

California Environmental Protection Agency



Air Resources Board

PROCEDURE FOR THE DETERMINATION OF SULFUR IN FUELS BY U.V. FLUORESCENCE

SOP MV-FUEL-123
Revision No.5.1
Effective Date: July 1, 2014

FUEL ANALYSIS & METHODS EVALUATION SECTION
CHEMICAL ANALYSIS & EMISSIONS RESEARCH BRANCH
EMISSIONS COMPLIANCE, AUTOMOTIVE REGULATIONS & SCIENCE DIVISION

HAAGEN-SMIT LABORATORY
9528 TELSTAR AVENUE
EL MONTE, CA 91731

This page is intentionally left blank.

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 (mm²/S) at room temperature. This procedure is applicable to naphthas, distillates, motor fuels and oils containing 1.0 to 8000 mg/kg (referred to as ppm by this SOP) 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 9000, 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 is 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 has side arms for the introduction of oxygen and carrier gas.

- 3.3 Flow controllers -- the instrument is equipped with flow controllers capable of maintaining a constant supply of oxygen and carrier gas.
- 3.4 Drier tube -- the instrument is 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 UV 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 9000 or equivalent -- the microlitre syringe that is used in the autosampler should be capable of accurately delivering 10 to 20 μL quantities. The needle should be 50 mm \pm 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 10 to 20 μL quantities. The needle should be 50 mm \pm 5 mm long.
- 3.7 Direct Injection -- Robotic Liquid Autosampler, Antek Model 748, 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 or higher.
- 4.2 Calibration Standards -- suggested compounds are Dibenzothiophene, FW184.26 or Thionaphthene (Benzothiophene), FW 134.20.
- 4.3 Quality Control Sample — ASTM Crosscheck 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 or higher.

5 Calibration Standards Preparation

5.1 SULFUR STOCK SOLUTION, 1000 ppm range ($\pm 10\%$)

5.1.1 Prepare a stock solution gravimetrically by accurately weighing 0.4000 ± 0.0400 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. Record sulfur concentration of the stock solution with four significant figures.

5.1.2 The stock solution should be tightly capped and refrigerated. It is checked against a freshly opened NIST SRM sample at least once a year (see Quality Control Section 8.3). If the results indicate that the stock solution could be problematic, a new stock solution should be made.

5.2 CALIBRATION RANGE FOR ANTEK 9000, MITSUBISHI TS-100V, OR EQUIVALENT

5.2.1. 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 QC sample (see Quality Control Section 8.3). Because almost all of the samples we receive nowadays are below 50 ppm, a single calibration curve is suggested, as is listed in the following table. Note that except for the blank which is isooctane, the actual concentration of each level should be no more than $\pm 10\%$ away from the listed value. Samples of higher concentrations can be diluted and measured against this curve, as long as the lowered precision due to dilution is still deemed acceptable. Otherwise, a calibration curve of lower sensitivity would be used.

Sulfur, ppm
0.00 (blank)
1.00
2.50
5.00
10.00
25.00
50.00
Injection size 10-20 microlitres

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 9000 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

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 9000

Syringe drive: 1 μ L /s
Sample injection volume varies with the sulfur concentration of the sample:
suggested sample volume ~15 μ L

6.5.2 Typical Autosampler Operating Conditions—Mitsubishi TS-100V

Syringe drive: 1.2 μ L /s
Sample injection volume is 20 μ L .

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. For the suggested calibration curve, if the blank is greater than 1 ppm, the contamination sources must be corrected and the blank must be repeated 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^2 of least square fit must be 0.98 or greater. If it falls below 0.98, the instrument should be checked for possible malfunction or required maintenance; the calibration standards should be re-prepared if necessary; and the calibration should be rerun..

8.3 CONTROL SAMPLE ANALYSIS

- 8.3.1 For analyses that require three injections per sample, the control sample is analyzed at the beginning of the sample set, after at most every ten samples, and at the end of the sample set. For screening purposes with single injection analyses the control sample is analyzed at the beginning of the sample set, after at most every 25 samples and at the end of the sample set. A control chart is maintained for the control sample.
- 8.3.2 A control sample is out-of-control when the measured value of sulfur exceeds the control limit. The QC sample must be rerun if it is out-of-control. If it continues to be out-of-control, discard results of all samples after the last passing QC; determine the cause of the problem and pass the QC before analyzing any samples again on the instrument.

- 8.3.3 The QC sample shall be an ASTM round robin reformulated gasoline sample that contains sulfur at an appropriate level. The ASTM round robin robust mean is adopted as the average value of the QC sample. The control limit is set at within two times the ASTM repeatability, 2r.
- 8.3.4 A NIST SRM sample, currently SRM2723a, shall be analyzed on a quarterly basis. The control limit is two times the ASTM repeatability, 2r ($r = 0.1867 \times 11.0^{0.63} = 0.85$ for SRM2723a, so the measured value must be within 11.0 ± 1.7 ppm).

8.4 REPLICATE ANALYSIS

- 8.4.1 Replicate analyses must be performed at least once each of the days when at least one sample is analyzed. For three-injection analyses, a replicate analysis is performed after at most every ten samples and/or at the end of the sample set when at least six samples are run. For single-injection screening, or if three-injection and single-injection samples are mixed in the same QC bracket, a replicate run is performed after at most every 25 injections. 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 after the last passing replicate 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. A 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 LOD must be 1.0 ppm or lower.

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.
8.4.1-1.1 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.

11.8 Revision No. 5 Effective date: 1/01/2014

Significant changes: 1.3 – Noted mg/kg is referred to as ppm by this SOP
5.1, 5.2 – Defined 10% range for the calibration standards; use one unified recommended calibration curve from 1 to 50 ppm for both the Antek and the Mitsubishi
6.4 – Simplified Typical Instrument Operating Conditions
8.2.1 – Changed from $r > 0.99$ to $r^2 > 0.98$
8.3.3 – Changed the control criteria for the NIST SRM standard to ASTM's method reproducibility
8.3.4 – Adopted ASTM robust mean and robust standard deviation as the mean and standard deviation for the QC
8.4 – Clarified languages of requirements for replicate analysis
Various locations: – Updated the model number of our Antek and its autosampler

Formatting changes are not listed.

11.9 Revision No. 5.1 Effective date: 7/01/2014

Significant changes: 5.1 – now 5.1.1 is for preparation of the stock solution only; added 5.1.2 for storage and the annual checkup.
8.3 – set the QC control limits to be two times the ASTM repeatability ($2r$), and eliminate the warning limits. Set NIST SRM control limits also to $2r$; clarified that results of all samples that followed the last passing QC must be discarded.
8.4.2 – changed from “all samples for the day from this instrument must be reanalyzed” to “all samples after the last passing replicate must be reanalyzed”.