State of California
California Environmental Protection Agency
Air Resources Board

STAFF REPORT: INITIAL STATEMENT OF REASONS FOR PROPOSED RULEMAKING

PUBLIC HEARING TO CONSIDER AMENDING THE TEST METHOD DESIGNATED FOR DETERMINING THE OXYGEN CONTENT OF GASOLINE

Date of Release: May 12, 1995
Scheduled for Consideration: June 29, 1995

I. INTRODUCTION

We are proposing that the Air Resources Board (ARB or Board) amend its designation of the test method for determining the oxygen content of gasoline. The ARB's regulations now designate American Society of Testing and Materials (ASTM) test method D 4815-93. We are proposing that the designation be amended to identify ASTM test method D 4815-94, an updated version which provides more precise results.

The updated method would be used in determining whether motor vehicle gasoline complies with the ARB's requirements regarding minimum and maximum oxygen content. These limits currently apply during winter months only; starting in March 1996 there will be year-round requirements. The updated method would also be used for determining the ethanol content of gasoline under the ARB's regulation limiting the Reid vapor pressure (RVP) of gasoline.

In an October 6, 1994 letter, the Western States Petroleum Association (WSPA) petitioned the ARB to amend its regulations to update the method for measuring oxygen in gasoline by designating ASTM method D 4815-94. WSPA noted that the precision of the method had been improved with the addition of tighter procedures for calibration. In a letter dated November 15, 1994, the ARB's Executive Officer granted the petition. He indicated that the requested rulemaking would be scheduled in time for the updated test method to apply when the 1995-1996 wintertime oxygenate season starts on October 1, 1995. In the interim, ASTM method D 4815-94 was identified as an equivalent method for determining the oxygen content of gasoline. Copies of these two letters are appended in Attachment A.

II. BACKGROUND

The ASTM is a prominent not-for-profit organization that provides a forum for manufacturers and users of products, as well as academicians and government representatives, to prepare standards based on a consensus approach. Among the standards adopted by the ASTM are test methods. The ARB often identifies ASTM test methods as the means to determine compliance

with its standards for motor vehicle fuels. The last two digits of an ASTM test method represent the year of adoption or last revision.

In late 1991, the Board adopted a regulation establishing minimum and maximum oxygen content requirements for gasoline sold in the wintertime from November 1992 through February 1996. Around the same time, the Board also adopted the Phase 2 reformulated gasoline (Phase 2 RFG) regulations, which establish a set of specifications for eight properties of California gasoline starting in March, 1996. These include year-round minimum and maximum oxygen content limits. In both programs, the regulations originally identified ASTM Method D 4815-89 as the method for determining compliance with the oxygen content requirements. At the time, this was the most recent version of the ASTM's method for determining oxygenates in gasoline by gas chromatography.

Although ASTM Method D 4815-89 was the best one available when the regulations were adopted, both ARB staff and industry recognized that it had several shortcomings. The test method did not provide results in the same units as the regulations and, therefore, required a supplementary conversion table. In addition, it did not test for all of the common oxygenates that could potentially appear in gasolines. Finally, the precision of the test method was poor. In adopting the regulations, the Board accordingly directed staff to work with industry to identify improved test procedures.

In cooperation with WSPA and the ARB, the ASTM Subcommittee on Hydrocarbon Analysis revised the method and subjected it to interlaboratory testing. The revised version, designated as ASTM D 4815-93, improved the scope of the method to include additional oxygenates and broader concentration ranges. Additionally, the 1993 version specified gravimetric calibration techniques which allow the weight percent of oxygen to be measured directly. Following a September 1993 hearing, the Board amended its regulations to designate the revised method D 4815-93, "Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography." The ASTM has now revised the method again, as ASTM D 4815-94.

III. RECOMMENDATION

We recommend that the Board amend Sections 2258(c) and 2263(b) of Title 13, California Code of Regulations. The amendments would update the method designated for determining the oxygen content of gasoline from ASTM D 4815-93 to ASTM D 4815-94. Section 2258(c) applies to the ARB's currently applicable requirements regarding the oxygen content of gasoline in the wintertime. Section 2263(b) is part of the ARB's Phase 2 RFG regulations, which apply starting in March 1996.

We recommend that the Board also amend its currently applicable regulation on the RVP of gasoline, section 2251.5 of Title 13, California Code of Regulations. The proposed amendment, to Section 2251.5(c)(2), would update the method used in determining the ethanol content of gasoline from ASTM D 4815-93 to ASTM D 4815-94 and would eliminate the assumed

density of gasoline used in converting results from weight percent to volume percent. The density of gasoline will be measured using the method referenced in ASTM D 4815-94. The regulation identifies a method for determining ethanol content because under some circumstances, blends of gasoline having a specified minimum ethanol content, determined in volume percent, are subject to a less stringent RVP standard.

The text of the proposed amendments is set forth in Attachment B. A copy of ASTM D 4815-94 is appended as Attachment C.

IV. RATIONALE FOR PROPOSED ACTION AND ALTERNATIVES

A. Comparison of Current and Proposed Test Methods

Both test methods, D 4815-93 and D 4815-94, use identical or nearly identical instrumentation, materials, operating parameters and procedures. However, test method D 4815-94 contains an improved calibration procedure which improves the precision of the test method.

The calibration procedure in the test method is significant because it defines how the concentration of an oxygenate relates to the response of an instrument. In ASTM D 4815-93, the instrument response is determined from the measurement of response of a single sample of a known oxygenate concentration. In ASTM D 4815-94, the relationship is determined by measuring the response at five known oxygenate concentration levels, which is more accurate and less prone to variability. ASTM D 4815-94 is also more explicit in its description of the preparation of calibration standards, providing greater detail on reagent purification, sample transfer, weighing, and storage.

One measure of precision particularly applicable to interlaboratory comparisons is reproducibility. The ASTM uses the following language to characterize its measurement of 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 exceed the following values [in the reproducibility table] in one case in twenty.

Table 1 compares the reproducibilities of ASTM D 4815-94 to D 4815-93 for the two most widely used oxygenates in California gasoline. As Table 1 indicates, ASTM D 4815-94 has a substantially lower reproducibility level than ASTM D 4815-94, resulting in less uncertainty in the measurement of these oxygenates when using the proposed method.

Table 1

Reproducibility of ASTM D-4815 at Allowable Oxygenate Levels

mass% Oxygen	MTBE -94	MTBE -93	Ethanol -94	Ethanol -93
1.80	0.10	0.38	0.20	0.46
2.00	0.11	0.42	0.22	0.48
2.20	0.12	0.46	0.23	0.52

B. Alternative Methods

1. Gas Chromatograph/Fourier Transform Infra Red (GC/FTIR)

The ARB's regulations on the oxygen content of gasoline allow an alternative test method to be used if the Executive Officer determines that the alternative method produces results equivalent to those obtained with the designated method.

In the fall of 1993, the Executive Officer's designee determined that a Gas Chromatograph/Fourier Transform Infra Red (GC/FTIR) method was equivalent to ASTM 4815-93 for determining the oxygen content of gasoline. This determination was based on a request from Mobil Research and Development Company which developed the test method. The method is very selective for oxygenates because it utilizes infra-red absorbances for quantification, reducing the possibilities for interferences and ensuring that the scope of the method can readily be expanded to test for oxygenates not currently included.

The GC/FTIR method has been revised by Mobil to include a determination of benzene and total aromatics. The revised method has undergone ASTM-sponsored round robin testing with ARB participation; however, its reproducibility values are not yet available.

The GC/FTIR equivalency determination is based on a comparison to the currently designated test method. If the Board updates the designation of ASTM D 4815-93 to ASTM D 4815-94, the Executive Officer may be requested to determine if Mobil's GC/FTIR method yields results equivalent to results using the updated ASTM method.

2. Gas Chromatograph/Oxygen Flame Ionization Detector (GC/OFID)

The U.S. Environmental Protection Agency (U.S. EPA) administers regulations requiring that gasoline sold in various areas with poor air quality meet standards for "federal" reformulated gasoline. These regulations have applied in most of Southern California since December 1994.

One requirement is that the gasoline must meet year-round minimum oxygen content standards. The federal regulations provide that oxygen and oxygenate content is to be determined by a gas chromatographic procedure using an oxygen-selective flame ionization detector (GC/OFID). Until January 1, 1997, refiners and importers are allowed to use ASTM D 4815-93 as long as the results are correlated with U.S. EPA's GC/OFID method. (40 C.F.R. sec. 80.46(g).) The federal regulations allow producers and importers of California gasoline to use a test method specified in the ARB's Phase 2 RFG regulations in lieu of the otherwise applicable federal method. (40 C.F.R. sec. 80.81(h).)

The GC/OFID method, like the GC/FTIR method, is highly selective for oxygenates and therefore is less prone to interferences. In addition, the OFID method can be applied to a larger list of oxygenates than ASTM D 4815-94. However, interlaboratory testing of the method has shown the OFID method to have poor reproducibility compared to ASTM D 4815-94 and OFID instruments are reported to have greater than normal down time.

In a letter dated April 11, 1995, a representative of Wasson-ECE Instrumentation--a major vendor of OFID instruments--stated that recent ASTM round-robin data showed the OFID method to be at least as reproducible as ASTM D 4815-94. She also indicated that the problems leading to OFID instrument failure have been solved. Staff responded in a letter dated April 24, 1995, explaining that even with the improved reproducibility values for the 1995 draft version of the OFID method, the reproducibility of ASTM D 4815-94 is still significantly better for determining MTBE and ethanol content at the two mass percent oxygen level. Copies of the two letters are appended in Attachment D. The staff will continue to monitor the development of the OFID method. When issues of precision and reliability are resolved, staff is prepared to allow use of the OFID method as an equivalent method and, if appropriate, recommend its adoption in a future rulemaking.

IV. AIR QUALITY, ENVIRONMENTAL AND ECONOMIC IMPACTS

A. Air Quality and Environmental Impacts

The proposed change in test procedure will not result in air quality impacts because the underlying standards for gasoline oxygen content will remain the same. The staff has not identified any significant adverse non-air quality environmental impacts that would result from the proposal.

B. Economic Impacts

This section evaluates the potential economic impact of the proposed change in test method on business enterprises in California. A recent amendment to Section 11346.53 of the Government Code requires that, in proposing to adopt or amend any administrative regulation, state agencies shall assess not only the potential for adverse economic impact on California business enterprises and individuals, but also the ability of

California businesses to compete with businesses in other states. Also a new section to the Government Code (Section 11346.54) requires state agencies to assess the potential impact of their regulations on California jobs and business expansion, elimination, or creation.

