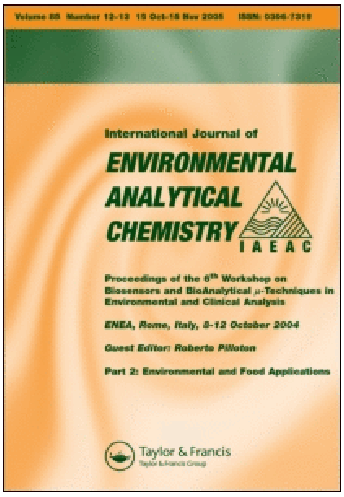

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Detection and Determination of Cyanide—A Review

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Detection and Determination of Cyanide—A Review

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Cyanides, whether organic or inorganic, are highly toxic to all forms of life, i.e., animals and plants alike. This necessitates its detection and determination even when present in trace amounts. Various optical, electrometric, radiochemical and chromatographic methods so far reported for this purpose have been reviewed. An exhaustive bibliography of 154 references is given.

KEY WORDS: Toxicity, lethal dose, trace amount, environmental matrices, waste waters, blood.

INTRODUCTION

Detection and determination of poisons is one of the important tasks which confronts a chemist, particularly a forensic scientist, quite frequently. Cyanides, both organic as well as inorganic, though industrially very important, e.g., in the manufacture of textiles, plastics and synthetic rubber, agricultural chemicals, metals and their electrolytic purification, photography etc., are highly toxic to all forms of life; a lethal dose being 100–150 mg for an adult human being. Death has even been attributed to as low a dose as 0.57 mg/kg body weight of HCN which is known to have a powerful action on the tissues because of its rapid absorption and circulation in blood plasma.[1] It inhibits the enzyme, cytochrome oxidases, responsible for utilising the oxygen being carried by blood. This results in a steady increase in oxyhaemoglobin level and a bright pink colour of the blood at death. On autopsy, the concentration of cyanide in brain tissues etc. has been found to be considerably lower than in blood.[2, 3] In general, inorganic cyanides are more poisonous than organic cyanides. Both are known to cause serious damage to eyes, central nervous system (CNS), body fluids and, grave after-effects and teratogenic effects when consumed accidentally or otherwise in non-lethal doses.

Cyanides may enter the body by inhalation, oral or skin absorption. A 2% concentration of HCN in air may cause poisoning in 3 minutes, 1% is dagerous in 10 minutes and even 0.05% may produce symptoms when inhaled through a gas or air mask.[4]

Most of the existing methods of analysis of CN^- involve its conversion to hydrogen cyanide. Of the most widely used methods the one by Williams[5] involves the decomposition of the complex cyanide by addition of an acidic solution of cuprous chloride to give HCN, while in Kruse and Mellon's[6] method, the latter is generated by distillation of the complex cyanide with phosphoric acid and EDTA under reduced pressure. On the contrary, the reduction to primary amines, hydrolysis to corresponding amides or to ammonia forms the basis of identification and determination of organic cyanides, commonly called nitriles.

Highly toxic nature of a cyanide necessitates its rapid and accurate detection and estimation. It can be determined by titrimetric (including complexometric), potentiometric, polarographic, atomic absorption spectroscopic techniques. In fact, there is a constant increase in the type of procedures being developed for the analysis of cyanides. Reviews by Hirata[7] and Pohlandt[8] have appeared in the recent past but these deal respectively with the methods suitable for determination of cyanides in water/process streams and effluents. In this review, methods reported for the detection and determination of cyanides present in a variety of matrices have been summarised primarily from the practising analyst's point of view.

TITRIMETRIC METHODS

Titrimetric methods described below are suitable for determination of cyanide present in macro quantities, e.g., $\geq 1.0\,\mathrm{mg}$.

The earliest report on the determination of cyanide is Liebig's argentometric method.[9] It is based on the appearance of turbidity due to formation of silver argentocyanide, $Ag[Ag(CN)_2]$, erroneously called 'insoluble silver cyanide' in alkaline or ammonical medium.[10]

$$\begin{tikzcd}
Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^- \arrow[d, "Ag^+"] \\
Ag[Ag(CN)_2]
\end{tikzcd}$$

(Silver argentocyanide)

Dengies[11] modified this method and used KI as a visual indicator in the presence of NH_4OH. Though excess of ammonium hydroxide does not seriously affect the results, more accurate determination can be made if its concentration is suitably regulated.[10]

