

NOTICE: This standard has either been superseded and replaced by a new version or discontinued.  
Contact ASTM International (www.astm.org) for the latest information.



Designation: D 936 - 89

AMERICAN SOCIETY FOR TESTING AND MATERIALS  
1916 Race St., Philadelphia, Pa. 19103  
Reprinted from the Annual Book of ASTM Standards, Copyright ASTM  
If not listed in the current combined index, will appear in the next edition.

An American National Standard

## Standard Test Method for Aromatic Hydrocarbons in Olefin-Free Gasolines by Silica Gel Adsorption<sup>1</sup>

This standard is issued under the fixed designation D 936; 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 reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

*This standard has been approved for use by agencies of the Department of Defense and replaces Method 3702 of Federal Test Method Standard No. 791b. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.*

### 1. Scope

1.1 This test method covers the determination of total aromatic content of gasolines and other debutanized hydrocarbon mixtures that distill below 204°C (400°F) and contain less than 1 % of olefinic hydrocarbons.

1.2 The values stated in SI units are to be regarded as the standard. The values in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems 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 hazard statements are given in Section 7 and Annex A1.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D941 Test Method for Density and Relative Density (Specific Gravity) of Liquids by Lipkin Bicapillary Pycnometer<sup>2</sup>

D 1319 Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption<sup>2</sup>

E 11 Specification of Wire-Cloth Sieves for Testing Purposes<sup>3</sup>

### 3. Summary of Test Method<sup>4</sup>

3.1 The sample is passed downward through a column packed with fine, activated silica gel and, when all of the sample has been adsorbed on the gel, alcohol is added as an eluent. The alcohol causes desorption of the hydrocarbons, forcing them down the column. In this process of adsorption and desorption, the hydrocarbons are separated according to their adsorption affinities so that the components issue from the bottom of the silica gel column in the following order:

saturates, saturates plus aromatics, aromatics, aromatics plus alcohol, and alcohol. The percolate is collected in small fractions and the aromatic content of the sample is calculated from measured volumes and refractive indices of the fractions. Samples containing less than 4 % aromatics are fortified with a known amount of toluene and those containing more than 80 % aromatics are diluted with a saturated hydrocarbon or hydrocarbon mixture boiling in the gasoline range; correction is made in the calculation for the toluene or diluent added.

### 4. Significance and Use

4.1 A precise knowledge of the liquid volume percent of the aromatic hydrocarbons of gasolines and petroleum fractions from which gasolines are blended is of value in assessing the performance properties of the gasolines. Such knowledge is also of value in measuring the conversion of paraffins and cycloparaffins to aromatics by catalytic reforming. This test method provides a procedure for making such a precise determination.

### 5. Interference

5.1 Paraffins and cycloparaffins do not interfere, regardless of their concentration. Olefinic hydrocarbons, when present in concentrations greater than one percent, interfere in the normal use of this test method. Compounds containing sulfur or nitrogen interfere by being included with the aromatic hydrocarbons.

### 6. Apparatus

6.1 *Adsorption Column*, as shown in Fig. 1, consisting of an eluent reservoir, a sample reservoir, and wide and narrow sections of a water-jacketed tubing. The column should be surrounded with a transparent protective shield when operating at pressures in excess of 69 kPa (10 psi).

6.2 *Receiver*, graduated, of 11-mL capacity, as shown in Fig. 2.

NOTE 1—While not strictly required, a cathetometer, capable of measuring liquid levels to  $\pm 0.1$  mm, is desirable for more accurate and convenient calibration of the receiver (see Section 9).

6.3 *Sample Containers*, of approximately 5, 10, and 25-mL capacities. It is convenient to use sets of numbered sample vials with molded plastic caps, each set supported in a drilled wooden block.

6.4 *Vibrator*, for packing of the silica gel. (A rubber padded vibrator of the type used by barbers is satisfactory.)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

Current edition approved Oct. 27, 1989. Published December 1989. Originally published as D 936 - 47. Last previous edition D 936 - 83.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>4</sup> For a more complete discussion of this test method, see Mair, B. J., "Separation and Determination of Aromatic and Monoolefin Hydrocarbons in Mixtures with Paraffins and Naphthenes by Adsorption," *Journal of Research*, National Institute of Standards and Technology. JRMSB, Vol 34, No. 5, 1945, p. 435.

