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## Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration<sup>1</sup>

This standard is issued under the fixed designation D 4377; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reappraisal. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reappraisal.

*This standard has been approved for use by agencies of the Department of Defense.*

<sup>ε1</sup> NOTE—Footnote 1 and the Referenced Documents were corrected editorially to comply with the ASTM-API joint standard contract in October 2002.

### 1. Scope

1.1 This test method covers the determination of water in the range from 0.02 to 2 % in crude oils. Mercaptan and sulfide ( $S^-$  or  $H_2S$ ) sulfur are known to interfere with this test method (see Section 5).

1.2 This test method is intended for use with standard Karl Fischer reagent or pyridine-free Karl Fischer reagents.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 7.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

D 4006 Test Method for Water in Crude Oil by Distillation (API MPMS Chapter 10.2)<sup>3</sup>

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products (API MPMS Chapter 8.1)<sup>3</sup>

D 4177 Practice for Automatic Sampling of Petroleum and Petroleum Products (API MPMS Chapter 8.2)<sup>3</sup>

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and the API Committee on Petroleum Measurement, and is the direct responsibility of Subcommittee D02.02/COMQ, the joint ASTM-API Committee on Static Petroleum Measurement.

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<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 05.02.

E 203 Test Method for Water Using Volumetric Karl Fischer Reagent<sup>4</sup>

#### 2.2 API Standards:<sup>5</sup>

MPMS Chapter 8.1 Manual Sampling of Petroleum and Petroleum Products (ASTM Practice D 4057)

MPMS Chapter 8.2 Automatic Sampling of Petroleum and Petroleum Products (ASTM Practice D 4177)

MPMS Chapter 10.2 Determination of Water in Crude Oil by Distillation (ASTM Test Method D 4006)

### 3. Summary of Test Method

3.1 After homogenizing the crude oil with a mixer, an aliquot of the crude, in a mixed solvent, is titrated to an electrometric end-point using Karl Fischer reagent.

### 4. Significance and Use

4.1 A knowledge of the water content of crude oil is important in the refining, purchase, sale, or transfer of crude oils.

### 5. Interferences

5.1 A number of substances and class of compounds associated with condensation or oxidation-reduction reactions interfere in the determination of water by Karl Fischer. In crude oils, the most common interferences are mercaptans and sulfides. At levels of less than 500  $\mu\text{g/g}$  (ppm) (as sulfur) the interference from these compounds is insignificant. For more information on substances that interfere in the determination of water using the (Karl Fischer reagent) titration method see Test Method E 203.

<sup>4</sup> Annual Book of ASTM Standards, Vol 15.05.

<sup>5</sup> Published as Manual of Petroleum Measurement Standards. Available from the American Petroleum Institute (API), 1220 L St., NW, Washington, DC 20005-4070.

## 6. Apparatus

6.1 *Karl Fischer Apparatus*, using electrometric end-point. A suggested assembly of the apparatus is described in Annex A2.

6.1.1 Presently there is available on the market commercial Karl Fischer titration assemblies, some of which automatically stop the titration at the end-point. Instructions for operation of these devices are provided by the manufacturer and not described herein. This test method is not intended for use with coulometric Karl Fischer titrators.

6.2 *Mixer*, to homogenize the crude sample.

6.2.1 *Non-Aerating, High-Speed, Shear Mixer*,<sup>6</sup> capable of meeting the homogenization efficiency test described in Annex A1. The sample size is limited to that suggested by the manufacturer for the size of the probe.

6.3 *Syringes*:

6.3.1 Samples and base liquid are most easily added to the titration vessel by means of accurate glass syringes with LUER fittings and hypodermic needles of suitable length. The bores of the needles used should be kept as small as possible, but large enough to avoid problems arising from back pressure/blocking whilst sampling. Suggested syringe sizes are as follows:

6.3.1.1 *Syringe*, 10  $\mu\text{L}$ , with a needle long enough to dip below the surface of the base solution in the cell during the standardization procedure (see Section 9).

6.3.1.2 *Syringes*, 2.5 mL, 5 mL, and 10 mL for crude oil samples (see Section 10).

6.3.1.3 *Syringe*, 20 mL or larger for sample solvent.

## 7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>7</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type IV of Specification D 1193.

