A New Spectrophotometric Method for the Determination of Cyanide from Waste Water

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(Received 17th April, 1994, revised 12th August, 1995)

Summary: Cyanide reacts with *N*-Bromosuccinimide followed by the reaction with pyridine-barbituric acid to produce a pink colour having maximum absorbance at 580 nm, the method is reasonably sensitive, accurate, precise and less time consuming. This method was successfully applied for the determination of cyanide from waste water.

Introduction

Cyanide from industrial wastes is placed in the most hazardous categories due to its toxic effect, so its determination is important in monitoring quality control of water. Many methods of determination of cyanide are reported in literature. In the fluorometric procedures [1,2] cyanide was reacted with quinone monoxide benzene sulfonate ester to produce a green fluorescent compound [1] and to further increase the sensitivity more derivatives of quinone were investigated [2]. In the spectrophotometric determination [3,4] neutral *di*-cyano-*bis*(1,10-phenanthroline)-iron II complex [3] and insoluble Tris (1,10-phenanthroline) iron II *tri*-iodide complexes were studied, specially the later gave a red cation complex with cyanide [4]. In another procedure cyanide ion catalyzed the reduction of *o*-dinitro-benzene by *p*-nitrobenzaldehyde [5].

Trace quantities of cyanide were determined colorimetrically [6] by conversion to cyanogen halide followed by reaction with pyridine and condensing agents like benzidine or pyrazolone, but the colour rapidly faded. This reaction was modified [7] by using *p*-aminophenylamine benzidine and *p*-phenyldiamine using bromine water as oxidant, but benzidine being carcinogenic, *p*-phenyldiamine was mostly used from sensitivity and safety view point [8]. In the indirect atomic absorption spectrophotometric method [9,10,11]

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extraction of cyanide complex with tris [1-10] phenanthroline) iron II [9] and precipitation as silver cyanide [10] were carried out. Palladium was also used to form a tetracyano palladate complex followed by extraction with *n*-butyl alcohol. The amount of Pd was related to the concentration of cyanide in water [11].

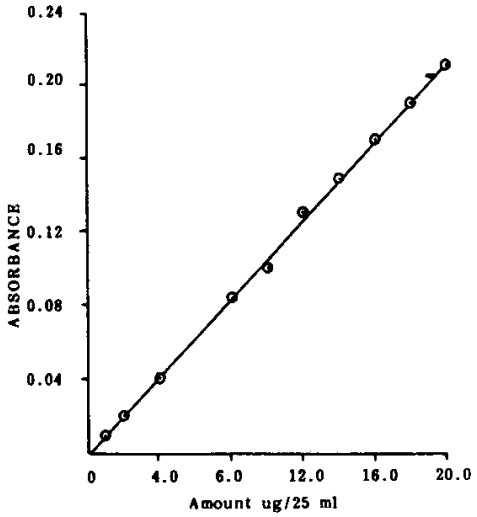

Fig. 1: Calibration curve of cyanide

Besides spectrophotometry numerous gas chromatography [12,13] ion chromatography [14-17] and potentiometric [18,19] procedures were also reported in literature. Most of these methods have certain disadvantages like time consumption, complex instrumentation, unavailability of the reagents and insufficient accuracy.

In the present investigation Konig's procedure [20,21] is modified by using *N*-Bromosuccinimide as an oxidizing agent while pyridine-barbituric acid is used as coupling reagent. The method is reasonably sensitive, accurate, precise and less time consuming.

Results and Discussion

Cyanide reacts with *N*-bromosuccinimide and is oxidized to CN^+ which further reacts with pyridine/barbituric acid to produce pink colour. The colour reaction has an absorption maxima at 580 nm (Fig. 2), hence all absorbance measurements were carried out at this wavelength.

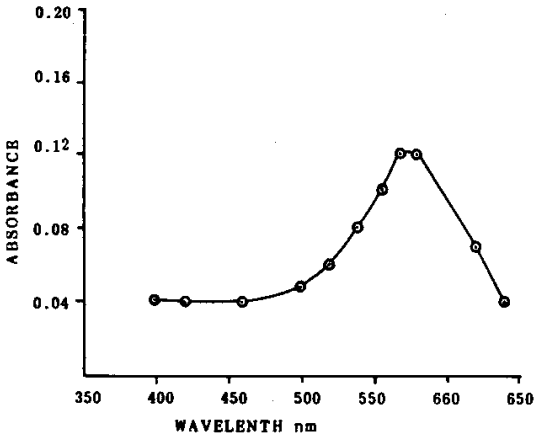

Fig.2: Absorption spectrum of cyanide complex

Effect of pH

During the systematic study it was found that colour intensity was maximum at pH 6.0, which was the pH of the resulting coloured solution. Above and below this pH the colour decreased. Therefore, all determinations were carried out at this pH.

Effect of temperature

The effect of temperature on colour intensity was studied (Fig. 3) and it was found that maximum colour intensity was obtained between 20-50°C, above this temperature the intensity decreased and the colour faded completely at 100°C. So all absorbance measurements were carried out at room temperature.

