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Flow-injection photometric determination of manganese(II) based on its catalysis of the periodate oxidation of *N,N′*-bis(2-hydroxy-3-sulfopropyl)tolidine☆

Shigenori Nakano*, Yuko Matumoto[1], Masahiro Yoshii

Department of Regional Environment, Faculty of Regional Sciences, Tottori University, Koyama-cho, Tottori 680-8551, Japan

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Abstract

A novel flow-injection spectrophotometric method has been developed for the determination of manganese(II) at sub-nanogram/ml levels. The method is based on its catalytic effect on the oxidation of *N,N′*-bis(2-hydroxy-3-sulfopropyl)tolidine (HSPT) by periodate. The catalytic effect of manganese(II) was enhanced by the presence of 2,2′-bipyridine as an activator. By monitoring the change in absorbance of the oxidation product of HSPT at 670 nm, manganese(II) ranging 0.02–3.0 ng ml^{-1} could be determined with the relative standard deviations of less than 2%. The interfering ions were effectively suppressed by the addition of 2,2′-iminodiethanol and citric acid. The proposed method is directly applicable to the determination of manganese in lake and river water samples.
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Keywords: Kinetic-catalytic method; Flow injection analysis; Spectrophotometry; Manganese; *N,N′*-Bis(2-hydroxy-3-sulfopropyl)tolidine; Periodate

1. Introduction

Manganese is well known as one of the essential trace elements for human beings. It is a component of enzymes, such as superoxide dismutase, glutamine synthetase and arginase [1]. This element is widely utilized in metallurgic and chemical industry, which emitted it into the atmosphere, hydrosphere and biosphere. Prolonged exposure to low levels of manganese may enhance the onset of Parkinsonian disturbances [2]. In order to understand its behavior and fate in human body and environment, highly sensitive and selective methods for the determination of manganese is necessary.

A variety of methods have been reported on the manganese determination. Atomic absorption spectrometry [3,4], inductively coupled plasma atomic emission spectroscopy [5,6] and neutron activation analysis [7] have high sensitivity, but they require special and expensive instruments. Electrochemical stripping methods such as cathodic stripping voltammetry [8,9] and adsorptive stripping voltammetry [10] have been employed for the determination of manganese; their selectivity is relatively poor. Although conventional spectrophotometry based on stoichiometric reactions was used [11], these methods necessitated preconcentration owing to their low sensitivity [12,13]. Kinetic-catalytic spectrophotometry offers simple and inexpensive alternative for the determination of trace levels of manganese(II) [11,14,15]. The reactions of rhodamine B [16], 3,3′,5,5′-tetramethylbenzidine [17], naphthol blue black [18] and dahlia violet [19] with periodate were used as indicator reactions for its manual catalytic determination. The oxidative coupling of 3-methyl-2-benzothiazolinone hydrazone with *N,N*-dimethylaniline by dissolved oxygen was also used for the manganese(II) determination [20]. These methods are capable of determining manganese(II) at ng/ml levels, but care must be taken in the timing of mixing the sample and reagent solutions to obtain highly accurate results. In the flow injection analysis (FIA), the reaction time can be easily controlled by using an adequate length of reaction coil and an adequate flow rate of the reagent solutions [14,15]. The adaptation of FIA to catalytic methods can lead to advantages such as higher precision and rapid sampling frequency. Table 1 shows pertinent FIA for the spectrophotometric determination of manganese(II) based on its catalysis [21–30]. To attain lower limit of detection, 1,10-phenanthlorine [24,25], triethylenetetramine [26], tri-

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* Corresponding author. Fax: +81 857 31 5109.
E-mail address: nakano@rstu.jp (S. Nakano).
[1] Present address: Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan.

