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Method 602: Purgeable Aromatics

APPENDIX A TO PART 136
METHODS FOR ORGANIC CHEMICAL ANALYSIS OF MUNICIPAL AND INDUSTRIAL WASTEWATER

METHOD 602—PURGEABLE AROMATICS

1. Scope and Application

1.1 This method covers the determination of various purgeable aromatics. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Benzene	34030	71-43-2
Chlorobenzene	34301	108-90-7
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
Ethylbenzene	34371	100-41-4
Toluene	34010	108-88-3

1.2 This is a purge and trap gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR Part 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 624 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above.

1.3 The method detection limit (MDL, defined in Section 12.1)[1] for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR Parts 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5 mL water sample contained in a specially-designed purging chamber at ambient temperature. The aromatics are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the aromatics are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the aromatics onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the aromatics which are then detected with a photoionization detector.[2,3]

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from interferences that may occur.

3. Interferences

3.1 Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high aromatic levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in an oven at 105˚C between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[4-6] for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene and 1,4-dichlorobenzene. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25 mL capacity or larger, equipped with a screw cap with a hole in the center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105°C for one hour before use.

5.2 Purge and trap system—The purge and trap system consists of three separate pieces of equipment: A purging device, trap, and desorber. Several complete systems are now commercially available.

5.2.1 The purging device must be designed to accept 5 mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device illustrated in Figure 1 meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in.

5.2.2.1 The trap is packed with 1 cm of methyl silicone coated packing (Section 6.4.2) and 23 cm of 2,6-diphenylene oxide polymer (Section 6.4.1) as shown in Figure 2. This trap was used to develop the method performance statements in Section 12.

5.2.2.2 Alternatively, either of the two traps described in Method 601 may be used, although water vapor will preclude the measurement of low concentrations of benzene.

5.2.3 The desorber must be capable of rapidly heating the trap to 180˚C. The polymer section of the trap should not be heated higher than 180˚C and the remaining sections should not exceed 200°C. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge and trap system may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3, 4, and 5.

5.3 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.3.1 Column 1 - 6 ft long x 0.082 in. ID stainless steel or glass, packed with 5% SP1200 and 1.75% Bentone-34 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 12. Guidelines for the use of alternate column packings are provided in Section 10.1.

5.3.2 Column 2 - 8 ft long x 0.1 in ID stainless steel or glass, packed with 5% 1,2,3-Tris (2-cyanoethoxy)propane on Chromosorb W-AW (60/80 mesh) or equivalent.

5.3.3 Detector—Photoionization detector (h-Nu Systems, Inc. Model PI-51-02 or equivalent). This type of detector has been proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 12. Guidelines for the use of alternate detectors are provided in Section 10.1.

5.4 Syringes— 5 mL glass hypodermic with Luerlok tip (two each), if applicable to the purging device.

5.5 Micro syringes—25 µL, 0.006 in. ID needle.

5.6 Syringe valve—Two-way, with Luer ends (three each).

5.7 Bottle—15 mL, screw-cap, with Teflon cap liner.

5.8 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water— Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon (Filtrasorb-300, Calgon Corp., or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, 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 and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Hydrochloric acid (1+1)—Add 50 mL of concentrated HCl (ACS) to 50 mL of reagent water.

6.4 Trap Materials

6.4.1 2,6-Diphenylene oxide polymer—Tenax, (60/80 mesh), chromatographic grade or equivalent.

6.4.2 Methyl silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.5 Methanol-Pesticide quality or equivalent.

6.6 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

6.6.1 Place about 9.8 mL of methanol into a 10 mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.6.2 Using a 100 µL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

6.6.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in µg/µL from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.6.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4°C and protect from light.

6.6.5 All standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

6.7 Secondary dilution standards—Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.3.1 or 7.4.1 will bracket the working range of the analytical system. Secondary solution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.8 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 minutes once daily prior to use.

7.2 Connect the purge and trap system to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate conditions equivalent to those given in Table 1. Calibrate the purge and trap-gas chromatographic system using either the external standard technique (Section 7.3) or the internal standard technique (Section 7.4).

7.3 External standard calibration procedure

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µL of one or more secondary dilution standards to 100 mL, 500 mL, or 1000 mL of reagent water. A 25 µL syringe with a 0.006 in. ID needle should be used for this operation. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.3.2 Analyze each calibration standard according to Section 10, and tabulate peak height or area responses versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.4 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compound, α,α,α,-trifluorotoluene, recommended as a surrogate spiking compound in Section 8.7 has been used successfully as an internal standard.

