Automatic Determination of Aniline Point of Petroleum Products

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An apparatus is described for the automatic determination of aniline point of petroleum products. The basic principle involved comprises the use of the electric eye as a substitute for visual observation. The test sample is internally heated or cooled, the temperature is maintained uniform by stirring, and temperature equilibrium is automatically accomplished by a relay system. The relay system which controls the heating or cooling is activated by directing a light beam through the sample on a photocell, the light beam being interrupted periodically as the sample clears or clouds with slight temperature change. The flashing of a lamp bulb indicates when equilibrium temperature is reached.

THE A.S.T.M. defines aniline point (*1*) as "the minimum equilibrium solution temperature for equal volumes of aniline and petroleum product".

Many attempts have been made to adapt the test to dark-colored products. Donn (*3*) proposed determining the temperature at which a break occurred in the viscosity-temperature curve. Van Wijk and Boelhouwer (*8*) proposed the detection of a change in transparency to infrared radiation by the use of a thermopile, while Matteson, Zeitfuchs, and Eldredge (*6*) described an apparatus also employing infrared radiation but using a photocell and microammeter. Williams and Dean (*9*) suggested a "circulating test tube" with visual observation through a 2.0-mm. layer. Carr and Agruss (*2*) and Madsen (*5*) recommended an apparatus for determining equilibrium temperature visually through a film of the sample.

Geddes (*4*) in order to overcome the difficulty and hazard involved in determining high aniline points of highly paraffinic lubricating oils proposed substituting *N*-methylaniline for aniline. Data indicate that *N*-methylaniline points are approximately 77° C. lower than aniline points.

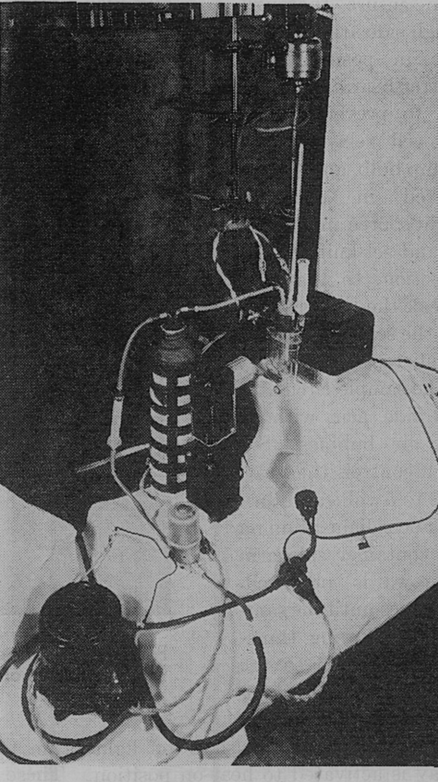

Figure 2. General View of Apparatus

The purpose of this paper is to describe an apparatus that determines aniline points automatically and has the definite advantage that at equilibrium temperature the thermometer mercury column remains practically constant, varying usually not more than 0.2° C.

APPARATUS

1. Air-drying tubes, 12.0 cm. × 17 mm. in outside diameter, filled with 8-mesh Drierite.
2. Bunsen valve 2.5-inch piece of gum tubing, 9 mm. in outside diameter, 5-mm. in inside diameter.
3. Indicating lamp bulb, ordinary, frosted.
4. Knife-switch, double-pole, single-blade.

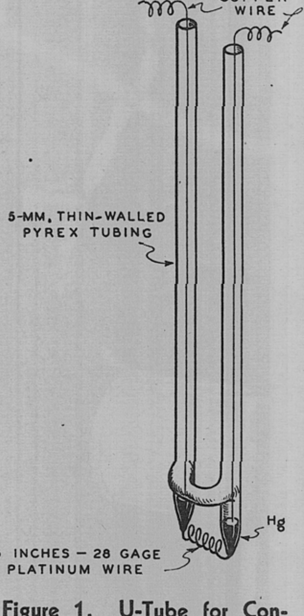

Figure 1. U-Tube for Conducting Cold Carbon Dioxide–Air Mixture

Contains heating unit

5. Light source, General Electric Catalog 98 × 264 Mazda 1133, 32 C, 6- to 8-volt. 3.8-cm. condensing lens. General Electric transformer, Catalog 71G620 KVA 0157, 50/60-cycle 115-volt to 4.8-volt.
6. Photocell and relay Photoelectric relay CR7505 K100-GZ, 115-volt 50/60-cycle. Connections K-6919764, phototube 923 (2nd tube ZG-479).
7. Platinum heating unit, 15.0 cm. of No. 28 gage (see Figure 1).
8. Plexiglas air-jacket, made from 0.15-cm. sheet.
9. Sample container, modified Thiele melting point tube. Over-all length, 17.8 cm. Main body: length 8.25 cm. diameter 2.54 cm. Top opening, 3.5 cm. Charging opening, approximately 12 mm.

