

## Note

### **Ion chromatographic determination of cyanide compounds by chloramine-T and conductivity measurement**

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Ion chromatography (IC) is a powerful technique for the separation and determination of anions and cations<sup>1</sup>. However, cyanide ion cannot be directly detected by the conductivity detector due to its low dissociation constant ( $pK=9.2$ ). Therefore, other means such as electrochemical detection (ED)<sup>2-6</sup>, or derivatization to a conducting form<sup>7-10</sup>, should be employed. Though ED methods are sensitive and selective for cyanide ion, the detectors are too expensive. Derivatization methods are time consuming and troublesome.

One of us previously reported an IC method for the determination of free cyanide and metal cyanide complexes using a conductivity detector<sup>11</sup>, and applied it to plating solutions and waste-waters<sup>12</sup>. It was based on the oxidation of cyanide ion by sodium hypochlorite to give cyanate ion ( $CNO^-$ )<sup>10,11</sup>. Since the dissociation constant of hydrogen cyanate is fairly high ( $pK=3.66$ ), cyanate ion can be measured by a conventional conductivity detector. However, a rather large chloride ion peak was observed, and the resin in the column was damaged during analysis.

Then, we attempted to replace sodium hypochlorite by a weaker oxidizing agent, chloramine-T, which is generally used in colorimetry<sup>13-15</sup>. The resin in a separator column is less damaged and the chloride ion peak is smaller than with sodium hypochlorite. Since the present method does not need buffer solution, colour developing agent and long standing time, it is much simpler than the usual one<sup>13-15</sup>.

Various parameters such as the amount of chloramine-T, temperature, standing time, and the stability of  $CNO^-$  formed were optimized to provide a quantitative conversion of  $CN^-$  into  $CNO^-$ . The calibration graph for  $CN^-$ , interferences from diverse anions and reducing agents and the applicability to the determination of metal cyanide complexes were also investigated. The method was applied successfully to the determination of cyanide compounds in waters and waste-waters.

## EXPERIMENTAL

*Apparatus and reagents*

Chromatography was performed on a Dionex system 2010i ion chromatograph equipped with a conductivity detector. A separator column (HPIC-AS4A) with a guard column (HPIC-AG4) and a fibre suppressor (AFS-1) were used. The volume of the sample loop was 50  $\mu$ l. The reagents used, except for chloramine-T solution, were as in ref. 11. Chloramine-T solution (5 or 10% w/v) was prepared daily.

*Procedure*

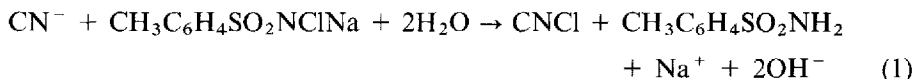
In a 50-ml volumetric flask were placed 5.0 ml of cyanide solution (10 mg/l, 0.01 *M* sodium hydroxide) and 4.5 ml of 0.1 *M* sodium hydroxide solution and the volume was made up to 50 ml with deionized water. A 50- $\mu$ l volume of chloramine-T solution was added and mixed thoroughly. The mixture was kept at 80°C for 10 min, then cooled in a water-bath (5 min). An aliquot of the solution was injected into the ion chromatograph.

For real sample analysis, an aliquot of sample solution and 0.1 *M* sodium hydroxide solution were mixed and diluted to 50 ml in deionized water (pH 12). Then, the procedure mentioned above was followed.

## RESULTS AND DISCUSSION

*Chromatogram of cyanate ion*

The overall reactions leading to cyanate ion may be written as follows<sup>13,16,17</sup>:



Cyanide ion reacts with chloramine-T to produce cyanogen chloride (CNCl) (reaction 1). When heated at alkaline pH, CNCl is hydrolyzed to CNO<sup>-</sup> (reaction 2). Typical chromatograms of cyanate ion are shown in Fig. 1.

A small peak, corresponding to only 5.4% of CN<sup>-</sup>, appeared when the reaction was performed at room temperature (25°C) for 10 min (A). However, when heating at 80°C is carried out for 10 min (B) the reaction proceeds quantitatively. The chromatogram of a blank is shown in Fig. 1 (C).

As shown in Fig. 1, a positive peak, called the "pseudopeak", appears first. Peaks of chloride and cyanate ions (A,B) follow. Their retention times are *ca.* 2.3 and 3.0 min, respectively. In this case, the peak of chloride ion was smaller than that produced when sodium hypochlorite was used<sup>11</sup>. The size is dependent on the concentration of cyanide ion (reaction 2).