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Table 1
Flow-injection spectrophotometric methods for the catalytic determination of manganese(II)

Indicator reaction	Activator	Dynamic range (/ng ml^{-1})	Application	Reference
Succinide dioxime + O_2		0.2–1300	Chemicals and food	[21]
N,N-Diethylaniline + IO_4^-		0.02–1.0	Water	[22]
Malachite green + IO_4^-		0.25–100		[23]
Tiron + H_2O_2	Phen	5.5–22	Stopped-flow/water	[24]
MBTH + DMA + H_2O_2	Phen + citrate	4–30	Plants	[25]
DPD + PDA + H_2O_2	Trien + tiron	0.05–1	Water	[26]
DHBA + H_2O_2		0.5–15	Solar salts	[27]
Diphenylcarbazone + O_2	TEA	0.1–4000	Plants	[28]
ABTS + IO_4^-		0.05–1	Water	[29]
Tetrabase + IO_4^-	NTA	0.07–20	Stopped-flow/water	[30]
HSPT + IO_4^-	bpy	0.02–3	Water	This work

Tiron, 1,2-dihydroxybenzene-3,5-disulfonate; phen, 1,10-phenanthlorine; MBTH, 3-methyl-2-benzothiazolinone hydrazone; DMA, *N,N*-dimethylaniline; DPD, *N,N*-dimethyl-*p*-phenylenediamine; PDA, *m*-phenylenediamine; trien, triethylenetetramine; DHAB, 3,4-dihydroxybenzoic acid; TEA, triethanolamine; ABTS, 2,2′-azinobis(3-ethylbenzothiazoline)-6-sulfonic acid; Tetrabase, 4,4′-bis(dimethylamino)diphenylmethane; NTA, nitrilotriacetic acid; HSPT, *N,N*′-bis(2-hydroxy-3-sulfopropyl)tolidine; bpy, 2,2′-bipyridine.

ethanolamine [28] and nitrilotriacetic acid [30] were used as activators in these methods, which could determine nanogram amounts of manganese(II).

N,N′-Bis(2-hydroxy-3-sulfopropyl)tolidine (HSPT) was employed as a new substrate for peroxidase assay instead of *o*-phenylenediamine and 3,3′,5,5′-tetramethylbenzidine [31]. The oxidation of HSPT by bromate was used as an indicator reaction for the catalytic FIA of ultratrace amounts of vanadium(IV, V) [32]. The authors found that manganese(II) acts as a catalyst in the periodate oxidation of HSPT and 2,2′-bipyridine (bpy) enhances the catalytic effect of manganese(II). This paper describes a novel FIA for the spectrophotometric determination of manganese(II) based on these findings. The proposed method can be used for the determination of sub-ng/ml levels of manganese. The method has been successfully applied to the determination of manganese in fresh water samples without preconcentration and separation.

2. Experimental

2.1. Reagents

All chemicals used were of analytical-reagent grade and water purified with a Millipore Milli-Q water-purification system was used for preparation of solutions.

A manganese(II) standard solution (1.0 mg ml^{-1} Mn(II) in 0.1 mol l^{-1} nitric acid) was obtained from Wako Junyaku Co., Japan. The working standard solutions were prepared daily by diluting the stock solution with 1.0×10^{-3} mol l^{-1} hydrochloric acid. *N,N*′-bis(2-hydroxy-3-sulfopropyl)tolidine, disodium salt, tetrahydrate (HSPT) was obtained from Dojin Kagaku, Japan. A 5.0×10^{-3} mol l^{-1} HSPT stock solution was prepared by dissolving 0.302 g of the compound in 100 ml of 5.0×10^{-3} mol l^{-1} sulfuric acid. The working HSPT solution (3.0×10^{-4} mol l^{-1}) was prepared from the stock solution by diluting with the acid. A 1.0×10^{-2} mol l^{-1} periodate stock solution was prepared by dissolving 0.230 g of potassium periodate (Wako Junyaku, Japan) with 100 ml of water. The working periodate solution (3.0×10^{-4} mol l^{-1}) was obtained by diluting the stock solution with water. Stock solutions of 3,3-dimethylglutaric acid (DGA, 0.1 mol l^{-1}), 2,2′-bipyridine (bpy, 5.0×10^{-3} mol l^{-1}), 2,2′-iminodiethanol (IDE, 0.1 mol l^{-1}) and citric acid (0.1 mol l^{-1}) were also prepared. A mixed solution of 1.0×10^{-2} mol l^{-1} DGA, 5.0×10^{-5} mol l^{-1} bpy, 2.0×10^{-4} mol l^{-1} IDE and 1.0×10^{-4} mol l^{-1} citric acid was prepared from these stock solutions and adjusted to pH about 12.6 with 1.0 mol l^{-1} sodium hydroxide solution.

