METHOD 35

REF: Regs 8-49 and 8-51

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS (VOC) IN SOLVENT BASED AEROSOL PAINTS AND ADHESIVES

1) PRINCIPLE

1.1 This method is applicable to the determination of % Volatile Organic Compounds (VOC) in solvent based aerosol paints and adhesive products, that may or may not contain 1-1-Difluoroethane (Dymel 152a), an exempt solvent.

1.2 The % VOC (w/w) is determined by spraying an aliquot of the paint into an adapter glass tube assembly and heating in an oven for one hour at $110^{o} \pm 5^{o}C$.

1.3 The concentration of 1,1-Difluoroethane if present, must be determined by gas chromatography, only if the % VOC (w/w) as calculated in (4.2.2) exceeds the limit set in the regulations.

1.4 This method excludes 1,1-Difluoroethane and water when calculating the % VOC (w/w) content of aerosol paints and adhesives. If water is present in the sample, it must be determined by Method 36, Section 4.4.

1.5 This method may not be applicable to all types of aerosol paints and adhesives. Other procedures may be substituted with mutual agreement of the manufacturer, user and the Air Pollution Control Officer (APCO).

2) APPARATUS

2.1 Gas Chromatograph. This unit is fitted with a flame ionization detector, a manually actuated ten port valve with a 2.3 ml gas sampling loop, a temperature programmer and a compatible integrator or data station. The operating parameters are as follows:

2.3.6 Glass Wool, 0.0029" to 0.0032" diameter. (Fisher Cat. #11-390)

2.3.7 Activated Charcoal, 8-12 Mesh.

2.3.8 Tygon Tubing, Thick Wall (1/4" ID x 1/2" O.D).

2.3.9 Iron Stands.

2.3.10 Utility Clamps.

2.4 Vacuum Pump.

2.5 Drying oven, forced air, capable of maintaining a temperature of 110 ± 5°C.

2.6 Actuators with Extension tube. Available from Spray On Products 26300 Fargo Ave., Bedford Heights, Ohio 44146.

2.7 Top loading balance, capable of weighing to 0.01 gm.

2.8 Eberbach Shaker (Fig. 2)

2.9 Flask Assembly. (Fig. 3)

2.9.1 Erlenmeyer Flask, 24/40 Standard Joint, 1 liter.

2.9.2 Adapter, Gas Inlet, with stopcock, Male, 24/40 Standard Joint. (Cat. #211300 - 2440, Kontes).

2.9.3 Joint Clamps, 24/40. (Cat. #7598-24, Ace Glass, Inc.)

2.9.4 Masking Tape.

2.10 Mercury Manometer (Fig. 3)

2.11 Syringe, 30 ml size.

2.12 Hypodermic Needle, 17 to 22 gauge x 6".

2.13 Rubber Septum.

2.14 Gas-Tight Syringe, 50 ml with 1 ml graduation (Cat. #2 - 1532 M, Supelco, Inc.)

3) REAGENTS

3.1 1,1-Difluoroethane ("Dymel" 152a). This product is available from DuPont Chemicals, 1007 Market St., Wilmington, DE 19898.

3.2 Cylinder Nitrogen or Helium.

3.3 Cylinder Hydrogen.

3.4 Cylinder Air.

4) ANALYTICAL PROCEDURE

4.1 Determination of Total Volatiles

4.1.1 Mix the aerosol can thoroughly using an Eberbach Shaker for 15 minutes at the low speed setting (Fig. 2). It is essential that the samples be well mixed to obtain valid results.

4.1.2 Weigh accurately to 0.01 g, a pre-conditioned sample adapter tube (2.3.1). Record the weight. (NOTE 1)

NOTE 1: Use a pair of gloves when handling the sample adapter tube.

4.1.3 Remove the cap and actuator from the mixed can. Replace the actuator with one having an extension tube (2.6).

4.1.4 Test the actuator with extension tube for leaks by spraying some contents out of the can for about five (5) seconds. If a leak is observed, replace with a better fitting actuator with extension tube.

4.1.5 Take the gross weight of the aerosol can with actuator and extension tube to 0.01 g. Record the weight. Spray about 3 to 5 g of aerosol into the adapter tube assembly (about 3 inches from the exit end of the sample adapter tube), spreading out the coating by moving the extension tube around the wall of the adapter tube. The spraying is done under vacuum.

