

TRACE DISSOLVED OXYGEN IN LIQUIDS

UOP Method 364-85

SCOPE

This method is for determining dissolved oxygen in concentrations as low as 0.1 mass-ppm in liquefied petroleum gases, and in aqueous or organic solutions, including caustic, liquid hydrocarbons, glycols and phenols. The determination of combined oxygen is not within the scope of this procedure.

OUTLINE OF METHOD

Oxygen-free nitrogen is passed through a measured volume of a sample that is normally a liquid to remove dissolved oxygen. The oxygen-bearing nitrogen is passed over freshly cleaned copper wire. If the sample is a liquefied gas, a measured weight of the gas is expanded and passed over the clean copper wire. In either case, copper oxide is formed and then recovered as cuprous ion in ammoniacal ammonium chloride solution. The cuprous ion is oxidized by atmospheric oxygen to the cupric ion which is determined colorimetrically by complexing with sodium diethyldithiocarbamate stabilized with gum arabic. The oxygen content of the sample is then calculated from the amount of copper dissolved as a result of the oxidation process.

APPARATUS

Balance, electronic, top-loading platform, 8000-g capacity, readability 0.1-g

Balance, readability, 0.1-mg

Beads, glass, 3- to 5-mm diameter, Sargent-Welch Scientific, Cat. No. S-39838, or equivalent

Bottle, glass, 500-mL, wide-mouth, Sargent-Welch Scientific, Cat. No. S-8300-E, or equivalent

Cylinder, sampling, one-liter, 304 SS, 1/2-inch NPT female opening on each end, Hoke, Cat. No. 8HD1000, or equivalent

Dissolved oxygen apparatus, UOP Inc., or equivalent, see Fig. 1. On the equipment, each stopcock shall be numbered, and each arm from the stopcocks shall bear a letter designation. All stopcock plugs are made of Teflon.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Flasks, volumetric, (8) 100-mL, (2) 500-mL, (1) 1000-mL

Flowmeter, 1 to 280 mL/min., Sargent-Welch Scientific, Cat. No. S-39827-10B, or equivalent

Heating tape, silicone rubber covered, 115V, Sargent-Welch Scientific, Cat. No. S-40853-20D, or equivalent

Pipets, 1-, 2-, 5-, 10-, 15-, 20- and 50-mL

Regulator, nitrogen, two-stage, Matheson, Model 8-580, or equivalent

Rubber bulb, pressure or suction, 75-mL capacity, Sargent-Welch Scientific, Cat. No. S-73125, or equivalent

Rubber stoppers, solid, Size No. 13-1/2, Sargent-Welch Scientific, Cat. No. S-73305-W, or equivalent

Spectrophotometer, capable of reading at 420 nm, Beckman Model 35, equipped with 20-mm cells, Beckman Instruments, Inc., or equivalent

Thermometer, -20 to 110 C

Transformer, variable, 1.4 kVA, 10A, 120V, Sargent-Welch Scientific, Cat. No. S-30940, or equivalent

Valves, Globe, 316 SS, 1/2-inch NPT male inlet, 1/4-inch female NPT outlet, Hoke, Cat. No. 22154844, 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 are available, unless otherwise specified. References to water mean deionized or distilled water.

Acetone

Air, compressed, 99.9%

Ammonium chloride, ammoniacal solution. Dissolve 300 ± 0.1 g of ammonium chloride in one liter of water. Add one liter of 14-M ammonium hydroxide solution and filter. This solution is hereafter referred to as "ACAS."

Ammonium hydroxide, 7- and 14-M

Copper, wire, No. 24, Sargent-Welch Scientific, Cat. No. SC11545, or equivalent

Copper solution, standard, 0.02 mg Cu/mL. Dissolve 0.2 ± 0.1 mg of copper wire in 20 mL of concentrated nitric acid and dilute to one liter with distilled or deionized water. Dilute 50 mL of this solution to 500 mL with water.

Gum arabic solution. Dissolve 5 ± 0.01 g of gum arabic in 100 mL of water at room temperature and filter. Add 5 mL of methanol as a preservative.

