State of California
Air Resources Board

Method 401

Determination of the Weight Percent of Volatile Organic Compounds in Waste Products (Gravimetric Purge and Trap)

Adopted: March 28, 1986

1.0 Principle and Applicability

1.1 Principle

The weight percent of volatile organic compounds (VOC) is determined by measuring the amount of VOC removed from a known amount of waste. An inert hydrogen free gas, such as Nitrogen or Helium is bubbled through a sample of waste thereby stripping out the VOC. The VOC is removed from the gas stream by a sorbent trap. The VOC collected on the sorbent trap is determined gravimetrically.

1.2 Applicability

This method is applicable for determining the weight percent of VOC in a solid or liquid waste as defined by the method. This method is designed to detect the presense of 1.0 percent or more of VOC in waste.

2 Apparatus

2.1 Gravimetric Purge and Trap Setup

A schematic of the gravimetric purge and trap (GP&T) is shown in Figure I. The GP&T setup consists of the following equipment:

Purging System

Purging Chamber

Glass Sparging Tube

Thermometer (1 @ 0-100°C $\pm$ 1°C)

Electric Stirrer

Tru Bore Stirrer Rod

Connecting Tubing (1/4 inch Teflon)

Constant Temperature Bath ($\pm$1.0°C)

Rotameters (2 @ 0-20 Lpm)

Pressure Gauge (0-20 psi)

Trap System

Coalescing Filter

Primary Activated Charcoal Tube

Secondary Activated Charcoal Tube

Analytical Micro Balance (± .1 mg)

Analytical Top Loading Balance (± .1 gm)

Thermometer Well (Thermometer 0-30°C ± 1°C)

2.1.1 Purging Chamber

The purging chamber shall be constructed as detailed in Figure II. The construction material of the chamber is glass. The bushings of the Ace-Thred fittings* shall be nylon and the associated O-ring shall be Buna-N rubber. Both the thermometer[+] (0-100°C ± 1C) and Tru-Bore stirrer[#] shall also be made of glass. The glass sparger** shall have 10 holes less than 1.0 mm in size and all holes shall be within 1.0 cm of the tip.

2.1.2 Coalescing Filter

The coalescing filter shall be constructed as detailed in Figure III. The construction material of the filter shall be glass. The bushings of the Ace-Thred fittings shall be nylon and the associated O-Ring shall be Buna-N rubber. The frit shall have an extra coarse porosity.

2.1.3 Constant Temperature Bath

The depth of the bath is to be at least 10 inches or sufficient to cover purging chamber to a depth of 10 inches. The bath must be able to maintain a temperature of 100°C (±1°C). The bath solution must be chosen with this temperature in mind. If a commercial antifreeze solution is chosen, caution must be taken due to the ethylene glycol content. The OSHA allowable concentration of ethylene glycol in occupational air is 125 mg/m3 (50 ppm) therefore antifreeze must be used in a well ventilated location.

2.1.4 Balances

A top-loaded balance with an accuracy of 0.1 grams shall be used to weight out 10 grams of waste sample. A micro balance with an accuracy of 1.0 milligram shall be used for weighing activated carbon traps. One balance can be used if it accommodates both levels of precision.

2.1.5 Organic Traps

2.1.5.1 Preliminary Organic Trap

The first trap (primary) shall contain four grams of coconut shell charcoal. The charcoal shall have a mesh size of 12 x 30. The charcoal shall be contained in a 14 mm ID glass tube of length 150 mm. Column connectors constructed of Ace-Thred fittings are to be used to connect the traps to the gas lines. Assembly of the organic trap is shown in Figure V.

2.1.5.2 Secondary Organic Trap

The second trap shall contain two grams of coconut shell charcoal. The charcoal shall have a mesh size of 12 x 30. The charcoal shall be contained in a 14 mm ID glass tube of length 75 mm. Column connectors constructed of Ace-Thred fittings are to be used to connect the traps to the gas lines. Assembly of the organic traps is shown in Figure V.

