United States
Environmental Protection Agency
Office of Transportation and Air Quality
National Vehicle and Fuel Emissions Laboratory
2565 Plymouth Road
Ann Arbor, MI 48105

Method for Analysis of Sulfur in Petroleum Fuels by X-ray Fluorescence

This procedure is written for the Environmental Protection Agency, National Vehicle and Fuel Emissions Laboratory (NVFEL) internal use. The use of specific brand names by NVFEL in this procedure are for reference only and are not an endorsement of those products. This document may be used for guidance by other laboratories.

NVFEL Reference Number

127

Implementation Approval

Original Procedure Authorized by EPCN # 319 on 05-03-2002

Revision Description

Table of Contents

1.0 Scope 3
2.0 Summary of Method 3
3.0 Significance 3
4.0 Applicable Documents 3
5.0 Definitions 3
6.0 Interference's and/or Limitations 4
7.0 Safety 4
8.0 Apparatus 5
9.0 Reagents and Materials 6
10.0 Sampling 8
11.0 Calibration 9
12.0 Analytical Procedure 14
13.0 Calculations and Reporting 18
14.0 Performance Criteria 19

Attachments

Attachment A, Instrument-Generated Sample Analysis Report (Diesel Fuel) 21
Attachment B, Instrument-Generated Sample Analysis Report (Gasoline) 22

1.0 Scope

This specific procedure has been written for samples in the range of 0.001%-0.50% sulfur in diesel fuel, or 10 ppm-1500 ppm in gasoline, both on a weight basis (w/w). The working range of this procedure may be extended up to 5.0% by calibrating with additional, higher-concentration standards.

2.0 Summary of Method

Diesel fuel samples of at least 20 ml, containing 0.001%-0.50% (w/w) sulfur, or gasoline samples of at least 20 ml, containing 10 ppm-1500 ppm (w/w) sulfur are analyzed directly by x-ray fluorescence spectrometry.

Samples containing higher levels of sulfur may also be diluted for analysis.

3.0 Significance

This test procedure covers the determination of total sulfur in diesel fuel or gasoline. It is the Laboratory Operation Division (LOD) version of American Society for Testing and Materials (ASTM) Standard D 2622, Standard Test Method for Sulfur in Petroleum Products by X-Ray Spectrometry, for performing the sulfur analysis required in petroleum products.

4.0 Applicable Documents

4.1 ASTM Standard D 2622, “Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-Ray Fluorescence Spectrometry”

4.2 ASTM Standard Practice E-177-86, “Standard Practice for the Use of the Terms Precision and Bias in ASTM Methods”

4.3 40 CFR 80.2, as published in the Federal Register, Tuesday, August 21, 1990, Vol. 55, No. 162, p34137

40 CFR 80.46, as published in the Federal Register, Wednesday, February 16, 1994, Vol 59, No. 32, p7826

4.4 Rigaku Instrument Manual, Rigaku Software Manual

4.5 Testing Services Group (TSG) Chemical Hygiene Plan, Appropriate Material Safety Data Sheets, and the TSG Chemical Inventory

5.0 Definitions

N/A

6.0 Interference's and/or Limitations

6.1 Matrix of standards needs to be as close as reasonably possible the matrix of samples.

6.2 M85 and M100 fuels have high oxygen content leading to significant absorption of sulfur K and radiation.

6.3 Standards produced from simulated gasoline can produce results that are more accurate than results obtained using white oil standards.

6.4 For other interfering species and their tolerance levels, refer to ASTM D2622, Table 3.

7.0 Safety

7.1 Diesel fuel is flammable under some conditions. As a precaution, exposure to sparks and open flames should be minimized.

Gasoline is highly flammable. Exposure to sparks or flames must be eliminated.

7.2 Exposure to excessive quantities of x-ray radiation is injurious to health. X rays are ionizing radiation which, in large doses, will cause radiation sickness and death. The x-ray spectrometer should be operated in accordance with regulations and recommendations governing the use of ionizing radiation.

