P. KIERLIK*#, A. HANC-KUCZKOWSKA*, R. MĘCZYŃSKI*, I. MATUŁA*, G. DERCZ*

PHASE COMPOSITION OF URBAN SOILS BY X-RAY DIFFRACTION AND MÖSSBAUER SPECTROSCOPY ANALYSIS

The main purpose of this study was to identify the mineral composition of soil sample taken from the upper layer of topsoil. High absorption of chemical substance is a characteristic for humus-organic layer of topsoil. The source of those substance could be a pollutant emitted to the atmosphere by human activity. The research area includes Upper Silesia region, which is the most industrial region of Poland. In the present study, the phase composition of the top soil separates were analyzed by using X-ray diffraction and Mössbauer spectroscopy. X-ray diffraction analysis revealed the presence of seven mineral phases in the material magnetic separated by lower current (quartz, illite, kaolinite, Fe^{3+} oxides, hematite, magnetite and pyrite). In case of higher current were identified four phases (quartz, muscovite, kaolinite and $K_{0.94}Na_{0.06}(AlSi_3O_8)$). Mössbauer spectroscopy was used for an extensive analysis of iron-containing phases (pyrrhotite, magnetite, aluminosilicate oxides with Fe^{3+} and kaolinite/Fe^{2+} silicate).

Keywords: Mössbauer spectroscopy, X-ray diffraction, environmental protection, qualitative phase analysis, topsoil

1. Introduction

Nowadays, the urban areas are exposed to the impact of anthropogenic pollution. The accumulation of pollutants occurs in the upper soil layer and their complex composition is difficult to identify. In this work, the authors have attempted to characterize the phase composition of pollutants accumulated in the soil from the steal and coke industry.

Accumulation of pollutant in the environment was investigated with the use of various methods, which provided analysis of different parts of the environment elements such as: snow [1], street dust [2], industry dust [3], tree leaves [4]. However, the long-time contribution of pollutants could be characterized by phase composition of soil [5]. There is a possibility of identifying chemical composition of pollutants accumulated in the soil applying chemical and iron-containing phases analysis. The long term contribution of pollutants is one of the most important to be investigated, because it gives information about the main sources of pollutant emission in the examined region [6].

In present paper we combine X-ray diffraction analysis and Mössbauer spectroscopy in a detailed characterization of soil sample collected in the region of Upper Silesia in Poland, which is influenced by coke industry and power plant.

2. Material and methods

The study was conducted in the area influenced by a power plant and the coke industry located in Dąbrowa Górnicza in Upper Silesia region. The investigated material came from the upper layer of the soil and was taken with a soil core sampler. The sample was taken from woodland areas around industrial region of the north-eastern part of Dąbrowa Górnicza. Soil core was 30 cm long and was the base for selection of humus-organic layer. The preparation of soil core consisted of cleaving off the humus and organic layer from the top soil profile, which was followed by homogenization. In this material homogenization involves the equalization of the soil. After a standard initial preparation, the separation process was carried out in two steps: sieve separation and magnetic separation. In this way, three granulometric fractions were obtained: (I) Ø = (0.05-0.1) mm, (II) Ø = (0.1-0.25) mm and (III) Ø = (0.25-0.5) mm which then underwent magnetic separation with a isodynamic magnetic separator operated on different currents: 0.2 A and 1.2 A. Every granulometric fraction was divided into two groups of samples – separated with low (A) and high (B) currents. In the following paper IA, IB, IIA, IIB, IIIA, IIIB will be used for designation of the examined material.

The phase composition of the material after different stages of separation were studied with X-ray diffraction (XRD) method. The measurements were performed with the use of an X-ray X'Pert diffractometer (Phillips), with a copper anode ($Cu_{K\alpha} - \lambda = 1.54178$ Å) powered by an electric current of 30 mA, voltage of 40 kV and a curved graphite monochromator to determine the wavelengths emitted by the Cu anode. The diffraction patterns were recorded by "step-scanning" of 0.04°2θ steps within an angular range 2θ = 10÷140°.

Iron-containing phases identification was carried out with the use of ^{57}Fe Mössbauer spectroscopy. The Mössbauer spectra

* UNIVERSITY OF SILESIA, INSTITUTE OF MATERIALS SCIENCE, 1A 75 PULKU PIECHOTY STR., 41-500 CHORZOW, POLAND
# Corresponding author: pkierlik@us.edu.pl

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were recorded with conventional spectrometer at room temperature with a constant acceleration with ^{57}Co:Rh source (activity ~50mCi) in transmission geometry. The metallic iron powder (α-Fe) absorber was used for velocity and isomer shift calibration of the Mössbauer spectrometer. Author's numeric program MOSS 2.0 was used to fit recorded spectra. The mineralogical analysis of the spectra was based on the Mössbauer Mineral Handbook [7].

