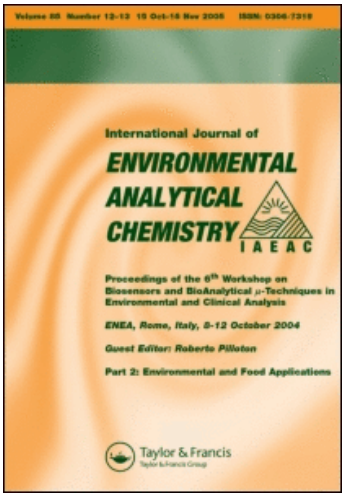

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Extractive Spectrophotometric Method for the Determination of Hydrogen Cyanide in Environmental Samples Using 4-Amino Salicylic Acid

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EXTRACTIVE SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF HYDROGEN CYANIDE IN ENVIRONMENTAL SAMPLES USING 4-AMINO SALICYLIC ACID

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A new spectrophotometric determination of the widely used fumigant hydrogen cyanide in air is described. The method is based on Konig reaction. The hydrogen cyanide from air is collected in a dilute solution of sodium hydroxide, brominated and reacted with pyridine to form glutaconic aldehyde. This is coupled with 4-aminosalicylic acid to form a yellow orange polymethine dye, which is extractable in *n*-butanol. The extracted dye shows an absorbance maximum at 520 nm. Beer's law is accomplished in the range of 0.03 to 0.2 mg l^{-1}. The application of the method for the analysis of hydrogen cyanide in cigarette smoke, cysteine and blood plasma is reported.

KEY WORDS: Hydrogen cyanide, air, spectrophotometry.

INTRODUCTION

Hydrocyanic acid, also known as hydrogen cyanide, finds its application as fumigant in ships, buildings and on citrus trees. It is also emitted as bye product from plastic industry, coal tar, in the manufacture of acrylonitrile, electroplating and coke ovens in steel plants. It is also present in cigarette smoke[1,2] and in some plants like peaches, apricots and plums[3].

Hydrogen cyanide is extremely toxic to warm blooded animals as it enters through skin and respiratory tract, resulting in irritation of throat, watering of eyes, salivation, headache and weakness of arms and legs. The threshold limit value for hydrogen cyanide is 10 $\mu g\ m^{-3}$ given by ACGIH[2,4].

Apart from the various instrumental methods[5–9] hydrogen cyanide is normally determined spectrophotometrically using the highly sensitive and selective Konig reaction[10,11].

In this paper an extractive spectrophotometric method is reported for the determination of hydrogen cyanide making use of Konig reaction and employing 4-aminosalicylic acid as coupling reagent. Solvent extraction has been applied here to develop a highly sensitive method for the determination of hydrogen cyanide in air, that can also be applied for the detection of hydrogen cyanide in cigarette smoke, cysteine and blood plasma.

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EXPERIMENTAL

Apparatus

A Carl Zeiss spekol spectrophotometer with 1 cm matched silica cell was used for all spectral measurements. Midget impingers of 35 ml capacity and a rotameter to check air flow were used.

Reagents

All chemicals used were of analytical reagent grade and were prepared in de-mineralised water.

Standard cyanide solution A 1 mg ml^{-1} of cyanide was prepared by dissolving 0.250 g of potassium cyanide in 100 ml of water. Working standard of 10 μg ml^{-1} was prepared by appropriate dilution of the stock.

Pyridine reagent 3 ml of concentrated hydrochloric acid and 18 ml of freshly distilled pyridine were mixed and diluted with 12 ml of de-mineralised water.

4-*Aminosalicylic acid* 1% (w/v) aqueous solution.

Tris-HCl buffer 0.2 M, pH 7.6, prepared by dissolving 0.60 g of tris(hydroxymethyl)aminomethane and 2.36 g of tris(hydroxymethyl)aminomethane hydrochloride in 100 ml of water.

Cysteine solution Prepared by placing 50 mg of L-cysteine hydrochloride monohydrate in a test tube, after which one drop of bromocresol green indicator solution was added. NaOH (0.5 M) was added dropwise until all the cysteine was dissolved. Tris-HCl buffer (10 ml) was added to neutralise the cysteine and thoroughly mixed. The pH of the solution should be 7.4.