7.4.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.3.1.

7.4.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 6.6 and 6.7. It is recommended that the secondary dilution standard be prepared at a concentration of 15 µg/mL of each internal standard compound. The addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 µg/L.

7.4.3 Analyze each calibration standard according to Section 10, adding 10 µL of internal standard spiking solution directly to the syringe (Section 10.4). Tabulate

peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using Equation 1.

Equation 1

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard.
C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s / A_{is}, vs. concentration rario C_s / C_{is}.

7.5 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of a QC check sample.

7.5.1 Prepare the QC check sample as described in Section 8.2.2.

7.5.2 Analyze the QC check sample according to Section 10.

7.5.3 For each parameter, compare the response (Q) with the corresponding calibration acceptance criteria found in Table 2. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual Q falls outside the range, a new calibration curve, calibration factor, or RF must be prepared for that parameter according to Section 7.3 or 7.4.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 10 µg/mL in methanol. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Prepare a QC check sample to contain 20 µg/L of each parameter by adding 200 µL of QC check sample concentrate to 100 mL of reagent water.

8.2.3 Analyze four 5 mL aliquots of the well-mixed QC check sample according to Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter of interest using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all

parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

NOTE: The large number of parameters in Table 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.3.

8.2.6.2 Beginning with Section 8.2.3, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.3.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to 10 samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or one to five times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 20 µg/L or one to five times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.2 Analyze one 5 mL sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second 5 mL sample aliquot with 10 µL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100(A-B)%/T, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be

accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[7] If spiking was performed at a concentration lower than 20 µg/L, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (X′) using the equation in Table 3, substituting the spike concentration (T) for C; (2) calculate overall precision (S′) using the equation in Table 3, substituting X′ for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as (100 X′/T) ±2.44(100 S′/T)%.[7]

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 10 µL of QC check sample concentrate (Section 8.2.1 or 8.3.2) to 5 mL of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}$=90% and s_p=10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each parameter on a regular basis (e.g., after each 5-10 new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas

chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.7 The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with surrogate compounds (e.g.,α,α,α,-trifluorotoluene) that encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 6.6, add a volume to give 750 µg of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix and dilute to volume for a concentration of 15 mg/µL. Add 10 µL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. Prepare a fresh surrogate spiking solution on a weekly basis. If the internal standard calibration procedure is being used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 7.4.2).

9. Sample Collection, Preservation, and Handling

9.1 The samples must be iced or refrigerated from the time of collection until analysis. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottle just prior to shipping to the sampling site. EPA Method 330.4 or 330.5 may be used for measurement of residual chlorine.[8] Field test kits are available for this purpose.

9.2 Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding 1+1 HCl while stirring. Fill the sample bottle in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 All samples must be analyzed within 14 days of collection.[3]

10. Procedure

10.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and MDL that can be achieved under these conditions. An example of the separations achieved by Column 1 is shown in Figure 6. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

10.2 Calibrate the system daily as described in Section 7.

10.3 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device, and set the purge and trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

10.4 Allow the sample to come to ambient temperature prior to introducing it to the syringe. Remove the plunger from a 5 mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just

short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 µL of the surrogate spiking solution (Section 8.7) and 10.0 µL of the internal standard spiking solution (Section 7.4.2), if applicable, through the valve bore, then close the valve.

10.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

10.6 Close both valves and purge the sample for 12.0 ± 0.1 minute at ambient temperature.

10.7 After the 12-minute purge time, disconnect the purging device from the trap. Dry the trap by maintaining a flow of 40 mL/min of dry purge gas through it for six minutes (Figure 4). If the purging device has no provision for bypassing the purger for this step, a dry purger should be inserted into the device to minimize moisture in the gas. Attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 5), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 mL/min for four minutes. If rapid heating of the trap cannot be achieved, the GC column must be used as a secondary trap by cooling it to 30°C (subambient temperature, if poor peak geometry and random retention time problems persist) instead of the initial program temperature of 50°C.

10.8 While the trap is being desorbed into the gas chromatograph column, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5 mL flushes of reagent water.

10.9 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.10 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.11 If the response for a peak exceeds the working range of the system, prepare a dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

11. Calculations

11.1 Determine the concentration of individual compounds in the sample.

11.1.1 If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the peak response using the calibration curve or calibration factor determined in Section 7.3.2.

11.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.4.3 and Equation 2.

Equation 2

$$\text{Concentration } (\mu g/L) = \frac{(A_s)\ (C_{is})}{(A_{is})\ (RF)}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard.