## D 936

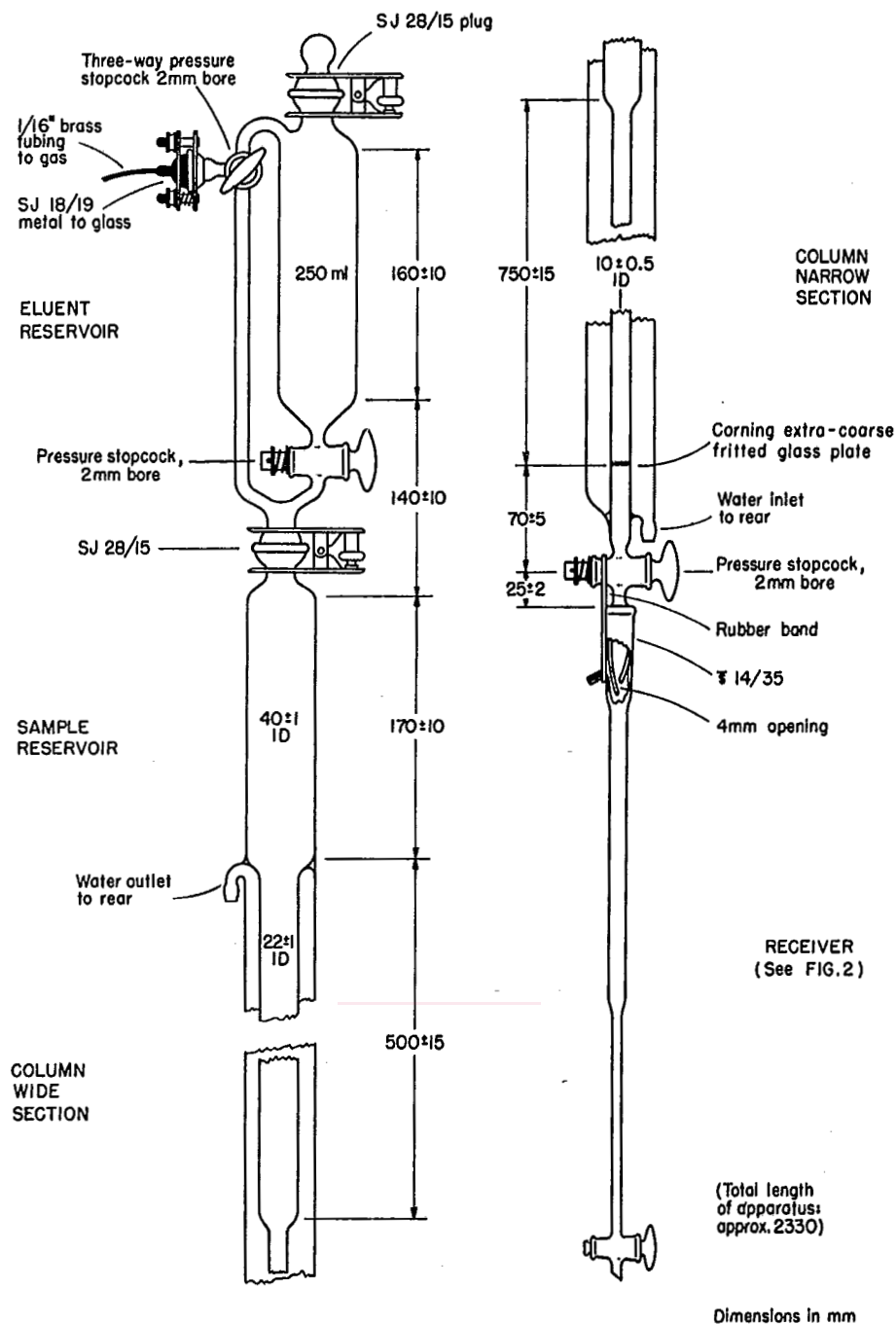


FIG. 1 Analytical Adsorption Column

Proper packing can also be accomplished by tapping with a padded rod.

6.5 *Plastic Tubing*, 4.8-mm ( $3/16$ -in.), for column flushing.

6.6 *Refractometer*, capable of measuring refractive indexes to  $\pm 0.0001$  unit of less than 1 mL of liquid at 20 or 25°C.

