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TRACE DETERMINATION OF CYANIDE BY DERIVATIZATION AND FLAME THERMIONIC GAS CHROMATOGRAPHY

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SUMMARY

A sensitive gas chromatographic method for the determination of cyanide at trace levels is described. The method is based on the derivatization of cyanide to benzonitrile, which is extracted with benzene and determined by flame thermionic gas chromatography. In the derivatization reaction, aqueous cyanide reacts with aniline and sodium nitrite in the presence of copper(II) sulphate and forms benzonitrile. Cyanide at concentrations between 3 ng/ml and 1.0 $\mu\text{g}/\text{ml}$ can be detected with a linear response. Several anions tested do not interfere. The method was evaluated by analysing wastewater samples collected from various factories and by comparing the values obtained with those obtained by the pyridine-pyrazolone method, which has been used widely for the determination of cyanide. Good agreement was found between the two methods.

INTRODUCTION

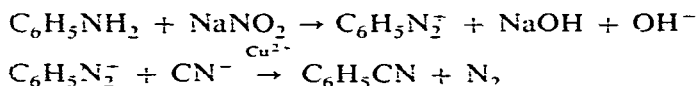
Because of its extremely toxic properties, cyanide represents a significant waste disposal problem in various industries, such as metal plating and petroleum refining. A variety of techniques for the determination of trace amounts of cyanide exist. Of these methods, the recommended method¹ is the pyridine-pyrazolone method², which is a modification of the pyridine-benzidine method³. In the pyridine-pyrazolone method, cyanide is determined spectrophotometrically after conversion to cyanogen chloride followed by reaction with pyridine and 1-phenyl-3-methyl-5-pyrazolone. However, the colour development is very slow and the colour developed tends to fade. Therefore, this method is time consuming and tedious. Recently, a method using a cyanide ion-selective electrode has frequently been used, but it is subject to interferences from several anions, such as iodide and thiocyanate.

A few sensitive gas chromatographic (GC) methods have been developed. One of the methods is based on the evolution of hydrogen cyanide from cyanide ion by acidification and the determination of the resulting hydrogen cyanide by the head-

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space technique and GC with flame thermionic detection^{4,5}. Several groups have reported another method based on the derivatization of cyanide to cyanogen halide, followed by the GC determination with electron-capture detection⁶⁻⁹. This method has also been used for the determination of thiocyanate at trace levels⁸⁻¹⁰.

We have investigated the determination of inorganic anions by GC with derivatization¹¹⁻¹⁷, and reported a method for the determination of cyanide together with other inorganic anions in which cyanide is methylated to acetonitrile with dimethyl sulphate and determined by GC. As preliminary work, we have also published another technique for the determination of cyanide¹². In the method, cyanide reacts with aniline and sodium nitrite in the presence of copper(II) sulphate and the derivatized benzonitrile is determined by GC with flame-ionization detection. The derivatization reaction, which is similar to the Sandmeyer reaction, seems to proceed as follows:



Because of the use of a flame-ionization detector, this technique is not sensitive enough to detect cyanide at concentrations lower than 3 $\mu\text{g}/\text{ml}$. In this paper, this technique is extended to the determination of cyanide at ng/ml levels by using a flame thermionic detector, which is much more sensitive to benzonitrile than a flame-ionization detector. This method has been applied to the analysis of cyanide in various wastewater samples.

EXPERIMENTAL

Apparatus

A Shimadzu GC-6AM gas chromatograph equipped with a flame thermionic detector (Shimadzu, Kyoto, Japan) was used. A stainless-steel column (3 m \times 3 mm I.D.) was packed with 5% PEG-HT on 60-80-mesh Uniport HP. Nitrogen was used as the carrier gas at a constant flow-rate of 20 ml/min. The detector, injection port and column temperatures were maintained at 230, 230 and 170°C, respectively. The peak areas were measured with a Shimadzu Chromatopac E1A digital integrator.

