



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).

© COPYRIGHT 2011, 2015 UOP LLC. All rights reserved.

Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

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 SO₂ 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- μ L, 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 *Procedure, 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 *Procedure, 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:

Dibenzothiophene stock solution, 1000- μg S/mL

1. Tare a clean, dry, 100-mL volumetric flask. Dispense 0.575 g of dibenzothiophene and record the mass to the nearest 0.0001 g.
2. Dilute to the mark with toluene. Cap and mix well.
3. Calculate the actual concentration of the stock solution using Equation 1:

$$S, \mu\text{g/mL} = \frac{A(0.1740)10^6}{100} \quad (1)$$

where:

- A** = mass of dibenzothiophene, g
- 0.1740** = S mass-fraction of dibenzothiophene (32.066/184.26)
- 32.066** = molecular mass of sulfur, g/mol
- 184.26** = molecular mass of dibenzothiophene, g/mol
- 100** = dilution volume, mL
- 10^6** = factor to convert g to μg

Dibenzothiophene stock solution, 10- μg S/mL

1. Dispense 1.0 mL of the 1000- μg /mL S stock solution using a volumetric pipet into a clean, dry, 100-mL volumetric flask.
2. Dilute to the mark with low S isooctane. Cap and mix well.
 - The actual concentration is 1/100th the concentration of the stock solution above.

Calibration standard solution, 1500-ng S/mL

1. Dispense 15.0 mL of the 10- μg /mL S stock solution using a volumetric pipet into a clean, dry, 100-mL volumetric flask.
2. Dilute to the mark with low S isooctane. Cap and mix well.
 - The actual concentration is 15/100th the concentration of the nominal 10- μg S/mL stock solution above.

Calibration standard solution, 1000-ng S/mL

1. Dispense 10.0 mL of the 10- μg /mL S stock solution using a volumetric pipet into a clean, dry, 100-mL volumetric flask.
2. Dilute to the mark with low S isooctane. Cap and mix well.
 - The actual concentration is 1/10th the concentration of the nominal 10- μg S/mL stock solution above.

Calibration standard solution, 500-ng S/mL

1. Dispense 5.0 mL of the 10- μg /mL S stock solution using a volumetric pipet into a clean, dry, 100-mL volumetric flask.
2. Dilute to the mark with low S isooctane. Cap and mix well.
 - The actual concentration is 1/20th the concentration of the nominal 10- μg S/mL stock solution above.

Calibration standard solution, 200-ng S/mL

1. Dispense 2.0 mL of the 10- μg /mL S stock solution using a volumetric pipet into a clean, dry, 100-mL volumetric flask.

2. Dilute to the mark with low S isooctane. Cap and mix well.
 - The actual concentration is $1/50^{\text{th}}$ the concentration of the nominal 10- μg S/mL stock solution above.

Calibration standard solution, 100-ng S/mL

1. Dispense 1.0 mL of the 10- μg /mL S stock solution using a volumetric pipet into a clean, dry, 100-mL volumetric flask.
2. Dilute to the mark with low S isooctane. Cap and mix well.
 - The actual concentration is $1/100^{\text{th}}$ the concentration of the nominal 10- μg S/mL stock solution above.

Calibration standard solution, 50-ng S/mL

1. Dispense 10.0 mL of the 500-ng/mL S calibration standard solution using a volumetric pipet into a clean, dry, 100-mL volumetric flask.
2. Dilute to the mark with low S isooctane. Cap and mix well.
 - The actual concentration is $1/10^{\text{th}}$ the concentration of the nominal 500-ng S/mL calibration standard solution above.

Calibration standard solution, 20-ng S/mL

1. Dispense 10.0 mL of the 200-ng/mL S calibration standard solution using a volumetric pipet into a clean, dry, 100-mL volumetric flask.
2. Dilute to the mark with low S isooctane. Cap and mix well.
 - The actual concentration is $1/10^{\text{th}}$ the concentration of the nominal 200-ng S/mL calibration standard solution above.

The stock solutions can be retained, if refrigerated, for up to six months. The calibration standard solutions of 100-ng S/mL and higher can be retained, if refrigerated, for up to 3 months. The 20- and 50-ng S/mL standard solutions should be made fresh daily.

