



Standard Test Method for Chemical Composition of Gases By Mass Spectrometry¹

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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 Electro-dynamics 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 problems, 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.* For a specific precautionary statement, see Note 5.

2. Referenced Documents

2.1 ASTM Standards:

- D 1137 Method for Analysis of Natural Gases and Related Types of Gaseous Mixtures by the Mass Spectrometer²
- D 1145 Method of Sampling Natural Gas³
- D 1247 Method of Sampling Manufactured Gas³

¹ 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 Analyses.

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² Discontinued; see 1980 Annual Book of ASTM Standards, Part 26.

³ Discontinued; see 1986 Annual Book of ASTM Standards, Vol 05.05.

D 1265 Practice for Sampling Liquefied Petroleum (LP) Gases (Manual Method)⁴

D 1302 Method for Analysis of Carbureted Water Gas by the Mass Spectrometer⁵

3. Terminology

3.1 Definitions:

3.1.1 *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).

3.1.2 *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.

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

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

3.1.5 *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.

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

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

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

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

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

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

⁴ Annual Book of ASTM Standards, Vol 05.01.

⁵ Discontinued; see 1968 Annual Book of ASTM Standards, Part 19.

TABLE 1 Calculation Procedures for Mass Spectrometer Gas Analysis

NOTE 1—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	D 1137 ^A Natural Gas			D 1302 ^B Carbureted Water Gas			H ₂ -C ₆			Reformer Gas			C ₃ ,C ₄			iC ₄		
Component	O	P	M	O	P	M	O ^C	P ^C	M	O	P	M	O ^C	P ^C	M	O	P	M
Hydrogen	6	2	M	16	2	U	17	2	M	0
Methane	15	16	U	7	15 ^{1/6}	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
n-Pentane	4	72	M2	2	72	U	7	72	M2	5	72	M
Benzene	2	7	4	78	M
Hexanes	2	7	M
C ₆ 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

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 ^C	P ^C	M	O	P	M	O	P	M	O	P	M	O ^C	P ^C	M
Hydrogen	15	2	M	10	2	M	16	2	M
Methane	14	16	M	9	16	M	15	16	M
Ethylene ^E	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 ^F	^F	M	1	^F	^F	9	39	M	1	^F	...	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
n-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
n-Pentane	6	72	M	5	72	M
Benzene	H	H	D
Hexanes	H	H	D
C ₆ cyclic paraffins	H	H	D
Hexanes	H	H	D
Toluene	H	H	D
Hydrogen sulfide	/	...	C	/	/	C	/	/	C
Carbon dioxide	/	...	C	/	/	C	/	/	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 ^E	8	27	M	8	27	M	10	27	M	16	14	M	5	27	M	11	14	M	17	14	M
Residual ^E	9	29	M	9	29	M	11	29	M	17	15	M	6	29	M	12	15	M	18	15	M
Residual ^E	18	27	M	13	27	M	19	27	M
Residual ^E	19	29	M	14	29	M	20	29	M
Serial No.	14						15						16								
Name or Application	H ₂ -C ₆ Cracked Gas						H ₂ -C ₆ Straight Run Gas						Light Refinery Gas								
Component	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 ₆ 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				

^A Method D 1137.

^B Method D 1302.

^C 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.

^D 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 %.

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

^H Removed from sample by distillation.

^I Chemically removed.

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