2.1.6 Miscellaneous Equipment

All gas lines shall be ¼ - inch teflon tubing. A variable speed electric or air-driven stirrer, torque of ½-1 inch-lb shall be used in conjunction with the Tru-Bore glass stirrer. Two 0-20 Lpm rotameters shall be used to monitor flows into and out of the GP&T. A 0-20 psi pressure gauge will be placed up stream of the inlet rotameter. A thermometer 10-30°C $\pm$1°C held in a glass thermometer well, Figure IV, shall be used at the outlet of the secondary trap to measure the gas stream temperature.

3.0 Reagents

3.1 Sodium Thiosulfate—(ACS) Granular

3.2 Trap Materials

3.2.1 Activated Carbon-Coconut Shell-12 x 30 mesh

3.3 Organic-Free Water

3.3.1 Organic-free water is water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water or well water through a carbon filter bed containing about 1 lb. of activated carbon. The organic-free water must not contain more than 1 ppm of organics.

3.3.2 A water system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

3.3.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

3.4 Organic Free-Gas

An inert and non-reactive gas supply can be substituted for a nitrogen supply. Helium could forexample be substituted for nitrogen. The gas supply must not contain more than 1 ppm of water or of organic compounds.

4.0 Procedure

4.1 Sample Collection, Preservation and Handling

Grab samples must be collected in glass containers^{++} of approximately one liter. Completely fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottles so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

The sample must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium

thiosulfate preservative (10 ug/40 ml) to the empty sample bottles just prior to shipping to the sample site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

All samples must be analyzed within two weeks after the time of collection. Samples must be refrigerated between time of collection and analysis.

Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) into the sample during sampling, shipment and storage. A field blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

4.2 Sample Preparation

Blend one liter sample by hand using a large spoon or electrical blender for several minutes. An emulsification agent can be added to provide a uniform mixture if it can be shown not to cause interferences. Sand or diatomaceous earth might be used as an emulsification agent.

4.3 Organic Trap Preparation

Weigh out 4 gm of activated charcoal and put into an appropriate glass tube. Weigh out an additional 2 gm and place in a second tube. Use glass wool as a plug to hold activated charcoal in glass tubes. Label tubes primary and secondary. Weigh activated charcoal tubes. Record weights to one mg on an appropriate data sheet. The balance must be accurate to within one milligram. Assemble traps and place in setup as shown in Figure I. Caution must be used in the amount of glass wool inserted as a plug into the traps. To much glass wool causes large pressure buildup. It is recommended that the operator, on a weekly basis, batch dry an appropriate amount of activated charcoal.

4.4 GP&T System Setup

Set up apparatus as shown in Figure I. Due to the pressure in the purging chamber and the temperature of the bath the apparatus should be placed in a hood. It is recommended that the operator clean a gallon of Dioctyl phthalate at a time.

4.5 Sample Analysis

Step 1. Set up apparatus as shown in Figure I, leaving purging chamber out of bath.

Step 2. Disassemble chamber and place chamber base, Figure II, on a balance. Using a large spoon, mix and spoon out a sample from the glass sample jar then add to chamber until the weight change is 10 grams $\pm$ 0.1 grams. Record weight change to the nearest tenth of a gram on a data sheet.

Step 3. Add 100 ml $\pm$ 10 ml of Dioctyl Phthalate (DOP).

Step 4. Reassemble chamber. Thermometer must extend into DOP. Stirring rod must be within 1 cm of bottom and not interfere with sparger.

Step 5. Place chamber into temperature bath. The bath temperature should be at 100°C $\pm$ 1°C.

Step 6. Weigh out 4 gm $\pm$ .1 gm of activated charcoal and put into appropriate glass tube. Weigh out 2 gm $\pm$.1 gm and place in a second tube. The activated charcoal is held in the tube with small amounts of glass wool plugs. Weigh both adsorption tubes to the nearest .1 mg and record weights.