Part A – Samples between 100- and 1500-ng/g Sulfur

Preparation of Apparatus

1. Set up the instrument according to the manufacturer's instructions. New combustion tubes need to be conditioned with catalyst before use, following the manufacturer's procedure. **For Mitsubishi instruments, procedure ZINF026 MUST be followed.** Connect the membrane drier in series between the combustion tube and the detector. Allow the instrument to warm up and the baseline to stabilize before injecting samples. Suggested Operating Conditions for the Mitsubishi TS-100V analyzer are listed in Table 1 and for the NSX-2100V in Table 2.
2. Set the STC-210 temperature controller set points to 15°C (see *Note 1*) for both the sample tray and the syringe. Allow at least 30 minutes for the temperature to stabilize before injecting samples.
 - For samples that do not contain volatiles such as pentane, the temperature of the sample tray may be set at 20°C. For heavier samples, such as n-paraffins in the C_{16} to C_{18} range which may solidify upon cooling, maintain the sample tray above room temperature (see *Note 1*).
3. Fill the rinse and pre-fill bottles with low sulfur isooctane. Empty the waste bottle.

- Dispose of all materials in an environmentally safe manner according to local regulations.
4. Before starting to measure either calibration standards or samples, run an instrument program with 3 (or more) injections of isooctane to condition the instrument. The response should be a stable, level baseline, free of drift before proceeding.

Table 1
Operating Conditions for Mitsubishi TS-100V/SD-100

Upper temperature ^a	900°C
Lower temperature ^b	1000°C
Argon main	250 mL/min
Oxygen main	150 mL/min
Argon auxiliary	50 mL/min
Oxygen auxiliary	400 mL/min
Gain	Ultra
Normal end	Off
Timer start	3 sec
Timer end	400 sec
Minimum area	40000
Base line	25%
Syringe pre-fill	10 µL
Sample volume	80 µL
Injection rate	1.2 µL/sec

^aCombustion tube, upper portion

^bCombustion tube, lower portion

Table 2
Suggested Operating Conditions for Mitsubishi NSX-2100V/SD-210

Inlet heater temperature	900 °C
Outlet Heater temperature	1000 °C
Argon	100 mL/min
Oxygen	500 mL/min
Dryer gas flow	1000 mL/min (or higher)
Argon Time	30 sec
Oxygen Time	120 sec
PMT Sensitivity	High (For Low Concentration)
Type	Timer
Waiting Time	10 sec
Measurement Time	300 sec
Syringe pre-fill	10 µL
Sample Volume	80 µL
Injection rate	1.2 µL/sec
Precedent Rinse	Enable

Calibration

Calibrate the instrument weekly when in use. Check the calibration daily when in use, by analyzing one of the calibration standards or a reference material. Calibration data are in a separate program from the sample analysis with the TS-100V, but part of the same sample schedule when using the NSX-2100V. Calibration samples should be within the Repeatability Allowable Difference.

1. Fill autosampler vials, one each, with the solvent used to make the standard solutions (solvent blank) and the 100-, 200-, 500-, and 1000-ng S/mL calibration standards. Rinse each autosampler vial with approximately 1 mL of the material, empty, and then fill with the material.
 - The 1500-ng/mL standard is optional if calibration above 1 mass-ppm is desired.
2. Cycle the instrument (Step 4 in *Preparation of Apparatus*) while the temperature of the standard solutions equilibrates to 15°C.
 - Approximately 10 minutes is required for temperature equilibration of the standards, much less than that required by the instrument cycling and analyses of the blank.
3. Run a calibration program with multiple 80-μL injections of the solvent blank and each standard. It is recommended to inject each standard or blank at least 4 times. The injections contain approximately 0, 8, 16, 40, and 80 ng of added sulfur.
 - The average of the replicate injections is calculated by the instrument software.
 - Relative standard deviation (RSD), as calculated by the instrument for the blank, should be within 25%. The RSD for the standards should be within 10%. If greater deviations occur, make certain that there are no problems with the equipment or the procedure, and then make additional runs until the expected repeatability is obtained.
4. Create a regression line using the instrument software using the blank and the four standards (or five, if the 1500 ng S/mL standard is used). Set the regression line to the “ $y=bx+c$ ” option for this calibration.