7.3 *1-Ethylpiperidine* (99 + percent). (**Warning**—Irritant. Flammable.)

7.4 *Karl Fischer Reagents*, Standard reagent containing pyridine (7.4.1) or pyridine-free reagent (7.4.2).

7.4.1 *Karl Fischer Reagent Ethylene Glycol Monomethyl Ether Solution*, stabilized, containing pyridine, (1 mL = 5 mg

<sup>6</sup> The following mixers were used in a cooperative program and have been found satisfactory for samples under 300 mL; Ultra Turrax Model TP 18/10, available from Tekmar Co., P. O. Box 37202, Cincinnati, OH 45222; Brinkman Polytron Model PT 35, Available from Brinkman Instruments Inc., Cantiagu Road, Westbury, NY 11590; and Kraft Apparatus Model S-25, SGA, Bloomfield, NJ.

<sup>7</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U. S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

of water)—Fresh Karl Fischer reagent must be used. Must be used with solvent in 7.6.1. (**Warning**—Combustible. Harmful if swallowed, inhaled, or absorbed through the skin.)

7.4.2 *Pyridine-Free Karl Fischer* (one-component) reagent diluted with xylene—Dilute three parts pyridine-free Karl Fischer (one-component) reagent<sup>8</sup> (1 mL = 5 mg water) to 1 part xylene. Fresh Karl Fischer reagent must be used. (**Warning**—See 7.4.1) Must be used with solvent in 7.6.2.

7.5 *Methanol (anhydrous)*, Maximum 0.1 % water but preferably less than 0.05 % water. (**Warning**—Flammable. Vapor harmful. May be fatal or cause blindness if swallowed or inhaled. Cannot be made nonpoisonous.)

7.6 *Sample Solvent*—Use 7.6.1 for standard Karl Fischer reagent containing pyridine and 7.6.2 for pyridine-free Karl Fischer reagent.

7.6.1 *Sample Solvent*—Mix 40 mL of 1-ethylpiperidine, 20 mL of methanol, and 40 mL of Karl Fischer reagent in a sealable glass bottle. Allow this mixture to sit overnight before adding 200 mL of xylene. Additional methanol may be required in some cases for the proper function of the electrodes. (**Warning**—see 7.3.)

7.6.2 *Sample Solvent for Pyridine-Free Reagents*—Mix 3 parts chloroform to 1 part pyridine-free solvent using solvent part of two-component reagent<sup>8</sup> (contains SO<sub>2</sub> and odorless amine dissolved in methanol) and store in a sealable glass bottle. An evaluation of a number of crude oils has demonstrated that xylene can be substituted for chloroform with no apparent change in accuracy of this test method. (**Warning**—Flammable. Vapor harmful.) (Also, see 7.4.1.)

7.7 *Xylene*, reagent grade. Less than 0.05 % water.

7.8 *Chloroform*, reagent grade. (**Warning**—Harmful if inhaled or swallowed. Carcinogen (animal positive). Skin and eye irritant. May produce toxic vapors if burned.)

## 8. Sampling and Test Samples

8.1 Sampling, is defined as all the steps required to obtain an aliquot representative of the contents of any pipe, tank, or other system, and to place the sample into the laboratory test container. The laboratory test container and sample volume shall be of sufficient dimensions and volume to allow mixing as described in 8.1.2.1.

8.1.1 *Laboratory Sample*—Only representative samples obtained as specified in Practice D 4057 (API MPMS Chapter 8.1) and Practice D 4177 (API MPMS Chapter 8.2) shall be used for this test method.

8.1.2 *Test Samples*—The following sample handling procedure shall apply in addition to those covered in 8.1.1.

8.1.2.1 Mix the test sample of crude oil immediately (within 15 min) before analysis to insure complete homogeneity. Mix the test sample at room temperature (25°C) in the original container.

NOTE 1—The sample should be mixed at room temperature (25°C) or

<sup>8</sup> Pyridine-free Karl Fischer reagent and two-component solvent used in the cooperative program and found to be satisfactory are available from Crescent Chemical Co., Inc., 1324 Motor Parkway, Hauppauge, NY 11788 under the name of Hydranal a registered trademark of Riedel Dehaen—Composite 5 and Hydranal—solvent.

less. Mixing of the sample should not increase the temperature of the sample more than 10°C, or a loss of water may occur. The type of mixer depends on the quantity of crude. Before any unknown mixer is used, the specifications for the homogenization test, Annex A1, must be met. The mixer must be re-evaluated for any changes in the type of crude, quantity of crude, or shape of the sample container.

