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ORIGINAL ARTICLE

Factors affecting the determination of iron species in the presence of ferric iron

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Abstract
The high concentration Fe^{3+} in sample had interference on the determination of iron species by spectrophotometric method in which 1,10-phenanthroline was used to as a chromogenic agent. The F^- could mask absolutely the effect of Fe^{3+} when F^-/Fe^{3+} molar concentration ratio was 13.3. The temperature or light did not affect the masking action of F^-. Low temperature and dark conditions favored the stability of chromophoric complex. This method is suitable for the measure of iron species where the concentration of Fe^{3+} is far more than that of Fe^{2+} in samples.

Keywords Iron species · Spectrophotometric · Fluorine ion · Masking action · Storage condition

Introduction

Acid mine drainage (AMD) is produced when sulfide minerals are exposed to oxic conditions. AMD distributes widely around the world, like USA (Nordstrom et al. 2000), South Africa (Tutu et al. 2008), Australia (Webb and Sasowsky 1994), Ireland (Gray 1998) and China (Wu et al. 2009). AMD is characterized by low pH values (Blowes et al. 2003; Nordstrom et al. 2000), high iron concentration and various heavy metals (As, Hg, Sb et al.) (Arnold et al. 2011; Iakovleva et al. 2015). Iron species and contents can affect the transport and transformation of heavy metals (Matlock et al. 2002; Zhu et al. 2017). So, it is important to exactly determine iron species in the investigation of environmental behavior of heavy metals in AMD.

The spectrophotometric methods have been commonly used for the analysis of iron content such as 2,2′-bipyridyl and 2,2′,2″-terpyridyl 4,7-diphenyl-1 method (Moss and Mellon 1942), 4,7-diphenyl-1,10-phenanthroline method (Clark 1962), ferrozine method (Herrera et al. 1989) and 1,10-phenanthroline method (Tamura et al. 1974). The 1,10-phenanthroline method is used widely due to its high sensitivity (Tong et al. 2016; Amonette and Matyáš 2016; Sumitomo et al. 2017). The high concentration Fe^{3+} affects the analysis of Fe^{2+} in the process of colorimetry by the 1,10-phenanthroline method such as AMD samples, so F^- is added into the solution to eliminate interferences (Herrera et al. 1989). The F^- reacts with Fe^{3+} to form ferric fluoride which does not react with 1,10-phenanthroline, so F^- was a complexing agent to modify the 1,10-phenanthroline method (Herrera et al. 1989). The studies on the usage rules of F^- and reaction conditions of chromophoric complexes by the 1,10-phenanthroline method are few. Besides, the stability of chromophoric complexes under different temperatures or lights is not known.

The objectives of this study were to investigate the effects of Fe^{3+}, obtain a suitable dosage of F^- which can mask the interference of Fe^{3+} and assess the effects of light, reaction temperature and time. And then, the solutions after chromogenesis were stored under different conditions to evaluate the stability of chromophoric complex.

Materials and methods

Chemicals

Ferrous sulfate (99.9%), ferric chloride (99.9%), sodium fluoride (99.9%), ammonium acetate (99.9%), acetic acid (99.9%) and 1,10-phenanthroline (99.9%) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. The

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deionized water prepared by a Milli-Q water purification device (Millipore, USA) was used in all experiments.

Batch experiments

Different amounts of 400 mg/L Fe^{3+} and 100 mg/L Fe^{2+} solutions were added to deionized water to produce modified AMD. In modified AMD, the molar ratios of Fe^{3+}/Fe^{2+} were 0, 0.1, 0.5, 1, 2, 4, 8, 16, respectively. These samples were used to assess the interferences of Fe^{3+} on the measurement of Fe^{2+}.