Sample Analysis

1. Rinse the autosampler vial with approximately 1 mL of the sample, empty and then fill the autosampler vial with the sample. Place the vial onto the autosampler rack and repeat for all remaining samples.
 - Approximately 10 minutes is required for temperature equilibration of the samples.
2. Fill the rinse and pre-fill vials with isooctane, if not already full. Empty the waste vial.
3. Enter the sample parameters into the software to create a sample method. Set injection volume to 80 μL. Each sample should be injected at least three times.
 - The 80-μL injection volume is necessary for the required sensitivity. Do not inject less than 80 μL for samples containing less than 200-ng S/g.
4. Combust and analyze at least 3 injections of isooctane to condition the instrument before starting the samples. A level baseline with no drift should be obtained before proceeding.
5. Inject and analyze the samples using 80-μL injections.
 - If the detector becomes contaminated (trace off scale), continue to analyze isooctane blanks until the response stabilizes. Then, confirm that the sensitivity has not changed by analyzing a calibration standard or a control standard.
 - Integration and calculations are done automatically. The average of the replicate injections is calculated by the instrument software.
 - Multiple injections of the same sample are averaged by the instrument software. The values from each of the replicate runs should not deviate from the average by more than 0.03 mg/kg. If greater deviations occur, make certain that there are no problems with the equipment or the procedure, and then make additional runs until the expected repeatability is obtained.

Part B – Samples between 10- and 200-ng/g Sulfur, using the Trap and Release Unit

Preparation of Apparatus

- Set up the instrument according to the manufacturer's instructions. New combustion tubes need to be conditioned with catalyst before use, following the manufacturer's procedure. **For Mitsubishi instruments, procedure ZINF026 MUST be followed.** Connect the membrane drier in series between the combustion tube and the detector. Note that the detector flow is reversed when using the TS-100V with the TRU-100 Trap and Release Unit. A 250- μ L syringe must be installed.
 - The set up is shown in the instrument manual, and is demonstrated during initial instrument installation.
- Allow the instrument to warm up and the baseline to stabilize before injecting samples. Suggested Operating Conditions for the Mitsubishi TS-100V analyzer are listed in Table 3 and for the NSX-2100V in Table 4.

Table 3
Operating Conditions for Mitsubishi TS-100V/SD-100/TRU-100

Upper temperature ^a	900°C
Lower temperature ^b	1000°C
Argon main	170 mL/min
Oxygen main	150 mL/min
Argon auxiliary	50 mL/min
Oxygen auxiliary	400 mL/min
Gain	Ultra
Normal end	Off
Trap time	400 sec
Timer start	400 sec
Timer end	760 sec
Minimum area	40000
Base line	75%
Sample volume	240 μ L
Injection rate	1.2 μ L/sec

^aCombustion tube, upper portion

^bCombustion tube, lower portion

Table 4

Suggested Operating Conditions for Mitsubishi NSX-2100V/SD-210/TRU-210

Inlet heater temperature	900 °C
Outlet Heater temperature	1000 °C
Argon	100 mL/min
Oxygen	500 mL/min
Dryer gas flow	1000 mL/min (or higher)
Argon Time	30 sec
Oxygen Time	90 sec
PMT Sensitivity	High (For Low Concentration)
Type	Timer
Waiting Time of integration start	473 sec

Measurement Time	713 sec
Syringe pre-fill	10 µL
Sample volume	240 µL
Injection rate	1.2 µL/sec
Precedent Rinse	Enable
Startup Preparation Time	180 sec
Wait Time after Release	30 sec
Trap Standby Time	220 sec
Trap Time	453 sec
Trap Temp.	200°C
Release Temp.	800°C
Prebake Temp.	950°C

- Set the STC-210 temperature set points to 15°C (see *Note 1*) for both the sample tray and the syringe. Allow at least 30 minutes for the temperature to stabilize before injecting samples.
 - For samples that do not contain volatiles such as pentane, the temperature of the sample tray may be set at 20°C. For heavier samples, such as n-paraffins in the C16 to C18 range which may solidify upon cooling, maintain the sample tray above room temperature (see *Note 1*).
- Fill the rinse and pre-fill bottles with low sulfur isooctane. Empty the waste bottle.
 - Dispose of all materials in an environmentally safe manner according to local regulations.
- Before starting to measure either calibration standards or samples, run an instrument program with 3 (or more) injections of isooctane to condition the instrument. The response should be a stable, level baseline, free of drift before proceeding.

