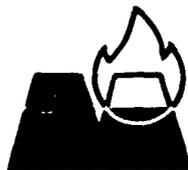MINTEK

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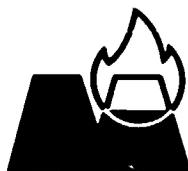THE DETERMINATION OF TOTAL CYANIDE IN SOLUTIONS
CONTAINING URANIUM AND GOLD

by

M. Solomons and K. Dixon

3rd January, 1983

(ANALYTICAL CHEMISTRY DIVISION)

REPORT
No. M67

THE DETERMINATION OF TOTAL CYANIDE IN SOLUTIONS CONTAINING URANIUM AND GOLD

by

Mathew Solomons and Kenneth Dixon

SYNOPSIS

This report gives the results of a limited investigation of three distillation procedures and their variants for the separation of cyanide. The spectrophotometric measurement, which follows the distillation, uses either a mixture of pyridine and pyrazolone, or a mixture of pyridine and barbituric acid.

It was found that the method published in the South African *Government Gazette* in 1969 gives quantitative recoveries from potassium cyanide solutions but not in the presence of gold.

The ligand-displacement method did not give quantitative recoveries in the presence of gold, except when zinc was added to the distilland, and it then failed to give a quantitative recovery of cyanide from ferrocyanide. These two methods were therefore rejected as unsuitable for the determination of cyanide in solutions containing small amounts of uranium and gold.

The procedure of the American Public Health Association (APHA) was found to give quantitative recoveries in the presence of gold, uranium, thiocyanate, and ferrocyanide when cuprous chloride, or cuprous chloride with magnesium chloride, are added to the distilland. The spectrophotometric measurement using a mixture of pyridine and barbituric acid is preferred. The calibration range of the method is 0,5 to 6 μg of cyanide, and the limit of determination is 0,04 μg/cm^3. (The relative standard deviation of the method is 0,05.) The distillation time in the APHA method is approximately $2\frac{1}{2}$ hours; with 3 distillation trains, up to 9 distillations can be made per day, plus a further 2 hours for the spectrophotometric determination.

The preferred laboratory method is detailed in an appendix.

SAMEVATTING

Hierdie verslag gee die resultate van 'n beperkte ondersoek van drie distilleerprosedures en hul variante vir die skeiding van sianied. Die spektrofotometriese meting wat op die distillering volg, gebruik 'n mengsel van piridien en pirasoloon, of 'n mengsel van piridien en barbituursuur.

Daar is gevind dat die metode wat in 1969 in die Suid-Afrikaanse *Staatskoerant* gepubliseer is, kwantitatiewe herwinnings uit kaliumsianiedoplossings gee, maar nie in die aanwesigheid van goud nie.

Die ligandverplasingsmetode het nie kwantitatiewe herwinnings in die aanwesigheid van goud gegee nie, behalwe toe sink by die distilland gevoeg is, en dit het nie 'n kwantitatiewe herwinning van sianied uit ferrosianied gegee nie. Hierdie twee metodes is dus afgekeur as ongeskik vir die bepaling van sianied in oplossings wat klein hoeveelhede uraan en goud bevat.

Daar is gevind dat die prosedure van die American Public Health Association (APHA) kwantitatiewe herwinnings in die aanwesigheid van goud, uraan, tiosianaat en ferrosianied gee wanneer kuprochloried, of kuprochloried tesame met magnesiumchloried, by die distilland gevoeg word. Die spektrofotometriese meting met gebruik van 'n mengsel van piridien en barbituursuur word verkies.

Die kalibrasiebestek van die metode is 0,5 tot 6 μg sianied en die bepalingsgrens is 0,04 μg/cm^3. (Die metode se relatiewe standaardafwyking is 0,05.) Die distilleertyd in die APHA-metode is ongeveer $2\frac{1}{2}$ uur; met 3 distilleeropstellings kan daar tot 9 distillerings per dag gedoen word, plus 'n verdere 2 uur vir die spektrofotometriese bepaling.

Die voorkeurlaboratoriummetode word in besonderhede in 'n aanhangsel uiteengesit.

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1. INTRODUCTION

The determination of cyanide is required in effluent and intermediate solutions produced in metallurgical plants for the recovery of gold.