Other indicators used include murexide,[12] *p*-dimethylaminobenzylidine rhodanine[13] and dithizone.[10] In case of dithizone, a sharp colour change from orange yellow to deep red-purple is observed owing to the formation of silver-enol-dithizone complex. Sarwar[14] used Bodeaux Red as indicator in the titration of solution containing cyanide and N-bromo-succinimide as titrant. The colour change at the end point is from rose-red to yellow. This method has been successfully employed for the microdetermination of cyanide (1–6 mg/ml) in electrolytic baths; the average coefficient of variation is ~0.66% but I^-, SCN^-, HSO_3^-, $S_2O_3^{2-}$, SO_3^{2-} and S^{2-} interfere seriously. Precision of the determination can be improved by using photoelectric colorimeter or turbidimeter for the detection of the end point.[15] Titrimetric methods are useful for the determination of cyanide in water and solid wastes.[16]

INSTRUMENTAL METHODS

Instrumental methods of analysis of cyanide ion can be classified into four main groups as follows:

i) Electrometric
ii) Opticometric
iii) Radiochemical
iv) Chromatographic

Though some of the above mentioned techniques can be used for detection only, most of the colorimetric methods are employed both for detection as well as determination.

I. Electrometric methods

Potentiometric methods Potentiometric titrations of cyanide with silver nitrate have been carried out by various workers[17, 18] and have been reported to be[19] superior to Liebig's method for determining cyanide in plating solution.[20] L. L. Gerchman[21] used a cation sensitive electrode which indicated the completion of complexation reaction. A silver iodide membrane electrode is most suitable for determining cyanide in the concentration range of 10^{-3} to 10^{-5} M. It can also be successfully used at both higher and lower concentrations of this limit.[22] Theoretically, every halide membrane electrode can be converted into a cyanide electrode[23, 24] but in practice, the cyanide electrode based upon silver iodide is the most suitable because of its high sensitivity.

The response of the cyanide selective electrode operated at different flow rates has been studied.[25] Ion selective electrodes based on silver iodide and sulphide[26, 27] have been widely used for the determination of 0.1 nM to 1.0 mM of cyanide in river water.[28] This method has also been automated using semiautomatic titrimeter.[29]

Fleet's method[30] is also an automated method and is based on a computerised Gran plot technique using ion-selective electrode. The solutions have to be passed through an auto-analyser system and a Gran plot generated with use of a suitable computer programme to facilitate calculations. By this method 0.1 to 6.0 mM of cyanide can be determined. Conrad[31] and others[32] used silver ion selective electrode as indicator electrode. Mayer[34] used a packed-bed silver electrode. In this method the standard current-potential curves are obtained and a rectilinear relationship between plateau current and cyanide exists. This method is used to determine cyanide in the concentration range 1 μM to 10 mM even in the presence of Cl^- but interference is caused by Br^-, I^- and S^{2-} whereas the dissolved oxygen can be tolerated. Estimation has also been carried out by a micro-diffusion method using NAS-11-18 electrode in an argentimetric microtitration of cyanide.[35] The use of gold gas-porous electrode has also been suggested.[36] Common electrodes used have been given in Table I.

TABLE I

Common Electrodes used for detection of cyanide

S. No.	Electrode	Conc. range	Interfering ions	Ref.
1.	Cyanide-selective electrode	$10^{-5}-10^{-2}M$	Cations which form complex with CN^-	25
2.	Silver-ion selective electrode	$3.8\times10^{-7}-3.8\times10^{-5}M$	—	31
3.	Silver iodide/silver sulphide-electrode	$10^{-5}-10^{-3}M$	—	26
4.	Silver iodide membrane electrode	$10^{-5}-10^{-3}M$	—	22
5.	Silver sulphide membrane electrode	$10^{-5}-10^{-3}M$	Zn^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, $S_2O_3{}^{2-}$, SCN^-, Cl^-, Br^- & I^-	27
6.	Packed bed silver electrode	$10^{-4}-10^{-3}M$	S^{2-}, Br^- & I^-	34

Polarographic and amperometric methods Anodic reactions take place in aqueous solution of cyanide (as low as 2 ppm conc.) at a dropping mercury electrode[37, 38] Canterford[39] reported rapid direct current polarography for the simultaneous micro determination of cyanide and sulphide using $NaOH\text{-}H_3BO_3$ supporting electrolyte. The electrolytic process in the dil. NaOH (0.01–0.10 M) is:

$$Hg + 2CN^- \rightleftharpoons Hg(CN)_2 + 2e^-$$

It has been established that the limiting current is linearly dependent on cyanide concentration and not on pH. Interference is caused by I^- and $S_2O_3{}^{2-}$. This method is recommended for monitoring industrial effluents. Humphrey[40] and Wisser[41] used differential pulse polarographic method for determination of cyanide. The method was found superior to conventional dc polarography and is based on the principle that cyanide ion reacts with mercuric iodate to form soluble, undissociated mercuric cyanide and releases iodate ions (Eq. 1) which undergoes reduction at DME (Eq. 2).