*Optimum oxidizing condition*

The volume of chloramine-T solution for the conversion of CN<sup>-</sup> into CNO<sup>-</sup> was optimized by using 5% chloramine-T solution for 1 mg/l cyanide solution and 10% solution for 10 mg/l cyanide solution. The results are shown in Fig. 2.

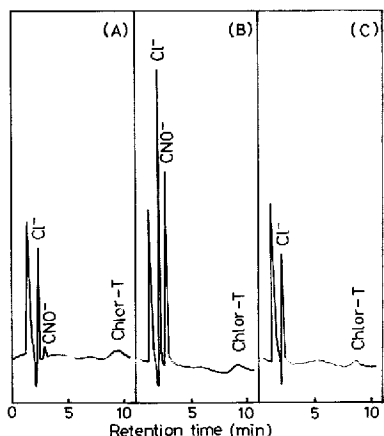


Fig. 1. Chromatogram of cyanate ion: (A)  $\text{CN}^-$  (1 mg/l, 50 ml) + chloramine-T (Chlor-T) (5%, 50  $\mu\text{l}$ ), 25°C, 10 min; (B)  $\text{CN}^-$  (1 mg/l, 50 ml) + chloramine-T (5%, 50  $\mu\text{l}$ ), 80°C, 10 min; (C) water (pH 12, 50 ml) + chloramine-T (5%, 50  $\mu\text{l}$ ), 80°C, 10 min. Column: HPIC-AS4A. Eluent: 2.2 mM  $\text{Na}_2\text{CO}_3$ . Detector: conductivity: full scale, 3  $\mu\text{S}$ .

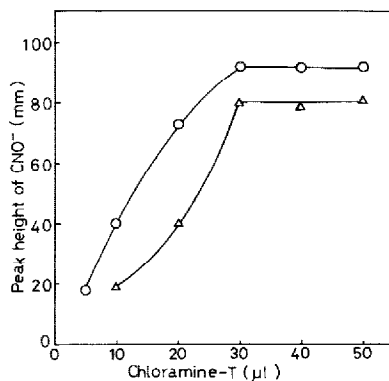


Fig. 2. Effect of the volume of chloramine-T solution added: ○ =  $\text{CN}^-$  (1 mg/l, 50 ml) + chloramine-T (5%, 10 – 50  $\mu\text{l}$ ); △ =  $\text{CN}^-$  (10 mg/l, 50 ml) + chloramine-T (10%, 10 – 50  $\mu\text{l}$ ). Conditions: 80°C, 10 min stand; Column: HPIC-AS4A; eluent, 2.2 mM  $\text{Na}_2\text{CO}_3$ ; detector, conductivity, full scale, 3  $\mu\text{S}$  (○), 30  $\mu\text{S}$  (△).

In both cases, when 30 – 50  $\mu\text{l}$  of the solution were added the peak heights were almost constant. Therefore, the volume of chloramine-T solution was fixed at 50  $\mu\text{l}$ .

The effect of temperature on the conversion of  $\text{CN}^-$  into  $\text{CNO}^-$  was examined. Results are shown in Fig. 3. The peak height of cyanate ion increases with temperature to a maximum at 70°C and was almost constant between 70 and 90°C.

The effect of reaction time was examined at 80°C (Fig. 4). No differences were observed for reaction times of 10 – 30 min. Cyanate ion formed at pH 12 was stable for 45 min. Therefore, 80°C and 10 min were chosen.

#### Calibration graphs

Two calibration graphs for cyanide ion concentration ranges of 0.05 – 1.0 and 1.0 – 10.0 mg/l, are shown in Fig. 5. Both plots are essentially linear, which indicates that the oxidation reaction is almost stoichiometric. The correlation coefficients were 0.9996 (for 0.05 – 1.0 mg/l) and 0.9992 (for 1.0 – 10.0 mg/l).

#### Interferences

The effects of diverse anions and reducing agents on the cyanide analysis were examined. The results are presented in Table I.

Common anions do not interfere. When the concentration of chloride ion is 50 times larger than that of cyanide ion the separation of cyanate ion from chloride ion is incomplete, which gives a negative error. The retention time of nitrite ion (2.7 min) almost coincides with that of cyanate ion (3.0 min), which gives a positive error. The latter can be avoided by decomposing nitrite ion with amidosulphuric acid<sup>11</sup>.

