

When setting up the apparatus, the "Set Current" control is adjusted for maximum current and the oscillator frequency control (0.001 μ F variable capacitor) is adjusted until a flash-over discharge can be heard from within the precipitator, with the carrier gas flowing. This capacitor is then readjusted until the discharge ceases. The "Set Current" control may now be used.

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Comparison of two partitioning phases for gas-liquid chromatography with two types of detectors utilizing four halogenated hydrocarbons

Several halogenated hydrocarbons have been separated by gas-liquid chromatography. PERCIVAL¹ separated trichlorofluoromethane and dichlorofluoromethane using di-*n*-octyl phthalate as the liquid stationary phase and obtained quantitative recoveries of 98-102%. ZWEIG AND ARCHER², ZWEIG, ARCHER AND RUBENSTEIN³, and COULSON, CAVANAGH, DE VRIES AND WALTHER⁴ utilized silicone grease as the stationary phase for the separation of organo-halogenated compounds.

The present work was undertaken to investigate a suitable column packing for the efficient separation of *cis*-, and *trans*-1,3-dichloropropene, 1,2-dichloropropane, and 1,2-dibromo-3-chloropropane. Data are presented on a comparison of two column packings at two temperature levels together with a comparison of the sensitivities of the hot-wire katharometer detector and the microcoulometer cell.

Experimental

Apparatus and procedure. Gas chromatographic data were obtained by two types of apparatus: (a) Burrell Kromo-Tog, Model K-1 equipped with a hot-wire katharometer detector and an 8 ft. \times 0.25 in. o.d. U-shaped glass column, using helium as the carrier gas. (b) Microcoulometer gas chromatograph Model G-100 (Dohrmann Instruments Company, Palo Alto, California) using a 6 ft. \times 0.25 in. o.d. spiral aluminum or stainless steel column and nitrogen as the carrier gas.

Column packings were (a) silicone grease, 20% w/w (Dow-Corning, high methyl polymer) and (b) di-*n*-decyl phthalate, 30% w/w (Eastman Organic Chemicals); each coated on 30-60 mesh acid-washed Chromosorb (Johns-Manville).

Chemical compounds were 1,2-dichloropropane (b.p. 95-97°), *cis*-1,3-dichloropropene (b.p. 104-105°), *trans*-1,3-dichloropropene (b.p. 110-111°), and 1,2-dibromo-3-chloropropane (b.p. 196°).

The compounds were purified by gas chromatography, using a di-*n*-decyl phthalate column either at 83° or 132°. The desired fractions were collected in acetone-dry ice cold traps and qualitatively identified by infrared analysis. The infrared spectra⁵ of the four compounds were similar to published spectra or available reference compounds after chromatographic purification.

Results

Table I shows the data for the relative retention volumes of the halogenated hydrocarbons studied. The data were obtained by means of a gas chromatographic apparatus equipped with a hot-wire detector and an 8-foot column. Table II illustrates the

TABLE I
RELATIVE* RETENTION VOLUMES ON GLC-KATHAROMETER
DETECTOR WITH EIGHT-FOOT COLUMN**

Column Compound	b.p. °C	Silicone grease		Di- <i>n</i> -decyl phthalate	
		83° ml	132° ml	83° ml	132° ml
1,2-Dichloropropane	95-97	300	113	1488	408
1,3-Dichloropropene (<i>cis</i> -)	104-105	353	120	1920	510
1,3-Dichloropropene (<i>trans</i> -)	110-111	408	150	2742	654
1,2-Dibromo-3-chloropropane	196	3240	390	> 7400	5400

* Relative retention volume was calculated by multiplying the carrier gas flow rate, as measured at the column exit, by the total retention time as measured from the point of sample injection to the point of total elution of each component.

** Helium flow rate 60 ml/min.

TABLE II
COMPARISON OF RELATIVE SENSITIVITY OF KATHAROMETER AND
MICROCOULOMETER DETECTORS USING A DI-*n*-DECYL PHTHALATE COLUMN

Compound	Detector				Sensitivity increase ^b
	Katharometer		Microcoulometer a		
	µg added	sq. in. per µg	µg added	sq. in. per µg	
1,2-Dichloropropane ^c	30.2	0.013	2.0	0.75	58 ×
1,3-Dichloropropene ^c (<i>cis</i> -)	37.2	0.013	2.0	0.66	51 ×
1,3-Dichloropropene ^c (<i>trans</i> -)	32.6	0.013	1.5	0.72	56 ×
1,2-Dibromo-3-chloropropane ^d	52.0	0.009	3.1	0.62	69 ×

a 128 Ω resistance of the attenuator.

b Relative greater sensitivity of microcoulometer detector based upon katharometer detector as unity.

c 83°.

d 132°.

relatively greater sensitivity of the microcoulometer detector when compared to the hot-wire detector which was arbitrarily expressed as unity.

