DETERMINATION OF HEAVY METALS FROM ENVIRONMENT SAMPLES BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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Abstract. In the studied area with geological and mining activities of ore extraction containing heavy metals, the environment is polluted with dusts resulted from these activities. From the technological processes of each stage, the environment accumulates sedimentable and suspension dusts, which contribute to the high pollution of air, soil and plants. The paper pursues the determination of Pb and Zn in the ore mines from the area, mining concentrations, sedimentable dusts from air, soil and plants of nettle and spinach. The analytical techniques used must have low detection limits, the lowest matrix effects possible and they must allow the determination, as precise as possible, of the major components as well as of the minor ones and in traces. We used the inductively coupled plasma atomic emission spectrometry (ICP-AES) and the atomic absorption spectrometry (AAS) for the experimental determinations. BAIRD ICP 2070 and AAS 3 spectrometers were used. The experimental results show high concentrations of the two metals even in the sedimentable dusts in soils and plants. The distribution and the mobility of the heavy metals are determined by the environment in which they are emitted and by the type of combinations in which they are found. In the air, metal mobility will be determined by both the nature of chemical combinations in dusts and by the weather factors as wind and precipitations. The type of soil, organic material content, pH and the potential of oxidation-reduction determine the mobility in soil, while in plants mobility is determined by the specific biochemical mechanisms of each plant.
Keywords: AAS, dusts, ICP-AES

1. Introduction

Baia Mare is situated in the NW of Romania, being limited at N by hills with 500-600 m height, and at E and NE height is more than 1000 m.

The processing and extraction of non-ferrous metal ores, which realize an advanced pollution of air, water, soil and plants with Pb, Cu, Zn, Cd, Mn, Mo was developed in this area.

It's a possibility that soil and air pollution is realized by powders resulted from burned fuels, but because the metallurgical processes are much extended it is impossible to appreciate the contribution of each pollutant agent. In the Eastern and North-Eastern parts of the town are placed two economic agents, which are considered to be the main pollutant agents. Their placement is unfavorable from the point of view of local meteorological conditions; they contribute to the dispersion of pollutants.

Meteorology studies done over 10 years concluded that the winds are blowing especially from E, W, NW and SE. Considering the blowing rate of the winds, it is predominantly under 4 ms-1, in 70% of the cases, the rate is less than 2,2 ms-1. Counting that the atmosphere grades are stable, we can conclude that local meteorological factors do not create the necessary conditions for pollutants' dispersion and these are moved towards the highly populated areas of the town.

2. Method and samples

In order to weather ore samples, sedimentable dust samples, soils and plants, we can use various methods according to the sample composition [1],[2].

After being collected, the samples were dried at 120oC and calcified at 500oC, and then submitted to disintegration under pressure in a CEM MDS 2000 microwave. A mixture of Merck acids formed of 5 cm3 fluorhydric acid, 8 cm3 chlorhydric acid and 8 cm3 nitric acid was used. The parameters programmed for the microwave are: 10 minutes time, 50% power and 120 psi pressure. After the total solubilisation, the solutions were passed in quoted balloons of 50 cm3 and brought to this volume with bi-distilled water. The obtained solutions were submitted for analysis to determine the concentrations of heavy metals, the analysis being made with a BAIRD ICP 2070 spectrometer, which was calibrated with a standard Merck solution. The spectrometer operated at a power of 900 W, a flux of the cooling gas of 9 l Ar. min-1 and an auxiliary flux of 1,5 l Ar. min^{-1} [3], [4].

Pb and Zn in sedimentable dust were determined with AAS 3 spectrometer too.

Before starting the experimental determinations, some preparing operations were done, such as selecting the wavelength for each element, drawing the calibration curves and optimising the work conditions, in order for the analytic performances to be maxim.

The AAS spectrometer was calibrated with solutions of solid standards which are prepared in a similar manner to the one presented for the solubilization of samples.

The BAIRD ICP 2070 spectrometer was calibrated in two stages: the calibration of the monochromator and the calibration of the wavelength of each element to be determined.

The monochromator was calibrated using the zero order of the network and the wavelength of 415.859 nm of the argon in the plasma.

The calibration of wavelength was done with a Merck standard solution, containing 1g/dm3 of 20 elements among which Pb and Zn. From this standard we prepared a solution which contains 10 ppm out of the two elements which is introduced into the inductively

coupled plasma. We selected and analyzed the wavelength of each element which is accessible and does not present interferences.

