Spectrophotometric Determination of Cyanide by Silica Supported Tris(Pentane-2,4-dionato) Iron(III) Reagent

M. MAZHAR*, G.AFSHAN, S.ALI, S. IKRAM AND A. AHMAD
Department of Chemistry, Quaid-i-Azam University, Islamabad.

(Received 11th March, 1989, revised 20th September, 1989)

Summary: A fast and accurate spectrophotometric method has been investigated for the quantitative evaluation of free cyanide ions in the concentration range of 25 ppb by using silica supported tris(pentane-2,4-dionato)iron(III)column

Introduction

The toxicity of cyanide in ionic form is well known. Cyanide is also widely used in industry. Being a soft base it forms a lot of stable complexes with transition metals which find uses in various fields e.g. ferrocyanides are extremely useful in the production of various types of commercial pigments, photography, and in bleaching agents [1]. In addition to this cyanide consitutes a considerabe part of the polymer industry. The quantitative determination of cyanide ions in various sources including food is necessitated because of its toxic properties. A method to determine cyanide in very low concentration is thus required to be developed. Cyanide complexes are coloured and in order to avoid any interaction between the reagent and the complex cyanide a separation of free cyanide from the complex cyanide was desired and tried.

Kurse and Thibault [2] tried to determine free cyanide in ferri and ferrocyanides by use of titration and colorimetric techniques. These methods were limited in application for general use. Epstein [3] also developed a procedure for the microquantities of cyanide using pyrazine-pyrazalone reagent, but it was rather cumbersome. Two methods for the estimation of cyanide with picric acid [4] and with the formation of prussian blue [5] are comparatively insensitive. Lambert and Manzo [6] also published a method for the estimation of cyanide ions with tris - 1,10-phenanthroline-iron(II) triodide ion association reagent. Other methods for the estimation of cyanide which lack precision are by displacement titration [7] and the one reported by Konig [8].

Our procedure describes a rapid and sensitive method for the routine measurements of free cyanide ions in 25 ppb limits concentration range in all samples including commercial and food materials.

* whom correspondence should be addressed

Materials and Methods

E. Merck analytical grade chemicals were used without further purification. U.V. spectrum were recorded on Hitachi Model (100- 50) spectrophotometer in 1 cm quartz cells using pet-ether (40-60°) as solvents.

Preparation of Silica Supported Tris(Pentane-2,4-dionato)Iron(III)

Feric chloride solution (1.00M: 60 ml) was added in a 250 ml. Erlenmeyer flask containing 28.00 ml. of acetylacetone. The mixture was heated to 65°C by swirling it in hot water bath. Silica 18.00 g. was added and contents were vigorously stirred. Aqueous sodium acetate solution (3.00 M; 34 ml) was then added and temperature raised to 65°C in hot water bath. The reaction flask was gradually cooled in an ice bath and the desired reagent collected on the Buchner funnel by filtration and repeatedly washed with distilled water, air dried before storing in an amber glass bottle.

Calibration Curve

A stock solution of 20 ppm was prepared by dissolving 20 mg. of pentane-2,4-dione in 1000 ml. of pet-ether. Further five solutions in the concentration range of 10 ppb-50 ppb were prepared by diluting the stock solution. The absorbance of each solution was determined in the U.V. region at wavelength 295 nm. A calibration curve using five concentrations versus absorbance was plotted as shown in Fig. 1.

Evaluiation of Cyanide

One gram of the dry reagent silica supported tris-pentane-2,4- dionato) iron(III) was packed in a glass column of 12 cm x 1 cm. The lower end of the glass column was blocked with glass wool. A cyanide solution of 25 ppb was prepared in distilled water. 2 ml was poured into the column. After 20 minutes the column was eluted with water and eluent was extracted with pet-ether. The pet-ether layer containing the eluted pentane-2,4-dione was separated from the aqueous layer and absorbance was determined. The concentration of cyanide is thus calculated from the concentration of pentane-2,4-dione elutions from the column.

