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New Method for the Direct Determination of Dissolved Fe(III) Concentration in Acid Mine Waters

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A new method for direct determination of dissolved Fe(III) in acid mine water has been developed. In most present methods, Fe(III) is determined by computing the difference between total dissolved Fe and dissolved Fe(II). For acid mine waters, frequently Fe(II) ≫ Fe(III); thus, accuracy and precision are considerably improved by determining Fe(III) concentration directly. The new method utilizes two selective ligands to stabilize Fe(III) and Fe(II), thereby preventing changes in Fe reduction−oxidation distribution. Complexed Fe(II) is cleanly removed using a silica-based, reversed-phase adsorbent, yielding excellent isolation of the Fe(III) complex. Iron(III) concentration is measured colorimetrically or by graphite furnace atomic absorption spectrometry (GFAAS). The method requires inexpensive commercial reagents and simple procedures that can be used in the field. Calcium(II), Ni(II), Pb(II), Al-(III), Zn(II), and Cd(II) cause insignificant colorimetric interferences for most acid mine waters. Waters containing >20 mg of Cu/L could cause a colorimetric interference and should be measured by GFAAS. Cobalt(II) and Cr(III) interfere if their molar ratios to Fe(III) exceed 24 and 5, respectively. Iron(II) interferes when its concentration exceeds the capacity of the complexing ligand (14 mg/L). Because of the GFAAS elemental specificity, only Fe(II) is a potential interferent in the GFAAS technique. The method detection limit is 2 μg/L (40 nM) using GFAAS and 20 μg/L (0.4 μM) by colorimetry.

Introduction

Accurate and precise measurements of Fe reduction−oxidation (redox) species are particularly important in the study of acid mine waters because Fe is a major component in such waters. Charge balance calculations for acid mine waters depend strongly on the Fe(II)/Fe(III) ratio. Aqueous speciation is sensitive to the absolute concentrations of Fe-(II) and Fe(III) as well as the Fe(II)/Fe(III) ratio. Iron(III) precipitates readily, forming hydrous ferric oxide, which adsorbs trace metals. Thus, Fe controls the mobility and toxicity of other metals. A method for determining Fe(III) concentration is needed to accurately predict the fate and mobility of metals in high-Fe aquatic environments.

Dissolved Fe(II) concentrations in waters are commonly determined by a colorimetric technique using a ferroin complexing reagent; it is also preferable to determine total dissolved Fe (Fe_T) concentrations by colorimetry. In a study comparing analytical methods for the determination of major and trace constituents in acid mine waters, Ball and Nordstrom (*1*) found that colorimetric determination of Fe_T using FerroZine as the complexing agent was more reliable, precise, and sensitive than inductively-coupled plasma or direct−current plasma spectrometry.

Most methods for determining Fe(III) concentration are based on colorimetric determination of the Fe(II) concentration, followed by a separate determination of the Fe_T concentration after reduction of Fe(III) (*2*). The difference between the concentrations of Fe_T and Fe(II) is taken as the Fe(III) concentration. One major problem with this approach is that both accuracy and precision of the Fe(III) concentration are compromised as the proportion of Fe(II) increases, with determinations often overestimating actual Fe(III) concentrations. The differencing approach often yields highly imprecise values for Fe(III) in acid mine waters because these waters usually contain much more Fe(II) than Fe(III), and the difference between Fe_T and Fe(II) is comparable to the error of the determination. Prompt on-site determination of the Fe species may be important because the relative concentrations of the Fe redox states may change in the presence of oxygen, light, and biocatalysts (*3*). Portable UV−visible spectrophotometers allow colorimetric Fe measurements to be taken immediately after sample collection.

Many of the published Fe(III) methods cannot be used in the field. Some spectrophotometric analyses for Fe(III) are based on the ability of a trace analyte to catalyze the reaction of a species present at much higher concentration (*4*). Catalytic techniques are sensitive to the composition of the matrix and may exhibit inconsistent behavior. Complexing can affect the catalytic activity of Fe(III), resulting in erroneous Fe(III) values. Since reaction kinetics are sensitive to temperature fluctuations, adapting catalytic techniques for field use may be difficult because of variations in ambient temperatures (*5*).

Thiocyanate (CNS^-) has been used for Fe(III) determination in strongly acidic samples. Iron(III) thiocyanate has analytical limitations including deviation from Beer's law and fading of the iron(III) thiocyanate color. Errors larger than 6% for standards prepared with hydrochloric acid solution and a 10% decrease in the complex color in 10 min were observed (*6*).

A method for the simultaneous determination of Fe(II) and Fe(III) in atmospheric water has been described (*7*). This method yields detection limits of 4 nM (about 0.0002 mg/L) when combined with a solvent concentration step and 0.1 μM (about 0.006 mg/L) without solvent concentration. However, the color reagent for the technique is not commercially available and thus must be synthesized. The reagent also reacts with other transition metals such as Co, Cu, Ni, and Zn. While the probability that these metals will interfere with the determination of Fe in cloudwater is remote, interferences are far more likely if the method were applied to acid mine waters. Finally, while determination by difference of one Fe valence state is a simple matter when $0.2 \leq$ Fe(II)/Fe(III) ≥ 5, it becomes far more difficult at very large or very small ratios. In such instances, reagents are needed that are specific for the respective oxidation states.

