

## 여러 가지 시료 중에 p-Aminoacetanilide를 사용하여 Cyanide와 Hydrogen Cyanide 흔적량의 신속한 분광광도법 측정

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### Rapid Spectrophotometric Determination of Trace Amounts of Cyanide and Hydrogen Cyanide Using p-Aminoacetanilide in Various Samples

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#### INTRODUCTION

A highly toxic substance, cyanide is widely used for the extraction of metals in electroplating industry, for surface treatments and in the production of various resin monomers. Major sources of cyanide in addition to those from the above mentioned industries include, exhaust from vehicle emissions and cigarette smoke.<sup>1</sup> Typical signs of acute cyanide poisoning include tachypnoea, headache, vertigo, lack of motor coordination, weak pulse, cardiac arrhythmias, vomiting, stupor, convulsions, eye irritation coma and death.<sup>2</sup>

Hydrogen cyanide is reported to be present in cigarette smoke, the concentration of which varies according to the variety of the cigarette. A cigarette without filter is reported to liberate 500 µg of hydrogen cyanide while filtered cigarettes liberate only 100 µg.<sup>3-4</sup> Cyanide is well absorbed *via* gastrointestinal tract or skin and rapidly absorbed *via* respiratory tract. Once absorbed, cyanide is rapidly and ubiquitously distributed throughout the body, although the highest level is typically found in liver, lungs, blood and brain.<sup>5</sup> The lethal dose for human beings normally varies between 0.5 to 3.5 mg/kg of body weight.<sup>6</sup>

Due to its highly toxic nature, a method for its determination has been an area of interest for analytical chemists. Several methods have been developed for the determination of cyanide, which include HPLC,<sup>7</sup> GC-MS,<sup>8</sup> capillary electrophoresis,<sup>9</sup> photometry,<sup>10</sup> electrochemical sensor,<sup>11</sup> ion chromatography,<sup>12</sup> chromatography,<sup>13</sup> indirect determination by atomic absorption

spectrometry,<sup>14</sup> electrochemical method,<sup>15</sup> spectrofluorimetry,<sup>16</sup> and spectrophotometry.<sup>17-21</sup>

In this communication, a spectrophotometric method has been proposed which is based on the earlier reported method of conversion of cyanide to cyanogen chloride by chloramine-T.<sup>22</sup> Cyanogen chloride thus produced is reacted with pyridine to form an additional product which subsequently condenses with p-aminoacetanilide to form a coloured product measurable at 485 nm. Although a number of spectrophotometric methods have been reported for the determination of cyanide, the most of them use bromine water which is toxic in nature, few of the reported method use benzidine and other amino like p-phenylene diamine, compounds for coupling which are carcinogenic (Table 4). Both these drawbacks are removed by using chloramine-T and p-aminoacetanilide.

#### EXPERIMENTAL

##### Apparatus and reagents

A Toshniwal model TVSP 25 spectrophotometer was used for spectral measurements. pH measurements were made with systronics pH meter model 331. Fritted midget impingers (diameter~10 mm) of 35 mL capacity were used for air sampling. Flow rate adjustable calibrated rotameters were used for measuring the air flow. All chemicals used in this work were of analytical grade, double distilled water was used throughout.

Cyanide stock (Merck) -1 mg mL<sup>-1</sup> stock solution of cyanide

was prepared by dissolving 250 mg of potassium cyanide in 100 mL<sup>-1</sup> water. Working standards were prepared from this stock by appropriate dilution. Pyridine reagent –3 mL of concentrated hydrochloric acid was mixed with 18 mL of pyridine (Merck) and 12 mL of water followed by addition of 30 mL of 0.5% aqueous solution of p-aminoacetanilide (Merck). Chloramine-T (Merck) –0.03% (w/v) chloramine-T solution was prepared by dissolving 0.03 g chloramine-T in distilled water and diluting it to the mark in a 100 mL volumetric flask. Stock Solution of fenvalerate Pesticide (Northern Mineral Limited, India) 1 mg mL<sup>-1</sup> was prepared in ethanol. Working standards were prepared by appropriate dilution of the stock. Sodium hydroxide solution (Loba chemie, Mumbai) 2 M aqueous solution was prepared.

### Procedure

**Preparation of calibration curve:** To an aliquot of an aqueous solution containing 0.4 ~ 5.0 µg of cyanide was taken in a 25 mL graduated test tube series. To it 1 mL of pyridine-p-aminoacetanilide reagent was added followed by addition of 1 mL of chloramine-T and reaction condition thermostated at 30 °C. The solution was diluted with double distilled water and allowed to stand for 2 ~ 3 min for complete colour development. The absorption of the standard solution of the cyanide with different concentrations was recorded at 485 nm against reagent blank.