For effluent solutions (waste waters), a method has been published in the South African *Government Gazette*[1]. This is based on the liberation of hydrogen cyanide from complex metal cyanides and simple cyanides by distillation from a sulphuric acid solution containing magnesium chloride and mercuric chloride, and subsequent photometric measurement of the cyanide ions that have been collected in sodium hydroxide solution. This method is an adaptation of a method published by the American Public Health Association (APHA)[2], which claims that cyanide can be recovered from all complex metal cyanides except cobalticyanide. The Association gives procedures for the removal of interfering compounds, such as sulphide, and oxidizing agents.

A later edition[3] of this publication recommends distillation from a sulphuric acid solution containing either magnesium or cuprous chlorides. The magnesium salt is preferred in the presence of thiocyanate, and a mixture of pyridine and barbituric acid is used for the photometric measurement instead of the pyridine-pyrazolone reagent given in the method published in the South African *Government Gazette*. The use of barbituric acid means that the critical pH-adjustment step required in the pyrazolone procedure is not necessary.

Ingersoll *et al.*[4] describe a ligand-displacement procedure that allegedly recovers cyanide from many metal and complex anionic metal cyanides, but again not from cobalticyanide. Its advantage appears to be a shorter distillation time, 45 minutes as against 2 hours for the other methods. The reagents added to the sample before distillation are 4,5-dihydroxy-m-benzene disulphonic acid disodium salt monohydrate (TIRON), tetra-ethylenepentamine, lead acetate, and an acetate buffer to maintain the distilland at a pH value of 4,5.

The apparatus required for all three procedures and their variants is the same. Although these methods are allegedly applicable to the determination of cyanide in many metal cyanides and complex anionic cyanides with the exception of cobalticyanide, they make no mention of the determination of cyanide in the presence of gold or uranium, or of cyanide, in the presence of these elements and thiocyanate.

The three methods and their variants were therefore examined so that their relative merits could be determined in relation to the analysis of solutions that could contain small amounts of gold, uranium, and thiocyanate together with cyanide in parts-per-billion (10^9) to parts-per-million amounts. The South African Government specification for maximum cyanide in effluents is 0,5 p.p.m.

2. APPLICABILITY OF THE VARIOUS PROCEDURES

As the solutions for analysis would almost certainly contain gold, uranium, and thiocyanate as well as the more common metal cyanides, the three procedures with their modifications were applied to synthetic solutions containing known amounts of potassium cyanide (200 to 600 μg of cyanide) with and without the addition of gold cyanide (as potassium aurocyanide), uranium sulphate, thiocyanate (as ammonium thiocyanate), and one of the reputedly most stable of the base-metal cyanides, potassium ferrocyanide. The amounts of metals in the distillands were 12,6 mg of uranium, 0,2 to 2,4 mg of gold, 2 mg of mercury, 0,3 mg of nickel, and 0,21 mg of iron. The amount of ammonium thiocyanate was 15 mg.

The cyanides of mercury and nickel were analysed for CN only by the ligand-displacement method.

The experimental conditions and the results obtained are given in Tables 1 and 2 respectively. It is evident that quantitative recoveries are obtained from potassium cyanide solutions by all the methods tested. Subsequent tests using mercuric chloride alone, rather than the recommended mixture of mercuric and magnesium chlorides as catalyst, gave recoveries of only 5 per cent, and it is therefore possible that the presence of mercuric chloride inhibits the quantitative liberation of hydrogen cyanide. The presence of gold and uranium was not specifically mentioned in the various methods. A quantitative recovery in the presence of gold was obtained with the APHA method only when cuprous chloride was used as catalyst. A near-quantitative recovery was obtained for a mixed catalyst of cuprous chloride and magnesium chloride. The use of the mixed salts was prompted by the reported need for the use of magnesium chloride in the presence of thiocyanate[3], and by the observation that an addition of cuprous chloride was essential for the determination of cyanide in the presence of gold. The possibility of interference from thiocyanate in the ligand-displacement method of Ingersoll may arise from the formation of sulphide when solutions containing thiocyanate are acidified and distilled. The sulphide may then interfere with the measurement by selective electrode. Subsequent tests carried out with the addition of only cuprous chloride to solutions containing thiocyanate and thiocyanate plus gold as the complex potassium salt gave recoveries of cyanide that were quantitative. Quantitative recoveries were obtained in the presence of uranium salts by two of the methods tested, *Government Gazette* and APHA, and for ferrocyanide by all the procedures excepting that where zinc was present as an additive.