8.1.2.1.1 For small sample volumes, 50 to 500 mL, a non-aerating, high speed, shear mixer is required. Use the mixing time, mixing speed, and height above the bottom of the container found to be satisfactory to Annex A1. Clean and dry the mixer between samples.

8.1.2.2 The test sample size is selected as indicated in Table 1 based on the expected water content.

## 9. Calibration and Standardization

9.1 Standardize the Karl Fischer reagent at least once daily.

9.2 Add enough solvent to the clean, dry titration vessel to cover the electrodes. The volume of solvent depends on the size of the titration vessel. Seal all openings to the vessel and start the magnetic stirrer for a smooth stirring action. Turn on the indicating circuit and adjust the potentiometer to give a reference point with approximately 1 µA of current flowing. Add Karl Fischer reagent in suitable amounts to the solvent to cause the needle to deflect from the reference point. At first the needle will deflect due to local concentration of the unreacted reagent about the electrodes but will fall back to near the reference point. As the end-point is approached, the needle will fall back more slowly after each addition of Karl Fischer reagent. The end-point is reached when, after the addition of a single drop of reagent, the needle remains deflected at least 1 µA from the reference point for at least 30 s. Swirl the titration vessel to dry the inside walls of the vessel. Add more Karl Fischer reagent, if needed, until a steady end-point is reached for at least 30 s.

9.3 Standardize the Karl Fischer reagent with distilled water by one of the following methods:

9.3.1 From a water filled weighing pipet or syringe previously weighed to the nearest 0.1 mg, add 1 drop of distilled water (about 20 mg) to the sample solvent at end-point conditions and reweigh the syringe. Record the weight of the water added. Titrate the water with Karl Fischer reagent added from the buret until a steady end point is reached for at least 30 s. Record to the nearest 0.01 mL the volume of the Karl Fischer reagent needed to reach the end-point.

NOTE 2—After adding water do not shake the cell.

NOTE 3—When wiping the needle exercise care, so not to siphon liquid through the tip of the needle.

9.3.2 Fill a 10-µL syringe with water taking care to eliminate air bubbles, wipe the needle with a paper tissue to remove any residual water from the needle and accurately determine the weight of syringe plus water to 0.1 mg. Add the contents of

the syringe to the sample solvent in the cell which has been adjusted to the end point ensuring that the tip of the needle is below the surface of the sample solvent. Reseal the vessel immediately. Remove any solvent from the needle by wiping with a paper tissue and reweigh the syringe to 0.1 mg. Titrate the water with Karl Fischer reagent as in 9.3.1.

9.4 Calculate the water equivalence of the Karl Fischer reagent as follows:

$$F = W/T \quad (1)$$

where:

$F$  = water equivalence of the Karl Fischer reagent, mg/mL,

$W$  = water added, mg, and

$T$  = reagent required for titration of the added water, mL.

9.5 Duplicate values of water equivalence should agree within 2 % relative. If the variation between the two titrations is greater than 2 % relative, discard the contents of the titration vessel. Introduce a further portion of sample solvent into the vessel and repeat the standardization procedure. If the titrations for two further portions of distilled water still vary by more than 2 %, it is likely that either the Karl Fischer reagent or the sample solvent, or both, have aged. Replace these with fresh reagents and repeat the procedure for calibration and standardization.

9.6 Determine and record the mean water equivalence value.

## 10. Procedure

10.1 Add the fresh sample solvent to the titration vessel and bring the solvent to end-point conditions as described in 9.2.

10.2 Add the crude to the titration vessel immediately after the mixing step described in 8.1.2.1 using one of the following methods:

10.2.1 Starting with a clean, dry syringe (10 or 5 mL), rinse the syringe two times with the sample and discharge to waste. Withdraw the required amount of sample and discharge any air bubbles. Weigh the syringe to the nearest 0.1 mg. Inject the sample into the titration vessel, clean the needle with a paper tissue, and reweigh the syringe. Titrate the sample until a steady end-point for at least 30 s is reached and record the volume of Karl Fischer reagent to the nearest 0.01 mL (see Note 2 and Note 4).

