

Determination of inorganic anions via postcolumn reaction with iodide in ion chromatography

Yuko Kitamaki^a, Ji-Ye Jin^b, Toyohide Takeuchi^{a,*}

^a Department of Chemistry, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

^b Instrumental Analysis Center, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan

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Dedicated to Professor Terumichi Nakagawa on the occasion of his retirement and 63rd birthday.

Abstract

Inorganic anions were determined as triiodide by postcolumn reaction with iodide under an acidic condition with help of α -cyclodextrin in ion chromatography. Analytes reacting with iodide to produce iodine could be determined by the present method. The analytes were indirectly detected at 287 or 355 nm. The presence of α -cyclodextrin caused an increase in the concentration of triiodide, leading to improvement of the sensitivity. The present system achieved good selectivity to iodate, bromate and nitrite as well as good repeatability under the optimum conditions. The determination of nitrite in river water was possible.

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1. Introduction

It is necessary to determine various trace inorganic ions for the estimation of the environmental water pollution degree. For example, the determination of iodide in seawater is helpful for understanding the marine environment [1]. And nitrite in environmental water is the index for understanding the water pollution because nitrite in the water is produced by oxidation of ammo-

nium ion, which is included in factory drainage, manure, or other things.

It is known that only several chemical species such as iodate, nitrite, bromate and hypochlorite react with iodide to produce iodine (I_2) [2–5], and the presence of excessive iodide produces triiodide (I_3^-), which strongly absorbs UV light at 287 and 355 nm [3]. At such relatively high UV wavelengths, most of inorganic anions are transparent. This means that if triiodide is detected at the above wavelengths, analytes producing iodine by the postcolumn reaction with iodide can be selectively detected.

Nowack and Gunten [4] reported an osmate-catalyzed postcolumn reaction of chlorate with

* Correspondence author. Tel./fax: +81-58-293-2806

E-mail address: takeuchi@apchem.gifu-u.ac.jp (T. Takeuchi).

iodide and UV-detection of triiodide for the determination of chlorate. They achieved a detection limit of 0.4 $\mu\text{g/l}$ chlorate. Miura and Hamada [5] also measured triiodide formed by a reaction of nitrite with iodide for the determination of nitrite in lake water and they achieved a detection limit of 4.6 $\mu\text{g/l}$ nitrite.

As in the case of triiodide, tribromide (Br_3^-) is also produced by postcolumn reaction for the determination of oxyhalides. Inoue et al. [6] proposed a sensitive and selective determination method of bromate with postcolumn conversion into tribromide. Weinberg and Yamada [7] also proposed postcolumn conversion of the eluting oxyhalides such as bromate and iodate into the tribromide ion under acidic conditions.

It is expected from the previous work that the addition of α -cyclodextrin (α -CD) increases the absorbance of the reactant owing to the equilibrium shift [3].

This paper describes the determination of inorganic anions via postcolumn reaction with iodide under an acidic condition with the help of CDs in ion chromatography.

2. Experimental

2.1. Apparatus

The eluent and the postcolumn mixing reagent solution were supplied by using PU-980 intelligent HPLC pumps (Jasco, Tokyo, Japan) at 1.0 ml/min, respectively. These solutions were degassed in vacuo under ultrasonic vibration before use. Samples were injected with a model 7000 valve injector with a 28- μl loop (Rheodyne; Cotati, CA, USA). TSKgel IC-Anion PW_{XL} (35 \times 4.6mm i.d.; Tosoh, Tokyo, Japan) was operated in the anion-exchange mode. The eluent and the mixing reagent solutions were mixed at a PEEK T-joint (GL Science, Tokyo, Japan), followed by passing into a PTFE reaction tube (0.25mm i.d.). A Yamato thermo-Mate BF-200 water-bath (Tokyo, Japan) was used to control the reaction tube temperature. The effluent was monitored by a UV-970 UV/VIS detector (Jasco). The detector was operated at 287 or 355 nm. Chromatopac C-R4AX (Shimadzu,

Kyoto, Japan) was used as a data processor. Absorption spectra were measured by using a UV-210 double beam spectrometer (Shimadzu) in the stopped flow mode.