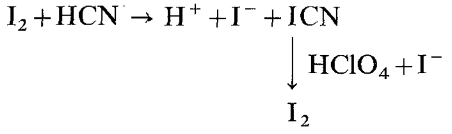
$$\mathrm{Hg(IO_3)_2{}^+ + CN^- \rightarrow HgCH + 2IO_3{}^-} \qquad (1)$$

$$\mathrm{IO_3{}^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O} \qquad (2)$$

Bark[42] suggested an indirect method for the determination of as low as 0.0025 ppm of cyanide in natural water and sewage effluent. In this method cyanide is complexed with Cu(II) and the excess of the latter is determined polarographically. From the amount of uncomplexed copper, concentration of cyanide is calculated.

T. Nomura[43] developed a single-drop method for determination of cyanide in solution with Piezoelectric quartz crystal wherein the frequency of a quartz crystal in contact with a single drop of solution containing CN^- is measured. Change in the frequency due to dissolution of gold electrode of the crystal is linearly proportional to cyanide ion concentration in the range 10^{-4}–10^{-3} M. Only Ag^+ and Hg^{2+} are reported to interfere because of formation of stable complexes. The square wave polarographic[44] and oscillopolarographic[45] determination of cyanide has also been reported.

Of several amperometric titration methods known, Premys Beran *et al.*'s[46] method has been most widely used for determination of ng amounts of CN^- in water and waste water. In this method cyanide rapidly reacts with iodine, forming iodine cyanide which regenerates iodine on treatment with perchloric acid.



$$\begin{array}{l} \mathrm{I_2 + HCN \rightarrow H^+ + I^- + ICN} \\ \qquad\qquad\qquad\qquad\quad \big\downarrow \mathrm{HClO_4 + I^-} \\ \qquad\qquad\qquad\qquad\quad \mathrm{I_2} \end{array}$$

This regenerated iodine, which is equivalent to the amount of cyanide present is transferred to the gas phase by purging with nitrogen and subsequently determined at gold gas-porous electrode by electrooxidation to iodate. Interference due to the presence of a number of ions was checked; Ag^+, Cu^{2+} and NO_3^- do not interfere provided sufficient excess of iodine is used. Mercury(II)-chloranilate when added to an aqueous alcoholic solution containing cyanide ions, forms mercury(II) cyanide and releases chloranilate ions, which can be determined amperometrically.[47]

$$\mathrm{HgCh} + 2\mathrm{CN}^- \rightarrow \mathrm{Hg(CN)_2} + \mathrm{Ch}^{2-}$$

(Ch = chloranilate)

II. Opticometric methods

Spectrophotometric method These are of two types.

i) Methods based on the formation of coloured metal complexes or increase in extinction coefficient.

These methods are quite sensitive for the detection and determination of traces of cyanide. The formation of red coloured ferric ferrithiocyanate produced on reaction with ammonium polysulphide and ferric chloride is an excellent spot test for CN^- [48,49] (Table II). Another extremely sensitive test for cyanide is the formation of Prussian blue.[59,51]

$$\begin{tikzcd}
\mathrm{FeSO_4} + 2\mathrm{NaOH} = \mathrm{Fe(OH)_2} + \mathrm{Na_2SO_4} \arrow[d, "\mathrm{KCN}"] \\
\mathrm{K_4[Fe(CN)_6]} + 2\mathrm{KOH} \arrow[d, "\mathrm{FeCl_3}"] \\
\mathrm{KFe[Fe(CN)_6]} + 3\mathrm{KCl}
\end{tikzcd}$$

(Prussian blue)

Hyde[52] used this method for quantitative determination by comparing the blue spots produced by the sample with that of standard using a densitometer. The method has been used to estimate cyanide in animal and plant tissues. Formation of coloured palladium

TABLE II

Spot test reagents for detection of cyanide ions

S. No.	Reagent	Colour produced	Sensitivity (μg/mL)	Interfering ions	Ref.
1.	Ferric chloride-ammonium polysulphide	Red	1.00	S^{2-}, SO_3^{2-}	48, 49
2.	Ferrous sulphate-ferric chloride	Prussian blue	0.20	$Fe(CN)_6^{4-}$	50, 51
3.	Copper acetate-benzidine	Blue	0.25	Oxidising ions	93
4.	Copper sulphate-amm. molybdate	Blue	>0.15	Fe^{2+}, Sn^{2+}, Sb^{3+} I^-, SO_4^{2-}	55
5.	Copper-ethyl acetoacetate	Blue	1.00	S^{2-}	56
6.	Copper sulphide	Colourless	1.25	—	95
7.	Copper phenolphthalein	Red	0.1 – 10.0	Oxidising ions	99
8.	Copper ethyl acetoacetate-4,4′-tetramethyldiaminodiphenylmethane	Blue	0.50	CrO_4^-, Cl^-, Br^-, I^-, and ammonia and lead	94
9.	Iodopalladate-triphenylstibine	Colourless	0.25	No_2^-, CNO^-, BrO_3^-, IO_3^-, CIO_3^-, CIO^-, S^{2-}	53
10.	4-(2-pyridylazo)-resorcinol palladium(II)	Yellow	1.00	CIO^-, oxidising ions	54
11.	Silver dithizonate	Colourless	0.50	Usual interfering ions do not interfere	58
12.	Picolinealdehyde	Orange	5.00	Strong reducing and oxidising ions	97
13.	Picric acid	Red	<3.00	I^-, S^{2-}, $Fe(CN)_6^{4-}$	96
14.	*O*-Dinitrobenzene-*p*-nitrobenzaldehyde	Deep purple	0.003	Hg^{2+}, Cu^{2+}, Co^{2+} CIO^-, S^{2-}	98

