α-Chloroacetophenone*

Measurements Research Branch

Analytical Method

Analyte:	α-Chloroacetophenone	Method No.:	P&CAM 291
Matrix:	Air	Range:	0.18-0.62 mg/cu m
Procedure:	Adsorption on Tenax GC, thermal desorption, GC/FID	Precision:	0.061
		Classification:	E (Proposed)
Date Issued:	9/22/78		
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1. Synopsis

1.1 A known volume of air is drawn through two glass tubes in series containing Tenax GC to trap α-chloroacetophenone vapors.

1.2 The sample is thermally desorbed from the Tenax GC, and the α-chloroacetophenone is analyzed by gas chromatography with a flame ionization detector.

2. Working Range, Sensitivity, and Detection Limit

2.1 This method was evaluated over the range of 0.18-0.62 mg/cu m at an average atmospheric temperature of 23°C and atmospheric pressure of 763 mm Hg, using a 12-liter sample. The method may be capable of measuring smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.

2.2 The upper limit of the range of the method depends on the adsorptive capacity of the Tenax GC. This capacity may vary with the concentrations of α-chloroacetophenone and other substances in the air. Breakthrough is defined as the time that the effluent concentration from the collection tube (containing 35 mg of Tenax GC) reaches 5% of the concentration in the test gas mixture. Breakthrough did not occur after sampling for 3.5 hours at an average sampling rate of 0.183 liter/minute and relative humidity of 87% and temperature of 23°C. The breakthrough test was conducted at a concentration of 0.778 mg/cu m.

*Phenacylchloride

3 Under the instrumental conditions used in the study, a 2-microliter injection of 0.958 microgram/microliter α-chloroacetophenone solution spiked onto 35 mg of Tenax GC and thermally desorbed resulted in a peak whose height was 30% of full scale on a 1 millivolt recorder. The amplifier of the gas chromatograph was set on range 100 and attenuation 8.

The detection limit of the method is estimated to be 20 ng of α-chloroacetophenone.

3. Interferences

3.1 When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.

Any compound that has the same retention time as α-chloroacetophenone at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.

4. Precision and Accuracy

The Coefficient of Variation for the total analytical and sampling method in the range of 0.18-0.62 mg/cu m was 0.061. This value corresponds to a 0.02 mg/cu m standard deviation at 0.05 ppm (0.3 mg/cu m). Statistical information can be found in Reference 11.1. Details of the test procedures are found in Reference 11.2.

The accuracy of this method has not been determined. In the studies, a reliable independent measure of dynamically generated test atmospheres was not found. The desorption efficiency was determined to be 1.034 for a collector loading of 1.916 microgram. In storage stability studies, the mean of samples analyzed after 7 days were within 1.2% of the mean of samples analyzed immediately after collection. Experiments performed in the study are described in Reference 11.2.

Advantages and Disadvantages

5 1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those that occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

5.2 One disadvantage of the method is that the amount of sample that can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of α-chloroacetophenone found on the backup Tenax GC tube exceeds 25% of that found on the front tube, the probability of sample loss exists.

The precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate

and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

Personal Sampling Pump. A calibrated personal sampling pump whose flow rate can be determined within 5% at the recommended flow rate.

Tenax GC Tubes. Separate front and backup sampling tubes are used in this method. The tubes are constructed of glass tubing with both ends unsealed. The tubes are 13 cm long with a 6-mm O.D. and a 4-mm I.D. The front tube contains 35 mg of 35/60 mesh Tenax GC*, and the backup tube contains 17 mg. Tenax GC is held in place in the tube with 3-mm plugs of glass wool. The Tenax GC is placed within 4 cm of one end of the tube. The sample tube length may need to be adjusted to accommodate the GC inlet. The pressure drop across the tubes must be less than 10 mm of mercury at a flow rate of 0.2 liter/minute.

Immediately prior to packing, the empty glass tubes should be acetone rinsed and dried to eliminate the problem of Tenax GC adhering to the walls of the glass tubes. Before use, each tube must be thermally desorbed for 3 minutes at 285°C using nitrogen flow through the tube to rid the Tenax GC of any interfering substances. The front and backup tubes are joined together with a short piece of flexible tubing, and the ends of the sampling train are capped with plastic caps on the tubes.