The proposed change in test method would have minimal impact, if any, on California business enterprises. Because the instrumentation, materials, and operating parameters of the updated method are unchanged from ASTM D 4815-93, the updated method is unlikely to impose any additonal costs on businesses. The updated method may require additional time for calibration; however, such calibration practices have already been adopted by many laboratories as part of Good Laboratory Practices. We also expect no significant change in employment, business creation, elimination, or expansion; and business competitiveness due to the change of test method because the updated method would impose no additional costs on business enterprises in California.

REFERENCES

1. ASTM D 1298-85, "Standard Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method," Annual Book of ASTM Standards, Vol 05.01.

2. ASTM D 1744-92, "Standard Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent," Annual Book of ASTM Standards, Vol 05.01.

3. ASTM D 3606-92, "Standard Test Method for Determination of Benzene and Toluene in Fininshed Motor and Aviation Gasoline by Gas Chromatography," Annual Book of ASTM Standards, Vol 05.02.

4. ASTM D 4052-91, "Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter," Annual Book of ASTM Standards, Vol 05.02.

5. ASTM D 4057-88, "Standard Practice for Manual Sampling of Petroleum and Petroleum Products," Annual Book of ASTM Standards, Vol 05.02.

6. ASTM D 4307-93, "Standard Practice for Preparation of Liquid Blends for Use as Analytical Standards," Annual Book of ASTM Standards, Vol 05.02.

7. ASTM D 4420-89, "Standard Test Method for Aromatics in Finished Gasoline by Gas Chromatography," Annual Book of ASTM Standards, Vol 05.02.

ATTACHMENT A

October 6, 1994 Letter from Gina Grey of WSPA to James D. Boyd
(without attachments)

November 15, 1994 Letter from James D. Boyd to Gina Grey

WSPA
Western States Petroleum Association

October 6, 1994

Gina Grey
Managing Coordinator

Mr. James D. Boyd
Executive Officer
California Air Resources Board
1102 Q Street
P.O. Box 2815
Sacramento, CA 95812

RE: Petition For Acceptance of Revised Test Method for Oxygenates In Phase II Gasoline

Dear Mr. Boyd:

This letter is being sent to request that ARB amend the California Code of Regulations in order to clarify the method required for measuring oxygen in gasoline. California regulations currently specify that ASTM Method D-4815-93, Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C1 to C4 Alcohols in Gasoline by Gas Chromatography, be used for determining compliance with the oxygen content limitations. ASTM D02 Subcommittee 4 on Hydrocarbon Analysis has conducted a round robin program to improve the precision of ASTM D-4815 with the addition of tighter procedures for calibration. This revision of D-4815 has been approved by ASTM and has now been published as ASTM D-4815-94.

Since method D4815-94 is somewhat improved over the 1993 version, we recommend that ARB consider amending the regulations at this time to allow the use of the revised method D4815-94 for oxygenates in gasoline testing. Copy both the 1994 and the 1993 versions of D4815 are attached.

If there are any questions concerning this petition, please contact James M. McCann of Texaco, Inc. (Chairman of ASTM D02.04 on Hydrocarbon Analysis) at 914-838-7351.

Very truly yours,

Gina Grey

AA:jm

Attachments

505 N. Brand Blvd., Suite 1400 • Glendale, California 91203 • (818) 543-5352 • FAX (818) 545-0954

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STATE OF CALIFORNIA—CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY PETE WILSON, Governor

AIR RESOURCES BOARD
2020 L STREET
P.O. BOX 2815
SACRAMENTO, CA 95814-2815

November 15, 1994

Ms. Gina Grey
Managing Coordinator
Western States Petroleum Association
505 N. Brand Boulevard, Suite 1400
Glendale, CA 91203

Dear Ms. Grey:

Thank you for your letter of October 6, 1994, in which you request that the Air Resources Board (ARB) amend the California Code of Regulations in order to update the test method specified for measuring oxygen in gasoline. You note that the ARB's regulations currently provide that ASTM Method D 4815-93 is to be used to determine compliance with the oxygen content requirements. You ask that ASTM D 4815-94, which identifies tighter procedures for calibration, be allowed to be used in gasoline testing.

My staff has reviewed your request and has confirmed that ASTM D 4815-94 contains improvements over ASTM D 4815-93. Accordingly, I am granting your petition. As you know, currently applicable ARB requirements regarding the oxygen content of gasoline apply only in the winter months, from October through February. The procedural requirements for rulemakings are such that it would not be practical to amend our regulations in time to affect the 1994-1995 wintertime oxygen content requirements. Thus, we plan to schedule the rulemaking according to a timetable that will enable us to have the updated test method in place by the time the 1995-1996 season begins in October 1995. Under this schedule, the amendments will of course also be in place by the time our Phase 2 reformulated gasoline requirements apply starting in March 1996.

As you are aware, Title 13, California Code of Regulations, sections 2258(c) and 2263(c) authorize the Executive Officer to permit use of an alternative oxygen content test method in addition to ASTM D 4815-93 upon a determination that the alternative test method produces results equivalent to the results with ASTM D 4815-93. Pending completion of our rulemaking, we plan to designate ASTM D 4815-94 as an equivalent method for determining the oxygen content of gasoline. Our equivalency determination will be the subject of a separate letter.

If you have any questions on this matter, please contact Jim Shikiya at (818) 575-6815.

Sincerely,

James D. Boyd
Executive Officer

cc: W. Loscutoff
J. Shikiya

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ATTACHMENT B

Proposed Regulation Order

Proposed Amendments to Title 13, California Code of Regulations,
Sections 2258(c), 2251.5(c), and 2263(b)

PROPOSED REGULATION ORDER

Amend Section 2258(c), Title 13, California Code of Regulations, to read as follows:

Section 2258. **Oxygen Content of Gasoline in the Wintertime**

[no amendments to section (a) or (b)]

(c) Sampling Procedures and Test Methods

Compliance with the oxygen content standards in this regulation shall be determined by use of an applicable sampling methodology set forth in Title 13, California Code of Regulations, section 2296, and use of American Society for Testing and Materials Test Method ASTM D ~~4815-93~~ 4815-94, which is incorporated herein by reference. Another test method may be used following a determination by the executive officer that the other method produces results equivalent to the results obtained with ASTM D ~~4815-93~~ 4815-94.

[No amendments to sections (d) through (f)]

NOTE: Authority cited: Health and Safety Code Sections 39600, 39601, 43013, 43018, and 43101; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal. 3d 411, 121 Cal. Rptr. 249 (1975). Reference: Health and Safety Code Sections 39000, 39001, 39002, 39003, 39500, 39515, 39516, 41511, 43000, 43016, 43018, and 43101; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal. 3d 411, 121 Cal. Rptr. 249 (1975).

Amend Section 2251.5(c), Title 13, California Code of Regulations, to read as follows:

Section 2251.5. Reid Vapor Pressure of Gasoline Sold After January 1, 1992, and Before March 1, 1996.

[No amendments to section (a) or (b)]

(c) **Sampling and Test Methods.**

(1) Compliance with the standards set forth in section (a)(1) and (2) shall be determined by use of an applicable sampling methodology set forth in 13 CCR section 2296, and by use of either (A) the American Society for Testing and Materials Test Method ASTM D 328-58 (which is incorporated by reference herein), deleting paragraph 4(b) concerning sampling or (B) the test method set forth in Section 2297.

(2) For purposes of section (a)(3), the ethanol content of gasoline shall be determined by: (A) ~~Use~~ use of American Society of Testing and Materials Test Method D ~~4815-93,~~ 4815-94 (which is incorporated by reference herein) to determine the mass percent of ethanol in the gasoline, and (B) conversion of the concentration of ethanol from percent by mass to percent by volume according to ~~Equation 5~~ Section 14.3 of ASTM D ~~4815-93~~ 4815-94 ~~using a fuel density of 0.742 gram per milliliter~~. The volume of ethanol shall include the volume of any denaturant approved for that purpose by the United States Bureau of Alcohol, Tobacco and Firearms, provided those denaturants do not exceed 5 percent of the volume of alcohol (including denaturants).

[No amendments to sections (d) through (f)]

NOTE: Authority cited: Health and Safety Code Sections 39600, 39601, 43013, 43018, 43101, and 43830; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975). Reference: Health and Safety Code Sections 39000, 39001, 39002, 39003, 39500, 39515, 39516, 39606, 41511, 43000, 43016, 43018, 43101, and 43830; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975).

Amend section 2263(b), Title 13, California Code of Regulations, to read as follows:

Subarticle 2. Standards for Gasoline Sold Beginning March 1, 1996

* * * *

Section 2263. Sampling Procedures and Test Methods

[No amendments to section (a)]

(b) **Test Methods.**

(1) In determining compliance with the standards set forth in this subarticle 2, the test methods presented in Table 1 shall be used. All identified test methods are incorporated herein by reference.

Table 1

Section	Gasoline Specification	Test Method
2262.1.	Reid Vapor Pressure	ASTM D 323-58 a/ or 13 C.C.R. Section 2297
2262.2.	Sulfur Content	ASTM D 2622-87
2262.3.	Benzene Content	ASTM 3606-87 or ARB MLD 116 b/
2262.4.	Olefin Content	ASTM D 1319-89
2262.5	Oxygen Content	ASTM D ~~4815-93~~ 4815-94
2262.6.	T90 and T50	ASTM D 86-90
2262.7.	Aromatic Hydrocarbon Content	ARB MLD 116 b/

a/ Delete paragraph 4(b) concerning sampling.

b/ Air Resources Board, Monitoring and Laboratory Division, "Procedure for the Analysis of Benzene and Other Aromatic Components of Gasoline," dated November 1991. This method is to be used instead of ASTM 3606-87 to determine benzene content if ethanol is present.

NOTE: Authority cited: Health and Safety Code Sections 39600, 39601, 43013, 43018 and 43101; and Western Oil and Gas Ass'n. v. Orange County Air

Pollution Control District, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975). Reference: Health and Safety Code Sections 39000, 39001, 39002, 39003, 39010, 39500, 39515, 39516, 39606, 41511, 43000, 43016, 43018, and 43101; and Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975).

ATTACHMENT C

American Society of Testing and Materials Method D 4815-94

Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, tertiary-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography

Designation: D 4815 – 94

AMERICAN SOCIETY FOR TESTING AND MATERIALS
1916 Race St. Philadelphia, Pa 19103
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If not listed in the current combined index, will appear in the next edition.

Standard Test Method for Determination of MTBE, ETBE, TAME, DIPE, *tertiary*-Amyl Alcohol and C_1 to C_4 Alcohols in Gasoline by Gas Chromatography[1]

This standard is issued under the fixed designation D 4815; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is designed for the determination of ethers and alcohols in gasolines by gas chromatography. Specific compounds determined are: methyl *tert*-butylether (MTBE), ethyl *tert*-butylether (ETBE), *tert*-amylmethylether (TAME), diisopropylether (DIPE), methanol, ethanol, isopropanol, *n*-propanol, isobutanol, *tert*-butanol, *sec*-butanol, *n*-butanol, and *tert*-pentanol (*tert*-amylalcohol).

