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Title: Test Method for Evaluation of Hexane
Emissions from Vegetable Oil
Manufacturing

PEDCo Environmental Inc.

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AP-42 Section	<u>9.11.1</u>
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Report Sect.	_____
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TEST METHOD FOR EVALUATION
OF HEXANE EMISSIONS FROM
VEGETABLE OIL MANUFACTURING

PRELIMINARY DRAFT

Prepared by

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Contract No. 68-02-2811
Task No. 7
PN 3333-G

Prepared for

U.S. ENVIRONMENTAL PROTECTION AGENCY
Emission Measurement Branch
Research Triangle Park, N. C. 27711
Nancy D. McLaughlin, Project Officer

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SECTION I

TEST METHOD FOR THE EVALUATION OF HEXANE EMISSIONS FROM VEGETABLE OIL MANUFACTURING

1. Principle and Applicability

1.1 Principle. A sample is drawn from the stack at a constant rate through a series of midget impingers. Carbon disulfide is used in the impingers as a collecting media for hexane vapor. The carbon disulfide solution is then recovered and analyzed on a gas chromatograph with a flame ionization detector (FID) to determine the amount of hexane collected.

1.2 Applicability. This method was developed to measure hexane emissions from solvent extraction processes such as those employed in the vegetable oil processing industry. This method may be applicable for other hydrocarbon sources where only one or two compounds are being emitted provided that these compounds are highly soluble in carbon disulfide and can be easily separated by gas chromatography for analysis.

2. Range and Sensitivity

Laboratory tests have shown the method has a collection efficiency of better than 99 percent when sampling sources with concentrations ranging from 90 ppm to 8.5 percent by volume. In one field study conducted at a vegetable oil plant the method was compared with bag samples drawn from the stack and found to be accurate for sources having concentrations of 10 and 50 ppm hexane.

Possible interferences are any other compounds present which have the same retention time as the hexanes with the gas chromatograph operating conditions described in this method. When other compounds are suspected or known to exist in the sampled gas stream, such information, including their suspected identities, should be transmitted with the samples. If the possibility of interferences does exist, chromatographic conditions may be changed to circumvent analytical difficulties.

3. Apparatus

3.1 Sampling. (See Figure 1.)

3.1.1 Probe. Glass or Teflon tubing. A glass wool plug may be added to remove particulate if needed.

3.1.2 Impinger Train. Two midjet impingers and three midjet bubblers are connected in series with leak-free glass connectors. Silicone grease may be used if applied sparingly. The impinger train must be kept in an ice bath to allow condensation of the hexane vapor and to minimize the vapor pressure of the carbon disulfide.

The first impinger contains 15 ml of distilled water and removes moisture and some hexane from the gas stream. Alternately, the first impinger may be left dry, provided that carbon disulfide is added to the condensate in the impinger immediately after the test to prevent the rapid loss of hexane due to evaporation (see recovery of sample, section 5.2).

Following the first impinger are three fritted impingers, or bubblers, each containing approximately 15 ml of carbon disulfide

