Enrichment of Trace Iron with Activated Carbon for Its Spectrophotometric Flow Injection Determination in Tap and River Water Samples

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Abstract

A FIA system with an activated carbon (AC) microcolumn was developed for the enrichment and sensitive determination of trace iron. In the FIA system, iron was adsorbed on AC as iron(II) complex with 1,10-phenanthroline at pH 4.5 in the presence of L-ascorbic acid and eluted with 10 M acetone. Absorbance of the complex was monitored at 510 nm. Sample volume injected was controlled by the pumping time of the sample. A calibration curve was linear up to at least 1.2 mg l^{-1} iron for 2 ml of sample. The detection limit was 2 μg l^{-1}. A typical sampling rate was 25 samples h^{-1}. The maximum sample volume was 4 ml for the complete adsorption of iron on AC. The presence of a higher concentration of humic acid (HA) interfered with the iron determination. In this case, HA and other adsorptive organic compounds were eliminated by adsorbing them on AC in a separate column. The proposed method was successfully applied to analyses of river and tap water samples. Recycle of wastes was also studied.

Keywords Activated carbon, enrichment, iron determination, FIA, 1,10-phenanthroline, river and tap water, recycle of wastes.

1. Introduction

The spectrophotometric method with 1,10-phenanthroline (Phen) is widely used for the simple and low-cost determination of iron. This method was applied to FIA of water samples [1,2], but its determination or detection limit was insufficient for natural and tap water samples [3,4] containing iron at 1 - 10 μg l^{-1} levels. Therefore, the enrichment of iron is required for the flow injection determination. The enrichment of iron as iron(II)-Phen complex is useful to simplify the flow system and to eliminate the additional reagents. This paper describes the on-line enrichment of Fe(II)-Phen by an activated carbon (AC) microcolumn and the spectrophotometric flow injection determination of iron in water samples. For water analysis, the complexation of iron with 8-Qunolinol [5,6] or L-ascorbic acid (AA) [7] and its adsorption on AC were used for the iron determination by X-ray fluorescence or spark-source mass spectrometry. However, no report was found for Fe(II)-Phen. In our study, the FIA system was optimized for the complete adsorption and effective elution of iron. The recycle of wastes was also studied. The proposed method could successfully be applied to analyses of tap and river water samples.

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2. Experimental

2.1. Reagents

De-ionized and distilled water was used throughout. A high-purity NaOH solution was prepared by diluting Ultrapur reagent (Kanto Chemical) with water. The other chemicals used were of analytical reagent grade. A Phen solution (10 mM) was prepared by dissolving 1,10-phenanthroline monohydrate (Wako Pure Chemical Industries) in water. Buffered Phen solutions were prepared by mixing 10 mM Phen solution and an acetate buffer solution (2 M sodium acetate and 2.7 M acetic acid). An AA

solution (10 or 100 mM) was prepared by dissolving L-ascorbic acid in water just before use. Stock iron(II) and (III) solutions (1.00 g l^{-1} Fe) were prepared by dissolving $FeSO_4 \cdot 7H_2O$ and $FeNH_4(SO_4)_2 \cdot 12H_2O$ (purity≥99%), respectively, in 0.1 M HCl. The concentration of iron(II) in the stock solution was standardized by the redox titration with potassium dichromate. Working iron standard solutions were prepared by diluting the stock solution with water or 0.1 M HCl just before use.

Chromatographic-grade AC reagent (Wako Pure Chemical Industries) was used. Before use, 1 g of AC was washed with 100 ml of ethanol by decantation and finally the sedimented fraction with particle size of 20 - 200 μm (mainly 50 μm) was collected on a filter paper. After drying, the fractionated AC powder was dispersed into ethanol (0.5 g in 50 ml) and subsequently packed into a microcolumn (PTFE tubing with 1 mm i.d. and 2 mm o.d.). Silica glass wool was placed both the ends of the column.

One gram of the above AC reagent was packed in a polystyrene syringe (2.3 cm i.d.) and used for the elimination of humic substances (HSs) in the sample. This syringe column was conditioned by washing three times with 10 ml of 40 M acetone, 8 times with 10 ml of water and finally three times with 10 ml of 0.1 M HCl. AC packed was renewed, when HSs was detected spectrofluorometrically [8] in the eluent of 0.1 M HCl.