3. Results and discussion

The X-ray diffraction (XRD) patterns of subsamples are present in Fig. 1 and Fig. 2. The XRD analysis revealed the multiphase composition of the studied materials. In case of samples separated by low current (series A) were identified 7 phases: illite, kaolinite, muscovite, quartz and 3 an iron based chemical compounds (pyrite, iron oxide, and magnetite). Due to the pollution the significant group of compounds containing iron and sulphur can be distinguished. Additionally, the diffraction pattern of this series of subsamples revealed different participation of mineralogical phases in studied materials in term of used parameters of sieve separation. On the other hand, the XRD phase analysis revealed only three of the above phases (quartz, muscovite, kaolinite) in the subsamples series B (I B, II B, III B). Moreover, an additional $(K_{0.94} Na_{0.06})(AlSi_3O_8)$ phase is visible.

The presence of iron in the chemical composition of the sample is significant in the study of the pollution of the environment pollution. For this reason, it is vital to conduct deeper analyses related to the establishment of accurate iron-containing compounds, hence the Mössbauer spectroscopy is used. This method allows identifying the mineralogical transformation in the components of the iron-containing soils. Furthermore, it enables us characterize iron oxides and hydroxides [8].
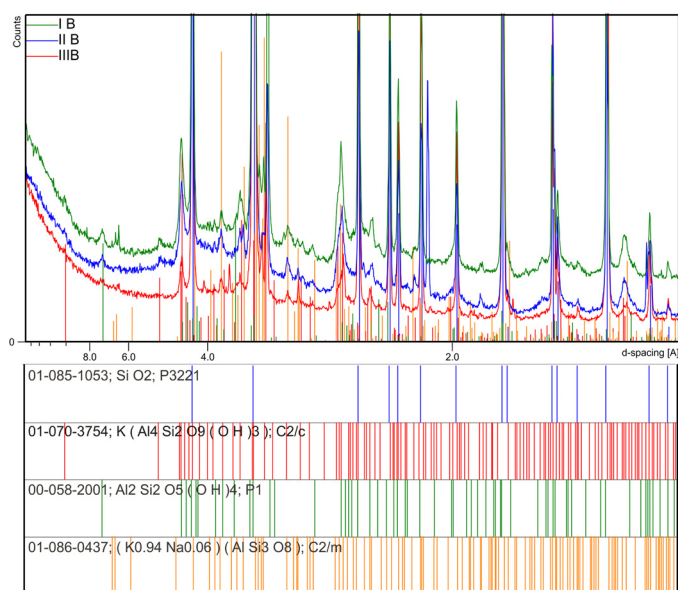

Fig. 1. The X-ray diffraction patterns of the topsoil after first step magnetic separation (with isodynamic magnetic separator working at 0.2A current in sieve separation: I – (0.05 – 0.1) mm, II – (0.1-0.25) mm, III – (0.25-0.5) mm
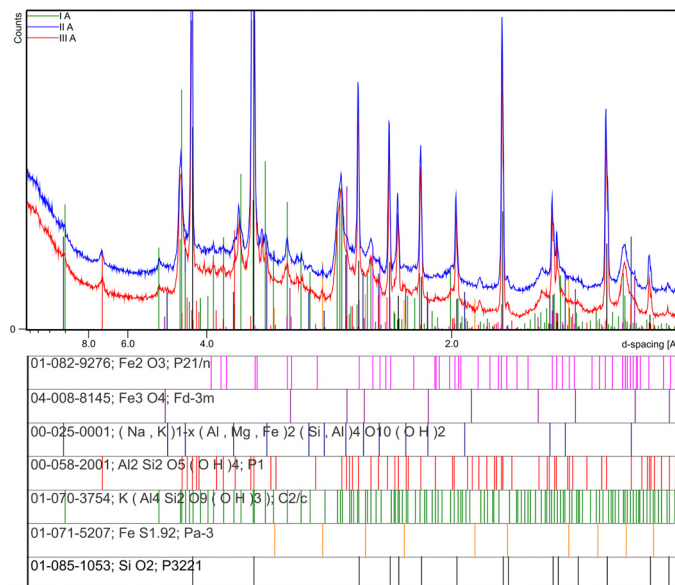