11.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[1] The MDL concentrations listed in Table 1 were obtained using reagent water.[9] Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.2 This method has been demonstrated to be applicable for the concentration range from the MDL to 100 x MDL.[9] Direct aqueous injection techniques should be used to measure concentration levels above 1000 x MDL.

12.3 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1-550 µg/L.[9] Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

References

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7. Provost, L.P. and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, *15*, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3. is two times the value 1.22 derived in this report.)

8. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268. March 1979.

9. "EPA Method Study 25, Method 602, Purgeable Aromatics," EPA 600/4-84-042, National Technical Information Service, PB84-196682, Springfield, Virginia 22161, May 1984.

Table 1—Chromatographic Conditions and Method Detection Limits

Parameter	Retention time (min)		Method detection limit (µg/L)
	Column 1	Column 2	
Benzene	3.33	2.75	0.2
Toluene	5.75	4.25	0.2
Ethylbenzene	8.25	6.25	0.2
Chlorobenzene	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4

Column 1 conditions: Supelcoport (100/120 mesh) coated with 5% SP-1200/1.75% Bentone-34 packed in a 6 ft x 0.085 in ID stainless steel column with helium carrier gas at 36 mL/min flow rate. Column temperature held at 50°C for two minutes then programmed at 6°C/min to 90°C for a final hold.

Column 2 conditions: Chromosorb W–AW (60/80 mesh) coated with 5% 1,2,3-Tris(2-cyanoethyoxy) propane packed in a 6 ft x 0.085 in ID stainless steel column with helium carrier gas at 30 mL/min flow rate. Column temperature held at 40°C for two minutes then programmed at 2°C/min to 100°C for a final hold.

Table 2—Calibration and QC Acceptance Criteria-Method 602[a]

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P_s (%)
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in µg/L (Section 7.5.3).
$\bar{s}$ = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).
P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).
[a]Criteria were calculated assuming a QC check sample concentration of 20 µg/L.

NOTE: These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

Table 3—Method Accuracy and Precision as Functions of Concentration—Method 602

Parameter	Accuracy, as recovery, X′ (µg/L)	Single analyst precision, s′ (µg/L)	Overall precision, S′ (µg/L)
Benzene	0.92C + 0.57	$0.09\bar{X}$ + 0.59	0.0.21$\bar{X}$ + 0.56
Chlorobenzene	0.95C + 0.02	$0.09\bar{X}$ + 0.23	$0.17\bar{X}$ + 0.10
1,2-Dichlorobenzene	0.93C + 0.52	$0.17\bar{X}$ - 0.04	$0.22\bar{X}$ + 0.53
1,3-Dichlorobenzene	0.96C - 0.05	$0.15\bar{X}$ - 0.10	$19\bar{X}$ + 0.09
1,4-Dichlorobenzene	0.93C - 0.09	$0.15\bar{X}$ + 0.28	$0.20\bar{X}$ + 0.41
Ethylbenzene	0.94C + 0.31	$0.17\bar{X}$ + 0.46	$0.26\bar{X}$ + 0.23
Toluene	0.94C + 0.65	$0.09\bar{X}$ + 0.48	$0.18\bar{X}$ + 0.71

X′ = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.
s′ = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.
S′ = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.
C = True value for the Concentration, in µg/L.
$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

