Integrated System for Microreactor Gas Chromatography[1]

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Abstract

A compact unit has been constructed to control and to supply a microreactor apparatus. Features are an ozone generator, gas flow rotameters, solenoid-operated six-way gas valve and a combination temperature-and-ozone meter. The meter monitors and, by means of a built-in relay, controls reaction temperature. It also affords a visual indication of ozone concentration during reactions. Basic electronic circuits and common laboratory items simplify the unit's construction. Some possible microreactions to which this integrated system may be applied are ozonization-pyrolysis, esterification, transesterification, saponification, reduction and halogenation.

Introduction

Chemical transformations of samples in the microreactor before introduction into a gas chromatograph increase the applicability of this already powerful analytical tool. In concept, any chemical treatment which can be made in an open test tube may also be carried out in the microreactor but with added advantages of microliter samples, quantitative transfer to the chromatograph and ease and rapidity of operation. Basic requirements of the microreactor system are heat and temperature control, sample and reagent introduction in liquid and gas phases, a monitor to determine reaction progress and carrier gas to transfer the reaction products to the chromatograph. The wide range of chemical reactions which may be conducted in the microreactor assembly (MRA) include esterifications, saponifications, reductions, halogenations, pyrolysis and ozonolysis.

Many types of instrumentation have been used in the process of ozonolysis and structure determination on a variety of compounds (2,10,12). One of the latest developments was a soldering gun microtechnique for analytical determination of double bond positions (8,9,11). The associated control and supply equipment was a complex interconnection of individual units, consisting of a pyrometer, flow meters, ozone generator and meter, soldering gun and gas valves. Such an array presents a complicated arrangement for the analyst. It became apparent that an improvement in versatility and simplicity of operation would be accomplished by integrating the units into one compact system. Such a unit has now been constructed and is described in this article. The use of basic electronic circuits, common laboratory items and readily available components should facilitate construction.

Description of Apparatus

Figure 1 is a photograph of the MRA front panel showing placement of controls. All gas controls are on the left side of the panel to obtain the shortest possible tubing lengths which aid in the use of ozone and its measurement. A detailed description of the soldering gun microreactor has already been published (8,9).

Figure 2 is a simplified block diagram of the complete MRA system. Note that there are two centers of operation in the diagram—the six-way valve for gas flow and the meter for electronic control and monitoring. The block diagram of Figure 2 should be studied along with the pictorial diagram of Figure 3 for a thorough understanding of gas flow paths and electrical circuits.

In Figure 3 the six-way valve (Wilkens Instrument and Research, Inc., Walnut Creek, Calif.) is shown in the GLC injection position (helium flowing through gun). In this position the needle on the gun can be inserted into the injection septum of a GLC, a mass spectrometer or other analytical instrument; the reaction products are then transferred by

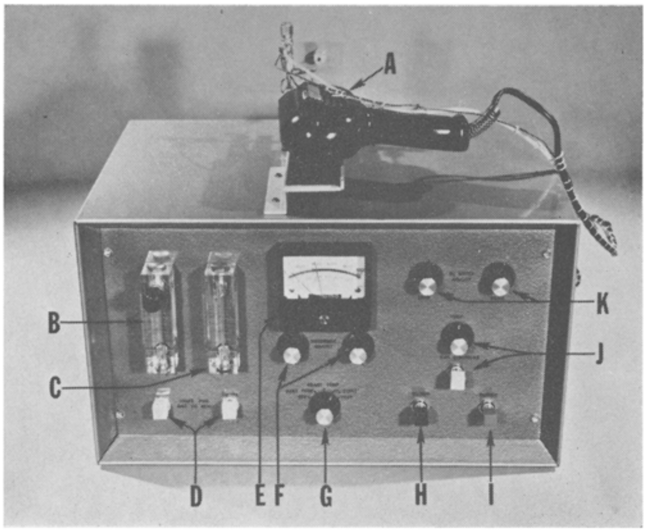

FIG. 1. Front panel of integrated microreactor (MRA) system: A, microreactor gun; B and C, gas flowmeters; D, indicating switches for six-way value control; E, multifunction meter; F, recorder controls; G, function switch; H, ozone generator switch; I, power switch; J, gun temperature controls; K, ozone meter controls.