Thermal Desorption Apparatus. This apparatus is designed to use the gas chromatograph inlet heater as the source of heat for thermal desorption. The inlet should have an opening of at least 6 mm in diameter and be deep enough to allow the sample tube to be inserted. The apparatus consists of three parts as illustrated in Figures 291-1 and 291-2.

6.3.1 Sample Tube Holder (Figure 291-1A). This assembly is composed of a Swagelok Quick-Connect** stem (stainless steel #QC6-S-600) with a 3/8-in tube fitting on the opposite end. The fitting is drilled out to allow the 6-mm O.D. sample tube to pass through it. A Teflon tube (4 cm long with a 3/8-in O.D. and 5.5 mm I.D.) connects the stem to a 3/8 in to 1/4 in tube fitting reducer. Teflon ferrules are used with the connecting nuts to hold the Teflon tube. The sample tube is inserted through the stem and into the Teflon tube. Tightening the connecting nut to finger tightness secures the sample tube in place. The Teflon tube may have to be replaced after excessive use.

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*Tenax GC is a solid adsorbent manufactured by Enka, N.V., The Netherlands. It is available through most gas chromatographic equipment suppliers.

**Patented by Crawford Fitting Company.

6.3.2 Gas Chromatograph Inlet Fitting (Figure 291-1B). This assembly consists of a Swagelok Quick-Connect body (stainless steel #QC6-B-4PF) which has been rethreaded to fit onto the gas chromatograph injection port. The ball and spring in the body must be removed to allow the sample tube to pass through. This fitting replaces the septum nut. Other injector parts that interfere with insertion of the sample tube must be removed.

The inlet fitting is sealed to the injection port with a Teflon gasket.

6.3.3 Valves and Carrier Gas Lines (Figure 291-2). The flow of carrier gas is regulated by a system incorporating two needle valves and two 3-way valves. The carrier gas is split into two lines regulated by needle valves. When a sample tube is being thermally desorbed, the majority of carrier gas flows through the sample tube. A minor flow enters at the normal GC inlet port to allow additional carrier gas to flow over the sample tube. Three-way valve #1 is used to split the carrier flow as described above or route the entire flow to the inlet port for normal use of the GC or injection of standards. Three-way valve #2 is used to vent the carrier flow when the sample tube holder is being loaded with a sample tube. It is also used to relieve pressure before disconnecting the desorber from the inlet after a sample is analyzed. A 0.02-in flow limiting orifice is placed at the valve #2 vent so that pressure is relieved slowly. Sudden changes in pressure may disrupt the gas chromatographic column packing or the sorbent in the sample tube. The thermal desorption assembly is connected to valve #2 with a 1/4-in O.D. Teflon tubing.

6.4 Gas chromatograph equipped with a flame ionization detector.

Column (10 ft long x 1/8-in O.D. stainless steel) packed with 5% OV-17 on 80/100 mesh Chromosorb W DMCS.

An electronic integrator or some other suitable method of determining peak areas.

Microliter Syringes: 10-microliter and other convenient sizes for preparing standards.

Pipets: Delivery type, 1.0-mL and other convenient sizes.

6.9 Volumetric Flasks: 10-mL and other convenient sizes for preparing standard solutions.

6.10 Stopwatch.

6.11 Manometer.

7. Reagents

All reagents used must be ACS reagent grade or better.

7.1 α-Chloroacetophenone.

7.2 Hexane

7.3 Stock Standard α-Chloroacetophenone Solution. Weigh out 354 mg of α-chloroacetophenone and dilute to 100 mL with hexane.

7.4 Nitrogen, purified

7.5 Hydrogen, prepurified.

7.6 Air, filtered, compressed.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed, thoroughly rinsed with tap water and distilled water, and dried.

Calibration of Sampling Pumps. Each personal sampling pump must be calibrated with representative Tenax GC tubes in the line to minimize errors associated with uncertainties in the volume sampled.

