Sampling Aerosol GLC Peaks for Spectroscopy[1]

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Abstract

A brief summary of devices and techniques which have been used for trapping GLC fractions is presented together with a new, simple, and efficient technique especially suited for collection of aerosol samples. The apparatus is described and a typical application of its use in collecting samples for spectroscopic analyses is presented together with a brief theory of the principles involved.

Introduction

PREPARATIVE SCALE gas chromatography may be divided into four types depending on the amount of separated material needed: Pilot-plant scale GC, when liters or gallons of product are desired; large-scale preparative GC, when 1 to 100 ml of product are needed; preparative GC, when 0.1 to 1 ml of sample is wanted for physical measurements, pharmacological tests, and small-scale chemical reactions; and analytical preparative GC, when 1 to 100 mg are required for further microchemical or instrumental analysis.

This paper is concerned with the last type of preparative GC, with emphasis on use of the separated and collected sample for any spectroscopic analysis.

Numerous methods and devices for trapping GLC fractions have been described. Some of these are:

Absorption of eluate from eluent by contact with a solvent at, or below, ambient temperature. In this method the desired fraction is partially extracted from the carrier gas and is dissolved in the collection solvent in accordance with conventional principles of physical chemistry. The efficiency of this method is fixed by the equilibrium constants between the vapor pressures of solute and solvent and their partial pressures in the discarded effluent gas mixture.

Condensation of eluate from the eluting gas as a dew or frost at ambient or reduced temperatures. Collection of the droplets adhering to a suitable condensing surface may be accomplished by centrifugation or washing with a volatile solvent. The so-called thermal-gradient system is used for eluates of low volatility and utilizes a small collection device such as a small capillary tube (glass or metal) for collecting small quantities, e.g., 1 to 10 μliters, of sample. The collection device is inserted directly into the exit vent of the chromatograph. Traps with large surface area and volume, such as sand traps, have been described. These require washing the condensed droplets out with a relatively large volume of solvent.

Total collection methods include (a) condensation at liquid nitrogen temperatures of an appropriate carrier gas together with the desired eluate and subsequently allowing the liquefied carrier gas to evaporate at subambient temperatures, and (b) collection of the total gaseous effluent, containing the desired fraction in a trap of relatively large volume at ambient temperature. In the latter case the desired eluate is extracted batchwise from the total gaseous mixture by a suitable solvent.

In the "packed-trap" method the desired gaseous fractions are passed through either a GC column or small tube containing suitable GC packing material, which may be used to accumulate one or more identical fractions by adsorption on the packing material. Subsequent elution or evaporation of the sample directly into the analytical instrument (e.g., mass spectrometer) may then be accomplished for very small quantities (0.1 to 10 μliters).

For collecting fractions for analytical purposes (1 to 100 mg) analytical-type, packed columns, with their desirable separating and monitoring (by recorder) characteristics, may be used. When quantities of the desired fraction larger than the single pass capabilities of the column are needed, a collection system which accumulates several identical fractions is helpful. With nondestructive detectors, such as the thermal conductivity detector, the effluent may be passed directly into the collection trap. When the flame ionization, electron capture, argon, or other detectors which destroy or modify the desired eluate are used, sample splitting or diversion to bypass the detector must be employed.

In any method of trapping used, trouble may be encountered with aerosol formation by the less volatile eluates. These aerosols consist of smoke (composed of a gaseous suspension of extremely fine particles of condensed solid), or fog (comprising fine, condensed liquid particles), or a combination of both. This combination is called "smog" by meteorologists. These dispersions of solid or liquid particles of eluate in the effluent carrier gas can be easily seen by the naked eye, especially if a light beam is directed through them. It is an exasperating experience to see a highly desired GLC fraction pass completely through collecting apparatus and emerge into the atmosphere as smoke. The collection techniques described in this paper were developed to deal with these aerosols.

It was reasoned that the extremely small particles of desired sample, emerging as smoke or fog from the gas chromatograph, bore like electrical charges which caused them to repel one another and stay apart—rather than coalesce into droplets on the inner surfaces of the trap, as desired. Electrostatic precipitation devices have been employed, but it was felt that a simpler and more effective method for capturing these particles is needed.

It is a well-known fact that condensation of moisture in the atmosphere to form rain from saturated air is facilitated by electrically charged particles of dust. These serve as nuclei for condensation of droplets of water or crystals of snow from supercooled, saturated air.

With these practical physical facts in mind a system was devised for trapping aerosol particles in the effluent of the gas chromatograph.

Experimental Procedures

Apparatus

A Kromo-Tog K-5 double gas chromatograph consisting of two independent units—each with its own

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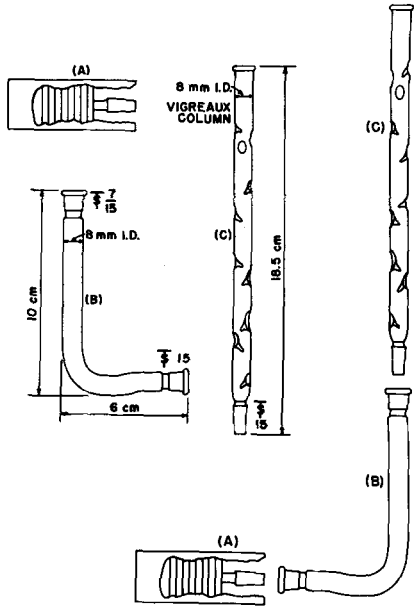

FIG. 1. Exploded view and dimensions of entrapment apparatus as used with the Burrell Kromo-Tog K-5 Gas Chromatograph. A. Heated exit port of gas chromatograph. B. Glass sample collection tube. C. Glass Vigreaux Column.

eluting gas supply, heaters, column, detector, and recorder—was used. The experiments which will be described may be considered to have been performed on a single instrument, the double instrument simply supplies two independent chromatographs in a small space for convenience.

U-shaped ¼-in. glass or stainless steel columns up to 9 ft in length were used, according to the need for separating the desired peaks.

Each column in this instrument is equipped with a preheater at the on-column injection port, thermal-mass-stabilized column, and TC detector ovens. A heated manifold with five manually controlled ball valves for selecting the desired collection device is an integral part of the instrument. Temperatures at each of the above locations are registered and may be controlled either manually or automatically. The manifold has 5 metal standard-taper male tubular connections to which either glass or metal fittings may be attached. The entire assembly is designed to minimize dead space in the gas flow system. Fig. 1 shows a diagram of an exploded view of one of the 5 ejection port nozzles together with the two-piece glass collection trap devised for the purpose. The figure shows details and dimensions of the parts. Using one of the exits for by-passing the collection traps, the other four may be used to collect as many desired fractions for each injected sample.

To prevent premature condensation of eluate the fraction collection manifold and exit ports were maintained at a temperature at least 5C higher than the detector bath. In practice, the glass collection devices were attached to the desired exit ports by a slight twisting action to insure gas tight connections. It is important that the temperature of the ejection ports have been stabilized. It the metal standard-taper port rises in temperature the attached glass connector will be broken by the expansion of the metal. The hot metal exit connection was lubricated each time by wiping it with polyethylene plastic immediately prior to attaching the glass connector. Rubber bands or small springs may be attached as a precaution to hold the traps firmly but gently on the apparatus.

Immediately upon attaching each trap, reagent grade carbon tetrachloride was added from a wash bottle to the desired level. Boiling of the CCl_4 begins immediately. The Vigreaux-type air condenser is then attached and the apparatus is ready to collect the desired fraction.

While other volatile solvents, with suitable physical and chemical properties, could be used with this technique, reagent grade carbon tetrachloride was selected for the following illustrations. This solvent, which boils at 77C, is relatively chemically inert. It is inexpensive and easily obtained in pure form. Its volatility is such that it condenses readily in the short Vigreaux column used and yet is easily removed by distillation or evaporation from the relatively high boiling substances of which most aerosols are composed. Furthermore, it is a commonly used solvent in IR, NMR, UV, and visible spectroscopic analysis. It is a good solvent for many organic compounds and thus the CCl_4 solutions of the compounds of interest may be used directly, if desired. However, in the collection method described herewith, it is not necessary that the desired collected fraction be completely dissolved in the trapping liquid. Once it has served the purpose of trapping the particles (in solution or suspension) the aggregate of solvent and collected fraction may be transferred to any type of small container by washing with more of the same solvent which may be removed by distillation or evaporation in accordance with the usual analytical techniques. The collected fraction may then be used in the pure state or it may be dissolved in any other suitable solvent.

