Standard Analytical Methods for Determining Therminol®:

- Viscosity
- Acidity
- Moisture

TECHNICAL BULLETIN O/FF-18

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STANDARD ANALYTICAL METHOD

Product: Pydraul and Therminol fluids

Test: Viscosity by Modified Ostwald Viscometer for Transparent and Opaque Liquids

SCOPE

This method is used to determine the viscosity of the fluids by using a modified Ostwald viscometer and is in accordance with ASTM Standard Test D 445-65, *Viscosity of Transparent and Opaque Liquids.* Viscosity is determined by measuring the time of flow of a fixed volume of liquid at a given temperature through a calibrated glass capillary instrument using "gravity flow".

EQUIPMENT

a. Viscometers — Calibrated glass capillary type, capable of measuring viscosity within repeatable limits. Viscometers such as Cannon-Fenske Routine, Cannon-Manning Semi-Micro, and Cannon-Fenske Opaque in sizes 100, 150, 200 and 300 are recommended.

	Viscosity Range	
Size	*Centistokes*	*SSU*
100	3-12	36-66
150	7-28	49-133
200	20-80	98-370
300	50-200	230-930

These items available from Cannon Instrument Co., State College, Pennsylvania.

b. Viscometer Holder or Frames — Any suitable holder to suspend viscometer securely in constant temperature bath in same vertical position as when calibrated.

c. Constant Temperature Bath — Any transparent liquid bath of sufficient depth to cover within 2 cm the sample in the viscometer.

Temperature control of the bath must be such to maintain ± 0.02°F. between 60° and 212°F over the length of the viscometer.

d. Timer — Any timing device graduated in divisions of not more than 0.2 seconds and having an accuracy of ± 0.05 percent.

Note: Items a through c are available from Cannon Instrument Company in State College, Pennsylvania.

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Safety

The Pydraul or Therminol fluids can be irritating to the skin. The vapors of the hot materials can be irritating to the eyes and upper respiratory system. If accidental contact is made with the eyes, flush immediately with large quantities of water and get immediate medical attention. Exercise caution to avoid possible thermal burns through contact with hot materials or equipment.

Determination

1. Determine the viscosity of the sample using the following table to determine the proper tube size and bath temperatures:

Product	*Temperature*	*Tube Series No.*
Therminol FR Lo-Temp	100°F/37.8°C	100
Therminol FR-0	100°F/37.8°C	100
Therminol FR-1	100°F/37.8°C	150
Therminol FR-2	100°F/37.8°C	200
Therminol 55	100°F/37.8°C	200
Therminol 66	100°F/37.8°C	200
Therminol 77	100°F/37.8°C	300

Note: Therminol fluids showing increased viscosity as result of decomposition may require next larger size viscometer.

2. Connect the large side of the tube, by means of a piece of rubber tubing to a water aspirator (vacuum source) for cleaning.
3. Apply gentle suction by means of the aspirator.
4. Place the capillary arm of the tube in a beaker containing ca. 100 ml of filtered benzene and suck the solvent through the tube.
5. Repeat step 4 using ca. 100 ml of filtered acetone.
6. Dry the tube by sucking a gentle stream of dry air through it.

Note: If the tube is not completely clean, it will be necessary to repeat Steps 4 and 5.

7. Insert the proper range thermometer in the bath.
8. Maintain the bath at the desired temperature ± 0.05°F.

Note: At temperatures of 100°F or lower, it may be necessary to circulate cooling water through the coils to maintain the desired temperature.

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9. To the large side arm of the viscometer tube, connect a piece of clean rubber tubing which is connected to the vacuum source.

10. Invert the viscometer tube and place the capillary side into a beaker containing the sample. The sample should be hot enough to be fluid.

Note: If the material to be tested is not *completely* free of residue and suspended solids, it must be filtered. This can be done by placing a 1" x 6" test tube in a 500 ml suction flask. Insert a medium porosity (70 micron) Selas glass crucible into a rubber adapter. Place the adapter in the top of the suction flask with the glass tube extending into the test tube. Filter, by suction, enough of the sample to fill the test tube ca. ¾ full.