Circulating side arm, 12-mm. outside diameter. Pyrex tubing, approximately 7.6 cm. over-all length, with flattened area of approximately 2.0-mm. inside diameter and with a centered bulls-eye of about 0.6-cm. diameter, the sides of which are just close enough together to allow a thin layer of sample to circulate between.

Interchangeable ground-glass joints have been tried, but cork has proved satisfactory.

10. Solenoid valve, General Electric CR9503,115-volt.
11. Stirrer, steel, 0.3-cm. diameter, 41.6-cm. shaft, equipped with 1.3-cm. vertical blades.
12. Stirrer-motor equipped with rheostat.
13. Thermos bottle. Quart size filled with pieces of dry ice stoppered with a rubber equipped with 5- to 6-mm. Pyrex tubes, outlet tube extending to bottom. Wrapped for protection against breakage.
14. Thermometer, A.S.T.M. aniline point. It is believed that one thermometer of suitable range can be used in view of constancy of the temperature at equilibrium point.
15. U-tube. 5.0-mm. Pyrex tubing for circulating cold air and

containing heating unit (Figure 1). Thin-walled tubing is necessary for efficient cooling.

PROCEDURE

For Aniline Points above Room Temperature. Measure sufficient sample aniline through the charge inlet into the sample container to ensure thorough mixing through side arm. Place thermometer in position and attach to stirrer bearing with an elastic band to prevent vibration. (Photocell relay circuit, indicating lamp bulb, and Variac are connected in parallel.) Switch on light source and photocell circuits and set knife switch blade in position, so that the relay will break the heating unit circuit when the solution is clear. Start the stirrer and adjust speed until the sample circulates through the side arm without drawing in air bubbles. Set Variac, which controls the heating unit, to 3 to 5 volts and turn on switch. Focus light beam on flat area of container side arm and direct towards photocell. Heating continues until the sample clears, thus allowing transmittance of light beam to the photocell and thereby breaking the heating circuit. The sample cools immediately, clouds, and shuts off light beam to photocell, and relay is activated to heat-on position. These clearing and clouding cycles are uniform and of very short duration and are indicated by the flashing lamp bulb.

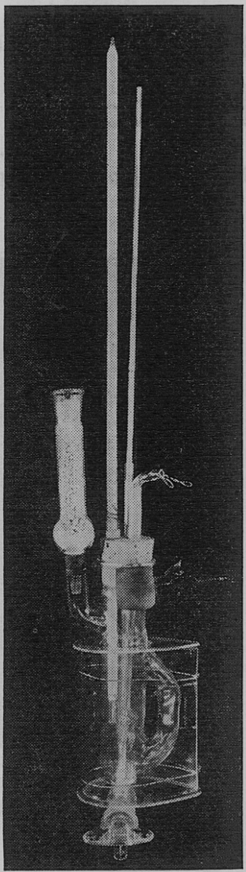

Figure 3. Close-Up of Container

Table I. Aniline Point Determinations

Sample No.	Description	Results: Proposed automatic ° C.	A.S.T.M. ° C.
1	65 ml. of benzene diluted to 100 ml. with *n*-heptane	−11.15, −11.4	−11.4
2	60 ml. of benzene diluted to 100 ml. with *n*-heptane	−3.4, −3.6	−3.7
3	50 ml. of benzene diluted to 100 ml. with *n*-heptane	10.05, 10.2	10.1, 10.1
4	43 ml. of benzene diluted to 100 ml. with *n*-heptane	20.3	20.2
5	Gasoline cut from still	30.8	31.0
6	34 ml. benzene diluted to 100 ml. with *n*-heptane	31.2	31.3
7	Light-colored naphtha	35.7, 35.7	35.9
8	Gasoline cut from still	39.1	39.2
9	Gasoline cut from still	40.8	40.8
10	Light-colored naphtha	49.6, 49.7, 49.6	49.7
11	Diesel fuel	62.0	62.0
12	*n*-Heptane	68.9, 68.9, 69.0	69.1, 69.2
13	Light-colored naphtha	77.6, 78.0, 77.7	77.8
14	Lubricating oil, NPA color 3	111.0	111.2