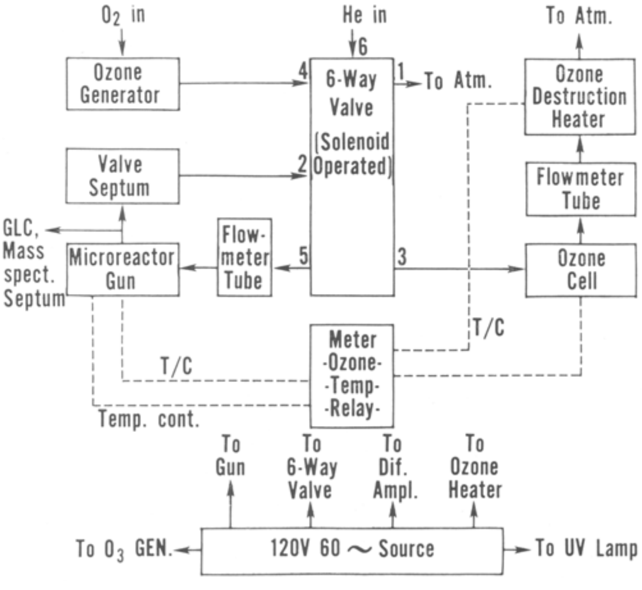

FIG. 2. Block diagram of MRA system. Solid lines (except from voltage source) indicate metal or Tygon tubing connections; dashed lines are electrical connections.

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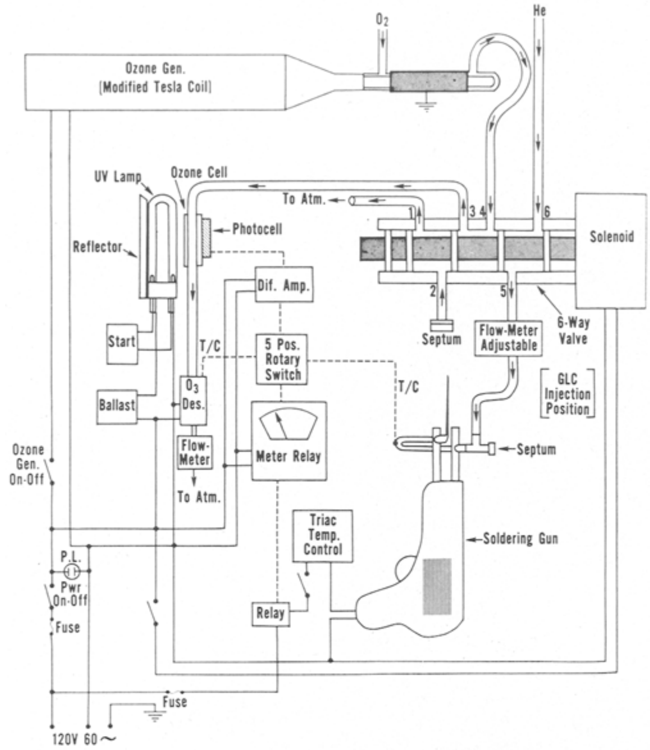

FIG. 3. Pictorial diagram of unitized MRA system. Dashed lines indicate electrical signal paths; solid lines, electrical power source; and arrows, direction of gas flow.

vaporizing them with heat. Actuating the six-way valve moves the position of the O-rings and changes the route of oxygen-ozone flow through the gun for ozonizing. The gun should then be inserted into the valve septum which permits the oxygen-ozone mixture to flow through the ozone cell and heater for monitoring and destruction. Other features to be noted in Figure 3 are the flow meters, meter-relay and Triac temperature control. Two flow meters are incorporated, one in the gas stream going to the gun (adjustable) and one in the oxygen flow (nonadjustable). In preparing the instrument, flow rates of both gases can be monitored, and gun flow can be adjusted readily on the front panel. The meter relay, as the name implies, is a combination indicating meter and controlling relay. Ozone destruction temperature, reaction chamber temperature, ozone concentration or a simple test of meter functionality are displayed by moving the five-position switch to one of four labeled points (fifth position being "off").