High selectivity is needed to isolate Fe(III) for reliable measurement in the presence of other metal ions, particularly when concentrations of Fe(II) are high. Many of the published

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methods for Fe(III) determination are not suitable for use with acid mine waters because they have not been tested for major potential interferences, particularly high levels of Fe(II), at realistic levels relative to Fe(III) (*8*−*14*). The proposed method uses selective complexing agents for both Fe(II) and Fe(III). The new method corrects for the shortcomings of many reported methods and current practices and provides accurate and precise measurements of Fe(III) in the presence of other metals including Fe(II). Desirable features of the method include reliability, portability, and low costs.

Two groups of compounds (catechols and hydroxamates) are formed naturally by microorganisms to chelate Fe(III) in Fe-deficient environments (*15*). Acetohydroxamic acid was selected as the Fe(III) chelator because it has a high selectivity for Fe(III) (*16*−*18*), it is commercially available, and it is inexpensive. Derivatives of this compound could be used to further enhance the molar absorptivity and sensitivity of the method.

Experimental Section

Sample Collection and Preservation. Samples collected in the field are immediately filtered through a 0.1-μm tortuous path membrane, acidified to pH of about 1 with hydrochloric acid (2 mL of 6 M HCl/250 mL of sample), and stored in acid-washed opaque plastic bottles at 4 °C. Samples collected and preserved in this manner may be stored for up to 6 months without significant changes in the Fe redox distribution because microbial catalysts are removed, the pH is low enough to keep metals solubilized, and the iron oxidation rate is negligible.

Apparatus. A diode-array spectrophotometer (HP8452A) with 5-cm cells, Zeeman atomic absorption spectrometer (PE 4110ZL), Alltech maxi-clean C_{18} cartridges containing 900 mg of absorbent, and plastic syringes (10 and 30 mL) were used.

Reagents. Double-distilled water; 1.0 M acetohydroxamic acid ($C_2H_4NO_2$), Aldrich, 98%; 4.9×10^{-3} M FerroZine iron reagent ($C_{20}H_{13}N_4S_2O_6Na{\cdot}H_2O$), Hach, 95.2% pure; 6 M redistilled hydrochloric acid (HCl); methanol (CH_3OH), 99.9%, ACS HPLC grade; hydroxylamine hydrochloride solution ($NH_2OH{\cdot}HCl$), 10% w/v; and ammonium acetate buffer solution (CH_3COONH_4), pH 7−7.5. The buffer was prepared by diluting 467 mL of reagent grade (28−30%) ammonium hydroxide (NH_4OH) and 230 mL of ultrapure glacial acetic acid (CH_3COOH) to 1 L. Iron(III) standard stock solution: 10.0 mg/L as ferric sulfate hexahydrate ($Fe_2(SO_4)_3{\cdot}6H_2O$) in double distilled water containing 1% (v/v) of 6 M redistilled HCl. The Fe in the standard was greater than 99.0% Fe(III), as determined by the FerroZine method. Iron(II) standard stock solution: 100 mg/L as ferrous ammonium sulfate hexahydrate ($Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$) in double distilled water containing 1% (v/v) of 6 M redistilled HCl. The Fe in the standard was greater than 99.0% Fe(II), as determined by the FerroZine method.

The following single-element standards were used for interference studies: Cu(II), 1000 ± 3 mg/L in 2% HNO_3; Ca(II), 10 000 ± 5 mg/L in 5% HNO_3; Cr(III), 1000 ± 3 mg/L in 5% HCl and 1% HNO_3; Al(III), 1000 ± 5 mg/L in 5% HCl and 1% HNO_3; Co(II), 1000 ± 3 mg/L in 2% HNO_3; Ni(II), 1000 ± 5 mg/L in 5% HNO_3; Pb(II), 1000 ± 3 mg/L in 2% HNO_3; Zn(II), 1000 ± 5 mg/L in 5% HNO_3; and Cd(II), 1000 ± 3 mg/L in 2% HNO_3.

Procedure. (A) Determine dissolved Fe(II) and Fe_T using the FerroZine method as follows:

(a) Pipet an adequate volume of acidified sample (up to 20 mL maximum) that will yield 0.004−1.6 mg/L Fe when diluted to volume into a 25-mL volumetric flask.

(b) Prepare appropriate blanks and standards in 25-mL volumetric flasks.

(c) If solution is a standard or blank, add 0.25 mL of hydroxylamine hydrochloride solution (reduces Fe(III) to Fe(II)).

(d) Add 0.5 mL of FerroZine reagent and mix (the FerroZine forms a complex with Fe(II)).

(e) Add 1.25 mL of buffer solution (buffers the pH near neutrality), rinse down neck of flask, shake well, and allow at least 5 min for full color development.

