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Indian Standard (Reaffirmed 1998)

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTE WATER

PART 27 CYANIDE

(First Revision)

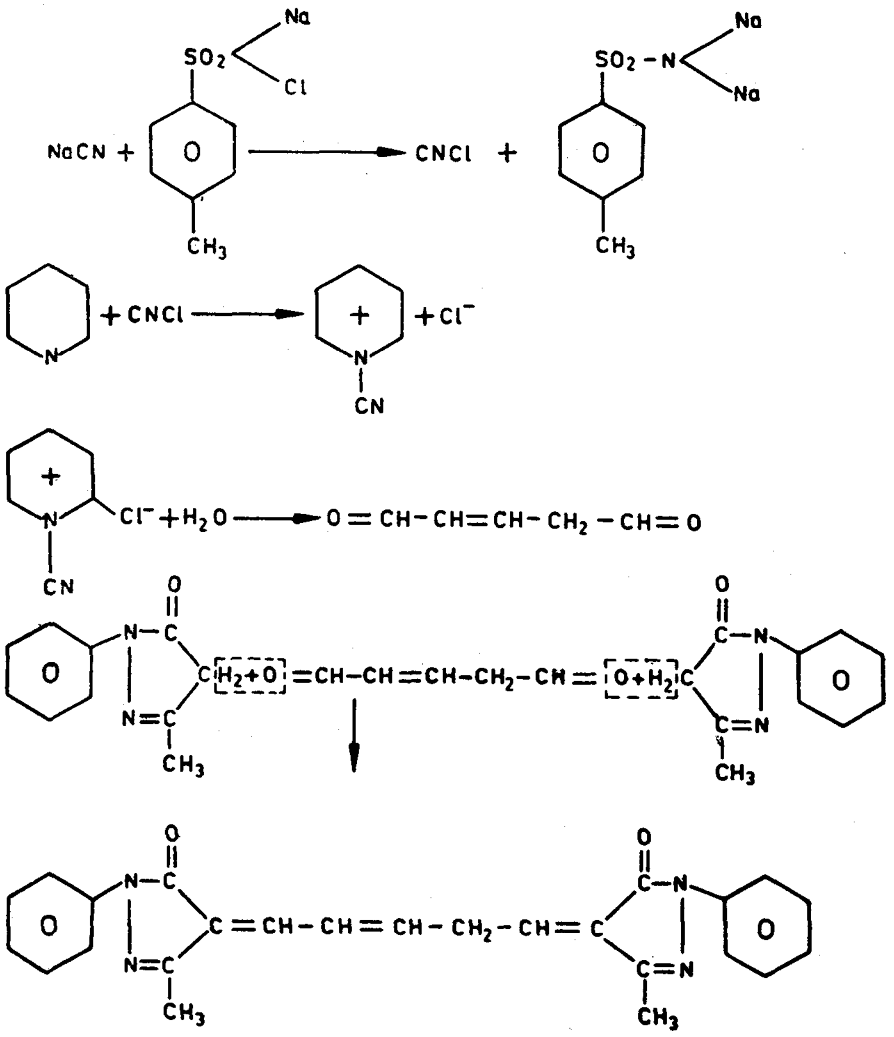
1. Scope — Prescribes two methods for determination of total cyanides in water and waste waters. The total cyanides after distillation method prescribes the determination of total cyanides which distil over on treatment with sulphuric acid. This method is applicable to the determination of cyanide in surface, waste and sea water. The method is suitable for cyanide concentration to a lower limit of 20 μg/l. The selective electrode method is applicable to solution in the concentration range of 0·05 to 10 mg/l.

2. Determinatian of Total Cyanides After Distillation

2.1 *Principle* — Distillation of sample in the presence of sulphuric acid converts simple and complex cyanides into hydrocyanic acid. The hydrogen cyanide gas is absorbed in a solution of sodium hydroxide and the cyanide is determined colorimetrically.

$$Fe(CN)_6^{-4} + 6H^+ \longrightarrow 6HCN + Fe^{+2}$$
$$HCN + NaOH \longrightarrow NaCN + H_2O$$

2.2 In the colorimetric measurement, the cyanide in the sodium hydroxide solution after distillation is converted to cyanogen chloride by reaction with chloramine-T. The cyanogen chloride then forms a blue dye on the addition of pyridine-pyrazolone reagent and the absorbance is measured at 620 nm. The reaction may be expressed by the following equations:



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Water Sectional Committee, CDC 26, Panel for Methods of Test for Water and Effluents, CDC 26 : P1 [Ref : Doc : CDC 26 (9092)]

2.3 *Interferences*

2.3.1 Sulphides and nitrite interfere, and should be removed prior to distillation (*see* **2.7**).

2.3.2 Other interfering substances are removed by distillation.

2.4 *Sampling Procedure and Storage*

2.4.1 The samples should be collected in 2-litre polyethylene bottle and analyzed as soon as possible after collection.

2.4.2 Samples should be preserved by addition of sufficient sodium hydroxide to raise the *p*H to 11·0 or above and be stored in a cool place.