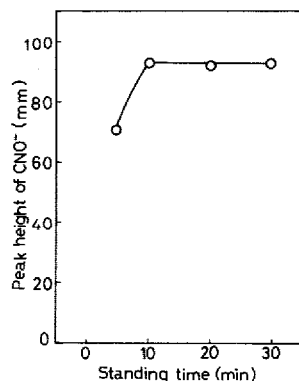
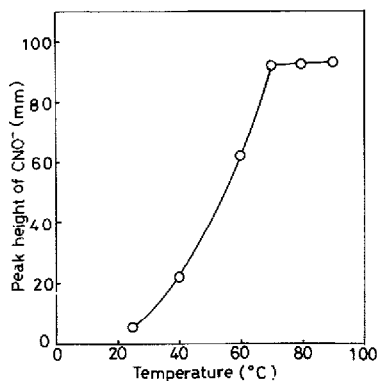


Fig. 3. Effect of temperature (25–90°C). Conditions:  $\text{CN}^-$  (1 mg/l, 50 ml) + chloramine-T (5%, 50  $\mu\text{l}$ ), 10 min; Column: HPIC-AS4A. Eluent: 2.2 mM  $\text{Na}_2\text{CO}_3$ . Detector: conductivity: full scale, 3  $\mu\text{S}$ .

Fig. 4. Effects of reaction time (5–30 min). Conditions:  $\text{CN}^-$  (1 mg/l, 50 ml) + chloramine-T (5%, 50  $\mu\text{l}$ ), 80°C; Column: HPIC-AS4A. Eluent: 2.2 mM  $\text{Na}_2\text{CO}_3$ . Detector: conductivity: full scale, 3  $\mu\text{S}$ .

Large amounts (10 mg/l) of reducing agents such as sulphide, thiosulphate and ascorbic acid cause serious interferences. However, at less than 1 mg/l, interference only from sulphide ion is considerable. Sulphite, hypophosphite, phosphite and arsenite ions cause no interference, even when the amount is 10 times larger than that of cyanide ion.

Thiocyanate ion gives cyanate ion upon reaction with chloramine-T<sup>17</sup> and heating. Therefore, even a small amount of this ion causes serious interference.

#### Analysis of metal cyanide complexes

In order to study the applicability to metal cyanides, solutions of zinc, cad-

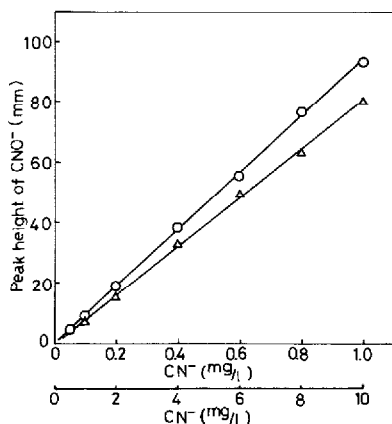


Fig. 5. Calibration graphs: ○ =  $\text{CN}^-$  (0.05–1 mg/l, 50 ml) + chloramine-T (5%, 50  $\mu\text{l}$ ); △ =  $\text{CN}^-$  (1–10 mg/l, 50 ml) + chloramine-T (10%, 50  $\mu\text{l}$ ). Conditions: 80°C, 10 min stand; Column: HPIC-AS4A. Eluent: 2.2 mM  $\text{Na}_2\text{CO}_3$ ; detector, conductivity, full scale, 3  $\mu\text{S}$  (○), 30  $\mu\text{S}$  (△).

TABLE I

## INTERFERENCES FROM ANIONS AND REDUCING AGENTS

Volumes of cyanide solutions: 1 mg/l, pH 12, 50 ml, full scale, 3  $\mu$ S; 10 mg/l, pH 12, 50 ml, full scale, 30  $\mu$ S. Volume of chloramine-T (5 or 10%) solution: 50  $\mu$ l. Conditions: 80°C, 10 min stand; column, HPLC-AS4A; eluent, 2.2 mM Na<sub>2</sub>CO<sub>3</sub>; detector, conductivity.

