



## Standard Test Method for Aromatic Types Analysis of Gas-Oil Aromatic Fractions by High Ionizing Voltage Mass Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D 3239; 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 method<sup>2</sup> 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 *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.*

1.3 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.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 2549 Test Method for Separation of Representative Aromatics and Nonaromatics Fractions of High-Boiling Oils by Elution Chromatography<sup>3</sup>

D 2786 Test Method for Hydrocarbon Types Analysis of Gas-Oil Saturate Fractions by High Ionizing Voltage Mass Spectrometry<sup>4</sup>

E 137 Practice for Evaluation of Mass Spectrometers for Quantitative Analysis from a Batch Inlet<sup>5</sup>

### 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:

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

##### 3.1.3 Class II:

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

##### 3.1.4 Class III:

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

##### 3.1.5 Class IV:

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

##### 3.1.6 Class V:

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

##### 3.1.7 Class VI:

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

##### 3.1.8 Class VII:

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

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 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

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

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>5</sup> Discontinued—See 1992 *Annual Book of ASTM Standards*, Vol 05.03.

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,<br>$C_nH_{2n-20}$                            |
| 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,<br>$C_nH_{2n-14}$ 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                                                         |

obtained by liquid elution chromatography (see Test Method D 2549).

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  $C_nH_{2n-11}$  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 D 2786, 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 E 137.

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

NOTE 3—**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  $\mu$ A is used.

NOTE 4—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, the results should agree with those shown in Table 4.

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   SUBROUTINE 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

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TABLE 2 *Continued*

```

SUBROUTINE AROMTC
C
C THIS ROUTINE GIVES THE ANALYSIS OF AROMATICS FRACTIONS FROM PETROLEUM
C USING THE PROCEDURE DESCRIBED IN ANAL CHEM 41, 1548-54 (1969)
C
COMMON TITLE(20), H(758), HDI(758)
DIMENSION AIN(7,7), RA(7), BB(7), SR(758)
DATA AIN /+1.8094,-.1952,+.0124,-.0027,-.0015,-.0011,-.0028,
2      -.1601,+2.0479,-.2806,-.0401,+.0082,+.0012,+.0000,
3      -.0943,-.2287,+2.3024,-.4936,-.0601,-.0155,-.0089,
4      -.0292,+.0033,-.0580,+1.9404,-.1337,-.0117,-.0043,
5      -.0022,-.0003,-.0026,-.0195,+1.9773,-.1823,+.0123,
6      -.0420,+.0026,-.0018,-.0151,-.0584,+2.0616,-.4193,
7      -.2346,-.1069,-.0267,-.0019,-.0057,-.0904,+1.9904/
C
C INITIALIZE SQUARE ROOT ARRAY
C
DO 2132 I=12,750
2132 SR(I) = 0.0
C
C ASSEMBLE APPROPRIATE PEAKS IN MASS SPECTRUM OF AROMATIC FRACTION
C FOR PROCESSING IN A 7 X 7 MATRIX. QUANTITIES A6,A7,A8,ETC. REFER
C INITIALLY TO SUMS OF PEAKS AT Z NUMBERS 6,7,8,ETC. A6,A8,ETC. ARE
C LATER REDEFINED TO INCLUDE THE ODD Z-NUMBER SUM CORRESPONDING TO
C THE PARENT-1 SERIES (A6 = A6 + A7, A8 = A8 + A9, ETC.)
C
A6 = 0.0
DO 2106 M=78,750,14
2106 A6 = A6 + H(M)
A7 = 0.0
DO 2107 M=91,750,14
2107 A7 = A7 + HDI(M)
A6 = A6 + A7
A8 = 0.0
DO 2108 M=104,750,14
2108 A8 = A8 + H(M)
A9 = 0.0
DO 2109 M=117,750,14
2109 A9 = A9 + HDI(M)
A8 = A8 + A9
A10 = 0.0
DO 2110 M=130,750,14
2110 A10 = A10 + H(M)
A11 = 0.0
DO 2111 M=129,750,14
2111 A11 = A11 + HDI(M)
A10 = A10 + A11
A12 = 0.0
DO 2112 M=128,750,14
2112 A12 = A12 + H(M)
A13 = 0.0
DO 2113 M=141,750,14
2113 A13 = A13 + HDI(M)
A12 = A12 + A13
A14 = 0.0
DO 2114 M=154,750,14
2114 A14 = A14 + H(M)
A15 = 0.0
DO 2115 M=167,750,14
2115 A15 = A15 + HDI(M)
A14 = A14 + A15
A16 = 0.0
DO 2116 M=166,750,14
2116 A16 = A16 + H(M)
A17 = 0.0
DO 2117 M=179,750,14
2117 A17 = A17 + HDI(M)
A16 = A16 + A17
A18 = 0.0
DO 2118 M=178,750,14
2118 A18 = A18 + H(M)
A19 = 0.0
DO 2119 M=191,750,14

