

USABILITY OF PORTABLE X-RAY SPECTROMETERS FOR DISCRIMINATION OF VALENCE STATES

I.A.Brytov, R.I.Plotnikov, B.D.Kalinin
Bourestnik Research & Manufacturing Co.,
68 Malookhtinsky Pr., 195112 St.Petersburg, Russia

In some studies, besides the quantitative content of an element in a sample, it is necessary to distinguish between its different valence states (phase composition studies, etc.). This information may sometimes be obtained from X-ray diffraction data, but this method is imprecise and time-consuming.

Other possible methods to determine the ratio of compounds with different valence states of the given element are to study changes in the shape of X-ray emission lines ("fingerprints method"[1]) or their displacement (chemical shift[2]). These methods proved efficient on precision spectrometers with high spectral resolution. Studies of chemical shifts on flat-crystal scanning spectrometers have also been reported[3].

The paper demonstrates the usability of mass-produced portable X-ray spectrometer with a 150-mm focal circle (Johannsson type) and a 9-watt X-ray tube to measure chemical shifts and estimate the content ratio of oxidation states of transition metals. Compounds of iron and chromium in different oxidation states are used as an example. Chemical shifts are measured with a 0.01 – 0.02 eV precision.

In a sample containing compounds of a transition metal in different oxidation states, their content ratio may be estimated with a 3 – 5% precision from count rates on the opposite slopes of the \hat{E}_{β_1} line. An algorithm for chemical shift evaluation from the ratio of count rates on the two line slopes is presented and errors are estimated.

Chemical shift-induced quantitative analysis errors caused by different oxidation states of the element in the sample and the reference are evaluated. For example, the use of metallic titanium as a reference for titanium X-ray assay in oxide materials may lead to an error of 0.3 – 0.4%.

[1] Brytov I.A. Doctoral dissertation, St. Petersburg, 1978.

[2] Narbutt K.I. Izv. AN USSR, ser. Phys., 1972, 36, 354.

[3] Hoffer H.E. Brey G.P.Schulz-Dobrick B.Oberhansli R.Eur .J.Mineral.1994,6,407-418