Step 7. When the temperature of the DOP reaches 100°C, start the flow through the sparger. The outlet rotameter is to be set to the required flowrate of 15 Lpm $\pm$ 1 Lpm. The inlet rotameter is to have its reading corrected to atmospheric pressure and checked against the outlet rotameter. If the two flowrate readings after the pressure corrections are not within 10 percent of each other, the run is invalid and is to be terminated. Leak checking is to be conducted before rerunning the test.

CAUTION: Required flowrate causes high pressure in a glass vessel. Proper care must be taken.

Step 8. The temperature at the outlet of the secondary trap be 30°C $\pm$ 5°C. A temperature variation ($\pm$ 5°C) will be seen during run. The temperature of 30°C is necessary to eliminate water retention on the activated carbon.

Step 9. Continue the flow for 30 minutes recording pertinent data. Total analysis time, which includes: sample preparation, run time, data reduction and cleanup, may be in excess of one hour.

4.6 VOC Measurement

Step 1. Remove tubes and swab clean exposed surfaces of glass tube to remove any residual water droplets.

Step 2. Weigh tubes and record results to the nearest 0.1 mg on data sheet.

4.7 Sample Disposal

Contents of the sample jar and purging chamber are considered to contain hazardous material and must be disposed of in a proper manner.

5.0 VOC Calculations

5.1 Calculations

The percent of VOC in the waste sample is determined from the weight gain of the organic adsorption trap.

$$\% \text{ VOC} = \frac{\text{Weight Change of Primary + Weight Change of Secondary}}{\text{Weight of Sample}} * 100$$

5.2 Acceptability of Results

If the weight change of the secondary organic trap is greater than the weight change of the primary trap and the calculated percent VOC is less than 1.0 percent, then the test must be rerun. If the results described above are duplicated then the test procedure is not applicable to this waste. Contact the appropriate agency for an alternative test method.

6.0 Validation

Validation of the purge and trap setup must be performed when a new batch of activated carbon is used. The validation consist of testing 100 mg of tridecane, decane, octane, isopropanol, mixed xylenes, butyl cellosolve, methanol, acetone, and dichloromethane individually in 10 gms of water. Capture of these compounds on the activated charcoal traps should be greater than 99 percent for all organic compounds listed except methanol which should be less than 1.0 percent.

Before processing any samples, the analyst should demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free.

7.0 Quality Assurance

See ARB quality assurance manual entitled

AIR MONITORING QUALITY ASSURANCE, VOLUME VI, STANDARD OPERATING PROCEDURES FOR STATIONARY SOURCE EMISSION MONITORING AND TESTING, Air Resources Board, Stationary Source Division, January 1979

8.0 Bibliography

8.1 ASTM Standards: Part 23

D 270 Sampling Petroleum and Petroleum Products
D 4057 Manual Sampling of Petroleum/Petroleum Products

8.2 EPA Methods

Method 624, Purgeables, Pg. 69532, FR Volume 44, No. 233, Dec. 3, 1979
Method 602, Purgeable Aromatics, Pg. 69474; ibid.

8.3 EPA Reports

EPA-600/2-80-018: “Samples and Sampling Procedures for Hazardous Waste Streams.”

8.4 ARB unpublished report entitled

Technical Support Document
Experimental Data in Support of
Proposed ARB Method 401-
Determination of the Weight Percent of
Volatile Organic Compounds in Waste Products
(Gravimetric Purge and Trap)

9.0 Safety

As a precaution against laboratory personnel being exposed to hazardous materials or injured by projectiles from pressurerized equipment, stringent chemistry laboratory safety practices shall be followed and appropriate apparel worn when conducting this method. Operation of the GP&T is recommednded to

be preformed in a hood with a pull down safety face. As with all safety questions this is the responsibility of the laboratory performing the test.

10.0 Alternative Test Methods or A Modified Test Method

Methods, other than specified above, or a modified test method may be used if prior approval is obtained from the Executive Officer of the Air Resources Board or appropriate officer of the responsible control agency. In order to secure the Executive Officer's approval the proponent is responsible for demonstrating to the Executive Officer's satisfaction that the alternative method is equivalent to the adopted method or that the modification to the method does not alter the results obtained by the adopted method.

