

# **Exhibit 177**

## **(Part 3)**

**PREAMBLE (NOT PART OF THE STANDARD)**

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**END OF PREAMBLE (NOT PART OF THE STANDARD)**

Designation: D 2597 – 94 (Reapproved 1999)

An American National Standard

## **Standard Test Method for Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography<sup>1</sup>**

This standard is issued under the fixed designation D 2597; 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 analysis of demethanized liquid hydrocarbon streams containing nitrogen/air and carbon dioxide, and purity products such as an ethane/propane mix that fall within the compositional ranges listed in Table 1. This test method is limited to mixtures containing less than 5 mol % of heptanes and heavier fractions.

#### **1.2**

The heptanes and heavier fraction, when present in the sample, is analyzed by either (1) reverse flow of carrier gas after *n*-hexane and peak grouping or (2) precut column to elute heptanes and heavier first as a single peak. For purity mixes without heptanes and heavier no reverse of carrier flow is required.

Note 1—**Caution:** In the case of unknown samples with a relatively large C<sub>6</sub> plus or C<sub>7</sub> plus fraction and where precise results are important, it is desirable to determine the molecular weight (or other pertinent physical properties) of these fractions. Since this test method makes no provision for determining physical properties, the physical properties needed can be determined by an extended analysis or agreed to by the contracting parties.

#### **1.3**

The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

#### **1.4**

*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. For specific hazard statements see Annex A3.*

### **2. Referenced Documents**

#### **2.1**

*ASTM Standards:*

D 3700 Practice for Containing Hydrocarbon Fluid Samples Using a Floating Piston Cylinder<sup>2</sup>

#### **2.2**

*Other Standard:*

GPA Standard 2177 Analysis of Demethanized Hydrocarbon Liquid Mixtures Containing Nitrogen and Carbon Dioxide by Gas Chromatography<sup>3</sup>

TABLE 1 Components and Compositional Ranges Allowed

Components	Concentration Range, Mol %
Nitrogen	0.01–5.0
Carbon Dioxide	0.01–5.0
Methane	0.01–5.0
Ethane	0.01–95.0
Propane	0.01–100.0
Isobutane	0.01–100.0
<i>n</i> -Butane and 2, 2-Dimethylpropane	0.01–100.0
Isopentane	0.01–15.0
<i>n</i> -Pentane	0.01–15.0
2,2-Dimethylbutane	0.01–0.5
2,3-Dimethylbutane and 2-Methylpentane	
3-Methylpentane and Cyclopentane	0.01–15.0
<i>n</i> -Hexane	
Heptanes and Heavier	0.01–5.0

### 3. Summary of Test Method

#### 3.1

Components to be determined in a demethanized hydrocarbon liquid mixture are physically separated by gas chromatography and compared to calibration data obtained under identical operating conditions. A fixed volume of sample in the liquid phase is isolated in a suitable sample inlet system and entered onto the chromatographic column.

##### 3.1.1

Components nitrogen/air through *n*-hexane are individually separated with the carrier flow in the forward direction. The numerous heavy end components are grouped into an irregular shape peak by reversing direction of carrier gas through the column by means of a switching valve immediately following the elution of normal hexane. (See Fig. 1.) Samples that contain no heptanes plus fraction are analyzed until the final component has eluted with no reverse of carrier flow.

##### 3.1.2

An alternative to the single column backflush method is the use of a precut column which is backflushed to obtain the heptanes plus as a single peak at the beginning of the chromatogram. Two advantages of the alternate method are as follows: (1) better precision in measuring the C<sub>7</sub> plus portion of the sample and (2) reduction in analysis time over the single column approach by approximately 40 %.

<sup>1</sup> This test method is under the jurisdiction of Committee D–2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.H on Liquefied Petroleum Gas.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 05.02.

<sup>3</sup> Available from Gas Processors Assn., 6526 E. 60th St., Tulsa, OK 74145.

#### 1 FIG. 1 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Frontal Carrier Gas Flow Through *N*-Hexane, Reverse Grouping Heptanes Plus)

#### 3.2

The chromatogram is interpreted by comparing the areas of component peaks obtained from the unknown sample with corresponding areas obtained from a run of a selected reference standard. Any component in the unknown, suspected to be outside the linearity range of the detector, with reference to the known amount of that component in the reference standard, must be determined by a response curve. Peak height method of integration can be used only if the Chromatograph is operating in the linear range for all components analyzed. Linearity must be proved by peak height for all components, when using peak height method. (See Section 6 for further explanation of instrument linearity check procedures.)

### 4. Significance and Use

#### 4.1

The component distribution of hydrocarbon liquid mixtures is often required as a specification analysis for these materials. Wide use of these hydrocarbon mixtures as chemical, feedstocks or as fuel require precise compositional data to ensure uniform quality of the reaction product. In addition, custody transfer of these products is often made on the basis of component analyses of liquid mixtures.

#### 4.2

The component distribution, data of hydrocarbon mixtures can be used to calculate physical properties such as specific gravity, vapor pressure, molecular weight, and other important properties. Precision and accuracy of compositional data are extremely, important when these data are used to calculate physical properties of these products.

## 5. Apparatus

### 5.1

Any gas Chromatograph can be used that meets the following specifications.

#### 5.1.1

*Detector*—The detector shall be a thermalconductivity type. It must be sufficiently sensitive to produce a deflection of at least 0.5 mv for 1 mol % of *n*-butane in a 1.0- $\mu$ L sample.

#### 5.1.2

*Sample Inlet System, Liquid*—A liquid sampling valve shall be provided, capable of entrapping a fixed volume of sample at a pressure at least 200 psi (1379 kPa) above, the vapor pressure of the sample at valve temperature, and introducing this fixed volume into the carrier gas stream ahead of the analyzing column. The fixed sample volume should not exceed 1.0  $\mu$ L and should be reproducible such that successive runs agree within  $\pm 2$  % on each component peak area. The liquid sampling valve is mounted exterior of any type heated compartment and thus can operate at laboratory ambient conditions.

#### 5.1.3

*Sample Inlet System, Gas (Instrument Linearity)*—Provision is to be made to introduce a gas phase sample into the carrier gas stream ahead of the chromatographic column so that linearity of the instrument can be estimated from response curves. The fixed volume loop in the gas sample valve shall be sized to deliver a total molar volume approximately equal to that delivered by the liquid sample valve in accordance with 5.1.2. (See Section 6 for further explanation of instrument linearity check procedures.)

#### 5.1.4

*Chromatographic Columns:*

##### 5.1.4.1

*Column No. 1*—A partition column shall be provided capable of separating nitrogen/air, carbon dioxide, and the hydrocarbons methane through normal hexane. (See Fig. 1 and Fig. 2.) Separation of carbon dioxide shall be sufficient so that a 1- $\mu$ L sample containing 0.01 mol % carbon dioxide will produce a measurable peak on, the chromatogram. (The silicone 200/500 column, containing a 27 to 30 weight % liquid phase load, has proven satisfactory for this type of analysis.)

##### 5.1.4.2

*Column No. 2*—A partition column similar, to Column No. 1. It shall be of the same diameter as Column No. 1. The column shall be of an appropriate length to clearly separate the heptanes plus fraction from the hexanes and lighter components.

##### 5.1.5

*Attenuator*—A multistep device shall be included in the detector output circuitry to attenuate, the signal from the detector to the recorder when using manual calculation methods. The attenuation between steps shall be accurate to  $\pm 0.5$  %.

##### 5.1.6

*Temperature Control*—The chromatographic column(s) and the detector shall be maintained at their respective temperatures, constant to  $\pm 0.3^\circ$  during the course of the sample and corresponding reference standard runs.

### 5.2

*Carrier Gas*—Pressure-reducing and control devices to

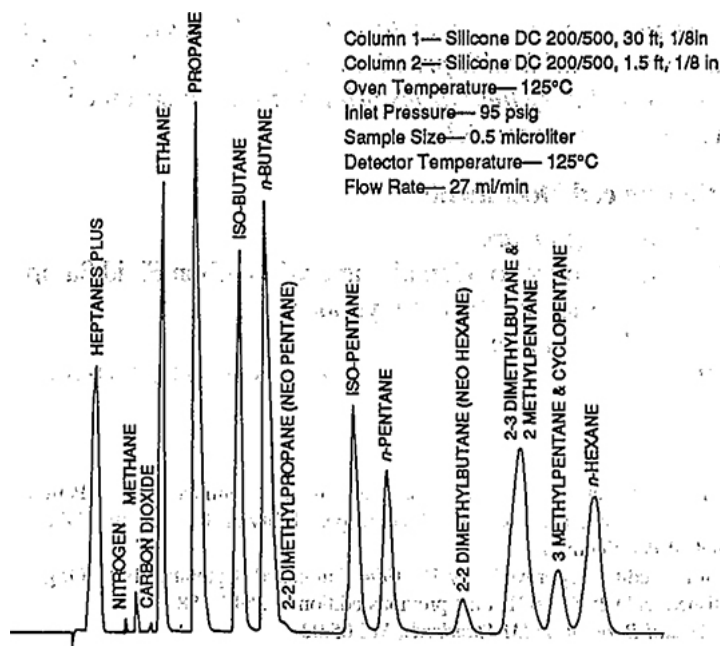


FIG. 2 Chromatogram of Demethanized Hydrocarbon Liquid Mixture (Precut Column Grouping Heptanes Plus, Frontal Carrier Gas Flow Remaining Components)

2 give repeatable flow rates.

### 5.3

**Recorder**—A strip chart recorder with a full-scale range of 1 mv shall be required when using manual calculation methods. A maximum pen response time of 1 s and a minimum chart speed of 1 cm/min (0.5 in./min accepted) shall be required. Faster speeds up to 10 cm/min (3 in./min accepted) are required if the chromatogram is to be interpreted using manual methods to obtain areas.

**Note 2**—A strip chart recorder is recommended for monitoring the progress of the analysis if an electronic digital integrator without plotting capability is in service.

### 5.4

**Electronic Digital Integrator**—A strongly preferred and recommended device for determining peak areas. This device offers the highest degree of precision and operator convenience.

**Note 3—Caution:** Electronic digital integrators are able to integrate peak areas by means of several different methods employing various correction adjustments. The operator should be well versed in integrator operation, preventing improper handling and manipulation of data—ultimately resulting in false information.

### 5.5

**Ball and Disk Integrator**—An alternative device in the absence of an electronic digital integrator for determining peak areas. This device gives more precise areas than manual methods and saves operator time in interpreting the chromatogram.

### 5.6

**Manometer**—Well type, equipped with an accurately graduated and easily readable scale covering the range from 0 to 900 mm of mercury. The manometer is required in order to charge partial pressure samples of pure hydrocarbons when determining response curves for linearity checks when using the gas sampling valve.

### 5.7

**Vacuum Pump**—Shall have the capability of producing a vacuum of 0.1 mm of mercury absolute or less. Required for linearity checks when using the gas sampling valve.

### 5.8

**Sample Filter**—An optional device to protect the liquid sampling valve from scoring due to the presence of foreign contaminants such as metal shavings, dirt, and so forth, in a natural gas liquid (NGL) sample. The filter can be of a small total volume, or an in-line type design and contain a replaceable/disposable element.

**Note 4—Caution:** A filter can introduce error if not handled properly. The filter should be clean and free of any residual product from previous samples so that a buildup of heavy end hydrocarbon components does not result. (Can be accomplished by a heating/cooling

process or inert gas purge, etc.) The filter element should be 15- $\mu\text{m}$  size or larger so that during the purging process NGL is not flashed, preventing fractionation and bubble formation.

## 5.9

### Sample Containers:

#### 5.9.1

**Floating Piston Cylinder**—A strongly preferred and recommended device suitable for securing, containing, and transferring samples into a liquid sample valve and which preserves the integrity of the sample. (See Fig. 3 and Test Method D 3700.)

#### 5.9.2

**Double-Valve Displacement Cylinder**—An alternate device used in the absence of a floating piston cylinder suitable for securing, containing, and transferring samples into a liquid sample valve. (See Fig. 4 and Fig. 5.)

Note 5—**Caution:** This container is acceptable when the displacement liquid does not appreciably affect the composition of the sample of interest. Specifically, components such as  $\text{CO}_2$  or aromatic hydrocarbons are partially soluble in many displacement liquids and thus can compromise the final analysis. This caution is of the utmost importance and should be investigated prior to utilizing this technique.

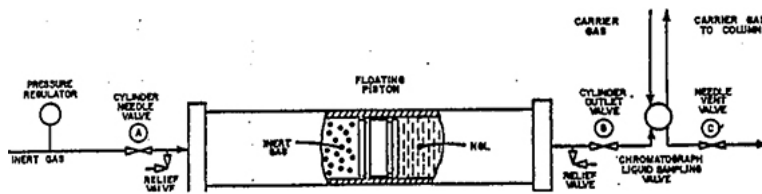


FIG. 3 Repressuring System and Chromatographic Valving with Floating Piston Cylinder

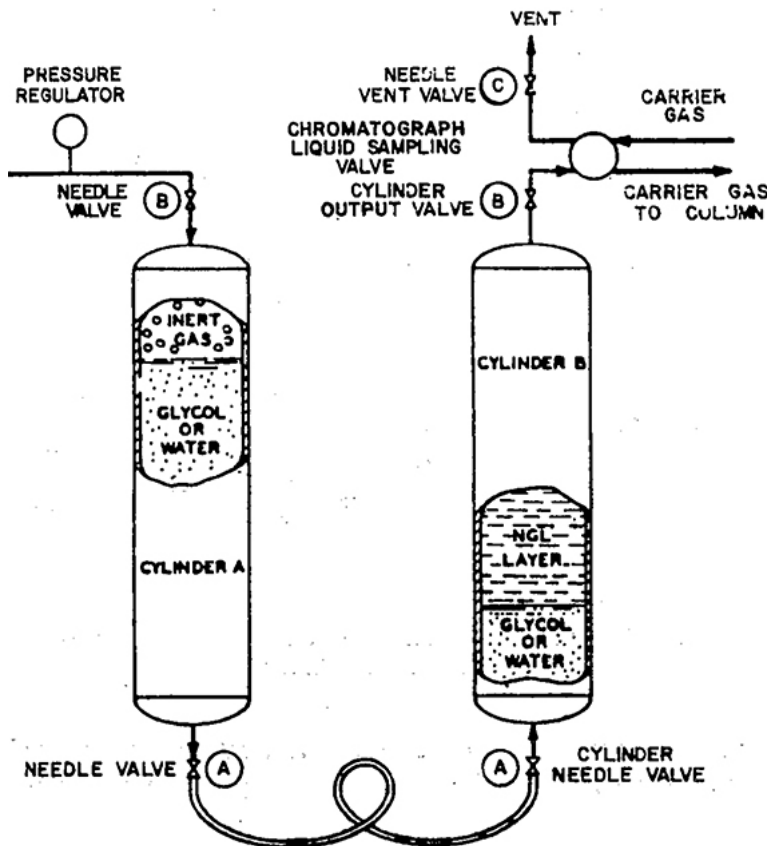


FIG. 4 Repressuring System and Chromatographic Valving with Double-Valve Displacement Cylinder

## 6. Calibration

### 6.1

In conjunction with a calibration on any specific chromatography, the linear range of the components of interest shall be determined. The linearity is established for any new Chromatograph and reestablished whenever the instrument has undergone a major change (that is, replaced

detectors, increased sample size, switched column size, or dramatically modified run parameters).

### 6.1.1

The preferred and more exacting procedure is to prepare response curves. The procedure for developing the data necessary to construct these response curves for all components nitrogen through n-pentane is set forth in Annex A2.

