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The Determination of Dissolved Total Fe by Flow Injection Analysis in Environmental Samples.

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Abstract : There has been an increasing need for analytical methods of dissolved total iron (tFe) that are highly sensitive, rapid, inexpensive and simple for environmental samples. A sensitive flow injection analysis (FIA) method for determining the concentration of tFe in environmental samples was developed. The proposed method required 10 minutes and only 500 μL of sample for an analysis. The standard deviation was 5.0 % at 0.5 μgL^{-1} (n=6), and the detection limit was 0.075 μgL^{-1}. The developed method was applied to environmental samples such as tap water, mineral water, rain, snow and cloud water. Since this FIA system was free from interferences of coexisting ions commonly found in samples, sub- μgL^{-1} level of tFe could be easily determined without further preconcentration and separation.

Key words : FIA, dissolved total Fe (tFe), environmental samples

1. Introduction

Iron is the fourth most abundant element in the earth's crust; it is present in the variety of rock and soil minerals as both Fe^{2+} and Fe^{3+}. In particular, dissolved iron compounds are one of the most important metals in environmental samples, because they are present at trace level concentrations that are at least an order of magnitude higher than those of other metals and also they rapidly react with many of the oxidants, reductants in natural waters and atmospheric water droplets[1-4]. Recently, there has been an increasing need for an analytical method of iron that is highly sensitive, rapid, inexpensive and simple. However, the sensitivity of most spectrophotometers is insufficient for determining dissolved total iron (tFe) at the sub- μgL^{-1} levels[5,6]. Preconcentration and separation techniques such as chelating and extraction, which require a large volume of sample, are usually needed prior to the analysis. The tFe could not be determined by inductively coupled plasma mass spectrometry (ICP-MS) directly because of the severity of isobaric interferences from ArO and ArN polyatomic species on the major isotope of Fe[7]. Electrothermal vaporizing system for sample introduction of ICP-MS (ETV-ICP-MS) and furnace atomic absorption spectrometry(furnace AAS) have a high sensitivity but the analysis time is longer than other methods and the cost is high. Hirayama and Unohara described a catalytic kinetic method to achieve ultratrace determination of Fe in water based on the oxidation of N, N-dimethyl-p-phenylenediamine (DPD) with hydrogen peroxide[8]. The catalytic nature of the reaction enhanced the sensitivity of the method since the amount of oxidized DPD

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was proportional to the amount of Fe and the length of the reaction time. The time dependency of the sensitivity of the catalytic reaction was ideally suited to flow injection analysis (FIA) since it was capable of providing good reproducible reaction time.

The aim of this work was to establish a rapid, inexpensive, simple, new, and sensitive FIA method for determining the concentration of tFe in aqueous solution and then to apply to tap water, mineral water, rain, snow, and cloud water.

2. Experimental section

2.1. Reagents

Fe working solutions were prepared by diluting a commercial atomic absorption spectrometer standard solution (Wako chemical. Co.) containing 1000 mgL^{-1} of Fe. Hydrogen peroxide (H_2O_2) was of the TAMAPURE-AA100 purchased from Tama chemicals. N, N-dimethyl-p-phenylenediamine dichloride (DPD, Wako chemical. Co.), hydrochloric acid (HCl, 35 %), acetic acid (99.7 %), ammonium water (NH_4OH, 25 %) and other reagents were of super special grade (Katayama Chemicals) and used without further purification. SLRS-4 was used for certified reference material from National Research Council of Canada. Carrier solution was with Milli-Q water (MQW, < 18.2 MΩ) and acetate buffer solution was prepared by mixing 2 M acetic acid and 2 M ammonium solution adjusted to pH 5.75 ±0.01. DPD reagent was prepared daily since the solution slowly oxidized and became discolored in the bottle.

2.2. Instruments, apparatus and experimental proceeding

The FIA system for determination of tFe is shown in *Fig.* 1. The system consists of a 4-channel peristaltic pump, a 6-port injection valve attached to a 500 μL sample loop, and a 8-hydroxyquinoline mini column (8-HQ column, 0.14 cm I.D. x 0.5 cm length). The 8-HQ column prepared by a modification of the procedure of Landing et al[9]. A UV-Visible spectrophotometer (JASCO 870UV) was used for the detection of semiquinone derivatives of DPD at 514 nm. The inlet and outlet tubings of flow cell were replaced with 0.5 mm I.D. tubings to minimize backpressure in the system. The signal intensity was recorded with a strip chart recorder. All other tubings used were 0.5 mm I.D. PTFE tubing. Teflon tubing and peristaltic pump tubing were pre-cleaned by passing 0.4 % HCl for 1 hour. All plastic ware was leached with 10 % HNO_3 for 2 days, and then with 24 % HCl for another 2 days, and was finally rinsed three times with MQW. To minimize the effect of air-borne contamination, all experiments were carried out in a clean room (class 100).

