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Flow injection determination of hydrogen peroxide using catalytic effect of cobalt(II) ion on a dye formation reaction

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ABSTRACT

A novel flow injection photometric method was developed for the determination of hydrogen peroxide in rainwater. This method is based on a cobalt(II)-catalyzed oxidative coupling of 3-methyl-2-benzothiazolinone hydrazone (MBTH) with *N*-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxyaniline (DAOS) as a modified Trinder's reagent to produce intensely colored dye ($\lambda_{max} = 530$ nm) in the presence of hydrogen peroxide at pH 8.4. In this method, 1,2-dihydroxy-3,5-benzenedisulfonic acid (Tiron) acted as an activator for the cobalt(II)-catalyzed reaction and effectively increased the peak height for hydrogen peroxide. The linear calibration graphs were obtained in the hydrogen peroxide concentration range 5×10^{-8} to 2.2×10^{-6} mol dm^{-3} at a sampling rate of 20 h^{-1}. The relative standard deviations for ten determinations of 2.2×10^{-6} and 2×10^{-7} mol dm^{-3} hydrogen peroxide were 1.1% and 3.7%, respectively. The proposed method was successfully applied to the determination of hydrogen peroxide in rainwater samples and the analytical results agreed fairly well with the results obtained by different two reference methods; peroxidase method and hydrogen peroxide electrode method.

1. Introduction

Hydrogen peroxide has very important role in many fields, such as biochemistry, clinical chemistry, industrial chemistry, atmospheric chemistry and analytical chemistry. In the atmospheric chemistry, oxidizing power of the troposphere has recently attracted attention in relation to the removal of air pollutants, the origin of acid rain [1] and the decline of forests [2,3]. Hydroxyl radical and ozone are important oxidants in the atmosphere and are responsible for the oxidizing power of troposphere, *e.g.*, nitrogen oxide NO_x, which is emitted by fossil fuel combustion, is oxidized to nitric acid mainly by hydroxyl radical $^{\bullet}OH$ and ozone O_3 in the troposphere [1]. Hydrogen peroxide is also an important atmospheric oxidant in the troposphere. Recently, the importance of hydrogen peroxide as a tropospheric oxidant has been revealed [4–7]. In the troposphere, hydrogen peroxide is produced from self-reaction of hydroperoxy radical $^{\bullet}O_2H$, which is generated by the reaction of hydroxyl radical with carbon monoxide. Since hydrogen peroxide is highly soluble in water, it works as a tropospheric oxidant mainly in aqueous phase, such as cloud droplets and raindrops. It has been shown by research on the origin of acid rain that sulfur dioxide is oxidized to sulfuric acid mainly in cloud droplets and raindrops by hydrogen peroxide [4,5]. It shows the importance of aqueous phase hydrogen peroxide as a tropospheric oxidant. The direct effects of rainwater hydrogen peroxide on ocean phytoplankton growth [6] and decline of forests [7] also attract attention in relation to the removal of atmospheric carbon dioxide. In these studies, the concentrations of hydrogen peroxide in rainwater samples show wide variation and sometimes values below the detection limit [7,8]. Therefore, highly sensitive analytical methods for the determination of hydrogen peroxide in rainwater are required.

A number of analytical methods have been reported for the determination of hydrogen peroxide by using photometric [9–12], fluorometric [8,13–16], chemiluminescent [17,18] and electrochemical [19–22] detections. Most of the analytical methods widely used are enzymatic methods using peroxidase [8,12,14–16], which are very popular especially in clinical chemistry [23,24], but enzymatic methods have the disadvantages of the use of expensive and unstable isolated enzymes. For the field-work of environmental analyses, inexpensive and high sensitive non-enzymatic methods using stable reagents are preferable to enzymatic methods [8]. And the employment of flow injection photometric analysis technique in environmental analyses leads to the many advantages, such as simple and automated instrumentation, easy handling, high sensitivity, good reproducibility and high sample throughput [9,11,12].

