# A GAS-CHROMATOGRAPHIC APPARATUS FOR THE STUDY OF THE HOT-ATOM CHEMISTRY OF ORGANIC HALIDES<sup>1</sup>

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### ABSTRACT

The construction of an easily assembled and inexpensive gas-chromatographic apparatus is described. This system has been designed to determine  $\beta$ -active materials. The operation of this instrument involves the use of a temperature program in order to resolve materials boiling over a wide range of temperature.

# INTRODUCTION

Libby (1, 2) made the first attempts to isolate and identify the individual organic products from neutron-irradiated alkyl halides. From the reaction,  $Br^{\$1}(n,\gamma)Br^{\$2}$ , in *n*-propyl bromide he separated some eight active organic products using the technique of fractional distillation. Willard (3) using the same compound and separational method later increased the number of products to 11.

The technique of fractional distillation suffers from one great disadvantage. It cannot operate at the tracer level; carriers must be added for all components present. If carriers are not added the tracers will tend to contaminate each other or any carriers that are present.

Willard and Evans (4, 5) were the first to adapt gas-chromatographic methods to the study of hot-atom reactions of alkyl halides. From neutron-irradiated *n*-propyl bromide they obtained more than 20 active organic products without prior addition of macro amounts of inactive carrier. They had thus shown that gas chromatography was a method of analysis that was suitable not only for operation at the macro level, but also at a tracer level.

# EXPERIMENTAL

In Fig. 1 is shown a schematic diagram of the gas-chromatographic apparatus constructed for determination of the  $\beta$ -active products from the hot-atom reactions of alkyl halides. The detection system employed was one designed for detection of active products; it is conceivable, however, that it could be substituted by or complemented with a conventional type of gas-chromatographic detection system for detection of inactive materials or added carriers.

The gas entered through a fine capillary (A) whose resistance to flow was greater than that of the column; thus it determined the flow rate of carrier through the entire system. With this device it was possible to program the column temperature with a minimum variation in flow rate.

The sample introduction system (D) shown in Fig. 2 had been designed to make use of the micropipettes commonly used in gas-chromatographic analysis. The pipette, filled by capillary action, was inserted through the rubber seal up to the stopcock. The stopcock was then opened and the pipette inserted until its tip plugged the hole in the silicone rubber disk. This blocked the normal carrier gas flow and thus forced the carrier gas to flow through the pipette, blowing the measured volume of liquid into the system. The pipette could then be withdrawn.

<sup>1</sup>Manuscript received November 3, 1960.

Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario. This paper was presented at the Third Symposium on Nuclear Chemistry and Radiochemistry held at Atomic Energy of Canada Limited, Chalk River, Ontario, September 6–8, 1960.

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FIG. 1. Schematic diagram of gas-chromatographic apparatus.
A. Capillary flow restriction. B. Flowmeter. C. Mercury manometer. D. Sample introduction system.
E. Column, F. Flow counter. G. Methane inlet. H. High-voltage supply and linear pulse amplifier. I. Rate meter. J. Recorder.

Solid lines indicate gas flow. Broken lines indicate electrical connections.



FIG. 2. Sample introduction system. I. Normal flow. II. Sample introduced. A. Micropipette. B. Rubber seal. C. Large stopcock. D. Silicone rubber disk. E. Column.

A second sample-introduction system made use of a microsyringe and a puncture seal. The sample volume could be increased as a function of time thereby correcting for radioactive decay and normalizing all chromatograms to the same starting time after irradiation.

The column (E in Fig. 1) was heated by an air oven. This consisted of a metal can 30 cm high and 13 cm in diameter. It was wrapped with asbestos, nichrome wire, and aluminum foil. Temperature programing was achieved by increasing the voltage to the nichrome wire heater at preset time intervals.

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The column was a helix of 6-mm O.D. pyrex tubing coiled to an outside diameter of 6.5 cm. Lengths of 2 and 4 meters were used. The packing was 30% by weight General Electric SF-96 (40) silicone oil coated on Johns-Manville Chromosorb P (30-60 mesh). This packing gave good resolution and short analysis times for alkyl halides. It also had the property of allowing the components to emerge in order of their boiling points, a help in identification.