2.2. FIA system

Figure 1 shows the FIA system used in this study. PTFE tubing (0.5 mm i.d.) and Daiflon connectors were used throughout. Two double plunger pumps (P_1, Nihon Seimitsu Kagaku NP-FX-6U and P_2, a pumping part in Hitachi 655A-11 liquid chromatograph) were used for propelling sample (S), reagent (R_1) and carrier (R_2) solutions and eluent solution (R_3). Sample volume injected was controlled by the pumping time of the sample. A chromatographic valve (V) was used to exchange the adsorption and elution modes of iron on/from the AC column (ACC). A Shimadzu UV-140-01 double-beam spectrophotometer with a silica glass flow cell (optical path, 10 mm long and 18-μl) and a strip-chart recorder was used for absorbance measurements.

2.3. Sample pretreatment

A sample collected was immediately filtered through a membrane filter with a pore size of 0.45 μm. The filtrate was acidified to 0.1 M HCl and allowed to stand for one or a half day in order to dissolve particulate or colloidal iron(III) hydroxide and liberate iron ions from humic aggregates [9]. The resulting solution less than 100 ml was passed into the syringe column to adsorb HSs on AC. The residual iron ions were recovered by washing the column three times with 10 ml of 0.1 M HCl. Just before FIA, the AA solution and then 1 M NaOH were added into the effluent to be 0.05 mM AA and pH 2 or 3.

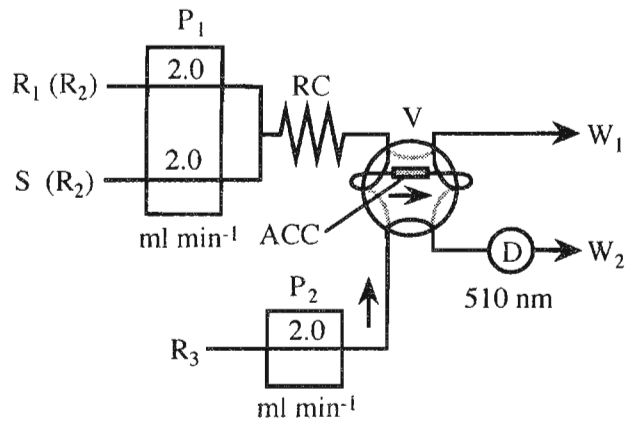

Fig. 1 FIA system with activated carbon column. S : sample; R_1 : 0.5 mM Phen - 0.1 M AcONa - 0.135 M AcOH (pH 4.5); R_2 : carrier (0.05 M AcONa - 0.0675 M AcOH); R_3 : 10 M acetone; P_1 and P_2 : double plunger pumps; RC : reaction coil (0.5 mm i.d., 2 m); ACC : activated carbon column (1 mm i.d., 5 cm); V : valve (solid line for adsorption mode and half-tone line for elution mode); D : flow cell (1.5 mm i.d., 10 mm); W_1 and W_2 : wastes.

2.4. FIA procedure

The reagent solutions were set up as indicated in Fig. 1. The valve (V in Fig. 1) was set to the adsorption mode. The sample (S) and the Phen solution (R_1) were introduced into the FIA system by a pump (P_1). The introduced volumes of S and R_1 were controlled by the pumping time of sample. The acetate buffer carrier (R_2) was pumped for 30s to carry all the sample and Phen solutions into the AC column. After exchanging the valve to the elution mode, iron adsorbed on AC was eluted by introducing an acetone solution (R_3) into the AC column by a pump (P_2). The absorbance of Fe(II)-Phen eluted was monitored at 510 nm. The height of the resulting peak signal was measured

for the determination. Iron - 0.05 mM AA solutions with pH 2 or 3 (see Section 2.3) prepared from the iron(III) standard solutions were used for the calibration curve.

