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## ELECTRON-CAPTURE GAS CHROMATOGRAPHIC DETERMINATION OF CYANIDE AS PENTAFLUOROBENZYL CYANIDE

HSIN-LUNG WU\* and WEN-RUNG HWANG

*School of Pharmacy, Kaohsiung Medical College, Kaohsiung 800 (Taiwan)*

KOICHI FUNAZO

*Department of Chemistry, Osaka Prefectural Technical College, Neyagawa, Osaka 572 (Japan)*

MINORU TANAKA and TOSHIYUKI SHONO

*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565 (Japan)*

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### SUMMARY

A simple, sensitive and specific method was established for the determination of cyanide as pentafluorobenzyl cyanide, based on the derivatization of cyanide anion in an alkaline medium with pentafluorobenzyl bromide. The derivative formed in the reaction solution was injected directly into a gas chromatograph equipped with an electron-capture detector. The detection limit was about 0.2 ng of cyanide anion in 0.1 ml of aqueous sample (2 ppb). The effects of base, amount of pentafluorobenzyl bromide, solvents, reaction temperature and reaction time on the derivatization were investigated, and the optimal derivatization conditions were established. Interferences due to some anions commonly found in wastewater were examined and were found to be minimal except for thiocyanate ion. The proposed method was applied to the determination of cyanide in industrial wastewater and the results agreed well with those obtained using the pyridine-pyrazolone spectrophotometric method.

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### INTRODUCTION

Cyanides are used in electroplating, in precious metal refining, in syntheses of cyanopolymer-based materials and in many other chemical processes. Small amounts of cyanide can cause rapid death owing to its extremely toxic action against cytochrome *c* oxidase<sup>1</sup>, and the measurement of cyanide at trace levels is therefore of great importance.

A variety of methods have been reported for the determination of cyanide, spectrophotometry being the most widely used, based on the oxidation of cyanide to cyanogen chloride or cyanogen bromide and further reaction with pyridine-benzidine<sup>2</sup>, pyridine-barbituric acid<sup>3</sup> or pyridine-pyrazolone<sup>4</sup> to form coloured compounds. However, improvements to these methods are necessary in order to increase the specificity, sensitivity and simplicity.

An electrochemical method using the cyanide ion-selective electrode has also been used<sup>5,6</sup> because of its simplicity, but it is subject to interferences from halides, sulphide, etc.

Several gas chromatographic (GC) methods based on chemical derivatization have been established for the determination of cyanide, in which the cyanide was oxidized with bromine or chloramine-T to form cyanogen bromide<sup>7</sup> or cyanogen chloride<sup>8</sup>, respectively. Before GC analysis, care should be taken to prevent losses of these highly volatile cyanogen halides. Fagile and Klockow<sup>9</sup> reported another GC method in which cyanide and several other anions were converted into their *n*-decyl derivatives by a procedure involving ion-pair formation with tetra-*n*-butylammonium sulphate and then alkylation of the anions with methanesulphonic acid *n*-decyl ester under anhydrous conditions. In this method, therefore, lyophilization of water samples is inevitable. Cyanide has also been determined by GC as methyl benzoate<sup>10</sup> produced by the cyanide-catalysed cleavage of benzil in the presence of methanol. However, the hydroxide concentration in the reaction mixture needs to be carefully controlled in order to avoid non-cyanide-catalysed production of methyl benzoate at high base concentrations.

In the derivatization GC analysis of inorganic anions, we have devised several sensitive methods for the determination of cyanide, as follows. Cyanide was converted into acetonitrile<sup>11</sup> or benzonitrile<sup>12</sup> by methylation with dimethyl sulphate or by the Sandmeyer reaction, respectively. The derivative formed was transferred into an organic layer and determined by GC with flame thermionic detection. We have further developed an approach for microgram levels of cyanide involving pentafluorobenzoylation of cyanide to give pentafluorobenzyl cyanide<sup>13</sup>, which is subsequently detected by GC with a flame-ionization detector. Obviously, this derivative is designed for GC determination with electron-capture detection, based on the high electron affinity of the pentafluorobenzyl moiety and the optimal volatility of the derivative.

