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MULTICOLUMN RADIO-GAS- CHROMATOGRAPHIC ANALYSIS OF RECOIL TRITIUM REACTION PRODUCTS

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### Publication Date

1972-09-01

Submitted to  
Analytical Chemistry

LBL-1249  
Preprint ?/

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September 1972

Prepared for the U. S. Atomic Energy Commission  
under Contract W-7405-ENG-48

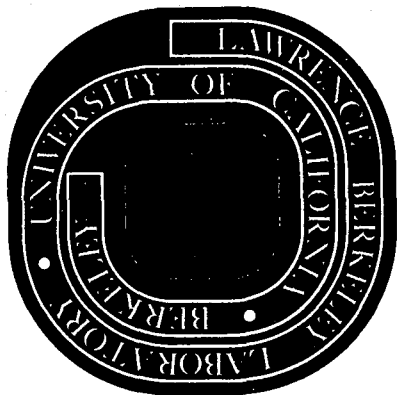
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## INTRODUCTION

Gas chromatography has been widely applied in the separation and analysis of multicomponent systems. If the components are radioactive, the effluent from a chromatographic column may be mixed with a counting gas and the radioactivity measured as the mixture flows through an internal proportional counter (1). This immediate radio-assay is called radio-gas-chromatography. The radio-gas-chromatographic analysis of tritium-labeled hydrocarbons is of particular interest to us. We are studying the reactions of recoil tritium atoms.

There were several a priori considerations for the design of a general radio-gas-chromatographic analysis system for the products of recoil tritium reactions: 1) the expected (tritium labeled) products differed widely in boiling points and physico-chemical properties. The expected products ranged from HT and CH<sub>3</sub>T to the tritiated parent hydrocarbon (we intended to eventually study the recoil tritium reactions of cyclohexene and methylcyclohexene) and included nearly every straight chain alkane-t and alkene-t species in between (for a review of recoil tritium reactions see References 2 and 3). In addition, we wanted to separate the methylcyclohexene-t isomers. (This would determine whether or not direct T-for-H substitution was accompanied by a shift of the double bond (2-4).) A normal "boiling point" column would not separate 3-methylcyclohexene-t from 4-methylcyclohexene-t. The three methylcyclohexene isomers had been individually resolved on a saturated silver nitrate/ethylene glycol column (5). The methylcyclohexene-t isomers and the smaller tritiated alkenes from recoil tritium reaction would be individually resolved on a saturated silver nitrate/ethylene glycol column. However, all alkane-t species would

emerge as one peak from such a column (6). This suggested an aliquoting procedure. The tritiated alkenes and the methylcyclohexene-t isomers could be assayed using one aliquot. The tritiated alkanes could be assayed using another aliquot. Upon further consideration, we decided that no aliquoting procedure would be possible. Aliquoting might lead to unequal fractionation of low vapor pressure parent compounds. Consequently, we decided to inject the entire sample at once. The typical gaseous sample was contained in a glass capsule, 6 cm long with an internal diameter of 1.5 cm. (The dimensions of the capsule are fixed at such large values to minimize the loss of recoil tritons to the capsule wall following the  $^3\text{He}(n,p)\text{T}$  reaction (7).) The glass capsule would be mechanically crushed directly in the stream of the chromatograph.

This led to: 2) a large sample injection volume. The sample is initially distributed throughout the  $20\text{ cm}^3$  volume of the mechanical crusher. This sample volume is swept onto the gas chromatographic column in about 100 sec, assuming typical radio-gas-chromatographic flow rates and pressure drops (8). In contrast, the typical residence time in the 85 ml internal proportional counter is only 60 sec (8). The residence time in the counter is smaller than the sample injection interval. Although the proportional counter has a large volume compared to conventional GC detectors, the volume of the counter is not a limiting factor. The large sample injection volume is the most important factor affecting peak resolution.