2.2. Apparatus

A flow diagram for the manganese(II) determination is shown in Fig. 1. Two double-plunger micropumps (Sanuki Kogyo DMX-2000T, Japan) were used to propel the carrier and reagent solutions. A six-way injection valve (Sanuki Kogyo SVM-6M2, Japan) was used for the injection of the solutions of manganese(II) standard and sample into the carrier stream. A spectrophotometer (Soma Kogaku S-3250T, Japan) equipped with a flow cell (8 μl volume, 10 mm path length) was used for absorbance measurements. A Rika Denki R-61 recorder was used for recording the absorbance. A circulating thermostated bath (Taitek DX-10T, Japan) and an immersion cooler (Tokyo

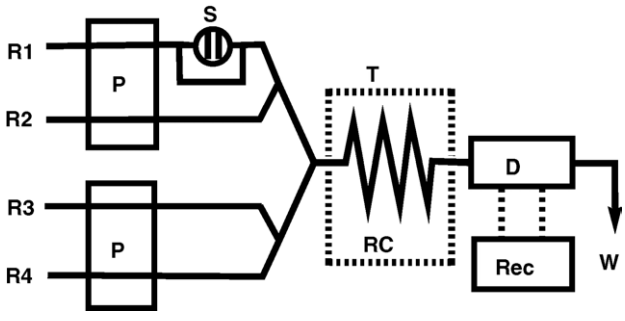

Fig. 1. Flow system for the manganese(II) determination. R1–R4, reservoir; P, pump; S, sample injector; RC, reaction coil; T, thermostated bath; D, detector (spectrophotometer); Rec, recorder; W, waste. Conditions as in Table 2.

Table 2
Optimized conditions for the determination of manganese(II)

Reservoir	
R1	HCl (1.0×10^{-2} mol l^{-1}, carrier solution)
R2	DGA (1.0×10^{-2} mol l^{-1})/bpy (5.0×10^{-5} mol l^{-1})/IDE (2.0×10^{-4} mol l^{-1})/citric acid (1.0×10^{-4} mol l^{-1})
R3	HSPT (3.0×10^{-4} mol l^{-1})
R4	KIO_4 (3.0×10^{-4} mol l^{-1})
Flow rate	0.6 ml min^{-1}
Sample volume	270 μl
Reaction coil	6 m
Reaction temperature	15 °C
Reaction pH	7.3
Detector	Spectrophotometer (670 nm)

Rika ECS-0SST, Japan) were used to adjust the reaction temperature. All connecting lines containing a sample loop and reaction coil were made from 0.5 mm i.d. poly(tetrafluoroethylene) (PTFE) tubing. A Toa Denpa IM-40ST pH meter was used for pH measurements. A Shimadzu MultiSpec-1500 photodiode array spectrometer was used for the measurement of absorption spectra.

2.3. Procedure

The optimized conditions are shown in Table 2. In the flow system (Fig. 1), a carrier solution (R1, 10^{-2} mol l^{-1} hydrochloric acid), a mixed solution (R2) of DGA, bpy, IDE and citric acid, HSPT solution (R3) and periodate solution (R4) were pumped to the flow line at a flow rate of 0.6 ml min^{-1}. An aliquot of the sample solution (270 μl) was injected into the carrier stream by a sample injector and then mixed with the reagent solutions. The catalyzed reaction proceeded in the reaction coil (6 m) at 15 ± 0.1 °C. The absorbance of the colored product was continuously measured at 670 nm.

3. Results and discussion

HSPT is slowly oxidized by periodate to form a blue compound which has an absorption maximum at 670 nm in neutral pH media. The rate of oxidation of HSPT is catalytically accelerated by trace amounts of manganese(II). According to the literature [20], manganese(II) is oxidized by periodate to manganese(III) or (IV) which accelerates the oxidation of HPTS. The reduced manganese(II) during the reaction is then oxidized again to manganese(III) and/or (IV) by periodate; the oxidation of HSPT is catalyzed by manganese(II) as a result of its regeneration. Therefore, trace amounts of manganese(II) can be determined by measuring the change in absorbance of oxidation product of HSPT at a fixed time.

