

MONSANTO CHEMICAL COMPANY
W. G. KRUMMRICH PLANT LABORATORY
**STANDARD ANALYTICAL
METHOD**

DATE ISSUED 11/1/57	PAGE 1 OF 6	NUMBER 10,100
WRITTEN BY EOM		APPROVED BY RFS
ATTACHMENTS WGK Drawing 142		

PRODUCT

General Method No. 7

TEST

Water

THIS FORM

☐ SUPERSEDES METHOD
☒ REVISES INSTRUCTIONS

ISSUED ON 9/3/54

SCOPE

This method determines water in most organic and inorganic compounds using the Karl Fischer reagent "one-solution" technique. An electrometric "Dead stop" procedure is used for greater accuracy. A visual technique is described for application where no "Dead Stop" indicating device is available and where such increased accuracy is not necessary.

EQUIPMENT

- Special titration vessel, equipped with Platinum electrodes and an electric motor stirrer with a paddle type glass stirrer (see attached drawing).
- Schilling Automatic Buret Assembly, 10 ml. or 25 ml. capacity, as indicated by the specific determination (Ace Glass Co., Vineland, N. J., Catalog No. 5751).
- Rheostat to control stirrer speed.
- 500 ml. ggs 24/40 Erlenmeyer flask with stoppers.
- "Magic-Eye Dead-Stop End Point Indicator" as described by C. A. McCauley and W. J. Gresham, Anal. Chem., 27, 1955, p. 1847, or equivalent.

REAGENTS

- Dry Methanol (< 0.01% water).
- Dry Benzene (< 0.01% water).
- Dry Toluene (< 0.01% water).
- Glacial acetic acid.
- Pyridine (2°C. boiling range).

DSW 551048

Product: General Method No. 7
Test: Water

Method No. 10,100
Page 2 of 6 pages

f. Karl Fischer Reagent:

1. Pyridine (2°C. boiling range).
2. Iodine, A.R. grade, Mallinckrodt Chem. Co., Cat. No. 1008, or equivalent.
3. Dry Methanol (< 0.01% water).
4. Liquid sulfur dioxide (< 0.005% water).

Dissolve 254 g. of iodine in 800 ml. of pyridine in a brown gallon jug. Swirl until all of the iodine is in solution. Then, add 2 liters of dry methanol. Cool the mixture to 0°C. or below in an ice and salt bath. After the mixture has cooled to 0°C. or below, slowly add 100 ml. of liquid SO₂, with constant stirring. After the solution is thoroughly mixed, stopper the gallon jug with a Bunsen valve and remove the jug from the ice bath. After the solution is at room temperature, replace the Bunsen valve with a rubber stopper and store for 24 hours before using.

NOTE: A Bunsen valve is a rubber stopper with a short piece of glass tubing fitted through it. To this tube, a short piece of rubber tubing is attached with a glass rod sealing the open end. A slit is cut ca. 1/2 way through the rubber tubing on an approximately 45° angle. Bunsen valves are used to stopper vessels that need protection from the atmosphere but need to have pressure relief. (See attached drawing)

STANDARDIZATION OF KARL FISCHER REAGENT

NOTE: The standardization must be performed in duplicate.

1. Fill the Schilling Automatic Buret Assembly with Karl Fischer Reagent. Shake the contents thoroughly and flush out the buret by pumping the reagent into it and draining back into the reservoir several times. (NOTE: Check drying tubes to see that they are still active. If they are spent, replace the desiccant with fresh Drierite, Fisher Scientific Co., Cat. No. 7-577).
2. Pour 100 ml. of dry methanol into the special titration vessel. Titrate with the unstandardized reagent to the end point as directed under the determination portion of this method, steps 1 - 6.

DSW 551049

Product: General Method No. 7
Test: Water

Method No. 10,100
Page 3 of 6 pages

3. Using an analytical balance, weigh (to the nearest 0.0001 g.) into the blanked out methanol one drop of distilled water (ca. 0.05 g.) from a dropper type weighing bottle. (NOTE: Be sure that the drop of water falls directly into the blanked out methanol.)
4. Titrate immediately with the Karl Fischer reagent to the same end point as in step 2 above.
5. Repeat the standardization as above.

Calculation

$$\text{H}_2\text{O Factor} = \frac{\text{Weight of water added to flask}}{\text{ml. of titration}} = \text{g. water/ml. reagent}$$

Record the H₂O factor to the nearest 0.00001 g./ml.

Duplicate results should check within 0.00001 g./ml.