2.5 *Apparatus*

2.5.1 *Boiling flask* — 1 litre, with inlet tube and provision for water-cooled condensers (*see* Fig. 1).

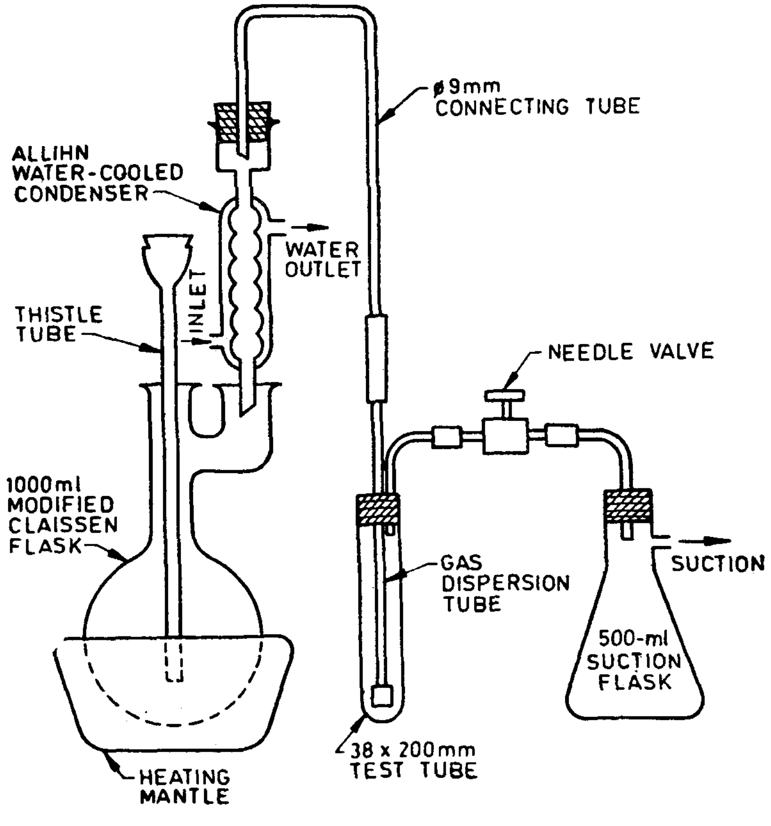

FIG. 1 CYANIDE DISTILLATION APPARATUS

2.5.2 *Heating mantle*

2.5.3 *Gas absorber* — with gas dispersion tube equipped with medium-porosity fritted outlet.

2.5.4 *Ground glass ST joints* — TFE sleeved or with an appropriate lubricant for the boiling flask and condenser. Neoprene stopper and plastic threaded joints may also be used.

2.5.5 *Spectrophotometer* — for use at 620 nm, providing a light path of 1 cm.

2.6 *Reagents*

2.6.1 *Sodium hydroxide solution* — Dissolve 50 g sodium hydroxide in 1 litre distilled water.

2.6.2 *Lead carbonate* — Powdered.

2.6.3 *Sulphamic acid* (NH_2SO_3H)

2.6.4 *Magnesium chloride solution* — Dissolve 51 g magnesium chloride ($MgCl_2.6H_2O$) in 100 ml distilled water.

2.6.5 *Sulphuric acid concentrated*

2.6.6 *Sodium hydroxide solution* (0·2 *N*) — Dissolve 8·0 g sodium hydroxide in 1 litre distilled water.

2.6.7 *Acetic acid* — Make by diluting 1 part of glacial acid with 4 parts of water.

2.6.8 *Stock cyanide solution* — Dissolve 2·51 g potassium cyanide, in 1 litre water, standardize this solution with 0·019 2 N silver nitrate solution. The solution loses strength gradually and must be rechecked every week.

(1 ml of this solution = 1 mg CN)

Caution: Potassium cyanide is highly toxic, take care to avoid ingestion; use gloves while preparing solution.

2.6.9 *Standard cyanide solution* — Dilute 10 ml stock cyanide solution (**2.6.8**) to 1 litre with distilled water; mix and make a second dilution of 10 ml to 100 ml.

One ml = 1 μgCN

Note — This solution must be prepared daily.

(*Caution*: Toxic, take care to avoid ingestion.)

2.6.10 *Chloramine* — T-Dissolve 1 g of chloramine — T in 100 ml distilled water. Prepare daily.

