

TOTAL CYANIDE IN REFINERY WATERS BY VISIBLE SPECTROPHOTOMETRY

UOP Method 682-84

SCOPE

This method is for determining cyanide in aqueous solutions in the presence of large quantities of sulfide. The lower limit of detection in the presence of 1.0% or 0.1% sulfide is 0.2 or 0.02 mass-ppm cyanide, respectively. The upper limit of detection can range from 200 ppm to 10,000 ppm cyanide depending on the size of the sample selected for analysis. Thiosulfate above a level of 0.1% will interfere with the test. Significant amounts of sulfite, thiocyanate, aldehydes, amines and other materials can also interfere with the analysis. The instability of cyanide in the presence of air requires that the analysis be performed as soon as possible after sampling.

OUTLINE OF METHOD

The sulfide content of the sample is determined by UOP Method 683, or equivalent, to determine the sample size required for sulfide removal using cadmium carbonate. The cyanide released after acidification is distilled and swept into an alkaline absorption solution. After neutralization and the addition of chloramine-T and barbituric acid-pyridine, the absorbance of the solution's red-blue color is measured spectrophotometrically at 578 nm. The mass-ppm cyanide is determined from a previously prepared calibration curve.

APPARATUS

Balance, readability, 0.1-mg

Beakers, graduated, 100-, 250- and 400-mL

Cotton balls, medium size

Cyanide micro distillation apparatus, fabricated and described as shown in Figs. 1 through 5, available from UOP Inc., or equivalent

Absorber tube, with a Teflon stopcock metering valve, Lab Glass Inc., Cat. No. LG-9606T-100, Fig. 1, "C"

Distillation tube, with built-in condenser and charger funnel, Fig. 1, "A"

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Filter assembly, consisting of a Millex Filter, Millipore, Type HA, 0.45 μm , Cat. No. SLHA0250S, inserted into a shortened Luer Lok stainless steel needle (0.065-inch OD, 16 gauge). A length of Teflon tubing (400-mm, 0.125-inch OD) connected to the needle, leads directly onto the stopcock inside the charger funnel of the distillation tube through a tight fitting neck (5-mm OD) of the ground glass joint (19/38), Fig. 3, "B".

Flow manometer, with a 300-mm length of capillary glass tubing (0.25-mm ID) immersed into a test tube. A short piece of the same tubing is used as an air flow restrictor, Fig. 2.

Gas scrubber, hydrogen sulfide, Fig. 1, "B"

Heating jacket fluid circulation system, Fig. 5, arranged so that a heating jacket surrounding the distillation tube is positioned higher than the circulator pump, Haake, Model D3. Make all connections using heavy wall rubber tubing secured with stainless steel clamps.

Syringe assembly, consisting of a 50-mL (1-mL graduations) Plastipak Disposable Syringe with Luer Lok, Becton Dickinson, Cat. No. 5663, fitted with a stainless steel Luer Lok stopcock, Millipore, Cat. No. XX30-025-65, Fig. 3, "A"

Vacuum source, consisting of a vacuum pump and a 2-liter filtering flask with side tube as a trap, Fig. 4

Flask, Erlenmeyer, 250-mL capacity, narrow neck, T stopper, Sargent-Welch Scientific, Cat. No. S-34147-F, or equivalent

Flasks, volumetric, 50-, 100-, 250-, 500-, 1000- and 2000-mL

Pipets, dispensing, Eppendorf multivolume micropipet, Sargent-Welch Scientific, Cat. No. SC69721-10C & 10J, or equivalent

Pipets, disposable, glass, 145-mm length, Pasteur, capillary, Sargent-Welch Scientific, Cat. No. S-69647-A, or equivalent

Pipets, volumetric, 1-, 2-, 5-, 10-, 20-, 25- and 50-mL

Pipets, graduated, 10- and 25-mL

pH meter, Orion, Model No. 611, Sargent-Welch Scientific, Cat. No. S-30030-90, or equivalent

