

# Simultaneous Dual Column Gas Chromatography

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► A gas chromatography apparatus which employs two columns having different liquid phases and which displays simultaneously the chromatograms obtained from each column on separate channels of a dual channel recorder is described. The apparatus is capable of providing from one sample injection the necessary data for qualitative analysis by means of retention volume constants. Performance data for the measurement of both retention times and peak areas are given.

A NUMBER of two-stage systems for series operation of different columns have been described (1-3, 5), as well as the parallel operation to two chromatographs (6). An instrument which incorporates two columns in a single oven is also available commercially (Aerograph Model A-350-B, Wilkins Instrument and Research, Inc., Walnut Creek, Calif.), but the use of separate injection ports and only one detector limit its utility. Many advantages may be derived from a system which permits two chromatograms to be obtained with a single sample injection. A gas chromatograph which employs two columns having different liquid phases and which displays simultaneously the chromatograms obtained from each column on separate channels of a dual channel recorder has been devised.

The simultaneous dual column gas chromatograph was developed primarily to provide a simple and convenient means of acquiring the necessary data for carrying out qualitative gas chromatographic analyses by means of retention volume constants (4). Two chromatograms, each from a different column, may be obtained in the time normally required for one, yet under exactly the same conditions of either constant or programmed temperature. The instrument may also be used effectively to perform simultaneous chromatographic analyses on different columns when the available amount or nature of the sample will permit only a single sample injection. Furthermore, the inherent reproducibility of experimental conditions for the two columns is ideally suited to studies involving the comparison of effect of column param-

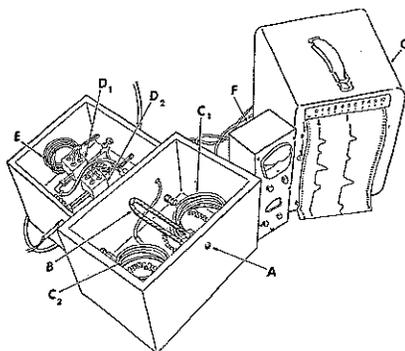


Figure 1. Simultaneous dual column gas chromatograph

- A. Syringe injection port
- B. Sample evaporator and premixer
- C<sub>1</sub>, C<sub>2</sub>. Chromatograph columns
- D<sub>1</sub>, D<sub>2</sub>. Matched kathemeters
- E. Carrier gas preheating coil
- F. Kathemeter controls
- G. Dual channel strip chart recorder

eters such as liquid phase, temperature, flow rate, column length.

## EXPERIMENTAL

**Apparatus.** A sketch of the chromatograph is shown in Figure 1. The apparatus consists of a single, rubber-septum, syringe injection port, a sample splitter, two packed, coiled columns, two thermal conductivity detectors (Model 9193 (TE-11), Gow-Mac Instrument Co., Madison, N. J.) with separate controls and a dual

channel strip chart recorder (Model G-22, Varion Associates, Palo Alto, Calif.). The columns and detectors are mounted in separately heated chambers to provide separate temperature control. The column oven is equipped with suitable voltage controls for the heating elements to provide, in addition to constant temperature control, either a linear or nonlinear temperature program from 25° to 175° C. at rates ranging from 2° C. per minute to 10° C. per minute. A pre-heating coil is employed between the carrier gas source and the reference sides of the detectors to help eliminate base line drift during programmed temperature runs.

The flow of gas in the apparatus is indicated in Figure 2. Helium carrier gas enters through the pre-heating coil located in the detector oven and passes successively through the reference sides of the detectors 1 and 2. The carrier gas then passes by the sample injection port and through a length of tubing approximately 12 inches long which is heated to the same temperature as the injection port. The purpose of this tube is to allow sufficient time for the sample to become completely vaporized and mixed with the carrier gas before reaching the splitter. The homogeneous mixture of sample and carrier gas then passes through the splitter (a three-way, brass tee, compression fitting). One half of the sample passes into column A and the other half into column B. The portions of the gas stream passing through columns A and