2.2. Reagents and materials

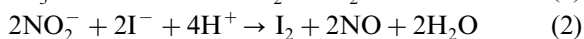
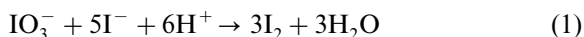
All reagents were obtained from Nacalai Tesque (Kyoto, Japan). Purified water was prepared in the laboratory by using a GS-590 water distillation system (ADVANTEC, Tokyo, Japan). All of the reagents were used as received.

Water samples were filtered with a 0.45- μm membrane filter, and hydrophobic components were then removed by passing into a laboratory-made pre-column (10 \times 0.25 mm i.d.) packed with Develosil C30 (Nomura Chemical, Seto, Japan).

3. Results and discussion

3.1. Detection principle

It is known that several chemical species react with iodide to produce iodine [2]. For example, iodate and nitrite react with iodide to produce iodine under acidic conditions as shown by the following reactions:



The presence of excessive iodide produces triiodide, as shown by the following equilibrium:



Since triiodide strongly absorbs ultraviolet to visible light, iodate and nitrite can be indirectly, selectively and sensitively detected by monitoring triiodide at the wavelengths where most inorganic anions are transparent.

CDs are cyclic oligosaccharides produced from D-glucose by α -1,4 unit. CDs having six, seven, and eight D-glucopyranose units are called α -, β -, and γ -CD with internal diameters of 4.7–5.3, 6.0–6.5, and 7.5–8.3 Å, respectively [8]. Due to the specific molecular cavity structure, CDs can include various guest substances with hydrophobic to ionic properties in aqueous solution [9–11].

CDs form inclusion complexes in aqueous solution with a number of substances, where complexation has been attributed to hydrophobic interaction, hydrogen bonding and/or non-specific van der Waals forces [9]. In case CD is added into the above solution, the inclusion complexes between CD and the existing chemical species are formed, among which the inclusion complex between α -CD and triiodide is the most stable, as shown by the following equation:

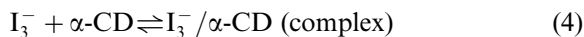


Fig. 1 shows the absorption spectra of aqueous solutions containing iodine and iodide in the presence or absence of CD. Each CD was dissolved in aqueous solution containing 0.001% iodine and 0.01% sodium iodide. It is seen that the addition of α -CD increases the absorbance of the solution to a further degree than β - and γ -CD. The gain in the absorbance was negligibly small for γ -CD. This is because the inclusion complex between triiodide and α -CD is more stable than other complexes, and more triiodide ions are formed to maintain the equilibrium shown by Eq. (3) in the case of the addition of α -CD. It is presumed in the present work that the increase in the absorption is not caused by the increase in the molar extinction coefficient but by the increase in total concentration of triiodide.

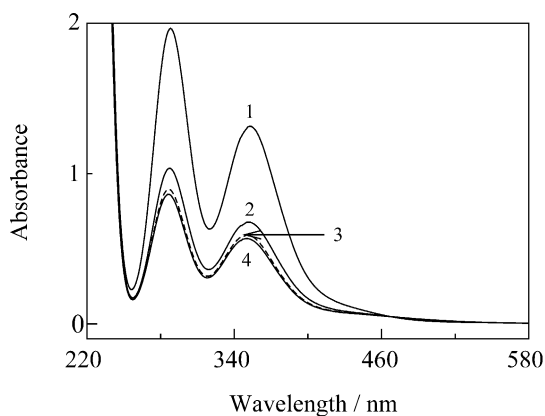


Fig. 1. Absorption spectra of solutions containing iodine and iodide in the presence or absence of CD. Solutions: aqueous solutions containing 0.001% iodine and 0.01% sodium iodide with 0.1 mM α -CD (1), 0.1 mM β -CD (2), 0.1 mM γ -CD (3), or without CD (4).

Actually, the equilibrium equations involved in the mixture of iodide, iodine, triiodide and α -CD are much more complex than the above discussion [12,13]. Iodide and iodine can also form inclusion complexes with α -CD as in the case of triiodide. More experiments will be required to discuss the results quantitatively.

The maximum absorbance was observed at 287 and 355 nm. It is expected that higher sensitivity can be achieved for the detection at 287 nm, whereas the selectivity can be improved for the detection at 355 nm.