Materials

All reagents were of analytical-reagent grade and were used without purification, except benzene and deionized water, which were distilled before use.

Stock cyanide solution

A 1.0 mg/ml solution of cyanide was prepared by dissolving 2.51 g of potassium cyanide in 1.0 l of distilled water. The solution was prepared immediately before the experiment and was standardized by titration with silver nitrate¹. A 10.0-ml volume of the solution was added to 100 ml of 2% (w/v) sodium hydroxide solution, and the mixture was diluted to 1.0 l. Subsequently, 10.0 ml of this alkaline solution was diluted to 100 ml with distilled water to give the stock cyanide solution (1.0 $\mu\text{g}/\text{ml}$). Standard solutions of various concentrations were prepared by diluting this stock cyanide solution.

Samples

Wastewater samples were collected from various factories using cyanide, such as metal refining and plating factories. Instantly after collection, sodium hydroxide was added to the samples, and the solution was adjusted to pH 12–13 in order to prevent the evolution of hydrogen cyanide. These samples were analysed after the distillation of hydrogen cyanide.

Procedure

Alkaline sample solutions or standard solutions of various concentration are neutralized with 1.0 *N* sulphuric acid before derivatization. The recommended procedure for the determination of cyanide in the neutralized solution is as follows, in which cyanide is derivatized under the optimum derivatization conditions (see Results and Discussion). To a 2.0-ml volume of the neutralized solution in a reaction vessel (*ca.* 10 ml) are added aqueous solutions of aniline ($6.0 \cdot 10^{-2}$ *M*, 2.0 ml), sodium nitrite ($2.5 \cdot 10^{-2}$ *M*, 0.5 ml) and copper(II) sulphate ($3.0 \cdot 10^{-1}$ *M*, 0.5 ml). The vessel is then allowed to stand for 20 min in a water-bath maintained at 80°C. At the end of the reaction period, 1.0 ml of benzene containing *p*-dichlorobenzene ($1.0 \cdot 10^{-3}$ or $1.5 \cdot 10^{-4}$ *M*) as an internal standard is added and the derivatized benzonitrile is extracted by shaking the vessel for 10 min at room temperature (*ca.* 18°C).

In the determination of cyanide at concentrations lower than 0.2 µg/ml, the concentration of the internal standard is $1.5 \cdot 10^{-4}$ *M*, whereas it is $1.0 \cdot 10^{-3}$ *M* in the determination of 0.05–1.0 µg/ml of cyanide (internal standard at both concentrations was used for 0.05–0.2 µg/ml of cyanide). The benzene layer is centrifuged if it contains an insoluble solid, which probably consists of azo coupling compounds produced as by-products. An aliquot (1.0 µl) of the clean benzene extract is injected into the gas chromatograph after washing with hydrochloric acid (2.0 *N*, 3.0 ml), and benzonitrile is determined with a flame thermionic detector.

RESULTS AND DISCUSSION

Optimum derivatization conditions

In order to perform the derivatization under the optimum derivatization conditions, we investigated the effects of reaction temperature, reaction time, pH and the concentration of each reagent on the derivatization of a 1.0 µg/ml cyanide solution. The results are shown in Figs. 1–3.

The highest derivatization yield is obtained at a reaction temperature of 80°C in only a few minutes (Fig. 1).

The effect of pH (Fig. 2) was examined as follows. To a 2.0-ml volume of an aqueous solution of cyanide, sodium hydroxide solution or sulphuric acid (0.20 ml) of different concentrations was added before derivatization. Fig. 2 shows that the derivatization proceeds with a constant yield as long as the reaction solution is neither strongly basic nor strongly acidic. Usually the sample solution is made strongly basic to prevent the evolution of hydrogen cyanide. Therefore, it is necessary to neutralize the basic solution before derivatization.