TABLE 1

Conditions of test (volumes added in cubic centimetres)

	Government Gazette method	APHA method			Ligand-displacement method
		MgCl$_2$	CuCl$_2$	CuCl$_2$ + MgCl$_2$	
Sample volume	250	250	250	250	250
H$_2$SO$_4$ (1-to-1)	25	50	50	50	–
HgCl$_2$ (68 g/l)	20	–	–	–	–
MgCl$_2$·6H$_2$O (510 g/l)	10	20	–	20	–
Cu$_2$Cl$_2$ (20 g/l)	–	–	10	10	–
Pb acetate (2,4 M)	–	–	–	–	2,5
TIRON (0,64 M)	–	–	–	–	5,0
TEPA (250 g/l, pH 4,5)	–	–	–	–	2,5
Acetate buffer (11,7 N, pH 4,5)	–	–	–	–	5,0

TABLE 2

The recovery of cyanide under the conditions shown in Table 1*

Distilland (containing from 200 to 600 µg of CN$^-$)	Recovery*, %					
	Government Gazette method†	APHA method‡			Ligand-displacement method‡	
		MgCl$_2$	CuCl$_2$	CuCl$_2$ + MgCl$_2$	As given	+ Zn
KCN	101 ± 2 (4)	104 ± 8 (2)	99 (1)	100 (1)	102 (1)	101 ± 1 (2)
KAu(CN)$_2$ (Au/CN = 3,9, Au = 1,9 mg)	61 ± 2 (2)	70 (1)	100 ± 1 (3)	94 ± 2 (2)	3 ± 0 (3)	90 ± 5 (2)
KCN + Au^{3+} (Au/CN = 12, Au = 2,4 mg)	–	–	101 ± 1 (2)	–	–	–
KCN + Au^{3+} (Au/CN = 1, Au = 0,2 mg)	–	–	97 (1)	–	–	–
KAu(CN)$_2$ + UO$_2$SO$_4$ (U = 12 mg)	70 ± 4 (2)	80 ± 1 (2)	99 ± 1 (2)	–	–	–
KCN + UO$_2$SO$_4$ (U = 12 mg)	98 ± 1 (2)	96 ± 4 (2)	99 (1)	–	–	–
K$_4$Fe(CN)$_6$ (1,38 mg)	99 ± 1 (2)*	98 ± 0 (2)	99 ± 2 (2)	98 ± 2 (2)	106 ± 3 (2)	1 ± 0 (2)
KCN + NH$_4$CNS (15 mg)	–	100 (1)	98 ± 2 (2)	100 ± 0 (2)	–	–
KAu(CN)$_2$ + NH$_4$CNS (15 mg)	–	88 ± 2 (2)	97 ± 3 (2)	–	–	–

* In this report *recovery* means the amount of constituent determined as a percentage of the amount present.

† Pyrazolone–pyridine reagent

‡ Barbituric acid–pyridine reagent

( ) = number of determinations

Ratios of Au to CN expressed by mass

– not determined

The results reported in Table 2 immediately preclude the use of the *Government Gazette* and ligand-displacement methods for the determination of cyanide from solutions associated with the recovery of gold and uranium from mine dumps. Whereas the addition of zinc to the distilland enables an almost quantitative (90 ± 5 per cent) recovery of cyanide in the presence of gold to be obtained by the ligand-displacement method[4], this addition almost totally inhibits the recovery of cyanide from potassium ferrocyanide. Apart from this, recoveries of only 88 per cent for mercury and 84 per cent for nickel cyanide were obtained.

As the recoveries with cuprous chloride as an additive for all the tests were all quantitative, the precision of the determination was calculated from the sets of replicate data. A value of 0,050 for the relative standard deviation was obtained.