3.2. Effect of the eluent and its concentration in the mobile phase

The effect of the eluent on the retention of iodate and nitrite was examined. When the eluent concentration was kept constant at 1 mM, the nitrite peak was broadened due to the increase in the retention time when sodium chloride and sodium dihydrogen phosphate were used as the eluent. It was observed that sodium sulfate has larger elution strength than the other eluents.

The sodium sulfate concentration on the retention of analytes was then examined. It was found that the peak height increased with increasing concentration of sodium sulfate, but two peaks could not be separated completely when the concentration of sodium sulfate was higher than 5 mM. Therefore, 1 mM sodium sulfate was selected as the eluent in the following experiments.

3.3. Effect of sulfuric acid concentration

The signal intensity was affected by the acid concentration as can be expected from Eqs. (1) and (2). When the post-column reaction was carried out at room temperature (ca. 20 °C) through a 10 m \times 0.25 mm i.d. reaction tube by using a post-column reagent solution containing 3 mM α -CD, 10 mM sodium iodide and sulfuric acid, the signal intensity for iodide increased with increasing sulfuric acid concentration up to 4 mM in the post-column reagent solution and was nearly constant at higher sulfuric acid concentration. On the contrary, the signal for nitrite increased

linearly with increasing sulfuric acid concentration up to 8 mM in the post-column reagent solution.

3.4. Effect of cyclodextrin in the mixing reagent solution

The effect of CDs in the postcolumn mixing reagent solution on the signal intensity was studied. As expected from the results in Fig. 1, the addition of CD increases the concentration of triiodide. The signal intensities observed in the presence or in the absence of CD are compared in Table 1. It is observed that α -CD achieved the largest signal intensity. It can be concluded again that α -CD has the most suitable cavity size for forming a stable complex with triiodide.

The larger the concentration of α -CD, the better sensitivity was observed for nitrite as demonstrated in Fig. 2. On the contrary, in the case of iodate the effect of α -CD concentration is very small and little increase is observed when the concentration of α -CD is higher than 3 mM. Considering these results, the concentration of α -CD in the mixing solution was set at 3 mM in the following experiments.

3.5. Effect of the length and temperature of reaction tube

Fig. 3 shows the effect of the reaction tube length on the detection signal. It is found that the sensitivity of iodate does not change very much.

Table 1

Effect of CD in the mixing reagent solution on the signal intensity

Analyte	Peak height/abs			
	Without CD	α -CD	β -CD	γ -CD
Iodate	0.236	0.388	0.301	0.224
Nitrite	0.0007	0.0046	0.0026	0.0015

Column: TSKgel IC-Anion PW_{XL} (35 × 4.6 mm i.d.; Tosoh, Tokyo, Japan). Eluent: 1 mM sodium sulfate. Mixing reagent solution: aqueous solution containing 1 mM α -CD, 10 mM sodium iodide and 1 mM sulfuric acid. Flow rate: 1.0 ml/min each. Sample: 0.1 mM each. Wavelength of UV detection: 287 nm. Reaction tube: 10 m × 0.25 mm i.d. Reaction temperature: room temperature (ca. 20 °C).

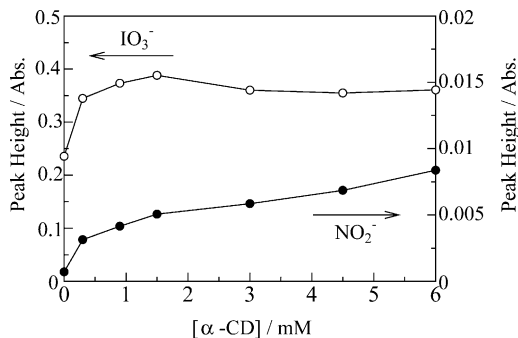


Fig. 2. Effect of the α -cyclodextrin concentration in the mixing reagent solution on the signal intensity. Operating conditions as in Table 1 except for the sulfuric acid (1 mM) and α -CD concentration as indicated.

On the contrary, the longer the reaction tube, the better the sensitivity is achieved for nitrite. These results indicate that the postcolumn reaction is still incomplete for nitrite. It should be noted that in the case of the 10-m reaction tube, the reaction time is about 15 s.

