

METHOD 38

REF: Reg. 8-17-303.1

**DETERMINATION OF PETROLEUM (STODDARD) SOLVENT
IN DRY CLEANING FILTRATION WASTES****1) PRINCIPLE**

- 1.1 This method is applicable to the determination of petroleum (Stoddard) solvent in filtration wastes from dry cleaning operations.
- 1.2 The Stoddard solvent is extracted from the filtration waste using carbon disulfide (CS_2), and the extract is analyzed by gas chromatography.
- 1.3 The detection limit of this method is 0.50% (W/W) stoddard solvent in the sample.

2) APPARATUS

- 2.1 **Gas Chromatograph.** This unit is fitted with a flame ionization detector (FID), a glass sieve injection port, a temperature programmer and a compatible integrator capable of performing time slice integration. Operating parameters are as follows:

	<u>Initial</u>	<u>Final</u>
Oven Temperature (°C)	50	200
Iso Time (min)	5.0	10.0
Program Rate (°C/min)	5.0	
Injector Temperature (°C)	250	
Detector Temperature (°C)	250	
Carrier Gas	He or N	
Carrier Gas Flow, (cc/min)	20.0	
Injection Sample Size, μl	2.0	

2.2 Analytical Column.

2.2.1 6' x 1/8" OD SS Column packed with 1.5% SE 52, 1.5% OV 225 on Chrom W, HP, 8/100 mesh.

2.3 10 µl Syringe.

2.4 Centrifuge tube, 15 ml, graduated in 0.1 ml subdivision with screwcap.

2.5 Metal quart can, wide mouth with cover

2.6 Pipets, Various sizes as needed.

2.7 Refrigerator

2.8 Volumetric Flasks, 10 ml

2.9 Spatula

3) REAGENTS: Reagents must be ACS analytical reagent quality. Reagents should be refrigerated when not in use.

3.1 Carbon Disulfide, (CS₂), Reagent Grade.

3.2 Stoddard Solvent. A minimum of 99% purity is acceptable.

3.3 Cylinder Hydrogen

3.4 Cylinder Helium or Nitrogen

4) ANALYTICAL PROCEDURE

4.1 The sample is collected in a metal quart can, and must be refrigerated immediately after it is received in the laboratory.

- 4.1.1 Take the filter waste sample out of the refrigerator at least 30 minutes prior to analysis. This will allow the sample to reach equilibrium at room temperature.
- 4.1.2 Open the can and mix the sample thoroughly using a spatula. It is essential that the sample be well mixed to obtain valid results.
- 4.1.3 Preweigh a 15 ml graduated centrifuge tube. As rapidly as possible, weigh accurately 0.8 to 1 g (± 0.0001 g) of the mixed sample in the tared 15 ml graduated centrifuge tube. Record the net weight of the sample.
- 4.1.4 Using a pipet, add 10.0 ml of CS₂ to the sample in the centrifuge tube. Cap and invert the tube several times. This will allow the CS₂ to extract the stoddard from the waste sample.
- 4.1.5 Let the mixture set for 10 to 15 minutes undisturbed to allow the CS₂ layer to completely separate from the other waste materials.
- 4.1.6 Inject 2 μ l of the CS₂ into a gas chromatograph set-up with the parameters described in Section 2.1.
- 4.1.7 Record the retention times and the sum of the peak areas of the hydrocarbon compounds in the chromatogram. Run duplicates, peak areas should agree to within $\pm 5\%$ of the mean.
- 4.1.8 Samples with Stoddard solvent concentrations higher than three (3) times the concentration of the standard must be diluted with CS₂. Record the dilution factor (DF) required to bring the sample to the range of the standard.

5) STANDARDIZATION

- 5.1 **Standard Solution.** Accurately weigh approximately 200 mg (± 0.1 mg) of Stoddard solvent in a 10 ml volumetric flask and dilute to the mark with CS₂. This solution contains approximately 20 mg Stoddard solvent per ml. Stopper the flask, and thoroughly mix by inverting the flask several times. This standard solution is always prepared fresh prior to use.
- 5.2 The CS₂ used for sample extraction and standard preparation must be checked for contamination. Inject 2 μ l of the CS₂ blank into the gas chromatograph. Record the retention times and peak areas of the compounds, if any are present. Retain the chromatogram. (NOTE 1)

NOTE 1: CS₂ may contain some benzene and thiophen. These compounds do not, however, interfere with the Stoddard solvent determination.

5.3 Set the gas chromatograph parameters as described in Section 2.1.

5.3.1 Inject 2 μl of the standard solution (5.1) into the gas chromatograph using a 10 μl syringe. Record the retention time and peak area of the hydrocarbon compounds in the chromatogram. Retain the chromatogram. Run duplicates, peak areas should agree to within ± 5% of the mean.

6) CALCULATION FOR COMPLIANCE:

6.1 Compare the chromatograms of (5.3.1) to (4.1.7). Quantitate the concentration of Stoddard solvent in the sample using the following equations:

$$6.1.1 \quad \text{Weight Stoddard (mg)} = \frac{(\text{Conc})_{\text{std}} \times (\text{Total PA})_{\text{HC}} \times 10 \times \text{DF}}{(\text{Total PA})_{\text{std}}}$$

Where:

(Total PA)_{HC} = Sum of the peak areas of the hydrocarbon compounds in the sample chromatogram (4.1.7).

(Conc)_{std} = Weight of Stoddard in mg/ml CS₂ in the standard.

(Total PA)_{Std} = Sum of the peak areas of the hydrocarbon compounds in the stoddard standard chromatogram (5.3.1).

10 = Volume of CS₂ in ml, used in sample extraction.

DF = Dilution factor. Where no dilution is made, DF = 1.

$$6.1.2 \quad \% \text{ Stoddard Solvent (W/W)} = \frac{(6.1.1) \times 100}{W_s}$$

W_s = Weight of sample in mg (4.13).

7) REFERENCES

- 6.1 Control Techniques for VOC Emissions from Stationary Sources, EPA 450/7-78-023, May 1978.
- 6.2 Boiling Range Distribution of Petroleum Fractions by Gas Chromatography, ASTM D 2887-84, 1986 Annual Book of ASTM methods, Section 5.