Nitric acid, concentrated

Nitrogen, 99.99% minimum purity

Mercury

Methanol

Sodium diethyldithiocarbamate solution. Dissolve 0.2 ± 0.01 g of sodium diethyldithiocarbamate in 100 ± 0.5 mL of water.

Stopcock lubricant, Dow Corning high vacuum grease, Fisher Scientific, Cat. No. 14-635-5D, or equivalent

PREPARATION OF COLORIMETRIC STANDARDS AND CALIBRATION CURVE

Pipet accurately into 100-mL volumetric flasks, 1-, 2-, 5-, 10- and 15-mL of the standard copper solution containing 0.02 mg Cu/mL. Add 10 mL of 7-M ammonium hydroxide. Add water to dilute to about 90 mL. Add one milliliter of gum arabic solution and mix thoroughly. Add 2 mL of sodium diethyldithiocarbamate solution to assure an excess of this reagent. Fill each flask to the 100-mL mark with water and shake well.

After 10 minutes, but before one hour, determine the absorbances of these solutions against water as a blank (the absorbance of water is assumed to be 0.0), at 420 nm. Plot absorbances against milligrams of copper per 100 mL on linear graph paper. This calibration curve should be a straight line for the range of copper concentration indicated.

PREPARATION OF APPARATUS

Cut enough copper wire to fill the upper chamber of the nitrogen scrubber and the reactor into 12 ± 0.5 mm lengths. Wash the pieces with acetone to remove grease and dry with a stream of clean air. Pack the upper chamber of the nitrogen scrubber with the wire pieces. Loosely pack the space around the joint, between the upper and lower chamber, with glass beads to prevent entrainment of liquid in the gas outlet of the scrubber. Then pack the reactor with the remaining pieces of the copper wire.

The ACAS supply is contained in a 3-liter flask fitted with a standard taper joint. The ACAS flask closure is equipped with a fritted plate bubbler connect to Stopcock 1B. A liquid outlet tube is connected to Stopcock 12B, and a third outlet is connected to Stopcock 14. The bubbler permits first stage deaeration of the ACAS.

Fill the pressure relief valve to a depth of approximately 100 mm with mercury. Place a beaker or other container under the outlet to collect mercury if over pressuring occurs.

The nitrogen supply is connected to the system via a needle valve which is used to control nitrogen flow.

All glass tubing connections are 12/5 spherical joints. Organic tubings of all kinds are sufficiently permeable by oxygen to preclude their use in the apparatus (see Note 1). Apply water-insoluble stopcock grease to all ball joints. Assemble apparatus as indicated in Fig. 1.

Stopcocks 1 and 4 are 2-bore, 4-way, so that arms AD and BC can be simultaneously connected, or AB and CD can be connected.

Stopcock 3 is 1-bore, 4-way, so that any 2 adjacent arms may be connected.

Stopcock 14, on the ACAS supply flask closure, is 3-way 2-diagonal bore, so that the gas phase in the ACAS supply flask may be vented to the atmosphere or connected to Stopcock 1C by capillary glass tubing.

Stopcocks 2 and 5 through 13 are 3-way 120°.

Stopcock 12C connects to Stopcock 13B to permit transfer of ACAS to the nitrogen scrubber.

First Stage ACAS Deaeration

Turn Stopcock 1 to connect A to B and C to D. Turn Stopcock 14 to vent gas from the ACAS supply flask to the atmosphere. The position of other valves are not important. Adjust the nitrogen to provide a brisk bubbling rate in the ACAS supply flask. Purge with nitrogen for 15 minutes to reduce the dissolved oxygen of the ACAS to a low level.

Nitrogen Scrubber Filling

Turn Stopcock 14 to “off” position. Turn Stopcock 2 to connect AC, and Stopcock 3 to connect CD. Turn Stopcock 12 to BC, and Stopcock 13 to BA. The nitrogen pressure will increase in the ACAS supply flask and ACAS will flow from the supply flask to the nitrogen scrubber. When the ACAS reaches a level about 25 mm below the perforated plate in the lower section of the nitrogen scrubber, turn Stopcock 13 to “off” but not to “drain” position.

ACAS Scrubber Filling

Turn Stopcock 12 to BA position, and let the ACAS fill the ACAS scrubber to about 50 mm from the outlet capillary. Turn Stopcock 12 to “off” position, preferably a 60° turn clockwise from the BA position (see Note 2).