Collection and Shipping of Samples

8.3.1 Immediately before sampling, remove the caps from the ends of the Tenax GC tubes. All tubes must be packed with Tenax GC from the same manufacturer's lot.

8.3.2 The tube containing the smaller amount of Tenax GC is used as a backup tube and should be positioned nearer the sampling pump. Air should flow through the front tube before entering the backup tube.

8.3.3 The tubes should be placed in a vertical direction during sampling to minimize channeling through the Tenax GC.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the Tenax GC tubes.

8.3.5 A sample size of 12 liters is recommended. Sample at a flow rate between 0.01 and 0.2 liter/minute. Do not sample at a flow rate less than 0.010 liter/minute. Record sampling time, flow rate, and type of sampling pump used.

8.3.6 Set the flow rate of the sampling pump as accurately as possible using the manufacturer's directions. The temperature, pressure, and relative humidity of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The Tenax GC tubes should be separated and capped individually with plastic caps immediately after sampling. Under no circumstances should rubber caps be used. Each set of tubes should be marked to identify the front Tenax GC tube with its corresponding backup tube.

8.3.8 With each batch or partial batch of 10 samples, submit one set of tubes (a front adsorbing tube containing 35 mg of Tenax GC and a backup tube containing 17 mg of Tenax GC) from the same lot of tubes used for sample collection. These tubes must be subjected to exactly the same handling as the samples except that no air is drawn through them. These tubes should be labeled as the blanks.

8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.

8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap or equivalent. This sample should not be transported in the same container as the Tenax GC tubes. A minimum of 18 extra Tenax GC front and backup tubes should be provided for desorption efficiency determinations.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. Remove the caps from the ends of the sample tube. Wipe off the outside of the tube with a clean lab wiper.

8.4.2 Thermal Desorption of Samples

1. Place auxillary valves in position so that the carrier gas is split between the sample tube holder and the inlet (valve #1 dividing flow) and so that flow to the sample tube holder is vented (valve #2 open to vent). Valves are in "load/vent mode" (see Figure 291-2).

2. Load the sample tube holder by inserting the sample tube through the stem and just into the Teflon tube with the connecting nut loose. Tighten the connecting nut to finger tightness to secure the sample tube in place. The sorbent material should be at the end opposite the connecting nut.

3. Insert the sample tube into the gas chromatograph inlet, joining the stem of the sample tube holder to the body of the gas chromatograph inlet fitting.

4. Turn the carrier gas valve #2 to allow the carrier gas to pass through the sample tube. Valves are in "desorption mode" (see Figure 291-2).

5. Allow the sample to thermally desorb for 3 minutes at an inlet temperature of 285°C onto the head of the GC column which is set at 95°C.

6. Program the column oven temperature from 95°C to 150°C at a rate of 15°C/minute.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are the following.

40 mL/min nitrogen carrier gas flow through sample tube holder

30 mL/min nitrogen carrier gas flow to GC inlet

50 mL/min hydrogen gas flow to detector; 500 mL/min (50 psig) air flow to detector

8.4.4 The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of Tenax GC to another. Thus, it is necessary to determine the fraction of the specific compound that is removed in the desorption process for a particular batch of Tenax GC.

8.5.2 Tenax GC sample tubes containing 35 mg of Tenax GC from the same batch as that used in obtaining the samples are used to determine the desorption efficiency. A known amount of a hexane solution of α-chloroacetophenone is injected directly onto the Tenax GC with a microliter syringe, and the tube is capped. The amount injected is equivalent to that present in a 12-liter air sample at the selected level. The solutions of α-chloroacetophenone in hexane are prepared so that the amount injected is no more than 8.0 microliters.

Six tubes at each of three levels (0.5X, 1X, and 2X the OSHA standard) are prepared and allowed to stand for at least overnight to assure complete adsorption of the α-chloroacetophenone onto the Tenax GC. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are thermally desorbed and analyzed in exactly the same manner as the sampling tubes described in Section 8.4.