4.1.6 Weigh the aerosol can with actuator and extension tube to 0.01 g after spraying out the sample. Record the weight.

4.1.7 Place the sample adapter tube in the drying oven for one hour at 110 ± 5°C. Cool the sample in a desiccator and weigh to 0.01 g. Record the weight.

4.1.8 Samples must be run in duplicate and must agree within ± 5% of the mean.

4.2 **Calculation for Compliance in the absence of 1,1-Difluoroethane.**

4.2.1

$$\% \text{ NV (w/w)} = \frac{[(4.1.7) - (4.1.2)]}{(4.1.5) - (4.1.6)} \times 100$$

Where:

(4.1.7) - (4.1.2) = Weight of Non-Volatile (g).

(4.1.5) - (4.1.6) = Weight of Sample (g)

4.2.2 % VOC(w/w) = 100.0 - (4.2.1).

4.3 **Determination of 1,1-Difluoroethane content of the aerosol paint or adhesive by gas chromatography. (NOTE 2).**

NOTE 2: **It is not necessary to determine 1,1-Difluoroethane if the VOC content of the sample is within the limit of the applicable regulation, as calculated in Section 4.2.2.**

4.3.1 **Calibration of the Flask (2.9.1) with Gas Inlet Adapter (2.9.2).**

4.3.1.1 Weigh the flask with gas inlet adapter to ± 0.01 g.

4.3.1.2 Remove the gas inlet adapter and fill the flask with water to the neck at 25°C.

4.3.1.3 Reattach the gas inlet adapter to the flask and add water up to the stopcock by using a syringe.

4.3.1.4 Weigh the flask with the water to ± 0.01 g.

4.3.1.5 Calculation for total volume of the flask.

$$\text{Total Volume} = \frac{(4.3.1.4) - (4.3.1.1)}{d_{H_2O}}$$

Where d_{H_2O} = Density of H_2O = 1.0 g/ml.

4.3.2 **Sample Preparation**

4.3.2.1 Assemble the calibrated flask (2.9.1) with gas inlet adapter (2.9.2) and joint clamp (2.9.3.) as shown in Fig. 3. **(NOTE 3).**

NOTE 3: Tape the exterior of the flask with masking tape (2.9.4) for safety.

4.3.2.2 Using a thick wall tygon tubing, connect the gas inlet adapter tube of the flask assembly to the vacuum pump.

4.3.2.3 Turn on the vacuum pump, open the stopcock of the gas inlet adapter and evacuate the flask for about 10 minutes.

4.3.2.4 After evacuating the flask, close the stopcock of the gas inlet adapter disconnect the tygon tubing and shut off the vacuum pump. Plug the gas inlet adapter with a rubber septum. (2.13).

4.3.2.5 Repeat Sections 4.1.1, 4.1.3 and 4.1.4.

4.3.2.6 Attach a hypodermic needle (2.12) to the end of the extension tube.

4.3.2.7 Weigh the aerosol can with the actuator, extension tube and needle to ± 0.01 g. Record the weight.

4.3.2.8 Push the needle at the end of the extension tube through the rubber septum of the flask.

4.3.2.9 Open the stopcock and push the needle deeper into the stopcock until the end of the extension tube snugly rests on top of the rubber septum.

4.3.2.10 Spray approximately 0.4 to 0.8 g of the aerosol sample into the evacuated flask. Withdraw the extension tube with the needle from the flask. Close the stopcock and swirl the flask to disperse the sample.

4.3.2.11 Reweigh the can with the actuator, extension tube and needle to ± 0.01 g. Record this weight as the final weight.

4.3.2.12 Allow the flask to reach atmospheric pressure by opening the stopcock to allow room air into the flask. Close the stopcock.

4.3.2.13 Connect the gas inlet adapter to the mercury manometer using a Tygon tubing.

4.3.2.14 Open the stopcock. Pressurize the content of the flask to 960 mm Hg with compressed air. Close the stopcock, disconnect from the Tygon tubing and plug with the rubber septum (2.13). Close the main valve of the compressed air cylinder.

4.3.2.15 Allow the content of the flask to reach equilibrium at room temperature by leaving the flask undisturbed for at least one hour.