Anion or reducing agent	Retention time (min)	ppm ratio (CN <sup>-</sup> /A <sup>n-</sup> )	Recovery (%)
F <sup>-</sup>	1.6	1/10	101.0
Cl <sup>-</sup>	2.3	1/10	100.0
Cl <sup>-</sup>	2.3	1/50	92.6
Cl <sup>-</sup>	2.3	10/100	102.0
Cl <sup>-</sup>	2.3	10/500	82.3
NO <sub>2</sub> <sup>-</sup>	2.7	1/1	101.0 <sup>a</sup>
NO <sub>2</sub> <sup>-</sup>	2.7	1/10	98.0 <sup>a</sup>
NO <sub>2</sub> <sup>-</sup>	2.7	10/10	101.0 <sup>a</sup>
HPO <sub>4</sub> <sup>2-</sup>	7.6	1/10	100.0
Br <sup>-</sup>	3.7	1/10	96.9
NO <sub>3</sub> <sup>-</sup>	4.3	1/10	101.0
SO <sub>4</sub> <sup>2-</sup>	7.8	1/10	100.0
S <sup>2-</sup>		1/1	64.5
S <sup>2-</sup>		1/10	0.0
SO <sub>3</sub> <sup>2-</sup>	7.7	1/1	101.0
SO <sub>3</sub> <sup>2-</sup>	7.7	1/10	97.8
S <sub>2</sub> O <sub>4</sub> <sup>2-</sup>		1/1	100.0
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>		1/10	10.8
PO <sub>3</sub> <sup>3-</sup>		1/1	102.0
PO <sub>3</sub> <sup>3-</sup>		1/10	102.0
PO <sub>3</sub> <sup>3-</sup>	5.3	1/1	101.0
PO <sub>3</sub> <sup>3-</sup>	5.3	1/10	101.0
C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> <sup>-</sup>		1/1	101.0
C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> <sup>-</sup>		1/10	89.2
AsO <sub>2</sub> <sup>-</sup>		1/1	101.0
AsO <sub>2</sub> <sup>-</sup>		1/10	100.0
SCN <sup>-</sup>		0/1	34.3
SCN <sup>-</sup>		1/1	130.2

<sup>a</sup> Measured after the decomposition of NO<sub>2</sub><sup>-</sup> (ref. 11).

mium, copper, silver, nickel, iron, gold and cobalt cyanides were examined. The results are presented in Table II together with those obtained by using 1% sodium hypochlorite solution.

Weak cyanide complexes (Category 1) such as Zn(CN)<sub>4</sub><sup>2-</sup>, Cd(CN)<sub>4</sub><sup>2-</sup> and Cu(CN)<sub>4</sub><sup>3-</sup> can be quantitatively determined as CNO<sup>-</sup> after oxidation with chloramine-T.

Cyanate ion peaks were detected from moderately strong cyanide complexes (Category 2) such as Ag(CN)<sub>2</sub><sup>-</sup> and Ni(CN)<sub>4</sub><sup>2-</sup>. The peak height of CNO<sup>-</sup> from Ag(CN)<sub>2</sub><sup>-</sup> is about 38% of that with sodium hypochlorite.

Strong cyanide complexes (Category 3) such as Fe(CN)<sub>6</sub><sup>4-</sup>, Fe(CN)<sub>6</sub><sup>3-</sup>, Au(CN)<sub>2</sub><sup>-</sup>, Au(CN)<sub>4</sub><sup>-</sup> and Co(CN)<sub>6</sub><sup>3-</sup> are stable. Therefore, almost no CNO<sup>-</sup> peaks were detected even after heating at 80°C, except for Au(CN)<sub>4</sub><sup>-</sup>. The reason why the

TABLE II

## OXIDATION YIELDS OF METAL CYANIDE COMPLEXES WITH CHLORAMINE-T AND SODIUM HYPOCHLORITE

Volumes: cyanide ion (ca. 1 mg/l, pH 12) 50 ml; chloramine-T (5%) solution 50  $\mu$ l; NaClO (1%) solution 50  $\mu$ l. Standing time: 80°C, 10 min. Column: HPIC-AS4A, AFS. Eluent: 2.2 mM Na<sub>2</sub>CO<sub>3</sub>. Detector: conductivity: full scale; 3  $\mu$ S.

