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Inductively Coupled Plasma Atomic Emission Spectrometry - Air Quality Monitoring

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Abstract

The concentration levels of heavy and toxic elements circulating in the environment increase due to various industrial activities. Now it is well understood that the environmental particles influence directly the cloud properties and atmosphere visibility, and indirectly change the global climate. Particles with aerodynamic diameter larger than approx. 10 μm were collected by Bergerhoff's method around metallurgical works "Kremicovtzi" in Sofia, Bulgaria. Samples of atmospheric particles smaller than approx. 10 μm were collected by filter technique from the meteorological stations Milesovka and Kopisty, located in a highly polluted industrial region of the Czech Republic. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was applied in this study for quantitative determination of traces of elements after sample extraction with *aqua regia* according to ISO 11466:1995. The accuracy is ensured by the following ICP–AES methodology: (a) quantification of spectral interferences in the presence of Al, Ca, Mg, Fe and Ti as a complex environmental matrix around the prominent lines of the analytes, and (b) line selection for trace analysis. The content of some pollutants (As, Ba, Cu, Mn, Pb, Zn, Al, Ca, Mg, Fe and Ti) was compared to the corresponding threshold concentration levels and to the results from the chemical analysis of hundreds of individual particles by using Electron Probe X–ray Micro-Analyses (EPXMA).

Keywords: ICP-AES, trace determination, atmospheric particles, EPXMA

1. Introduction

The coarse atmospheric aerosol fraction (particulates with aerodynamic diameter above 10 μm) determines dry sedimentation. The nature and magnitude of the hazards in a given situation depend on the complex combination of many factors, including particle size distribution, particle morphology, mineralogy and chemical composition. The chemical analysis

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of the coarse atmospheric particles is of interest for industrial hygiene chemistry whose main functions are screening for chemical stressors during the recognition phase and monitoring of specific hazard concentrations during the evolution [1].

Exposure to airborne ambient fine particulate matter (defined as particles with aerodynamic diameter < 2.5 μm) contributes to a variety of adverse health effects including asthma, lung cancer, cardiopulmonary disease and even mortality [2]. In addition to epidemiological studies, this type of aerosols and its elemental concentration data are employed as inputs to source–receptor models to identify emission sources necessary to develop effective air quality management strategies [3].

The contribution of environmental solid particles to atmospheric processes is of great importance. Dust particles scatter the light and influence visibility and climate; they act as cloud condensation nuclei and modify cloud properties and precipitations [4]. The ambient atmospheric aerosol is composed by natural and anthropogenic constituents. The latter are most often enriched in heavy metals or toxic trace elements [5-8].

Various instrumental methods are used to monitor airborne particulate outdoors and to safeguard occupational health in industrial workplace [9-14] as well as for the purposes of meteorology [5-8, 15, 16].

As the number of ecological and health problems associated with environmental contamination continues to rise, the determination of trace heavy metals in environmental samples becomes more and more important.

The present paper is aimed at demonstrating the possibilities of inductively coupled plasma atomic emission spectrometry (ICP-AES) by using Q-values [17]: (a) in the determination of Ba, Cd, Cr, Mn, Pb and Zn in atmospheric particulate matter, collected by Bergerhoff's method [18]. Comparative data for the concentration of the above mentioned elements will be obtained by flame atomic absorption spectrometry (FAAS) and direct current arc atomic emission spectrographic method (Dc arc-AES); (b) in the determination of As, Ba, Cu, Mn, Zn, Pb, Fe, Mg, Ca, Al and Ti, sampled on nitrocellulose membrane filters with pore size of 0.45 μm. Some results from Electron Probe X–ray Micro-Analyses (EPXMA) are added that concern the single particles, located on the filters and their enrichment in the above mentioned elements.

2. Experimental

2.1. Instrumentation

2.1.1. Inductively coupled plasma atomic emission spectrometry (ICP-AES)

The emission spectral measurements were performed with the Jobin Yvon JY ULTIMA 2 instrument (Longjumeau, France) equipped with a 1 m Czerny-Turner monochromator (practical bandwidth 5 pm in the second order from 160 to 320 nm), and a 40.68 MHz radial viewing ICP. Table 1 lists the operating conditions.

Table 1. Operating conditions

Generator Power (kW)	1.0
Plasma gas flow rate (L min^{-1})	12
Auxiliary gas (L min^{-1})	0
Sample uptake rate (mL min^{-1})	2.0
Nebulizer pressure flow (psi)	50
Nebulizing gas flow (L min^{-1})	1.0

2.1.2. Electron Probe X-ray Micro-Analysis EPXMA

EDX-ray analysis (Electron Probe X-ray Micro-Analysis EPXMA) performed on the JSM-6390 and JXA-733, JEOL apparatuses was applied for detailed investigation of single atmospheric particles collected on nitrocellulose filters [19]. The elemental spectrum of each particle was collected for about 60 s at 20 KeV. Elements with an atomic number less than that of nitrogen are not included in the determination of the elements weight percentage (wt%).

An observation in SEI mode (image formed by secondary electrons) reveals the morphology and surface texture of the objects. In BEI mode (image formed by back-scattered electrons) it is influenced by the atomic number of the chemical elements and, as a result, the objects rich in heavy-metals look bright shining on the dark background of the nitrocellulose filter and the rest of other particles (alumosilicates, calcites, etc.).

2.2. Sampling

Atmospheric particles with aerodynamic diameters larger than approx. 10 μm are collected by Bergerhoff’s method [18] around the “Kremicovtzi” metallurgical works, Sofia, Bulgaria. This place located in the North-East part of Sofia is well known as one of the most intensive industrial pollutants of the capital. The samples were air-dried and ground in a rotating plastic drum.

Samples of atmospheric particles, most of them smaller than 10 μm, are collected by filter technique (nitrocellulose membrane filters with pore size of 0.45μm) from one of the most polluted regions of the Czech Republic, near the meteorological stations Milesovka (837 m above sea level) and Kopisty (240 m above sea level), situated at 22 km from each other. This region, known as the "black triangle", is one of the most polluted industrial areas near the border of the Czech Republic with Poland and Germany [5, 20]. Nitrocellulose filters "MILLIPORE RAWP04700" with pore size of 0.45μm, diameter 47 mm and thickness of 1.2 mm were used. They were elevated about 2 m above ground and sheltered against falling precipitations. An exposure of 48 hours was used for the samples from Kopisty (K) and 48 - 96 hours for those from Milesovka (M). The samples were dried and prepared for observation in an electron microscope by their covering with mono-atomic layer of carbon.

2.3. Dissolution procedures

2.3.1. Reagents and test solutions

Reagents of highest purity grade (Suprapur Merck) were used: 30 % HCl, 65 % HNO_3, and tri-distilled water from a quartz apparatus.

2.3.2. Dissolution of samples of atmospheric particles

The samples of atmospheric particles, collected by the Bergerhoff's method, were dissolved in accordance with ISO 11466 [18].

0.5 g sub - sample was weighed accurately in a reaction vessel. 0.5 mL of tri-distilled water was added to obtain a slurry, followed by 4.5 mL of hydrochloric acid (12 mol L^{-1}) and 1.5 mL nitric acid (15.8 mol L^{-1}). Then 10 mL of 0.5 mol L^{-1} nitric acid were added to the absorption vessel which was connected to the reflux condenser. The apparatus was placed on the top of the reaction vessel. The samples were allowed to stay for 16 h at room temperature for slow oxidation of the organic matter and reduction of the gases produced during the subsequent heating cycle. They were boiled under reflux for 2 h and allowed to cool slowly at room temperature. The content of the reaction vessel was transferred quantitatively to a 25 mL graduated flask and filled up to the mark with nitric acid (0.5 mol L^{-1}). After the undissolved material has settled, the supernatant solution was subjected to analysis by ICP-AES. A blank sample, containing the acids used for digestion, was prepared in the same way.

2.3.3. Dissolution of nitrocellulose filters with a pore size of 0.45μm

The apparatus described in Ref. [21] was used.