Sodium arsenite 1.5% (w/v) aqueous sodium arsenite solution. Saturated bromine water, 5 M sulphuric acid, 6 M sodium hydroxide.

Procedure

A controlled amount of hydrogen cyanide vapours was generated by the dropwise addition of potassium cyanide solution containing 100 μg ml^{-1} of cyanide to 5 ml of 5 M sulphuric acid taken in a midget impinger at different time intervals. The flask was connected to two impingers each containing 10 ml of absorbing solution and connected in series to the source of suction. Hydrogen cyanide generated in air was passed through the impingers at a flow rate of 1 l min^{-1} for 30 minutes. After sampling, pure air was passed through the impingers for 5 minutes to sweep the residual vapours.

Analysis in aqueous medium

After sampling, aliquots of the absorbed solution were transferred into 10 ml volumetric flasks. Bromine water (0.3 ml) was added to the flasks and kept for 2 minutes for complete bormination. The excess of bromine was then destroyed by dropwise addition of sodium arsenite solution. Then, 0.4 ml of freshly prepared pyridine reagent followed by 2 ml of 1% 4-aminosalicylic acid were added, thoroughly shaken and kept for 5 minutes. A few drops of 6 M sodium hydroxide were added for colour development and made up to the mark with demineralised water (final pH ~ 8). The absorbance was measured at 400 nm using de-mineralised water as reference. The blank gave no colour under these conditions.

Extraction with organic solvents

In order to enhance the sensitivity of the method, some organic solvents were tried for the extraction of the dye from the aqueous medium. For this purpose, 100 ml of sample containing 3 to 20 μg of hydrogen cyanide (0.03 to 0.2 mg l^{-1}) were taken in a separatory funnel and the procedure of the aqueous medium was followed to obtain the dye. The dye was extracted in acidic medium with *n*-butanol. The *n*-butanol extract was dried over anhydrous sodium sulphate and the absorbance was measured at 520 nm against *n*-butanol as reference.

RESULTS AND DISCUSSION

Generation of hydrogen cyanide

Hydrogen cyanide was quantitatively generated by the reaction of sulphuric acid with potassium cyanide. The liberated hydrogen cyanide was trapped in 0.002 M solution of sodium hydroxide (Table 1A) by passing purified air through the solution at a rate of 1 l min^{-1} (Table 1B). Sampling was carried out for 30 minutes (Table 1C). The absorbing solution was then neutralised with 1 to 2 drops of 3 M hydrochloric acid and then determined by the proposed procedure. The generation of hydrogen cyanide was quantitative.

Effect of varying reaction conditions

A minimum of 0.3 ml of saturated bromine water was needed for complete bromination of cyanide to cyanogen bromide (Figure 1). The amount of pyridine reagent needed for conversion of cyanogen bromide into glutaconic aldehyde was also checked. A minimum of 0.4 ml of pyridine reagent was needed for the reaction. There was practically no change in absorbance value by the addition of 1–6 ml of 1% 4-aminosalicylic acid (Figure 1).

The effect of time and temperature on colour development were studied and it was found that 5 minutes were needed for full colour development and the colour remained stable for 45 minutes. A variation of the temperature between 15–30°C had no adverse effect on the final absorbance values.

Table 1a Effect of concentration of sodium hydroxide on absorption efficiency

(*Flow rate* = 1 *l min*$^{-1}$; *Sampling time* = 30 *minutes*)

Concentration of sodium hydroxide (M)	*Equivalent of hydrogen cyanide liberated added as KCN (μg)*	*Amount of hydrogen cyanide liberated (μg)*	*% Absorption*
0.001	10	9.85	98.5
	20	19.64	98.2
	30	29.46	98.2
0.002	10	9.98	99.8
	20	20.00	100.0
	30	29.94	99.8
0.008	10	9.95	99.5
	20	19.80	99.0
	30	29.91	99.7
0.01	10	9.95	99.5
	20	19.96	99.8
	30	29.91	99.7
0.1	10	9.98	99.8
	20	19.92	99.6
	30	29.55	98.6

