



**PROCEDURE FOR THE DETERMINATION OF OLEFINS IN GASOLINE BY  
SUPERCRITICAL FLUID CHROMATOGRAPHY AND FLAME IONIZATION  
DETECTOR**

SOP MV-FUELS-134  
Version 3.1  
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Fuels Analysis and Methods Evaluation Section  
Chemical Analysis and Emissions Research Branch  
Mobile Source Laboratory Division

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## 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.
- 1.3 This procedure is based on American Society for Testing and Materials (ASTM) D6550-10<sup>1</sup>, 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 different method reproducibility.
- 1.4 Total olefins are determined from 0.3 to 25 mass percent.

## 2 Method

- 2.1 A representative sample is injected onto a set of two chromatographic columns and transported using supercritical carbon dioxide (CO<sub>2</sub>) 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.

$$\text{Olefins (Volume \%)} = 0.857 * \text{Olefins (Mass \%)}$$

## 3 Instrument

- 3.1 Supercritical fluid chromatograph (SFC), equipped with SFC Pump, a Liquid Autosampler, a silica column, a silver column, two six-way switching valves, Flame Ionization Detector (FID), and a computer system running automation software.

#### **4 Reagents**

All chemicals are reagent grade or higher.

- 4.1 2,2,4-trimethylpentane (isooctane), 99% minimum purity
- 4.2 Commercial Calibration Standards Set of five or more levels between 0.5% and 25%. Or
- 4.3 Standard Materials for Preparation of Calibration Standards:
  - 4.3.1 1-Methyl-1-cyclohexene, 97% minimum purity
  - 4.3.2 1-Octene, 98% minimum purity
  - 4.3.3 1-Hexene, 99% minimum purity
  - 4.3.4 1-Pentene, 99% minimum purity
- 4.4 Toluene, 99% minimum purity
- 4.5 Benzene, 99% minimum purity
- 4.6 Air, "Zero" grade or higher
- 4.7 Carbon dioxide, supercritical fluid chromatographic grade, 99.995% minimum purity, supplied in a pressurized cylinder equipped with a full dip tube.
- 4.8 Hydrogen, 99.99% minimum purity
- 4.9 Nitrogen, 99.99% minimum purity

#### **5 Preparation of Instrument**

- 5.1 Before analysis, the SFC instrument need to be on and warmed up until all the gas flows, the CO<sub>2</sub> pressure, the FID, oven and column temperatures are stabilized.
- 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 The cut times can be determined in many ways. The use of a gasoline sample such as the quality control sample that contains alkanes, benzene

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and mono-aromatics, and olefins to determine the cut times is described below. Other methods such as using a mixture of 5% benzene and 5% cyclohexene in isooctane are also okay.

5.2.3 To determine the first cut time,  $t_L$  set the valve 1 to on and valve 2 to off, so that the silver column is bypassed. Run the gasoline sample until everything elutes.  $t_L$  should be set to after the saturates and the olefins elute but before the aromatics does.

5.2.4 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.

5.2.5 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.

The total run time should be long enough to make sure 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

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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.

Alternatively, a commercial set of olefins calibration standards (see section 4.2) made for the ASTM-6550 can be used instead.

- 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.
- 7.2 The autosampler delivers 25 L of sample to the injector, which sends 0.5 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. A fume hood with adequate ventilation is needed. Reagents and samples are kept in an explosion-proof cabinet and/or refrigerator.

## 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.

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- 9.2 A National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) is run at least once per quarter. The total olefin concentration reported must agree with the certified value within two times the repeatability of the test method (see 9.4). For SRM 2294, 2296 and 2297 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.

- 9.5 Replicate Analysis

A replicate analysis is performed every 10 samples or at the end of sample set. It is recommended to run the replicate immediately after the original sample. A quality control chart is maintained for the replicates.

If the difference is greater than the repeatability specified in section 9.4 the sample should be repeated. If the closest two values of the three analyses still show a difference greater than the repeatability, all samples from this instrument must be reanalyzed. Steps should be taken to determine the cause of the problem.

- 9.6 Limits of Detection

The limits of detection (LOD) are determined annually. The LOD for olefin can be calculated using the following equation

$$\text{LOD} = t * \text{SD}$$

Where t is the Student's t value associated with a 98% confidence interval. When the sample is analyzed eight times in a row, t = 3. SD is the standard deviation of a replicate analysis of a low concentration sample (0.3 to 1 mass percent).

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The LOD must be below 0.30 mass percent.

10 **References**

1. Standard Test Method Determination of Olefin Content of Gasolines by Supercritical Fluid Chromatography, Method D6550-10, *Annual Book of ASTM Standards*, Vol. 05.04.

11 **Revision History**

11.1 Version 1.0: Effective Date: 1/1/2002

11.2 Version 2.0: Effective Date: 1/1/2014

Significant changes:

Section 9.5 – Addition of replicate analysis requirement

Section 9.6 – Addition of limits of detection (LOD) determination. Update the instruments used and valve settings and cutting times

11.3 Version 3.0 Effective Date: 5/1/2017

Significant changes:

Sections 1.3 and 10 – Updated the ASTM D6550 to the 2010 version.

Section 3 – Removed SFC vendor-specific information.

Sections 4 and 6.4 – Added commercial sets of calibration standards as an alternative.

Section 5 – Changed typical procedure to determine the cut time  $t_c$

Section 9.2 – Revised the requirement of the NIST SRM to within two times repeatability as defined in section 9.4

Section 9.5 – Use our own repeatability formula of section 9.4

Section 9.6 – Revised the limits of detection (LOD) to 0.30 mass%, and any sample with between 0.3% and 1% olefins can be used, and clarified that the sample is repeated eight times for the determination of LOD

Other changes:

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Deleted references to instruments we no longer use.

Revised the safety section.

Added the dip tube requirement to the CO<sub>2</sub> cylinder in section 4.7

11.4 Version 3.1            Effective Date: 12/1/2019

SOP format updated for ADA compliance