The nitrocellulose filter was weighed and placed in a reaction vessel. 1.0 mL of tri-distilled water was added, followed by 7.0 mL of hydrochloric acid (12 mol L^{-1}) and 2.0 mL of nitric acid (15.8 mol L^{-1}). The nitric acid was added dropwise. The samples were allowed to stay for 1 h at room temperature. They were heated on the water bath under reflux for 8 h and allowed to cool slowly at room temperature. After that the solution was heated over plate (the distance between the plate and the reaction vessel was 5 mm). The solution was evaporated to a volume of 2 mL. The content of the reaction vessel was transferred quantitatively to a 10 mL graduated flask and filled up to the mark with tridistilled water. A blank sample was prepared in the same way. It contained the acids used for digestion and an unused nitrocellulose filter.

3. Results and discussion

3.1. Data base of Q-values

Spectral interferences, especially line overlaps, are major problems in atomic emission radiation sources, but they are emphasized with ICP-AES because of the richness of the spectra. A detailed experimental study of spectral interferences in ICP-AES encountered with environmental materials was shown in our previous papers [18, 22]. Table 2 lists the selected prominent lines of analytes As, Ba, Cd. Cr, Cu, Mn, Pb and Zn, $Q_{WJ}(\Delta\lambda_a)$ for wing background interference and $Q_{IJ}(\lambda_a)$ values for line interference, measured in the presence of 2 mg mL^{-1} Al, Ca, Mg, Fe and Ti, respectively, as interferents. The term $Q_I(\lambda_a)$ is expressed as the ratio $S_{IJ}(\lambda_a)$ / $S_{A,}$ where $S_I(\lambda_a)$ is the partial sensitivity of the interfering line, determined as the signal per unit interferent concentration produced by the interfering line at the peak wavelength of the analysis line λ_a, and S_A is the sensitivity of analysis lines (signal per unit analyte concentration).The term $Q_{WJ}(\Delta\lambda_a)$ is expressed as the ratio $S_{WJ}(\lambda_a)$ / S_A, where $S_{WJ}(\Delta\lambda_a)$ is the wing sensitivity of the interfering line in the spectral window $\Delta\lambda_a$ and S_A is as stated above.

These data were used for calculation of the true detection limits in the case of the multi-component system by using Equation 1 [17];

$$C_{L,\,true} = 2/5\Sigma_J\, Q_{IJ}(\lambda_a)\times C_{IJ} + C_{L,\,conv} \qquad (1)$$

$$C_{L,\,conv} = 2\sqrt{2}\ 0.01\times RSDBL\times[BEC + \Sigma_J\, Q_{IJ}(\lambda_a)\times C_{IJ} + \Sigma_J\, Q_{WJ}(\Delta\lambda_a)\times C_{IJ}] \qquad (2),$$

where $C_{L,conv}$ is the conventional detection limit; BEC – background equivalent concentration in pure solution; RSDBL – relative standard deviation of blank samples; C_{IJ} – matrix concentration; and J – Al, Ca, Mg, Fe, Ti.

An interfering line signal in the presence of a given matrix has to be considered as contribution to the background that can be measured only with a far larger uncertainly than continuous background. It was this insight that prompted the introduction of the concept of "true detection limits" (Eq. 1) to be distinguished from the "conventional detection limit" (Eq. 2) and the common detection limits (C_L) for pure solvent (Eq. 3):

$$C_L = 2\sqrt{2}\ 0.01\times \text{RSDB}\times\text{BEC} \qquad (3),$$

where RSDB is the relative standard deviation of the background in pure solvent.

Table 2 lists all investigated analysis lines and the interferents concentration C_{IJ} for which $Q_{IJ}(\lambda_a) = 0$ for Al, Fe and Ti as matrix elements. The line interference level at the peak wavelength of the analysis line λ_a, is determined by the magnitude of $Q_{IJ}(\lambda_a)$. Eq. 4 was used for calculation of C_{IJ} for which $Q_{IJ}(\lambda_a) = 0$ [20]:

$$C_{IJ} = C_L / Q_{IJ}(\lambda_a) \qquad (4)$$

The prominent lines of the analytes follow the sensitivity order in pure solvent in accordance with ICP Line Coincidence Tables [23]. The selected analysis lines are presented in bold.