chelates have also been similarly used.[53,54] Tobia[55] developed a new spot test ($>1.5\,\mu g$); a blue colour is formed on adding 0.01% copper sulphate followed by 1 or 2 drops of 5% ammonium molybdate to a solution containing cyanide ion. The colour is due to reduction of ammonium molybdate to molybdenum blue in the presence of Cu^+.

$$Cu^{2+} + CN^- \longrightarrow Cu^+ \xrightarrow[(NH_4)_6Mo_7O_{24}\,.\,4H_2O]{\text{Conc. HCl}} 2MoO_3\,.\,Mo_2O_5$$

(Molybdenum blue)

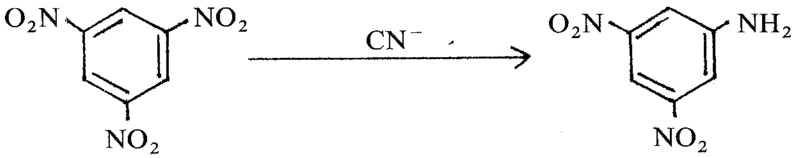
A blue stain is also obtained with as little as $1\,\mu g$ of cyanide and copper ethylacetoacetate.[56] This method has been used for the detection of cyanide in wines and spirits.

Tanaka and Yamato[57] recommended a method involving the use of mercuric diphenylcarbazide. Paper impregnated with this reagent changes from blue-violet to red in presence of $\geqq 0.5\,\mu g/mL$ of cyanide ions in a neutral or weakly basic solution. Ferrocyanides interfere in this reaction. Similarly a paper impregnated with silver-dithiazonate is treated with a drop of test solution. The area of white spot on violet pink background is proportional to the amount of cyanide present.[58] Kopec[59] suggested a method where cyanide and copper(II) give a green-yellow complex in presence of pyridine and potassium thiocyanate. 0.96 to $14.40\,\mu g/mL$ of CN^- can be determined. Tanaka[60] reported an indirect spectrophotometric determination of cyanide using Hg(II) and Cu(II). Aqueous solution of Hg(II) complex of bis(4-sulphobenzyl)-di-thiocarbamic acid and Cu(II) complex of nitrilotriacetic acid react with CN^-; the intensity of the resulting brown colour is proportional to cyanide concentration. By this method $2\,\mu g/mL$ of cyanide can be determined accurately; I^-, $S_2O_3^{2-}$, S^{2-} and cations that form stable cyano complexes interfere. Several iron complexes have been used for the spectrophotometric determination of cyanide.[61–64]

Verma *et al.*[65] developed a sensitive chromogenic complexometric reagent for mercury(II) using ammonium-*p*-(2-amino-3-hydroxypyridil-4-azo) benzene-arsonate (AHP−4A). The complex formed undergoes a ligand exchange reaction with CN^- libearting the free dye quantitatively as follows

$$\begin{array}{l}
\mathrm{Hg(AHP\text{-}4A)^+ + CN^- \rightarrow NC\text{-}Hg\text{-}(AHP\text{-}4A)} \\
\hspace{9em}\text{(Ternary complex)} \\
\hspace{10em}\Big\downarrow \mathrm{CN^-} \\
\hspace{9em}\mathrm{HgCN_2 + (AHP\text{-}4A)^-} \\
\hspace{9em}\text{(free dye)}
\end{array}$$

Picric acid[66, 67] has also been widely used for the determination of cyanide. Red colour is formed due to reduction of one of the nitro groups of picric acid or sodium picrate to an amino group



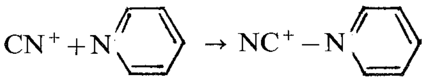
(2, 4, 6-Trinitrophenate)

(red colour)

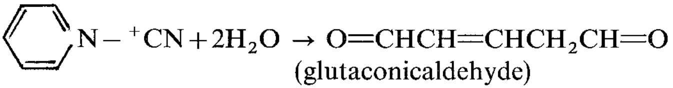
This reagent has also been used for automated analysis of cyanide.[68]