Nitrogen Purification and Apparatus Purging

Turn Stopcock 1 to AD-BC position. Nitrogen will now enter the side loop of the nitrogen scrubber at a point below the level of ACAS in the lower section of the nitrogen scrubber. The nitrogen will entrain ACAS and lift it into the copper-packed upper section of the scrubber. Repeated recycling of the nitrogen and ACAS will continuously reduce the surface of the copper in the upper section. The reduced copper surfaces thus exposed to the nitrogen will rapidly remove oxygen from the nitrogen.

Final Deaeration of ACAS

Bubble the deoxygenated nitrogen through the ACAS in the ACAS scrubber for 10 minutes at about 100 mL per minute to remove the last traces of oxygen.

Deaeration of Apparatus

Pass the nitrogen from the ACAS scrubber through the apparatus. Set Stopcock 3 at CB, Stopcock 4 at AD and CB, Stopcock 10 at CB, Stopcock 11 at CA. Set Stopcocks 5, 6, 8 and 9 to guide the nitrogen through the reactor on the first deaeration. Thereafter, nitrogen will bypass the reactor except during deaeration of a sample, or bubbling of ACAS in the reactor during flushing and draining.

Preparing the Reactor

With Stopcock 2 at AC, turn Stopcock 3 to AB, 9 to BC, 8 to CA, 6 to BC, and 7 to AC. Place a 100-mL volumetric flask under Arm C of Stopcock 7. The buildup of nitrogen pressure in the ACAS scrubber will force deoxygenated ACAS into the reactor. When the ACAS level reaches the top of the bed of copper wire in the reactor, turn Stopcock 9 to AB, 2 to AB, 4 to AB, 5 to AC. The nitrogen will bubble through the ACAS in the reactor and help to dissolve the oxidized copper in the ACAS. Some of the ACAS may be carried into the 100-mL flask at 7C. Pass nitrogen through the ACAS for 15 seconds.

Flush the ACAS from the reactor, refill with ACAS, and bubble nitrogen through the ACAS. Repeat this cycle for a total of 9 flushes. The sequence of stopcock manipulations is as follows:

To flush: Turn Stopcock 6 to AC, 5 to AB, 8 to AB and collect the ACAS escaping at 8B. Turn 8 counterclockwise to “off” position for about 10 seconds to permit ACAS to drain in the cell. Again turn 8 to AB and collect the ACAS.

To refill: Turn 8 counterclockwise to AC, 2 to AC, 9 to BC and 6 to BC. This order is required to ensure that nitrogen or ACAS pressure is imposed on the reactor before Stopcock 6 is opened to vent. Let in enough ACAS to cover the copper. Meanwhile turn 5 to AC and place the flask at 7C.

To bubble: Turn 2 to AB, and 9 to AB. Bubble for about 15 seconds and flush.

This sequence of bubbling, flushing and filling will be repeated for each blank determination and for each analysis. About 90 mL of ACAS is obtained from the reactor for a blank determination or for an analysis, requiring about 9 flushings of ACAS (see Note 3).

Apparatus Conditioning

Continue repeated reactor washings with deoxygenated ACAS until successive washings yield a constant absorbance with sodium diethyldithiocarbamate when measured at 420 nm. See *Blank Determination* for the true blank used in the calculations.

Blank Determination

Flush ACAS from the reactor and bubble the deoxygenated nitrogen through the reactor for 45 minutes at 40 to 60 mL per minute, the time required to thoroughly deaerate a liquid sample. Wash the reactor with deoxygenated ACAS as described under *Preparing the Reactor*. Obtain the absorbance of the washings from this blank run, and the equivalent in copper from the calibration curve. This blank is to be used as specified under *CALCULATIONS* (see Note 4).

PROCEDURE FOR LIQUID SAMPLES

Sampling

Determine the density of the sample using ASTM Method D 4052 or equivalent at the temperature of test. Two kinds of containers can be used for samples, either a 500-mL bottle or a stainless steel cylinder. In either case the sampling must be performed so as to exclude all oxygen (air) from the container. Bottle samples can be used when the analytical laboratory is located in the proximity of the sample source. The steel cylinder samples are used where samples are to be shipped.

