

WATER IN GLYCOL

UOP Method 300-61

SCOPE

The procedures given are control analyses for determining the water content of Udex glycol streams.

OUTLINE OF METHOD

Four procedures of satisfactory accuracy are available for determining the water content of glycol samples. Each has its advantages and disadvantages with regard to convenience and necessary equipment. The latter consideration should govern the procedure chosen.

The first procedure is a modified ASTM method for determining the water content of petroleum products. The glycol sample is mixed with a water-immiscible solvent and distilled. The condensate is collected in a graduated trap and the volume of the water phase read directly. This procedure has the advantage of requiring only readily available equipment. The total time required is from two to four hours.

The second procedure is similar in principle, except that a solvent heavier than water is used and a specially-designed water trap is required. The total time required for each analysis is reduced to one-half hour.

The third procedure is a refractive index method which requires a shorter analysis time than either of the previous methods. The refractive index of the sample is measured by a refractometer and the water content read from a calibration curve. This procedure is more susceptible to interference from foreign materials (e.g., hydrocarbons) in the glycol, which limits the application of the method (see UOP Method 390).

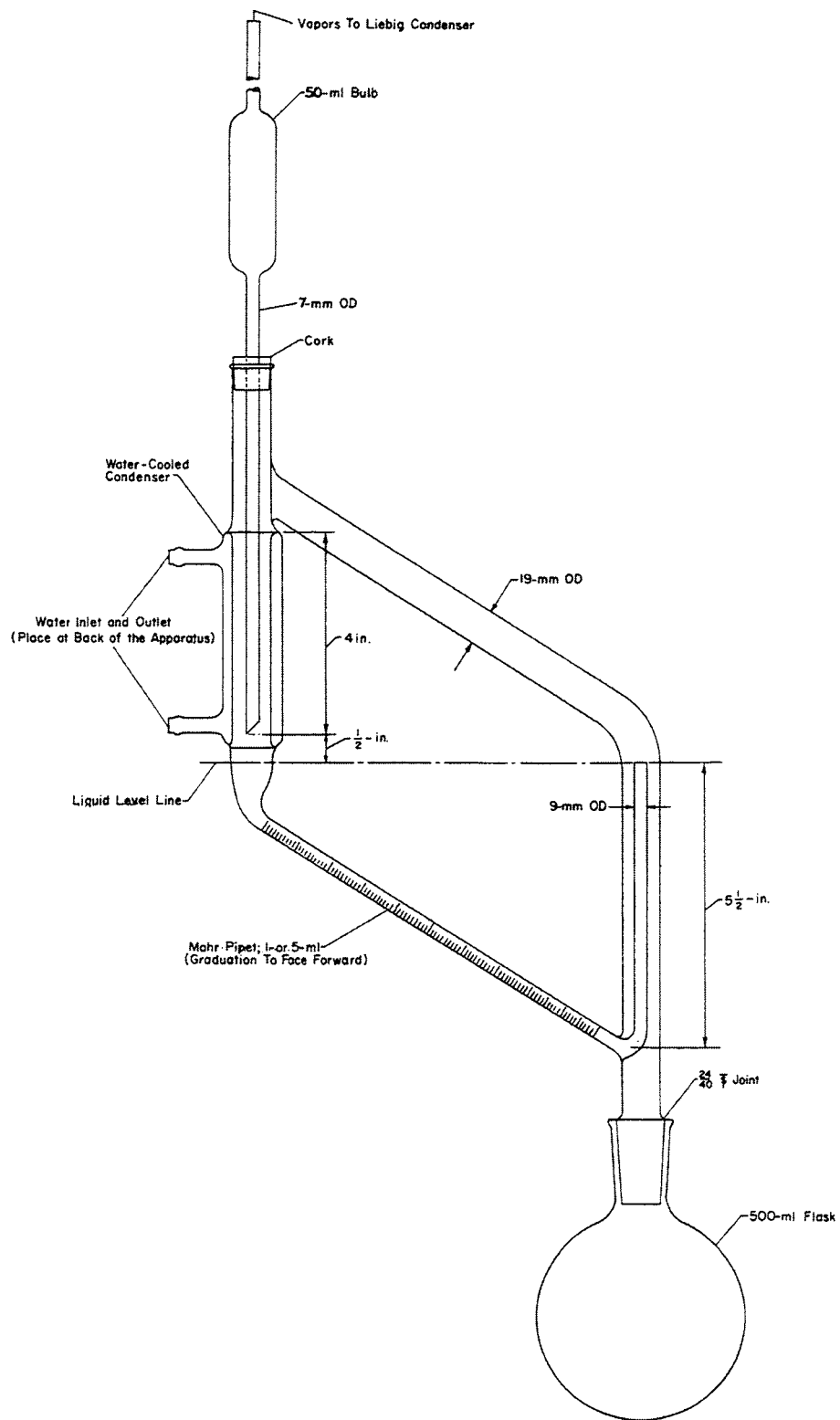
The fourth procedure is a titration method in which Karl Fischer reagent (see UOP Method 206) is the titrant.

Procedure A

APPARATUS

As specified in ASTM Method D 95

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).



Modified Lindsay Trap For Water Determination

REAGENTS

Benzene, “Udex quality,” dry

PROCEDURE

Weigh about 50 ± 1 g into the flask, add boiling chips and 100 ml of benzene. Apply heat and bring the contents to reflux temperature. When this temperature is reached, carefully mix the contents of the flask to produce a single liquid phase. Reflux until the water level remains constant in the water trap, which usually requires 2 to 4 hours. Read the volume of water collected.

