Acta Physica Universitatis Comenianae
Vol. XLVI–XLVII, (2005–2006) 73–82

Concentration of Elements in Atmospheric Aerosol in Bratislava

J. Merešová[1], M. Florek[1], K. Holý[1], I. Sýkora[1],
M. V. Frontasyeva[2], S. S. Pavlov[2]

[1]Department of Nuclear Physics and Biophysics, Comenius University, Bratislava, Slovak Republic
[2]Frank Laboratory of Neutron Physics, JINR, Dubna, Russia

Abstract: The concentrations of 41 chemical elements (heavy metals, rare earths, and actinides) were determined in atmospheric aerosol using nuclear and related analytical techniques. The sampling location was in Bratislava (Slovak Republic). The main goal of this study is the quantification of the atmospheric pollution and its trend. The elemental content in filters was measured using instrumental neutron activation analysis at IBR-2 reactor in JINR Dubna and by atomic absorption spectrometry in Bratislava. The obtained results confirm the decreasing trend of pollution by most of the heavy metals in Bratislava atmosphere, and they are compared with the contents of pollutants in atmosphere of other cities. We determined also the composition of clear filter materials.

1. Introduction

Atmospheric aerosols are submicron particles, on which the elements of solid or liquid state present in the air are captured. The aerodynamic size of aerosol determined the degree of biological effect on human organism. Aerosol particles are sorted according to their size into three modes:

(a) Aitken nuclei mode (from 0.003 to 0.07 m, average 0.015 m).
(b) Accumulation mode (from 0.07 to 2 m, average 0.3 m).
(c) Coarse mode (from 2 to 36 m, average >10 m).

Besides other elements aerosol particles contain heavy metals, too. Some heavy metals play important role in the nutrition of plants, animals or humans (Mn, V, Cr, Ni, Cu, Zn), but if they occur in excess, they may produce toxic effects. The others (Cd, Hg, Pb) are toxic even in very low contents. Heavy metals are released to the environment from a great number of sources like different industrial activities or combustion of fossil fuels. These elements are components of traffic emissions and they are emitted into atmosphere in form of fine dust and aerosols. Velocity of dry deposition of heavy metals in atmospheric aerosols is usually less than 0.5 cm.sec ^{1} and the medium residence time is supposed to be about 5 days [1]. Airborne soil particles, volcanic aerosols and forest fires contribute to natural emissions of trace elements. The current anthropogenic metal emissions are up to several orders of magnitude higher than natural contents [2].

Nowadays several methods are available to determine elemental composition of matter. We had been using instrumental neutron activation analysis (INAA) to determine elemental content of atmospheric aerosol samples. Along with the relatively new analytical

techniques, like inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS), INAA is the most sensitive method for multi-element analysis. Each of these techniques has its own benefits and disadvantages. Main advantages of instrumental activation analysis (IAA) in connection to high-resolution gamma-ray spectroscopy are simultaneous multi-elemental determination. These contributed mainly to its extensive application in trace element analysis. It should be noted that INAA technique does not require sample dissolution, therefore it has a great advantage if the total concentration is the aim of the analysis. The main disadvantage of NAA is the high cost of the appropriate neutron source.

2. Experimental and Methods

The sampling location is at the Meteorological Station near the Faculty of Mathematics, Physics and Informatics (FMPI), Comenius University, Bratislava. Using the sampler device with an air-flow rate of 30 $m^3.h^{-1}$ aerosol particles are collected on the nitro-cellulose membrane filters (PRAGOPOR, pore size 0.85 m, the collection efficiency approximately 100 %). Two samplings were realised using the textile filters. The collection efficiency of this type of filters was evaluated to be approximately 80 %. Also the permeability of the textile filter was much larger than in the case of nitro-cellulose filter, therefore the total volume of pumped air was greater. The sampler device is situated at height of 2.85 m above the ground at the Meteorological Station near the FMPI. The filters are changed every week and about 3000 m^3 of air is pumped through each sample. In September 2004 the new sampling device was launched and the volume of pumped air increased twice.