3.1. Selection of activator

The catalytic effect of a metal ion on redox reactions is remarkably enhanced by the presence of a ligand, i.e., an activator [14,15]. Highly sensitive catalytic methods can be developed by utilizing the activating effect of the ligand on the metal-catalyzed reaction. If the activator also acts as a masking agent for interfering ions, the selectivity of the method is improved. In the present reaction system, ligands acted as possible activators for the manganese(II)-catalyzed reaction were examined: they were acetylacetone (acac), bpy, ethylenediamine (en), iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), 1,10-phenanthroline (phen), triethylamine (TEA), 1,2-dihydroxybenzene-3,5-disulfonate (tiron) and triethylenetetramine (trien). A 0.5 ng ml^{-1} manganese(II) solution in the presence of each ligand in the concentration range 10^{-6}–10^{-4} mol l^{-1} was introduced into the flow system. Among them, bpy, TEA and trien showed larger activating effect for manganese(II) (Fig. 2). The rate of the manganese(II)-catalyzed reaction was dependent on the concentration of TEA and trine, but it was independent on the bpy concentration; bpy was selected as an activator in this reaction system. The effect of bpy concentration in the range 0–8.0×10^{-5} mol l^{-1} was examined by adding the bpy solution to the reservoir R2. The peak height due to the catalyzed reaction increased with increasing bpy concentration up to 3.0×10^{-5} mol l^{-1}, and then it was almost constant at the concentrations above 3.0×10^{-5} mol l^{-1} (Fig. 3). On the other hand, the absorbance of baseline due to the uncatalyzed reaction scarcely increased with increasing the bpy concentration. A 5.0×10^{-5} mol l^{-1} bpy concentration was thus chosen for the procedure.

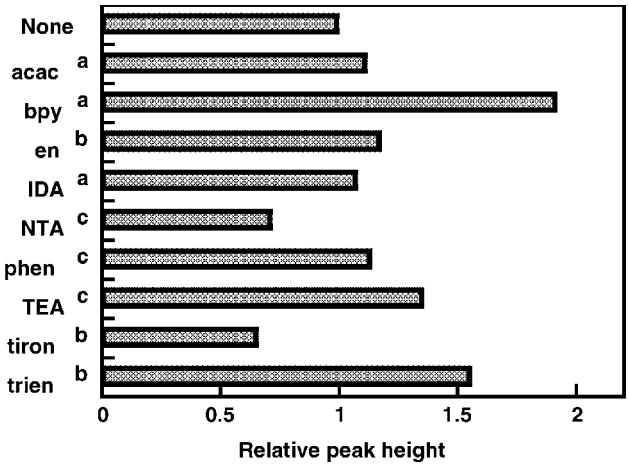

Fig. 2. Effect of ligands on the manganese(II)-catalyzed reaction. Ligand concentration (mol l^{-1}): (a) 1×10^{-4}; (b) 1×10^{-5}, (c) 1×10^{-6}. $C_{Mn(II)}$, 0.5 ng ml^{-1}. Conditions are as in Table 2 except for the ligand concentration. Abbreviations are as in the text.

3.2. Optimization of reaction variables

The variables such as flow rate, coil length, reaction temperature, reaction pH, reagent concentrations were optimized by injecting a 0.5 ng ml^{-1} manganese(II) solution.

The effect of flow rate on the peak height was examined by using a 6 m coil length at 15 °C. The height of peak and the absorbance of baseline increased with decreasing the flow rate. The flow rate was selected as 0.6 ml min^{-1} because lower flow rates led to slower sampling frequency. The effect of reaction

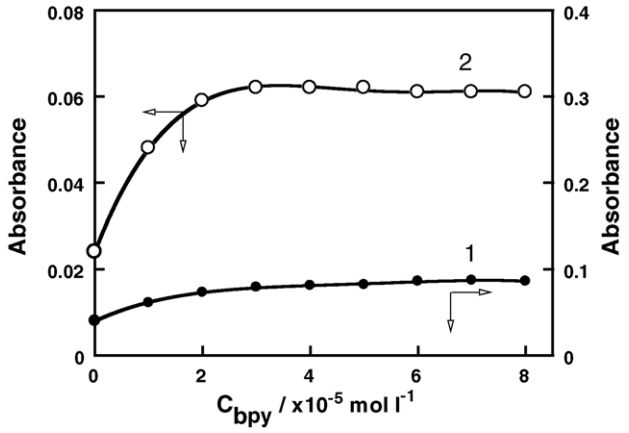

Fig. 3. Effect of bpy concentration on the color development. (1) Baseline; (2) 0.5 ng ml^{-1} Mn(II). Conditions are as in Table 2 except for the bpy concentration.

