XRF with chemometric data processing for analysis of iron oxidation state

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XRF (X-ray fluorescence) analysis is a widely employed spectroscopic method for elemental analysis which allows for determination of quantitative content for elements from beryllium to uranium. Iron is involved in many geological formations (hematite, magnetite, hydrogoethite etc.) and it is important for various construction materials. It is not only quantitative content which is important when analyzing such objects, but also the oxidation state of iron. To solve the last problem one can use the phase analysis methods. On the other hand the energy (or wavelength) of some X-ray fluorescence lines depends on the energy of the atom valence levels. X-ray fluorescence lines shift can be used to determine oxidation state and this was shown in numerous studies. However, the practical implementation of this approach is associated with certain difficulties mainly due to insufficient energy resolution of spectrometers and uncertain interpretation of results. The purpose of this work is to determine oxidation states of the iron atoms from X-ray fluorescence lines shifts using logistic regression, PCA and PLS-DA.

Solid samples containing iron with different oxidation states were analyzed: a-Fe, Fe_2O_3, $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]*3H_2O$, $FeCl_2*4H_2O$, $FeCl_3*6H_2O$. The L - series lines of iron ($FeL_{\alpha1-2}$, $FeL\beta_{1-3}$) were employed as analytical signals for determination of the iron atoms oxidation states. The reason for this choice is the energy of these lines which mostly depends on the energy of 3d electron levels involved in formation of chemical bonds.

Spectra of the samples were measured by wavelength dispersive X-ray fluorescence spectrometer with high resolution (Shimadzu XRF-1800). Measurement conditions were: TAP crystal with first order of reflection; X-ray tube with Rh anode, voltage 90 kV and current 45 mA. These conditions allowed for the largest changes in X-ray lines, good reproducibility and reasonable accumulation time.

The spectra were decomposed into single lines followed by logistic regression, PCA and PLS-DA. It was shown that all three methods can solve the task of oxidation state analysis.