly variations of the content of elements in air) and on the contamination level in air. Usually, analysts have to deal with a wide range of R_i.

Results and Discussion

The NAA of atmospheric air samples was fulfilled with the use of different small-pore filters. The characteristics of two of them, F1 and F2, and the regimes of air aspiration are presented in Table 1. The average concentrations of elements in blank F1 and F2 home filters were determined and are shown in Columns 1-2 in Table 2. Ten filters of each type were analysed.

Table 1. The characteristics of F1 and F2 filters and the regimes of air aspiration

	S	m	V_{air}	V_{air}/S	V/t
F1	0.5—2 cm^2	5—10 mg	20 m^3	10—40 m^3/cm^2	0.8 m^3/hour
F2	50 cm^2	150—200 mg	200 m^3	4 m^3/cm^2	8 m^3/hour

Table 2

	Concentr. in F1 (ppm)	Concentr. in F2 (ppm)	Content, ng per filter [5]	$R_{1,i}$	$R_{2,i}$	Remote reg. (ng/m^3)	Industr. reg. (ng/m^3)
Na	9.01E+1(32)	≤ 2.0E+2	160–9700	18	4	5.91E+2(21)	7.04E+2(30)
Al	9.38E–0.25)			97		3.38E+2(38)	
Mg	≤ 5.0E–0		28–1600	≥ 90		1.75E+2(31)	
Cl	1.17E+2(30)	1.10E+5(14)		8.6		3.77E+2(25)	
K	≤ 1.3E+1	≤ 3.3E+3		≥ 200	≤ 3	1.06E+3(37)	3.61E+3(70)
Ti	≤ 2.0E–0	≤ 3.0E+1		≥ 1000	≥ 100	7.87E+2(63)	2.65E+3(34)
Mn	3.55E–0(16)		< 2	13		1.78E+1(40)	
Sc	2.70E–3(25)	2.80E–2(15)		96	36	9.70E–2(42)	8.90E–1(42)
Cr	1.34E–0(18)	1.05E+1(35)	7–320	12	≤ 3	5.90E–0(66)	8.48E–0(56)
Ni	9.96E–1(21)	5.67E–0(13)	< 5	13	≤ 3	5.10E–0(45)	2.68E–0(71)
Fe	2.61E+1(33)	1.16E+2(20)	< 1000	15	14	1.45E+2(62)	2.60E+3(46)
Co	2.12E–1(17)	7.26E–1(50)	< 0.5	11	≤ 3	8.60E–1(80)	9.20E–1(48)
Cu	≤ 9.5E–0		5–60	≥ 20		7.41E+1(27)	
Zn	1.68E–0(23)	8.85E—0(43)	3–330	116	4.5	7.30E+1(82)	3.33E+1(24)
Se	1.11E–1(31)	≤ 5.0E–2					1.74E–0(51)
As	2.62E–2(36)	≤ 3.1E–0	< 5	37	5	3.60E–1(75)	1.41E+1(41)
Br	4.11E–1(27)	2.18E+2(10)		10	≤ 3	1.60E–0(45)	6.54E+1(31)
Sr	≤ 1.5E–1	≤ 3.7E–1	0.1–16		≥ 70		2.31E+1(33)
Rb	2.49E–2(42)	2.84E–1(10)	< 1	280	90	2.60E–0(54)	6.11E–0(42)
Zr	≤ 3.0E–1	≤ 1.4E–0			≥ 28		3.42E+1(47)
Mo	6.00E–2(60)	≤ 8.1E–1	< 1	44	≤ 3	1.00E–0(62)	2.04E–0(70)
Ag	7.30E–2(15)	1.26E–1(35)		12	≤ 3	3.40E–1(94)	2.05E–1(85)
Sn	1.20E–0(30)	≤ 4.0E–1			≥ 120		4.21E+1(59)
Cd	1.26E–2(76)	≤ 1.5E–0		100	5	4.70E–1(27)	6.70E–0(72)
Sb	1.50E–2(27)	1.96E–1(22)		7	7	3.90E–2(18)	1.38E–0(51)
Ba	4.32E–1(33)	5.30E–0(32)	2–10	47	9	7.70E–0(46)	4.10E+1(40)
Cs	1.97E–3(15)	1.18E–2(21)	< 0.3	40	36	3.01E–2(55)	3.70E–1(42)
La	3.75E–1(58)	1.44E–0(22)	< 0.3	≥ 3	≤ 3	5.80E–2(95)	2.92E–0(44)
Ce	8.76E–1(46)	4.77E–0(66)			≤ 3		5.60E–0(43)
Nd	6.71E–1(55)	≤ 6.5E–1			≥ 13		7.65E–0(38)
Sm	7.67E–4(22)	1.56E–2(50)		70	25	2.03E–2(53)	3.43E–1(43)
Eu	6.97E–3(20)	9.87E–2(45)		40	4.5	1.08E–1(48)	3.93E–1(40)
Tb	1.85E–3(68)	9.53E–3(25)		≥ 28	6	< 2.0E–2	4.84E–2(48)
Yb	1.20E–2(30)	≤ 1.5E–2			≥ 35		4.58E–1(63)
Hf	≤ 4.0E–3	5.05E–2(25)			13		4.49E–1(44)