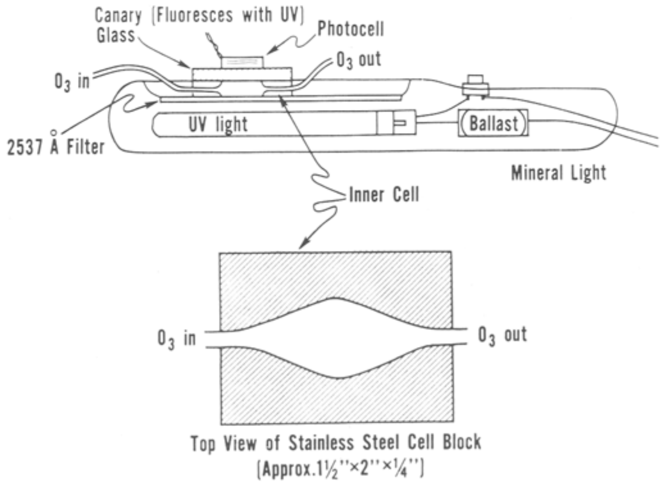

FIG. 4. Construction of prototype ozone cell.

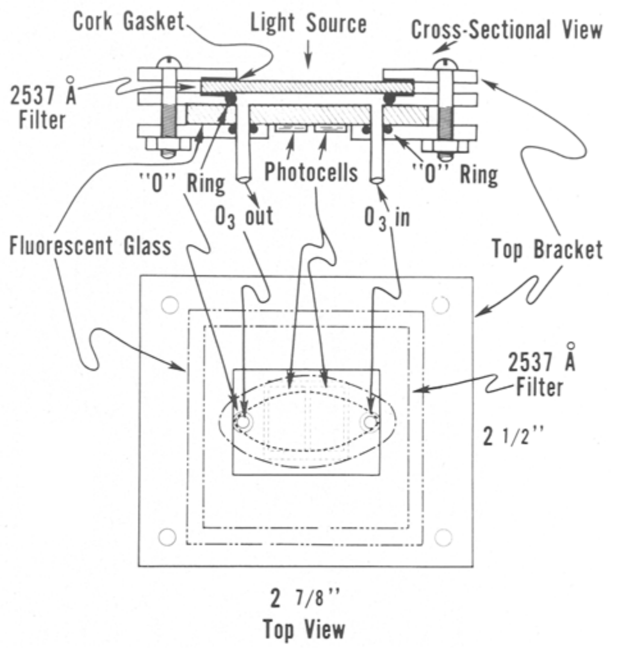

FIG. 5. Redesigned model of ozone cell.

Temperature of the gun's reaction chamber is controlled by two devices: the Triac control, which acts as a variable power source, and the meter relay, which turns the gun off and on at a preset temperature. Temperatures can easily be held constant (30–400 C within ±1 C) for reactions or injections.

Figure 4 shows the construction of an ozone monitoring cell used in the prototype design. The cell

