



Designation: ~~D2650-04~~ Designation: D2650 - 10

## Standard Test Method for Chemical Composition of Gases ~~By~~ Mass Spectrometry<sup>1</sup>

This standard is issued under the fixed designation D2650; 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.

### 1. Scope\*

1.1 This test method covers the quantitative analysis of gases containing specific combinations of the following components: hydrogen; hydrocarbons with up to six carbon atoms per molecule; carbon monoxide; carbon dioxide; mercaptans with one or two carbon atoms per molecule; hydrogen sulfide; and air (nitrogen, oxygen, and argon). This test method cannot be used for the determination of constituents present in amounts less than 0.1 mole %. Dimethylbutanes are assumed absent unless specifically sought.

NOTE 1—Although experimental procedures described herein are uniform, calculation procedures vary with application. The following influences guide the selection of a particular calculation: qualitative mixture composition; minimum error due to components presumed absent; minimum cross interference between known components; maximum sensitivity to known components; low frequency and complexity of calibration; and type of computing machinery.

Because of these influences, a tabulation of calculation procedures recommended for stated applications is presented in Section 12 (Table 1).

NOTE 2—This test method was developed on Consolidated Electrodynamics Corporation Type 103 Mass Spectrometers. Users of other instruments may have to modify operating parameters and the calibration procedure.

1.2

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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*:<sup>2</sup>

D1137 Method for Analysis of Natural Gas and Related Types of Gaseous Mixtures by the Mass Spectrometer<sup>3</sup> ~~D1145~~ Test

Method  
for  
Sam-  
pling  
Natu-  
ral  
Gas<sup>3</sup>

ASTM D2650-10

<https://standards.iteh.ai/catalog/standards/sist/3a0ea9a9-1601-4921-898a-48085dce6997/astm-d2650-10>

D1247 Method of Sampling Manufactured Gas<sup>3</sup>

D1265 Practice for Sampling Liquefied Petroleum (LP) Gases, Manual Method

D1302 Method for Analysis of Carbureted Water Gas by the Mass Spectrometer<sup>3</sup>

2.2 *American Petroleum Institute Standards*:<sup>4</sup>

MPMS 14.1 Collecting and Handling of Natural Gas Samples for Custody Transfer

2.3 *Gas Producers Association Standards*:<sup>5</sup>

GPA 2166 Obtaining Natural Gas Samples for Analysis by Gas Chromatography

<sup>1</sup> 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 Hydrocarbon Analysis—Mass Spectroscopy.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Withdrawn. The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>4</sup> Crout, P. D., "A Short Method for Evaluating Determinants and Solving Systems of Linear Equations with Real or Complex Coefficients," *Marchant Calculating Machine Co., Bulletins MM-182 and 183*, ASTBA, September 1941. Dwyer, P. S., *Psychometria*, Vol 6, 1941, p. 101. Hotelling, H., *Am. Math. Stat.*, Vol 14, 1943, p. 1.

<sup>5</sup> Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, <http://www.api.org>.

<sup>6</sup> "Triangular Inverse Method," *Analytical Chemistry*, Vol 30, 1959, p. 877.

<sup>7</sup> Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145, [www.gpaglobal.org](http://www.gpaglobal.org).

\*A Summary of Changes section appears at the end of this standard.

**TABLE 1 Calculation Procedures for Mass Spectrometer Gas Analysis**

NOTE—Coding of calculation procedures is as follows:

O = Order peaks are used in the calculation expressed serially from 1 to *n*, *n* being the total number of components.

P = *m/e* of peak used and prefix, *M*, if monoisotopic.

M = Method of computation

U = Unicomponent Peak Method

*M<sub>a</sub>* = Simultaneous equations where “*a*” identifies the particular set of equations if more than one is used.

C = Chemically removed.

Residual = *m/e* of peak suitable as an independent check on the method.