NOTES

* Whenever in this procedure that use of an “Ace-Thred fitting” is specified, another equally effective fitting may alternatively be used.

\+ Whenever in this procedure the use of a “Thermometer” is specified, another equally effective temperature sensing device may alternatively be used.

\# Whenever in this procedure the use of a “Tru-Bore stirrer” is specified, another equally effective stirrer may alternatively be used.

** Whenever in this procedure the use of a “glass sparger” is specified, another equally effective sparger may alternatively be used.

++ Whenever in this procedure the use of a “glass container” is specified, another equally effective container may alternatively be used.

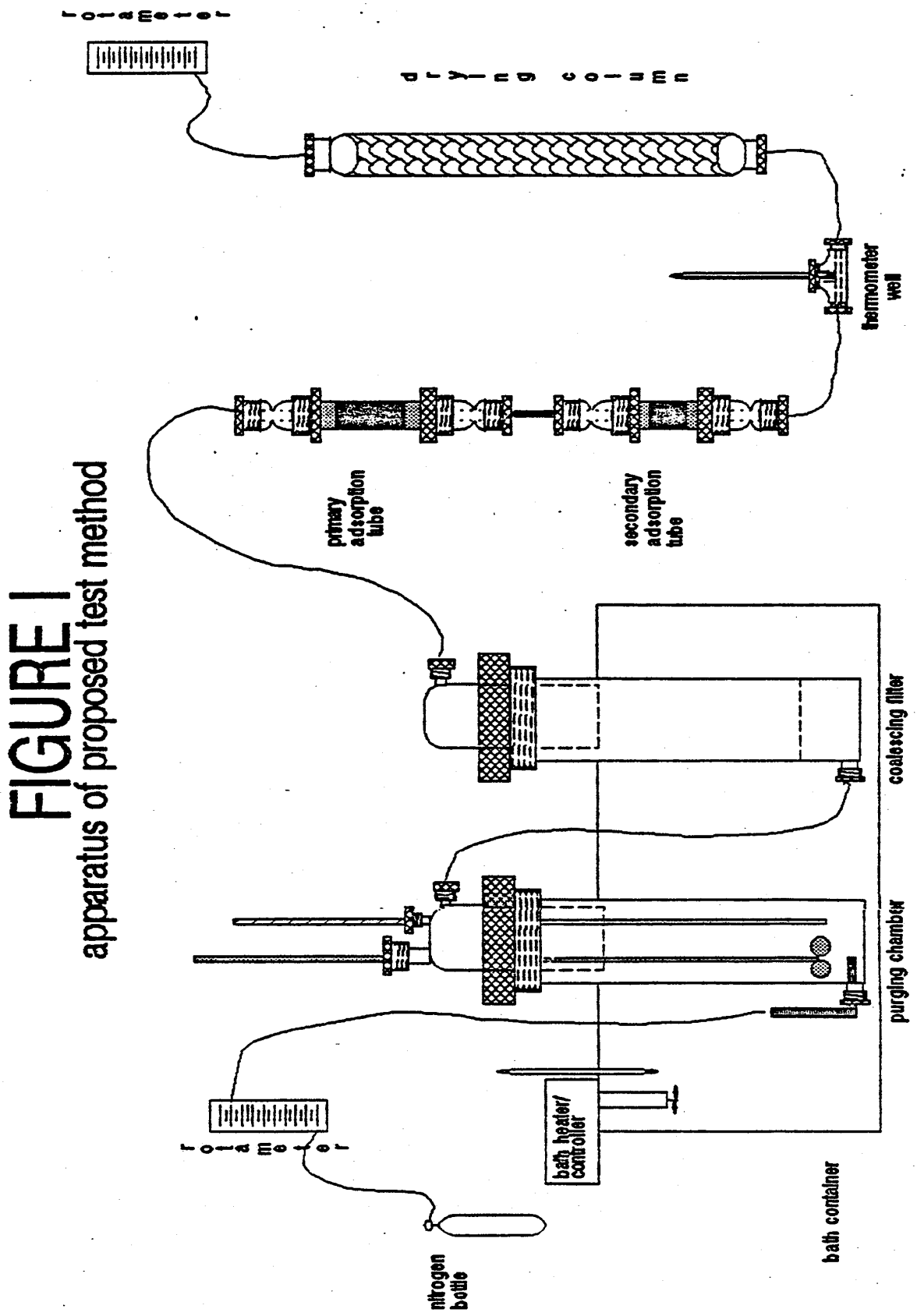


FIGURE I
apparatus of proposed test method

FIGURE II

THE GP&T PURGING CHAMBER

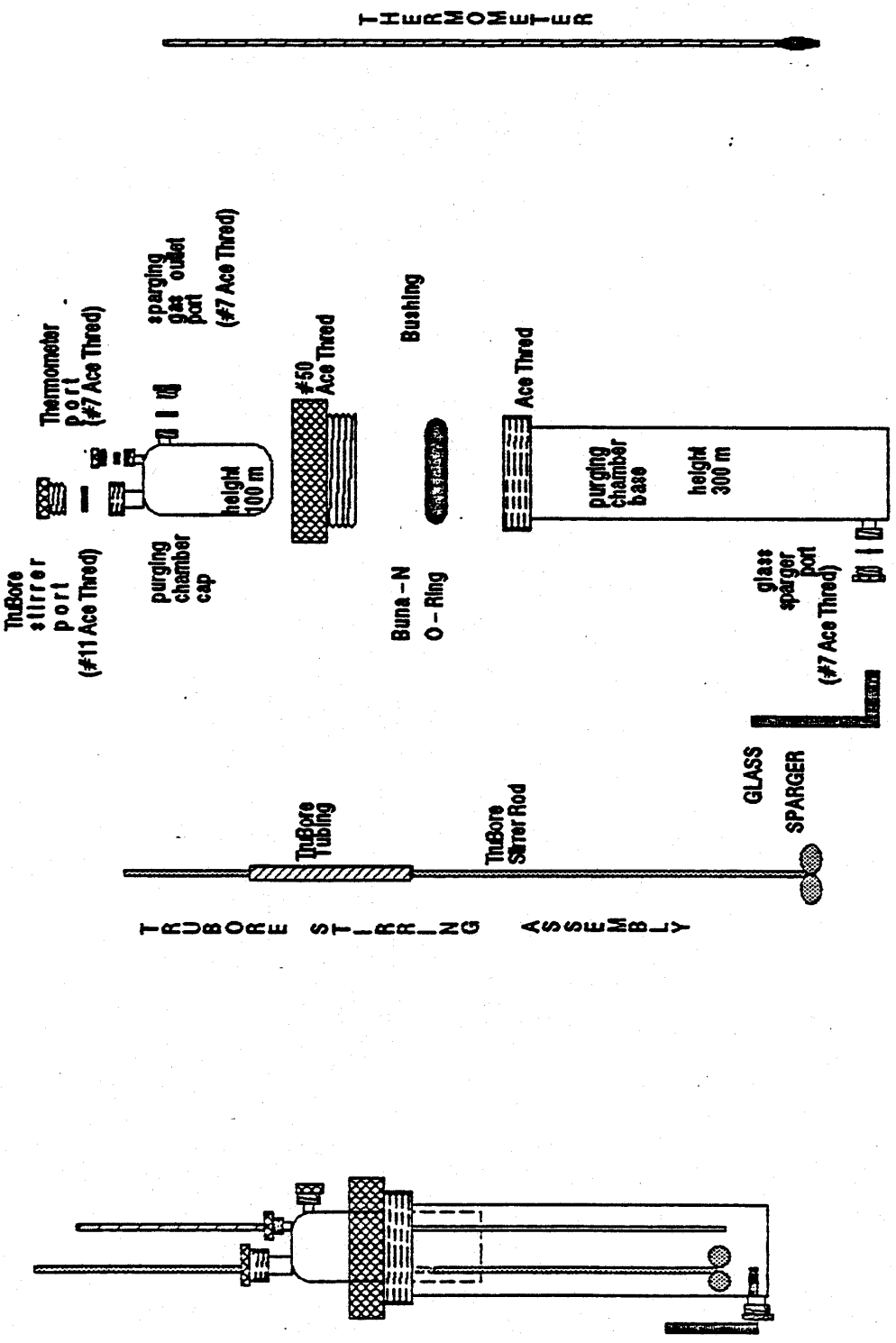
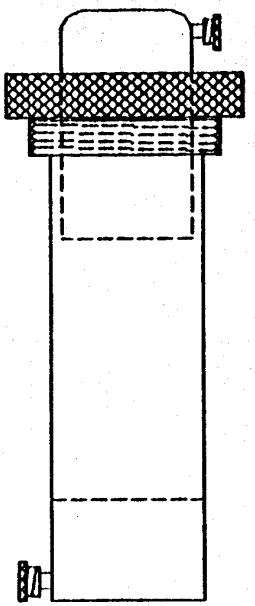