Fig. 3 shows the effect of the concentration of each reagent solution added to the sample. The yield becomes constant when the concentration is higher than $2.0 \cdot 10^{-2}$ *M* (aniline), $1.0 \cdot 10^{-1}$ *M* [copper(II) sulphate] or $9.0 \cdot 10^{-3}$ *M* (sodium nitrite).

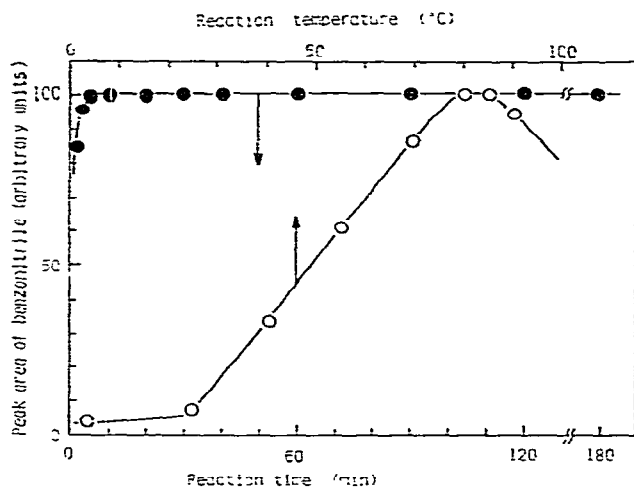


Fig. 1. Effects of reaction temperature (O) and reaction time at 80°C (●) on derivatization of cyanide (1.0 $\mu\text{g/ml}$).

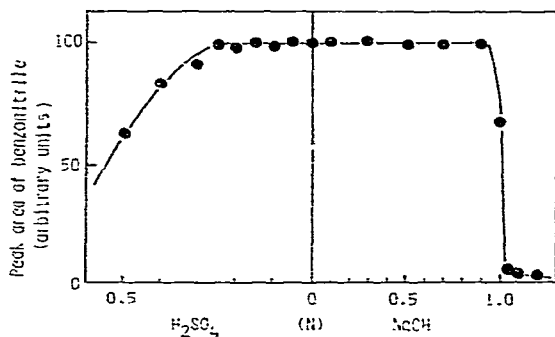


Fig. 2. Effect of normality of added acid or base on derivatization of cyanide (1.0 $\mu\text{g/ml}$).

From these results, the optimum derivatization conditions described in the Experimental section were chosen.

Calibration graph and derivatization yield

Calibration graphs were constructed by plotting the benzonitrile peak area against cyanide concentration. Good linearity was obtained in the concentration ranges 0.01–0.20 and 0.05–1.0 $\mu\text{g/ml}$ (Fig. 4), but the graphs did not pass through the origin, probably owing to the appearance of the reagent blank peak.

The detection limit was obtained as follows. A commonly accepted definition of the detection limit is the concentration of analyte giving a signal twice the average noise. However, the detection limit was not obtained according to this definition, because the peak of benzonitrile overlapped the small blank peak. Therefore, the mean value (M) and standard deviation ($S.D.$) of the blank peak area were obtained