Table 2. Interferent concentration C_{IJ} for which $Q_{IJ}(\lambda_a) = 0$ for Al, Fe and Ti

Analysis lines, nm	Interferent concentration C_{IJ} (in μg mL^{-1}) for which $Q_{IJ}(\lambda_a) = 0$		
	Al	Fe	Ti
As I 193. 695	0.8	-	-
As I 189.042	-*	-	-
As I 197.198	0.3	24.0	-
As I 200.334	-	-	-
As I 228.812	-	-	-
As I 234.984	-	-	250
Ba II 455.403	-	-	-
Ba II 493.409	-	200	-
Ba II 233.527	-	700	-
Ba II 230.424	-	1400	-
Cd II 214.438	-	-	-
Cd II 228. 802	-	-	-
Cd II 226.502	1000	-	-
Cd II 205.552	-	1200	-
Cd II 206. 149	-	-	1200
Cr II 267.716	-	-	1800
Cr II 283.563	-	-	-
Mn II 257.716	-	-	-
Mn II 259. 373	-	-	350
Cu I 324. 754	-	-	-
Cu II 224. 700	-	-	-
Cu I 327. 396	-	-	250

(Table 2 continued)

Analysis lines, nm	Interferent concentration C_{IJ} (in μg mL^{-1}) for which $Q_{IJ}(\lambda_a) = 0$		
	Al	Fe	Ti
Pb II 220.610	-	-	-
Pb I 216. 999	400	1500	-
Pb I 261.418	-	200	-
Pb I 283. 306	-	600	-
Zn I 213. 856	-	1500	-
Zn II 202.548	-	-	-
Zn II 206. 200	-	-	-

- $Q_{IJ}(\lambda_a) = 0$ for $C_{IJ} = 2000$

Table 2 shows that in all cases the first prominent lines were selected as the “best” analysis lines with two exceptions: As I 189.042 nm and Zn II 206.200 nm. The information can be used for additional line selection depending on the concentrations of matrix elements in the samples. In this way the accuracy of the results can be improved by using two and more analysis lines in the determination of the impurities in different environmental materials.

Table 3. Values of $Q_{WJ}(\lambda_a)$ and $Q_{IJ}(\lambda_a)$ for the selected analysis lines of analytes

Selected analysis lines, nm	Interferent	$Q_{WJ}(\Delta\lambda_a)$	$Q_{IJ}(\lambda_a)$
As I 189.042	Al	4.0×10^{-4}	0
	Ca	0	0
	Mg	0	0
	Fe	0	0
	Ti	0	0
Ba II 455.403	Al	0	0
	Ca	0	0
	Mg	0	0
	Fe	0	0
	Ti	0	0
Cd II 214.438	Al	0	0
	Ca	1.3×10^{-5}	0
	Mg	0	0
	Fe	6.0×10^{-5}	0
	Ti	8.0×10^{-5}	0
Cr II 267.716	Al	0	0
	Ca	0	0
	Mg	0	0
	Fe	0	0
	Ti	0	0

(Table 3 continued)

Selected analysis lines, nm	Interferent	QWJ(Δλa)	QIJ(λa)
Mn II 257.610	Al	0	0
	Ca	0	0
	Mg	0	0
	Fe	0	0
	Ti	0	0
Cu I 324.754	Al	0	0
	Ca	0	0
	Fe	0	0
	Mg	0	0
	Ti	0	0
Pb II 220.353	Al	2.8×10^{-4}	0
	Ca	4.0×10^{-5}	0
	Fe	1.2×10^{-4}	0
	Mg	0	0
	Ti	0	0
Zn I 202.548	Al	0	0
	Ca	6.0×10^{-6}	0
	Fe	0	0
	Mg	1.7×10^{-4}	0
	Ti	0	0

The selected analysis lines and the corresponding $Q_{IJ}(\lambda_a)$ and $Q_{WJ}(\Delta\lambda_a)$ values are listed in Table 3.

The ICP-AES determination of the matrix components Al. Ca, Mg, Fe and Ti was performed after digestion of the corresponding samples using the procedures described in sections 2.3.2 and 2.3.3. The accuracy was improved by using two selected analysis lines for each element, which were free from inter-element interferences: Al II 237.324 nm, Al I 394.401 nm, Ca I 422.673 nm, Ca II 315.887 nm, Fe II 238.204 nm, Fe II 239.562 nm, Mg II 279.806 nm, Mg I 265.213 nm, Ti II 334.941 nm and Ti II 336.121 nm.