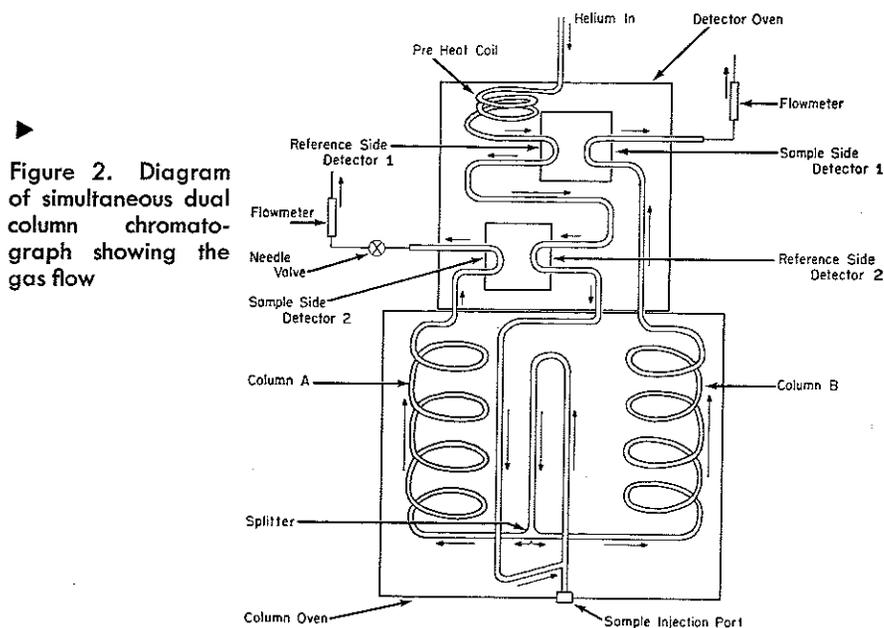


Figure 2. Diagram of simultaneous dual column chromatograph showing the gas flow

*B* are directed, respectively, into the sample sides of detectors 1 and 2. As the components pass through the separate detectors, the respective chromatograms representing the separations obtained on columns *A* and *B* are traced simultaneously on a dual channel recorder.

To obtain an even split of the sample, the flow rate of carrier gas must be maintained at equal values on each side of the splitter. The flow rate on each side is measured by a flow meter at the exit end of the sample side of each detector and is adjusted by means of needle valves inserted between the exit end of the detectors and the flow meter.

**Performance.** The apparatus has been used routinely for investigations in this laboratory for several months. Chromatograms have been obtained of a large number of a wide variety of compounds, both singly and in mixtures, and under both isothermal and programmed temperature conditions of operation. Compounds have represented eight different types of functionality and have ranged in boiling point from 35° to 185° C. (4).

The performance of the splitter is precise. Some representative data are given in Table I. These data were obtained under typical operating conditions for a routine isothermal gas chromatographic analysis, that is, column temperature 120° C., injection port temperature 175° C., detector temperature 150° C., flow rate 75 ml. per minute. The columns were coated respectively with 25% by weight of Carbowax 20-M and Silicone SF-96 on

60 to 80 mesh firebrick. The columns employed in this study, although inferior to the OPN/CW-4000 or the CW-20M/CW-4000 combinations cited in reference (4) for optimum utility, nevertheless provide suitable retention volume constants and were necessarily chosen to illustrate this work because they constitute the only pair which showed a change in order of elution of components. The precision of splitting was estimated by measuring the area under the peak on each chromatogram and calculating the ratio of peak areas. The ratio of splitting is also expressed

as a percentage. Variation in the ratio was randomly distributed, thereby indicating that no geometrical asymmetry existed. The measures of precision applied—e.g., small average deviation—showed that the splitting ratio can be set reproducibly by an appropriate adjustment of the flow rate in each column.

The data for evaluating the reliability of the splitter were obtained from chromatograms of pure compounds injected singly. The behavior of the compounds in mixtures was evaluated from data obtained under the same operating conditions from replicate (five) simul-

Table I. Reproducibility of 1 to 1 Splitting Ratio on Simultaneous Dual Column Chromatograph

Compound	Approximate Sample Size, $\mu$ l.	Peak Area, Sq. Cm. (by Triangulation)		Ratio of Peak Areas	Average Splitting Ratio, %
		on Carbowax 20-M	on Silicone SF-96		
<i>n</i> -Pentane	2.2	2.81	2.79	1.007	50.20/49.80
	2.7	3.44	3.41	1.009	
<i>n</i> -Amyl acetate	2.7	1.92	1.90	1.010	50.59/49.41
	2.8	2.06	1.95	1.056	
	2.3	1.68	1.67	1.006	
<i>n</i> -Decane	3.3	2.02	2.11	0.957	49.42/50.58
	3.2	2.05	1.99	1.030	
	2.9	1.75	1.85	0.946	
Toluene	2.1	2.72	2.57	1.058	50.27/49.73
	2.4	2.95	2.95	1.000	
	2.3	2.79	2.86	0.976	
<i>n</i> -Butanol	2.8	3.65	3.45	1.058	50.46/49.54
	2.9	3.62	3.54	1.023	
	2.7	3.28	3.36	0.976	