Concentrations of elements were determined by instrumental neutron activation analysis (INAA) on pulsed fast reactor IBR-2 in FLNP JINR, Dubna, Russia. The experimental setup consists of four channels for irradiation (Ch1–Ch4) and the pneumatic transport system REGATA. It provides activation with thermal, epithermal and fast neutrons [3]. Two channels are cadmium screened for activation with epithermal neutrons [4]. Thermal NAA takes advantage of the high intensity of neutrons available from the thermalisation of fission neutrons and the large thermal neutron cross sections for most isotopes. Epithermal NAA (ENAA) is a useful extension of INAA in that it enhances the activation of a number of trace elements relative to the major matrix elements. Epithermal is taken to be neutrons with energies from the Cd cut-off of 0.55 eV up to approximately 1 MeV. In general, the activation cross sections of the matrix elements of environmental samples are inversely proportional to the neutron energy (1/v low). The trace elements also follow this general trend but many of them (rare earth elements in particular) have large resonance activation integrals at specific energies in the epithermal energy region.

Table 1. Characteristics of four irradiation channels of the experimental setup REGATA.

Irradiation site	Neutron flux density 10^{12}. F [$cm^{2}.s^{1}$]			T [^{0}C] Inside Ch	Ch diam. [mm]	Ch length [mm]
	Thermal	Epithermal	Fast			
Ch1	Cd-coated	3.31	4.32	70	28	260
Ch2	1.23	2.96	4.10	60	28	260
Ch3	Cd-coated	7.5	7.7	30 40	30	400
Ch4	4.2	7.6	7.7	30 40	30	400

The main parameters (for reactor's power 2000 MW) of the irradiation channels are presented in Table 1, where the temperature inside channels, the diameter and the length of channel *are shown*. The neutron flux density (for thermal or epithermal neutrons) inside channels is of the order of 10^{12} $cm^{2}.s^{1}$ [5]. The channels Ch3, Ch4 are cooled by water, and the channels Ch1, Ch2, connected with the pneumatic transport system, are cooled by air. That is reason why the temperature in channels Ch3 and Ch4 is lower than the temperature in channels Ch1 and Ch2 in spite of the greater neutron flux density. The time of sample irradiation in channels Ch3, Ch4 depends on the operation cycle duration of the reactor and is equal to 4–12 days. Each channel consists of two concentric pipes made from stainless steel. They are placed into an aluminium box filled with biological shield. Samples are transported through one of the pipes of 28 mm in diameter. Compressed air flows through the second pipe.

Filters were packed in polyethylene foil bags for short-term irradiation. Aluminium containers *were* used for long-term irradiation. Short-term irradiation preceded 3–5 min to determine short-lived isotopes. After a decay-period of 5 to 7 min the irradiated samples were measured twice, first for 3–5 and then for 10–15 min. A long-term irradiation of 4–5 days was used to measure long-lived radionuclides. After irradiation the samples were re-packed and measured twice, first after 4–5 days for 40–50 min and after 20 days for 2–4 hours. The induced activity was measured using -spectrometers with Ge(Li) or HPGe detectors and ORTEC electronics. Data processing was carried out using software developed in FLNP JINR [6], and element contents were determined on the basis of certified reference materials and flux comparators. The mentioned method can determine up to 45 elements [7]. The neutron flux is controlled by monitors (Au, Zr, etc.). The reduction of the neutron flux density along the channel length is gradual, but significant, up to 30–50 %. That phenomenon should be taken into consideration while data processing.

In addition the contents of Cr, Ni, Cu, Zn, Cd and Pb were determined using atomic absorption spectrometry at Institute of Geology at the Faculty of Natural Sciences, Comenius University, Bratislava.

3. Results and Discussion

Using INAA at IBR-2 reactor in Dubna with combination of AAS concentrations of 41 elements in 8 selected samples (Table 2) of atmospheric aerosol were determined. Table 3 presents which elements were determined using NAA (short-term or long-term irradiation

mode) or AAS methods. As and Sb were determined not only via short-term but via long-term irradiation, too. Ni and Zn were measured using NAA and AAS.

Table 2. Eight selected samples of atmospheric aerosol.

Date of the sample		Volume of air [m^3]	Type of filter
18.07.2001	16.7. 19.7.01	4274.2	nitro-cellulose
14.09.2001	11.9. 17.9.01	4419.4	nitro-cellulose
01.10.2001	28.9. 3.10.01	3505.5	nitro-cellulose
13.01.2004	7.1. 19.1.04	3507.7	nitro-cellulose
28.03.2004	12.5. 25.5.04	3555.7	nitro-cellulose
10.10.2004	6.10. 15.10.04	7582.5	nitro-cellulose
15.01.2005	13.1. 18.1.05	23195.2	textile
17.04.2005	14.4. 20.4.05	25554.3	textile

Table 3. Schedule of elements according to method of determination.

Method	Number of elements	Elements (Uncertainty of determination [%])
NAA short-term	15	Na (9), Al (8), Cl (11), K (6), Ca (20), Ti (24), V (8), Mn (6), As (14), Br (17), In (20), Sb (22), I (8), Dy (26), W (48), U (16)
NAA long-term	23	Fe (6), Co (20), Ni (34), Zn (7), As (16), Se (34), Rb (16), Sr (70), Zr (82), Mo (14), Ag (14), Sb (8), Cs (20), Ba (15), La (13), Ce (31), Sm (10), Gd(32), Tb (35), Hf (27), Ta (99), Au (16), Th (12)
AAS	6	Cr (6), Ni (6), Cu (2), Zn (10), Cd (10), Pb (3)

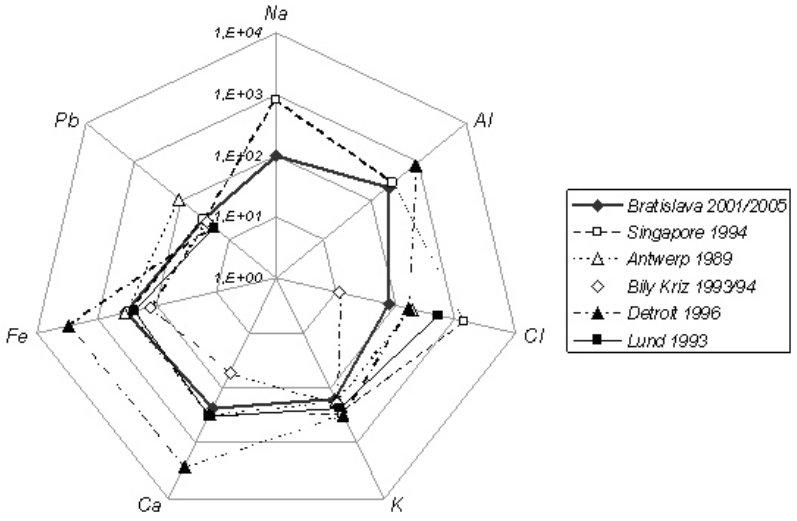


Fig. 1. Concentrations [ng.m ^{3}] of elements in atmospheric aerosol for six locations.

Table 4 shows average, median, minimum and maximum values of concentrations of 41 elements in atmospheric aerosol measured using the above mentioned analytical methods. Figs. 1–3 present the concentrations of elements in atmospheric aerosol for six locations. These results are presented in Table 5, too. Relatively low values comparing of Cl, Na and Br to the values from the coastal localities indicate the sea spray origin. The small contents of V, Ni and As can by attributed to weaker frequency of oil and coal combustion in Bratislava compared to other locations. Oil combustion is practically the only source of V, while Ni can be emitted also from a high quality steel production plants and Ni smelters [8]. Al, Ca and Ti are typically soil derived elements. Non-ferrous smelters are the sources of Zn, Cu, Cd and Pb. Cd and Pb are released into the environment also via fossil fuel combustion. The measured contents of almost all elements are lower in Bratislava comparing to other localities. It can be caused by the small number of sources of pollution near the sampling site. On the other side this location is typical with the high number of windy days per year.

Table 4. Average, median, minimum and maximum values of concentrations [ng.m ^{3}] of 41 elements in atmospheric aerosol determined from analyses of 8 filter samples.

Element	Average	Median	Minimum	Maximum
Na	100	83	47	253
Al	231	183	40	682
Cl	79	41	26	276
K	158	150	101	212
Ca	228	256	52	345
Ti	12	10	3	23
V	1.05	0.93	0.56	1.7
Cr	0.45	0.40	0.26	0.68
Mn	5.0	4.3	1.9	9.2
Fe	317	317	129	505
Co	0.10	0.10	0.04	0.16
Ni	0.68	0.56	0.39	1.08
Cu	5.9	5.1	4.3	8.3
Zn	28	25	20	45
As	0.51	0.48	0.21	0.83
Se	2.0	2.0	1.0	2.9
Br	2.59	2.34	0.68	4.07
Rb	0.75	0.75	0.42	1.08
Sr	1.08	1.08	0.65	1.52
Zr	3.96	3.96	1.65	6.27
Mo	0.35	0.35	0.27	0.42
Ag	0.104	0.104	0.029	0.179
Cd	0.098	0.108	0.068	0.120
In	0.0020	0.0016	0.0007	0.0046
Sb	1.01	0.90	0.33	2.29

Continued (Table 4)

I	1.15	1.12	0.79	1.65
Cs	0.058	0.058	0.035	0.081
Ba	4.2	4.2	1.7	6.6
La	0.35	0.35	0.17	0.53
Ce	0.39	0.39	0.10	0.68
Sm	0.028	0.028	0.006	0.050
Gd	0.31	0.31	0.06	0.57
Tb	0.0034	0.0034	0.0007	0.0061
Dy	0.017	0.014	0.010	0.036
Hf	0.027	0.027	0.009	0.046
Ta	0.0081	0.0081	0.0021	0.0140
W	0.37	0.13	0.09	1.46
Au	0.0011	0.0011	0.00078	0.0013
Pb	34	25	23	55
Th	0.045	0.045	0.009	0.080
U	0.018	0.016	0.010	0.031

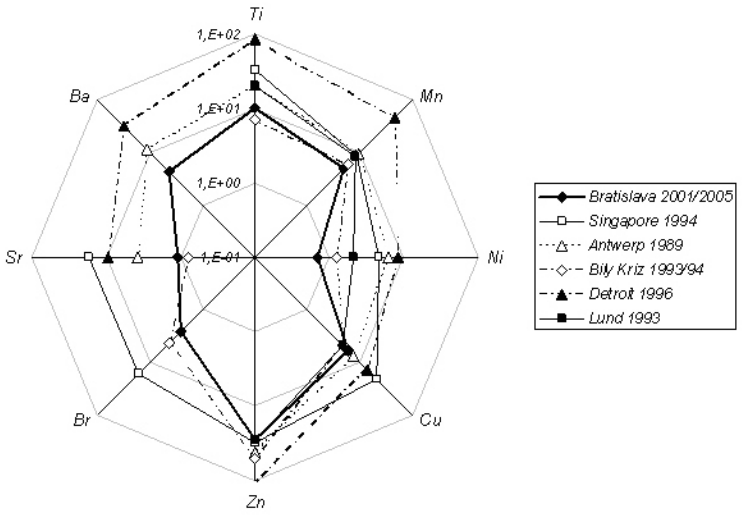


Fig. 2. Concentrations [ng.m ^{3}] of elements in atmospheric aerosol for six locations.

Table 5. Concentrations [ng.m ^{3}] of elements in atmospheric aerosol for six locations.

