

California Environmental Protection Agency
 **Air Resources Board**

**PROCEDURE FOR THE DETERMINATION OF SULFUR CONTENT IN
PETROLEUM PRODUCTS BY X-RAY SPECTROMETRY**

SOP NO. MLD 130

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SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

1 Introduction

- 1.1 The Air Resources Board (ARB) uses this Standard Operating Procedure (SOP) to determine sulfur (S), and to screen for lead (Pb), manganese (Mn), and phosphorus (P) in gasoline and diesel fuels.
- 1.2 This SOP is based on ASTM D2622-94 "ASTM Standard Test Method for Sulfur in Petroleum Products by X-ray Spectrometry", for the determination of sulfur content (concentration > 10 ppm) in gasoline and diesel fuel.
- 1.3 This SOP also incorporates modifications for the determination of low sulfur content (10-100 ppm sulfur) in gasoline specified in Title 13, California Code of Regulations, Section 2263 (b).
- 1.4 This SOP covers sulfur concentration from 10 ppm to 5 mass%.

2 Method Summary

- 2.1 An X-ray spectrometer is used to measure S and screen for Pb, Mn, and P contents in gasoline and diesel fuels. The sample is placed in the X-ray beam, and the intensity of the elements listed in the Table 1 are measured. The intensities of S, Mn and P are corrected from the sulfur background intensity. The resultant net intensity is then compared to previously prepared calibration curves to obtain the concentration of these elements.
- 2.2 A calibration is performed for the routine operation of the XRF to screen for sulfur in gasoline and diesel covering the sulfur concentration range of 10-500 ppm. This calibration method was developed to cover the sulfur concentration range encountered in both gasoline and diesel and is used to screen for lead, manganese, and phosphorus in fuels.
- 2.3 Following the calibration standard preparation procedures outlined in California Code of Regulations, Title 13, Section 2263 (b), a second calibration is performed using thiophene and 2-methylthiophene with a toluene and iso-octane mixture for the low concentration sulfur gasoline covering the 10-100 ppm sulfur concentration range.

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

Table 1 Element Measured by XRF

Element	Line	Wave Length (Å)
Sulfur	K _α	5.373
Sulfur Background	K _α	5.437
Manganese	K _α	2.103
Lead	L _β	0.982
Lead background	L _β	1.194
Bismuth	L _α	1.144
Phosphorous	K _α	6.155

- 2.4 A third calibration, based on ASTM D 2622-94, is performed using di-n-butyl sulfur in white oil for high concentration sulfur in gasoline and in diesel fuels.

3 Instrumentation and Apparatus

- 3.1 Oxford X-ray Spectrograph -- equipped for X-ray detection of elements listed in Table 1.
- 3.1.1 Optical path of helium -- for liquid samples such as gasoline and diesel fuels.
- 3.1.2 Detector for long wavelength X-rays -- flow type gas filled proportional counters which are fitted with a continuous flow of argon/methane for S, S background, P, and Mn. Sealed type proportional counters for Pb, Pb background, and Bi.
- 3.1.3 Analyzing Crystal -- set at a particular angle to the beam, X-rays of a certain wavelength will be diffracted into an X-ray detector.
- 3.1.4 X-ray Tube -- tube with anode supplies and a filament, requiring 40 kV and 5 mA for normal operation.
- 3.2 Class A volumetric flasks (100 mL and 250 mL).
- 3.3 Analytical balance with readability of 0.1 mg.