However, the use of the counter does add one limitation, namely, 3) the flow rate through the counter must remain constant (8). The limitation of a constant flow rate through the counter is, in practice, a limitation to a constant flow rate for the helium carrier gas. The helium flow rate is

usually changed in programmed temperature gas chromatography (9) and in programmed pressure gas chromatography (10) and in sequential applications of the two techniques (11). Consequently, these powerful techniques for gas chromatographic separations over a wide range of boiling points have not been used in radio-gas-chromatography. However, a stepwise change in column temperature accompanied by a stepwise change in column inlet pressure could be used in radio-gas-chromatography. The simultaneous change of two factors which affect the helium flow rate could be pre-calibrated so that the resultant helium flow rate is unchanged. The simultaneous stepwise change of both temperature and pressure could cause large perturbations in the helium flow rate. The time interval between the radioactivity peaks would have to be large enough so that the helium flow rate was stabilized before the next peak was counted.

Another standard gas chromatographic technique which has not been used in radio-gas-chromatography is post-injector splitting of the helium flow stream (12). With flow splitting, the effluent from each column must be individually monitored. This is often prohibitive in radio-gas-chromatography because it means duplication of relatively expensive counting equipment.

4) All counting of radioactivity must be done with only one counting system.

The four design criteria discussed above are not unique to the radio-gas-chromatographic analysis of recoil tritium reaction products. The same criteria are individually met elsewhere in the application of gas chromatography. Consequently, there remained three avenues of attack: a) Trapping and re-injecting. The disadvantages of trapping are the tedious procedure involved in the addition of non-radioactive carrier and the nagging worry about trapping efficiency (13).

b) Backflushing (14). Backflushing offers no advantage in the radio-gas-chromatographic analysis of recoil tritium reaction products. Although the parent hydrocarbon certainly makes up the bulk of the sample, there is no sharp break in the boiling points between the parent hydrocarbon and the other tritiated products. In addition, tritiated products of higher boiling point than the parent are formed (15). Backflushing would not resolve these products from the parent hydrocarbon.

c) Multiple columns in series. Theoretically, the separating efficiency of each individual column may be reduced if the sample is passed through more than one column before reaching the detector (16). However, useable separations have been made with columns of different liquid phases in series. No one column completely resolved all the peaks. All peaks were resolved when the sample was passed through more than one column in series (17). It is not feasible to pass all sample components through all columns if the sample components differ widely in boiling points and physico-chemical properties. The column in a series which gives good resolution of the low-boiling components gives unuseable peak shapes for the high-boiling components, and vice-versa. The obvious solution was to arrange the column in the series in the order: injector, high-boiling component column, low-boiling component column, detector. The trick was to pass the low-boiling components through both columns while passing the high-boiling components through the high-boiling column only. Three methods of solution have been developed: i) Rabinovitch and co-workers start with the columns in series but at the appropriate time during analysis change to have the columns in parallel (18). This requires multiple detectors.



ii) Rowland and co-workers start with the columns in series but reverse the order of the columns at the appropriate time during the analysis (19). Some or all of the low-boiling components pass through the high-boiling component column twice. This "recycling", using match columns, has been used to achieve difficult isotopic separations (20). With the unmatched column required in a general radio-gas-chromatographic analysis system, the recycled peaks and the high-boiling component peaks may overlap.

iii) Borfitz had discovered that the helium flow through a column may be stopped and peaks in that column may be "stored" for analysis at a later time (21). The intuitive prediction is that the shape of the peaks would deteriorate rapidly once the flow through the column was stopped. In practice, useable peak shapes were obtained later when flow was routed through the column in the same direction as before the flow stoppage. Several authors (22-24) had applied the stop-flow technique to a series of multiple columns. In this multicolumn stop-flow method, the order of the columns remains unchanged.