Spectrophotometer, with 10-mm matched silica cells, Bausch and Lomb, Model 710, or equivalent

Stirring apparatus, magnetic, variable speed, Sargent-Welch Scientific, Cat. No. S-76506, or equivalent

Sulfide in Refinery Waste Water test apparatus, see UOP Method 683

Timer

Weighing dishes, polystyrene, disposable, capacity approximately 5.5 g, Sargent-Welch Scientific, Cat. No. S-3860-C, or equivalent

REAGENTS AND MATERIALS

All reagents shall conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, when such specifications exist, unless otherwise specified. References to water shall mean deionized by polystyrene amberlite type resins. The water must meet Type II requirements described in ASTM D 1193. Unqualified references to solutions mean aqueous solutions.

Acetic acid, glacial

Alcoholic sodium hydroxide absorber solution. Dissolve 64 ± 0.1 g of reagent grade NaOH pellets in approximately 1600 mL of water in a 2000-mL volumetric flask, cool and dilute to volume with methanol. Shake to mix.

Barbituric acid, 98% minimum purity, Sargent-Welch Scientific, Cat. No. EK1090-100GM, or equivalent

Buffer solution, sodium acetate pH of 6. Dissolve 40.0 ± 0.1 g of anhydrous sodium acetate in 60 ± 2 mL of water, using a 250-mL beaker. Bring to a pH of 6 as measured with a pH meter using about 6-8 mL of glacial acetic acid. Transfer and dilute to volume in a 100-mL volumetric flask.

Cadmium carbonate, powder, 98% minimum purity, Sargent-Welch Scientific, Cat. No. SC16016-500GM, or equivalent

Chloramine-T solution. Dissolve 1.0 ± 0.01 g of hydrated Chloramine-T (Sargent-Welch Scientific, Cat. No. EK1022-250GM, or equivalent) in a 100-mL volumetric flask in water. Dilute to volume and mix. Prepare fresh weekly.

Hydrochloric acid, concentrated

Lead acetate solution, 5%. Dissolve 25 ± 0.1 g of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (Sargent-Welch Scientific, Cat. No. SC13088-500GM, or equivalent) in approximately 300 mL of water in a 500-mL volumetric flask. Add 125 mL of glacial acetic acid, swirl to dissolve, dilute to volume with water and mix.

Magnesium chloride catalyst solution. Dissolve 51 ± 0.1 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Sargent-Welch Scientific, Cat. No. SC13291-500GM, or equivalent) in water in a 100-mL volumetric flask. Dilute to volume with water and mix.

Methanol, HPLC grade (not more than 3 ppm acetone or aldehydes), Fisher Scientific, Cat. No. A-452, or equivalent

Phenolphthalein indicator, 1% solution in methanol, Sargent-Welch Scientific, Cat. No. SC14007-500ML, or equivalent

Potassium cyanide, 96% minimum purity, Sargent-Welch Scientific, Cat. No. SC17216-125GM, or equivalent

Potassium Cyanide Stock Solution, 250 ppm. Dissolve $0.6258 \text{ g} \pm 0.1 \text{ mg}$ of KCN in approximately 200 mL of water containing 1.6 g of NaOH pellets in a 1000-mL volumetric flask, dilute to volume with water and mix. Prepare monthly.

Potassium Cyanide Standard Solution, 10 ppm. Pipet 20 mL of the potassium cyanide stock solution into a 500-mL volumetric flask, dilute to volume using the alcoholic sodium hydroxide solution and mix. Prepare weekly.

Potassium Cyanide Working Solution, 1 ppm. Pipet 25 mL of the potassium cyanide standard solution into a 250-mL volumetric flask, dilute to volume using the alcoholic sodium hydroxide solution and mix. Prepare on a daily basis as needed, within two hours of analysis, and protect from light.