NOTE 4—The solvent should be changed when the sample content exceeds 2 g of crude per 15 mL of solvent or when 4 mL of titrant per 15 mL of solvent has been added to the titration vessel.

10.2.2 For viscous crudes, add the sample to a clean, dry dropper bottle and weigh the bottle and crude. Quickly transfer the required amount of sample to the titration vessel with the dropper. Reweigh the bottle. Titrate the sample as in 10.2.1.

NOTE 5—After adding the sample do not shake the cell.

## 11. Calculations

11.1 Calculate the water content of the sample as follows:

$$\text{water, mass \%} = CF/W(10) \quad (2)$$

where:

**TABLE 1 Test Sample—% Water Content Based on Sample Size**

Expected Water Content, %	Sample Size, g
0–0.3	5
0.3–1	2
1–2	1

- $C$  = Karl Fischer reagent required to titrate the sample, mL,  
 $F$  = water equivalence of Karl Fischer reagent, mg/mL,  
 $W$  = sample used, g, and  
 10 = factor for converting to percent.

## 12. Precision and Bias <sup>9</sup>

12.1 The precision of this test method as determined by the statistical examination of interlaboratory test results is as follows:

12.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only in one case in twenty. (See Table 2.)

12.1.1.1 *Standard Karl Fischer Reagents:*

$$r = 0.034 (X^{1/3}) \quad (3)$$

12.1.1.2 *Pyridine-Free Karl Fischer Reagents:*

$$r = 0.032 (X^{1/3}) \quad (4)$$

where:

$X$  = sample mean from 0.0 to 2 %.

12.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty.

<sup>9</sup> Supporting data are available from ASTM Headquarters. Request RR: D02-1173.

**TABLE 2 Precision Intervals<sup>A</sup>**

Mass % Water	Standard Karl Fischer Reagents		Pyridine-Free Reagents	
	$r$	$R$	$r$	$R$
0.05	0.013	0.041	0.012	0.035
0.1	0.016	0.052	0.015	0.044
0.3	0.023	0.074	0.021	0.064
0.5	0.027	0.088	0.025	0.075
0.7	0.030	0.099	0.028	0.084
1.0	0.034	0.111	0.032	0.095
1.3	0.037	0.121	0.035	0.104
1.5	0.039	0.127	0.037	0.109
1.7	0.041	0.132	0.038	0.113
2.0	0.043	0.140	0.040	0.120

<sup>A</sup> $r$  = repeatability and  $R$  = reproducibility.

12.1.2.1 *Standard Karl Fischer Reagents:*

$$R = 0.111 (X^{1/3}) \quad (5)$$

12.1.2.2 *Pyridine-Free Karl Fischer Reagents:*

$$R = 0.095 (X^{1/3}) \quad (6)$$

where:

$X$  = sample mean from 0.00 to 2 %.

12.2 *Bias:*

12.2.1 Compared to the results of Test Method D 4006 (API *MPMS* Chapter 10.2), no significant bias was found.

12.2.2 The interference from mercaptan sulfur follows the theoretical stoichiometry of 1 to 0.28, that is 1000 µg/g (ppm) of mercaptan sulfur can generate a response equivalent to 280 µg/g (ppm) (0.03 mass %) water by this test method. The validity of correcting measured water contents for known mercaptan/sulfide sulfur levels has not been evaluated.

## ANNEXES

### (Mandatory Information)

#### A1. HOMOGENIZATION EFFICIENCY OF UNKNOWN MIXERS

A1.1 The homogenization efficiency of each unknown mixer must be evaluated before use. The grade of crude oil, the sample size, and the sample container expected to be used with the mixer should be used in this test. The specifications of this test should be met before running this method and any changes in the mixing procedure should be re-evaluated by this test. The crude oil used in this test should be dry (less than 0.1 % water).