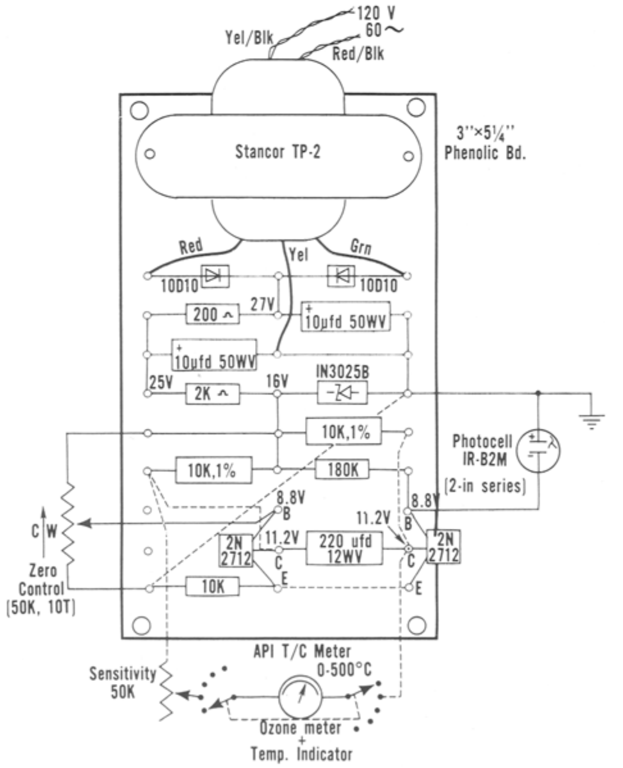

FIG. 6. Difference amplifier pictorial diagram of ozone meter electronics. Dashed lines are connections made under the board. All resistors ½ W, 5% unless otherwise noted. Voltages measured with a VTVM.

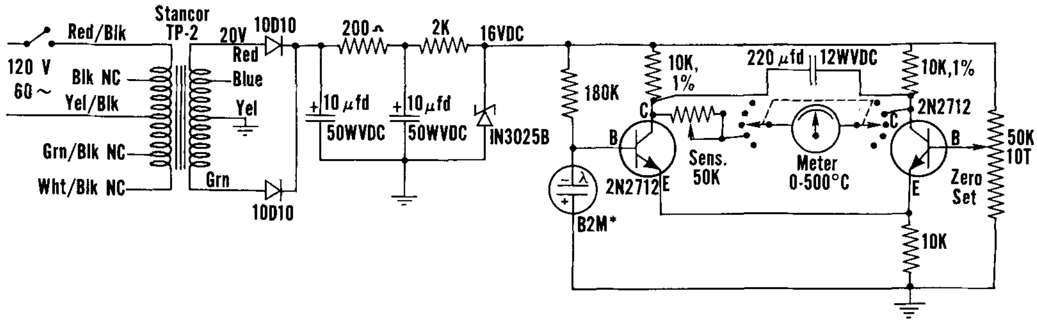

FIG. 7. Schematic of difference amplifier. All resistors ½ W, 5% unless otherwise noted. *Two B2M photocells are used—wired in series.

incorporates a Mineral Light (Ultra-Violet Products, Inc., San Gabriel, Calif.) as an ultraviolet (UV) source and filter, a stainless steel spacer block, fluorescent canary glass (Corning Glass No. 3750) and a photocell. While this unit is readily constructed and works very well, the physical dimensions exclude convenient chassis packaging; therefore, the design shown in Figure 5 was constructed. Although components are the same as in the prototype cell, they are arranged in a more convenient form with stainless steel brackets and Viton O-rings for cell walls or separators. This arrangement is pressure tight and more adaptable to chassis mounting. In addition, the cell depth (14) has been changed from 8 to 1 mm for optimum sensitivity under our conditions, and small holes were drilled through the fluorescent glass to permit gas flow into the cell.

Figure 6 illustrates the component arrangement of the transistorized difference amplifier, which forms the heart of the ozone meter electronics. The unit is packaged on a single phenolic board. The only components not mounted directly on the board are the front panel controls, zero control, sensitivity control and meter along with the photocells that are on the ozone detector. Components are identified in Figure 6 and working voltages are given at critical points. Voltages shown at the transistor terminals are present when the difference amplifier is balanced (meter reading zero on Fahrenheit scale). If ozone is present in the cell, the voltages at the transistor will vary.

A schematic diagram of the difference amplifier is shown in Figure 7. The left of the diagram, up to and including the point marked 16VDC, is the power supply; whereas the right portion forms the difference amplifier (13). The meter is connected between the collectors (c) of the transistors. Thus, no current will flow through the meter (zero meter reading) when equal voltages appear on the collectors but will flow when the voltages are unequal (measuring ozone concentration). The addition of the large capacitor, 220 μf (microfarad), connected between the collectors of the transistors dampens meter movements caused by voltage transients. Note that the biasing of the transistor is controlled by the photocell. Two or more

