



Standard Test Method for Aromatic Types Analysis of Gas-Oil Aromatic Fractions by High Ionizing Voltage Mass Spectrometry¹

This standard is issued under the fixed designation D3239; 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 (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method² covers the determination by high ionizing voltage, low resolution mass spectrometry of 18 aromatic hydrocarbon types and 3 aromatic thiophenotypes in straight run aromatic petroleum fractions boiling within the range from 205 to 540°C (400 to 1000°F) (corrected to atmospheric pressure). Samples must be nonolefinic, must contain not more than 1 mass % of total sulfur, and must contain not more than 5 % nonaromatic hydrocarbons. Composition data are in volume percent.

NOTE 1—Although names are given to 15 of the compound types determined, the presence of other compound types of the same empirical formulae is not excluded. All other compound types in the sample, unidentified by name or empirical formula, are lumped into six groups in accordance with their respective homologous series.

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

1.3 *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.*

2. Referenced Documents

2.1 ASTM Standards:³

[D2549 Test Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography](#)

[D2786 Test Method for Hydrocarbon Types Analysis of Gas-Oil Saturates Fractions by High Ionizing Voltage Mass Spectrometry](#)

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04.0M on Mass Spectroscopy.

Current edition approved Oct. 1, 2011. Published October 2011. Originally approved in 1973. Last previous edition approved in 2006 as D3239 – 91 (2006). DOI: 10.1520/D3239-91R11.

² Robinson, C. J., and Cook, G. L., *Analytical Chemistry* (ANCHA), Vol 41, 1969, p. 1548.

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

E137 Practice for Evaluation of Mass Spectrometers for Quantitative Analysis from a Batch Inlet⁴

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 Characteristic Mass Summations— Classes I–VII:

3.1.2 Class I:

$$\begin{aligned} \Sigma 78 = & 78 + 92 + 106 + 120 + \dots \text{to end, polyisotopic} \\ & + 91 + 105 + 119 + \dots \text{to end, monoisotopic} \end{aligned} \quad (1)$$

3.1.3 Class II:

$$\begin{aligned} \Sigma 104 = & 104 + 118 + 132 + 146 + \dots \text{to end, polyisotopic} \\ & + 117 + 131 + 145 + \dots \text{to end, monoisotopic} \end{aligned} \quad (2)$$

3.1.4 Class III:

$$\begin{aligned} \Sigma 129 = & 130 + 144 + 158 + 172 + \dots \text{to end, polyisotopic} \\ & + 129 + 143 + 157 + 171 + \dots \text{to end, monoisotopic} \end{aligned} \quad (3)$$

3.1.5 Class IV:

$$\begin{aligned} \Sigma 128 = & 128 + 142 + 156 + 170 + \dots \text{to end, polyisotopic} \\ & + 141 + 155 + 169 + \dots \text{to end, monoisotopic} \end{aligned} \quad (4)$$

3.1.6 Class V:

$$\begin{aligned} \Sigma 154 = & 154 + 168 + 182 + 196 + \dots \text{to end, polyisotopic} \\ & + 167 + 181 + 195 + \dots \text{to end, monoisotopic} \end{aligned} \quad (5)$$

3.1.7 Class VI:

$$\begin{aligned} \Sigma 166 = & 166 + 180 + 194 + 208 + \dots \text{to end, polyisotopic} \\ & + 179 + 193 + 207 + \dots \text{to end, monoisotopic} \end{aligned} \quad (6)$$

3.1.8 Class VII:

$$\begin{aligned} \Sigma 178 = & 178 + 192 + 206 + 220 + \dots \text{to end, polyisotopic} \\ & + 191 + 205 + 219 + \dots \text{to end, monoisotopic} \end{aligned} \quad (7)$$

3.1.9 *Classes, Compound Types, Empirical Formulae*—See [Table 1](#).