Table 1b Effect of flow rate on absorbing efficiency
(Concentration of NaOH = 0.002 M; Sampling time = 30 minutes)

Equivalent of hydrogen cyanide added as NaCN (μg)	*Flow rate (l min*$^{-1}$)							
	0.25		0.50		1.0		2.0	
	*a**	*b**	*a**	*b**	*a**	*b**	*a**	*b**
10	9.92	99.2	9.9	99.0	10.0	100.0	9.84	98.4
20	19.8	99.0	19.9	99.5	19.9	99.8	19.4	97.8
30	29.7	99.1	29.8	99.3	29.9	99.8	29.4	98.0

Table 1c Effect of time on absorption efficiency
(Flow rate = 1 l min^{-1}; Concentration of NaOH = 0.002 M)

Equivalent of hydrogen cyanide added as KCN (μg)	*Sampling time (in minutes)*									
	10		15		20		30		40	
	*a**	*b**	*a**	*b**	*a**	*b**	*a**	*b**	*a**	*b**
10	9.72	97.2	9.95	99.5	9.97	99.7	9.98	99.8	9.35	93.5
20	19.50	97.5	19.9	99.8	19.9	99.8	20.0	100.0	18.8	94.0
30	29.4	98.0	29.9	98.8	30.0	100.0	29.9	99.8	28.2	94.1

a*—amount of hydrogen cyanide found (μg); b*—% absorbed.

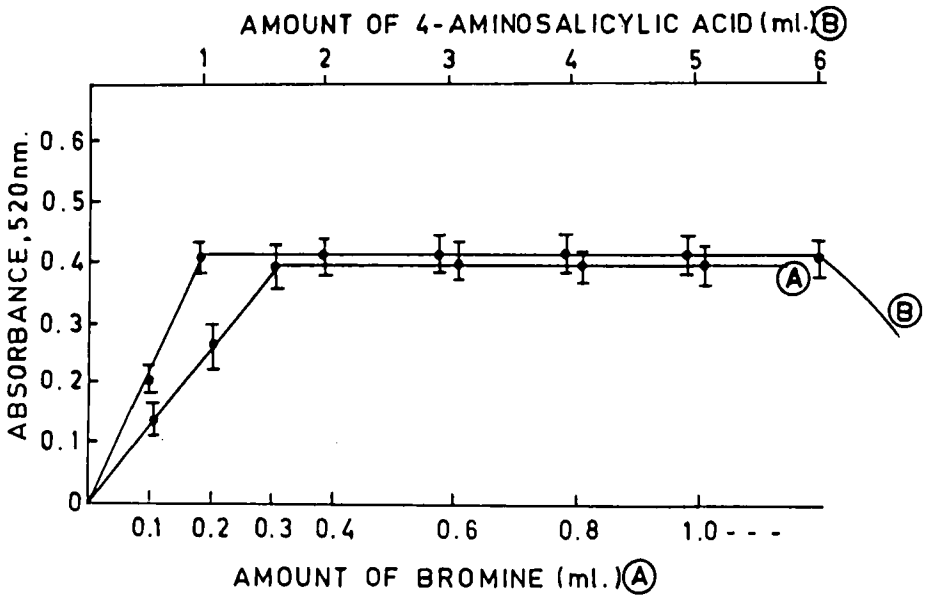

Figure 1 Effect of amount of bromine and 4-amino salicylic acid on colour reaction. Concentration of hydrogen cyanide = 10 μg 100 ml^{-1} (as cyanide).