Fig. 2. The X-ray diffraction patterns of the topsoil after last step magnetic separation (with isodynamic magnetic separator working at 1.6A current) in sieve separation: I – (0.05 – 0.1) mm, II – (0.1-0.25) mm, III – (0.25-0.5) mm

The central part of Mössbauer spectra which are shown at Fig. 3 is a dominant one. This part is connected with the presence of non-magnetic phases in the examined material. The
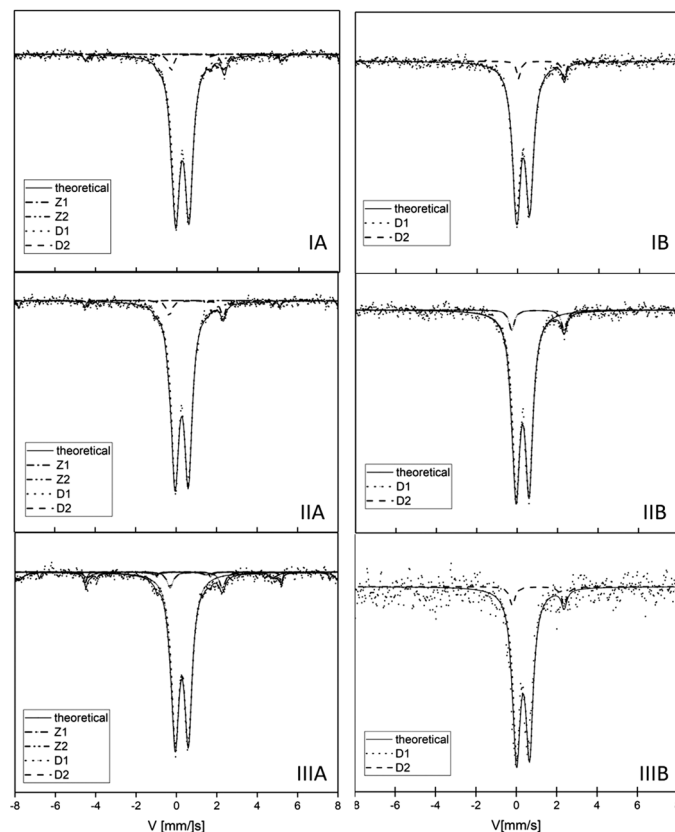

Fig. 3. The experimental Mössbauer spectra measured at room temperature in transmission geometry for subsamples of the topsoil after magnetic separation: A – 0.2 A, B – 1.2 A and in sieve separation: I – (0.05-0.1) mm, II – (0.1-0.25) mm, III – (0.25-0.5) mm. Fitted components are presented on the figure as: D1, D2, Z1, Z2

peripheral part of the spectrum is associated with the occurrence of magnetic hyperfine interactions. The central part of spectra was fitted with two doublets components (D1 and D2) while two Zeman sextet components (Z1 and Z2) were used to describe the peripheral part. Some differences between those compounds were found in hyperfine parameters. The results of fitting process are presented in Table 1.

TABLE 1

Fitted Mössbauer parameters for spectra of subsamples IA, IB, IIA, IIB, IIIA, IIIB. IS – isomer shift (with reference to metallic iron), QS – quadruple splitting, H – magnetic hyperfine filed, A – relative area fraction with respect to whole fitted spectrum. Where doublet compounds have been described as D1 and D2 and Zeman sexted compounds have been described Z1 and Z2

Compo-nent	IS [mm/s]	QS [mm/s]	H [T]	A [%]	IS [mm/s]	QS [mm/s]	A [%]
	IA				IB		
D1	0.36	0.64	0.00	84.80	0.37	0.64	94.00
D2	1.08	2.60	0.00	8.00	1.09	2.62	6.00
Z1	0.63	0.38	27.80	3.40			
Z2	0.30	−0.10	49.80	3.80			
	IIA				IIB		
D1	0.37	0.66	0.00	84.70	0.36	0.64	91.00
D2	1.06	2.68	0.00	8.00	1.10	2.62	9.00
Z1	0.59	0.28	28.40	3.20			
Z2	0.23	−0.03	49.60	4.10			
	IIIA				IIIB		
D1	0.37	0.64	0.00	78.90	0.38	0.64	93.00
D2	1.05	2.60	0.00	8.00	1.10	2.58	7.00
Z1	0.49	0.26	28.40	4.70			
Z2	0.24	−0.04	49.70	8.40			

The component (D1) is dominant in all spectra and contribution of it in the whole spectra (79-94%) and it is characterized by hyperfine parameters such as isomer shift IS = (0.36-0.38) mm/s, and quadruple splitting QS = (0.64-0.66) mm/s. Those parameters are identified as oxide iron-aluminosilicates. The similar component were presented for dust samples from steel and coke plants, where hyperfine parameters were described as: isomer shift IS = (0.32-0.35) mm/s, and quadruple splitting QS = (0.66 = 0.67) mm/s. [9,10].