FIGURE III

The Coalescing Filter



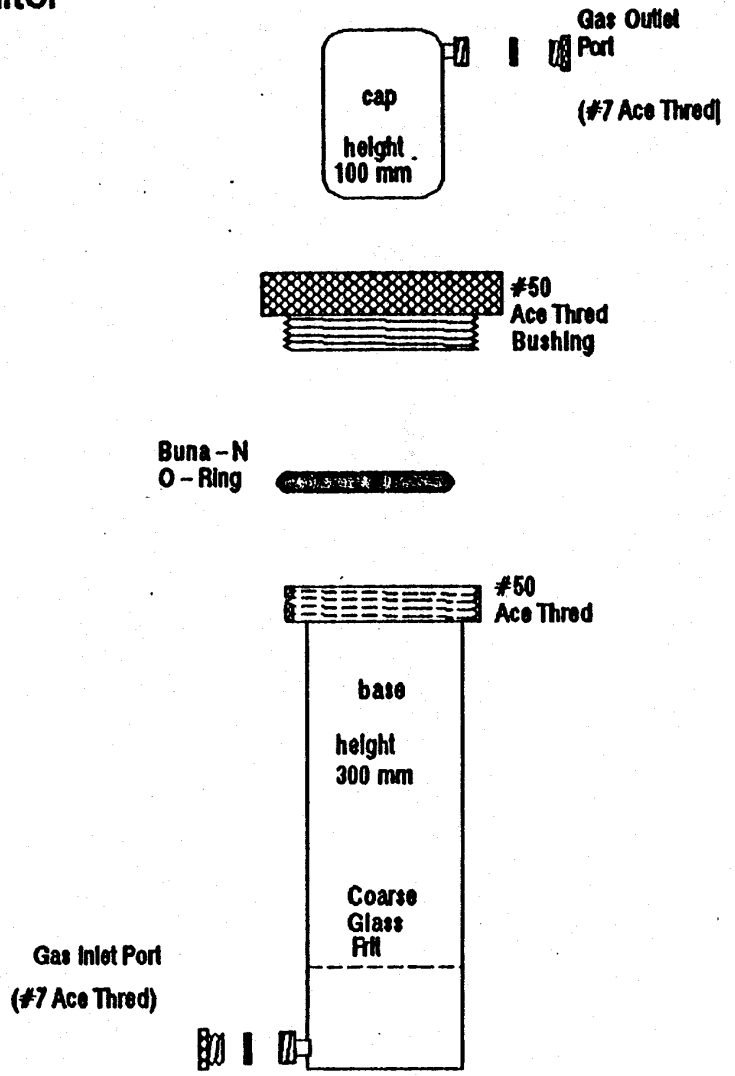
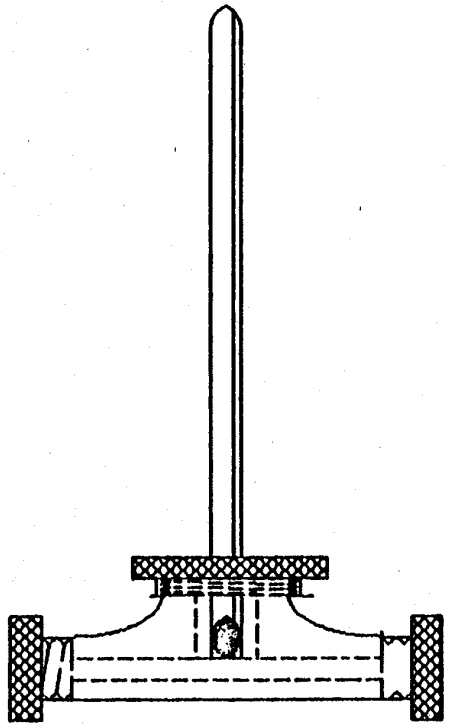


