Flow Injection Determination of Manganese Using Malachite Green - Periodate Catalytic Reaction

Susumu Kawakubo, Tsugio Fukasawa, Masaaki Iwatsuki
and Tsutomu Fukasawa*

Department of Applied Chemistry, Faculty of Engineering, Yamanashi University, Takeda-4, Kofu-shi 400 (Japan)

Abstract

The method is based on the catalytic effect of manganese(II) on the oxidation reaction of a 2.2×10^{-5} M Malachite Green (MG) with 8.5×10^{-4} M periodate in acetate buffer medium (pH 4.4). The colour fading of MG after reaction in a 2-m or 4-m reaction tubing at 50°C is measured at 615 nm and recorded on a strip chart as a minus peak. For both the reaction tubings, the calibration curves of peak height vs. manganese amount in 20-ul sample are linear in the range of 0 - 2 ng manganese, and the relative standard deviations are within 2 % in determination of 1-ng manganese. Nine or eight samples can be analyzed in an hour. The interferences of foreign ions are also described.

Introduction

Reference to the available literatures indicated that there are not so many papers so far on the flow injection analysis (f.i.a.) using catalytic reaction, which seems to require often additional attention compared with the ordinary f.i.a. using the reactions in conventional spectrophotometric method. And among them were found two papers on the sensitive catalytic spectrophotometric determination of down to ca. 0.02-ng manganese by f.i.a.; one uses oxidation reaction of 3,4-dihydroxybenzoic acid with hydrogen peroxide at pH of 5 to 7 [1] and the another the oxidation reaction of succinimido dioxime with dissolved oxygen in a strong basic medium [2]. However, these methods are subject to interference from foreign ions such as magnesium, iron(III) and chromium(III).

Previously, the authors proposed a batchwise spectrophotometric catalytic method using a Malachite Green (MG)- periodate redox reaction for determination of ng-level manganese, and successfully applied it to the analyses of some chemicals and high purity materials [3-5]. However, the procedure was a little sophisticated and time-consuming. Recently, the same reaction was studied further, and a simpler and rapid method was developed, which includes measurement of colour fading in the initial reaction of the much more concentrated reactants at higher reaction temperature [6]. In the newly developed method, the determination was not subject to interference even from magnesium of 1600-fold amounts, and iron(III) and chromium(III) of 30-fold amounts as much as manganese amounts to be determined.

In the present paper, a sensitive f.i.a. for the determination of down to 0.03-ng manganese is studied on the basis of the preceding paper[6] with extended allowances of the foreign ions. Some additional problems accompanyed with using catalytic reaction are also described.

Experimental

Reagents and Apparatus

Metal manganese (99.99 %) of 125 mg was dissolved in 10 ml of 1 M nitric acid, and diluted to 250 ml with 0.05 M sulphuric acid to make a stock solution (500 μg ml^{-1}). Manganese standard solutions (20 to 100 ng ml^{-1}) were prepared by diluting the stock solution with water before use.

A buffer solution of pH 4.4 was prepared by mixing 100 ml of 2 M sodium acetate with 40 ml of 10 M acetic acid. The solution of different pH value was prepared by mixing different volume ratio of 10 M acetic acid to 2 M sodium acetate.

A stock Malachite Green (MG) solution (2.2×10^{-3} M) was prepared by dissolving MG (oxalate) in water. Working MG solution (4.4×10^{-5} M) of pH 4.4 was prepared by mixing 2.00 ml of the stock MG solution with 14 ml of the pH 4.4 buffer solution in a 100 ml measuring flask and diluting to the mark with water.

A stock periodate solution (1.7×10^{-2}M) was prepared by dissolving potassium periodate in water. Working periodate solutions were

prepared by diluting the stock solution with water before use.

The all reagents used were of reagent grade. Deionized and distilled water was used.

An Atto SJ-1220 peristaltic pump was used with silicone tubings of 1 mm i.d. and 0.4 m length. Absorbance was measured using a flow-through cell of 18-μl (1.5-mm i.d., 10-mm light path) and a Shimadzu UV-140-01 double-beam spectrophotometer with a strip chart recorder. The cell chamber of the spectrophotometer was maintained at 22$\pm$0.1 °C by circulating a thermostated water. The recording chart speed was 1 mm min^{-1}.