### 6.1.2

A second procedure utilizes gravimetrically constructed standards of a higher concentration than is contained in the unknown. A set of response factors are first determined for all components by means of a blend mix. (See 6.3.) A second (or third) gravimetrically determined standard (either purity or blend) can then be run, using the originally obtained

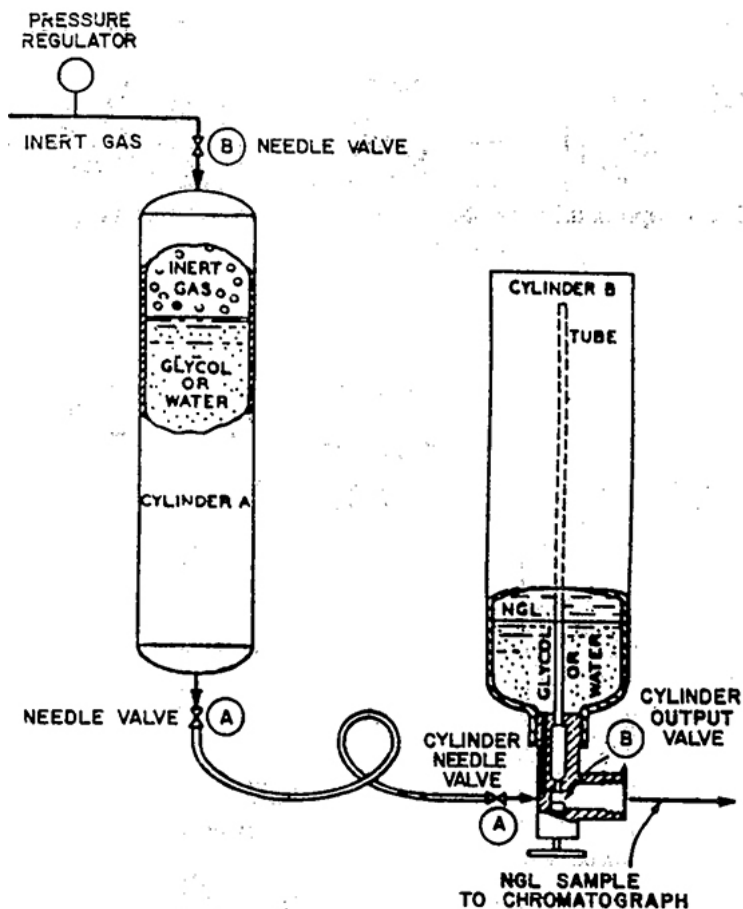


FIG. 5 Alternate Repressuring System with Double-Valve Displacement Cylinder

response factors, which contain a concentration of individual components exceeding the expected amounts in the unknowns.

When both (or all three) runs match their respective standards within the precision guidelines allowed in Section 10, then the instrument can be considered linear within that range.

Note 6—This test method omits the need of a gas sample valve on the chromatographic instrument. However, several accurate primary NGL standards are required and the exact point at which nonlinearity occurs is not determined.

## 6.2

For routine analysis using this procedure it is intended that calibration be accomplished by use of a selected reference standard containing known amounts of all components of interest. It is recommended that the reference standard composition be similar to the one shown in Table 2, or closely resemble the composition of expected unknowns. This approach is valid for all components that lie within the proven linear range for a specific gas Chromatograph.

Note 7—Check the reference standard for validity when received and periodically thereafter. Annex A1 details one procedure for making the validity check.

## 6.3

Using the selected liquid reference standard, obtain a chromatogram as outlined in Section 7.

### 6.3.1

Determine peak areas (or peak heights) from the chromatogram for all components. These data shall be used to calculate response factors in accordance with 9.1.

### 6.3.2

Repeat 6.3 through 6.3.1 until a satisfactory check is obtained. Usually two runs will suffice.

## 7. Procedure

### 7.1

*General*—In the routine analysis of samples described in the scope of this procedure, it is possible to obtain all components of interest from a single run. Response factors,

TABLE 2 Example of Response Factors Determined from Reference Standard

Component	Mol % in Referenced Standard	Peak Area Referenced Standard Run	Mol % Response Factors ( $\times 1000$ )	Relative Response Factor (C <sub>3</sub> Reference Peak)
Nitrogen/air	0.10	311	$\frac{0.10}{311} = 3.2154$	$\frac{0.10}{311} \times \frac{122825}{28.05} = 1.4080$
Methane	1.49	3552	$\frac{1.49}{3552} = 4.1948$	$\frac{1.49}{3552} \times \frac{122825}{28.05} = 1.8368$
Carbon dioxide	0.50	1568	$\frac{0.50}{1568} = 3.1888$	$\frac{0.50}{1568} \times \frac{122825}{28.05} = 1.3963$
Ethane	53.90	182108	$\frac{53.90}{182108} = 2.9598$	$\frac{53.90}{182108} \times \frac{122825}{28.05} = 1.2960$
Propane	28.05	122825	$\frac{28.05}{122825} = 2.2837$	$\frac{28.05}{122825} \times \frac{122825}{28.05} = 1.0000$
Isobutane	3.05	15306	$\frac{3.05}{15306} = 1.9927$	$\frac{3.05}{15306} \times \frac{122825}{28.05} = 0.8726$
<i>n</i> -Butane 2,2-Dimethylpropane	6.01	30834	$\frac{6.01}{30834} = 1.9491$	$\frac{6.01}{30834} \times \frac{122825}{28.05} = 0.8535$
Isopentane	1.00	5856	$\frac{1.00}{5856} = 1.7077$	$\frac{1.00}{5856} \times \frac{122825}{28.05} = 0.7478$
<i>n</i> -Pentane	2.00	12280	$\frac{2.00}{12280} = 1.6287$	$\frac{2.00}{12280} \times \frac{122825}{28.05} = 0.7132$
2,2-Dimethylbutane	0.02	132	$\frac{0.02}{132} = 1.5152$	$\frac{0.02}{132} \times \frac{122825}{28.05} = 0.6635$
2,2-Dimethylbutane 2-Methylbutane	0.64	4513	$\frac{0.64}{4513} = 1.4181$	$\frac{0.64}{4513} \times \frac{122825}{28.05} = 0.6210$
3-Methylbutane Cyclopentane	0.41	2401	$\frac{0.41}{2401} = 1.7076$	$\frac{0.41}{2401} \times \frac{122825}{28.05} = 0.7477$
<i>N</i> -Hexane	0.74	5064	$\frac{0.74}{5064} = 1.4613$	$\frac{0.74}{5064} \times \frac{122825}{28.05} = 0.6399$
Heptanes Plus	2.09	14851	$\frac{2.09}{14851} = 1.4073$	$\frac{2.09}{14851} \times \frac{122825}{28.05} = 0.6162$

4 determined in duplicate runs on a selected reference standard, are used to convert peak areas (or peak heights) of the unknown sample to mol percent.

### 7.2

*Apparatus Preparation*—With the proper column(s) and liquid sample valve in place, adjust operating conditions to optimize the resultant chromatogram. Using the reference standard, introduce the sample in the following manner.

### 7.3

*Introduction of Sample:*

#### 7.3.1

*Floating Piston Cylinders*—For floating piston cylinders, refer to Fig. 3 and proceed as follows: connect a source of inert gas to Valve A so that pressure can be applied to the sample by means of the floating piston. Apply a pressure not less than 200 psi (1379 kPa) above the vapor pressure of the sample at the temperature of the sample injection valve.

#### 7.3.2

Thoroughly mix the sample.

#### 7.3.3



Connect the sample end of the cylinder, Valve B, to the inlet of the Chromatograph liquid sample valve. All connections and tubing are to be made of material impervious to the sample composition and of as small diameter and shortest length of plumbing as is practical, thereby minimizing dead space. All tubing between sample cylinder and liquid sampling valve shall be the same diameter.

#### 7.3.4

With Valve C closed, open Valve B to fill the sample valve and associated lines.

#### 7.3.5

Slowly crack Valve C to purge the sample valve. When the purge is complete, close Valve C. **Caution**—Use extreme care to ensure that no flashing of sample occurs in the inlet sampling line and valve system. Always meter at sample purge Valve C, never at sample Valve B. The sample line and valve system should remain at 1379 kPa (200 psi) above the vapor pressure of the product.

#### 7.3.6

Operate the liquid sample valve either manually or automatically to inject the liquid sample into the carrier gas flow immediately ahead of the chromatographic column. Actuate the sample valve quickly and smoothly to place the sample on the column all at once and to ensure continuous carrier gas flow through the column.

#### 7.3.7

*Double-Valve Displacement Cylinders*—For doublevalve displacement cylinders refer to Fig. 4 and Fig. 5 and proceed as follows: Connect the sample Cylinder B to Cylinder A so repressurizing fluid can be entered into the bottom of Cylinder B. With this configuration the hydrocarbon sample is taken from the upper portion of the cylinder. Pressurize Cylinder A with an inert gas and maintain a pressure at least 200 psi (1379 kPa) above the vapor pressure of the hydrocarbon sample at operating conditions. Open the necessary valves to admit pressurizing fluid into the sample Cylinder B.

#### 7.3.8

Mix the sample thoroughly by gently inverting Cylinder B several times. Fix the cylinder in a vertical position by means of a ringstand, or similar device.

#### 7.3.9

Connect the sample outlet Valve B on Cylinder B to the inlet of the Chromatograph liquid sample valve. All connections and tubing are to be made of material impervious to the sample composition and of as small diameter and shortest length of plumbing as is practical, thereby minimizing “dead space.” All tubing between sample cylinder and liquid valve should be the same diameter.

#### 7.3.10

With Valve C closed, open Valve B to fill the sample valve and associated lines.

#### 7.3.11

Slowly crack Valve C to purge the sample valve. When the purge is complete close Valve C. **Caution**—Use extreme care to ensure that no flashing of sample occurs in the inlet sampling line and valve system. Always meter at sample purge Valve C, never at sample Valve B. The sample line and valve system should remain at 1379 kPa (200 psi) above the vapor pressure or the product.

#### 7.3.12

Operate the liquid sample valve either manually or automatically to inject the liquid sample into the carrier gas flow immediately ahead of the chromatographic column. The liquid sample valve should be actuated quickly and smoothly to place the sample on the column all at once and to ensure continuous carrier gas flow through the column.

### 7.4

#### *Valve Switching:*

#### 7.4.1

After the elution of *n*-hexane the carrier gas flow is reversed by means of a backflush valve operated manually or automatically. (An acceptable backflush valve configuration is shown in Fig. 6.) Reversing carrier flow causes severe baseline deviations (see Fig. 1). When using electronic digital integrators, exercise care to ensure integration does not occur until baseline is adequately reestablished. The resulting irregular shaped C<sub>7</sub> plus peak is eluted over a period of time equivalent to time on forward flow minus the retention time for the air peak. Only after baseline is reestablished should the run be terminated and carrier flow returned to original direction.

#### 7.4.2

An alternative to backflushing after normal hexane is the use of a precut column to group the  $C_7$  plus fraction at the beginning of the chromatogram as a single peak. (An acceptable valve configuration for the precut method is illustrated in Fig. 7.) The valve position is switched when normal hexane and lighter components have traveled through Column 2 and are in Column 1. At this point, heptanes and heavier components are retained in Column 2. When the valve is reversed, the heptanes plus fraction will elute from Column 2 first. Baseline must be clearly and distinctly established before elution of the  $C_7$  plus peak so an accurate measurement of this peak can be obtained. After the elution of  $n$ -hexane, terminate the run and return the valve to the initial position.

## 8. Unknown Sample Run

### 8.1

Obtain a chromatogram of the unknown sample in accordance with instructions outlined in Section 7.

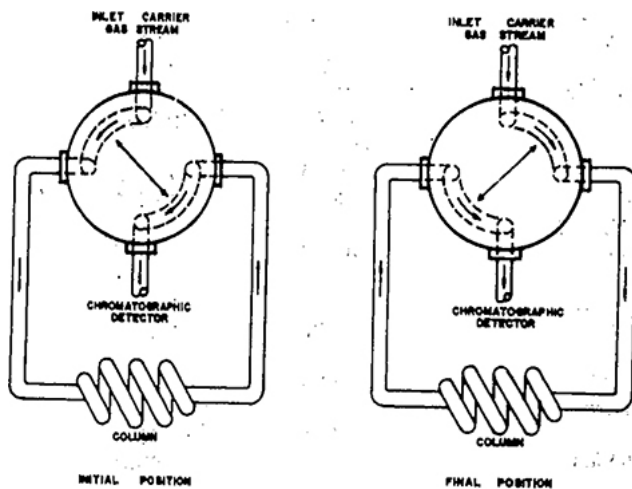


FIG. 6 Backflush Valve Configuration

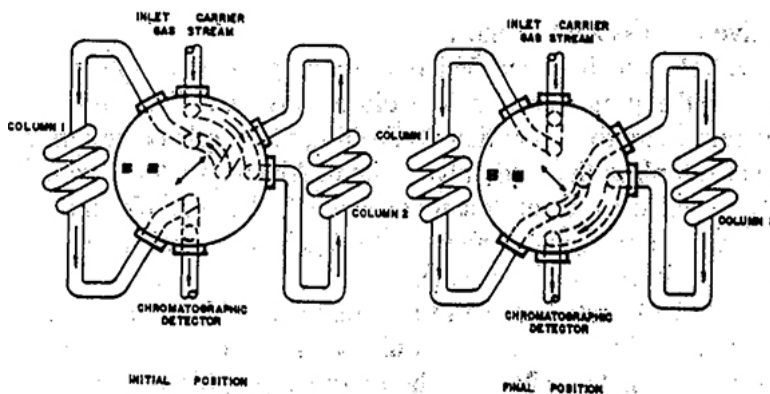


FIG. 7 Precut Valve Configuration

#### 8.1.1

Determine peak areas (or peak heights) from the chromatogram for all components. These data shall be used to calculate composition of the unknown in accordance with instructions outlined in 9.2.

## 9. Calculation

### 9.1

*Calculation of Response Factors Using a Known Reference Standard:*

#### 9.1.1

Determine the peak area (or peak height) of each component nitrogen/air through heptanes plus (if applicable) from the chromatogram of the known reference standard.

Note 8—The backflush peak (where applicable) for heptanes plus is considered to be a single component for the purpose of this calculation. In addition, the peak area method shall be used in calculating the heptanes plus fraction.

#### 9.1.2

Calculate a response factor for each of the preceding components in accordance with the following equation (see Table 2):

$$K = \frac{M}{P} \quad (1)$$

where:

$K$	=	response factor,
$M$	=	mol percent of component in reference standard, and
$P$	=	peak area or peak height in arbitrary units (millimetres, square inches, counts, and so forth) corrected to maximum sensitivity.

### 9.1.3

An alternative method of determining response factors is the use of a single reference component in the standard. Calculate a relative response factor for each component in accordance with the following equation (see Table 2):

$$KF_i = \frac{M_i}{P_i} \times \frac{P_{RP}}{M_{RP}} \quad (2)$$

where:

$KF_i$	=	relative response factor for component $i$ ,
$M_i$	=	mol percent of component $i$ in reference standard,
$P_i$	=	peak area (or peak height) in arbitrary units corrected to maximum sensitivity for component $i$ ,
$P_{RP}$	=	peak area (or peak height) of the component selected as the reference peak, and
$M_{RP}$	=	mol percent of the component in reference standard as the reference peak.

From the equation defining the relative response factor, the component chosen as the reference peak always has a response factor of 1.000.

## 9.2

*Calculation of Mol Percent of Components in Unknown Sample:*

### 9.2.1

Determine peak area (or peak height) of each component nitrogen/air through heptanes plus from the chromatogram of the unknown sample using the same arbitrary units as in 9.1.

