A Method for Obtaining the Emission Spectra of Organic Compounds Utilizing the Microwave Emission Detector for the Gas Chromatograph

by E. M. BELLET, W. E. WESTLAKE, and F. A. GUNTHER
Department of Entomology
University of California Citrus Research Center
and Agricultural Experiment Station, Riverside, California

During evaluation of the performance and operating characteristics of the microwave-powered emission gas chromatographic detector developed by McCormack, et al. (4) it became apparent that a means for scanning the emission spectra of organic compounds would be of value both for locating the more intense lines for use in quantitation and for utilization in characterizing unknowns. As this type of detector has been used routinely for measuring residues of organophosphorus pesticides by Bache and Lisk (1), compounds of this type were selected for initial study. A continuous flow system for the gas chromatographic component of the total apparatus that permits the scanning of the emission spectrum of any diatomic or polyatomic organic compound having sufficient vapor tension, over the entire range of the monochromator used, is described herein.

Basic Equipment

Equipment used was essentially the microwave emission detector of McCormack, et al. (4), coupled to a gas chromatograph in a manner similar to that used by Bache and Lisk (1).

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Several modifications were made, however, to simplify alignment of optical components and to facilitate maintenance of the total system. The quartz capillary tube in which the emitting plasma is created was connected to the gas chromatograph column by a rigidly mounted Swagelok® union fitted with a Teflon® ferrule to form a gas-tight seal and also to facilitate easy removal and replacement of the tube through the top of the oven. This quartz tube, encased in a machined aluminum block fitted with heating elements, was maintained at a temperature of 225° C. The waveguide, emission tube block, lens and monochromator were mounted on an alignment bench (Figure 1) to permit the independent adjustment of the monochromator and lens in the three Cartesian directions, while the waveguide is adjustable in two directions, to allow exact and reproducible alignment of all three components for maximum optical efficiency.

Continuous-flow System

The attachment for continuous scanning consists of a 12 x 5 cm. stainless steel cylinder fitted with the valve system shown diagrammatically in Figure 2, inserted in the carrier gas line immediately before the line enters the injection port. A photograph of the system is shown in Figure 3. One end of the cylinder is permanently closed while the other is fitted with a threaded plug sealed with a Buna-N "O" ring to facilitate insertion of samples and cleaning of the interior. Buna-N was