	Concentr. in F1 (ppm)	Concentr. in F2 (ppm)	Content, ng per filter [5]	$R_{1,i}$	$R_{2,i}$	Remote reg. (ng/m^3)	Industr. reg. (ng/m^3)
Ta	8.77E–4(68)	2.11E–3(30)		70	36	2.30E–2(45)	6.69E–2(37)
W	1.75E–1(37)	7.00E–0(31)		12		8.10E–1(64)	
Au	2.08E–3(25)	1.20E–2(42)		14	≤ 3	1.10E–2(63)	5.80E–3(33)
Th	1.53E–3(47)	1.90E–2(15)	< 0.1	100	40	5.90E–2(41)	6.65E–1(38)
U	2.73E–3(16)	≤ 2.1E–1	< 0.1	36	≤ 3	3.71E–2(25)	4.23E–1(20)

In brackets ( ) — confidence intervals in percents.

The content of elements in a clean and more expensive F1 blank filter is sufficiently low and is comparable with the quantitative content of some other ones [5] (clm.3, Tab.2). The contents of elements in the F1 filter do not cause any trouble to NAA of aerosol samples. This explains frequent use of F1 filters in the study of atmospheric aerosols. The element concentrations in the second F2 filter which is not expensive are higher for most elements, especially, for Cl and Br ($\approx 10^5$ and ≈ 220 ppm). Because of a very high content of Cl, the NAA of short-life nuclides is practically impossible. The nuclide of Br^{82} with medium half-life of 35 hours emits several strong gamma-lines. A high level of its Compton background reduces the sensitivity or makes it impossible to determine elements with the use of nuclides with medium half-lives, such as Na^{24}, K^{42}, Ca^{47}, Sc^{48}, Ni^{57}, Cu^{64}, Zn^{69m}, Ga^{72}, As^{76}, Ge^{77}, Zr^{97}, Mo^{99}, Pd^{109}, Cd^{115}, Sb^{122}, La^{140}, Pr^{142}, Ce^{143}, Eu^{152m}, Sm^{153}, Gd^{159}, Ho^{166}, Er^{171}, Yb^{175}, Lu^{177}, Re^{186}, Re^{188}, W^{187}, Pt^{191}, Os^{191m}, Ir^{194}, Hg^{197}, Pt^{197}, Hg^{197m}, Au^{198}, Pb^{203}, Np^{239}. The data obtained with F2 filters are discussed in this paper to find how results depend of unfavourable quantitative element contents in blank filters or, in similar circumstance, an excessive abundance of Br in atmospheric air ($n_{Br} \approx 220$ ng/m^3).