Manifold and Procedure

The manifold of the f.i.a. is shown in Fig.1. Except the tubings of the pump, all reactor system was made of PTFE tubing (0.5-mm i.d.) connected with Daiflon joints. Buffered 4.4x10^{-5} M MG and 1.7x10^{-3} M periodate solutions are pumped at the same flow rate of 0.06 ml min^{-1}, and mixed each other at point M (T-shaped joint) to make a reacting stream. It should be noted for the subsequent discussion that the initial concentrations of MG and periodate after mixing are 2.2x10^{-5} M and 8.5x10^{-4} M, respectively, equivalent to one half the concentrations of their pumped solutions. The MG concentration of 2.2x10^{-5} M has absorbance of ca. 2 vs. water. A 20-μl sample is injected into the reacting stream through a septum-type injector (S) by a microsyringe. The reaction is mainly proceeded in a coiled reaction tubing of 2 or 4 m (C_1) submerged in a thermostated water bath (T_1) of 50$\pm$0.1 °C. The absorbance decrease at 615 nm based on the catalyzed colour fading of MG is recorded on a strip chart as a minus peak under the base-line defined by uncatalyzed reaction as shown later in Fig. 7. A plastic absorption plate with absorbance of ca. 1.0 is used as a reference for precise measurements of absorbance decreasing from about 2.0 to 1.0 against water. The amount of manganese is found from the calibration curve of minus peak height vs. manganese amount, which was previously prepared using the manganese standard solutions.
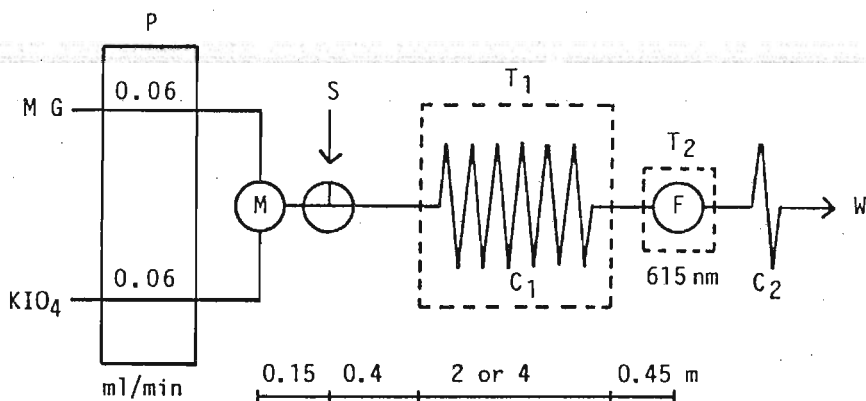
Fig. 1 Manifold of recommended f.i.a. system. (P) peristaltic pump; (M) mixing joint; (S) sample injector; (C_1) reaction tubing (2 or 4 m long, 0.5 mm i.d.); (T_1) thermostated water bath (50 °C); (F) flow-through cell; (T_2) thermostated cell chamber(22°C); (C_2) back-pressure tubing (1 m long, 0.25 mm i.d.); (W) waste.

Results and Discussion

At first, the study was performed using a reaction tubing of 2 m nearly equivalent to the reaction time of 5 min which is described in the preceding paper [6], provided that the flow rate of reacting solution is 0.12 ml min^{-1}. The minus peak is caused not only by the catalyzed reaction but also by temporary dilution of the reacting solution based on injection of a colourless sample solution. The contribution of the catalytic effect is shown by the difference between peak heights of manganese-containing sample and blank sample (water). Then, the sensitivity is defined as the difference between peak heights of 1-ng manganese and water samples.