3. Results and Discussion

3.1. Adsorption and elution of iron(II)-Phen complex

To study adsorption and elution properties of iron(II)-Phen complex, 2 ml of 0.2 mg l^{-1} of iron(III) solution (Fig. 1, S) containing 0.05 mM AA and 2 ml of the Phen solution (R_1) were introduced into the FIA system. The complete adsorption of iron was confirmed by the AAS determination of iron in the effluent (W_1). The elution with 10 M acetone gave a profile A (Fig. 2) with two peaks a and b. The profile B was obtained by the introduction of the acetate buffer carrier (R_2) in the place of S and R_1. This profile also had similar two peaks even in the absence of Phen as the color-producing reagent. In this case, two peaks were caused by the reflection change at the interface between the acetate buffer and acetone solutions. From the comparison between the profiles A and B, the peak b is corresponding to iron(II)-Phen. Therefore, the peak height of b was measured for the determination of iron.

Acetone, methanol and ethanol were effective for the elution of iron(II)-Phen. At their concentrations giving a comparable peak height of b in the presence of iron(II)-Phen, acetone performed lowest ghost peaks, *i.e.*, the peaks a and b caused only by the reflection change. The decrease in acetone concentration decreased the height of the ghost peaks. However, it broadened the peak width of iron(II)-Phen and consequently decreased the analytical sensitivity. On the other hand, at a higher concentration (> 25 M), a lower solubility of air in the acetone solution generated bubbles by mixing with the residual carrier in the AC column. Therefore, 10 M acetone (Fig. 1, R_3) was used as an eluent, although the elution of iron(II)-Phen was incomplete as described below.

Under the elution condition in Fig. 1, a ratio (R) of residual iron to the total iron adsorbed on AC was 0.15±0.08 from AAS determination results of the effluents (W_2). When R is constant, $P_n=R^nP_0+(1-R^n)P_\infty$, where P is peak height and the subscripts of P are the number of successive injection/elutions of the same sample, after a different sample giving P_0 was injected. The peak height reached to a constant value (P_∞) by repeated injections of the same sample (Fig. 5). For three microcolumns prepared, the peak height in n=1 and the above equation gave R=0.14±0.04, which was consistent with the above AAS results. With this R value, the equation led to that $P_n \geq 0.99P_\infty$ was obtainable at n=3 in setting $P_0=0$. In this study, a constant peak height after repeated injections was measured for the determination of iron.

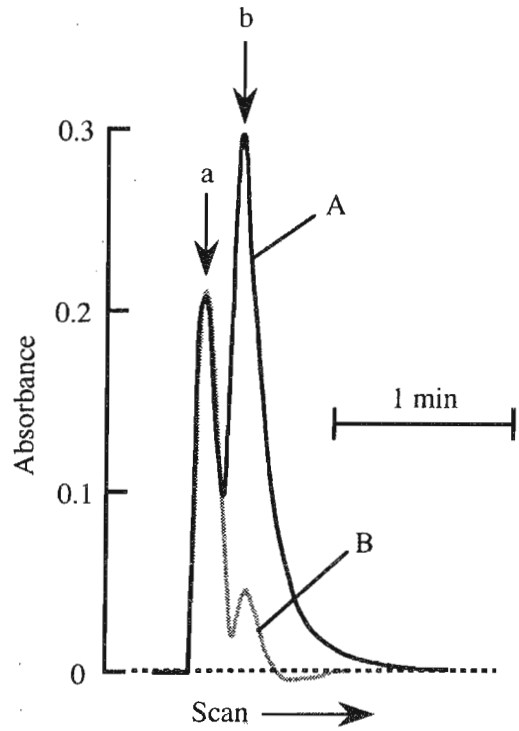

Fig. 2 Elution profiles after 1-min introduction of 0.2 mg Fe l^{-1} and Phen (A) and acetate buffer carrier (B).

3.2. Optimization of reagent concentrations

Absorbance of iron(II)-Phen formed at pH 4.5 was measured at 510 nm [10]. The effects of reagent concentrations on the peak height for the reagent blank and 0.2 mg l^{-1} of iron(II) were investigated for effective adsorption and elution of iron. Figure 3 shows the effects of Phen, AA and acetate concentrations on the peak height. By the batch method, 0.2 mM or more of Phen was required for the complete formation of Fe(II)-Phen. From the results in Fig. 3 (A), 0.5 mM of Phen giving the maximum peak height of iron was adopted as the optimized concentration. A decreased peak height at 0.2 mM was caused by the broadening of peak. Over 0.5 mM, the peak height decreased with an increase in Phen concentration. The AAS determination of iron in