Serial No. . . . .	1			2			3			4			5			6		
Name or Application	D1137 <sup>A</sup> Natural Gas			D1302 <sup>B</sup> Carbureted Water Gas			H <sub>2</sub> -C <sub>6</sub>			Reformer Gas			C <sub>3</sub> ,C <sub>4</sub>			<i>i</i> C <sub>4</sub>		
Component	O	P	M	O	P	M	O <sup>C</sup>	P <sup>C</sup>	M	O	P	M	O <sup>C</sup>	P <sup>C</sup>	M	O	P	M
Hydrogen	...	...	...	6	2	M	16	2	U	17	2	M	0	...	...	...	...	...
Methane	15	16	U	7	15/16	M	15	16	U	16	16	M	0	...	...	...	...	...
Ethylene	13	27	M2	12	27	M	13	26	U	15	26	M	0	...	...	...	...	...
Ethane	12	30	M2	8	30	M	12	30	U	13	30	M	0	...	...	...	...	...
Propene	10	42	M2	11	42	M	8	42	M2	12	42	M	6	42	M	...	...	M
Propane	9	29	M2	9	29	M	3	44	M1	14	29	M	9	29	M	3	29	M
Butadiene	...	...	...	9	...	...	3	...	...	10	54	M	9	...	M	...	...	M
Butene-1	8	56	M2	5	56	U	9	41	M2	8	56	M	8	41	M	...	...	M
Butene-2	8	56	M2	5	56	U	10	55	M2	8	56	M	4	56	M	...	...	M
Isobutene	8	56	M2	5	56	U	11	56	M2	8	56	M	5	39	M	...	...	M
Isobutane	7	43	M2	5	...	...	4	M43	M1	11	43	M	7	43	M	2	43	M
<i>n</i> -Butane	6	58	M2	4	58	U	5	58	M1	6	58	M	2	58	M	1	58	M
Pentenes	...	...	...	3	70	U	2	70	U	9	55	M	3	70	M	...	...	M
Isopentane	...	...	...	3	...	...	6	M57	M1	7	57	M	1	72	M	...	...	...
<i>n</i> -Pentane	4	72	M2	2	72	U	7	72	M2	5	72	M	...	...	...	...	...	...
Benzene	...	...	...	2	...	...	7	...	...	4	78	M	...	...	...	...	...	...
Hexanes	...	...	...	2	...	...	7	...	...	...	...	M	...	...	...	...	...	...
C <sub>6</sub> cyclic paraffins	...	...	...	2	...	...	7	...	...	3	84	M	...	...	...	...	...	...
Hexanes	5	57	M2	2	...	...	1	71	U	2	86	M	...	...	...	...	...	...
Toluene	...	...	...	2	...	...	1	...	...	1	92	M	...	...	...	...	...	...
Hydrogen sulfide	2	34	M1	2	...	...	1	...	...	21	34	M	...	...	...	...	...	...
Carbon dioxide	11	44	M2	10	44	M	1	...	C	20	44	M	...	...	...	...	...	...
Carbon monoxide	...	...	...	13	12	M	1	...	C	18	28	M	...	...	...	...	...	...
Nitrogen	14	28	M2	14	14	M	14	28	U	19	14	M	...	...	...	...	...	...
Air	3	32	M1	1	32	U	14	...	...	22	32	M	1	32	U	...	...	...
Helium	1	4	U	1	...	...	14	...	...	<sup>D</sup>	<sup>D</sup>	...	...	...	...	...	...	...

