California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR THE DETERMINATION OF ETHERS AND ALCOHOLS IN GASOLINE BY GAS CHROMATOGRAPHY

Standard Operating Procedure MV-FUEL-115

Version 2.1

Effective: July 12, 2010

Fuel Analysis and Methods Evaluation Section
Chemical Analysis & Emissions Research Branch
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1 Introduction

1.1 This document describes an automated method of analyzing C1 to C4 alcohols, tertiary amyl alcohol, and four ethers in gasoline by gas chromatography.

1.2 This method provides a procedure for the analysis of methanol (MeOH), ethanol (EtOH), isopropanol (iPA), n-propanol (nPA), isobutanol (iBA), sec-butanol (sBA), tertiary-amyl alcohol (tAA or tertiary pentanol), tertiary-butanol (tBA), and n-butanol (nBA) in gasoline in the range of 0.2 to 12.0 mass %.

1.3 Methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary-amyl methyl ether (TAME), and diisopropyl ether (DIPE) in gasoline are determined from 0.2 to 20.0 mass %.

1.4 This method is based on ASTM D 4815-04.

2 Summary of Procedure

2.1 Gasoline samples are collected and brought to the laboratory. An internal standard, 1,2-dimethoxyethane (ethylene glycol dimethyl ether), is added gravimetrically to the samples prior to analysis. The internal standard weight is used to calculate the mass percent of each oxygenate as compared to the response for internal standard and the same oxygenate in the calibration standard.

2.2 Samples are injected by auto sampler into a gas chromatograph (GC) equipped with a polar pre-column, non-polar analytical column, column switching valve, and flame ionization detector (FID). The pre-column retains the oxygenated and heavier hydrocarbons, while allowing the faster eluting light hydrocarbons to vent. The pre-column is then back flushed onto the analytical column, which separates the individual C1 to C4 alcohols, ethers, and tert-pentanol from the remaining heavier hydrocarbons. These heavy compounds are then backflushed from the analytical column upon elution of the last oxygenate of interest.

2.3 The data system identifies the oxygenate associated with each chromatographic peak. Oxygenate concentrations are determined by integrating and comparing the areas of sample peaks and calibration standard peaks, with reference to the internal standard.

3 Measurement Interferences and Limitations

3.1 The known interference or limitation to this procedure is hydrocarbon contamination. If the valve back flush time is not set correctly, hydrocarbon peaks (particularly olefins) may co-elute with the oxygenates. This can be detected and minimized by setting the back flush time according to ASTM D4815-04 and analyzing an unoxygenated gasoline blank daily to check for any hydrocarbon peaks.

4 Instrument and Reagents

4.1 Gas chromatograph, Bruker Scion 456 or equivalent, equipped with FID, 1,2,3-tris-2-cyanoethoxypropane (TCEP) or equivalent pre-column and DB-1 (J & W) or equivalent analytical column, connected by a 10-port valve.

4.2 Liquid Autosampler, Bruker CP- 8400 or equivalent.

4.3 Digital Data Acquisition System, Bruker MS Workstaion or equivalent.

4.4 Methanol, isopropanol, n-propanol, isobutanol, sec-butanol, tert-butanol, n-butanol, tert-pentanol, ethanol, MTBE, ETBE, TAME, and 2,2,4-trimethylpentane, reagent grade or equivalent, free of other components to be analyzed. A refinery CARBOB, verified as being free of oxygenates, is used for preparation of blank standards.

4.5 A daily control standard, of typical sample concentration, is prepared as described in 9.4.

4.6 Gas requirements:

4.7.1 Air, "Zero" grade.

4.7.2 Helium, 99.995% or better.

4.7.3 Hydrogen, 99.995% or better.

4.8 The forms needed are the instrument notebook, spreadsheets for reporting results, and spreadsheets for quality control reports.

5 Procedure

5.1 A 5 or 10 ml volumetric flask is placed on an analytical balance, which is tared. 250 uL (for 5mL) or 500 uL (for 10 mL) of internal standard (DME) is pipetted into the flask and is weighed. The balance is retared. A gasoline sample is added in sufficient quantity to bring the solution to volume. The weight of the sample is obtained. The weights of the internal standard and sample are recorded in the instrument notebook.