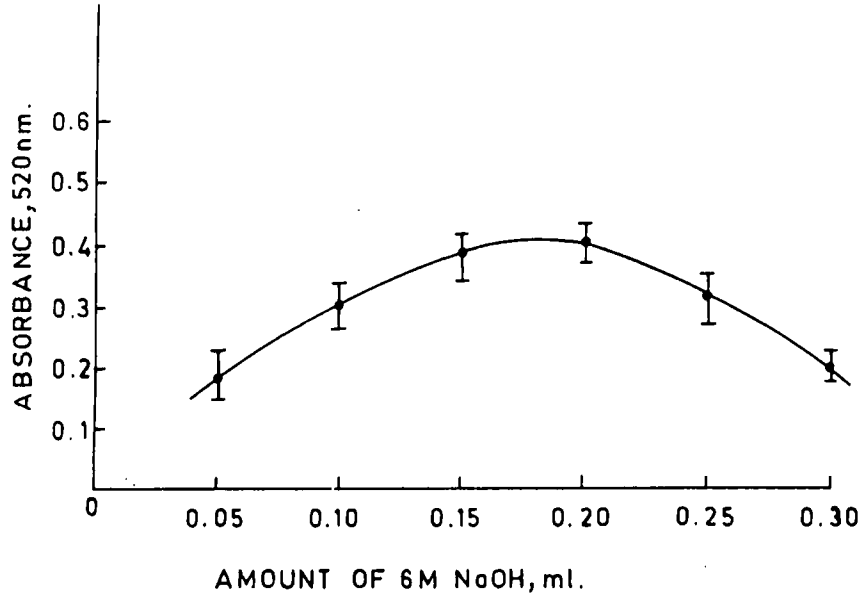

Figure 2 Effect of amount of alkali on colour reaction. Concentration of hydrogen cyanide = 10 μg 100 ml^{-1} (as cyanide).

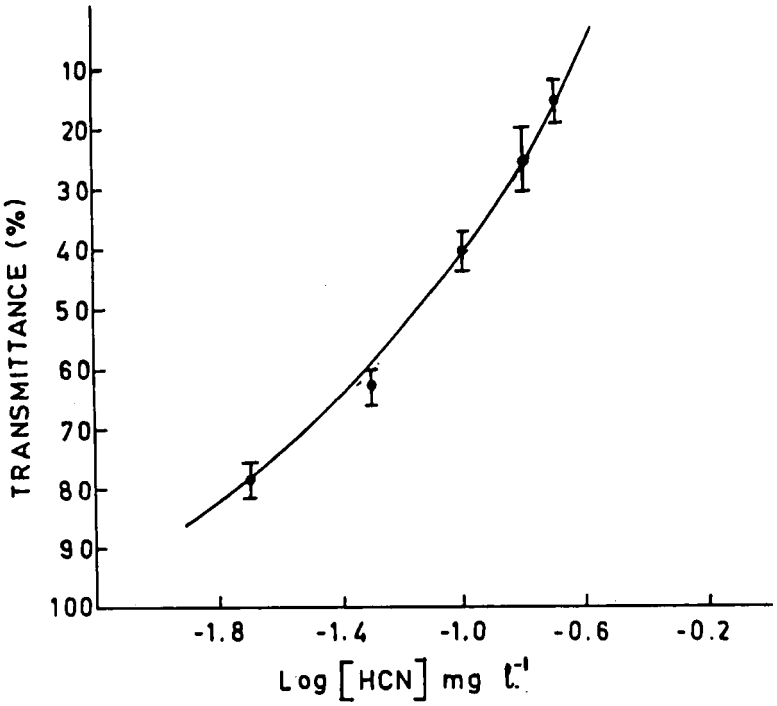

Figure 3 Ringbom's plot to determine the effective photometric range of hydrogen cyanide hydrogen cyanide concentration = 0.03–0.2 mg l^{-1} λ_{max} – 520 nm.

The effect of alkali was studied and it was found that 0.2 ml of 6 M NaOH (pH ~ 8) was needed for colour development (Figure 2). With increase of alkali and in acidic medium there was a decrease in absorbance values.

Beer's law and Sandell's sensitivity

Beer's law was accomplished in the range of 0.4 to 4 mg l^{-1} in the aqueous medium and 0.03 to 0.2 mg l^{-1} in *n*-butanol extract. Ringbom's curve[19] was also drawn by plotting the percentage of transmittance against the log concentration of hydrogen cyanide (Figure 3), to evaluate the optimum photometric range and analytical accuracy. The molar's absorptivity and Sandell's sensitivity were found to be 5.8×10^3 (± 100) l mol^{-1} cm^{-1} and 0.004 μg cm^{-2} in the aqueous medium and after extraction these were 12.3×10^4 (± 100) l mol^{-1} cm^{-1} and 0.00022 μg cm^{-2} respectively.

