

Species distribution of polymeric aluminium-ferrum—timed complexation colorimetric analysis method of Al-Fe-Ferron

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Abstract: The effects of the colorimetric buffer solutions were investigated while the two colorimetric reactions of Al-ferron complex and Fe-ferron complex occurred individually, and the effects of the testing wavelength and the pH of the solutions were also investigated. A timed complexation colorimetric analysis method of Al-Fe-ferron in view of the total concentration of $[Al + Fe]$ was then established to determine the species distribution of polymeric Al-Fe. The testing wavelength was recommended at 362 nm and the testing pH value was 5. With a comparison of the ratios of n_{Al}/n_{Fe} , the standard adsorption curves of the polymeric Al-Fe solutions were derived from the experimental results. Furthermore, the solutions' composition were various in both the molar n_{Al}/n_{Fe} ratios, i. e. 0/0, 5/5, 9/1 and 0/10, and the concentrations associated with the total $[Al + Fe]$ which ranged from 10^{-5} to 10^{-4} mol/L.

Keywords: polymeric aluminum-ferrum; species distribution; timed complexation colorimetric analysis method; Al-Fe-ferron

Introduction

Turner first adopted the Al-ferron method as an indirect analysis method to determine the species distribution of Al-solutions in 1969 (Turner, 1969). This method has been improved and is still used at present and it plays a key role in studying the distribution and transformation of species in the solutions containing Al^{3+} and Fe^{3+} . Ferron (7-iodo-8-hydroxy quinoline-5-sulfonic acid) was first used in analyzing the Fe-forms under a given condition (Yoe, 1937). Ferron is reactive with the free ions of Fe to form a series of green Fe-ferron complexes such as FeL^+ , FeL_2^- , $Fe(OH)L$, $Fe(OH)_2L^-$, FeL_3^{3-} and $Fe(OH)L_2^{2-}$ and other forms, which were bound by hydroxide bridge (Davenport, 1949). Davenport (1949) reported that the monomeric ion of Al was reactive with ferron to form Al-ferron complexes such as AlL^+ , $Al(OH)L$, $Al(OH)_2L^-$, AlL_2^- , $Al(OH)L_2^{2-}$ and AlL_3^{3-} and other forms (Langmuir, 1961), which yielded an absorption maximum at 370 nm. He also reported that two absorption maximums for the Fe-ferron complex species arose at 600 nm and 370 nm, respectively (Davenport, 1949). Therefore, it was impossible to determine the forms of Al and Fe simultaneously based on the above mentioned reaction law.

In order to identify the species distribution of the acidic Al-Fe coexisting solutions, Li (Li, 1998) used the above mentioned ferron-reaction method through measuring the absorbances of the Al-Fe solutions to determine the species concentration of Al and Fe at 370 nm and 600 nm, respectively. In the process of determining the Al-forms, there was an interfering factor that the green color of the Fe-ferron complexes could completely sheltered the yellow color of the Al-ferron complexes, so the results were inaccurate. The yellow of the Al-complexes was weak in strength, so aluminum did not interfere with the determination of the green Fe-complexes too much. According to this fact, Tian (Tian, 1998) derived the species distribution in the solutions of hydroxyl polymeric aluminum-ferric chloride (HPAFC) by determination of the Fe-forms of them. Because the contribution of the Al-forms to the species distribution of the HPAFCs could not be distinguished from by this method, thus the result could not really reflect the species distribution of the Al-Fe coexisting solutions.

In this paper, the authors proposed an improved timed complexation colorimetric analysis method of Al-Fe-ferron, which could be used to determine the species distribution in the Al-Fe coexisting solutions quantitatively.

1 Improvement to the timed complexation colorimetric method

The composition of the colorimetric buffer solution used for the Al determination was not as same as that used for the Fe-determination. Hydroxylamine hydrochloride could reduce Fe^{3+} to Fe^{2+} , the latter then be complexed by orthophenanthroline to form a stable complex ion of $[(C_{12}H_8N_2)_3Fe^{2+}]$ at pH ranging from 3 to 9, and therefore the formation of Fe-ferron complex could be minimized. The ions of Cu^{2+} , Ni^{2+} , Zn^{2+} , Hg^{2+} , Ca^{2+} and Mn^{2+} could be masked by orthophenanthroline, so their interference could be avoided in the Al determination (Wuhan University, 1995).

Literatures (Tian, 1998; Li, 1998) indicated that the HPAFC was a collection made up of following species, such as polymeric Al, polymeric Fe and co-polymeric Al-Fe. It was impossible to identify the species distribution of the HPAFC solution based on either Al-species distribution or Fe-species distribution individually. However, if we considered Al-Fe species as a whole, the species distribution of the Al-Fe coexisting solutions could be described simply by the summation of the Al-Fe species. The timed complexation reaction curve of Al-Fe-ferron could be divided into three phases: the $[Al + Fe]_a$ that reacted rapidly, the $[Al + Fe]_b$ that reacted slowly, and the $[Al + Fe]_c$ of inertial reaction. This could somewhat reflect the whole situation of the species distribution of the Al-Fe solutions. However, the orthophenanthroline and hydroxylamine

hydrochloride could not be added into the colorimetric buffer reaction solutions during the period of reaction.