5.2 The gasoline/internal standard mixture is transferred into an auto sampler vial.

5.3 Steps 5.1 and 5.2 are repeated for each sample.

5.4 A 2.0 uL aliquot of each sample is injected via an auto sampler into a GC configured as follows:

5.4.1 Pre-column --- TCEP, 20% (m/m) on 80/100 Chromosorb P(AW), stainless steel, 560 mm x 1.6 mm OD.
Analytical --- DB-1, 30 m x 0.53 mm ID, 3.0 micron film thickness.

Helium flow: 5 mL/min
Hydrogen: 40 mL/min
Air: 400 mL/min

Detectors: FID, 250 C
Injector: 200 C, split/splitless with split ratio 15:1
Column Temp.: 60 C (isothermal)
Data system: Varian Star data station

Back flush time: approximately 0.20 min, or the time necessary to vent light hydrocarbons without losing the oxygenates of interest.
Reset time: approximately 8.0 min, or any time after TAME has eluted.

5.5 Column and split vent flows are adjusted previous to a multi point calibration.

5.6 One control standard and one stock gasoline blank are analyzed daily at the beginning of each set of samples.

5.7 The control standard is repeated at the end of the run.

5.8 A replicate analysis is performed daily.

5.9 Peak identifications provided by the data system are checked and corrected, if necessary. Any misplaced baseline segments are corrected in the reconstructed chromatogram.

5.10 The level of peak rejection is set below the lowest peak area equivalent to 0.2 mass percent as per 1.3 and 1.4.

6 Safety Precautions

6.1 Standard laboratory safety procedures and equipment should be used in performing this method. For example, safety glasses and gloves should be worn. All standard and sample preparation should be done in the fume

hood. Gasoline contains compounds known to be toxic and carcinogenic. The internal standard, 1,2-dimethoxyethane (DME), is a known teratogen.

7 Calibration

7.1 Normally, calibration is performed once a year. When modifications or repairs change the calibration curves, or when quality control measurements (Section 9) indicate that the calibration is no longer valid, additional calibrations are required.

7.2 Two types of calibrations may be used for this method. The first type uses commercially available calibration standard sets. Depending on the vendors and their products, such a calibration standard set can contain eight to thirteen compounds listed in sections 1.2 and 1.3. The second incorporates only ethanol and MTBE and the calibration standard is prepared in the laboratory.

Ethanol is the only oxygenate used in California, and MTBE is the only other oxygenate used in the Phase II certification fuel. TAME was phased out of use by American refiners several years ago. No other oxygenate has been detected in the history of ARB's fuel program. Moreover, the prohibited concentrations of non-ethanol oxygenates are below the scope of D4815-04. Therefore, in normal analyses oxygenates other than MTBE and ethanol need not be quantified, and either type of calibrations is adequate. For special projects, calibration of some or all of the other oxygenates may be needed.

7.3 2-compound Calibration:

Calibration standards are prepared by using the appropriate amounts of ethanol and MTBE with a gasoline base (CARBOB or isooctane) which contains no oxygenates. Internal standard is added to each standard at the same concentration as it is added to samples. Each component is weighed and the mass of each component is recorded. A minimum of five calibration levels spanning the range of the oxygenates expected in the samples is prepared.

7.4 Calibration with Commercially Available Calibration Standards:

Calibration standards which are National Institute of Standards and Technology (NIST) traceable by weight are purchased as needed and stored below 5 degrees C. Commercially available calibration sets may contain as few as eight or as many as all the 13 oxygenates described in the ASTM method. The purchased calibration standard set can come with or without internal standard. It comes with appropriate ranges for the oxygenates as stated in the ASTM D4815 method. If it comes without any internal standard, then internal standard is added to each standard at the

same concentration as it is added to samples, each standard is weighed and the mass of each standard is recorded.