the wastes (W_1 and W_2 in Fig. 1) indicated a decrease in peak height was caused by incomplete adsorption of iron on AC. The effect of AA was studied for iron(III) (Fig. 3, B). A peak signal in the absence of AA indicated that a part of iron(III) was reduced to Fe(II) by AC. At 0.05 mM AA, the peak height was the maximum and equal to that of iron(II). At higher concentration of AA, the peak height became lower because of incomplete adsorption of iron on AC. The effects of AA and Phen at higher concentrations suggested that the adsorption of the organic matter on AC decreased the adsorption capacity for Fe(II)-Phen. The effect of acetate concentration was investigated at pH 4.5 which was adjusted by changing the concentration of acetic acid (Fig. 3, C). Over 0.1 M, an increase in acetate concentration decreased the peak height, which was caused by the decrease in peak height of ghost peaks and the broadening of peak. On the other hand, the effect of acetate was negligible at lower concentrations. Therefore, 0.1 M was adopted as an appropriate concentration.

Variation of peak height under the same condition (Figs. 2 - 5) was caused by the use of microcolumns prepared separately (see Section 3.4).

3.3. Optimization of FIA system

Higher pumping rates were preferred for the rapid analysis. However, the total flow rate in the AC column should not be over 4 ml min^{-1}, because it decreased the life of the column and finally broke down the column. Therefore, the pumping rates indicated in Fig. 1 was used. The column can