Standards are prepared by spiking the same amount of the hexane solution of α-chloroacetophenone used for spiking samples above onto 35 mg of Tenax GC and thermally desorbing immediately

Standards are desorbed as in Section 8.4.2.

The desorption efficiency (D.E.) equals the average weight in μg recovered from the tube divided by the weight in μg added to the tube, or

$$D.E. = \frac{\text{Average Weight recovered } (\mu g)}{\text{Weight added } (\mu g)}$$

The desorption efficiency is dependent on the amount of α-chloroacetophenone collected from the Tenax GC. Plot the desorption efficiency versus weight of α-chloroacetophenone found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standardization

A series of standards, varying in concentration over the range corresponding to approximately 0.1 to 3 times the OSHA standard for the sample under study, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in μg/sample versus peak area. Standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

9.1 From the stock standard solution (Section 7.3), appropriate aliquots are withdrawn and dilutions are made in hexane. Prepare at least 5 working standards to cover the range of 0.4-10 micrograms/sample. This range is based on a 12-liter sample and 4-microliter injections.

Standards are prepared by spiking 4 microliters of the standard solution onto 35 mg of Tenax GC and thermally desorbing immediately.

Prepare a standard calibration curve by plotting μg/sample versus peak area.

10. Calculations

10.1 Read the weight, in μg, corresponding to each peak area from the standard curve.

10.2 Corrections for the blank must be made for each sample.

$$\mu g = \mu g \text{ sample} - \mu g \text{ blank}$$

where:

μg sample = μg found in front sample tube
μg blank = μg found in front blank tube

A similar procedure is followed for the backup tubes.

10.3 Add the weights found in the front and backup tubes to determine the total weight of the sample.

10.4 Read the desorption efficiency from the curve (Section 8.5.2) for the amount found in the front tube. Divide the total weight by this desorption efficiency to obtain the corrected μg/sample.

$$\text{Corrected } \mu g/\text{sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 For personal sampling pumps with rotameters only the following correction should be made.

$$\text{Corrected Volume} = f \times t \left(\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}\right)$$

where:

f	=	flow rate sampled (liters/min)
t	=	sampling time (minutes)
P_1	=	pressure during calibration of sampling pump (mm Hg)
P_2	=	pressure of air sampled (mm Hg)
T_1	=	temperature during calibration of sampling pump (°K)
T_2	=	temperature of air sampled (°K)

10.6 The concentration of α-chloroacetophenone in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \mu g/\text{liter} = \frac{\text{Corrected } \mu g \text{ (Section 10.4)}}{\text{Corrected air volume sampled (L) (Section 10.5)}}$$

10.7 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{P} \times \frac{T + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liters/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of α-chloroacetophenone
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 Documentation of NIOSH Validation Tests, National Institute for Occupational Safety and Health, Cincinnati, Ohio (DHEW-NIOSH-Publication #77-185), 1977. Available from Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., Order No. 017-033-00231-2.

11 2 Backup Data Report No. 291 for α-Chloroacetophenone, prepared under NIOSH Contract No. 210-76-0123.