In this work, the improved simplicity, specificity and sensitivity of the method were studied, and the method was applied to the determination of cyanide in industrial effluents with satisfactory results.

## EXPERIMENTAL

### *GC conditions*

A Varian 3700 gas chromatograph equipped with a <sup>63</sup>Ni pulsed linearized electron-capture detector was used. The column was a coiled stainless-steel tube (2 m × 2 mm I.D.) packed with 10% OV-210 silicone on Chromosorb W HP (80–100 mesh). The temperatures of the injection port, column and detector were kept at 250, 200 and 270°C, respectively. Nitrogen was used as the carrier gas at a flow-rate of 30 ml/min. A Varian 9176 recorder was utilized at a chart-speed of 2.5 mm/min.

### *Materials*

$\alpha$ -Bromo-2,3,4,5,6-pentafluorotoluene (PFBBr; pentafluorobenzyl bromide) and *p*-nitrophenyl phenyl ether (Aldrich, Milwaukee, WI, U.S.A.) and 10% OV-210 on Chromosorb W HP (80–100 mesh) (Alltech Assoc., Deerfield, IL, U.S.A.) were used without further treatment. Potassium cyanide (Wako, Osaka, Japan), acetone

and other reagents were of analytical-reagent grade. Deionized and distilled water was used to prepare aqueous solutions. Solutions of the internal standard (I.S.) were prepared by dissolving *p*-nitrophenyl phenyl ether ( $37.2 \mu\text{M}$ ) in acetone. Solutions of the reference standard were prepared by dissolving suitable amounts of potassium cyanide in  $0.015 \text{ M}$  potassium hydroxide solution. Before analysis, industrial waste-water samples were filtered and diluted with an equal volume of  $0.03 \text{ M}$  potassium hydroxide solution. Further dilution with  $0.015 \text{ M}$  potassium hydroxide solution was performed, if necessary. PFBBr solution ( $1.62 \text{ mM}$ ) was prepared by diluting suitable amounts of PFBBr with acetone.

### Procedure

A  $0.65\text{-ml}$  volume of PFBBr solution was introduced into a  $10\text{-ml}$  glass-stoppered test-tube containing  $0.1 \text{ ml}$  of the reference standard solution or sample solution, then  $0.25 \text{ ml}$  of the internal standard solution was added. The reaction mixture was stirred magnetically for  $90 \text{ min}$  at  $30^\circ\text{C}$ , then an aliquot of the reaction solution was subjected to GC analysis.

## RESULTS AND DISCUSSION

In order to establish the optimal derivatization conditions for pentafluorobenzoylation of cyanide ( $15.4 \mu\text{M}$ ), several parameters including concentration of potassium hydroxide solution, amount of PFBBr, the water-soluble organic solvent, reaction temperature and reaction time were examined. The formation of the cyanide derivative was evaluated by measuring the ratio of the peak height of the derivative to that of the internal standard.

### Effect of concentration of base

The effect of different concentrations of potassium hydroxide ( $0.005\text{--}0.025 \text{ M}$ ) in  $0.1 \text{ ml}$  of aqueous solution on the formation of the cyanide derivative was investigated. The results are shown in Fig. 1. The optimal concentration is about  $0.015 \text{ M}$ , and this was selected for the derivatization reaction except where indicated otherwise. Derivatization of cyanide in acidic medium was not performed owing to the volatility and toxicity of the hydrocyanic acid formed.

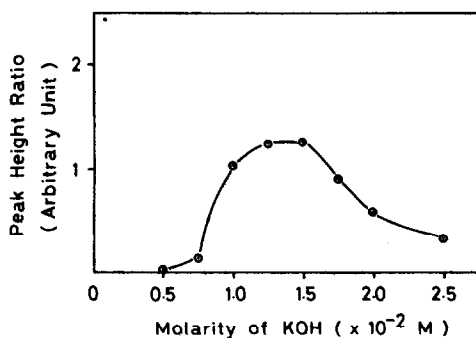


Fig. 1. Effect of concentration of base on the formation of cyanide derivative.