The operator must avoid exposing any part of his or her person, not only to primary x rays but also to secondary or scattered radiation that might be present. No maintenance is to be performed on the instrument when the x-ray source is on.

7.3 The x-ray unit must not be operated if any interlocks are open or if any radiation seals are suspected of being faulty.

A radiation badge must be worn when operating the x-ray unit.

7.4 Prior to performing the analysis, the analyst must be familiar with the Material Safety Data Sheets (MSDS) for materials used in this analysis.

8.0 Apparatus

8.1 Rigaku 3271 X-Ray Spectrometer, equipped for soft x-ray detection in the 5.37 Å range

For optimum sensitivity to sulfur, the instrument should be equipped with the following:

8.1.1 Optical path of helium

8.1.2 Pulse-height analyzer or other means of energy discrimination

8.1.3 Detector designed for the detection of long wave-length x rays

8.1.4 Analyzing crystal, suitable for the dispersion of sulfur K_α x rays within the angular range of the spectrometer employed

For this analysis, a germanium crystal will be used.

8.1.5 X-ray tube, capable of exciting sulfur K_α radiation

For this analysis, a tube with a rhodium anode will be used.

8.2 Laboratory Supplies

8.2.1 Sample cups with plastic snap rings

8.2.2 Polypropylene film (0.2-mil)

8.2.3 5-mL automatic pipette and disposable pipette tips

8.2.4 1-, 5-, and 50-mL syringes and suitable needles

8.3 Analytical balance with an NIST-traceable calibration

200-g capacity, 0.1-mg resolution, or equivalent

8.4 Transfer documents for each sample.

9.0 Reagents and Materials

9.1 Di-n-Butyl Sulfide (DNBS)

This is a high-purity standard material rated 96% or higher purity, confirmed to be at least 99% pure.

A DNBS sample with certified analysis designed specifically for this analysis is also acceptable as a source of DNBS. If this material is used for calibration, the certified sulfur concentration should be used to calculate the weight fraction sulfur in the prepared standards.

Note: Although 96% is the highest guaranteed purity available commercially for DNBS, in practice the actual purity is much higher. Before beginning calibration with a new bottle of DNBS, it should be analyzed by gas chromatography (GC) using a flame ionization detector (FID) to establish its purity. A general analysis with a slow ramp is preferred, with an integration format of normalized area percent. With this method, a result indicating more than 2% area impurities would indicate a suspect standard material. Using this setup for GC, a 2% area for impurities would roughly correspond to better than 99% purity of the DNBS.

9.2 Blank Stock

A blank stock is used as the diluent for all calibration standards and sample dilutions. The blank stocks are prepared as outlined below. The weight tolerances are ±5% for each compound. These materials should have a minimum purity of 98%, and must each contain less than 1 ppm total sulfur.

9.2.1 Diesel Blank Stock

This mixture is designed to simulate the boiling point range and density of diesel fuel, and is prepared by combining the following substances:

15 g	tert-butylbenzene
15 g	decane
15 g	dodecane
15 g	tetradecane
15 g	hexadecane
15 g	tetralin
5 g	octadecane
5 g	naphthalene

9.2.2 Gasoline Blank Stock

A similar blank stock is prepared for analyses of gasoline. This mixture is prepared by combining:

5 g n-pentane
10 g n-hexane
10 g cyclo-hexane
15 g n-heptane
20 g 2,2,4 trimethyl-pentane
10 g n-octane
5 g n-decane
15 g toluene
10 g mixed xylenes

9.3 Calibration Standards

Calibration standards are made from sulfur (DNBS) diluted in the appropriate blank stock in various concentrations. Once the calibration is completed, these standards may be used as check standards for subsequent analysis sessions.

9.4 Check Standard

The check standard is prepared in the same manner as the calibration standards, except that it need not be prepared in a sealed container. This standard is used only to verify calibration, not for the initial calibration itself. This standard is normally prepared in a larger quantity, e.g., 100 mL.