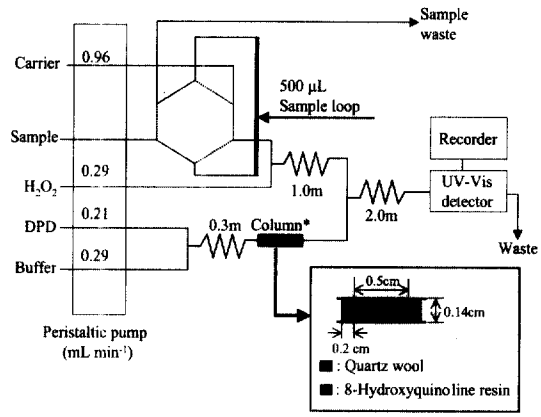

Fig. 1. Schematic diagram of FIA system for determination of tFe.

2.3. Samples

Tap water and mineral water in Korea were used without preparation. Rain and snow samples were collected in polyethylene (PE) bottles equipped with Teflon-coated PE funnels (all acid-cleaned) on the roof of the Higashi Hiroshima campus building of Hiroshima University at Higashi-Hiroshima, Japan. Snow sample was stored in a refrigerator for about 2 hours until the sample analysis. The samplers were set up just before precipitation events. Cloud water was collected by airplane over the Sea of Japan near Oki Island (N 35°52'- 35°59', E 132°06'- E 132°35' and altitude 1524-1676.4m) for 12 minutes (from 15:53 to 16:05) on December 14, 1999[10].

All the samples were filtered with 0.45 μm membrane filters, and then acidified to about pH 2 with HCl.

3. Results and discussion

3.1. Optimization of the FIA system

We investigated optimum condition for fixed reaction time (1 min., 2 m reaction coil). *Fig.* 2 shows the effect of H_2O_2 concentration on the signal intensity of tFe in FIA. The absorbance of standard (S_{abs}), blank (B_{abs}), and standard minus blank (I_{abs}) increased continually up to 0.65 % H_2O_2 concentration. Because there was no appreciable increase at higher than 0.65 % H_2O_2, this value has been adopted for the experiment. The effect of DPD concentration on the signal intensity of tFe was also examined in case of 0.65 % H_2O_2 as shown in *Fig.* 3.

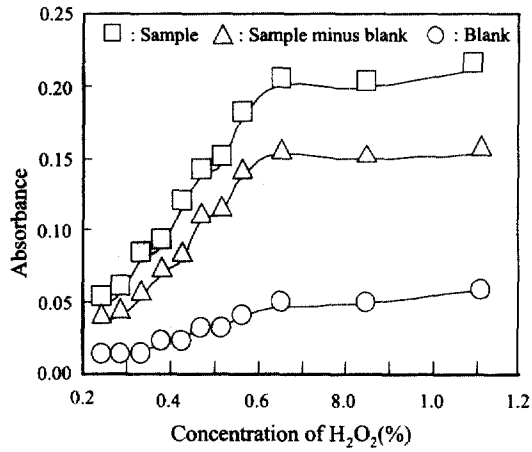

Fig. 2. The effect of H_2O_2 concentration on the absorbance of 2 μgL^{-1} tFe and 3mM DPD.

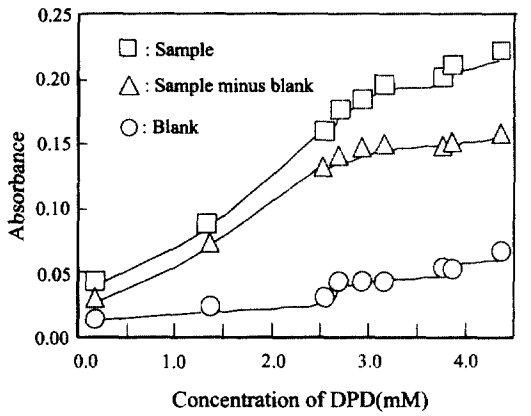

Fig. 3. The effect of DPD concentration on the absorbance of 2 μgL^{-1} tFe and 0.65% H_2O_2.