When the reaction tube is less than 4 m, the background noise level is slightly higher. This may be because the use of a longer reaction tube leads to uniform mixing. However, the peak width and the pressure drop across the reaction tube increase with increasing reaction tube length. Considering these results, a 10 m length of the reaction tube was employed in the following experiments.

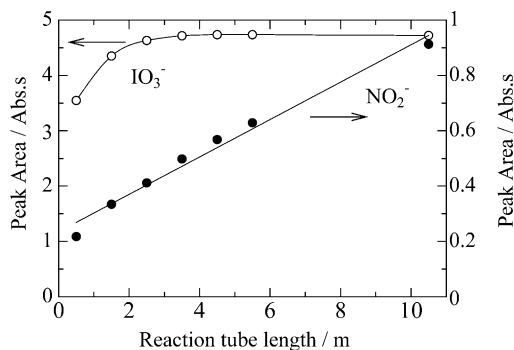


Fig. 3. Effect of reaction tube length on the signal intensity. Postcolumn mixing reagent solution: aqueous solution containing 3 mM α -CD, 10 mM sodium iodide and 5 mM sulfuric acid. Sample: 0.05 mM iodate and 0.1 mM nitrite. Reaction temperature: 65 °C. Other operating conditions as in Table 1.

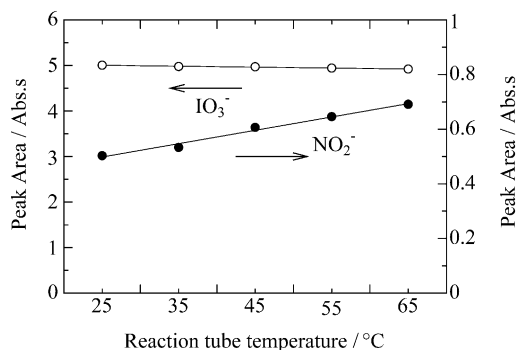


Fig. 4. Effect of reaction tube temperature on the signal intensity. Reaction temperature: as indicated. Other operating conditions as in Fig. 3 except for the reaction temperature.

Fig. 4 shows the effect of the reaction tube temperature on the detection signal. It is found that the signal intensity for nitrite increases as the tube temperature increases. On the other hand, the signal intensity for iodate is almost independent of the reaction temperature. This indicates that the reaction rate for iodate is faster than that for nitrite, and the former reaction rate is fast enough even at room temperature, whereas higher reaction temperature is favored for nitrite.

3.6. Interference from other inorganic anions

Table 2 shows the signal intensity for various inorganic anions. It is seen that the present detection system is selective to iodate and nitrite. Bromate can also be detected under the conditions in Table 1 although its sensitivity is not high. Hypochlorite (ClO^-) and nitrate gave very small

signals, and perchlorate and bromide gave no signal. It is shown that the sensitivity of nitrite is about seven times worse than that of iodate. This result is reasonable considering the retention time of these two anions and the detection principle involved in this method. As follows from Eqs. (1) and (2), the signal intensity of this method for iodate ion must be six times as large as that for nitrite.

Fig. 5 demonstrates the detection of an authentic mixture of iodate, bromate and nitrite under the optimum conditions. In Fig. 6, 0.01 mM (1.8 mg/l) iodate, 1 mM (1.3×10^2 mg/l) bromate and 0.1 mM (4.6 mg/l) nitrite are injected. It is seen that iodate is the most sensitive and bromate is the least sensitive among the three analytes.

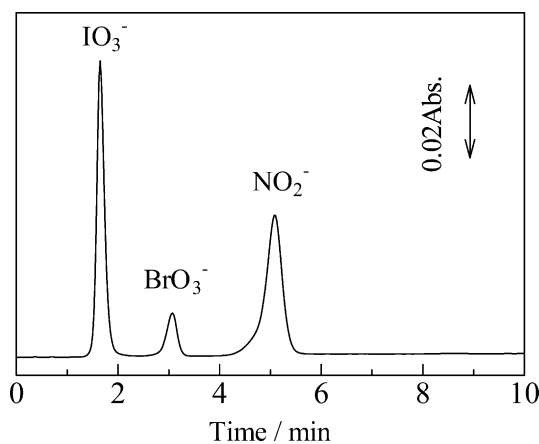


Fig. 5. Detection of iodate, bromate and nitrite. Operating conditions as in Fig. 3 except for the sample concentration: 1.8 mg/l iodate, 1.3×10^2 mg/l bromate and 4.6 mg/l nitrite.

