Spectrophotometric Determination of Cyanide and Hydrogen Cyanide Using *p*-Aminobenzoic Acid as a New Reagent and Its Application in Steel Industries

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A new reagent system is proposed for the determination of cyanide and hydrogen cyanide. Cyanide is reacted with bromine and pyridine to form glutaconic aldehyde, which is then condensed with *p*-aminobenzoic acid to give a yellow orange dye extractable in *n*-butanol. Beer's law is obeyed over a concentration range of 0.02–0.2 ppm of cyanide at 410 nm. The molar absorptivity and Sandell's sensitivity were found to be 1.3×10^4 L mol^{-1}cm^{-1}, and 0.002 µg cm^{-1} respectively. The analytical parameters have been optimised and applied for the determination of cyanide in industrial effluent and air. The method has been favourably compared with ion selective electrode and other methods normally used in steel industries and found to be sensitive and specfic.

INTRODUCTION

Cyanides are extremely toxic chemicals extensively employed by several industries. They enter into the environment through various industries like electroplating, extraction of precious metals, chemicals, plastics, resins, fertilisers and combustion of coal. In steel industries considerable amount of cyanide is liberated in coke oven and blast furnace operations due to combustion of coal[1] in absence of air. Small amounts of cyanide (0.1–0.5 ppm) are also present in the effluents of coke oven battery.[2] Cyanide salts and aerosols can cause upper respiratory irritation, enlargement of the thyroid glands, anoxia, eye irritation, and giddiness.[3, 4] The current permissible exposure limit value for cyanide is 5 mg/ m^3. Water containing cyanide above 0.01 ppm is unfit for drinking as per WHO guidelines.[5] The lethal dose for human beings normally varies between 0.5 to 3.5 mg per kg of body weight.[6] Looking to the toxicology of cyanide there is a prime need to control the emission of cyanide from steel industries by means of regular monitoring and implementation of adequate control measures. Large number of methods have been reported for the determination of cyanide. Popular instrumental methods are amperometric,[7] coulometric,[8] polarographic,[9] potentiometric,[10] atomic absorption spectrophotometric,[11] and ion selective electrode.[12] Owing to simplicity and ease of application spectrophotometric methods are much more popular than others. Most of them are based on complex formation reactions and Konig reaction,[13] using various reagents. Though many of the methods are quite sensitive, methods using reagents like benzidine, phenylene diamine are not advisable because of the associated hazards. To overcome many of the defects with the above reagents a new reagent *p*-aminobenzoic acid is proposed as a

simple, sensitive and selective reagent for the analysis of cyanide based on Konig reaction. In the proposed method cyanide is reacted with bromine and pyridine to form glutaconic aldehyde, which is then condensed with *p*-aminobenzoic acid to form a yellow dye, extractable in *n*-butanol. Beer's law is obeyed in the range of 0.02–0.2 ppm of cyanide at 410 nm. The standard deviation for 7 replicate measurements for 0.08 ppm of cyanide was ± 0.03 absorbance units. The method is simple and it has been applied for the determination of cyanide in coke oven effluents and hydrogen cyanide in ambient air of steel plant area, and also compared with the ion selective electrode and other methods normally used in steel plants for estimation of cyanides. Results are reported in Table-2.

TABLE-1
RESULTS OF ANALYSIS: COKE OVEN EFFLUENTS

Sample (5 mL)	Cyanide found(µg/L)	
	Present method	Ion selective electrode method
A	0.19*	0.22*
B	0.21	0.20
C	0.23	0.25
D	0.18	0.16
E	0.30	0.27

*Means of three replicate analysis

TABLE-2
RESULT OF ANALYSIS—STEEL PLANT AIR

Air samples	Cyanide found (mg/m^3)	
	Coke oven	Blast furnace
(a) Present method	3.88^a	1.55^a
	5.90	1.91
	3.75	2.0
(b) Drager tube method	4.0^b	1.50^b
	6.0	2.0
	4.0	2.10

* Results of three replicate analysis:
  (a) Sampled volume 1 ltr.   (b) Sampled volume 1 ltr.

