SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF IRON SPECIES IN THE PRESENCE OF FERRIC IRON

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ARTICLE DETAILS

ABSTRACT

Article History:

Received 02 october 2017

Accepted 06 october 2017

Available online 11 october 2017

Keywords:

Iron species,
Spectrophotometric method,
Fluorine ion, Masking action,
Storage condition.

The high concentration of ferric(Fe^{3+}) in sample has interference on the determination of ferrous(Fe^{2+}) concentration by spectrophotometric method which 1, 10-phenanthroline is used to as chromogenic agent. Appropriate concentration of fluorine ion (F^-) can complex Fe^{3+} to eliminate interferences which the F^- concentration is 13.3 time greater than that of Fe^{3+} . The temperature and light do not affect the masking action of F^- . Low temperature and dark conditions favour the stability of chromophoric complex. This method is suitable for determination iron species in the presence of high concentration of Fe^{3+} in sample.

1. INTRODUCTION

Acid mine drainage (AMD) is caused by oxidation of sulfide minerals exposed to atmospheric oxygen. It distributes widely around the world, like USA [1], South Africa [2], Australia [3], Ireland [4] and China [5]. AMD is characterized by the low pH values [1,6], the high iron concentrations and various heavy metal (such as As, Hg, Sb) [7-8]. Iron species and content can affect transport and transformation of heavy metal. So, the determination of iron species concentrations is practical important in investigation of heavy metal.

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-1,10-phenanthroline method [9], 4,7-diphenyl-1,10-phenanthroline method [10], ferrozine method [11] and 1, 10-phenanthroline method [12]. 1, 10-phenanthroline method has been published and implemented as standard specifications of Ministry of Environmental Protection of the People's Republic of China due to its high sensitivity. The concentrations of Fe^{2+} and Fe^{3+} in AMD are very high, which reaches several hundreds and even thousands of mg/L. The high concentration Fe^{3+} affect analysis of Fe^{2+} in the process of spectrophotometric method using 1, 10-phenanthroline, so we need a method to mask the effect of Fe^{3+} . The F^- react with Fe^{3+} to form ferric fluoride [11] which do not react with 1,10-phenanthroline, so F^- was used to a complexing agent to modify the 1,10-phenanthroline method. The study about method of application of F^- and storage conditions of chromophoric complexes are few.

The objectives of this study were to investigate affects of Fe^{3+} and choice of suitable reagent to mask the effect of Fe^{3+} , assess effect of reaction temperature, light and time. At last, the solutions after chromogenesis were stored under different conditions to evaluate the stability of chromophoric complex.

2. Materials and methods

2.1 Chemicals

Ferrous sulfate (99.9%), ferric chloride (99.9%), sodium fluoride (99.9%), ammonium acetate (99.9%), acetic acid (99.9%), 1, 10-phenanthroline

(99.9%) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. The deionized water prepared by a Milli-Q water purification device (Millipore) was used in all experiments.

2.2 Batch experiments

Different volumes 400 mg/L Fe^{3+} solution were added to 2 mg/L Fe^{2+} solution respectively to form different Fe^{3+} concentrations. The molar ratios of Fe^{3+} to Fe^{2+} respectively were 0, 0.1, 0.5, 1, 2, 4, 8, 16. These samples were used to assess the interferences of Fe^{3+} on measurement of Fe^{2+} .

To get appropriate concentration of F^- to mask Fe^{3+} , we added different concentrations F^- into solutions which contain 2 mg/L Fe^{2+} and 8 mg/L Fe^{3+} to make molar ratio of F^- to Fe^{3+} respectively be 0, 1, 2, 4, 6, 8, 12, 18, 36 and 72. To evaluate the influence of temperature on masking action of F^- , we made solution temperature to be 5, 15 and 30°C. To examine stability of chromophoric complexes, solutions were stored in different temperature and light conditions.

2.3 Chemical analysis

The concentration of Fe^{2+} was measured by the 1,10-phenanthroline analytical method at 510 nm using a UV-vis spectrophotometer [12]. Total iron concentrations were measured through 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+} .