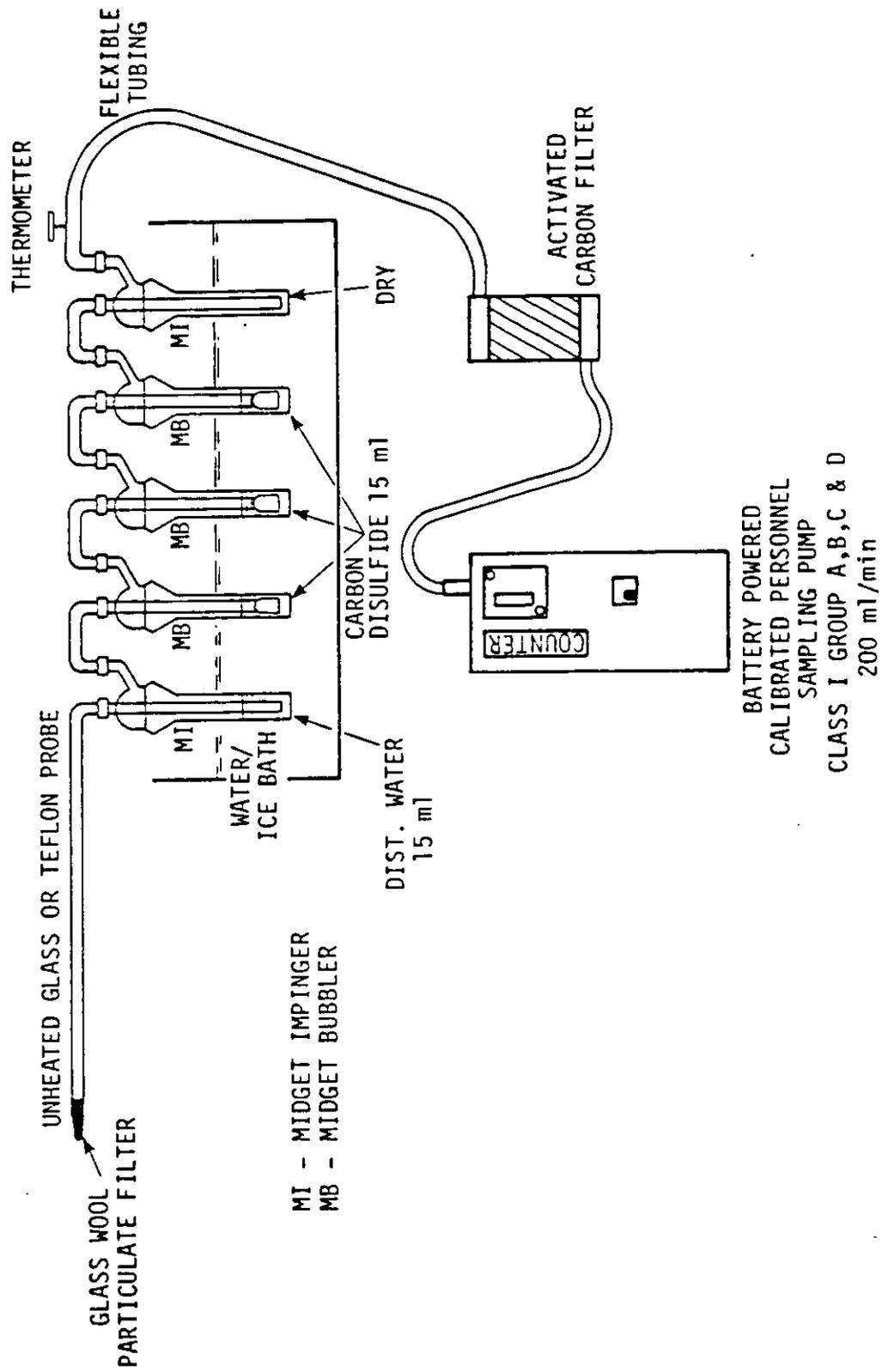


FIGURE 1. HEXANE SAMPLING APPARATUS.

(CS₂). The final impinger is left dry to knock out vapor carried over from the carbon disulfide impingers.

3.1.3 Activated Carbon Filter. Placed between the impinger train and the pump, the filter absorbs carbon disulfide vapor thus protecting the pump and allowing a truer measurement of sample volume.

3.1.4 Sample Pump. Battery operated personnel sampling pump, intrinsically safe for Class I, groups A, B, C, and D hazardous environments. Pump must be calibrated to maintain a constant sampling rate in the range of 150 to 500 ml/min., and should be able to pull a vacuum of 3-4 in. Hg.

3.1.5 Temperature Gauge. Dial thermometer, or equivalent, to measure temperature of gas leaving the impinger train to within $\pm 1^\circ\text{C}$.

3.1.6 Bubble Meter. To check calibration setting on pump before and after each test.

3.1.7 Barometer. To measure atmospheric pressure to within 0.1 in. Hg.

3.2 Analysis.

3.2.1 Gas Chromatograph. Commercially available with flame ionization detector.

3.2.2 G.C. Column. To separate hexanes from carbon disulfide, 10 or 20-ft. x 1/8 in. stainless steel column packed with 10 percent SP-1000 on 80/100 suplecoport.

3.2.3 Recorder. Continuous strip chart type with millivolt input to match detector electrometer output. Optional electronic peak area integrator.

3.2.4 Microliter Syringe. Glass, 10 microliter or other size convenient for sample injection and preparation of standards.

3.2.5 Standard Vials. Glass with replacable Teflon backed septum caps.

3.3 Sample Recovery.

3.3.1 Sample Storage Bottles. Glass, 4 oz. size (~ 120 ml) with tight fitting Teflon backed rubber septum caps for impinger sample storage.

3.3.2 Pipettes. Volumetric type, 5 ml and 15 ml sizes.

3.3.3 Graduate Cylinder. 25 ml size.

3.3.4 Syringe. 5 ml size to draw water layer from sample bottle.

3.3.5 Balance. To weigh sample containers to 0.1 g.

4. Reagents

4.1 Sampling.

4.1.1 Carbon Disulfide. Chromatographic grade.

4.1.2 Distilled, deionized water.

4.2 Analysis.

4.2.1 n-hexane. 99 mole percent n-hexane for calibration standards.

4.2.2 Carbon Disulfide. Chromatographic grade for preparation of standards.

5. Procedure

5.1 Sampling.

5.1.1 Preparation of Collection Train. Assemble glassware as shown in Figure 1. Place impingers in the ice water bath before adding carbon disulfide. With a graduate cylinder, measure 15 ml of distilled water and add to the first impinger. Add approximately 15 ml of carbon disulfide to each of the next three impingers (sufficient quantity to cover the fritted end of the impinger).

5.1.2 Pump Calibration. Pump must be capable of holding a steady sampling rate in the range of 150 to 500 ml/min. for the duration of the test period. Pump should be tested and leak checked before use in the field. Calibration should be checked before and after each test using a bubble meter or similar flow measurement device. Pump must be calibrated with sample train and carbon tube in line.

5.1.3 Leak Check Procedure. Leak check sampling train before and after each sampling run. Plug the inlet to the probe and turn on pump. If system is leak free, pump-stroke counter will stop or pump float chamber will indicate zero flow. Observe this condition for 15 seconds, then slowly release the vacuum from the probe end, and turn off the pump.

5.1.4 Sample Collection. Record the initial pump-stroke counter reading, if applicable. Record the starting time for the test and the ambient temperature and pressure. Position the tip of the probe at the sampling point and start the pump. Periodically record the temperature of the gas leaving the impinger train. Check the system

during the test to see that all connections remain tight and pump is operating. Add more ice to the train as required. Sampling time is variable depending on source concentration. Sources with a low concentration should be sampled for at least one hour.

At the end of the sampling period, turn off the pump and remove the probe from the stack. Record the time and pump counter reading if applicable. Conduct a leak check as in section 5.1.3. If a leak is found, void the test run. Cap off train to prevent evaporation losses and return to the sample recovery area.