The concentrations of elements in atmospheric air of two, a remote and an inductrial (not highly comtaminated), Siberian regions were obtained using F1 and F2 filters (clms.6—7, Tab.2). The concentrations are the result of averaging over 25 samples of daily aspirated atmospheric air from both regions. In accordance with these data the content of elements in the air of the industrial region is higher. The number of the elements determined with the use of medium-life and long-life nuclides do not differ significantly for these regions. Some elements were determined quantitatively using the medium-life nuclides, as Na^{24}, K^{42}, As^{76}, Mo^{99}, Cd^{115}, Sb^{122}, La^{140}, Sm^{153}, Au^{198}, and U(Np^{239}) in the air of the industrial region. The $R_{1,i}$ and $R_{2,i}$ (clms 4—5, Tab.2) determined as a ratio of the accumulated net concentration of the i-th element to the background concentration in blank F1 and F2 filters show that $R_{2,i}$ are systematically lower than $R_{1,i}$. Some $R_{2,i}$ are low (less than 10). This indicates a decrease in the reliability of quantitative determination of the corresponding elements.

Decreasing of reliability is caused by significantly higher concentrations of some elements in blank F2 filters and longer confidence intervals for some of them. More reliable data on element contents in blank F2 filters and significantly shorter confidence intervals are required not to make the concentrations of these elements in atmospheric air too high.

However, it is an established fact that there exists the real possibility of determination of the content of nearly 30 elements in atmospheric air using filters with a high Br concentration in the conditions similar to those of a high content of Br (or some other elements, such as La, As, Mo, Sb, W, U, etc., with medium-life nuclides) in air. This is certainly connected with the right choice of sampling conditions, i.e., aspiration of large volumes of air through F2 filters (and also with a higher content of elements in the air of the industrial region).

Table 3

	Det. Lims. with F1 and F2 filters, (ng/m^3)	South Pole [7], (ng/m^3)	Highly contaminated. regs. [6], (ng/m^3)
Na	1.2 – 22	3.3E – 0	200–1200
Al	0.5 – 660	0.82	600–1500
Mg	1.2 – 33000	0.73	100–2600
Cl	0.5 – 290	2.4	200–7000
K	105 – 1800	2.4	400–4000
Ti	> 0.5	0.1	80–140
Mn	0.05 – 330	0.012	30–390
Sc	0.00093 – 0.0037	0.00016	0.2–1.3
Cr	0.13 – 0.5	0.04	5–590
Ni	0.029 – 0.13		10–300
Fe	2.5 – 11	0.62	500–8100
Co	0.0017 – 0.0062	0.0005	0.5–3.1
Cu	280 – 910	0.03	10–350
Zn	0.033 – 0.13	0.033	80–1200
Se	0.0033 – 0.032	< 0.8	1–20
As	0.0034 – 0.19	0.031	2–4
Br	0.0022 – 0.28	2.6	4–30
Sr	0.11 – 0.43	0.052	20–50
Rb	0.012 –0.045	0.002	2–20
Mo	0.0063 – 0.52		1–10
Ag	0.0023 – 0.0055	< 0.0004	1–10
Sn	0.093 – 0.31		1–20
Cd	0.013 – 1.0	< 0.015	2–20
Sb	0.0004 – 0.0013	0.0008	0.5–10
Ba	0.20 – 0.45	0.016	30–100
Cs	0.0004 – 0.0015	0.0001	0.2–10
La	0.0023 – 0.095	0.00045	0.6–12
Ce	0.024 – 0.19	0.004	1–30
Sm	0.00013 – 0.0081	0.0001	0.1–2.8

	Det. Lims. with F1 and F2 filters, (ng/m^3)	South Pole [7], (ng/m^3)	Highly contaminated. regs. [6], (ng/m^3)
Eu	0.0018 – 0.0086	0.00002	0.1–10
Tb	0.00024 – 0.0011		
Yb	0.0027 – 0.017	< 0.05	0.04–0.6
Hf	0.0018 – 0.0065	0.00006	
Ta	0.00018 – 0.00054	0.00007	0.04–0.2
W	0.0073 – 0.44	0.0015	0.7–20
Au	0.00004 – 0.0017	0.00004	0.01–0.5
Hg	0.015 – 0.66	0.17	0.5–10
Th	0.00043 – 0.0018	0.00014	0.1–3.0
U	0.001– 0.093		0.1–0.3