Since the B_{abs} increased with increasing DPD concentration, but I_{abs} did not increase over 3.5 mM, we selected 3.7 mM DPD as the optimal concentration. The optimal pH of buffer solution was found to be between 5.50 and 6.00. (*Fig.* 4). Flow rate of each reagents were

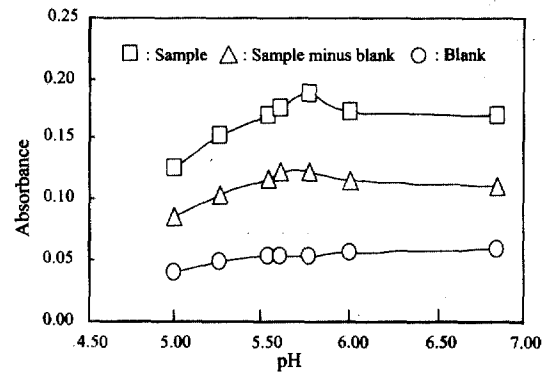

Fig. 4. The effect of pH on on the absorbance of 2 μgL^{-1} tFe, 3.7mM DPD and 0.65% H_2O_2.

important parameter in FIA because it affected reaction time, backpressure and consumption of reagents in FIA system. Although initial experiments were carried out using flow rate at 12 rpm, we adopted 9.5 rpm because it minimized the possibility that tubing junctions would be broken and decreased the consumption of reagents. At 9.5 rpm, B_{abs} was higher than that at 12 rpm, but I_{abs} increased because residence time of the reaction mixture increased in reaction coil. The flow rates of each reagent are shown in *Fig.* 1. In our FIA system, Fe in DPD solution and buffer solution increased B_{abs}. However, it could be effectively removed by passing the 8-HQ column with acetate buffer (pH 5.50-6.00).

Table 1. The effect of various ions on the recovery of 1 μgL^{-1} Fe

Ion added	Conc. (μgL^{-1})	Recovery (%)	Ion added	Conc. (μgL^{-1})	Recovery (%)
Ca(II)	1000	99	Bi(II)	100	102
K(I)	1000	98	B(III)	100	98
Mg(II)	1000	98	Al(III)	100	100
Mn(II)	100	97	Li(I)	100	99
Na(I)	1000	98	Zn(II)	100	99
Ni(II)	100	99	V(V)	100	98
Si(IV)	100	98	Ba(II)	100	99
Sr(II)	1000	98	Pb(II)	100	99

We checked the interference of other metals at our FIA system, but most metal ions did not interfere with tFe analysis (*Table* 1). Cr, Mn, and Bi gave minor negative interferences, even at concentrations that were 50 times higher than those in rain samples[11]. Although Cu(II) gave positive interference above 10 μgL^{-1}, adding triethylenetetramine to the buffer solution as a masking reagent could eliminate this interference (*Table* 2).

Table 2. The effect of Cu(II) on the recovery of 1 μgL^{-1} Fe

Cu(II) Conc. (μgL^{-1})	Conc.[a] (mM)	Recovery(%)
5	0	103
50	0	161
50	1	99

[a] : The conc. was concentration of triethylenetetramine.

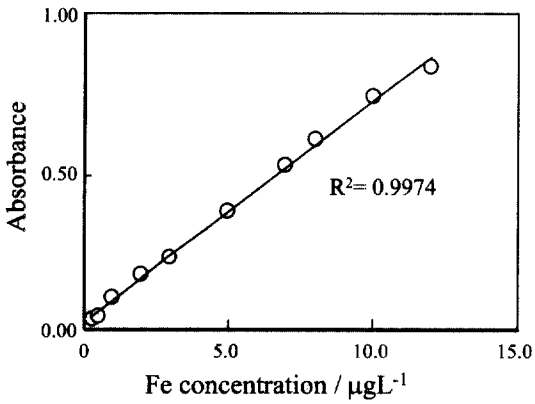

Fig. 5. The calibration curve for different Fe concentration at optimum condition.

Calibration curve of tFe by our FIA system is shown in *Fig.* 5. Our FIA system could analyze from 0.5 μgL^{-1} to 12 μgL^{-1} of tFe, and had a sufficient sensitivity to detect total dissolved iron in aquatic environmental samples. The detection limit of this method was estimated from three times the standard deviation of the concentration determined from a low-level iron standard. The relative standard deviation for a sample with 0.5 μgL^{-1} tFe was 5.0 % (n=6), implying the detection limit of 0.075 μgL^{-1}. *Fig.* 6. showed typical signal outputs of rain samples and standard solution. Six samples could be measured within an hour.