5.2. Sample Recovery. This procedure must be carried out in a well ventilated area away from all possible ignition sources. If an exhaust hood is available, sample recovery should be carried out under the hood. Note: carbon disulfide (CS_2) is extremely flammable and toxic. Exercise caution when handling the solvent and avoid prolonged contact with the skin or contact with the eyes.

Leave impinger train in the ice bath during the rinsing and place the tared sample recovery bottle in ice. Proceed with recovery as follows:

- 1) Rinse probe with 10-15 ml of CS_2 .
- 2) Add 15 ml of CS_2 to the first impinger containing water and shake.
- 3) Starting with the last impinger and proceeding to the first, pour all contents into a glass sample bottle. Close and return impingers to the ice bath. Replace the lid on sample bottle between additions.
- 4) Place 15 ml of CS_2 in the last impinger and shake to remove hexane from the interior surface.

- 5) Pour the rinse solution in the last impinger into the next to the last impinger and shake. Continue this procedure until all impingers have been rinsed. Then add rinse solution to the sample bottle.
- 6) Repeat steps #4 and #5 with a second 15 ml portion of carbon disulfide.
- 7) Rinse all connecting glassware.
- 8) Seal sample container, mark the solution level, and label the sample for analysis.

5.3 Analysis.

5.3.1 Sample Preparation. Shake sample container well and when contents settle, use a 5 ml gas tight syringe to extract the water layer from the carbon disulfide. Measure the volume of water collected. Next, weigh the CS₂ solution and sample container to the nearest 0.1 g or better. Sample volume is determined by dividing the weight of the solution by the density of the solution. Density should be corrected for hexane content if significant.

5.3.2 Gas Chromatograph Conditions. When using a column with 10 percent SP-1000 packing, use the following conditions:

Nitrogen carrier gas	20-30 cc/min.
Injection temperature	125°C
Column temperature	70°C
FID temperature	250°C

Other columns and conditions may also prove applicable.

5.3.3 Calibration. Calibration is done with solutions of known concentration of n-hexane in carbon disulfide. In analyzing samples, all isomer peaks are summed and concentrations are calculated based on the response for n-hexane.

6. Calculations

6.1 Hexane Collected. To determine the amount of hexanes collected in the impinger solution, use the following:

$$\frac{\epsilon H_{sa}}{l} \times RF \times \frac{1}{V_i} \times \frac{V_{sl}}{l} = H \text{ mg.}$$

where: ϵH_{sa} - combined area under peaks for n-hexane and isomers in sample, area units

RF - response factor for n-hexane ug injected/area unit response

V_i - volume of sample injected - ul

V_{sl} - total volume of sample solution ml

H - milligrams of hexane collected.

(Note: ug/ul is equivalent to mg/ml.)

6.2 Sample Volume. Pumps used in this method are not metered. Therefore, it is critical that the pumps be calibrated to a set sampling rate prior to each test and checked after each test to insure that the sampling rate remained the same during the test period. The volume of gas sampled is then calculated as such:

$$V_{sg} = R \text{ ml/min} \times t \text{ min} \times \frac{293}{T_i} \times \frac{P_b}{760} \times \frac{10^{-3} l}{ml}$$

where: V_{sg} - volume of gas sampled - standard liters

R - sampling rate ml/min

t - sampling period min

T_i - temperature of gas stream to pump from impinger train °K

P_b - barometric pressure mm Hg.

6.3 Source Concentration. Use the following to calculate the source concentration in part per million by volume.

$$V_H = H \text{ mg} \times \frac{10^{-3} \text{ g}}{\text{mg}} \times \frac{1 \text{ gmole}}{86.17 \text{ g}} \times \frac{24.04 \text{ l}}{\text{gmole}}$$

$$C \text{ ppm} = \frac{V_H}{V_H + V_{sg}} \times 10^6$$

- where: V_H - volume, as vapor, of collected Hexane standard liters
 H - total milligrams of hexane collected
 V_{sg} - volume of gas sampled - standard liters
 C - concentration of hexane in source - part per million by volume

SECTION II
METHODS DEVELOPMENT

The vegetable oil extraction plants have several problems with regard to developing a simple, precise and reproducible test method. The problems are as follows:

- Low flow rates through some exhaust stacks
- Explosive atmosphere in stacks and around plant
- High moisture in some emissions discharges
- Wide variation in emissions concentration
- High concentration of emissions from some ducts
- The hexane used for vegetable oil extraction varies in the amounts of isomers present.

The sample method must have the ability to remove moisture from the vent gas and be adaptable for sampling at low and high concentration of hexane. The Monsanto bag method as designed for benzene sampling could not be used in this industry due to condensation in the bag that would occur from the streams that are saturated in water vapor and/or hexane. Also, the varying concentrations would require that the sampling loop be changed on the GC and/or some bag dilution technique be developed for analyzing the different stacks.

Taking into account the high moisture content, the varying concentrations, and the explosive atmosphere, PEDCo originally proposed the sample train shown in Figure 1. After working with known concentrations to determine collection efficiencies and problems, PEDCo now proposes that the sample train be set-up as shown in Figure 2. This sample train removes the moisture and