Table II. Mixed Aniline Point Determinations

Sample No.	Description	Results: Proposed automatic ° C.	A.S.T.M. ° C.
7	Light-colored naphtha	53.2	53.4
10	Light-colored naphtha	59.8	60.0
13	Light-colored naphtha	73.0	73.2

Temperature is maintained practically constant, holding usually within 0.2° C. Adjust Variac, if necessary, according to the difference between test and room temperatures.

Shut off electric circuits upon completion of test. Drain sample by opening stopcock. Rinse sample container thoroughly with suitable solvent (acetone, benzene, or mixture of both) through charge opening and then apply vacuum through stopcock to dry container.

For Aniline Points below Room Temperature. The presence of water seriously interferes with the accuracy of aniline point determinations (7). In determining aniline points occurring below room temperature, air will be drawn into the sample container as cooling takes place. This might be serious in locations where excessive humidity is common. Therefore, the following precautions should be observed.

Make certain that the stopper and fittings are tight. Fit a drying tube into the charge opening by means of a rubber stopper, after sample and aniline are in the container, to act as dry-air breather opening. Insert the thermometer into position through a snug-fitting rubber sleeve.

Replace heating unit circuit with solenoid-activated cooling circuit and set Variac to 115 volts. (Solenoid, photocell relay circuit, and indicating lamp bulb are in parallel.) Insert Bunsen valve in air line between laboratory air supply and solenoid valve. connect the outlet of the solenoid valve to a drying tube, which in turn is connected to the thermos bottle containing the dry ice; make final connection to U-tube in sample container. Turn on the air until an excess blows through the Bunsen valve. Switch on light source, photocell circuit, and stirrer, and reverse knife switch blade in position so that relay breaks circuit to solenoid when the sample clouds. Cooling continues until clouding occurs, thus interrupting the light beam to the photocell which breaks circuit to solenoid, closes valve instantly, and diverts the air through the Bunsen valve. The sample warms immediately and clears, again allowing transmittance of the light beam to the photocell, which activates relay to close solenoid circuit and thereby opens air valve. These clearing and clouding cycles are indicated by the flashing of the lamp bulb and produce a practically constant equilibrium temperature.

Shut off electric circuits and clean container as directed above:

