

AIR RESOURCES BOARD

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PROCEDURE FOR THE DETERMINATION OF OLEFINS IN GASOLINE BY
SUPERCRITICAL FLUID CHROMATOGRAPHY

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CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

Procedure for the Determination of Olefins in Gasoline by Supercritical Fluid Chromatography

1 Introduction

- 1.1 This document describes an automated method for the determination of olefins in gasoline.
- 1.2 This test method covers gasolines and gasoline blendstocks.
- 1.4 Total olefins are determined from 0.3 to 25 mass percent.
- 1.3 This procedure is based on ASTM D6550-00¹, as modified by footnotes g, h, and i in section 2263 of the California Code of Regulations. These modifications include a mass-volume percent correlation, a change in the method scope, and a different method reproducibility.

2 Method

- 2.1 A representative sample is injected onto a set of two chromatographic columns and transported using supercritical carbon dioxide (CO₂) as the mobile phase. The first column is packed with silica and the second column contains a material loaded with silver ions.
- 2.2 Upon sample injection, saturates flow through both columns to the detector, while aromatics and oxygenates are retained on the silica column and olefins are trapped on the silver column. After elution of the saturates, the aromatics and oxygenates are backflushed from the silica column to the detector. Finally, the olefins are backflushed from the silver column.
- 2.3 The mass concentration of olefins is determined by multiplication of the olefin peak area by detector response factors determined by external standard calibration.
- 2.4 The volume concentration of olefins is determined by multiplication of the mass

concentration by a correlation factor.

3 **Instrumentation**

- 3.1 Agilent/Berger Supercritical Fluid Chromatograph (SFC)
 - 3.1.1 Agilent 5890 SFC
 - 3.1.2 Agilent G1205A SFC pump
 - 3.1.3 Alcott model 700 liquid autosampler
 - 3.1.4 0.5 microliter sample loop
 - 3.1.5 Phenomenex Selectosil SCX column, 50 mm long, 4.6 mm i.d., 5 micron particle size or equivalent
 - 3.1.6 Agilent hydrocarbon group separation column, 250 mm long, 4.6 mm i.d., 5 micron particle size or equivalent
 - 3.1.7 Two six-way switching valves
 - 3.1.8 Berger SFC Chemstation software
- 3.2 Selerity SFC
 - 3.2.1 placeholder

4 **Reagents**

- 4.1 2,2,4-trimethylpentane (isooctane), reagent grade or equivalent.
- 4.2 1-Methyl-1-cyclohexene, 97%
- 4.3 1-Octene, 98%

- 4.4 1-Hexene, 99%
- 4.5 1-Pentene, 99%
- 4.6 Toluene, 99%

- 4.7 Benzene, 99%
- 4.8 Air, "Zero" grade
- 4.9 Carbon dioxide, supercritical fluid chromatographic grade, 99.99%
- 4.10 Hydrogen, 99.99%
- 4.11 Nitrogen, 99.99%

5 **Preparation of Instrument**

- 5.1.1 CO₂ outlet pressure: 220 bar
- 5.1.2 Detector air: 400 mL/min
- 5.1.3 Detector hydrogen: 50 mL/min
- 5.1.4 Detector temperature: 375 °C
- 5.1.5 Oven temperature: 75 °C

5.2 **Timing**

- 5.2.1 Cut and backflush times vary from instrument to instrument and column to column and may require adjustment.
- 5.2.2 Solutions of 5% benzene in isooctane and 5% cyclohexene in isooctane are used to determine the cut times.

- 5.2.3 The first cut time, t_L should be set to the longest time which allows benzene to completely elute in the aromatic region (approximately 3-3.5 minutes) and not in the olefin region (approximately 7 minutes). Also, no more than 25% of cyclohexene's area counts should appear in the aromatic region. If these two conditions cannot both be met, then the silica column may need cleaning or replacement. t_L is typically approximately 1.45 minutes.
- 5.2.3 The second cut time, t_A , should be long enough to ensure that the FID signal returns to baseline after the elution of the aromatics in real samples. t_A is typically approximately 4.50 minutes.
- 5.2.4 The third cut time, t_C , should be long enough to ensure that the FID signal returns to baseline after any heavy saturates have eluted from the olefin trap. Most samples do not give any significant signal in this time range. t_C is typically approximately 5.50 minutes.
- 5.2.4 The total run time should be long enough to allow at least one minute of flat baseline after the olefin peak has finished eluting.