Serial No. . . . .	7			8			9			10			11			12			13		
Name or Application	Commercial Propane			Commercial Butane			BB Stream (Cracked Butanes)			Dry Gas Cracked Fuel Gas			Mixed Iso and Normal Butanes			Reformer Make-Up Gas			Unstabi- lized Fuel Gas		
Component	O	P	M	O	P	M	O <sup>C</sup>	P <sup>C</sup>	M	O	P	M	O	P	M	O	P	M	O <sup>C</sup>	P <sup>C</sup>	M
Hydrogen	...	...	...	...	...	...	...	...	...	15	2	M	...	...	...	10	2	M	16	2	M
Methane	...	...	...	...	...	...	...	...	...	14	16	M	...	...	...	9	16	M	15	16	M
Ethylene <sup>F</sup>	7	26	M	...	...	...	...	...	...	12	26	M	...	...	...	...	...	...	13	26	M
Ethane	6	30	M	...	...	...	...	...	...	11	30	M	...	...	...	7	30	M	12	30	M
Propene	5	42	M	7	42	M	6	42	M	10	42	M	...	...	...	...	...	...	8	42	M
Propane	3	44	M	4	44	M	4	44	M	7	44	M	3	44	M	5	44	M	6	44	M
Butadiene	...	...	...	...	...	...	1	54	M	3	54	M	...	...	...	...	...	...	2	54	M
Butene-1	1	56	M	1	56	M	7	41	M	1	...	...	...	...	...	...	...	...	9	41	M
Butene-2	1	56	M	1	56	M	8	56	M	1	56	M	...	...	...	...	...	...	10	56	M
Isobutene	1 <sup>F</sup>	<sup>F</sup>	M	1	<sup>F</sup>	<sup>F</sup>	9	39	M	1	<sup>F</sup>	...	4	43	M	...	...	...	11	39	M
Isobutane	4	43	M	5	43	M	5	43	M	8	43	M	1	58	M	6	43	M	7	43	M
<i>n</i> -Butane	2	58	M	2	58	M	2	58	M	4	58	M	...	...	...	2	58	M	3	58	M
Pentenes	...	...	...	6	70	M	<sup>G</sup>	70	U	9	70	M	...	...	...	3	57	M	...	70	U
Isopentane	...	...	...	3	57	M	3	57	M	5	57	M	2	57	M	4	72	M	4	57	M
<i>n</i> -Pentane	...	...	...	...	...	...	...	...	...	6	72	M	...	...	...	...	...	...	5	72	M
Benzene	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	<sup>H</sup>	<sup>H</sup>	D
Hexanes	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	<sup>H</sup>	<sup>H</sup>	D
C <sub>6</sub> cyclic paraffins	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	<sup>H</sup>	<sup>H</sup>	D
Hexanes	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	<sup>H</sup>	<sup>H</sup>	D
Toluene	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	<sup>H</sup>	<sup>H</sup>	D
Hydrogen sulfide	...	...	...	...	...	...	...	...	...	<sup>I</sup>	...	C	...	...	...	<sup>I</sup>	<sup>I</sup>	C	<sup>I</sup>	<sup>I</sup>	C
Carbon dioxide	...	...	...	...	...	...	...	...	...	<sup>I</sup>	...	C	...	...	...	<sup>I</sup>	<sup>I</sup>	C	<sup>I</sup>	<sup>I</sup>	C
Carbon monoxide	...	...	...	...	...	...	...	...	...	13	28	M	...	...	...	8	28	M	14	28	M
Nitrogen	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Air	...	...	...	...	...	...	...	...	...	2	32	M	...	...	...	1	32	M	1	32	M

**TABLE 1** *Continued*

Serial No. . . . .	7			8			9			10			11			12			13		
Name or Application	Commercial Propane			Commercial Butane			BB Stream (Cracked Butanes)			Dry Gas Cracked Fuel Gas			Mixed Iso and Normal Butanes			Reformer Make-Up Gas			Unstabilized Fuel Gas		
Acid Gases	...	...	...	...	...	...	...	...	...	/	...	C	...	...	...	/	/	C	/	/	C
Residual <sup>E</sup>	8	27	M	8	27	M	10	27	M	16	14	M	5	27	M	11	14	M	17	14	M
Residual <sup>E</sup>	9	29	M	9	29	M	11	29	M	17	15	M	6	29	M	12	15	M	18	15	M
Residual <sup>E</sup>	...	...	...	...	...	...	...	...	...	18	27	M	...	...	...	13	27	M	19	27	M
Residual <sup>E</sup>	...	...	...	...	...	...	...	...	...	19	29	M	...	...	...	14	29	M	20	29	M

  