The best known method for the spectrophotometric determination of cyanide are based on Konig synthesis.[69–71] In this method cyanogen bromide or chloride quantitatively reacts with pyridine giving glutaconicaldehyde which on coupling with an aromatic amine form a coloured polymethine dye. The reaction is given below:

$$\mathrm{CN^- + Br_2 - Water \rightarrow CNBr}$$



(pyridine)



(glutaconicaldehyde)

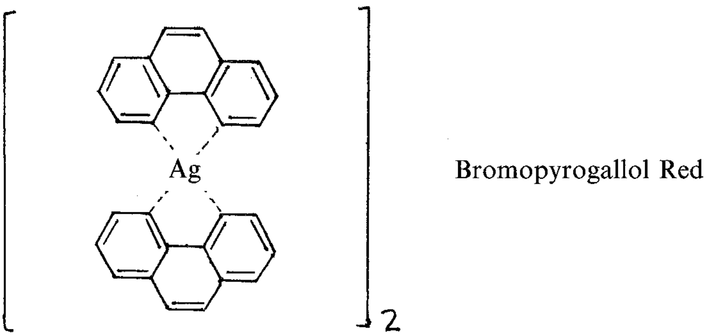
$$\Big\downarrow \text{pr. amine}$$

(coloured species)

This method is widely used for the determination of cyanide in water and solid wastes, 0.1 to 10.0 μg of cyanide having been determined precisely.[72] CN^- gives a blue coloured complex in the presence of isonicotinic acid—barbituric acid reagent and chloramine T. Zheng and Yuan[73] reported the λ max of this complex at 590 nm with detection limit 0.1 $\mu g/mL$ while Xiang[74] has used this reagent for CN^- detn. in waters with detection limit of 4 ppb at 595 nm.

(ii) Methods based on the formation of colourless metal complex or decrease in extinction coefficient.

The ability of cyanide to form stable colourless complexes and cause demasking of complexed transition metal ions has been studied by various workers from analytical standpoint. Brooke[75] selected palladium α-furildioxime as the most sensitive reagent for determining cyanides in the range 0.5 to 3.0 ppm in refinery waste waters. Cyanide breaks the yellow chelate and forms colourless species. Several methods involving demasking effect of mercury(II) have been used for the detection and determination of cyanide ion.[76–81] Cyanide (0.5 to 5.0 $\mu g/mL$) can be determined using mercury(II)-*p*-dimethylaminobenzylidenerhodanine complex.[82] Similarly, coloured mercury(II)-chloranilate, when added to an ethanol-water mixture containing cyanide ion, forms mercury(II) cyanide and liberates an equivalent amount of colourless chloranilate.[83] The formation of the silver(I)-1,10-phenanthroline-bromopyrogallol red ternary complex is inhibited by cyanide ion.



(deep blue triple complex)

On this basis cyanide can be determined in the concentration range of 0.25 to 2.60 ppm.[84, 85] Similarly silver(I)-1,10-phenanthroline iodine complex decomposes at pH 9.5. By this method 0.2–0.5 $\mu g\, CN^-/mL$ can be detected.[86] An ultraviolet spectrophotometric method for determination of cyanide (0.5–20.0 ppm) in biological materials has also been developed.[87]

Silver and copper give sensitive colour reaction with Cadion 2B in the presence of a neutral surfactant, Triton X-100.[88, 89] The suppression of colour formation between Ni^{2+} and 2-(5-bromopyridylazo)-5-diethylaminophenol by CN^- has been utilised in the determination of CN^- in industrial waste waters.[90, 91]

Recently, a highly sensitive indirect spectrophotometric method has been reported by Blanco and Maspoch.[92] It is based on inhibition of extraction of Pd-5-phenylazo-8-aminoquinoline in the presence of cyanide. The detection limit is 0.005 $\mu g/mL$ of cyanide; sulphide interferes.

Table III lists the reagents commonly used for the spectrophotometric determination of cyanide.[93–117]

Fluorometric method Pilipenko[118] and others[119, 120] suggested an indirect chemiluminescence determination of cyanide in which the oxidation of immoluminol by Cu^{2+} at pH 1.40 is suppressed in presence of cyanide. This method is widely used even for the determination of traces of cyanide. Ag^+, Mn^{2+}, Co^{2+}, Hg^{2+}, Ni^{2+}, Fe^{3+}, Cr^{3+} interfere. Hanker *et al.*[121] had earlier developed a method involving the formation of a fluorescent compound by reaction of nicotinamide and cyanogen chloride. Hanker[122] has also suggested a method based on demasking of 8-hydroxy-5-quinolinesulphonic acid from non-fluorescent potassium di(5-sulphoxino)-palladium(II) with cyanide and resulting species forms a fluorescent chelate with Mg^{2+}. By this method 0.02 $\mu g/mL$ of cyanide can be determined.