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

4 Reagents and Materials

- 4.1 Detector Gas (P10) -- 90 % argon and 10% methane, inlet pressure ~ 7 psi, flow rate 20-30 mL/min.
- 4.2 Purge Gas -- helium gas with at least 99.5 % purity, inlet pressure ~ 6-8 psi.
- 4.3 Restandardization materials -- available from Oxford, are lithium tetraborate fusion beads made by fusing lithium borate mixed with oxides of the element of interest at very high temperature. These materials are in a glass matrix which reduces any matrix effect.
- 4.4 Thiophene -- at least 99% purity.
- 4.5 2-Methylthiophene -- at least 98 % purity.
- 4.6 Di-n-Butyl Sulfide -- a high-purity grade standard with a certified analysis.
- 4.6 Iso-octane -- should be a sulfur-free (analyzed by ASTM D5453 to confirm low sulfur concentration) solvent.
- 4.7 Toluene -- should be a sulfur-free (analyzed by ASTM D5453 to confirm low sulfur concentration) solvent.
- 4.8 White Oil -- Containing less than 5 mg/L sulfur.
- 4.9 Pb, P, Mn Primary Standard -- 5000 ppm single-element standard in white oil (obtained from Chemplex).

5 Preparation of Calibration Standards

5.1 Preparation of Stock Standard (~10,000 ppm S)

- 5.1.1 Weigh standard material thiophene (~0.7290 g) and 2-methylthiophene (~0.7031g) separately onto a tared 100 mL volumetric flask and record the individual mass to 0.1 mg.
- 5.1.2 Add mixed solvent containing 25% toluene and 75% iso-octane (by volume) into the flask to a net weight of approximately 50 g and record the weight.
- 5.1.3 The actual sulfur concentration can be calculated as follows;

Sulfur from thiophene (g) =

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

weight of thiophene x 32.06 x purity / 84.14
Sulfur from 2-methylthiophene (g) =
weight of 2-methylthiophene x 32.06 x purity / 98.07
Sulfur concentration of Stock Standard (w/w) =
(sulfur thiophene + sulfur from 2-methylthiophene) / net weight of the
Stock Standard
Multiply the sulfur concentration by 1000 to convert to mg/g.

5.2 Preparation of Calibration Standard for low concentration sulfur in gasoline

- 5.2.1 Pipet 2.5 mL of the Stock standard to 250 mL flask and dilute with the mixed solvent to the mark. The "Diluted Standard" contains approximately 100 mg/kg sulfur.
- 5.2.2 Pipet 5, 10, 20, 30, 50, 75 mL of the Diluted Standard into 100 mL flasks, and dilute with the mixed solvent to the mark to prepare 5, 10, 20, 30, 50, and 75 ppm calibration standards respectively.
- 5.2.3 The actual concentration of the calibration standards should be determined from the stock standard. The standards with sulfur concentration range from 5 to 100 ppm and the mixed solvent are to be used for calibrating the instrument.

5.3 Preparation of calibration standard sulfur in diesel fuel

- 5.3.1 Prepare calibration standards by weight dilution of the certified di-n-butyl sulfide with white oil. The following concentrations listed in Table 2 are recommended.

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

Table 2 Sulfur Standard

Sulfur Concentration, ppm	Sulfur Concentration, ppm	Sulfur Concentration, ppm
50	1000	10000
100	2500	20000
250	5000	30000
500	-	40000
750	-	50000

5.4 Preparation of calibration standards for sulfur, lead, manganese, & phosphorus

5.4.1 Follow procedure 5.1 to prepare 10,000 ppm sulfur stock solution.

5.4.2 To prepare approximately 2500 ppm of diluted standard for sulfur, pipet 25 mL of the sulfur stock solution. To prepare diluted standard for Pb, Mn, and P, weigh 4 mL of each Pb, Mn, and P from the 5000 ppm standards (available from Chemplex) to a 100 mL flask and dilute with the mixed solvent to the mark.

5.4.3 The concentration (g/gal) of each diluted Pb, Mn, and P calibration can be calculated as follows:

ie., Pb (g/gal) =

Weight of 4 mL (5000 ppm) Pb standard (g) x Pb standard concentration (ppm)/
(100 mL x 1L/ 1000 mL x 1 gal/ 3.7853 L)

5.4.4 Pipet 0.4, 1, 1.6, 2.5, 5, 10, 15, 20 mL of the diluted standard into a 100 mL flask, respectively, and dilute with the mixed solvent to the mark to prepare 0.8, 2.3, 2.5, 5, 10, 20, 30, and 40 ppm Pb, Mn, and P calibration standards. The range for the sulfur calibration standards will be 10-500 ppm S.