3. SPECTROPHOTOMETRIC MEASUREMENT OF CYANIDE

Apart from the variations in the distilland reagents, two spectrophotometric procedures were used as recommended. Both methods suffer from the disadvantage that the absorbance of the coloured complex decreases with time as illustrated in Figure 1.

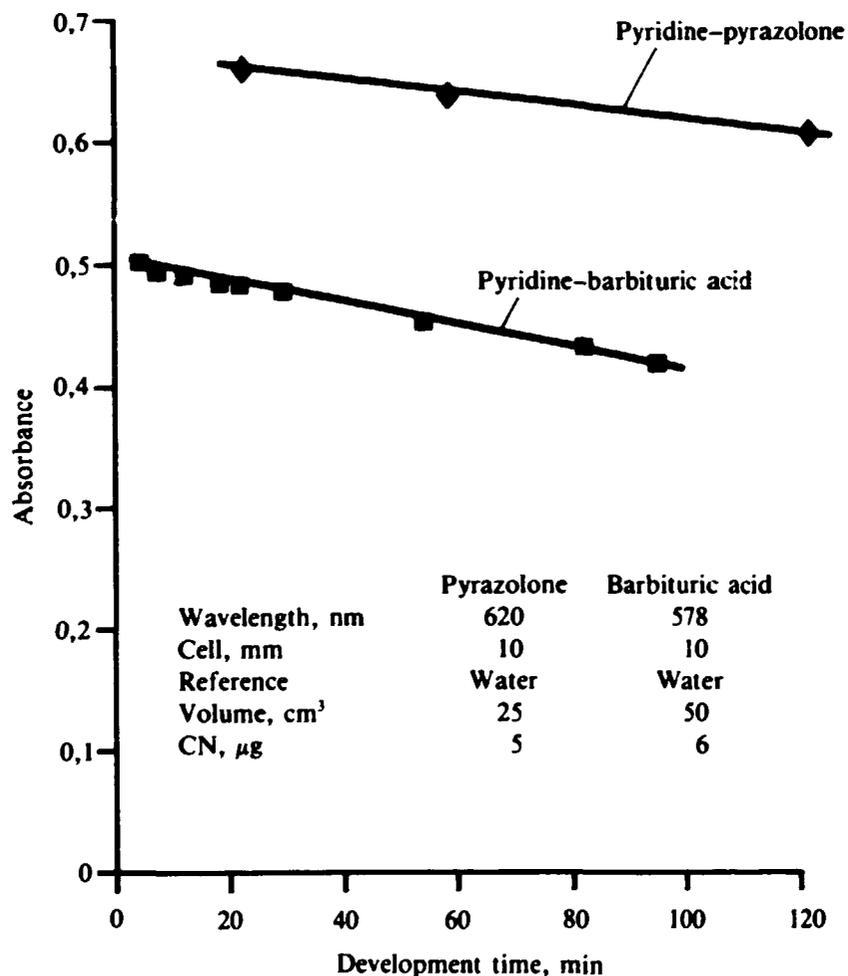|	Pyrazolone	Barbituric acid
Wavelength, nm	620	578
Cell, mm	10	10
Reference	Water	Water
Volume, cm^3	25	50
CN, μg	5	6

FIGURE 1. The effect of time of development on the absorbance of cyanide complexes

This is more critical when a mixture of pyridine and barbituric acid is used than with pyridine-pyrazolone. The respective rates of decrease are 0,00088 and 0,00053 absorbance unit per minute.

As a result of differences in manipulation, it was found convenient for the absorbance of the barbituric acid complex to be measured 10 to 15 minutes after the addition of the barbituric acid reagent, and the absorbance of the pyrazolone complex 30 to 40 minutes after the addition of the reagent. The change in absorbance after these times was 0,01 unit.

Less manipulation is involved with barbituric acid because it does not require the adjustment of pH, which is difficult and time-consuming. Thus, despite the more rapid change of absorbance of the barbituric acid complex this method is preferred.

4. TIME FOR ANALYSIS

The bulk of the analysis time is associated with the distillation, for which 15 minutes are required for the warm-up, 2 hours for the distillation itself, and a further 15 minutes without heat. With three distillation trains, up to nine distillations can be completed in one day, a further one to two hours being required for the spectrophotometric measurement. These nine determinations would normally include a control standard.