5.3 Valve Settings and Cut Times

- 5.3.1 At the start of the run, valves 1 and 2 are on.
- 5.3.2 At time t_L , valves 1 and 2 are switched off.
- 5.3.3 At time t_A , valves 1 and 2 are switched on.
- 5.3.4 At time t_C , valve 1 is switched off.
- 5.3.5 At the end of the run, valve 1 is switched on.

6 Calibration

- 6.1 This test method is based on external standard calibration.
- 6.2 An olefin stock solution is prepared by mixing 5 mL 1-pentene, 10 mL 1-hexene, 2 mL cyclohexene, and 3 mL 1-octene.

- 6.3 A dilution stock solution is prepared by mixing 50 mL toluene, 75 mL xylene, and 375 mL isooctane. This solution should give no response in the olefin portion of the chromatogram.
- 6.4 Five calibration standards are prepared by mixing varying volumes of olefin stock solution with dilution stock solution to a final volume of 50 mL. The amounts of each solution should be weighed to the nearest 0.001 g. Suggested nominal volume percent olefin concentrations of the calibration solutions are 0.5, 1.0, 4.0, 7.0, and 12.0.
- 6.5 The five calibration standards are injected into the instrument. The instrument's software is used to generate a calibration curve from the resulting chromatograms. The R-squared value for the calibration must be at least 0.99.
- 6.6 Calibration is performed when analysis of quality control samples, round robin samples, or standard reference materials indicates that the instrument is producing inaccurate results. Instrument repairs or maintenance, such as installing new columns, may trigger a need for recalibration.

7 Procedure

- 7.1 2 mL of each sample is transferred into a glass autosampler vial which is then capped. Red rubber septa should not be used with the Alcott autosampler.
- 7.2 The autosampler delivers 25 μ L of sample to the injector, which sends 0.5 μ L to the column.
- 7.3 The chromatographic response is integrated by the software. Results in weight percent are calculated from the calibration curve by the software.
- 7.4 Volume percent results are calculated using the following equation:

$$\text{Vol}\% = 0.857 * \text{Wt}\%$$

8 Safety

- 8.1 Gasoline and many of its various components are toxic. Persons using this method must

wear protective gloves and eyewear when working with reagents and samples. Reagents and samples are kept in a fume hood with adequate ventilation.

9 **Quality Control**

- 9.1 A blank sample containing no olefins (typically the dilution stock described in section 6.3), is analyzed at the beginning of each set of samples. If the blank chromatogram shows more than 0.1 volume percent olefins then the blank is repeated or the instrument hardware checked.
- 9.2 A NIST SRM is run at least once per quarter. The total olefin concentration reported must agree with the certified value within the repeatability of the test method (see 10.4). For SRM 2294 and 2296, the repeatability is approximately 0.27 weight%.
- 9.3 A control standard is analyzed at the beginning and end of each set of samples. The control standard should be an ASTM crosscheck sample or some other sample with a consensus olefin concentration. The control standard analyses are recorded on a quality control chart. A result is considered to be out of control if its difference from the consensus value is greater than twice the repeatability of the test method (see 9.4). In this event, corrective action must be taken prior to analyzing samples.
- 9.4 For total olefin measurements, the repeatability is given by the following equation:

$$r = 0.13(X)^{0.5}$$

where r is the repeatability and X is the measured concentration in weight percent.

10 **References**

1. Standard Test Method Determination of Olefin Content of Gasolines by Supercritical Fluid Chromatography, Method D6550-00, *Annual Book of ASTM Standards*, Vol. 05.04.

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11. **Standard Operating Procedure Revision History**

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