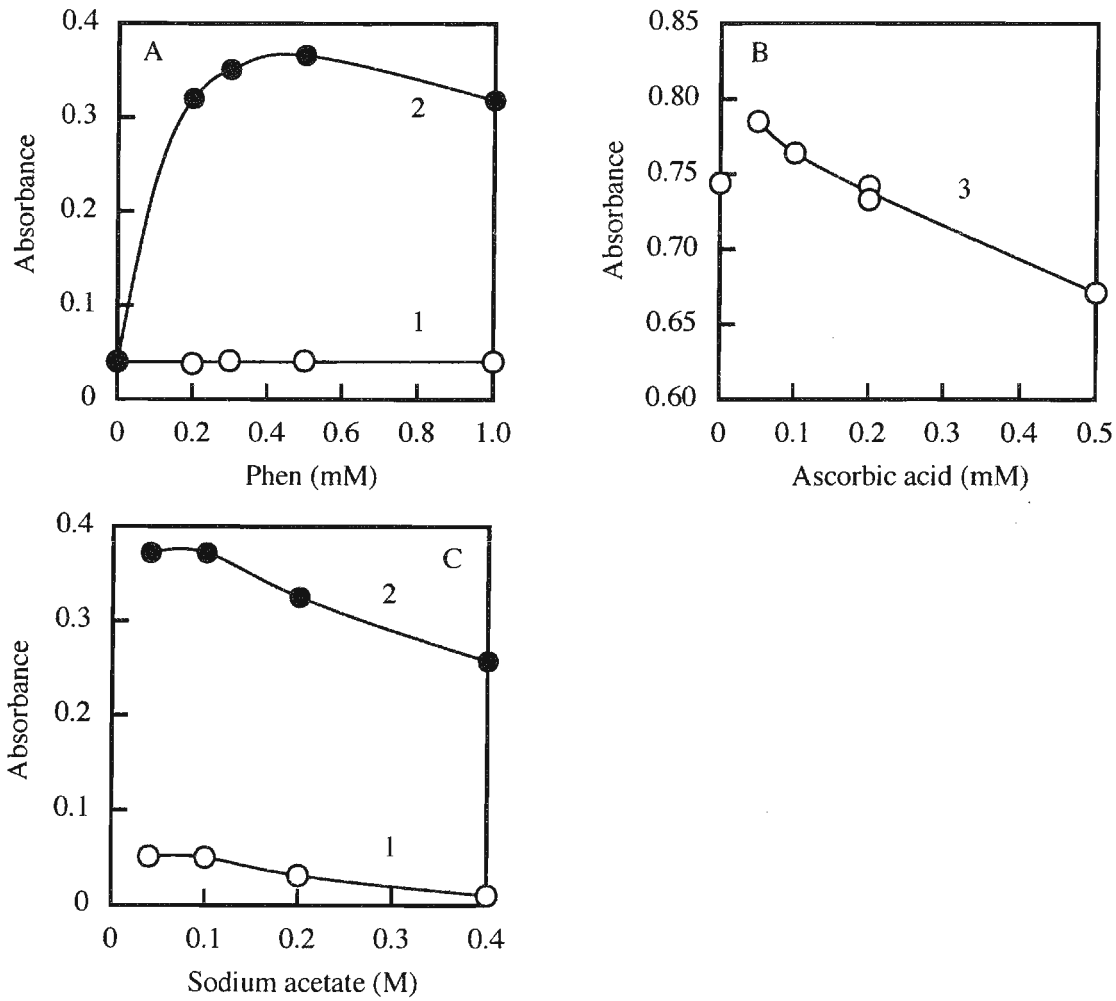

Fig. 3 Effects of Phen (A), ascorbic acid (B) and sodium acetate (C) concentrations on absorbance of peak height for the reagent blank (1) and 0.2 mg Fe(II) l^{-1} (2) or 0.5 mg Fe(III) l^{-1} (3) under the conditions as shown in Fig. 1 and with 1 min of sampling time.

be used for at least 200 enrichment runs. Figure 4 shows the effects of the length of reaction coil (Fig. 1, RC) and sample volume on the peak height for the reagent blank and 0.2 mg l^{-1} iron(II) or 0.5 mg l^{-1} iron(III). The length (1 to 4 m) of reaction coil did not influence the peak height, indicating the complete formation of Fe(II)-Phen and its adsorption on AC. We adopted 2 m. The peak height increased linearly with increasing the sample volume up to 4 ml. Over 4 ml, iron was adsorbed incompletely on AC. Therefore, 4 ml of sample were the maximum volume injected. A decrease in the flow rate of the eluent broadened the peak width and thereby decreased the peak height of iron. In our FIA system, 2 ml min^{-1} was adopted.

3.4. Determination characteristics

Under the conditions optimized above and the introduction of 2 ml of sample, typical peak signals were recorded for different concentrations of iron (Fig. 5). The variation (s) of the peak height for the reagent blank was used to estimate a detection limit (DL) of iron corresponding to $3s$. From the result in Fig. 5, the DL was 2 μg l^{-1}; about 10-times lower than that without the AC microcolumn and a few time lower than that by direct AAS or inductively-coupled plasma atomic emission spectrometry. The calibration curve by the proposed FIA method was linear up to at least 1.2 mg l^{-1} iron. The sampling rate for 0.2 mg l^{-1} iron was 25 samples h^{-1}. For 4 ml of the sample, about 30-times enrichment was estimated from the slope of the calibration curve with and without the AC column.

The use of separate microcolumns prepared by the same manner changed the slope and intercept of the calibration curve; their variations were about 10 and 30%, respectively. On the other hand, the variations were not significant (≤ 5%) in about 50 enrichment runs for the same microcolumn.

3.5. Interferences

The interference from many foreign ions is probably negligible for natural and tap water samples [10]. However, from the effect of Phen or AA concentration (Fig. 3), the adsorption of organic compounds on AC may interfere with the determination of iron. The interference from humic acid (HA) as a major organic constituents in river water was investigated for a synthetic sample containing iron(III) and HA. This sample was prepared in the presence of 0.1 M HCl. After the addition of AA, pH was adjusted, as described in Section 2.3. In the determination of 0.2 mg l^{-1} iron, the presence of 0.1 mg l^{-1} HA gave a lower determined value (0.071 mg l^{-1}). Such serious interference is not acceptable for the analysis of natural water. Therefore, HA was eliminated by its adsorption on a separate AC column (see Sections 2.1 and 2.3). The acidification of sample with 0.1 M HCl liberates iron ions from humic aggregates [9]. For a synthetic sample (80 ml) containing 0.5 mg l^{-1} iron(III) and 2 mg l^{-1} HA, a