4.3.2.16 Calculate the total volume of the sample as follows:

$$(Vt)s = (4.3.1.5) \times 1.2632$$

Where: 1.2632 = Ratio of the final pressure in the flask assembly (960 mm) to the initial pressure (760 mm) at 25°C.

(Vt)s = Total volume (ml) of the diluted sample in the flask.

4.4 Determination of 1,1-Difluoroethane By Gas Chromatography.

4.4.1 Set up the GC as described in (2.1).

4.4.2 Using a 30 ml syringe inject 15 to 20 ml of the sample into the gas chromatograph through the 2.3 ml sample loop.

4.4.3 Record the retention time and the peak area of the 1,1-Difluoroethane. Retain the chromatogram. (Fig. 4)

4.4.4 Samples with concentrations greater than two (2) times the standard must be diluted with compressed air and re-analyzed. Record the dilution factor (DF) required to bring the sample into the range of the standard. (NOTE 4.)

NOTE 4: To dilute the sample, open the stopcock and release the contents until atmospheric pressure is reached. Repeat Sections 4.3.2.13 through Section 4.3.2.15.

4.4.5 Samples must be run in duplicate. Duplicate results must agree to within ± 5% of the mean.

5) STANDARDIZATION

5.1 Repeat Sections 4.3.2.1 to 4.3.2.4.

5.2 Using a 50 ml gas-tight syringe inject 30 ± 0.5 ml of gaseous 1,1-Difluoroethane into the evacuated flask assembly. (NOTE: 5)

NOTE 5: **Prepare the 1,1 Difluoroethane standard under the hood and away from open flame.**

5.3 Repeat Sections 4.3.2.12 to 4.3.2.15.

5.4 Calculate the concentration of 1,1-Difluoroethane $(Conc)_{std.}$ in the standard as follows:

$$(Conc)_{std}\ (mg/ml) = \frac{30\ ml \times 2.7\ mg/ml}{(Vt)_{std.}}$$

Where:

2.7 mg/ml = the factor for converting ml 1,1-Difluoroethane to mg 1,1-Difluoroethane

$(Vt)_{std}$ = (4.3.1.5) x 1.2632

5.5 Using a 30 ml syringe inject 15 to 20 ml of standard into the gas chromatograph through the 2.3 ml sample loop. Record the retention time and peak area of 1,1-Difluoroethane. Retain the chromatogram.

6) CALCULATION FOR % 1,1-DIFLUOROETHANE (W/W)

6.1 Compare the chromatograms of (5.5) to (4.4.3) to confirm the identify of 1,1-Difluoroethane. Calculate % 1,1-Difluoroethane in the sample using the following equation:

6.1.1 Weight of 1,1-Difluoroethane (mg) =

$$\frac{(Conc)_{std} \times (PA)_{1,1\text{-}DFE} \times DF \times (4.3.2.16)}{(PA)_{std}}$$

Where:

$(Conc)_{std}$ = Concentration in mg/ml of 1,1-Difluoroethane in the standard (5.4)

$(PA)_{1,1\text{-}DFE}$ = Peak area of the 1,1-difluoroethane in the sample chromatogram (4.4.3).

$(PA)_{std}$ = Peak area of the 1,1-difluoroethane in the standard chromatogram (5.5).

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

6.1.2 $$\% \text{ 1,1-difluoroethane} = \frac{(6.1.1) \times 100}{Ws}$$

Where:

Ws = Weight of sample in mg, (4.3.2.7 - 4.3.2.11) x 1000 mg/g

7) CALCULATION FOR COMPLIANCE IN THE PRESENCE OF 1,1-DIFLUOROETHANE

7.1 % VOC (W/W) = (4.2.2) - (6.1.2).

8) REFERENCES

8.1 "Volatile Content of Paint". ASTM Designation D2369-92, Annual Book of ASTM Standards, Vol 6.01.

8.2 "BAAQMD Manual of Procedures", Vol 3, Method 22.

8.3 "BAAQMD Manual of Procedures", Vol 3, Method 36.

8.4 **"Method for Determining % VOC in Aerosol Paint, which May or May Not Contain Water".** National Paints and Coatings Association Method.

8.5 **"Practice for Packed Column Gas Chromatography"** ASTM Designation E260, Annual Book of ASTM Standards, Vol 14.01.