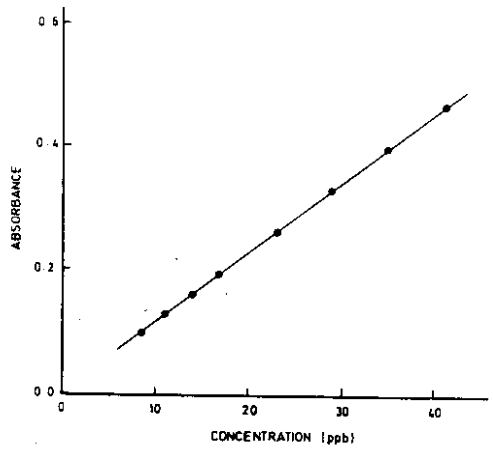

Fig.A: Calibration plot of concentration of Pentane-2, 4-dionete (ppb) versus absorbance at 295 nm.

Study of Interference

The presence of chloride, bromide, carbonate, sulphate, acetate and fluoride ions along with cyanide ions do not interfere with the procedure. Nitrate ions are likely to interfere in this estiation. Interference due to the presence of organic acids, ketones, esters etc. can be eliminated by taking blank reading before passing the sample through the reagent column.

Discussion

Tris(pentane 2,4-dionato) iron(III) does not dissociate significantly when neutral or slightly basic aqueous solutions are used to elute a column of the complex supported on silica. However cyanide ion cuases the stepwise release of pentane-2,4- dione according to the following reactions.

$$[Fe(acac^-)_3] + 2CN^- \longrightarrow [Fe(acac)_2(CN)_2]^- + acac^- \quad (I)$$

$$[Fe(acac)_2(CN)_2]^- + 2CN^- \longrightarrow [Fe(acac)(CN)_4]^{2-} + acac^- \quad (II)$$

$$[Fe(acac)(CN_4]^{2-} + 2CN^- \longrightarrow [Fe(CN)_6]^{3-} + acac^- \quad (III)$$

Exhaustion of the column is indicated by the colour change of the supported material from brown red to deepred as $[Fe(CN_6)]^{3-}$ is formed.

*acac = pentane-2,4-dione

Recovery Experiment and Determination of Cyanide ions in Commercial and Food Stuff Samples

No.	Sample	Amount of cyanide determined* in gram (a)	Known Amount of cyanide in gram added in the sample (b)	Total Amount of cyanide determined in gram (c)	% recovery c- a/b x 100
1.	Steel industry	50×10^{-6}	1.58×10^{-6}	51.504×10^{-6}	95.2
2.	Prussian blue	25×10^{-6}	2.5×10^{-6}	27.478×10^{-6}	99.12
3.	Nail after fusing with sodium metal	1.952×10^{6}	5.00×10^{-6}	6.89×10^{-6}	98.76
4.	Cyanide dopped metal oxide sample	30.807×10^{-6}	Nil	30.807×10^{-6}	-
5.	Apple	Nil	30×10^{-6}	27.8×10^{-6}	92.67
6.	Degraded polyacrylonitrile	45×10^{-6}	3.5×10^{-6}	48.339×10^{-6}	95.4

* Sample taken in 1 ml. solution.

The liberated pentane-2,4-dione elutes down the column in the aqueous phase which is subsequently extracted with pet-ether and absorbance is noted at 295 nm. From the calibration plot amount of peatane-2,4-dione liberated can be found. Amount of cyanide ion present in the sample can be calculated as an equivalent of pentane-2,4-dione corresponds to two cyanide ions.

This method is highly sensitive and cyanide ions can be accurately evaluated in the concentration range upto 25 ppb without the interference of chloride, bromide floride, acetate, carbonate etc. ions.

References

1. Dictionary of Chemistry Ed. John Daintith International Book Production 62 (1981).
2. J.M. Kruse and L.E. Thibault; *J.Anal.Chem.*, **45**, 2260 (1973).
3. J. Epstein, *J.Anal.Chem.* **19**, 272 (1947).
4. A.D. Waller, *J.Anal.Chem.* 35, 406 (1910).
5. A. Vichoever, C.O. Jhons, *J.Chem.Soc.* **37**, 601 (1916).
6. Jack L. Lambert and David J. Manzo, *J.Anal.Chem.* **40**, 1354 (1968).
7. A.I. Vogal "Quantitative Inorganic Analysis" English Language Book Soc. London, 68(1961).
8. W. Konig, *J. Prakt.Chem.* 69 (1904).