Table 2
Comparison of the signal intensity for inorganic anions.

Analyte ions	Concentration (mM)	Peak area (mAbs s)	Relative intensity
IO_3^-	0.05	4744	100
NO_2^-	0.05	673	14
BrO_3^-	20	3946	0.21
ClO^-	20	124	0.0065
NO_3^-	20	82	0.0043
ClO_4^-	20	0	0
Br^-	20	0	0

Mixing reagent solution: aqueous solution containing 3 mM α -CD, 10 mM sodium iodide and 5 mM sulfuric acid. Reaction temperature: 65 °C. Other operating conditions are as in Table 1.

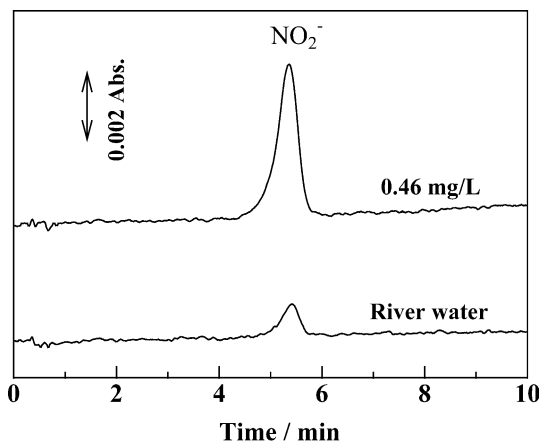


Fig. 6. Detection of nitrite in river water sample. Operating conditions as in Fig. 5 except for the detection wavelength and the sample. Wavelength of UV detection: 355 nm. Sample: 0.46 mg/l nitrite (upper trace) and Izira-river water sample (lower trace).

3.7. Determination of nitrite

The relative standard deviations (RSDs) of the retention time of iodate and nitrite for five successive measurements under the conditions in Fig. 5 were 0.26 and 0.73%, respectively. On the other hand, RSDs of the peak area were 0.20 and 0.46% for iodate and nitrite, respectively, whereas those of the peak height were 0.41 and 0.95%, respectively. It is found that good repeatability can be achieved under the conditions in Fig. 5. The detection limits at signal-to-noise ratio (S/N) 3 were 2.6 and 15.0 $\mu\text{g/l}$ for iodate and nitrite, respectively. Optimizing the reaction condition or adding a catalyst may improve the sensitivity of nitrite.

Good linear relationships between the peak height and the analyte concentration up to 0.1 and 0.5 mM for iodate and nitrite, respectively. The linear-regression coefficients for the plots were 0.999 for the both plots. It should be noted that the signal was not linear at the concentrations higher than 0.1 mM for iodate because its signal intensity was beyond the linearity of the detector.

The present method could be applied to the determination of nitrite in river water samples. Fig. 6 demonstrates the chromatogram for a river water sample. The water samples were passed

through a short column packed with Develosil C30 to remove hydrophobic compounds. It is found in Fig. 6 that nitrite is selectively detected and its concentration was determined to be 0.071 mg/l. Direct UV detection can achieve nearly the same detection limits for nitrite as in the present system and it also allows the determination of nitrite in environmental waters. However, the direct UV detection method would have inconvenience caused by interferences.

In addition, the solutions employed were degassed in vacuo under ultrasonic vibration before use. Under such conditions oxygen dissolved did not affect the detectability of the present method.

4. Conclusions

It is effective to use sodium sulfate as the eluent to elute iodate and nitrite in a reasonable time. The addition of α -CD in the postcolumn reaction solution improved the sensitivity. The longer the reaction tube, the better is the sensitivity for nitrite, indicating that the postcolumn reaction is still incomplete. Good repeatability was achieved under the optimum conditions. The present system allowed selective determination of iodate and nitrite. The determination of nitrite in river water was possible.

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