

**California Environmental Protection Agency**  
 **Air Resources Board**

**PROCEDURE FOR THE DETERMINATION OF SULFUR IN FUELS  
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SOP No. MLD 123  
Revision No.4.2  
Effective Date: September 30, 2010

FUEL ANALYSIS AND METHODS EVALUATION SECTION  
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## **1 Introduction**

- 1.1 This procedure describes the determination of sulfur content in both gasoline and diesel by ultraviolet fluorescence.
- 1.2 The Air Resources Board utilizes this procedure to analyze sulfur content of gasoline and diesel to determine compliance with the sulfur specifications of California RFG and Clean Diesel regulations and to support various research projects requiring sulfur analysis.
- 1.3 This method determines total sulfur in liquid hydrocarbons with a boiling point range from approximately 25 to 400 degrees Celsius, with viscosities between approximately 0.2 and 10 cSt (mm<sup>2</sup>/S) at room temperature. This procedure is applicable to naphthas, distillates, motor fuels and oils containing 1.0 to 8000 mg/kg total sulfur.
- 1.4 This procedure is based on ASTM D 5453-93.

## **2 Method**

- 2.1 Fuel samples are injected into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide in an oxygen rich atmosphere. The water produced during the sample combustion is removed and the sample combustion gases are then exposed to ultraviolet (UV) light.
- 2.2 The sulfur dioxide absorbs the energy from the ultraviolet light and is converted to excited sulfur dioxide. The fluorescence emitted from the excited sulfur dioxide as it returns to a stable state sulfur dioxide is detected by a photomultiplier tube and the resulting signal is a measure of the sulfur contained in the sample.
- 2.3 The data system identifies the peaks and quantifies the sulfur content by integrating and comparing the areas of sample and calibration standard peaks.

## **3 Instrumentation and Apparatus**

- 3.1 Furnace--Antek model 7000VLAS, Mitsubishi model TS-100V, or equivalent, should be equipped with an electric furnace capable of a maximum temperature of 1100 degrees Celsius.
- 3.2 Combustion tube--The instrument must be equipped with a quartz combustion tube constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace. The combustion tube must have side arms for the introduction of oxygen and carrier gas.

- 3.3 Flow controllers--The instrument must be equipped with flow controllers capable of maintaining a constant supply of oxygen and carrier gas.
- 3.4 Drier tube--The instrument must be equipped with a membrane drying tube for the removal of water vapor. The oxidation reaction products include water vapor which must be eliminated before the sample is measured by the detector.
- 3.5 Detector--The U.V. Fluorescence detector is a qualitative and quantitative detector capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.
- 3.6 Microlitre syringe--
  - 3.6.1. Antek model 7000VAS or equivalent--The microlitre syringe that is used in the autosampler should be capable of accurately delivering 5 to 20 uL quantities. The needle should be 50 mm (+/- 5 mm) long.
  - 3.6.2. Mitsubishi model TS-100V or equivalent-- The microlitre syringe that is used in the autosampler should be capable of accurately delivering 25 to 40 uL quantities. The needle should be 50 mm (+/- 5 mm) long.
- 3.7 Direct Injection--Robotic Liquid Autosampler, Antek Model 738, Mitsubishi model ASC-150L, or equivalent.
- 3.8 Data system--IBM Compatible Data System with Antek Elemental Software, or Mitsubishi TS-100V Software, or equivalent. System should provide autosampler control, sample identification, concentration, statistics and disk storage of results for data manipulation.

#### **4 Reagents and Materials**

- 4.1 Solvent--Isooctane, Reagent grade.
- 4.2 Calibration Standards--Suggested compounds are Dibenzothiophene, FW184.26 or Thionaphthene (Benzothiophene), FW 134.20.
- 4.3 Quality Control Sample--Gasoline samples with a sulfur concentration between 5-300 ppm.
- 4.4 Carrier gas--Argon or helium, high purity grade (chromatography or zero grade), 99.998% minimum purity.
- 4.5 Oxidizing reagent--Oxygen, high purity grade (chromatography or zero grade), 99.75% purity.

## 5 Calibration Standards Preparation

### 5.1 SULFUR STOCK SOLUTION, 1000 ppm S

5.1.1 Prepare a stock solution gravimetrically by accurately weighing 0.4000 g of Dibenzothiophene into a tared 100 mL volumetric flask. Dissolve the dibenzothiophene with approximately 50 mL isooctane. Add isooctane to the mark on the flask and weigh. This solution may be diluted to desired sulfur concentrations. Working standards should be prepared on a regular basis depending upon frequency of use and age. The suggested shelf life of the standards is about one year. The calibration standards have maintained their integrity for one year in refrigerated storage.

### 5.2 CALIBRATION RANGE

5.2.1 Calibration Range for Antek 7000 VAS or equivalent.

5.2.1.1 Prepare a series of calibration standards by making dilutions of the stock solution to cover the range of operation. Calibrate the analyzer as per manufacturer's instructions using the average response for each standard. This curve should be linear and the instrument performance must be checked with the Q.C. sample (see Quality Control Section 8.3). The following is a table of the suggested calibration curves. Note that the volume injected varies with the concentration range.