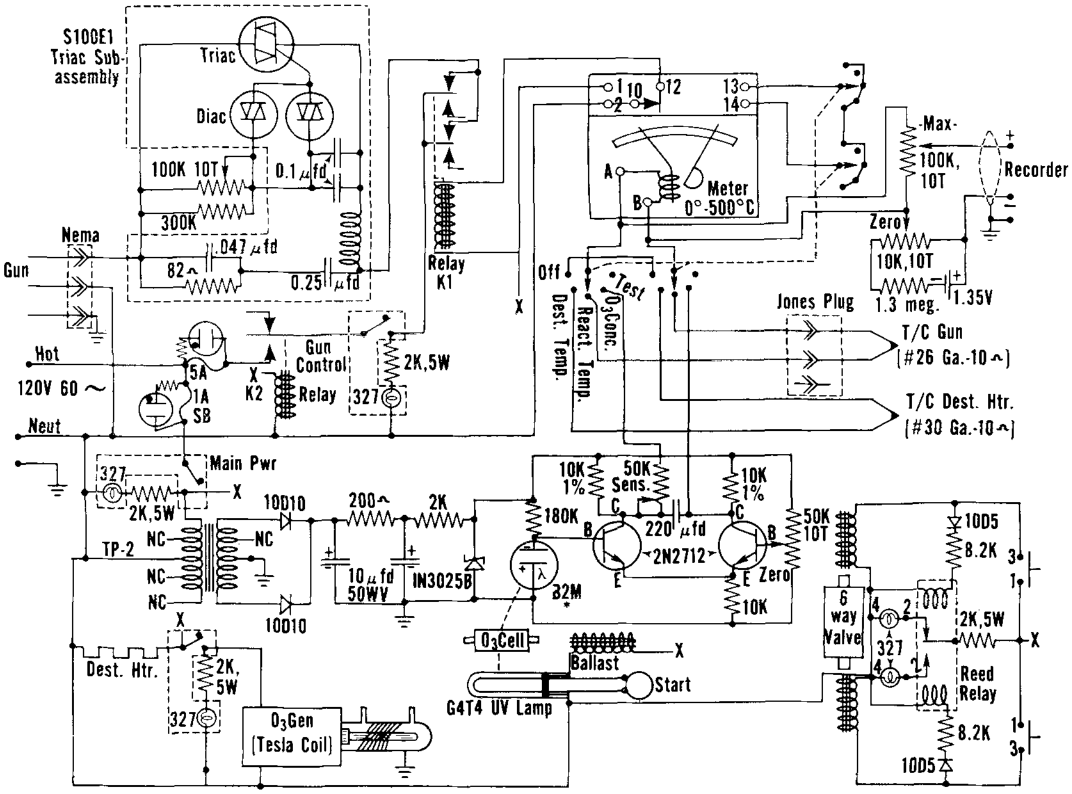

FIG. 8. Complete schematic of integrated system for MRA gun. All resistors ½ W, 5% unless otherwise noted. *Two B2M photocells are used—wired in series.

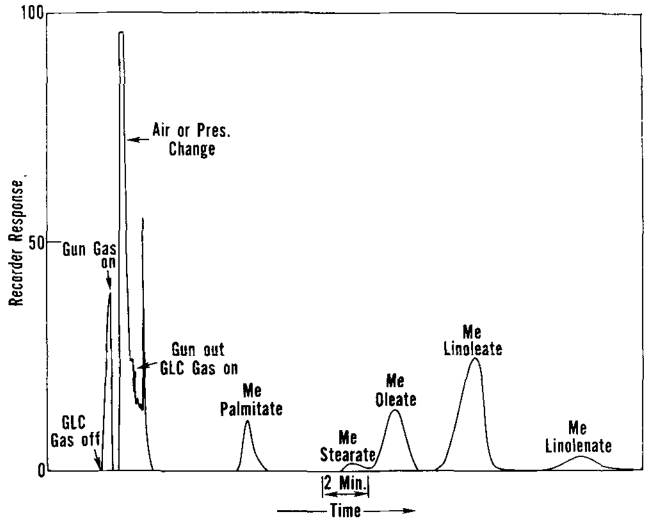

FIG. 9. Chromatograph of transesterification of refined soybean oil using MRA system. Thermoconductivity GLC used. Helium flow rate, 50 cc/min. Column temperature, 170 C. Column packing, 25% DEGS on Chromosorb W, 60/80 mesh. Column dimensions, 5 ft. long × ¼ in. diameter.

photocells may be used of the many different ones available, as well as the type we selected, but each will require a specific resistance in series with it to obtain proper bias. The least complicated method of determining this resistance is to substitute a potentiometer (ca. 1 meg) in place of the 180 K ohm resistor, adjust for zero reading on the meter with a base voltage close to 8.8 volts and then install an appropriate fixed resistor.