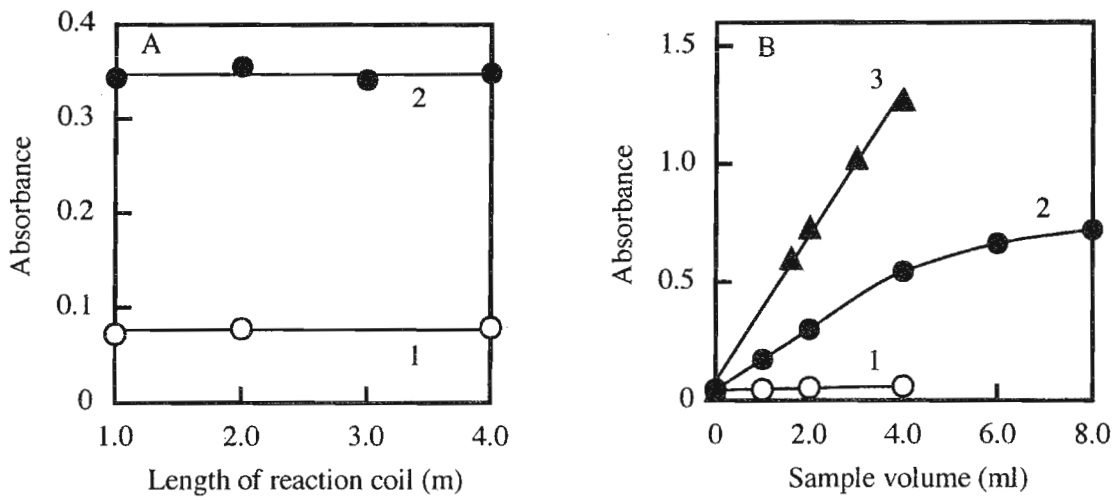

Fig. 4 Effects of length of reaction coil (A) and sample volume (B) on absorbance of peak height for the reagent blank (1) and 0.2 (2) and 0.5 mg Fe(III) l^{-1} (3) under the conditions as shown in Fig. 1.