Species	Formation Constant	Chloramine-T(5%)	NaClO(1%)
Zn(CN) <sub>4</sub> <sup>2-</sup>	16.7	88.0 <sup>a</sup>	86.5 <sup>a</sup>
Cd(CN) <sub>4</sub> <sup>2-</sup>	18.8	98.0	96.0
Cu(CN) <sub>4</sub> <sup>3-</sup>	30.3	91.0	94.0
Ag(CN) <sub>2</sub> <sup>-</sup>	21.2	36.0	95.0
Ni(CN) <sub>4</sub> <sup>2-</sup>	31.3	106.0	106.0
Fe(CN) <sub>4</sub> <sup>4-</sup>	35	1.0	13.0
Fe(CN) <sub>6</sub> <sup>3-</sup>	42	0.0	0.0
Au(CN) <sub>2</sub> <sup>-</sup>	38.3	0.0	0.0
Au(CN) <sub>4</sub> <sup>-</sup>	—	21.0	20.0
Co(CN) <sub>6</sub> <sup>3-</sup>	64	0.0	0.0

<sup>a</sup> Peak height of CNO<sup>-</sup> formed (mm).

CNO<sup>-</sup> peak was detected from Au(CN)<sub>4</sub><sup>-</sup> is considered to be that a part of Au(CN)<sub>4</sub><sup>-</sup> was decomposed to Au(CN)<sub>2</sub><sup>-</sup> and CN<sup>-</sup>. Therefore, it was oxidized to CNO<sup>-</sup> by chloramine-T at 80°C.

*Real sample analysis*

The proposed method was applied to the determination of cyanide ion in drinking water, river-water and plating waste-waters. As no detectable amount of cyanide

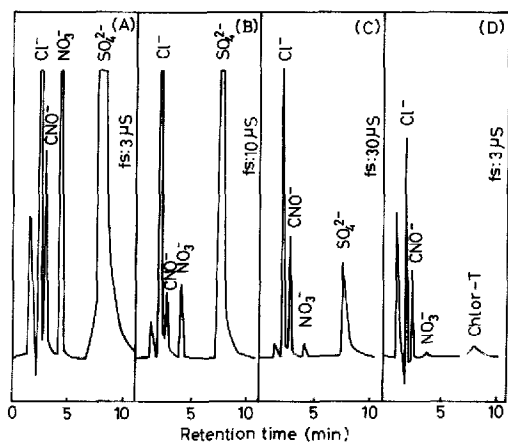


Fig. 6. Determination of cyanide in real samples: (A)= Drinking water spiked with 1.0 mg/l cyanide ion; (B)= River-water spiked with 1.0 mg/l cyanide ion; (C)= Plating waste-water before treatment; (D)= Plating waste-water after treatment, distillation was performed. Conditions: 80°C, 10 min stand; column: HPIC-AS4A; eluent: 2.2 mM Na<sub>2</sub>CO<sub>3</sub>; detector: conductivity. fs = Full scale.

TABLE III  
DETERMINATION OF CYANIDE IN REAL SAMPLES

Sample	CN <sup>-</sup> (mg/l) mean <sup>a</sup>	S.D.	C.V. (%)
Drinking water <sup>b</sup>	0.98	0.008	0.8
River-water <sup>b</sup>	0.95	0.022	2.3
Plating waste-water <sup>c</sup>	173.0	1.24	0.7
Plating waste-water <sup>d</sup>	0.46	0.004	0.9

<sup>a</sup> Five samples at each concentration. Column: HPIC-AS4A. Eluent: 2.2 mM Na<sub>2</sub>CO<sub>3</sub>. Detector: conductivity. Chloramine-T, 50 μl; 80°C, 10 min stand.

<sup>b</sup> Spiked with 1.0 mg/l cyanide ion.

<sup>c</sup> Before treatment of cyanide by alkaline chlorination.

<sup>d</sup> After treatment of cyanide by alkaline chlorination; distillation was performed (total cyanide).

ion was found, a small amount of cyanide ion (50 μg) was added to 50 ml of drinking water (A) and river-water (B), and the recoveries were checked. Plating waste-water (C) was diluted 25 times in deionized water. Waste-water (D) was distilled and this distillate was directly measured for its cyanide concentration. The results are presented in Table III and Fig. 6.

The recoveries of cyanide ion from the spiked drinking water and river-water were 98 and 95%, respectively. The coefficients of variation (%) of samples A (1.0), B (1.0), C (173) and D (0.96 mg/l, CN<sup>-</sup>) were 0.8, 2.3, 0.7 and 0.9%, respectively.

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