11. Using a gentle suction, draw enough sample to fill both bulbs and into the capillary up to the mark etched on it.

12. Remove the vacuum tubing and return the tube to an upright position. Wipe the outside of the tube to remove any excess sample.

13. Fit the tube in the viscosity tube holder and immerse it in a constant temperature bath to such a level that the top bulb is completely immersed but allowing ¼" of the tube to protrude above the holder. Adjust the tube to a verticle position by visual inspection.

14. Allow the sample and viscometer tube to come to a temperature equilibrium with the bath. This will require a minimum of 10 minutes.

15. After the tube and sample have attained the bath temperature, draw the sample up to a point ca. 5 mm above the mark between the bulbs using a rubber bulb attached to the capillary arm.

16. Withdraw the rubber bulb and as the meniscus of the liquid passes the upper mark start the stop watch.

17. As the meniscus of the liquid passes the lower mark, stop the stop watch.

18. Record, to the nearest 0.2 second, the time required for the fluid to pass between the upper and lower marks. This is the efflux time.

19. Make a check determination by repeating steps 15 through 18. It is not necessary to refill the viscometer. Efflux times should agree with 0.2%.

Calculation

$V_K = Ct$

where V_K = viscosity in centistokes at T°F

C = tube constant at T°F

t = efflux time in seconds T°F

Determine V_K to the nearest 0.05 centistokes.

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Conversion of Centistokes (Cs) to Saybolt Universal Seconds (SUS)

Centistokes (Cs)	Saybolt Universal Seconds (SUS) At 100°F. and 130°F.	Saybolt Universal Seconds (SUS) At 210°F.	Centistokes (Cs)	Saybolt Universal Seconds (SUS) At 100°F. and 130°F.	Saybolt Universal Seconds (SUS) At 210°F.
2.0	32.6	32.9	36.0	168.2	169.4
2.5	34.4	34.7	37.0	172.7	173.9
3.0	36.0	36.3	38.0	177.3	178.5
3.5	37.6	37.9	39.0	181.8	183.0
4.0	39.1	39.4	40.0	186.3	187.6
4.5	40.8	41.0			
5.0	42.4	42.7	41.0	190.8	192.1
			42.0	195.3	196.7
6.0	45.6	45.9	43.0	199.8	201.2
7.0	48.8	49.1	44.0	204.4	205.9
8.0	52.1	52.5	45.0	209.1	210.5
9.0	55.5	55.9			
10.0	58.9	59.3	46.0	213.7	215.2
			47.0	218.3	219.8
11.0	62.4	62.9	48.0	222.9	224.5
12.0	66.0	66.5	49.0	227.5	229.1
13.0	69.8	70.3	50.0	232.1	233.8
14.0	73.6	74.1			
15.0	77.4	77.9	51.0	236.7	238.4
			52.0	241.3	243.1
16.0	81.3	81.9	53.0	245.6	247.7
17.0	85.3	85.9	54.0	250.6	252.4
18.0	89.4	90.1	55.0	255.2	257.0
19.0	93.6	94.2			
20.0	97.8	98.5	56.0	259.8	261.6
			57.0	264.4	266.3
21.0	102.0	102.8	58.0	269.1	270.9
22.0	106.4	107.1	59.0	273.7	275.6
23.0	110.7	111.4	60.0	278.3	280.2
24.0	115.0	115.8			
25.0	119.3	120.1	61.0	282.9	284.9
			62.0	287.5	289.5
26.0	123.7	124.5	63.0	292.2	294.2
27.0	128.1	129.0	64.0	296.8	298.8
28.0	132.5	133.4	65.0	301.4	303.5
29.0	136.9	137.9			
30.0	141.3	142.3	66.0	306.0	308.1
			67.0	310.6	312.8
31.0	145.7	146.8	68.0	315.3	317.4
32.0	150.2	151.2	69.0	319.9	322.1
33.0	154.7	155.8	70.0	324.4	326.7
34.0	159.2	160.3			
35.0	163.7	164.9	Over 70.0	SUS = Cs × 4.635	SUS = Cs × 4.667

Viscosities not listed, but which are within the range given in this table, are obtained by linear extrapolation.