Effect of pH

Figure 2 shows the effect of pH on the peak heights for injection of 1-ng manganese and water (blank), and on the sensitivity. The peak height of the blank decreased with increasing pH value. The decrease of the peak height is well explained as the pH dependence of the suppressed uncatalyzed reaction in the temporarily diluted reacting solution by sample injection, because the dilution peak of MG should be

constant under the same sample volume. The absorbance level of base-line defined by continuous uncatalyzed reaction also decreased from ca. 2 to 1.8 showing the same pH dependence as that of the blank. A smaller peak height of the blank is desirable to allow recording a larger catalytic peak. On the other hand, the maximum sensitivity, i.e., the maximum difference between the blank and 1-ng manganese, was given around pH 4.1. Therefore, pH 4.4 was selected to be used as a point of compromise between smaller peak height of the blank and higher sensitivity.

Effect of Periodate Concentration

As shown in Fig. 3, the peak height of 1-ng manganese did not depend on the periodate concentration higher than 1.0×10^{-3} M. The peak height of the blank also was nearly constant at least up to 4.3×10^{-3} M periodate. These results were similar to the effect of periodate on the zero-order reaction constant in the preceding study [6]. As clearly understand from the difference between the two curves, the sensitivity was also nearly constant in the periodate concentration higher than 1.0×10^{-3} M. These results means little dilution effect of sample injection on both the catalyzed and uncatalyzed reactions, when concentrated reactant solution of more than 1.0×10^{-3} M is used. The continuous base-line level defined by the uncatalyzed reaction also remained constant throughout all the concentration examined. Therefore, 1.7×10^{-3} M periodate was used in the recommended f.i.a.

Effect of Reaction Temperature

As shown in Fig. 4, the blank peak height slightly depended on the temperature, whereas the peak height of 1-ng manganese had a characterized temperature dependence with a maximum value at 50 °C. These temperature dependences did not follow the Arrhenius' equation. From the difference between the two curves, it is clear that the highest sensitivity also is given at 50 °C. The base-line level remained nearly constant throughout the temperature examined.

Effect of Flow Rate

Figure 5 shows that the peak heights of 1-ng manganese as well as

the sensitivity, i.e., the difference between the two curves, significantly decreased with increasing flow rate, whereas the blank peak height slightly depended on the flow rate at more than 0.05 ml min^{-1}. These results are explained by the facts that a high flow rate gives a short reaction time in the f.i.a. system, consequently poorly progressed catalytic reaction. The base-line absorbance remained nearly constant throughout all the flow rate. On the other hand, the lower flow rate made the broader peak width because of the time-consuming passage of the reaction zone through the flow cell, which reduced the sampling rate of analysis. The flow rate of 0.06 ml min^{-1} was used as a compromise among the sensitivity, the blank peak height and the sampling rate of analysis.

Effect of Length of Reaction Tubing

Figure 6 shows the peak height of 1-ng manganese as well as the sensitivity increased with increasing the length of reaction tubing up to 4 m, whereas the peak height of the blank sample decreased. And a longer reaction tubing resulted in a broader peak. The depression of the peak height at the tube length of more than 4 m can be explained by the peak broadening. For a 2-m reaction tubing, the reaction time was 3.3 min, and the time required for measurement of a whole peak was ca. 6.5 min which was 13 % shorter than that for a 4-m reaction tubing. Therefore, the 2-m tubing was useful for the rapid analyses of many samples. A 4-m reaction tubing was recommended for the more sensitive determination with smaller peak of the blank sample. In this case, the reaction time and the peak width were 6.5 and 7.5 min, respectively.

