Iron, manganese and sulphur valence state determination by wavelength-dispersive X-ray fluorescence analysis

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The wavelength-dispersive X-ray fluorescence method is widely used for elemental composition determination in analyzing geological objects, such as minerals, rocks and ores. The position of peak, shape and intensity of some emission lines and satellites are affected by the chemical bond. It allows using of X-ray fluorescence method also for determination of valence state and speciation of elements presented in rocks and ores in different chemical states (Fe^{2+} and Fe^{3+}, Mn^{2+}, Mn^{3+} and Mn^{4+}, S^{2-}, S^{4+} and S^{6+}). We investigated influence of chemical bond on intensity of X-ray fluorescence emission spectra and have developed the number of techniques for determination some elements valence state and speciation in geological objects. Due to intensity of all spectral lines depends on total content of element, we used ratio of chosen lines intensity to intensity of line in lowest rate affected by chemical state.

For iron valence state determination in rocks we used ratio of $FeK\beta_5$ line, caused by transition from valence level (M_4M_5), to intensity of $FeK\beta_{1,3}$ line as the analytical parameter. Those investigations are important in geological, geochemical and petrologic studies, for example to identify oxygen activity in magma and equilibrium between minerals and silicate melts. Precision of Fe^{2+} content determination in igneous and sedimentary rocks by our technique was comparable with precision of volumetric technique that is more labor-consuming and longer than our X-ray fluorescence technique and does not allow analyzing of some object with high manganese contents such as ferromanganese nodules.

Satellites of emission Kβ spectrum of manganese (MnKβ', MnKβ'', $MnK\beta^x$) caused by transition from valence levels were used for estimation of speciation (oxides, silicates or carbonates) and valence state of manganese in ores. The line intensities of $MnK\beta_5$ and MnKβ' satellites are least influenced by speciation, and they may be used for evaluating the manganese valence state for the samples containing low iron. The line intensities of MnKβ'' and $MnK\beta^x$ satellites may be employed for assessing the manganese speciation. Those data can be used for estimation of ores quality and further mining.

Another element that can be used for ores quality estimation is sulphur. Using ratio of SKβ' satellite and $SK\beta_{1,3}$ line intensities ratio allows us to distinguish S^{2-} from S^{4+} and S^{6+}, due to SKβ' satellite preconditioned by transition from molecular orbital formed by oxygen and absent in spectra of pure sulphides. Chemical shifts of $SK\beta_{1,3}$ and $SK\alpha_{1,2}$ lines allow to determine sulphide sulphur content with precision compared with gravimetric technique.

Therefore wavelength-dispersive X-ray fluorescence analysis can be useful tool not only for gross contents of iron, manganese and sulphur in rocks and ores, but also for express estimation of their valence state and speciation.

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