

Determination of Ultratrace Amounts of Iron in Concentrated Acids by Flow Injection Spectrophotometric Method Based on the Catalytic Effect of Iron Ion on the Oxidation Reaction of *N,N*-dimethyl-*p*-phenylenediamine with Hydrogen Peroxide

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Abstract

A spectrophotometric flow injection system is described for the determination of iron in acid samples. The detection method is based on the catalytic action of iron(III) on the oxidation reaction of *N,N*-dimethyl-*p*-phenylenediamine (DPD) in the presence of hydrogen peroxide. An increase in absorbance of oxidized DPD was measured spectrophotometrically at 514 nm. The proposed method allows the dynamic linear calibration of 0.1 to 1.0 $\mu\text{g L}^{-1}$ of iron. The method showed high sensitivity (LOD 0.008 $\mu\text{g L}^{-1}$) with good repeatability (RSD below 2%). And was also successfully applied to the determination of ultratrace amounts of iron in commercially available concentrated acids, such as hydrochloric, sulfuric and acetic acid.

Keywords: Iron, flow injection analysis, catalytic reaction, hydrogen peroxide, spectrophotometry, concentrated acids.

1. Introduction

Commonly used acids, such as hydrochloric, nitric, sulfuric and acetic acid, are often requisite for the decomposition of solid samples and/or the preparation of solutions prior to chemical analysis. In trace and ultratrace analysis, high purity acids are necessary because they provide low background and lead to lower limit of detection.

In electronic industries, several kinds of highly pure acids are required for cleaning and etching processes in order to improve product quality. Such acids are often different in their contaminant compositions and their concentrations, which mean that real-time analyses for contaminants are needed for process controls and for quality controls of products. Therefore, automated and rapid methods, as well as highly sensitive analytical methods for ultratrace analysis of ultrapure chemicals, are required.

Conventional methods for the determination of trace and ultratrace amounts of metal ions have been carried out by atomic absorption spectrophotometry (AAS), inductively coupled plasma - atomic emission spectrometry (ICP-AES) and -mass spectrometry (ICP-MS) ¹. Such methods can provide relatively high sensitivity. However, the analytical systems used are somewhat expensive and sophisticated. Furthermore, tedious sample pretreatment procedures, such as solvent extraction, ^{2, 3} evaporation, ⁴ and solid phase extraction with ion exchange column, ⁵ are usually required prior to the measurement. In contrast, a flow injection analysis (FIA) system equipped with such a simple detection apparatus as a spectrophotometric detector is cost effective, simple and sometimes provides high sensitivity.

Trace amounts of iron in highly pure acids are one of the most important indicators for the contamination from the process, vessels and environment.

Usually, the iron contents in such acids are considerably low. Therefore, the highly sensitive method for the determination of ultratrace iron is necessary.

Recently, Lunvongsa et al. reported a simple flow injection spectrophotometric method for the determination of dissolved and total amounts of iron in tap and natural water samples ⁶. The method is based on the catalytic effect of iron(III) on the oxidation reaction of *N,N*-dimethyl-*p*-phenylenediamine (DPD) with hydrogen peroxide. The increase in the absorbance of an oxidized product of DPD was measured spectrophotometrically at 514 nm. This detection reaction has been proposed firstly by Hirayama and Unohara ⁷. In addition, copper also has catalytic action on the oxidation of DPD, and therefore, this reaction has been also applied to the sequential determination of iron and copper in water samples ⁸.

In this work, the catalytic oxidation reaction of DPD by iron was also employed for the determination of ultratrace amounts of iron in pure acid samples. An FIA system modified from the previous work was used. The improved method was applied to the determination of trace and ultratrace amounts of iron in various acid samples, which are often used for trace chemical analyses and semiconductor industries, such as acetic, hydrochloric, nitric and sulfuric acid.

2. Experimental

All lab-wares used were cleaned by soaking them in 1 M hydrochloric acid before use, followed by rinsing them thoroughly with ultrapurified water. All standard and sample solutions were prepared using the ultrapurified water obtained by using an Elix 3/ Milli-Q Element System (Nihon Millipore, Japan).