1.2 Individual ethers are determined from 0.1 to 20.0 mass percent. Individual alcohols are determined from 0.1 to 12.0 mass percent. Equations used to convert to mass percent oxygen and to volume % of individual compounds are provided.

1.3 Alcohol-based fuels such as M-85 and E-85, MTBE product, ethanol product and denatured alcohol are specifically excluded from this method. The methanol content of M-85 fuel is considered beyond the operating range of the system.

1.4 Benzene, while detected, cannot be quantified using this test method and must be analyzed by alternate methodology (Test Method D 3606 or D 4420).

1.5 SI (metric) units are preferred and used throughout this standard. Alternate units, in common usage, are also provided to increase clarity and aid the users of this test method.

1.6 *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 1298 Test Method for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method[2]

D 1744 Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent[2]

D 3606 Test Method for Benzene and Toluene in Finished Motor and Aviation Gasoline by Gas Chromatography[3]

D 4052 Test Method for Density and Relative Density of Liquids by Digital Density Meter[3]

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products[3]

D 4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards[3]

D 4420 Test Method for Aromatics in Finished Gasoline by Gas Chromatography[3]

3. Terminology

3.1 *Descriptions of Terms Specific to This Standard:*

3.1.1 *low volume connector*—a special union for connecting two lengths of tubing 1.6 mm inside diameter and smaller. Sometimes this is referred to as zero dead volume union.

3.1.2 *MTBE*—methyl *tertiary*-butylether.

3.1.3 *ETBE*—ethyl *tertiary*-butylether.

3.1.4 *TAME*—*tertiary*-amyl methylether.

3.1.5 *DIPE*—diisopropylether.

3.1.6 *tertiary-amyl alcohol*—*tertiary*-pentanol.

3.1.7 *oxygenate*—any oxygen-containing organic compound which can be used as a fuel or fuel supplement, for example, various alcohols and ethers.

3.1.8 *split ratio*—in capillary gas chromatography, the ratio of the total flow of carrier gas to the sample inlet versus the flow of the carrier gas to the capillary column, expressed by

$$\text{split ratio} = (S + C)/C \quad (1)$$

where:

S = flow rate at the splitter vent, and

C = flow rate at the column outlet.

3.1.9 *TCEP*—1,2,3-tris-2-cyanoethoxypropane—a gas chromatographic liquid phase.

3.1.10 *WCOT*—a type of capillary gas chromatographic column prepared by coating the inside of the capillary with a thin film of stationary phase.

4. Summary of Test Method

4.1 An appropriate internal standard such as 1,2-dimethoxyethane (ethylene glycol dimethyl ether) is added to the sample which is then introduced into a gas chromatograph equipped with two columns and a column switching valve. The sample first passes onto a polar TCEP column which elutes lighter hydrocarbons to vent and retains the oxygenated and heavier hydrocarbons.

4.2 After methylcyclopentane, but before DIPE and MTBE elute from the polar column, the valve is switched to backflush the oxygenates onto a WCOT non-polar column.

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analysis.

Current edition approved Feb. 15, 1994. Published April 1994. Originally published as D 4815 – 89. Last previous edition D 4815 – 93.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vol 05.02.

The alcohols and ethers elute from the non-polar column in boiling point order, before elution of any major hydrocarbon constituents.

4.3 After benzene and TAME elute from the non-polar column, the column switching valve is switched back to its original position to backflush the heavy hydrocarbons.

4.4 The eluted components are detected by a flame ionization or thermal conductivity detector. The detector response, proportional to the component concentration, is recorded; the peak areas are measured; and the concentration of each component is calculated with reference to the internal standard.

5. Significance and Use

5.1 Ethers, alcohols, and other oxygenates can be added to gasoline to increase octane number and to reduce emissions. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Drivability, vapor pressure, phase separation, exhaust and evaporative emissions are some of the concerns associated with oxygenated fuels.

5.2 This test method is applicable to both quality control in the production of gasoline and for the determination of deliberate or extraneous oxygenate additions or contamination.

6. Apparatus

6.1 *Chromatograph*—While any gas chromatographic system, which is capable of adequately resolving the individual ethers and alcohols that are presented in Table 1, can be used for these analyses, a gas chromatographic instrument which can be operated at the conditions given in Table 2, and having a column switching and backflushing system equivalent to Fig. 1 has been found acceptable. Carrier gas flow controllers shall be capable of precise control where the required flow rates are low (Table 2). Pressure control devices and gages shall be capable of precise control for the typical pressures required.

6.1.2 *Detector*—A thermal conductivity detector or flame ionization detector, can be used. The system shall have sufficient sensitivity and stability to obtain a recorder deflection of at least 2 mm at a signal-to-noise ratio of at least 5 to 1 for 0.005 volume % concentration of an oxygenate.

TABLE 1 Pertinent Physical Constants and Retention Characteristics for TCEP/WCOT Column Set Conditions as in Table 2

Component	Retention Time, Min.	Relative Retention Time (MTBE = 1.00)	Relative Retention Time (DME = 1.00)	Molecular Weight	Relative Density at 15.56/15.56°C
Water	2.90	0.53	0.43	18.0	1.000
Methanol	3.15	0.63	0.46	32.0	0.7963
Ethanol	3.48	0.69	0.51	46.1	0.7939
Isopropanol	3.83	0.76	0.56	60.1	0.7899
tert-Butanol	4.15	0.82	0.61	74.1	0.7922
n-Propanol	4.56	0.90	0.67	60.1	0.8060
MTBE	5.04	1.00	0.74	88.2	0.7460
sec-Butanol	5.36	1.06	0.79	74.1	0.8114
DIPE	5.76	1.14	0.85	102.2	0.7300
Isobutanol	6.00	1.19	0.88	74.1	0.8058
ETBE	6.20	1.23	0.91	102.2	0.7452
tert-Pentanol	6.43	1.28	0.95	88.1	0.8170
1,2-Dimethoxyethane (DME)	6.80	1.35	1.00	90.1	0.8720
n-Butanol	7.04	1.40	1.04	74.1	0.8137
Benzene	7.41	1.47	1.09	78.1	0.8830
TAME	8.17	1.62	1.20	102.2	0.7758

TABLE 2 Chromatographic Operation Conditions

Temperatures		Flows, mL/min		Carrier Gas: Helium	
Column Oven	60	to injector	75	Sample size, µL[A]	1.0–3.0
Injector, °C	200	Column	5	Split ratio	15:1
Detector—TCD, °C	200	Auxiliary	3	Backflush, min	0.2–0.3
—FID, °C	250	Makeup	18	Valve reset time	8–10 min
Valve °C	60			Total Analysis time	18–20 min

[A] Sample size must be adjusted so that alcohols in the range of 0.1 to 12.0 mass % and ethers in the range of 0.1 to 20.0 mass % are eluted from the column and measured linearly at the detector. A sample size of 1.0 µL has been introduced in most cases.

6.1.3 *Switching and Backflushing Valve*—A valve, to be located within the gas chromatographic column oven, capable of performing the functions described in Section 11 and illustrated in Fig. 1. The valve shall be of low volume design and not contribute significantly to chromatographic deterioration.

6.1.3.1 *Valco Model No. A 4C10WP*, 1.6 mm (1/16 in.) fittings. This particular valve was used in the majority of the analyses used for the development of Section 15.

6.1.3.2 *Valco Model No. C10W*, 0.8 mm (1/32 in.) fittings. This valve is recommended for use with columns of 0.32 mm inside diameter and smaller.

6.1.3.3 Some gas chromatographs are equipped with an auxiliary oven which can be used to contain the valve and polar column. In such a configuration, the nonpolar column is located in the main oven and the temperature can be adjusted for optimum oxygenates resolution.

6.1.4 An automatic valve switching device must be used to ensure repeatable switching times. Such a device should be synchronized with injection and data collection times.

6.1.5 *Injection System*—The chromatograph should be equipped with a splitting-type inlet device if capillary columns or flame ionization detection are used. Split injection is necessary to maintain the actual chromatographed sample size within the limits of column and detector optimum efficiency and linearity.

6.1.5.1 Some gas chromatographs are equipped with on-column injectors and autosamplers which can inject small samples sizes. Such injection systems can be used provided that sample size is within the limit of the column and detectors optimum efficiency and linearity.

6.1.5.2 Microlitre syringes, automatic syringe injectors, and liquid sampling valves have been used successfully for introducing representative samples into the gas chromatographic inlet.

6.2 *Data Presentation or Calculation, or Both:*

6.2.1 *Recorder*—A recording potentiometer or equivalent with a full-scale deflection of 5 mV or less can be used to monitor detector signal. Full-scale response time should be 1 s or less with sufficient sensitivity and stability to meet the requirements of 6.1.2.

6.2.2 *Integrator or Computer*—Means shall be provided for determining the detector response. Peak heights or areas can be measured by computer, electronic integration or manual techniques.

6.3 *Columns, Two as Follows:*

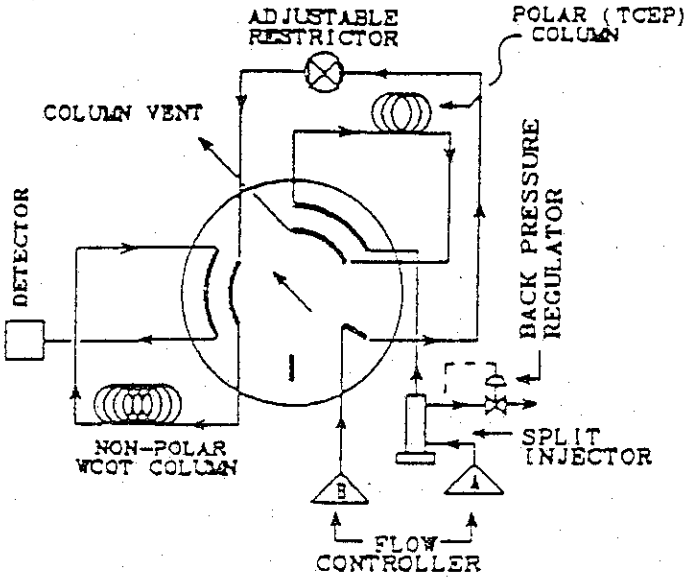

FIG. 1 Analysis of Oxygenates in Gasoline Schematic of Chromatographic System

6.3.1 *Polar Column*—This column performs a preseparation of the oxygenates from volatile hydrocarbons in the same boiling point range. The oxygenates and remaining hydrocarbons are backflushed onto the non-polar column in 6.3.2. Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.1.1 can be used. The column shall perform at the same temperature as required for the column in 6.3.2, except if located in a separate auxiliary oven as in 6.1.3.3.