Bottle samples: Extend a sample line to the bottom of a clean 500-mL bottle. Permit the liquid to overflow the bottle until a volume equal to the capacity of the bottle has overflowed. Insert a rubber stopper in the neck of the bottle, displacing liquid as the sample line is withdrawn from the bottle. This procedure is designed to ensure complete removal of air-contaminated liquid from the bottle, and minimize diffusion of atmospheric oxygen through the closure into the liquid.

Stainless steel cylinder samples: Purge the cylinder for 5 to 10 minutes with high purity nitrogen, close the cylinder valves allowing 70-140 kPa (10-20 psig) nitrogen pressure on the cylinder, disconnect from the nitrogen tank, and take the cylinder to the sample location. Arrange the cylinder in a *vertical* position and bring the sample line to the cylinder. Purge all air from the sample line by flushing with the sample, connect it to the lower cylinder valve, open both valves, and allow the sample to flow upward through the cylinder. Permit 2 to 3 liters of sample to flow through the cylinder and discard this material. Close both cylinder valves and disconnect the sample line. To avoid hydrostatic pressure buildup, immediately remove a small amount of sample from the cylinder by connecting the cylinder to a high purity nitrogen source and pressuring out about 100 mL of the liquid. Thoroughly purge the gas line before connecting it and maintain a slow nitrogen flow while the connection is being made.

Transfer of Sample into Liquid Sample Tube

The liquid sample tube of the apparatus (Fig. 1) has a volume of about 50 mL. A mark at the 25-mL level indicates the amount of liquid sample to be used. The tube is equipped with 120° 3-way Stopcocks 10 and 11, at the top and bottom ends, respectively, female spherical joints for attachment at Stopcock 4; a side tube (10A to 11C) and a vent (11B).

Connect a glass tube to Arm B of Stopcock 11, making a glass-to-glass connection (see Note 1).

Drain the ACAS from the reactor by displacing it with nitrogen.

Turn Stopcock 11 to BC and divert the deoxygenated nitrogen through the sample transfer line for one minute. Remove the stopper from the sample bottle, stop the flow of deoxygenated nitrogen and insert the sample line in the bottle, closing the neck of the sample bottle by wrapping it with aluminum foil.

Set Stopcocks 10 at BC, 4 at AB and DC, 5 at AC, 9 at AB, 8 at AC, 6 at BC and 7 at AC. Allow the deoxygenated nitrogen to vent from Stopcock 7 for one minute. Turn Stopcock 7 to “off” position, so that no deoxygenated nitrogen is being vented. Turn Stopcock 3 to DC to vent deoxygenated nitrogen. Turn Stopcock 4 to AD and BC and place a slight vacuum, through the use of a rubber bulb, on Stopcock 7 at C. Turn Stopcock 7 to AC and Stopcock 11 to AB. Allow the liquid to be slowly drawn up into the sample tube to the 25-mL mark. Turn Stopcock 7 to the “off” position. Turn Stopcock 3 to BC, 4 to AB and DC, to break the partial vacuum with deoxygenated nitrogen. Remove the rubber bulb from Stopcock 7 at C.

Remove the sample transfer line from the bottle and re-stopper the bottle. Blow out the remaining sample in the sample transfer line into a beaker by turning Stopcock 4 to AD and BC and Stopcock 11 to BC. Immediately start stripping the liquid sample in the sample tube with deoxygenated nitrogen as described under *Analysis*.

Analysis

Set Stopcocks 11 at AC and 7 at AC. The flow of deoxygenated nitrogen will displace oxygen from the sample and carry it into the reactor. Pass deoxygenated nitrogen through the sample for 45 minutes at a flow rate of 40 to 60 mL/minute.