The plotting of the calibration curve was done with standard solutions containing 0; 1; 10 and 15 ppm from each element.

For experimental determination we used wavelengths of 220.412 nm for Pb and 213.856 nm for Zn.

3. Results and Discussions

The experimental determinations from Pb and Zn concentrations in the sedimentable dusts are presented in figure 1, in soils in figure 2 and in plants in figure 3.
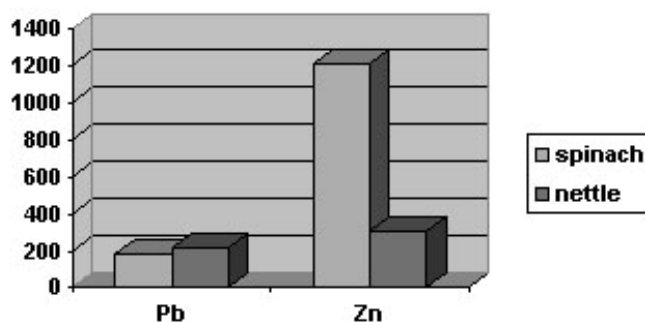
In figure 4 we presented graphically a comparison between the results in percentages obtained in the same sample for Pb and Zn, by the AAS and by the ICP-AES method.
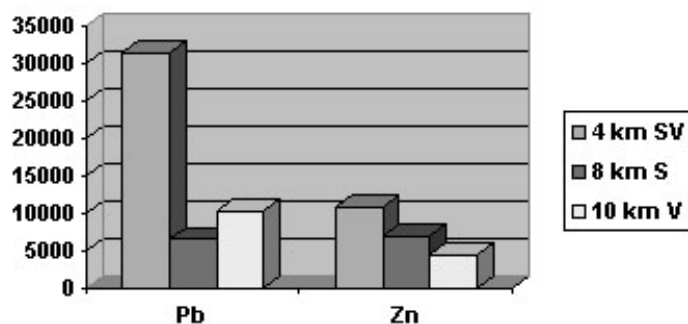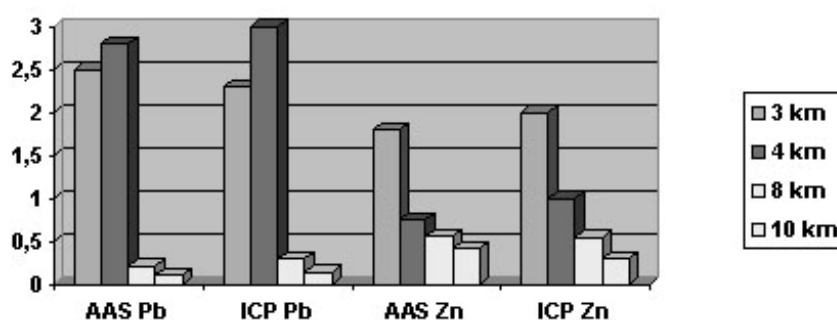

FIGURE 1. The variation of Pb and Zn concentration with the distance in sedimentable dust
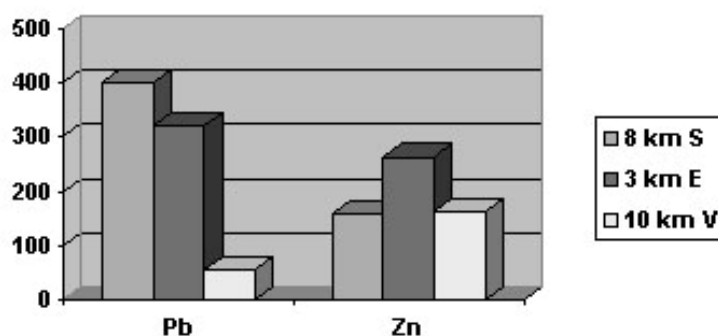
FIGURE 2. The variation of pb and zn concentration in soil with the distance

FIGURE 3. Pb, Zn and Mn concentration in plants

FIGURE 4. Comparison between the results obtained by aAAS and ICP-AES methods

The experimental data obtained for the three metals show high concentrations in the sedimentable dusts collected in spots situated at small distances from the main polluting source of the air with dusts.

This repartition can be explained considering the types of chemical combinations in which each chemical element is found in the prime matter, the chemical combination types which can form as a result of processing the prime matter, but also the transformations suffered by these combinations once they get into the atmosphere.

As a result of speciation analyses, the following percentages of Pb combinations in ores were obtained: 85,62% sulphide; 9,51% oxide and carbonate and 4,87% sulphate, the report being done for the entire quantity of lead.