The outlet of the column was connected to the flow counter (F in Fig. 1) which is shown in detail in Fig. 3. The connection was kept at 200° C in order to prevent condensa-



FIG. 3. Cross section of flow counter. A. UG 931/U high-voltage connector. B. Teflon plug. C. Teflon plug grooved to permit flow of gas. D. 0.05-mm tungsten wire. E. Ball joint. F. Methane inlet. G. Connection to column, 7/25 standard taper ioint.

tion of the high-boiling components. The carrier gas was mixed with methane (natural gas was also found suitable) before entering the active volume of the counter. The active components present in the carrier gas were then counted as part of the counting gas, inside the counter with a very high efficiency. This system was the most sensitive of all present day systems of monitoring gas streams. The relative sensitivity and resolution could be varied by adjusting the flow of the methane relative to the carrier gas as this determined the length of time the active fraction remains in the counter. A trap was connected to the exit of the counter using a spherical ground joint; this was necessary to dispose of the active waste.

The output of the flow counter was fed into a linear pulse amplifier and rate meter. The rate meter ran a standard 10-mv potentiometer recorder which plotted the radiochromatogram.

# RESULTS

Figure 4 shows chromatograms of the products from the reaction  $Br^{79}(n,\gamma)$   $Br^{80}$ in pure n-propyl bromide. Results are shown for irradiation at liquid air temperature

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FIG. 4. Radiochromatograms of the products of the  $Br^{79}(n,\gamma)Br^{80}$  reaction in *n*-propyl bromide. I, at liquid N<sub>2</sub> temperature (-196° C). II, at core temperature (30° C). III, elemental bromine scavenged (30° C). IDENTIFICATION OF PRODUCTS:

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2)	Methyl bromide	
5)	Vinyl bromide	

- Ethyl bromide  $\begin{pmatrix} c \\ (d) \end{pmatrix}$ *i*-Propyl bromide *n*-Propyl bromide
- (e) (f)
- Methylene bromide
- (g) 1,1-Dibromoethane

1,2-Dibromoethane (h)1,2-Dibromopropane

- (i)Bromoform
- $\stackrel{(j)}{(k)}$ 1,3-Dibromopropane
- (l) 1,1,2-Tribromoethane
- Carbon tetrabromide (m)(n)1,2,3-Tribromopropane

Vertical axis represents relative response of the recorder.

 $(-196^{\circ} \text{C})$  and at the reactor temperature (30° C). At the reactor temperature the effects of elemental bromine scavenger are also shown.

The samples sealed in quartz were irradiated in the Rabbit System of the McMaster Nuclear Reactor for 30 seconds at a flux of  $5 \times 10^{12}$  n/cm<sup>2</sup> sec. The background  $\gamma$  field, as determined by cobalt glass, was 10<sup>5</sup> r integrated over this 30-second irradiation period.

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# DISCUSSION

The detection system used in this apparatus was a gas-flow proportional counter designed to operate with a mixture of helium and methane. It was of similar design to the counter described by Wolfgang and Rowland (6) for studies of tritiated compounds.

The great advantage of this detection method was its great sensitivity. As the counting was done internally the counter was essentially 100% efficient for  $\beta$  radiation.

Both Willard (4, 5) and Herr (7) passed the carrier gas through external tubing close to scintillation crystals, thereby incurring loss due to both geometry and crystal efficiency. The literature also described several other systems which externally monitor the gas stream; these, however, lose sensitivity by geometrical losses. These included both Geiger-Müeller (7, 9) and scintillation (10) detection systems.

Harris (8) collected fractions in charcoal traps which were counted in a well-type crystal. Although this method is very sensitive it does not give continuous chromatograms and is not as convenient.

Ionization chambers have been described (11, 12) using continuous flow systems. The geometrical losses have thus been reduced but the sensitivity remains less than that of a proportional counting system.

The proportional counter suffers from the big disadvantage that it can not be used at elevated temperatures. In general, Geiger-Müeller and proportional counters do not perform satisfactorily above 75° C. Wolfgang and Rowland (6) have found, however, that their design performed satisfactorily up to 200° C, the only change having been a shortening in the length of the plateau. This result was confirmed with the flow counter used in this laboratory.

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