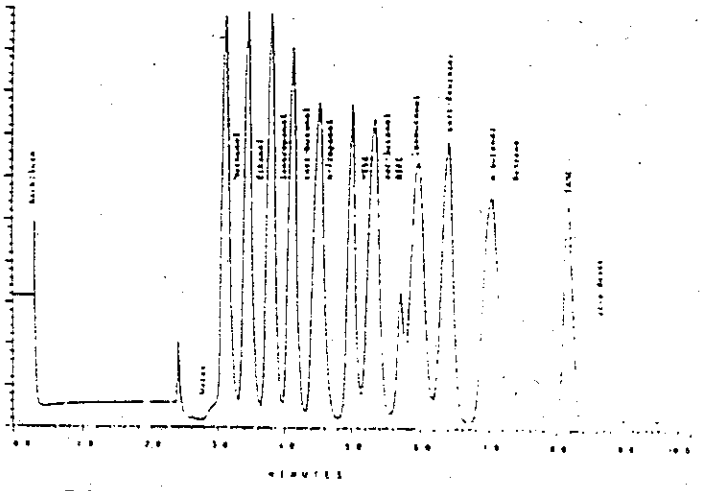

FIG. 2 Analyses of Oxygenates in Gasoline Example Chromatogram Showing Oxygenates

6.3.1.1 *TCEP Micro-Packed Column*,[4] 560 mm (22 in.) by 1.6 mm (1/16 in.) outside diameter by 0.38 mm (0.015 in.) inside diameter stainless steel tube packed with 0.14 to 0.15 g of 20 % (mass/mass) TCEP on 80/100 mesh Chromosorb P(AW). This column was used in the cooperative study to provide the precision and bias data referred to in Section 15.

6.3.2 *Non-Polar (Analytical) Column*—Any column with equivalent or better chromatographic efficiency and selectivity to that described in 6.3.2.1 and illustrated in Fig. 2 can be used.

6.3.2.1 *WCOT Methyl Silicone Column*, 30 m (1181 in.) long by 0.53 mm (0.021 in.) inside diameter fused silica WCOT column with a 2.6 µm film thickness of cross-linked methyl siloxane. This column was used in the cooperative study to provide the precision and bias data referred to in Section 15.

7. Reagents and Materials

7.1 *Carrier Gas*—Carrier gas appropriate to the type of detector used. Helium has been used successfully. The minimum purity of the carrier gas used must be 99.95 mol %.

7.2 *Standards for Calibration and Identification*—Standards of all components to be analyzed and the internal standard are required for establishing identification by retention time as well as calibration for quantitative measurements. These materials shall be of known purity and free of the other components to be analyzed.

NOTE 2: Warning—These materials are flammable and can be harmful or fatal if ingested or inhaled.

7.3 *Methylene Chloride*—Used for column preparation Reagent grade free of non-volatile residue.

NOTE 3: Warning—Harmful if inhaled. High concentrations may cause unconsciousness or death.

8. Preparation of Column Packings

8.1 *TCEP Column Packing:*

8.1.1 Any satisfactory method, used in the practice of the art that will produce a column capable of retaining the C

[4] Available from Hewlett Packard Co., Avondale, PA.

C4 alcohols and MTBE, ETBE, DIPE and TAME from components of the same boiling point range in a gasoline sample. The following procedure has been used successfully.

8.1.2 Completely dissolve 10 g of TCEP in 100 mL of methylene chloride. Next add 40 g of 80/100 mesh Chromosorb P(AW) to the TCEP solution. Quickly transfer this mixture to a drying dish, in a fume hood, without scraping any of the residual packing from the sides of the container. Constantly, but gently, stir the packing until all of the solvent has evaporated. This column packing can be used immediately to prepare the TCEP column.

9. Sampling

9.1 Every effort should be made to ensure that the sample is representative of the fuel source from which it is taken. Follow the recommendations of Practice D 4057 or its equivalent when obtaining samples from bulk storage or pipelines.

9.2 Upon receipt in the laboratory, chill the sample in its original container to 0 to 5°C (32 to 40°F) before any subsampling is performed.

9.3 If necessary, transfer the chilled sample to a vapor tight container and store at 0 to 5°C (32 to 40°F) until needed for analysis.

10. Preparation of Micro-Packed TCEP Column

10.1 Wash a straight 560 mm length of 1.6 mm outside diameter (0.38 mm inside diameter) stainless steel tubing with methanol and dry with compressed nitrogen.

10.2 Insert 6 to 12 strands of silvered wire, a small mesh screen or stainless steel frit inside one end of the tube. Slowly add 0.14 to 0.15 g of packing material to the column and gently vibrate to settle the packing inside the column. When strands of wire are used to retain the packing material inside the column, leave 6.0 mm (0.25 in.) of space at the top of the column.

10.3 *Column Conditioning*—Both the TCEP and WCOT columns are to be briefly conditioned before use. Connect the columns to the valve (see 11.1) in the chromatographic oven. Adjust the carrier gas flows as in 11.3 and place the valve in the RESET position. After several minutes, increase the column oven temperature to 120°C and maintain these conditions for 5 to 10 min. Cool the columns below 60°C before shutting off the carrier flow.

11. Preparation of Apparatus and Establishment of Conditions

11.1 *Assembly*—Connect the WCOT column to the valve system using low volume connectors and narrow bore tubing. It is important to minimize the volume of the chromatographic system that comes in contact with the sample, otherwise peak broadening will occur.

11.2 Adjust the operating conditions to those listed in Table 2, but do not turn on the detector circuits. Check the system for leaks before proceeding further.

11.2.1 If different polar and nonpolar columns are used, or capillary columns of smaller ID are used, or both, it can be necessary to use different optimum flows and temperatures.

11.3 *Flow Rate Adjustment:*

11.3.1 Attach a flow measuring device to the column vent with the valve in the RESET position and adjust the pressure to the injection port to give 5.0 mL/min flow (14 psig). Soap bubble flow meters are suitable.

11.3.2 Attach a flow measuring device to the split injector vent and adjust the flow from the split vent using the A flow controller to give a flow of 70 mL/min. Recheck the column vent flow set in 11.3.1 and adjust if necessary.

11.3.3 Switch the valve to the BACKFLUSH position and adjust the variable restrictor to give the same column vent flow set in 11.3.1. This is necessary to minimize flow changes when the valve is switched.

11.3.4 Switch the valve to the inject position RESET and adjust the B flow controller to give a flow of 3.0 to 3.2 mL/min at the detector exit. When required for the particular instrumentation used, add makeup flow or TCD switching flow to give a total of 21 mL/min at the detector exit.

11.4 When a thermal conductivity detector is used, turn on the filament current and allow the detector to equilibrate. When a flame ionization detector is used, set the hydrogen and air flows and ignite the flame.

11.5 *Determine the Time to Backflush*—The time to backflush will vary slightly for each column system and must be determined experimentally as follows. The start time of the integrator and valve timer must be synchronized with the injection to accurately reproduce the backflush time.

11.5.1 Initially assume a valve BACKFLUSH time of 0.23 min. With the valve RESET, inject 1 to 3 µL of a blend containing at least 0.5 % or greater oxygenates (7.3), and simultaneously begin timing the analysis. At 0.23 min, rotate the valve to the BACKFLUSH position and leave it there until the complete elution of TAME is realized. Record this time as the RESET time, which is the time at which the valve is returned to the RESET position. When all of the remaining hydrocarbons are backflushed the signal will return to a stable baseline and the system is ready for another analysis. The chromatogram should appear similar to the one illustrated in Fig. 2.

11.5.1.1 Ensure that the BACKFLUSH time is sufficient to quantitatively transfer the higher concentrations of the ethers, specifically MTBE, into the nonpolar column.

11.5.2 It is necessary to optimize the valve BACKFLUSH time by analyzing a standard blend containing oxygenates. The correct BACKFLUSH time is determined experimentally by using valve switching times between 0.20 and 0.35 min. When the valve is switched too soon, C5 and lighter hydrocarbons are backflushed and are co-eluted in the C4 alcohol section of the chromatogram. When the valve BACKFLUSH is switched too late, part or all of the ether component (MTBE, ETBE or TAME) is vented resulting in an incorrect ether measurement.

11.5.2.1 DIPE may require a BACKFLUSH time slightly shorter than the other ethers. The system may require reoptimization if the analysis of DIPE is required.

11.5.3 To facilitate setting BACKFLUSH time, the column vent in Figure 1 can be connected to a second detector (TCD or FID) as described in Test Method D 4420 and used to set BACKFLUSH TIME based on the oxygenates standard containing the ethers of interest.

12. Calibration and Standardization

12.1 *Identification*—Determine the retention time of each component by injecting small amounts either separately, or in known mixtures or by comparing the relative retention times with those in Table 1.

12.1.1 In order to ensure minimum interference from hydrocarbons, it is strongly recommended that a fuel devoid of oxygenates be chromatographed to determine the level of any hydrocarbon interference.

12.2 *Preparation of Calibration Samples*—Prepare multicomponent calibration standards of the oxygenates and concentration ranges of interest by mass according to Test Method D 4307. For each oxygenate, prepare a minimum of five calibration standards spanning the range of the oxygenate in the samples. As an example, for full range calibration, 0.1, 0.5, 2, 5, 10, 15, and 20 mass percent of each oxygenate may be used. Before preparing the standards, determine the purity of the oxygenate stocks and make corrections for the impurities found. Whenever possible, use stocks of at least 99.9 % purity. Correct the purity of the components for water content determined by Test Method D 1744. To minimize evaporation of light components, chill all chemicals and gasoline used to prepare standards. Prepare standards by transferring a fixed volume of oxygenates using pipettes or eye droppers (for volumes below one volume percent) to 100 mL volumetric flasks or septum capped vials as follows. Cap and record the tare weight of the volumetric flask or vial to 0.1 mg. Remove the cap and carefully add the oxygenate to the flask or vial. Do not contaminate with sample the part within the flask or vial which contacts the cap. Cap and record the net mass (*Wi*) to 0.1 mg of the oxygenate added. Repeat the addition and weighing procedure for each oxygenate of interest. Similarly, add 5 mL of the internal standard (DME) and record its net mass (*Ws*) to 0.1 mg. Dilute each standard to 100.0 mL with oxygenate-free gasoline or a mixture of hydrocarbons such as isooctane/mixed xylenes (63.35 volume percent). Do not exceed 30 volume percent for all oxygenates, including the internal standard added. Store the capped calibrations standards below 5°C (40°F) when not in use.