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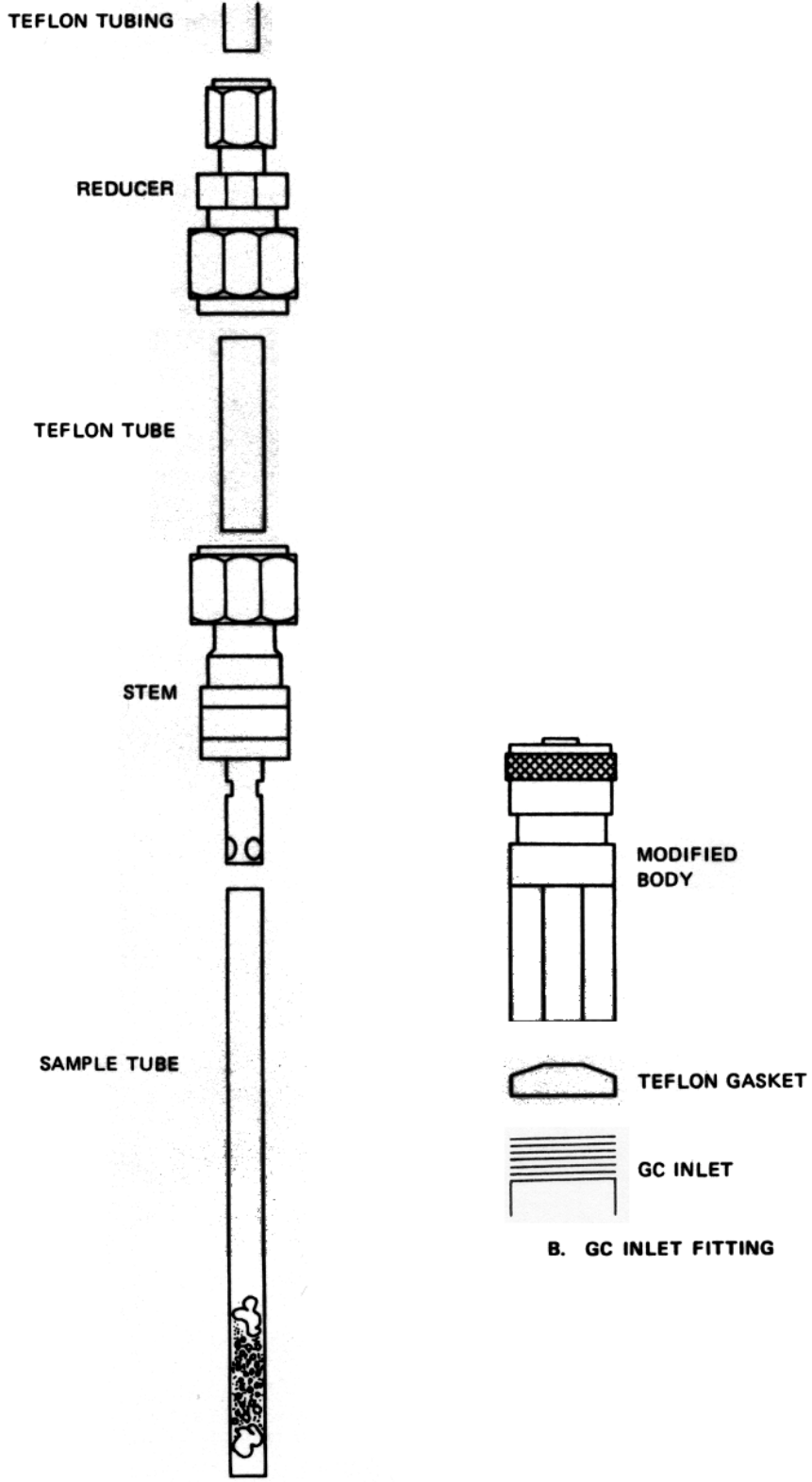
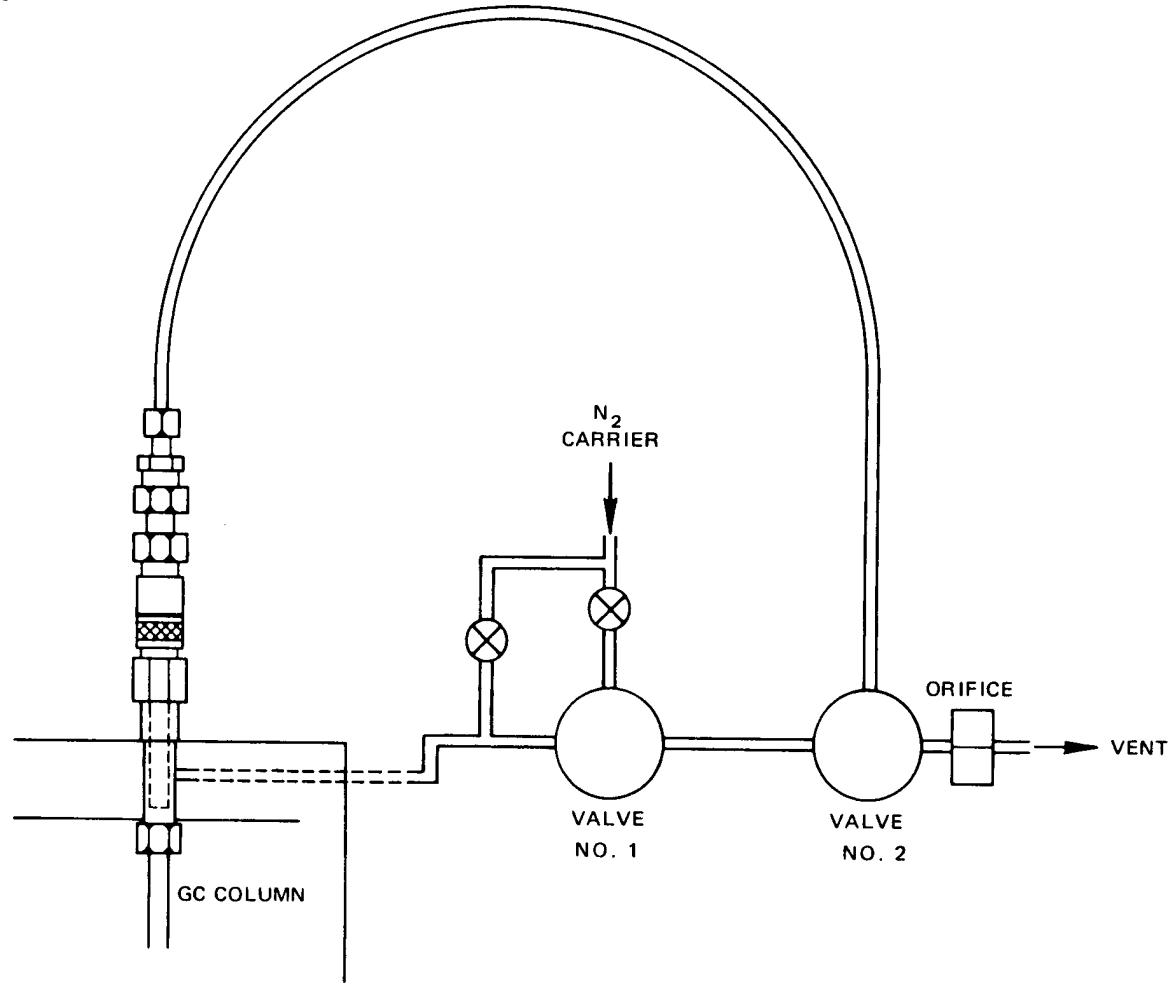