5. CONCLUSIONS AND RECOMMENDATIONS

The limited number of tests carried out led to the following conclusions.

(a) The use of mercuric chloride without magnesium chloride in the distilland when the *Government Gazette* method was used inhibited the distillation of hydrogen cyanide from potassium cyanide. In the presence of both salts, quantitative recovery of cyanide (101 ± 2 per cent) was obtained from solutions of potassium cyanide.

(b) In the presence of gold (1,9 mg) added as the complex potassium gold cyanide, quantitative recoveries were obtained only by the APHA method using cuprous chloride, or cuprous chloride plus magnesium chloride, as an additive to the distilland.

(c) The presence of uranium salts (12,6 mg of uranium) did not affect the recovery by the *Government Gazette* method or the various modifications of the APHA method.

(d) Cyanide in the presence of thiocyanate can be determined quantitatively by the APHA method with cuprous chloride as an additive to the distilland.

(e) Of the spectrophotometric procedures, that using the pyridine–barbituric acid reagent is preferred. Despite the higher rate of colour fading, the procedure is simpler and avoids the problems associated with the adjustment of pH, which is required in the alternative technique.

(f) It is recommended that the APHA method[3] using cuprous chloride as catalyst should be used for the determination of cyanide in effluents and solutions containing gold or thiocyanate, or both, such as those pertaining to the recovery of gold from mine dumps.

(g) Either the calibration should be carried out with the analysis, or suitable control solutions containing potassium cyanide should be included so that corrections can be made for day-to-day variations in the calibration.

(h) The literature indicates that the APHA method recommended in (f) is not applicable to cobalticyanide[3], but this was not confirmed because this cyanide chemical was not available. However, full recoveries from the stable ferrocyanide were obtained.

6. REFERENCES

1. REPUBLIC OF SOUTH AFRICA. *Government Gazette,* no. 2512. Pretoria, Government Printer, 29th Aug., 1969. pp. 30–34.

2. AMERICAN PUBLIC HEALTH ASSOCIATION. Standard methods for the examination of water and wastewater. 11th edition. New York, the Association, 1962. pp. 350–358.

3. AMERICAN PUBLIC HEALTH ASSOCIATION. Standard methods for the examination of water and wastewater. 14th edition. Washington D.C., the Association, 1976. pp. 361–379.

4. INGERSOLL, D., HARRIS, W.R., and BOMBERGER, D.C. Ligand displacement method for the determination of total cyanide. *Analyt. Chem.,* vol. 53. 1981. pp. 2254–2258.

APPENDIX

THE DETERMINATION OF CYANIDE BY DISTILLATION AND SPECTROPHOTOMETRIC MEASUREMENT USING A PYRIDINE-BARBITURIC ACID COMPLEX
(Laboratory Method No. 7/28)

1. OUTLINE

This method is basically that of the American Public Health Association (APHA)[1]. Its application has been tested at the Council for Mineral Technology (Mintek) in the presence of gold, uranium, and thiocyanate, either individually or in combination.

After treatment for the removal of any sulphides or oxidizing agents, the sample is reacted with sulphuric acid and cuprous chloride as catalyst, and the evolved hydrogen cyanide is absorbed in a sodium hydroxide solution. The resulting solution is reacted with a mixture of pyridine and barbituric acid, and the absorbance of the coloured complex formed is measured. The concentration of cyanide is determined from a calibration curve.

2. APPLICATION

The method is applicable to the determination of total cyanide in the form of free cyanide and complex anionic cyanides with the possible exception of cobalticyanide (Note 1). It can be used in the presence of gold, thiocyanate, and uranium in amounts up to 2,4 mg, 11 mg, and 12 mg respectively. The range of the calibration curve is from 0,5 to 6 μg for a 1 cm cell, and the precision of determination (relative standard deviation) is 0,05. With a single distillation train, three distillations can be made per day and, with three trains, up to nine distillations can be completed in one day.

3. APPARATUS

    (1) Distillation Apparatus

    As illustrated in Figure I-1.

    All joints should be glass standard-taper joints.