### 9.2.2

Calculate the concentration in mol percent of each of these components in accordance with the following equation (see Table 3):

$$M = P \times K \quad (3)$$

where:

$M$	=	mol percent of component in unknown,
$P$	=	peak area (or peak height) of each component in unknown sample, and

TABLE 3 Calculation of Unknown Sample Using Response Factors from Table 2

Component	Peak Area	Mol % Response Factor ( $\times 10\ 000$ )	Unnormalized Mol %	Normalized Mol %	Relative Response Factor ( $C_3$ Reference Peak)	Unnormalized Area $\times$ RRF	Normalized Mol %
Nitrogen/Air	91	3.2154	0.02926	0.04	1.4080	128	0.04
Methane	4720	4.1948	1.97995	2.85	1.8368	8670	2.85
Carbon Dioxide	2615	3.1888	0.83387	1.20	1.3963	3651	1.20
Ethane	64090	2.9598	18.96936	27.27	1.2960	83061	27.27
Propane	113346	2.2837	25.88483	37.21	1.0000	113346	37.21
Isobutane	31590	1.9927	6.29494	9.05	0.8726	27565	9.05
<i>n</i> -Butane	33672	1.9491	6.56301	9.44	0.8535	28739	9.44
2,2-Dimethylpropane							
Isopentane	16368	1.7077	2.79516	4.02	0.7478	12240	4.02
N-Pentane	17235	1.6287	2.80706	4.04	0.7132	12292	4.04
2,2-Dimethylbutane	75	1.5152	0.01136	0.02	0.6635	50	0.02

Component	Peak Area	Mol % Response Factor (×10 000)	Unnormalized Mol %	Normalized Mol %	Relative Response Factor (C <sub>3</sub> Reference Peak)	Unnormalized Area × RRF	Normalized Mol %
2,3-Dimethylbutane	4027	1.4181	0.57107	0.82	0.6210	2501	0.82
2-Methylpentane							
3-Methylpentane	1584	1.7076	0.27048	0.39	0.7477	1184	0.39
Cyclopentane <i>n</i> -Hexane	4521	1.4613	0.66065	0.95	0.6399	2893	0.95
Heptanes Plus	13335	1.4073	1.87663	2.70	0.6162	8217	2.70
			69.54763	100.00		304537	100.00

6  $K$  = response factor as determined in 9.1.

#### 9.2.2.1

Total the mol percent values and normalize to 100 %.

#### 9.2.3

Using the relative response factors calculate the concentration in mol percent of each of these components in accordance with the following equation (see Table 3):

$$M_i = \frac{KF_i \times P_i}{\sum_{i=1}^n (KF_i \times P_i)} \times 100 \quad (4)$$

where:

$M_i$	=	mol percent of component $i$ in unknown,
$KF_i$	=	relative response factor for component $i$ ,
$P_i$	=	peak area (or peak height) of component $i$ in unknown, and
$\sum_{i=1}^n (KF_i \times P_i)$	=	summation of all relative response areas in the chromatogram.

#### 9.2.3.1

Total mol percent values and normalize to 100 %.

## 10. Precision and Bias

### 10.1

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

#### 10.1.1

*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 following values only in one case in twenty:

Component	Mol % Range	Percent Relative Repeatability
Nitrogen	0.01–.89	9
Carbon Dioxide	0.01–2.3	4
Methane	1.6–4.5	4
Ethane	27.–54.	.5
Propane	28.–34.	.5
Isobutane	3.0–8.8	1
<i>n</i> -Butane	6.0–9.3	1
Isopentane	1.0–3.9	2
<i>n</i> -Pentane	2.0–3.8	2
C <sub>e</sub> <sup>+</sup>	3.6–5.7	2

#### 10.1.2

**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 following values only in one case in twenty:

### 10.1.2

Component	Mol % Range	Percent Relative Reproducibility
Nitrogen	0.01–89	60
Carbon Dioxide	0.01–2.3	30
Methane	1.6–4.5	10
Ethane	27–54	2
Propane	38–34	2
Isobutane	3.0–8.8	4
<i>n</i> -Butane	6.0–9.3	4
Isopentane	1.0–3.9	6
<i>n</i> -Pentane	2.0–3.8	6
C <sub>e</sub> <sup>+</sup>	3.6–5.7	10

Note 9—The repeatability and reproducibility statements for this procedure are from the statistical data obtained in a GPA cooperative test program completed in 1986. The testing program included six samples analyzed in a round robin by eight laboratories.

### 10.2

**Bias**—The bias of the procedure in this test method has not been determined but is now under consideration.

## 11. Keywords

### 11.1

chromatography; demethanized hydrocarbons; liquefied petroleum gases; natural gas liquids

## ANNEXES

### (Mandatory Information)

## A1. FIDELITY OF SELECTED REFERENCE STANDARDS

### A1.1

Referring to Section on Summary of Test Method, it is noted that the test method is based on response factors calculated from a selected reference standard using peak area measurements. Liquid reference standards are difficult to prepare and are subject to change in composition during use. Hence it is virtually mandatory that the reference standard be authenticated in some manner when received and periodically during use. One simple approach is described as follows:

#### A1.1.1

Determine mol percent response factors for normal hydrocarbons using area measurements of peaks recorded on chromatogram of reference standard run (see 9.1.2).

#### A1.1.2

Determine molecular weight corresponding to each component hydrocarbon in A1.1.1.

#### A1.1.3

Using log/log paper plot the response factor on the vertical scale versus molecular weights on the horizontal scale (see Fig. A1.1).

#### A1.1.4

If all is in order the resultant plot will be essentially a straight line with a negative slope. For a specific instrument, the slope of the plot should remain essentially constant. A change in the angle usually indicates a change in blend composition.

#### A1.1.5

An example follows using data from Table 2 in this test method (see Table A1.1).

**A1.2**

It should be noted, the relationship described in A1.1.1-A1.1.5 is valid for reference blends in the vapor state as well as the liquid state, so long as the following conditions are met.

**A1.2.1**

Chromatogram is obtained using a thermal conductivity detector.

**A1.2.2**

Peak areas in arbitrary units are used for peak measurements.

**A1.2.3**

Known concentrations of hydrocarbon components  
7 in the known reference blend are expressed in mol %.

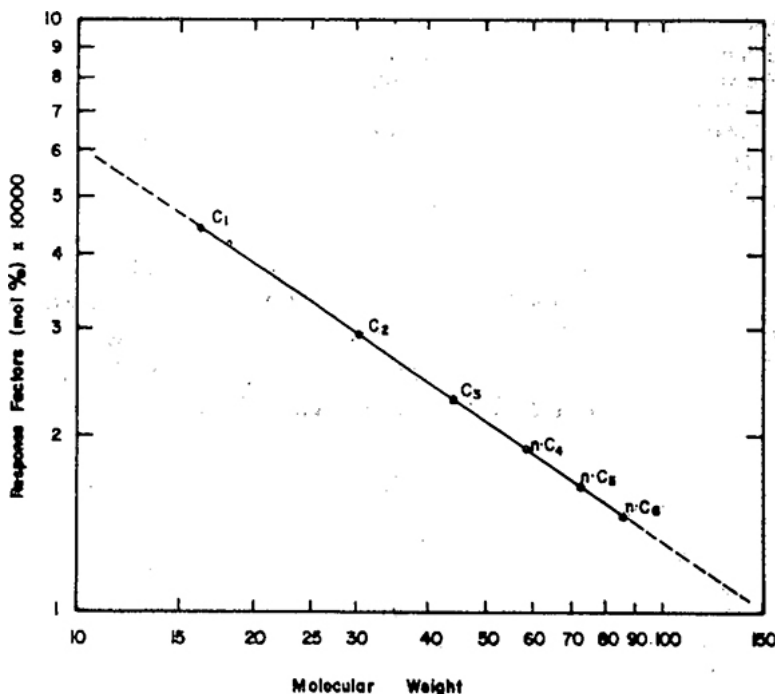


FIG. A1.1 Response Factors (mol %) Versus Molecular Weight

TABLE A1.1 Response Factors and Mol Weights Normal Hydrocarbon Components<sup>A</sup>

Component	Response Factor × 10 <sup>-4</sup>	Mol Weight
Methane	4.195	16.043
Ethane	2.960	30.070
Propane	2.284	44.097
<i>n</i> -Butane	1.949	58.123
<i>n</i> -Pentane	1.629	72.150
<i>n</i> -Hexane	1.461	86.177

<sup>A</sup>Initially with a new system and a new blend this check should be performed often, say once a day for the first week to satisfy the operator that the component analysis furnished with the blend is essentially correct. After this time the check should be performed each time a calibration run is made to verify the continued fidelity of the selected reference blend.

**A1.3**

In addition to authentication of reported composition of a new blend and periodically verifying its validity, this plot can be used to:

**A1.3.1**

Reduce the frequency of calibrations required.

**A1.3.2**

Reveal calculation and interpretation errors in calibration runs.

### A1.3.3

Pick off factors for components not in the standard by extrapolating the plot. A factor for the back flush peak can be picked off if the molecular weight can be satisfactorily estimated.

## A2. DETERMINATION OF RESPONSE FACTORS

### A2.1 Linearity Check

#### A2.1.1

In order to establish linearity of response for the thermal conductivity detector, it is necessary to carry out the procedure outlined as follows:

#### A2.1.2

The major component of interest (methane for natural gas) is charged to the Chromatograph by means of the fixed-size sample loop at partial pressure of 100 to 700 mm of Hg in increments of 100 mm. The peak area of the methane is plotted versus partial pressure. Any deviation from linearity indicates the fixed volume sample loop is too large. The sample size should be reduced until the pure major component is linear over the concentration range expected in the samples.

#### A2.1.2.1

Connect the pure component source to the sample entry system. Evacuate the sample entry system and observe manometer for any leaks. (See Fig. A2.1 for a suggested manifold arrangement.) The sample entry system shall be vacuum tight.

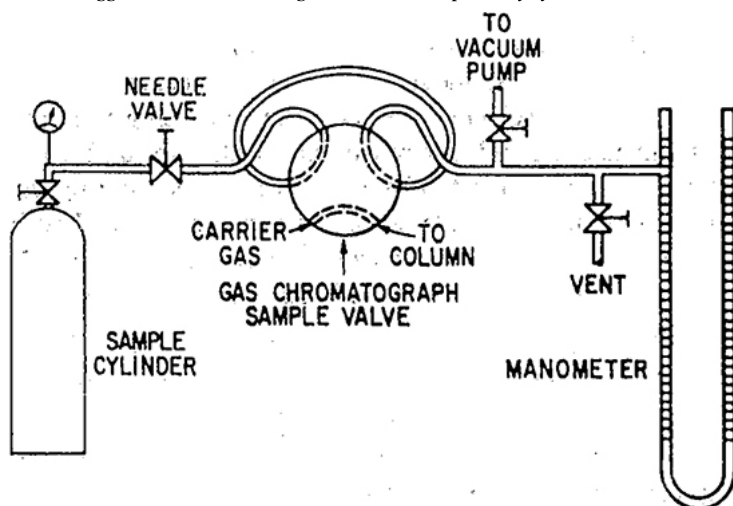


FIG. A2.1 Suggested Manifold Arrangement for Entering Vacuum Samples

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#### A2.1.2.2

Carefully open the needle valve to admit the pure component up to 100 mm of partial pressure.

#### A2.1.2.3

Record exact partial pressure and actuate sample valve to place sample onto column. Record peak area of pure component.

#### A2.1.2.4

Repeat A2.2.3 for 200, 300, 400, 500, 600, and 700 mm of mercury. Record peak area obtained at each pressure.

#### A2.1.2.5

Plot the area data versus partial pressure on the  $x$  and  $y$  axes of linear graph paper as shown in Fig. A2.2.

Note A2.1—Experience has shown that if the major component is linear over the expected concentration range in the sample, the lesser components will also be linear. Methane and ethane exhibit less than 1 % compressibility at 760 mm Hg and are therefore the components of choice for linearity checks.

Note A2.2—**Caution:** *n*-Butane at atmospheric pressure exhibits 3.5 % compressibility, which, if the detector response is linear, will produce a nonlinear response opposite to detector non-linearity.

## A2.2 Calibration Procedure

### A2.2.1

Response factors of the components of interest can be established in two ways. The routine method is to use a gas reference standard of known composition to determine response factors, provided all components in the reference standard and in the unknown samples lie within the proven linear range for a specific chromatography instrument. An acceptable non-routine method of determining response factors is to charge the pure components to the Chromatograph. The latter method is described in Annex A1.

#### A2.2.1.1

Connect the reference standard gas to the sample entry system. Evacuate the sample entry system and observe the manometer for any leaks.

#### A2.2.1.2

Carefully open the needle valve to admit reference standard gas up to some predetermined partial pressure.

Note A2.3—The use of some constant partial pressure below atmospheric pressure avoids variations in sample size due to changes in barometric pressure.

#### A2.2.1.3

Record the partial pressure and operate the gas sampling valve to place the sample onto the column. Record the chromatogram, integrator/computer peak areas, and peak retention times.



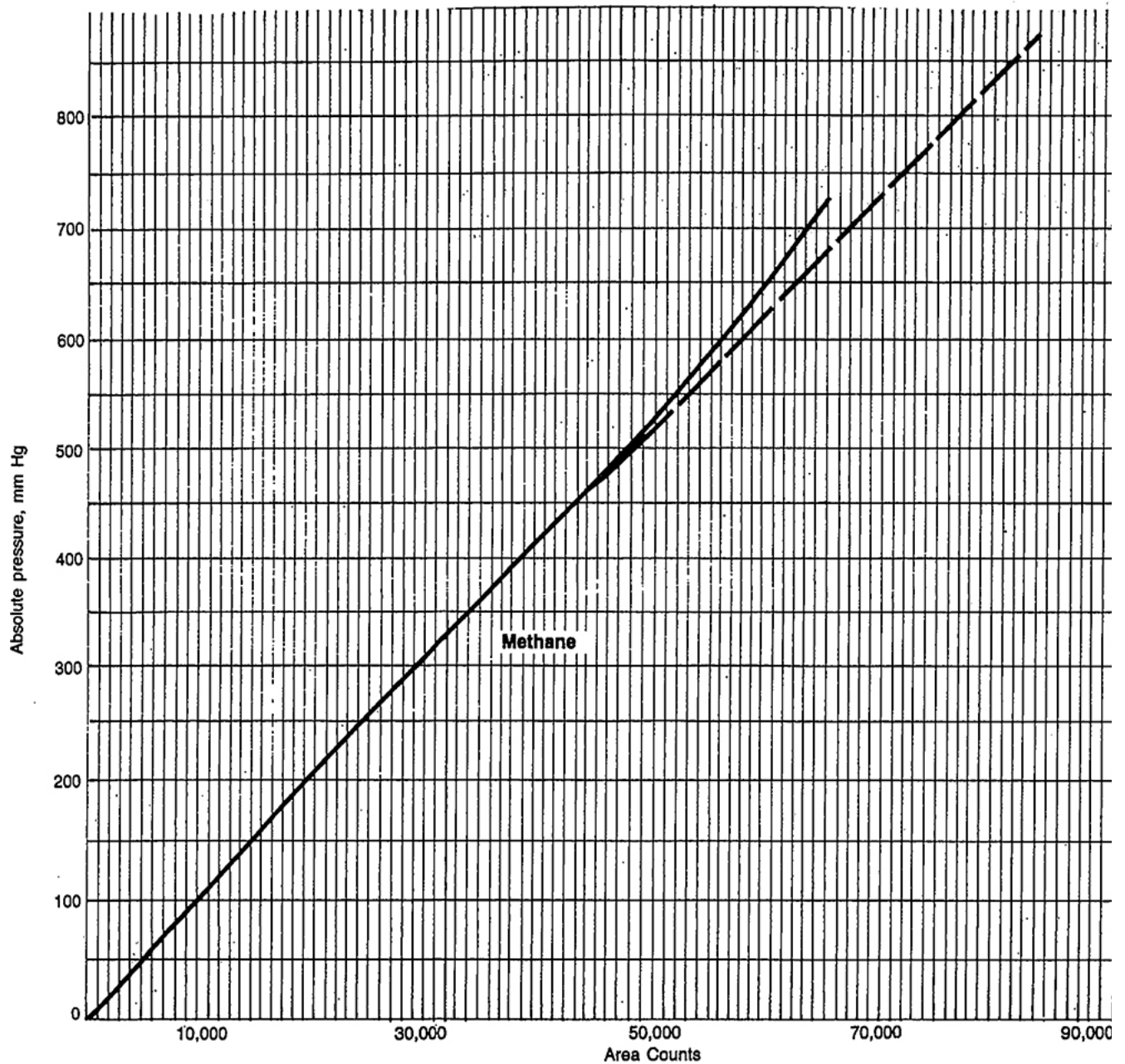


FIG. A2.2 Linearity of Detector Response

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Note A2.4—It is recommended that the integrator/computer has the capability to print out retention times of peak maxima to aid in peak identification and to monitor instrument conditions for unknown changes.