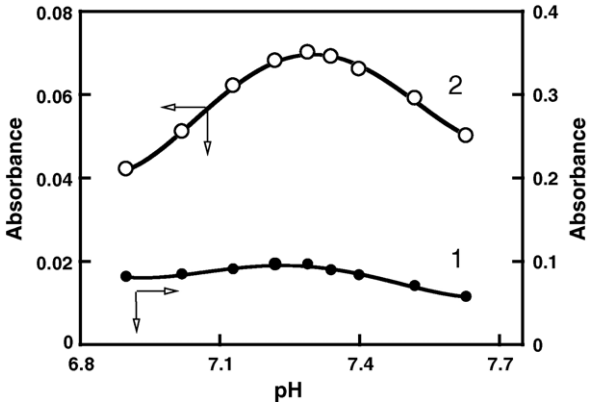

Fig. 5. Effect of the pH on the color development. (1) Baseline; (2) 0.5 ng ml^{-1} Mn(II). Conditions are as in Table 2 except for the reaction pH.

temperature was examined in the range 2–30 °C by using reaction coils of 4 and 6 m. In general, the rate of both catalyzed and uncatalyzed reactions proceed more quickly at higher temperature. Although the peak height increased with increasing temperature up to 15 °C in this reaction system, it decreased above 15 °C as shown in Fig. 4, because the decomposition of the blue compound proceeded at temperatures above 15 °C. The reaction was carried out at this temperature. An increase in the length of reaction coil also increased the height of peak and the absorbance of baseline because of longer reaction time. A 6 m coil length was chosen taking account the sensitivity and sampling frequency. The effect of the sample volume was examined in the range 110–360 μl. The height of peak increased with increasing the sample volumes up to 270 μl. At above this volume, a slight increase in the peak height was observed because of dispersion of sample zone; a sample volume of 270 μl was selected for the procedure.

Fig. 5 shows the effect of the reaction pH ranging 6.9–7.6 in the presence of DGA as a buffer agent. As the optimum pH was found to be around 7.3, the reaction was carried out at this pH. Some buffer agents having a buffer capacity in the pH range 6–8 were examined in the presence of 0.5 ng ml^{-1} manganese(II). The following buffers were examined; DGA, *N*-(2-acetamido)-2-aminoethane sulfonic acid (ACES), 2-hydroxy-3-morpholinopropanesulfonic acid (MOPSO), *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES), 3-morpholino-propanesulfonic acid (MOPS), *N*-tris(hydroxymethyl)methyl-2-aminoethane sulfonic acid (TES), 2-[4-(2-hydroxyethyl)-1-piperazinyl] ethanesulfonic acid (HEPES). Among them, DGA was selected as a buffer agent because the peak height was scarcely affected by its concentration up to 1.0×10^{-2} mol l^{-1}. The DGA concentration was fixed at 1.0×10^{-2} mol l^{-1}.

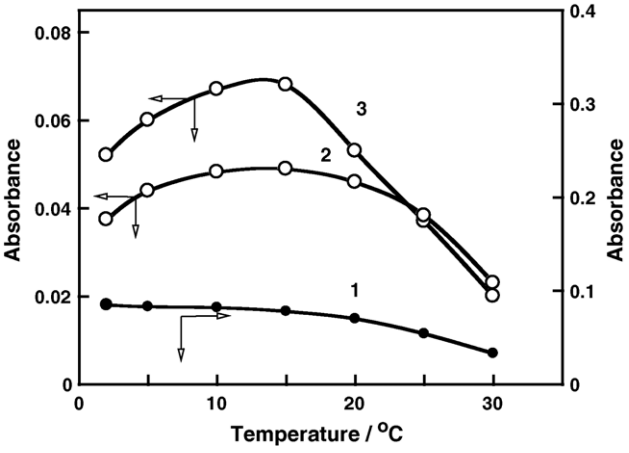

Fig. 4. Effect of reaction temperature on the color development. (1) Baseline; (2) and (3) 0.5 ng ml^{-1} Mn(II). Reaction coil length: 1 and 3, 6 m; 2, 4 m. Conditions are as in Table 2 except for the reaction temperature.