The continuing interest in isotopic separations in general (13) and our specific interest in separating species which differ only by the position of the radioactive label (see References 25 and 26) led us to create a multicolumn series with stop flow and recycle capability. We decided to maintain a constant flow rate through the detector in stop-flow applications by stepwise pressure programming instead of using preset needle valves (as in References 18, 22-24). A radio-gas-chromatographic system with stepwise pressure programming capability would also have stepwise temperature programming capability as discussed earlier. Later we were forced to develop the ability to remove

and further separate unresolved peaks emerging in the middle of the analysis. This is known as taking a center cut. We are reporting a general radio-gas-chromatographic system which operates under the design criteria discussed earlier: 1) The components of the hydrocarbon mixture differ widely in boiling point and physico-chemical properties. 2) The sample injection volume is large; namely the whole sample. 3) The flow rate through the detector is constant. 4) All peaks are monitored with the same detector (beta proportional counter). This system uses four columns in series and has the capability for 1) stop flow, 2) recycle, 3) center cut, 4) stepwise pressure programming, and 5) stepwise temperature programming applications.

#### EXPERIMENTAL

Pressure control and valve arrangement. Pressure regulation of the helium carrier gas began at the commercially available tank with a standard two stage regulator. This regulator maintained a pressure of 100 psi in the ballast tank. The ballast tank was a common input to five single-stage regulators used for pressure programming. These single stage regulators each exhausted through a check valve (on/off) into a common manifold. Only one pressure regulator was open to the manifold at any time. That pressure regulator was preset for a specific series of columns. The preset pressure maintained a helium flow rate through the counter of 30 cc/min. Removing (or adding) a column from (or to) the series required a shift to a lower (or higher) preset pressure to maintain a 30 cc/min flow rate. The pressure in the manifold was changed by first shutting off the pressure regulator in current use. The manifold pressure was then bled off to the atmosphere. Following bleed-off,

the new preset pressure regulator was opened to the manifold. This made a sharp pressure change. Reproducible flow rates were obtained with these "presettings" over long periods of time. During an analysis, the flow rate obtained through use of preset pressure regulators was more constant than the flow rate obtained using a commercial constant flow controller (#63-BU-L, Moore Products Co.); particularly during stepwise temperature programming and reversing the order of the columns in the flow stream. This manifold was the beginning of the arrangement of columns and 4-way valves shown in Figure 1.

The flow down stream from the manifold was through 1/6 inch o.d. stainless steel tubing. The 4-way valves were #P26-418 from Circle Seal Corp. The stainless steel tubing and 4-way valves were operated at 25 °C. The exhaust from the buffer column passed through the detector side of a standard thermistor cell (plus power supply and bridge circuit) from Gow-Mac Corp. The thermistor detector was, of course, not sensitive enough to measure carrier-free amounts of tritium labeled hydrocarbons. The thermistor detector was used to determine retention times of standards and to monitor the parent hydrocarbon peak during an actual analysis. The thermistor response was printed out by one pen of a Leeds and Northrup 10 mV dual pen strip chart recorder. Following the thermistor the helium flow stream was mixed with propane in a standard 1/4 inch Swagelock Tee. The propane flow stream similarly consisted of a commercial tank, two-stage regulator, ballast tank, single stage regulator, check valve, dummy column to give a useable pressure drop, then the mixing Tee. The combined helium and propane flow passed through the counter, through a soap bubble flow meter and was then exhausted into a hood. The combined flow rate was maintained at 83 cc/min., giving the desired 1.8/1.0 propane to helium mixture (8). The propane pressure was not changed during an analysis.