2.1. Reagents

Iron(III) standard solutions for the preparation of a calibration graph were prepared daily by diluting a 1000 mg L^{-1}

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standard iron(III) solution for atomic absorption spectrometry (Wako Pure Chemicals, Japan) with 2 M ammonium acetate buffer (pH 5.7). A carrier solution, CS, and a buffer solution, BS, were 2 M ammonium acetate buffer (pH 5.7), prepared by mixing an appropriate amounts of 2 M acetic acid prepared by diluting a glacial acetic acid (electronic grade, Mitsubishi Chemicals, Japan) with 4 M ammonia solution (electronic grade, Mitsubishi Chemicals, Japan). An oxidizing solution, OS, was 0.5 M hydrogen peroxide solution prepared from a 30 % hydrogen peroxide (electronic grade, Cica Kanto Chemicals, Japan). A reagent solution, RS, was a 0.012 M *N,N*-dimethyl-*p*-phenylenediamine (DPD: Wako Pure Chemicals, Japan). DPD was dissolved in a 0.01 M hydrochloric acid. In the interference study, all standard solutions of metal ions were prepared by appropriate dilution of stock solutions of metal ions with 0.1 M hydrochloric acid.

2.2. Sample preparation

Concentrated acid samples, which were commercially available, can not be injected into the FIA system directly

because their acidity is too high and the coloration reaction can not proceed.

To adjust the pH of the coloration reaction to the suitable value, acid sample solutions for the analysis were prepared by appropriate dilution of the samples with 2 M ammonium acetate buffer solution (pH 5.7).

2.3. FIA configuration

A schematic diagram of the FIA system employed in this work is shown in Fig. 1. All tubings used for the connection of the components were 0.5 mm i.d. poly(tetrafluoroethylene) (PTFE). The system consisted of two double plunger pumps (F.I.A. Instrument, model 201, Tokyo), which were used for propelling a carrier and a reagent stream. Samples and the standard solutions were introduced into the carrier stream using a six-way injection valve with a 500 μ L sample loop. Absorbance was measured with a Soma model S-3250 spectrophotometer equipped with a 4-cm path length flow through cell. Data acquisition was accomplished by using a data processor, FIA monitor (F.I.A. Instrument, Japan). A TCI model GAS DIF dry thermostat bath was used to keep the reaction coil temperature at 50 $^{\circ}$ C.

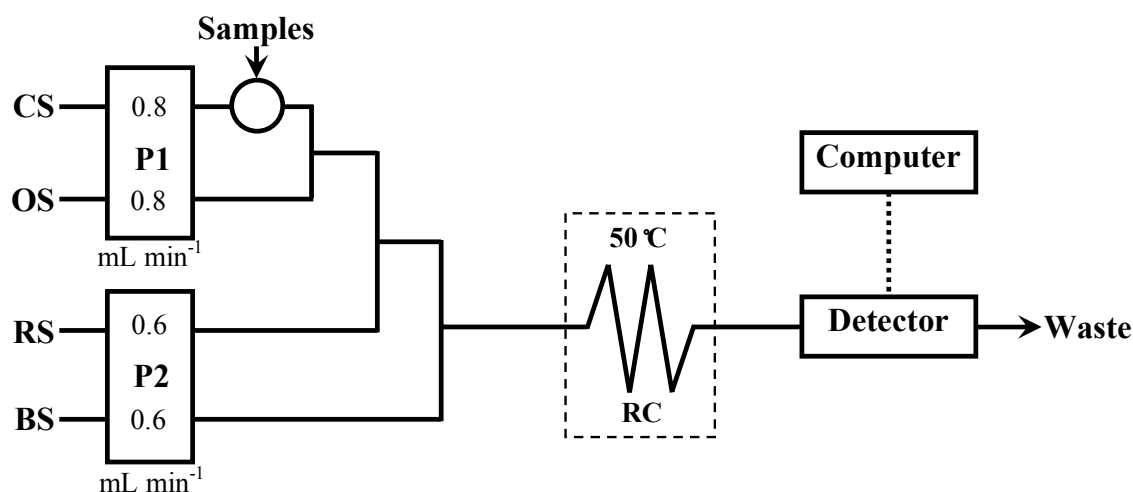


Fig. 1 Flow injection system for the determination of iron in acid samples: CS, 2 M ammonium acetate buffer (pH 5.7); OS, 0.5 M hydrogen peroxide; RS, 0.012 M *N,N*-dimethyl-*p*-phenylenediamine; BS, 2 M ammonium acetate buffer (pH 5.7); RC, reaction coil (400 cm x 0.5 mm i.d.), Dotted box is a thermostated bath.