Sample Volume

The effect of sample volume was also examined using the f.i.a. system with the 2-m reaction tubing. The peak height of the blank and 50-ppb manganese linearly increased up to 20 μl of sample volume, and the increments of peak height were gradually depressed at more than 20 μl. Therefore, the sample volume of 20 μl or less was recommended.
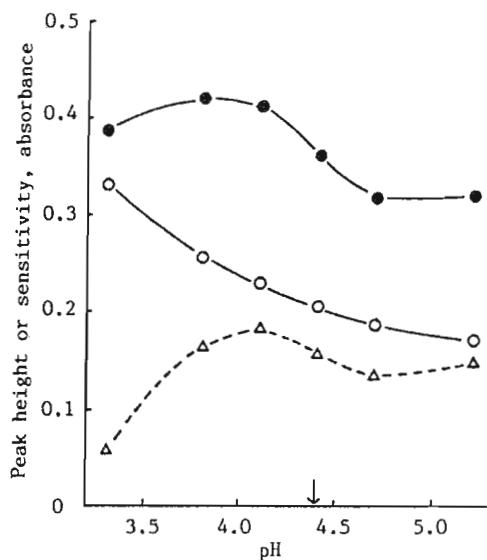
Fig. 2 Effect of pH on peak height and sensitivity. (○) blank; (●) 1-ng Mn(II); (△) sensitivity; 4.4x10^{-5} M MG in 0.2 M acetate buffer; 1.7x10^{-3} M potassium periodate; 2 m of reaction tubing; the other conditions are shown in Fig.1. Base-line : changed from ca. 2 to 1.8 A vs. water; ↓: used.
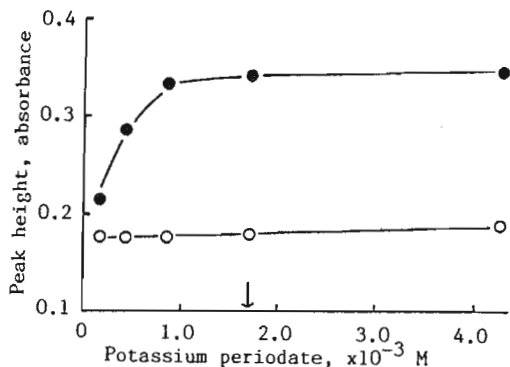

Fig. 3 Effect of potassium periodate concentration on peak height. (○) blank; (●) 1-ng Mn(II); 2 m of reaction tubing; the other conditions are shown in Fig. 1. Base-line : 2±0.02 A vs. water; ↓: used.
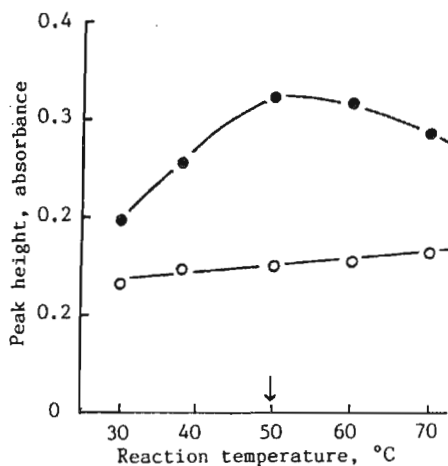

Fig. 4 Effect of reaction temperature on peak height. (○) blank; (●) 1-ng Mn(II); 2 m of reaction tubing; the other conditions are shown in Fig. 1. Base-line : 2±0.02 A vs. water; ↓: used.
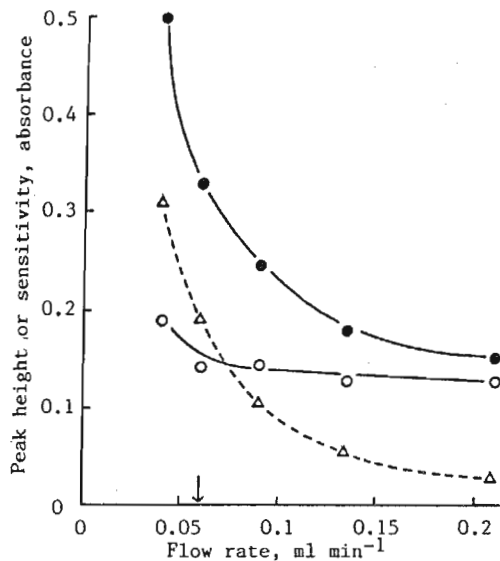