Metal ion catalyzed oxidation reactions provide sensitive, selective and inexpensive non-enzymatic methods for the determination of hydrogen peroxide [9,11]. Iron(III) catalyzed oxidative coupling reactions of 4-aminoantipyrine (4AA) with *N*,*N*-dimethylaniline (DMA) [9] and 5-dichloro-2-hydroxybenzenesufonic acid (DCPS) [11] have been used for the flow injection photometric determination of hydrogen peroxide.

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Although the combination of metal ion catalyzed reaction and flow injection photometric technique provides the most convenient analytical method for the determination of hydrogen peroxide, such methods reported so far do not give enough sensitivity for environmental analysis [9,11].

Recently, several new compounds have been synthesized as new Modified Trinder's reagents for enzymatic determination of hydrogen peroxide based on peroxidase catalyzed oxidative coupling of 4AA with these compounds [12,24]. On the other hand, these new Modified Trinder's reagents also provide highly sensitive spectrophotometric method for determination of metal ions based on the catalytic effect of metal ions. Among these Modified Trinder's reagents, *N*-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxyaniline (DAOS) is the most useful reagent for the determination of metal ions [25–27]. Highly sensitive flow injection spectrophotometric methods have been reported for the determinations of copper(II) [25,26] and cobalt(II) [27] based on the catalytic effects of these metal ions on the oxidative coupling reaction of DAOS with 3-methyl-2-benzothiazolinone hydrazine (MBTH). In the presence of hydrogen peroxide and cobalt(II) as a catalyst, MBTH reacts with DAOS to form an intensively colored dye (λ_{max} = 530 nm) [27]. In this cobalt(II)-catalyzed reaction, the presence of hydrogen peroxide is essential for the progress of the reaction. Therefore, this cobalt(II)-catalyzed reaction can be used for the determination of trace amount of hydrogen peroxide and provide the highly sensitive and inexpensive non-enzymatic analytical method.

This paper describes a novel highly sensitive spectrophotometric flow injection method for the determination of hydrogen peroxide based on the cobalt(II)-catalyzed oxidative coupling of MBTH with DAOS. The use of 1,2-dihydroxy-3,5-benzenedisulfonic acid (Tiron) as an activator and polyoxyethylene(20) sorbitan monolaurate (Tween 20) as a surfactant improves the sensitivity and reproducibility. The proposed method was successfully applied to the determination of hydrogen peroxide in rainwater.

2. Experimental

2.1. Reagents

The water used to prepare the reagents and buffer solutions was obtained from a Milli-Q water purification system (Millipore). All reagents used were of analytical grade and used without further purification.

Working solutions of hydrogen peroxide were freshly prepared daily by the stepwise dilution of a stock solution, which was standardized by permanganate titration.

A stock solution of 8×10^{-3} mol dm^{-3} MBTH was prepared by dissolving 0.43 g of 3-methyl-2-benzothiazolinone hydrazone hydrochloride (Tokyo Kasei) in 250 cm^3 of water. A stock solution of 5×10^{-3} mol dm^{-3} DAOS was prepared by dissolving 0.17 g of *N*-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3,5-dimethoxyaniline sodium (Dojindo Lab.) in 100 cm^3 of water. A 0.05 mol dm^{-3} AMP buffer was prepared by dissolving 1.3 g of 2-amino-2-methyl-1,3-propanediol (Wako Junyaku) in 250 cm^3 of water. A stock solution of 2.0×10^{-2} mol dm^{-3} cobalt(II) was prepared by dissolving 2.38 g of cabalt chloride hexahydrate (Wako Junyaku) in 1×10^{-3} mol dm^{-3} hydrochloric acid. A stock solution of 1×10^{-3} mol dm^{-3} Tiron and 0.1% Tween 20 were prepared from the commercial reagents. Working solutions of these reagents were prepared from these stock solutions.