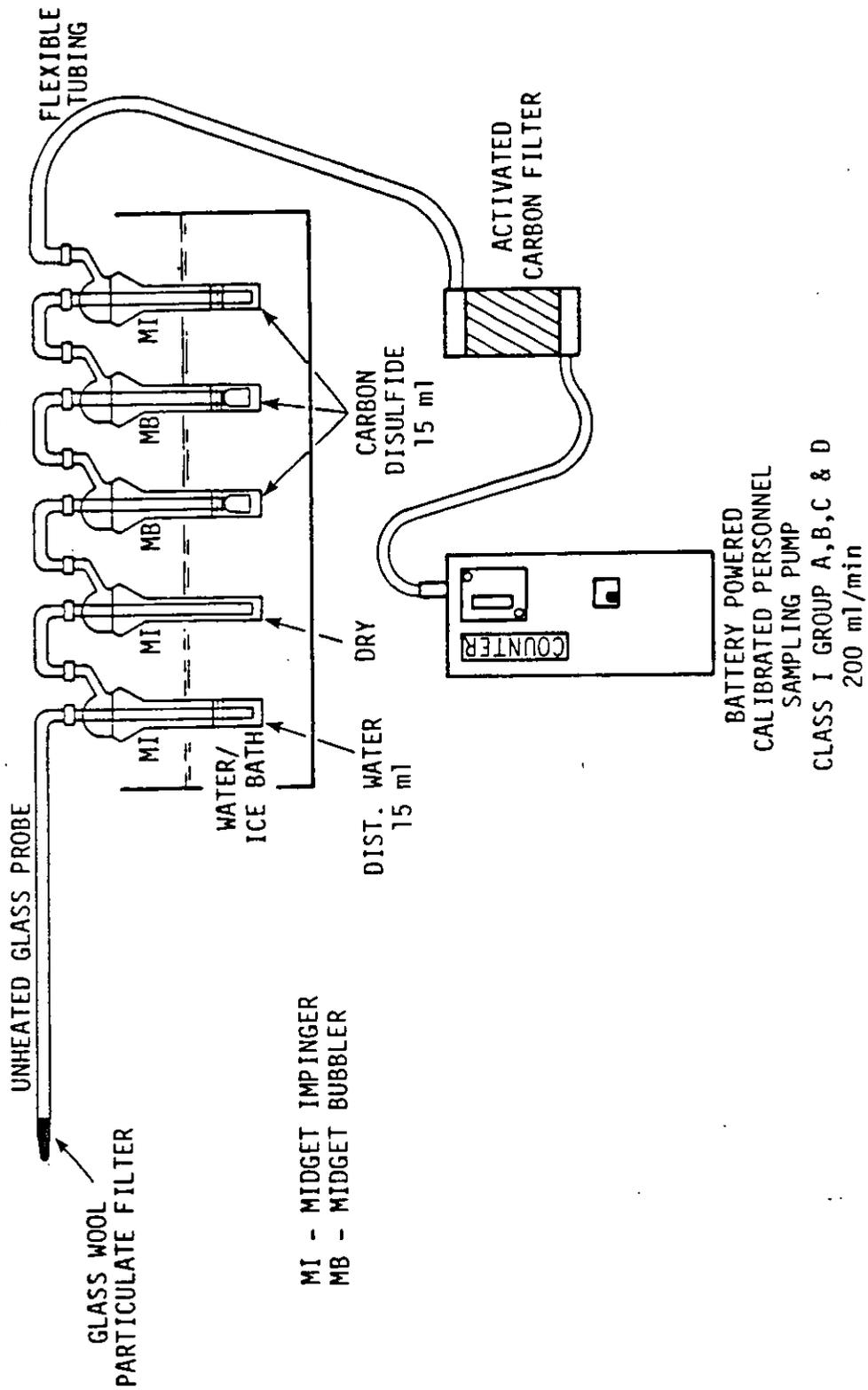


Figure 1. ORIGINAL PROPOSED HEXANE SAMPLING TRAIN

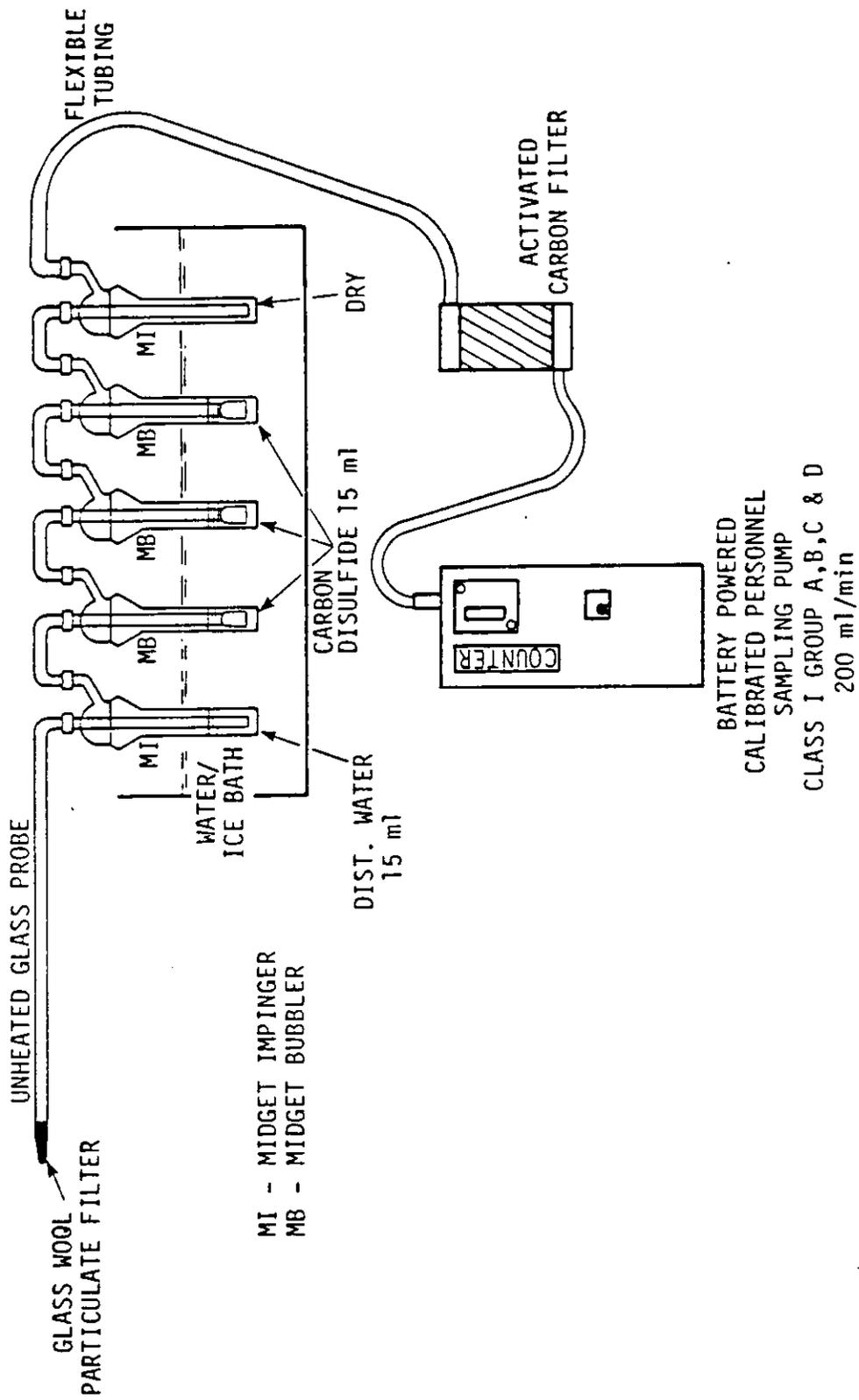


Figure 2. PROPOSED HEXANE SAMPLING TRAIN

allows flexibility of analysis on a wide range of concentrations by varying the sampling rate, the sampling time and/or the amount of liquid injected into the GC. The first impinger removes excess moisture and possibly some hexane. The next three impingers/bubblers remove in excess of 99 percent of the remaining hexane vapors. The sample recovery is performed as follows:

- 1) Add 15 ml of fresh CS₂ to the first impinger containing the water and shake.
- 2) Starting with the last impinger and proceeding to the first, pour all contents into a glass sample container. Close and replace the impingers back into the ice/water bath. Replace the lid on the container between additions.
- 3) Place 15 ml of fresh CS₂ into the last impinger and shake to remove hexane from the interior surface.
- 4) Pour the rinse solution in the last impinger into the next to last impinger and shake. Continue this procedure until all impingers have been rinsed. Then add the rinse solution to the glass sample container.
- 5) Repeat #4 with a second 15 ml of fresh CS₂.
- 6) Seal the container, mark the solution level, and label the container for transfer to the laboratory for analysis.

Recovery of the sample is the most critical step in the test procedure. Loss of hexane from the sample is most likely to occur during this step. For this reason, the sample train and sample container should be kept in an ice bath throughout the rinsing.

The proposed method gives only one sample container per run that must be analyzed. The concentration of hexane in the CS₂ portion of this container could vary over several orders of magnitude depending on the stream sampled and the sampling conditions. This does not affect the method since the FID response on the Hewlett-Packard 5830A G.C. has been shown to be linear between 500 ppm and 25,000 ppm (See Figure 3 and Table 1). If the hexane concentration