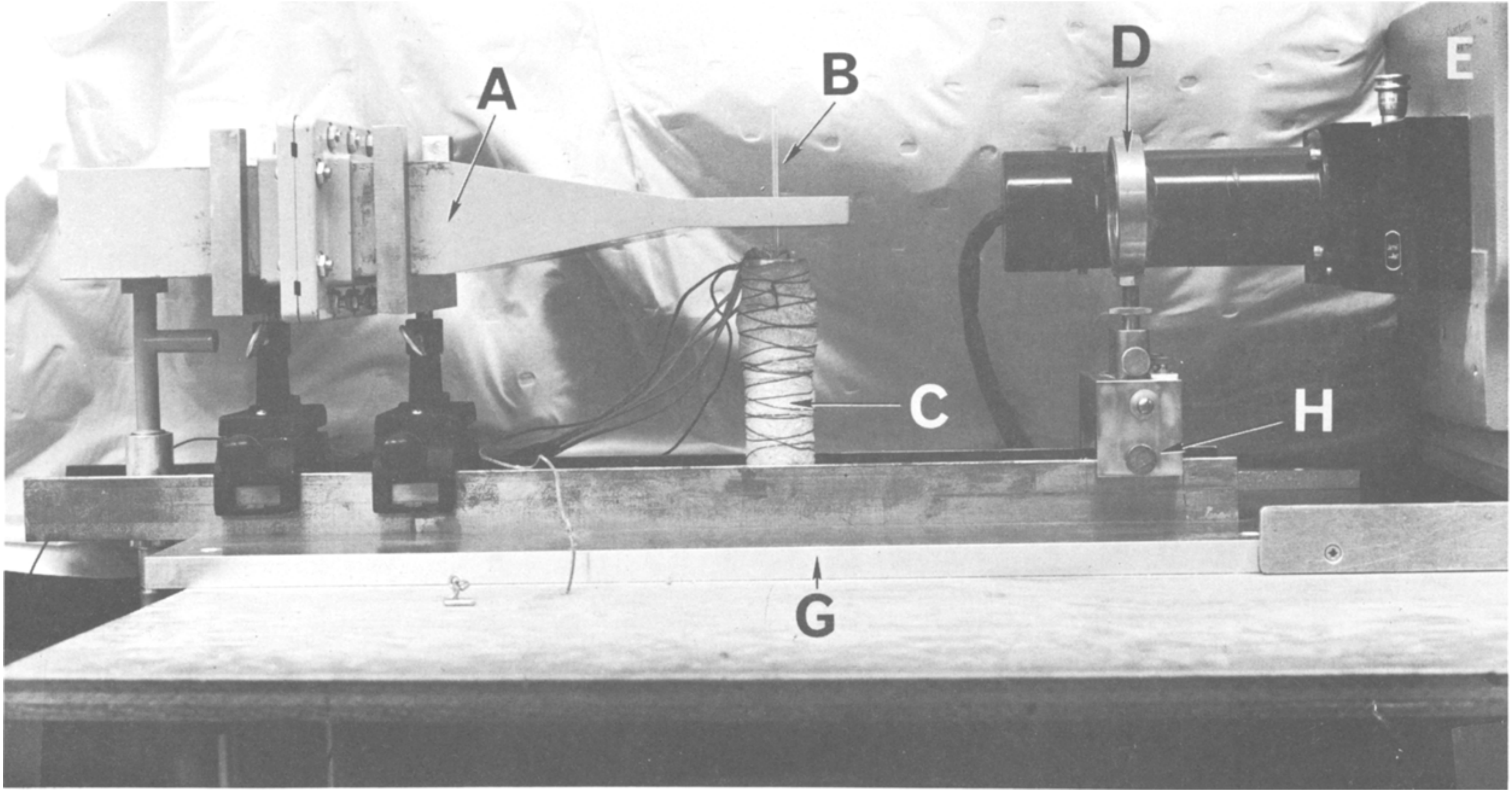

Figure 1. Photograph showing alignment bench and components of detection system. A = waveguide, B = quartz emission tube, C = heating block, D = quartz lens, E = monochromator, G = alignment bench, and H = lens alignment adjustment.

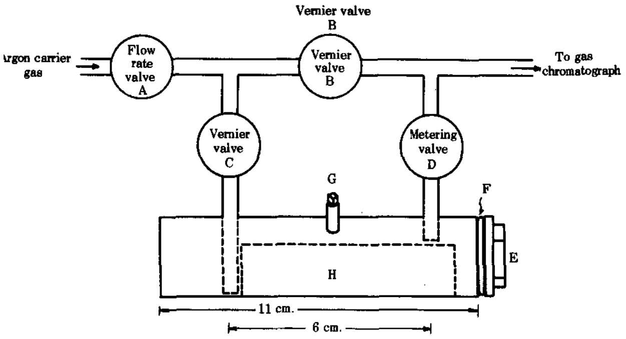

Figure 2. Diagram of cylinder and valve arrangement for continuour scanning. A and D = needle valves, B and C = micrometer valves, E = stainless steel cylinder with threaded plug, F = "O" ring, G = pressure release with threaded tapered plug, and H = glass boat

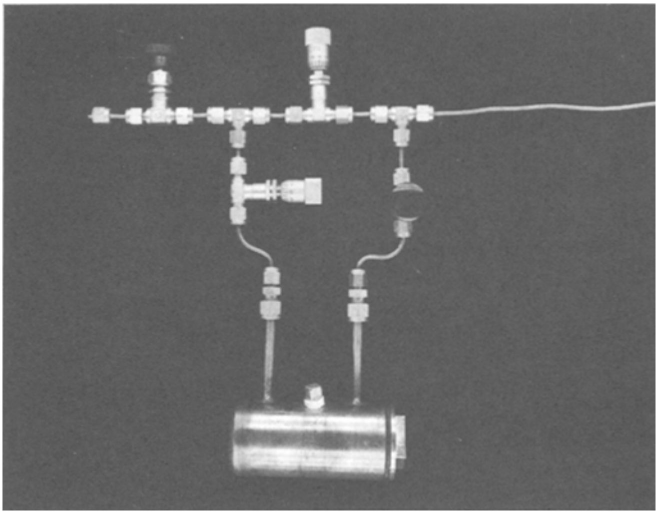

Figure 3. Photograph of cylinder and valve assembly for continuous scanning, showing arrangement of components.

found to be resistant to attack by organophosphorus compounds and was selected for this reason and because the "O" rings are readily available. The compound to be studied is placed in a glass boat having the same curvature as the cylinder to avoid gross contamination of the cylinder walls. Quantities of less than a gram are used and presumably less than milligram amounts of many compounds would suffice although no attempt has been made, to date, to determine the minimum amounts required. The cylinder is fitted with a small threaded tapered plug as a pressure release.

With valves A and B open and C and D closed (Figures 2 and 3), there is no gas flow through the cylinder, permitting operation of the gas chromatograph in the normal manner. Valve A is always set to allow a flow rate slightly higher than required and the micrometer valve B is used to obtain the desired precise flow rate.

When valves C and D are opened and valve B partly closed, a portion of the carrier gas is diverted through the cylinder, where it becomes mixed with the vapor phase of any organic compound present, thus carrying a constant concentration of the compound into the injection port of the gas chromatograph. Regulation of the gas flow through the cylinder is accomplished with the micrometer valves B and C; these can be adjusted to divert whatever part of the total gas flow necessary to obtain the desired concentration of the compound being studied in the gas stream entering the gas chromatograph. Because the detector responds to exceedingly small amounts (as little as a few ng. per second) of organic compounds, micrometer valves are used to control the gas flow and to allow diversion of a very small part through the cylinder when necessary. The gas flow required through the cylinder is a function of the vapor pressure of the compound of interest.

Results

Attention was initially directed to the four atomic phosphorus lines at 2534.01, 2535.65, 2553.28, and 2554.93 A. because of the extreme sensitivity of the detector to organophosphorus pesticides reported by Bache and Lisk (1). The scans of the spectral region including these lines, for triethyl and triphenyl phosphite, are shown in Figure 4. The vapor tension of triethyl phosphite is 4 mm. at 20° C., while that of triphenyl phosphite is reported by Forsman (3) to be 5 mm. at 200-206.5° C.

Guthion (O,O-dimethyl S-4-oxo-1,2,3-benzo-triazin-3(4H)-ylmethyl phosphorodithioate) is a crystalline compound with a vapor tension of less than 3.78×10^{-5} mm. at 20° C., according to Burchfield and Johnson (2). The scan of the region encompassing the four atomic phosphorus lines of interest is shown in Figure 5. Despite the low vapor tension of Guthion, a good response was obtained. Many organic compounds of interest may have vapor tensions too low to permit their examination at

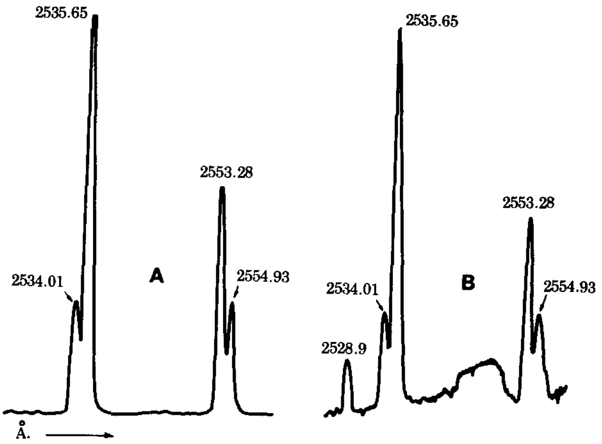

Figure 4. Spectra of triethyl phosphite (A) and triphenyl phosphite (B).

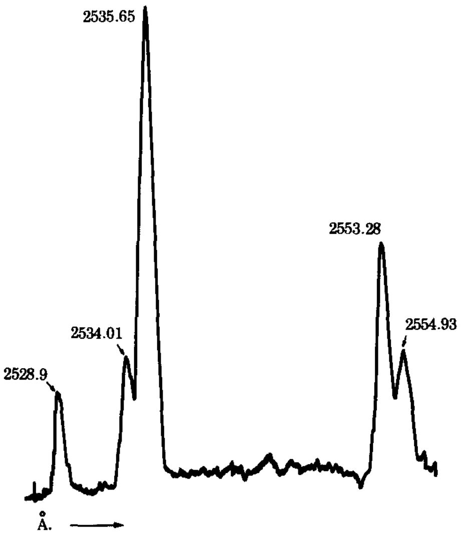

Figure 5. Spectrum of Guthion.

ambient temperatures, but the useful range can undoubtedly be extended by providing for moderate heating of the cylinder and the tubing between the injection port and the cylinder. This could easily be accomplished by wrapping these parts with electric heating tape.

Precautions

Vapor tension is probably the most significant factor involved in obtaining this type of emission spectrum of both liquid and solid samples. Care should be taken to allow a minimum flow of the compound of interest through the column to prevent the deposition of interfering contaminants in the lines or on the inside of the quartz tube and possible breakdown of the liquid phase in the column. Cleaning of the cylinder is simplified by using the previously mentioned glass boat and careful insertion of the compound of interest in this vessel will prevent gross contamination of the cylinder walls. Immersing the cylinder in concentrated sulfuric acid was necessary to remove deposited contaminants when the compounds were placed directly in the cylinder and may occasionally be required even when the glass boat is used.

Other Applications

Obviously the range of the instrument is not limited to the region of the phosphorus lines. By completely enclosing the optical system it is possible to scan the spectrum through the visible range and well into the infrared without appreciable baseline drift. This affords a means for locating the more intense emission lines for any given organic compound for possible quantitative work and may assist in establishing the identity of unknowns by comparison with the spectra of pure known compounds.

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