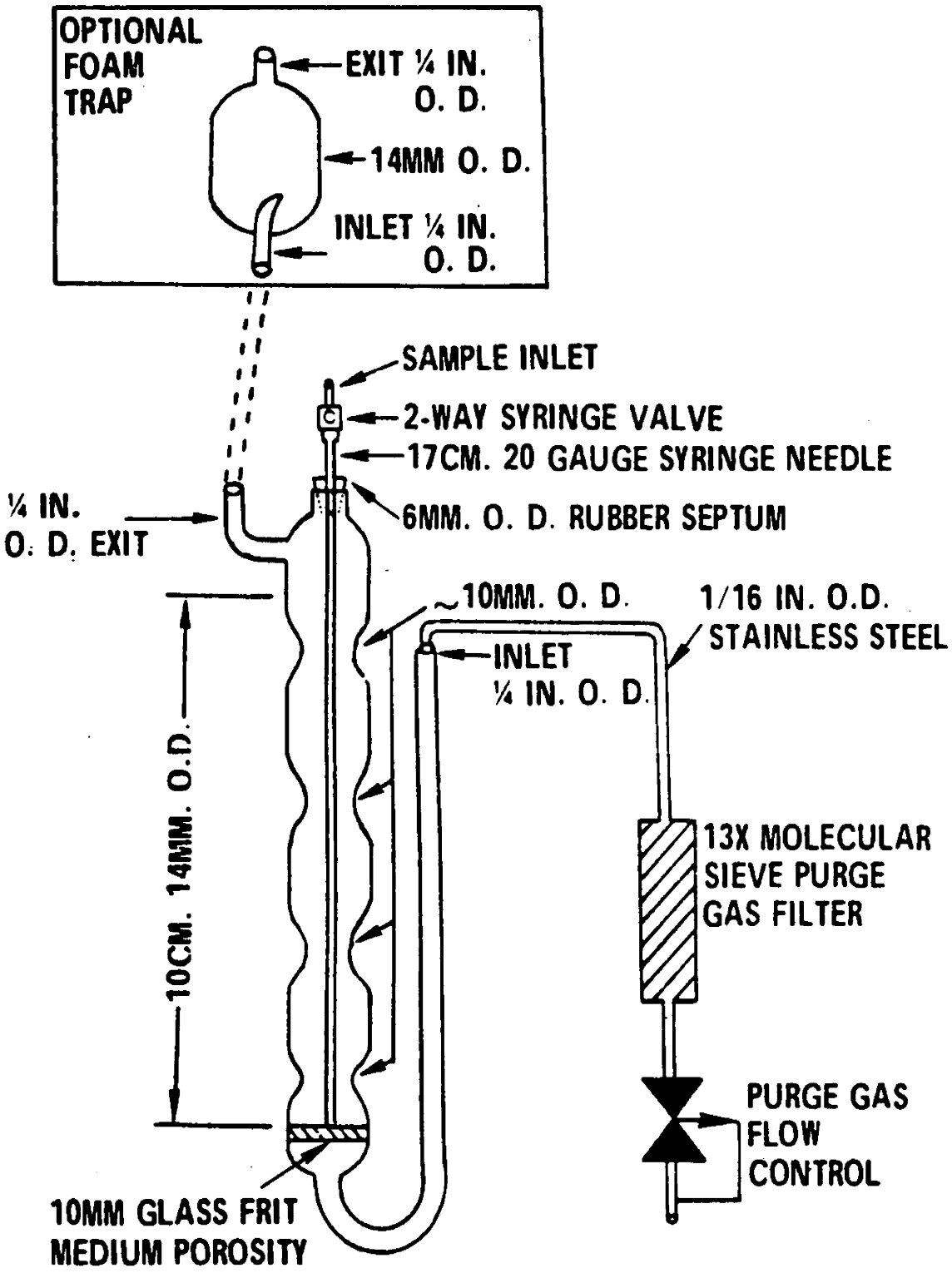

Figure 1. Purging device.