Pyridine, 99.8% minimum purity, Sargent-Welch Scientific, Cat. No. SC14376-500ML, or equivalent

Pyridine-barbituric acid reagent. Weigh 15 ± 0.1 g of barbituric acid into a 400-mL beaker. Stir with a magnetic stirrer while wetting the powder with a little water to make a smooth paste. Carefully, in a fume hood, add 75 mL of pyridine, followed by 15 mL of concentrated HCl and stir until all lumps are dispersed. Dilute to about 200 mL with water and stir until a clear yellow solution is formed. Transfer into a 250-mL volumetric flask, allow to cool, dilute to volume and mix. Prepare fresh weekly or discard sooner if the solution severely darkens or if a precipitate forms.

Sodium hydroxide, 10% in water

Stopcock grease, silicone

Sulfuric acid, 1:1. Carefully pour 100 mL of concentrated H_2SO_4 into 100 mL of water in a 250-mL glass stoppered Erlenmeyer flask, cool and mix.

Triethylene glycol, 97% minimum purity, Sargent-Welch Scientific, Cat. No. EKP2828-001KG, or equivalent

CALIBRATION

To minimize the possibility of oxidation, prepare the standards for the calibration curve while distilling the last sample to be analyzed. Using a graduated 10-mL pipet, transfer 0.5, 2.0, 5.0 and 8.0 mL of the one-ppm *Potassium Cyanide Working Solution* into four, labeled 50-mL volumetric flasks. Using a graduated pipet add to the respective flasks 9.5, 8.0, 5.0 and 2.0 mL of alcoholic sodium hydroxide absorber solution to bring the volume in each flask to 10 mL. To a fifth flask add by pipet 10 mL of alcoholic sodium hydroxide absorber solution. Continue the procedure as described under *Spectrophotometric Determination*.

PROCEDURE

Preparation of Distillation Apparatus

Assemble the apparatus as shown in Figs. 1 through 5 and rinse the micro cyanide distillation apparatus with water. All ground glass joints should be greased lightly with silicone stopcock grease. Start and adjust the heater-circulator pump to maintain the triethylene glycol temperature at 120 C. Disconnect the gas scrubber (Fig. 1B) and prepare it by packing 3 cotton balls inside and thoroughly soaking the cotton with lead acetate solution by allowing 15 ± 0.5 mL of the solution to drain through the packed scrubber into a 100-mL beaker. Remove the excess solution by touching the vacuum hose to the male ball joint for about 30 seconds, secure the gas scrubber to the distillation tube with spring hooks and connect the ball joint with the clamp.

Pipet 20 mL of water into the absorber tube and add about 50 ± 1.0 mL of water into the charger funnel. Connect the flow manometer (Fig. 2) to the charger funnel and apply a vacuum equivalent to 100-120 mm of water (to which a few drops of food coloring has been added) in the capillary column, by adjusting the Teflon stopcock metering valve (Fig. 1C). Once the metering valve is properly adjusted, a smooth, steady and reproducible air flow is obtained for many successive distillations. Remove the flow manometer glass joint from the charger funnel. Turn off the pump circulating the triethylene glycol heating fluid around the heating jacket and by opening the pinch clamp, allow air to enter into the jacket and to gravity-drain the heater fluid into the circulator. Remove the gas scrubber and cool the interior of the distillation tube by flushing it with cold water added above the condenser while simultaneously vacuum siphoning it off from the charger funnel with a piece of plastic tubing connected to a vacuum hose. (The apparatus is cleaned out in the same manner between distillations.) Reconnect the gas scrubber and secure with the spring hooks. Drain the water from the absorber tube, rinse with acetone and dry using vacuum. Pipet 20 mL of alcoholic absorber solution into the absorber and reconnect the calibrated metering valve on top of the absorber tube. Connect and clamp the ball joints, and then place the syringe/filter assembly (Fig. 3) into position on the charger funnel making sure that the Teflon sample tubing ends close above the stop-cock inside the charger funnel. When the apparatus is on stand-by or not in use, keep both the distillation and absorber tube clean by leaving each filled with a 1:10 aqueous dilution of alcoholic absorber solution.