Serial No. . . . .	14						15						16					
Name or Application	H <sub>2</sub> -C <sub>6</sub> Cracked Gas						H <sub>2</sub> -C <sub>6</sub> Straight Run Gas						Light Refinery Gas					
Component	O	P	M	O	P	M	O	P	M	O	P	M	O	P	M			
Hydrogen	1	2	M	1	2	M	20	2	U									
Methane	2	16	M	2	16	M	17	16	M									
Ethylene	4	26	M	...	...	...	14	26	M									
Ethane	7	30	M	5	30	M	13	30	M									
Propene	11	42	M	...	...	...	12	42	M									
Propane	6	29	M	4	29	M	10	29	M									
Butadiene	15	54	M	...	...	...	...	...	...									
Butane-1	...	...	...	...	...	...	11	56	M									
Butene-2	16	56	M	...	...	...	...	...	...									
Isobutene	...	...	...	...	...	...	...	...	...									
Isobutane	12	43	M	9	43	M	9	43	M									
n-Butane	18	58	M	14	58	M	8	58	M									
Pentenes	21	70	M	...	...	...	15	70	M									
Isopentane	17	57	M	13	57	M	7	57	M									
n-Pentane	22	72	M	18	72	M	6	72	M									
Benzene	...	...	...	19	78	M	5	78	U									
Hexanes	23	84	M	...	...	...	4	84	U									
C <sub>6</sub> cyclic paraffins	...	...	...	20	84	M	...	...	...									
Hexanes	...	...	...	17	71	M	3	86	U									
Toluene	...	...	...	21	92	M	...	...	...									
Hydrogen sulfide	9	34	M	7	34	M	1	34	U									
Carbon dioxide	13	44	M	10	44	M	16	44	U									
Carbon monoxide	...	...	...	...	...	...	18	12	U									
Nitrogen	5	28	M	...	...	...	19	28	U									
Air	8	32	M	6	32	M	2	32	U									
Water	3	18	M	3	18	M	...	...	...									
Cyclobutane	...	...	...	12	56	M	...	...	...									
Cyclopentene	20	67	M	...	...	...	...	...	...									
Pentadienes	20	67	M	...	...	...	...	...	...									
Cyclopentane	...	...	...	16	70	M	...	...	...									
Methylmercaptan	14	48	M	11	48	M	...	...	...									
Ethylmercaptan	19	62	M	15	62	M	...	...	...									
Residual 41	10	41	M	8	41	M	...	...	...									
Residual 14	24	14	M	22	14	M	...	...	...									

<sup>A</sup> Method D1137.

<sup>B</sup> Method D1302.

<sup>C</sup> The mass spectrometer analysis for isomeric butenes is far less accurate than for the other hydrocarbon components. The inaccuracies involved in the isomeric butene analysis by mass spectrometer range from 1.0 to 4.0 mole %, depending upon the concentration, ranges, and extent of drifts in instrument calibrations. These inaccuracies will range still higher when pentenes are present in larger than 0.5 % concentrations. See *Analytical Chemistry*, Vol 22, 1950, p. 991; *Ibid*, Vol 21, 1949, p. 547; and *Ibid*, Vol 21, 1949, p. 572.

<sup>D</sup> In Method 4, butylenes and pentenes spectra are composites based on typical GLC analyses. Hexene and hexane spectra are from appropriately corrected spectra of representative fractions.

<sup>E</sup> Residuals Groups A: *m/e* 72, 58, 57, 44, 43; Group B: *m/e* 56, 42, 30, 29, 14. All Group A residual shall be 0.2 division or less with the residual of the largest peak also being less than 0.3 % of its total peak height. All Group B residuals shall be less than 1 % of the peak height or 0.2 division, whichever is greater.

<sup>F</sup> Butenes are grouped if they are less than 5 %.

<sup>G</sup> If pentenes exceed 1 %, they are determined by other means and the spectrum removed from the poly spectrum.

<sup>H</sup> Removed from sample by distillation.

<sup>I</sup> Chemically removed.

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *base peak of a compound*—the peak used as 100 % in computing the cracking pattern coefficient.

3.1.2 *cracked gases*—hydrocarbon gases that contain unsaturates.

3.1.3 *cracking pattern coefficient*—the ratio of a peak at any *m/e* relative to its parent peak (or in some cases its base peak).