A1.2 Weigh the sample container to the nearest 0.01 g. Fill the container half way (or the level normally used) with the dry crude. Immerse the mixer into the crude with the bottom of the mixer 5 mm above the bottom of the container and mix the crude at the speed and for the amount of time you expect to use. Suggested mixing time is between 1 and 5 min at 5 to 7

thousand rpms. Immediately determine the water content in duplicate (10.1) of the dry crude. Obtain the average of the duplicate results.

A1.3 Weigh the crude and container to the nearest 0.01 g. Immerse the mixer into the crude as in A1.2. Knowing the weight of the crude, add enough water to increase the water content 1 % above the base level found in A1.2. From a water filled syringe previously weighed (nearest 0.1 mg), inject the water below the surface of the crude near the inlet to the mixer. Reweigh the syringe (to the nearest 0.1 mg) and determine the amount of water added. Wipe any oil on the needle off before weighing. Mix the sample in the same manner as in A1.2. Determine the water content of the crude immediately after

mixing. Sample the crude just below the liquid level.

A1.4 Without additionally mixing the crude, determine the water content of the crude 15 and 30 min after the initial mixing in A1.3.

A1.5 Remix the sample in the same manner as A1.2. Immediately after mixing, determine the water content in duplicate.

A1.6 The water contents of the crude determined in A1.3, A1.4, and A1.5 minus the base determined in A1.2 should agree within 0.05 % absolute of the added water and to each other. If they do not agree, this test should be repeated while changing the mixing time, the mixing speed, or the height of the mixer, in the crude or a combination thereof, until these conditions are met.

## A2. APPARATUS

### A2.1 Titration Assemblies

A2.1.1 The titration assembly (Fig. A2.1) shall include the following:

A2.1.1.1 *Buret*—A 10-mL buret graduated 0.05-mL subdivisions and fitted within a three-way stopcock. Some stopcock greases are affected by Karl Fischer reagent.

A2.1.1.2 *Reagent Reservoir*, any convenient-size glass bottle.

A2.1.1.3 *Stirrer*, magnetic stirrer.

A2.1.1.4 *Titration Flask*, a three-neck flask of approximately 500-mL capacity.

A2.1.1.5 Assemble the apparatus as shown in Fig. A2.1. All possible precautions must be taken to prevent absorption of moisture from the atmosphere. Cracks between glass and stoppers should be sealed with a suitable sealing material and necessary openings should be protected by the use of drying tubes containing anhydrous calcium sulfate.

### A2.2 Electrical Circuit

A2.2.1 The electrical circuit (Fig. A2.1) shall include the following:

A2.2.1.1 *Microammeter*, A d-c microammeter having a range from 0 to 50  $\mu$ A and internal resistance of approximately 1500  $\Omega$ .

A2.2.1.2 *Battery*, a 1.5-V dry cell.

A2.2.1.3 *Electrodes*—Suitable electrodes (Fig. A2.2) can be constructed as follows. Seal a piece of platinum wire approximately 25 mm (1 in.) in length (diameter of wire 0.3 to 0.8 mm (0.01 to 0.03 in.)) into a piece of small bore soft glass tubing approximately 160 mm long. Approximately 7.1 mm (0.28 in.) of the wire should extend above the seal on the inside of the tubing and approximately 15.2 mm (0.60 in.) extend outside of the seal. Bend the glass tubing slightly about 20 to 30 mm above the seal as shown in Fig. A2.2. Make a small loop approximately 6.4 mm (0.25 in.) in diameter in the end of the platinum wire. Place sufficient mercury in the glass tube to provide contact for the leads to complete the circuit. Two electrodes are required. Exercise care so that cracks do not develop around the seal, which will make the electrodes useless.

A2.2.1.4 *Potentiometer*, a potentiometer having a resistance of 2000  $\Omega$ .

A2.2.1.5 Assemble the circuit as shown in Fig. A2.1.