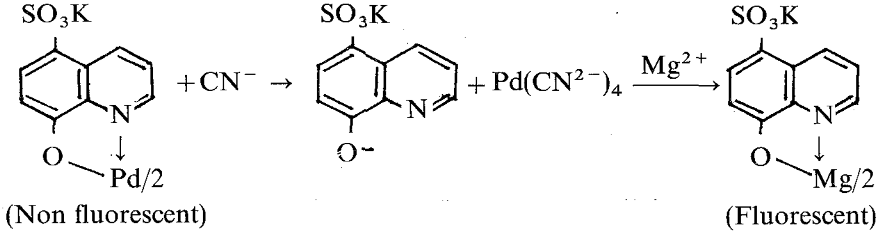


TABLE III

Reagents for spectrophotometric determination of cyanide ion

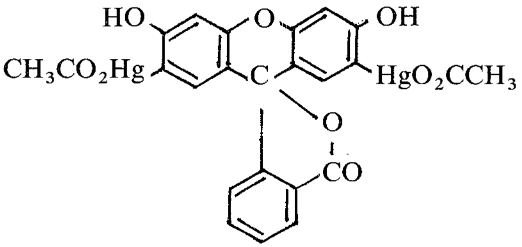
S. No.	Reagent	Colour	pH	λ max (nm)	Sensitivity (μg/ml)	Interfering ions	Ref.
1.	Mercury-metaphthalein	Purple	9.6–10.3	583	0.02–0.40	Ag^+, Hg^{2+}, S^{2-}	77
2.	Mercury-methylthymol blue	Purple-blue	7.2–7.6	615	0.10–1.60	Co^{2+}, I^-, Br^-, Cl^-	103
3.	Mercury-diphenylcarbazone	Violet-red	7.0	562	0.02–0.60	Ni^{2+}, Cu^{2+}, S^{2-}, SCN^-, Cl^-, Br^-, I^-	82
4.	Mercury-EDTA	—	6.0–8.0	250	0.20–28.00	Ni^{2+}, Cu^{2+}, Co^{2+}, SCN^-, S^-, Br^-, I^-	80
5.	Mercury-*p*-dimethylamino-benzylidinerhodanine	Brick red	11.0–11.3	452	0.10–1.00	$S_2O_3{}^{2-}$, S^{2-}, I^-	82
6.	Mercury-chloranilate	Red-violet	6.45	525 330	0.40–4.00	$S_2O_3{}^{2-}$, S^{2-}	83
7.	Mercury-(AHP-4A)	Magenta	7.2	535	0.04–0.37	Ag^+, Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Cl^-, Br^-, I^-, $SO_3{}^{2-}$, $S_2O_3{}^{2-}$	65
8.	Mercury-carbazone	Violet-red	4.0–8.0	560	0.005–0.600	Ag^+, Cu^{2+}, Cl^-, Br^-, SCN^-	111
9.	Mercury-bis(4-sulphobenzyl)dithiocarbamic acid	Brown	6.0	433	2.0–10.0	Ag^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, I^-, $S_2O_3{}^{2-}$, S^{2-}	60
10.	Mercury-iodide	—	4.0–8.0	323	1.3–13.0	Rb^+, Fe^{2+}	79
11.	Mercury-iodate	Blue	7.0	595	0.04–0.10	S^{2-}, $S_2O_3{}^{2-}$, Cl^-, Br^-, I^-, SCN^-	78
12.	Mercury-bis(2-hydroxyethyl)diethyldithiocarbamic acid	Yellow	5.4–5.7	383	5.0–100	Fe^{2+}, Hg^{2+}, $S_2O_3{}^{2-}$, I^-	81
13.	Mercury-EDTA-iodide	—	5.0–8.0	260	$\leqq$250	S^{2-}, $S_2O_3{}^{2-}$, I^-	76

TABLE III (continued)