12.3 *Standardization:*

12.3.1 Run the calibration standards and establish the calibration curve for each oxygenate. Plot the response ratio (rsp_i):

$$rsp_i = (Ai/As) \tag{2}$$

where:
Ai = area of oxygenate, and
As = area of internal standard.
as the *y*-axis versus the amount ratio (amt_i):

$$amt_i = (Wi/Ws) \tag{3}$$

where:
Wi = mass of oxygenate, and
Ws = mass of internal standard.
as the *x*-axis calibration curves for each oxygenate. Check the correlation r^2 value for each oxygenate calibration. The r^2 value should be at least 0.99 or better. r^2 is calculated as follows:

$$r^2 = \frac{(\Sigma xy)^2}{(\Sigma x^2)(\Sigma y^2)} \tag{4}$$

where:

$$x = X_i - \bar{X} \tag{5}$$
$$y = Y_i - \bar{y} \tag{6}$$

and:
X_i = amt_i ratio data point,
$\bar{X}$ = average values for all (amt_i) data points,
Y_i = corresponding rsp_i ratio data point, and
$\bar{y}$ = average values for all (rsp_i) data points.

12.3.2 Table 3 gives an example on the calculation of r^2 for an ideal data set X_i and Y_i:

12.3.3 For each oxygenate *i* calibration data set, obtain the linear least-squares fit equation in the form:

$$(rsp_i) = (m_i)(amt_i) + b_i \tag{7}$$

where:
(rsp_i) = response ratio for oxygenate *i* (*y*-axis),
m_i = slope of linear equation for oxygenate *i*,
amt_i = amount ratio for oxygenate *i* (*x*-axis), and
b_i = *y*-axis intercept.

12.3.4 The values m_i and b_i are calculated as follows:

$$m_i = \Sigma xy/\Sigma x^2 \tag{8}$$

and

$$b_i = \bar{y} - m_i\bar{x} \tag{9}$$

12.3.5 For the example in Table 3:

$$m_i = 5/10 = 0.5 \tag{10}$$

and

$$b_i = \bar{y} - m_i\bar{x} = 1.5 - (0.5)(3) = 0 \tag{11}$$

Therefore, the least-squares fit (Eq 7) for the above example in Table 3 is:

$$(rsp_i) = 0.5\ amt_i + 0 \tag{12}$$

NOTE 5—Normally the b_i value is not zero and may be either positive or negative. Figure 3 gives an example of a linear least-squares fit for MTBE and the resulting equation in the form of Eq 7 above.

12.3.6 For an optimum calibration, the absolute value of the *y*-intercept b_i must be at a minimum. In this case, A_i approaches zero when w_i is less than 0.1 mass percent. The equation to determine the mass percent oxygenate *i* or w_i reduces to Eq 13. The *y*-intercept can be tested using Eq 13 below:

$$w_i = (b_i/m_i)(W_s/W_g)100\ \% \tag{13}$$

where:
w_i = mass % oxygenate *i*, where w_i is <0.1 mass %,
W_s = mass of internal standard added to the gasoline samples g, and

TABLE 3 Example Calculation of Correlation Coefficient

X_i	Y_i	$x = X_i - \bar{x}$	$y = Y_i - \bar{y}$	xy	x^2	y^2
1.0	0.5	−2.0	−1.0	2.0	4.0	1.0
2.0	1.0	−1.0	−0.5	0.5	1.0	0.25
3.0	1.5	0.0	0.0	0.0	0.0	0.0
4.0	2.0	+1.0	0.5	0.5	1.0	0.25
5.0	2.5	+2.0	1.0	2.0	4.0	1.0
$\bar{x} = 3.0$	$\bar{y} = 1.5$			$(\Sigma xy)^2 = 25.0$	$\Sigma x^2 = 10.0$	$\Sigma y^2 = 2.5$

$$r^2 = \frac{(\Sigma xy)^2}{(\Sigma x^2)(\Sigma y^2)} = \frac{25.0}{(10.0)(2.5)} = 1.0$$

W_g = mass of gasoline samples, g.

NOTE 6—Since in practice W_s and W_g vary slightly from sample to sample, use average values.

12.3.7 The following gives an example of the calculation for the *y*-intercept (b_i) test using Fig. 3 for oxygenate *i* (MTBE) for which b_i = 0.015 and m_i = 1.83. From 13.1, a typical sample preparation may contain approximately W_s = 0.4 g (0.5 mL) of internal standard and approximately W_g = 7 g (9.5 mL) of a gasoline sample. Substituting these values into Eq 13 yields:

$$w_i = (0.015/1.83)(0.4 \text{ grams}/7 \text{ grams})\ 100\ \% = 0.05 \text{ mass } \% \quad (14)$$

12.3.8 Since w_i is less than 0.1 mass percent, the *y*-intercept b_i has an acceptable value for MTBE. Similarly, determine w_i for all other oxygenates. For all oxygenates, w_i must be less than 0.1 mass percent. If any of the w_i values are greater than 0.1 mass percent, rerun the calibration procedure for oxygenate *i* or check instrument parameters and hardware or check for hydrocarbon interferences.

13. Procedure

13.1 *Preparation of Sample*—Transfer 0.5 mL of internal standard (*Ws*) by a volumetric pipette into a tared and capped 10 mL volumetric flask. Record weight to nearest 0.1 mg. Record the net mass of the internal standard added. Retare the capped flask. Fill the 10 mL volumetric flask to volume with sample, cap and record the net mass (*Wg*) to the nearest 0.1 mg of the sample added. Mix thoroughly and inject into the gas chromatograph. If using an automatic sampler then transfer an aliquot of the solution into a glass gas chromatographic (GC) vial. Seal the GC vial with a Teflon-lined septum. If the sample is not immediately analyzed, store below 5°C (40°F).

13.2 *Chromatographic Analysis*—Introduce a representative aliquot of the sample, containing internal standard, into the gas chromatograph using the same technique and sample size as used for the calibration analysis. An injection volume of 1.0 to 3.0 µL with a 15:1 split ratio has been used successfully. Start recording and integrating devices in synchronization with sample introduction. Obtain a chromatogram or integrated peak report or both which displays the retention times and integrated area of each detected component.

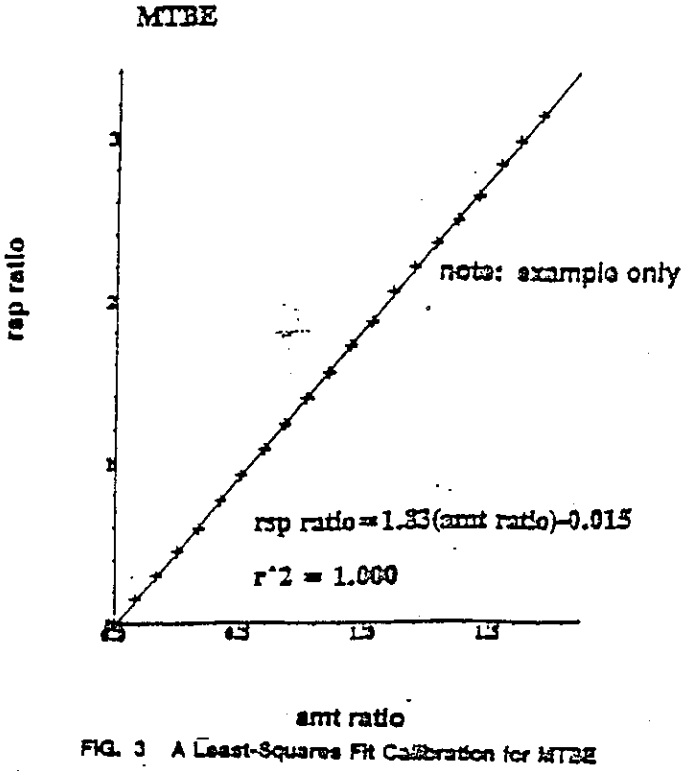

FIG. 3 A Least-Squares Fit Calibration for MTBE

13.3 *Interpretation of Chromatogram*—Compare the retention times of sample components to those of the calibration analysis to determine the identities of oxygenates present.

14. Calculations and Reporting

14.1 *Mass Concentration of Oxygenates*—After identifying the various oxygenates measure the area of each oxygenate peak and that of the internal standard. From the least-squares fit calibrations, as depicted in the MTBE example in Fig. 3, calculate the mass of each oxygenate (W_i) in the gasoline samples using the response ratio (rsp_i) of the areas of the oxygenate to that of the internal standard as follows:

$$rsp_i = (m_i)(amt_i) + b_i \quad (7)$$

where:

m_i = slope of the linear fit,
b_i = *y*-intercept, and
amt_i = amount ratio as defined by Eq 3.

or

$$amt_i = \frac{Wi}{Ws} = (rsp_i - b_i)/m_i \quad (15)$$

or

$$Wi = [(rsp_i - b_i)/m_i]Ws \quad (16)$$
$$= [(Ai/As - b_i)/m_i]Ws \quad (17)$$

To obtain mass percent (w_i) results for each oxygenate:

$$w_i = \frac{Wi(100\ \%)}{W_g} \quad (18)$$

where:

W_g = weight of gasoline sample.

14.2 Report the mass percent of each oxygenate to the nearest 0.01 mass percent.

14.3 *Volumetric Concentration of Oxygenates*—If the volumetric concentration of each oxygenate is desired, calculate the volumetric concentration according to Eq 14:

$$V_i = wi\left(\frac{D_f}{D_i}\right) \quad (19)$$

where:

w_i = mass percent of each oxygenate as determined using Eq 13,
V_i = volume percent of each oxygenate to be determined,
D_i = relative density at 15.56°C (60°F) of the individual oxygenate as found in Table 2, and
D_f = relative density of the fuel under study as determined by Test Method D 1298 or D 4052.