Mean Ratio of Peak Areas = 1.008  $\delta_R = 0.028$   
Mean Splitting Ratio, % = 50.20/49.80  $\delta_{\%} = 0.42$

Table II. Simultaneous Dual Column Chromatographic Analyses of Five-Component Heterologous Mixture<sup>a</sup>

	Di- <i>n</i> -butyl ether		<i>n</i> -Butanol		Toluene		<i>n</i> -Heptanal		<i>n</i> -Propylbenzene	
	14.4 <sup>b</sup>	15.0 <sup>c</sup>	20.0	17.2	20.6	21.6	16.1	16.3	29.3	29.8
	13.1	15.0	19.4	17.5	20.6	20.5	16.2	16.9	29.4	30.0
	13.6	14.1	20.0	17.3	21.1	20.2	16.5	16.1	29.8	30.8
	14.4	14.6	19.2	17.6	20.7	20.2	16.2	17.1	29.6	29.6
	14.7	14.4	19.3	17.3	20.5	20.1	16.0	16.7	29.6	30.2
Mean ( $\bar{x}$ )	14.0	14.6	19.6	17.4 <sup>d</sup>	20.7	20.5	16.2	16.6	29.5	30.1
Av. dev. ( $\delta$ )	0.57	0.30	0.34	0.14	0.16	0.42	0.12	0.34	0.16	0.34

Mean average deviation =  $\bar{\delta} = 0.29$

Mean relative error of analyses =  $\frac{\sum(\delta/\bar{x})}{n} = \sim 1.5\%$

<sup>a</sup> Expressed as per cent of component computed from peak areas in sq. centimeters obtained by triangulation.

<sup>b</sup> Values obtained from chromatograms given by Carbowax 20-M column.

<sup>c</sup> Values obtained from chromatograms given by Silicone SF-96 column.

<sup>d</sup> Discrepancy in *n*-butanol analysis is due to tailing of the peak on the Silicone SF-96 column. Measurement of peak area by counting squares method gives a closer result.

Table III. Simultaneous Dual Column Chromatographic Analyses of Five-Component Homologous Mixture<sup>a</sup>

	Benzene		Toluene		Ethylbenzene		<i>n</i> -Propylbenzene		<i>n</i> -Butylbenzene	
	17.1 <sup>b</sup>	17.2 <sup>c</sup>	18.5	17.3	17.1	17.6	27.5	27.4	19.9	20.4
	16.7	17.2	18.4	17.3	17.2	17.7	27.1	27.6	20.4	20.1
	17.1	17.3	18.5	17.8	17.3	17.2	28.3	28.6	20.1	19.3
Mean ( $\bar{x}$ )	17.0	17.2	18.5	17.5	17.2	17.5	27.6	27.9	20.1	19.9
Av. dev. ( $\delta$ )	0.17	0.03	0.03	0.23	0.07	0.20	0.43	0.5	0.13	0.43

Mean average deviation =  $\bar{\delta} = 0.22$

Mean relative error of analyses =  $\frac{\sum(\delta/\bar{x})}{n} = \sim 1\%$

<sup>a</sup> Expressed as per cent of component computed from peak areas in sq. centimeters obtained by triangulation.

<sup>b</sup> Values obtained from chromatograms given by Carbowax 20-M column.

<sup>c</sup> Values obtained from chromatograms given by Silicone SF-96 column.