Element	**Bratislava Slovakia** 2001/2005 (this paper)	**Singapore Singapore** 1994 [9]	**Antwerp Belgium** 1986 [10]	**Bily Kriz Czech Rep** 1993/1994 [8]	**Detroit USA** 1996 [11]	**Lund Sweden** 1993 [12]
Na	100	802				
Al	231	281			861	
Cl	79	1376	190	11	163	514
K	158	280	170	191	313	224
Ca	228	303	300	54	2630	320
Ti	10.1	33.0	21.0	7.1	86.0	20.0
V	1.05	4.08	13.00	2.32	8.58	
Cr	0.446		2.100		2.730	21.580
Mn	4.97	8.63	9.60	5.87	45.20	8.37
Fe	317	296	330	130	3080	233
Co	0.100				0.320	
Ni	0.682	4.675	6.100	1.260	8.200	2.080
Cu	5.90	20.50	7.50	4.71	13.70	4.57
Zn	27.8	30.5	41.0	50.8	103.0	28.5
As	0.512		8.900	4.000	2.070	
Se	1.97		5.70	1.01		1.26
Br	2.59	16.08		4.12		
Rb	0.751	1.450			0.360	
Sr	1.08	17.20	3.80	0.78	9.59	
Mo	0.346				1.050	
Ag	0.104				0.048	
Cd	0.098				0.450	
Sb	1.01				1.81	
Ba	4.15		11.00		30.70	
La	0.353				0.530	
Ce	0.388				0.940	
Sm	0.028				0.071	
W	0.367				0.240	
Pb	34.2	33.8	110.0	28.7	21.5	19.8

Fig. 4 shows decreasing trend of air pollution by heavy metals (Mn, Cu, Zn, Cd and Pb) in Bratislava since the year 1981. The emissions of Pb have decreased, reflecting the shift from leaded to unleaded gasoline. The main reason of this decreasing trend is the decline of the industry production in Slovak Republic after the year 1989. The emissions of pollutants

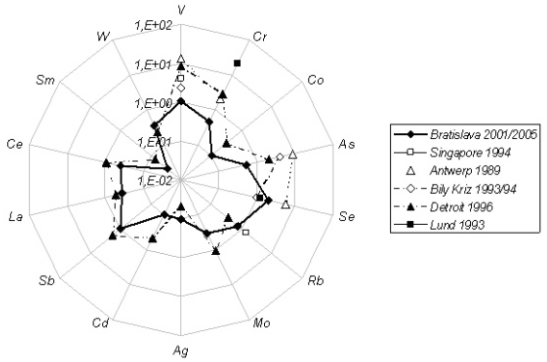
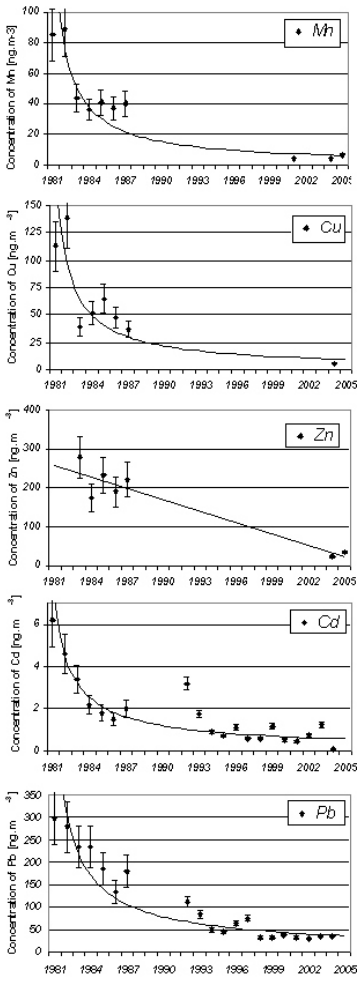


Fig. 3. Concentrations [ng.m ^{3}] of elements in atmospheric aerosol for six locations.



were reduced via application of more strict requirements in the environmental legislative, too.

We determined also the content of clear filters. Table 6 shows the concentrations of the measured elements in two different filtration materials, nitro-cellulose and textile. Because of the nitro-cellulose material this type of filter could not be irradiated in long-term mode. Therefore for the nitro-cellulose filters only the elements determined short-term irradiation and AAS are available. On the other side the textile filters were not measured using AAS.

The concentrations of elements in both analysed filtration materials are comparable within the bounds of uncertainties except for Al, Ti, In and W.
As the Fig. 5 shows, the concentration of these elements is much higher for the textile filter.

Fig. 4. Concentrations of Mn, Cu, Zn, Cd and Pb in atmospheric aerosol in Bratislava since 1981. The data of period 1981 1987 are from [1]; the data of period 1992 2003 for Cd and Pb are from [13]. Our data are marked by arrow.

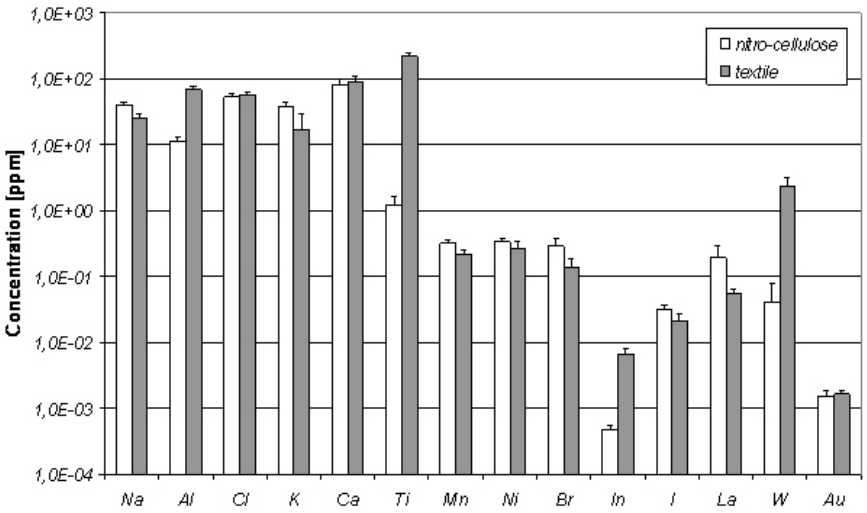


Fig. 5. Concentrations [ppm] of elements in two different types of filters used for sampling of atmospheric aerosol particles.

Table 6. Concentrations of elements [ppm] in two different types of filters used for sampling of atmospheric aerosol particles.

Element	Nitro-cellulose filter	Textile filter	Element	Nitro-cellulose filter	Textile filter
Na	39.4 ± 4.7	25.4 ± 3.5	**Zr**		0.808 ± 0.328
Al	11.3 ± 1.4	68.7 ± 7.0	**Mo**		0.0214 ± 0.0039
Cl	53.3 ± 6.2	57.0 ± 6.0	**Ag**		0.0215 ± 0.0031
K	38.2 ± 6.0	17.0 ± 12.4	**Cd**	0.0297 ± 0.0030	
Ca	81.8 ± 15.2	90.4 ± 19.8	**In**	0.0005 ± 0.00001	0.0066 ± 0.0015
Ti	1.24 ± 0.42	219.4 ± 26.2	**Sb**		0.0156 ± 0.0021
V	0.0119 ± 0.0038		**I**	0.0318 ± 0.0045	0.0210 ± 0.0061
Cr		8.32 ± 1.13	**Cs**		0.0034 ± 0.0008
Mn	0.321 ± 0.039	0.222 ± 0.037	**Ba**		0.672 ± 0.112
Fe		21.8 ± 3.6	**La**	0.192 ± 0.102	0.0555 ± 0.0076
Co		0.0877 ± 0.0122	**Ce**		0.131 ± 0.026
Ni	0.335 ± 0.034	0.262 ± 0.073	**Sm**		0.0027 ± 0.0003
Cu	1.24 ± 0.24		**Hf**		0.0063 ± 0.0015
Zn		2.30 ± 0.26	**Ta**		0.0076 ± 0.0030
Se		0.0973 ± 0.0247	**W**	0.0398 ± 0.0372	2.38 ± 0.80
Br	0.291 ± 0.084	0.137 ± 0.049	**Au**	0.0015 ± 0.0004	0.0017 ± 0.0002
Rb		0.0433 ± 0.0095	**Th**		0.0037 ± 0.0005
Sr		0.307 ± 0.086	**U**	0.0032 ± 0.0007	