To visualize the interconnection of all parts, a complete schematic of the integrated system is given in Figure 8. The Triac subassembly, in the upper left quadrant surrounded by dashed lines, can be purchased as a single unit (1). Slight modifications in the wiring were necessary in the S100E1 Triac we used, but other designs have become available (S100F1) which should not require changes. Gun temperature is readily controlled by varying the 100 K, 10 T potentiometer.

In the upper right quadrant of Figure 8 is shown the meter with its multifunction switch and the strip chart recorder connection. Any function that is indicated on the meter can also be recorded. A 1 mv recorder is recommended.

The lower portion of Figure 8 contains the difference amplifier, ozone generator and UV source. The exact components of the difference amplifier can be easily identified from the enlarged diagram of Figure 7. A starter and ballast must be used with the UV lamp, as with any conventional fluorescent lamp. Although other designs could be used to get high voltage for producing ozone, the cost and simplicity of Tesla coils preclude construction. The ozone generator chamber is made by inserting a stainless-steel rod through a Teflon stopper into a glass tube containing two sidearms, wrapping the tube first with aluminum foil and then with enamel-covered wire and sealing with electrical tape. Connecting the Tesla coil to the stainless-steel rod, grounding one end of the coil and sealing the glass tube, Teflon stopper and rod with epoxy cement complete the construction.

The six-way valve with its associated components appears in the lower right corner of Figure 8. It is operated by two solenoids, one at each end. Position of the valve is indicated by the lighting of either of the No. 327 lamps. A latching-type reed relay must be used to control the lamps since the valve is only momentarily actuated.

Experimental Procedures

Two different experiments were performed to demonstrate the usefulness of the MRA system. The first was transesterification of a refined soybean oil and the second consisted of two ozonization-pyrolyses.

A typical transesterification procedure consists of injecting 8 μliters of sodium methoxide and 3 μliters of refined soybean oil into the gun reaction chamber, heating for 1 min at 50 C and then neutralizing the mixture with 0.4 μliter formic acid. Helium is slowly passed through the mixture to evaporate the solvent and excess acid until indicator paper held at the tip of the needle reveals no acidity. The products are transferred to a GLC by inserting the needle of the MRA gun and vaporizing between 300 and 400 C for 1 min with helium flow rate at 50 cc/min.

The procedure for ozonization-pyrolyses consists of turning on the ozone generator, positioning the six-way valve to pass ozone through the MRA, injecting approximately 0.2 μliter of sample into the reaction chamber and noting reaction completion by meter deflection. Transferring the sample to a GLC is done as in the transesterification procedure.

Samples treated in the MRA may vary in amount from 0.1 to 10 μliters depending on the number of components present and sensitivity of the analytical instrument used. A thermoconductivity isothermal GLC was used for the transesterification reaction, whereas a flame ionization temperature-programmed unit was used for ozonization-pyrolyses.

Results

Transesterification of refined soybean oil in the MRA is shown in Figure 9. The response curve for methyl esters of soybean oil is typical with the exception of the injection period. Various responses will occur initially with the thermoconductivity detector, depending on injection technique employed. When carrier gas is turned off, the pen travels upscale; when zero pressure is attained and MRA gas flow is started, the pen returns to the baseline. During vaporization, desorbed hot gases, traces of solvents and higher or lower gas pressure cause additional response until the MRA gun is removed, the usual carrier gas supply is established and column condition is returned to normal.