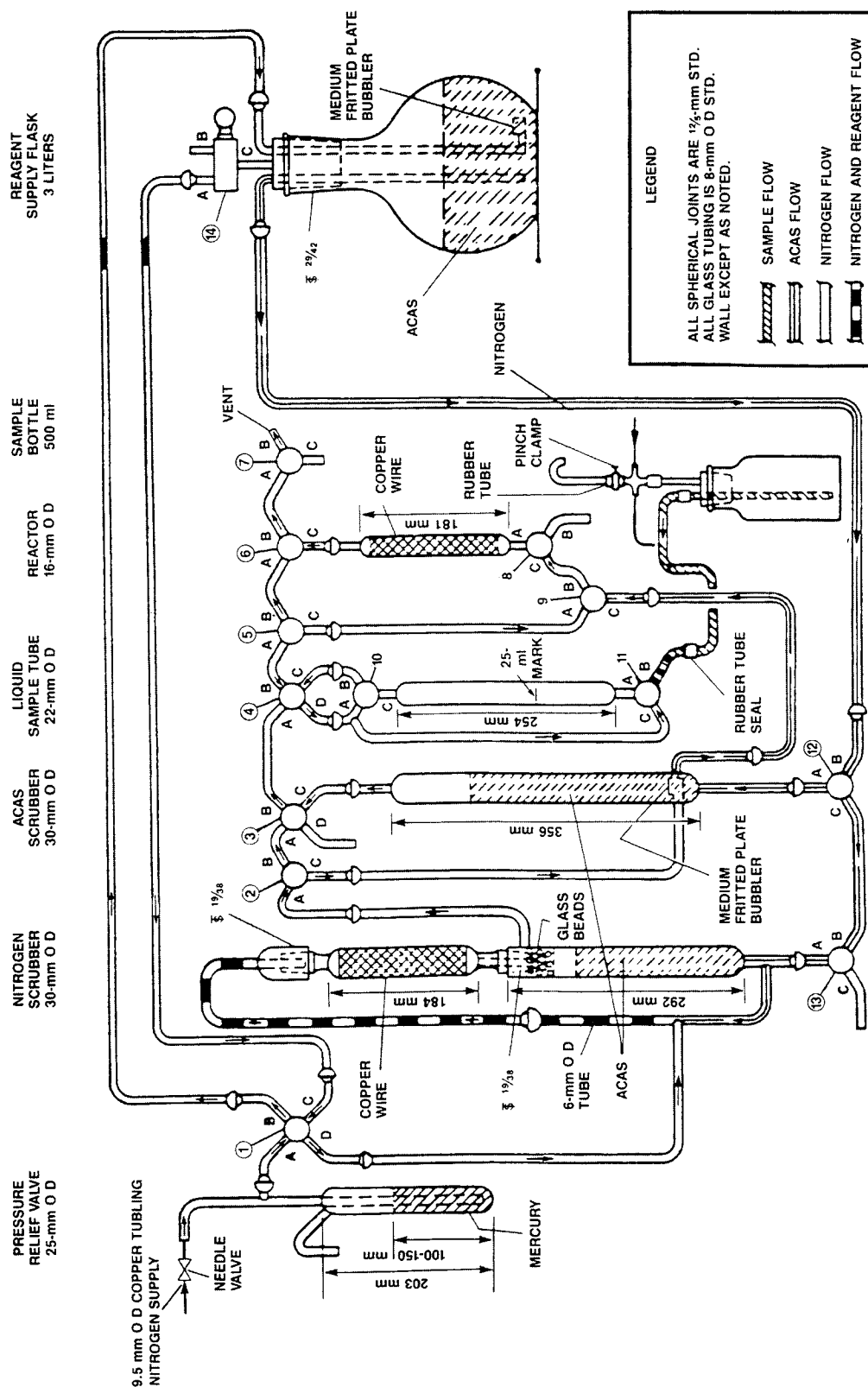


Figure 1

Apparatus for Determination of Dissolved Oxygen

Turn Stopcock 4 to AB and DC. Fill the reactor with ACAS. Bubble deoxygenated nitrogen for 15 sec, flush, fill and bubble 9 times, as when obtaining a blank determination. Collect the ACAS in a 100-mL volumetric flask and determine the amount of copper collected by the following procedure:

If the solution is water-white, signifying a low concentration of copper, fill the 100-mL volumetric flask with washings to no more than about 90 mL. Add one milliliter of gum arabic solution and mix thoroughly. Add 2 mL of sodium diethyldithiocarbamate solution, dilute to a final volume of 100 mL with water, and mix. Read the absorbance at 420 nm of the colored solution after 10 minutes, but before one hour, against water as reference.