Reproducibility of the method

The reproducibility of the method was checked by replicated analysis of hydrogen cyanide over a period of 7 days. The standard and relative standard deviations were found to be ± 0.012 and $\pm 2.64\%$ for the samples, containing 10 μg cyanide.

Table 2 Effect of foreign species
(Concentration of hydrogen cyanide = 10 μg)

*Foreign ions (tolerance limit in μg)**
Ni^{2+} (20,000), Pb^{2+}, K^{+}, Cd^{2+}, (10,000). Ca^{2+}, Mg^{2+} (5,000)
F^{-}, Cl^{-} (1,000), Zn^{2+}, Se^{4+} (500), Fe^{2+} (250), Cr^{3+} (200)
Benzene (2,000), *m*-Dinitrobenzene, Phenol (1,000)
Aniline (200), Ammonia (15), Thiocyanate (+ve interference)

* Amount of foreign species that caused ±2% error.

Effect of foreign species

Organic pollutant viz., benzene, phenol, aniline, m-dinitrobenzene, benzaldehyde and metal ions such as zinc, cadmium, lead, mercury, chromium do not interfere. Oxidising and reducing agents, if present in small amounts, are removed by sodium arsenite and bromine water, respectively, and hence do not interfere. Other gases present in normal air also do not interfere. The tolerance limits are shown in Table 2.

Effect of solvents on extraction

Various solvents were selected for the extraction of the polymethine dye (Table 3). *n*-Butanol was found to be best as it gave maximum absorbance, better stability and quantitative results.

It was also found that solvent extraction was accomplished only in acidic medium. The optimum results were obtained by addition of 10 ml of 6M HCl to the sample, before extraction, was found to be best (approx. 0.5 M HCl final solution). Acidity higher and lower than this resulted in lower absorbance values (Figure 4).

Applications of the method

Determination of hydrogen cyanide in cigarette smoke:

Various brands of cigarettes were used for detection of hydrogen cyanide in cigarette smoke. Cigarettes were attached to an air sampling train. The cigarettes were lit and the smoke was drawn through dilute sodium hydroxide solution taken

Table 3 Effect of various solvents on extraction

Solvent used	λ_{max}, *nm*		*Optical density*
Water	400		0.30
iso-Pentanol	520		0.39
n-Hexanol		No extraction	
Methyl butanol	520		0.42
n-Butanol	520		0.45
Chloroform		Incomplete extraction	

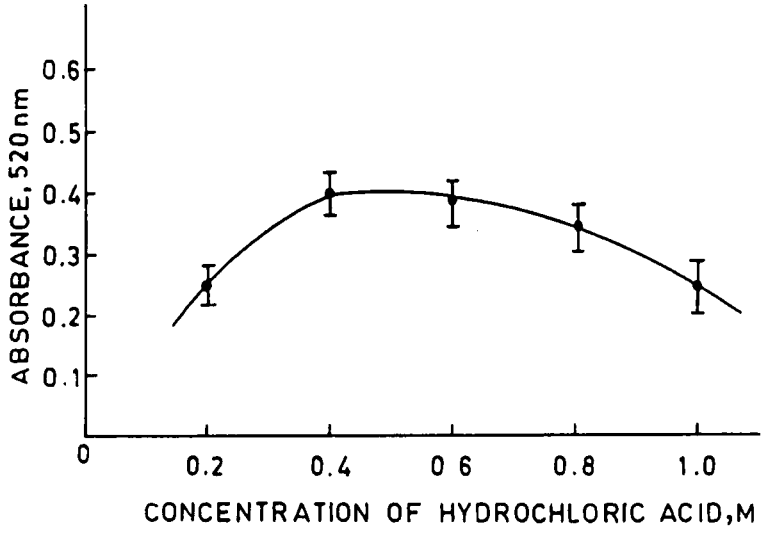

Figure 4 Effect of acidity on extraction Concentration of hydrogen cyanide = 10 μg 100 ml^{-1} (as cyanide).

in two impingers connected in series to a sampling train attached to a source of suction at a flow rate of 0.25 to 0.5 l min^{-1} for 15–30 minutes. The solutions were then analysed both by the present method and a previously reported method[12,13]. The results obtained were in good agreement (Table 4). Amounts ranging from 6 to 15 μg of hydrogen cyanide were found in each cigarette by this method.