A. SAMPLE TUBE HOLDER

B. GC INLET FITTING

Figure 291-1



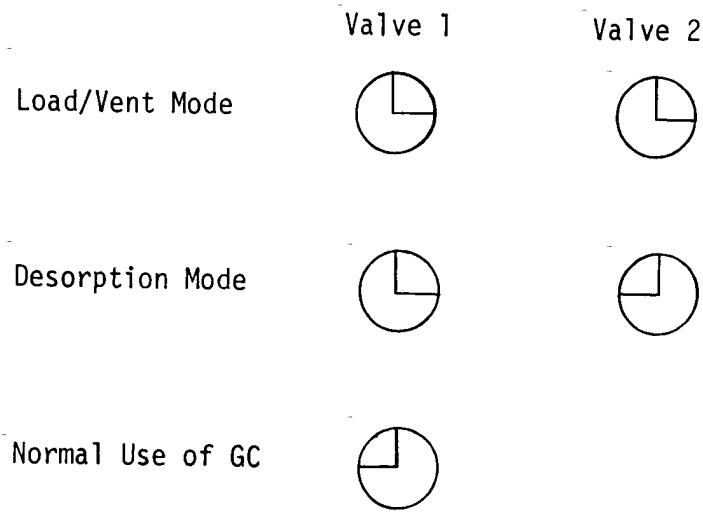


Figure 291-2 VALVES AND CARRIER GAS LINES