9.5 Control Fluid

The control fluid for each diesel analysis is the current diesel certification fuel, typically containing 0.03 to 0.05 weight percent sulfur. Similarly, the control fluid for gasoline analyses is test fuel, which is based on the sulfur results of the samples coming in, typically 20 ppm to 300 ppm sulfur. The control fluids are used for routine quality control measurements. The control limits for these materials are established by multiple sample analyses of the fuel.

9.6 Drift-Correction Fluid

The drift-correction fluid for the diesel analysis is a stable diesel fuel containing 0.15% to 0.20% (w/w) sulfur. This fluid is typically prepared by the addition of 13 ml of di-n-butyl-disulfide (practical purity) to 1 gallon of certification diesel fuel: however, any diesel fuel available in moderate quantity with sulfur concentration near the suggested range is adequate.

The drift correction fluid for the gasoline analysis is made in similar fashion to that for gasoline, in that it is a diesel fuel that either lies, or has been sulfur fortified to lie in the upper range of the current calibration curve. Diesel fuels are used as the base for this gasoline analysis because they are more resistant to weathering, and thus more stable in the long term. The sulfur concentration for this fluid is typically between 1000 and 1500 ppm.

9.7 National Institute of Standards and Technology (NIST) Standard (for diesel fuel analysis)

This standard is made from sulfur in fuel oil (or kerosene), of suitable concentration for this analysis, and is principally used to ensure the accuracy of instrument calibration.

The NIST-determined concentration of this standard is used as the basis for quality control limits placed on the NIST standard analysis.

9.8 Helium, typically 99.99% purity, for the atmosphere of the analysis chamber

9.9 P-10 Gas

This is a mixture of 10% methane in argon blended specifically as a scintillation gas for x-ray detectors.

10. Sampling

10.1 Ensure that the samples do not contain sediment or separated phases prior to filling the sample cups.

If samples do contain sediments, they must be thoroughly mixed prior to analysis.

Multi-phase samples should have each phase analyzed separately if possible.

In both cases, the situation should be noted and initialed by the analyst on the instrument-generated sample analysis report (Attachments A and B.)

10.2 If the samples are for enforcement/litigation purposes, ensure that the sample bottles are tightly closed and labeled properly.

10.3 If a sample is to be split and redirected to another laboratory or other location outside the present facility, a copy of the traveler document will accompany this sample. It must be filled out to include all pertinent information and sent with the newly sealed sample. The original COC form is to remain in the Chem Lab files.

10.4 Ensure that there are adequate quantities of helium and P-10 gas to complete the test sequence. At least 200 PSI in all cylinders is prudent.

10.5 For normal operation in the analysis of sulfur in either fuel, the following settings and flow rates should be verified:

10.5.1 Ensure that a helium atmosphere is selected and that helium is flowing to the instrument at the specified flow rate of 1.0 L/minute.

10.5.2 Ensure that P-10 gas is flowing to the instrument at the specified flow rate of 50 mL/minute.

10.5.3 Ensure that the x-ray unit is on and operating at 30 kV and 80 mA.

10.5.4 Ensure that no warning messages are appearing on the instrument display.

11. Calibration

11.1 Determine if instrument calibration is required. The following are guidelines for this determination:

Calibration will be necessary for a new instrument, or one not previously used for these analyses. Calibration will be required if current calibrations are lost or damaged. Calibration may be required after reconfiguration or repair of an existing instrument.

A new calibration may be necessary if the current check standard, control fluid, or NIST or independent standard results fall outside acceptance criteria.

If calibration is not required, proceed to Section 12 of this procedure.

If calibration is required, complete the remaining steps in Section 11.

Consult the laboratory manager if there are any questions regarding the need for a new instrument calibration.

11.2 Prepare the calibration standards. Standards are created by diluting pure DNBS with the appropriate blank stock. Standards are analyzed along with the blank stock used in making up standards to produce a linear calibration. When this line is saved, an NIST standard is analyzed to verify the accuracy of the calibration. If this analysis falls within control limits, it is followed by a control-fluid sample, and the two initial instrument drift-correction-fluid samples.