Figure 10 plots the ozonization-pyrolsis of methyl oleate. As in Figure 9, the initial injection peaks occur and then the expected major peaks for C_9 aldehyde and C_9 aldehyde ester appear (8).

An ozonization-pyrolysis chromatogram for a complex mixture of oleate isomers is reproduced in Figure 11. The sample consisted of the methyl esters of C_{18} *trans* monoenes of hydrogenated soybean oil. Although chain lengths of the aldehydic fragments are noted, together with the corresponding aldehyde ester portions of the monoenoic fatty acid esters, no attempt was made to identify each peak. Figures 9 to 11 illustrate how the integrated system may be used in determining the composition of reaction products.

Discussion

Reaction chromatography is an opening field of research for broadening the utility of the already in-

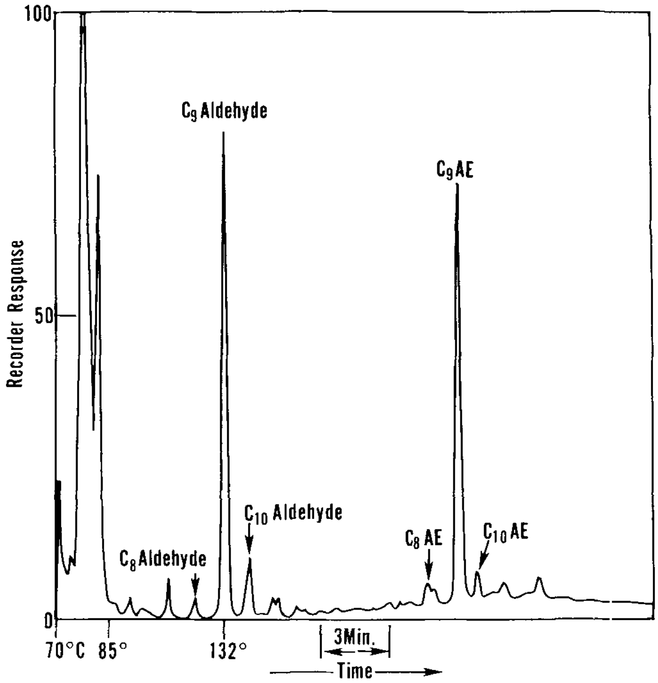

FIG. 10. Ozonization-pyrolysis of methyl oleate with MRA system. GLC: Temperature program, 6 C/min up to 200 C, hydrogen flame detector. Column: 25% DEGS on Chromosorb W, 60/80 mesh, 5 ft. long × ⅛ in. diameter, 20 cc/min N_2 flow rate. AE, aldehydic ester.

valuable gas chromatograph. Progress has already been reviewed by Beroza and Coad (5) who distinguish the "on column" from the "precolumn" reactions. Our work reported here falls under the second category and is primarily concerned with instrumentation. It illustrates the applicability of the new equipment with two common and published laboratory operations; namely, the comparatively simple transesterification of glycerides and the more complex ozonization-pyrolysis of unsaturated fatty acids.

Many and different individual pieces of apparatus have been constructed for ozonization (3,4,7,12,15) and for measuring ozone (12,14), but little attention has been given to the integration of isolated units into a usable, single, compact system. An attempt has been made in our apparatus not only to combine the required components for ozonization-pyrolysis and for a multiplicity of other pre-gas chromatographic chemical treatments, but still to maintain the prime requisite of portability. The only external equipment required is a source of oxygen and of carrier gas, e.g., helium.

The applications presented in this article are by no means intended to indicate the limit of the instrument's usefulness. The apparatus can also be used for esterification, saponification followed by esterification, hydrazine reduction or halogenation. Many of these reactions have been examined with promising results and details will be described later. In addition, the equipment has the advantage of versatility in instrumentation. For example, a small test tube can be used for a reaction chamber rather than the soldering gun (especially for large samples); the temperature controller will control any type of heater up to approximately 600 watts; and ozone concentration can also be monitored when generated from an external source.

The ozone monitors of Figures 4 and 5 are designed about the UV absorption properties of ozone (14).