8.6 **"Test Method for the Determination of Weight Percent Volatile Content of Solvent-Borne Paint in Aerosol Cans."** ASTM Designation D5200-92, Annual Book of ASTM Standards, Vol. 6.01.

8.7 "Determination of Weight Percent Volatile Content of Solvent-Borne Paints in Aerosol Cans", ASTM D5200-92. 1993 Annual Book of ASTM Standards, Vol. 6.01.

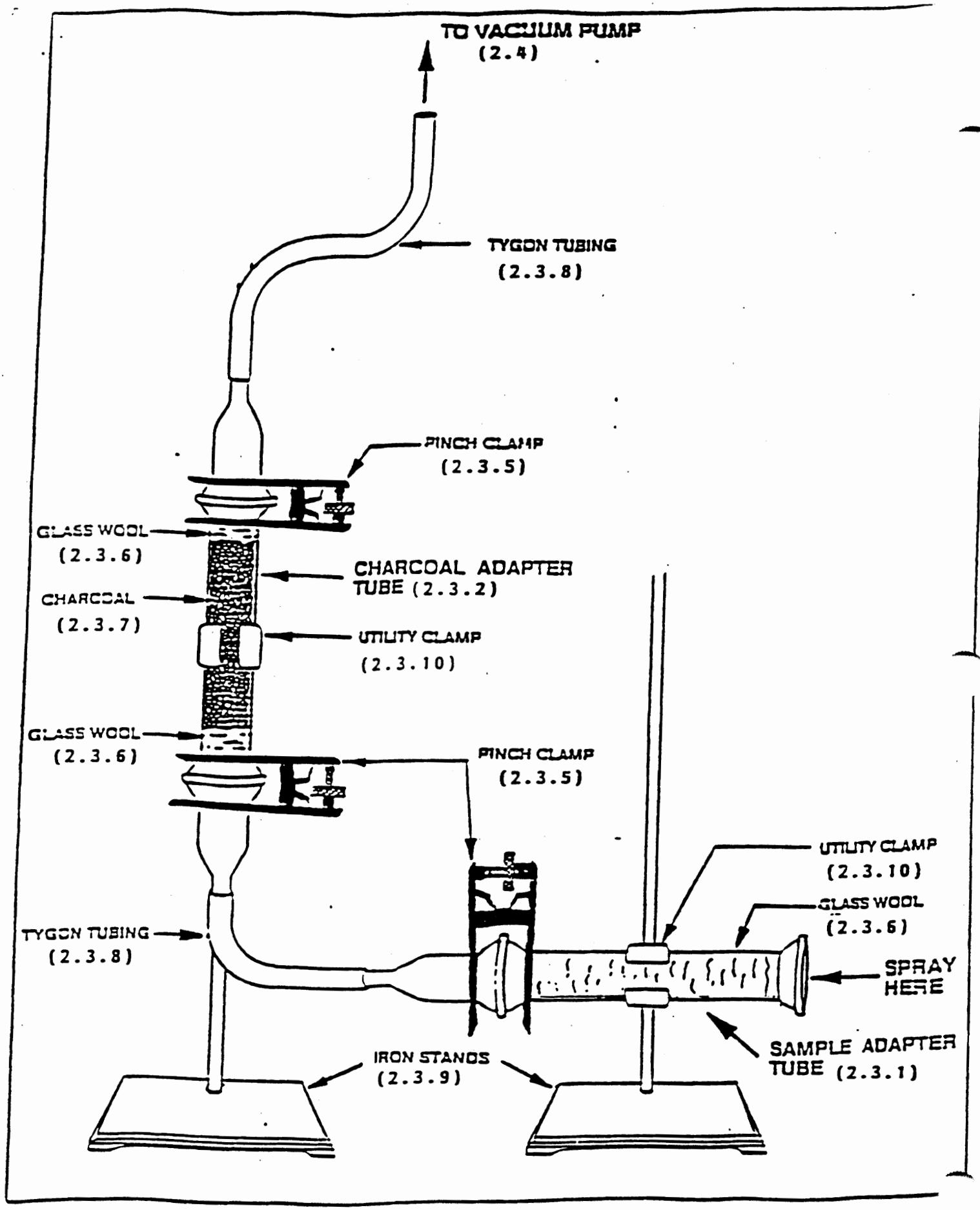