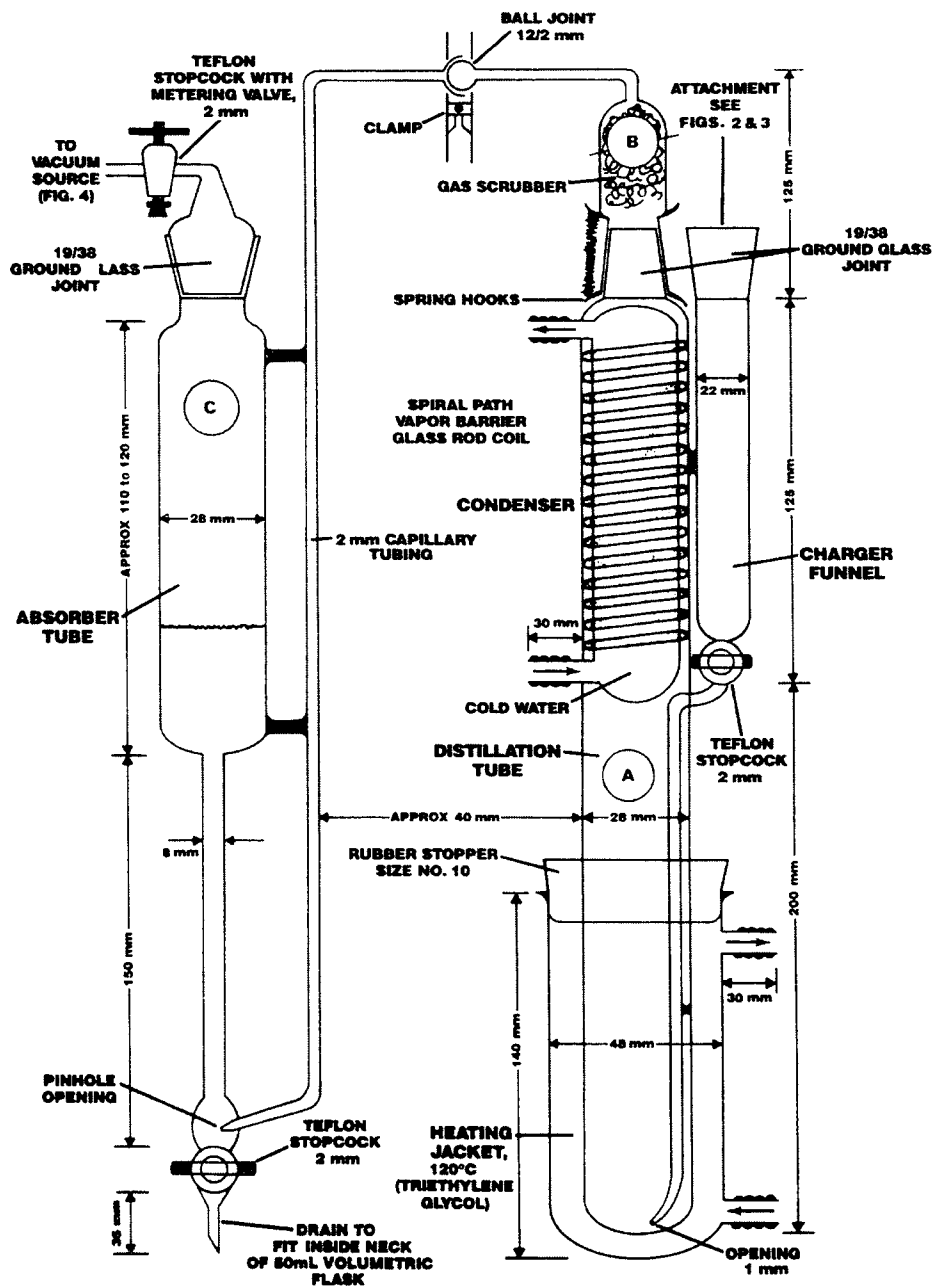


Figure 1

Cyanide Micro Distillation Apparatus

NOT TO SCALE

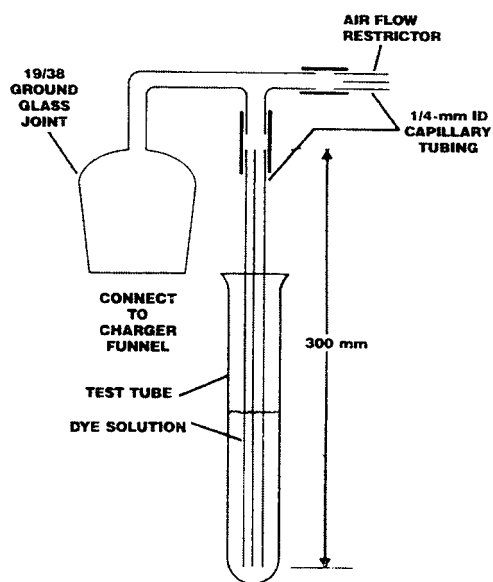


Figure 2

Flow Manometer

(NOT TO SCALE)