CALCULATIONS

$$\text{Water, wt-\%} = \frac{V \times 100}{W}$$

where:

V = volume of water in trap

W = weight of sample, g

Procedure B

This procedure is similar in principle to *Procedure A*. However, a solvent heavier than water (such as chloroform) is used, requiring a specially - designed water trap. The reflux time for this procedure is about 20 to 30 minutes.

APPARATUS

Balance, triple beam, capacity 500 g

Condenser, Liebig

Cylinder, graduated, 100-ml

Flask, 500-ml, round-bottom with T 24/40 joint

Flask, suction, 250-ml

Heater, electric. “Ful-Kontrol” or equivalent

Traps, Lindsay, modified, 1-ml capacity calibrated in 0.01-ml units, and 5 ml capacity calibrated in 0.1-ml units. Modify as shown in the drawing.

REAGENTS

Carborundum crystals

Chloroform, USP

“Desicote” Available from Beckman Instrument Co., South Pasadena, Calif.

Glycol

PREPARATION OF APPARATUS

The trap - condenser section of the reflux apparatus must be treated with "Desicote" before use. "Desicote" is a silicone compound which, when applied to a glass surface, makes it water-repellent. Thoroughly wash the apparatus with hot soapy water. Use a brush if necessary but exercise caution not to scratch the glass surface. Rinse thoroughly with water, follow by a rinse with distilled water. Dry completely in an oven and cool it to room temperature.

The following operations using "Desicote" should be done in a well - ventilated hood while wearing rubber gloves. Pour about an ounce of "Desicote" into the condenser, being careful to keep the trap tilted so as not to spill the contents through the return tube. Swirl and move the trap to completely wet the inside wall of the condenser tube. Pour the remaining "Desicote" back into the bottle and allow the trap to drain for several minutes. Rinse with acetone and air dry. The trap is now ready for service.

When the trap loses its water - repellancy, coat it again with "Desicote".

PROCEDURE

Estimate the sample size to yield a volume of water commensurate with the volume of the graduated portion of the trap being used. Charge the glycol sample to a tared round - bottom flask containing a few carborundum crystals and reweigh. Add 90 ml of chloroform and swirl until the sample is completely dissolved. Set the flask on the heater and fit the trap in place.

Put 10 ml of chloroform into the trap. (*Note:* If an air bubble forms in the trap, rock the trap back and forth to displace the bubble.) Insert the vent tube in place so that the tip is 1/2-inch above the liquid level. Connect the vent tube with rubber tubing to the top of a Liebig condenser that has the bottom end connected by means of a cork stopper to a suction flask containing some glycol to act as a diluent for any chloroform condensate. Attach a drying tube to the side arm of the suction flask. Leave the flask open to the atmosphere.

Start the flow of water through the condenser jacket. Check to be sure that the trap is correctly positioned to provide the proper liquid level when the trap is returning liquid to the flask (see drawing). Apply heat to bring the chloroform solution to a gentle reflux and continue for 20-30 minutes at a rate which does not permit the chloroform vapor condensation line to rise into the bulb section of the vent tube. *Note:* A too rapid reflux rate will cause vapors to enter the vent tube and at this stage of reflux very likely may cause the loss of water, yielding low results. If droplets of water are still clinging to the inside wall of the condenser tube after 20-30 minutes of refluxing increase the reflux rate for a few minutes. Now allow the chloroform condensation line to rise well up into the vent tube; it may actually spill over into the Liebig condenser. If this additional refluxing does not wash down all the water, then the trap is dirty and should be cleaned and recoated (see *PREPARATION OF APPARATUS*).

After the water has been collected in the trap, turn off the heater, raise the apparatus and place a piece of transite board over the heater to permit rapid cooling and thus prevent the formation of bubbles and the subsequent movement of trap liquid back into the flask. When refluxing has stopped, tilt the flask and trap to permit the water to enter the graduated portion of the trap. Read and record the volume of water collected. Rinse the trap with acetone and air dry after each determination.

USP chloroform usually contains a small amount of water (about 0.01 ml per 100 ml chloroform.) Therefore, run a blank determination on each new batch of chloroform using a total of 200 ml of chloroform and following through the above procedure. Use half of the value so obtained for a blank correction.

CALCULATIONS

$$\text{Water, wt-\%} = \frac{A - B}{W} \times 100$$

where:

A = volume of water collected, ml

B = blank correction, ml

W = weight of sample, g

NOTES AND PRECAUTIONS

In rare cases, glycol samples have been found that would not completely dissolve upon mixing with the chloroform. Upon heating such solutions, however, a single phase was obtained.

PRECISION

Duplicate determinations should not differ by more than 5% of the average value of the 2 determinations.

Procedure C

APPARATUS

As specified in ASTM Method D 1218 or equivalent

REAGENTS

Glycol, "Udex quality." Redistill and take an 80% heart - cut.

Water, distilled or deionized

PREPARATION OF CALIBRATION CURVE

Prepare a series of glycol samples containing known concentrations of water. Determine the refractive index of these samples at a convenient reference temperature and plot the data. Use this calibration plot to determine the water content from the refractive index of the unknown sample.

In using the refractive index procedure on glycols from commercial Udex units, remember that it is reliable *only* for glycols which have been completely stripped of hydrocarbon. It cannot be used on the rich glycol streams.

Procedure D

APPARATUS

As specified in UOP Method 206

REAGENTS

As specified in UOP Method 206

PROCEDURE

Follow the *PROCEDURE* section under the subheading *Titration* specified in UOP Method 206.

REFERENCES

ASTM Methods, D 95 and D 1218, www.astm.org
UOP Method 206
UOP Method 390
Lindsay, W. N., *Ind. Eng. Chem., Anal. Ed.*, **18**, 69 (1946)