## 7. Reagents and Materials

7.1 *Silica Gel*,<sup>5</sup> activated, conforming to the sieve test

<sup>5</sup> Silica gel, Grade 922, from the Davison Chemical Corp., Baltimore, MD, is satisfactory.

requirements shown in Table 1, and containing not more than 0.01 % of extractable impurities (Section 8). Make a performance test on each lot of gel that passes the test for impurities, as follows: Percolate through the packed column, as directed in Section 10, a mixture of 80 mL of essentially pure 2,2,4-trimethylpentane (**Warning**—See Note 2) and 20 mL of essentially pure toluene (**Warning**—See Note 3) and elute with alcohol as described in Section 10. Consider the lot as having satisfactory adsorptive properties if there is obtained not more than 3 mL of percolate of refractive index,  $n_D^{20}$ , between 1.3970 and 1.4920, or  $n_D^{25}$ , between 1.3940 and 1.4890.

ASTM D 936

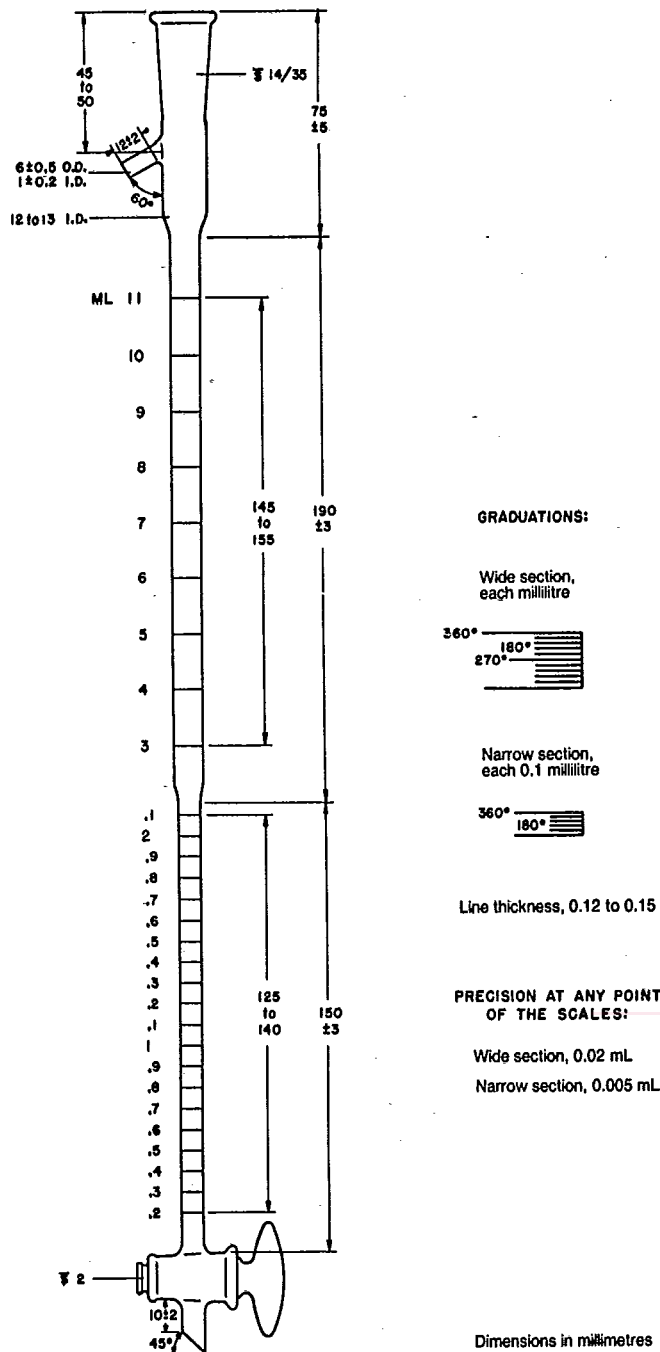


FIG. 2 Receiver for Analytical Adsorption Column

NOTE 2: Warning—Extremely flammable. Harmful if inhaled. Vapors can cause flash fire. See Annex A1.1.

NOTE 3: Warning—Flammable. Vapor harmful. See Annex A1.2.

7.2 Silica Gel, activated, 28 to 200-mesh<sup>6</sup> (for 10-mm layer above fritted glass plate, see 10.2).

7.3 Alcohol, Ethyl or Isopropyl, cp absolute:

NOTE 4: Warning—Flammable. Denatured—cannot be made non-toxic. See Annex A1.3 and A1.4.

<sup>6</sup> Silica gel, Code No. 12, from the Davison Chemical Corp., Baltimore, MD, is satisfactory.

7.4 Toluene, cp, at least 99 % pure:

NOTE 5: Warning—Flammable. Vapor harmful. See Annex A1.2.