Columns. HT, CH<sub>3</sub>T, ethane-t, and ethylene-t were resolved on a 50 ft column of 10% propylene carbonate (PCA) on 60/70 mesh activated alumina F-1 in 1/4 inch o.d. copper tubing. The method of column preparation and typical retention times are given elsewhere (27). This column was operated at two temperatures: -78 °C, maintained by immersing the column in a dry ice-acetone slurry, and -8 °C, maintained by immersing the column in an acetone bath inside a commercial freezer. The temperature change from -78 °C to -8 °C (or -8 °C to -78 °C) was made by physically removing the PCA column from one temperature bath and placing the column in the other temperature bath. Tritiated C<sub>3</sub> and C<sub>4</sub> hydrocarbons were resolved on a 50 ft. column of 25% 2,4-dimethyl sulfolane (DMS) on 30/60 mesh acid-washed Chromosorb P in 1/4 inch o.d. copper tubing. Typical retention data for this column are given in References 28. This column was operated at room temperature. Tritiated C<sub>5</sub> - C<sub>7</sub> hydrocarbons were resolved on a 4.5 ft. column of 22% di-n-butyl tetrachlorophthalate (DBTCP) on 30/60 mesh acid-washed Chromosorb P in 1/4 inch o.d. copper tubing. Typical retention data for this column are given in Reference 29. This column was operated at room temperature. During the course of our work, it became necessary to separate 1,3 butadiene-t from 1,3 butadiene-d<sub>5</sub>t (30,31). This separation was done on a 25 ft. column of saturated silver nitrate/ethylene glycol (AgNO<sub>3</sub>) on 30/60 mesh acid-washed Chromosorb P in 1/4 inch o.d. stainless steel tubing. The method of column preparation and typical retention data are given in Reference 5. This column was operated at room temperature. A buffer column was placed immediately before the counter to minimize the flow perturbations caused by changing the order of the columns in the series. The buffer column was 25 ft. of 60/80 mesh glass beads in 1/4 inch o.d. copper tubing and was operated at room temperature.

Counting. The 85 ml counter has been described (8). The high voltage on the centerwire of the counter was maintained by a 5 kV power supply. A pre-amplifier of our own design (schematics are available on request) was coupled to the counter. The pulses from the pre-amplifier went through a standard amplifier and single-channel analyzer, before passing through a standard anticoincidence network. An anticoincidence screen of plastic scintillator as well as an arrangement of lead bricks shielded the counter from background radiation. This lowered the background of the counter to typically 10 counts/min. The train of pulses emerging from the anticoincidence network was divided. One branch went to a rate meter. The rate meter response on a logarithmic scale was printed out on one pen of the dual pen recorder. During an actual analysis, this gave a continuous plot of the log of activity (monitored by the counter) versus time. The other branch passed through a variable time control unit and into a 1024-channel analyzer (Technical Measurements Corp.). The 1024-channel analyzer was used in the multiscaler mode. The length of the time during which the response of the counter was recorded in a single channel was set by the variable time controller unit. At the end of the preset length of time the controller unit advanced the counter response to the next channel. The controller was started when the sample was injected.

At the end of analysis the number of counts recorded in each channel had been stored in the memory of the analyzer. The memory could be printed out in both analog and digital fashion. Qualitative information could be obtained from the analog printout on a Hewlett-Packard X-Y plotter. The analog printout was a plot of counts (in each channel) versus channel number. The channel number could be converted to time from knowledge of the settings of the

time controller. A typical radio-chromatogram is shown in Figure 2. Quantitative information could be obtained from the digital printout of a Hewlett-Packard model 562A printer.

Sample preparation. The procedure employed for sample preparation was similar to that described previously (32). The sample was a 1720 Pyrex capsule (14 ml internal volume) to which 8.5 cm 3-methylcyclohexene, 2.6 cm of 4-methylcyclohexene, 1.5 cm butadiene-d<sub>6</sub> and 30 cm of <sup>3</sup>He had been added (pressures corrected to 130 °C). The irradiation was for 24 hours at a flux of  $3.9 \times 10^8$  n cm<sup>-2</sup> sec<sup>-1</sup> in the Hohlraum of the Berkeley Campus Nuclear Reactor. The temperature of the sample during irradiation was maintained at  $130.0 \pm 0.5$  °C by a specially designed irradiation container which will be described elsewhere (33). The sample capsule was placed in the sample injector and the injector was heated to 130 °C before injection.

