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A novel kinetic procedure for the determination of iron in environmental samples

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Abstract: A novel kinetic procedure for the determination of trace iron(III) was proposed based on the aerial oxidation of Gallocyanine by oxygen dissolved in water at pH 7.0. The calibration graph is linear for 0.05—0.6 $\mu\text{g/ml}$, and the detection limit is 0.01 $\mu\text{g/ml}$ (Fe). The present procedure is selective for iron(III) and very easy to control compared with kinetic procedures for iron. It had been used to the determination of trace iron in environmental samples, and the results were satisfactory.

Key words: kinetic spectrophotometry; Gallocyanine; iron; determination

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Introduction

The determination of iron received extensive attention because of its increasing importance in biochemical and environmental studies, and kinetic procedures played an important rule among the techniques for it (Crouch, 1998). The main advantage of catalytic procedure is that for most indicator reactions the only instrumentation required is a spectrophotometer. Most kinetic procedures for iron were developed based on the oxidation of organic compounds by hydrogen peroxide or periodate: such as the oxidation of chlorpromazine (Tomiyasu, 1996), 2-hydroxybenzaldehyde thiosemicarbazone (Moreno, 1984), and chromotropic acid (He, 1995) by hydrogen peroxide, and the cooperative oxidation of chromotrope 2R by hydrogen peroxide and potassium periodate (Fang, 1997). The oxidation of PHA (Zheng, 1998) and dichlorofluorescein (Zhang, 1994) by hydrogen peroxide, and the oxidation of *o*-tolidine by periodate with 2, 2-bipyridine as an activator (Dolmanova, 1977) are all very sensitive for iron(III), but these reactions must be performed at higher temperature, and manganese seriously interfere in the later case. Up till now, kinetic procedures for iron based on the aerial oxidation had been rarely reported, except for one that based on the aerial oxidation of sodium 4, 8-diamino-1, 5-dihydroxyanthraquinone-2, 6-disulphonate (Navas, 1984).

Consequently, novel kinetic procedures for iron are still urgently needed, and the following points should be taken into consideration for developing new indicator reactions: short reaction time with preferably a simple mechanism, the reaction should be carried out at room temperature, and can be followed spectrophotometrically (Snezana, 1995).

On the basis mentioned above, we studied the catalytic effect of iron(III) on the aerial oxidation of Gallocyanine at pH 7.0, and based on which a procedure for the determination of iron was proposed.

1 Experimental

1.1 Reagents

Standard solution of 100 $\mu\text{g/ml}$ (Fe) was prepared by dissolving 0.2158g of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot$

2H₂O in 2.5 ml H₂SO₄ and diluted to 250 ml with water. Working solution of 10 μg/ml was made by appropriate dilution.

Gallocyanine (GC) solution of 5.0×10^{-4} mol/L was prepared by dissolving 0.085g of GC in 0.0001 mol/L NaOH by heating and diluted to 500 ml with water.

Phosphate buffer solution of pH 7.0 was prepared by dissolving 7.8g of NaH₂PO₄·2H₂O and 11.5g of Na₂HPO₄·12H₂O in water and diluted to 500 ml.

All the solutions were prepared with analytical grade chemicals and redistilled water.

1.2 Apparatus and recommended procedure

The reaction was monitored by measuring the absorbance at 620 nm with 722 spectrophotometer, the temperature was controlled by a WC/09-05 thermostat, and the acidity was measured by a pHT-pH meter.

To a series of colorimetric tubes certain amount of iron(III) standard or sample solutions were added (cover the range of 0—0.6 μg/ml), 1.5 ml of buffer solution and 1.0 ml of GC solution were then added successively. The mixture was diluted to 10 ml with water and stirred vigorously. The solution was transferred to a 10 mm cell and the absorbance was measured at 620 nm with water as the reagent blank. The absorbance difference of catalytic and non-catalytic systems was calculated as $\Delta A = A_0 - A$.

2 Results and discussion

2.1 The absorption spectra

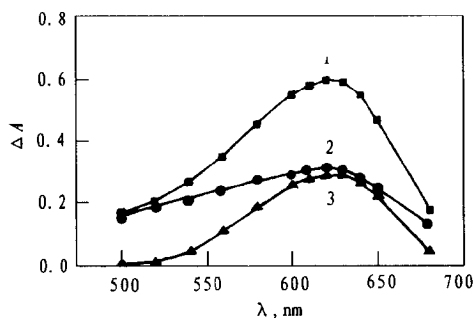


Fig. 1 The absorption curves

[GC] = 5.0×10^{-5} mol/L; pH 7.0; 0.25 μg/ml (Fe)

1: GC/O₂ system (A_0); 2: GC/O₂/F₂³⁺ system (A);

3: difference of 1 and 2 (ΔA)

Fig. 1 shows the absorption spectra of catalytic and non-catalytic reaction systems that determined under the optimized conditions discussed below. It is obvious that the absorbance difference ΔA reached maximum near 620 nm, and the absorbance of other species at this wavelength are negligible. The determinations were carried out at 620 nm.