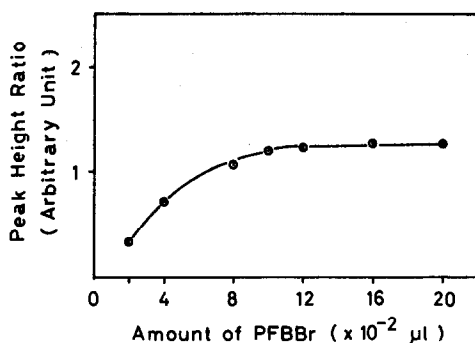


Fig. 2. Effect of amount of PFBBr on the formation of cyanide derivative.

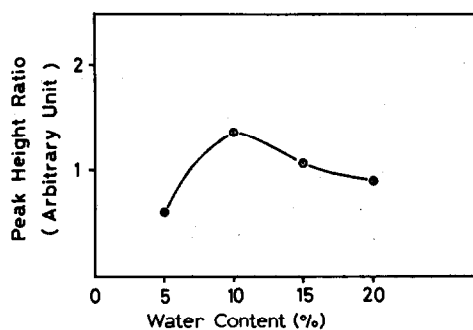


Fig. 3. Effect of volume ratio of alkaline aqueous solution to acetone on the formation of cyanide derivative.

#### *Effect of amount of PFBBr*

To establish the optimal amount of PFBBr required for pentafluorobenzoylation of 1.54 nmol of cyanide anion, different volumes of PFBBr (0.02–0.20  $\mu\text{l}$ ) were tried in the derivatization. To achieve a constant formation of the cyanide derivative, the amount of PFBBr needed is about 0.12  $\mu\text{l}$ , as shown in Fig. 2. For definite derivatization of cyanide, 0.16  $\mu\text{l}$  of PFBBr, which is equivalent to 0.65 ml of 1.62 mM PFBBr solution, was subsequently used.

#### *Effects of solvent and reaction temperature*

An aliquot of 0.9 ml of various water-miscible organic solvents containing I.S. and PFBBr was added to 0.1 ml of 0.015 M potassium hydroxide solution containing cyanide to establish the optimal solvent for the derivatization. Of the solvents tested, acetone is much better than ethanol or methanol, in which nearly no formation of the derivative was observed. Owing to overlapping of the chromatographic peak of the reagent blank with that of the cyanide derivative, acetonitrile could not be used. The volume ratio of 0.015 M potassium hydroxide solution to acetone has a significant effect on the formation of the cyanide derivative as shown in Fig. 3. About 10%

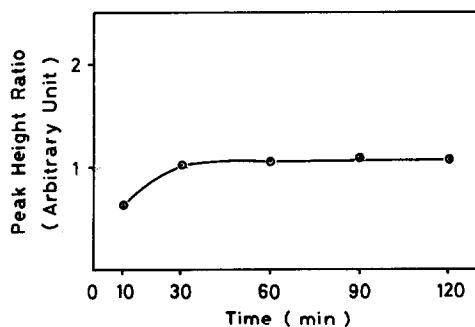


Fig. 4. Effect of reaction time on the formation of cyanide derivative.

(v/v) alkaline solution in acetone is the best for the derivatization of cyanide, probably owing to the homogeneity of the reactants in the test-tube.

The derivatization yield of cyanide increases with increasing reaction temperature. However, the peak of the reagent blank formed at temperatures above 40°C overlaps with that of the cyanide derivative. Therefore, the reaction temperature was set at 30°C. To improve the derivatization yield and the sensitivity for the analysis further, resolution of the cyanide derivative from the reagent blank with reaction at higher temperatures is under investigation using a high-performance glass capillary column.

#### Effect of reaction time

The reaction time required to give a constant formation of the cyanide derivative was examined at different time intervals from 10 to 120 min, as shown in Fig. 4. The results indicated that about 60 min are required for plateau formation of the derivative. A period of 90 min was set for subsequent derivatization reactions.

In some instances when using an electron-capture detector, it is well known that the detector temperature considerably affects the detector response<sup>14</sup>. Therefore, the effect of detector temperature was tested in the range 230–300°C. The results revealed that a small increments in the detector response was observed on increasing the temperature, but that the fluctuation of the baseline was also elevated. As a compromise, a detector temperature of 270°C was employed.