2.2. Apparatus

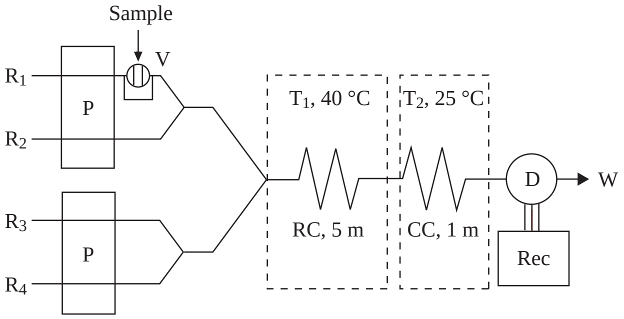

Fig. 1. Flow system for the determination of hydrogen peroxide. R$_1$, water; R$_2$, mixed solution of 2.0×10^{-3} mol dm^{-3} Co(II) and 5.0×10^{-4} mol dm^{-3} Tiron; R$_3$, mixed solution of 0.025 mol dm^{-3} 2-amino-2-methyl-1,3-propanediol (AMP) buffer (pH 9) and 2.5×10^{-3} mol dm^{-3} DAOS; R$_4$, mixed solution of 4.0×10^{-3} mol dm^{-3} MBTH and 0.05% Tween 20; P, pump (1.0 cm^3 min^{-1} for each pump); V, sample injection valve; RC, reaction coil (5 m); CC, cooling coil (1 m); T$_1$ and T$_2$, thermostated baths (40 °C and 25 °C); D, detector (530 nm); Rec, recorder; W, waste.

A schematic diagram of the flow injection system for the determination of hydrogen peroxide is shown in Fig. 1. The system consisted of two double-plunger micro-pumps (Sanuki Kogyo, DMX-2000), a six-way injection valve (Sanuki Kogyo, SVM-6M2), a thermostated bath (Taitec, SJ-10R), a spectrophotometer (Soma Optics, S-3250) equipped with a 10 mm micro flow cell (8 mm^3) and a recorder (Chino, EB 22005). The flow lines were made from Teflon tubing (0.5 mm i.d.).

2.3. Procedure

In the flow system (Fig. 1), water as a carrier (R$_1$), a mixed solution of 2.0×10^{-3} mol dm^{-3} Co(II) and 5.0×10^{-4} mol dm^{-3} Tiron (R$_2$), a solution of 2.5×10^{-3} mol dm^{-3} DAOS containing 0.025 mol dm^{-3} AMP buffer (R$_3$), and a solution of 4.0×10^{-3} mol dm^{-3} MBTH containing 0.05% Tween 20 (R$_4$) were pumped into the flow lines at a flow rate of 1.0 cm^3 min^{-1} for each pump. A 242 mm^3 of sample solution was injected into the carrier stream. The color development proceeded in the reaction coil of 5 m length at 40 °C, and then the colored solution was passed through the cooling coil of 1 m length at 25 °C and the flow-through cell. The absorbance of product was measured at 530 nm with a spectrophotometer and continuously recorded on a recorder.

3. Results and discussion

In the presence of hydrogen peroxide and cobalt(II) as a catalyst, MBTH reacts with DAOS to form an intensively colored red dye [27]. Since the reactions involve the oxidation of cobalt(II) to cobalt(III) by hydrogen peroxide, hydrogen peroxide can be determined by measuring the absorbance of the reaction product. The absorption maximum of the product was found at around 530 nm. The change in the absorbance was continuously monitored at this wavelength in the FI system.

3.1. Optimization of reaction variables

In order to find the optimum conditions for the determination of hydrogen peroxide, the flow injection variables, such as flow rate, reaction temperature, reaction pH and reagent concentrations were studied by injecting a 2.2×10^{-6} mol dm^{-3} hydrogen peroxide solution into the system shown in Fig. 1.