However the advantage of using filters with lower element contents is considerable. Lower concentrations of elements in the atmospheric air of the investigated remote region were determined with F1 filters in the regime of small-volume air aspiration in field conditions. The comparison of the detection limits (clm.1, Tab.3) obtained with F1 and F2 filters confirms this fact. With the F1 filter, a significantly higher sensitivity of the analysis using short-life (Al^{27}, Mg^{27}, Cl^{38}, Mn^{56}, Cu^{64}, etc.) and medium-life (Na^{24}, As^{76}, Mo^{99}, Cd^{115}, Br^{82}, La^{140}, Sm^{152}, Au^{198}, Np^{239}) nuclides can be achieved (200–10^4 and 30-500 times higher, respectively). These detection limits demonstrate the possibilities of the analysis for two cases, i.e., favourable and unfavourable, in which the advantages of NAA as an analytical method can be realized to a more or less significant extent. The conditions of analysis in these cases can be conventionally called the «Soft» and «Hard» regimes.

The following general conclusion can be made on the basis of these results. The «Soft» regime is most productive for the reliable determination of the majority of elements in case of their low contents in atmospheric air. Therefore, the strategy of sampling and NAA must be oriented to the realization of a more preferable «Soft» regime. This means that for the determination of contents in highly contaminated air not excessive (optimal for NAA) quantities of elements must be accumulated on filters. The concentrations of elements in a highly contaminated air of industrial regions [6] are examplified in clm.3, Tab.3. In the analysis of clean (or very clean) air it is desirable to accumulate the quantities of elements reliably exceeding their contents in blank filters. However, the use of optimal aspiration conditions and NAA cannot guarantee the reliable determination of low concentrations of some elements in the presence of some other elements, whose concentrations are significantly higher. In such a case, NAA is not a panacea and the concentrations of these elements can be determined by other analytical methods.

The results of determination of the content of elements in atmospheric air in the South Pole [7] (clm.2, Tab.3) confirm the importance of the realization of optimal strategy. Suitable conditions for sampling and NAA were maintained by these authers and allowed them to obtain very good results, namely, to determine low concentrations of trace-elements in Antarctic air.

reactor allows one to achieve a high sensitivity of analysis due to large cross sections of a significant part of medium and heavy nuclei in the epithermal neutron energy region and lower activation of nuclei with low resonance integrals if the irradiation in Cadmium is used.

Conclusions

In NAA study of the quantitative content of atmospheric aerosols with a wide spectrum of sizes the NAA analytical possibilities must be realized in full extent. The number of the analysed elements and the reliability of obtained results are determined by many factors and strongly depend on the main ones, i.e., individual content of elements in samples of atmospheric aerosol, the small-pore filters used, and the regimes of air aspiration and NAA.

The author is grateful to collaboration from the Institute of Chemical Kinetics and Combustion of SB RAS, Prof. K.P.Koucenogii, and collaborators from the Frank Laboratory of Neutron Physics, T.M.Ostrovnaya, S.F.Gundorina, V.P.Chinaeva for their help on the project, and to T.F.Drozdova for help in the preparation of the English version of this manuscript.

References

1. Koutzenogii K.P., Valendik E.N., Bufetov N.S., Ivanova G.A., Peresedov V.F. — IV Russian-French Seminar on the Applications of Neutrons and Synchrotron Radiation for Condensed Matter Investigation. Novosibirsk—Irkutsk, Russia, June 25 — July 3, 1996. JINR, E14-96-191, Dubna, 1996.
2. Koutzenogii K.P., Efremov S.P., Efremova T.T., Peresedov V.F. — Ibid.
3. Koutzenogii K.P., Smirnova A.I., Peresedov V.F. et al. — Atmospheric and Oceanic Optics, 1997, v.7, No.6, p.1–9.
4. Peresedov V.F., Rogov A.D. — Journ. of Radioanal. and Nucl. Chem., 1996, v.214(4), p.277–283.
5. Berg T., Royset O., Steinnes E. — Atmospheric Environment, 1993, v.27A(15), p.2435–2439.
6. Pushkin S.G., Michailov V.A. — Comparative Neutron Activation Analysis: Study of Atmospheric Aerosols. Science, Siberian Branch. Novosibirsk, 1989.
7. Maenhaut W., Zoller W.H. — Journ. of Radioanal. and Nucl. Chem., 1977, v.37, p.637–650.

Received on May 30, 1997.