### A3. PRECAUTIONARY STATEMENTS

#### A3.1 Flammable Liquefied Gases

##### A3.1.1

Keep away from sparks and open flame.

##### A3.1.2

Keep container closed.

##### A3.1.3

Use with adequate ventilation.

##### A3.1.4

Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosive electrical devices and heaters.

**A3.1.5**

Avoid prolonged breathing of vapor or spray mist.

**A3.1.6**

Avoid prolonged or repeated skin contact.

**A3.2 Compressed Gases (Helium, Nitrogen)****A3.2.1**

Keep container closed.

**A3.2.2**

Use adequate ventilation.

**A3.2.3**

Do not enter storage areas unless adequately ventilated.

**A3.2.4**

Always use a pressure regulator.

**A3.2.5**

Release regulator tension before opening cylinder.

**A3.2.6**

Do not transfer to cylinder other than one in which gas is received.

**A3.2.7**

Do not mix gases in cylinders.

**A3.2.8**

Do not drop cylinders.

**A3.2.9**

Make sure cylinder is supported at all times.

**A3.2.10**

Stand away from cylinder outlet when opening cylinder valve.

**A3.2.11**

Keep cylinder out of sun and away from heat.

**A3.2.12**

Keep cylinder from corrosive environment.

**A3.2.13**

Do not use cylinder without label.

**A3.2.14**

Do not use dented or damaged cylinder.

**A3.2.15**

For technical use only. Do not use for inhalation purposes.

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**Designation: D 3120 – 96**

An American National Standard

# Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry<sup>1</sup>

This standard is issued under the fixed designation D 3120; 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 determination of sulfur in the range from 3.0 to 100 ppm (ug/g) in light liquid hydrocarbons boiling in the range from 26 to 274°C (80 to 525°F).

### 1.2

This test method may be extended to liquid materials with higher sulfur concentrations by appropriate dilution.

### 1.3

The preferred units are micrograms per grams. Values stated in SI units are to be regarded as the standard. Values in inch-pound units are for information only.

## 1.4

*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. For specific hazard statements, see 6.3, 6.4, 6.8, and 6.10.*

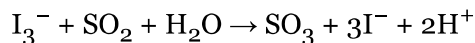
## 2. Summary of Test Method

### 2.1

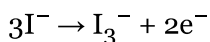
A liquid sample is injected into a combustion tube maintained at about 800°C having a flowing stream of gas containing about 80 % oxygen and 20 % inert gas (for example, nitrogen, argon, etc.). Oxidative pyrolysis converts the sulfur to sulfur dioxide which then flows into a titration cell where it reacts with triiodide ion present in the electrolyte. The triiodide thus consumed, is coulometrically replaced and the total current required to replace it is a measure of the sulfur present in the sample injected.

### 2.2

The reaction occurring in the titration cell as sulfur dioxide enters is:



The triiodide ion consumed in the above reaction is generated coulometrically thus:



### 2.3

These microequivalents of triiodide (iodine) are equal to the number of microequivalents of titratable sample ion entering the titration cell.

## 3. Significance and Use

### 3.1

This test method is used to determine trace quantities of sulfur in reformer charge stocks and similar petroleum fractions where such trace concentrations of sulfur are deleterious to the performance and life of the catalyst used in the process. Higher concentrations of sulfur in products analyzed by this test method after appropriate dilution are often detrimental to the use of the product.

## 4. Interferences

### 4.1

This test method is applicable in the presence of total halide concentrations of up to 10 times the sulfur level and total nitrogen concentrations of up to 1000 times the sulfur level.

## 4.2

This test method is not applicable in the presence of total heavy metal concentrations (for example, Ni, V, Pb, etc.) in excess of 500 µg/g (ppm).

Note 1—To attain the quantitative detectability that the method is capable of, stringent techniques must be employed and all possible sources of sulfur contamination must be eliminated.

## 5. Apparatus<sup>2</sup>

### 5.1

*Pyrolysis Furnace*—The sample should be pyrolyzed in an electric furnace having at least two separate and independently controlled temperature zones, the first being an inlet section that can maintain a temperature sufficient to volatilize all the organic sample. The second zone shall be a pyrolysis section that can maintain a temperature sufficient to pyrolyze the organic matrix and oxidize all the organically bound sulfur. A third outlet temperature zone is optional.

#### 5.1.1

Pyrolysis furnace temperature zones for light liquid petroleum hydrocarbons should be variable as follows:

Inlet zone	up to at least 700°C
Center pyrolysis zone	800 to 1000°C
Outlet zone (optional)	up to at least 800°C

### 5.2

*Pyrolysis Tube*, fabricated from quartz and constructed in such a way that a sample, which is vaporized completely in the inlet section, is swept into the pyrolysis zone by an inert gas where it mixes with oxygen and is burned. The inlet end of the tube shall hold a septum for syringe entry of the sample and side arms for the introduction of oxygen and inert gases. The center or pyrolysis section should be of sufficient volume to ensure complete pyrolysis of the sample.

### 5.3

*Titration Cell*, containing a sensor-reference pair of electrodes to detect changes in triiodide ion concentration and a generator anode-cathode pair of electrodes to maintain constant triiodide ion concentration and an inlet for a

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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<sup>2</sup> The apparatus described in Sections 5.1 to 5.5 inclusive, is similar in specifications to equipment available from Dohrmann Div. of Rosemount, 3240 Scott Blvd., Santa Clara, CA 95050. For further detailed discussions, in equipment, see: Preprints—Division of Petroleum Chemistry, American Chemical Society, Vol 1, No. 3, Sept. 7–12, 1969, p. B232 “[ ] Determination of Sulfur, Nitrogen, and Chlorine in Petroleum by Microcoulometry,” by Harry V. Drushel.

284 gaseous sample from the pyrolysis tube. The sensor electrode shall be platinum foil and reference electrode platinum wire in saturated triiodide half-cell. The generator anode and cathode half-cell shall also be platinum. The titration cell shall require mixing, which can be accomplished through the use of a magnetic stirring bar, stream of inert gas, or other suitable means.

**Note 2: Caution**—Excessive speed will decouple the stirring bar, causing it to rise in the cell and damage the electrodes. The creation of a slight vortex is adequate.

## 5.4

*Microcoulometer*, having variable attenuation, gain control, and capable of measuring the potential of the sensing-reference electrode pair, and comparing this potential with a bias potential, amplifying the potential difference, and applying the amplified difference to the working-auxiliary electrode pair so as to generate a titrant. Also the microcoulometer output voltage signal shall be proportional to the generating current.

## 5.5

*Recorder*, having a sensitivity of at least 0.1 mV/in. with chart speeds of 1/2 to 1 in./min. Use of a suitable electronic or mechanical integrator is recommended but optional.

## 5.6

*Sampling Syringe*—A microlitre syringe of 10- $\mu$ L capacity capable of accurately delivering 1 to 10  $\mu$ L of sample into the pyrolysis tube. 3-in. by 24-gage needles are recommended to reach the inlet zone of the pyrolysis furnace.

**Note 3**—Since care must be taken not to overload the pyrolyzing capacity of the tube by too fast a sample injection rate, means should be provided for controlling the sample addition rate (0.1 to 0.2  $\mu$ L/s).

## 6. Reagents and Materials

### 6.1

*Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>3</sup>

Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

## 6.2

*Purity of Water*—The water used in preparing the cell electrolyte should be demineralized or distilled or both. Water of high purity is essential.

Note 4—Distilled water obtained from an all borosilicate glass still, fed from a demineralizer, has proven very satisfactory.

## 6.3

*Acetic Acid* (rel dens 1.05)—Glacial acetic acid ( $\text{CH}_3\text{COOH}$ ).

Note 5: **Warning**—Poison. Corrosive. Combustible. May be fatal if swallowed. Causes severe burns. Harmful if inhaled.

## 6.4

*Argon, Helium, or Nitrogen*, high purity grade (HP),<sup>4</sup> used as carrier gas.

Note 6: **Warning**—Compressed gas under high pressure. Gas reduces oxygen available for breathing.

## 6.5

*Cell Electrolyte Solution*—Dissolve 0.5 g of potassiumiodide (KI) and 0.6 g of sodium azide ( $\text{NaN}_3$ ) in approximately 500 mL of high-purity water, add 5 mL of acetic acid( $\text{CH}_3\text{COOH}$ ) and dilute to 1000 mL.

Note 7—Bulk quantities of the electrolyte should be stored in a dark bottle or in a dark place and be prepared fresh at least every 3 months.

## 6.6

*Gas Regulators*—Two-stage gas regulators must be used on the reactant and carrier gas.

## 6.7

*Iodine* (I), 20 mesh or less, for saturated reference electrode.

## 6.8

**Isooctane**<sup>5</sup> (2,2,4-trimethylpentane).



Note 8: **Warning**—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire.

Note 9—The most reliable solvent is a sulfur-free form of the sample type to be analyzed. Alternatively, use a high-purity form of cyclohexane [boiling point 80°C (176°F)], isooctane (2,2,4-trimethyl pentane) [boiling point, 99.3°C (211°F)], or hexadecane [boiling point, 287.5°C (549.5°F)].

## 6.9

*n*-Butyl Sulfide (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>S.

## 6.10

Oxygen, high purity grade (HP),<sup>4</sup> used as the reactant gas.

Note 10: **Warning**—Oxygen vigorously accelerates combustion.

## 6.11

Potassium Iodide (KI), fine granular.

## 6.12

Sodium Azide (NaN<sub>3</sub>), fine granular.

Note 11: **Warning**—Toxic, causes eye and skin irritation; explosive.

## 6.13

*Sulfur, Standard Solution (approximately 30 μg/g (ppm))*—Pipet 10 mL of sulfur stock solution (reagent 6.14) into a 100-mL volumetric flask and dilute to volume with isooctane.

Note 12—The analyst may choose other sulfur compounds for standards appropriate to sample boiling range and sulfur type which cover the concentration range of sulfur expected.

## 6.14

*Sulfur, Standard Stock Solution (approximately 300 μg/g (ppm))*—Weigh accurately 0.5000 g of *n*-butyl sulfide into a tared 500-mL volumetric flask. Dilute to the mark with isooctane and reweigh.

$$S, \text{ ppm } (\mu\text{g/g}) = \frac{\text{g of } n\text{-butyl sulfide} \times 0.2187 \times 10^6}{\text{g of } (n\text{-butyl sulfide} + \text{solvent})}$$

## 7. Preparation of Apparatus

### 7.1

Carefully insert the quartz pyrolysis tube in the pyrolysis furnace and connect the reactant and carrier gas lines.

## 7.2

Add the electrolyte solution to the titration cell and flush several times. Maintain an electrolyte level of  $\frac{1}{8}$  to  $\frac{1}{4}$  in. (3.2 to 6.4 mm) above the platinum electrodes.

## 7.3

Place the heating tape on the inlet of the titration cell.

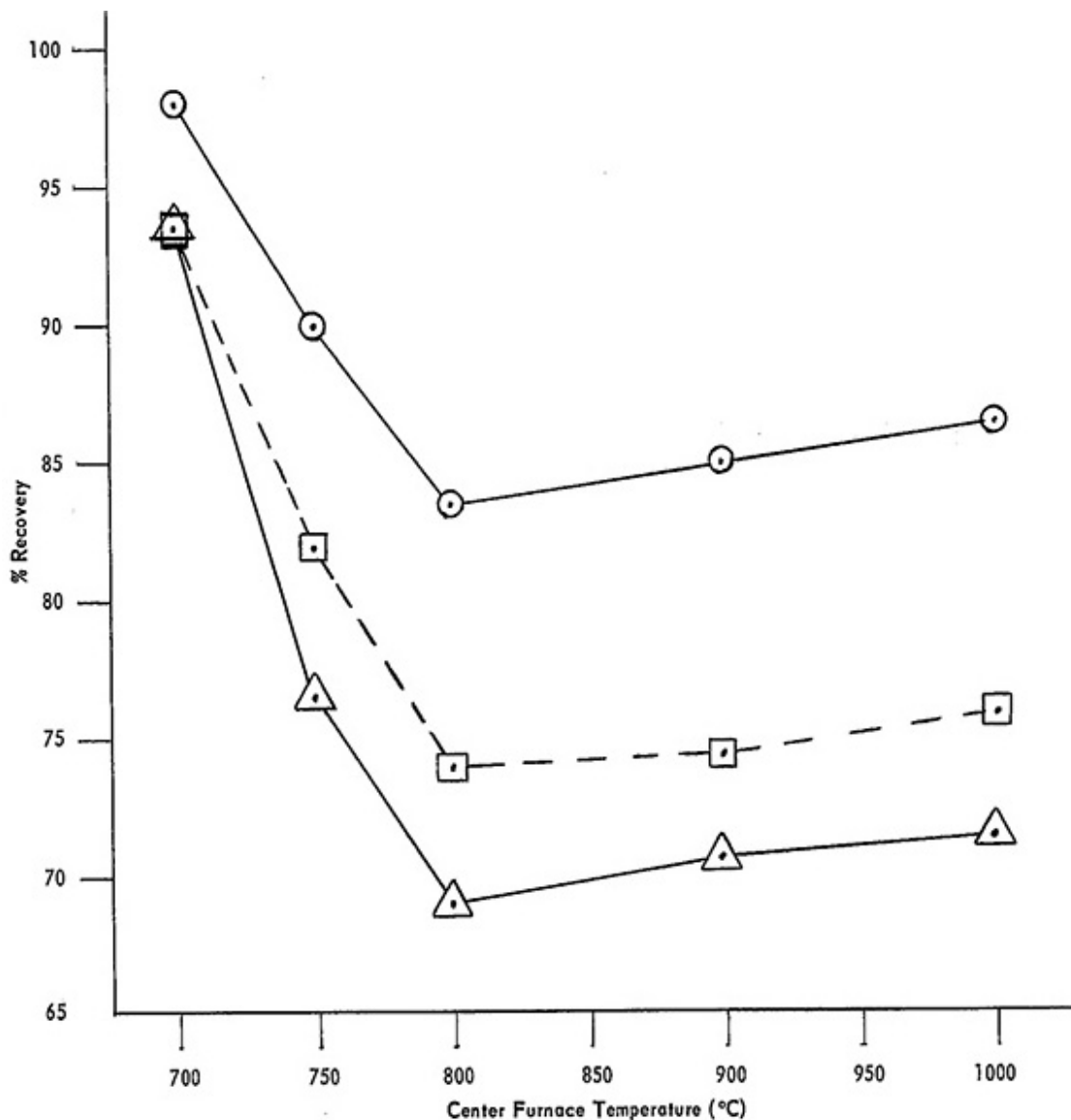
## 7.4

Position the platinum foil electrodes (mounted on the moveable cell head) so that the gas inlet flow is parallel to the electrodes with the generator anode adjacent to the generator cathode. Assemble and connect the coulometer and recorder (integrator optional) as designed or in accordance with the manufacturer's instructions. Figure X1.2 illustrates the typical

<sup>3</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

<sup>4</sup> High-purity grade gas has a minimum purity of 99.995 %.

