Improvements to the Quantitative Assay of Nonrefractory Minerals for Fe (II) and Total Fe Using 1,10-Phenanthroline

James E. Amonette[1] and J. Charles Templeton[2]

[1] Environmental and Health Sciences Division, Pacific Northwest National Laboratory, Richland, Washington 99352
[2] Department of Chemistry, Whitman College, Walla Walla, Washington 99362

Abstract: A method using 1,10-phenanthroline (phen) to quantify Fe(II) and total Fe in nonrefractory minerals was modified to improve the accuracy and precision and to eliminate the inconvenience of performing much of the analysis under darkroom conditions. Reagents were combined to minimize solution-handling errors, volumes of the reagent additions were determined gravimetrically and the acid-matrix solution was preheated to near-boiling before sample contact. The darkness requirement, which stems from the photoreduction of Fe(III) to Fe(II) in the presence of phen, was eliminated by the use of opaque amber-colored high-density-polyethylene bottles during the digestion step and for storage of the digestate and subsequent dilutions before Fe(II) analysis. Reduction of Fe(III) for total-Fe analysis was accomplished either by exposure to light from a Hg-vapor lamp or by reaction with hydroxylamine, NH_2OH. Although the minimum periods required for adequate reduction ranged from 1.5 to 4 h, the optimum reduction periods were between 6 and 10 h. When standard samples containing Fe(II) and $MnCl_2$ were digested and analyzed for total-Fe using the light treatment (with incidental heating to $35-45\ ^\circ C$), significant decreases and in some instances, oscillations, in absorptivity were obtained. Similar experiments with NH_2OH, or with $CrCl_3$ showed no effect. The absorptivity of most digestates stored in opaque bottles was stable for at least 2 weeks, although digestates with Mn concentrations above 3 $\mu g\ mL^{-1}$ showed proportional decreases in absorptivity. Analysis of 8 geochemical reference materials by the modified method (using NH_2OH) yielded excellent agreement with published values and a mean relative standard deviation of 0.6%. Total-Fe results obtained using the light treatment, however, were generally lower ($\sim$2% relative) than the NH_2OH values, although this difference decreased with longer irradiation periods. Use of NH_2OH was deemed preferable because it was simpler, faster, minimized interferences from Mn and eliminated the need for specialized apparatus. Lastly, MICA Fe was shown to be unreliable as a primary reference material for Fe(II) determinations.

Key Words: 1,10-Phenanthroline • Belousov-Zhabotinsky Reaction • Fe • Fe(II) • Ferrous Iron • Hydroxylamine • Oscillatory Reaction • Photoreduction • Total Iron

Clays and Clay Minerals; February 1998 v. 46; no. 1; p. 51-62; DOI: 10.1346/CCMN.1998.0460106

Clay Minerals Society (www.clays.org)