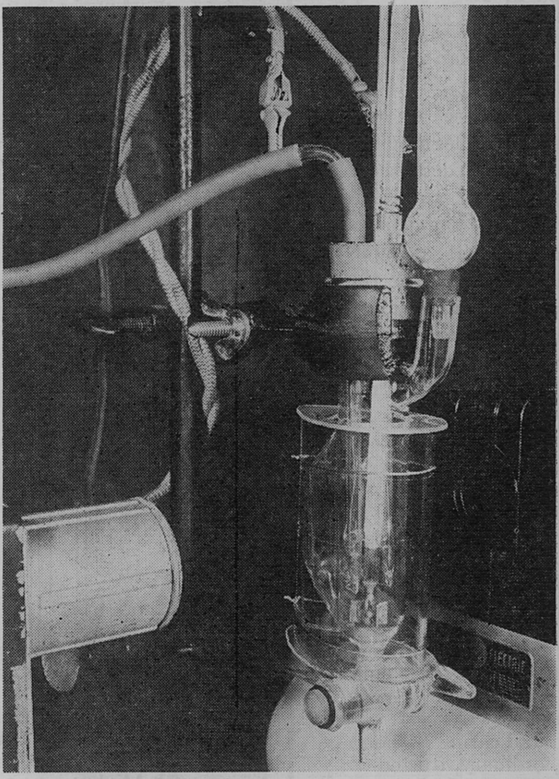

Figure 4. Light Source and Photocell

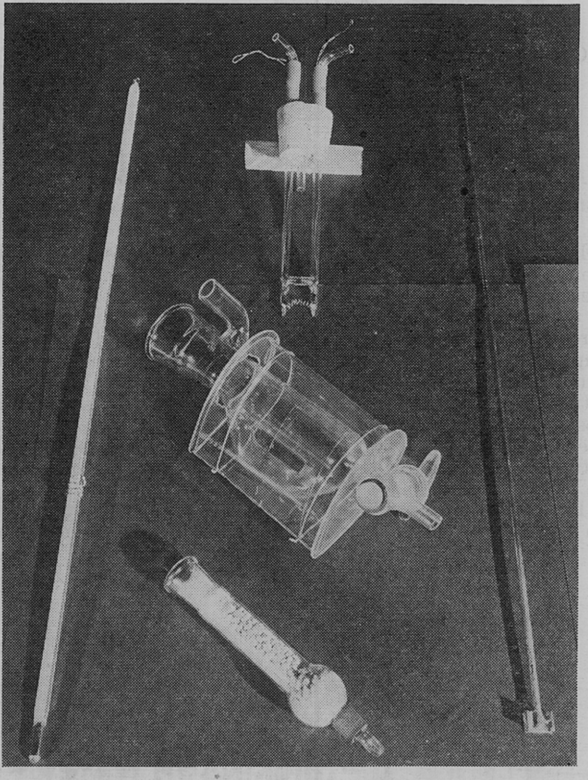

Figure 5. Sample Container Disassembled

Tables I and II show the reproducibility with the apparatus and the close agreement with results obtained by the A.S.T.M. procedure.

Table III covers a few tests which indicate the adaptability of this apparatus to dark petroleum products. The samples cover the A.S.T.M. color range from −7 to very much darker than 8. Incidentally, while there is no doubt a limit of sample color beyond which this apparatus may not function, changes in sample container design and a more sensitive light source (possibly infrared) and photocell combination may permit the testing of practically all dark products.

Table III. Aniline Point of Dark-Colored Petroleum Products

No.	Sample Color, Lovibond (500 Amber Series), 0.25-Inch Cell: As is	Diluted with kerosene 9 to 1	A.S.T.M.	Results Proposed Automatic, ° C.
A	350	...	7−	82.2
B	450	...	8−	116.8
C	700	...	8+	95.5
D	>750	95	8+	104.4
E	>750	>750	8+	81.3

Figure 2 shows the general setup.

Figure 3 pictures the sample container plus jacket, etc., and Figure 4 pictures container in position between light source and photocell. The clip which prevents the thermometer from slipping through the glass sleeve in the stopper is replaced by a tight-fitting rubber sleeve when testing samples whose aniline points are below room temperature.

Figure 5 pictures sample container, U-tube, stirrer, and thermometer disassembled.

Tentative steps are under way for the manufacture of this apparatus by the Precision Scientific Company, Chicago, Ill.

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An Automatic-Recording Ultraviolet Photometer for Laboratory and Field Use

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The rates of adsorption processes or chemical reactions involving a gas which absorbs ultraviolet light can be followed readily with an ultraviolet photometer. An automatic-recording instrument is described capable of detecting concentrations of the order of a part per million. This apparatus has been applied to the evaluation of the efficiency of adsorbents against toxic gases, to field studies of the travel of gas clouds, and to fundamental investigations in the kinetics of gaseous reactions.

IN TESTS of the protection of absorbents against toxic gases and in field studies of the travel of gas clouds, it is highly desirable to have an instrument which will follow rapid changes in concentration and will detect minute quantities of certain test gases. In laboratory tests of the efficiency of adsorbents, a knowledge of the variation of effluent concentration with time is necessary for both practical and theoretical assessment, and since this concentration-time curve (Figure 1) is frequently very steep, a rapid, recording analyzer is most desirable. In field tests a cloud of toxic gas may pass a station in less than a minute and may exhibit large variations in concentration within that short period (Figure 2), so that a rapid-recording device becomes essential.

A number of the important war gases—for example, phosgene (*2*) and chloropicrin (*4*)—exhibit strong absorption of ultraviolet radiation. This property may be used to advantage as an analytical tool and has been so applied by Woodson (*9*) and others (*1*, *3*, *6*). The instrument described in this paper has a number of advantages over those previously described. For increased precision in analysis, a null-point measuring circuit has been introduced similar to one already described (*3*). To avoid the neces-