    (2) Gas-absorption Bottle

    This should be of the Fisher–Milligan or Friedrich type with a helical gas-absorbing path of about 900 mm.

    (3) Heating Mantle

    (4) Spectrophotometer
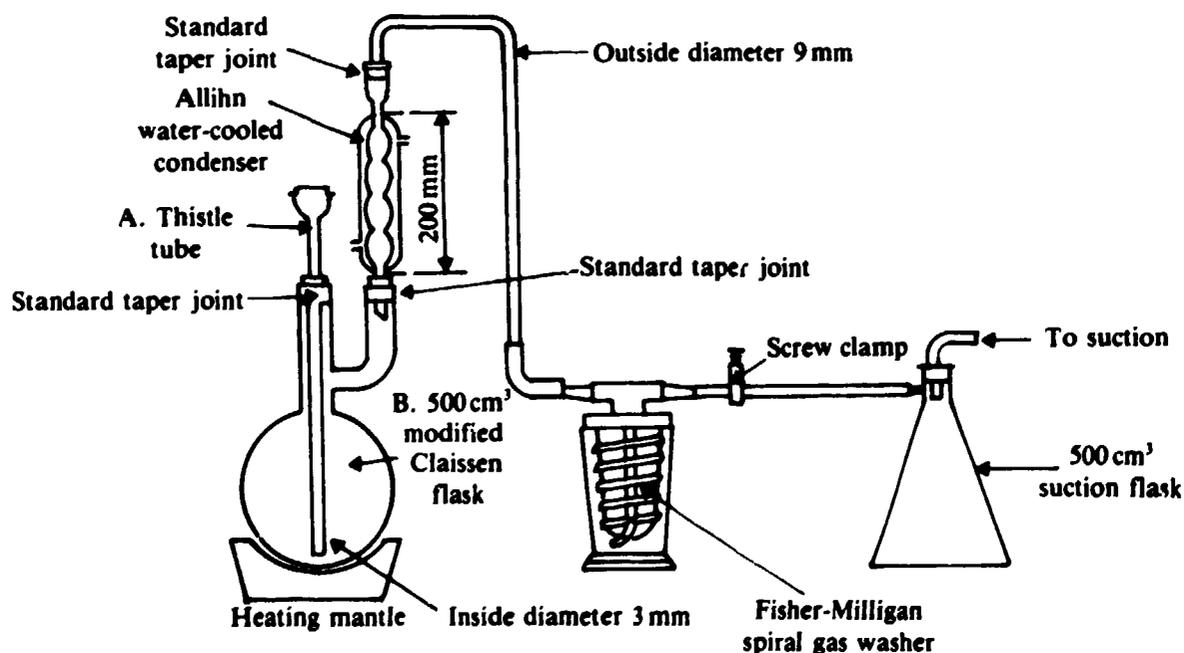
    For use at 578 nm.

FIGURE I-1. The apparatus used for the distillation of cyanide

4. REAGENTS

(1) Sodium Hydroxide Solution, 1,25 M

Dissolve 50 g of NaOH in water and dilute to 1 litre. (Store in a polythene container.)

(2) Sodium Hydroxide Solution, 0,25 M

Dissolve 10 g of NaOH in 1 litre of distilled water. (Store in a polythene container.)

(3) Cuprous Chloride

Weigh 20 g of finely powdered Cu_2Cl_2 into an 800 cm³ beaker. Wash twice by decantation with 250 cm³ portions of 1:49 sulphuric acid, and then gently wash twice with water. Add about 250 cm³ of water and approximately 125 cm³ of hydrochloric acid until the salt dissolves. The reagent should be clear; a dark discoloration indicates the presence of cupric salts. Metallic copper inserted into the reagent will reduce the cupric ions. Dilute to 1 litre with water. If precipitation occurs, add more hydrochloric acid. Store in a tightly stoppered bottle containing a few lengths of pure copper wire or rod extending from the bottom to the mouth of the bottle. If smaller reagent bottles are used, keep completely filled and tightly stoppered. Refill to the top from the original 1 litre of stock solution after each use to avoid the oxidation of the cuprous salt by air.

(4) Sodium Dihydrogen Phosphate, 1 M

Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 litre of distilled water. Refrigerate.