Table 1 Optimal conditions of the FIA system for the determination of iron in highly pure acid samples.

Variables	Range examined	Optimal conditions
Carrier, CS		2 M ammonium acetate buffer (pH 5.7)
Buffer solution, BS		2 M ammonium acetate buffer (pH 5.7)
Concentration of hydrogen peroxide, OS	0.24 to 2.4 x 10 ⁻² M	1.2 x 10 ⁻² M
Concentration of DPD, RS	0.1 to 1.5 M	0.5 M
Sample volume	100 to 750 μ L	500 μ L
Flow rate of Pump 1	0.8 to 2.0 mL min ⁻¹ (total flow rate)	1.6 mL min ⁻¹
Flow rate of Pump 2	0.8 to 2.0 mL min ⁻¹ (total flow rate)	1.2 mL min ⁻¹
Reaction coil length	50 to 700 cm	400 cm
Reaction temperature	30 to 60 $^{\circ}$ C	50 $^{\circ}$ C

3. Results and discussion

3.1. Optimization and modification of FIA system

The reaction conditions and FIA experimental variables were optimized in details in order to get the higher sensitivity than that described in the previous report ⁶. The experimental conditions optimized and used in this work were summarized in Table 1. In order to maintain suitable pH for the optimal color reaction, the system was modified by changing a carrier stream of 0.1 M HCl for 2 M ammonium acetate buffer (pH 5.7).

3.2. Effect of coexisting ions

The effect of potential interfering ions was examined by using the solutions containing 1.0 µg L⁻¹ Fe (III) and one of other foreign ions. The tolerable concentration of each coexisting ion was taken as a highest concentration causing an error of ± 5 %. The results were summarized in Table 2. Most of the investigated ions did not interfere with the determination of iron, while copper (II) was found to cause serious interference effect. However, the effect of copper could be eliminated by adding triethylenetetramine (TETA) as a masking agent. The tolerable amount of TETA was found to be 6.7 × 10⁻⁴ M, at the concentration of which the determination of iron was not interfered. The interference from copper(II) up to 400 µg L⁻¹ was completely eliminated in the presence of 6.7 × 10⁻⁴ M TETA as shown in Table 3.

Table 2 Maximum tolerance concentrations of coexisting ions on the determination of 1.0 µg L⁻¹ Fe(III).

Coexisting ions	Tolerable concentration* (mg L ⁻¹)
Li ⁺	600
Na ⁺ , K ⁺ , Ca ²⁺	200
Mg ²⁺	15
Mn(II), V(V)	4.0
Al ³⁺	2.0
Cd(II), Ni(II), Pb(II), Zn(II), Co(II)	1.0
Cr(III), Mo(VI)	0.25
PO ₄ ³⁻	20
SO ₄ ²⁻	50

Iron(III) : 1 µg L⁻¹.

*Maximum tolerable concentrations for ions, in which errors are within ± 5 %.

3.3. Analytical characteristics

Under the optimal conditions, a linear response was observed for iron(III) concentrations, as well as iron(II) concentrations in the range of 0.1 to 1.0 µg L⁻¹ with a correlation coefficient of 0.9967. Linear equation is $A = 689.7 C + 16.96$, where A and C are signal reading in absorbance and iron concentration in µg L⁻¹, respectively. A detection limit was estimated to be 0.008 µg L⁻¹ for the signal to noise ratio of three. A relative standard deviation for ten injections of 0.5 µg L⁻¹ of iron(III) was less than 2 %. The practical sampling frequency of 25 samples h⁻¹ could be achieved.

Table 3 Effect of Cu(II) on the determination of 1.0 µg L⁻¹ Fe(III).

Cu(II) concentration (µg L ⁻¹)	Error (%)	
	Without TETA*	With TETA
10	+35	- 0.8
20	+124	- 0.5
50	+340	- 1.2
200	+795	3.5
400	+1150	5.0
500	**	15.0

Iron(III) : 1 µg L⁻¹.