#### Interferences

In order to apply the method to the determination of cyanide in environmental

TABLE I  
RESULTS OF INTERFERENCE STUDY

Cyanide concentration: 0.4 µg/ml.

<i>Ion</i>	<i>Concentration (µg/ml)</i>	<i>Added as</i>	<i>Peak-height ratio*</i>
None			100.0 ± 1.4
F <sup>-</sup>	100	NaF	100.5 ± 3.0
Cl <sup>-</sup>	100	NaCl	100.2 ± 1.6
Br <sup>-</sup>	100	KBr	98.5 ± 3.6
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	100	NaH <sub>2</sub> PO <sub>4</sub>	100.3 ± 5.1
HPO <sub>4</sub> <sup>2-</sup>	100	Na <sub>2</sub> HPO <sub>4</sub>	99.3 ± 1.1
Fe(CN) <sub>6</sub> <sup>3-</sup>	100	K <sub>3</sub> Fe(CN) <sub>6</sub>	100.7 ± 2.7
Fe(CN) <sub>6</sub> <sup>4-</sup>	100	K <sub>4</sub> Fe(CN) <sub>6</sub>	101.4 ± 1.3
CO <sub>3</sub> <sup>2-</sup>	100	K <sub>2</sub> CO <sub>3</sub>	99.8 ± 1.1
HCO <sub>3</sub> <sup>-</sup>	100	NaHCO <sub>3</sub>	101.2 ± 1.1
SO <sub>4</sub> <sup>2-</sup>	50	Na <sub>2</sub> SO <sub>4</sub>	101.2 ± 3.1
NO <sub>3</sub> <sup>-</sup>	50	NaNO <sub>3</sub>	99.1 ± 4.3
CH <sub>3</sub> COO <sup>-</sup>	50	CH <sub>3</sub> COONa · 3H <sub>2</sub> O	100.5 ± 2.9
S <sup>2-</sup>	10	Na <sub>2</sub> S · 9H <sub>2</sub> O	99.8 ± 3.9
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	10	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	102.5 ± 2.9
I <sup>-</sup>	10	NaI	100.1 ± 2.4
SCN <sup>-</sup>	0.5	KSCN	142.4 ± 3.2

\* Mean ± standard deviation of three replicate analyses.

samples, the effects of several common anions that could coexist in industrial wastewater on the cyanide determination were examined and the results are presented in Table I.  $F^-$ ,  $Cl^-$  and  $Br^-$  at 100 ppm and  $I^-$  at 10 ppm do not interfere in the determination. The method is not affected by cyanide complexes of iron such as  $Fe(CN)_6^{4-}$  and  $Fe(CN)_6^{3-}$ , which are not dissociated in alkaline solution. Other common anions ( $H_2PO_4^-$ ,  $HPO_4^{2-}$ ,  $CO_3^{2-}$ ,  $HCO_3^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$  and  $CH_3COO^-$ ) at 50 or 100 ppm do not interfere. Sulphide and thiosulphate anions do not interfere at 10 ppm, which is acceptable in view of the fact that sulphide interferes in many of the methods reported for the determination of cyanide. On the other hand, thiocyanate definitely interferes, giving high cyanide values. This is probably due to the presence of cyanide dissociated from thiocyanate in alkaline medium, as indicated by the appearance of a peak with the same retention time as that of the cyanide derivative on the chromatogram of the derivatization product of thiocyanate. When cyanide coexists with thiocyanate in a water sample, it is possible to distil off hydrocyanic acid from thiocyanic acid after acidifying the water, based on the non-volatility of thiocyanic acid<sup>15</sup>.