The basic sample solutions were diluted (dilution factor = 5) in order to eliminate the multiplicative interferences [17]. The reference solutions were prepared on the basis of an acid blank.

The detection limits (in ng mL^{-1}) and BEC (in μg mL^{-1}) in pure solvent are shown in Table 4.

Table 4. Detection limits C_L(in ng mL^{-1}) and BEC (in μg mL^{-1}) in pure solvent

Analysis lines, nm	BEC, μg mL^{-1}	C_L, ng mL^{-1}
As I 189.042	0.10	3.0
Ba II 455.403	0.0042	0.12
Cr II 267.716	0.025	0.7
Cd II 214. 438	0.035	1.0
Mn II 257.610	0.0047	0.13
Cu I 324.754	0.045	1.3
Pb II 220.353	0.18	5.0
Zn II 202.548	0.0124	0.35

3.1.1. Determination of Ba, Cd, Cr, Mn, Pb and Zn in samples of atmospheric particulate matter

Table 5 lists the concentration of analytes by ICP-AES (column 2), obtained under the operating conditions shown in Table 1. The results obtained in the determination of Ba, Cd, Cr, Mn, Pb and Zn in samples of atmospheric particulate matter by ICP-AES method agree well with the corresponding values, derived by both FAAS (column 3) and dc arc –AES (column 4) methods.

Table 5. Element determination in samples of atmospheric particulate matter (mean values of six replicates)

Selected analysis lines, nm	Concentrations, μg g^{-1}		
	ICP-AES	FAAS	d.c. Arc -AES
Ba II 455.403	695 ± 10	700 ± 10	690 ± 25
Cd II 214.438	1.52 ± 0.05	1.53 ± 0.05	1.58 ± 0.1
Cr II 267. 716	250 ± 5	242 ± 5	245 ± 20
Mn II 257 610	355 ± 8	356 ± 6	360 ± 15
Pb II 220.353	165 ± 5	176 ± 5	169 ± 10
Zn II 202.548	495 ± 10	495 ± 10	510 ± 25

Using Student's criterion, no statistical differences between the results obtained by ICP-AES, FAAS and dc arc –AES methods were found. It should be noted that the dc arc –AES method is a direct method for analysis of solid samples. In this way the efficiency of extraction of the above mentioned analytes from samples of atmospheric particulate matter in *aqua regia* was experimentally demonstrated.

Table 6. Content of Al, Ca, Mg, Fe and Ti in solution (μg mL^{-1}) after dissolution of the sample

Matrix element	Concentration (μg mL^{-1}) (mean values of six replicates)
Al	200
Ca	1115
Mg	150
Fe	990
Ti	5.9

Table 6 lists the content of major elements in μg mL-1. These data and Q-values were needed for estimation of the true detection limits by using Eqs. 1 and 2. In this case all selected analysis lines are free of line interferences (Table 3), QIJ(λa) = 0, QWJ(Δλa) > 0. Hence, CL, true = CL, conv, i.e. the detection limits will be estimated by Eq. 2. Table 7 lists the conventional detection limits.

The results for Ba, Cr, Mn, Pb and Zn given in Table 5 show that the analyte concentrations substantially exceeded the detection limits (Table 7). In this case the use of a second analysis line with $Q_{IJ}(\lambda_a) = 0$ was justified. The interferent concentration C_{IJ} for which $Q_{IJ}(\lambda_a) = 0$ (Table 2) and the dilution factor of the sample solution were determined. When necessary, more than two analysis lines could be used for improving the accuracy of the analytical determination.

Table 7. Conventional detection limits (in μg g^{-1})

Element	Concentration (μg g^{-1})
Ba	0.006
Cd	0.15
Cr	0.90
Mn	0.0065
Pb	0.57
Zn	0.063

3.1.2. Determination of As, Ba, Cu, Mn, Pb, Zn, Al, Ca, Mg, Fe and Ti in dust particles collected by filter technique

The nitrocellulose filters with the collected samples were dissolved by using the digestion procedure described in 2.3.3. The final solutions were introduced into the ICP. Tables 8 and 9 list the concentration levels of elements in the samples collected from the Czech meteorological stations Milesovka and Kopisty, respectively. As the chemical composition of the studied samples is closely related to the meteorological conditions, the available data are given in the lower parts of both tables for comparison. The highest concentration of a given element among the studied samples is printed in bold as is also the respective threshold concentration level.