FIGURE IV
thermometer well



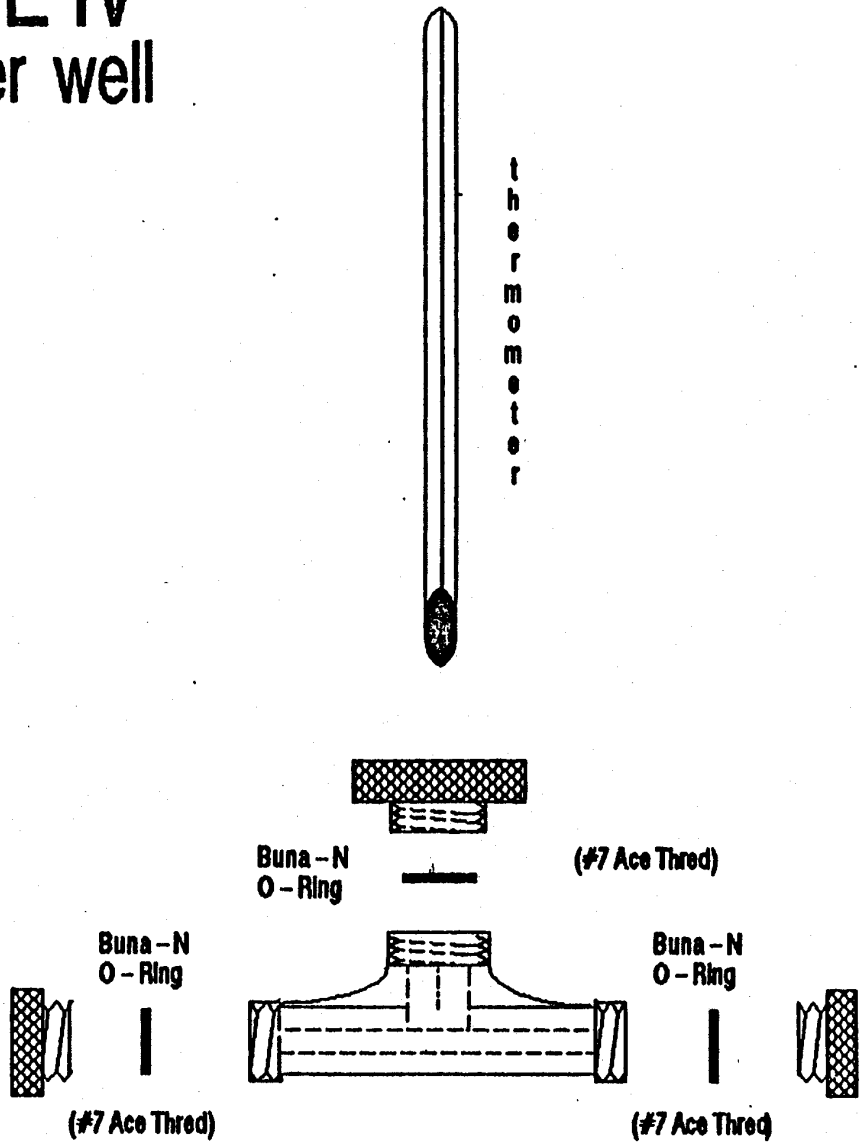


FIGURE V
the organic trap