Curve I Sulfur, ppm	Curve II Sulfur, ppm	Curve III Sulfur, ppm
0.50	1.00	10.00
1.00	5.00	100.00
2.50	25.00	500.00
5.00	50.00	1000.00
10.00	100.00	
Injection size 10-20 microlitres	Injection size 5-10 microlitres	Injection size 5-10 microlitres

5.2.2 Calibration Range for Mitsubishi TS-100V or equivalent.

5.2.2.1 Prepare a series of calibration standards by making dilutions of the stock solution to cover the range of operation. Calibrate the analyzer as per manufacturer's instructions using the average response for each standard. This

curve should be linear and the instrument performance must be checked with the Q.C. sample (see Quality Control Section 8.3). The following is a table of the suggested calibration curves.

Curve I Sulfur, ppm	Curve II Sulfur, ppm	
0.50	2.50	
1.00	10.00	
2.50	25.00	
5.00	50.00	
10.00	100.00	
25.00	500.00	
Injection size 40 microliters	Injection size 40 microliters	

## 6 Procedure

- 6.1 Fuel samples are collected in bottles or metal canisters and delivered to the laboratory.
- 6.2 The calibration standards and fuel samples are transferred into autosampler vials.
- 6.3 A sample is drawn from the vial by the autosampler and is run in triplicate to obtain the average value.

### 6.4 TYPICAL INSTRUMENT OPERATING CONDITIONS

- 6.4.1 Typical Instrument Operating Conditions--Antek 7000VAS or equivalent:
  - Furnace Temperature (Pyro A): 1100 C
  - Furnace Oxygen Flowmeter Setting: 3.5
  - Inlet Oxygen Flowmeter Setting: 0.5
  - Inlet Carrier Flowmeter Setting: 2.0

Low level sulfur @ 1-10 ppm  
 Chan. B Gain: HIGH  
 Gain Factor: X25  
 PMT Voltage: ~650 V

Mid level sulfur @ 10-100 ppm  
Chan. B Gain: HIGH  
Gain Factor: X1  
PMT Voltage: ~650 V

High level sulfur @ 100-1000 ppm  
Chan. B Gain: LOW  
Gain Factor: X1  
PMT Voltage: ~650 V

- 6.4.2 Typical Instrument Operating Conditions—Mitsubishi TS-100V or equivalent:  
Furnace Temperature (Inner): 1075 C  
Furnace Temperature (Outer): 850 C  
Main Oxygen Setting: 400 mL/min.  
Main Argon Setting: 350 mL/min  
Auxiliary Oxygen Setting: 150 mL/min.  
Auxiliary Argon Setting: 150 mL/min.

## 6.5 TYPICAL AUTOSAMPLER OPERATING CONDITIONS

- 6.5.1 Typical Autosampler Operating Conditions—Antek 7000VAS  
Syringe drive: 1 uL/s  
Sample injection volume varies with the sulfur concentration of the sample:  
Low level sulfur suggested sample volume- ~15 uL  
Midlevel sulfur suggested sample volume- ~8 uL  
High level sulfur suggested sample volume- ~8 uL
- 6.5.2 Typical Autosampler Operating Conditions—Mitsubishi TS-100V  
Syringe drive: 1.2 uL/s  
Sample injection volume is 40 uL.

## 7 **Calculation of Results**

- 7.1 The sulfur concentrations, given in ppm, are calculated by the data system using external multipoint calibration standards. The area count measured from the sample is compared to the area counts measured from the multipoint calibration.
- 7.2 Check each run for proper quantification of the sulfur peak. If necessary, omit the outlier from the triplicate runs.

7.3 The result of the sulfur concentration needs to be corrected for density. The densities of isooctane and of the sample are measured. The formula to calculate the corrected concentration in ppm is shown below:

$$\text{ppm} = \frac{A \times B}{C}$$

A = Average result from the triplicate runs

B = Density of isooctane

C = Density of the sample

## 8 Quality Control

### 8.1 BLANK ANALYSIS

8.1.1 A sample of isooctane is used as a blank and analyzed daily to check the analytical system for contamination. If the blank analysis shows an area count greater than the 0.5 ppm standard for the low-level sulfur or 1 ppm standard for the mid-level sulfur, the blank should be repeated. If the blank still shows sulfur content greater than 0.5 ppm or 1 ppm, the contamination sources must be corrected before analyzing samples. The system should be checked for possible saturation or soot accumulation.

### 8.2 CALIBRATION STANDARDS ANALYSIS

8.2.1 Calibration standards are prepared as needed. It is estimated that the standards will maintain a shelf life of about one year. This depends on how often the standards are uncapped. Working standards are stored in the refrigerator. The multi-level calibration is run as needed and should be linear. The r of least square fit must be 0.99 or greater. If it falls below 0.99, the calibration should be rerun and/or the instrument should be checked for possible malfunction or required maintenance.