4. Conclusion

The concentrations of chemical elements in Bratislava show typical values for European area. Comparing to other locations the most heavy metals exhibited the lowest concentration. Our data confirm the decreasing trend of atmospheric pollution by heavy metals (Mn, Cu, Zn, Cd, and Pb) in period of the last 20 years, too. The obtained data may be useful as a reference level for comparison with the future measurements of atmospheric pollution by heavy metals in Bratislava city.

Analyses of clear filtration materials (nitro-cellulose and textile) shown, that the concentrations of elements in both analysed filtration materials are comparable except for Al, Ti, In and W. Their concentrations are much higher for textile filters.

References

[1] M. Brezna, D. Zavodsky: Heavy Metals in Atmospheric Aerosols in the Region of Slovakia (in Slovak) Air Protection **6** (1989)144 148.
[2] E. Chmielewska, H. Spiegel: Some Control of an Amplified Heavy Metal Distribution at Immission Sites of Danube Lowland Refineries. Environment Protection Engineering **29** (2003) 23 32.
[3] M. V. Frontasyeva, S. S. Pavlov: Analytical Investigation at the IBR-2 Reactor in Dubna. Proceedings of the VII International Seminar on Interaction of Neutrons with Nuclei, Dubna, May 17 20, 2000, E3-2000-192, JINR (2000) 219 227.
[4] M. V. Frontasyeva, E. Steinnes: Epithermal Neutron Activation Analysis for Studying the Environment. Proc. Int. Symposium M.V. on Harmonization of Health Related Environmental Measurements Using Nuclear and Isotopic Techniques (Hyderabad, India, 4 7 November, 1996), IAEA (1997) 301 311.
[5] V. F. Peresedov, A. D. Rogov: Simulation and Analysis of Neutron Energy Spectra from Irradiation Channels of the IBR-2 reactor. J. Radioanal. and Nucl. Chem., Letters **214** (4)(1996) 277 283.
[6] T. M. Ostrovnaya, L. S. Nefedyeva, V. M. Nazarov, S. V. Borzakov, L. P. Strelkova: Software for INAA on the Basis of Relative and Absolute Methods Using Nuclear Data Base. In Proceedings "Activation Analysis in Environment Protection", D14-93-325, JINR, Dubna, (1993) 319 325.
[7] V. F. Peresedov: Atmospheric Aerosols and Possibilities of their Analysis for Elemental Content at the IBR-2 reactor. JINR Rapid Communications, No. 5[85]-97, Dubna, (1997) 43 50.
[8] E. Swietlicky, R. Krejci: Source Characterisation of the Central European Atmospheric Aerosol Using Multivariate Statistical Methods. Nuclear Instruments and Methods in Physics Research B 109/110. (1996) 519 525.
[9] I. Orlic, W. Bao, F. Watt, S. M. Tang: Air Pollution in Singapore: its Multielemental Aspect as Measured by Nuclear Analytical Techniques. Environmental Monitoring and Assessment **44** (1997) 455 470.
[10] W. A. V. Born, F. C. Adams, W. Menhaut: Atmospheric Environment **23** (1989) 1139 1151.
[11] S. Utsunomiya, K. A. Jensen, G. J. Keeler, R. C. Ewing: Direct Identification of Trace Metals in Fine and Ultrafine Particles in the Detroit Urban Atmosphere. Environmental Science and Technology **38** (2004) 2289 2297.
[12] P. S. Swietlicky, H. Ch. Hansson, H. Edner: Urban Air Pollution Source Apportionment Using a Combination of Aerosol and Gas Monitoring Techniques. Atmospheric Environment **30** (1996) 2795 2809.
[13] Air pollution in the Slovak Republic, Reports of Slovak Hydrometeorological Institute for years 1992 2003.