<sup>5</sup> Pesticide test grade such as Mallinckrodt "Nano-grade" isooctane has been found satisfactory.



Oxidative sulfur system: Thiophene in cyclohexane (10 ppm S) using 0.06% azide electrolyte

Legend	Flow rate (cc/min)		
	Oxygen	Argon	O <sub>2</sub> /Ar ratio
○—○	40	160	1:4
□- -□	100	100	1:1
△—△	160	40	4:1

**Fig. 1 Percent Recovery versus Temperature (°C)**

assembly and gas flow through a coulometric apparatus.

**7.4.1**

Turn the heating tape on.

**7.5**

Adjust the flow of the gases, the pyrolysis furnace temperature, titration cell, and the coulometer to the desired operating conditions. Typical operational conditions are given in Table 1.

## 8. Calibration and Standardization

### 8.1

Prepare a series of calibration standards covering the range of sulfur concentration expected. Follow instructions in 6.13, 6.14, or dilute to appropriate level with *isooctane*.

### 8.2

Adjust the operational parameters (7.5).

Note 13—See Fig. 1 for the variance of percent recoveries with gas ratios and temperature.

### 8.3

The sample size can be determined either volumetrically or by mass. The sample size should be 80 % or less of the syringe capacity.

#### 8.3.1

Volumetric measurement can be obtained by filling the syringe with about 8  $\mu\text{L}$  or less of sample, being careful to eliminate bubbles, retracting the plunger so that the lower liquid meniscus falls on the 1- $\mu\text{L}$  mark, and recording the volume of liquid in the syringe. After the sample has been injected, again retract the plunger so that the lower liquid meniscus falls on the 1- $\mu\text{L}$  mark, and record the volume of liquid in the syringe. The difference between the two volume

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TABLE 1 Typical Operational Conditions

Reactant gas flow (oxygen), $\text{cm}^3/\text{min}$	160
Carrier gas flow (Ar, He, N) $\text{cm}^3/\text{min}$	40
Furnace temperature; $^{\circ}\text{C}$ :	
Inlet zone	700
Pyrolysis zone	800
Outlet zone	800
Titration cell	set to produce adequate mixing
Coulometer:	
Bias voltage, mV	160
Gain	low (approximately 200)

readings is the volume of sample injected.

### 8.3.2

Alternatively, the sample injection device may be weighed before and after the injection to determine the amount of sample injected. This technique provides greater precision than the volume delivery method, provided a balance with a precision of  $\pm 0.00001$  g is used.

## 8.4

Insert the syringe needle through the inlet septum up to the syringe barrel and inject the sample or standard at an even rate not to exceed 0.1 to 0.2  $\mu\text{L/s}$ . If a microlitre syringe is used with an automatic injection adapter, the injection rate (volume/pulse) should be calibrated to deliver 0.1 to 0.2  $\mu\text{L/s}$ .

## 8.5

Repeat the measurement of each calibration standard at least three times.

Note 14—Not all of the sulfur in the sample comes through the furnace as titratable  $\text{SO}_2$ . In the strongly oxidative conditions of the pyrolysis tube some of the sulfur is also converted to  $\text{SO}_3$  which does not react with the titrant. Accordingly, sulfur standards of n-butyl sulfide in *isooctane* or sulfur standards appropriate to sample boiling range and sulfur type and sulfur concentration should be prepared to guarantee adequate standardization. Recoveries less than 75 % are to be considered suspect. Low recoveries are an indication to the operator that he should check his parameters, his operating techniques, and his coulometric system. If the instrument is being operated properly, recoveries between 75 and 90 % are to be expected.

Satisfactory standard materials<sup>6</sup> are given in Table 2.

## 8.6

If the fraction of sulfur converted to  $\text{SO}_2$  drops below 75 % of the standard solutions, fresh standards should be prepared. If a low conversion factor persists, procedural details should be reviewed.

## 9. Procedure

### 9.1

Flush the 10- $\mu\text{L}$  syringe several times with the unknown sample. Determine the sulfur concentration in accordance with 8.2 to 8.6.

### 9.2

Sulfur concentration may require adjustment of sensitivity settings or sample volume or both.

## 10. Calculation

**10.1**

Calculate the sulfur content of the sample in parts per million, ppm  $\mu\text{g/g}$ , by mass as follows:

$$\text{Sulfur, ppm } \mu\text{g/g} = (A \times 1.99)/(R \times M \times F) \quad (1)$$

$$\text{Sulfur, ppm} = (A \times 1.99 \times 10^3)/(R \times V \times D \times F) \quad (2)$$

where:

$A$	=	area under curve, in. <sup>2</sup>
1.99	=	derivation will be found in X1.3,

TABLE 2 Satisfactory Standard Materials

Sample Type	Boiling Point Range °C(°F)	Sulfur Compound
Naphthas	26 to 204	cyclohexane sulfide
	(80 to 400)	
Jet fuels and stove oil	177 to 274	benzyl-thiophene
	(350 to 525)	

$R$	=	coulometer range switch setting, $\Omega$
$M$	=	mass of sample, g (volume $\times$ density),
$V$	=	volume of sample, $\mu\text{L}$ ,
$D$	=	density of sample, g/mL, and
$F$	=	recovery factor, fraction of sulfur in standard that is titrated, ratio of ppm sulfur determined in standard divided by the known ppm sulfur in standard. $F = (A \times 1.99)/(R \times M \times C_{\text{std}}$

where:

$C_{\text{std}}$	=	concentration of standard, ppm.
------------------	---	---------------------------------

**10.2**

Derivation of the calculation equation will be found in X1.3.

Note 15—The calculation equation is valid only when the chart speed is 0.5 in./min and a 1-mV (span) recorder with a sensitivity of 0.1 mV/in. is used.

Note 16—If a disk integrator is used, see X1.3 for calculations, derivations, and equations.

Note 17—A more general form of the equation in 10.1 which is not dependent on the use of a particular recorder scale nor a disk integrator is as follows:

$$\text{sulfur, ppm } (\mu\text{g/g}) = \frac{(A) (X) (0.166)}{(R) (Y) (M) (F)}$$

where:

A	=	area in appropriate units,
X	=	recorder sensitivity for full-scale response (mv),

$$0.166 = \frac{(16 \text{ gS/eq}) (10^{-3} \text{ V/mV}) (10^6 \mu\text{g/g})}{(96 \ 500 \text{ coulombs/eq})},$$

R	=	resistance, $\Omega$ ,
Y	=	area equivalence for a full-scale response on the recorder per second ... area units per second,
M	=	mass of sample, g, and
F	=	recovery factor.

## 11. Precision and Bias

### 11.1

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

#### 11.1.1

*Repeatability*—The difference between successive 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 28 % of the average value only in one case in twenty.

#### 11.1.2

*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 38 % of the average only in one case in twenty.

### 11.2

*Bias*—Since there is no accepted reference material suitable for determining the bias for the procedure in this test

<sup>6</sup> Wallace, L. D., "Comparison of Oxidative and Reductive Methods for the Microcoulometric Determinations of Sulfur in Hydrocarbons," *Analytical Chemistry*, Vol 42, March 1970, p. 393.

method, no statement on bias is made.<sup>7</sup>

## 12. Keywords

### 12.1

light hydrocarbons; microcoulometry; sulfur

## APPENDIX

### X1. DERIVATION OF COULOMETRIC CALCULATIONS USED IN SECTION 10.1

#### (Nonmandatory Information)

#### X1.1

The configuration of the pyrolysis tube and furnace may be constructed as is desirable as long as the operating parameters are met. Figure X1.1 is typical of apparatus currently in use.

#### X1.2

A typical assembly and oxidative gas flow through a coulometric apparatus for the determination of trace sulfur is shown in Fig. X1.2.

#### X1.3 Derivation of Equations:

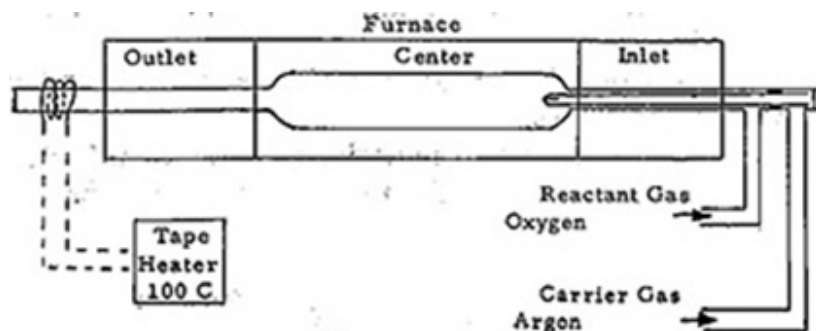


Fig. X1.1 Pyrolysis Tube

#### X1.3.1

The derivation of the equations used in the calculation section is based on the coulometric replacement of the triiodide (iodine) ions consumed in the micro-coulometric titration cell reaction ( $I_3^- + 2e^- \rightarrow 3I^-$ ). The quantity of the reactant formed (triiodide ions) between the beginning and the interruption of current at the end of the titration is directly proportional to the net charge transferred,  $Q$ .

#### X1.3.2



In most applications a constant current is used so that the product of current,  $i$ , in amperes (coulombs per second), multiplied by the time,  $T$  (seconds), required to reach the end point provides a measure of the charge,  $Q$  (coulombs), necessary to generate the iodine equivalent to the reactant; that is,  $Q = it$ . Therefore, the number of equivalents of reactant is equal to  $Q/F$ , where  $F$  is the Faraday constant, 96 500 C per equivalent.

### X1.3.3

Therefore, the expression to be solved to find the mass of reactant is:

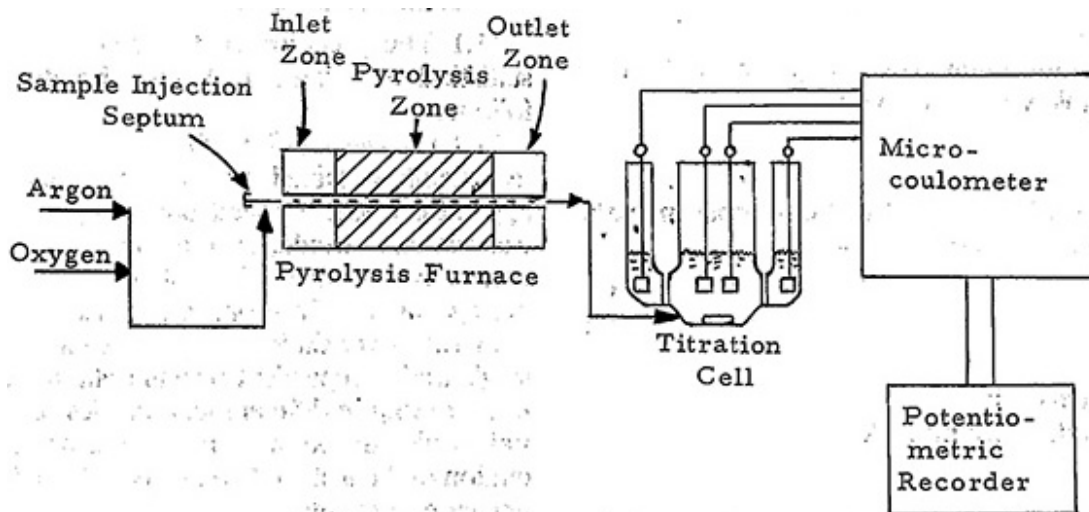


Fig. X1.2 Flow Diagram for Coulometric Apparatus for Trace Sulfur Determination

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$$\text{Concentration of sulfur} = \frac{\text{mass of sulfur, g}}{\text{mass of sample, g}} = \frac{\frac{Q(C)}{FC} \times \frac{16 \text{ g}}{\text{eq}}}{\text{mass of sample, g}} \quad (\text{X1.1})$$

$$\mu\text{g S} = A \text{ in.}^2 \times \frac{\frac{0.1 \text{ mV}}{\text{in.}} \times \frac{2 \text{ min}}{\text{in.}} \times \frac{60 \text{ s}}{\text{min}} \times \frac{10^{-3} \text{ V}}{\text{mV}} \times \frac{16 \text{ g}}{\text{eq}} \times \frac{10^6 \mu\text{g}}{\text{g}}}{R(\Omega) \times \frac{96\,500 \text{ C}}{\text{eq}} \times \frac{\text{A} \cdot \text{s}}{\text{C}} \times f)} \quad (\text{X1.2})$$

where:

$A \text{ in.}^2$	=	peak area measured in square inches,
$0.1 \text{ mV/in}$	=	millivolt span of upscale deflection for the recorder
$2 \text{ min/in.}$	=	chart speed in minutes per inch,
$60 \text{ s/min}$	=	conversion of time in minutes to seconds,
$10^{-3} \text{ V/mV}$	=	conversion of volts to millivolts,
$16 \text{ g/eq}$	=	gram-equivalent of sulfur,
$10^6 \mu\text{g/g}$	=	micrograms per gram conversion factor,
$R(\Omega)$	=	microcoulometer range switch setting in ohms,
substituting $V/R$	=	1 (amps)

$$Q(A \cdot s) = \frac{A \text{ in.}^2 \times \frac{0.1 \text{ mV}}{\text{in.}} \times \frac{2 \text{ min}}{\text{in.}} \times \frac{60 \text{ s}}{\text{min}} \times \frac{10^{-3} \text{ V}}{\text{mV}}}{R(\Omega)} \quad (\text{X1.3})$$

$F$	=	96 500 C/eq
	=	Faraday's constant <sup>8</sup> (electrical equivalence of one gram-equivalent mass of any substance)
A·s/C	=	conversion of coulombs to ampere-seconds, and
$f$	=	recovery factor (ratio of ppm S determined in standard versus known ppm S in standard),

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3} \text{ A} \cdot \text{s} \times \frac{16 \text{ g}}{\text{eq}} \times \frac{10^6 \mu\text{g}}{\text{g}}}{R \times \frac{96 \ 500 \text{ C}}{\text{eq}} \times \frac{\text{A} \cdot \text{s}}{\text{C}} \times f} \quad (\text{X1.4})$$

Therefore,

$$\mu\text{g S} = \frac{A \times 12 \times 10^{-3} \times 16 \times 10^6 \mu\text{g}}{R \times 96 \ 500 \times f} \quad (\text{X1.5})$$

Therefore,

$$\mu\text{g S} = (A \times 1.99)/(R \times f) \quad (\text{X1.6})$$

Since ppm =  $\mu\text{g/g}$ :

$$\text{ppm S} = \frac{A \times 1.99}{R \times f \times \text{volume, } \mu\text{L}} \times 10^{-3} \frac{\text{mL}}{\mu\text{L}} \times \text{density, } \frac{\text{g}}{\text{mL}} \quad (\text{X1.7})$$

$$\text{ppm S} = \frac{A \times 1.99 \times 10^3}{R \times f \times \text{volume} \times \text{density}} \quad (\text{X1.8})$$

since mass = volume  $\times$  density

$$\text{ppm S} = (A \times 1.99)/(R \times f \times \text{mass, g}) \quad (\text{X1.9})$$

### X1.3.4

*Derivation with Disk Integrator*— $A$  in Eq X1.6 is expressed as  $\text{in.}^2$ . However, it may also be expressed as counts. Therefore,  $A \text{ in.}^2 = \text{counts} \times 10^{-3}$  since  $1 \text{ in.}^2 = 1000 \text{ counts}$ . Therefore, substituting  $\text{counts} \times 10^{-3}$  for  $A$  in Eq X1.6 gives

$$\mu\text{g S} = (\text{counts} \times 1.99 \times 10^3)/(R \times f)$$

Then:

$$\text{ppm S} = \frac{\text{counts} \times 1.99}{R \times \text{volume, } \mu\text{L} \times \text{density, } \frac{\text{g}}{\text{mL}} \times f} \quad (\text{X1.10})$$

$$\text{ppm S} = (\text{counts} \times 1.99 \times 10^{-3})/(R \times \text{mas, g} \times f)$$

Note X1.1—Counts =  $100 \times$  number of integrator per full-scale excursions.