#### Analytical calibration

To evaluate the quantitative applicability of the method, eight standard ref-

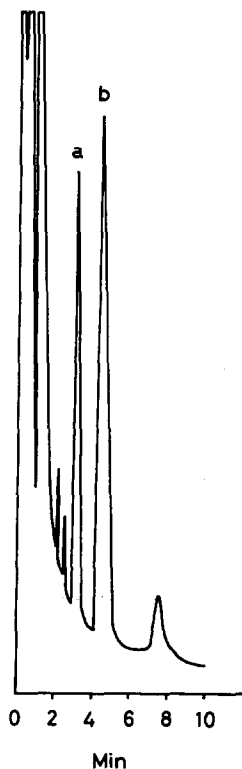


Fig. 5. Typical gas chromatogram for cyanide determination. Peaks: a = cyanide derivative; b = *p*-nitrophenyl phenyl ether (I.S.).

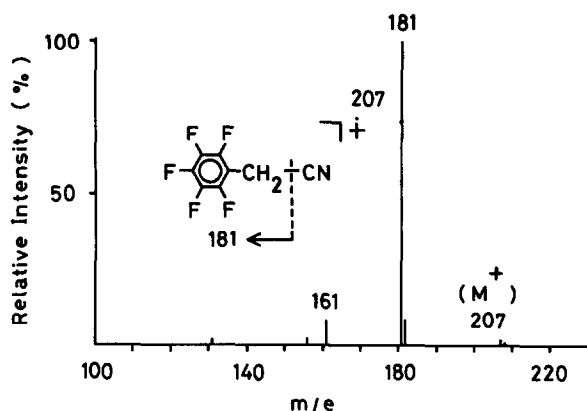


Fig. 6. Mass spectrum of cyanide derivative.

erence samples containing cyanide over the range of 1–40 ng were determined and a calibration graph was constructed of amount of cyanide ( $x$ ) versus peak-height ratio of the cyanide derivative to I.S. ( $y$ ). A linear regression equation,  $y = 0.0377x + 0.0201$ , was obtained with a correlation coefficient of 0.999, which indicates good applicability of the method to cyanide quantitation. The detection limit, based on the concentration of analyte giving a signal twice the average noise, is about 0.2 ng of cyanide in 0.1 ml of sample solution. The derivatization yield of cyanide is about 70%, determined using the authentic cyanide derivative synthesized and isolated in our laboratory.

The typical gas chromatogram in Fig. 5 indicates the good chromatographic properties of the cyanide derivative, with a short retention and a symmetrical peak. The peak of the cyanide derivative in Fig. 5 (a) was examined by GC-mass spectrometry (MS) under the conditions used previously<sup>13</sup>. The mass spectrum exhibits a molecular ion at  $m/e = 207$  and a base ion at  $m/e = 181$ , equivalent to the ion fragment  $C_6F_5CH_2^+$ , as shown in Fig. 6. For further confirmation of the cyanide derivative, the synthesized and purified cyanide derivative was identified by infrared (IR) spectrometry. The IR spectrum showed a weak absorption at  $2250\text{ cm}^{-1}$ , which

TABLE II

COMPARISON OF METHODS FOR THE DETERMINATION OF CYANIDE

Sample	Cyanide concentration ( $\mu\text{g/ml}$ )	
	Spectrophotometry*	GC**
A	0.34	$0.31 \pm 0.008$
B	0.05	$0.05 \pm 0.003$
C	0.45	$0.47 \pm 0.009$
D	0.19	$0.18 \pm 0.016$
E	0.14	$0.13 \pm 0.001$

\* Pyridine-pyrazolone method.

\*\* Mean  $\pm$  standard deviation of three replicate analyses.

is characteristic of the stretching vibration of cyanide substituted with electronegative groups<sup>16</sup>. Based on the GC-MS and IR analyses, the cyanide derivative is identified as pentafluorobenzyl cyanide.

### Applications

The method was applied to the measurements of cyanide in industrial wastewater from an electroplating works and the results were compared with those obtained by the pyridine-pyrazolone spectrophotometric method<sup>4</sup> (Table II). The results agree well and demonstrate the high reliability of the proposed method. As the sample size used is small (0.1 ml), a modified method may be useful for the determination of cyanide in biological specimens. In addition, it may be possible to develop the method to determine hydrogen cyanide in polluted air using an alkaline aqueous solution as the absorbent.

### ACKNOWLEDGEMENT

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