(f) If the magenta color of the FerroZine complex is masked or discolored by a brick or rust red color due to the presence of high Fe(III) concentrations, add 1.50 mL of 6 M HCl after color development. If Fe(III) interference is suspected but not noticeable to the eye, check duplicates, one with acid against one without: absorbances should be nearly identical if no interference is present.

(g) Dilute to the mark and shake well.

(h) Measure absorbance at 562 nm. Solutions must be measured *within 1*−*2 h*.

(i) For Fe_T, use the same procedure with the addition of step c to all samples.

(B) Transfer a maximum of 18.25 mL of sample containing no more than 14 mg/L Fe(II) and no more than 1.2 mg/L Fe(III) when diluted to volume to a 25-mL volumetric flask.

(C) Add the following reagents in the order listed:

(a) 5.0 mL of FerroZine solution.

(b) 0.5 mL of acetohydroxamic acid (the acetohydroxamic acid will form a complex with Fe(III)).

(c) 1.25 mL of ammonium acetate buffer (buffers the pH near neutrality).

(D) Dilute to volume with double distilled water.

(E) Remove the Fe(II)−FerroZine complex from the sample as follows:

(a) Attach a new or regenerated C_{18} cartridge to a 10-mL plastic syringe.

(b) Condition C_{18} cartridge by passing through it 5 mL of methanol followed by 5 mL of double distilled water. Do not allow cartridge to dry before sample processing.

(c) Remove C_{18} cartridge from syringe and attach it to a new 30-mL syringe.

(d) Remove plunger, transfer sample into the syringe, then force sample through cartridge at a fast, steady drip (2−3 drops/s). Discard first 5 mL of filtrate and collect remaining 20 mL for Fe(III) determination.

(F) Determine the Fe(III) concentration colorimetrically (within 5 h) or by Zeeman-corrected graphite furnace atomic absorption spectrometry (GFAAS).

(G) Regenerate C_{18} cartridge by passing 10 mL of methanol through it.

Results and Discussion

Typical calibration curves for Fe(III) by colorimetric and GFAAS analyses are shown in Figures1 and 2, respectively. The visible absorption spectrum of the Fe(III)−acetohydroxamic acid complex exhibits a single peak with maximum absorbance at 424 nm. At this wavelength, the molar absorptivity is 2583 cm^{-1} mol^{-1}, and Beer's law is obeyed to approximately 16 mg/L. The Fe(III)−acetohydroxamic acid complex is stable for up to 5 h. The redox stability of the combined Fe(II) and Fe(III) complexes was tested by time series determinations. No change in Fe(II)/Fe(III) ratio was found for up to 3 h.

Accuracy of Direct Fe(III) Measurements in Acid Mine Waters. The accuracy of the new method was estimated by performing spike recoveries. Two or three additions of Fe(III) standard solution were added to six different samples and treated with the described procedure. The samples were collected from three different acid mine effluents including Summitville Mine, Rio Grande County, CO; Paradise Portal in the Upper Animas Mine Drainage, San Juan County, CO; and Iron Mountain Mine, Shasta County, CA. GFAAS

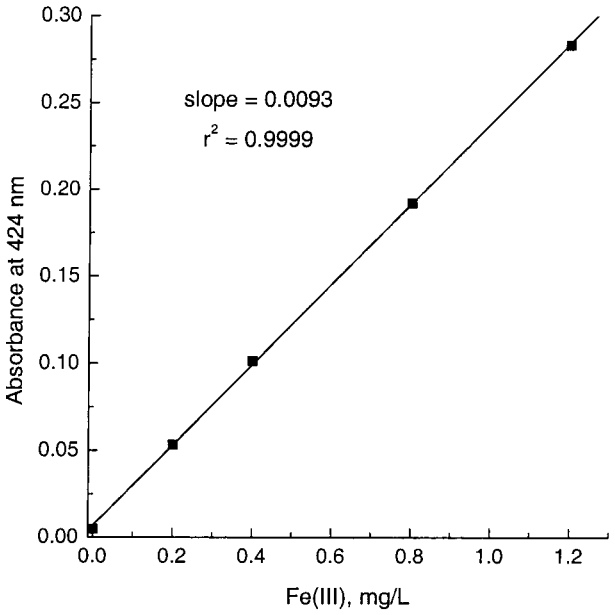

FIGURE 1. Standard curve for colorimetric determinations.