If the ACAS washings contain over 0.3 mg of cupric ion per 100 mL, the ACAS will be bluish. The aliquot size to be taken for color development is dependent on how blue the washings are; the bluer the washings, the smaller the aliquot size. Dilute the washings in the 100-mL volumetric flask with water and mix. Transfer an appropriately sized aliquot to a second 100-mL flask. Add 10-mL of 7-M ammonium hydroxide and dilute to about 90 mL with water. Add one milliliter of gum arabic solution and mix thoroughly. Add 2 mL of sodium diethyldithiocarbamate solution and dilute to a final volume of 100 mL with water. Shake the flask well and after 10 minutes, but before one hour, determine the absorbance of the colored solution at 420 nm against water as reference. Take a smaller aliquot if the absorbance is greater than 0.4 absorbance and repeat the above procedure.

PROCEDURE FOR LIQUEFIED GAS SAMPLES

Sampling

When sampling a liquefied gas, connect a clean, dry one-liter stainless steel cylinder so that it is in a vertical position with the sample line connected to the lower valve. Completely open both valves of the cylinder and allow 1 to 2 volumes of the liquefied gas to flow through the cylinder. Close the bottom valve first, then close the top valve and disconnect the cylinder from the unit. With the cylinder in a vertical position, open the bottom valve to allow 40-50 mL of the liquid sample to flow out thereby preventing hydrostatic pressure from developing.

Analysis

Passage of the gas sample over clean copper surfaces in the reactor is carried out by employing an electrically-heated gas expansion valve. Fig. 2 shows the cylinder attached to the expansion valve apparatus. Wrap the heating tape around the valve only, and not on the tubing upstream from the valve. Heating of the tubing upstream from the valve causes boiling of the liquid in the sample line, and allows the volatile oxygen to migrate back into the cylinder. The temperature of the expansion valve, 38-43 C, is controlled by a variable transformer. During sampling, the valve on the sample cylinder is opened all the way and the expansion valve is used to control the flow. The sample quantity is determined by cylinder mass difference. Weigh the cylinder and contents to the nearest 0.1 g and connect to the system.

Set Stopcock 4 at AB, 5 at AB, 6 at AC, 8 at AB and drain ACAS from the reactor.

Set 8 at AC, 9 at AB, 5 at BC, 6 at AB, and 7 to AB.

Set 3 at CD and 2 at AC to deoxygenate the ACAS.

Attach the tubing downstream from the expansion valve to Stopcock 8 at B. Set Stopcock 8 at BC. Open the bottom valve of the sample cylinder all the way, and slightly open the heated gas expansion valve. Allow a *small* volume of the expanded gas to sweep out any atmospheric oxygen that might be entrapped in the tubing. Set Stopcock 8 at AB and 6 at BC. Attach a length of tubing from the vent, B at Stopcock 7, to a flowmeter and vent the gas to a safe area.

Adjust the flow rate of the expanded gas through the reactor to 40 to 60 mL/minute.

Pass a volume of gas through the unit as indicated in the following table:

Estimated O₂ Content, mass-ppm	Gas Sample mL
50-200	1200-1300
10-50	2500-2600
0-10	5000-5200

When the desired volume of gas has been passed through the reactor, close the valve of the sample cylinder and allow the remaining gas in the tubing to pass through the reactor. To determine whether all of the gas in the tubing has passed through the reactor, place the end of the vent tubing into a beaker of water and observe whether any bubbles are formed. Then close the gas expansion valve. Reweigh the sample cylinder to the nearest 0.1 g.

Set Stopcock 5 at AC, 7 at AC, 8 at AC, 9 at CB and 3 at AB and fill the reactor with ACAS. Collect any overflow at Stopcock 7 C.

Proceed with the sequence of bubbling, flushing and filling to recover reacted copper from the reactor until a total of 90 mL of ACAS washings has been collected.

Proceed with the color development step as directed in the last two paragraphs of *PROCEDURE FOR LIQUID SAMPLES*.