* TETA : 6.7 × 10⁻⁴ M triethylenetetramine.

** Off-scale

3.4. Appropriate dilution of acid samples

Appropriate dilution of the acid samples prior to the injection into the FIA system must be carried out. The optimization for sample preparation depends on the pH of final solutions: a low dilution factor is recommended. It was found that most of the acid sample could be prepared under suitable pH range with a low dilution factor, except for sulfuric acid (AR grade).

Dilution effect for the sample preparation of concentrated sulfuric acid was studied by diluting with 2 M ammonium acetate buffer solution (pH 5.7). Dilution factor examined were in the range of 10 to 60. The results are shown in Table 4. When the dilution factors were 10 to 20, the pH of the solutions was considerably low, which was not suitable for the coloration of the detection reaction. The results in Table 4 also indicate that the dilution factor of 30 is the most appropriate: the pH of the solution was adjusted to be about 3.7 and at higher dilution factor the concentration of iron is too low to be determined.

Table 4 Dilution effect on the determination of iron in concentrated sulfuric acid.

Dilution factor	pH of sample solution	Fe found (µg L ⁻¹)
10	0.01	ND
15	0.55	ND
20	1.08	ND
30	3.65	0.093 ± 0.018
40	4.27	ND
50	4.54	ND
60	4.72	ND

ND: Not detectable

3.5. Application of the proposed method to the analysis of commercially available acid samples

The proposed method was applied to the determination of ultratrace amounts of iron in commercially available acid samples, which are of analytical reagent grade (AR) and of electronic (EL) grade. The iron contents obtained for the acid samples are summarized in Table 5. Iron contents of hydrochloric and acetic acid of EL grade were very scarce and were below the detection limit of 0.08 µg L⁻¹, whereas the AR grade acid contains relatively high concentrations of iron. Good recoveries for iron were obtained in the range of 96 – 108 %.

Table 5 Iron contents ($\mu\text{g L}^{-1}$) in commercially available acid samples and their recoveries.

Sample	pH	Dilution factor	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Iron concentration ($\mu\text{g L}^{-1}$)	Recovery (%)
Hydrochloric acid, EL grade	3.75	10	-	$< 0.008^*$	$< 0.08^{**}$	-
Hydrochloric acid, AR grade	3.75	10	0.480	0.475 ± 0.005	-	99
Hydrochloric acid, EL grade	3.70	10	-	0.147 ± 0.003	1.47 ± 0.03	-
Hydrochloric acid, AR grade	3.70	10	0.480	0.657 ± 0.01	-	107
Acetic acid, EL grade	4.60	10	-	$< 0.008^*$	$< 0.08^{**}$	-
Acetic acid, AR grade	4.60	10	0.607	0.585 ± 0.013	-	96
Acetic acid, EL grade	4.59	10	-	0.344 ± 0.001	3.44 ± 0.01	-
Acetic acid, AR grade	4.59	10	0.480	0.838 ± 0.009	-	103
Nitric acid, AR grade	4.60	25	-	0.115 ± 0.001	2.89 ± 0.05	-
Nitric acid, AR grade	4.60	25	0.480	0.625 ± 0.004	-	106
Sulfuric acid, AR grade	4.40	40	-	$< 0.008^*$	$< 0.34^{**}$	-
Sulfuric acid, AR grade	4.40	40	0.480	0.518 ± 0.007	-	108
Sulfuric acid, AR grade	3.65	30	-	0.093 ± 0.018	2.78 ± 0.53	-

* System detection limit, SDL, is 0.008, which corresponds to the signal to noise ratio of 3.

** Method detection limit, MDL, corresponds to (SDL x Dilution factor).

4. Conclusions

The FIA system for the determination of ultratrace amounts of iron could be successfully developed. The principle of the detection method is based on the catalytic action of iron(III) on the oxidation reaction of *N,N*-dimethyl-*p*-phenylenediamine with hydrogen peroxide. The advantages of the proposed method, compared other methods reported so far, are high sensitivity (the LOD of 8 ppt levels of iron without any preconcentration procedure), fast analysis time, and good reproducibility. Application of the proposed method to the determination of ultratrace amounts of iron in commercially available acid samples could be achieved.

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