8 Calculation of Results

8.1 Calibration and Control Standard Concentrations

The concentration of each oxygenate in the calibration and control standard is determined by the following equation.

$$\text{Concentration (Mass \%)} = \frac{\text{Mass of Oxygenate}}{\text{Total Mass}} \times 100$$

Establish the calibration curve for each oxygenate. Plot the response ratio:

$rsp_i = (A_i / A_s)$

where:

A_i = area of oxygenate, and
A_s = area of internal standard

as the y-axis versus the amount ratio (amt_i) = (W_i/W_s) where

W_i = mass of the oxygenate, and
W_s = mass of the internal standard.

as the x-axis calibration curves for each oxygenate. Check the correlation r squared value for each oxygenate. The r^2 value should be at least 0.99 or better. R^2 is calculated as follows:

$$R^2 = \frac{(\Sigma xy)^2}{(\Sigma x^2)(\Sigma y^2)}$$

where:

$x = X_i - x_a$, and
$y = Y_i - y_a$

and

X_i = amt_i ratio data point,
x_a = average values for all (amt_i) data points,
Y_i = corresponding rsp_i ratio data point, and
y_a= average values for all (rsp_i) data points.

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

$(rsp_i) = (m_i)(amt_i) + b_i$

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.

The values of m_i and b_i are calculated as follows:

$m_i = \Sigma xy/\Sigma x^2$, and
$b_i = y_a - m_i x_a$

For an optimum calibration, the absolute value of the y-intercept b_i must be at a minimum. The equation to determine the mass percent reduces to the following. The y-intercept can be tested using the same equation.

$w_i = (b_i/m_i)(W_s/W_g)100\%$

where :

w_i = mass % oxygenate *i*, where w_i is <0.2 mass %,
W_s = mass of internal standard added to the gasoline sample, and
W_g = weight of gasoline sample.

8.2 Sample Concentrations

The concentration of each oxygenate in a sample is determined by the following equation:

$rsp_i = (m_i)(amt_i) + b_i$

where:

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

or

$amt_i = W_i = [(rsp_i)-b_i]/m_i$.

To obtain mass percent (w_i) results for each oxygenate

$w_i = (W_i\, 100\%)/W_g$

where:

W_i = mass of each oxygenate *i.*
W_g = weight of the gasoline sample.

Volumetric concentrations of oxygenate in a sample, if desired can be calculated using the following equation:

$V_i = w_i (D_f/D_i)$

where:

w_i = mass percent of each oxygenate as determined in the equation above.
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 1.
D_f = relative density of the fuel under study as determined by ASTM Test Method D 1298 or D 4052.

8.3 Determination of Total Oxygen

8.3.1 The sum of the mass % oxygen of the individual oxygenates constitutes the total mass % oxygen in the sample.

$\text{Oxygen Total} = \text{Oxygenate}_1 + \text{Oxygenate}_2 + ... + \text{Oxygenate}_n$

where:

Oxygen Total = total mass % oxygen in the fuel, and
Oxygenate *i* = concentration of each oxygenate (mass % oxygen)

8.3.2 Alternatively, total oxygen may be determined directly from the individual oxygenate concentrations, in mass %, as follows:

$OX_{TOT} = C\ OX_1 \times 16.0 \times N_1/M_1 + C\ OX_2 \times 16.0 \times N_2/M_2 + ...$

where:

OX_{TOT} = total mass % oxygen in the fuel,
$C\ OX_i$ = concentration of each oxygenate (mass %),
Atomic weight of oxygen = 16.0,
N_i = number of oxygen atoms in the oxygenate molecule, and
M_i = molecular weight of the oxygenate.

9 Quality Control and Assurance

9.1 Blank Analysis

A stock gasoline blank free of oxygenate is analyzed daily to check the analytical system for contamination. If the blank chromatogram shows a peak greater than 0.2 mass percent (as specified in 1.3 and 1.4) in the region of interest, the blank is repeated. If necessary, the back flush time is readjusted according to ASTM D 4815-94. All oxygenate concentrations must be below 0.2 mass percent before the analysis may proceed.

9.2 Calibration Standard Analysis

Calibration standards are purchased (NIST traceable by weight) or prepared yearly and stored below 5 degrees C. The five level calibration for each oxygenate of interest is performed as needed, and must be repeated if the linearity or intercept tests fail the specification of ASTM D 4815-04.