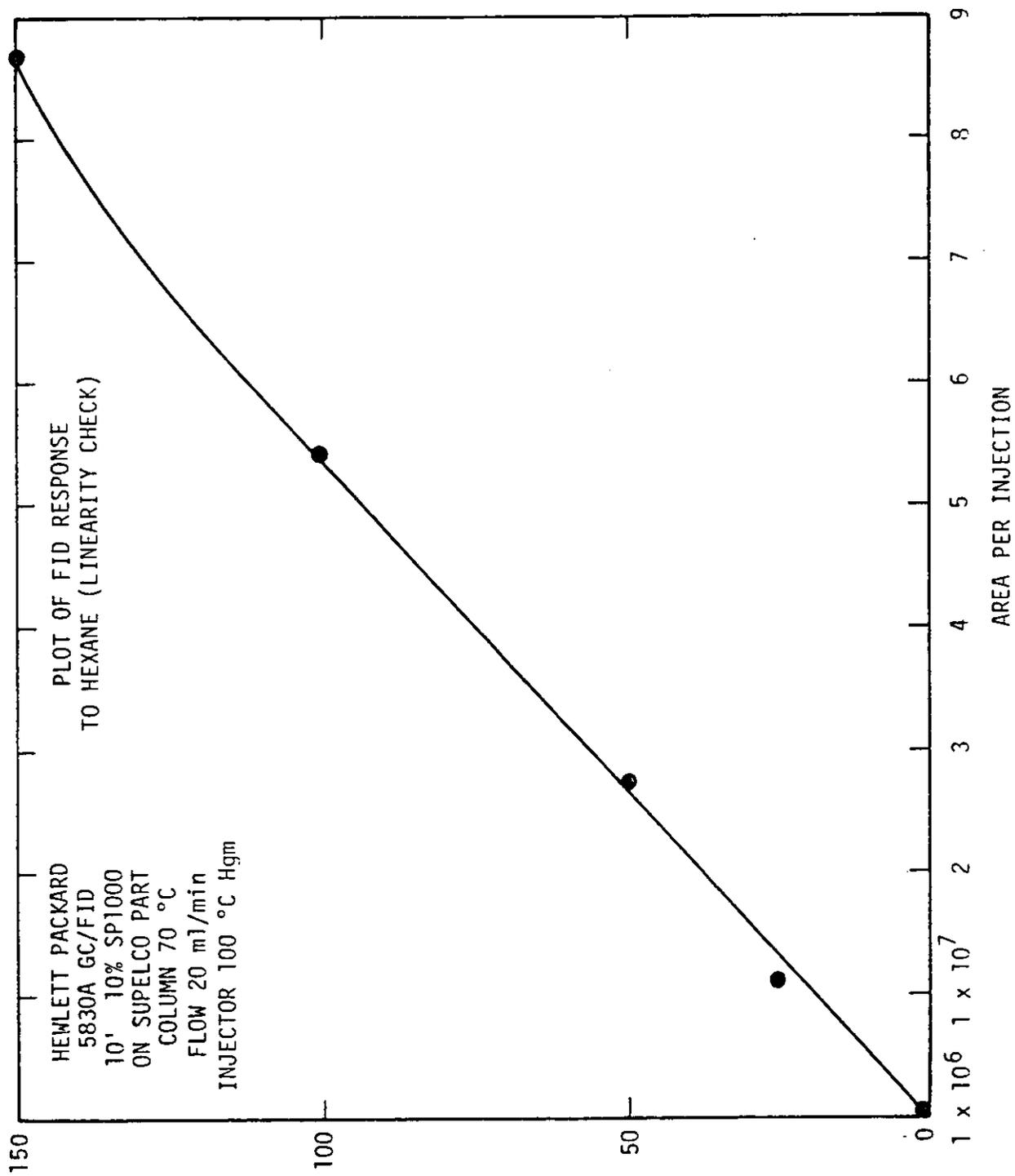


Figure 3. FID RESPONSE TO HEXANE

Table 1
Hexane Response Study Standards

Run#	ppm	µg/µl	µl inj.	Area	µg/ unit area	Area % from mean
1	500	0.3295	1.5	245,500	2.013×10^{-6}	+3.44
2	500	0.3295	1.5	225,560	2.192×10^{-6}	-4.98
3	500	0.3295	1.5	250,600	1.972×10^{-6}	+5.59
4	500	0.3295	1.5	227,700	2.171×10^{-6}	-4.06
Average				237,325	2.087×10^{-6}	
1	1000	0.659	1.5	467,400	2.115×10^{-6}	+1.60
2	1000	0.659	1.5	448,600	2.203×10^{-6}	-2.48
3	1000	0.659	1.5	464,100	2.130×10^{-6}	+0.88
Average				460,033	2.149×10^{-6}	
1	25037.94	16.5	1.5	11,180,000	2.214×10^{-6}	-0.62
2	25037.94	16.5	1.5	11,190,000	2.212×10^{-6}	-0.53
3	25037.94	16.5	1.5	11,380,000	2.175×10^{-6}	+1.15
Average				11,250,000	2.200×10^{-6}	
1	50075.87	33	1.5	27,240,000	1.817×10^{-6}	-1.01
2	50075.87	33	1.5	26,480,000	1.869×10^{-6}	-3.77
3	50075.87	33	1.5	28,720,000	1.723×10^{-6}	+4.37
4	50075.87	33	1.5	27,630,000	1.791×10^{-6}	+0.41
Average				27,517,500	1.800×10^{-6}	
1	100000	65.9	1.5	53,650,000	1.842×10^{-6}	-1.52
2	100000	65.9	1.5	57,380,000	1.723×10^{-6}	+5.33
3	100000	65.9	1.5	51,680,000	1.913×10^{-6}	-5.13
4	100000	65.9	1.5	55,200,000	1.791×10^{-6}	+1.33
Average				54,477,500	1.817×10^{-6}	
1	150,000	98.9	1.5	88,620,000	1.674×10^{-6}	+1.69
2	150,000	98.9	1.5	78,580,000	1.888×10^{-6}	-9.93
3	150,000	98.9	1.5	94,240,000	1.574×10^{-6}	+8.14
Average				87,150,000	1.712×10^{-6}	

is too high, the liquid sample can be easily diluted for analysis.

The average recovery for four trials with the original train and recovery method was 99.4 percent \pm 11.9 percent. With the new train and recovery method, the average recovery for three trials was 99.2 percent \pm 2.2 percent. These seven trials include gas samples containing 23 percent, 16 percent, and 1 percent hexane in air.

Analysis of individual impingers in the train showed that at the low concentration of hexane, only 0.3 percent of the hexane recovered was found in the first impinger while 94 percent was recovered in the second, 5 percent in the third, 0.2 percent in the fourth, and 0.02 percent in the last impinger. At the higher concentrations of hexane in air, significant amounts of hexane condensed in the first impinger. The amount in this impinger has amounted to as much as 70 percent of the total hexane recovered. This is not unexpected. This condensation of liquid hexane is why fresh CS₂ is added to the first impinger before the contents are transferred to the sample container. The CS₂ should reduce any loss of hexane due to evaporation. The amount of hexane collected in the other impingers of the train decreases to a value no higher than 0.2 percent of the total in the last impinger even at the highest concentration of hexane in air.

