Effect of fluorescence on quantitative X-ray diffraction estimates of crystalline and amorphous phases in Fe-rich geologic samples using Co and Cu radiations

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The effect of iron (Fe) fluorescence on background and peak intensities in X-ray diffraction (XRD) analyses of banded iron formation, mine-waste samples, steel and copper (Cu) pyrometallurgical slags, and Fe-rich synthetic mixtures was investigated using Cu and cobalt (Co) target radiations. The strong fluorescence of Fe by Cu radiation compared to Co radiation influences crystalline and amorphous phase estimates by Rietveld refinements.

Background intensities are consistently lower in XRD patterns collected from samples containing Fe phases using Co radiation compared to Cu radiation; this is observed for samples containing as little as 2 weight percent (wt. %) Fe. Net peak heights (peak minus background) are higher using Co radiation compared to Cu radiation for samples containing greater than approximately 25 wt. % Fe. Furthermore, the differences in net peak intensities between Co and Cu increase with increasing Fe content above 25 wt. % with improvement by a factor of up to 3 (i.e., 3 times higher net peak intensities) for samples with 60 wt. % Fe. The higher net peak intensities for Fe-rich samples in Co radiation is likely due to X-rays penetrating deeper into the sample and thus having a larger diffracting volume because Fe has an absorption edge between Cu and Co Kα radiations. The mineralogy of Fe phases in the samples may influence optimal diffracting conditions: mine waste containing Fe-oxide minerals (i.e., hematite, jarosite, and goethite) irradiated with Co produced higher net peak intensities than when irradiated with Cu even at only 15-20 wt. % Fe; whereas mine waste containing Fe sulfides (i.e., pyrite and pyrrhotite) as the predominant Fe-bearing mineral produced diffractograms with higher net peak intensities in Cu radiation at similar total Fe concentrations (i.e., 15-20 wt. % Fe).

Differences in background and peak intensities resulting from different radiation sources influence phase abundance estimates by Rietveld refinement. Quantification of synthetic mixtures consistently underestimates the abundance of the Fe-oxide mineral hematite using both Cu and Co radiations; however, the Fe-mineral abundance is more accurately estimated for patterns collected with Co radiation. Using Cu radiation, higher amorphous amounts are estimated for Fe-rich samples that do not contain a separate amorphous phase, likely from the higher backgrounds and lower overall peak intensities. Interestingly, the summation of the Fe-mineral abundance plus amorphous content, determined by spiking with ZnO, is remarkably comparable to the amount of the Fe-bearing mineral for both Cu and Co radiation sources.

In multi-phase Fe-rich geologic samples containing glass or poorly crystalline Fe oxides, the abundance of amorphous material is generally estimated to be higher for patterns collected using Cu radiation compared to Co radiation. In contrast, for samples with < 15 wt. % Fe, the abundance of amorphous material estimated is generally less for Cu radiation compared to Co radiation. When evaluating Rietveld-based amorphous quantifications, factors such as the nature of the amorphous component, fluorescence effects, as well as the presence of poorly-crystalline Fe oxides and clays will all likely contribute to amorphous phase overestimation. Significant Fe fluorescence does have a measurable effect on crystalline and amorphous phase quantification using Cu radiation and effects can be minimized with the use of Co radiation.