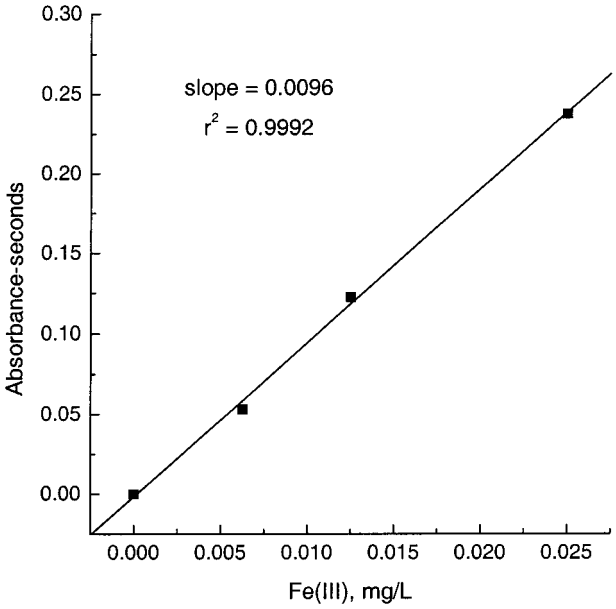

FIGURE 2. Standard curve for GFAAS determinations.

determinations were performed for samples found to contain less than 0.02 mg/L Fe(III) by colorimetric analysis. Recoveries were 93−101% for colorimetric determinations and 89−91% for GFAAS (Figure 3, Table 1).

Analytical Considerations. The C_{18} cartridges retain some Fe(II)−FerroZine complex. Thus, for best accuracy and precision at Fe(III) concentrations below about 0.2 mg/L, it is critical to preclean C_{18} cartridges by processing a blank solution through them. The C_{18} cartridges can be regenerated virtually indefinitely when used to determine Fe(III) concentrations higher than 0.2 mg/L. The pH of the final solution should be between 4 and 7. The yellow Fe(III)−acetohydroxamic acid complex (Figure 4) and the Fe(II)−FerroZine (*19*) complex will form completely in aqueous solution in this pH range.

The detection limit by colorimetric analysis using a 5-cm cell is 0.02 mg/L Fe(III). Standards for colorimetric determinations were prepared in the same way as samples and contained 0, 0.2, 0.4, 0.8, and 1.2 mg/L Fe(III) when diluted to volume. The detection limit by Zeeman-corrected GFAAS

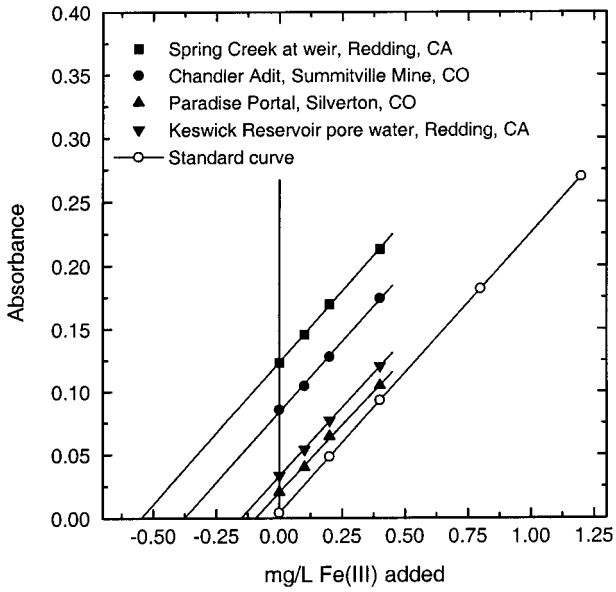

FIGURE 3. Method of standard additions for Fe(III) using the acetohydroxamic acid method.

TABLE 1. Iron(III) Spike Recoveries Using the Acetohydroxamic Acid Method

sample ID	Fe(III) added (mg/L)	recovered mg/L	recovered %	analysis
Alamosa River below	0.010	0.009	91	GFAAS
Terrace Reservoir	0.020	0.018	89	GFAAS
Spring Creek at weir	0.100	0.100	100	color
	0.200	0.203	101	color
	0.400	0.403	101	color
Chandler adit of	0.100	0.097	97	color
Summitville Mine	0.200	0.197	98	color
	0.400	0.400	100	color
Paradise Portal	0.100	0.093	93	color
	0.200	0.198	99	color
	0.400	0.384	96	color
Keswick Reservoir	0.100	0.097	97	color
pore water	0.200	0.198	99	color
	0.400	0.396	99	color

is 0.002 mg/L Fe(III). The less-sensitive colorimetric analysis is preferred only when Fe(III) concentrations are above its detection limit and results are needed in real time, such as during field studies. GFAAS determinations were standardized by programming the instrument to dilute a standard, prepared in the same way as samples, containing 0.03 mg/L Fe(III). For instruments without this capability, separate standards must be prepared. Non-Zeeman-corrected GFAAS may be applicable to the Fe determination, but this should be tested before routine use.

The sample should be filtered through a 0.1-μm or smaller pore-sized membrane. In a study of filter pore-size effects on the analysis of dissolved Fe, Al, Mn, and Ti in natural water, errors of 1 order of magnitude or more in the measurement of the dissolved metals were found when a 0.45-μm filter was used (*20*). This was caused by fine-grained particulate material passing through the membrane. Compared with a 0.45-μm membrane, the 0.1-μm membrane reduces the passage of particulate materials without significantly increasing filtration time. More recently, investigators have demonstrated that iron colloids also can pass through a 0.1-μm membrane (*21*).