The apparatus shown in Figure 2.2 was used to determine the amount of hexane which passes through the impinger train during a sampling run. Laboratory tests were conducted with source concentrations of 91.4 ppm and 85,866 ppm or 8.59 percent by volume

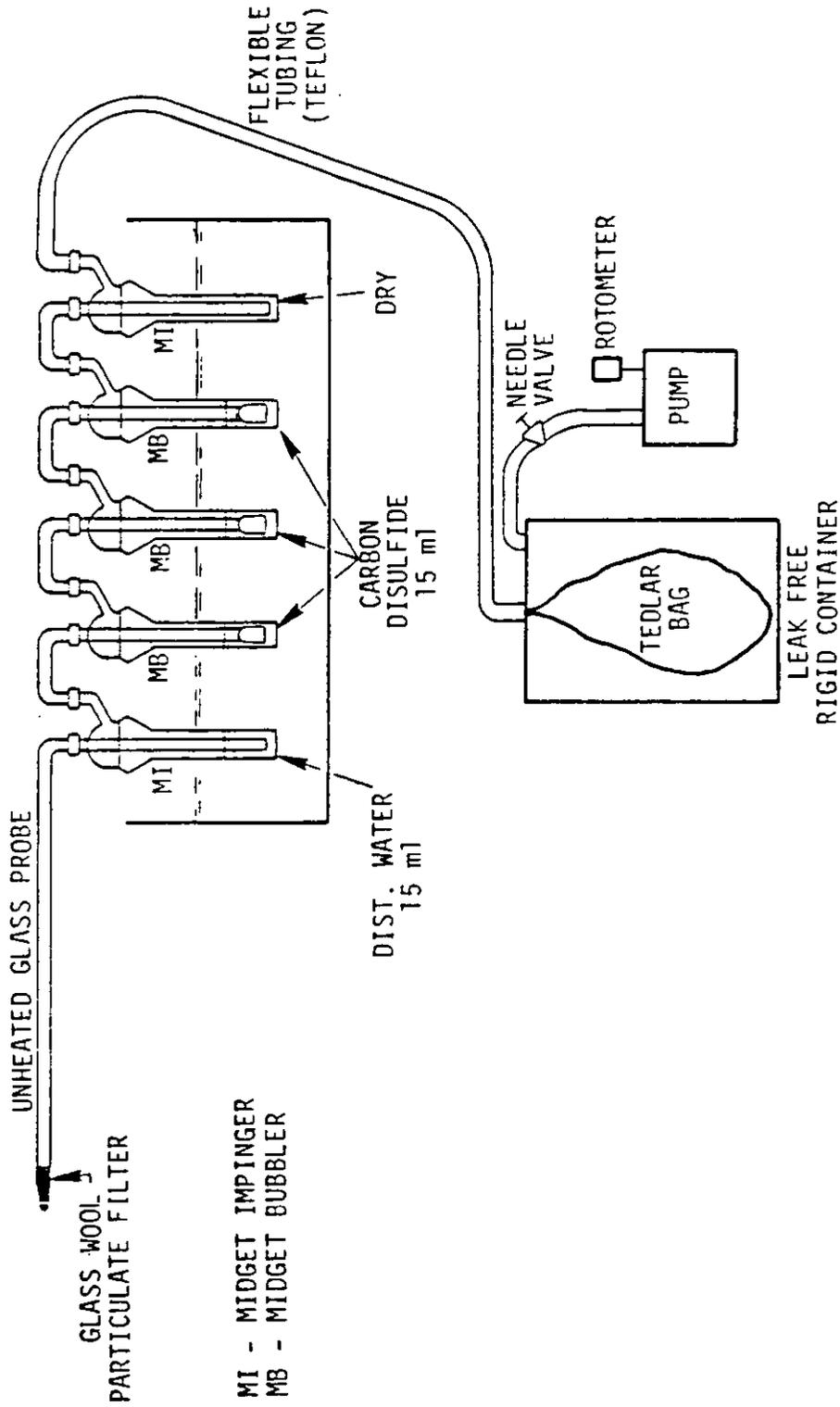


Figure 2.2. COLLECTION EFFICIENCY SAMPLING TRAIN

n-hexane. The collection efficiency was calculated by comparing the amount of hexane collected in the bag to the amount collected in the impinger train sample. Three tests were run with each of the source concentrations. The average collection efficiency for all six tests was 99.61 percent \pm 0.35 percent. One field study was conducted with this apparatus. In seven tests from sources with concentrations ranging from 58 ppm to 95,800 ppm, the average collection efficiency was 98.31 percent \pm 1.82 percent with a range in values of 94.95 percent to 99.39 percent.

The amount of hexane dissolved in water contained in the sample bottle is insignificant. The results of a study on the distribution of hexane between water and carbon disulfide showed that an average of only 0.010 percent \pm 0.003 percent of recovered hexane remained in the aqueous layer. The average recovery in the CS₂ layer was 99.7 percent \pm 6.8 percent. The values represent triplicate determinations at two different concentrations. Each determination used 20 ml of water and 30 ml of CS₂. Three contained 30 μ l of hexane, the other three contained 300 μ l of hexane.

Stability of carbon disulfide solutions of hexane has been determined to be stable over a period of four days at least. Three 60 ml bottles with screw teflon coated septum tops containing 25 ml of a solution of 1 μ l hexane per ml were prepared. Their concentrations versus a standard were found to be 99.2 percent \pm 1.9 percent of the listed value on the day prepared. The following day the samples were found to contain 98.8 percent \pm 3.0 percent of the listed values. On day four, the samples were found to

contain 102.7 percent \pm 8.8 percent of the listed values. This may represent some loss of solvent by evaporation thru the punctures in the septa.

In a field study, 19 samples, analyzed on site, were reanalyzed in the laboratory two weeks later. The values of concentration obtained in the laboratory were 105.5 percent \pm 7.72 percent of the on site analysis. The fact that both lab samples and field samples tend to become more concentrated with time, suggests that some solvent is being lost. However, the amount of carbon disulfide lost is not necessarily equal to the percent difference in concentration. The accuracy of the analytical procedure is estimated to be \pm 5 percent.