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<sup>7</sup> Supporting data are available from ASTM. Request RR: D02-1036.

<sup>8</sup> The value of the Faraday has been redetermined in 1960 by the National Bureau of Standards: the new value is  $96\,489 \pm 2$  coulombs (chemical scale).

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Designation: D 4891 – 89 (Reapproved 2006)

# Standard Test Method for Heating Value of Gases in Natural Gas Range by Stoichiometric Combustion<sup>1</sup>

This standard is issued under the fixed designation D 4891; 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 determination of the heating value of natural gases and similar gaseous mixtures within the range of composition shown in Table 1.

1.2 *This standard involves combustible gases. It is not the purpose of this standard to address the safety concerns, if any, associated with their 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>

D 1826 Test Method for Calorific (Heating) Value of Gases in Natural Gas Range by Continuous Recording Calorimeter

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

## 3. Terminology

3.1 All of the terms defined in Test Method D 1826 are included by reference.

### 3.2 Descriptions of Terms:

3.2.1 *combustion ratio*—the ratio of combustion air to gaseous fuel.

3.2.2 *stoichiometric ratio*—the combustion ratio when the quantity of combustion air is just sufficient to convert all of the combustibles in the fuel to water and carbon dioxide.

3.2.3 *burned gas parameter*—a property of the burned gas after combustion which is a function of the combustion ratio.

3.2.4 *critical combustion ratio*—for a specific burned gas parameter, the combustion ratio at which a plot of burned gas parameter versus combustion ratio has either maximum value or maximum slope.

**TABLE 1 Natural Gas Components and Range of Composition Covered**

Compound	Concentration Range, mole, %
Helium	0.01 to 5
Nitrogen	0.01 to 20
Carbon dioxide	0.01 to 10
Methane	50 to 100
Ethane	0.01 to 20
Propane	0.01 to 20
<i>n</i> -butane	0.01 to 10
isobutane	0.01 to 10
<i>n</i> -pentane	0.01 to 2
Isopentane	0.01 to 2
Hexanes and heavier	0.01 to 2

## 4. Summary of Test Method

4.1 Air is mixed with the gaseous fuel to be tested. The mixture is burned and the air-fuel ratio is adjusted so that essentially a stoichiometric proportion of air is present. More exactly, the adjustment is made so that the air-fuel ratio is in a constant proportion to the stoichiometric ratio which is a relative measure of the heating value. To set this ratio, a

characteristic property of the burned gas is measured, such as temperature or oxygen concentration.

## 5. Significance and Use

5.1 This test method provides an accurate and reliable procedure to measure the total heating value of a fuel gas, on a continuous basis, which is used for regulatory compliance, custody transfer, and process control.

5.2 Some instruments which conform to the requirements set forth in this test method can have response times on the order of 1 min or less and can be used for on-line measurement and control.

5.3 The method is sensitive to the presence of oxygen and nonparaffin fuels. For components not listed and composition ranges that fall outside those in Table 1, modifications in the method may be required to obtain correct results.

## 6. Apparatus

6.1 A suitable apparatus for carrying out the stoichiometric combustion method will have at least the following four components: flow meter or regulator, or both; combustion chamber; burned gas sensor; and electronics. The requirement for each of these components is discussed below. The detailed

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D03 on Gaseous Fuels and is the direct responsibility of Subcommittee D03.03 on Determination of Heating Value and Relative Density of Gaseous Fuels.

Current edition approved June 1, 2006. Published June 2006. Originally approved in 1989. Last previous edition approved in 2001 as D 4891-89 (2001).

<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.

design of each of these components can vary. Two different apparatus are shown in Fig. 1 and Fig. 2. In each figure the equivalent of the four necessary components are enclosed in dashed lines.

6.2 *Overview*—Air and fuel enter the apparatus and the flow of each is measured. Alternatively, only one gas flow need be measured if the flow of the other is kept the same during measurement and calibration. This is illustrated in Fig. 2. Next there is a combustion chamber in which the air and fuel are mixed and burned. This can be as simple as a bunsen or meeker burner, but precautions should be taken that subsequent measurements of burned gas characteristics are not influenced by ambient conditions. Finally, there is a sensor in the burned gas which measures a property of this gas that is sensitive to the combustion ratio and has a unique feature at the stoichiometric ratio. Two such properties are temperature and oxygen concentrations, and either can be measured.

6.3 *Flow Meter and/or Regulator*—The flow measurement part of the apparatus should have an accuracy and precision of the order of 0.1 %. Likewise, if the flow is to be kept

constant, the flow regulator should maintain this constant value within 0.1 %. The meter or regulator for natural gas must maintain this precision and accuracy over the density and viscosity ranges consistent with the composition range in Table 1.

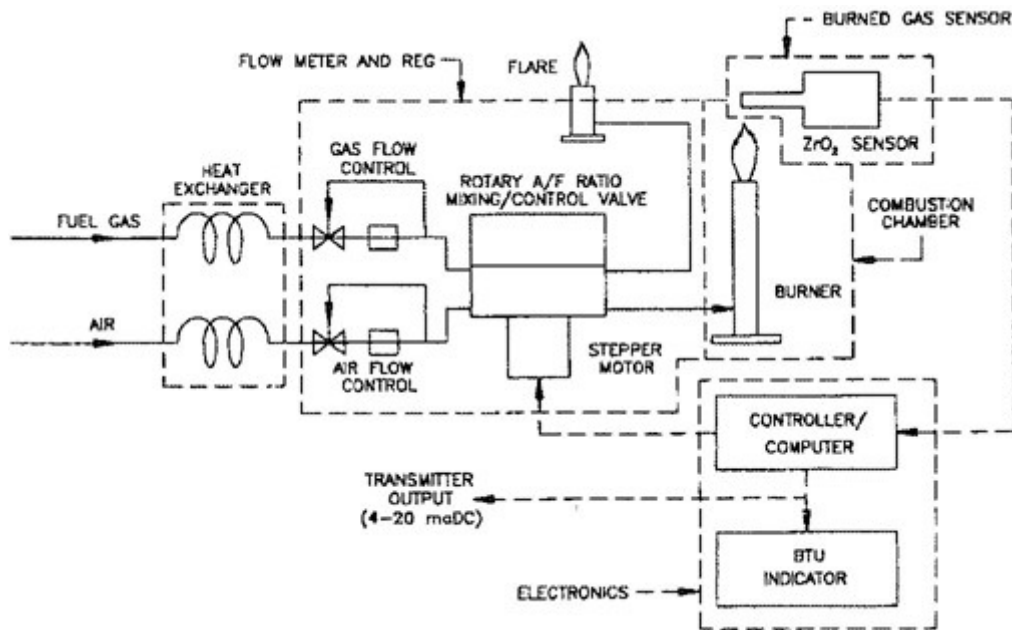
#### 6.4 Combustion Chamber:

6.4.1 There are two different types of combustion chambers that may be used. In the first type the air and fuel are mixed and burned in a single burner. The apparatus shown in Fig. 1 has this type of combustion chamber.

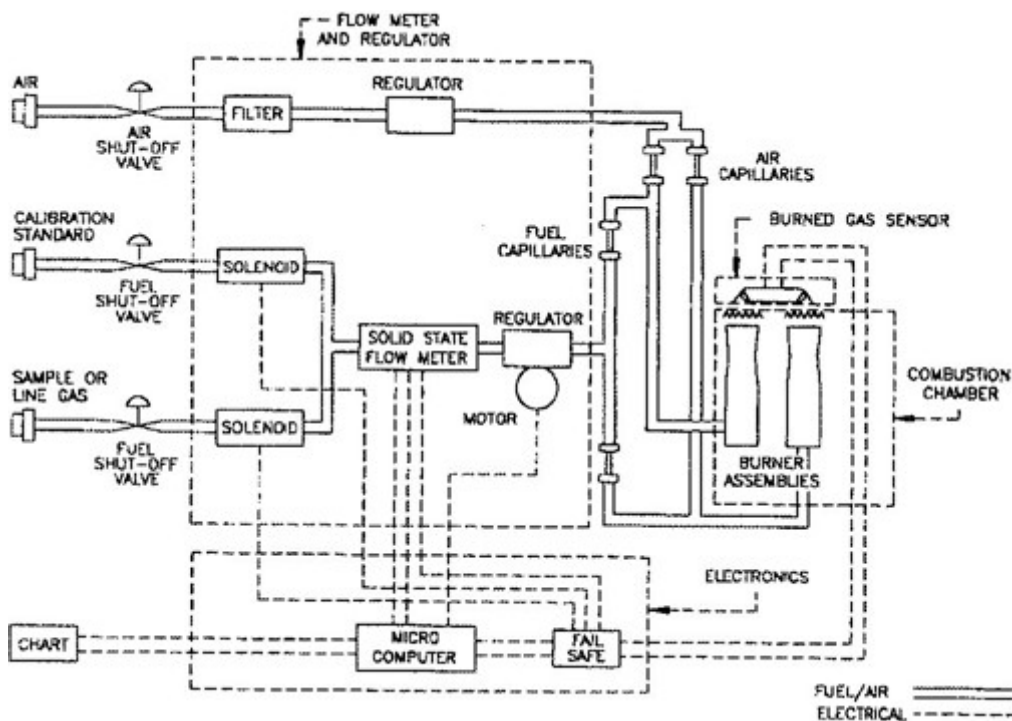
6.4.2 In the second type of combustion chamber, the air and fuel are each divided into two streams, and combustion takes place simultaneously in two burners. The division of air flow must be such that the proportion of air going to each burner always remains the same. Likewise the division of fuel flow must always remain the same even through fuel composition changes. Another requirement is that the flow divisions be such that one burner has a mixture with a slightly higher combustion ratio than the other. The apparatus shown in Fig. 2 has this type of combustion chamber.

#### 6.5 Burned Gas Sensor:

6.5.1 The burned gas sensor must measure a characteristic of the burned gas which is a function of the combustion ratio and for which there is a critical combustion ratio related to the



**FIG. 1 Gas Btu Transmitter (Functional Overview)**



**FIG. 2 Stoichiometric Combustion Apparatus**

stoichiometric ratio. A combustion chamber of the first type (Fig. 1) would have one sensor in the burned gas and its output signal would constitute the desired measurement. In a combustion chamber of the second type (Fig. 2) there would be a sensor in the burned gas from each burner. The difference between the two output signals would constitute the desired measurement.

6.5.2 There are several properties of the burned gas which are related uniquely to the combustion ratio. A burned gas sensor may be selected which provides a measure of any one of these, for example, either temperature or oxygen partial pressure.

6.6 *Electronics*—Electronics are used to receive the signals from the components described above to control the flow of gases into the combustion chamber in response to the signal from the burned gas sensor and to provide a digital or analog output signal, or both, which is proportional to the heating value of the gaseous fuel.

6.7 *Temperature Stability and Operating Environment*— The method is capable of operating over a range of temperatures limited only by the specific apparatus used to realize the method. It is desirable to equilibrate the air and fuel temperatures before the gases are measured. The electronics should also be stabilized against temperature changes and the burned gas sensor should be insensitive to changes in the ambient conditions.

## 7. Reagents and Materials

7.1 *Physical Contamination*—The air and gas must be free of dust, liquid, water, liquid hydrocarbons, and other entrained solids. Foreign materials should be removed by a sample line filter. To avoid any problems in the line from any liquid accumulation, pitch the line to a low point and provide a drip leg.

7.2 *Chemical Contamination*—The air must be free of combustible compounds. The oxygen content and the absolute humidity of the air should be the same during measurement



as during calibration.

2

## 8. Calibration and Standardization

8.1 The calibration factor,  $F$ , and the constant,  $B$ , in the equation,  $C = F \cdot R + B$ , are determined through an initial calibration, in which the critical combustion ratios of at least two standard gases of known but different heating values are measured using the procedure described in 9.1.

8.2 The calibration factor,  $F$ , is routinely redetermined at regular intervals under field conditions using a calibration gas of known heating value. The constant,  $B$ , is not adjusted in the routine calibrations. The interval between routine calibrations must be determined under the specific operating conditions, and is usually of the order of 24 h. Determination of  $F$  establishes the amount of net oxygen per standard volume of combustion air. Variations in net oxygen constant can be caused by several factors, such as changes in absolute humidity or the presence of contaminants in the air supply.

## 9. Procedure

9.1 Measure the burned gas parameter at different combustion ratios and determine that combustion ratio for which the parameter has a specified characteristic such as a maximum, minimum, or maximum rate of change.

9.1.1 Use an apparatus such as in Fig. 1 or Fig. 2 where the components of the apparatus meet the requirements of Section 6. If the apparatus has two flow meters, the combustion ratio is the ratio of the output of the air flow meter divided by the output of the fuel flow meter. If the apparatus has only one flow meter, then the combustion ratio is set numerically equal to either the output of the air flow meter or the reciprocal of the output of the fuel flow meter. The burned gas parameter is a function of the combustion ratio and is measured at different combustion ratios. The critical combustion ratio,  $R$ , is taken as that point where this function has a maximum value, minimum value, or maximum rate of change. The heating value,  $C$ , is calculated from the equation

$$C = F \cdot R + B, \quad (1)$$

where the constants  $B$  and  $F$  are determined as described in 8.1 and 8.2.

9.1.2 This procedure may be automated, for example, by using a microprocessor in the electronics.

9.2 For making laboratory measurements of highest precision, use the following procedure:

9.2.1 First calibrate the instrument as described in 8.2. Then, before measuring the test gases, measure two other standard gases of known heating value. After the test gas measurements, measure the two standard gases again. The known heating values of these standard gases, CAL.VAL. LOW and CAL.VAL.HIGH, should bracket that of the unknown gas. Combine the measured values of the standard gases and the test gases to obtain a best estimate of the heating value of the test gas. Do this using the following calculation procedure.

9.2.1.1 *Step 1*—There are four measured values for the calibration gases, two for the high calorific gas and two for the low calorific gas. Average these four measurements together. The

result is represented by the symbol, AV.STD.GASES.

9.2.1.2 *Step 2*—Average the two known heating values of the standard gases together. The result is represented by the symbol, AV.CAL.VAL. Thus,  $AV.CAL.VAL = [(CAL.VAL.HIGH) + (CAL.VAL.LOW)]/2$ .

9.2.1.3 *Step 3*—Calculate a correction to the test gas measurements. This correction is represented by the symbol, CORR. The calculation is as follows:  $CORR = (AV.STD.GASES) - (AV.CAL.VAL)$ .