EXPERIMENTAL

A Carl Zeiss spekol with 10 mm optically matched silica cells was used for all spectrophotometric measurements. 35 mL midget impingers, and Pimco make calibrated rotameters were used for air sampling. A Systronics pH meter model no. 331 was used to measure the pH. Orion ion selective electrode and

Drager multi-gas detector for detection of cyanide in water and air, were also used.

All chemicals used were AnalaR grade or the best quality available. Double distilled deionised water was used throughout.

Cyanide stock: 1 mg mL^{-1} stock solution of cyanide was prepared by dissolving 250 mg of potassium cyanide in 100 mL water. Working standard was prepared from this stock by appropriate dilution.

Pyridine reagent: 3 mL of concentrated HCl was mixed with 18 mL of pyridine and 12 mL of water was added to it.

Bromine water: Saturated solution of bromine in water.

p-Aminobenzoic acid (PABA): 1% (m/v) aqueous solution.

Procedure

Preparation of calibration curve: To an aliquot of sample (100 mL) containing cyanide in the range of 2–20 μg, 0.5 mL of bromine water was added and shaken for 2 min. The excess of bromine was removed by adding 2–3 drops of sodium arsenite solution. Then 0.5 mL pyridine, 2 mL of each PABA and 6 M sodium hydroxide solution were added and allowed to stand for 5 min, for complete colour development. Then 5 mL of *n*-butanol were added to the flask and shaken thoroughly. Butanol extract was then separated and dried over anhydrous sodium sulphate. The absorbance of dye was measured at 410 nm against distilled water as reference.

Determination of hydrogen cyanide in air and water: Contaminated air of nearby locations of coke ovens and blast furnace was drawn into two midget impingers each containing 10 mL of 0.1 M sodium hydroxide solution connected to a source of suction in the environment at a flow rate of 0.25 L min^{-1} for 5–15 min. After sampling aliquots of absorbing solution were analysed as described above. Analysis of contaminated air was also done by Drager multigas detector method which uses a quantitative detector tube. In this method both ends of the tips of the cyanide tubes were broken and inserted in the pump head, so that the arrow of the tube points towards inlet of the pump. For taking the air samples from the contaminated area, the pump bellows are compressed completely and then released, the air sample is drawn through the drager tubes, the colour change gives the concentration of HCN in ppm. The suction rate of the pump is 100 cm^3 per stroke. The result of the analysis was compared with the reported method (Table-3).

For estimation of cyanide in coke oven effluents, samples were collected from 3 places of outlet sampling pit, treated with 3–4 drops of lead acetate. Filtrate was taken and analysed by PABA method as described above. Results are reported in Table-1.

RESULTS AND DISCUSSION

Absorption spectra: The yellow dye extractable in butanol shows maximum absorbance at 410 nm whereas reagent blank has negligible absorbance

at this wavelength. Beer's law is obeyed over the concentration range of 0.02–0.2 ppm of cyanide. The molar absorptivity and Sandell's sensitivity are 1.3×10^4 L mol^{-1} cm^{-1} and 0.002 μg cm^{-2} respectively.

Effect of reagent concentration: Effects of different reagent concentrations on absorbance values were evaluated. It was found that 0.5 mL of bromine water, 0.5 mL of pyridine reagent and 2 mL *p*-aminobenzoic acid were required for complete colour development. Two drops of sodium arsenite solution were found to be sufficient for removal of excess bromine.

Effect of temperature and time: It was found that temperature range of 10–40°C had no adverse effect on colour development. The colour development was complete within 5 minutes after addition of the reagent.

Effect of pH on extraction: It was found that the dye can be extracted into *n*-butanol in the pH range of 2–5 maintained by 0.25 mol L^{-1} sulphuric acid.

Effect of foreign species: Effect of other pollutants on absorbance value was studied and it was found that the method was free from common interference present in steel plant environment. The tolerance limits of different pollutants are presented in Table-3.