To obtain appropriate fluorine ion (F^-) concentration to mask Fe^{3+}, different amounts of F^- were added into modified AMD which contains 2 mg/L Fe^{2+} and 8 mg/L Fe^{3+} to make F^-/Fe^{3+} molar concentration ratio be 0, 1, 2, 4, 6, 8, 12, 18, 36, respectively. To evaluate the influence of temperature on chromogenic reaction, chromogenic reaction has been performed under 5, 15 or 30 °C, respectively, where solutions contained 2 mg/L Fe^{2+}, 8 mg/L Fe^{3+} and with or without the addition of 36.1 mg/L F^-. To examine the stability of chromophoric complexes, solutions after color reaction were stored under room light illumination at 25 °C, dark at 25 °C or dark at 5 °C, respectively.

Chemical analysis

Dissolved Fe^{2+} was measured by the 1,10-phenanthroline analytical method at 510 nm using a UV–Vis spectrophotometer (Tamura et al. 1974). Total iron concentrations were measured through the reduction of Fe^{3+} to Fe^{2+} by hydroxylamine HCl. The concentration of Fe^{3+} was calculated as the difference in concentrations between total iron and Fe^{2+}.

Results and discussion

Analysis of the error of determination of Fe^{2+} in the presence of Fe^{3+}

The chromophoric complexes by 1, 10-phenanthroline and high concentration of Fe^{3+} could increase the absorbance of samples at 510 nm. To analyze the effect of Fe^{3+} on the measurement of Fe^{2+}, different concentrations of Fe^{3+} were added to 2 mg/L Fe^{2+} solution. The absorbance of solutions at 510 nm increased with the increase in concentrations of Fe^{3+}, as shown in Fig. 1. The error reached 22.6% when the concentration of Fe^{3+} was 16 times more than that of Fe^{2+} which is common in AMD. The error was more than 50% when Fe^{3+} was not complexed and Fe^{2+} was less than 1% of the total iron (Herrera et al. 1989). So, Fe^{3+} obviously affects the measurement of Fe^{2+} when the concentration of Fe^{3+} was more than that of Fe^{2+} in solution.

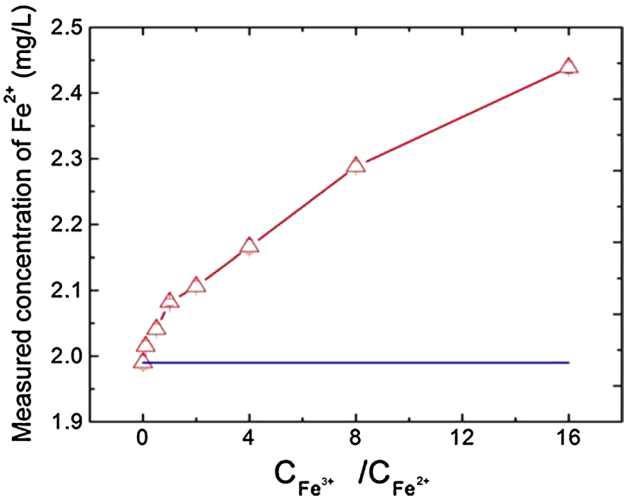

Fig. 1 Interference of Fe^{3+} on the measured concentration of Fe^{2+}. C^{3+}_{Fe}/C^{2+}_{Fe} was molar concentration ratio. Experimental conditions: 2 mg/L Fe^{2+} and different concentrations of Fe^{3+}