3. Results and discussion

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

Fig. 1 Interference of Fe^{3+} on measurement concentration of Fe^{2+} . $C_{\text{Fe}^{3+}}/C_{\text{Fe}^{2+}}$ was molar concentration ratio. Experiment conditions: 2 mg/L Fe^{2+} and different concentration of Fe^{3+} .

To analyze the effect of Fe^{3+} on measurement of Fe^{2+} , different concentrations of Fe^{3+} were added to 2 mg/L Fe^{2+} solution. The resulting absorbance (510 nm) increased with the concentrations of Fe^{3+} , as shown in Fig. 1. The error of result reached to 22.6% when the concentration of Fe^{3+} was 16 times than that of Fe^{2+} which is common in AMD. So, high concentration of Fe^{3+} obviously affect measurement of Fe^{2+} .

3.2 Determination of F^- dosage

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+} and 8 mg/L Fe^{3+} , $C_{\text{F}}/C_{\text{Fe}^{3+}}$ was molar concentration ratio.

The F^- react with Fe^{3+} to form ferric fluoride [11] to make Fe^{3+} do not react with 1,10-phenanthroline, so F^- was selected as the complexing agent to modify the 1,10-phenanthroline method. The effect of F^- on the determination of Fe^{2+} in the presence of Fe^{3+} was shown in Fig. 2, which 2 mg/L Fe^{2+} and 8 mg/L Fe^{3+} were in solution. It should be noted that absorbance of sample after chromogenesis decreased with the increase of concentrations of F^- (Fig. 2). In combination with effect of F^- dosages, we concluded that there was an optimal dosage for masking Fe^{3+} which the concentration of F^- was 13.3 time than that of Fe^{3+} (Fig. 2). So, the amount of F^- required depends on the expected Fe^{3+} concentration in the sample. With less or more dosage of F^- , the masking effect of F^- was not best.

3.3 Effect of temperature on reaction

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 of 36.1 mg/L F^- under room light illumination.

Because temperature affect chemical reaction ratio, we evaluated the influence of temperature on F^- -masking action. The sample which contain 2 mg/L Fe^{2+} , 8 mg/L Fe^{3+} and with or without addition of F^- were respectively stored at 5, 15 and 30 °C. The Fig. 3 showed that temperature did not effect masking action of F^- , but affect significantly chromogenic reaction ratio at 5-30 °C. The chromogenic reaction of Fe^{2+} has been finished within 15 minute, and the complexes from the reaction of Fe^{2+} with 1,10-phenanthroline keep stable in 1 hour at 15-30 °C. The chromogenic reaction of Fe^{2+} has been finished within 45 minute at 5 °C. This suggested that chromogenic reaction of Fe^{2+} need more time in lower temperature.

3.4 Effect of storage condition

To further evaluate the stability of chromophoric complexes, the solution with and without F^- after chromogenesis were stored different conditions which including room light illumination at 25 °C, dark at 25 °C and dark at 5 °C. The temperature and light did not affect the masking action, but affect the stability of chromophoric complexes (Fig. 4). The effect of temperature on breaking complex was greater than the light (Fig. 4). The chromophoric complexes were stable under dark condition and 5 °C within 12 h.

Fig. 4 Effect of light and temperature on chromophoric complexes. Experimental conditions: 2 mg/L Fe^{2+} , 8 mg/L Fe^{3+} and with or without of 36.1 mg/L F^- after chromogenesis.

4. Conclusion

The high concentration Fe^{3+} in water sample affect analysis of Fe^{2+} concentration in the process of spectrophotometric method by 1, 10-phenanthroline method. Appropriate concentration of F^- can mask the effect of Fe^{3+} which the F^- concentration is 13.3 time greater than that of Fe^{3+} . The temperature and light do not affect the masking action of F^- . Low temperature and dark conditions favour the stability of chromophoric complex. This method is suitable for determination of concentration of iron species in the presence of high concentration of Fe^{3+} in sample.

Acknowledgments

This work was supported by the Science and Technology Foundation of Guizhou Province [No. J- LKN[2013]27].

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