7.5 Isooctane, 2,2,4-trimethylpentane, at least 99 % pure:

NOTE 6: Warning—Extremely flammable. Harmful if inhaled. Vapors can cause flash fire. See Annex A1.1.

7.6 Diluent, an aromatic-free, saturated hydrocarbon or a mixture of hydrocarbons boiling in the gasoline range:

NOTE 7: Warning—Extremely flammable. Harmful if inhaled. Vapors can cause flash fire. See Annex A1.5.

7.7 Pressurizing Gas, nitrogen or air, delivered to the top of the column at a regulated pressure, constant to 7 kPa (1 psi):

NOTE 8: Warning—Compressed gas under high pressure. See Annex A1.6.

7.8 Stopcock Lubricant, hydrocarbon-in-soluble.<sup>7</sup>

7.9 Mercury, redistilled (for calibration of receiver):

NOTE 9: Warning—Poison. Can be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds threshold limit value for occupational exposure. See annex A1.7.

7.10 Chromic Acid Cleaning Solution:

NOTE 10: Warning—Causes severe burns. A recognized carcinogen. Strong oxidizer; contact with other material can cause fire. Hygroscopic. see Annex A1.8.

7.11 Acetone:

NOTE 11: Warning—Extremely flammable. Vapors can cause flash fire. Vapors can spread long distances and ignite explosively. See Annex A1.9.

8. Test for Impurities in Silica Gel

8.1 On each lot of silica gel, determine the amount of impurities by adding about 200 mL of alcohol (Warning—See Note 12) to the column packed with silica gel as specified in Section 10, using a weighed charge. Force the alcohol through the adsorbent at a rate of descent of 7 to 13 mm/min (0.3 to 0.7 mL/min). Collect the percolate in a tared glass evaporation dish, evaporate almost to dryness on a steam bath, dry the outside of the dish with a clean lint-free cloth, and heat to constant weight in an oven at 100 to 105°C. Cool under a dust-protective cover, and weigh to 0.1 mg.

NOTE 12: Warning—Flammable. Denatured—cannot be made non-toxic. See Annex A1.3 and A1.4.

8.2 The extractable, nonvolatile residue should not be more than 10 mg/100 g of silica gel (0.01 %). (See 7.1)

NOTE 13—Commercial silica gel has been found to contain varying amounts of a waxy material that appears in the fractions containing the saturates, thus causing results for aromatics to be low. It has also contained a small amount of colored organic material desorbed by alcohol, which appears in the fractions containing mixtures of aromatics and alcohol, thus giving an apparent aromatic content slightly greater than is actually present. Since it is difficult to determine these two kinds of impurities separately and derive corrections, lots of silica gel having an amount of total impurities greater than 0.01 % should be considered unsatisfactory.

<sup>7</sup> For a suitable recipe, see T. P. Sager, "An Esterification Resin as a Ground Joint Lubricant," *Industrial and Engineering Chemistry, Analytical Ed.*, Vol 4, No. 4, 1932, p. 388.

 D 936

TABLE 1 Sieve Acceptance Tests of Silica Gel

Sieve Size		Particles Passing Through Sieve, %
$\mu\text{m}$	Designation <sup>A</sup>	
150	No. 100	95 min
75	No. 200	80 min
45	No. 325	25 max

<sup>A</sup> Detailed requirements for these sieves are given in Specification E 11.

## 9. Calibration of Receiver

9.1 Clean the receiver with chromic-sulfuric acid (Warning—See Note 14), water and acetone, and dry by evacuation. Grease the stopcock and weigh the receiver on a draft-protected balance to  $\pm 0.001$  g.

NOTE 14: Warning—Causes severe burns. A recognized carcinogen. Strong oxidizer; contact with other material can cause fire. Hygroscopic. See Annex A1.8.

9.2 Close the stopcock and leave it closed during the calibration. Fill the receiver with pure mercury (Warning—See Note 15) to a point between the 0.2 and 0.3 marks and tap gently to remove entrapped air and droplets of mercury adhering to the glass. Weigh and calculate the weight of the mercury to  $\pm 0.001$  g.

NOTE 15: Warning—Poison. Can be harmful or fatal if inhaled or swallowed. Vapor harmful; emits toxic fumes when heated. Vapor pressure at normal room temperature exceeds Threshold limit value for occupational exposure. See Annex A1.7.

9.3 Clamp the receiver firmly in a vertical position and provide a source of indirect illumination adjusted so that the meniscus is sharply defined. Note on the scale the observed volume,  $V_{\text{obs}}$ , indicated at the top of the meniscus.