Potential Interferences. The FerroZine and ammonium acetate reagents did not interfere with the Fe(III)−acetohydroxamic acid complex. Acid mine water may contain at

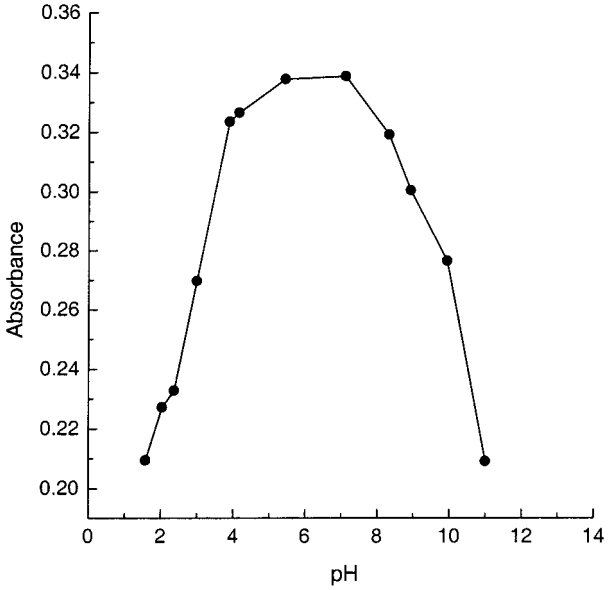

FIGURE 4. Effect of pH on the formation of Fe(III)−acetohydroxamic acid complex.

least 31 major chemical species with concentrations that vary up to several orders of magnitude. Many of those constituents may cause interferences in the colorimetric determination of Fe(III). Ten metals found in a typical acid mine effluent that may cause interferences have been tested. Chromium(III) was selected because of its chemical similarity to Fe(III). The remaining metals were selected based on their reported binding constants with acetohydroxamic acid (*22*).

Under the conditions used in this study, actetohydroxamic acid forms a tris complex with Fe(III) and has a reported binding constant, *K*, of $10^{26.9}$. The metals, in decreasing value of their reported binding constant with acetohydroxamic acid, are as follows: Al(III) (log $K = 21.47$), Pb(II) (log $K = 10.7$), Zn(II) (log $K = 9.6$), Co(II) (log $K = 8.9$), Fe(II) (log $K = 8.5$), Cu(II) (log $K = 7.9$), Ni(II) (log $K = 7.8$), Cd(II) (log $K = 7.8$), and Ca(II) (log $K = 2.4$). Because of the elemental specificity of the GFAAS technique, only Fe(II) is a potential interferent in the GFAAS measurement.

In the initial colorimetric interference study, the absorbance of each metal combined in solution with 2.5 mL of acetohydroxamic acid and 4.0 mL of ammonium acetate buffer solution and diluted to 25 mL was measured. Only Cr(III) (0.023) and Cu(II) (0.010) had absorbances above the blank (0.005). All metals except Ca(II) (400 mg/L) were tested at 40 mg/L. The level of interference by each metal with the quantitation of Fe(III) was determined by using the new method to measure the change in apparent Fe(III) content in the presence of each metal. Individual solutions containing 0 or 0.4 mg/L Fe(III) were analyzed in triplicate with up to 40 mg/L of potential interferent, except for Ca(II) (400 mg/L), added. The change in apparent Fe(III) content in the presence of 40 mg/L Al(III), Pb(II), Zn(II), Ni(II), and Cd(II) and 400 mg/L Ca(II) was less than ±0.008 mg/L. This change is considered insignificant because it is well below the minimum difference in Fe(III) content measurable by the new method.

The apparent Fe(III) content increases by 0.052 mg/L in the presence of 40 mg/L Cu(II). The tested Cu(II)/Fe(III) molar ratio was 88, whereas the ratio found in acid mine samples is typically less than 1. Of 25 samples taken from the Leviathan Mine drainage basin, located in California and Nevada, the average Cu(II)/Fe(III) ratio was 0.18 with two samples having a ratio slightly greater than 1 (*23*). In the presence of 20 mg/L Cu(II), the change in apparent Fe(III) content was less than 0.008 mg/L (Figure 5a).