2.6.11 *Pyridine*

2.6.12 *1—phenyl—3—methyl—5 pyrazolone solution* — Prepare a saturated aqueous solution (approximately 0·5 g/100 ml) by adding the pyrazolone to water at 75°C. Agitate occasionally as the solution cools to room temperature. If necessary, the pyrazolone (melting point 127° to 128°C) can be purified by recrystallisation from ethyl alcohol. Usually this is not required.

2.6.13 *Bis—pyrazolone* (*3,3'—dimethyl—1—diphenyl*) (*4,4'—bis—2—pyrazolone)—(5,5'dione*).

2.6.14 *Mixed pyridine — Pyrazolone reagent* — Mix 125 ml of the filtered saturated aqueous solution of pyrazolone with a filtered solution containing 0·025 g bis-pyrazolone dissolved in 25 ml pyridine. Several minutes of mixing is usually necessary to dissolve the bis-pyrazolone in pyridine.

Note — Prepare this reagent daily. This reagent develops a pink colour on standing.

2.6.15 *Standard silver nitrate solution* — Dissolve 3·27 g of silver nitrate in 1 litre of distilled water. Store in dark bottle.

1 ml of this solution = 1·00 mg CN.

2.7 *Procedure*

2.7.1 *Distillation*

2.7.1.1 Add 500 ml sample to the boiling flask. Add 10 ml of sodium hydroxide solution to gas scrubber and dilute, if necessary, with distilled water to obtain an adequate liquid depth in the absorber. Do not use more than 225 ml total volume of absorber solution. When sulphide generation from the distilling flask is anticipated, add 50 or more mg powdered lead carbonate to the absorber solution to precipitate sulphide. Connect the train, consisting of boiling flask air inlet, flask condenser, gas washer, suction flask trap and aspirator. Adjust suction so that approximately 1 air bubble per second enters the boiling flask. This air rate will carrying hydrogen cyanide gas from flask to absorber and usually will prevent a reverse flow of hydrogen cyanide gas through the air inlet. If this air rate does not prevent sample backup in the delivery tube, increase air flow rate to 2 air bubbles per second. Observe air purge rate in the absorber where the liquid level should be raised not more than 6·5 to 10 mm. Maintain airflow through the reaction.

2.7.1.2 Add 2 g of sulphamic acid through the air inlet tube and wash down with distilled water.

2.7.1.3 Add 50 ml of concentrated sulphuric acid through the air inlet tube with distilled water and let air mix flask contents for 3 minutes. Add 20 ml of magnesium chloride reagent through air inlet and wash down with stream of water. A precipitate that may form redissolves on heating.

2.7.1.4 Heat with rapid boiling, but do not flood condenser inlet or permit vapours to rise more than halfway into condenser. Adequate refluxing is indicated by reflux rate of 40 to 50 drops/min from the condenser lip. Reflux for at least 1 hour. Discontinue heating but continue air flow. Cool for 15 minutes and drain gas washer contents into separate container. Rinse connecting tube between condenser and gas washer with distilled water, and rinse water to drained liquid, and make upto 250 ml in a volumetric flask.

2.7.2 *Procedure for colorimetric measurement*

2.7.2.1 Transfer 15 ml of distillate to a 50 ml beaker.

2.7.2.2 To prepare standard solutions for the calibration curve, use cyanide standard 1 ml = 1 mgCN. Pipette 0 (blank), 0·2, 0·5, 0·8 and 1·0 ml into 50 ml beaker and make up to 15 ml with 0·2 N sodium hydroxide solution (**2.6.6**). Proceed with **2.7.2.3**, treating samples and standards in the same manner.

2.7.2.3 Adjust *p*H at 6-7 with acetic acid (**2.6.7**). Transfer to 25 ml volumetric flask.

2.7.2.4 Add 0·2 ml chloramine-T solution (**2.6.10**) and mix. Allow 2 minutes for the reaction.

2.7.2.5 Add 50 ml mixed pyridine-pyrazolone reagent (**2.6.14**) and make up to the mark, mix. Allow 20 minutes for colour development.

2.7.2.6 Read absorbance at 620 nm in a 1-cm cell.

2.7.2.7 As a check on the distillation step, periodically process cyanide standard solutions through the complete procedure.

2.8 *Calculations*

2.8.1 Prepare a calibration curve derived by plotting concentrations versus absorbances.

2.8.2 Determine the micrograms of cyanide in the samples by comparing on calibration curve.

2.8.3 Calculate the cyanide concentration as follows:

$$\text{mg/l, CN} = \frac{A \times B}{C \times D}$$

where

A = cyanide determined in mg by calibration graph,

B = diluted absorbing solution in ml (as obtained in **2.7.1.4**),

C = original sample in ml, and

D = sample taken for colorimetric measurement in ml (*see* **2.7.2.1**).

