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Article 155

EFFLUENT COLLECTOR FOR GAS CHROMATOGRAPHY

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Abstract.—The authors have designed a convenient effluent collector for gas chromatographic samples. This collector eliminates contamination of one component by another as well as contamination from other sources. The collector provides an individually complete assembly for each component, it pockets and magnifies the sample, and it has its own heat sink. Importantly, the sample is collected close to the end of the analytical column.

Gas chromatography is being used increasingly for the analysis of volatile organic compounds and of those substances that can be made volatile. However, the collection of pure fractions of gas chromatographic samples from analytical columns presents a problem, particularly where several close-boiling components are involved. Contamination of one component by another can occur readily in the effluent line and at the exit port. The effluent line can also serve as a condensation chamber in which the column substrate may accumulate.

Although several types of collectors are described in the literature (Grasselli and Snavely, 1962; Hajra and Radin, 1962; Haslam and others, 1961; and Lesser, 1959), all the collectors examined used the existing effluent line and exit port. Some collectors provided excellent trapping, but all were deficient in preventing contamination of one component by another.

To avoid contamination of gas chromatographic samples, the samples must be collected at or near the end of the analytical column and not at a common exit port supplied by a common effluent line. The collector should pocket the sample so that it can be readily withdrawn by a hypodermic needle. The collector should be relatively inexpensive, easily handled, individually cooled, and conveniently sealed from atmospheric moisture and coolant-bath vapor before and after collection.

An especially designed collector that embodies these principles is shown in figure 155.1. The admission

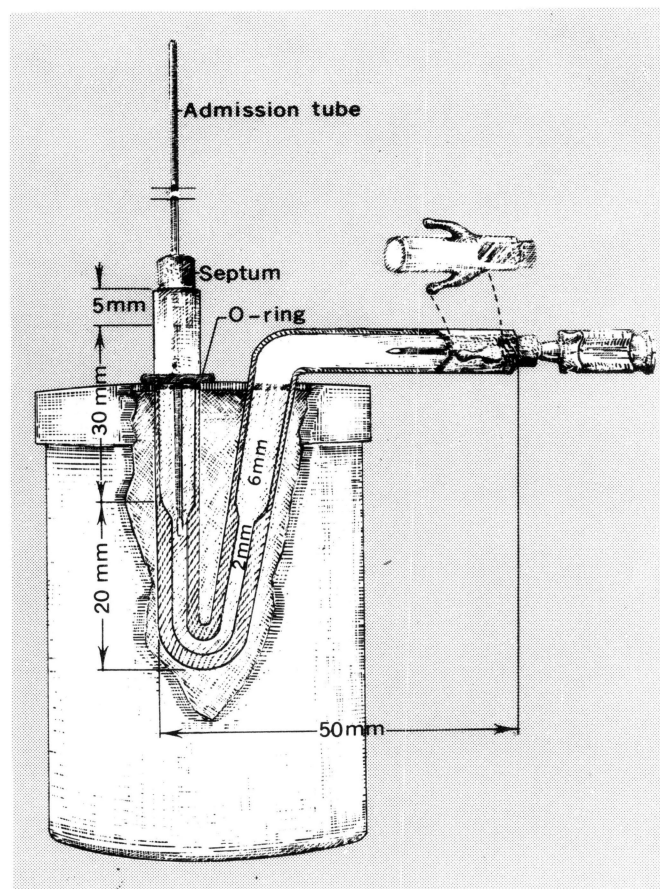


FIGURE 155.1.—Effluent collector.

tube is 18-gage stainless-steel hypodermic tubing; it has a 17-degree bent point on one end and a square cut on the other. The part of the admission tube that extends beyond the rubber septum should be just less than the length of the common effluent line, so that when the tube is inserted, the septum will seal the exit port. Before and after use, the end of the admission tube can be sealed with an inverted septum if desired.

The carrier gas is vented through a hypodermic needle that is inserted in the discharge arm of the collector. The silicone-rubber septums are the standard half-drilled type that fit 6-mm ID tubing. The coolant-bath holder for each collector consists of a snap-on-cap polyethylene container $1\frac{1}{2}$ inches in diameter by $2\frac{1}{4}$ inches high. Two holes and a connecting slit were made in each cap. An O-ring cut from rubber tubing positions the collector in the coolant-bath holder.

The admission tube may be placed in the horizontal or vertical arm of the collector, depending upon the access to the detector vent. In order to reach the detector vent with an admission tube, the gas chromatograph must have a sufficiently straight common effluent line. In some gas chromatographs the end of the column is at the bottom of the instrument and the common effluent line is arranged so that it is not possible to reach the detector vent with an admission tube. However, these gas chromatographs can be modified so that the components can be collected from the bottom of the instrument.

For example, a Perkin-Elmer Model 154-D gas chromatograph was modified by drilling a $\frac{5}{8}$ -inch hole in the bottom of the oven cabinet. The hole was aligned with the exit "tee" of the detector so that a 4-inch length of straight $\frac{1}{8}$ -inch stainless-steel tubing attached to the exit "tee" just protruded outside the oven chamber. A $1\frac{1}{4}$ -inch length of $\frac{1}{2}$ -inch copper tubing was inserted and crimped to line the hole and keep the insulation in place. The exit end of the $\frac{1}{8}$ -inch stainless-steel tube was fashioned so that the entry was conical, to facilitate insertion of the admission tube. The inside of the exit tube was polished to a smooth finish with emery powder on a cotton-swab stick. The upstream end of the tube was swaged to the detector-outlet "tee." Access to the new exit port was made by supporting the gas chromatograph cabinet on a frame. The original effluent line was removed.

EFFLUENT COLLECTION PROCEDURE

The collection apparatus is assembled and a suitable coolant is placed into the coolant receptacle. A sample is injected into the gas chromatograph, and just before the desired component emerges, the admission tube of the collector is started into the exit port of the chromatograph. At the time the recorder indicates the emergence of the component, the admission tube is inserted all the way to the rubber septum and held firmly in place. The uncontaminated component in the carrier gas passes through the individual admission tube and is condensed in the pocket of the glass collector. During waiting periods, the collectors and bath holders may be kept in a flat pan of crushed ice or on a slab of dry ice.

EXPERIMENTAL RESULTS

Methyl caproate was selected to demonstrate the suitability of the apparatus for collecting components with comparatively low boiling points, and the dimethyl esters of fumaric and malonic acids were used to show the effectiveness of the apparatus for the separate collection of two partially overlapping compounds.

A 20-microliter sample containing 0.00023 g of methyl caproate in absolute methanol was injected into the gas chromatograph. Collection of the sample was begun when the recorder pen left the base line and ended when the pen returned to the line. The collected sample was transferred from the collector to a micro-cavity cell (0.2–0.3 μ l minimum volume) with a total of 5 μ l of carbon disulfide by using a microliter syringe. Infrared analysis was made after the solvent was evaporated down to about 1 μ l under the gentle heat of an infrared heat lamp. Evaporation was halted by closing the cell with a drop of mercury. Another infrared scan was made after replacing the carbon disulfide with carbon tetrachloride by dilution and evaporation. A $\times 4$ infrared beam condenser was used for these analyses.

A 20- μ l aliquot of a solution containing 0.0124 g of dimethyl malonate and 0.0119 g of dimethyl fumarate in 1.00 ml of absolute methanol was injected into the gas chromatograph. As shown in figure 155.2 the resulting chromatograph is a good example of closely eluting, partially overlapping compounds. The collections were timed to eliminate the unseparated part of the elution. The overlapping part, comprising 20 percent of the dimethyl malonate and 40 percent of the dimethyl fumarate, was discarded by venting. The infrared spectrum of each of these components was obtained as described in the preceding paragraph except that only carbon tetrachloride was used with dimethyl fumarate. In addition, the dimethyl fumarate was collected for infrared analysis by the potassium bromide micropellet technique.

RESULTS AND DISCUSSION

Each component eluted by the gas chromatograph is collected close to the end of the analytical column in an individually complete assembly. An excellent infrared spectrum for methyl caproate was obtained from a single collection of an injection of only 0.00023 g of the ester. This demonstrated the application of this apparatus for the collection of components with comparatively low boiling points.

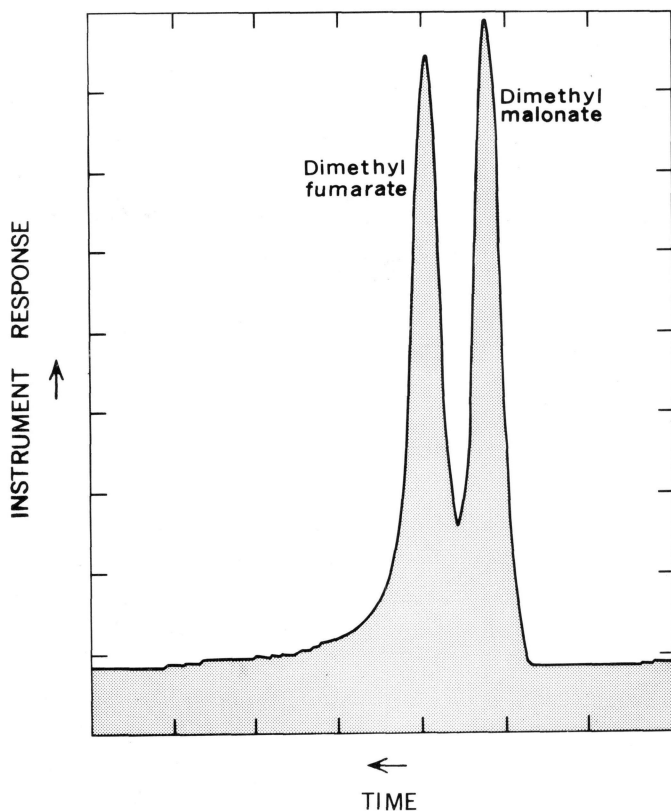


FIGURE 155.2.—Chromatograph of overlapping compounds.

A separate collection of closely eluting and partially overlapping components was equally successful as demonstrated by the injection of a sample containing dimethyl malonate and dimethyl fumarate. Two injections were required because it was necessary to vent the overlapping part of the elution. Each of the 2 injections contained 0.00025 g of dimethyl malonate and 0.00024 g of dimethyl fumarate. From these injections, each component was collected separately and placed in a microcavity cell for infrared analysis. No contamination of one of these esters by the other could be observed in the infrared spectra.

To test another handling technique, two collections of dimethyl fumarate were pressed in a micropellet of potassium bromide. Again, no contamination of this ester was observed in the infrared spectrum that was obtained with a $\times 4$ beam condenser and $\times 5$ scale expansion.

An important feature of the apparatus described here is the completely individual system for the collection of each component very near the end of the column. Thus, contamination of one component by another as well as contamination from condensation of column substrate can be eliminated. This collector has several other distinct advantages. For example, the condensing surface can be easily washed with a small amount of solvent, and the thickened glass section magnifies and pockets the collected material. The collector can be completely sealed during cool-down or waiting periods, thus avoiding contamination by atmospheric moisture and cold-bath solvents. The collector is always maintained in its own heat sink that will not warm up before the collection is completed.

This collector also enhances a collection and reinjection technique developed by the authors. With this technique the components are individually collected and reinjected into a different gas chromatographic column to obtain two characteristic retention volumes for each component. This provides a salient advantage in the identification and confirmation of the organic components in a sample.

REFERENCES

- Grasselli, J. G., and Snaveley, M. K., 1962, Analysis of organic reaction products by combined infrared-gas chromatography techniques: *Appl. Spectroscopy*, v. 16, p. 190-194.
- Hajra, A. K., and Radin, N. S., 1962, Collection of gas-liquid chromatographic effluents: *Lipid Research Jour.*, v. 3, p. 131-134.
- Haslam, J., Jeffs, A. R., and Willis, H. A., 1961, Applications of gas-liquid chromatography: *Analyst*, v. 86, p. 44-53.
- Lesser, J. M., 1959, Device for isolation of components separated by gas chromatography: *Anal. Chemistry*, v. 31, p. 484.