Calibration

Calibrate weekly when in use. Calibration data are in a separate program from the sample analysis with the TS-100V, but part of the same sample schedule when using the NSX-2100V.

- Fill autosampler vials, one each, with the 20-, 50-, 100-, and 200-ng S/mL calibration standards. Rinse the autosampler vial with approximately 1 mL of the material, empty, and then fill with the material. Place an empty vial in the first position.
 - The empty vial serves as an instrument blank for the calibration.
- Cycle the instrument (Step 4 in *Preparation of Apparatus*) while the temperature of the standard solutions equilibrates to 15°C.
 - Approximately 10 minutes is required for temperature equilibration of the standards, much less than that required by the instrument cycling and analyses of the blank.
- Run a calibration program with multiple 240-µL injections of the isooctane blank and each standard. It is recommended to inject each standard or blank at least 3 times. The injections contain approximately 0, 4.8, 12, 24, and 48 ng of added sulfur.
 - The average of the replicate injections is calculated by the instrument software.
 - Relative standard deviation (RSD), as calculated by the instrument for the blank, should be within 25%. The RSD for the standards should be within 10%. If greater deviations occur, make certain that there are no problems with the equipment or the procedure, and then make additional runs until the expected repeatability is obtained.
- Create a regression line using the instrument software using the blank and the four standards. Set the regression line to the “ $y=bx+c$ ” option for this calibration.

Sample Analysis

1. Rinse the autosampler vial with approximately 1 mL of the sample, empty and then fill the autosampler vial with the sample. Place the vial onto the autosampler rack and repeat for all remaining samples.
 - Approximately 10 minutes is required for temperature equilibration of the samples.
2. Fill the rinse and pre-fill vials with isooctane, if not already full. Empty the waste vial.
3. Enter the sample parameters into the software to create a sample method. Set injection volume to 240 μ L. Each sample should be injected at least four times.
 - The amount of sulfur injected should not exceed 50 ng per measurement.
4. Combust and analyze at least 3 injections of isooctane to condition the instrument before starting the samples.
5. Inject and analyze the samples using 240- μ L injections.
 - If the detector becomes contaminated (trace off scale), continue to analyze isooctane blanks until the response stabilizes. Then, confirm that the sensitivity has not changed by analyzing a calibration standard or a control standard.
 - Integration and calculations are done automatically. The average of the replicate injections is calculated by the instrument software.
 - Multiple injections of the same sample are averaged by the instrument software. The values from each of the replicate runs should not deviate from the average by more than 3 ng/g (Part B). If greater deviations occur, make certain that there are no problems with the equipment or the procedure, and then make additional runs until the expected repeatability is obtained.

Calculations

All calculations are performed by the software, and results are displayed and printed in mass-ppm (mg/kg) or mass-ppb (ng/g). The density of the sample is input during sample data entry and is used by the instrument to convert results from mass/volume to mass/mass. If the density of the sample is unknown, it can be determined by ASTM D4052, "Density and Relative Density of Liquids by Digital Density Meter."

Report

For *Part A*, report mg/kg (mass-ppm) results to two decimal places. For *Part B*, report ng/g (mass-ppb) to the nearest whole number.

Notes and Precautions

1. Highly volatile samples (e.g. pentane, hexane) are cooled to 15°C. Other sample matrices (e.g. light aromatics, naphtha) should be held at 15 or 20°C, since the temperature control improves measurement precision. Heavy samples, such as n-paraffins in the C₁₆ to C₁₈ range which may solidify on cooling, may need to be heated to approximately 27-40°C to prevent solidification.
2. The membrane drier is used to remove the water produced during combustion. If not removed, the water vapor would result in a loss of SO₂ causing a low recovery. The membrane drier consists of a thin walled Nafion™ tube within a larger plastic tube. The combustion product gas flows through the Nafion tube. Dry air or other dry gas flows counter-current through the outer plastic tube. The Nafion membrane allows water to pass through and be carried away by the air stream on the other side.
3. Since this method is for use with very low levels of sulfur, care must be taken to prevent contamination of the sample. The containers used for the samples and standards must not

contaminate the solutions. The autosampler vial septum could also be a source of sulfur contamination. Fill an autosampler vial with isooctane and cap. Analyze immediately from this container, and again several hours later. Any increase in sulfur level is an indication of contamination from the container. Autosampler bottles, such as the recommended part from Grace, do not contribute S to the samples. The samples should not be left uncovered any longer than necessary. This prevents loss of volatile components and/or entry of contaminants.

