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Research Methods of Atmospheric Solid Pollutants

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Abstract. Gravitation dust sediment, which surface of particles is enriched by volatile toxic elements in industrial sites, is created by particles, with diameter greater than 10 μm. The studied samples of the gravitation dust were collection near U. S. Steel s. r. o., so they represent pollutants of a metallurgy industry. In this place it is assumption of maximum amount of collected samples. Characteristics of gravitation dust were studied by various analytical methods and after determination of particles size these were applied for study of original samples and size fractions.

Phase composition of gravitation dust sediments was detected by three methods of qualitative analysis (thermal differential analysis, X-ray phase diffraction analysis and local electron microanalysis). The total content of major and trace elements was determined by methods of quantitative analysis after total decomposition of samples. The content of major elements was determined by atomic emission spectrometry with inductive coupled plasma after decomposition by HF, $HClO_4$ and HNO_3. The total content of matrix elements from this region decreases in the order Fe, Ca, Mg, Al, Mn. Other risk elements in samples occur on the trace level and their content decrease in the order Pb, Zn, Cu, Hg, Cd, Sb, Ni, Co. As and Sb was determined by atomic absorption spectrometry with hydride generation, Hg by atomic absorption spectrometry with thermal-oxidative generation and amalgamation after decomposition by aqua regia. Other elements by FAAS were determined.

Mobile and mobilizable element forms were determined by extraction with enable extraction agent. Extraction conditions were specified on the Košice-city sample and these conditions were applied for single step extraction of gravitation dust samples from the U. S. Steel region. For determination of mobile form of risk element samples were extracted by 0.1 mol NH_4NO_3 and for determination of mobilizable element forms by 0.1 mol.dm^{-3} EDTA. It was found, that in these samples elements in the dangers mobile forms consist mainly of Zn, Cd, Cu and in the mobilizable form of Cd, Zn and Cu.

The analyses of the acquired data from metallurgical industry region revealed that: applied research procedure enables to find complex data about characteristic of gravitation dust sediment; characteristic of gravitation dust sediment are significantly changing with specific region and single step extraction of dust enough inform about soils contamination.

Key words: gravitation dust sediments, fractionation, single-step extraction

Introduction

Dust particles in atmosphere of industry regions contain higher content of risk elements as dust particles of other regions. Toxic elements evaporated during high-temperature processes (such are e. g. combustion or metallurgical processes) have a trend to condense on surfaces of solid pollutants. Dust particles have a variety range size and from their size depend not only rapidity and way their removal from atmosphere, but their ecological impact to other environmental components too.

Gravitation dust sediment is created by particles with diameter higher as 10 μm, which are capable of spontaneous sedimentation. Its delay time in atmosphere is very short and its effect on living organisms is minimal. On this account the quantity of gravitation dust sediment is not able criteria for evaluation of situation of atmosphere pollution. The quantity of gravitation dust, which is expressed in g.m^2 in 30 days is related on the area of sedimentation and express of pollution extent of soils or vegetation. Particles, after its sedimentation, can contaminate soils by those toxic element forms, which are able of transport to the soil system. Consequently their biological mobility can enter from soil to food-chain a secondary contaminate living organisms.

For completely study of gravitation dust sediment can apply a lot of analytical methods, by help whom can study their physical and chemical properties. Our research program was concentrated on:

- determination of the particles size;
- determination of the major mineralogical composition in original samples and size fractions;
- determination of the total content of major elements in original samples and size fractions;
- determination of the total content of risk toxic elements in original samples and size fractions;
- determination of the content of risk elements in various physical – chemical forms (fractionation analysis) in original samples and size fractions;
- study of the pre-concentration method (SPE analysis) for directly risk elements determination in sorbet or elements determination after elution.

Research methods applied for study of atmospheric pollutants particles consisted especially from X-ray phase diffraction analysis, thermal differential analysis, local electron microanalysis, atomic absorption and emission spectrometry, roentgen fluorescence spectrometry and single step extraction by various extraction agents. By application of this methods were estimated necessary characteristics of atmospheric solid samples.