Due to the low transformation efficiencies, the existent combinations in the concentrate are also found in sedimentable dusts in different percentages. Depending on the collecting places, the medium percentages of different lead combinations in dusts are: 46% sulphides, 21% oxides and carbonates and 33% sulphates. Considering this compositional structure of conglomerate of the sedimentable dusts, the distribution of lead in proportion of

71,7% - 86,2% up to the distance of 3,5 – 4 km from the main pollution source can be explained.

The speciation of zinc pursues the determination of sulphate, oxide and carbonate, silicate and sulphide. Reported to the total quantity of Zn, the proportion of combinations is: 0,19% sulphate, 1,33% oxide and carbonate, 2,50% silicate and 95,98% sulphide. In the pollutant dusts of the atmosphere, zinc is found as 30% sulphate, 17% oxide and carbonate, 11% silicate and 42% sulphide. In the case of zinc, the un-soluble forms also predominate; this explains their repartition in proportions of 85,4% - 95,7% at distances of 4 – 6 km from the main source.

The predominant wind contributes to this distribution, having directions to west, north-west and south-east, and in 70% of the cases it has speeds less than 2.2 m/s.

In the case of soils, the maximum concentrations of Pb admitted, of 100 ppm, are exceeded in all the analyzed samples, Zn having high concentrations.

The analyzed soil is of podsolic river-clay type, poorer in clays and richer in quartz and it has a pH of 4.5 – 5.5. The clay part and the high content of organic material determine a high capacity to retain metals in their insoluble state.

Comparing the Pb concentrations in soils with the normal concentrations of 50 ppm, we observe that this value is exceeded.

In plants, the concentrations of the two minerals are higher than in the soil samples from which they were collected. This can be explained by the assimilation of the soluble soil formations, by the deposit of solid dusts on plants and by the pollution of waters which penetrate the soil.

For plants, in the speciality literature, typical concentrations which are of 20 ppm for Pb, 100 ppm for Zn were presented. For the analyzed plants, these typical concentrations are exceeded by Pb and Zn, as well for nettle as for spinach.

Although the two plants were collected from the same soil, the share of each element reported to the others is different.

4. Conclusions

The studied area is strongly polluted with heavy metals coming from mining activities, concentrating and industrial processing of raw materials.

In order to appreciate the level of pollution in the area, the identification of the main local pollution sources was necessary. We find that it is not possible to exactly precise the

contribution of each source to the global pollution of the area, the fact that the main sources of pollution are the two non-ferrous metallurgical plants being only an appreciation.

The experimental findings can be explained only if we consider the emission rates of the pollution sources, geographic, meteorological and geological factors, which contribute to the dispersion and accumulation of pollutants, the nature and characteristics of the soil and of the chemical combinations in which metals are found.

The pollutant emissions are transported to different distances, depending on the geographic area, its geology and the local meteorological factors: fog, wind, rains, thermal inversions. All these natural factors of environment, specific to the area, do not contribute to a fast dispersion of pollutants and thus, the level of momentary pollutant concentrations is not reduced, because in situations of atmospheric instability, pollutants are transported to highly populated areas, and in situations of atmospheric calm, the diffusion of pollutants is very weak.

The type of chemical combinations in which they are found also determines the mobility of metals in soil. Considering the compositional structure of conglomerate in which these combinations are found, some of them hardly soluble and with great molecular mass, the distribution of pollutants at small distances from the pollution sources can be explained.

The results obtained by analysing spinach and nettle samples allow formulating the appreciation that, although plants were collected from the same soil, the heavy metals concentrations in them are the same, because the mechanisms of metals' accumulation are different in the two plants. Generally, the heavy metals concentration is 3 – 8 times higher in plants from the researched area, compared to the plants collected from unpolluted area.

The same sample was analysed also by AAS, the atomic absorption spectrometry, where the quantity of solution was sufficient. A good concordance was found between the obtained results in the case of high concentrations, and the appearance of some differences in the case of low concentrations, when the values are higher in ICP-AES than in AAS. The better atomising and exciting conditions in ICP-AES than in AAS explain this, allowing even the determination in ICP-AES of the concentration of elements in traces. The ICP-AES analysing method allowed the determination with the same precision in large concentration limits and in a short time, for the determination of 12 elements only 8 – 10 minutes being necessary.

By determining the concentration of heavy metals in sedimentable dusts, in soil and in plants with, we can appreciate that Baia Mare area is strongly aggressed by the anthropic activity.

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