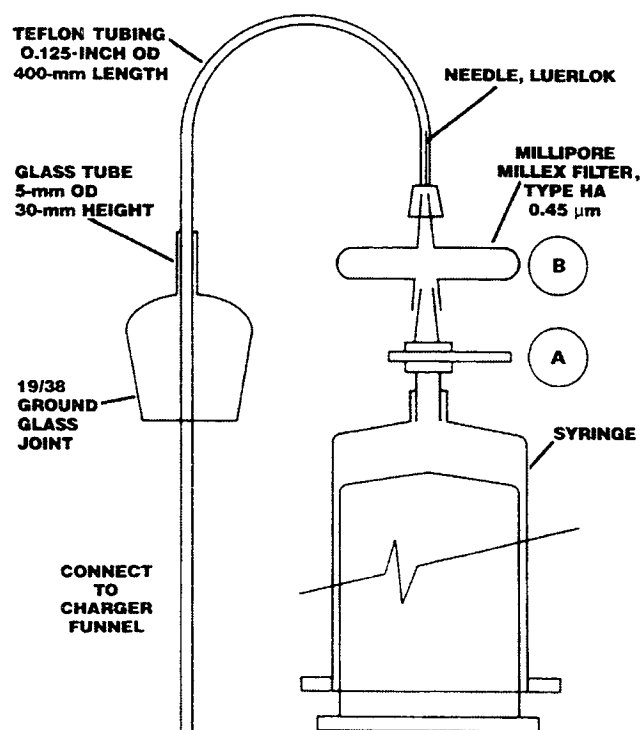


Figure 3

Syringe/Filter Assembly

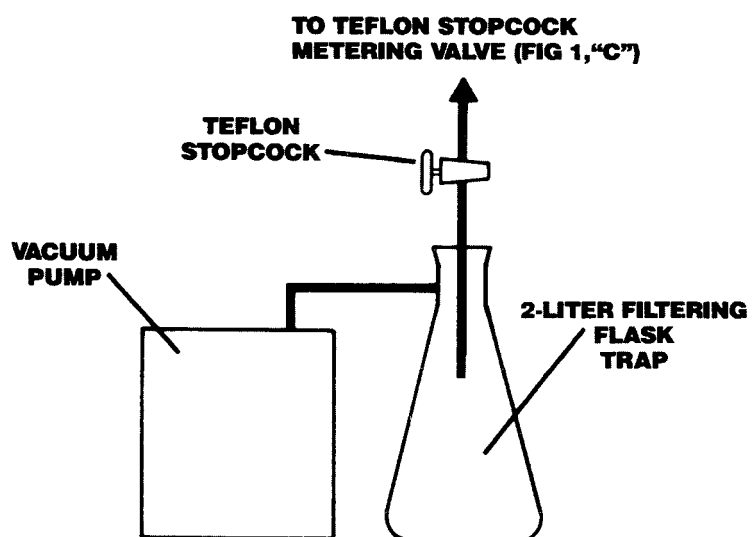


Figure 4
Vacuum Source and Trap

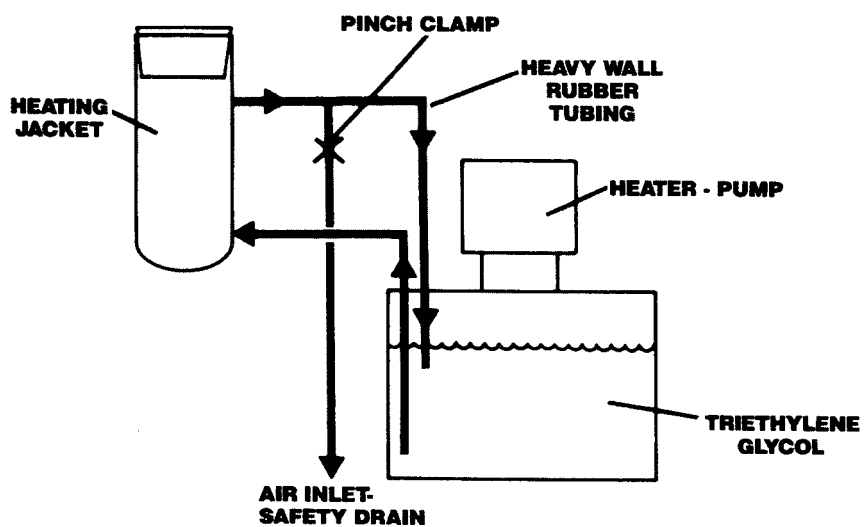


Figure 5
Heating Jacket Fluid Circulation

Sample Size Determination

Determine the sulfide content of the sample using UOP Method 683, or equivalent. Determine the density of the sample using ASTM Method D 1298. Dilute the sample as specified in Table 1. Pipet the required aliquot of sample into a 100-mL volumetric flask. Add two drops of phenolphthalein and shake the flask. If the solution turns red (see *NOTE*), titrate with glacial acid, using a disposable pipet, to a colorless endpoint. Dilute to 100 mL with water immediately prior to sulfide removal and shake to mix

Table 1

Sulfide, %	Sample Aliquot Diluted to 100 mL (Item C in Calculations)
2.1 - 5.0	2.0
1.1 - 2.0	5.0
0.51 - 1.0	10.0
0.21 - 0.5	20.0
0.11 - 0.2	50.0
0.1 or less	90.0

Sulfide Removal

Remove the plunger from the 50-mL plastic syringe, close the stainless steel stopcock and place the syringe with the open end at the top in a 400-mL beaker. Pipet 50 mL of the sample solution from the volumetric flask into the syringe. To the syringe, add 500 ± 10 mg of preweighed cadmium carbonate from a plastic weighing dish and 2.0 mL of sodium acetate buffer solution using a volumetric pipet. *IMMEDIATELY* insert the plunger. Use both hands to hold the plunger firmly in line with the syringe barrel to prevent gas or liquid leakage. Vigorously shake the syringe for 2 minutes holding it horizontally so that the mixture travels along the length of the barrel. Hold the syringe upright for 20 to 30 seconds to allow most of the solids to settle onto the plunger. Connect the syringe-stopcock to the Millex filter assembly (Fig. 3) previously connected to the charger funnel. While keeping the syringe upright, open the syringe-stopcock and slowly filter-inject 40 ± 0.05 mL of the clear filtrate through the charger tube and into the distillation apparatus. Disconnect the Teflon tubing from the Millex filter at the Luer Lok. Allow the contents of the tubing to drain into the charger funnel. Remove the remaining ground glass joint.