14.4 Report the volume percent of each oxygenate to the nearest 0.01 volume percent.

14.5 *Mass Percent Oxygen*—To determine the oxygen content of the fuel, convert and sum the oxygen contents of

TABLE 4 Precision Interval as Determined from Cooperative Study Data

Component	MEOH	EtOH	iPA	tBA	nPA	MTBE	sBA	DIPE	iBA	ETBE	tAA	nBA	TAME	Total Oxygen
Repeatability														
Wt. %														
0.20	0.04	0.02	0.02	0.02	0.01	0.02	0.01	0.03	0.03	0.01	0.02	0.02	0.02	
0.50	0.06	0.04	0.03	0.03	0.02	0.03	0.02	0.05	0.05	0.03	0.03	0.04	0.03	
1.00	0.09	0.06	0.04	0.04	0.03	0.05	0.03	0.08	0.08	0.05	0.04	0.06	0.05	0.02
2.00	0.14	0.09	0.06	0.06	0.05	0.07	0.05	0.12	0.12	0.09	0.06	0.09	0.08	0.05
3.00	0.17	0.12	0.07	0.07	0.06	0.09	0.06	0.15	0.15	0.12	0.08	0.12	0.11	0.08
4.00	0.20	0.14	0.09	0.09	0.07	0.11	0.07	0.17	0.17	0.16	0.09	0.14	0.13	0.12
5.00	0.23	0.16	0.10	0.10	0.08	0.12	0.08	0.20	0.20	0.19	0.11	0.16	0.15	0.15
6.00	0.26	0.18	0.11	0.11	0.08	0.14	0.09	0.22	0.22	0.22	0.12	0.18	0.17	
10.00	0.35	0.24	0.15	0.15	0.11	0.18	0.12	0.29	0.29	0.33	0.16	0.24	0.25	
12.00	0.39	0.27	0.16	0.16	0.12	0.20	0.14	0.32	0.32	0.38	0.18	0.27	0.29	
14.00						0.22		0.35		0.44			0.32	
16.00						0.24		0.38		0.49			0.35	
20.00						0.27		0.43		0.58			0.41	
Reproducibility														
Component	MEOH	EtOH	iPA	tBA	nPA	MTBE	sBA	DIPE	iBA	ETBE	tAA	nBA	TAME	Total Oxygen
Wt. %														
0.20	0.14	0.09	0.14	0.07	0.04	0.04	0.15	0.14	0.14	0.11	0.06	0.09	0.14	
0.50	0.24	0.16	0.26	0.12	0.07	0.08	0.28	0.26	0.26	0.21	0.10	0.15	0.22	
1.00	0.37	0.23	0.42	0.19	0.11	0.12	0.44	0.42	0.42	0.46	0.15	0.22	0.31	0.09
2.00	0.57	0.34	0.67	0.30	0.16	0.19	0.70	0.67	0.67	0.81	0.22	0.33	0.44	0.22
3.00	0.72	0.43	0.80	0.40	0.21	0.25	0.92	0.88	0.88	0.83	0.28	0.41	0.54	0.36
4.00	0.86	0.51	1.06	0.48	0.24	0.30	1.11	1.06	1.06	1.03	0.33	0.49	0.63	0.52
5.00	0.99	0.58	1.23	0.56	0.28	0.35	1.29	1.23	1.23	1.22	0.38	0.55	0.70	0.70
6.00	1.10	0.64	1.40	0.63	0.31	0.40	1.46	1.40	1.40	1.41	0.42	0.61	0.77	
10.00	1.51	0.86	1.97	0.89	0.41	0.56	2.06	1 97	1.97	2.07	0.56	0.82	1.00	
12.00	1.68	0.95	2.22	1.00	0.45	0.63	2.33	2.22	2.22	2.38	0.62	0.91	1.10	
14.00						0.70		2.46		2.68			1.19	
16.00						0.77		2.59		2.96			1.28	
20.00						0.89		3.13		3.51			1.43	

all oxygenated components determined above according to the following equation:

$$W_{tot} = \Sigma \frac{w_i \times 16.0 \times N_i}{M_i} \quad (20)$$

or

$$W_{tot} = \frac{w_1 \times 16.0 \times N_1}{M_1} + \frac{w_2 \times 16.0 \times N_2}{M_2} + \ldots \quad (21)$$

where:

w_i = mass percent of each oxygenate as determined using Eq 13,
W_{tot} = total mass percent oxygen in the fuel,
M_i = molecular mass of the oxygenate as given in Table 2,
16.0 = atomic mass of oxygen, and
N_i = number of oxygen atoms in the oxygenate molecule.

14.6 Report the total mass percent of oxygen in the fuel to the nearest 0.01 mass percent.

15. Precision and Bias[5]

15.1 *Precision*—The precision of this test method as determined by a statistical examination of interlaboratory test results is as follows:

15.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test materials would, in the long run, in the normal and the correct operation of the test method exceed the following values in Table 4 only in one case in twenty.

Repeatability Estimates for Oxygenates in Gasoline

Component	Repeatability
Methanol (MeOH)	0.09 ($X^{0.59}$)
Ethanol (EtOH)	0.06 ($X^{0.41}$)
Isopropanol (iPA)	0.04 ($X^{0.56}$)
tert-Butanol (tBA)	0.04 ($X^{0.56}$)
n-Propanol (nPA)	0.003 ($X^{0.57}$)
MTBE	0.05 ($X^{0.56}$)
sec-Butanol (sBA)	0.003 ($X^{0.61}$)
DIPE	0.08 ($X^{0.56}$)
Isobutanol (iBA)	0.08 ($X^{0.56}$)
ETBE	0.05 ($X^{0.62}$)
tert-Pentanol (tAA)	0.04 ($X^{0.61}$)
n-Butanol (nBA)	0.06 ($X^{0.61}$)
TAME	0.05 ($X^{0.70}$)
Total Oxygen	0.02 ($X^{1.26}$)

where X is the mean mass percent of the component.

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical material would, in the long run, exceed the following values in Table 4 only in one case in twenty.

[5] Supporting data available from ASTM Headquarters. Request D02-1296.

Reproducibility Estimates in Oxygenates in Gasolines

Component	Reproducibility
Methanol (MeOH)	$0.37 (X^{0.61})$
Ethanol (EtOH)	$0.23 (X^{0.57})$
Isopropanol (iPA)	$0.42 (X^{0.67})$
tert-Butanol (tBA)	$0.19 (X^{0.67})$
n-Propanol (nPA)	$0.11 (X^{0.57})$
MTBE	$0.12 (X^{0.67})$
sec-Butanol (sBA)	$0.44 (X^{0.67})$
DIPE	$0.42 (X^{0.67})$
Isobutanol (iBA)	$0.42 (X^{0.67})$
ETBE	$0.36 (X^{0.74})$
tert-Pentanol (tAA)	$0.15 (X^{0.57})$
n-Butanol (nBA)	$0.22 (X^{0.57})$
TAME	$0.31 (X^{0.51})$
Total Oxygen	$0.09 (X^{1.27})$

where X is the mean mass percent of the component.

15.2 *Bias*—The National Institutes of Standards and Technology (NIST) provides selected alcohols in reference fuels. As an example the following standard reference materials (SRM) in reference fuels are available as described in the NIST Standard Reference Catalog.[6]

16. Keywords

16.1 alcohols; ethers; oxygenates; gasoline; gas chromatography; MTBE (Methyl tert-butylether); ETBE (Ethyl tert-butylether); TAME (Tert-amylmethylether); DIPE (Disopropylether)

[6] NIST Special Publication 260; NIST Standard Reference Materials 1990–1991.

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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, 1916 Race St., Philadelphia, PA 19103.

ATTACHMENT D

April 11, 1995 Letter from Lynn Hunter of Wasson-ECE to Dr. Shiou-Mei Huang

April 24, 1995 Letter from Paul Rieger to Lynn Hunter

WASSON·ECE
INSTRUMENTATION

11 April 1995

Dr. Shiou-Mei Huang
California Air Resources Board
9530 Telstar Avenue
El Monte, CA 91731-2990
ph. 818-575-6875
FAX 818-575-6818

Dear Dr. Huang:

Thank you for all the help which you provided to me which allowed me to attend the workshop which you hosted last Wednesday. I found the workshop to be very interesting and informative and specifically wanted to present some information which I hope you will find valuable. If this information should not be addressed to you, please forward this document to the proper party.

Oxygenates in Gasoline
As I understood it, the Board has chosen to use ASTM method D-4815-94 because it is perceived as the most reproducible and reliable method. As I remember it from my notes, I believe that you showed a reproducibility for the ASTM D-4815-94 method of approximately 2.5% and a reproducibility for the OFID method of 10%. Please tell me where the reproducibility for the OFID came from? My guess was that the reproducibility was actually pulled from the CFR rather than from experimental results, is this true?

I have contacted Ms. Cherlyn Bradley of Amoco in Naperville with regards to providing me with ASTM round-robin experimentally produced data showing the reproducibility of the OFID to be less than 2.5% in the concentration range of interest for all components. I have enclosed a copy of that data for your review. I am sure that Ms. Bradley, the chair for the committee charged with evaluating and creating the OFID method for ASTM, would be happy to provide you with the raw data and calculations which she used to generate those numbers. Ms. Bradley may be reached by phone at 708-420-5216 or by FAX at 708-420-5252.

1305 Duff Drive
Fort Collins, Colorado 80524
(303) 221-9179
FAX (303) 221-9364

Your concern about the historic reliability of the OFID is founded based on the performance of the OFID during the months of December '94 and January '95. I would estimate that Wasson-ECE has provided more than 95% of the OFID's purchased in the U.S. thus far and that during those months, we saw failures of the catalytic cracking reactor which may have been due to materials problems.

All of those cracking reactor units which failed were replaced under warranty. We began intensive research to eliminate the materials problem. Design changes have been made, including rector composition and dimensions. We began releasing the redesigned reactors to our customer base in mid-January and have not seen any failures of the new reactor design thus far. We are confident that the reliability problem has been solved.

Another criterion that was mentioned for other analyses (not particularly for oxygenates) was the stability of calibration. Because of the use of the TCEP column in the D-4815 method, the calibration and timing of that configuration is particularly subject to change. This is because of the high bleed rate of the TCEP column. If you consult with some of the WSPA members who have both OFID and 4815 instruments, I think that you will find that the 4815 requires much more constant maintenance (with regard to valve timing) and calibration than the OFID and is subject to change more often than the OFID.

The CFR OFID method requires control charting for the OFID which requires users to recalibrate if the independent or routine reference standards fall outside the control parameters. Ms. Sonia Bain of Ashland Petroleum Research and Development reports that her laboratory uses a 3% RSD control point on 10% MTBE and a 2% RSD on 12% ethanol (both of these are more stringent than the EPA specifications) and that she has not needed to recalibrate in 6 months, even after changing cracking reactors. If you have specific questions for Ms. Bain, she may be reached by phone at 606-921-6369 or by FAX at 606-921-2580.

Finally, the OFID method is more selective than the 4815 method. High concentrations of olefinic compounds in gasolines have caused interferences with MTBE in the ASTM D-4815 method. I know that several of the WSPA members have seen this interference and that the capability of running a clean "blank" using gasoline has been difficult, if not impossible, below the 0.5% level. By comparison, the OFID method allows clean blanks to be run down to a limit of about 0.005%.

With regards to combination of methods, it is possible to install both the OFID configuration and the ASTM D-5580 configuration in the same gas chromatograph. While these two methods could be combined in the same GC, they could not run simultaneously.