S. No.	Reagent	Colour	pH	λ max (nm)	Sensitivity (μg/ml)	Interfering ions	Ref.
14.	Copper-EDTA	—	9.6 – 12.10	—	—	—	101
15.	Copper-*o*-cresolphthalein	Purple-red	—	568	< 5.0	Cu^{2+}, Ni^{2+}	100
16.	Copperethylenediamine sulphate	Violet-red	6.0 – 10.0	550	20 – 200	$Fe(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$	—
17.	Copper-*o*-hydroxyquinol-phthalin	Purple-red	7.4	565	< 5.20	Al^{3+}, Fe^{3+}, In^{3+}, $VO_3{}^-$	102
18.	Nickel cyanide	—	7.0 – 12.0	267	0.5 – 2.0	S^{2-}, $S_2O_3{}^{2-}$	87
19.	Nickel-α-furildioxime	Orange-red	9 – 11	480	0.5 – 5.0	—	110
20.	Nickel-3,4-diaminobenzoic acid	—	10.0 – 12.0	730	10.0 – 40.0	Fe^{3+}, Rb^+	106
21.	Nickel-2-(5-Br-pyridylazo) -5-diethylaminophenol	Violet-red	8.0	560	0.20	S^{2-}	91
22.	Silver-1,10-phenanthroline bromopyrogallol red	Blue	3.0 – 10.0	635	0.26 – 2.60	Au^{3+}, Hg^{2+}, Cd^{2+} SCN^-, Br^-, I^-	84 85
23.	Silver-1,10-phenanthroline torsine	—	9.5	—	0.2 – 0.5	—	86
24.	Tris-iron(II) 1,10-phenanthroline triiodide	Red	5.0 – 6.0	514	0.40	Ag^+, Fe^{3+}, $S_2O_3{}^{2-}$, SCN^-, I^-	63
25.	Tris-1,10-phenanthroline iron(II)	Violet	9.2 – 9.7	597	1.0 – 25.0	Co^{2+}, Ni^{2+}, Cu^{2+}, $CdI_4{}^-$, $ClO_4{}^-$, $IO_4{}^-$, I^-, CNS^-	61
26.	Aquopentacyanoferrate(II)	Blue	3.0 – 7.0	658	0.16 – 1.06	—	62
27.	Potassium-di-(7-iodo-5-sulphonoxino)palladium(II) -ferric chloride	Blue	8.0	650	1.00	SCN^-, SH^-, S^{2-}	105

28.	5,5′-Dithiobis-(2-nitrobenzoic acid)-cetyl trimethyl amm. bromide	Brown	8.0	433	0.8 – 28.0	$S_2O_3^{2-}$, S^-, SCN^-, I^-, mercaptans	107
29.	*p*-Nitrobenzaldehyde	Deep purple	9.0	560	0.1 – 1.0	Hg^{2+}, Co^{2+}, ClO^-, S^{2-}	98
30.	Picric acid	Red	11.0	520	2.0 – 3.0	—	—
31.	5,5′-Dimethylcyclohexane-1,3-dione	Violet-red	—	550	1.0 – 4.0	Reducing ions	108
32.	2,2′-Dithiodipyridine	—	9.7	340	0.2 – 5.0	Cu^{2+}, Hg^{2+}, SH^-, $S_2O_3^{2-}$, S^{2-}	109
33.	4,4′-Dithiodipyridine	—	9.0	324	0.2 – 5.0	Cu^{2+}, Hg^{2+}, SH^-, $S_2O_3^{2-}$, S^{2-}	109
34.	2,2′-Dithiodipyrimidine	—	7.0 – 9.0	277	0.2 – 5.0	Cu^{2+}, Hg^{2+}, SH^-, $S_2O_3^{2-}$, S^{2-}	109
35.	5,5′-Dithio-bis-2-nitrobenzoic acid	—	7.0 – 9.0	412	0.2 – 5.0	Cu^{2+}, Hg^{2+}, SH^-, $S_2O_3^{2-}$, S^{2-}	109
36.	Haemoglobin	Brown	6.9	422	0.1	S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$,	104
37.	Pyridinebarbituric acid	Violet-red	8.0 – 9.0	560	0.01 – 1.00	Cl^-, SCN^-	113
38.	Pyridinebenzidine	Red	7.0	520	3.0	SCN^-, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$	117
39.	Pyridine-pyrazolone	Blue	7.0 – 9.0	630	1.2	S^{2-}, complex cyanides	115
40.	Pyridine-diphenylenediamine	Red	—	515	0.1 – 1.0	—	116
41.	Barbituric acid-isonicotonic acid	Blue-violet	5.2	600	0.5	S^{2-}, SCN^-	114
42.	4-Picoline-barbituric acid	Blue-violet	5.2	605	0.5	SCN^-	112

The use of quinones has also been reported for the fluorometric determination of cyanide (5.0 ng/mL), only $Cr_2O_7^{2-}$ and S^{2-} interfere.[123, 124] On the other hand, decrease in intensity of fluorescence of 2,7-bis(acetoxymercuric-fluorescein (AMF) on addition of cyanide ions has also been used for analytical purpose.[125]



AMF (fluorescent)

McKinney[126] developed a mothod of determination based on breaking up of $Pb_2(DANSe)_2Cl_2$ complex by cyanide ions and giving fluorescent DANS species (DAN = 2,3-diaminonaphthalene). Groff[127] has automated this method for the determination in blood. Another rapid and simple fluorometric method for determination of CN^- in human blood has been discussed by Suzuki *et al.*[128] CN^- in water (0.8 ppb) can also be determined using colourless fluorescein at pH 8.0–9.0; the excitation and emission wavelengths are 500 and 520 nm respectively.[129]