Comparison of the mean concentrations of the selected elements shows everywhere higher values for K(average) than for M(average) with only one exception - for calcium. This result is expected and reasonable, having in mind the additional influence in the case of Kopisty of the urban area of town Most with its chemical industry as well as the possible influence of background rocks in vicinity of Milesovka mountain.

Table 8. Content of As, Ba, Cu, Mn, Pb, Zn, Al, Ca, Mg, Fe and Ti in samples, collected from Czech meteorological stations Milesovka (M)

Selected analysis lines, nm	Threshold concentration levels, ng m^{-3}	Concentration, ng m^{-3}				
		M4	M5	M6	M8	M average
As	**3000**	2	**6**	3	2	3
Mn	**10 000**	**13**	2	3	1	5
Cu	**10 000**	**213**	41	20	10	70
Zn	**50 000**	**287**	93	116	90	147
Pb	**1700**	**36**	9	**31**	12	22
Ba		**6**	4	2	1	4
Fe		**704**	239	180	270	350
Mg		10	**55**	36	18	30
Ca		**2828**	420	300	**2600**	1540
Al		**745**	74	114	133	267
Ti		13	10	6	6	9
Wind direction, degrees		290÷320	260÷300	300	240÷260	240÷320
Wind speed, m s^{-1}		6.0÷12.7	15.0÷21.4	9.8÷11.2	8.7÷16.9	6÷21
Air flow volume, m^3		79.313	37.721	77.615	77.328	68
Collection time, h		96	96	48	48	72
T_{min}÷T_{max}, °C		-13.4÷2.4	-6.8÷0.8	-6.5÷0.2	-5.4÷1.3	-13÷2
Relative humidity, %		40÷97	94÷100	80÷95	94÷97	90

3.2. Data base from EPXMA analysis of single particles.

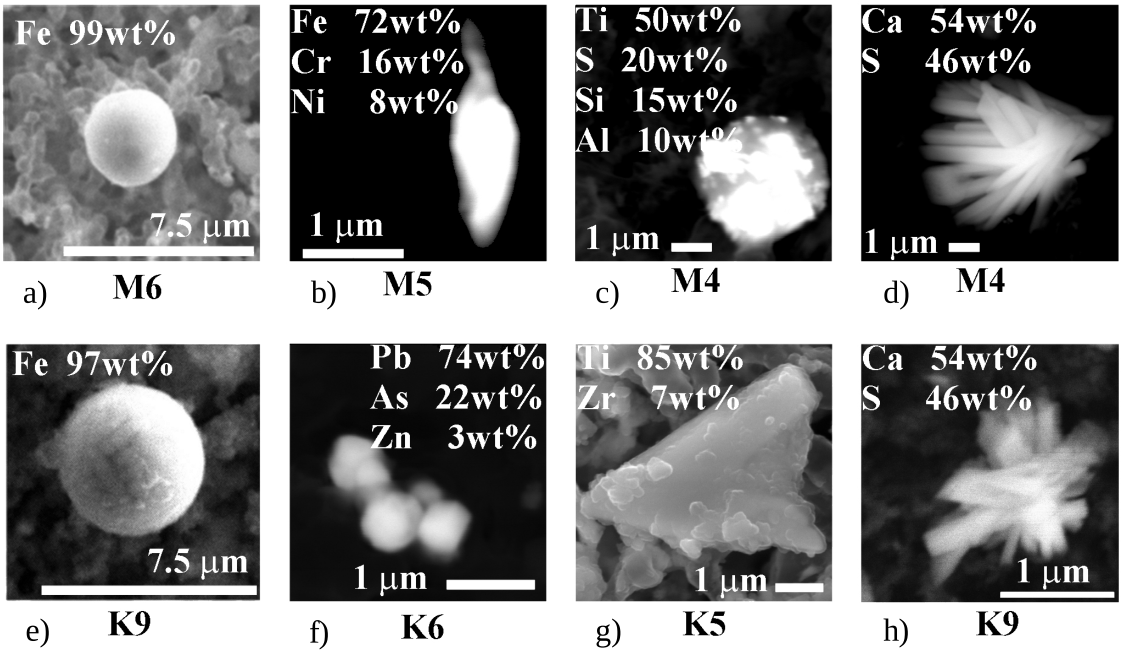
About 700 single particles (247 from Milesovka and 443 from Kopisti) are EPXMA-analyzed. In BEI-mode of observation one has the privilege to find easily a great variety of heavy and toxic elements and to determine their distribution in single particles, which is not possible by usage of bulk methods of analysis like ICP-AES.