9.2.1.4 *Step 4*—Subtract the quantity, CORR, that is calculated in Step 3 from each of the test gas measurements to give the corrected value.

9.2.2 *Example 1*—Standard gas low has CAL.VAL-LOW = 1000 Btu/standard cubic foot and measured values after calibration are 1002.0 and 1002.8. (All heating values in Example 1 and Example 2 have units of Btu per standard cubic foot.) Standard gas high has CAL.VAL.HIGH = 1200 and measured values of 1202.0 and 1203.2.

$$AV.STD.GASES = (1002.0 + 1002.8 + 1202.0 + 1203.2)/4 = 1102.5.$$

$$AV.CAL.VAL = (1000.0 + 1200.0)/2 = 1100.0$$

$$CORR = 1102.5 - 1100 = 2.5$$

$$TEST\ GAS\ MEASUREMENT = 1080.6$$

$$CORRECTED\ VALUE = (1080.6 - 2.5) = 1078.1$$

9.2.3 *Example 2*:

CAL.VAL.LOW = 1000 Btu/standard cubic foot.

Measured values are 998.0 and 998.2.

CAL.VAL.HIGH = 1200

Measured values are 1199.0 and 1199.2

$$AV.STD.VAL = (998.0 + 998.2 + 1199.0 + 1199.2)/4 = 1098.6$$

$$AV.CAL.VAL = 1100$$

$$CORR = (1098.6 - 1100) = -1.4$$

$$TEST\ GAS\ MEASUREMENT = 1076.7$$

$$CORRECTED\ VALUE = [1076.7 - (-1.4)] = 1078.1$$

## 10. Precision and Bias

10.1 To determine precision and bias, an interlaboratory study was carried out using two types of commercial instruments that implement the stoichiometric method. For each type of instrument six different laboratories each measured five different reference gases. Cylinders containing these reference gases were transported from laboratory to laboratory. Each laboratory used its own instrument and personnel to measure the heating values of the gases in these cylinders. The same calibration gas was used to calibrate each instrument.

10.2 The heating values of the reference gases were determined prior to the study by the Institute of Gas Technology. These values were established by averaging three recording calorimeter measurements. The values were unknown to the participants in the interlaboratory

test program. At the end of the study, the heating values were remeasured at the Institute of Gas Technology to establish that the gas compositions did not change. The statistical analysis of the results was in accordance with the procedures in Practice E 691.

10.2.1 *Repeatability*—The root mean square estimate of the within laboratory component of standard deviation was 0.76 Btu/standard cubic foot. The corresponding 95 % confidence repeatability interval was 2.1 Btu/standard cubic foot.

3 10.2.2 *Reproducibility*—The root mean square estimate of the between laboratory component of standard deviation was 1.67 Btu/standard cubic foot. The corresponding 95 % confidence reproducibility interval was 5.1 Btu/standard cubic foot.

10.2.3 *Bias*—The average of all measurements agreed with the average reference value within 0.1 %.

## 11. Keywords

### 11.1 natural gas range by stoichiometric conversion

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**Designation: D 5257 – 97**

# Standard Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 5257; 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 procedures for the determination of dissolved hexavalent chromium in waste water, surface water, and drinking water.

### 1.2

The precision and bias of this test method has been tested in reagent water and industrial waste water and has been found suitable over the range of approximately 1 to 1000  $\mu\text{g/L}$ . See Table 1 for details. Higher levels can be determined by appropriate dilution.

### 1.3

Samples containing very high levels of anionic species (that is, chloride, sulfate, etc.) may cause column overload. Samples containing high levels of reducing species (that is, sulfides, sulfites, etc.) may cause reduction of Cr(VI) to Cr(III). This can be minimized by buffering the sample to a pH of 9 to 9.5, filtering it, storing it at 4°C and analyzing it within 24 h.

#### 1.4

The values stated in SI units are to be regarded as the standard.

#### 1.5

*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:

D 1066	Practice for Sampling Steam <sup>2</sup>
D 1129	Terminology Relating to Water <sup>2</sup>
D 1192	Specification for Equipment for Sampling Water and Steam in Closed Conduits <sup>2</sup>
D 1193	Specification for Reagent Water <sup>2</sup>
D 2777	Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water <sup>2</sup>
D3370	Practices for Sampling Water from Closed Conduits

### 2.2 EPA Standard:

EPA Method 218.6 Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography<sup>3</sup>

TABLE 1 Determination of Precision and Bias for Hexavalent Chromium

Water Matrix	Amount Added, µg/L	Amount Found, µg/L	$S_t$	$S_o^A$	Bias, %
Reagent	1.2	1.40	0.16	0.15	+ 16.6
	1.6	1.87	0.65	...	+ 16.9
	6.0	6.68	1.03	0.53	+ 11.3
	8.0	8.64	1.10	...	+ 8.0
<sup>A</sup> Each Youden pair was used to calculate one lab data point, $S_o$ .					

Water Matrix	Amount Added, µg/L	Amount Found, µg/L	$S_t$	$S_o^A$	Bias, %
	16.0	17.4	2.25	0.77	+ 8.8
	20.0	21.4	2.31	...	+ 7.0
	100	101	1.91	3.76	+ 1.0
	140	143	5.52	...	+ 2.1
	800	819	24.3	12.7	+ 2.4
	960	966	18.5	...	+ 7.3
Waste	6.0	5.63	1.17	0.55	-6.2
	8.0	7.31	1.91	...	-8.6
	16.0	15.1	2.70	1.85	-5.6
	20.0	19.8	1.01	...	-1.0
	100	98.9	4.36	3.31	-1.1
	140	138	8.39	...	-1.4
	800	796	60.6	27.1	-0.5
	960	944	8.1	...	-1.7

<sup>A</sup> Each Youden pair was used to calculate one lab data point,  $S_o$ .

### 3. Terminology

#### 3.1

*Definitions*—For definitions of terms used in this test method, refer to Terminology D 1129.

#### 3.2 *Definitions of Terms Specific to This Standard:*

##### 3.2.1

*eluant*—the ionic mobile phase used to transport the sample through the ion exchange column.

##### 3.2.2

*resolution*—the ability of a column to separate constituents under specified test conditions.

### 4. Summary of Test Method

#### 4.1

A fixed volume of buffered and filtered sample, typically 100  $\mu\text{L}$ , is injected into the eluant flow path and separated by anion exchange using an ammonium sulfate based eluant.

## 4.2

After separation, the sample is reacted with an acidic solution of diphenylcarbohydrazide. Hexavalent chromium reacts selectively with this reagent to form the characteristic violet colored complex.

## 4.3

The eluant stream passes through a photometric detector

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

Current edition approved Dec. 10, 1997. Published December 1998. Originally published as D 5257 – 92. Last previous edition D 5257 – 93.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>3</sup> Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

626 for detection of the chromium diphenylcarbohydrazide complex by visible absorbance at 530 nm. Absorbance is proportional to the hexavalent chromium concentration.

## 5. Significance and Use

### 5.1

Hexavalent chromium salts are used extensively in the metal finishing and plating industries, in the leather industry as a tanning agent, and in the manufacture of paints, dyes, explosives, and ceramics. Trivalent chromium salts are used as mordants in textile dyeing, in the ceramic and glass industry, and in photography. Chromium, in either oxidation state, may be present in waste water from these industries and may also be discharged from chromate-treated cooling waters.

### 5.2

Hexavalent chromium is toxic to humans, animals, and aquatic life. It can produce lung tumors when inhaled and readily induces skin sensitization. It is not known whether cancer will result from ingestion of chromium in any of its valence states.

### 5.3

Ion chromatography provides a means of separating the hexavalent chromium from other species present in the sample, many of which interfere with other detection methods. The combination of this separation with a sensitive colorimetric detection method provides a

selective and sensitive analytical method for hexavalent chromium with minimal sample preparation.

## 6. Interferences

### 6.1

By virtue of the chromatographic separation essentially all interfering species are removed from the hexavalent chromium before detection.

### 6.2

Interferences may result from overloading of the analytical column capacity with high concentrations of anionic species in the sample. Concentrations of chloride ion or sulfate ion up to the equivalent of 1 % NaCl and 3 % Na<sub>2</sub>SO<sub>4</sub> do not affect the separation or detection when using an anion exchange column, and a 100 µL sample loop.

### 6.3

The response, of 1 mg/L of hexavalent chromium is not affected by 1 g/L of chromic ion.

### 6.4

Reducing species may reduce hexavalent chromium in acidic matrices. Preservation at a pH 9 to 9.5 will minimize the effect of these species.

### 6.5

Trace amounts of Cr are sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this test method to adjust the pH of samples, reagent blanks should be analyzed to assess the potential for Cr(VI) contamination. Contamination can also come from improperly cleaned glassware or contact with caustic or acidic reagents with chromium containing stainless steel or pigmented materials.

## 7. Apparatus

### 7.1

*Ion Chromatograph*—An ion chromatograph having the following components configured as shown in Fig. 1.

#### 7.1.1

*Pump*, capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 200 to 2000 psi.

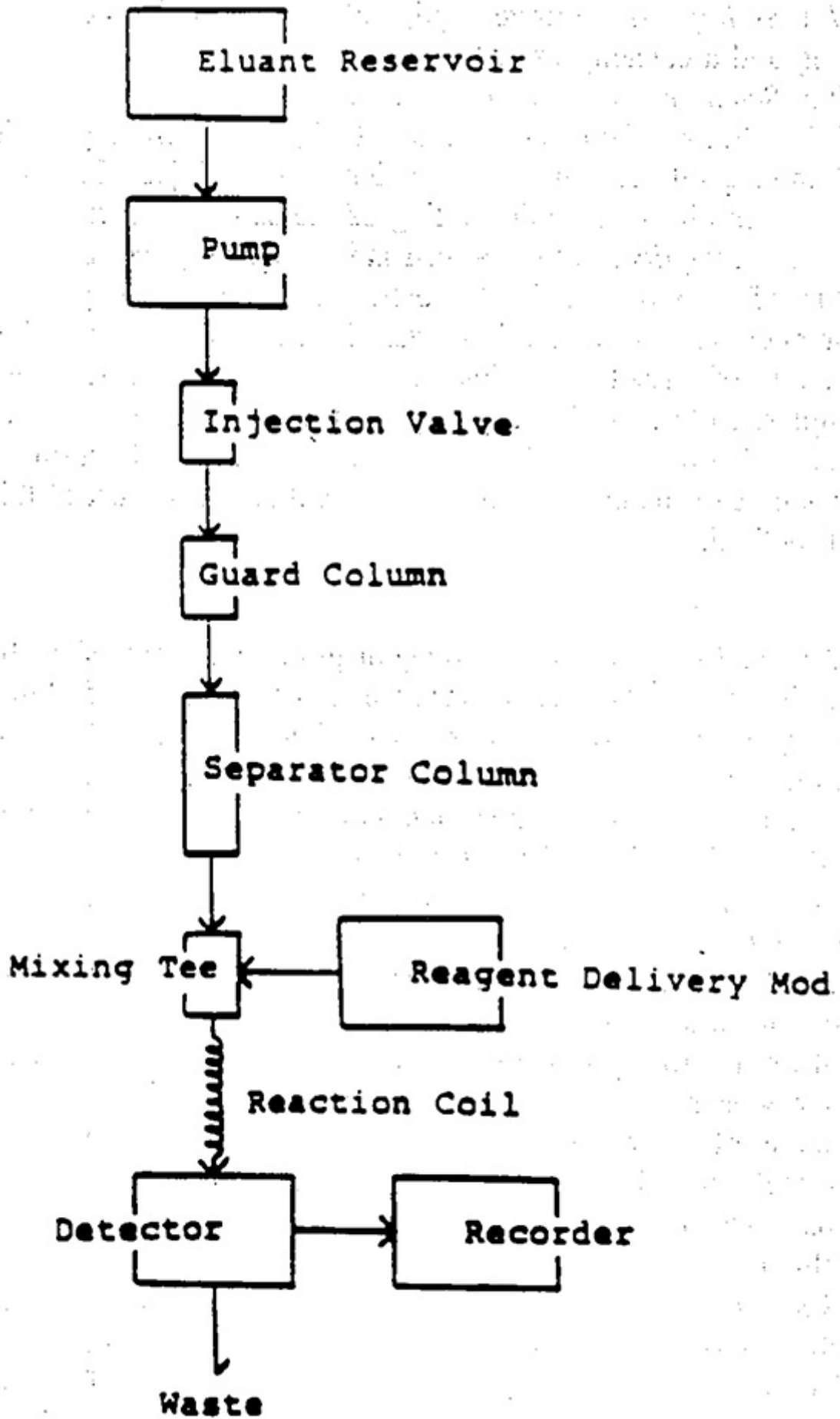


**7.1.2**

*Injection Valve*—A high pressure, low dead volume valve that allows introduction of 50 to 250  $\mu\text{L}$  of sample into the eluant stream at up to 2000 psi.

**7.1.3**

*Guard Column*—A column placed before the separator column to protect the separator column from fouling by particles or strongly absorbed organic constituents.



## FIG. 1 Diagram of an Ion Chromatograph Using Post-Column Reagent Addition and Photometric Detection

### 7.1.4

*Analytical Column*—A liquid chromatographic column packed with a polymeric anion exchange resin capable of separating chromate from other anions in a sample containing high total dissolved solids (for example 3 % Na<sub>2</sub>SO<sub>4</sub>).

### 7.1.5

*Reagent Delivery Module*—A device capable of delivering 0 to 2 mL/min of reagent against a backpressure of up to 60 psi.

### 7.1.6

*Mixing Tee and Reaction Coil*—A device capable of mixing two flowing streams providing a sufficient reaction time for post column reaction with minimal band spreading.

### 7.1.7

*Detector*—A low-volume, flow-through UV-visible absorbance detector with a non-metallic flow path. The recommended detection wavelength for hexavalent chromium is 530 nm.

## 7.2

*Recorder, Integrator, Computer*—A device compatible with detector output, capable of recording detector response as a function of time for the purpose of measuring peak height or area.

## 7.3

*Eluant Reservoir*—A container suitable for storing eluant.

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## 7.4

*Syringe*—A syringe equipped with a male luer type fitting and a capacity of at least 1 mL.

## 7.5 Summary of Column Requirements:

### 7.5.1

*Guard Column*—A short liquid chromatographic column capable of removing organics from the injected sample so as to minimize organic fouling of the separator column.

## 7.5.2

*Analytical Column*—An anion exchange column capable of providing suitable retention and chromatographic efficiency for chromate ion even in the presence of high amounts of dissolved solids that can occur in waste water samples. Note that high capacity columns will tolerate higher dissolved solids before becoming overloaded. See Section 13 for details of the columns used in the collaborative test of this test method.

## 8. Reagents

### 8.1

*Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>4</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

### 8.2

*Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type I. Other reagent water types may be used provided it is first ascertained that the water is of sufficiently high purity to permit its use without adversely affecting the bias and precision of the test method. Type II water was specified at the time of round robin testing of this test method.

### 8.3

*Chromium Solution, Stock* (1000 mg Cr/L)—Dissolve 0.2828 g of potassium dichromate ( $K_2Cr_2O_7$  that has been dried at 105°C for 1 h) in water. Add 0.1 mL of eluant concentrate (8.6) to ensure analyte stability. Dilute to 100 mL in a volumetric flask.

### 8.4

*Chromium Solution, Standard* (1000 µg Cr/L)—Pipet 1.00 mL of chromium stock solution, (see 8.3) and 1 mL of eluant concentrate into a 1L volumetric flask. Dilute to volume with, water.

### 8.5

*Reagent Blank*—Add 1 mL of eluant concentrate (8.6) to a 1 L flask and dilute to volume with the water used to prepare the chromium standards.

