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Fluorescence Detection-FIA for ppb Levels of Bromate with Trifluoperazine

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Abstract

The fluorescence of tifluoperazine at EX:300 nm and EM:485 nm was changed into non-fluorescent substance in the presence of bromate under acidic conditions, and the fluorescence detection-FIA of trace amounts of the bromate was developed using this phenomenon. In the concentration range of 1-15 μg L^{-1}, the bromate analysis was able to obtain a good straight line and eighteen samples per hour were measured. For 7.5 μg L^{-1} of bromate, the relative standard deviation(RSD) was 2.03 %(n=5) and the detection limit (3σ) was 1.47 μg L^{-1}.

Keywords: FIA, bromate ion, trifluoperazine, ppb levels determination

1. Introduction

As for the bromate ion (BrO_3^-), the bromine ion contained in water reacts with ozone during ozonization (advanced clean water processing) in order to decompose trihalomethane. It is an odor material that exists in raw water. Also, it is the causative agent that causes hepatic toxicity and renal damage when the drinking water is manufactured, and the bromate ion is generated. Moreover, the bromate ion is classified into group 2B(group in which the possible carcinogenicity for humans occurs) according to the International Agency of Research on Cancer of World Health Organization (WHO) (IARC and International Agency for Research on Cancer) [1)]. In Japan, it was added to the water standard law revised in 2003. Furthermore, a standard value {10 ppb(μg L^{-1})} was determined for drinking water. Therefore, since safe water that can be ingested is requested to be easily offered in order to preserve our health, it is necessary to manage it based on a highly sensitive analysis method of the bromate ion in the drinking water. For example, HPLC such as ion chromatography post column absorption spectrophotometry has now been adopted as the test methodology of the bromate ion in the quality test of the water supply in Japan [2)]. However, expensive equipment, the corrosion control of the device, the stability of the baseline etc. have become important problems. Moreover, the test time has become a problem as a nine minute measurement time per one sample using the ion-exchange column for the absorbance detection-FIA of the bromate ion is required [3)]. Therefore, a low-cost and simple method should be developed, and the analytical method with a commercial instrument such as FIA is requested.

In this study, FIA for the trace amounts of bromate ion at the standard water quality level was developed using the change to non-fluorescenct substance of tifluoperazine at EX:300 nm and EM:485 nm.

2. Experimental

2.1 Reagents

Trifluoperazine dihydrochloride was obtained from the Sigma-Aldrich Co. (St. Louis, USA). Potassium bromate and hydrochloric acid were provided by Kanto Chemicals (Tokyo, Japan). All other reagents were of analytical grade.

2.2 Apparatus

The fluorescence spectra were measured using an F-400 fluorescence spectrophotometer (Hitachi Co.). Also, FIA fluorescence detection was done using an FP-920 instrument (JASCO Co.). Two TCI-NOX1000ω (TOKYO KASEI KOGYO Co.) components were used as the double plunger-type pump.

The injector was used as the 100 μl loop injector built into the pump. A PFA (Tetra fluoroethylene-perfluoroalkylvinyl ether copolymer) tube (external diameter: 2.0 mm; internal diameter: 1.0 mm; GL Sciences Co.) was used as the flow tubing and mixing coil.

2.3 Procedure

The determination of bromate ion (bromate)

The proposed flow system is shown in Fig.1. The length of the reaction coil (inside diameter =1mm) was 230 cm. Flow passage A injected the sample solution (100 μL) into a flowing 5.7×10^{-5} M trifluoperazine solution using the injector (I). Flow passage B adds the 2.5 M hydrochloric acid solution, and the flow velocity in each flow passage was set at 1.0 mL min^{-1}. Moreover, aluminum foil covered all the flow passages, because the trifluoperazine was extremely influenced by light. Hence, it was covered during the experiment. Furthermore, after flow passage A and flow passage B were joined, two minutes to the detector was assumed and the measurement wavelength was set to EX: 300 nm and EM 485 nm for the measurement time. The difference in the fluorescence intensity of the empty examination reaction is indicated by ΔF [= F sample－F blank]. Here, the difference between the fluorescence intensity of the empty examination reaction and the sample reaction after two minutes is indicated by F blank and F sample, respectively. The determination of the bromate ion is measured using the calibration curve which was obtained from the previously developed flow signal.