Figure 1 - Adapter Glass Tube Assembly

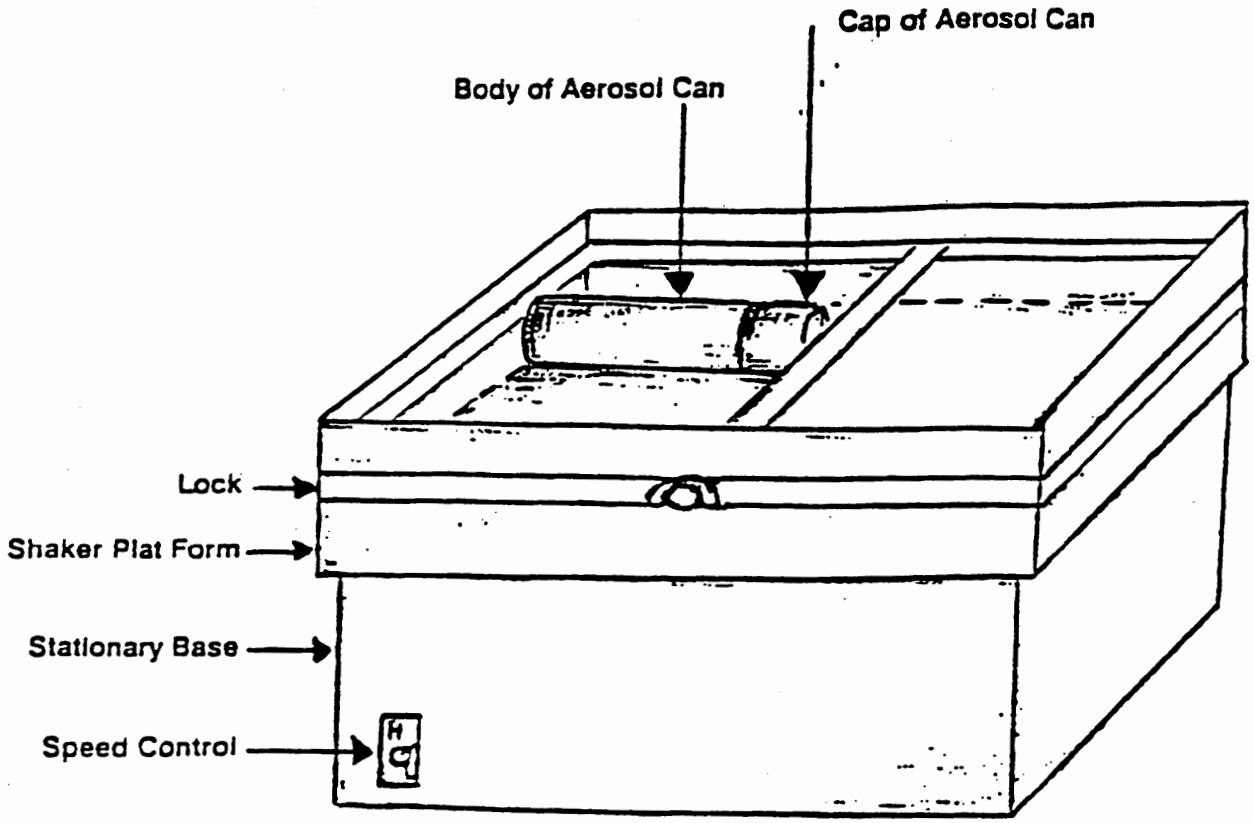


Figure 2 - Aerosol Can On Eberbach Shaker

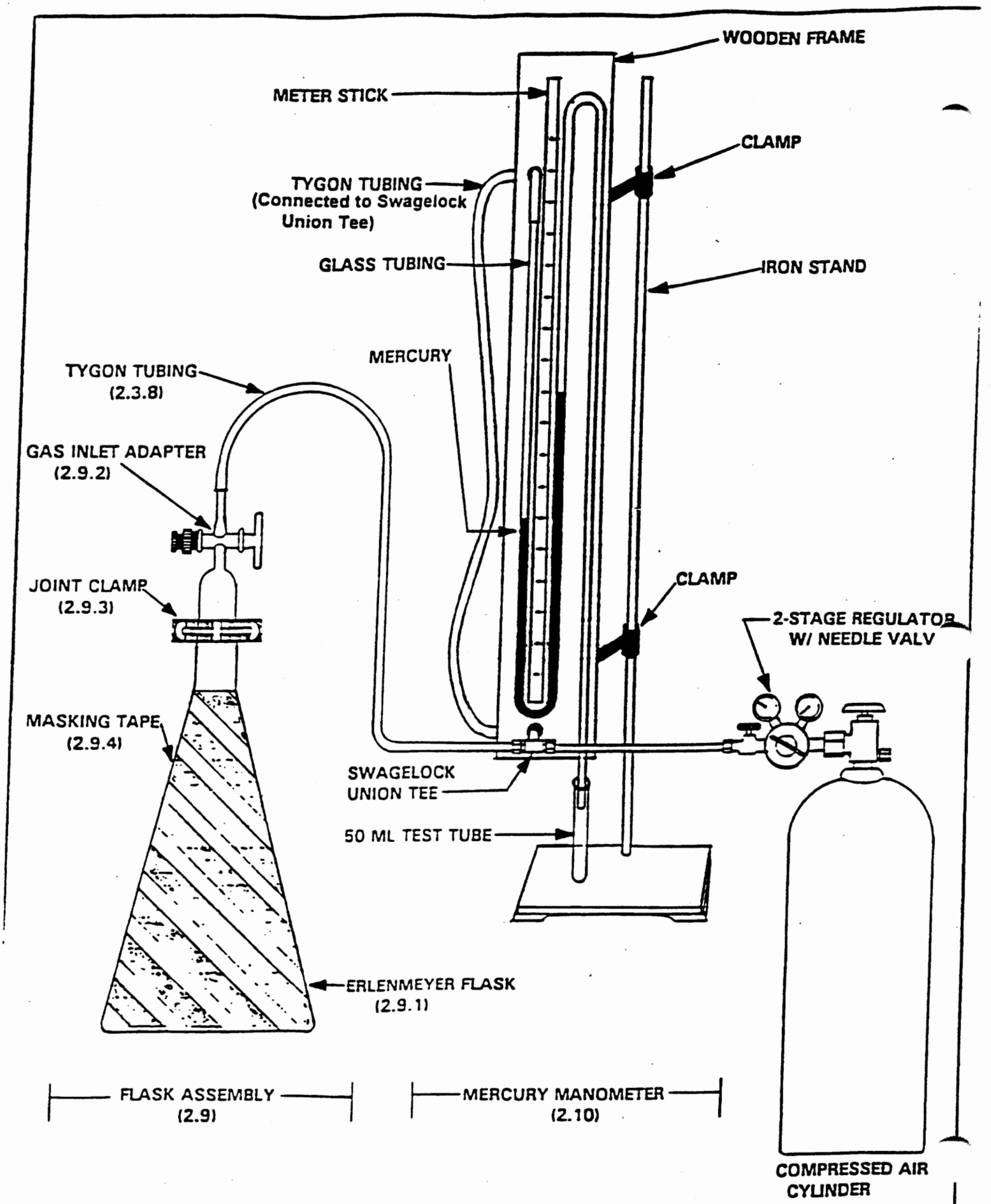
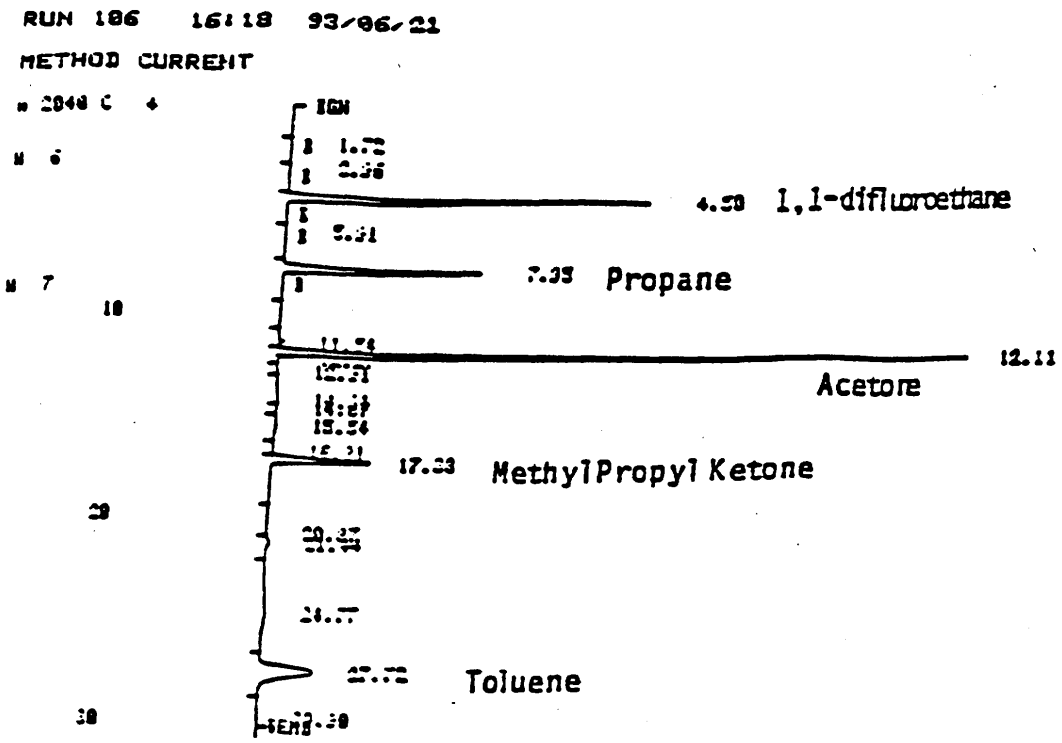