3. Selective Electrode Method

3.1 *Principle* — Cyanide in the alkaline distillate from the preliminary treatment, as given in **2.7.1**, can be determined potentiometrically by using a cyanide in selective electrode in combination with a double junction reference electrode and a *p*H meter having an expanded millivolt scale, or specific ion meter.

3.2 *Apparatus*

3.2.1 *Expanded-scale pH meter or specific ion meter*

3.2.2 *Cyanide-ion-selective electrode**

3.2.3 *Reference electrode, double-junction*

3.2.4 *Magnetic mixer with TFE-coated stirring bar*

3.3 *Reagents*

3.3.1 *Stock standard cyanide solution — see* **2.6.8**.

3.3.2 *Sodium hydroxide diluent* — Dissolve 1·6 g sodium hydroxide in water and dilute to 1 litre.

3.3.3 *Intermediate standard cyanide solution* — Dilute a calculated volume (approximately 100-ml) of stock potassium cyanide solution, based on the determined concentration, to 1 000 ml with sodium hydroxide diluent. Mix thoroughly; 1 ml = 100 μg CN^-.

3.3.4 *Dilute standard cyanide solution* — Dilute 100 ml intermediate cyanide standard solution to 1 000 ml with sodium hydroxide diluent; 1·00 ml = 10·0 μg CN^-. Prepare daily and keep in a dark, glass-stoppered bottle.

3.3.5 *Potassium nitrate solution* — Dissolve 100 g potassium nitrate in water and dilute to 1 litre. Adjust to pH 12 with potassium hydroxide. This is the outer filling solution for the double-junction reference electrode.

3.4 *Procedure*

3.4.1 *Calibration* — Use the dilute and intermediate standard cyanide solutions and sodium hydroxide diluent to prepare a series of three standards, 0·1, 1·0 and 10·0 mg CN^-/l. Transfer approximately 100 ml of each of these standard solutions into a 250 ml beaker pre-rinsed with a small portion of standard being tested. Immerse CN^- and double-junction reference electrodes. Mix well on a magnetic stirrer at 27°C, maintaining as closely as possible the same stirring rate for all solutions.

Always progress from the lowest to the highest concentration of standard otherwise equilibrium is reached only slowly. The electrode membrane dissolves in solutions of high cyanide concentration; do not use with a concentration above 10 mg/l. After making measurements remove electrode and soak in water.

After equilibrium is reached (at least 5 min and not more than 10 min), record potential (millivolt) readings and plot CN^- concentrations versus readings on semi-logarithmic graph paper. A straight line with a slope approximately 59 mV per decade indicates that the instrument and electrodes are operating properly. Record slope of line obtained (millivolts/decade of concentration). The slope may vary somewhat from the theoretical value of 59·2 mV per decade because of manufacturing variation and reference electrode (liquid-junction) potentials. The slope should be a straight line and is the basis for calculating sample concentration.

3.4.2 *Measurement of sample* — Place 100 ml of absorption liquid obtained in **2.7.1** into a 250 ml beaker. When measuring low cyanide concentrations, first rinse beaker and electrodes with a small volume of sample. Immerse cyanide and double-junction reference electrodes and mix on a magnetic stirrer at the same stirring rate used for calibration. After equilibrium is reached (at least 5 min and not more than 10 min), record values indicated on ion meter or found from graph prepared above. Calculate concentration as given below.

3.4.3 *Calculation*

$$\text{Cyanide, mg/l} = \frac{A \times B}{C}$$

where

A = mg cyanide per litre found from meter reading or graph;

B = total volume of absorption solution after dilution, ml; and

C = volume of original sample used in the distillation, ml.

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*Orion Model 94-06A or equivalent.

EXPLANATORY NOTE

Cyanide refers to all the CN groups in cyanide compounds that can be determined as cyanide ion by the method used. The great toxicity to aquatic life of molecular HCN is well known, it is formed in solutions of cyanides by hydrolytic reaction of cyanide ion with water. After removal of interfering substances, the metal cyanide is converted into hydrogen cyanide gas, which is distilled and absorbed in sodium hydroxide solution. The absorption liquid is analysed by titrimetric, colorimetric or cyanide ion selective electrode procedure. This method supersedes **15** of IS : 2488 (Part 1)-1966 'Methods of sampling and test for industrial effluents: Part 1' and **27** of IS : 3025 - 1964 'Methods of sampling and test (physical and chemical) for water used in industry'.

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IS 3025 (PART 27) : 1986 METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTEWATER

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(*Page* 4, *clause* **2.7.2.5**, *line* 1) — Substitute '5.0 ml' *for* '50 ml'.

(CHD 32)

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