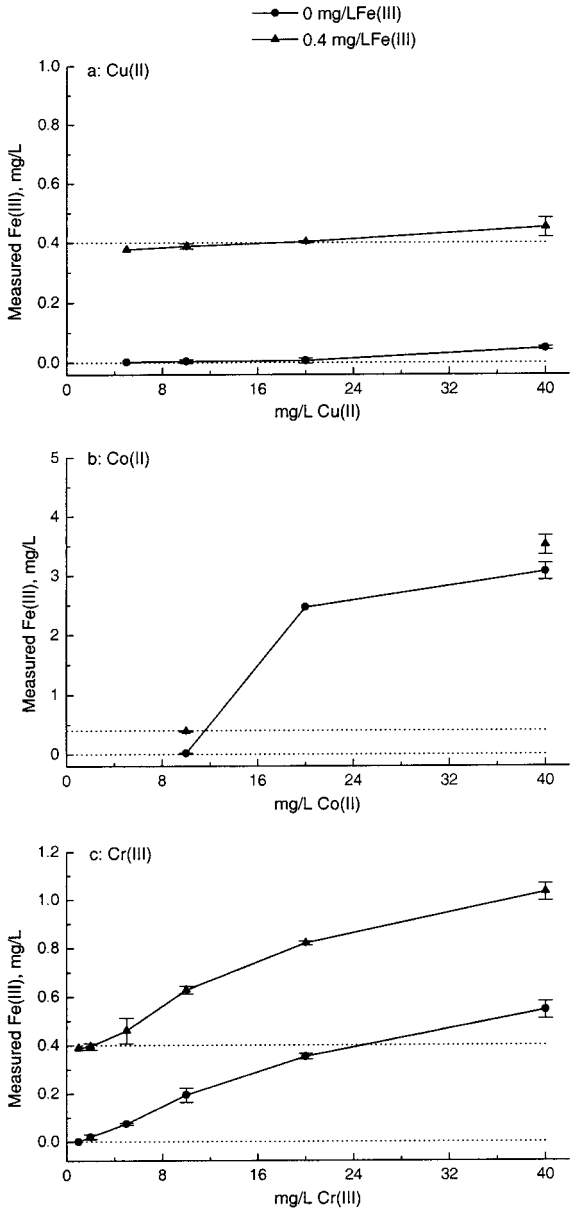

FIGURE 5. Apparent Fe(III) concentration in the presence of added Cu(II), Co(II), and Cr(III). [Error bars represent ±1 s for triplicate determinations.]

Co(II) forms a colored complex with FerroZine (*24*) that is not completely retained by the C_{18} cartridge at Co(II) > 10 mg/L and absorbs intensely at wavelengths less than 350 nm. The tail of the absorption band interferes with the 424-nm line. The highest Co(II)/Fe(III) molar ratio in the 25 Leviathan Mine drainage basin samples discussed above is 0.8. In the presence of 10 mg/L Co(II) (Co(II)/Fe(III) molar ratio of 24) the Co(II)−FerroZine complex is completely retained by the C_{18} cartridge. The change in apparent Fe(III) content was about +0.016 mg/L for a blank and about −0.008 mg/L in a 0.4 mg/L standard (Figure 5b). These deviations are not significant relative to the measured precision.

The apparent Fe(III) content increased by about 0.6 mg/L in the presence of 40 mg/L Cr(III). In the presence of 2 mg/L Cr(III) (Cr(III)/Fe(III) molar ratio of about 5), no change in the apparent content of Fe(III) in test solutions could be detected (Figure 5c). In most acid mine effluent samples the Cr(total)/Fe(III) molar ratio is usually well below 0.5. Cr, Co, and Cu are expected to interfere only under unusual conditions.

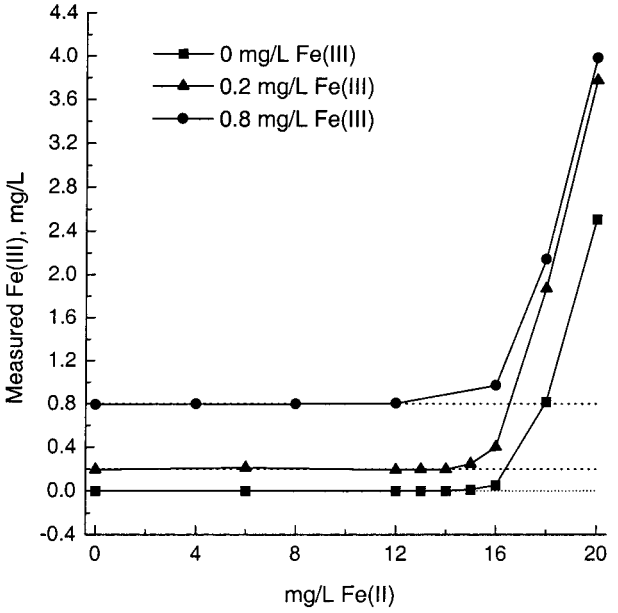

FIGURE 6. Iron(II) interferences and tolerance limits for direct determination of Fe(III) using the acetohydroxamic acid method.

Acetohydroxamic acid can oxidize Fe(II) to Fe(III), causing overestimation of the Fe(III) concentration. To control this source of error, it is necessary to add the FerroZine reagent before the acetohydroxamic acid so that the distribution of Fe redox species is stabilized. Separation of the two Fe complexes is necessary to prevent the strongly absorbing Fe(II)−FerroZine complex from interfering with the colorimetric determination of Fe(III). The Fe(II)−FerroZine complex exhibits a single peak with a maximum absorbance at 562 nm (*19*). The C_{18} cartridge retains the more hydrophobic Fe(II)−FerroZine complex while allowing the more hydrophilic Fe(III)−acetohydroxamic acid complex to pass into the effluent. The 562-nm absorbance remained at the baseline for synthetic Fe samples containing 0, 0.2, and 0.8 mg/L Fe(III) and 0−20 mg/L Fe(II), illustrating the completeness of the separation.