**Determination of hydrogen cyanide in air samples:** Contaminated air of nearby location of steel plant was drawn into two midjet impingers, each containing 10 mL of 0.1 M NaOH solution connected to a source of suction in the environment at a flow rate of 0.25 L min<sup>-1</sup> for 15 min. After sampling, aliquots of the absorbing solution were analyzed as described above and the results confirmed by a reported method<sup>20</sup> (Table 3).

**Determination of cyanide in pesticide:** Stock solution of fenvalerate pesticide (Northern mineral limited, India) 1 mg mL<sup>-1</sup> was prepared in ethanol. Working standards were prepared by appropriate dilution of the stock. To known amount of pesticide taken separately in a series of 25 mL graduate test tube, 1.0 mL of 2 M sodium hydroxide solution was added and allowed to stand for complete hydrolysis. After 5 min, 1 mL of 2 M hydrochloric acid, 1 mL of pyridine-p-aminoacetanilide reagent and 1 mL of chloramine-T were added in sequence. The solution was kept for 5 min for complete colour development. The resulting orange red dye was made up to the mark and measured at 485 nm against a reagent blank that gave negligible absorbance at this wavelength (Table 3).

**Coke oven effluents:** In coke oven effluent, 1 mL of pyridine-p-aminoacetanilide reagent and 1 mL of chloramine-T were added. The solution stand for 5 min, resulting orange red dye was made up to the mark and measured at 485 nm against a

reagent blank that gave negligible absorbance at this wavelength (Table 3).

## RESULT AND DISCUSSION

### Absorption spectra

Final colored product is stable for 30 min and shows maximum absorbance at 485 nm (Fig. 1) where as the reagent blank has negligible absorbance at this wave length. Linear range is obeyed over the concentration range of 0.016 to 0.2 µg mL<sup>-1</sup> of cyanide. The molar absorptivity and Sandell's sensitivity are  $9.63 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> and 0.0003 µg cm<sup>-2</sup> respectively. The slope, intercept, and the correlation coefficient evaluated by least squares regression analysis are also included (Table 1).

### Effect of reagent concentration

Effects of reagent concentration on the absorbance value were evaluated. It was found that 1 mL of chloramines-T (0.03%) and 1 mL of pyridine-p-aminoacetanilide reagent was required for complete colour development.

Table 1. Spectral characteristics, precision and accuracy of the presented method

Parameter	Results
$\lambda_{\max}$ (nm)	485
Limit of Beer's law (µg mL <sup>-1</sup> )	0.016 to 0.2
Molar absorptivity (L mol <sup>-1</sup> cm <sup>-1</sup> )	$9.63 \times 10^4$
Limit of detection (µg mL <sup>-1</sup> )	0.0011
Limit of quantification (µg mL <sup>-1</sup> )	0.0034
Sandell's sensitivity (µg cm <sup>-2</sup> )	0.0003
Standard deviation (±)	0.0015
Relative standard deviation (%)	0.23
Regression equation (Y = bx + a)*	
Correlation coefficient	0.9999
Slope b	4.57
Intercept a	0.0114

(Y = bx + a), x is the concentration in µg mL<sup>-1</sup>, \*\*n = 6.

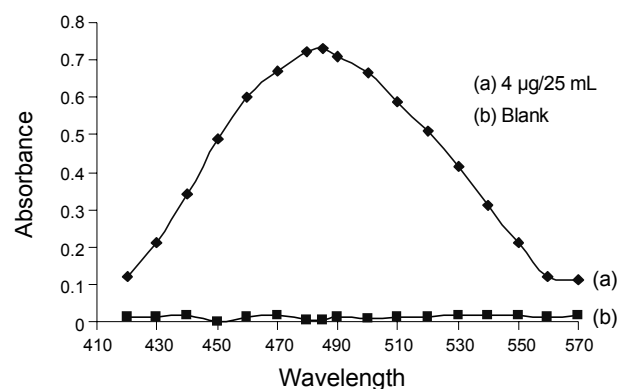


Fig. 1. Absorption spectra of the dye.