FIGURE 3 - FLASK ASSEMBLY AND MERCURY MANOMETER

Column: 4m x 1/8" Carbopack B/1% SP 1000
Sample Loop Volume = 2.3 ml 60/80 mesh



Analytical Column: 15' x 1/8" Chromosorb 102
Sample Loop = 2.3 ml 100/120 mesh

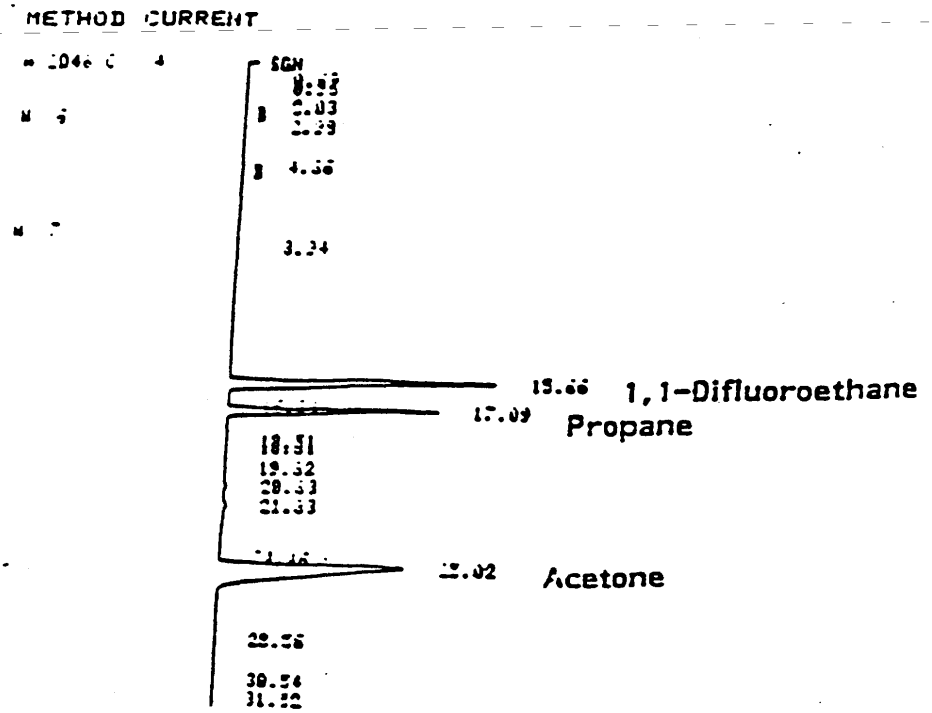


FIGURE 4 - TYPICAL CHROMATOGRAMS