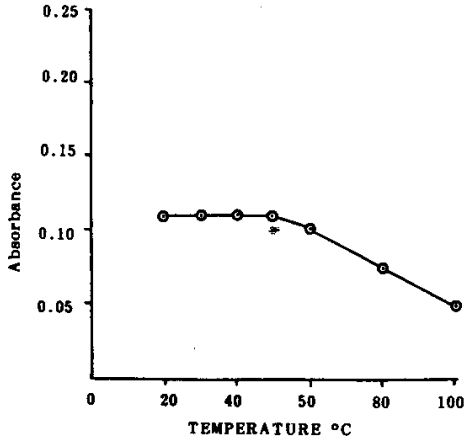

Fig. 3: Effect of temperature on colour intensity.

Effect of reagent concentration

The effect of reagent concentration is shown in Fig. 4. It was found that 1 mg of *N*-bromosuccinimide was sufficient to produce maximum absorbance for 10 μg of cyanide.

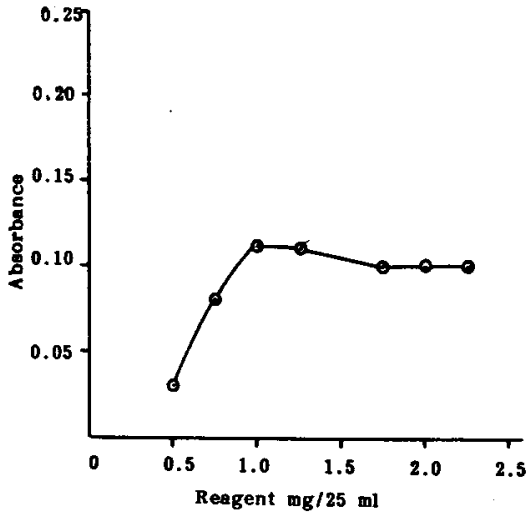

Fig. 4: Effect of reagent concentration on colour intensity.

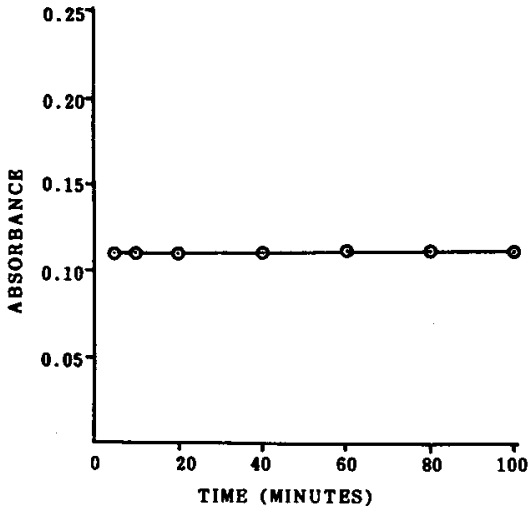

Fig. 5: Effect of time on colour intensity.

Effect of order of addition of reagents

The order of addition of reagents is important. *N*-bromosuccinimide is added to cyanide solution after the addition of potassium dihydrogen phosphate. The solution is mixed well and after two minutes barbituric acid/pyridine solution is added and absorbance is measured at 580 nm after diluting to 25 ml with distilled water.

Effect of time on colour stability

The effect of time on the stability of the colour is shown in Fig. 5. A pink coloured complex is formed within a few seconds after mixing the reagents. The colour is stable for more than an hour.

Precision and accuracy

With the objective of checking the reproducibility of the method, different solutions of cyanide were randomly examined by the above procedure for the absorbance. The percentage error is given in Table-1, which shows the reliability of the method.

Table-1: Determination of cyanide from pure solution

S.No.	Amount taken (μg/25 ml)	Amount found (μg/25 ml)	Error %
1.	5.0	5.0	+0.0
2.	6.0	5.8	-3.3
3.	10.0	10.2	+2.0
4.	12.0	12.3	+2.5
5.	15.0	15.2	+1.3
6.	18.0	17.5	-2.8
7.	20.0	20.7	+3.5

Every found value is an average of five determinations.

The method was successfully applied to the industrial waste water containing micro amounts of cyanide. The results are shown in Table-2. The method is reasonably precise and accurate. Even very small amounts of cyanide can be determined.

Table-2: Determination of cyanide in industrial waste water

S.No.	Industry	Amount of CN (ppm)
1.	A	0.005
2.	B	0.012
3.	C	0.010

Every found value is an average of five determinations.

Experimental

Reagents

All reagents were of analytical grade or comparable purity. Cyanide stock solution 1 mg/ml was prepared by dissolving 1.25 g KCN (E.Merck) in 0.2 N NaOH and volume was made upto 500 ml.

N-bromosuccinimide solution 0.1% in distilled water.

Potassium dihydrogen phosphate solution 150g/l in distilled water

Barbituric acid/pyridine solution was prepared by making a slurry of 15 g of barbituric acid in a little water and then completely dissolving it in 75 ml of pyridine and treating with 15 ml of concentration HCl. The solution was cooled and volume was made upto 250 ml.

Procedure

To an aliquot of cyanide (either synthetic or effluent water) containing 1-20 µg of cyanide was added 5 ml of potassium dihydrogen phosphate followed by 1 ml of 0.1% *N*-bromosuccinimide and mixed well by shaking. After about 2 minutes, 1 ml of barbituric acid-pyridine reagent was added, a pink colour appeared immediately. The solution was diluted to 25 ml with distilled water and the absorbance was measured at 580 nm against reagent blank employing spectronic 20 spectrophotometer. The experiment was repeated with different volumes of standard cyanide solution and a calibration graph was prepared shown in Fig. 1. The colour reaction obeyed Beer's law from 1.0 to 20 µg/25 ml.

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