2.2 The influence of variables

2.2.1 The acidity of the solution

The influence of acidity on the aerial oxidation of GC is shown in Fig. 2. It indicated that the acidity had remarkable effect on the reaction. The difference of absorbance reached maximum at pH 7.0, and the procedure was most sensitive for iron (III) at this acidity. Therefore the acidity of the system was controlled by phosphate buffer solution, and the experimental results showed that the appropriate amount of buffer should be 1.0—1.2 ml. We chose 1.5 ml in the determination.

2.2.2 The effect of GC concentration

The influence of GC concentration on the sensitivity of the determination had been investigated, the results showed that the sensitivity of the determination improved with the increase of GC concentration within the range of $(2.5-10) \times 10^{-5}$ mol/L, but the error for determination enhanced and the reproducibility deteriorated as GC concentration increased and out of certain range. We chose 5.0×10^{-5} mol/L in the determinations.

2.2.3 The influence of temperature and reaction time

The effect of temperature within the range of 20–50°C had been studied. It indicated that within 20–30°C, the absorbance difference, ΔA , reached maximum and there is a plateau, but it decreased slightly within 30–50°C, and the stability and reproducibility of the system deteriorated at higher temperature. The determinations were carried out at room temperature of about 25°C.

The results also showed that the sensitivity of the determination will reach maximum 1 minute after the reaction mixture had been mixed, and the absorbance difference, ΔA , will remain unchanged for hours. That means the influence of reaction time on the determination is negligible.

2.2.4 The influence of foreign ions

The effect of foreign ions on the determination were studied by combining sufficient amount of foreign ions with iron(III) solution to yield a final solution containing 0.15 $\mu\text{g/ml}$ Fe(III). If an error of $\pm 5\%$ was considered permissible, the tolerant amount for different ions are listed in Table 1.

Foreign ions	Tolerant ratio	Foreign ions	Tolerant ratio
K^+ , Na^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , F^- , CO_3^{2-} , Cl^- , Ac^- , S^{2-} , SO_4^{2-}	>1000	Mn^{2+} , Ce^{3+} , Hg^{2+} , MoO_4^{2-} , WO_4^{2-}	20
Zn^{2+} , Ni^{2+} , Ti^{4+}	30	Cr^{3+} , Cd^{2+}	10
		Ag^+ , VO_3^- , Co^{2+}	5
		Cu^{2+} , Fe^{2+}	3

We concluded from the above mentioned results that the content of iron can be determined directly without prior separation, as for most real samples the content of foreign ions can not exceed the tolerant amount listed in Table 1. The interference of excess Cu(II) was eliminated by extraction with Dithizone in chloroform, and iron(II) was oxidized to iron(III) with chlorine to eliminate its interference.

3 Calibration graph

The relationship between ΔA and iron concentration were investigated under the conditions mentioned above. It indicated that the calibration graph is linear for 0.05–0.6 $\mu\text{g/ml}$ Fe(III), the relationship is: $\Delta A = 0.4608C(\mu\text{g/ml}) + 0.1985$, with the correlation coefficient $r = 0.9989$. The detection limit of the procedure was determined to be 0.01 $\mu\text{g/ml}$ (Fe). A standard solution containing 0.25 $\mu\text{g/ml}$ Fe(III) had been determined for 6 times, the average recovery rate was 98.0%, and the relative standard deviation was 2.3%.

4 Applications of the procedure

The present procedure had been used to the determination of iron in simulate sample, tap

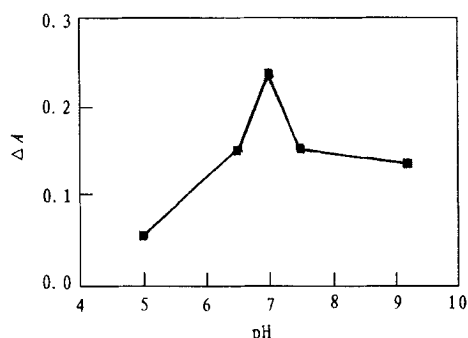


Fig. 2 The effect of acidity
[GC] = 5.0×10^{-5} mol/L; 0.25 $\mu\text{g/ml}$ (Fe)

water, human hair and floor, and the samples were treated as follows:

Simulate sample was prepared by combining certain amount of iron(III) standard solution with appropriate amount of foreign ions.

Tap water was determined directly after doubly charged iron(II) was oxidized to iron(III) by chlorine (Cl_2) at acidic medium.

Human hair and floor: 0.50g of human hair that had been washed and dried or 1.0g of floor was soaked overnight in 15 ml of HNO_3 , the mixture was digested gently with an electric heater for about 3 hours and cooling for 1h. Certain amount of perchloric acid was draped repeatedly until the mixture became clear, and the solution was then heated and kept smoking. About 2 ml of 0.1 mol/L HCl was added after cooling for 30 minutes, and diluted to 50 ml.

The content of iron in the above sample solutions were determined with the present procedure, and the results are listed in Table 2.

Table 2 The analytical results ($\mu\text{g/g}$)

Samples	Found ($n = 5$)	Added	Recovery rate, %	R. S. D, %
Standard solution *	0.245		98.0	2.3
Simulate sample *	0.246	0.150	103.5	2.5
Tap water *	0.121	0.200	102.6	2.6
Human hair	28.5	20.0	97.3	2.7
Floor	6.44	5.00	99.3	1.2

* $\mu\text{g/ml}$, the standard solution containing 0.25 $\mu\text{g/ml}$ Fe(III)

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