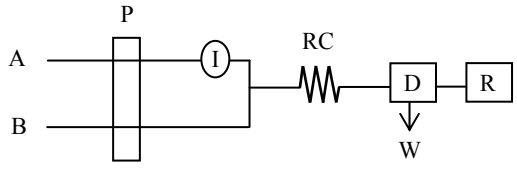

Fig.1 FIA system for determination of bromate with trifluoperazine soln.

A: 5.7×10^{-5} M Trifluoperazine soln . , 1.0 mL min^{-1};
B: 2.5 M HCl soln. , 1.0 mL min^{-1}; P: Pump; I: Injector (100 μL);
RC: Reaction coil (235 cm); R: Recorder; W: Waste;
D: Detector (EX: 300 nm、EM :485 nm)

3. Results and discussion

3.1 The fluorescence spectra in trifluoperazine

The fluorescence spectra of the trifluoperazine are shown in Fig.2. The phenomenon that changes into non-fluorescent substance can be confirmed by the addition of bromate ion. As a result, the non-fluorescent substance increased as the concentration of the bromate ion increased. Hanson et al. [4] reported that the phenothiazine was dimerized while being oxidized. Here, phenothiazine is the basic frame of trifluoperazine molecular structure. A similar reaction mechanism is also expected in the case oxidizing the trifluoperazine with the bromate ion. The reaction mechanism is shown in Fig.3. It is thought that the non-fluorescent substance occurred because the structure of the trifluoperazine changed. The FIA flow chart for the fluorescence intensity of tifluoperazine at EX: 300 nm and EM: 485 nm using this phenomenon is shown in Fig.4. The various conditions with this flow signal were optimized.

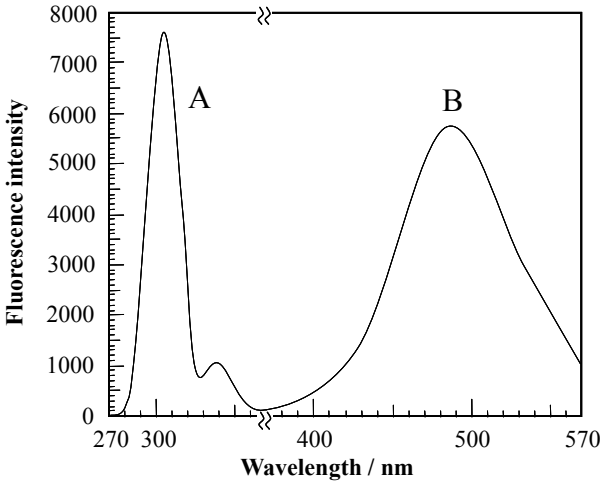

Fig.2 Fluorescence spectra of trifluoperazine （F-400 fluorescence spectrophotometer, PMT voltage: 950 V）
$[Trifluoperazine]_I=7.35\times10^{-6}$ M, $[HCl]_I$=1.0 M,
A: Excitation spectra at emission wavelength（485 nm）
B: Emission spectra at excitation wavelength（300 nm）

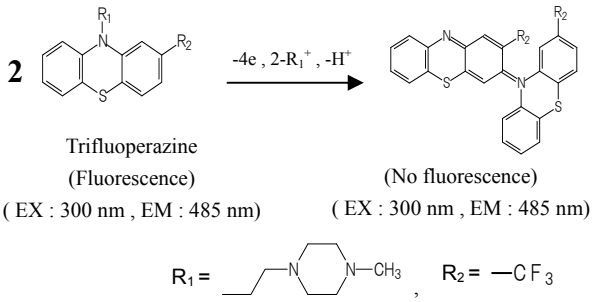

Fig.3 Estimated reaction scheme for fluorescence degradation of trifluoperazine with bromate

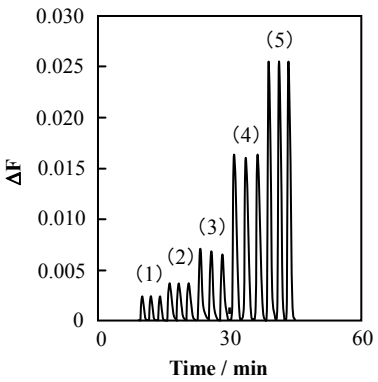

Fig.4 Flow signals of the FIA（FP-920 instrument, gain: 100）
$[Trifluoperazine]_T$ =5.7×10^{-5} M, $[HCl]_T$ =2.5 M
Signal: $[Bromate]_T$ =（1）1.0；（2）3.0；（3）5.0；（4）7.5，（5）15.0 ;μgL^{-1}