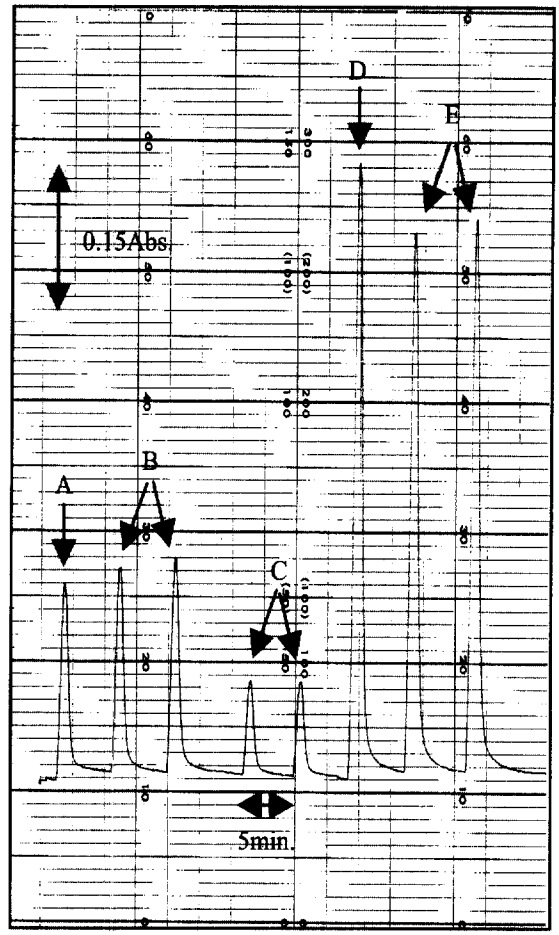

Fig. 6 Detector outputs of four rain samples and standard solution. A:rain 1 (3.3 μgL^{-1}), B:rain2 (3.4 μgL^{-1}), C:rain 3 (1.2 μgL^{-1}), D:11.0 μgL^{-1} standard solution, E: rain 4 (10.5 μgL^{-1}).

3.2. Total dissolved Fe in environmental samples.

The method was directly applied to the determination of tFe in environmental samples and certified reference material (SLRS-4) without preconcentration. The results shown in *Table* 3 were in good agreement with those obtained by furnace AAS and inductively coupled plasma atomic emission spectrometry (ICP-AES) performed for comparison that equipped with an ultrasonic neublizer.

Table 3. Determination of dissolved total iron in environmental samples

unit:μgL^{-1}

Sample	Sampling site	No.	FIA system	Other methods	%
SLRS-4			105.9	103[a]	103
Tapwater	Busan, Korea		13.5	14.1[b]	96
Mineral water	Busan, Korea	1	3.1	2.9[b]	107
		2	5.5	5.9[b]	93
Cloud water	over sea of Japan near Oki island		103.3	100.8[c]	102
Snow	Higashi-Hiroshima, Japan		50.1	48.7[c]	103
Rain	Higashi-Hiroshima, Japan	1	3.3	ND	
		2	3.4	ND	
		3	1.2	ND	
		4	10.5	10.2[c]	103
		5	8.7	8.9[c]	98
		6	11.3	11.0[c]	103
		7	12.7	12.0[c]	106
	Shichirui, Japan	1	8.3	7.9[c]	105
		2	60.7	58.1[c]	104

[a] : Certified value in SLRS
[b] : Values obtained by furnace AAS
[c] : Values obtained by ICP-AES equipped with an ultrasonic neublizer

4. Conclusion

A sensitive FIA system for determining the concentration of tFe in environmental samples was developed. The FIA system required only 500 μgL^{-1} of sample for an analysis, and the only coexisting ion that causes interference is Cu(II). However, masking with triethylenetetramine could eliminate the interference of Cu(II). The standard deviation was 5.0 % at 0.5 μgL^{-1} (n=6), and the detection limit was 0.075 μgL^{-1}. Since this FIA system was free from the interferences of coexisting ions commonly found in samples, tFe could be easily determined in environmental aquatic sample without further preconcentration and separation from 0.5 μgL^{-1} to 12 μgL^{-1}.

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