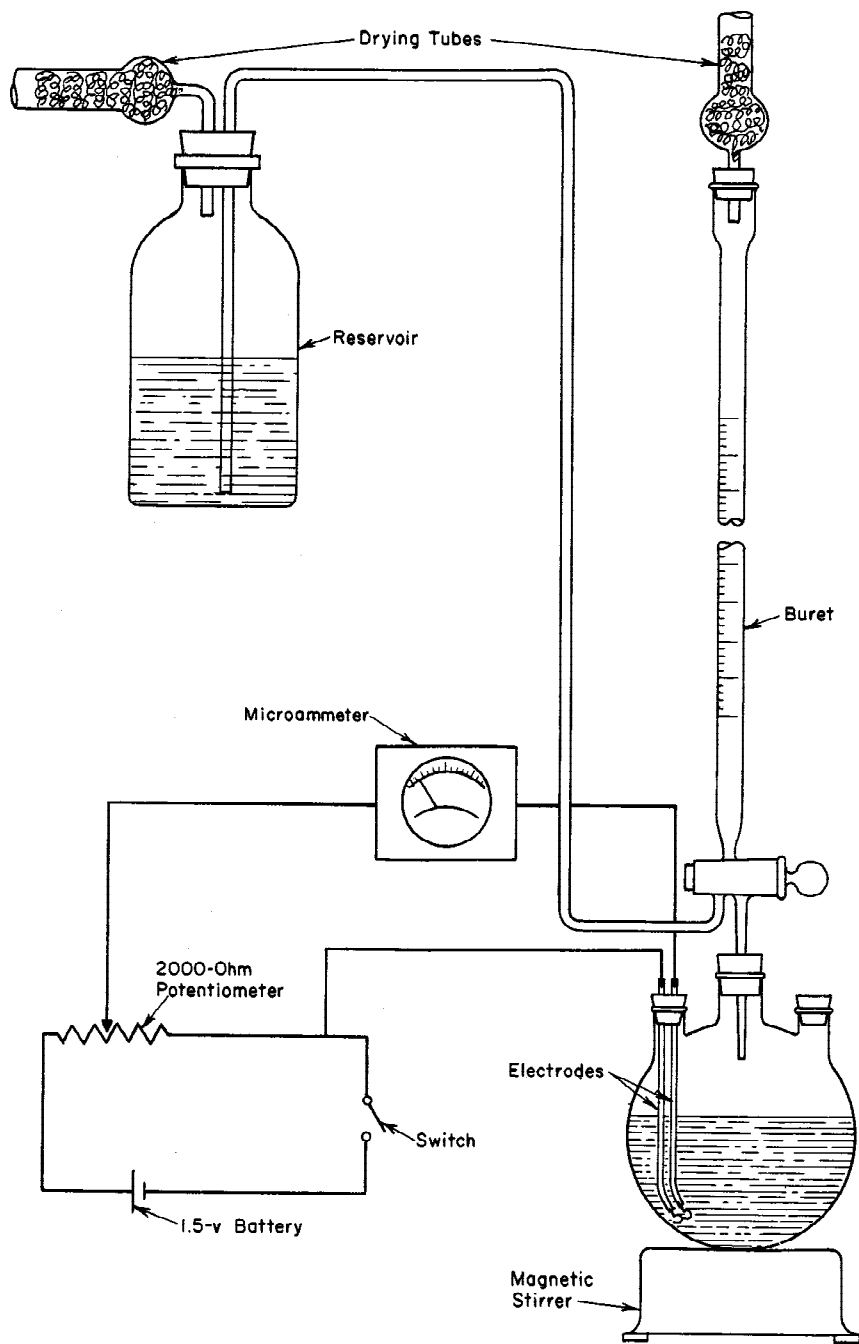


FIG. A2.1 Apparatus for Determination of Water by Karl Fischer Reagent

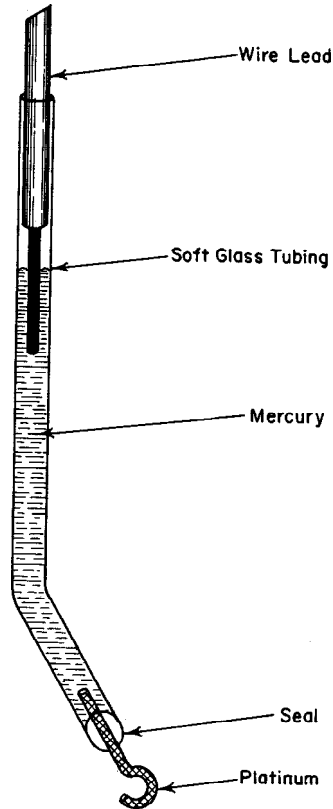


FIG. A2.2 Electrode

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