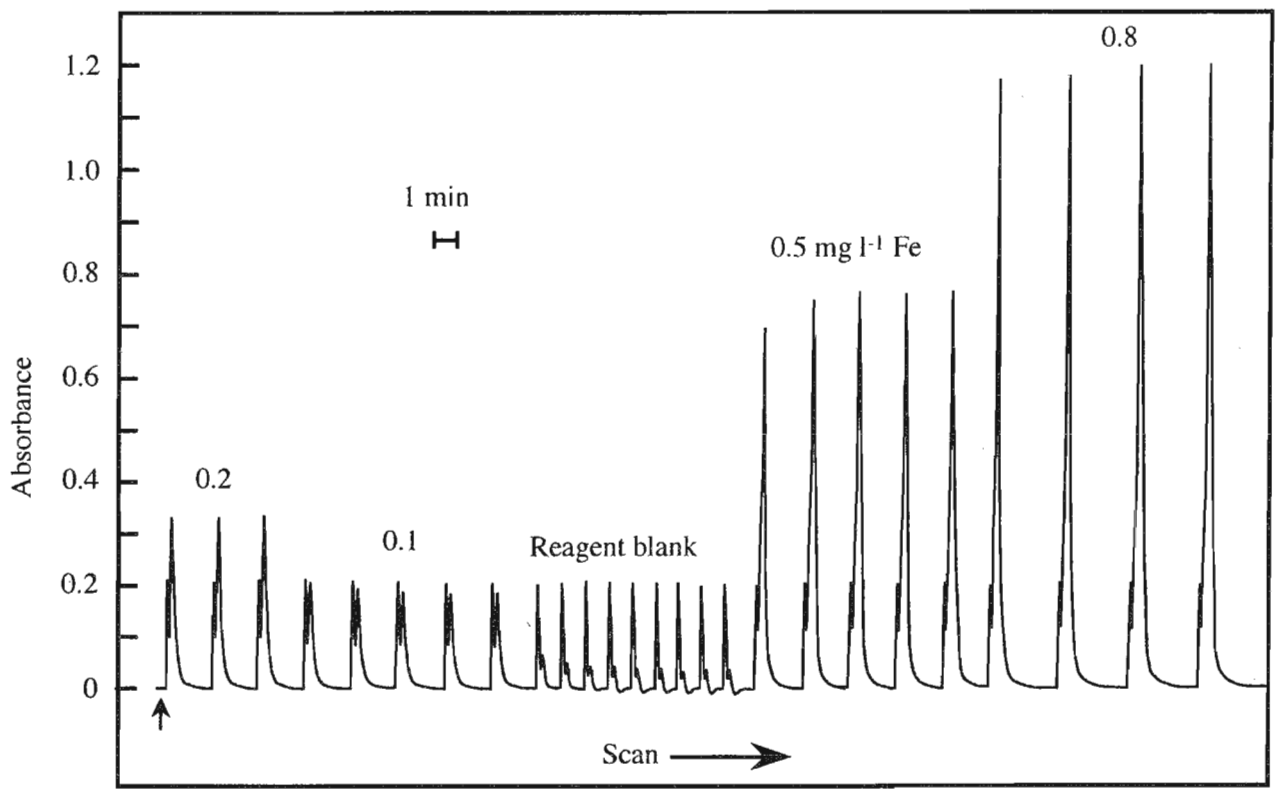

Fig. 5 Typical peak profiles for different concentrations of Fe(III) under the FIA conditions shown in Fig. 1. Arrow indicates a start point of elution. Sample volume was 2 ml.

Table 1 Determination of iron ($\mu g\ l^{-1}$) in tap and river water samples[a] by the FIA and atomic absorption spectrometric (AAS) methods

Sample No. and sampling data	Pretreatment[b]	FIA method		AAS method	
1 Tap water pH 7.3, 10/17/1999	No	65±2	(n=5)	66±3	(n=3)
		[5.2±0.5][c]	(n=3)	[64±1][c]	(n=3)
2 Tap water pH 7.2, 10/25/1999	No	9.8±0.3	(n=3)	10±1	(n=3)
3 Aikawa river pH 8.0, 10/19/1999	No	2.3±0.1	(n=3)	13±2	(n=3)
		[1.3±0.5][c]	(n=3)	[10±2][c]	(n=4)
	Yes	11±0.5	(n=5)	-	
4 Arakawa river pH 7.4, 2/2/2000	Yes	33±2	(n=3)	31±2	(n=3)
5 Nigorigawa river pH 7.1, 2/9/2000	Yes	667±5	(n=4)	684, 687	

[a]filtered through 0.45-μm filter and acidified to be 0.1 M HCl.
[b]elimination of HA by an off-line AC column.
[c]without the acidification.

satisfactory recovery of iron (≥ 95%) and no detection of HA (< 0.02 mg l^{-1}) after this pretreatment were confirmed by their AAS and fluorometric determinations, respectively.

3.6. Analysis of tap and river water samples

Tap and river water samples were collected in Kofu, Japan. Table 1 shows the analytical results obtained by both the proposed FIA and direct AAS methods. For acidified tap water samples (Nos. 1 and 2), the results obtained by the proposed FIA method agreed with those obtained by the AAS method. On the other hand, for non-acidified sample (No. 1), the result by the FIA method was much lower than that by the AAS method. Most of iron existed as $Fe(OH)_3$ at pH 7 [4]. The dissociation of $Fe(OH)_3$ by Phen may be ineffective for a short reaction time in the FIA system. Therefore, the acidification of sample was required for the dissolution of $Fe(OH)_3$.

For the river water sample (No. 3), even after the acidification, the analytical results by the FIA method were lower than those by AAS method. This sample contains 0.5 mg l^{-1} of HSs as HA. At this concentration level, HA obviously interferes with the FIA determination. By the elimination of HA and together with other adsorptive organic compounds, the results (Nos. 3 to 5) by the FIA method agreed with those by the AAS method, confirming the reliability of the proposed FIA method for the analysis of natural fresh water.

3.7. Recycle of wastes

Recycle of wastes (W_1 and W_2 in Fig. 1) was studied to minimize the wastes. The waste of W_1 was used as the acetate buffer (R_2) and for the preparation of the Phen-buffer solution (R_1). Acetone distilled from the waste (W_2) was used for the preparation of R_3. In a single cyclic use of W_1 for R_1 and R_2 and W_2 for R_3, the peak height for the reagent blank decreased comparable to that for the carrier (Fig. 2, B). Impurity iron in R_1 and R_2 was probably eliminated by passing through the AC microcolumn. Slopes of the calibration curve with and without the wastes agreed within an error of 5%. The waste of W_1 can be used, when it contains an tolerable concentration of acetone and has a sufficient buffer capacity.

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