(5) Indicator Solution

Dissolve 0,02 g of paradimethylamino-benzal-rhodamine in 100 cm³ of acetone.

(6) Pyridine

A.R. Grade.

(7) Chloramine-T Solution, 10 g/l

Dissolve 1 g of the reagent in 100 cm³ of distilled water. Prepare daily.

(8) Pyridine-Barbituric Acid Reagent

Place 15 g of barbituric acid in a 250 cm³ volumetric flask, and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 cm³ of pyridine and mix. Add 15 cm³ of concentrated hydrochloric acid, mix, and cool to room temperature. Dilute to the mark with water, and mix. Prepare the solution daily.

(9) Standard Silver Nitrate Solution, 0,0192 N

Dissolve 3,27 g of silver nitrate ($AgNO_3$) in 1 litre of distilled water. Standardize against standard sodium chloride solution using the Mohr method with potassium chromate (K_2CrO_4) indicator.
1 cm³ of 0,0192 N $AgNO_3$ ≡ 1,00 mg of CN.

(10) Stock Cyanide Solution

Dissolve approximately 2 g of potassium hydroxide and 2,51 g of potassium cyanide in 1 litre of distilled water. CAUTION — Because potassium cyanide is highly toxic, avoid contact or inhalation. Standardize against standard silver nitrate solution. Store in a polythene container. The standardization is carried out as follows. Take an aliquot portion (25 cm³) of the stock cyanide solution and adjust the pH value to 11 or above with sodium hydroxide solution. Dilute the aliquot portion to 250 cm³, add 0,5 cm³ of indicator solution (reagent 5), and titrate with the standard silver nitrate solution (reagent 9) to the first change from a canary yellow to a salmon hue. Titrate a blank solution containing a similar amount of alkali and water.
The concentration of the stock cyanide solution is as follows.

$$CN = \frac{(AgNO_3 \text{ for CN solution, cm}^3) - (AgNO_3 \text{ for blank, cm}^3)}{\text{Aliquot portion taken, cm}^3}, \text{ mg/cm}^3.$$

(11) Standard Cyanide Solution

1 cm³ ≡ 1 µg of CN in 0,25 M NaOH solution

Take a calculated volume (approximately 10 cm³) of the stock cyanide solution based on the determined concentration (see (10) of Section 4), and dilute it to 1 litre with 0,25 M sodium hydroxide so that the cyanide concentration is exactly 10 µg/cm³. Mix thoroughly. Make a second dilution by taking 10 cm³ of the diluted cyanide solution and diluting it to 100 cm³ with 0,25 M sodium hydroxide. Prepare this solution afresh daily, and keep in a glass-stoppered bottle.
1 cm³ of this solution ≡ 1 µg of CN.

5. AMOUNT OF SAMPLE TO BE USED

Table I-1 indicates the volume of sample required. When the ranges overlap, use the larger alternative volume.

TABLE I-1

Volume of sample to be used

Estimated CN in sample, $\mu g/cm^3$	Volume of sample, cm^3
0,04 to 0,32	250
0,20 to 1,60	50
1 to 8	10
5 to 40	2

6. PROCEDURE

a. If necessary, test for the presence of sulphides and oxidizing agents in the following manner.

    (i) Test for the presence of sulphide by using lead acetate paper, and remove the sulphide if it is present by adjusting the sample to a pH value of 12 and stirring with small portions of powdered cadmium nitrate. Filter off the yellow cadmium sulphide.

    (ii) Test for oxidizing agents using o-tolidine reagent and, if present, add a few crystals of ascorbic acid at a time until no colour is produced when the solution is retested.

b. Place $50 cm^3$ of sodium hydroxide solution (reagent 1 in Section 4) in the gas-absorption bottle, and dilute if necessary to ensure that the helical absorption path will be covered with the solution when the gas is passing through the system. Attach the flask to the train.

c. Place a suitable aliquot portion of the sample in flask B (Figure I-1), and dilute if necessary to about $250 cm^3$.

d. Adjust the suction so that about one bubble per second enters the distillation flask through A (Figure I-1), the air-inlet thistle tube (Note 2).