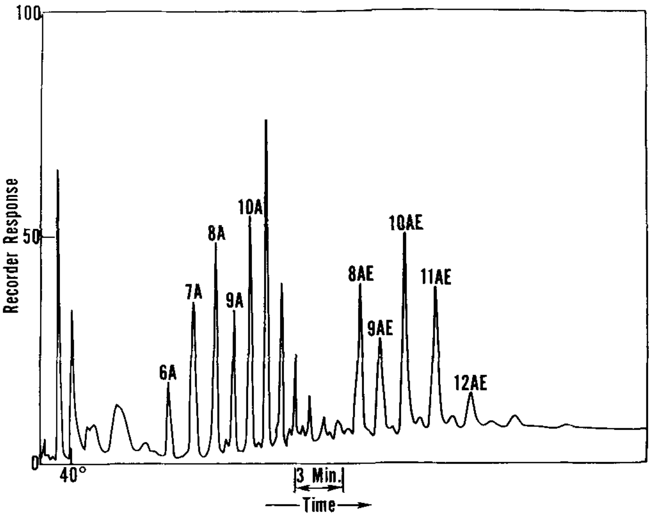

FIG. 11. Ozonization-pyrolysis of methyl esters of C_{18} *trans* monoenes with MRA system. GLC: Temperature program, 8 C/min to 200 C, hydrogen flame detector. Column: 25% DEGS on Chromosorb W, 60/80 mesh; 5 ft. long × ⅛ in. diameter; 20 cc/min N_2 flow rate. A, Aldehyde, AE, aldehydic ester.

The resonance line of mercury (2537 A) when passing through an ozone monitoring cell filled with air is only slightly absorbed and the canary glass of the cell is caused to fluoresce intensely. When ozone is present in the gas stream, UV light is absorbed, and the intensity of the fluorescence observed by the photocell is reduced. In contrast to a filament-type ozone detector, the cell is unaffected by many solvents. Consequently, reactions can be performed in any solvent that does not absorb UV light. Finally, the elimination of liquid ozone measurement as used in some types of apparatus (6) with its accompanying spillage, containers and other problems is another advantage of UV ozone detection.

The parts for our entire MRA apparatus cost approximately $450. Individual sections for specific applications could be constructed for much less; i.e., ozone detector, ozone generator, ozone meter or temperature controller.

ACKNOWLEDGMENTS

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REFERENCES

1. Allied Industrial Electronics Supplement Catalog, No. 671, Chicago, Ill., January 1967, p. 15.
2. Bailey, P. S., Chem. Rev. *58*, 925–1010 (1958).
3. Beroza, M., and B. A. Bierl, Anal. Chem. *38*, 1976–1977 (1966).
4. Beroza, M., and B. A. Bierl, Ibid. *39*, 1131–1135 (1967).
5. Beroza, M., and R. A. Coad, J. Gas Chromatog. *4*(6), 199–216 (1966).
6. Bersis, D., and E. Vassiliou, Analyst *91*, 499–505 (1966).
7. Bonner, W. A., J. Chem. Educ. *30*, 452–453 (1953).
8. Davison, V. L., and H. J. Dutton, Anal. Chem. *38*, 1302–1305 (1966).
9. Davison, V. L., and H. J. Dutton, J. Lipid Res. *8*, 147–149 (1967).
10. Kadesch, Richard G., "Progress in the Chemistry of Fats and Other Lipids," Vol. 6, Pergamon Press, Oxford, London, New York, 1963, p. 291–312.
11. Kleiman, R., V. L. Davison, F. R. Earle and H. J. Dutton, Lipids *2*, 339–341 (1967).
12. Long, Louis, Jr., Chem. Rev. *27*, 437–493 (1940).
13. "Military Standardization Handbook," Mil-Hdbk-215, Selected Semiconductor Circuits, U.S. Govt. Print. Office, Washington, D.C., June 1960, p. 2–8.
14. Welsbach Corporation, "Basic Manual of Applications and Lab Ozonizaton Technique," Ozone Processes Div., Philadelphia, Pa., p. 23–24.
15. Welsbach Corporation, "Organic Ozone Reactions and Techniques," 4th Rev., Ozone Processes Div., Philadelphia, January 1962.

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