#### ILLUSTRATION OF SYSTEM USE AND CAPABILITY

A typical analysis of the products of recoil tritium reactions with methylcyclohexene is shown in Figure 2. The sequence of operations used to obtain this radio-chromatogram is given in Table I. This sequence of operations, with the exception of the center cut of butadienes (265 to 300 min), represents a general radio-gas-chromatographic analysis scheme and has been successfully employed in the analysis of the products of recoil tritium reactions with ethylene, propylene, butane, 1-butene, isobutene, cis- and trans-2-butene, butadiene, cyclohexane, and cyclohexene as well as the more difficult case of 3- and 4-methyl cyclohexene shown in Figure 2. The timing of these operations is obviously specific for this choice of four columns. Table I

and Figure 2 are used to illustrate how the arrangement of 4-way valves shown in Figure 1 may be employed to utilize the gas chromatographic techniques discussed below. The techniques used in the analysis shown in Figure 2 in the order of their appearance are:

(1) Stop flow. At 30 min.,  $C_5$  product peaks are just about to emerge from the DBTCP column.  $C_4$  and lighter product peaks have already emerged and are in the DMS and PCA columns. At 30 min., the  $C_5$  and  $C_7$  product peaks are "stored" in the DBTCP column for future analysis when flow in the DBTCP column is stopped. At 38 min.  $C_3$  product peaks are just about to emerge from the DMS column.  $C_2$  and lighter product peaks have already emerged and are in the PCA column. At 38 min., the  $C_3$  and  $C_4$  product peaks are "stored" in the DMS column for future analysis.

At 165 min., flow is restarted in the DMS column. While the flow through the DMS column was stopped, the pressure equilibrated over the entire column. In restarting the DMS column, this causes a flow surge which lasts for 3.5 min. The first  $C_3$  product peak, propane-t, emerges and starts being counted 4 minutes after restarting. Consequently, the flow surge does not affect the analysis. Storage for a little over two hours has affected the peak shape. For example, the FWHM of a trans-2-butene mass peak increased by 10% because of peak storage. At 380 min., flow is similarly restarted in the DBTCP column. Again the flow surge does not affect the analysis. The FWHM of a cyclohexene mass peak increased by 15% because of peak storage in the DBTCP column for nearly six hours.

(2) Stepwise pressure programming. A constant helium flow rate through the detector was maintained when the DBTCP column and the DMS column were removed

from the flow stream by decreasing the manifold pressure at 30 and 38 min., respectively. Similar use of the pressure "presettings" is made at later times in the analysis when columns are added to or removed from the flow stream.

(3) Stepwise temperature programming. At 98 min. the operating temperature of the PCA column is changed from  $-78^{\circ}\text{C}$  to  $-8^{\circ}\text{C}$ . This shortens the elution time of the ethylene-t peak by 400 min. The stepwise temperature change causes a perturbation in the helium flow rate. This perturbation does not affect the analysis because no peaks are being counted. At 162 min., the  $\text{C}_2$  peaks in the PCA column have emerged and been counted. The temperature of the PCA column is then returned to  $-78^{\circ}\text{C}$  to minimize the number of pressure regulators required for analysis.

(4) Center cut. It is known from calibration data that the unresolved butadiene-t and butadiene-d<sub>5</sub>t peaks would have emerged from the DMS column and been counted at 275 to 290 minutes. The center cut of these peaks is made by placing the  $\text{AgNO}_3$  column down stream from the DMS column during that interval.

(5) Recycle. The inherent recycle capability of this system is displayed in the permutations of the column order at 265, 300, and 375 minutes. A careful analysis of Figure 1 will reveal a nested series of recycle loops. The recycle capability is used here to allow separation of the butadiene-t and butadiene-d<sub>5</sub>t peaks to proceed simultaneously with the counting of peaks emerging from the DMS and DBTCP columns. The recycling of the butadiene-t and butadiene-d<sub>5</sub>t peaks through the DBTCP column is unnecessary for the sake of resolution. However, this recycling is advantageous because after 380 min. the analysis is automatic.