I would request that you re-evaluate the OFID based on the information and resources provided. I suggest that CARB adopt the OFID method for the following reasons: 1) it is more reproducible and repeatable than the ASTM D-4815-94 method 2) it is more specific to oxygenates 3) it is easier to use than the ASTM D-4815-94 method because it does not require valve timing adjustments based on column degradation over time 4) the OFID method is more stable than the D-4815-94 method.

Some of the information presented here was not available to me until after I attended the meeting. I did not want to present some of the information during the workshop because I did not wish to turn your workshop into a Wasson-ECE info-mercial. If you have questions or would like additional information or resources, please call me.

Aromatics in gasoline

I believe that the board's choice of ASTM method D-5580 is correct and that it will provide a better analysis than D-3606. However, the method is not as accurate as the GC/MS method suggested by the USEPA because of the limited number of components which are assayed. Also, there are drawbacks to the analysis which I think that you should be aware of and for which you may want to consider soliciting solutions from the technical community.

One of the participants of the recent ASTM round-robin testing for the D-5580 method found that toluene and 2-hexanone (the internal standard) are not baseline resolved. The user does not wish to be identified for political reasons (within the ASTM). I have included an excerpt from the user's letter to USEPA for your review.

"We participated in both ASTM D 5580 round robins for benzene and aromatics and did well. ASTM did not accept our D 3606 round robin results because they were run using the modified method even though our results were in good agreement with other D 3606 participants, D 5580 and GC/MS results. The D 5580 separation between toluene and the internal standard, 2 hexanone, is not a baseline separation as seen in chromatogram II (enclosed). Chromatograms I (modified D 3606) and II (D 5580) were plotted using the same scale for comparison of resolution. All D 5580 round robin samples contained at least 2 volume % of toluene. Gasolines from refineries with BTX extraction processes typically contain less than 2 volume % toluene. This may be a problem since it will be difficult to quantify accurately the internal standard in the presence of diminutive amounts of toluene. The difference in retention time between ethanol and benzene by modified D 3606 is 1.336 minutes. The difference between 2-hexanone and toluene is only 0.56 minutes. This difference is not as bad as it looks since D 3606 is a packed column while D 5580 is megabore; and ethanol tails while 2 hexanone does not."

The chromatograms referred to are enclosed for your review. As with the D-4815-94 method, the D-5580 method uses a TCEP micro-packed stripper column which may also degrade over time and may possibly cause even more coelution of toluene and 2-hexanone. I think that this should be considered, even though the D-5580 method is more powerful than the D-3606 method with alternate columns which have been accepted for use by the USEPA. I would suggest that research be initiated for an alternate stripper column be used in place of the TCEP column which is used in the D-5580 method.

Also, please be aware (and make your constituents aware) that 2-hexanone is a volatile neural agent which may be adsorbed through the skin or mucous membranes. This fact is not prominent in the ASTM methodology, and anyone who is adding the component as an internal standard to samples is at risk. Also note that the effects of 2-hexanone are cumulative and are not dissipated over time.

As it was suggested during the workshop, should the board decide to stay with the D-4815 method, both configurations for D-4815 and D-5580 could be incorporated into the same GC, although they could not be run simultaneously.

Thank you again for your help, for hosting the workshop, and for this opportunity to present data and information to you. I hope that there will be a September 29 workshop. Barring that, I would like to submit alternate methods at the Board Hearing on October 26, once the logistics of that issue have been resolved. Please keep me informed of workshops and procedures for submitting alternate methods. If you have any questions or would like additional information, please call me at 303-221-9179.

Sincerely,

Lynn Hunter
Product Manager Chromatography

LH/ab
enc.
cc: D. Sanders, HP
R. Cherney, HP
S. Bain, Ashland
C. Bradley, Amoco

APR-11-1995 14:22 FROM AMOCO CORPORATION TO 93032219364 P.02

1994 Summer/Fall
OFID

Table 3

Precision Interval as Determined from Cooperative Study Data
Repeatability

Component Wt %	MeOH	EtOH	IPA	tBA	nPA	NTBE	sBA	DIPE	IBA	ETBE	tAA	nBA	TAME	TOTAL OXYGEN
0.20	0.03	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.01	0.01	0.03	0.03	0.02	-
0.50	0.05	0.02	0.03	0.03	0.03	0.03	0.02	0.03	0.02	0.01	0.04	0.04	0.03	-
1.00	0.07	0.03	0.04	0.05	0.04	0.05	0.03	0.05	0.03	0.04	0.05	0.06	0.04	0.03
2.00	0.10	0.06	0.06	0.08	0.05	0.07	0.04	0.08	0.05	0.07	0.07	0.08	0.06	0.06
3.00	0.12	0.08	0.07	0.10	0.06	0.09	0.05	0.10	0.07	0.10	0.08	0.10	0.08	0.08
4.00	0.13	0.11	0.08	0.12	0.06	0.11	0.06	0.12	0.09	0.13	0.09	0.11	0.09	0.11
5.00	0.15	0.13	0.09	0.14	0.07	0.13	0.07	0.14	0.11	0.16	0.10	0.13	0.10	0.13
6.00	0.17	0.16	0.10	0.16	0.07	0.14	0.08	0.16	0.12	0.19	0.10	0.14	0.11	-
10.00	0.22	0.25	0.14	0.22	0.09	0.19	0.10	0.22	0.18	0.29	0.13	0.17	0.15	-
12.00	0.24	0.29	0.15	0.25	0.09	0.21	0.11	0.25	0.21	0.34	0.14	0.19	0.17	-
14.00	-	-	-	-	-	0.23	-	0.28	-	0.39	-	-	0.18	-
16.00	-	-	-	-	-	0.25	-	0.30	-	0.43	-	-	0.20	-
20.00	-	-	-	-	-	0.28	-	0.35	-	0.53	-	-	0.23	-

APR-11-1995 14:22 FROM AMOCO CORPORATION TO 93032219364 P.03

1994 Summer/Fall
OF 1.0

TOTAL P.03

Recoverability

Component Wt %	MeOH	EtOH	IPA	tBA	nPA	MIBE	sBA	DIPE	IBA	EIBE	3AA	nBA	TAME	TOTAL OXYGEN
0.20	0.06	0.07	0.06	0.05	0.04	0.02	0.05	0.05	0.05	0.07	0.07	0.14	0.08	-
0.50	0.14	0.16	0.13	0.11	0.09	0.05	0.10	0.10	0.11	0.14	0.12	0.18	0.15	-
1.00	0.25	0.27	0.21	0.20	0.17	0.10	0.17	0.16	0.19	0.25	0.18	0.22	0.24	0.13
2.00	0.45	0.47	0.35	0.28	0.31	0.19	0.28	0.26	0.34	0.43	0.26	0.27	0.39	0.23
3.00	0.64	0.65	0.47	0.48	0.45	0.28	0.38	0.35	0.47	0.60	0.33	0.31	0.51	0.32
4.00	0.82	0.82	0.59	0.61	0.58	0.37	0.47	0.43	0.60	0.75	0.39	0.33	0.62	0.41
5.00	1.00	0.98	0.69	0.72	0.70	0.46	0.55	0.50	0.72	0.89	0.44	0.36	0.73	0.49
6.00	1.17	1.13	0.79	0.84	0.82	0.55	0.63	0.57	0.84	1.03	0.48	0.38	0.83	-
10.00	1.81	1.70	1.15	1.26	1.29	0.89	0.91	0.82	1.28	1.54	0.64	0.44	1.17	-
12.00	2.12	1.97	1.32	1.46	1.51	1.06	1.04	0.93	1.49	1.78	0.71	0.46	1.33	-
14.00	-	-	-	-	-	1.23	-	1.04	-	2.01	-	-	1.48	-
16.00	-	-	-	-	-	1.39	-	1.15	-	2.23	-	-	1.63	-
20.00	-	-	-	-	-	1.72	-	1.34	-	2.66	-	-	1.90	-

AMOCO RESEARCH CENTER

FAX COVER SHEET

DATE: 4-10-95

NO. OF PAGES: 3 (INCL. COVER)

FAX NUMBER: 303-221-9364

ATTENTION: Lynn Hunter

COMPANY: WASSON

FROM:

Cherlyn Bradley
AMOCO CORPORATION

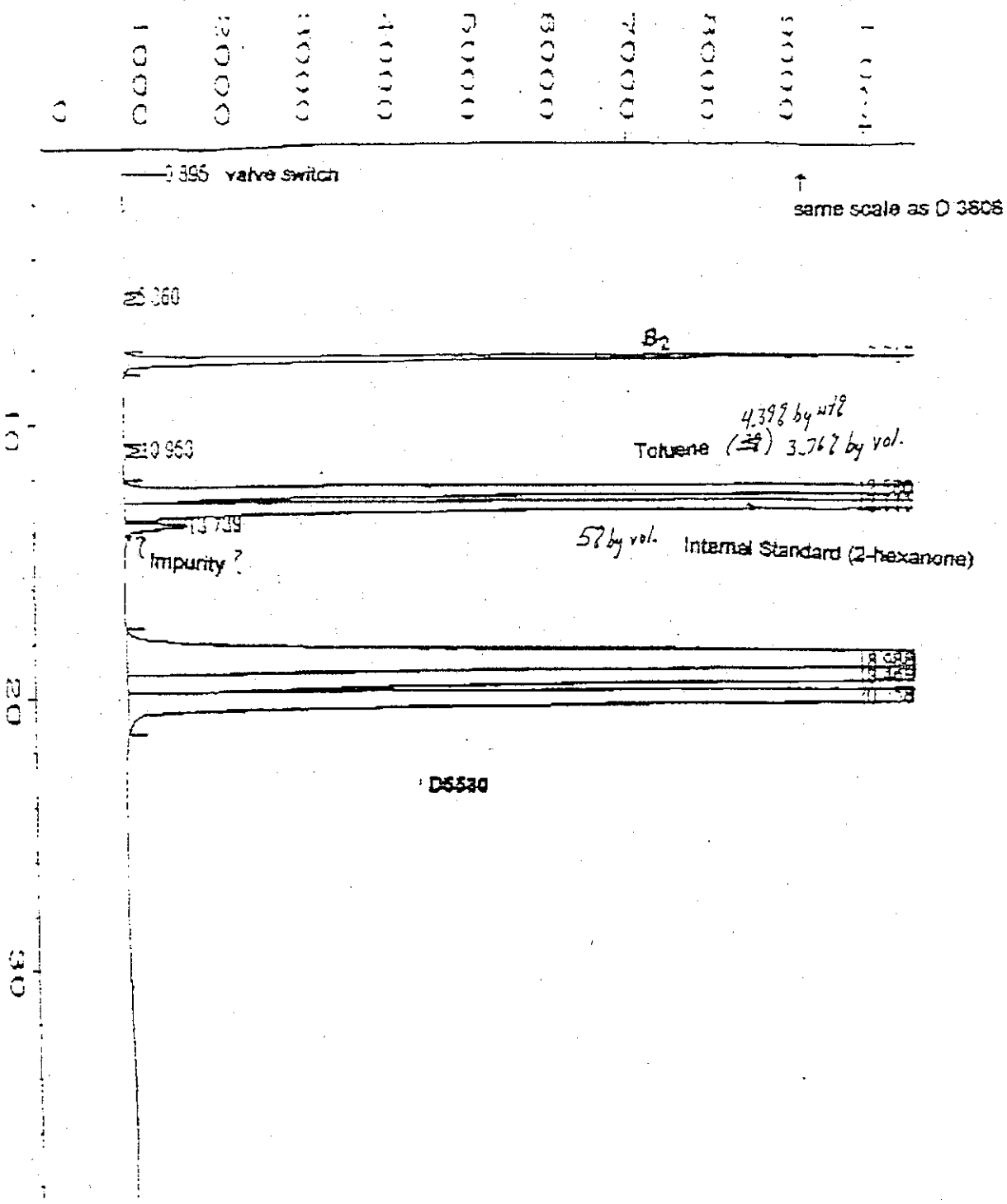
P.O. Box 3011,
NAPERVILLE, IL 60566

FAX NUMBER (708) 420-5252

NOTES: Latest RR OFID precision (from Summer/Fall Round Robin 1994)