3.2 Effect of various factors

3.2.1 Flow rate and reaction coil length

In this study, the reaction time was examined in the batch system under following conditions: $[Trifluoperazine]_T$= 7.35×10^{-6} M, $[HCl]_T$=1.0 M, $[Bromate]_T$=0, 7.5 μg L^{-1} and room temperature. As a result, the different of fluorescence intensity (ΔF) became to be constant in two minutes or later. Therefore, it is thought that this reaction reached to the equilibrium. Flow rate and reaction coil length in FIA were examined based on this result as follows. When changing the length of the reaction coil (inside diameter =1mm) in the range of 230-420 cm, and changing the flow velocity within the range of 0.8-1.7 ml/min, a bubble easily occurs and it hinders the measurement when the flow velocity is slow and when the length of reaction coil is short. Also, a sufficient reaction time is not obtained when the flow velocity is very fast, and as a result, the difference in fluorescence intensity becomes too small. When the length of the reaction coil is long and the flow velocity is fast, diffusion occurs and as a result, the difference in fluorescence intensity became very small so that the dilution and diffusion may happen though the reaction time was sufficient when the flow velocity is slow. Since the difference in the fluorescence intensity was the highest, the length of reaction coil was set at 230 cm and the flow velocity was also set at 1.0 ml/min.

3.2.2 Trifluoperazine concentration

The total concentration of the trifluoperazine was changed within the range of 2.0×10^{-5}-6.5×10^{-5} M. When the trifluoperazine concentration was higher than 5.70×10^{-5} M, the difference in the fluorescence intensity was lower. Thus, it is thought that the reaction rate at the 5.70×10^{-5} M trifluoperazine concentration is maximized. As a result, the total concentration of the trifluoperazine was set at 5.70×10^{-5} M.

3.2.3 Hydrochloric acid concentration

For the hydrochloric acid concentration, it is thought that the difference in the fluorescence intensity is small below 2.5 M because it was not a sufficient acidic condition so that the reaction may sensitively occur by changing the total concentration of the hydrochloric acid within the range of 2.0-3.0M. The difference in the fluorescence intensity became small for the hydrochloric acid above 2.5 M, because it became difficult for the reaction to occur in which the proton in the reaction formula of Fig.3 proceeded, and the dimerization had been hindered. Hence, the total concentration of the hydrochloric acid was set at 2.5 M, because the difference in the fluorescence intensity was the highest.

3.3 Calibration curve

The calibration curve of the bromate ion is shown in Fig.5. As a result, a good straight line was obtained in the concentration range of 1-15 μgL^{-1}. The relation between the concentration of the bromate ion and the difference in the fluorescence intensity (Δ F) that was obtained from this calibration curve was y=0.0018x (y: Δ F and x: concentration of the bromate ion[μ g L^{-1}]). Also, the correlation coefficient was 0.9737. The RSD was 2.03 %(n=5) at the bromate concentration of 7.5 μgL^{-1}, and the detection limit (3σ) was 1.47 μgL^{-1}.

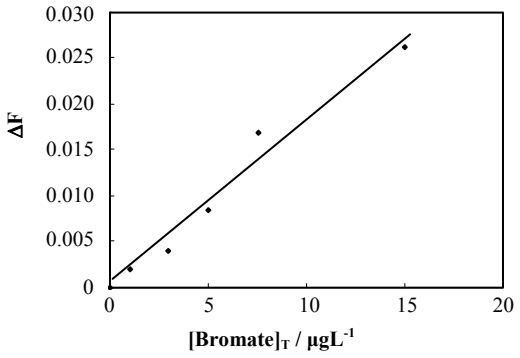

Fig.5 Calibration curve（FP-920 instrument, gain: 100）
$[Trifluoperazine]_T$=5.7×10^{-5} M, $[HCl]_T$=2.5 M