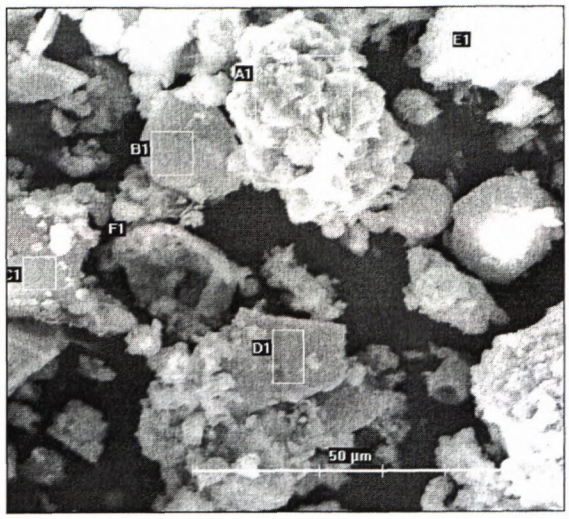
Results and discussion

The level of air pollution by solid particles has been monitored through concentration of fly dust couched in $\mu g.m^{-3}$. The overload of the highest admissible value of this concentration (60 $\mu g.m^{-3}$) in Košice region were registered on the monitoring station "Veľká Ida". This station occurs nearly of U. S. Steel s. r. o. (big metallurgical plant), which is the significant polluter of atmosphere in this region. The fly dust is created by particles, which diameter is less than 1 μm, with very small sedimentation power.

Gravitation dust sediment, which surface of particles is enriched by volatile toxic elements in industrial sites, which is created by particles, with diameter greater than 10 μm. The studied samples of the gravitation dust were collection near by U. S. Steel s. r. o., so that represented pollutants of a metallurgy industry. In this place it is assumption of maximum amount of collected samples. An overload of the highest admissible quantity of dust sediment (12.5 $g.m^{-2}$ for 30 days) it was registered here in each season of 2002 year. The total amount of collected samples into 12 settling glass vessels in time 3 months was from 6 g to 14 g approximately.

The phase composition of gravitation dust sediments was detected by three method of qualitative analysis (thermal differential analysis, X-ray phase diffraction analysis and local electron microanalysis). It was detected, that the particles matrix is created mainly by $CaCO_3$, SiO_2, $Fe_3Al_2(SiO_4)_3$, Fe_2O_3 and MgO. The Fe is presents in the carbonate form too. From elements representative an environmental risk was detected presence of Cd in the carbonate form and Cu as malachite ($CuCO_3.Cu(OH)_2$) and otavite ($Cu_3(OH)_2.(CO_3)_2$). The presence of Ni, Co, Zn and Mg in carbonate forms was detected only partly. A part of elements is bound as oxides. The example of configuration and composition shows Fig. 1.

The total content of major and trace elements was determined by methods of quantitative analysis after total decomposition of samples. Samples by HF, $HClO_4$ and HNO_3 were decomposed and content of major elements by atomic emission spectrometry with inductive coupled plasma was determined. The total content of matrix elements from this region decreases in the order Fe, Ca, Mg, Al, Mn. Other risk elements in samples occur on the trace level and their content decrease in the order Zn, Pb, Cu, Hg, Cd, Sb, As, Ni, and Co. As and Sb was determined by atomic absorption spectrometry with hydride generation, Hg by atomic absorption spectrometry with thermal-oxidative generation and amalgamation after decomposition by aqua regia. Other risk elements by method of F AAS were determined.



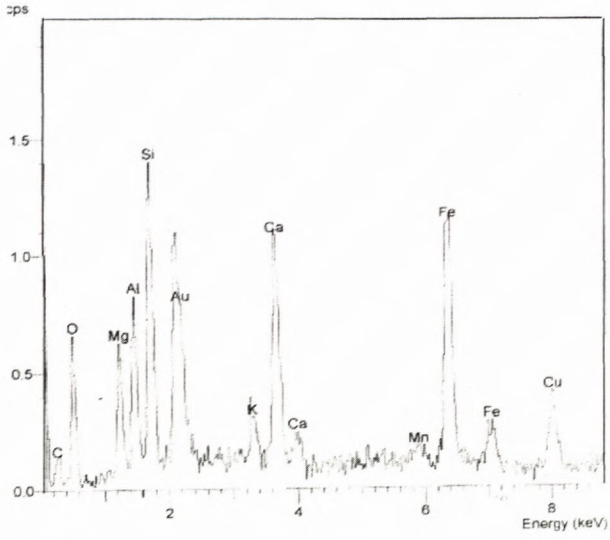


Fig. 1. The electron microscope picture and local element analysis of the dust particle (F1)

The fractionation is method used on the identification of element forms according to their various physical (solubility) or chemical (bonding) properties (Templeton et al., 2000). In the fractionation analysis of soils exist a lot of single-steps and sequential extraction procedures on the isolation of mobile and mobilizable element forms. From the standpoint of mobility in soil, the mobile forms (water-soluble and ion-exchangeable) constitute the highest danger. These forms are mobile in normal soil conditions. The mobilizable forms (mobile, organic, and carbonate) are mobile in changed soil conditions.