### CONCLUSIONS

A general radio-gas-chromatographic analysis system has been developed for hydrogen and C<sub>1</sub> to C<sub>7</sub> alkanes and alkenes. Although all peaks had to be monitored at a constant flow rate in the same detector and the injection volume was large, more than 20 peaks have been analyzed, with good resolution of most peaks, in a total time of 1000 minutes. We conclude that: (1) A recycle system of 4-way-valves and columns allows permutation to be made in the order of columns in a series. These permutations may be useful by themselves in addition to allowing peaks to be recycled and center cuts to be made. In addition, this system of 4-way-valves may shorten the time required for a particular analysis. (The long time required for the analysis shown here was due to the large injection volume.) (2) Stop flow chromatography is a useful technique if the accompanying increase in FWHM can be tolerated. (3) Stepwise inlet pressure programming can be used to maintain a constant flow rate through the detector when a column is removed from the series in stop-flow chromatography. Stepwise pressure programming is additionally advantageous because it allows utilization of powerful stepwise temperature programming techniques.

Therefore, we propose a new gas-chromatographic system that has broad application.

### ACKNOWLEDGMENTS

We would like to acknowledge a series of discussions on chromatography with Drs. F. S. Rowland, G. P. Miller, J. K. Garland, and D. H. Froemsdorf. We would like to thank Walt Niemi for assistance with the regulators and Fred Vogelsberg for handling the electronics.

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\* Work performed under the auspices of the U. S. Atomic Energy Commission.

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Table 1. Sequence of Operations