e. Through the thistle funnel, add $50 cm^3$ of 1-to-1 sulphuric acid followed after one minute by $10 cm^3$ of the cuprous chloride reagent (reagent 3 of Section 4).

f. Heat to boiling and reflux for at least two hours. Adjust the heating rate so that vapours do not rise more than half way up the condenser (Note 3).

g. Discontinue heating, and allow the air to continue bubbling for a further 15 minutes.

h. Quantitatively transfer the contents of the gas-absorption bottle, and of the connecting tube from the condenser to the bottle, into a $250,0 cm^3$ volumetric flask. Rinse the bottle and connecting tube with water, adding the washing solution to the $250,0 cm^3$ volumetric flask. Dilute to the mark with water.

i. Using distilled water instead of a sample, prepare a blank solution by following the procedure detailed in steps b to h.

j. Transfer $20,0 cm^3$ of the distillate obtained from step h, or a suitable aliquot portion diluted to $20,0 cm^3$ with 0,25 M sodium hydroxide, into a $50 cm^3$ volumetric flask.

k. Transfer two portions of $6,0 \mu g$ of cyanide ($6,0 cm^3$ of reagent 11 in Section 4) to two additional volumetric flasks, and dilute each to $20,0 cm^3$ with 0,25 M sodium hydroxide. These will be used for the determination of the recovery factor, F (Note 4).

l. Add $15 cm^3$ of the phosphate buffer (reagent 4 in Section 4), and mix thoroughly.

m. Add $2 cm^3$ of chloramine-T solution (reagent 7 in Section 4), and swirl to mix.

n. IMMEDIATELY after the addition of the chloramine-T solution, add $5 cm^3$ of the mixture of pyridine and barbituric acid (reagent 8 of Section 4), and swirl to mix.

o. Dilute to $50,0 cm^3$ with water, mix well, and allow the colour to develop.

p. Between 10 and 15 minutes after the addition of the pyridine and barbituric acid, measure the absorbance of the coloured complex, using a 10 mm cell at a wavelength of 578 nm. Use water as a reference.

q. Using the calibration graph, relate absorbance to mass of cyanide (in micrograms) in the aliquot portion used, having corrected for the absorbance of the blank solution.

7. CALIBRATION

a. Transfer 0, 0,5, 1,0, 2,0, 4,0, and 6,0 cubic centimetres of the standard cyanide solution (reagent 11 of Section 4) to $50,0 cm^3$ volumetric flasks. Dilute each to $20 cm^3$ with 0,25 M sodium hydroxide (reagent 1 of Section 4).

b. Proceed as from steps 1 to p in Section 6.

c. Prepare a graph relating absorbance and concentration of cyanide. having corrected the absorbances for the blank solution.

8. CALCULATION

$$\text{Concentration of } CN^-, \mu g/cm^3 = \frac{(M_1 - M_2) \times V_1 \times F}{V_2 \times V_3}$$

where

M_1 = CN in the aliquot portion used for the absorbance measurement, μg

M_2 = CN in the blank solution, μg

V_1 = Volume to which distillate was diluted, cm^3

V_2 = Volume of aliquot portion of distillate used for the absorbance measurement, cm^3

V_3 = Volume of sample distilled, cm^3

F = Recovery factor.

NOTES

1. It is claimed that cyanide is recovered from cobalticyanide by the use of ultraviolet irradiation as described by Goulden et al.[2].

2. The flowrate can be increased to two bubbles per second to prevent solution in the flask from being forced up into the thistle funnel. If the flowrate is too high, some hydrogen cyanide may escape absorption.

3. If the solution in the flask tends to be forced up through the thistle funnel, a cold, wet (previously prepared) pad of paper should be placed on the upper spherical surface of the flask.

4. The recovery factor is used to compensate for small variations arising from aging of the reagents and different batches of barbituric acid.

9. REFERENCES

1. AMERICAN PUBLIC HEALTH ASSOCIATION. Standard methods for the examination of water and wastewater. 14th edition. Washington, D.C., the Association, 1976. pp. 361–386.

2. GOULDEN, P.D., AFGHAM, B.K., and BROOKSHANK, P. Determination of nanogram quantities of simple and complex cyanides in water. *Analyt. Chem.*, vol. 44. 1972, p. 184.