The effects of concentrations of HSPT and periodate on the color development were examined in the range 0–5.0×10^{-4} mol l^{-1}. Both heights of peak and baseline remarkably increased with increasing HSPT and periodate concentrations. By considering the stability of baseline, the concentrations of HSPT and periodate were adjusted to 3.0×10^{-4} mol l^{-1}, respectively.

3.3. Calibration graph and reproducibility

Calibration curves were constructed under the optimized conditions as shown in Table 2. The curves were linear in the range of 0.02–3.0 ng ml^{-1} manganese(II). The regression equation is $A = 0.144 \times C_{Mn(II)} + 0.005$, with correlation coefficient of 0.998, where A and $C_{Mn(II)}$ denote absorbance and concentration of manganese(II), respectively. Detection limit (S/N = 3) was 0.01 ng ml^{-1} manganese(II) and sampling frequency was about 20 h^{-1}. The reproducibility of the method was satisfactory with relative standard deviations of 1.6 and 1.1% for five determinations of 0.2 and 0.5 ng ml^{-1} manganese(II), respectively.

3.4. Effect of diverse ions

In the presence of bpy, Fe(III) gave a positive error presumably because of its catalytic effect. In order to eliminate the interference from Fe(III), some complexing agents such as citrate, diphosphate, *N*-(2-hydroxyethyl)ethylendiamine-*N,N′,N′*-

Table 3
Tolerance limits for diverse ions in the determination of 0.5 ng ml^{-1} manganese(II)

Tolerance limit (ng ml^{-1})	Ion added
>10000	Ag(I), As(V), Ca(II), Hg(II), K(I), Na(I), NH_4(I), Se(IV), Sr(II), W(IV), BO_3^{3-}, Br^-, ClO_4^-, CO_3^{2-}, F^-, I^-, NO_3^-, PO_4^{3-}, SCN^-, SO_4^{2-}, citrate, oxalate, tartrate
1000	Ba(II), Bi(III), Co(II), Mg(II), Mo(VI), Zn(II)
500	Fe(III), Sn(IV), Te(IV)
100	Al(III), Cd(II), Cr(VI), Cu(II), Pb(II), Sn(II), V(V), NO_2^-, $P_2O_7^{4-}$
50	V(IV)
10	As(III)[a], Ce(III), Ce(IV), Fe(II)
5	Cr(III), Ni(II)
0.5	As(III)

[a] Oxidation with ozone.

Table 4
Determination of manganese in the certified reference materials of river water

Sample	Mn added (ng ml^{-1})	Mn found[a] (ng ml^{-1})	Mn in sample (ng ml^{-1})	Recovery (%)
JAC-0031[b]	0	0.231 ± 0.01	0.462 ± 0.02	–
	0.1	0.331 ± 0.01		100
	0.2	0.425 ± 0.01		97.0
	0.3	0.437 ± 0.01		102
JAC-0032[c]	0	0.277 ± 0.01	5.54 ± 0.15	–
	0.1	0.377 ± 0.01		100
	0.2	0.472 ± 0.02		97.5
	0.3	0.537 ± 0.01		98.7

[a] Average and standard deviations (n = 3).
[b] Dilution, 1/2; certified value (ng ml^{-1}), 0.46 ± 0.02.
[c] Dilution, 1/20; certified value (ng ml^{-1}), 5.4 ± 0.1.

triacetic acid, IDE, 2,6-pyridine dicarboxylic acid and sulfosalicylic acid were examined as a masking agent. Among these agents examined, the catalytic effect of 100 ng ml^{-1} Fe(III) was suppressed at the IDE concentrations above 1.0×10^{-4} mol l^{-1}; IDE was chosen as a masking agent for Fe(III) and its concentration was fixed at 2.0×10^{-4} mol l^{-1}.