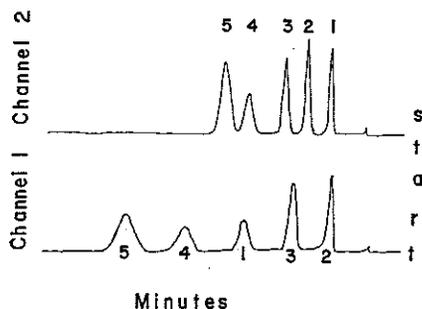


Figure 3. Chromatograms of five-component mixture obtained simultaneously from two different columns

Upper, Carbowax 20-M, lower, Silicone SF-96  
 Column chamber temperature, 125° C.  
 Injection port temperature, 175° C.  
 Detector chamber temperature, 150° C.  
 Helium flow rate, 75 ml./min. in each column  
 Sample size, 4  $\mu$ l.  
 Peak 1, di-*n*-butyl ether  
 Peak 2, *n*-butanol  
 Peak 3, toluene  
 Peak 4, *n*-heptanal  
 Peak 5, *n*-propylbenzene

taneous chromatograms of a five-component heterologous mixture. Typical chromatograms are shown in Figure 3. The results of the quantitative analyses are given in Table II. The precision of the determination of each component of the mixture on each column was computed and expressed as the average deviation of the mean. The over-all precision was also calculated. Similar data were obtained for triplicate simultaneous chromatograms of a five-component homologous series of alkyl benzenes (Table III).

Since the apparatus is used primarily for qualitative analysis, the reproducibility of retention volumes was also evaluated. The data are given in Table IV. The average deviation of the measurement of retention volume is less than the absolute error of one's ability to measure the distance on the

chart paper—i.e., 0.1 cm.—and meets the requirements for precision in the computation of retention volume constants (4).

To evaluate the performance of the apparatus under programmed temperature conditions, simultaneous chromatograms were obtained for an homologous series of normal alkyl benzenes (benzene, b.p. 80.1° C., through *n*-butylbenzene, b.p. 183.3° C.). The columns were programmed from 40° to 175° C. at a heating rate of 5° C. per minute, and the carrier gas flow was maintained at a constant rate of 75 ml. per minute. All components were eluted from both columns within 24 minutes. The separation of components was good with practically even spacing between components. Carbowax 20-M gave a separation factor of 6.2 cm. between members and Silicone SF-96 a factor of 4.4 cm. No appreciable base line drift was observed. Data on splitting ratios, precision of quantitative analyses, and reproducibility of

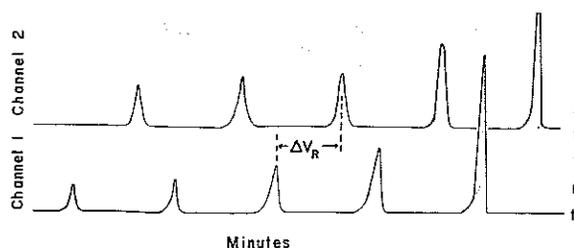


Figure 4. Simultaneous dual column programmed temperature chromatograms of homologous series of *n*-alkylbenzenes (C<sub>6</sub>-C<sub>10</sub>)

Columns, 5% didodecylphthalate (upper) and 5% squalane (lower) on 60-80 mesh firebrick  
 Heating rate, 3° C./min. from 30° to 100° C.  
 Injection port temperature, 175° C.  
 Detector chamber temperature, 150° C.  
 Argon flow rate, 80 ml./min. in each column  
 Sample size, 0.01  $\mu$ l.  
 Detectors, matched strontium-90 ionization cells

retention times indicated that performance under programmed temperature conditions of operation was comparable to the results obtained for isothermal operation.

#### DISCUSSION

There are two main advantages of using a simultaneous dual column chromatograph for qualitative analysis by means of retention volume constants in addition to the obvious savings in time and amount of sample required and the inherent reproducibility of operating parameters. First, it is extremely convenient to be able to compute the retention volume constants of unknown components directly from a single chromatogram. In the case of programmed temperature chromatograms, the evaluation of the retention volume difference is accomplished simply by measuring the

Table IV. Reproducibility of Retention Volumes

Retention volumes<sup>a</sup> from replicate simultaneous dual column chromatograms of five-component heterologous mixture

on Carbowax 20-M					on Silicone 96				
Di- <i>n</i> -butyl ether	Butanol	Toluene	Heptanal	<i>n</i> -Propylbenzene	<i>n</i> -Butanol	Toluene	Di- <i>n</i> -butyl ether	<i>n</i> -Heptanal	<i>n</i> -Propylbenzene
1.9	3.2	4.2	6.5	7.5	1.9	3.9	6.7	10.2	13.1
1.8	3.1	4.4	6.2	7.7	2.0	4.1	6.9	10.2	13.4
1.9	3.1	4.3	6.3	7.5	1.9	4.0	6.7	10.0	13.1
1.9	3.1	4.3	6.2	7.4	1.9	4.0	6.6	9.8	12.9
1.8	3.0	4.2	6.1	7.3	1.9	4.0	6.5	9.8	12.8
Mean	1.9	3.1	4.3	7.5	1.9	4.0	6.7	10.0	13.1
Av. dev.	0.04	0.04	0.06	0.12	0.02	0.04	0.10	0.16	0.16