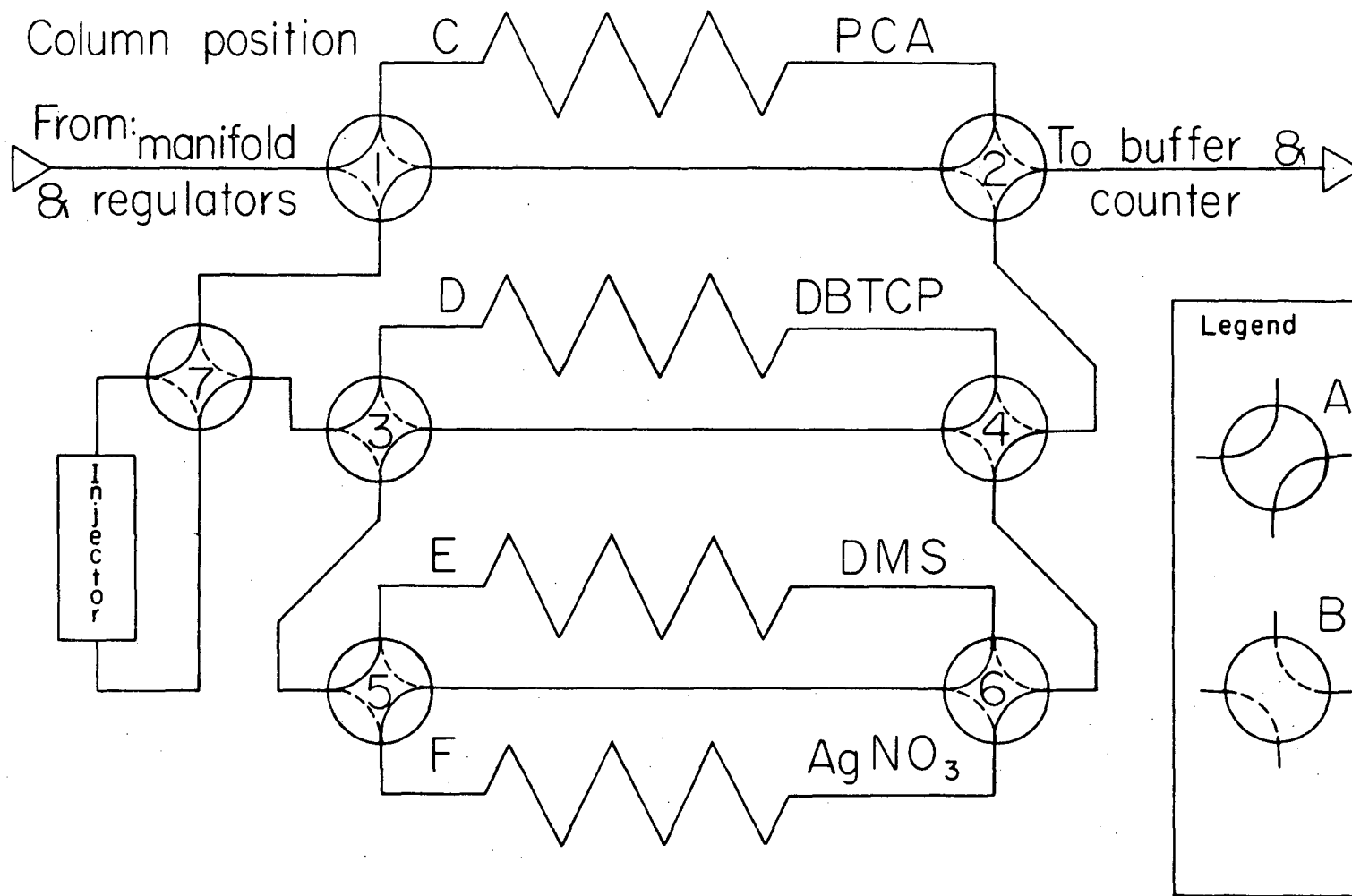
Time Min.	Manifold Pressure psi	Arrangement of Valves <sup>a</sup> 123 456 7	Column Order in Flow Stream <sup>b</sup>	Comment
-1	34.4	BBA AAB B	DBTCP, DMS, PCA-78	break capsule
0		BBA AAB A		inject sample; timing interval 0.5 min./channel
10		BBA AAB B		injector by passed
30	34.2	BBB AAB B	DMS, PCA-78	DBTCP by passed
38	28.0	ABB AAB B	PCA-78	DMS by passed
98	32.0		PCA-8	Temp. change -78 °C to -8 °C for PCA
162			PCA-78	Temp. change -8 °C to -78 °C for PCA
165	34.2	AAB AAB B	PCA-78, DMS	flow restarted in DMS
250				change timing interval to 1.5 min./channel
265	36.2	AAB AAA B	PCA-78, DMS, AgNO <sub>3</sub>	AgNO <sub>3</sub> center cut of butadienes
320		AAB ABB B	PCA-78, AgNO <sub>3</sub> , DMS	end center cut
375		AAB AAA B	PCA-78, DMS, AgNO <sub>3</sub>	order switched
380		AAB BAA B	PCA-78, DMS, AgNO <sub>3</sub> , DBTCP	flow restarted in DBTCP

a) See Figure 1.

b) With valves as indicated and propylene carbonate column (PCA) in position C in Figure 1, di-n-butyl tetrachlorophthalate column (DBTCP) in position D, 2,4-dimethyl sulfolane column (DMS) in position E, saturated silver nitrate/ethylene glycol column (AgNO<sub>3</sub>) in position F.

## Figure Captions

- Fig. 1. Schematic diagram of gas chromatographic flow stream. The columns are defined in the text. The choice of columns is specific for this analysis. The recycle arrangement of 4-way valves with positions for four columns is presented as a general gas chromatographic system.
- Fig. 2. Radio-gas-chromatogram of recoil tritium reaction products. Sample preparation is given in the text. The HT peak shown is 1/32 actual. Only the carbon skeleton is shown for the other radioactivity peaks. All mass peaks are shown on the same arbitrary scale. See Table I for an explanation of the time scale.



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Fig. 1



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