Designation: D2650 − 10 (Reapproved 2015)

Standard Test Method for Chemical Composition of Gases by Mass Spectrometry[1]

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 (ε) 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 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:*[2]

D1137 Method for Analysis of Natural Gases and Related Types of Gaseous Mixtures by the Mass Spectrometer (Withdrawn 1981)[3]

D1247 Test Method for Sampling Manufactured Gas (Withdrawn 1986)[3]

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

D1302 Test Method for Analysis of Carbureted Water Gas by the Mass Spectrometer (Withdrawn 1967)[3]

2.2 *American Petroleum Institute Standards:*[4]

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

2.3 *Gas Producers Association Standards:*[5]

GPA 2166 Obtaining Natural Gas Samples for Analysis by Gas Chromatography

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.

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

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[2] 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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, http://www.api.org.

[5] Available from Gas Processors Association (GPA), 6526 E. 60th St., Tulsa, OK 74145, www.gpaglobal.org.

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	D1137[A] Natural Gas			D1302[B] Carbureted Water Gas			H_2-C_6			Reformer Gas			C_3,C_4			*i*C_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	15/16	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	...	...	...
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	...	...	[D]	[D]	...	...	...	...	...	...	...

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		
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	...	...	...	...	...	...	...	...	...	[I]	...	C	...	...	...	[I]	[I]	C	[I]	[I]	C
Carbon dioxide	...	...	...	...	...	...	...	...	...	[I]	...	C	...	...	...	[I]	[I]	C	[I]	[I]	C
Carbon monoxide	...	...	...	...	...	...	...	...	...	13	28	M	...	...	...	8	28	M	14	28	M
Nitrogen	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Air	...	...	...	...	...	...	...	...	...	2	32	M	...	...	...	1	32	M	1	32	M
Acid Gases	...	...	...	...	...	...	...	...	...	[I]	...	C	...	...	...	[I]	[I]	C	[I]	[I]	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

TABLE 1 *Continued*

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 D1137.

[B] Method D1302.

[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.

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 D1247, 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	*n*-butane
2	*n*-butane
3	hydrogen
4	*n*-butane
5	hydrogen

10.1.2 If the 43/58 and 43/29 ratios of the first two runs do not agree with 0.8 %, further runs must be made until agreement is attained, either by adjusting the temperature of the ionization chamber or by other techniques commonly used by the laboratory. In any case, the three 43/58 and 43/29 ratios must agree within 0.8 % and the three butane sensitivities within 1 %. The two hydrogen sensitivities must agree within 1.5 %. A standard gas sample can also be used as an additional check.

10.2 *Reference Standards*—Check the entire range with the spectrometer evacuated. This check provides a blank or background spectrum. If the approximate composition of the mixture is not known, make a preliminary run over the entire operating mass range. If the composition is known, the necessary calibrating gases should have been run recently enough before the mixture to preclude pattern changes. The calibrating gases should be run in order of decreasing molecular weight. If isomers are present, do not run them in succession. Introduce the calibrating gases through the inlet system at a pressure closely approximating that used for the mixture spectrum. It is important that the recordings of the mass spectra of the calibrants and the gas mixture begin at the same ion accelerating voltage, the same magnetic field, and at the same interval after opening the sample volume to the leak manifold.

10.2.1 Run the hydrocarbon calibration gases as follows:

10.2.1.1 Introduce sufficient sample into the evacuated inlet system to give 4 Pa to 6.7 Pa (30 mtorr to 60 mtorr) pressure in the expansion reservoir of the instrument. (**Warning—**Samples and reference mixtures are extremely flammable. Keep away from heat, sparks, and open flames. Use with adequate ventilation. Cylinders shall be supported at all times. Hydrocarbon vapors that may be vented shall be controlled to assure compliance with applicable safety and environmental regulations.).

10.2.1.2 Adjust the magnetic field and the ion-accelerating voltage for the range m/e 2 to 4 on the collector.

10.2.1.3 Open the valve between the expansion reservoir and the leak manifold.

10.2.1.4 One minute later, start the recorder and sweep.

10.2.1.5 After sweeping over the above range, stop the sweep and recorder and quickly adjust the magnetic field and ion-accelerating voltage for the range m/e 12 to 100.