Cyanide Distillation

Following the sample injection, wash the charger funnel with 2 mL of magnesium chloride catalyst solution followed by 10 mL of H_2SO_4 (1:1) solution. Replace the flow manometer on the charger funnel and turn on the cooling water for the reflux condenser. Also turn on the heater fluid circulating pump with the pinch clamp closed, and set the timer to 30 minutes. The sample should be refluxing within 5 minutes. If the hot vapor zone climbs higher than 30% of the way up the condenser, immediately increase the cooling water flow. The flow manometer should indicate the proper preset vacuum air flow in the system producing a smooth bubble pattern through the absorber solution. The lead acetate soaked cotton of the gas scrubber may also begin to darken from gray to black, and elemental sulfur may precipitate in the boiling sample solution due to the degradation of the thiosulfate anion. The H_2S produced should not discolor more than about 2/3 of the cotton of the gas scrubber, since any H_2S passing through into the absorber solution will interfere with the analysis. If this occurs, repeat the analysis with a more dilute sample.

At the end of the 30 minute distillation time, turn off the circulating pump, open the pinch clamp to drain the heater fluid and then disconnect the ball joint. Gently lift and remove the glass joint from the top of the absorber tube (Fig. 1C) so as not to lose any absorber solution up into the capillary tubing. Then slowly drain the solution into a clean capped and labeled bottle.

Clean out the distillation apparatus and recharge the gas scrubber as detailed under *Preparation of the Distillation Apparatus* for additional distillations, if desired.

Spectrophotometric Determination

Due to the instability of the color developing reagents, mixing and subsequent spectrophotometric measurement must be done at a set time interval.

The cyanide concentration range to be covered determines the aliquot volume of absorber solution that must be brought to a volume of 10 mL and then mixed with the color developing reagents. These volumes are presented in Table 2 for several concentration ranges.

Table 2

Cyanide concentration range, ppm	Aliquot of absorber solution, mL (Item B in Calculations)	Volume of fresh absorber solution, mL
0.02 - 0.4	10.0	0
0.4 - 4.0	1.0	9.0
4.0 - 40	0.1	9.90
40 - 200	0.02	9.98
200 - 10,000*		

*If the cyanide concentration falls between 200 to 10,000 ppm, select a smaller sample volume than that presented in Table 1. Dilute to 100 mL and proceed with *Sulfide Removal*.

After selecting the cyanide concentration range, pipet the required volumes of absorber solution and fresh absorber solution into a 50-mL volumetric flask. Add one drop of phenolphthalein solution to the flask and carefully titrate the solution to just colorless using glacial acetic acid from a disposable pipet. Approximately 25-35 drops will be required. Do not use any more acetic acid than necessary, because cyanide will be lost.

In timed intervals of 1.5 minutes, add 2 mL of Chloramine-T solution to each flask of blank, standard or sample. Swirl for 30 seconds. Add 5 mL of pyridine-barbituric acid reagent, dilute to 50 mL with water and mix. Allow the color of the solutions to develop for exactly 14 minutes. Using the same interval of 1.5 minutes, read the absorbance of the solutions in a spectrophotometer at 578 nm in a 10-mm cell using water as a reference. A total of up to 9 samples and standards including a blank can usually be handled within the 14-minute time period with a 1.5 minute interval.

Draw a calibration curve by plotting the concentrations of the standards vs. absorbance after blank correction. The curve should follow Beer's Law. An example is shown in Fig. 6. From the net absorbance of the sample, determine the μg cyanide. If the absorbance of the sample is greater than the absorbance for the highest standard concentration, rerun the sample taking an aliquot of absorber solution from the next highest range. If the absorbance is less than 0.05, rerun the sample taking the volume of absorber solution from the next lower range.