The second doublet with a much lower share in the spectrum of no more than 9% is characterized by hyperfine interaction: isomer shift IS = (0.1.05-1.10) mm/s, quadruple splitting QS = (2.58-2.68) mm/s is identified as kaolinite / Fe^{2+} silicate on the basis of our XRD results and literature data. Those parameters could be identified as kaolinite with hyperfine parameters IS = (1.1-1.13) mm/s and QS = (2.53-2.61) mm/s [11], but some similarities to hyperfine parameters of Fe^{2+} silicate where IS = (1.05 -1.09) mm/s, QS = (2.67-2.73) mm/s [8] were found in the separate layers of soil profile in one of industrial regions of Ukraine. In X-ray diffraction analysis (Fig.1 and Fig. 2) was revealed the presence of kaolinite, illite, quartz and the group of Fe based oxides.

Magnetic components were only found in the group of subsamples separated with low current of 0.2A with was the first step

of magnetite separates (IA, IIA, IIIA). First magnetic component (Z1) was characterized by isomer shift IS = (0.49-0.63) mm/s, quadruple splitting QS = (0.26-0.38) mm/s and H = (27.8-28.4) T. Those parameters were identified as pyrrhotite. This mineral should be represented by three coexisting components, however due to low concentration of it in the examined material it is impossible to resolve them.

The differentiation of pyrrhotite hyperfine parameters is closely related to the chemical structure of this compound. Even the chemical formula ($Fe_{x-1}S_x$) suggests that there are significant number of chemical variety of this mineral. Subtle changes do not significantly affect the chemical composition but changing the geometry of the spatial relationship, hence affect the hyperfine interaction [11]. Pyrrhotite was found in the coke dust investigation, the fact that it was found in soil samples coming from the area which is affected by this industry is a logical consequence [12].

The next magnetic component (Z2), with isomer shift IS = (0.23-0.30) mm/s quadrupole splitting QS = (-0.1-0,03) mm/s and H = (49.6-49.8) T is associated with magnetite, which should be represented by two coexisting components. It is impossible to resolve this coexisting components in examined material due to low concentration in the sample.

Magnetite should be describe with two Zemman sexted, because in this mineral, Fe^{2+} and Fe^{3+} coexist. The Mössbauer parameters of this mineral, which chemical formula is $Fe^{3+}Fe^{2+}_2O_4$, was examined by Doriquetto et.all. (2003) Comparison of the values of parameters and results presented by the authors, allows to conclude that the component identified by us corresponds to the magnetite from Fe^{3+} [13].

The same component with similar hyperfine parameters was identified as magnetite [14,15] in the study of dust samples collected from the acoustic barriers of expressway. One possible source of magnetite could be a high temperature process of iron ore treatment [16].

Furthermore, a change in percentage share of both of them in the whole spectra was observed. In the first fraction (IA) component contribution is similar Z1-3% and Z2-4%, but in the smallest granulation (IIIA) the difference in participation is more significant Z1-5%, Z2-8%.

The analysis of Mössbauer spectra provides useful information regarding the relative fractions of paramagnetic and ferromagnetic minerals occurring at top-soil separates, which would be hard to clearly identify by XRD method.

4. Conclusion

The present study show that the top soil from the industrial region may have a varied chemical and magnetic composition. In the analysis of environmental samples, especially from industrial areas, use of the both methods seems to be necessary. This approach allow to achieve a more detailed analysis of the phase and chemical composition. What is more, analysis confirmed that the phase composition of collected sample is characteristic

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for coke industry based in the industrial region of Dąbrowa Górnicza.

The findings show that there are some differences between XRD and Mössbauer spectroscopy results. In XRD analysis of group B subsamples no iron-containing phases were found. In the same group the Mössbauer spectra revealed two iron-containing phases: aluminosilicate oxides with Fe^{3+} and Fe^{2+} silicate.

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