9.3 Standard Reference Material

A NIST Standard Reference Material (SRM) containing ethanol at approximately 10 mass percent is analyzed each quarter. If the determined concentration is not within 0.30 mass percent for ethanol, the instrument and situation are examined to find the problem and the SRM is reanalyzed. If the SRM value is still not within 0.30 mass percent for ethanol, the multiple point calibration is performed again and the SRM reanalyzed.

9.4 Control Standard Analysis

A control standard is analyzed every day to monitor changes or potential problems with the calibration or instrument. The control standard is prepared in the lab and consists of ethanol and MTBE target levels appropriate for California and federal gasoline. It is analyzed at the beginning and end of the analysis day. Whenever the control standard values differ from their predetermined value by more than twice the percent relative repeatability for a compound of interest, the standard must be reanalyzed. If the control analysis fails a second time, corrective action must be undertaken. The repeatabilities are shown in Table 2.

9.4 Quality Control Chart

A quality control chart is maintained for tracking the results of the control standard analyses. The chart calculates the percent difference from the predetermined value, and indicates whether each result passes or fails the quality control criteria.

9.5 Repeatability and Reproducibility

See Table 2 and 3.

10 **References**

10.1 ASTM D 4815-94, "Standard Test Method for Determination of C1 to C4 Alcohols and MTBE in Gasoline by Gas Chromatography," Annual Book of ASTM Standards, Vol. 05.03.

11 Revision History

Revision No. 6 Effective Date: 11/04/96 Approval Date: 12/27/96

Revision No. 7 Effective Date: 04/01/00

Significant changes: 5.1 - Allow use of 10 ml. Volumetric Flasks

9.2.1 - Change SRM 2294 Control limits

9.6. 1 - Update Violation duplicates

Revision No. 8 Effective Date: 01/01/03

Version 2.0 Effective Date: 4/1/05

Disclaimer on title page removed

1.3, 1.4 – Lower scope of method raised to 0.2 wt%. This change affects many other references to the lower scope of the method throughout the SOP.

4.1 – Instrument updated to Varian 3800

5.4.1 – FID gas flows changed

7 – 13-compound and 2-compound calibration options added

9.3 – Ethanol SRM now used instead of MTBE

9.4 – Control standards run twice per day

9.4.1 – Area counts are no longer tracked

9.5 – Replicate analyses removed. There has never been a failure of replicate analyses for this method. Moreover, with the new California fuel regulations, it is quite common for all of the samples analyzed in a typical day to be below the scope of the method. Analyzing replicate results for effectively blank samples is not useful.

9.6 – Violations section removed. Determination of violations is the responsibility of Enforcement Division.

9.7 – Limit of Detection test removed. This need is filled by the y-intercept test on the calibration curves as specified in section 8.1

9.9 – Documentation section removed. The use of the laboratory notebook is covered in section 5.1 and does not need to be repeated.

9.10 – Removed. Product sampling is handled by Enforcement Division and needn't be discussed in this SOP.

Version 2.1 Effective Date: July 12, 2010

Section 7 was revised to have other commercially available calibration sets allowed for use, such as an 8-compound set that we have purchased. More multi-compound standards with proven quality are available now.

Table 1. Densities of Oxygenates

COMPOUND	DENSITY (g/mL at 15.56 C)
Methanol	0.7963
Ethanol	0.7939
Isopropanol	0.7899
t-Butanol	0.7922
n-Propanol	0.8080
MTBE	0.7460
sec-Butanol	0.8114
DIPE	0.7300
Isobutanol	0.8058
ETBE	0.7452
t-Pentanol	0.8170
n-Butanol	0.8137
TAME	0.7758

Table 2. Repeatability Estimates of Oxygenates in Gasoline from ASTM D4815-04.

Component	Repeatability
Methanol (MeOH)	0.09 ($X^{0.59}$)
Ethanol (EtOH)	0.06 ($X^{0.61}$)
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	0.08 ($X^{0.56}$)
ETBE	0.05 ($X^{0.82}$)
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 ($X^{1.26}$)

Note: X = mass% of the oxygenate in the sample

Table 3. Reproducibility Estimates of Oxygenates in Gasoline from ASTM D4815-04.

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	0.42 ($X^{0.67}$)
ETBE	0.36 ($X^{0.76}$)
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 ($X^{1.27}$)

Note: X = mass% of the oxygenate in the sample