Polarimetric method Cyanide ions at concentration between 0.1 mM–0.001 mM can be determined in terms of change in optical rotation due to decrease in inhibitory effect of Hg^{2+} on the invertase catalysed hydrolysis of sucrose.[130]

Atomic absorption spectroscopic method Dicyanotris(1,10-phenanthroline)iron(II) complex has been used[131] for the determination of cyanide using AAS. It gives a linear response over the range 0.1 to 5.0 ppm of cyanide. Another method[132] is based on the principle that metallic silver reacts with cyanide to give soluble $Ag(CN)_2^-$ which may be determined by atomic absorption spectroscopy. Cyanide up to $\simeq$3.0 ppm can be determined. Br^-, I^-, SCN^- and SO_3^{2-} do not interfere while $S_2O_3^{2-}$ interferes by enhancing the signal. An alternative method based on the precipitation of silver cyanide and determination of excess of silver in supernatant solution is applicable up to 100 ppb of cyanide concentration.[133] A highly sensitive method based on the dissolution of copper carbonate by CN^- in an alkaline medium and subsequent determination of Cu by AAS has been developed.[134] The method has a sensitivity of 500 ppb.

Newton developed an indirect method of determining cyanide by Flameless Atomic Absorption using a wire loop atomiser and a loop of tungsten-rhenium alloy soaked in a solution of 0.01–0.10 ppm of $CdCl_2$.[135] 0.1 mM of CN^- can be detected by this method based on the interference in the absorption of Cd caused by CN^-. Recently Xu *et al.*[136] have developed an indirect method of determination of trace CN^- in water (0.1 μg/ml) based on the formation of a stable complex anion with Pd in alkaline solution. This complex anion forms an ion-association complex with tetraalkyl ammonium ions in BuOH. The extract is analysed for Pd (and hence indirectly for CN^-) by AAS.

III. Radiochemical methods

These methods have been successfully used for the determination of micro amounts of cyanide using radioactive silver.[137, 138] Bowen[139] has determined 0.5 μg to 10.0 mg of CN^- in aqueous solution by passing the solution through a column of silver iodide labelled with ^{110}Ag and counting the activity of the filtrate. Each mole of silver required two moles of cyanide (Table IV). This is an accurate, fast and sensitive method. Smith[140] has successfully determined cyanide

TABLE IV

KCN added (μ mole)	Average ^{110}Ag displaced (μ mole)
Blank	0.017
3.47	2.075
8.68	4.855
17.40	8.933
86.80	43.733
347.00	168.000

in slurries by irradiating pure silver in a nuclear reactor to form ^{110}Ag. It was then fixed inside a flow cell through which sulphide-free cyanide solution was passed. The method was applicable under controlled conditions. The calibration graph was rectilinear up to 1.0 g/L of cyanide. Mercury iodate labelled with ^{203}Hg has also been used[141] based on the principle that if solid water-insoluble mercuric iodate labelled with ^{203}Hg is added to a cyanide solution, a soluble nondissociating mercury(II) complex is quantitatively formed.

IV. Chromatographic methods

Gas liquid chromatography has been used for the determination of hydrogen cyanide.[142, 143] Bates *et al.* used this technique for the determination of cyanide in wines, distilled liquors and other alcoholic beverages, the lower limit of detection being 0.2 μg.[144] Nota *et al.*[145] developed a method for the determination of cyanide including complex cyanides, in water. The method is based on the reaction described by Schulek:

$$CN^- + Br_2 \rightarrow BrCN + Br^-$$

Cyanogen bromide is separated by gas chromatographic method and then detected by electron capture detector. No interference is observed from Cu^{2+}, Zn^{2+}, CNO^-, S^{2-}, $S_2O_3{}^{2-}$, glycine and urea when the amount of cyanide present is between 0.05 to 0.70 ppm. Several other workers[146–148] have also used gas chromatography for the determination of cyanide. A sensitive gas chromatographic method for CN^- determination at trace levels is based on the derivatisation of CN^- to benzonitrile which is extractable in benzene and determined by using flame thermionic detector.[149] Gallego[150] developed a new method based on thin layer chromatography of groups of anions. Best separation of SCN^-, CN^-, $Fe(CN)_6{}^{3-}$, $Fe(CN)_6{}^{4-}$ was achieved on microcrystalline cellulose incorporating a fluorescent indicator following use of wide range of developing solvents like acetone-water-methanol-propanol (4:1:1:1).

Thielemann[151] used paper chromatography for the separation of CN^-, OCN^- and SCN^- within 8 hours using methanol-pyridine-dioxan (7:2:1) as elutent. Cn^- and OCN^- are then identified by means of bromocresol purple; $CO_3{}^{2-}$ interfered.

Recently high performance liquid chromatography (HPLC), has also been employed for the determination of CN^- in blood plasma, red cells and human urine using fluorescent[152,153] or chromogenic derivative.[154]

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