4. Summary of Test Method

4.1 The relative abundance of seven classes (I–VII) of aromatics in petroleum aromatic fractions is determined by mass spectrometry using a summation of peaks most characteristic of each class. Calculations are carried out by the use of a 7 by 7 inverted matrix derived from published spectra of pure aromatic compounds. Each summation of peaks includes the

⁴ Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

TABLE 1 Classes, Compound Types, and Empirical Formulae

Class	Type	Formula
I	0	alkylbenzenes, C_nH_{2n-6}
I	1	benzothiophenes, $C_nH_{2n-10}S$
I	2	naphthenephenanthrenes, C_nH_{2n-20}
II	0	naphthenebenzenes, C_nH_{2n-8}
II	1	pyrenes, C_nH_{2n-22}
II	2	unidentified
III	0	dinaphthenebenzenes, C_nH_{2n-10}
III	1	chrysenes, C_nH_{2n-24}
III	2	unidentified
IV	0	naphthalenes, C_nH_{2n-12}
IV	1	dibenzothiophenes, $C_nH_{2n-16}S$
IV	2	unidentified
V	0	acenaphthenes + dibenzofurans, C_nH_{2n-14} and $C_nH_{2n-16}O$
V	1	perylene, C_nH_{2n-28}
V	2	unidentified
VI	0	fluorenes, C_nH_{2n-16}
VI	1	dibenzanthracenes, C_nH_{2n-30}
VI	2	unidentified
VII	0	phenanthrenes, C_nH_{2n-18}
VII	1	naphthobenzothiophenes, $C_nH_{2n-22}S$
VII	2	unidentified

polyisotopic homologous series that contains molecular ions and the monoisotopic homologous series one mass unit less than the molecular ion series. Using characteristic summations found in the monoisotopic molecular ion—1 series of peaks, each class is further resolved to provide relative abundances of three compound types: nominal (Type 0), first overlap (Type 1), and second overlap (Type 2). The aromatic fraction is obtained by liquid elution chromatography (see Test Method [D2549](#)).

NOTE 2—Monoisotopic peaks heights are obtained by correcting the polyisotopic heights for naturally occurring heavy isotopes, assuming that only ions of C_nH_{2n+2} to C_nH_{2-11} are present. This is not strictly accurate for aromatics, but the errors introduced by such assumption are trivial.

5. Significance and Use

5.1 A knowledge of the hydrocarbon composition of process streams and petroleum products boiling within the range 205 to 540°C (400 to 1000°F) is useful in following the effect of changes in process variables, diagnosing the source of plant upsets, and in evaluating the effect of changes in composition on product performance properties. This method, when used together with Test Method [D2786](#), provides a detailed analysis of the hydrocarbon composition of such materials.

6. Apparatus

6.1 *Mass Spectrometer*—The suitability of the mass spectrometer to be used with this method shall be proven by performance tests described both herein and in Practice [E137](#).

6.2 *Sample Inlet System*—Any inlet system may be used that permits the introduction of the sample without loss, contamination, or change in composition. The system must function in the range from 125 to 350°C to provide an appropriate sampling device.

6.3 *Microburet or Constant-Volume Pipet*.

6.4 *Mass Spectrum Digitizer*—It is recommended that a mass spectrum digitizer be used in obtaining the analysis,

because it is necessary to use the heights of most of the peaks in the spectrum. Any digitizing system capable of supplying accurate mass numbers and peak heights is suitable.

6.5 *Electronic Digital Computer*—The computations for this analysis are not practical without the use of a computer. Any computer capable of providing approximately 60 K bytes in core and capable of compiling programs written in FORTRAN IV should be suitable.

7. Reagent

7.1 *n-Hexadecane*. (**Warning**—Combustible-Very harmful.)

8. Calibration

8.1 Calibration equations in the computer program given in [Table 2](#) may be used directly provided the following procedures are followed:

8.1.1 *Instrumental Conditions*—Repeller settings are adjusted to maximize the m/e 226 ion of *n*-hexadecane. A magnetic field is used that will permit a scan over the mass range from 78 to 700. An ionizing voltage of 70 eV and an ionizing current in the range from 10 to 70 μ A is used.

NOTE 3—The instrument conditions and calibration equations described in this method are based on the use of a 180° magnetic-deflection type mass spectrometer (CEC Model 21-103). Satisfactory results have been obtained with some other magnetic deflection instruments. It is not known if the equations are suitable for use on all other mass spectrometer types.

8.1.2 *Computer Program*—The FORTRAN program given in [Table 2](#) contains all the equations for calculating the analysis, including those for calculating monoisotopic peak heights. The program is compiled and linked to create a computer load module that is available whenever needed. When the spectrum shown in [Table 3](#) is processed, these results should agree with those shown in [Table 4](#).

8.1.2.1 *Data Input Format*—The input format suggested in the main program may be changed to suit the needs of individual laboratories provided that true masses and peak heights are stored in the $H(M)$ array.