3.1.1. Effect of ligand

Since the present method is based on the cobalt(II)-catalyzed reaction in the presence of hydrogen peroxide, it is expected that the use of a suitable ligand as an activator makes the peak height

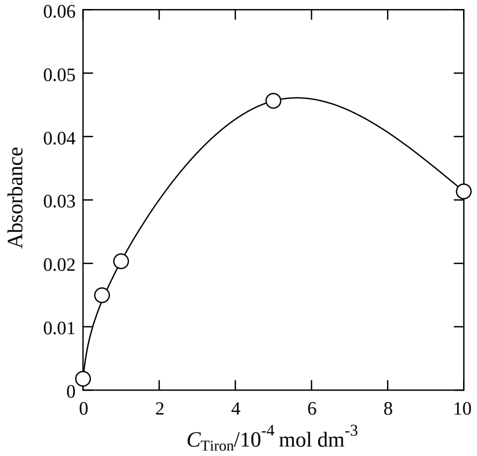

Fig. 2. Effect of Tiron concentration on the peak height by injecting a 2.2×10^{-6} mol dm^{-3} hydrogen peroxide solution. Other conditions as in Fig. 1.

increase and then improves the sensitivity for the determination of hydrogen peroxide. The use of a suitable ligand as an activator effectively accelerates the metal-catalyzed reaction [28] and thus increases the peak height for hydrogen peroxide. Therefore, the effect of some ligands on the peak height for hydrogen peroxide was examined. The ligands examined were Tiron, 2,2′-bipyridine, 1,10-phenanthroline and sodium hydrogencarbonate. Among the ligands tested, Tiron most effectively increased the peak height for hydrogen peroxide and was the most effective activator for the catalysis of cobalt(II). Fig. 2 shows the effect of Tiron concentration on the peak height over the range 5×10^{-5} to 1×10^{-3} mol dm^{-3}. The peak height showed a maximum at a Tiron concentration of 5×10^{-4} mol dm^{-3}. A 5×10^{-4} mol dm^{-3} Tiron concentration was selected for the procedure.

3.1.2. Effect of pH

The effect of pH on the peak height was examined over the pH range 7.5–8.6 by adding AMP solution and hydrochloric acid, and the results are shown in Fig. 3. The pH of the detector's outflow solution which was passed through the cooling coil of 1 m length at 25 °C was measured just after absorbance measurement. The peak height rapidly increased with increasing pH up to 8.4 and decreased at pH above 8.4. Therefore, the reaction was thus carried out at pH 8.4.

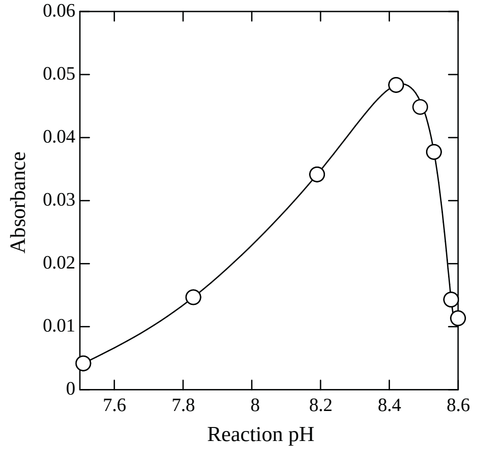

Fig. 3. Effect of the pH on the peak height by injecting a 2.2×10^{-6} mol dm^{-3} hydrogen peroxide solution. Other conditions as in Fig. 1.

3.1.3. Effect of reagent concentrations

The effect of cobalt(II) concentration on the peak heights was examined over the range 1×10^{-4} to 5×10^{-3} mol dm^{-3}. The peak height increased with increasing cobalt(II) concentration up to 2×10^{-3} mol dm^{-3}, and remained constant over the range 2×10^{-3} to 5×10^{-3} mol dm^{-3}. A 2×10^{-3} mol dm^{-3} of cobalt(II) was selected for the sake of sensitivity.