TABLE-3
EFFECT OF DIVERSE IONS—CYANIDE (8 μg/L)

Foreign ion	Tolerance limit (μg)	Foreign ion	Tolerance limit (μg)
Phenol	500	Ethanol	1000
Benzene	1000	Aniline	850
Toluene	650	Mg^{2+}, Co^{2+}	600
Formaldehyde	800	Mn^{2+}, Cu^{2+}	500
Ammonia	100	Fe^{3+}, Al^{3+}	300
SO_3^-	50	Pb^{2+}	200
NO_3^-	100	Hg^{2+}	50

* Tolerance limit may vary the relult by ± 2%.

Reproducibility: Reproducibility of the method was checked by 7 replicate analysis of cyanide solution containing 8 μg of cyanide in 100 mL final solution. The standard deviation and relative standard deviation was found to be 0.03 and ± 6.1% respectively.

Application: The proposed method has been satisfactorily applied for the determination of cyanide in coke oven effluent, and hydrogen cyanide in the ambient air of coke oven and blast furnace. The result of analysis has been reported in Tables 1 and 2. The results have also been compared with ion selective electrode method and result of air analysis was compared with drager multigas detector which uses drager tubes (Table-3).

The method has been compared with other recently reported spectrophotometric methods (Table-4). From the table it is evident that the method is sufficiently

sensitive for trace level analysis of cyanide in water and hydrogen cyanide in air. The method can be satisfactorily applied for industrial hygienic work.

TABLE-4
COMPARISON WITH OTHER SPECTROPHOTOMETRIC METHOD
REPORTED FOR CYANIDE

Method/Reference	λ_{max} (nm)	Range of determination ($\mu g/mL$)	Remarks
(1) Benzidine (14)	520	0.1–20	Benzidine is carcinogenic.
(2) p-Phenylene diamine (1)	575	0.005–100	p-Phenylene diamine is carcinogenic.
(3) Anthranilic acid (15)	400	1–7	Non-toxic reagent but less sensitive
(4) Sulphanilic acid (17)	480	0.5–3	Non-toxic reagent
(5) J-acid (16)	400	0.02–0.2	Sensitive, non-extractive
(6) Present method	410	0.02–0.2	Sensitive, extractive, applicable for effluent and flue gases

ACKNOWLEDGEMENT

REFERENCES

1. M.B. Jacobs, The Analytical Toxicology of Industrial Inorganic Poisons, Interscience Pub., p. 721 (1967).
2. L.S. Bark and H.G. Higson, *Talanta*, **11**, 621 (1964).
3. C. Zentz, Occupational Medicine, Principles and Practical Applications, Year Book Med. Pub., p. 192 (1988).
4. F.A. Patty, Industrial Hygiene and Toxicology, Interscience Pub., Vol. 2, p. 335.
5. World Health Organisation, Geneva, International Standards for Drinking Water (1958).
6. L. Permeggiani, Encyclopaedia of Occupational Health and Safety, ILO Pub., Geneva, p. 575 (1988).
7. J.A. Mecloswey, *Anal. Chem.*, **33**, 1842 (1961).
8. B. Pihlar and L. Kusta, *Talanta*, **26**, 805 (1979).
9. J.H. Karchmer and M.T. Walker, *Anal. Chem.*, **27**, 71 (1987).
10. J.C. Egekeze and W.F. Ochmn, *J. Anal. Toxicol.*, **3**, 119 (1980).
11. Z. Liang, J. Goi and X.L. Ceshi, **6**, 290 (1987).
12. V.M. Javanovic and M.S. Javanovic, **71**, 113 (1988).
13. W. Konig and Z. Angrew, *Z. Pract. Chem.*, **69**, 105 (1905).
14. S. Upadhyay and V.K. Gupta, *Analyst*, **109**, 1619 (1984).
15. S. Spurlin, *Anal. Chem.*, **19**, 272 (1947).
16. K.N. Ramachandran and V.K. Gupta, *Anal. Chem.*, **37**, 53 (1992).
17. S. Amlathe and V.K. Gupta, *Bull. Chem. Soc.*, **97**, 395 (1988).