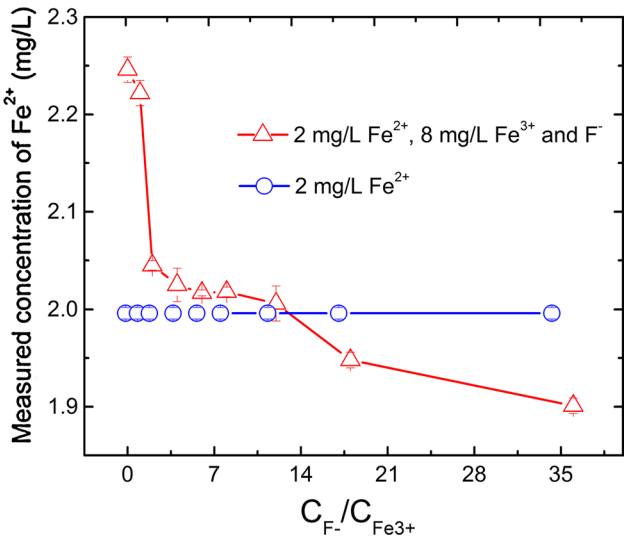

Fig. 2 Effect of dosage of F^- on the determination of Fe^{2+} in the presence of Fe^{3+}. Experimental conditions: 2 mg/L Fe^{2+}, 8 mg/L Fe^{3+} and with or without the addition of F^-; C^-_F/C^{3+}_{Fe} was molar concentration ratio

Determination of F^- dosage

The reaction of F^- with Fe^{3+} formed ferric fluoride (Herrera et al. 1989) which could make interference of Fe^{3+}, so F^- was selected as the complexing agent to modify the 1,10-phenanthroline method (Muir and Andersen 1977). The effect of F^- on the determination of Fe^{2+} in the presence of Fe^{3+} is shown in Fig. 2, where 2 mg/L Fe^{2+} and 8 mg/L Fe^{3+} were in solution. It should be noted that the absorbance of samples after chromogenesis decreased

with the increase in concentrations of F^- (Fig. 2). When F^-/Fe^{3+} molar concentration ratio was from 1 to 2, the errors of samples decreased quickly. And the errors of samples decreased slowly when F^-/Fe^{3+} molar concentration ratio was from 2 to 12. The F^- could eliminate absolutely the effect of Fe^{3+} when F^-/Fe^{3+} molar concentration ratio was 13.3(Fig. 2). But negative error was caused by excess F^- (Fig. 2). So, the amount of F^- depended on the Fe^{3+} concentrations in the sample. With less or more dosage of F^-, the masking effect of F^- was not best. The previous studies documented the error was decreasing with amount of F^-(Leandro et al. 1989; Tamura et al. 1974), but Tamura et al. found that a large excess of F^- has no effect on measurement of iron species (Tamura et al. 1974).

Effect of temperature on reaction

The temperature affects the chemical reaction ratio, but a few studies reported the effect of temperature on the 1,10-phenanthroline method and masking action of F^- (Anastácio et al. 2008; Leandro et al. 1989; Muir and Andersen 1977; Tamura et al. 1974). So we have evaluated the influence of temperature on color reaction and F^- masking action. The solutions which contain 2 mg/L Fe^{2+}, 8 mg/L Fe^{3+} and with or without the addition of F^- were stored under 5, 15 and 30 °C, respectively. Figure 3 shows that temperature did not affect the masking action of F^-, but affect significantly color reaction at 5–30 °C. The color reaction finished within 15 min, and the complexes from the reaction of Fe^{2+} with 1,10-phenanthroline kept stable within 1 h under 15–30 °C. The color reaction finished at 45 min under 5 °C. These suggested that color reaction needs more time at lower temperature. The experiment results of Herrera et al. (1989) show that the absorbance of solution increased after 5 min when all reagents were added at ambient temperature. The main reason may be that chromogenic reaction time was insufficient.

Effect of storage condition

To further evaluate the stability of chromophoric complexes, the solution with or without the addition of F^- after color reaction was stored at different conditions. The chromophoric complex concentrations decreased with time (Fig. 4). The chromophoric complexes were stable within 2 h and decomposed 24.0% in 96 h under light illumination and 25 °C. The chromophoric complexes were stable within 12 h and decomposed 6.3% in 96 h under dark and 25 °C. The chromophoric complexes were stable within 24 h and decomposed 1.9% in 96 h under dark condition and 5 °C. So, both light and temperature affected the stability of chromophoric complexes, and the effect of light on breaking chromophoric complexes was much greater than that of temperature. Because the absorbance of solutions with the addition of F^- was consistent with that without the addition of F^-, the light or temperature has not affected the masking action of F^-, and F^- had not affected the stability of chromophoric complexes. Verbeek (1961) found that the absorbance of solution increased because the Fe(III)-phen complex transformed Fe(II)-phen complex due to photoreduction when the solution was exposed to sunlight before the addition of F^-. Our procedure was completed in reference to Herrera's procedure (Tamura et al. 1974), so the absorbance of solutions not increased with time. The solutions after chromogenesis should be kept in dark and low temperature before they were measured.