A Hewlett Packard 5830-A G.C. with FID detector and a microprocessor was used for analysis. The column was a 10 ft. x 1/8 in. stainless steel containing 10 percent SP 1000 on 80/100 supelcoport. The conditions were inj. 125°C, column 70°C, FID 250°C, and a flow of 20 ml/min of nitrogen.

Standard bag samples are prepared by injecting a known quantity of 99+ percent n-hexane into the heated impinger in the apparatus shown in Figure 4. The volume, temperature and pressure are measured at the meter. The concentration is calculated as follows:

$$C_s = \frac{X(0.6603 \frac{\text{mg}}{\mu\ell}) \left(\frac{10^3 \mu\text{g}}{\text{mg}}\right) \left(\frac{\mu\text{g}\cdot\text{mole}}{86.17 \mu\text{g}}\right) \left(\frac{24.055 \mu\ell}{\mu\text{g}\cdot\text{mole}}\right)}{Y\left(\frac{10^6 \mu\ell}{\ell}\right) \left(\frac{293}{T_m}\right) \left(\frac{P_m}{760}\right)} \times 10^6$$

$$C_s = \frac{X(184.3)}{Y\left(\frac{293}{T_m}\right) \left(\frac{P_m}{760}\right)}$$

C_s = The hexane concentration in ppm

X = The number of $\mu\ell$ of hexane injected

Y = The dry gas meter reading, liters

P_m = The absolute pressure of the dry gas meter, mmHg

T_m = The absolute temperature of the dry gas meter, $^{\circ}\text{K}$

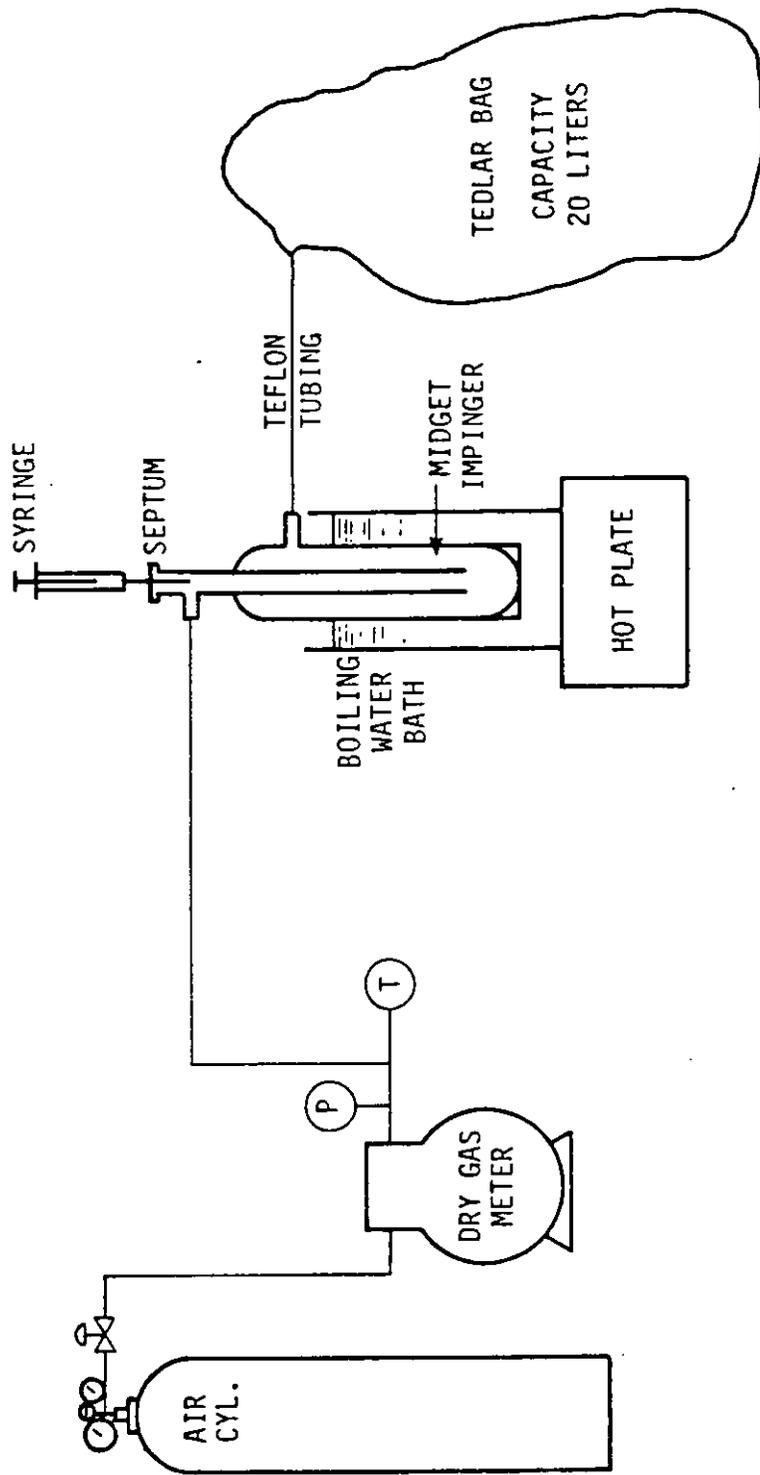


Figure 4. HEXANE STANDARD GAS PREPARATION

particular, more data is needed to validate the reproducibility of the results from test to test. This could be done by running two or more tests simultaneously or by repeated trials on a source with a consistent concentration.