

Designation: D2650 - 04

# 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  $(\varepsilon)$  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 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 Gases and Related Types of Gaseous Mixtures by the Mass Spectrometer <sup>3</sup>

D1145 Test Method for Sampling Natural Gas<sup>3</sup>

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>

### 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.

<sup>&</sup>lt;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 on Hydrocarbon Analysis.

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<sup>&</sup>lt;sup>2</sup> 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.

<sup>&</sup>lt;sup>3</sup> Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

#### 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

 $M_a$  = 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	N	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>			iC <sub>4</sub>		
Component	0	Р	М	0	Р	М	0 <sup>c</sup>	$P^{\mathcal{C}}$	М	0	Р	М	0 <sup>c</sup>	$P^{\mathcal{C}}$	М	0	Р	М	
Hydrogen				6	2	М	16	2	U	17	2	М	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	
n-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		h \	7	m	o r	4	78	M							
Hexanes				2		11 h	7		rait	AT P		M							
C <sub>6</sub> cyclic paraffins				2			7			3	84	M							
Hexanes	5	57	M2	2	• .!. /	040	111	71	U	2	86	M							
Toluene				2	• [] i	عيا 3	1	القا	ri 2	-1	92	M							
Hydrogen sulfide	2	34	M1	2			1			21	34	М							
Carbon dioxide	11	44	M2	10	44	M	1	4D	- C	20	44	М							
Carbon monoxide				13	12	M			C	18	28	M							
Nitrogen	14	28	M2	14	14	М	14	28	U	19	14	M							
Air	3	32	M1	1	32	U	14			22	32	М	1	32	U				
Helium	1	4	U	1		A for	14	0 6 7	0.77	D	D								

Name or Application		ommero Propan			mmerc Butane		(	3 Strea Cracke Butanes	d	(	Ory Gas Cracked uel Ga	d	ar	Mixed Is nd Norn Butane	nal		Reforme Make-U Gas			Jnstabi zed Fu Gas	
Component	0	Р	М	0	Р	M	0 <sup>c</sup>	P <sup>C</sup>	М	0	Р	М	0	Р	М	0	Р	М	0°	$P^{\mathcal{C}}$	М
Hydrogen										15	2	М				10	2	М	16	2	М
Methane										14	16	M				9	16	M	15	16	M
Ethylene <sup>E</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	М
Butene-2	1	56	M	1	56	M	8	56	M	1	56	M							10	56	М
Isobutene	1 <sup>F</sup>	F	M	1	F	F	9	39	M	1	F		4	43	M				11	39	М
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	G	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																			Н	Н	D
Hexanes																			Н	Н	D
C <sub>6</sub> cyclic paraffins																			Н	Н	D
Hexanes																			Н	Н	D
Toluene																			Н	Н	D
Hydrogen sulfide										1		С				1	1	С	1	1	С
Carbon dioxide										1		С				1	1	С	1	1	С
Carbon monoxide										13	28	M				8	28	M	14	28	M
Nitrogen																					
Air										2	32	M				1	32	M	1	32	М

TABLE 1 Continued

Serial No		7			8			9			10			11			12			13	
Name or Application		ommero Propan			ommero Butane		(	3 Strea Cracke Butanes	ed	(	Dry Ga Cracke uel Ga	d	ar	Mixed Is nd Norn Butane	nal	-	Reforme Make-U Gas			Jnstabi zed Fu Gas	
Acid Gases										1		С				1	1	С	1	1	С
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	М				14	29	М	20	29	М

Serial No.	4.4	45	10

Ochar IVO		1-7			10			10			
Name or Application	Н	<sub>2</sub> -C <sub>6</sub> Cracked Ga	as	H <sub>2</sub> -C	Straight Run	Gas	Light Refinery Gas				
Component	0	Р	М	0	Р	М	0	Р	М		
Hydrogen	1	2	М	1	2	М	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		
<i>n</i> -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		
<i>n</i> -Pentane	22	72	M	18	72	M	6	72	M		
Benzene				19	78	M	5	78	U		
Hexanes	23	84	M	tond	0 140 0		4	84	U		
C <sub>6</sub> cyclic paraffins		👢	TCII	20	84	M					
Hexanes				17	71	M	3	86	U		
Toluene		h 44 a	· //mto	21	92	M M					
Hydrogen sulfide	9	34	M /	JU (7 d.)	34	T M	1	34	U		
Carbon dioxide	13	44	M	10	44	M	16	44	U		
Carbon monoxide				4 T			18	12	U		
Nitrogen	5	28	M	eni P			19	28	U		
Air	8	32	M	6	32	М	2	32	U		
Water	3	18	M	3	18	M					
Cyclobutane				12	56	M					
Cyclopentene	20	67	MAST	M D2650-0	)4						
Pentadienes	20	67	M		2 1 2			***			
Cyclopentane and ards	.ıteh.ai/cat	alog/standai	rds/sist/b40	5tc2316-ab7	)-43 <sub>0</sub> e-a2	2e4-3 <b>m</b> b13	3ec260e/a	stm-d2650:	-04		
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>&</sup>lt;sup>A</sup> Method D1137.

## 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

<sup>&</sup>lt;sup>B</sup> Method D1302.

<sup>&</sup>lt;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>&</sup>lt;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.

E 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.

F Butenes are grouped if they are less than 5 %.

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

<sup>&</sup>lt;sup>H</sup> Removed from sample by distillation.

Chemically removed.