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STANDARD ANALYTICAL METHOD

Product: Pydraul and Therminol fluids

Test: Acidity (mg-KOH/g) or Neutralization Number

SCOPE

This test for the acidity of the fluid is in accordance with the ASTM Standard Test D664-58, *Standard Method of Test for Neutralization Number by Potentiometric Titration.* The acid number is determined by dissolving a quantity of the fluid in a mixture of toluene and isopropyl alcohol containing a small amount of water and then titrating potentiometerically with alcoholic potassium hydroxide. A glass indicating electrode and a calomel reference electrode are used in titrating. End points are taken as pH 11.

Equipment

a. Meter — Voltmeter or potentiometer with accuracy of plus or minus .005 v, sensitivity of ± .002 v, and a range of .5 v, such as Beckman Model 96A, Fisher Scientific Model 210, or equivalent.

b. Glass Electrode — Fisher Catalog No. 13-639-1, or equivalent.

c. Calomel Electrode — Sleeve type — Fisher Catalog No. 13-639-60, or equivalent.

d. Stirrer — Variable — speed mechanical stirrer of any suitable type.

e. Buret — Fisher Catalog No. 3-847, Size D, or equivalent.

f. Beaker — A 300 ml. beaker made with borosilicate glass.

g. Stand — A suitable stand to support stirrer, electrodes, and buret such that the beaker can be removed without disturbing the assembly is desirable.

Reagents

a. Buffer, Nonaqueous Basic — Add 10 ml of buffer stock solution A to 100 ml. of titration solvent. Use within 1 hour.

b. m-Nitrophenol (mol. wt. 139.11), conforming to the following requirements:

melting point — 96° to 97°C
color — pale yellow

Store in brown glass bottle.

c. Buffer Stock Solution A can be made or purchased as desired. Purchased solution available from Fisher Scientific or Micro Essential Laboratory (Brooklyn, New York). A pH 11 buffer is suggested. To make the buffer solution proceed as follows:

Accurately weigh 27.8 ± 0.1 g of m-nitrophenol and transfer to a 1-liter volumetric flask containing 100 ml. of isopropyl alcohol. Using a 250 ml. graduated cylinder, add to the flask while continuously stirring its contents, $50/N_1 \pm 1$ ml. of 0.2 N alcoholic KOH solution (N_1 being the exact normality of the KOH solution found by standardization). Dilute to the 100 ml. mark with iso-

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propyl alcohol, and mix thoroughly.

d. Potassium Chloride Electrolyte — Prepare a saturated solution potassium chloride (KCl) in water.

e. Potassium Hydroxide Solution, Standard Alcoholic (0.1N). Add 6 g of potassium hydroxide (KOH) to approximately 1 liter of anhydrous isopropyl alcohol. Boil gently for 10 min. to effect solution. Allow solution to stand for two days and then filter the supernatent liquid through a fine sintered — glass funnel. Store the solution in chemically resistant bottle. Dispense in such a manner that the solution is protected from atmospheric carbon dioxide (CO_2) by means of a soda lime or soda asbestos guard tube, and such that it does not come into contact with cork, rubber, or saponified stop-cock grease. Standardize frequently enough to detect normality changes of 0.0005.

f. Potassium Hydroxide Solution, Standard Alcoholic (0.2N) — Prepare, store and standardize as directed in paragraph (e), but use 12 to 13 g. of KOH to approximately 1 liter of isopropyl alcohol.

g. Titration solvent — add 500 ml of toluene and 5 ml. of water to 495 ml. of anhydrous isopropyl alcohol. The titration solvent should be made up in large quantities, and its blank value determined daily by titration prior to use.

Preparation of Apparatus

Use standard procedures for preparation and maintenance of electrode equipment.

Procedure for Acid Number

a. Into a 300 ml titration beaker, introduce a weighed quantity of Therminol or Pydraul of about 10 g $\pm$ 0.10 g, and add 125 ml of titration solvent. Make sure all surfaces of the electrode are wiped clean and wetted with electrolyte previous to titration. Place beaker on stand and adjust its position so that the electrodes are about half immersed. Start stirrer, and stir throughout titration at a rate sufficient to produce vigorous agitation without spattering or without stirring air into the solution.

b. Fill buret with the 0.1 N alcoholic KOH solution and place the buret into the titrating assembly so that the tip is about 1 inch into the liquid. Record the initial buret and meter (cell potential) readings. Add suitable small portions of 0.1N alcoholic KOH solution and, after waiting until constant potential has been established, record the buret and meter readings. In regions where 0.1 ml. of titration solution causes a change of 0.03 v (corresponding to 0.5 pH units), add 0.05 ml. portions. In regions where changes are less radical, add portions large enough to produce a change equal to, but not greater than 0.03 v. Titrate in this manner to an end-point of pH 11.

c. Blank — For each set of samples, make a blank titration of 125 ml. of titration solvent, adding 0.1N alcoholic KOH solution in 0.05 ml. increments to a meter of pH 11.

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Calculations

a. Note the volumes of the titrating solution for both sample and blank used to reach end-point of pH 11.

b. Calculate the acid number as follows in mg KOH per g:

$$\text{Acid Number} = \frac{(A\text{-}B) \times N \times 56.1}{W}$$

where:

A = milliliters of alcoholic KOH solution used to titrate the sample to its end point,
B = volume corresponding to A for the blank titration
N = normality of the alcoholic KOH solution, and
W = grams of sample.

Note: A colorimetric method, ASTM D 974-64, can be used, however, dark colored fluids will sometimes interfere with the colorimetric end points.

STANDARD ANALYTICAL METHOD

Product: Pydraul & Therminol Fluids

Test: Moisture (H_2O content)

SCOPE

This test for moisture content of the Pydrauls and Therminols is in accordance with the ASTM Standard Test D1744-64, *Standard Method of Test for Water* by Karl Fischer Reagent. The water content is determined by titrating the fluid with standard Karl Fischer reagent to an electrometric end point.

EQUIPMENT

a. Buret — Fisher Catalogue No. 3-847 Size D, or equivalent.

b. Stirrer — magnetic stirrer.

c. Titration Flask — Fisher Catalogue No. 10-163,500 ml capacity.

d. Meter System — A micro-ammeter circuit can be assembled according to the attached diagram and using the following components:

Microammeter — A dc meter having 0 to 50 micro amp range with internal resistance of 1500 ohms.

Battery — 1.5 volt dry cell.

Electrodes — a one inch long 0.01 to 0.03 inch diameter platinum wire sealed in soft glass tubing with tip extending approximately 0.6 inches. Fill glass tubing with mercury and seal wire lead into top of tubing with collodin.

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Potentiometer — having resistance of 2000 ohms.

A meter circuit can also be purchased.

Example: Precision titration No. 68880 or equivalent would be suitable. Attachments can also be purchased to convert PH meters to indicate Karl Fischer end points.

Interferences:

Free alkali; oxidizing and reducing agents; Mercaptans, certain basic nitrogenous substances, or other materials that react with iodine, interfere.

Reagents

a. Karl Fischer Reagent, Stock Solution — Can be purchased from Fischer Scientific Catalogue No. SO-K-2; or made as follows:

   For each liter of solution, dissolve 85 ± lg of iodine in 27° ± 2 ml of pyridine in dry, glass-stoppered bottle. Add 67° ± 2 ml of methanol (99.9 percent). Cool the mixture in an ice bath to below 3.9°C. Bubble gaseous sulfur dioxide (SO_2) through concentrated sulfuric acid (H_2SO_4, sp. gr. 1.84) into the cooled mixture. Continue the addition of SO_2 until the volume has increased 50 ± 1 ml. Alternatively, add 50 ± 1 ml freshly drawn liquid SO_2 in small increments to the precooled mixture in an ice bath. Mix well and set aside for at least 12 hours before using.

b. Karl Fischer Reagent, Dilute Solution — Can be purchased from Fischer Scientific Catalogue No. SO-K-5 or made from stock solutions as follows:

   Adjust the strength of the stock solution to a water equivalence of 2 to 3 mg. of water per ml by dilution with pyridine.

c. Sample Solvent — Mix 1 volume methanol with 3 volumes of chloroform.