The quantity of sample needed for spectroscopic analysis may be quite small if only a rough qualitative analysis is needed. For example, special sample holders with special condensing lenses may be used to obtain infrared absorption spectra of as little as one μliter of sample. However, if greater resolution is needed or desired, and if quantitative data are to be obtained, more sample is needed. In the case of NMR spectral analysis 100 μliters of sample may be necessary to obtain the best data. In this case the sample is not altered by the analysis and thus may be recovered by removal of the solvent (e.g., CCl_4 or CS_2) and volatile markers such as tetramethylsilane. Infrared and ultraviolet (and visible) spectral analyses are also nondestructive as a rule, and the original fraction, recovered either in solution or in pure form, may be used for other instrumental, microchemical, or biological tests. The mass spectrum may be obtained on as little as 1 mg of sample by transferring it to a capillary glass tube and placing it in the direct sampling port of an instrument such as the Consolidated Electrodynamics Corp. Model 110–21. This sample is destroyed during the analysis.

As in other analytical methods—chemical or biological—it is usually desirable to subject the sample under examination to a number of physical tests. This may often be true also of spectroscopic analysis. The purer a sample is, and the less extraneous material present, the more meaningful and informative are the derived analytical data.

While the apparatus and technique described were limited to manual selection of desired peaks, it is obvious that the principles can be applied to automatic fraction collection devices.

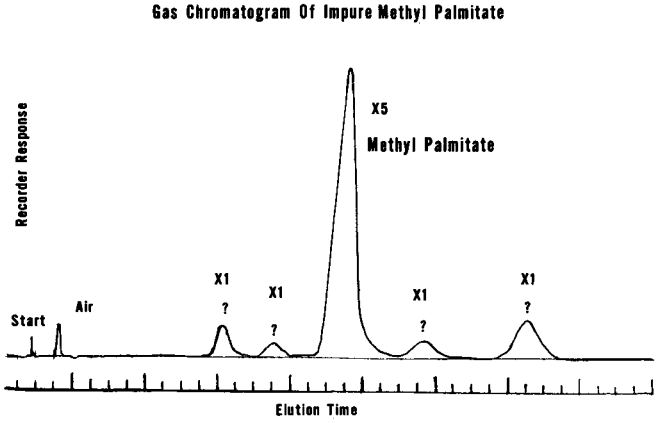

FIG. 2. Gas chromatogram of impure methyl palmitate.

Method

A typical example of application of the method is shown in the repurification of a sample of pure methyl palmitate obtained from one of the chemical supply houses. Fig. 2 shows the gas chromatogram obtained on the instrument described using a 9-ft column packed with 20% DEGSS at 200C in accordance with the AOCS method for quantitative fatty acid determination. Rate of helium gas flow was 50 ml/min. It is noted that four impurities are present in the amount of approximately 7%, and that the sample is not chromatographically pure.

The glass trap was attached to one of the exit ports and the bottom tube was filled to about one-half its length with reagent-grade CCl_4 from a wash bottle. Proper adjustment of the level of liquid and temperature of the discharge port manifold controls the rate of boiling of the trapping liquid. Incipient boiling is all that is needed to provide saturation of the eluting gas mixture with CCl_4 vapor at or near its boiling point. As the saturated gas moves up through the trapping liquid and comes into contact with the relatively cool walls of the Vigreaux condenser, the high-boiling eluate, containing the material of the desired peak, condenses with the CCl_4 vapor, either within the liquid or on the sides of the upper part of the trapping tube and condenser. Under these conditions a second portion of condensed liquid (CCl_4 solution) accumulates in the bottom of the condenser and serves as a second, and cooler, liquid trap. This may be returned to the bottom tube, when desired, simply by momentarily lifting the upper condenser. Loss of CCl_4 to the atmosphere by the sweeping action of the carrier gas which has been stripped of the desired sample fraction is minor. Periodic replacement may be made by adding CCl_4 from a wash bottle. If the instrument is situated in a draft hood or in a well ventilated room, contamination of the atmosphere by solvent vapor is no problem.

When an adequate number of desired fractions has accumulated in the trap, the CCl_4 is allowed to evaporate by removing the condenser and passing eluate-free carrier gas through it until the level is reduced to the bottommost depression of the trapping tube. The trap may then be removed and the collected sample washed quantitatively into a small beaker. Removal of solvent may be accomplished by careful distillation, or by allowing spontaneous evaporation of the CCl_4 in the hood or in a vacuum desiccator.