There was a maximum absorption at 370 nm for both the Al-feron and Fe-feron complexes. Based on this fact, Li (Li, 1998) determined the species distribution of HPAFC at 370 nm, but the measure result was just qualitative. The absorption maximum intensity of the Al-feron complex was not as same as that of the Fe-feron complex, the same absorption maximum intensity could be obtained from various Al-Fe solutions with different n_{Al}/n_{Fe} ratios, that is to say, the species concentration and the absorption intensity do not coincide. If the solutions of the Al-feron and Fe-feron complexes with the same concentration were measured by a UV/Vis spectrometer (Daojin UV2100), the testing results indicated that they both had a same absorption maximum intensity at 362 nm. The equal point in absorption maximum intensity was at 362 nm at which the absorption intensity was proportional to the total concentration of $[Al + Fe]$, and the pH value related to the solutions is about 5. This indicated that the quantitative analysis could be conducted for the Al-Fe coexisting solutions.

Based on classical instrument analysis theory, the wavelength of 362 nm would be determined as the testing wavelength in use of the timed complexation colorimetric method to analyze the Al-Fe species distribution quantitatively (Fig.1).

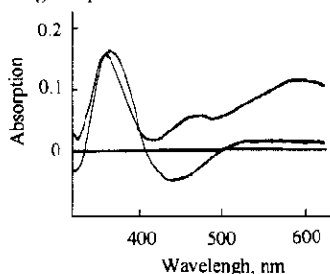


Fig.1 Complexation curves of Al-feron and Fe-feron

2 Effects of pH on the timed complexation colorimetric method

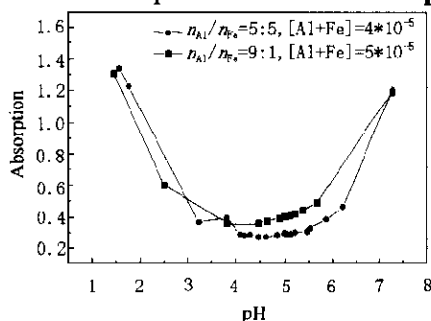


Fig.2 Effect of pH on Al-Fe-feron reaction

It was known many years ago that the effects of pH value were very important in use of the ferrorn-reaction method to determine the species distribution of Al^{3+} and Fe^{3+} in the solutions. The investigation undertaken by Hsu *et al.* (Hsu, 1991) has further improved the understanding for the following two effects of pH: (1) Species distribution of ferrorn is pH-dependent, the pH thereby affects the reaction of ferrorn with the monomeric Al^{3+} and Fe^{3+} , and it can also change the background absorption. (2) The changes in pH value can cause the instantaneous changes in species distribution of Al^{3+} and Fe^{3+} , so affecting the analysis results.

Luan *et al.* (Luan, 1988) indicated that Al-feron reactions could undertake properly at pH value ranging between 5.0 and 5.2. Tian (Tian, 1998) proposed that the pH of solution at 5 was good for Fe reaction with ferrorn. The Al-Fe-feron reactions were investigated at different pH values in this study to determine the

absorption intensities shown in Fig.2 where a platform appeared at the pH values ranging from 4.0 to 5.5 at which the Al-Fe-feron reactions could reach equilibrium point quickly.

3 The improved timed complexation colorimetric method

There are many personal factors that will occur in application of the timed complexation colorimetric method. The main reason was that none could identically operate. The authors proposed the following procedures through many experimental studies. The experimental reagent used should be of analytical grade, the instruments should be immersed in diluted HCl solution for a day and then washed with deionized water to prevent the interference of ions such as Zn^{2+} , Mn^{2+} and Cu^{2+} etc, eliminating the systematic error.

3.1 Colorimetric buffer solution

(1) Ferrorn solution (0.2%): 0.1000g of ferrorn was dissolved in boiled deionized water prior to dilution to 500 ml, and then stored in refrigerator. (2) NaAC solution (35%): 70.0g of NaAC (99.0%, wt/wt) was dissolved in deionized water prior to dilution to 200 ml, and then stored in refrigerator. (3) Hydrochloric acid (1:3): 25 ml HCl (~37%, wt/wt) was added to a 100 ml-volumetric flask, then diluted to 100 ml with deionized water.

3.2 Preparation of the standard aluminum solution

Standard aluminum solution, 0.01 mol/L: 0.2700g of aluminum (99.99%, wt/wt) was dissolved in some amount of HCl (1:1) solution before dilution to 1L. The final pH value of the stock solution was 0.7. The stock solution was diluted ten times to prepare the work solution with pH 1.65.

3.3 Preparation of the standard iron solution

Standard iron solution, 0.01 mol/L: 0.568 g of pure iron (99.99%, wt/wt) was dissolved in some amount of HCl (1:1) solution, then diluted to 1L. The final pH value of the stock solution was 0.7. The stock solution was diluted ten times to prepare the work solution with pH 1.65.