SAFETY

The solvents used in this determination are both toxic and flammable. Proper precautions should be taken to keep them off your person and away from sources of ignition. Karl Fischer reagent is toxic and can be absorbed through the skin. If it comes in contact with your skin, immediately wash the contaminated area with soap and water.

DETERMINATION

Part A. Electrometric "Dead Stop" Method

1. Snap the toggle switch on the front of the "Magic-Eye Dead-Stop End Point Detector" to the "ON" position and allow the instrument to warm up for 3 - 4 minutes.
2. Turn the "Solvent Selector Switch" knob to the position as specified by the method for material under test.

NOTE: The switch positions are: "NONE" (when no solvent other than methanol is used); "BENZENE" (for benzene-methanol mixtures); "TOLUENE" (for toluene-methanol mixtures); and "ACETIC ACID" (for acetic acid-methanol mixtures). "NONE" is used for the system pyridine-methanol.

3. Place 100 to 300 ml. of the solvent, as specified in the method of the material under test, into the titration vessel.

DSW 551050

STLCOPCB4089467

Product: General Method No. 7
Test: Water

Method No. 10,100
Page 4 of 6 pages

IMPORTANT: The stopper, which closes the charging opening of the titration flask, must be firmly in place before any attempt is made to proceed with the test. This applies to both the "blank" and the sample.

4. Start the stirring motor and adjust its speed so that effective agitation is achieved without splashing.
5. Slowly add the K. F. reagent to the titration flask. Observe that the shadows on the "Magic-Eye" tube open momentarily and then close, the length of the "open" time increasing as more K. F. reagent is added.
6. As the end point is approached, add K. F. reagent in 0.2 ml. increments. The solvent is "blanked" when the tube shadows remain fully open (ca. 100° each) for 30 seconds. Use a stop-watch.
7. Refill the buret with the K. F. reagent.
8. Weigh accurately (as prescribed in the specific method) a sample (not to exceed ca. 200 grams total weight) containing between 0.03 and 0.06 grams of water. Transfer quickly to the titration flask.

NOTE: Use a powder funnel if the sample is a powdered solid.

9. Allow the material in the flask to be agitated until all the sample is in solution or until the sample is well mixed if it is not soluble.
10. Titrate the solution with K. F. reagent to the end point described in step 6. Record the volume of K. F. reagent used.

CALCULATION

$$\% \text{ H}_2\text{O} = \frac{\text{ml. K. F. reagent} \times \text{H}_2\text{O factor} \times 100}{\text{Sample weight}}$$

Report the results as indicated under the specific method.

Part B. Visual Method (Alternate to Electrometric Method)

1. Place 100 to 300 ml. of the solvent, as specified in the method of the material under test, in a clean, dry 500 ml. Erlenmeyer flask.

DSW 551051

STLCOPCB4089468

Product: General Method No. 7
Test: Water

Method No. 10,100
Page 5 of 6 pages

2. Titrate the solvent with K. F. reagent to the visual end point i. e., the first change from the yellow to reddish orange that persists for 30 seconds. Use a stop-watch.
3. Refill the buret with the K. F. reagent.
4. Prepare a blank in the same manner until the color matches exactly that of the solution previously prepared.
5. Weigh accurately (as prescribed in the specific method) a sample (not to exceed ca. 200 grams total weight) containing between 0.03 and 0.06 grams of water. Transfer quickly to the titration flask.
6. Stopper and shake until the sample is in solution.
7. Titrate the solution with constant swirling, with K. F. reagent to the exact color of the blank prepared in step 4 above. Record the volume of K. F. reagent used.

CALCULATION

$$\% \text{ H}_2\text{O} = \frac{\text{ml. K. F. reagent} \times \text{H}_2\text{O factor} \times 100}{\text{Sample weight}}$$

Report the results as indicated under the specific method.

DISCUSSION

- a. Experience has shown that either of the two methods outlined above are precise to ca. $\pm 5\%$ of the water present.
- b. Dry benzene or other suitable dry solvent may be used together with methanol in order to render a sample soluble. Glacial acetic acid must be added in excess when amines are present in the sample to prevent interference in the water determination. Pyridine is added in excess to prevent interference by acids.
- c. In general, the K. F. technique is useful in determining water in a great number of organic and inorganic compounds. Usually, interferences will react with one or more of the components in the reagent giving erroneously high results. One caution is pointed out. Certain nearly anhydrous compounds tend to exhibit a false end point after addition of a small quantity of the reagent. Elimination of this phenomenon is best accomplished by adding an inert solvent (e.g., dry methanol).

DSW 551052

Product: General Method No. 7
Test: Water

Method No. 10,100
Page 6 of 6 pages

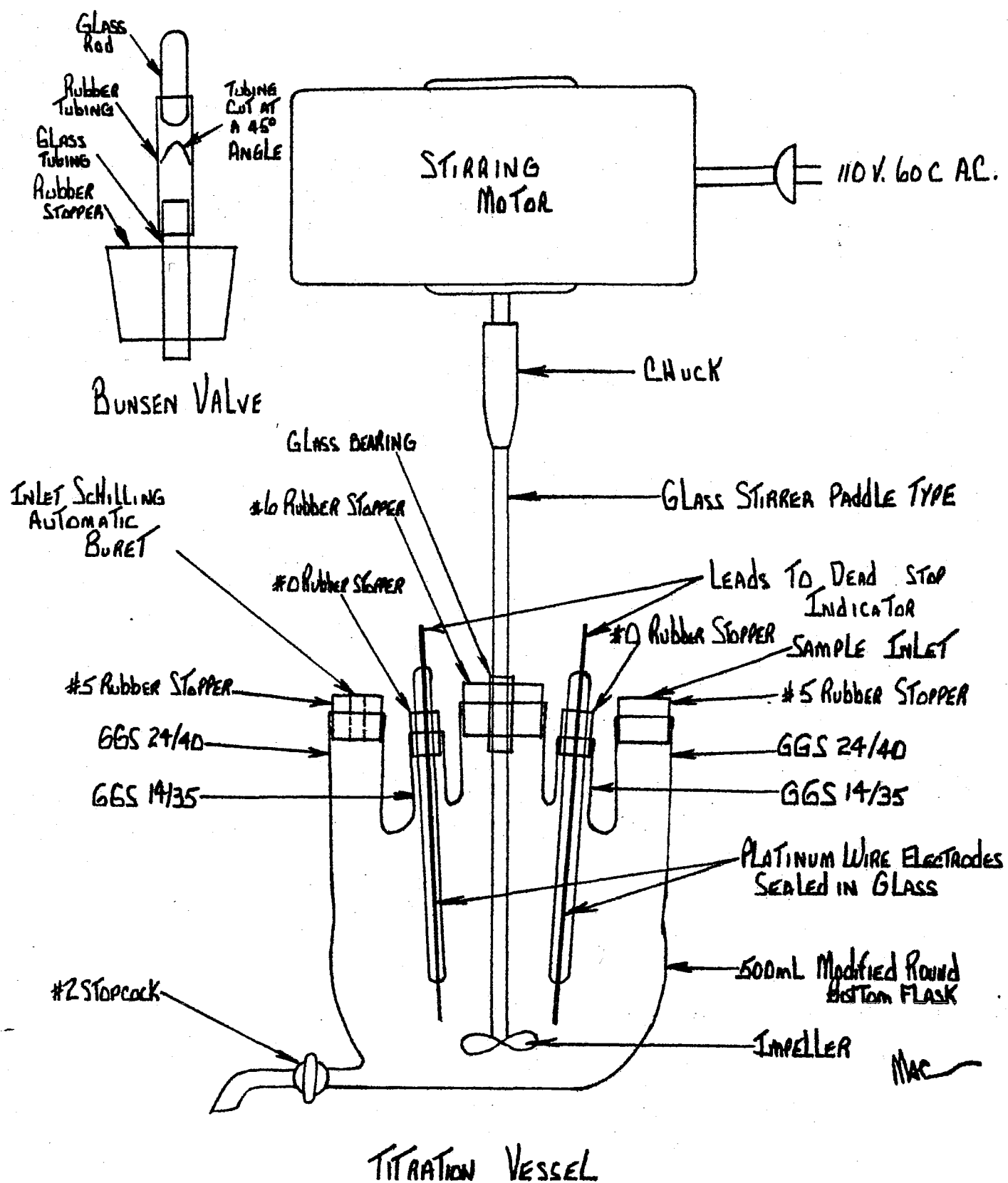
REFERENCE

- a. Mitchell, J. and Smith, D. M., "Aquametry" Application of the Karl Fischer Reagent to Quantitative Analyses Involving Water, Interscience Publishers Inc., N. Y. (1948).
- b. Frederickson's Report to Mehner, 5/23/50.

"The information contained herein is, to our best knowledge, accurate; but all recommendations or suggestions are made without guarantee, since the conditions of use are beyond our control. Monsanto disclaims any liability for loss or damage incurred in connection with the use of the above."

DSW 551053

STLCOPCB4089470



DRAWING NO. 142

DSW 551054

STLCOPCB4089471