Under the conditions stated in the procedure, Fe(II) concentrations less than14 mg/L do not interfere with the Fe(III) determination (Figure 6). The stated quantity of FerroZine has the capacity to complex a maximum of 350 μg of Fe(II). More FerroZine could be used, but the capacity of the C_{18} cartridge would be exceeded. Excess Fe(II) is oxidized and forms Fe(III)−acetohydroxamic acid. Iron(III) was separated (97−103% recovery) from synthetic iron samples containing Fe(II)/Fe(III) ratios from 0 to greater than 500. Using the stated procedure, Fe(III) can be measured colorimetrically in solution with Fe(II)/Fe(III) ratios up to 880 and by GFAAS in solutions with ratios up to 8800.

Naturally occurring organic substances such as humic and fulvic acids may contribute positive interferences by elevating the background absorbance of affected samples. Such interferences are corrected by analyzing a sample containing all reagents except FerroZine and acetohydroxamic acid and subtracting the resulting absorbance from the absorbance of an identical solution containing all reagents before calculating the Fe(III) concentration. Competitive complexation of Fe(II) and Fe(III) by dissolved organic substances could interfere with complexation by FerroZine and acetohydroxamic acid, but such reactions should be comparatively slow. No indication has appeared that such an interference is present in our samples. Such effects are minimized by complexing the iron redox species, before buffering, at a pH where most dissolved organic substances will be fully protonated and cannot complex metals.

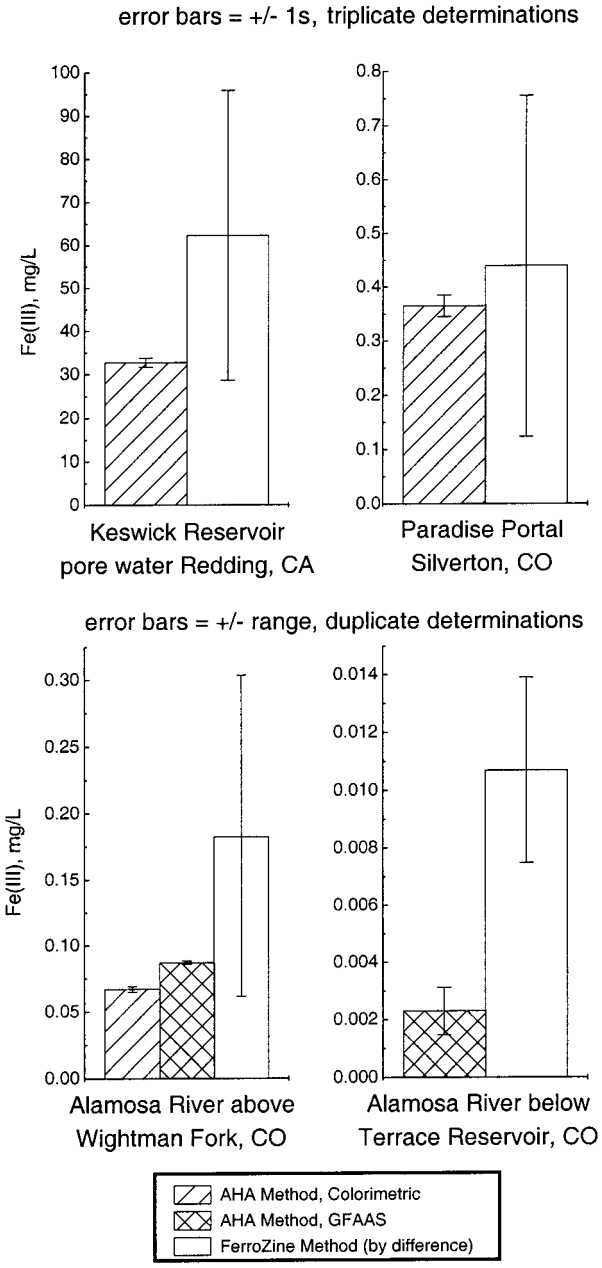

FIGURE 7. Comparison of Fe(III) concentrations determined directly using the acetohydroxamic acid (AHA) method with Fe(III) concentrations determined by difference using the FerroZine method.

Comparing the FerroZine Method with the New Method. The performance of the new method was compared with that of the FerroZine method for Fe(III) determinations. Ten representative samples were selected for the comparison (Table 2). Values of percent difference (Δ%), eq 1, were used for the comparison

$$\Delta\% = \frac{(\text{concentration}_{\text{method A}} - \text{concentration}_{\text{method B}})}{(\text{concentration}_{\text{method A}} + \text{concentration}_{\text{method B}})/2} \times 100 \quad (1)$$

where method A is the FerroZine method and method B is the new method with either colorimetric or GFAAS determinations. The maximum value of this function is ±200%. A Δ% value of 0 denotes a perfect match of the analytical values, while a value approaching ±200 means there is no similarity between values (*1*). A positive Δ% value indicates