9.4 Record the ambient temperature,  $t$ , to  $\pm 0.5^\circ\text{C}$  and calculate the volume of mercury,  $V_m$ , as follows:

Narrow Section of Receiver (9.6):

$$V_m = vW + 0.006 \quad (1)$$

Wide Section of Receiver (9.6):

$$V_m = vW + 0.023 \quad (2)$$

where:

$W$  = weight of mercury, g,

$v$  = volume of 1 g of mercury, mL at  $t^\circ\text{C}$  as shown in Table 2, and

0.006 and 0.023 are mercury meniscus corrections applicable to the two diameters of the receiver.

9.4.1 If a cathetometer is used in calibrating the receiver, make measurements to  $\pm 0.1$  mm at each of the following points:

$h_1$ , the first graduation line below the meniscus,

$h_m$ , the tangent to the apex of the meniscus, and

$h_2$ , the first graduation line above the meniscus.

TABLE 2 Volume of One Gram of Mercury at Various Temperatures

Temperature, $t$ , $^\circ\text{C}$	Volume, $v$ , mL	Temperature, $t$ , $^\circ\text{C}$	Volume, $v$ , mL
18	0.07379	24	0.07387
19	0.07380	25	0.07388
20	0.07382	26	0.07390
21	0.07383	27	0.07391
22	0.07385	28	0.07393
23	0.07386	29	0.07394

Calculate the observed volume,  $V_{\text{obs}}$ , as follows:

$$V_{\text{obs}} = V_1 + [(h_m - h_1)/(h_2 - h_1)][V_2 - V_1] \quad (3)$$

where:

$h_1$ ,  $h_m$ , and  $h_2$  = cathetometer scale readings, mm, and

$V_1$  and  $V_2$  = volumes indicated by the calibration marks at  $h_1$  and  $h_2$ , respectively.

Otherwise continue as directed in 9.4.

9.5 Calculate the calibration error,  $\Delta$ , at the point of checking as follows:

$$\Delta = V_{\text{obs}} - V_m \quad (4)$$

9.6 By successive addition of mercury, repeat the calibration at four well-spaced points on the narrow section of the receiver and at five points on the wide section. Reject the receiver if the difference between the highest and the lowest calibration error exceeds 0.005 mL for the narrow section and 0.02 mL for the wide section.

9.6.1 The receiver graduations need not be accurate in an absolute sense; that is, the indicated unit of volume does not need to be exactly 1 mm. However, the interrelationship of the graduations (and corresponding volumes) must be such that the tolerances indicated in 9.6 and in Fig. 2 are satisfied.

NOTE 16—If desired, a receiver that does not meet the specifications may be employed, provided volume corrections are made and introduced in the calculation procedure.

## 10. Preparation of Apparatus

10.1 Clean column and receiver with chromic-sulfuric acid, water, and acetone (Warning—See Note 17) or alcohol, and dry them by evacuation (Note 18). Lightly lubricate the stopcock at the bottom of the column and the receiver stopcock (but not the spherical joint of the sample reservoir or the standard taper joint of the receiver) with hydrocarbon-insoluble lubricant.

NOTE 17: Warning—Extremely flammable. Vapors can cause flash fire. Vapors can spread long distances and ignite explosively. See Annex A1.9.

NOTE 18—Clean the receivers with cleaning acid after each use and the column after about every third analysis.

10.2 Clamp the column (without eluent reservoir and receiver) to its stand and open the stopcock at the bottom. Add 28 to 200-mesh silica gel to the height of about 10 mm above the fritted glass plate and, while applying the vibrator (or tapping with a padded rod), slowly pour in silica gel through a funnel, as specified in 7.1, to a point 5 to 25 mm inside the reservoir. Immediately close the column stopcock and close the reservoir with a rubber stopper. Continue packing the gel by vibrating (or tapping) until the surface has dropped to a point 10 to 30 mm below the reservoir and does not move more than 1 mm during  $\frac{1}{2}$  min of vibrating (or 5 min of tapping). Toward the end of the packing period, remove the rubber stopper for a moment. Add more gel if the quantity proves insufficient. If not used immediately, leave the column closed to protect the gel from atmospheric moisture.

## 11. Procedure

11.1 For normal samples, pass tap water (below  $20^\circ\text{C}$ ) through the jacket; for samples containing appreciable quantities of material boiling below  $40^\circ\text{C}$ , circulate ice water. Attach the receiver to the column with the aid of a rubber