Table 2 Comparison with other methods

Methods	Indicator (Maximum wavelength)	Determination range ($\mu g\ L^{-1}$)	Detection limit (3σ) ($\mu g\ L^{-1}$)	Reference
Proposed method (Fluorescence photometry-FIA)	trifluoperazine (EX:300 nm, EM:485 nm)	1－15	1.47	This paper
Fluorescence photometry-FIA	carbostyril-124 (EX:339 nm, EM:421 nm)	4－200	0.9	7
Spectrophotometry-FIA	vanadium sulfate Nitro-PAPS (592 nm)	0－50	0.2	3
Fluorescence photometry using 1cm cell (batch method)	trifluoperazine (EX:300 nm, EM:485 nm)	0.8－15	0.58	8
Spectrophotometry using 10cm cell	trifluoperazine (504 nm)	1－700	0.67	5
Spectrophotometry using 1cm cell	triiodide (352 nm)	50－150	10	6
Post-column ion chromatography	tribromide (268 nm)	0.5－50	0.19	2

Nitro-PAPS: 2-(5-Nitro-2-pyridylazo)-5-[N-n-propyl-N-(3-sulfopropyl)amino]-phenol,disodium salt,dihydrate

3.4 Interference by foreign substances

The interference by foreign substances is shown in Table 1. As for the allowable limit, the change in time was within ±5 % based on the difference in the fluorescence intensity with the blank when no foreign substances were added. It was compared according to the molar ratio with the bromate ion. Although Fe^{2+}, Fe^{3+} and Mn^{2+} could be present up to 1-fold without affecting the results of the test, they could be masked up to 10-fold with the addition of EDTA as the masking reagent.

Table 1 Interference by foreign substances

Foreign substance [Foreign substance]/[Bromate]	Tolerance limit (±5%)
Al^{3+}, Ca^{2+}, K^{+}, Na^{+}, Ni^{2+} Mg^{2+}, Cl^{-}, NO_3^{-}, SO_4^{2-}	＞×1000
Zn^{2+}, IO_3^{-}, IO_4^{-}, EDTA $^{*}Fe^{2+}$, $^{*}Fe^{3+}$, $^{*}Mn^{2+}$	×10
Fe^{2+}, Fe^{3+}, Mn^{2+}	×1

$^{*}6.0\times10^{-7}$ M EDTA was added as a masking reagent.

$[Bromate]_T$: 6.0×10^{-8} M (7.5 μl L^{-1})

3.5 Practical application

3.5.1 Determination of bromate in mineral water and tap water

The determination of the bromate ion contained in commercially available mineral water was measured by the standard addition method as an application of this method. The correlation coefficient of the calibration curve was 0.9987. Moreover, it has been understood that the bromate ion is hardly contained from the calibration curve in the mineral water. Moreover, a 7.7 μgL^{-1} determination value was obtained as a satisfactory result, and the recovery percentage was 102 % for 7.5 μgL^{-1} of added potassium bromate to the mineral water. Furthermore, a 14.5 μgL^{-1} determination value was obtained, and the recovery percentage was 97 % for 15.0 μgL^{-1} added potassium bromate to the mineral water. Moreover, the determination of bromate ion contained in tap water (Hitachi city, Japan) was measured by the standard addition method. The correlation coefficient of the calibration curve was 0.9992. Moreover, it has been understood that the bromate ion is hardly contained from the calibration curve for tap water. Also, a 7.2 μgL^{-1} determination value was obtained, and the recovery

percentage was 96 % for 7.5 μgL^{-1} of potassium bromate added to the tap water. A 15.0 μgL^{-1} determination value was obtained, and the recovery percentage was 100 % for 15.0 μgL^{-1} of potassium bromate added to the tap water.

3.6 Comparison with other analysis methods

A comparison between this method and other methods is shown in Table 2. Since the easiness and the preprocessing are also unnecessary, the making of solution is extremely low-cost and simple though it is inferior to the other methods regarding the numerical value of the detection limit. Moreover, the proposed method was a rapid and simple analysis method because the number of samples (FIA method[7]:10 samples per hour, on the other hand, the proposed method:18 samples per hour) and temperature conditions (FIA method[7]:60 ℃, on the other hand, the proposed method: room temperature) are cost efficient compared to the fluorescence photometry-FIA.[7].

4. Conclusion

An analysis of the bromate ion which was developed in the present study, is more low-cost and simple than the ion chromatography-post column absorbance method. Thus, this FIA can be widely used for checking water quality. Moreover, the proposed method is expected to be more sensitive by combination of the micelle fluorescent sensitization method or the laser fluorescence detection method.

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