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

SOP MV-FUELS-123
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Fuels Analysis and Methods Evaluation Section
Chemical Analysis and Emissions Research Branch
Mobile Source Laboratory Division

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1 Introduction

1.1 This procedure describes the determination of sulfur content in gasoline and diesel fuels by ultraviolet fluorescence.

1.2 The California Air Resources Board (CARB) utilizes this procedure to analyze sulfur content of gasoline and diesel to determine compliance with the sulfur specifications of California Reformulated Gasoline (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/S) at room temperature. This procedure is applicable to naphthas, distillates, motor fuels and oils containing 1.0 to 8000 mg/kg (ppm) total sulfur.

1.4 This procedure is based on American Society for Testing Materials (ASTM) D 5453-93.

2 Method

2.1 Liquid fuel samples are injected into a high temperature combustion tube where the sulfur is oxidized to sulfur dioxide (SO_2) in an oxygen rich atmosphere. Water produced during the sample combustion is removed and the sample combustion gases are then exposed to ultraviolet (UV) light.

2.2 The SO_2 absorbs the energy from the UV 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 – The analytical instrument should be equipped with an electric furnace capable of maintaining a set temperature of 1100 degrees Celsius, which is sufficient to pyrolyze all of the sample and oxidize sulfur to SO_2.

3.2 Combustion tube – The analytical instrument should 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 analytical instrument should be equipped with flow controllers capable of maintaining a constant supply of oxygen and carrier gas.

3.4   Drier tube – The analytical instrument should 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   UV Fluorescence detector – The analytical instrument should be equipped with a qualitative and quantitative detector capable of measuring light emitted from the fluorescence of sulfur dioxide by UV light.

3.6   Microlitre syringe – A liquid autosampler should be equipped with a microliter syringe capable of delivering 5 to 20 microliter (µl) quantity of sample. The needle should be 50 mm ± 5 mm long.

3.7   Direct Injection – The liquid autosampler should be capable of automated injecting a set quantity of sample at a uniform speed of 0.2 to 1.0 µl/s with the capacity of 50 or more positions.

3.8   Data system -- The analytical instrument should include a data system which provide autosampler control, sample identification, calculation, 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 either one of the following:
            (Note that a correction for chemical impurity can be required.)

            Dibenzothiophene, FW184.26, 17.399% (m/m) S; or
            Butyl Sylfide, FW 146.29, 21.92% (m/m) S; or
            Thionaphthene (Benzothiophene), FW 134.20, 23.90% (m/m) S.

4.3   Quality Control Sample — ASTM Crosscheck gasoline samples with a sulfur concentration between 3 - 30 µg/kg (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 and Preparation of Standards

5.1   SULFUR STOCK SOLUTION, 1000 mg/kg (ppm) range (±10%)

     5.1.1   Prepare a stock solution gravimetrically by weighing either one of the following compounds into a tared 100 mL volumetric flask:

          Dibenzothiophene – 0.5748 g; or
          Butyl Sylfide – 0.4652 g; or
          Thionaphthene – 0.4184 g.

          Dissolve the compound 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 National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) sample at least once a year (see Quality Control Section 8.3.4). If the results indicate that the stock solution be problematic, a new stock solution should be made.

5.2   CALIBRATION RANGE

     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 of three injections for each standard. This curve should be linear and the instrument performance must be checked with a NIST SRM and the QC sample (see Quality Control Section 8.3).

5.2.2 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:

Sulfur, mg/kg (ppm)
0.00 (blank)
1.00
2.50
5.00
10.00
25.00
50.00
Injection size 10 - 20 µL

Note that except for the blank, which is isooctane, the actual concentration of each level should be no more than ± 10% away from the listed value.

5.2.3 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 required.

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 equipped with a microliter syringe. The syringe must be flushed several times with the sample prior to analysis. All samples are run in triplicate to obtain the average value.

6.4   TYPICAL INSTRUMENT OPERATING CONDITIONS

6.4.1 The instrument manufacturer usually suggests optimum operating conditions for their sulfur analyzer. Follow the manufacture's suggestion.

6.4.2   Typical Sulfur Analyzer Operating Conditions:

Furnace Temperature:	1100 ± 25 C
Furnace Oxygen Flowmeter Setting (3.8 – 4.1):	450 – 500 ml/min
Inlet Oxygen Flowmeter Setting (0.4 – 0.8):	10 – 30 ml/min
Inlet Carrier Flowmeter Setting (3.4 – 3.6):	130 – 160 ml/min

6.4.3   Typical Autosampler Operating Conditions:

Direct Injection Syringe Drive:	1 µL /s
Injection Volume:	10 – 20 µL

6.4.4   Sample injection volume should be the same as the injecting volume of the calibration standards.

7   Calculation of Results

7.1   The sulfur concentrations, given in mg/kg (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 sulfur concentration in mg/kg (ppm), is shown below:

Sulfur, mg/kg (ppm) = A x B / C

where: 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 system should be checked for possible

saturation or soot accumulation. The contamination sources must be corrected and the blank must be repeated before analyzing samples.

8.2   CALIBRATION STANDARDS ANALYSIS

8.2.1   Calibration standards and working standards are prepared as needed. All standards should be stored in the refrigerator. It is estimated that the standards will maintain a shelf life of about one year. This depends on how often the standards are uncapped.

8.2.2   The multi-level calibration analysis is performed as needed. The calibration should be linear, and the R^2 of least square fit be 0.995 or greater. If the R^2 falls below 0.995, the instrument should be checked for possible malfunction and may require repair and/or maintenance. The calibration standards should be re-prepared if necessary. The instrument should be recalibrated.

8.3   QUALITY CONTROL (QC) SAMPLE ANALYSIS

8.3.1   For analyses that require three injections per sample, the QC sample is analyzed at the beginning of the sample set, after every ten samples, and at the end of the sample set. For screening purposes with single injection analyses the QC sample is analyzed at the beginning of the sample set, after every 25 samples and at the end of the sample set. A control chart is maintained for the QC sample.

8.3.2   A QC 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, the analyst must discard results of all samples after the last passing QC, determine and correct the cause of the problem, and make sure the QC is within the limit of control before analyzing any samples again on the analyzer.

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 immediately after the multi-level calibration and on a quarterly basis. The control limit is two times the ASTM repeatability, 2r (r = 0.1867 x $11.0^{0.63}$ = 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 on the days
when at least one sample is analyzed. For three-injection analyses, a
replicate analysis is performed after 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 every 25
injections. It is recommended to run the replicate immediately after the
original sample. A 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 = $0.1867(Avg)^{0.63}$, the replicate analysis 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 and
correct 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.

LOD = (|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   The preparation of fuel samples and standards must be done in 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 body, 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: 03/13/2003

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: 11/01/2003

Significant changes:

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

11.4   Revision No. 4   Effective Date: 04/01/2006

Significant changes:

Addition of Mitsubishi TS-100V to the standard operating procedure (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

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

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.

Revision No 4.2   Effective Date: 09/9/2010

Significant changes:

8.4.2 – Modified Replicate QC requirements to use repeatability instead of 50% reproducibility.

11.5   Revision No. 5   Effective Date: 01/01/2014

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.

11.6   Revision No. 5.1   Effective Date: 07/01/2014

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".

11.7   Version 6.0   Effective Date: May 1, 2017

Significant Changes:

Removed of all the trade names of commercial products throughout the procedure.

11.8   Version 6.1   Effective Date: December 1, 2019

SOP format updated for ADA compliance