The effect of MBTH concentration was examined in the range 2×10^{-4} to 6×10^{-3} mol dm^{-3}. The peak height increased with increasing MBTH concentration up to 4×10^{-3} mol dm^{-3}, and maximum and almost constant peak height was obtained over the range 4×10^{-3} to 6×10^{-3} mol dm^{-3}. A 4×10^{-3} mol dm^{-3} MBTH concentration was selected. The effect of DAOS concentration was examined in the range 5×10^{-4} to 6×10^{-3} mol dm^{-3}. The peak height increased with increasing DAOS concentration up to 2.5×10^{-3} mol dm^{-3}, and maximum and almost constant peak height was obtained over the range 2.5×10^{-3} to 6×10^{-3} mol dm^{-3}. A 2.5×10^{-3} mol dm^{-3} DAOS concentration was selected.

3.1.4. Effect of temperature

The effect of reaction temperature on the peak height was examined over the range 30–60 °C. The peak height was almost constant in the whole temperature range examined, probably because the introduced hydrogen peroxide (2.2×10^{-6} mol dm^{-3}) as a sample was completely consumed under these reaction conditions. The baseline absorbance slightly increased with increasing temperature. Since, in the absence of hydrogen peroxide, the dissolved oxygen may work as the oxidant for the dye formation reaction, the increase of baseline absorbance indicates the increase of the reaction rate of dye formation reaction with dissolved oxygen. Thus a reaction temperature of 40 °C was selected for the sake of reproducibility.

3.1.5. Effect of flow rate

It is usually expected that the lower flow rate gives higher peaks because of longer reaction time. However, in this procedure the peak height was independent of the flow rate in the range 0.6–1.8 cm^3 min^{-1} for each pump. This result probably indicates the complete consumption of hydrogen peroxide introduce as a sample solution under these conditions, as mentioned above. The complete reaction of hydrogen peroxide is due to the extensive catalytic effect of cobalt(II)–Tiron complexes and contributes the high sensitivity of the present method. The baseline absorbance increased with decreasing flow rate. Since the baseline absorbance can be ascribed to the dye formation reaction with dissolved oxygen, the increase of baseline absorbance is due to the longer reaction time of this reaction at the lower flow rates. Considering sampling frequency and reagents consumption, a flow rate of 1.0 cm^3 min^{-1} for each pump was selected for the procedure.

3.1.6. Effect of surfactants

In the flow system shown in Fig. 1, Tween 20 was used as a surfactant. Without using surfactant, baseline absorbance was continuously increased during the measurements. It indicates the adsorption of a hydrophobic colored reaction product on the inside wall of the detector. In order to solve this problem, and also improve the sensitivity and reproducibility, we have examined the effects of some nonionic surfactants on the performance of the system. The surfactants examined were Tween 20, polyoxyethylene(20) sorbitan monooleate (Tween 80), polyoxyethylene(23) lauryl ether (Brij 35) and polyoxyethylene(10) octylphenyl ether (Triton X-100). Each surfactant was dissolved in the MBTH solution at a concentration of 0.05% (w/v), which is above the critical micelle concentrations (cmc) [29]. The peak height slightly increased in the presence of Tween 20, while the peak height decreased or remained

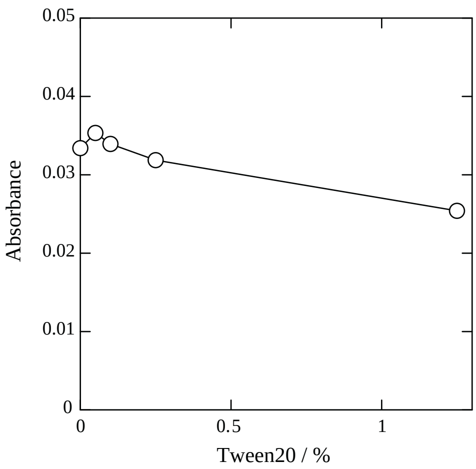

Fig. 4. Effect of Tween 20 concentration on the peak height by injecting a 2.2×10^{-6} mol dm^{-3} hydrogen peroxide solution. Other conditions as in Fig. 1.