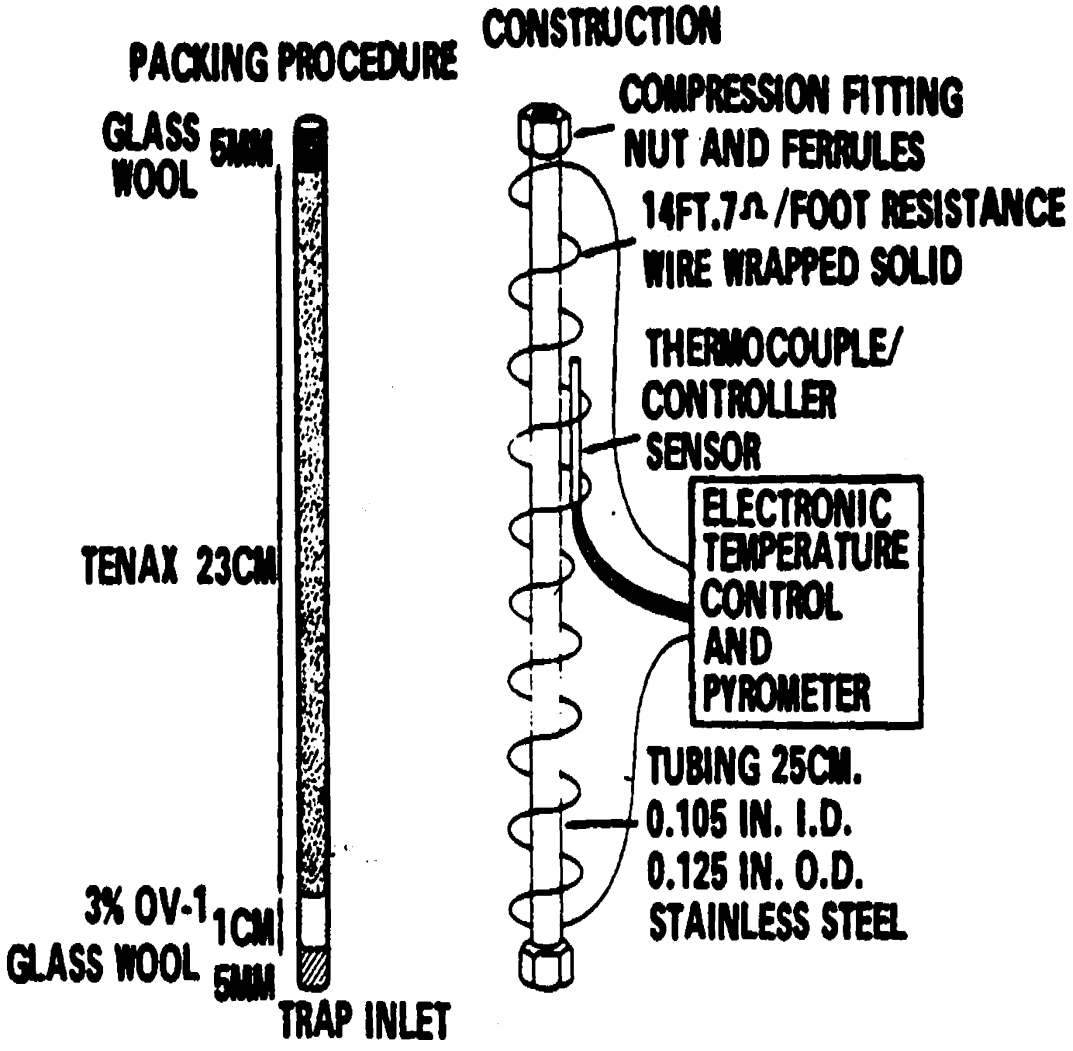

Figure 2. Trap packings and construction to include desorb capability.