This study is concentrated on particles smaller than 10 µm. They have different shape and elemental composition, as shown in Fig. 1.

Table 9. Content of As, Ba, Cu, Mn, Pb, Zn, Al. Ca, Mg, Fe and Ti in samples, collected from the Czech meteorological stations Kopisty (K)

Selected analysis lines, nm	Threshold concentration levels, ng m^3	Concentration, ng m^3					
		K5	K6	K7	K8	K9	K average
As	**3000**	2	10	**13**	10	9	9
Mn	**10 000**	13	27	26	25	24	23
Cu	**10 000**	18	18	**34**	14	20	21
Zn	**50 000**	165	364	160	343	345	271
Pb	**1700**	19	93	19	20	**116**	53
Ba		2	**32**	6	3	11	11
Fe		520	**1784**	**1522**	686	748	1052
Mg		37	120	97	87	**182**	105
Ca		514	1431	375	866	**2895**	1216
Al		242	804	803	772	643	653
Ti		7	13	16	13	**24**	15
Wind direction, degrees		220÷250	230÷300	230÷280	60÷120	70÷210	60÷300
Wind speed, m s^{-1}		3.9÷4.0	2.4÷3.0	1.5÷2.3	0.5÷0.9	0.4÷1.6	0.4÷4
Air flow volume, m^3		111.327	105.631	116.107	93.610	91.840	104
Collection time, h		48	48	48	48	48	48
T_{min}÷T_{max}, ^oC		-1.5÷4.9	-1.7÷2.9	-6.5÷5.3	-10.3÷3.5	-1.3÷7.3	-10÷7
Relative humidity, %		77÷84	76÷86	69÷74	82÷92	89÷97	82

Different in shape and size Fe-rich particles were found more often in the samples from Kopisty than in those from Milesovka. The observed abundance of iron-rich particles reflects the industrial-urban influence of the industrial zone of Most that is in the near vicinity of Kopisty. A great variety of particles enriched in non-ferrous heavy metals (Pb, Ba, Cu, Zn, Cr, Ni, Zr, Ti, Mn) was established in both locations. They were most often concentrated in the finest particles, usually smaller than 1 - 2 μm and rarely in the bigger ones. Some heavy elements, like Pb and Ba, were present in a great amount in single particles together with S, Cr and As; others, like Cu and Zn, were found combined together as well as with Cr, Ni, Mn and Fe [19]. The identified variety of non-ferrous heavy metals shows to a great extent similar quality and quantity of elements in both neighbor locations.



a) M6 b) M5 c) M4 d) M4

e) K9 f) K6 g) K5 h) K9

Fig.1. Atmospheric dust particles from Milesovka (M) and Kopisti (K) with different morphology, size and composition. By shape they are rounded (a, b, e, f), faceted (d, g, h), dendritic (d, h), etc. By surface structure they are smooth (a, d) or rough (e). By elemental composition they are often enriched in Fe (a, b, e) and other heavy elements (c, f, g) or in other elements such as Ca (d, h) or are of alum silicate type. Their size is in the micro- and nanometer scale, as seen from the corresponding white marker line under each photograph.

The obtained data offer a rich set of qualitative and semi-quantitative information that could be of importance to atmospheric pollution processes involving particles smaller than 10 μm. In order to give reliable results, the applied method of EPXMA-analysis of separated particles needs a great amount of statistical data. Despite of the existing uncertainty, caused by the relatively small number of studied particles (≤ 100), an attempt is done to compare the particles from Milesovka (Table 10) and Kopisty (Table 11), enriched in a given chemical element, with the analogous data from ICP-AES analysis. We have taken into account the single particles with enrichment ≥ 30 wt% in the elements mentioned in Tables 8 and 9, with exception of As, Mg and Mn for which this value is ≥ 10 wt%.