3.1.4 *GLC*—a gas-liquid chromatographic column that is capable of separating the isomers of butenes, pentenes, hexanes, and hexenes.

3.1.5 *IR*—infrared equipment capable of analyzing gases for the butene isomers.

3.1.6 *mass number or m/e value of an ion*—the quotient of the mass of that ion (given in atomic mass units) and its positive charge (number of electrons lost during ionization).

3.1.7 *parent peak of a compound*—the peak at which the *m/e* is equal to the sum of the atomic mass values for that compound. This peak is sometimes used as 100 % in computing the cracking pattern coefficients.

3.1.8 *partial pressure*—the pressure of any component in the inlet system before opening the expansion bottle to leak.

3.1.9 *sensitivity*—the height of any peak in the spectrum of the pure compound divided by the pressure prevailing in the inlet system of the mass spectrometer immediately before opening the expansion bottle to leak.

3.1.10 *straight-run gases*—hydrocarbon gases that do not contain unsaturates.

#### 4. Summary of Test Method

4.1 The molecular species which make up a gaseous mixture are dissociated and ionized by electron bombardment. The positive ions of the different masses thus formed are accelerated in an electrostatic field and separated in a magnetic field. The abundance of each mass present is recorded. The mixture spectrum obtained is resolved into individual constituents by means of simultaneous equations derived from the mass spectra of the pure compounds.

#### 5. Significance and Use

5.1 A knowledge of the composition of refinery gases is useful in diagnosing the source of plant upsets, in determining the suitability of certain gas streams for use as fuel, or as feedstocks for polymerization and alkylation, and for monitoring the quality of commercial gases.

#### 6. Interferences

6.1 In setting up an analysis, it is possible that a constituent was ignored. Also, an impure calibration may have been used. The spectrum calculated from the composition found is to, therefore, be compared with the observed spectrum of the mixture at masses independent of the original calculation. Differences so computed, called residuals, should as a general rule be less than 1 % of the original mixture peak for an acceptable analysis. Masses suitable for this calculation are tabulated with each calculation procedure.

NOTE 3—Another strategy employed to reduce interferences and increase accuracy consists of using spectra which have been corrected for contributions caused by the rare isotopes of carbon and hydrogen.

#### 7. Apparatus

7.1 *Mass Spectrometer*—Any mass spectrometer can be used with this test method that shall be proven by performance tests described herein.

#### 8. Reference Standards

8.1 The mass spectrometer must be calibrated with each of the components constituting the unknown mixture to be analyzed. The calibrating compounds must be of high purity. Research grade calibrants are readily available from a number of sources. In general, the mass spectrometer is capable of detecting impurities in calibrants and the contribution of such impurities to the calibration spectrum can be removed.

NOTE 4—Some of the calculation procedures require the use of combined spectra, for example, air and butylenes. Three frequently used possibilities for producing combined spectra are as follows:

- (1) Representative fraction from a specific source,
- (2) Multiplication factors to convert the spectrum of a pure constituent to a simulated spectrum of the mixture, and
- (3) Proportionality factors for combining actual calibrations.

A recommended concentration limit for combined mixtures is given. At the level recommended, the residual spectrum contribute less than 0.1 % error in any one result when the concentration of any constituent in the combined mixture is doubled.

#### 9. Sampling

9.1 Samples shall be collected by methods known to provide a representative mixture of the material to be analyzed. Samples can be collected in accordance with Test Method D1145 or Method D1247 or Practice, Practice D1265, API MPMS 14.1, or GPA 2166.

#### 10. Calibration and Standardization

10.1 *Apparatus*—Determine whether operating conditions remain normal by making certain tests periodically, following instructions furnished by the manufacturer of the apparatus. Include in these tests rate of leak, ion-beam control settings, pattern reproducibility, and galvanometer calibrations.

10.1.1 To ascertain pattern stability, the following schedule is provided both for laboratories that have mass spectrometers with conventional temperature control and for laboratories that vary the temperature of the ionization chamber to obtain constant patterns:

Run Number	Compound
1	<i>n</i> -butane