3.4 Experimental procedure (To establish the calibration curve)

(1) One milliliters of HCl (1:2) and 2.3 ml of NaAC (35%, wt/wt) were mixed well in a 50 ml volumetric flask. Then 5.0 ml of ferrorn solution was accurately added and mixed well again. (2) Each of both the standard aluminum solution and the standard iron solution was accurately added into 50 ml volumetric flasks individually in the order of 0, 0.5, 1.0, 2.0, 3.0 and 4.0 ml prior to dilution to 50 ml with deionized water and then mixed. The pH value of the above solutions was

about 5. Blank experiment of the ferron reagent was conducted, and the testing wavelength of 362 nm was selected to measure the absorbances.

4 Standard absorption curves of Al-Fe-ferron complexes

It is clear to obey the Beer's law under the condition that the total $[Al + Fe]$ concentration ranged from 10^{-5} mol/L to 10^{-4} mol/L at which the Al-Fe-ferron calibration curve was established. The absorption of the four groups of Al-Fe solution with different n_{Al}/n_{Fe} ratios were measured (data not shown), and then the Al-Fe-ferron calibration curves were established

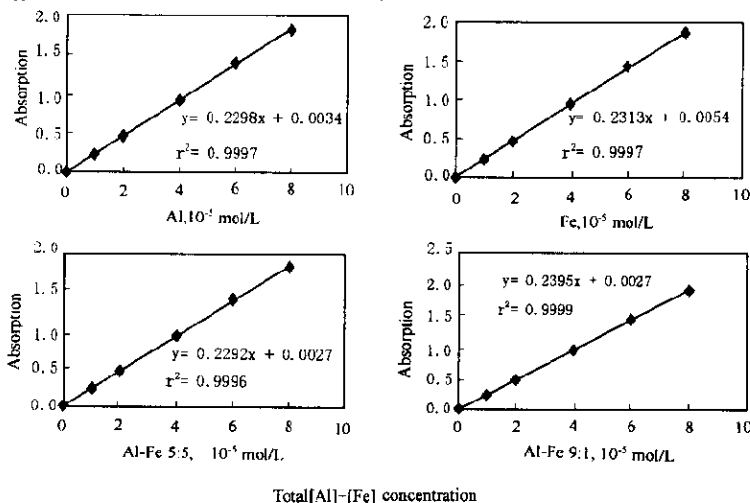


Fig.3 Standard absorption curve of Al-Fe-ferron complexes

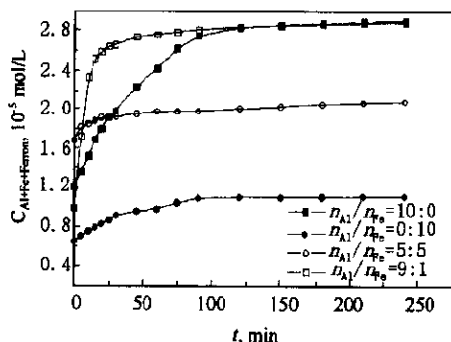


Fig.4 Four reaction kinetic curves of HPAFC-ferron complexes ($C = 4 \times 10^{-5}$ mol/L, $B = 2.0$)

shown in Fig.3. It was found that the complexes were very stable and they all had a stronger absorption maximum at pH 5. The regression coefficients of the calibration curves are over 0.99. The color of the ferron solution was dark yellow, so the blank absorption experiment of the ferron must be a concern at any time in measuring absorption. These Al-Fe-ferron solutions with different n_{Al}/n_{Fe} ratios all revealed the similarity in absorption trend. This indicated that little interference existed in the process of the determination of the species distribution in the Al-Fe coexisting solution at 362 nm.

Four reaction kinetic curves of different HPAFC-ferron complexes are shown in Fig.4 (data not shown), where the changes of reaction curves could apparently reflect the situation of the species distribution in the HPAFC solutions.

5 Discussion and conclusion

To ensure the correctness in use of the improved timed complexation colorimetric method of Al-Fe-ferron in the determination of the species distribution in the Al-Fe coexisting solutions, the preparative experiment for the standard solutions with differing n_{Fe}/n_{Al} ratios must be conducted to derive linear reaction kinetic curves. The absorption maximum could emerge in one or two minutes following the addition of the standard solutions that contained Fe^{3+} and Al^{3+} , highlighting that the reactions of Fe^{3+} and Al^{3+} with ferron could finish in a period of few minutes. The pH value of the standard solution should be paid attention to and it must be adjusted below 2 to restrain the hydrolysis reactions, so acid must be added to the solutions for dilution. This method could be used to determine the change of the total $[Fe + Al]$ concentration in Al-Fe-ferron reaction solutions, but it could not be quantitatively used to determine the individual species distribution (e.g. Fe-forms or Al-forms) associated with the reaction solutions that contained Fe^{3+} and Al^{3+} .

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