

Application of Mössbauer Spectroscopy in Environmental Research

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Abstract

Mössbauer spectroscopy is the technique of recoil-free resonant emission and absorption of gamma rays. It has the advantage of being sensitive only for one element. In the case of materials formed on the Earth's surface, such as soils and clays, the only propitious element is Fe.

Iron is the fourth most abundant element in the Earth's crust, it is essential for life, and almost all environmental materials contain at least some form of Fe. Not coincidentally the ⁵⁷Fe Mössbauer spectroscopy is among the most straightforward to operate. ⁵⁷Fe Mössbauer spectroscopy thus allows the characterization of iron speciation, and thereby of environmental conditions, over a wide range of concentrations, making it an extremely effective environmental technique. Straightforward, as it may seem, Mössbauer spectroscopy nevertheless has many pitfalls. Besides problems arising from the basic physics, complications can arise among other causes from imperfect crystallinity (small particle size), non-stoichiometry, interparticle effects and isomorphous substitutions.

The aim of the study was analysis of Mössbauer spectra of technogenic magnetic particles (TMPs), separated from various industrial dusts emitted from different sources and deposited in soil. TMPs can be used here as indicators of soil pollution with heavy metals, as they are one of the main carriers of metals from the emission source to the environment (soils, sediments, plants) (Magiera *et al.* 2011).

The analyzed samples of TMPs were separated from metallurgical and coke dusts as well as separated from organic horizon of the forest soil in the vicinity of relevant emission sources. Ash samples were obtained after coal combustion in domestic low-power boiler and biomass combustion in laboratory muffle furnace. Different kind of biomass was combusted: wooden pellets, straw pellets, oats, miscanthus. The ⁵⁷Fe Mössbauer spectra were

recorded at room temperature with a constant acceleration spectrometer with $^{57}\text{Co}:\text{Rh}$ source (activity $\sim 50\text{mCi}$). The metallic iron powder ($\alpha\text{-Fe}$) absorber was used for velocity and isomer shift calibration of the Mössbauer spectrometer. The mineralogical analysis of the spectra was based on the Mössbauer Mineral Handbook (Stevens *et al.* 2005).

Mössbauer spectra analyses revealed that TPMs formed during combustion of coal and biomass are more mineralogically homogeneous and contain mainly magnetite (TPMs after combustion of hard coal) or maghemite (after biomass combustion). It can be assumed that a higher degree of carbonization is associated with a higher concentration of TPMs in ash and as a consequence: higher magnetic susceptibility. The more complex mineralogy is exhibited in TPMs present in other industrial dusts (coking, metallurgy). They are differentiated by specific magnetic features. Steel and metalliferous dusts show significantly higher values of χ and SIRM than coking dusts. The latter, in turn, usually have higher values of coherence parameters due to a much greater share of antiferromagnetic and paramagnetic minerals in TPMs. Magnetite in fly ashes from hard coal combustion and in metallurgical dusts is more stoichiometric than in fly ashes after lignite and biomass combustion. In the second case, the finer maghemite and hematite are also present. The results of Mössbauer spectroscopy analysis showed that the magnetospheres consist of a core composed of magnetic spinels with complex internal structure that contains in addition to oxygen and iron (Fe^{3+} , Fe^{2+}) also Mn, Mg, Al, and Ti atoms. The outer shell of magnetospheres is composed of silica hyaline structure (glassy phase) containing iron. In metallurgical dust, additionally strongly magnetic metallic iron (αFe) and wustite were indicated. Ferrimagnetic sulphides as pyrrhotite are present in dust from coke production.

These results will be complemented with magnetic (bulk magnetic susceptibility and temperature dependence of magnetic susceptibility) and mineralogical (X-ray powder diffraction and scanning electron microscopy with energy dispersive spectroscopy – SEM/EDS) analyses.

Keywords: Mössbauer spectroscopy, technogenic magnetic particles, iron mineralogy.

References

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