Standards should span the analytical range of interest. For typical enforcement testing of on-highway diesel fuel, five to eight standards should be spaced across the range of 0.002 to 0.150 weight percent.

For typical enforcement analyses of gasoline, five to eight standards should be spaced across 25 to 1500 ppm.

These values are reached by varying the mass of DNBS added to each standard vial. All dilutions are accomplished gravimetrically in septum-capped vials by the following procedure:

11.2.1 Tare an empty vial, together with its septum and cap. Insert this weight into the bottle mass line of the spreadsheet calculator.

11.2.2 Introduce to the vial approximately 80 grams (approximately 100 ml) of the appropriate blank stock in such a manner as to avoid any spills, particularly those that may contact the outside of the container. This is typically accomplished with a large syringe and needle.

11.2.3 Cap, and precisely weigh the vial and its contents. Insert this weight into the bottle plus blank stock line in the spreadsheet calculator.

11.2.4 Add the sulfur source (typically DNBS) to the vial using a 1 ml syringe and needle. Each drop of DNBS will yield approximately a 0.01 increase in percent sulfur in the standard.

11.2.5 Precisely weigh the vial and its contents. Record this weight in the spreadsheet cell that represents the total weight of the vial with all contents.

11.2.6 The concentration of sulfur in ppm (w/w) and weight per-cent is calculated by the spreadsheet calculator. These results appear in red as the bottom two lines in the calculation section of the sheet.

For diesel fuel the weight percent sulfur is calculated as follows:

(mass DNBS)(weight fraction S)/(mass blank stock + mass DNBS) *100%

For gasoline the concentration of sulfur in ppm w/w is calculated as follows:

(mass DNBS)(weight fraction sulfur)/(mass blank stock + mass DNBS)*1,000,000ppm

In each equation, weight fraction S is the weight fraction of sulfur in the DNBS compound. If a DNBS compound of at least 99% purity is used, the weight fraction sulfur may be taken as 0.2191.

If a compound of less than 99% purity is used, the certified analysis provided by the chemical manufacturer must be used to calculate the true weight fraction sulfur.

Example: (0.2430g)(0.2191)/(39.1482g + 0.2430g)*100% = 0.1351 wt %

11.2.7 Label the vial with the calculated sulfur weight percent for diesel, or ppm w/w sulfur for gasoline, the date, and the analyst's initials.

11.2.8 Shake the vial to mix the contents.

11.3 Transfer the standards, control fluid, drift-correction fluid, blank-stock solution, or samples to sample cups as follows:

11.3.1 Label the appropriate sample cups on the flat, outer section of the cup with the standard concentration (or sample number) using a permanent marker.

11.3.2 Since automatic pipettes and disposable tips are typically used for routine analysis, no cleaning procedure is required for their use with samples.

If glass pipettes or syringes are used, the cleaning procedure is to rinse the pipette or syringe with a suitable low-volatility pure hydrocarbon (e.g., dodecane for diesel and pentane for gasoline) and once with the sample that is to be transferred.

11.3.3 Beginning with the blank stock, and continuing with the lowest standard through to the highest, precisely pipette or syringe 5.0 ±0.1 ml of standard (or sample) into a clean sample cup.

When the automatic pipette is used, it must be kept in a vertical position during the transfer. During aspiration of sample, the end of the disposable tip should remain immersed below the liquid surface.

11.3.4 Place a polypropylene film over the sample cup. Secure the film in place with a plastic snap ring.

11.3.5 Make sure that there are no wrinkles in the film. If there are wrinkles, discard the sample and transfer a new aliquot to a fresh sample cup.

11.3.6 Invert the filled sample cup, and ventilate the cup by piercing a small hole in the top with a push pin or similar instrument.

11.3.7 Carefully place the sample cup film down on a piece of absorbent paper for several seconds to determine whether or not the film window is leaking.

If the sample container is leaking, discard the sample and prepare a new one.

11.4 Load the autosampler and check the instrument setup for the calibration run.

11.4.1 One sample cup of each calibration standard and the blank stock solution must be included in the set of calibration standards inserted into the autosampler.

11.4.2 The nominal concentration of each standard and its position in the autosampler must be input to the instrument controller, together with the code describing them as standards and a "7" in the "RPT" column for gasoline analyses. Diesel analyses use a “1” in the RPT column.

Codes are readily available on the help screen in the analysis window of the software. Refer to the Rigaku Software Manual for additional details.

11.4.3 Each of these sample cups will be analyzed once, and only once, yielding a calibration intensity value.

11.4.4 Ensure that the instrument computer system date and time are correct.

11.5 Initiate the calibration analysis and perform the linear regression calculations according to the Rigaku Software Manual. For this calculation, a linear calibration fit should be used.

11.6 Following the completion of a calibration analysis and regression calculation, the calibration plot should be viewed to verify the linearity of the calibration. Any of the points that visually differ from linearity should be investigated.

Reanalyze standard samples or calculate the concentration of the calibration standards, based on the calibration line, and compare these values to the nominal concentration of the standards. The regression-determined concentration should be within the larger of ±5% or ±15 ppm of the nominal concentration. Investigate any points that do not meet this criterion. Failure to meet this criterion may mean that there was a problem in the preparation of one or more standards.

11.7 If the linearity of the calibration appears satisfactory, transfer an aliquot of an NIST standard to a sample cup per step 11.3, load it into the autosampler, and initiate analysis using the new calibration. The results from this analysis should be within ±3% or ±10 ppm (whichever is greater) of the named concentration of the standard**.**

If the results are not within these limits, the calibration is considered suspect, and the cause of the discrepancy must be resolved before the calibration can be accepted or samples analyzed.

11.8 If the result of the NIST sample analysis appears satisfactory, transfer an aliquot of the control fluid to a sample cup per Step 11.3, load it into the autosampler, and initiate analysis using the new calibration. The results from this analysis should be within the control fluid control limits.

11.9 If the data from both the NIST and the control fluid analysis appear satisfactory, the calibration must be saved within the data acquisition system.

11.9.1 The naming convention for saving a diesel calibration is the prefix SUL plus a sequential number. For example, the second calibration completed is named SUL2. The naming convention for gasoline calibrations is a prefix GA followed by a sequential number. (Options for this naming convention are restricted by the software limit of four characters.)

11.9.2 After saving the calibration, a plot of the calibration should be printed, along with a list of the calibration parameters. These printouts, together with the instrument-generated sample analysis reports for the control fluid and NIST standard, and a printed copy of the standard preparation table from the spreadsheet calculator that is signed and dates by the analyst are saved in the designated original results storage cabinet.

11.10 Following a successful save of the new calibration, transfer two aliquots of the drift correction fluid to sample cups per Step 11.3, load them into the autosampler, and initiate analysis. The first analysis is to be performed in an initial condition, and the second as an alpha standard. Refer to the Rigaku Software Manual for details of this setup. The result of this analysis will be an alpha-update value.

11.11 Check the alpha-update value. For this setup of the drift correction, the result would be suspect if this alpha value obtained were outside the range of 0.9 to 1.1. Values obtained on subsequent days may vary much more widely, but would be suspect if outside the range of 0.3 to 2.0.

12.0 Analytical Procedure

12.1 Place the sample in a sample cup using the technique described in Step 11.3.

12.2 Inspect each sample cup to verify that it is not leaking and to make sure that it is properly labeled.

12.3 For the first analysis performed each day, arrange the standards and test samples in the autosampler as described in the table below, and then input the sample and standard IDs to the Rigaku data system.

Blank
Control fluid
Check standard
Up to 12 individual samples
Duplicate
Control fluid
Up to 12 individual samples
Duplicate
Control fluid
Sample
etc.
Control fluid

12.4 At least one check standard is analyzed each day testing is performed. The analytical session is always nominally bracketed with analyses of the control fluid.

Additionally, a control fluid sample and a duplicate are to be run at least once every 12 samples.

If the analysis results of the initial preliminary sample set containing the blank, control fluid, and check standard analysis on a given day are not within the control limits, a drift correction should be run. The analysis sequence in this case becomes:

Blank
Control fluid
Check standard (Problem Discovered)
Drift Correction Fluid
Blank
Control fluid
Check standard
Up to 12 individual samples
Duplicate
Control fluid
Up to 12 individual samples
Duplicate
Control fluid
Sample
etc.
Control fluid

If the set of quality control samples following the drift correction are within the control limits, the session may be continued by analyzing the subsequent samples. If these limits are not met, the process must be halted and the cause investigated.

12.5 Set up the autosampler to perform one analysis per sample cup. For this procedure, all analyses are to be run only once per sample cup. If a sample must be reanalyzed, prepare a new sample cup.

12.6 Check the instrument notebook to verify that the active calibration is the most recent calibration for this working range. Ensure that the instrument time and date are set correctly and initiate the autosampler per the manufacturer's instructions to begin the analysis.

12.7 Check the alpha value of the drift correction fluid. Alpha values following drift correction must be within the range of 0.3 to 2.0, except immediately following calibration, when they must be within the range of 0.9 to 1.1

If the drift correction fluid results are not within these tolerances, investigate potential instrument problems. If the abnormal drift correction results can not be resolved, see the laboratory manager.

12.8 As each reading is being taken, the computer calculates and updates the database with a new standard deviation, average, 95% confidence level value, upper control limit, and lower control limit. The 95% confidence level is calculated as 1.96 times the standard deviation. The upper control limit is the average plus the 95% confidence level value. The lower control limit is the average minus the 95% confidence level value.

Confirm that the sulfur concentration of the control fluid is within the upper and lower control limits. Investigate any out-of-control conditions and take immediate corrective action. Record the action and its implications on the paper output.
If out-of-control occurrences cannot be reconciled, consult the laboratory manager.

12.9 Confirm that the check standard result is within 5% or 15 ppm, (whichever is greater) of the calculated nominal concentration of that standard.

If the check standard is not within the designated limits, analyze a NIST or independent standard. If this standard is within the greater of 3% or 10 ppm of its named value, discard the check standard and continue with the analysis. If the NIST or independent standard is out of specification, check the integrity of the standard materials, investigate for possible instrument malfunction, or consider recalibration of the instrument. Once the issue has been resolved, restart the analysis.

12.10 Confirm that the sulfur concentration of each subsequent control fluid analysis is within the control-fluid control limits.

If any control-fluid analysis indicates an out-of-control condition, halt the analysis and either perform a drift correction, or investigate for other possible sample or instrument problems. Record the action and its implications on the instrument-generated sample analysis report for the control fluid.

12.11 Repeat the control fluid analysis. If the post-correction analysis of the control fluid is acceptable, repeat the analysis of all samples run since the previous successful control fluid analysis. Discard the original results from these samples.

If out-of-control occurrences cannot be reconciled, consult the laboratory manager.

12.12 Check that the range of the duplicates is within the control limits. For this procedure, these control limits are defined as ±5% or 15 ppm, whichever is greater.

If the duplicate range is out of control, halt the analytical session and take immediate corrective action to resolve the abnormal analysis variability. Record the action and its implications on the instrument-generated sample analysis report. If out-of-control occurrences cannot be reconciled, consult the laboratory manager.

12.13 When the problem is resolved, repeat the duplicate analysis and ensure that the results are within the control limits before proceeding with the analysis.

If the investigation indicates that an out-of-control occurrence may have affected previously analyzed samples, repeat the samples analyzed since the last acceptable duplicate analysis. Discard the original results from these samples.

12.14 When the analysis batch has been completed, review the instrument-generated sample analysis reports to verify that all concentration values are within the working range of the current calibration.

If the analysis indicates that the sulfur concentration in any of the samples is greater than the calibration range, the original result must be supplemented with the analysis of an aliquot of the sample that has been diluted to fall within the calibration range. This is accomplished by w/w dilution with blank stock in a manner similar to that by which standards are prepared, except that the use of sealed vials is not necessary. (Refer to Step 7.4.)

12.15 When a sample must be diluted, the blank stock used for the dilution must also be analyzed with the diluted sample. For diesel analyses, the reported concentration of this blank stock must be below 0.002 weight percent sulfur for the diluted sample analysis to be valid. For gasoline analyses, the reported concentration of the blank stock must be below 10 ppm w/w sulfur.

If the analysis indicates a higher concentration of sulfur in the blank stock, discard the results from the diluted sample. A new batch of blank stock must be prepared and analyzed. If this blank stock yields a result of less than 0.002 weight percent sulfur for diesel analyses, or 10 ppm w/w sulfur for gasoline analyses, dilute again and reanalyze the out-of-range sample(s).

If the dilute analysis is satisfactory, calculate the concentration of sulfur in the undiluted sample as follows:

$$S = S_b * [(W_s + W_o)/ W_s]$$

where: S_b = concentration of sulfur in diluted sample
W_s = weight of the original sample in grams
W_o = weight of the diluent in grams

This calculation must be shown on the instrument-generated sample analysis report for the diluted sample.

12.16 Check that the sample numbers on the instrument-generated sample analysis report match those on the sample cups in the autosampler. If this number is missing on the sample analysis report, it should be hand entered and initialed by the operator.

12.17 Discard the contents of used sample cups in the appropriate container.

13.0 Calculations and Reporting

13.1 The identity of the sample cups and their autosampler position must be input to the data system before the start of each run. A report is generated by the Rigaku software for each analysis. The operator identifies each analysis and verifies that the printout contains the sample identification number written on the vial. If this number is missing on the printout, it should be hand entered and initialed by the operator.

13.2 If all acceptance criteria are met, the operator signs and dates the instrument-generated sample analysis report.

13.3 Sample results are transferred to the EPA-NVFEL Form. This form will eventually be filed in the Chemistry Laboratory secure data storage area when all required analyses are completed.

13.4 The spectrometer calculates the concentration of each sample based on the active calibration curve.

13.5 The analyst reviews the results of the control fluid, check standard (or NIST standard), drift-correction fluid, and range of duplicate analyses for conformance to acceptance criteria. The expected values for these standards must be written or printed on the Sample Analysis Report and each standard analysis value must be marked with an "OK" if it meets the acceptance limits.

13.6 If a calibration was performed, the analyst reviews the linearity of the curve and reanalyzes or calculates the concentration of the calibration standards, based on the calibration line. The resulting values are compared to the nominal concentration of the standards.

The results of the analyses of any calibration standards, NIST standards, control fluid, and blanks are reviewed for conformance to acceptance criteria.

13.7 If a sample dilution was required, the analyst checks the concentration of sulfur in the blank-stock solution. If that analysis conforms to the acceptance criteria, the concentration of sulfur in the undiluted sample is calculated as follows:

$$S = S_b * [(W_s + W_o)/ W_s]$$

where: S_b = concentration of sulfur in diluted sample
W_s = weight of the original sample in grams
W_o = weight of the diluent in grams

This calculation must be shown on the instrument-generated sample analysis report for the diluted sample.

13.8 The results are checked to ensure they have the proper sample ID number. If an error was made during log-in and was not corrected, then the results printout should show the correction. The analyst must initial and date any changes made to the instrument-generated sample analysis report

13.9 If all acceptance criteria are met, the operator signs the instrument-generated sample analysis report. This form is filed in the Chemistry Laboratory secure data storage area when all required analyses are completed.

13.10 The output from the analysis is an instrument-generated sample analysis report showing the various counting rates and the calculated concentration of each sample. This output is filed in the Chemistry Laboratory secure data storage area.

13.11 All results from samples diluted for analytical purposes must be clearly marked on the analysis report, describing the extent of dilution and the calculated concentration of the undiluted sample.

13.12 Sample results are transferred to the EPA-NVFEL Form. This form will eventually be filed in the Chemistry Laboratory secure data storage area when all required analyses are completed.

13.13 If a new calibration curve is generated, a plot of the calibration and a list of the calibration parameters along with the calibration analysis results of the control fluid, drift correction fluid, and NIST standard are filed in the results cabinet (the Chemistry Laboratory secure data storage area).

14.0 Performance Criteria

14.1 All points covered in Steps 13.10 through 13.13 must be correct before the data for each run can be accepted.

14.2 All analyses of the control fluid bracketing the analytical session must be compared to the control-fluid control limits. These comparisons must indicate that all samples were analyzed under conditions of known, stable accuracy.

14.3 Duplicate analyses must be compared to the applicable quality limits. These comparisons must indicate that all samples were analyzed under conditions of known, stable precision.

14.4 Check standards must be within the greater of ±5% or 15 ppm of their nominal value. NIST standards must be within ±3% or 10 ppm of their nominal value, whichever is greater.

14.5 Duplicates must be within ±5% or 15 ppm, whichever is greater.

14.6 The instrument-generated sample analysis report must be signed by the analyst before the results can be filed.

14.7 Alpha values following drift correction must be within the range of 0.3 to 2.0, except immediately following calibration, when they must be within the range of 0.9 to 1.1.

14.8 When calibrations are performed, a plot of calibration standard concentration versus instrument response must not indicate any visible departure from linearity. The concentration of each standard as calculated from the regression line should be within the greater of ±5% of point or ±15 ppm of the nominal concentration of the standard.

14.9 If samples are diluted, analysis of the blank stock must indicate that the concentration of sulfur in the blank stock is less than 0.002% (w/w) for diesel or 10 ppm w/w for gasoline.

14.10 Control fluid analysis before and after every 12 sample analyses to assess instrument drift.

Drift correction performed as necessary.

14.11 Analysis of external reference standards (NIST standards) to assure accuracy of calibration.

14.12 Analysis of laboratory duplicate samples to assure consistent precision.

14.13 Analysis of calibration or check standards to verify instrument accuracy.

14.14 Only one analysis is performed on each sample cup to minimize sample degradation.

14.15 Chain-of-custody provisions are followed to ensure sample integrity (for enforcement/litigation samples).

Attachment A
Instrument-Generated Sample Analysis Report
(Diesel Fuel)

```
      P#   JOB  CODE    SAMPLE  NAME       LOT #              94-04-28 14:06
 1-2  1:GRP SUL2 CERT DIESEL

                        S -KA
                        S

Peak  Int.   kcps   4.5160

BG    Int.   kcps   0.2778

Raw   Int.   kcps   4.2382

Net   Int.   kcps   1.5411

X-ray Int.   kcps   1.5411

Results     S

          0.0335
```

Attachment B

Instrument-Generated Sample Analysis Report (Gasoline)

```
 P#   JOB  CODE    SAMPLE  NAME        LOT #                    94-09-26 11:20
 1-1 1:GRP GAS1 CERT GASOLINE

Meas. Int.   kcps   S -KA    S -KA    S -KA
                    S 20     S 20     S 20
                    Peak     BG01     BG02
    Repeat   =  1  1.5050   0.4360   0.1703
                2  1.5154   0.4100   0.1708
                3  1.5297   0.4473   0.1643
                4  1.4974   0.4245   0.1678
                5  1.5189   0.4283   0.1678
                6  1.4745   0.4172   0.1641
                7  1.5018   0.4152   0.1678

    Average        1.5061   0.4255   0.1676
    Maximum        1.5297   0.4473   0.1708
    Minimum        1.4745   0.4100   0.1641
    Range          0.0552   0.0373   0.0067
    Std. Dev.      0.01780  0.01297  0.00261
    C.V. %           1.18     3.05     1.56
```

```
 P#   JOB  CODE    SAMPLE  NAME        LOT #                    94-09-26 11:20
 1-1 1:GRP GAS1 CERT GASOLINE

                     S -KA
                     S

Peak  Int.   kcps    1.5061

BG    Int.   kcps    0.2368

Raw   Int.   kcps    1.2693

Net   Int.   kcps    1.2691

Uncorrected Conc.      101.

Results    S

             101.
```