```

TABLE 2 *Continued*

```

2119 A19 = A19 + HDI(M)
      A18 = A18+ A19
C
C   CORRECT THE PEAK SUMS FOR THE PRESENCE OF IRRELEVANT IONS AT
C   MASSES 175,176,189,190,200,213
C
      CDI175 =HDI(161)-(HDI(161)-HDI(203))/3.0
      IF(HDI(175).GE.CDI175) GO TO 1046
      CDI175 = HDI(175)
C
C   ABOVE STATEMENTS CORRECT HDI(175)
C   NEXT STATEMENTS CORRECT H(176)
C
1046 CH176 = H(162)-(H(162)-H(204))/3.0
      IF(H(176).GE.CH176)GO TO 1048
      CH176 = H(176)
C
C   NEXT STATEMENTS CORRECT HDI(189)
C
1048 CDI189 = CDI175 - (CDI175-HDI(203))/2.0
      IF(HDI(189).GE.CDI189)GO TO 1049
      CDI189 = HDI(189)
C
C   NEXT STATEMENTS CORRECT H(190)
C
1049 CH190 = CH176-(CH176-H(204))/2.0
      IF(H(190).GE.CH190) GO TO 2101
      CH190 = H(190)
C
C   NEXT STATEMENTS CORRECT H(200)
C
2101 CH200 =(H(186)+H(214))/2.0
      IF(H(200).GE.CH200) GO TO 2102
      CH200 = H(200)
C
C   NEXT STATEMENTS CORRECT HDI(213)
C
2102 CDI213 =(HDI(199)+HDI(227))/2.0
      IF(HDI(213).GE.CDI213) GO TO 2103
      CDI213 = HDI(213)
C
C   NEXT STATEMENTS CORRECT THE A6,A8,ETC. SUMS
C
2103 A6 =A6-(HDI(175)+HDI(189) +H(176)+H(190))
      1 +CDI175 +CDI189+ CH176+ CH190
      A10 = A10-(H(200)+HDI(213))+CH200+CDI213
C
C   REDEFINE A6,A8,ETC. AS SUBSCRIPTED VARIABLE AND MULTIPLY BY THE
C   AROMATICS INVERSE AIN(I,J)
C
      RA(1) = A6
      RA(2) = A8
      RA(3) = A10
      RA(4) = A12
      RA(5) = A14
      RA(6) = A16
      RA(7) = A18
      DO 2125 J=1,7
        RB(J)=0.0
      DO 2124 I=1,7
2124 RB(J)=RB(J)+BA(I)*AIN(J,I)
2125 CONTINUE
      DO 2127 J=1,7
        IF(RB(J))2126,2127,2127
2126 RB(J)=0.0
2127 CONTINUE
      AA6 = RB(1)
      AA8 = RB(2)
      AA10 = RB(3)
      AA12 = RB(4)
      AA14 = RB(5)
      AA16 = RB(6)
      AA18 = RB(7)
      SUMAA = 0.0
      DO 2128 J=1,7

```