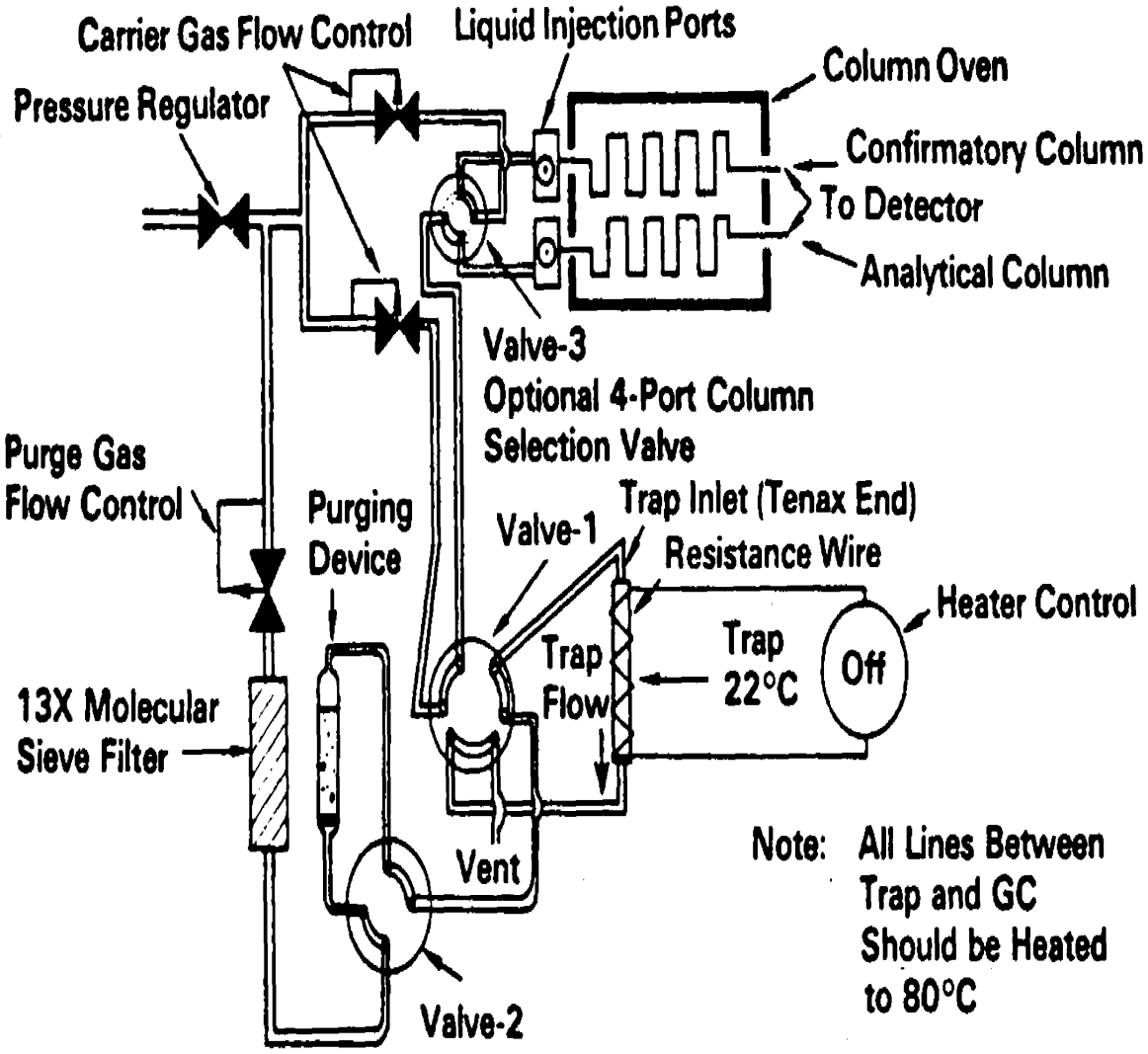

Figure 3. Purge and trap system - purge mode.