4. With direct injection instruments, it is recommended that the same injection volume be used for both the standards and the samples.
5. Nitrogen in excess of 100 times the sulfur content will result in a positive bias for Part A. This does not occur when the Trap & Release Unit is used for Part B.
6. When using the TS-100V, a separate calibration program and sample analysis program should be used. With the NSX-2100V, the calibration standards must be analyzed in the same schedule file as the samples.

Precision – Part A

Precision statements were determined using UOP Method 999, “Precision Statements in UOP Methods,” from precision data obtained using an autosampler. As described in the *Procedure and Calculations*, four replicate injections were averaged for each analysis.

Repeatability and Site Precision

A nested design was carried out for determining impurities in five samples of isooctane by one analyst on two separate days, performing two analyses each day, for a total of 16 analyses. A second series of analyses were performed on one sample so that site precision could be calculated. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 3. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 3 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 3 with 95% confidence.

Table 3
Repeatability and Site Precision for Procedure Part A, ng/g

<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
	<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
69	3.6	14	3.8	15
153	4.7	29		
202	7.5	46		
337	3.2	19		
1315	21.2	129		

The data in Table 3 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Precision – Part B

Precision statements were determined using UOP Method 999, “Precision Statements in UOP Methods,” from precision data obtained using an autosampler. As described in the *Procedure and Calculations*, four replicate injections were averaged for each analysis.

Repeatability and Site Precision

A nested design was carried out for determining impurities in four samples of isooctane by one analyst on two separate days, performing two analyses each day, for a total of 16 analyses. A second series of analyses were performed on one sample so that site precision could be calculated. Using a stepwise analysis of variance procedure, the within-day estimated standard deviations (esd) were calculated at the concentration means listed in Table 4. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Table 4 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Table 4 with 95% confidence.

The data in Table 4 represent short-term estimates of the repeatability of the method. When the test is run routinely, use of a control standard and a control chart is recommended to generate an estimate of long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Table 4
Repeatability and Site Precision for Procedure Part B, ng/g

<u>Mean</u>	<u>Repeatability</u>		<u>Site Precision</u>	
	<u>Within-Day esd</u>	<u>Allowable Difference</u>	<u>Within-Lab esd</u>	<u>Allowable Difference</u>
7	0.7	2	0.7	3
13	0.5	3		
26	2.0	9		
126	1.8	8		

Time for Analysis

The elapsed time for a calibration is approximately 3 hours for Part A and 5 hours for Part B. The labor requirement for either calibration is identical, 1 hour. Each succeeding analysis requires 0.5 hour (Part A) or 1 hour (Part B).

Suggested Suppliers

AccuStandard, 125 Market St., New Haven, CT 06513, USA (203-786-5290) AccuStandard.com

Burdick & Jackson, 1953 S. Harvey St., Muskegon, MI 49442, USA (973-455-5268)
www.burdickandjackson.com

COSA Xentaur, 84G Horseblock Rd., Yaphank, NY 11980, USA, 1-631-345-3434, distributor for
Mitsubishi Chemical Analytech, 370 Enzo, Chigasaki, Kanagawa Pref., 253-0084, Japan, +81-467-86-3864, cosaxentaur.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219, USA (412-562-8300) www.fishersci.com

Grace Davison Discovery Sciences, 2051 Waukegan Rd., Deerfield, IL 60015, USA (847-948-8600) www.discoverysciences.com

Matheson Tri-Gas, 166 Keystone Dr., Montgomeryville, PA 18936, USA (215-641-2700) www.mathesontrigas.com

Perma Pure Inc., 8 Executive Dr., Toms River, NJ 08754, USA (732-244-0010) www.permapure.com

Sigma-Aldrich, Milwaukee, WI 53201, USA (414-438-3850) www.sigma-aldrich.com

VHG Labs, 276 Abby Rd., Manchester, NH 03103, USA (603-622-7660) www.vhglabs.com

VWR International, 1310 Goshen Pkwy., West Chester, PA 19380, USA (610-431-1700) www.vwr.com