Standardization of Karl Fischer Reagent:

a. Add 50 ml. of the sample solvent to a clean, dry titration flask. Insert the stopper and adjust stirrer to give a smooth stirring action. Turn on the indicating circuit and adjust potentiometer to give a reference point with approximately 1μa of current flowing. Add Karl Fischer reagent in suitable amounts to the solvent to cause the needle to deflect from the reference. The end point is reached when after the addition of a single drop of reagent, the needle remains defected at least 1μa from the reference point for at least 30 seconds.

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b. To the solution in the titration flask add carefully, from a weighing pipet previously weighed to the nearest 0.1 mg., 1 drop of distilled water. Stopper the flask and reweigh the weighing pipet. Titrate to the end point as described in the above paragraph.

c. Calculate the water equivalence of the Karl Fischer reagent as follows:

$$F = \frac{W}{T}$$

where:

F = water equivalence of Karl Fischer reagent, in milligrams per milliliter,
W = milligrams of water added, and
T = milliliters of reagent required for the titration of the added water.

Procedure:

a. Add 50 ml. of solvent to the titration flask and titrate with the standardized Karl Fischer reagent to the end point as described in paragraph (a) of the previous section. Stopper the sample inlet tube as quickly as possible in order to prevent absorption of moisture from the atmosphere.

b. Weigh approximately 50 ml of the fluid and add to the titrating flask in any convenient manner.

c. Titrate the fluid to the end point as described above. Record the milliliters of reagent used.

Calculation:

Calculate the water content of the fluid as follows:

$$\text{water, ppm} = \frac{CF \times 1000}{W}$$

where:

C = milliliters of reagent required for titration of the Therminol or Pydraul,
F = water equivalence in milligrams of water per milliliter,
1000 = factor for converting to parts per million, and
W = grams of sample used.

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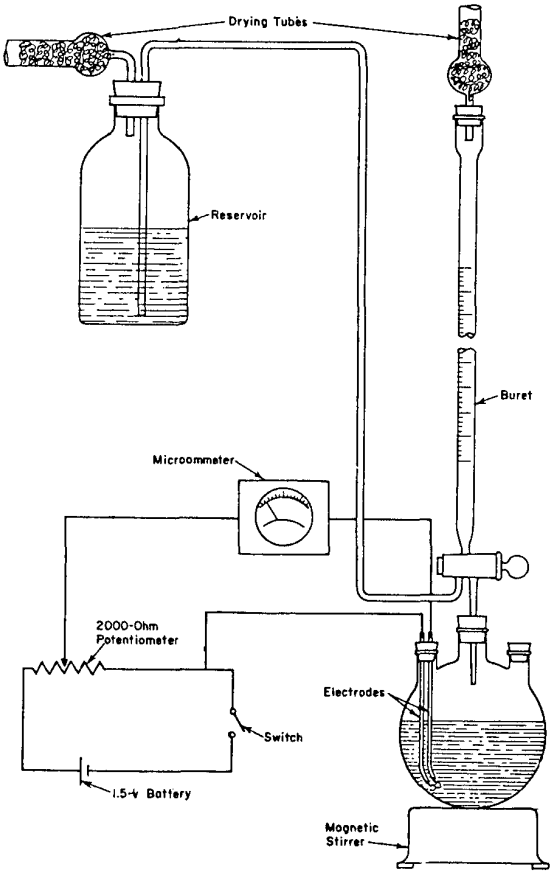

FIG. 1.—Apparatus for Determination of Water by Karl Fischer Reagent.

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