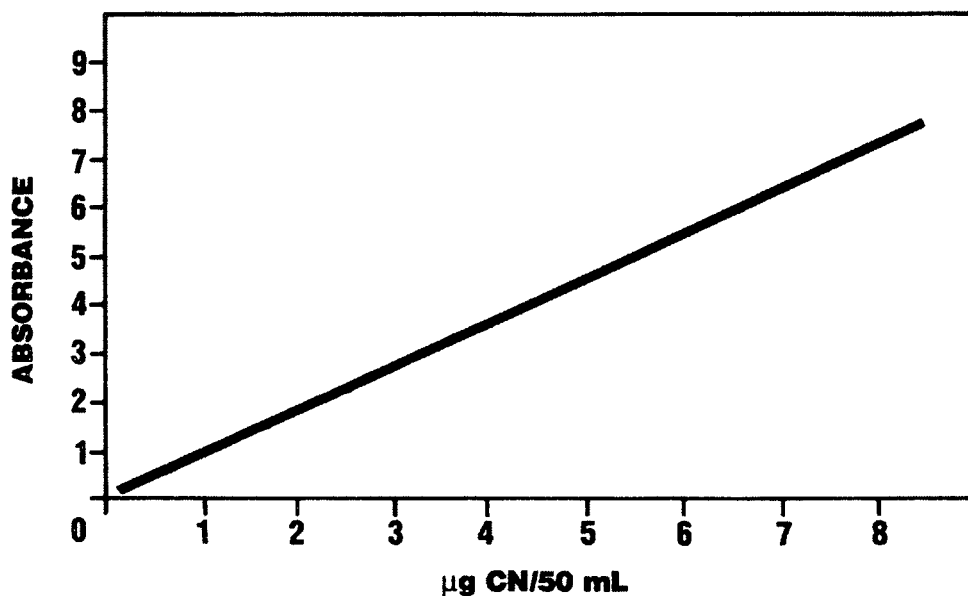


Figure 6

Visible Spectrophotometric Cyanide Calibration Curve at 578 nm

CALCULATION

Using the following equation determine the total cyanide concentration in mass-ppm.

$$\text{Cyanide, mass-ppm} = \frac{(20)(52)(100)A}{(40)(50)BCD}$$

where:

- A** = cyanide in absorber aliquot determined from calibration curve, µg
- B** = aliquot of absorber solution (Table 2), mL
- C** = sample volume taken for dilution to 100 mL (Table 1), mL
- D** = density of sample, g/mL
- 20** = total volume of absorber solution, mL
- 40** = aliquot of desulfurized sample injected into the distillation tube, mL
- 50** = aliquot taken from 100-mL sample dilution, mL
- 52** = total volume of syringe contents, mL
- 100** = final sample dilution volume, mL

NOTE

The lack of a red color at this point indicates that cyanide may have been lost from the sample due to improper stabilization.

PRECISION

Based on 5 replicate determinations, the estimated standard deviation (esd) for cyanide at the 0.2 ppm level was calculated to be 0.0017 ppm. Duplicate results by the same operator should not differ by more than 0.007 ppm (95% probability) at the stated level.

TIME FOR ANALYSIS

The elapsed time and labor requirement for one analysis are identical, 1.5 hours.

REFERENCES

1. UOP Method 683
2. "Determination of Micro Quantities of Cyanide in Presence of a Large Excess of Sulfide", M. O. Baker, R. A. Foster, Ben G. Post, and T. A. Hiett, *Analytical Chemistry*, **27**, p. 448, March 1955.
3. *Standard Methods for the Examination of Water and Wastewater*, 15th Edition, 1980.
4. ASTM D 1193, D 1298 and D 2036, www.astm.org

SUGGESTED SUPPLIERS

Bausch & Lomb, Spectroscopy Systems Div., 9545 Wentworth St., Sunland, CA 91350
Fisher Scientific Co., 1600 W. Glenlake Ave., Itasca, IL 60143
Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077
UOP Inc., 20 UOP Plaza, Des Plaines, IL 60016