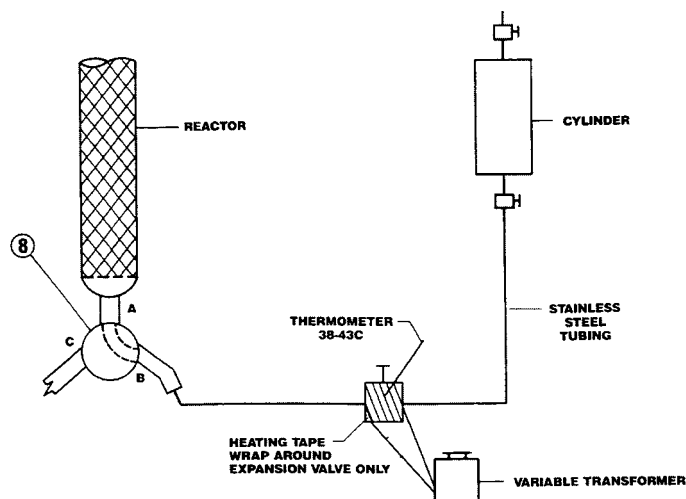


Figure 2
Gas Expansion Apparatus

CALCULATIONS

Determine the mass percent dissolved oxygen in liquids or liquefied gas samples as follows:

$$\text{Oxygen, mass-ppm} = \frac{126 \left(\frac{100S}{V} - B \right)}{W}$$

where:

B = copper in blank washings (read from the calibration curve), mg

S = copper in the aliquot taken for color measurement (read from the calibration curve), mg

V = volume of aliquot taken for absorbance measurement, mL

W = mass of sample, g. In cases where the sample measurement is volumetric, then $w = \text{volume (mL)} \times \text{density (g/mL)}$.

100 = volume to which the sample is diluted

126 = $\frac{16 (1000)}{2 (63.54)}$, atomic weight of oxygen divided by 2 times the atomic weight of copper.

This value is then multiplied by 1000 to convert mg to μg

NOTES AND PRECAUTIONS

1. Organic tubing may be used only to seal glass-to-glass or metal-to-glass connections for conduction samples into the apparatus. Expose the minimum surface of organic tubing to the sample. All sample lines must be stainless steel or glass.

2. ACAS must not be permitted to flow from the nitrogen scrubber to the ACAS scrubber or ACAS supply, or from the ACAS scrubber to ACAS supply. The ACAS in the nitrogen scrubber will quickly become filled with copper. Therefore, backflow to either the ACAS scrubber or ACAS supply will result in high blanks and erratic results.

3. All copper surfaces exposed to air become rapidly oxidized. Therefore, the ACAS from the first flushing of the reactor will contain considerable cuprous ion which, upon exposure to the air, will turn to blue cupric ammonium ion. Subsequent washings will contain less copper, and the solution will remain colorless when shaken with air. The presence of copper is then determined by complexing with sodium diethyldithiocarbamate as described under *PREPARATION OF COLORIMETRIC STANDARDS*.

4. If the absorbance of the blank is appreciably higher than the final absorbance obtained in the apparatus conditioning, the nitrogen scrubber is not removing all the oxygen from the nitrogen. This may be caused by either unsuitable nitrogen of high oxygen content (over 0.5%), or spent ACAS in the nitrogen scrubber which will occasionally require changing.

PRECISION

Based on 6 replicate determinations of liquid hydrocarbon samples, the estimated standard deviation (esd) was calculated for the dissolved oxygen concentration listed in the table below. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).

Level, Dissolved Oxygen, mass-ppm	esd, mass-ppm	Allowable Difference, mass-ppm
69	1.1	4.0
149	2.5	9.1

TIME FOR ANALYSIS

The elapsed time for one determination is 3 hours. The labor requirement is 2 hours.

REFERENCE

ASTM Method D 4052, www.astm.org

SUGGESTED SUPPLIERS

Beckman Instruments, Inc., Scientific Instruments Div., 2500 Harbor Blvd., Fullerton, CA 92634
 Fisher Scientific Company, 71 Forbes Ave., Pittsburgh, PA, 15219
 Hoke Inc., One Tenakill Park, Cresskill, NJ 07626
 Matheson, P.O. Box 85, East Rutherford, NJ 07073
 Sargent-Welch Scientific Co., 7300 N. Linder Ave., Skokie, IL 60077
 UOP Inc., 20 UOP Plaza, Des Plaines, IL 60016