California Environmental Protection Agency

Air Resources Board

PROCEDURE FOR THE DETERMINATION OF THE CARBON, HYDROGEN, OXYGEN, AND NITROGEN CONTENT OF LIQUID FUELS

Standard Operating Procedure MV-FUEL-153

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Fuel Analysis and Methods Evaluation Section
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SOP MV-FUEL-153 PROCEDURE FOR THE DETERMINATION OF THE CARBON, HYDROGEN, OXYGEN, AND NITROGEN CONTENT OF LIQUID FUELS

1 Introduction

1.1 This test method covers the determination of the carbon and hydrogen content of liquid fuels including gasoline, diesel, biodiesel blends, and gasoline-ethanol blends. When the only elements present in significant quantities are carbon, hydrogen, and oxygen, the oxygen content can be determined by difference.

1.1.1 MLD 131 (Determination of Hydrocarbon Types and Oxygenated Compounds in Gasoline) is the preferred test method for gasoline containing 15% or less of oxygenates by volume.

1.2 The repeatability and reproducibility equations in section 12 below are applicable for carbon in the range of 75 to 87 mass%, for hydrogen in the range of 9 to 16 mass%, and for nitrogen in the range of 0.1 to 2 mass%.

1.2.1 Most fuels in California contain less than 0.1 mass% nitrogen, so the nitrogen content reported will usually be zero.

1.3 This test method is based on ASTM D5291—02 (2007) method B.

2 Test Method

2.1 A small amount of the fuel to be analyzed is placed into a tared sample container. The container is closed, weighed, and transferred into an autosampler.

2.2 The autosampler delivers the sample container into the instrument's combustion tube and reduction tube. Carbon is converted into carbon dioxide, hydrogen is converted into water, and nitrogen is converted into nitrogen gas. Undesired materials such as excess oxygen and sulfur oxides are removed.

2.3 The product gases are homogenized and passed to a chromatographic column for separation, and then to a thermal conductivity detector for quantification.

3 Instrument

3.1 The instrumentation used in this analysis includes a PerkinElmer 2400 Series II CHNS/O Analyzer and a PerkinElmer AD6 microbalance.

3.2 Both the analyzer and the microbalance are connected to a Windows-based PC running Perkin Elmer's proprietary software.

4 Reagents

4.1 Helium: 99.995% or higher

4.2 Oxygen: 99.998% or higher

4.3 Acetanilide: reagent grade

4.4 Benzoic acid: reagent grade

4.5 2,2,4-trimethylpentane, reagent grade

4.6 Hexadecane, reagent grade

4.7 Combustion and reduction tube materials: as provided by Perkin Elmer

5 Preparation of Instrument

5.1 Set the helium regulator's output pressure to 18-20 psi. Set the oxygen regulator's output pressure to 16-18 psi. Set the pneumatic gas (house zero air) regulator to 60 psi.

5.2 Check and set (if necessary) the combustion and reduction temperatures. The combustion temperature should be 975 C; the reduction temperature should be 640 C.

5.3 Turn the gas saver off.

5.4 Create a new personal identification code (PID, which also serves as the data subdirectory) consisting of the current date in the format MMDDYY.

5.5 Purge the instrument with helium for 300 seconds.

6 Calibration

6.1 Calibrate the microbalance

6.1.1 Make sure the pans are empty. Close the doors and lower the pan arrest.
6.1.2 Press AUTOTARE and wait until the integration is complete.

6.1.3 Press RANGE until 200 mg appears.

6.1.4 Raise the pan arrest. Place the 100 mg calibration weight onto the sample pan. Close the door.

6.1.5 Lower the pan arrest. Type 100.00 using the numeric keypad. Press CALIB.

6.1.6 Calibration is now complete. Change the range back to 20 mg.

6.2 Calibration of the 2400 (called the determination of k-factors) is performed at the beginning of each analysis day.

6.3 Select a calibration material appropriate for the samples to be analyzed. 2,2,4-trimethylpentane or hexadecane should typically be used for liquid fuels. Acetanilide or benzoic acid is appropriate for solid samples, or for troubleshooting the instrument.

