A Honeywell Company

Low Trace Sulfur in Liquid Hydrocarbons by Oxidative Combustion with Ultraviolet Fluorescence Detection

UOP Method 987-15

Scope

This method is for determining sulfur in liquid hydrocarbons at concentrations ranging from 10 to 1500 ng/g (mass-ppb). A direct measurement procedure (Part A) is used for samples above 100 ng/g. A trap & release procedure (Part B) is used for samples between 10 and 200 ng/g where high precision is required. This method is applicable to highly volatile samples, such as pentane, through the use of a cooled sampling system.

Higher concentrations can be determined by ASTM Method D5453, "Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence," and D7183, "Standard Test Method for Determination of Total Sulfur in Aromatic Hydrocarbons and Related Chemicals by Ultraviolet Fluorescence," using the cooled sampling system described herein for highly volatile matrices.

Halogens interfere at concentrations greater than approximately 0.3%. The method has reduced sensitivity to sulfur present as sulfate. For Part A, nitrogen content must not exceed sulfur by more than 100-fold to prevent a positive bias to the results.

References

ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter," www.astm.org

ASTM Method D5453, "Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence" www.astm.org

ASTM Method D7183, "Standard Test Method for Determination of Total Sulfur in Aromatic Hydrocarbons and Related Chemicals by Ultraviolet Fluorescence" www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

A commercial instrument is set up and calibrated with liquid standards. For samples containing volatile components such as pentane, the sample tray is cooled (see *Note 1*). The sample is directly injected by autosampler into the combustion tube where it vaporizes into an argon carrier. The vapors

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

are mixed with oxygen at high temperature. The organic material is converted to carbon dioxide and water. The sulfur in the sample is converted to sulfur dioxide and measured by Ultraviolet Fluorescence (UVF) as described in *Part A*. For samples containing sulfur between 10 and 200 ng S/g, the SO_2 produced during sample combustion is preconcentrated using a Trap & Release Unit prior to measurement as described in Part B. Samples between 100 and 200 ng S/g can be analyzed either directly (*Part A*) or by preconcentration (*Part B*), although *Part B* will yield higher precision. The signal is proportional to the total sulfur in the sample.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, analytical, readable to 0.0001 g

Flasks, volumetric, Class A, borosilicate glass, 100- and 250-mL, Fisher Scientific, Cat. Nos. 10-210-8C and -8E, respectively

Pipet, volumetric, Class A, 1-, 2-, 5-, 10- and 15-mL, Fisher Scientific, Cat. No. 13-650-2B, -2C, -2F, -2L and -2M, respectively

Pipet filler, VWR, Cat. No. 53497-055

Refrigerator, flammable storage or explosion proof, Fisher Scientific, Cat. No. 55703-190

Regulator, argon, single-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3231, with connection fittings appropriate to the installation. This regulator is installed downstream of the two-stage regulator to provide better flow control.

Regulator, argon, two-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3122-580

Regulator, oxygen, single-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3231, with connection fittings appropriate to the installation. This regulator is installed downstream of the two-stage regulator to provide better flow control.

Regulator, oxygen, two-stage, with stainless steel diaphragm, delivery pressure range 30-700 kPa (4-100 psi), Matheson Tri-Gas, Cat. No. 3122-540

Sulfur analyzer, with attached furnace, autosampler, controls and computer. This method was developed and validated using the Mitsubishi analyzer Model TS-100V, with SD-100 Sulfur Detector, TRU-100 Trap & Release Unit and STC-210L Sample Temperature Controller, Mitsubishi Chemical Analytech, available from COSA Xentaur. Part A has also been validated on the Mitsubishi NSX-2100V, with SD-210 Sulfur Detector and STC-210L Sample Temperature Controller. Manufacturer recommended operation parameters for the use of the NSX-2100V with Part B of the method are also provided. The procedure for analysis may be different for other instruments and all other instruments need to be validated before using for this method. Not all combustion/UV fluorescence instruments are capable of running this analysis, since controlled temperature sampling is required. The Mitsubishi analyzer must be equipped with the following accessories:

Autosampler, Mitsubishi ASC-250L or ASC-150L, COSA Xentaur

Autosampler syringes, gas tight, 100-µL, Mitsubishi, Cat. No. MSSG10, COSA Xentaur (for Part A)

Autosampler syringes, gas tight, 250-µL, Mitsubishi, Cat. No. MSSGGQ, COSA Xentaur (for Part B)

Autosampler bottles, rinse, pre-fill, and waste, Mitsubishi, Cat. No. TX3LSW, COSA Xentaur

Membrane drier, Perma Pure MD-110-24F-4 or Tube Dryer, Mitsubishi, Cat. No. TN6RPC, COSA Xentaur (see *Note 2)*

Sample Temperature Controller, Mitsubishi STC-210L, COSA Xentaur

Trap & Release Unit, Mitsubishi TRU-100 or TRU-210, COSA Xentaur

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

The following items are required to perform the analysis. Additional reagents and materials may be required depending on the specific instrument.

Air, compressed, dry, oil-free, for membrane drier (if instrument does not purge the drier with argon), local supply

Alumina balls, Mitsubishi, Cat. No. TS3CAT, COSA Xentaur

Argon, compressed gas, 99.99% minimum purity. UHP, Matheson Tri-Gas or local supply

Autosampler vials, 15x45-mm, Grace Davison Discovery Sciences, Cat. No. 98008

Catalyst, Mitsubishi, Cat. No. TN5CAT, COSA Xentaur

Dibenzothiophene, 98%, VWR, Cat. No. AAA12288-14, optional (see *Procedur*e, *Preparation of Standards*)

Isooctane, should be as low in residual sulfur as possible to minimize the blank value, B&J Brand, Burdick & Jackson, Cat. No. BJ362-1, VWR or Fisher Pesticide grade, Fisher Scientific, Cat. No. O297-4. Test each new lot of solvent before use.

Oxygen, compressed gas, 99.98% minimum purity, UHP, Matheson Tri-Gas or local supply

Pipet, transfer, disposable plastic, 152-mm length, Fisher Scientific, Cat. No. 13-711-SA

Quartz wool, Mitsubishi, Cat. No. TNQWL, COSA Xentaur

Sulfur standard, commercial certified, Accustandard or VHG, optional (see *Procedur*e, *Preparation of Standards*). Purchase the lowest sulfur concentrations available, generally about 5 mg/kg.

Toluene, B&J Brand, Burdick & Jackson, VWR Cat. No. BJ347-4

Procedure

The analyst is expected to be familiar with general laboratory techniques, sulfur analysis, and the equipment being used.

Preparation of Standards

Calibration standards can be prepared as serial dilutions from a prepared volumetric standard solution or by diluting a commercial certified standard on a mass/volume basis. Suitable commercial standards are available, prepared in isooctane/toluene or diesel matrices, and sold by vendors such as AccuStandard and VHG. Prepare volumetric standard solutions as follows: