ALUMINUM COMPANY OF AMERICA

SAMPLING METHOD FOR THE DETERMINATION OF HYDROCARBONS EMISSIONS FROM COLD ROLLING MILLS - METHOD 1470-94 - REQUIRES METHOD 1471-94

1. Scope

1.1 This method applies to the sampling and analysis of exhaust from aluminum rolling mills that use lubricants amenable to analysis by gas chromatography, i.e., most mineral based oils.

1.2 The limit of detection is 0.05 mg/dscm based on a sampled air volume of 30 scf (840 Liters).

1.3 This method does not provide a simultaneous measure of gas moisture content for gas flow rate determination.

2. Summary of Method

2.1 Particulate and gaseous hydrocarbons are withdrawn isokinetically from the stack. The particulate or "mist" fraction of the emissions is removed from the gas stream by a stainless steel probe and glass cyclone operated at ambient temperature. The volatile or "vapor" fraction is removed by a charcoal sampling tube. A pitot tube and Method 5 metering console are used to determine gas flow rate, measure gas sample volume and maintain isokinetic sampling rate. Hydrocarbons in each fraction of the sample are analyzed by gas chromatography with flame ionization detection (GC/FID).

3. Apparatus

3.1 Sampling train. Figures 1 and 2 are schematics of the sampling train and charcoal tube.

3.1.1 Nozzles - stainless steel gooseneck type 0.1875 in. (4.7625 mm) through 0.5000 in. (12.7000 mm) diameter openings for use with heated probe.

3.1.2 Probe - Assembly of stainless steel probe, S-type pitot tube, probe thermocouple and stack temperature thermocouple.

3.1.3 Cyclone - Glass cyclone with collection flask.

3.1.4 Glass Adapters - Glass U-tube and ground-glass ball fitting with 0.375-inch O.D. glass tubing. (28/12 ball joint to 3/8-inch hose adapter).

3.1.5 Charcoal Sampling Tube - High density polyethylene tube, 8-inch long (20 cm)by 0.75-inch O.D. (1.9 cm), packed with activated charcoal.

3.1.6 Sampling Lines - Consisting of vacuuum tubing for sample line, 2 pitot tube lines and a thermocouple extension wire.

3.1.9 Meter console - Equipped with dry gas meter, dual inclined manometer, calibrated flow control orifice.

3.2 Sample recovery

3.2.1 Wash bottles - Teflon 500 mL

3.2.2 Sample storage bottles - glass with Teflon lined caps, 125 mL

4. Reagents and Materials

4.1 Sampling

4.1.1 Activated Charcoal - Fisher brand 6-14 mesh (No. 05-685 B)

4.1.2 Glass wool - borosilicate or quartz

4.1.3 Sampling tubes - High density polyethylene tubes, 8-inch long (20 cm)by 0.75-inch O.D. (1.9 cm), with end cap adapters to 0.375-inch. See Figure 2 for details.[Bell Art 8-inch drying tube No. 19962-000 - (Fisher No. 09-242C). SKC, INC., 3/8-inch end caps, No. 226-03-054].

4.1.4 Tygon - Tubing to connecting glass adapter to inlet of charcoal sampling tube, 3/8-inch I.D.

4.2 Sample recovery

4.2.1 Methylene chloride, HPLC grade

5. Procedure

5.1 Sampling

5.1.1 Charcoal tube preparation - Pack charcoal sampling tubes as illustrated in Figure 2, with charcoal divided into two sections separated by glass wool. The primary absorbing section should contain approximately 8 grams of charcoal and the backup section should contain approximately 2 grams. End cap adapters should be joined to polyethylene tubing with black electrical tape or equivalent to provide a leak-free seal. Charcoal tubes should be stored in a cool, vapor free environment and remain sealed prior to use in sampling.

5.1.1 Pretest preparation - All sampling equipment must be calibrated to meet EPA specifications (Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, J. J. Rom, U.S. EPA Report No. PB-209022 (NTIS), 1972 March).

5.1.2 Preliminary determinations - EPA Method 1 is used to select the sampling port location and the number of sampling points. EPA Method 2 is used to determine the stack pressure, temperature and the range of velocity heads for selecting nozzle size to maintain isokinetic sampling rates. Minimum sampling time is 1-hour for both inlets and outlets to emission control units and outlets of uncontrolled sources.

5.1.3 Preparation of sampling train - Pre-clean sample probe and cyclone by thoroughly rinsing with methylene chloride. Assemble the sample train as illustrated in Figure 1.

5.1.4 Leak check procedures - Leak check the assembled train by plugging the nozzle and pulling 15 in. Hg (380 mm Hg) vacuum. A leakage rate greater than 0.02 CFM (0.00057 m^3/min) is unacceptable. This check must be completed prior to and after each test run.

5.1.5 Train operation - Before starting a test run, record the initial dry gas meter reading. After starting the test, record the dry gas meter reading at the end of each time increment. Also record the vacuum, stack temperature, velocity head, pressure differential, gas sample temperature at dry gas meter (inlet and outlet). During the test, maintain an isokinetic sampling rate of 100% ±10%. Traverse the stack as required in EPA Method 1. At the end of the test, turn off the pump, remove nozzle and probe from the stack, record final dry gas meter reading.

5.2 Sample recovery

After the probe is removed from the stack and allowed to cool, wipe off all external particulate in the area near the nozzle tip. Leak check the sample train. Cap the nozzle, disconnect the probe at the cyclone inlet and cap both sections. Disconnect the charcoal tube and cap both ends. Transfer the probe, cyclone and charcoal tube to the clean-up area.

5.2.1 Nozzle and probe - Use methylene chloride to clean and rinse the internal area of the probe and nozzle into a labeled glass bottle with a Teflon lined cap. Rinse the nozzle and probe a minimum of three times.

5.2.2 Cyclone and connecting glassware - Use methylene chloride to clean and rinse the internal area of the cyclone, collection flask, U-tube and glass ball fitting into the same glass bottle used to collect the probe rinse. Rinse each section of glassware a minimum of three times. Seal the bottle with the Teflon lined cap.

5.2.3 Label the charcoal sampling tube and secure the end caps with masking tape. Store the tubes in a cool, vapor free environment until analysis in the laboratory.

5.3 Sample analysis

Analyze the samples for total mg of hydrocarbons according to Method 1471-94. By this method, the methylene chloride solution is concentrated by evaporation under an air stream and the charcoal tubes are desorbed using carbon disulfide. Both extracts are then analyzed by capillary gas chromatography with flame ionization detection.

6. Calibration

All calibrations must be completed in accordance with those outlined in EPA Reference Method 5 and Appendix A of 40 CFR Part 60. A laboratory log containing the following calibrations must be maintained.

6.1 Probe-nozzle
6.2 Pitot tube
6.3 Metering system (console)
6.4 Temperature gauges
6.5 Leak check of console
6.6 Barometer

7. Calculations

7.1 Summary of test data

7.1.1 Description of terms

V_s = Average stack or duct velocity, m/sec (ft/sec)

B_{wo} = Water vapor in gas stream proportion by volume (Determined separately by EPA Method 4)

C_p = Pitot tube coefficient, dimensionless

K_p = Pitot tube constant

= 34.97 m/sec Bbc[(f((g/g-mole)(mm Hg),(°K)(mm H_2O)))$^{1/2}$ (metric)

= 85.49 ft/sec Bbc[(f(lb/lb-mole (in. Hg),(°R) (in. H_2O)))$^{1/2}$ (English)

M_d = Molecular weigh of stack gas, dry basis, g/g-mole (lb/lb-mole)

M_s = Molecular weight of stack gas, wet basis, (lb/lb-mole) or M_d (1-B_{wo})

+ 18 B_{wo}

P_s = Absolute stack gas pressure, mm Hg (in. Hg) or $P_b \pm P_{static}$

P_b = Barometric pressure (atmospheric pressure), mm Hg (in. Hg)

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg)

P_m = Absolute pressure at the meter = P_b + DH/13.6

Q_{std} = Dry volumetric stack gas flow rate corrected to standard conditions, dscm/hr (dscf/hr)

t_m = Average dry gas meter temperature °C (°F)

T_m = Absolute dry gas meter temperature (°C + 273 = °K, °F + 460 = °R)

t_s = Stack temperature, °C (°F)

T_s = Absolute stack temperature (°C + 273 = °K, °F + 460 = °R)

T_{std} = Standard absolute temperature, 293°K (528°R)

A_s = Cross-sectional area of stack, m^2 (ft^2)

DP = Velocity head of stack gas, mm H_2O (in. H_2O)

3600 = Conversion factor, sec/hr

18 = Molecular weight of water, g/g-mole (lb/lb-mole)

V_m = Dry gas meter volume at meter conditions dcm (dcf)

$(V_m)_{std}$ = Dry gas meter volume corrected to standard conditions, dscm (dscf)

K_2 = 0.3858°K/mm Hg (metric)
17.64°R/in. Hg (English)

Y = Dry gas meter calibration factor

A_n = Area of sampling nozzle, m^2 (ft^2)

q = Total sampling time, minutes

C_{mist} = Concentration of particulate hydrocarbons or mist fraction, mg/scm (gr/scf)

C_{vapor} = Concentration of volatile hydrocarbons or vapor fraction, mg/scm (gr/scf)

C_{thc} = Concentration of total hydrocarbon, mg/scm (gr/scf)

W_{phc} = Weight of particulate hydrocarbons, mg

W_{vhc} = Weight of volatile hydrocarbons, mg

DH = Average pressure drop across orifice, mm H_2O (in. H_2O)

E_{mist} = Emissions of particulate hydrocarbons or mist fraction, kg/hr (lb/hr)

E_{vapor} = Emissions of volatile hydrocarbons or vapor fraction, kg/hr (lb/hr)

E_{thc} = Emissions of total hydrocarbons, kg/hr (lb/hr)

7.2 Dry volumetric gas flow rate corrected to standard conditions, dscm/hr (dscf/hr)

7.2.1 $V_s = K_p C_p\ (r(DP_{avg}))\ r(f(T_s, P_s M_s))$

7.2.2 $Q_{std} = 3600\ (1\text{-}B_{wo})\ V_s A_s\ \mathbf{Bbc}((f(T_{std}, T_{s(avg)}))\ \mathbf{Bbc}((f(P_s, P_{std}))$

7.2.3 $(V_m)_{std} = K_2 V_m Y\ f(P_b + (DH/13.6), T_m)$

7.3 Concentrations

7.3.1 Particulate hydrocarbon $C_{mist} = f(W_{mist}, (V_m)_{std})$

7.3.2 Volatile hydrocarbon $C_{vapor} = f(W_{vapor}, (V_m)_{std})$

7.3.3 Total hydrocarbons $C_{thc} = C_{mist} + C_{vapor}$

7.4 Emission rates

7.4.1 Particulate hydrocarbons

E_{mist}, kg/hr = $Q_{std}\ C_{mist} \times 1.0 \times 10^{-6}$

1.0×10^{-6} = conversion factor for mg to kg

E_{mist}, lb/hr = $Q_{std}\ C_{mist} \times 2.205 \times 10^{-6}$

2.205×10^{-6} = conversion factor for mg to lb

7.4.2 Volatile Hydrocarbons

E_{vapor}, kg/hr = $Q_{std}\ C_{vapor} \times 1.0 \times 10^{-6}$

E_{vapor}, lb/hr = $Q_{std}\ C_{vapor} \times 2.205 \times 10^{-6}$

7.4.3 Total Hydrocarbons

$E_{thc}, = E_{mist} + E_{vapor}$

7.5 Isokinetic variation

$I = f(100\ T_s\ [K_3 V_{lc} + (V_m/T_m)\ (P_b + DH/13.6)], 60\ q\ V_s\ P_s\ A_n)$

where:

K_3 = 0.003454 mm Hg - m^3/mL - °K for metric units
= 0.002669 in. Hg - ft^3/mL - °R for English units

Subscripts:

b = barometric
d = dry gas basis
m = at the meter
n = at nozzle
s = at the stack
scf = standard cubic feet
scm = standard cubic meter
std = standard conditions, 20°C, 760 mm Hg (68°F, 29.92 in. Hg)
mist = mist fraction or participate hydrocarbons
vapor= vapor fraction or volatile hydrocarbons
thc = total hydrocarbon

Figure 1
Sampling Train

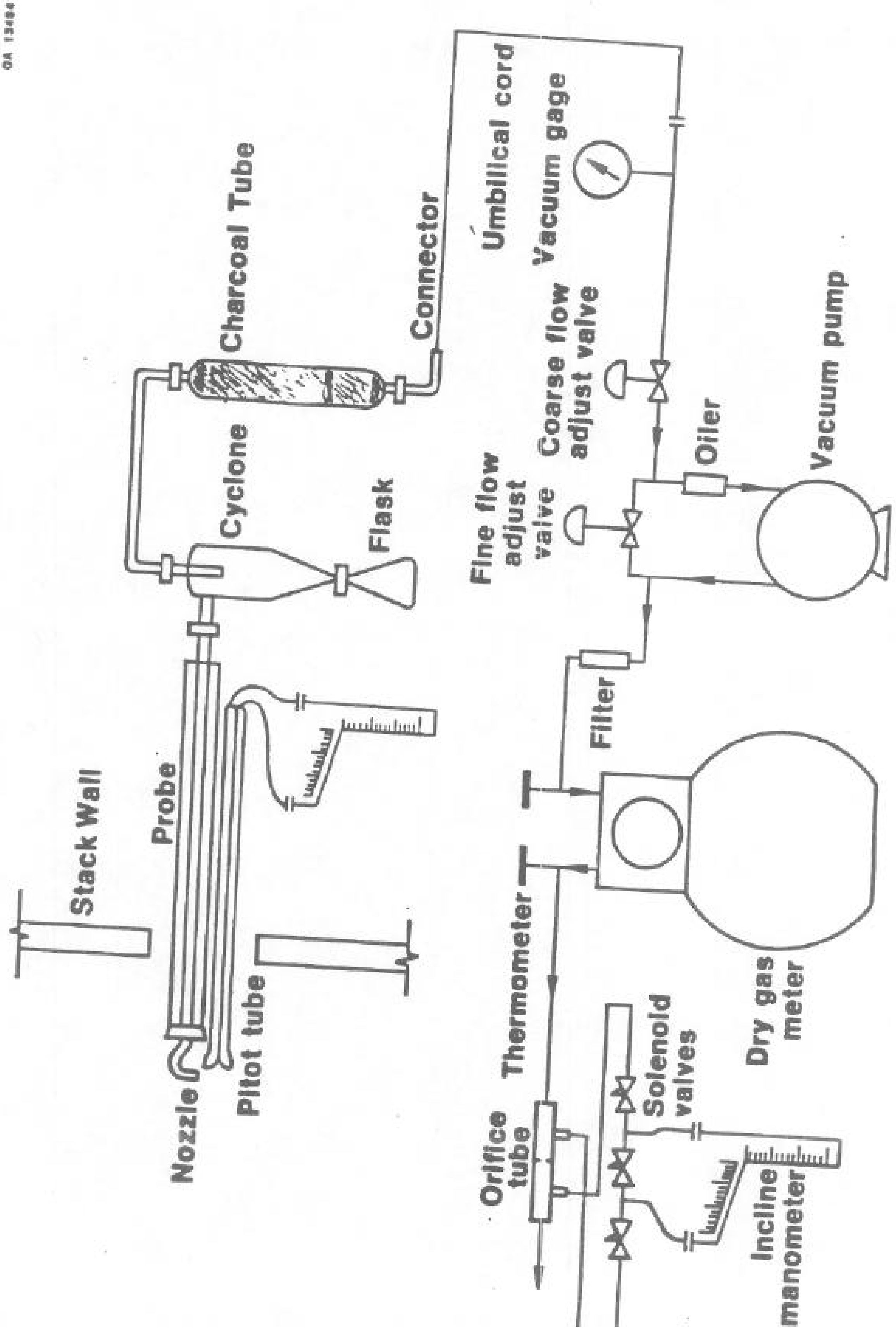
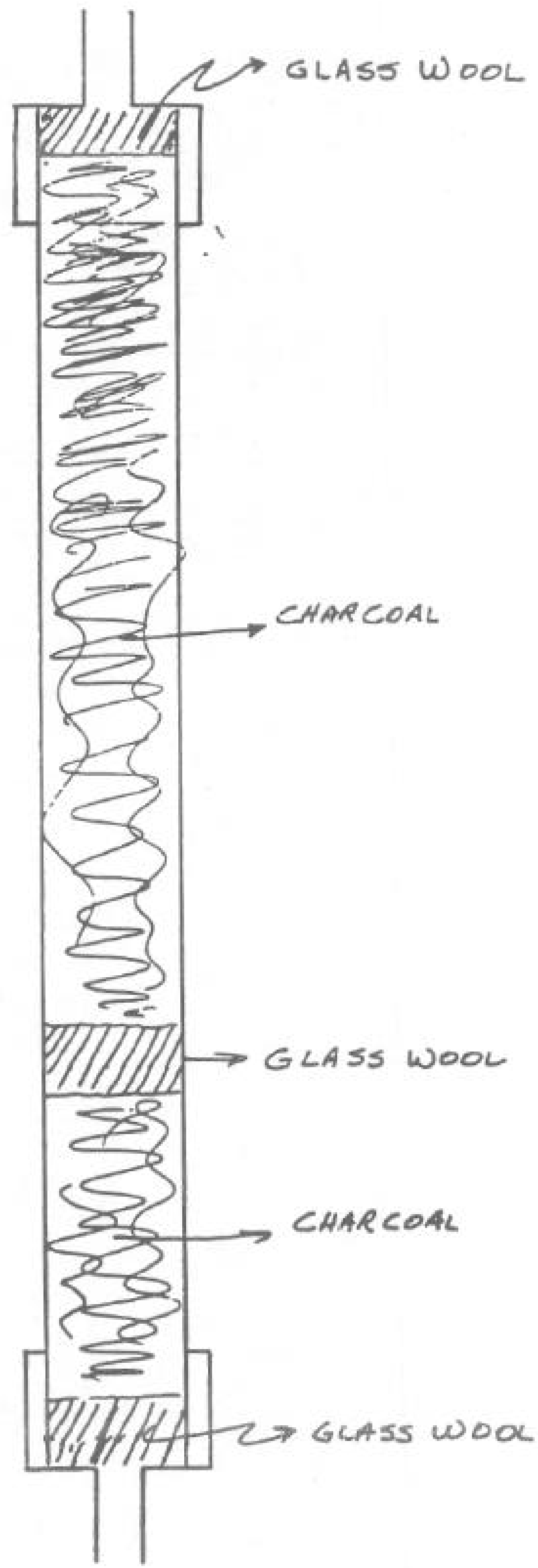


FIGURE 2



ALUMINUM COMPANY OF AMERICA

ANALYSIS METHOD FOR DETERMINATION OF HYDROCARBON EMISSIONS FROM ALUMINUM ROLLING MILLS - METHOD 1471-94

1. Scope

1.1 This method covers the analysis and quantification of rolling lubricants collected using a sampling probe and charcoal tube according to method 1470-94. The method is applicable to those lubricants which are amenable to analysis by gas chromatography, i.e., most mineral based oils.

1.2 The limit of detection is 0.05 mg/M^3 based on a sampled air volume of 30 scf (840 Liters).

2. Definitions

2.1 Refer to ASTM D1356 Standard Definitions of Terms Relating to Atmospheric Sampling and Analysis.

3. Summary of Method

3.1 The methylene chloride solutions from the sampling probes are concentrated by evaporation under an air stream. The charcoal tubes are desorbed using carbon disulfide. Both extracts are then analyzed by capillary gas chromatography with flame ionization detection.

4. Interferences

4.1 Any compound which co-elutes with the target lubricant under the chromatographic conditions used will be a positive interference.

4.2 Generally, the material collected on the charcoal tubes differs in composition from the base lubricant. The percentage of the more volatile components increases while the relative concentrations of the less volatile components decrease. These changes in composition must be taken into account when establishing the gas chromatographic conditions.

4.3 It may be difficult to quantify highly polar or ionic lubricants/surfactants using this method.

5. Apparatus

5.1 Vials, 40 mL with Teflon ™-lined caps.

5.2 Syringes, 10 uL and 100 uL.

5.3 Volumetric flasks, 10.0 mL and 100.0 mL for preparation of standards and controls.

5.4 Ultrasonic bath, 200 watt.

5.5 Evaporator, Zymark Turbo-Vap ™ or equivalent

5.6 Non-polar capillary column, Supelco SPB-1, 0.32 mm I.D., 30 meter in length or equivalent.

5.7 Gas chromatograph equipped with a capillary injection system and flame ionization detector.

6. Reagents

6.1 Carbon disulfide, chromatographic quality, benzene-free recommended.

6.2 Methylene chloride, pesticide grade.

6.3 Bulk lubricant to be used as a standard. It is recommended that the bulk be obtained on location during the sampling. SHIP THE BULK UNDER SEPARATE COVER FROM THE SAMPLES.

7. Calibration Standards

7.1 Place 5 mL of carbon disulfide into each of several 10.0 mL volumetric flasks. With a syringe, measure 5.0, 10.0, 25.0, 50.0 or 100.0 uL of the bulk lubricant into these vials and bring to volume with carbon disulfide. This will result in standards with concentrations of 0.5, 1.0, 2.5, 5.0 or 10.0 uL/mL. The density of the lubricant is used to determine the mg of lubricant/mL in each of the standards.

8. Control Standards (Recoveries and Desorption Efficiencies)

8.1 Probe Rinse Controls

8.1.1 Place 50 mL of methylene chloride in each of two clean bottles used to ship the probe rinses. Using a syringe, add 10.0 uL of the bulk lubricant to each bottle. Handle these controls in the same manner as the samples of probe rinses, Section 9.1, and then analyze as described in Section 10. Determine the percent recovery.

Note: The control solutions, once concentrated (Section 9.1.2), are equivalent in concentration to the 1.0 uL/mL calibration standard.

8.2 Charcoal Tube Controls

8.2.1 Place 50 mL of carbon disulfide in a 100.0 mL volumetric flask. Using a syringe, measure 100.0 uL of the bulk lubricant into the flask and bring to volume with carbon disulfide. This control solution is equivalent in concentration to the 1.0 uL/mL calibration standard.

8.2.2 Place 10g of clean charcoal in each of two 40 mL vials. Carefully add 30.0 mL of the control solution to each of the vials. CAUTION, a large amount of heat will be liberated.

8.2.3 Handle these controls in the same manner as the charcoal tube samples, Section 9.2. Analyze the controls as described in Section 10 and determine the desorption efficiency.

9. Sample Preparation

9.1 Probe Rinses

9.1.1 Quantitatively transfer the methylene chloride rinses to Turbo-Vap™ flasks and evaporate the solvent to under 5 mL. Do not evaporate the solvent to dryness.

9.1.2 Quantitatively transfer the concentrated extracts to 10.0 mL volumetric flasks and bring to volume with methylene chloride.

9.1.3 Remove an aliquot for analysis by gas chromatography.

9.2 Charcoal Tubes

9.2.1 Remove the front ("A") and back ("B") sections of charcoal from the tubes and place each section in separate 40 mL vials.

9.2.2 Carefully add 30.0 mL of carbon disulfide to each of the vials. CAUTION, a large amount of heat will be liberated.

9.2.3 Quickly cap the vials and place in an ultrasonic bath for 2 minutes.

9.2.4 Remove an aliquot for analysis by gas chromatography.

10. Gas Chromatographic Analysis

10.1 Chromatographic conditions

Initial temperature:	60° C
Initial hold:	5 minutes
Temperature rate:	10°C/minute
Final temperature:	300°C
Final hold:	6 minutes
Injector temperature:	220°C
Injection volume:	2.0 uL
Injection mode:	Splitless
Detector temperature:	260° C
Carrier gas:	Hydrogen or Helium
Carrier flow:	2 cc/minute

10.2 Analyze the standards, controls and samples. Standards should be re-analyzed approximately every 10-12 samples.

10.3 The linearity of the standards over the range of interest should be established. If the concentration of the lubricant in a sample exceeds the concentration of the maximum, linear standard, the sample should be diluted and re-analyzed.

10.4 Use a range of retention times which bracket the hydrocarbon peaks in the standards to determine the total peak area of the samples. Determine the concentrations using these integrated areas. It may be necessary to expand the range of retention times to include earlier eluting compounds in the samples from the charcoal tubes.

11. Calculations

$$C_l = \frac{A_s \times Rf \times EV \times Df}{DE \times AV}$$

Where C_l = The concentration of the lubricant in the stack effluent in mg/M^3.

As = Integrated total peak area of the sample in area counts.

Rf = Response factor determined from the standards in mg/mL-area count.

EV = Extraction volume of the sample in mL.

Df = Dilution factor (if necessary).

DE = Desorption efficiency or recovery (1.00 = 100%).

AV = Air volume sampled in M^3.