It is possible to applied of extraction procedures on samples of gravitation dust sediment in order to isolation of risk element forms, which are mobile from dust particles to soils. Application of money wise and time-consuming sequential extraction procedures for the dust samples is not necessary because dust particles have different matrix composition than soil particles. In the case of application of the single-step extraction is necessary regard the difference in amount of collected samples.

Table 1. The content of selected risk elements in gravitation dust sediment sample from locality Košice-Veľká Ida

Element		Zn	Pb	Cu	Hg	Cd	Sb	As
original sample	**weight %**	0.064	0.018	0.0063	0.0021	0.0004	0.0006	0.00041
d<36 μm		0.079	0.0224	0.0089	0.0025	0.0006	0.0006	0.00048
d>36 μm		0.053	0.0126	0.0056	0.0020	0.0004	0.00035	0.00037

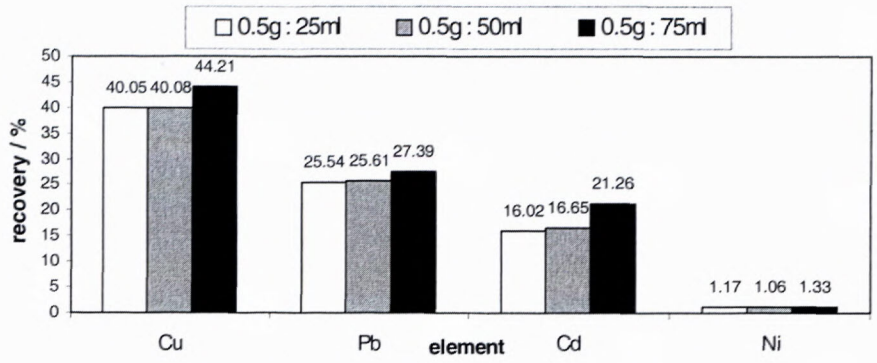


Fig. 2. The optimalization of extracting ratio for extraction by 0.05M EDTA.

For single-step extraction procedures following extracting reagents were used: distilled water, snow water, 0.1 mol.dm^{-3} $NaNO_3$, 0.1 mol.dm^{-3} NH_4NO_3, 0.1 mol.dm^{-3} $CaCl_2$ and 0.1 mol.dm^{-3} EDTA. By this reagents can extract mobile and mobilize element forms. In contrast of soil, we are applied the dust and the extracting ratio 1:150 (1g dust and 75 cm^3 extract agent). Other condition remained saved (Remeteiová et al., 2002). Extraction conditions were specified on the Košice-city sample and these conditions were applied for the single step extraction of gravitation dust samples from U. S. Steel region. For determination of mobile form of risk element samples were extracted by 0.1 mol NH_4NO_3 and for determination of mobilizable element forms by 0.1 mol.dm^{-3} EDTA. It was found, that from selected elements in dangers mobile forms are binding mainly Zn and Cd, and in the mobilizable forms Cd, Pb, Zn, and Cu.

Table 2. The percentage of selected risk elements in mobilizable forms.

Percentage / %	Zn	Pb	Cu	Cd
d<36 μm	48.3	65.1	39.5	81.2
d>36 μm	61.8	82.4	48.9	76.1

Because concentration of risk elements in extracts often is very low, we search possibility to find the able preconcentration method. We applied SPE extraction (solid phase extraction) and we are tested column from two various producers. Pre-concentrated risk elements can determine directly of sorbets by roentgen fluorescence spectrometry, or by analysis of pre-concentrated elute by other spectroscopic methods.

Conclusion

In consequence of acquired data from metallurgical industry region we can state that:

- applied research procedure enables to find complex data about characteristic of gravitation dust sediment particles;
- characteristic of gravitation dust sediment particles expressively changed with concrete region;
- single step extraction of dust sediments enough inform about soils contamination;
- spectroscopic methods provide relevant data information.

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