Table 2. Effect of diverse ions (concentration of Cyanide 0.5  $\mu\text{g}$  25  $\text{mL}^{-1}$ )

Foreign species	<sup>a</sup> Tolerance level ( $\mu\text{g mL}^{-1}$ )	Foreign species	Tolerance level ( $\mu\text{g mL}^{-1}$ )
$\text{Al}^{3+}$ , $\text{Fe}^{3+}$	250	Formaldehyde	10
$\text{Mn}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Co}^{2+}$	450	Ammonia	100
$\text{Ca}^{2+}$ , $\text{Mg}^{2+}$	500	Toluene	700
$\text{Hg}^{2+}$ , $\text{Pb}^{2+}$	100	Ethanol	950
$\text{SO}_3^{2-}$ , $\text{Cl}^-$ , $\text{IO}_4^-$	150	Aniline	800
$\text{S}^{2-}$	10	Carbonate	500

<sup>a</sup>The amount causing an error of  $\pm 2\%$  in absorbance value.

Table 3. results of analysis of different samples

<sup>b</sup> Air Sample	<sup>a</sup> Cyanide found, in $\text{mg/m}^3$	
	Present method	Reported method <sup>20</sup>
A	3.90	3.80
B	5.50	5.45
C	3.50	3.30

<sup>c</sup> Sample	Cyanide originally found ( $\mu\text{g}$ )	Total cyanide found ( $\mu\text{g}$ ) <sup>a</sup>	
		Present method	Reported method <sup>20</sup>
(A)	4.5	4.5	4.4
(B)	1.0	0.9	0.9
(C)	2.0	1.6	1.5

<sup>d</sup> Sample (5 mL)	Cyanide found, in $\text{ppm}$ <sup>a</sup>	
	Present method	Reported method <sup>20</sup>
A	0.11	0.10
B	0.19	0.17
C	0.31	0.30

<sup>a</sup>Mean of three replicate analysis. <sup>b</sup>Result of analysis of Plant Air. <sup>c</sup>Results of analysis of pesticide. <sup>d</sup>Result of analysis of coke oven effluents.

Table 4. Comparison with other spectrophotometric method

Reagents	$\lambda_{\text{max}}$	Range	Remark
p-aminobenzoic acid <sup>20</sup>	410	0.02 - 0.2	Extractive and less sensitive
J- Acid <sup>23</sup>	400	0.02 - 0.2	Less sensitive
Sulphanilic acid <sup>24</sup>	460	0.5 - 3	Less sensitive, toxic $\text{Br}_2$ water used
Anthranilic acid <sup>25</sup>	400	1 - 7	Non-toxic but less sensitive
Benzidine <sup>26</sup>	520	0.1 - 20	Carcinogenic reagent
Ninhydrin <sup>27</sup>	590	0.04 - 0.24	Less sensitive
Phloroglucinol <sup>28</sup>	540	0.4 - 3.4	Less sensitive
Aquacyanocobyrinic acid heptamethyl ester <sup>29</sup>	580	0.04 - 1.20	Less sensitive
p-phenylene diamine <sup>30</sup>	515	0.005 - 100	Carcinogenic reagent
p-aminoacetanilide (proposed method)	485	0.016 - 0.2	More sensitive

### Effect of temperature, time and pH

Optimum results were obtained when the pH of the final solution was between 5.0 ~ 5.5. Above this pH range decrease in the absorbance was observed and dye too became unstable. It was found that temperature range of 10 ~ 30  $^{\circ}\text{C}$  had no adverse effect on the colour development. The colour development was completed within 5 min after addition of the reagent and the colour remained stable for 30 min.

### Reproducibility

Reproducibility of the method was checked by 6 replicate analysis of the cyanide solution containing 0.3  $\mu\text{g}$  of cyanide in 25 mL final solution. The standard deviation and relative standard deviation were found to be  $\pm 0.0015$  and 0.26% respectively.

### Effect of foreign species

The possibilities of interference from ions, which generally co-exist with cyanide, were studied by adding known amounts of different organic pollutants and inorganic ions to the test solution containing a total amount of 4  $\mu\text{g}$  of cyanide per 25 mL of final volume. Interference from  $\text{NO}_2^-$  and  $\text{NO}_3^-$  was removed up to 100  $\mu\text{g mL}^{-1}$  by addition of 0.2% sulfamic acid. Interference from various organic pollutants and metal ions was not found. Masking of ions with EDTA solution increases the tolerance limit to a considerable extent. Thiocyanite shows positive interference since it also forms cyanogens chloride when treated with chloramines-T. The tolerance limit of various interferents is shown in Table 2.

**Application.** Previously, sample of industrial air, pesticides and coke oven effluent were analyzed by the recommended assay. The results of the determinations were in good agreement with those made with a well known spectrophotometric method.<sup>20</sup>

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