unchanged in the presence of other surfactants. Therefore, Tween 20 was used for the procedure, considering a stable baseline. Fig. 4 shows the effect of Tween 20 concentration on the peak height. The peak height increased at a concentration of 0.05% (w/v) and then gradually decreased with increasing the concentration of Tween 20 at concentrations above 0.05% (w/v). The increase in the peak heights at a Tween 20 concentration of 0.05% can be attributed to solubilization and stabilization of the hydrophobic dye product by Tween 20 micelles. At the higher Tween 20 concentrations, surfactant micelles incorporate hydrophobic reagent MBTH and isolate it from the bulk aqueous solution to inhibit the dye formation reaction. Thus a 0.05% (w/v) Tween 20 concentration was selected for the procedure.

3.2. Calibration graphs for hydrogen peroxide

The calibration graphs for hydrogen peroxide were prepared by the recommended procedure using the flow system shown in Fig. 1. The linear calibration graphs were obtained in the concentration range 5×10^{-8} to 2.2×10^{-6} mol dm^{-3}. The least squares regression equation was obtained as follows: $A = 2.3 \times 10^4 C$ with a correlation coefficient of 0.998, where A is the absorbance and C is the hydrogen peroxide concentration in mol dm^{-3}. Detection limit (signal to noise ratio S/N = 3) of the method was 1.3×10^{-8} mol dm^{-3}. It shows that the present method has extensively lower detection limit than other nonenzymatic methods, such as iron(III) catalyzed flow injection photometric method, which has the detection limit of 5×10^{-7} mol dm^{-3} (S/N = 2) [9]. The relative standard deviations for the ten determinations of 2.2×10^{-6} and 2×10^{-7} mol dm^{-3} hydrogen peroxide were 1.1% and 3.7%, respectively. The sampling frequency was 20 samples h^{-1}.

3.3. Effect of foreign ions

The effect of foreign ions on the determination of 1.0×10^{-6} mol dm^{-3} hydrogen peroxide was examined, considering the chemical species contained in rainwater [30]. The results are summarized in Table 1. A relative error of ±10% was considered to be tolerable. Most ions examined did not interfere in concentration up to 1×10^{-5} mol dm^{-3}. Fe(II) and Fe(III) at a concentration of 1×10^{-6} mol dm^{-3} gave negative errors, probably because of the decomposition of hydrogen peroxide by Fe(II) and Fe(III) catalyzed reactions known as Fenton like reactions [6]; that would not be the interference on the determination method but the natural chemical reaction in rainwater. At a concentration of 1×10^{-7} mol dm^{-3}, Fe(II) and Fe(III) did not interfere. Therefore, hydrogen peroxide can be determined by the dilution of sample solutions to avoid interference from these ions.

Table 1
Effect of foreign ions on the determination of 1×10^{-6} mol dm^{-3} hydrogen peroxide. A relative error of ±10% was considered to be tolerable.

Tolerance limit (mol dm^{-3})	Ions added
1×10^{-3}	Na^+, K^+, Cl^-, NO_3^-
1×10^{-4}	Mg^{2+}, Al^{3+}, Mn^{2+}, SO_4^{2-}
1×10^{-5}	Ca^{2+}, NH_4^+, PO_4^{3-}
1×10^{-7}	Fe^{2+}, Fe^{3+}

Table 2
The results of determination of hydrogen peroxide in rainwater samples by proposed method, peroxidase method and hydrogen peroxide electrode method. The samples were diluted 25 fold with water just before measurements.