After the collection trap was attached, successive portions of the impure methyl palmitate were injected and each time the single large peak, due to pure methyl palmitate, was trapped and collected in the hot CCl_4 trap. The amount of starting material which may be injected each time depends on the separating characteristics of the column and the eluting characteristics of the components of the mixture. The greater the difference in elution time of the components, the larger the amount of feed material which may be used at each injection. Complete separation is not necessary if the exit port valves are judiciously manipulated. Once the recorder trace of a single chromatogram is obtained, elution times may be used to judge the timing for the desired cuts. Twelve fractions, collected in this way, and desolventized as described above, yielded approximately 100 mg of a white solid which, when melted and reinjected, gave the chromatogram of Fig. 3 with 1 μliter. The retention time was that of pure methyl palmitate (as established from chromatograms of authentic mixtures of fatty acid methyl esters run through the instrument under identical conditions).

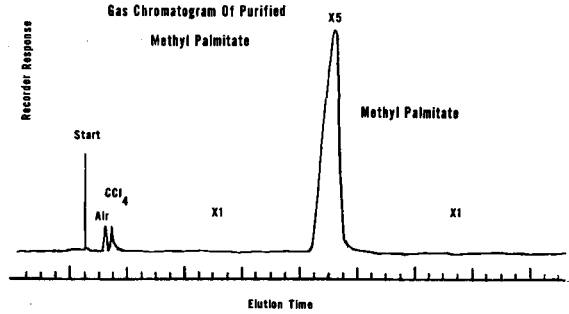

FIG. 3. Gas chromatogram of purified methyl palmitate.

The 100-mg collected fraction was redissolved in CCl_4, tetramethyl silane added as marker, and the NMR spectrum of Fig. 4 obtained.

The CCl_4 solution was again desolventized and the IR spectrum was obtained by melting the sample and placing a sufficient amount between sodium chloride crystals. This spectrum is shown in Fig. 5, together with that of the impure starting material. Two additional bands appear in the impure specimen just above the long-chain fatty acid band at 762 and 786 cm^{-1} which are exhibited by branched-chain fatty acid methyl esters (1). The identical NMR spectra of both the impure and purified material

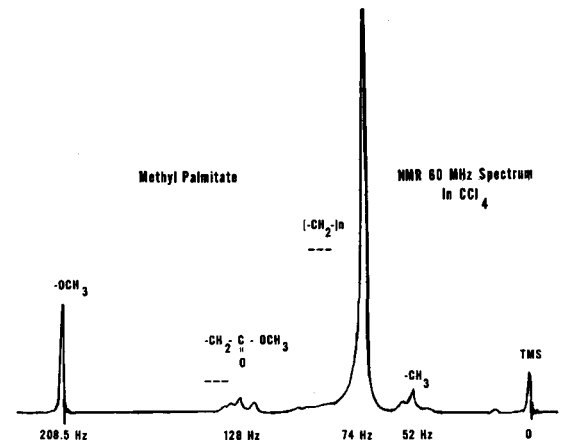

FIG. 4. NMR 60 MHz spectrum in CCl_4.

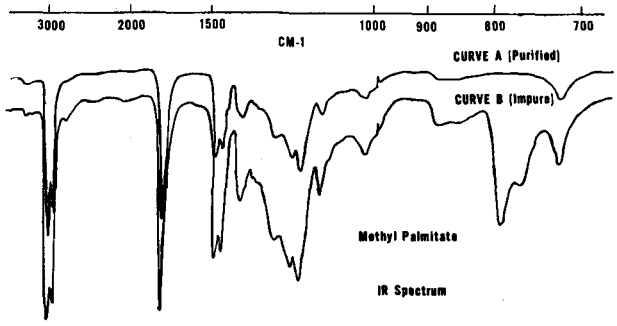

FIG. 5. Methyl palmitate IR spectrum.

show the usual groups to be expected in methyl esters of saturated fatty acids. The IR spectra for both the pure and impure samples are identical to that of the published authentic methyl palmitate spectrum, except for the bands between 700 and 800 cm^{-1} as noted above. The UV spectra of the recovered samples, dissolved in cyclohexane, showed no characteristic bands in either specimen.

Essentially quantitative recovery of the collected material, as compared to the amount injected, may be obtained, provided extreme care is exercised in eliminating leaks in the eluting gas system and quantitative microchemical techniques are employed.

The collection method described works consistently well. We have used it in our research and plan to use it extensively in the future.

REFERENCE

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