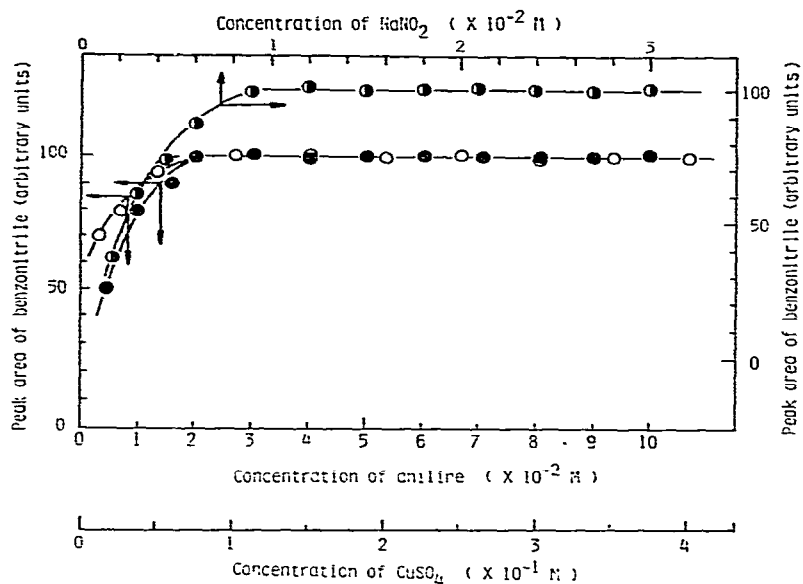


Fig. 3. Effects of concentrations of aniline (●), copper(II) sulphate (○) and sodium nitrite (●) on derivatization of cyanide (1.0 $\mu\text{g/ml}$).

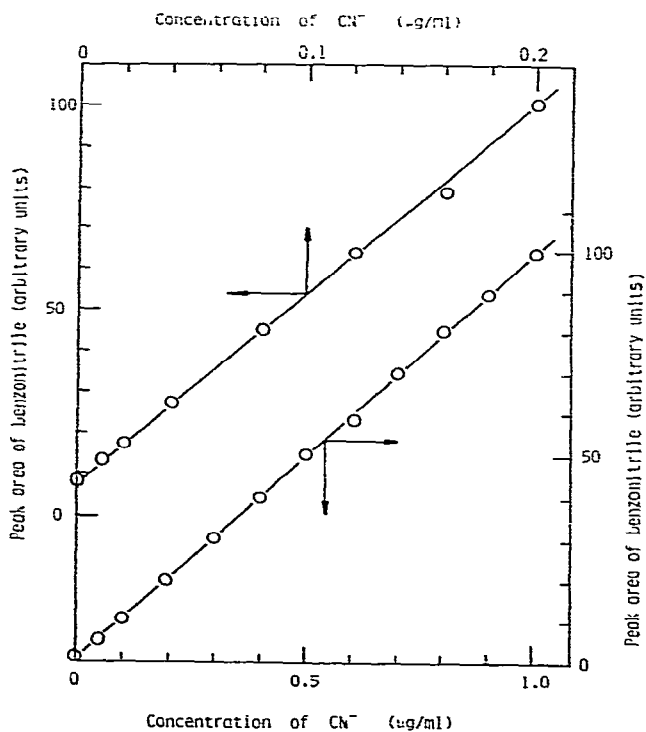


Fig. 4. Calibration graphs.

by performing five replicate analyses, and the detection limit was defined as the concentration of cyanide giving a peak area of $M + 3S.D.$ The detection limit measured in this way was 3 ng/ml, which is low compared with those of the pyridine-pyrazolone method (*ca.* 10 ng/ml) and of the method using a cyanide ion-selective electrode (*ca.* $1.0 \cdot 10^{-6} M = 26$ ng/ml).

The derivatization yield for cyanide was measured when cyanide was derivatized to benzonitrile under the optimum derivatization conditions described under Experimental. A yield of $71.5 \pm 1.8\%$ was obtained from five replicate measurements by derivatizing $2.0 \cdot 10^{-5} M$ (*ca.* 0.5 $\mu\text{g/ml}$) aqueous cyanide.

Interference study

The proposed method was tested in the presence of several ions normally found in environmental samples (Table I). The peak area of benzonitrile derivatized from the standard cyanide solution (0.5 $\mu\text{g/ml}$) was arbitrarily assigned a value of 100.

TABLE I
RESULTS OF INTERFERENCE STUDY

CN⁻ concentration: 0.50 $\mu\text{g ml}$.