Table 10. Number of the particles from Milesovka (M) studied by EPXMA. They are enriched in some of the chemical elements (mentioned in Table 8)

Elements, wt%	Number of particles enriched by given element					
	M4	M5	M6	M8	ΣMi / M(all) number	 %
As>10	0	0	0	0	0	0%
Mn>10	0	1	0	0	1	0.4%
Cu>30	**2**	0	1	0	3	1.2%
Zn>30	0	0	1	0	1	0.4%
Pb>30	**5**	1	1	1	8	3.2%
Ba>30	**2**	0	0	1	3	1.2%
Fe>30	**35**	25	**38**	24	122	49.4%
Mg>10	**4**	3	2	3	12	4.9%
Ca>30	**12**	9	8	**16**	39	15.8%
Al>30	4	11	3	5	23	9.3%
Ti>30	1	1	3	0	5	2.0%
All studied	78	74	72	60	M(all)=247	

Table 11. Number of the particles from Kopisti (K) studied by EPXMA. They are enriched in some of the chemical elements (mentioned in Table 9)

Elements, wt%	Number of particles enriched by given element						
	K5	K6	K7	K8	K9	ΣKi / K(all) number	 %
As>10	0	2	0	0	0	2	0.4%
Mn>10	9	0	1	0	3	13	2.9%
Cu>30	0	0	1	3	0	4	0.9%
Zn>30	0	0	0	3	0	3	0.7%
Pb>30	0	3	0	3	1	7	1.6%
Ba>30	1	2	1	0	0	4	0.9%
Fe>30	48	61	**81**	60	71	321	72.5%
Mg>10	4	0	0	2	2	8	1.8%
Ca>30	1	4	3	5	**6**	19	4.3%
Al>30	2	1	3	1	1	8	1.8%
Ti>30	3	2	0	2	0	7	1.6%
All studied	68	83	101	103	90	K(all)=443	

The maximum value of a given element among the studied samples is printed in bold in cases when it is in agreement with the analogous results from Tables 8 and 9. Good coincidence is obtained for As, Mn, Zn and Fe that are found at higher concentrations in Kopisty than in Milesovka, and for Ca, that shows the opposite relation. The poor coincidence of the light element Mg is most probably caused by the greater detection error given by EPXMA. The discrepancy for elements like Al and Ti is due to their more homogeneous distribution among all particles and the absence of enrichment in some particles that was confirmed by EPXMA-analysis of many particles. The number of particles enriched in Cu and Ba shows almost similar results for Milesovka and Kopisty. The disparate data for Pb may have an explanation because they are related to non-sufficient statistics and/or subjectiveness.

4. Conclusion

The chemical analysis of the atmospheric particles is of interest for atmospheric processes and industrial hygiene chemistry. The heavy metal traces, if present, could easily penetrate into the human body or contaminate the air, soil and underground water. That is why a combined study of the chemical properties of the bulk material and of single particles could better reveal their possible noxious ecological and human impact. The possibility of ICP-AES was shown in the quantitative estimation of pollutants around the “Kremicovtzi” metallurgical works “in Sofia, Bulgaria (Ba, Cd, Cr, Mn, Pb and Zn), and in the region of the meteorological stations Milesovka and Kopisty, located in one of the highly polluted industrial region of the Czech Republic (As, Ba, Cu, Mn, Zn, Pb, Fe, Mg, Ca, Al and Ti). The spectral interferences were quantified by Q-values, as was proposed by Boumans and Vrakking (Tables 2 and 3). Quantitative data on the concentration of the pollutants obtained by FAAS and Dc arc-AES were compared in Table 5. The semi-quantitative data, derived by EPXMA and concerning the enrichment of single particles in the above mentioned elements, were added in Tables 10 and 11. The last information is very interesting and can not be obtained by ICP-AES analysis only. The quantitative data derived by ICP-AES were compared also with the threshold concentration levels (Table 8, 9).

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