### 8.3 CONTROL SAMPLE ANALYSIS

8.3.1 The control sample is analyzed at the beginning of the sample set, after every ten samples, and at the end of the sample set. For the screening purposes with a single injection analyses the control sample is analyzed at the beginning of the sample set, after every 20-25 samples and at the end of the sample set. A control chart is maintained for the control sample. The upper and lower warning limits are set at two standard deviations ( $\pm 2s$ ). The upper and lower control limits are at three standard deviations ( $\pm 3s$ ).

8.3.2 A control sample is out-of-control when the measured value of sulfur exceeds the 3s limit or when two successive measurements of the control sample exceed the 2s limit. If the QC sample is out-of-control, the calibration and QC sample

must be rerun. If the control sample continues to be out-of-control, determine the cause of the problem before analyzing any samples.

8.3.3 A NIST SRM sample will be analyzed on a quarterly basis. The control limit must be within  $\pm 3$  ppm S of the certified value. This is determined from the sum of the uncertainty value ( $\pm 1$ ) and the ASTM D5453-93 repeatability value ( $\pm 1.93$ ), r., rounded off to a whole number.

8.3.4 The QC sample shall be an ASTM round robin reformulated gasoline sample that contains sulfur at the appropriate level. When a new ASTM sample is to be used as a QC sample, the determination of whether the QC is within an appropriate range shall be based on whether the sample is within the ASTM round robin robust standard deviation or on a 10% deviation from the ASTM robust mean, whichever is greater. Once 20 valid QC analyses have been performed, the control sample analysis shall revert to section 8.3.2.

#### 8.4 REPLICATE ANALYSIS

8.4.1 A replicate analysis is performed after every ten samples and/or at the end of the sample set when at least 6 samples are run. For a single injection screening analyses a replicate run is performed at least once per day and after every 20-25 samples. It is recommended to run the replicate immediately after the original sample. A quality control chart is maintained for the replicates.

8.4.2 If the difference is greater than the repeatability specified in the ASTM method D5453-93,  $r = 0.1867(\text{Avg})^{0.63}$ , the sample should be repeated. If the closest two values of the three analyses still show a difference greater than the repeatability, all samples for the day from this instrument must be reanalyzed. Steps should be taken to determine the cause of the problem.

#### 8.5 LIMIT OF DETECTION

8.5.1 The limit of detection (LOD) is determined annually from multipoint calibration data. The low level calibration curve is used to determine a linear regression.

$$\text{LOD} = \frac{|b| + (3.3)(s)}{m}$$

where:

b = intercept

m = slope

s = standard deviation of the lowest concentration

8.5.2 The L.O.D. must be at least 1.0 ppm.

## 9 Safety Precautions

- 9.1 Prepare fuel samples and standards under a fume hood.
- 9.2 Wear safety glasses and disposable gloves when handling fuels or solvents.
- 9.3 Fuels and solvents may be harmful or fatal if ingested or inhaled.
- 9.4 All fuels and solvents should be treated as extremely flammable and explosive.
- 9.5 The operator must exercise caution around the sulfur analyzer. Exposure to excessive quantities of ultraviolet light is harmful. The operator must avoid exposing any part of their person, their eyes, not only to direct UV light but also to secondary or scattered radiation that is present.

## 10 References

- 10.1 ASTM D 5453-93, "Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Oils by Ultraviolet Fluorescence", Annual Book of ASTM Standards, Vol 05.03

## 11 Revision History

- 11.1 Revision No. 2      Effective date: 03/13/03

Significant changes:

- 4.3 -      Extend a sulfur concentration range of Quality Control Sample.
- 5.2.1 -    Increase a sample injection size for the range of 100-1000 ppm sulfur.
- 6.3, 6.4 - Modify the Instrument Operating Conditions.
- 6.5 -      Modify the Autosampler Operating Conditions.

- 11.2 Revision No.3      Effective date: 11/01/03

Significant changes:

- 8.3.1-    Adjust the control sample runs for a single injection screening analyses.
- 8.4.1-1   Adjust the replicate runs for a single injection screening analyses.

- 11.3 Revision No.3.1    Effective date: 10/01/2005

Significant changes: 8.3.4 – Modification of Control Sample Analysis

- 11.5 Revision No. 4      Effective date: 4/01/2006

Significant changes: Addition of Mitsubishi TS-100V to SOP:

3.1, 3.6 – 3.8 – Addition of Mitsubishi TS-100V to Instruments and Apparatus

5.2.2 – Addition of suggested calibration curves for Mitsubishi TS-100V

6.4.2 – Addition of Mitsubishi TS-100V Instrument Operating Conditions

6.5.2 – Addition of Mitsubishi TS-100V Autosampler Operating Conditions

11.6 Revision No. 4.1 Effective date: 1/01/2007

Significant changes: 8.2.1- Calibration changed to only as needed

8.4.1 – Modification of replicate analysis to require replicates to be run only when at least 6 samples are being analyzed.

11.7 Revision No 4.2 Effective Date: 9/9/2010

Significant changes: 8.4.2- Modified Replicate QC requirements to use repeatability instead of 50% reproducibility.