Fig. 5 Effect of flow rate on peak height and sensitivity. (○) blank; (●) 1-ng Mn(II); (△) sensitivity; 2 m of reaction tubing; the other conditions are shown in Fig. 1. Base-line : 2±0.03 A vs. water; ↓: used.
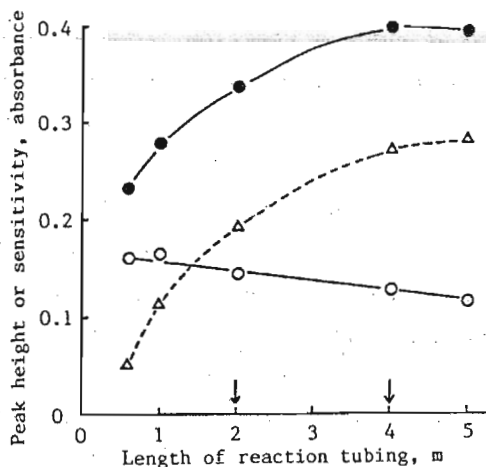
Fig. 6 Effect of length of reaction tubing on peak height and sensitivity. (○) blank; (●) 1-ng Mn(II); (△) sensitivity; see Fig. 1 for details of f.i.a. conditions. Base-line : 2±0.03 A vs. water; ↓ : used.
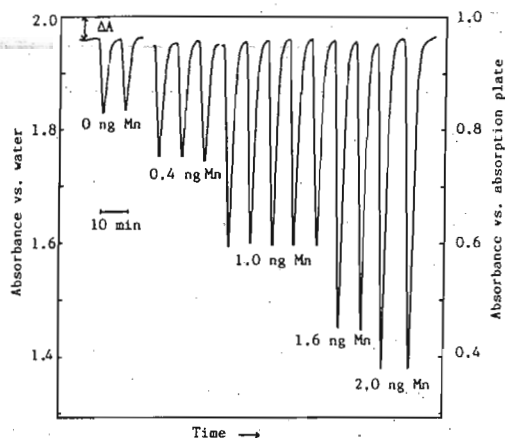
Fig. 7 Typical strip-chart recording obtained with the recommended f.i.a. system shown in Fig. 1. Standard manganese solutions were injected. 4 m of reaction tubing; Absorption plate : 1.0 A vs. water; ΔA : uncatalyzed reaction.

Table 1 Effect of foreign ions on determination of 1-ng manganese(II)

Foreign ion	Added (ng)	Mn found (ng)	Error (%)
Al(III)	200	0.71	−29
	40	1.05	+ 5
Fe(II)	200	0.64	−36
	40	0.84	−16
	10	0.94	− 6
	4	1.00	0
Fe(III)	400	0.77	−23
	100	0.93	− 7
Cu(II)	2000	0.58	−42
	200	0.89	−11
Br⁻	10000	1.26	+26
	2000	1.15	+15
I⁻	100	1.29	+29
	10	1.11	+11

Determination of Manganese

The calibration curve for the use of the 2-m reaction tubing was linear up to 2 ng of manganese, and the detectable absorbance of 0.001 was equivalent to 0.005 ng. The relative standard deviations (RSD) was 1.8 % in five determinations of 1-ng manganese, and the determination limit (DL), equivalent to 2xRSD, was 0.04 ng. Nine samples were analyzed in a hour. On the other hand, the linear range of the calibration curve for the 4-m reaction tubing was the same as that for the 2-m tubing, and the the detectable absorbance of 0.001 was equivalent to 0.004 ng. In this case, the RSD of 1-ng manganese and the DL were 1.3 % and 0.03 ng, respectively, which were ca. 20 % better than those in the 2-m tubing. And the value of DL was 1/50 or 1/100 that in the previous batchwise methods [3-6]. As an example, Fig. 7 shows peaks obtained by injection of 20 µl of blank sample (water) and manganese standard solutions into the f.i.a. system of 4-m reaction tubing. Eight samples were analyzed in one hour.

The interference of the typical foreign ions was investigated with the f.i.a. system of 4-m reaction tubing (Table 1). These interference levels were comparable to those of the tangent method by the batchwise procedure [6].

References
1. T. Yamane and Y. Nozawa, Bunseki Kagaku, 33, 652 (1984).
2. S. Maspoch, M. Blanco and V. Cerda, Analyst(London), 111, 69 (1986).
3. T. Fukasawa and T. Yamane, Bunseki Kagaku, 22, 168 (1973).
4. T. Fukasawa and T. Yamane, Bunseki Kagaku, 24, 120 (1975).
5. T. Fukasawa, T. Yamane and T. Yamazaki, Bunseki Kagaku, 26, 200 (1977).
6. T. Fukasawa, M. Mochizuki, M. Iwatsuki and S. Kawakubo, Mikrochim. Acta, 1986 III, No.1-2, 71 (1987).