8.1.2.2 *FORTRAN IV Language*—Changes in the program may be required for compatibility with the particular computing system to be used. These are permitted provided that the altered program gives the results shown in [Table 4](#) with the input data of [Table 3](#).

NOTE 4—The program, as shown in [Table 2](#), has run satisfactorily on IBM System 360 computers.

9. Procedure

9.1 If the mass spectrometer has been in continuous operation, no additional preparation is necessary before analyzing samples. However, if the spectrometer has been turned on only recently, check its operation according to the manufacturer's instructions to ensure stability before proceeding.

9.2 Obtain the mass spectrum of the sample, scanning from mass 76 to the high-mass end of the spectrum.

TABLE 2 High Ionizing Voltage, Low Resolution Mass Spectrometric Analysis of Gas Oil Aromatic Fractions

* The "end statement" designated is specific for IBM computers. The user may modify the FORTRAN program to suit his individual needs.

```

C
C IN THIS PROGRAM THE VARIABLE "H(M)" REPRESENTS THE HEIGHT OF THE
C POLYISOTOPIC PEAK AT MASS M. THE VARIABLE "HDI(M)" IS THE HEIGHT
C OF THE DEISOTOPED PEAK AT MASS M.
C
C THIS IS A POSSIBLE MAIN PROGRAM THAT READS INPUT DATA AND CALLS FIRST
C THE DEISOTOPING ROUTINE "SUBROUTINE DEISO" AND THEN THE
C CALCULATING AND REPORTING ROUTINE "SUBROUTINE AROMTC".
C
C      COMMON TITLE(20), H(758), HDI(758)
C      DIMENSION MASS(8), HITE(8)
C      1 READ(5,10,END=99)(TITLE(I),I=1,20)
C      10 FORMAT(20A4)
C
C A TITLE CARD FOR SAMPLE NAME, ETC. PRECEDES SPECTRAL DATA CARDS.
C FORMAT FOR TITLE IS 20A4 (20 4-CHARACTER WORDS IN 80 COLUMNS).
C FORMAT FOR SPECTRAL DATA IS MASS (I6) FOLLOWED BY HEIGHT (F4.0)
C WITH 8 PEAKS PER 80-COLUMN CARD.
C
C      DO 20 I=12,758
C      H(I) = 0.0
C      20 HDI(I) = 0.0
C      30 READ(5,40)(MASS(I),HITE(I),I=1,8)
C      40 FORMAT(8(I6,F4.0))
C      DO 50 I=1,8
C      IF(MASS(I).EQ.999999)GO TO 60
C
C ENTER "999999" IN A MASS POSITION ON A CARD TO DENOTE SPECTRUM END.
C
C      IF(MASS(I).EQ.0)GO TO 50
C      M = MASS(I)
C      H(M) = HITE(I)
C      50 CONTINUE
C      GO TO 30
C      60 CALL DEISO
C      CALL AROMTC
C      GO TO 1
C
C "GO TO 1" ALLOWS SUCCESSIVE SAMPLES TO BE COMPUTED BEFORE RELEASING
C COMPUTER.
C
C 99 STOP
C      END
C
C      SURROUTINE DEISO
C
C THIS SUBROUTINE COMPUTES MONOISOTOPIC PEAKS ASSUMING ALL IONS HAVE
C Z NUMBERS FROM +2 TO -11 IN THE FORMULA C(N)H(2N + Z).
C
C      COMMON TITLE(20), H(758), HDI(758)
C      DIMENSION NCARB(758), NHYD(758)
C      DO 10 I=12,758
C      NCARB(I) = 0
C      10 NHYD(I) = 0
C      DO 20 K=12,758
C      NCARB(K) = (K + 11)/14
C      NHYD(K) = K - 12*NCARB(K)
C      IF(NHYD(K).LT.0)NHYD(K) = 0
C      20 CONTINUE
C      DO 30 K=14,758
C      HDI(K) = H(K)-HDI(K-1)*(.010811*FLOAT(NCARB(K-1))+.00015*FLOAT
C      1(NHYD(K-1)))
C      HDI(K) = HDI(K)+HDI(K-2)*(.00005844*FLOAT(NCARB(K-2)*(1-NCARB(K-2)
C      1))+.1125E-7*FLOAT(NHYD(K-2)*(1-NHYD(K-2)))-.162165E-5*FLOAT(NCARB(
C      2K-2)*NHYD(K-2)))
C      IF(HDI(K).LT.0.0)HDI(K) = 0.0
C      30 CONTINUE
C      RETURN
C      END

```