In the presence of bpy and IDE, 0.5 ng ml^{-1} of As(III) negatively interfered with the manganese(II) determination, probably because As(III) acted as an inhibitor for the manganese(II)-catalyzed reaction. Therefore, masking agents for As(III) such as citric acid, maleic acid, malonic acid, oxalate, sulfosalicylic acid, succinic acid and tartrate were examined. Among them, the action of As(III) at the amount of 0.5 ng ml^{-1} was depressed at the citric acid concentrations above 2.5×10^{-5} mol l^{-1}. But, the peak height decreased at the concentrations above 2.0×10^{-4} mol l^{-1}. Thus, a 1.0×10^{-4} mol l^{-1} citrate solution was used for the procedure. The interference from As(III) at amounts higher than 0.5 ng ml^{-1} can be avoided by the oxidation of As(III) to As(V) which did not affect the manganese determination (Table 3); the amount of 10 ng ml^{-1} As(III) was easily oxidized to As(V) by bubbling ozone for 5 min.

The effect of diverse ions on the determination of 0.5 ng ml^{-1} manganese(II) was examined in the presence of bpy, IDE and citric acid. A ± 5% error was considered to be tolerable. The results are summarized in Table 3. Many foreign ions did not interfere with the determination of 0.5 ng ml^{-1} manganese(II) even at levels 100 times of manganese(II) concentration. Arsenic(III), Ce(III, IV) and Cr(III) caused negative interferences, and Fe(II) and Ni(II) showed positive ones when present in 100-fold excess. The effect of large amounts of interfering ions can be avoided by diluting the sample solutions because the proposed method has high sensitivity.

3.5. Application to water samples

In order to evaluate the reliability of the present method, it was applied to the determination of manganese in certified reference materials of river water issued by the Japan Society for Analytical Chemistry (JAC-0031 and JAC-0032). The samples unspiked and spiked with 0.1, 0.2 and 0.3 ng ml^{-1} of manganese(II) were analyzed after suitable dilution with 0.05 mol l^{-1} of nitric acid. The analytical values obtained are shown in Table 4; the recoveries of manganese(II) in the spiked samples are excellent.

Table 5
Determination of manganese in river and lake water samples

Sample[a]	Dilution	Mn in sample[b] (ng ml^{-1})		
		Present method		Reference method [26]
		(I)[c]	(II)[d]	
River water				
Sendai-gawa	1/20	3.75 ± 0.02	3.75 ± 0.02	3.71 ± 0.05
Ohro-gawa	1/250	96.6 ± 0.7	97.0 ± 0.9	96.4 ± 0.5
Kyufukurogawa	1/250	58.4 ± 0.6	58.5 ± 0.4	59.3 ± 0.8
Fukuro-gawa	1/100	26.5 ± 0.8	26.8 ± 0.2	27.0 ± 0.2
Lake water				
Hachiman-ike	1/250	76.9 ± 0.8	76.2 ± 0.4	74.9 ± 0.3
Mizushiri-ike	1/1000	129 ± 2	129 ± 2	130 ± 2

[a] Collected at Tottori Prefecture, Japan.
[b] Average and standard deviation (n = 3).
[c] Calibration curve method.
[d] Standard addition method.

The results obtained by the proposed methods were in good agreement with the certified values.

The proposed method was applied to the determination in river and lake water samples. After being collected, the samples were filtered with membrane filter (pore size 0.45 μm) and the filtrates were acidified at pH ca. 2 by adding 5 mol l^{-1} hydrochloric acid. Both calibration curve and standard addition methods were carried out. In order to validate the present method, the same samples were also analyzed by a reference method [26]. Analytical results are summarized in Table 5. These values obtained are in good agreement with each other.

4. Conclusions

The catalytic FIA for determining trace amounts of manganese(II) was presented by using the periodate oxidation of HSPT as a novel indicator reaction. The sensitivity of the method was enhanced by adding bpy as an activator; as low as 0.02 ng ml^{-1} manganese(II) could be easily determined. The reproducibility of the method was satisfactory with relative standard deviations of below 2%. The proposed method allowed direct application to the determination of manganese in river and lake water samples without the need for any separation and preconcentration steps.

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