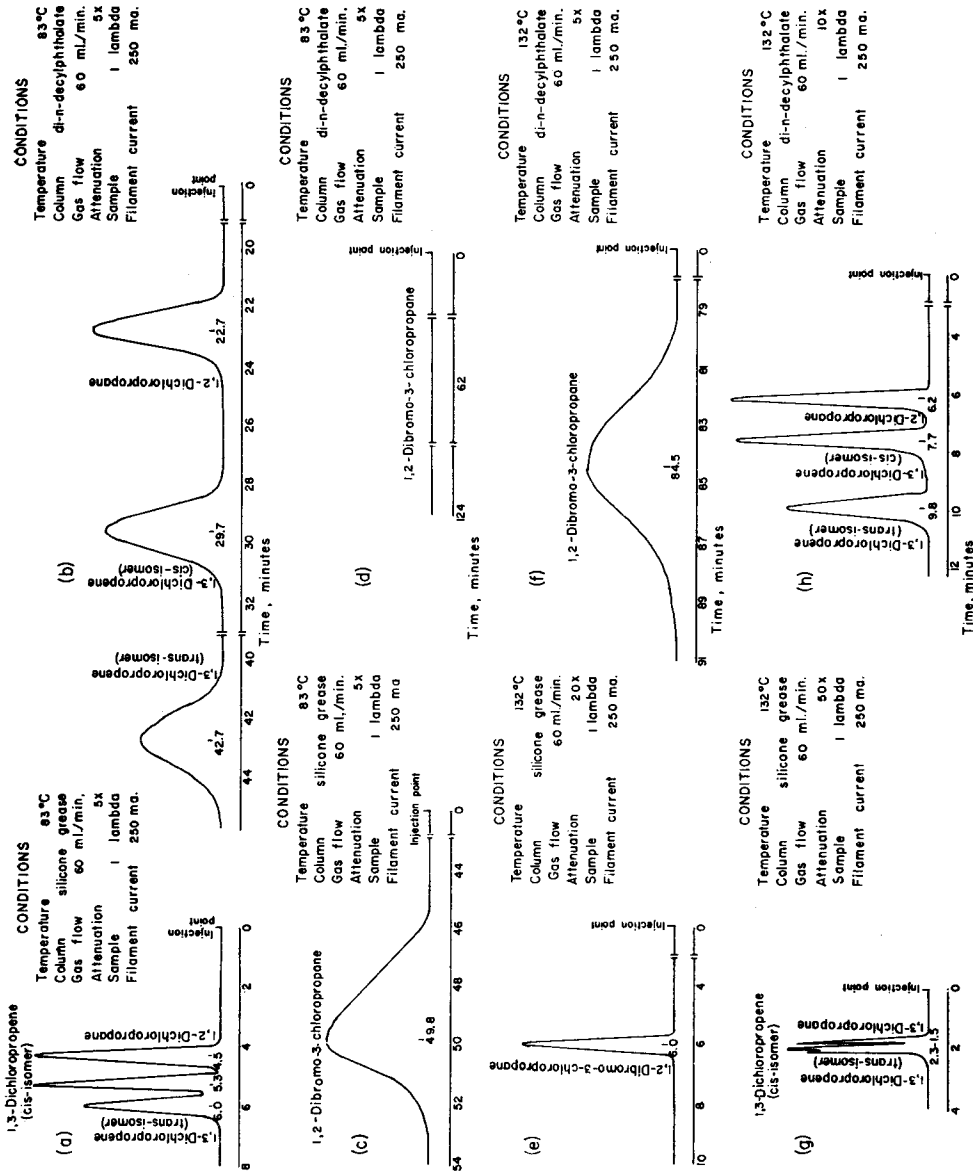


Fig. 1. Chromatograms of *cis*-1,3-dichloropropene, *trans*-1,3-dichloropropene, 1,2-dichloropropene, and 1,2-dibromo-3-chloropropene. Chromatograph: Burrell Model K-1. Columns: Silicone grease (Dow-Corning high methyl polymer) and di-*n*-decyl phthalate (Eastman Organic Chemicals). Column length: 8 ft. Column temperatures: 83° and 132°. Helium flow rate 60 ml/min.

COULSON *et al.*^{6,7} have discussed the technique of gas-liquid chromatography in combination with the microcombustion of the chromatographed sample followed by detection with microcoulometry. The sensitivity of the microcoulometer for the compounds studied was from 51 to 69 times greater than that of the hot-wire detector. The percentage recovery of each of the four halogenated hydrocarbons by the microcoulometer detector ranged from 75 % to 105 % on the silicone column and 85 % to 106 % on the di-*n*-decyl phthalate column at the temperatures used in this study.

Fig. 1 shows characteristic peaks for the four compounds obtained on the silicone grease and di-*n*-decyl phthalate columns at 83° and 132° with the gas chromatograph equipped with the katharometer detector. The silicone column separated 1,2-dibromo-3-chloropropane at 132° but it was unsatisfactory at 83°. The other three compounds were incompletely separated at 83° and almost wholly unresolved at 132°.

The di-*n*-decyl phthalate column (8 ft.) resolved the *cis*- and *trans*-1,3-dichloropropenes, and the 1,2-dichloropropane at the two temperatures studied. The 1,2-dibromo-3-chloropropane had a retention time of 90 min at 132°, but it was not eluted within a period of 124 min at 83°.

When all other conditions were constant, the compounds studied had the same elution characteristics with either helium or nitrogen as the carrier gas.

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