10.2.1.6 Two minutes after admission of sample to the leak, start the recorder and sweep.

10.2.1.7 After sweeping m/e = 100, pump out the reservoir and leak manifold. At least 5 min of pumping time should be allowed between each run.

10.3 *Calibration Data*—After the peaks of the calibration spectrogram have been measured, recorded, and corrected for background, transform them into a state appropriate for further computation. Obtain the sensitivities if desired by dividing the number of divisions of the base peak by the recorded sample pressure in the expansion reservoir of the mass spectrometer. Repeat the procedure for each calibrant.

11. Procedure

11.1 Introduce the sample without fractionation (see Section 9). Obtain the mass spectrum of the mixture under the same conditions as the calibration spectra (see Section 10). List the peak heights of the spectrum along with the appropriate *m/e* value.

12. Calculation

12.1 Schemes for calculating specific mass spectrometer gas analyses are shown in Table 1. Each results in a report of analysis on the samples as received in mole (gas-volume) percent unless otherwise noted. These schemes are possible procedures from which the user can make a choice on the basis of his particular problem.

12.2 The calculation basic to all mass spectrometric gas analysis is the solution of simultaneous equations. These are constructed in accordance with Eq 1:

$$m_i = \sum a_{ij} \times x_j \qquad (1)$$

where:

m_i = mixture peak height at the *i*th *m/e* used,
a_{ij} = pattern coefficient for the *j*th component on the *i*th peak, and
x_j = corrected base peak height of component *j*.

12.3 These equations will be solved, where indicated by the Unicomponent Peak Method:

$$x_j = \left(m_j - \sum_{k=1}^{k=j-1} a_{jk} \times x_k\right)/a_{jj} \qquad (2)$$

where k = 1 refers to the heaviest component.

12.4 Where simultaneous solution is indicated, a variety of direct arithmetic procedures may be used interchangeably.[6] Where increased precision or error control has been specified in this test method, more complex calculations must be used.[7]

12.5 In each of the above calculations, the *xj*'s must be divided by the sensitivity for *j* to get partial pressure. Sensitivity coefficients may be used instead of the a_{ij} in which case this step is not applicable.

12.6 The sum of the partial pressures should agree within 1 % with the pressure measured in the expansion reservoir of the mass spectrometer unless water vapor is present in the sample. Divide each partial pressure by the total calculated pressure and multiply by 100 to obtain mole percentages.

13. Report

13.1 Results shall be reported in mole (gas-volume) percent correct to one decimal place. Comments shall appear on the form in the event the sample is not reported on an "as received" basis. In any event the serial number of the calculation procedure shall appear on a report of analysis.

14. Precision and Bias

14.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

14.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in Table 2 and Table 3 only in one case in twenty.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values as shown in Table 2 and Table 3 only in one case in twenty.

NOTE 5—The precision for this test method was not obtained in accordance with RR:D02-1007.

14.2 *Bias*—A bias statement cannot be determined because there is no acceptable reference material suitable for determining the bias for the procedure in this test method.

15. Keywords

15.1 gas analysis; gas composition; mass spectrometry

TABLE 2 Summary of Results of Sample Calculated by Scheme 16

Component	Mole percent, Average	σ_r[A]	σ_R[B]
Hydrogen	20.6	0.2	2.2
Methane	34.1	0.4	1.4
Ethylene	5.4	0.1	0.2
Ethane	12.4	0.1	0.9
Propylene	7.9	0.1	0.6
Propane	5.8	0.3	0.3
Butylenes	2.6	0.1	0.2
Isobutane	2.5	0.1	0.4
Normal butane	1.2	0.1	0.2
Pentenes	0.4	0.1	0.1
Isopentane	0.5	0.1	0.2
Normal pentane	0.1	0.0	0.2
Nitrogen/carbon monoxide	0.5	0.1	0.5
Carbon dioxide	0.2	0.0	0.2
Hydrogen sulfide	5.8	0.1	0.9
Number of laboratories	14	6	14
Number of analyses	23	15	23

[A] σ_r repeatability standard deviation.
[B] σ_R reproducibility standard deviation.