5.4.5 The actual concentration of the calibration standards should be determined from the stock standard for sulfur. The Pb, Mn, and P standards are prepared gravimetrically.

5.5 Calibration standards, if commercially available, can also be used to calibrate the instrument.

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

6 Procedure

6.1 Instrument Calibration Procedure

The calibrations are performed as needed. The calibration method procedure is processed in two stages. The first step is to acquire the calibration data and the second step is to process the calibration data.

6.2 Establish calibration curve data by measuring the net intensities of each element in the calibration standards.

6.3 Once the parameters are set in the acquisition of the calibration data, the data can be processed for regression for the determination of each element.

6.4 Plot the intensity, in terms of net counts per second, against the concentration.

6.5 The set-up samples are selected for restandardization. The lower SUS should have an intensity similar to the low end calibration standard. The higher SUS should have an intensity similar to the high end calibration standard.

6.6 Measure the set-up samples to establish the counting rate of this standard by measuring its intensity at frequent intervals. This will be used to validate the calibration curve and to correct for the daily instrument sensitivity changes.

6.7 The analysis methods should be generated to use for the routine analysis. Three methods are generated for various purposes:

- 1) The first method is for screening of sulfur, phosphorus, manganese, and lead.
- 2) The second method is for the analysis of low concentration sulfur in gasoline.
- 3) The third method is for the analysis of diesel fuels.

6.8 Analysis Procedure

The P10 flow should be set @ 25 cc/min. During long periods of non-use the flow may be reduced to 10 cc/min. The XRF system should be turned on at least 4 hours before the start of analysis to allow the system to warm-up.

6.9 Fuel samples are collected in bottles or metal canisters and delivered to the laboratory.

6.10 To perform the routine analysis, select the method to be used and wait for the QX system to switch from vacuum to helium mode.

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

- 6.11 The setup samples (SUSs) are used to restandardize the XRF instrument. Before the SUSs are run, the polycarbonate film is changed on the secondary window sleeve. Once the SUSs are run the QX will prompt the system to the analyze mode.
- 6.12 Enter the sample label at the computer prompt for each sample and insert the sample in the sample port.
- 6.13 The computer software will give an update on the screen of the measured concentration for the sample as the run progresses. Acceptance of the result will store the result in a computer file and will simultaneously print the result.
- 6.14 If a gasoline sample is found to be a possible violation, the sample will need to be run in duplicate on the method that is used specifically for gasoline samples with the calibration range of 10-100 ppm sulfur.
- 6.15 If a diesel sample is found to be a possible violation, the sample will need to be run in duplicate on the method that is specific for diesel samples.
- 6.16 At the end of the analyses, the QX is to be set to the standby condition. If the QX is being operated on generators, the system should be turned off at the end of the analysis.

7 Safety Precautions

- 7.1 Standard laboratory safety procedures and equipment, for example, safety glasses and gloves, should be used in performing this SOP.
- 7.2 All standards and sample preparation should be done in the fume hood.
- 7.3 All the calibration standards, solvents, samples are known to be toxic and some are carcinogenic.
- 7.4 Exposure to excess quantities of X-ray radiation is injurious to health. Avoid exposure not only to primary X- rays but also to secondary or scattered radiation that may be present. The X-ray spectrometer should be operated in accordance with recommendations governing the use of ionizing radiation.

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

8 Calculations

8.1 The sulfur concentrations are calculated by the data system using external multipoint calibration standards. The net count rate after correction for the sensitivity correction factor and the background count rate at 5.190A measured from the sample is applied to the appropriate calibration curve.