Table 4 Determination of hydrogen cyanide in real samples

	Method I Proposed Method (*mg l*$^{-1}$)*	*Method II Aldridge's Method* (12) (*mg l*$^{-1}$)
A. *Cigarette smoke*:		
C_1	6.20	6.19
C_2	6.50	6.50
C_3	6.76	6.77
C_4	10.00	10.15
B. *In air***:		
S_1	10.40	10.50
S_2	12.40	12.40
S_3	19.10	19.00
S_4	25.30	25.50

* Mean of three repetitive analyses.
** Synthetic samples were prepared in laboratory by evaporating cyanide solution in fuming cupboards.

Table 5 Recovery of hydrogen cyanide from cysteine and blood plasma

Sample	*Amount of HCN added as cyanide μg*	*HCN found* (Present method) μg*	*Recovery %*	*HCN found* (Sulphanilic acid method) μg*	*Recovery %*
Cysteine	8	7.20	90.00	7.60	95.00
(3 ml)	15	14.70	98.00	14.90	99.30
	25	24.50	98.00	25.00	100.00
	30	29.40	98.00	29.50	98.30
Blood pasma	5	4.90	98.00	4.95	99.00
(1 ml)	15	14.80	98.60	14.75	98.30
	20	19.95	99.80	19.85	99.20
	35	34.90	99.70	34.90	99.70

* Mean of three repetitive determination

Determination of hydrogen cyanide in air:

Hydrogen cyanide was generated in a fume cupboard by gradual addition of sulphuric acid to a solution of potassium cyanide. The air from the fume cupboard was trapped in sodium hydroxide solution with the help of suction pump placed outside the chamber. The air was sampled for 30 minutes and then solution was analysed by the recommended procedure and compared with the standard benzidine method given by Aldridge[14]. The results obtained by both the methods were found to be almost identical (Table 4).

Determination of hydrogen cyanide in cysteine and blood plasma:

The method has been applied for the determination of cyanide in cysteine and blood plasma samples. It has been reported that cysteine reacts with cyanide in the body and helps in the detoxification of cyanide. Hence the determination of cyanide in cysteine is important from the biological point of view. A known amount of cyanide was added to 3 ml of cysteine solution and clean air was passed through the solution.

Table 6 Comparison of the spectrophotometric methods reported for hydrogen cyanide

Reagents	*λ_{max}, nm*	*Determination range (mg l^{-1})*	*Remarks*	*Reference*
1. Benzidine	524	0–20	Benzidine is carcinogenic	16
2. *p*-Phenylenediamine	515	0.005–100	*p*-Phenylenediamine is carcinogenic	17
3. Anthranilic acid	400	0.4–4	Less sensitive	14
4. Sulphanilic acid	460	0.08–0.75	Stability is 25 minutes	18
5. 4-Aminosalicylic acid	520	0.03–0.2	More sensitive More stable (45 minutes)	Present method

The liberated hydrogen cyanide was absorbed in 0.002 M sodium hydroxide solution and determined by the proposed procedure. The results in Table 5 shows 90–98% recovery of hydrogen cyanide from cysteine solution which is in agreement with the results of the sulphanilic acid method[18].

To determine the recovery of cyanide from blood known amounts of cyanide were added to blood plasma and cyanide was determined by the proposed method with excellent recoveries (>98%). The results are given in Table 5.

CONCLUSION

The proposed method for the determination of cyanide is fast and simple. No use of carcinogenic reagents is made and it can be applied to detect hydrogen cyanide in air, cigarette smoke and biological samples. The sensitivity of the method is comparable to most of the other reported colorimetric methods (Table 6).

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