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[6] 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.

[7] "Triangular Inverse Method," *Analytical Chemistry*, Vol 30, 1959, p. 877.

TABLE 3 Precision of Procedures for Mass Spectrometer Analysis

Serial No.	1		14	
Name	D1137 Natural Gas[A]		H_2-C_6 Cracked Gas	
Component	Repeatability	Reproducibility	Composition	Repeatability
Hydrogen	...	...	12.581	0.14
Methane	0.2	0.5	16.333	0.20
Ethylene	...	...	2.116	0.08
Ethane	0.1	0.3	7.367	0.10
Propene	0.02	0.04	7.883	0.16
Propane	0.02	0.06	6.601	0.12
Butene-1	...	...	...	...
Butene-2	...	...	5.333	0.19
Isobutene	...	...	...	...
Isobutane	...	...	5.528	0.18
n-Butane	...	...	1.484	0.09
Pentenes	...	...	1.015	0.10
Isopentane	...	...	1.270	0.11
n-Pentane	...	...	0.116	0.05
Hexanes	...	...	0.123	0.02
Carbon dioxide	0.02	0.03	...	...
Nitrogen	0.2	0.3	32.146	0.53
Cyclopentene	...	...	0.038	0.01
Degrees of Freedom	50 Laboratories	...	...	...

[A] Method D1137.

APPENDIX

(Nonmandatory Information)

X1. REFERENCE STANDARDS FOR PROCEDURES 14 AND 15

X1.1 *Butenes* —Butene-1, butene-2, and isobutene may be an average of equal ⅓ ’s. However, when a straight average is applied, limit the butenes total to 10 to 15 mole % to hold maximum error of lighter components to ±0.5 mole % and limited to 5 mole % to keep maximum error of lighter components to ±0.1 mole %. For a more accurate determination of lighter components, for example, ethylene, nitrogen, propylene, and propane—gases from representative refinery streams, are to be run by a GLC or IR method to obtain ratios of the butenes present. Weighted sensitivity coefficients allow accurate analyses for lighter components plus accurate total butene content through a 0 % to 100 % butene range. The continued accuracy obtained depends upon the stability of the refinery operation units; therefore, checks from time to time by an independent method (GLC or IR) enable mass spectrometric data processing groups to know the margins of error or to obtain new weighted sensitivity coefficients to maintain low deviations.

X1.2 *Pentenes* —Utilize weighted sensitivity coefficients at all times when pentenes content is likely to be above 1 mole %, due primarily to error caused in propane and propylene analysis.

X1.2.1 Gases from representative refinery streams can be run by a GLC method to obtain pentene ratios which then can be used to calculate weighted sensitivity coefficients. Alternatively, a C_5 cut could be obtained from a low-temperature fractional distillation of a sample of the type to be analyzed. The mass spectrum of this cut is recorded and the contributions of the normal and isopentane and normal butane present removed from the spectrum. The residual spectrum is typical of the pentenes present in samples of this type.

X1.2.2 Obtain checks from time to time on the pentene ratios to maintain low deviation.

X1.3 *Hexenes* —Obtain weighted sensitivity coefficients as explained in Appendix X1 for pentenes. However, a C_6 fraction from low-temperature distillation will be difficult to correct for pentenes present and if this approach is utilized it is suggested that a total C_6’s residual spectrum be calculated rather than attempting to correct out the C_6 saturates. If a C_6 fraction is used, regard samples with more than 1 mole % of C_6’s as inaccurate due to errors possible in incorrectly removing C_6 contributions to lighter components.

X1.3.1 If weighted sensitivities are employed, regard samples with over 2 mole % of C_6 as inaccurate due to probable variations in refinery units operation, since most operation units try to keep C_6’s to a minimum in gas streams.

X1.4 *Hexanes* —Obtain weighted sensitivity coefficients as described in X1.3. The amount of hexanes present in a gas sample are not to exceed 1 mole %, otherwise regard the analysis as inaccurate as described in X1.3.

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