8.2 If the sample is diluted, calculate the concentration of sulfur as follows:

$$S, \text{ ppm} = S(\text{dil.}) \times [(W_s + W_d) / W_s]$$

where:

S(dil) = ppm sulfur in diluted blend

W_s = mass of sample, g

W_d = mass of diluent, g

8.3 When analyzing M-85 or M-100 fuels, adjust the result as follows:

$$S \text{ (in M-85), ppm} = S, \text{ ppm} / 0.59$$

$$S \text{ (in M-100), ppm} = S, \text{ ppm} / 0.55$$

9 Quality Control

9.1 Blank Analysis

9.1.1 A sample of iso-octane is used as a blank and is analyzed daily to check the analytical system for contamination. If the blank analysis shows a concentration greater than 10 ppm, the blank should be repeated. If the blank still shows a sulfur content greater than 10 ppm, the contamination source should be corrected before analyzing samples.

9.2 Calibrations Standard Analysis

9.2.1 Calibration standards are prepared as needed. The system needs to be recalibrated after a major repair on the instrument (such as X-ray tube replacement), or after a failure to meet requirements on quality control sample and instrument sensitivity.

9.3 Control Sample Analysis

9.3.1 The control sample is analyzed at the beginning of the sample set, after every 15-20 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 for two standard deviations ($\pm 2\sigma$). The upper and lower control limits are at three standard deviations ($\pm 3\sigma$).

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

9.3.2 A control sample is out-of-control when the measured value of sulfur exceeds the 3σ limit or when two successive measurements of the control sample exceed the 2σ limit. If the Q.C. sample continues to be out-of-control, the calibration and Q.C. sample must be rerun. If the control sample continues to be out-of-control, determine the cause of the problem before analyzing any samples.

9.4 Sensitivity Analysis

9.4.1 The restandardization results for daily restandardization should be within 10% of the results determined at the time of calibration. For the blank, which has a low count rate a $\pm 20\%$ window is allowed. If the set-up sample (SUS) is not within the range of control, reanalyze the SUS. The instrument should be recalibrated or checked for possible causes of the instability of the instrument.

9.5 Replicate Analysis

9.5.1 A replicate analysis is performed after every ten samples and at the end of the sample set. It is recommended that the replicate is run immediately after the original analysis. A quality control chart is maintained for the replicates.

9.5.2 If the percent difference between the two analyses is greater than the limit listed in Table 3, reanalyze the sample. If the closest two values of the three analyses still show a percent difference greater than the limit, all the samples analyzed after the previous replicate must be reanalyzed. Steps should be taken to determine the cause of the problem.

Table 3 Replicate Control Limit

Average of Replicate (ppm)	Control Limit (%)
10-30	30
30 - 50	15
50 - 149	10
>150	5

SOP No. MLD 130 - Procedure for the Determination of Sulfur in Fuels by X-ray Fluorescence

9.6 Limit of Detection

- 9.6.1 The limit of detection (LOD) is determined when instrument is calibrated. The LOD can be calculated from multi point calibration data. The low level calibration curve is used to determine a linear regression.

$$\text{LOD} = [|b| + 3.3 * \sigma] / m$$

where:

|b| = absolute of intercept

m = slope

σ = standard deviation of the lowest concentration

- 9.6.2 The LOD for sulfur determination must not exceed 10 ppm.

10 Interferences and Limitations

- 10.1 Methanol containing fuels M-85 and M-100 may be analyzed with an accompanying loss of sensitivity and precision due to the high oxygen content of these fuels. Correction factors must be applied to obtain valid results (See section 8.3).

11 References

- 11.1 ASTM D 2622-94, "Standard Test Method for Sulfur in Petroleum Products by X-ray Spectrometry", Annual book of ASTM Standards, Vol 05.03.
- 11.2 California Code of Regulations, Title 13, Section 2263 (b) test Methods, Table 1, footnote c and d.