### 8.6

*Eluant Concentrate* (2.5 M  $(\text{NH}_4)_2\text{SO}_4$ , 1.0 M  $\text{NH}_4\text{OH}$ )—Dissolve 330 g of ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$  in about 500 mL of water. Add 65 mL of concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$  to sp gr 0.90). Mix well and dilute to 1 L in a volumetric flask.

## 8.7

*Eluant*—Two different analytical anion exchange columns proved satisfactory in the collaborative test that is summarized in Section 13. Accordingly, the eluant appropriate for each column is described in 8.7.1 and 8.7.2. Eluants should be filtered through a 0.45- $\mu\text{m}$  filter and degassed.

### 8.7.1

*Eluant for IonPac AS7 Column* (0.250 M  $(\text{NH}_4)_2\text{SO}_4$ , 0.1 M  $\text{NH}_4\text{OH}$ )—Add 100 mL of eluant concentrate (8.6) to a 1 L volumetric flask and dilute to volume with water.

### 8.7.2

*Eluant for IC Pac Anion HC Column* (0.025 M  $(\text{NH}_4)_2\text{SO}_4$ , 0.01 M  $\text{NH}_4\text{OH}$ )—Add 10 mL of eluant concentrate (8.6) to a 1 L volumetric flask and dilute to volume with water.

## 8.8

*Diphenylcarbohydrazide Reagent*—Dissolve 0.5 g of 1,5-diphenylcarbohydrazide in 100 mL of reagent grade methanol. Add to about 500 mL of water containing 28 mL of concentrated sulfuric acid. Dilute with water, while stirring, to 1 L in a volumetric flask. Filter and degas if necessary to ensure reliable delivery.

## 9. Sampling

### 9.1

Collect the sample in accordance with the applicable ASTM Standards as follows: Practice D 1066, Specification D 1192, or Practices D 3370.

### 9.2

Filter samples and adjust pH immediately upon sampling to minimize any interconversion between Cr III and Cr VI species. Filter the sample through a 0.45  $\mu\text{m}$  filter. Collect the filtrate and adjust its pH to 9 to 9.5 using the eluant concentrate (see 8.6). Ship and store samples at 4°C. Bring to ambient temperature prior to analysis. Analyze this stabilized filtrate within 24 h. Adjust final calculations to account for sample dilution.

## 10. Calibration

**10.1**

Prepare at least three levels of standards for each decade of the concentration range of interest. For standards of 1 to 1000 µg/L, prepare by diluting measured volumes of the standard chromium solution (see 8.4) with water in separate volumetric flasks.

**10.2**

Determine the chromium response for each of the standards and blank using the procedure defined in Section 11.

**10.3**

Prepare a calibration curve by using a linear plot of the peak height or area as a function of standard concentration. Do not force the calibration curve through zero. The response of the reagent blank should be less than 0.1 µg/L hexavalent chromium.

**10.4**

Prepare a new calibration curve when new reagents are made or the hardware is altered.

**11. Procedure****11.1**

Set up the ion chromatograph in accordance with the manufacturer's instructions.

**11.2**

Adjust the eluant flow rate to 1.5 mL/min. Increase the flow of the post-column reagent until the flow rate from the detector outlet line is 2.0 mL/min. so as to have a reagent flow of 0.5 mL/min under operating conditions. Measure the pH of the detector effluent to confirm it is 2 or lower.

**11.3**

After the flow rates are adjusted, allow the system to equilibrate for about 15 min.

**11.4**

If using a fixed volume sample loop (typically 100 µL), load at least 1 mL of sample through the sample port using an appropriate syringe. Inject the sample into the eluant stream and record the chromatogram (see Fig. 2). If using a variable volume injector, inject the desired sample volume into the eluant stream and record the chromatogram.

<sup>4</sup> "Reagent Chemicals American Chemical Society Specifications" Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American

Chemical Society, see "Analar Standards for Laboratory Chemicals," BDH Ltd., Poole, Dorset, U.K., and the "United States Pharmacopeia."

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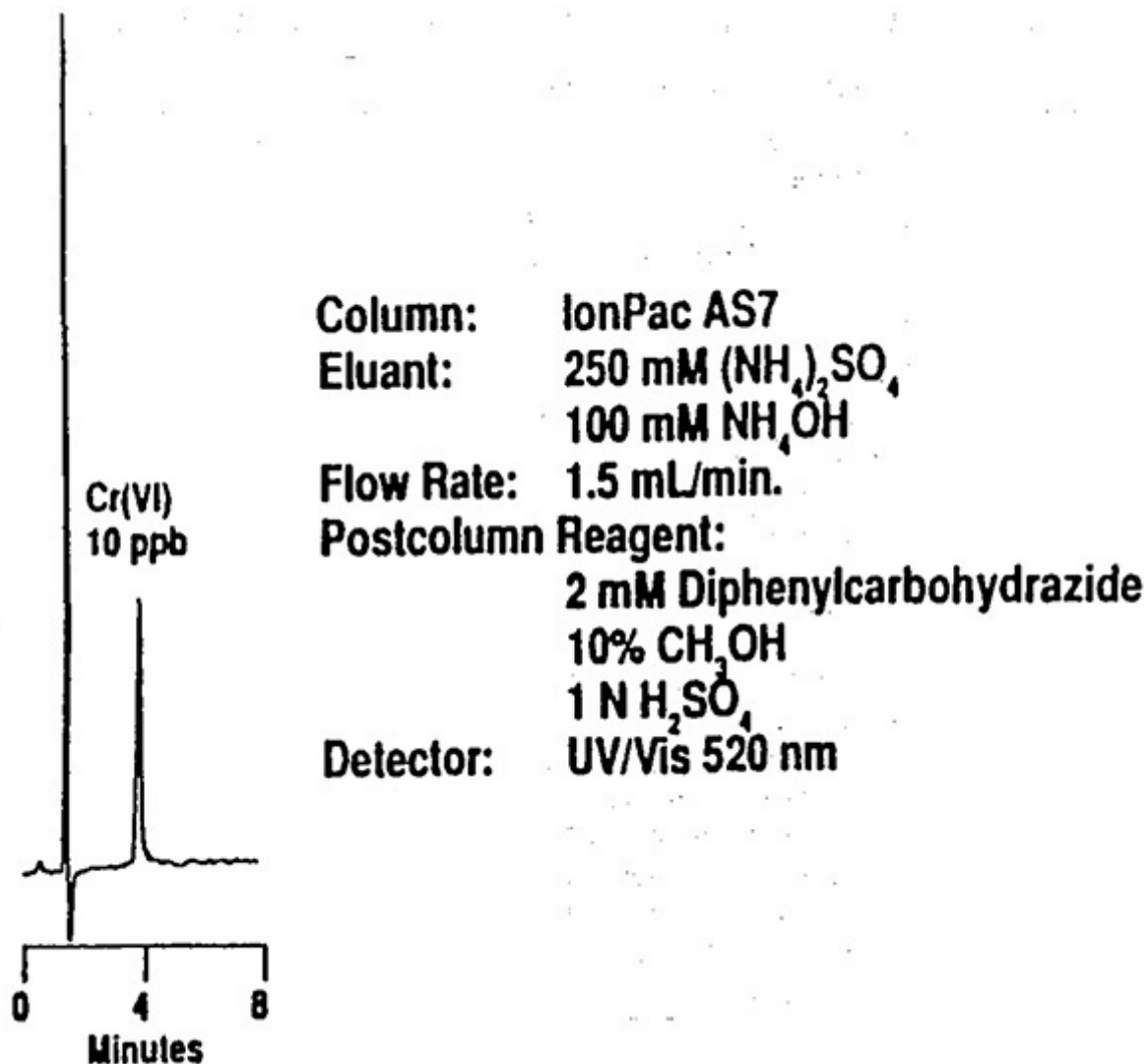


FIG. 2 Ion Chromatographic Determination of Hexavalent Chromium

## 12. Calculation

### 12.1

Refer the hexavalent chromium peak height or peak area to the calibration curve to determine the hexavalent chromium concentration of the injected sample in µg/L.

### 12.2

For samples that have been diluted, calculate the original hexavalent chromium concentration in µg/L by:

$$\mu\text{g Cr(VI)/L} = C \times F/V.$$

where:

$C$	=	µg Cr(VI)/L read from the calibration curve,
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$F$	=	volume of diluted sample, in mL, and
$V$	=	volume of undiluted sample in mL.

## 13. Precision and Bias

### 13.1

The precision and bias data presented in this test method meet the requirements of Practice D 2777 (see Annex A1 for details).

### 13.2

The following separator columns were used in the collaborative test high capacity separator column<sup>5</sup> and low capacity separator column.<sup>6</sup>

### 13.3

The collaborative test of this test method was performed in reagent water and waste water by fifteen laboratories using one operator each. For reagent water the test used ten levels of concentration comprised of five Youden pairs ranging from 1.2 to 960 µg/L of hexavalent chromium. For waste water the test used eight levels of concentration comprised of four Youden pairs ranging from 6 to 960 µg/L of hexavalent chromium. The precision and bias data are presented in Table 1. See the Annex for a detailed description of the collaborative test.

### 13.4

The results of this collaborative test can also be summarized as follows:

Number of laboratories: 15		
Range tested: 1.2 to 960 µg/L		
Matrix: Reagent Water:		
$S_o$	=	$0.033x + 0.106$
$S_t$	=	$0.050x + 0.559$
<i>Mean Recovery</i>	=	$1.04x + 0.183$
Matrix: Wastewater:		
$S_o$	=	$0.041x + 0.039$
$S_t$	=	$0.059x + 1.05$
<i>Mean Recovery</i>	=	$0.989x + -0.41$

## 14. Keywords

### 14.1



analysis; hexavalent chromium; ion chromatography; wastewater; water

<sup>5</sup> Model IonPac A57 column, available from Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088, has been found suitable for this purpose.

<sup>6</sup> Model IC Pac Anion HC, available from Millipore Corporation (Waters Division), 34 Maple Street, Milford, MA 01757.

## ANNEX

### A1. DUPLICATION OF QUALITY CONTROL MEASURES

#### (Mandatory Information)

#### A1.1

The precision and bias data cited in this test method were the result of a collaborative test designed and executed jointly by ASTM Committee D-19 on Water and the U.S. EPA Environmental Monitoring and Support Laboratory (Cincinnati). Participants were required to use this method or EPA Method 218.6, or both. These two methods are technically equivalent. The eleven reagent water samples consisted of a reagent water blank and five Youden pairs. The nine wastewater samples consisted of a waste-water blank and four Youden pairs. The following is a duplication of the test instructions that included the quality control measures that were part of this test method:

#### A1.2 Preparation

##### A1.2.1 Calibration Standard Preparation:

##### A1.2.1.1

A standard concentrate (green label) has been furnished with this study to minimize calibration standard biases. The Cr(VI) concentration contained within the standard concentrate ampul and the study range are listed in Table A1.1.

##### A1.2.1.2

Prepare a calibration curve according to 9.1 of

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**TABLE A1.1 Standard Ampul Concentration and Study Range**

Analyte	MDL, µg/L	STANDARD Ampul, µg/L	Study Range, µg/L
Cr(VI)	0.4	100,000	1–1000

EPA Method 218.6, revision 3.2 using a series of calibration standards prepared from the standard concentrate. The calibration curve must range from 1.0 µg/L to 1000 µg/L.

##### A1.2.2 Matrix Blanks:

**A1.2.2.1**

An analysis of each matrix water is required to determine potential background concentrations of Cr(VI). These blanks are referred to as *reagent water blank* and *wastewater blank*. The wastewater blank should be adjusted to pH 9.0 to 9.5 with the buffer solution (section 7.9, EPA Method 218.6) and passed through a 0.45 µm filter before analysis. Analyze a portion of the wastewater solution prepared in A1.2.4.2 as the blank.

**A1.2.3 Quality Control Sample Preparation:****A1.2.3.1**

Prepare the QC sample (laboratory fortified blank (LFB) as described in section 10.3.2, Method 218.6, revision 3.2) by pipetting a 1.0 mL aliquot from the QC sample concentrate ampul (blue label) and diluting to 100 mL with reagent water. The Cr(VI) concentration in the QC sample and the acceptance limits that are to be used for this study are presented in Table A1.2.

**A1.2.4 Sample Preparation:****A1.2.4.1 Reagent Water Samples:**

(a) Prepare the reagent water samples by transferring a 1.0 mL aliquot from each ampul labelled reagent water (yellow labels) to individual 100 mL volumetric flasks and dilute to volume with reagent water. These samples are now ready for analysis.

**A1.2.4.2 Wastewater Samples:**

(a) Collect at least 1 liter of a wastewater of your choice. Filter the wastewater matrix through a 0.45 µm filter then adjust the pH of the filtrate to 9.0 to 9.5 by adding dropwise a solution of the buffer (8.2, EPA Method 218.6). Prepare the individual wastewater samples by transferring a 1.0 mL aliquot from each ampul labelled wastewater (orange labels) to individual 100 mL volumetric flasks and dilute to volume with the pH adjusted wastewater. These samples are now ready for analysis. The wastewater matrix is not to be diluted prior to spiking regardless of the Cr(VI) background concentration.

**A1.3 Sample Analyses****A1.3.1**

Analyze each prepared sample in the order defined in Table A1.3. The sample names and numbers in Table A1.3 are the same as those on the data report forms. Be certain that the sample data is entered under the correct sample name.

**TABLE A1.2 Quality Control Sample Acceptance Limits**

Analyte	True Value (T.V.) µg/L	Acceptance Limits <sup>A</sup> µg/L
Cr(VI)	40.0	36–44
<sup>A</sup> Defined as T.V. ± 10 %.		

**TABLE A1.3 EPA Method Study 218.6 Injection Order**

Sample Name and Sample Order
QC Sample
Reagent Water Blank
Reagent Water—Sample #1
Reagent Water—Sample #2
Reagent Water—Sample #3
Reagent Water—Sample #4
Reagent Water—Sample #5
Reagent Water—Sample #6
Reagent Water—Sample #7
Reagent Water—Sample #8
Reagent Water—Sample #9
Reagent Water—Sample #10
QC Sample
Wastewater Blank
Wastewater—Sample #11
Wastewater—Sample #12
Wastewater—Sample #13
Wastewater—Sample #14
Wastewater—Sample #15
Wastewater—Sample #16
Wastewater—Sample #17
Wastewater—Sample #18
QC Sample

## A1.4 Quality Control (QC)

### A1.4.1

The QC sample is used to perform regular checks on the calibration curve. Only one QC sample need be prepared. However, three analyses of this QC sample will be required; one immediately following the last calibration standard, another immediately following the reagent

water sample series, and the third immediately following the wastewater sample series. If the Cr(VI) concentration in the QC sample falls outside of the acceptance limits found in Table A1.2, the analyst should reanalyze the QC sample. If the Cr(VI) concentration falls within the acceptance limits, continue with the sample analyses. If the Cr(VI) concentration is still outside of the acceptance limits, a new calibration curve is required and must be confirmed by a successful QC analysis before sample analyses can continue.

## **A1.5 Data Report Forms**

### **A1.5.1**

Analytical values reported on the data report forms must not be corrected for matrix background concentrations. Report measured concentrations of Cr(VI) as µg/L to three significant figures (that is, 2.35, 23.5, or 235).

## **A1.6 Questionnaire**

### **A1.6.1**

Operate your ion chromatograph according to manufacturer specifications and recommendations found in EPA Method 218.6 (revision 3.2) and the equivalent Test Method D 5257. A questionnaire is enclosed to record your specific operating conditions and equipment type.

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This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

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