Sample	$C_{H_2O_2}$ ($\times 10^{-5}$ mol dm^{-3})		
	Proposed method	Peroxidase method	Electrode method
Rainwater 1	2.51 (0.05)[a]	2.39 (0.07)	2.48 (0.01)
Rainwater 2	1.79 (0.03)	1.76 (0.04)	1.80 (0.03)
Rainwater 3	1.95 (0.03)	1.94 (0.05)	1.95 (0.05)
Rainwater 4	2.36 (0.03)	2.32 (0.04)	1.94 (0.03)
Rainwater 5	1.51 (0.03)	1.53 (0.02)	1.54 (0.04)
Rainwater 6	1.15 (0.03)	1.25 (0.01)	1.21 (0.04)
Rainwater 7	2.24 (0.07)	2.43 (0.01)	2.12 (0.02)

[a] The values in the parentheses indicate standard deviations for three determinations.

3.4. Application

The proposed method was applied to the determination of hydrogen peroxide in rainwater samples collected at Shizuoka University, Japan. In order to validate the present method, the analytical results were compared with those obtained by peroxidase method [24] and hydrogen peroxide electrode method. The analytical results were summarized in Table 2. In these measurements, the rainwater samples were filtered through a 0.45 μm membrane filter (MF-Millipore) and diluted 25 fold with water before measurements. For the peroxidase method of photometric determination of hydrogen peroxide, the reaction system of 4-aminoatipyrine with *N*-ethyl-*N*-(2-hydroxy-3-sulfopropyl)-3-methylaniline sodium salt (TOOS, Dojindo Lab.) was used as hydrogen donor for peroxidase catalyzed reaction under the reported conditions [24]. A MOPSO buffer was prepared by dissolving 2-hydroxy-3-morpholinopropanesulfonic acid (MOPSO, Dojindo Lab.) in water. The peroxidase solution (20 units cm^{-3}) was prepared by dissolving horseradish peroxidase in MOPSO buffer (pH 7.0). For the peroxidase method, another flow injection system similar to the system shown in Fig. 1 was constructed, and in this system water as carrier (R_1), 1×10^{-3} mol dm^{-3} TOOS solution (R_2), peroxidase solution (R_3) and 4-aminoantipyrine (R_4) were pumped at the flow rate of 1.0 cm^3 min^{-1}, and the absorbance of the colored product was monitored at 555 nm. The linear calibration graphs were obtained using this peroxidase method in the concentration range 2.0×10^{-7} to 1.0×10^{-6} mol dm^{-3}; $A = 3.2 \times 10^3 C$ with a correlation coefficient of 0.997, where A is the absorbance and C is the concentration of hydrogen peroxide in mol dm^{-3}. The slope of the calibration graph for this peroxidase method is much smaller than that for the proposed method. For the hydrogen peroxide electrode method, the commercially available hydrogen peroxide electrode (Able, Japan) was used. Using the electrode, the amperometric determinations of hydrogen peroxide were carried out by measuring the current by the following reaction on the electrode.

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$

The slightly downward curved calibration graphs were obtained for the electrode method in the concentration range 5.0×10^{-7} to 2.0×10^{-6} mol dm^{-3}. The measurements by these three different methods were carried out almost simultaneously. As shown in Table 2, the analytical results obtained by present method agreed fairly well with those obtained by other two methods. The analytical results by the proposed methods were compared with those by the other two methods using a paired two-sided Student's *t*-test. For the comparison between proposed method and peroxidase method, the *t* empirical value of 0.41 is less than the *t* critical value of 2.45 at 6 degrees of freedom and a 95% confidence level. It indicates that the two methods do not give significantly different values. For the comparison between the present method and the electrode method, the *t* empirical value of 1.07 also shows that there is no significant difference between the two methods.

4. Conclusions

A sensitive and inexpensive flow injection method for the determination of hydrogen peroxide was developed based on the reaction system of MBTH and DAOS in the presence of cobalt(II) as a catalyst in place of peroxidase. The sensitivity was enhanced by adding Tiron as an effective activator, which extensively increased the peak height for hydrogen peroxide. The proposed method was successfully applied to the analysis of rainwater samples.

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