Retention volumes<sup>a</sup> from replicate simultaneous dual column chromatograms of five-component homologous mixture

on Carbowax 20-M					on Silicone 96				
Benzene	Toluene	Ethylbenzene	<i>n</i> -Propylbenzene	<i>n</i> -Butylbenzene	Benzene	Toluene	Ethylbenzene	<i>n</i> -Propylbenzene	<i>n</i> -Butylbenzene
1.8	3.0	3.8	4.8	7.3	2.0	4.0	7.3	12.8	16.9
1.8	3.1	3.8	4.8	7.4	2.1	4.0	7.4	12.9	17.1
1.8	3.0	3.8	4.8	7.4	2.0	4.0	7.4	13.0	17.1
1.8	3.0	3.8	4.8	7.4	2.0	4.0	7.4	12.9	17.0

<sup>a</sup> Expressed as distance in centimeters from air peak.

distance along the chart paper between the corresponding peaks of each chromatogram (see Figure 4). Second, and more important, the quantitative analyses provided by the two chromatograms generally permit a reliable means of aligning corresponding peaks. For example, as seen in Figure 3, peak 1 (di-*n*-butyl ether) of the chromatogram obtained on the Carbowax 20-M column is eluted as the third peak from the Silicone SF-96 column. Such a change in order of elution of peaks may be encountered in the analysis of heterogeneous mixtures. In most cases, however, sufficient variation exists in the composition of a mixture to enable one to select corresponding peaks on the basis of the quantitative analyses.

Two features of the apparatus are recommended if the quantitative analyses are to be performed precisely enough to correlate the peaks of each chromatogram qualitatively. The sensitivity of the detectors should be matched and the gas stream must be split evenly. Although the amounts of the individual components of a mixture may be expressed as some fraction of the total for each chromatogram, presumably making the results independent of relative detector sensitivity and gas stream splitting ratio, studies in this laboratory have shown the analyses to be more precise when the response of the detectors is nearly equal.

The 12-inch piece of tubing which serves as sample evaporator and pre-mixer inserted between the sample injection port and splitter appears to be essential to achieve an equal split of the sample even when the flow rates in the columns have been equalized. In the first considerations of the design it was thought that the use of the premixer

tube might result in too much dead volume before the columns with consequent diffusion and spreading of the sample. In practice, no broadening nor overlapping of peaks which can be attributed to this cause has ever been observed. The presence of a large dead volume in the system does require, however, that the measurement of retention volumes be made relative to an air peak or some other reference compound. If a reference peak may not be used conveniently, the dead volume must be calculated and subtracted from the overall retention volume measured from the start of the chromatogram (sample back pressure peak). When applicable, correction must also be made for the difference in time base for each chromatogram if the pens of the dual recorder are offset. However, by setting the baseline on the chart for the two chromatograms at 0 and 50, respectively (as in Figure 4), the time base for the chromatograms may be synchronized.

As presently constituted, the apparatus accommodates only samples admitted by syringe injection. It is a simple matter to modify the apparatus to permit the use of capillary pipet or gas flow sample introduction systems.

To perform qualitative analyses by retention volume constants using simultaneous dual column chromatography over the full scope of chromatographic technique, the extension of this system to ionization detectors and capillary columns becomes necessary. The Research Specialties Co. Model 600 series gas chromatograph can be conveniently assembled from appropriate modules to provide any combination of operating parameters required. The oven will easily accommodate two columns and the streamsplitter, and can

be operated isothermally or with a linear temperature program. Matched detectors of either the katharometer or various ionization types can be mounted in parallel in a separately heated detector compartment. The appropriate detector controls are available as modules. Several simultaneous chromatograms obtained through the various modes of operation have been evaluated, and the instrument has been found to perform in a manner comparable to the apparatus initially constructed in this laboratory and described in detail herein. A typical linear programmed temperature chromatogram for packed columns employing strontium-90-argon ionization detectors is shown in Figure 4.

#### ACKNOWLEDGMENT

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