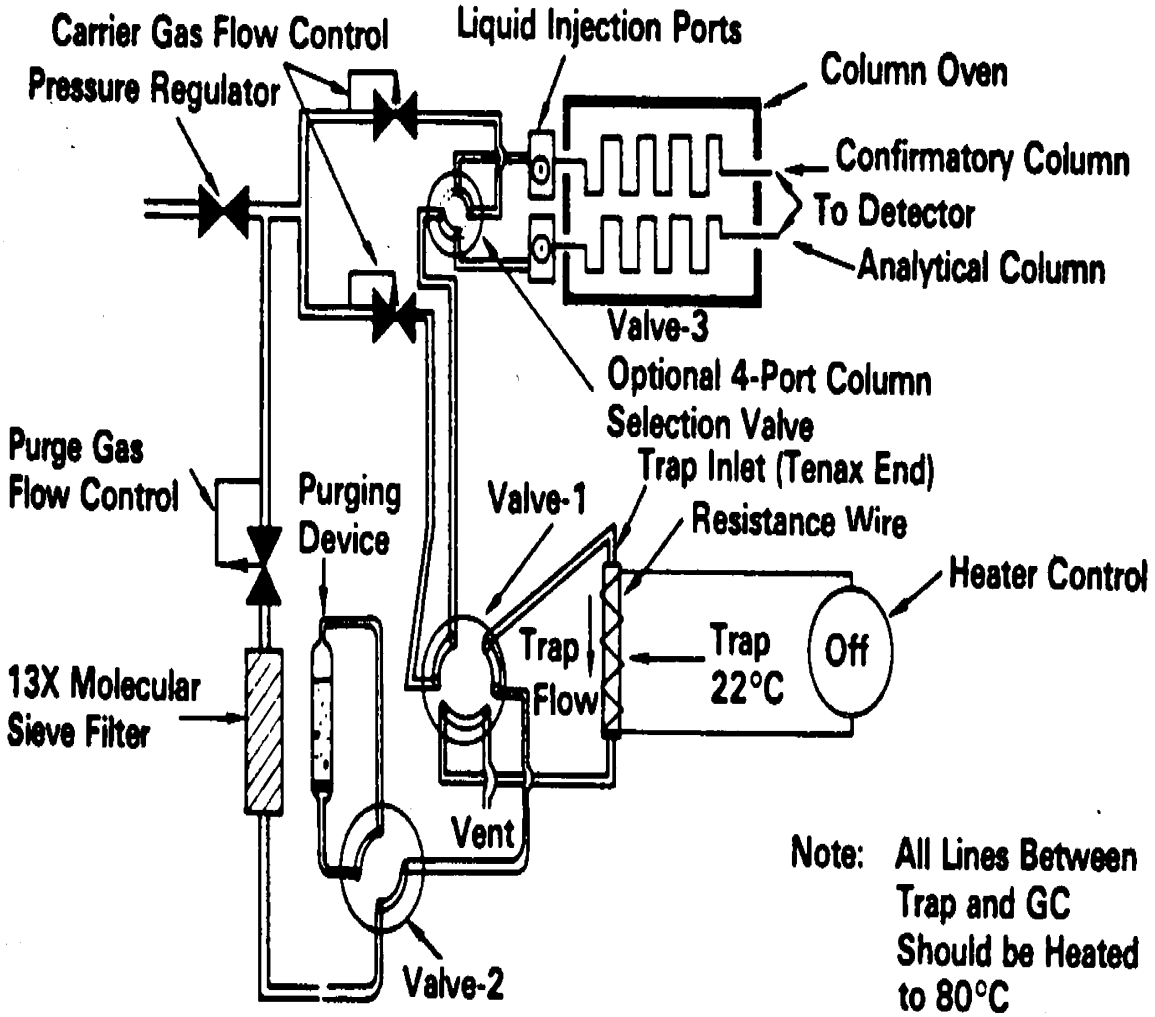

Figure 4. Purge and trap system-dry mode.

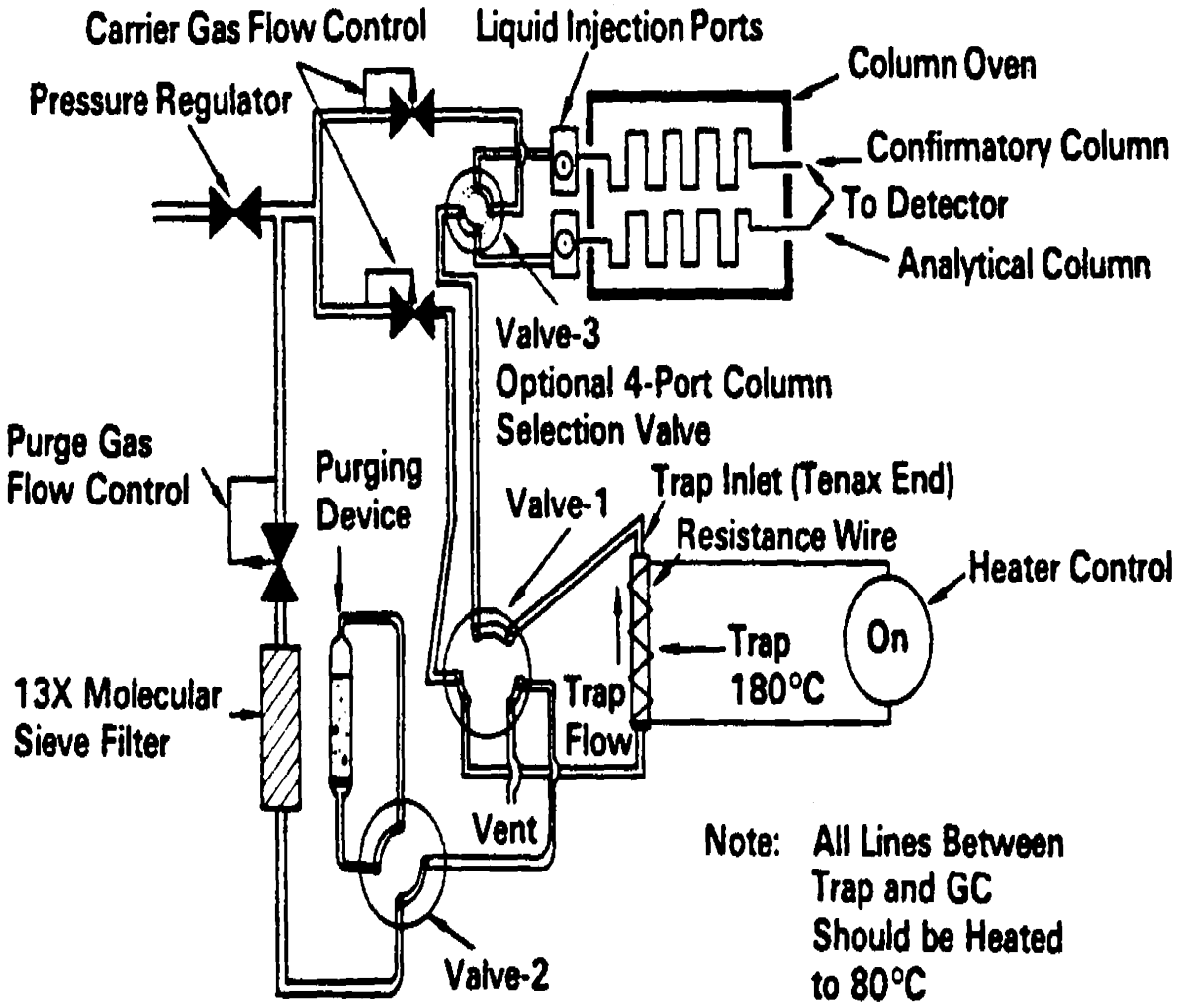

Figure 5. Purge and trap system-desorb mode.

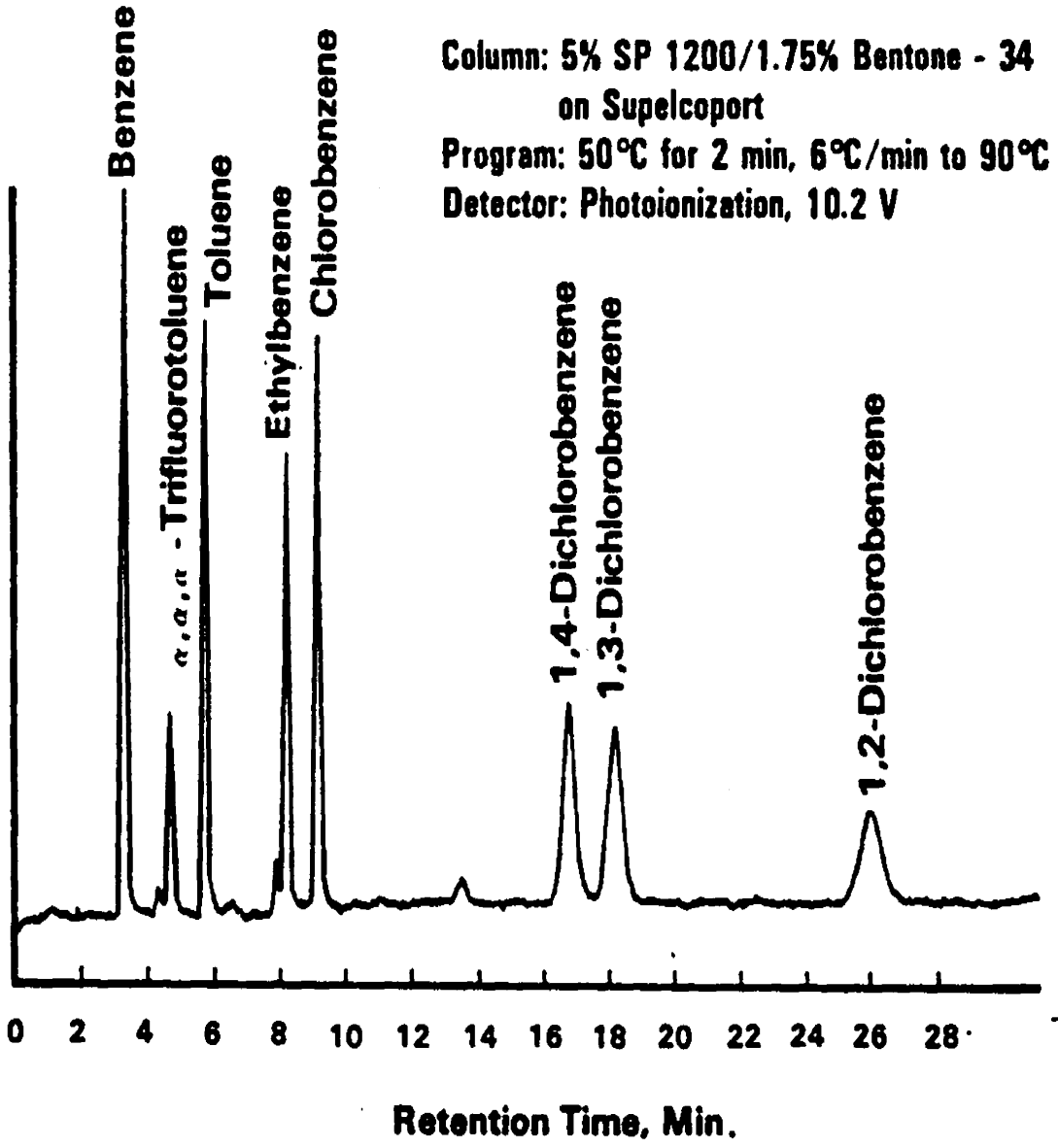

Figure 6. Gas chromatogram of purgeable aromatics.