C

Sample B. (from D5580 round robin)

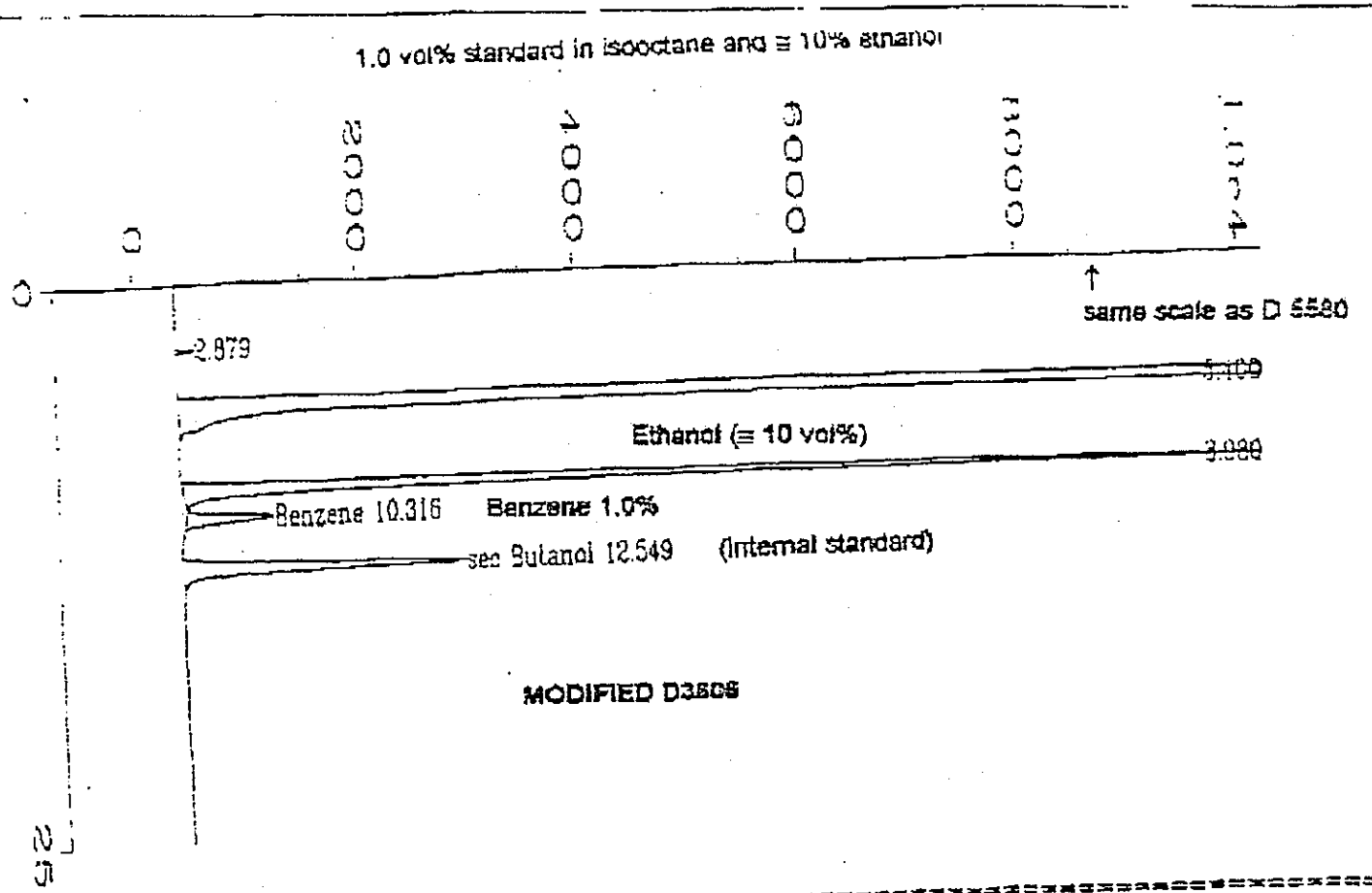


Data File Name : C:\HPCHEM\2\DATA\oct4a\002R0101.D
Operator : Kelly
Instrument : INSTRUMENT
Sample Name : B1
Run Time Bar Code:
Acquired on : 04 Oct 94 02:52 PM
Report Created on: 04 Oct 94 03:36 PM

Page Number : 1
Vial Number : 2
Injection Number : 1
Sequence Line : 1
Instrument Method: BENZENE.MTH
Analysis Method : BENZENE.MTH

Chromatogram II

D5580



Internal Standard Report

Data File Name	: C:\HPCHEM\1\DATA\1FEB1C\027F0101.D	Page Number	: 1
Operator	: RICK	Vial Number	: 27
Instrument	: ANALYZER1	Injection Number	: 1
Sample Name	: 1.0 BZ/ET RLA-2	Sequence Line	: 1
Run Time Bar Code:		Instrument Method	: D3606.MTH
Acquired on	: 01 Feb 95 01:49 PM	Analysis Method	: D3606.MTH
Report Created on	: 01 Feb 95 02:23 PM	Sample Amount	: 0
Last Recalib on	: 18 NOV 94 09:44 AM	ISTD Amount	: 4
Multiplier	: 1		

Sig. 1 in C:\HPCHEM\1\DATA\1FEB1C\027F0101.D

Ret Time	Area	Type	Width	Ref#	ng/ul	Name
10.316	15782	BB	0.307	1-R	1.008	Benzene
12.549	59578	BB	0.359	1-I	4.000	sec Butanol

Time Reference Peak	Expected RT	Actual RT	Difference
1	10.305	10.316	0.1%

Chromatogram I

STATE OF CALIFORNIA
AIR RESOURCES BOARD
HAGEN-SMIT LABORATORY
9528 TELSTAR AVENUE
EL MONTE, CA 91731-2990
PHONE: (818) 575-6800

PETE WILSON, Governor

April 24, 1995

Lynn Hunter
Product Manager Chromatography
Wasson-ECE Instrumentation
1305 Duff Drive
Fort Collins, Colorado 80524

Dear Ms. Hunter

Thank you for attending our workshop on Fuels Test Methods on April 5, 1995 and for your subsequent letter to Dr. Shiou-Mei Huang dated April 11, 1995. In your letter, you expressed some concerns about our proposed methods for the measurement of oxygenates and aromatics in Phase 2 gasoline.

In this letter I would like to address your concerns regarding our proposed oxygenates test methods. We will address your concerns regarding our proposed method for aromatics at the next workshop on fuels test methods, currently scheduled for September 19, 1995. For the sake of clarity, I will briefly restate the comments/questions raised in your letter and then provide a response.

Question Where did we obtain the data for the table of reproducibilities presented at the workshop comparing the OFID method to ASTM D4815-94 and why is the OFID reproducibility different from reproducibilities cited in the table recently obtained from the ASTM?

Response The table presented at the workshop indicated relative reproducibilities, that is, the actual reproducibility at a target concentration divided by the target concentration. The OFID data we used were from the Draft -94 method since the data from the Draft -95 method were not available to us at the time of the workshop.

The reproducibility data from the Draft -95 OFID method, provided with your letter, shows an improvement in reproducibilities but does not change the conclusion that the OFID method is not as reproducible as ASTM D4815-94 for MTBE and ethanol. The relative reproducibility of the two methods at the 2 mass % oxygen level is as follows:

	MTBE	Ethanol
ASTM D 4815-94	5.5 %	10.7 %
OFID Draft -95	8.8 %	18.8 %

Comment The reliability problems of the OFID detector have been resolved.

Response We were alerted to the OFID detector problem by several oil company laboratories who are participants in the WSPA/CARB Working Group on Test Methods. We are continuing our participation with this Working Group and will continue to monitor the development of the OFID method.

Comment Olefinic compounds may interfere with MTBE as determined by ASTM D 4815.

Response ASTM D 4815 has been in use in our laboratory for over six years. We have not observed any evidence of an olefin interference for MTBE nor has anyone reported such a problem to us. Phase 2 RFG specifications limit the olefin content to a relatively low level and therefore the potential for olefinic interference will be further reduced.. However, we would be very interested in obtaining additional information you may have about this interference.

Comment The OFID method is more stable and easier to use than ASTM D 4815-94.

Response Our instrument configured for ASTM D 4815-94 has been in operation on a mobile laboratory for well over six years. During that time only simple maintenance was required requiring very little down time. As to ease of use, we have not found it necessary to make the frequent valve timing adjustments suggested in your letter.

We are very supportive of the development of selective methods for the determination of regulated components in gasoline. For that reason we evaluated and approved the GC/FTIR method for the determination of oxygenates in gasoline as an equivalent method and participated in the ASTM round robin studies of the GC/FTIR method. We expect that when issues of reliability and precision are resolved, the oil industry will petition the ARB to evaluate the OFID method as an equivalent method to ASTM D 4815.

Thank you for your interest in fuels test methods development. I hope that this letter has addressed your concerns regarding the test method for oxygenates. The rulemaking scheduled for June and October of this year will not end our interest in methods improvement. We will continue to participate with industry and all interested parties in the refinement, updating, and replacement of methods.

If you have any questions please call me at (818) 575-6876, or Dr. Shiou-Mei Huang at (818) 575-6875.

Sincerely,

Paul Rieger, Spectroscopist
Monitoring and Laboratory Division