<i>Ion</i>	<i>Concentration</i>	<i>Added as</i>	<i>Peak area*</i>
	<i>($\mu\text{g ml}$)</i>		
None			100.0 \pm 2.0
F ⁻	500	NaF	99.2 \pm 1.7
Cl ⁻	500	NaCl	99.4 \pm 0.2
Br ⁻	500	NaBr	100.2 \pm 1.8
I ⁻	500	KI	98.6 \pm 1.3
SO ₂ ²⁻	500	Na ₂ SO ₂	100.4 \pm 3.2
NO ₃ ⁻	500	NaNO ₃	100.8 \pm 2.5
HCO ₃ ⁻	500	KHCO ₃	99.9 \pm 1.9
H ₂ PO ₄ ⁻	500	KH ₂ PO ₄	99.4 \pm 0.8
SCN ⁻	500	NaSCN	86.0 \pm 2.1
SCN ⁻	100	NaSCN	99.0 \pm 3.0
CNO ⁻	500	KCNO	104.1 \pm 0.7
CNO ⁻	100	KCNO	102.8 \pm 1.7
S ²⁻	0.1	Na ₂ S · 9H ₂ O	90.9 \pm 4.6
S ²⁻	0.05	Na ₂ S · 9H ₂ O	100.2 \pm 2.3
NH ₄ ⁻	500	(NH ₄) ₂ SO ₄	101.8 \pm 1.7

* Mean \pm S.D. of five replicate analyses.

None of the ions except thiocyanate, cyanate and sulphide interfered at a concentration of 500 $\mu\text{g/ml}$. At this concentration, thiocyanate interferes negatively and cyanate positively. However, these interferences are not observed at the 100 $\mu\text{g/ml}$ level. In the Sandmeyer reaction, halides and thiocyanate react together with cyanide to form the corresponding phenyl halides and phenyl thiocyanate, respectively. Therefore, these anions seem to affect this derivatization of cyanide, but interferences due to these anions were not observed because of the low yield of the derivatization of halides and thiocyanate and the high selectivity of a flame thermionic detector towards nitrogen-containing compounds. Sulphide ion interferes at relatively low con-

centrations; even at $0.10 \mu\text{g/ml}$, a negative interference is observed. Similar interferences of sulphide are well known in the pyridine-pyrazolone method and in the method using a cyanide ion-selective electrode. However, sulphide can be removed from the sample solution by treating the alkaline sample at pH 11.0 with small amounts of powdered lead carbonate¹.

Applications

In order to investigate the applicability of the method to analyses of real samples, factory wastewater samples were analysed both by this GC method and by the pyridine-pyrazolone method. The results are shown in Table II, and Fig. 5 shows a typical gas chromatogram obtained in the analysis of one of the wastewater samples. Table II reveals that the values measured by the two methods agree well.

TABLE II
COMPARISON OF SPECTROPHOTOMETRIC AND GC METHODS FOR THE ANALYSIS OF WASTEWATER SAMPLES

Sample	Cyanide concentration ($\mu\text{g/ml}$)	
	Spectrophotometric method*	GC method**
A	0.48	0.51 ± 0.015
B	0.20	0.20 ± 0.006
C	0.13	0.16 ± 0.002
D	0.03	$0.03 \pm <0.0005$
E	0.08	0.09 ± 0.002

* Pyridine-pyrazolone method.

** Mean \pm S.D. of five replicate analyses.

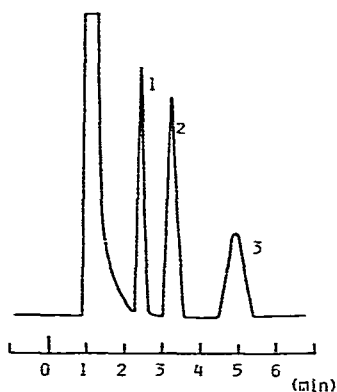


Fig. 5. Gas chromatogram obtained in the analysis of wastewater sample. Peaks: 1 = *p*-dichlorobenzene (internal standard); 2 = benzonitrile; 3 = aniline.

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