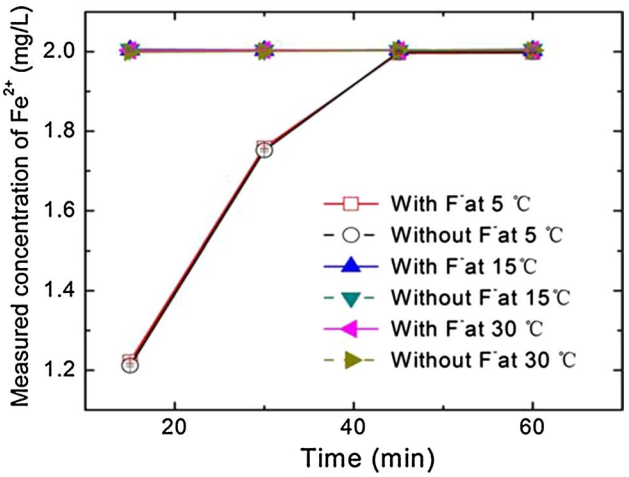

Fig. 3 Effect of temperature on the determination of Fe^{2+} in the presence of Fe^{3+}. Experimental conditions: 2 mg/L Fe^{2+}, 8 mg/L Fe^{3+} and with or without the addition of 36.1 mg/L F^- under room light illumination

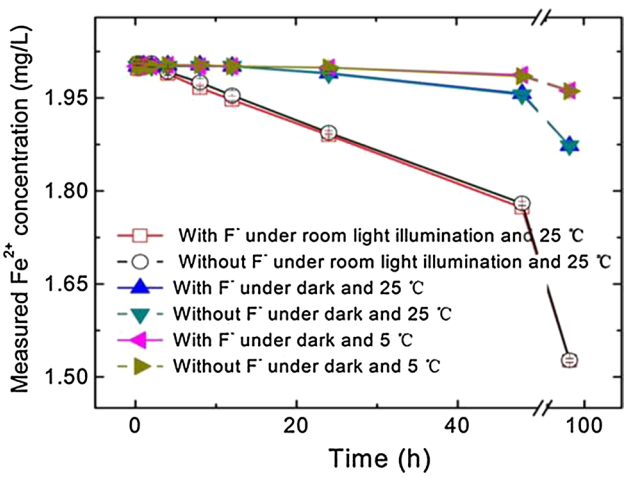

Fig. 4 Effect of light and temperature on chromophoric complexes. Experimental condition: solutions which contained 2 mg/L Fe^{2+}, 8 mg/L Fe^{3+} and with or without the addition of 36.1 mg/L F^- after chromogenesis was kept under different lights or temperatures

Conclusion

The high concentration Fe^{3+} in the sample interfered with the analysis of Fe^{2+} in the process of colorimetry by the 1,10-phenanthroline method. The previous studies modified spectrophotometric method which was based upon the addition of sodium fluoride to complex Fe(III) to eliminate interference (Leandro et al. 1989; Tamura et al. 1974). In this study, we found that F^- could mask absolutely the interference of Fe^{3+} when F^-/Fe^{3+} molar concentration ratio was 13.3. The low temperature reduces the rate of chromogenic reaction. The temperature or light did not affect the masking action of F^-. Low temperature and dark conditions favored the stability of chromophoric complex. This method is available to exactly determine the iron species in AMD.

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