TABLE 2. Chemical and Physical Parameters for 10 Water Samples[a]

sample ID	pH	spec cond	temp (°C)	Ca	Mg	Na	K	SO_4	HCO_3	Al	Mn	Cu	Fe_T	Fe(II)
Spring Creek at weir 11/97	NA	NA	NA	79	25	11	NA	NA	<1.0	17	4.6	1.2	112	102
Chandler Mine adit 6/97	2.6	5130	3.3	160	66	7.4	1.0	4780	<1.0	400	34	140	727	314
Paradise Portal 8/97	5.3	1950	4.8	370	58	9.0	3.4	1160	5.4	11	5.4	0.23	63.7	63.3
Keswick Reservoir pore water 9/97	5.7	4800	10.0	70	48	18	<0.7	4220	110	0.005	40	0.006	2100	2038
Alamosa River below Terrace Reservoir 6/97	6.7	122	9.3	14	2.2	1.6	<0.7	35	3.0	<0.1	0.25	<0.08	0.027	0.023
Alamosa River above Wightman Fork 10/97	5.8	154	0.1	17	3.7	2.3	<2.0	69	<5.0	0.42	0.29	0.01	2.86	2.70
Alamosa River above Wightman Fork 9/97	6.2	145	7.3	16	3.0	2.0	2.7	52	<5.0	<0.025	0.23	<0.003	2.10	1.92
Alamosa River above Jasper 9/97	6.2	311	9.9	45	4.9	3.7	<2.0	120	<5.0	<0.025	0.69	0.05	1.04	0.95
Wightman Fork at mouth 9/97	5.2	1010	7.8	200	13	9.5	3.5	580	<5.0	2.9	3.2	0.92	0.393	0.248
Wightman Fork at mouth 6/97	4.7	296	4.5	34	5.0	3.2	0.9	140	0.8	2.1	1.7	1.0	0.981	0.827

[a] Spec cond, specific conductance in μS/cm; all concentrations in mg/L. Maximum concentrations of Cd, Co, Cr, Pb, and Ni are less than 2 mg/L in all samples. Zn concentration is 38 mg/L in Chandler Mine adit sample and less than 2.5 mg/L in all other samples. NA, not analyzed.

TABLE 3. Precision and Percent Difference Calculations for Replicate Determinations on 10 Samples[a]

	FerroZine Fe(III)			AHA-colorimetric Fe(III)				AHA-GFAAS Fe(III)			
sample ID	*n*	mean (mg/L)	precision (mg/L)	*n*	mean (mg/L)	precision (mg/L)	Δ%	*n*	mean (mg/L)	precision (mg/L)	Δ%
Spring Creek at weir	3	10	0.77	3	8.97	0.17	3	NA			
Chandler Mine adit	3	410	4.7	3	367	11.1	3	NA			
Paradise Portal	3	0.4	0.32	3	0.36	0.021	5	NA			
Keswick Reservoir pore water	3	60.0	32.3	3	32.8	1.04	15	NA			
Alamosa River below Terrace Reservoir	3	0.01	0.003	NA				3	0.002	0.00008	32
Alamosa River above Wightman Fork 10/97	2	0.17	0.080	2	0.078	0.0025	18	2	0.10	0.002	12
Alamosa River above Wightman Fork 9/97	2	0.18	0.061	2	0.067	0.0010	23	2	0.087	0.0007	18
Alamosa River above Jasper	2	0.082	0.026	2	0.10	0.0005	−6	2	0.12	0.001	−9
Wightman Fork at mouth 9/97	2	0.14	0.005	NA				2	0.057	0.0076	22
Wightman Fork at mouth 6/97	2	0.15	0.028	NA				2	0.097	0.0084	11

[a] AHA, acetohydroxamic acid; precision, ±1 s for triplicate determinations, ± range for duplicate determinations; NA, not analyzed; Δ%, percent difference between FerroZine and AHA methods, calculated using eq 1.

that Fe(III) concentration determined by FerroZine is greater than the concentration measured by the new method. To compare the analytical results of direct Fe(III) determinations with the Fe(III) results obtained by difference using the FerroZine method, values of precision and the Δ% function were calculated (Table 3). In all but one case, Fe(III) concentrations obtained by difference using the FerroZine method were greater than those obtained using the new method. The value of the Δ% function was +32% in one case. A graphical representation of results for selected samples is shown in Figure 7.

The power of the new method lies in its capability to determine Fe(III) concentration in samples containing very high Fe(II)/Fe(III) ratios. As the Fe(II)/Fe(III) ratio increases, the relative standard deviation of Fe(III) concentrations obtained by difference generally increases. Relative standard deviations for Fe(III) determinations using the FerroZine method for 50 different samples collected from three different acid mine effluents including Summitville Mine, Rio Grande County, CO; Paradise Portal in the Upper Animas Mine Drainage, San Juan County, CO; and Iron Mountain Mine, Shasta County, CA, increased to over 50% in samples with Fe(II)/(III) ratios of 30 or higher. This uncertainty is often too large for Fe(III) concentrations determined by difference to be meaningful. The relative standard deviations for Fe(III) concentrations determined directly using the new method (Table 3) are generally less than 5%.

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