6.4 Run three blank samples (see 7.2 for sample preparation.) Check whether the blanks are reproducible to within the following limits:

6.4.1 Carbon: +/- 30; hydrogen: +/- 100; nitrogen: +/- 16

6.4.2 If the blanks are not reproducible, run more blanks.

6.5 Perform a conditioning run, a blank run, a conditioning run, a blank run, and three k-factor runs.

6.5.1 The conditioning runs should use the same material as the k-factor runs.

6.6 The three k-factors determined should differ from the mean value by no more than:

6.6.1 Carbon: +/- 0.15, hydrogen: +/- 3.75; nitrogen: +/- 0.50

6.6.2 If the k-factors are not sufficiently reproducible, perform up to two more k-factor runs. If the k-factors are still not sufficiently repeatable, repeat the procedure starting at 6.4.

7 Sample Preparation

7.1 The following instructions assume that the samples being analyzed are liquids. If the samples are solid, ignore all references to aluminum capsules, and skip steps 7.5 and 7.6. For blanks, do not perform any weighing.

7.2 Raise the microbalance's pan arrest. Place an empty tin capsule and an empty aluminum capsule on the microbalance's reference pan.

7.3 Place an empty tin capsule and an empty aluminum capsule on the microbalance's sample pan. Lower the pan arrest and press AUTOTARE.

7.4 Raise the pan arrest. Remove the aluminum capsule from the microbalance and

place it into the crimping tool.

7.5 Using a syringe, place approximately 3 microliters of sample into the aluminum capsule. The liquid level in the capsule should be just short of the top.

7.6 Crimp the aluminum capsule closed and place it into the tin capsule.

7.7 Using tweezers, fold the tin capsule into a minimal volume.

7.8 Place the tin capsule onto the microbalance's sample pan.

7.9 Lower the pan arrest and note the weight of the sample. If the weight does not fall within the range 1.5 – 3.0 mg, discard the sample and repeat from 7.2 above.

7.10 Record the sample weight. Place the tin capsule into the autosampler.

8 Procedure

8.1 Samples may be run individually using the Single Run function, or a queue can be entered using the Auto Run function. In either case, place the sample(s) into the autosampler.

8.2 Enter the sample numbers and weights into the instrument.

8.3 Run each sample at least two times. If the results differ by more than the method's repeatability (see 12.3 below), perform additional runs until there are two sufficiently close results.

8.4 At the end of the day's analyses, turn the gas saver on.

9 Calculation

9.1 Carbon and hydrogen content in weight percent are reported by the instrument software.

9.2 If the sample is known (from other analyses) to contain no oxygen, then normalize the results to a total of 100%

9.3 If the sample is known to contain oxygen, then the oxygen content in weight percent can be calculated as:

Oxygen = 100 – Carbon – Hydrogen

9.3.1 Alternately, if the oxygen content is known from another analysis, then normalize

the results to a total of (100 – oxygen content)%.

10 Maintenance

10.1 The combustion and reduction tubes need periodic replacement. Typical lifetimes are 1000 runs for the combustion tube and 250 runs for the reduction tube. The instrument has a countdown function which keeps track of the anticipated remaining lifetime of the tubes.

10.2 When the instrument indicates that a tube has reached its limit, or when poor blank or k-factor results indicate tube failure (see instrument manual), replace the applicable tube. Follow the instrument manual's procedure.

10.3 The materials used in preparing new tubes are potentially hazardous, especially the glass wool. Tube packing must be performed in a fume hood using gloves, a lab coat, safety glasses and a respirator. Extreme care should be taken with glass wool to avoid inhalation and contact with skin or eyes.

10.4 After replacing a tube, perform leak tests 1 and 2 (see instrument manual) and purge with helium for 300 seconds.

11 Safety

11.1 Acetanilide, gasoline, diesel and many of their various components are toxic. All volatile hydrocarbons are flammable. Persons using this method must wear protective gloves and eyewear when working with reagents and samples. The transfer of liquid fuels into sample capsules should be performed in a fume hood with adequate ventilation.

12 Quality Control

12.1 At the beginning of each analysis day, a quality control sample is analyzed. The sample should be a diesel fuel of known elemental composition (e.g. an ASTM crosscheck sample.)

12.2 The result of the quality control sample should differ from the consensus value by no more than twice the repeatability of the test method.

12.3 The repeatability of the test method is:

Carbon $r = 0.0072 * (x + 48.48)$
Hydrogen $r = 0.1162 * (x ^ 0.5)$

Where x = weight percent

13 References

1. "Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants," ASTM International, test method D5291-02 (2007).

2. "2400 Series II CHNS/O Analyzer User's Guide," PerkinElmer, Inc., 2003.

14 Revision History

Version 1.0 March 15, 2012

The quality control section has been updated to reflect a recent ASTM round robin. The absolute vapor pressure of 2,3-dimethylbutane has been re-determined as 7.50 psi.