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Chromatographic separation of carbon dioxide, argon and phosgene by temperature programming*

A simple chromatographic technique has been developed and is reported here for the resolution of gaseous mixtures of argon (or air), carbon dioxide and phosgene using a temperature-programmed silica gel column. The technique consists of separating the argon and carbon dioxide at 30° and then stepping the column temperature to 150° for the elution of the phosgene.

The isothermal separation of carbon dioxide from gas mixtures of chlorine, nitrogen, oxygen, hydrogen, nitrous oxide, etc. has been accomplished using silica gel columns¹⁻³. Low phosgene concentrations (less than 2 p.p.m.) can be separated from air and detected using a technique described by PRIESTLEY *et al.*⁴. These methods, however, do not appear applicable to the separation of argon, carbon dioxide and phosgene with a single column.

The isothermal separation of phosgene, carbon dioxide and other gases at 56.5° has been reported using a silica gel column 72 in. long⁵. Our attempts to separate argon, carbon dioxide and phosgene using an isothermal silica gel column were not successful. At temperatures of less than 100° the retention times for phosgene were greater than 60 min even for a 5-in. silica gel column. At column temperatures of greater than 100° the retention time for phosgene was reduced but poor resolution of the carbon dioxide and argon resulted.

It has been reported that a column of No. 10 Kel-F Oil on Haloport F can be used to obtain a separation of carbon dioxide from carbon monoxide, phosgene and other gases at 25° (ref. 6). However, an attempt to separate argon, carbon dioxide and

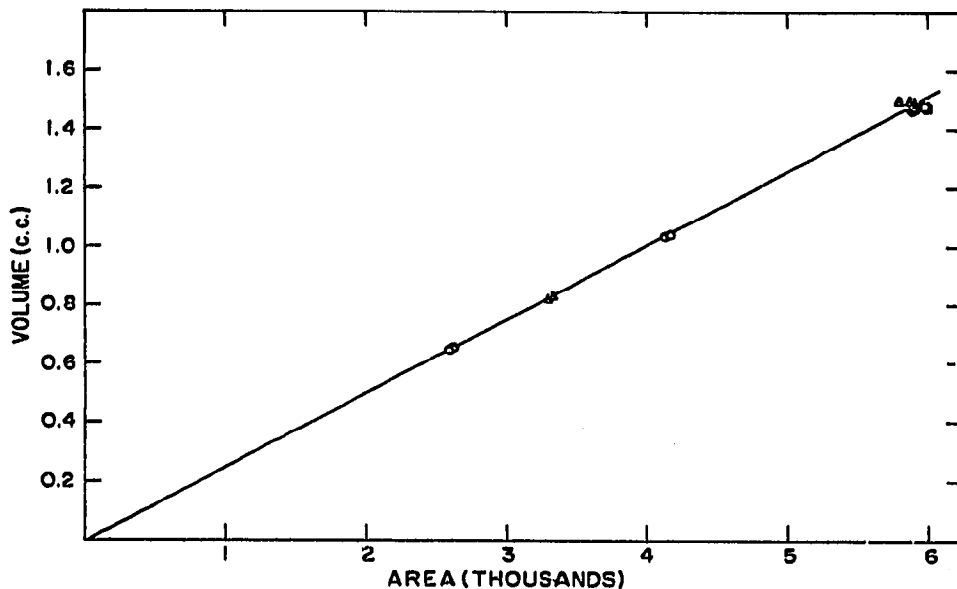


Fig. 1. Phosgene calibration curve: phosgene volume vs. peak area. Key: ○, run 1; □, run 2; △, run 3.

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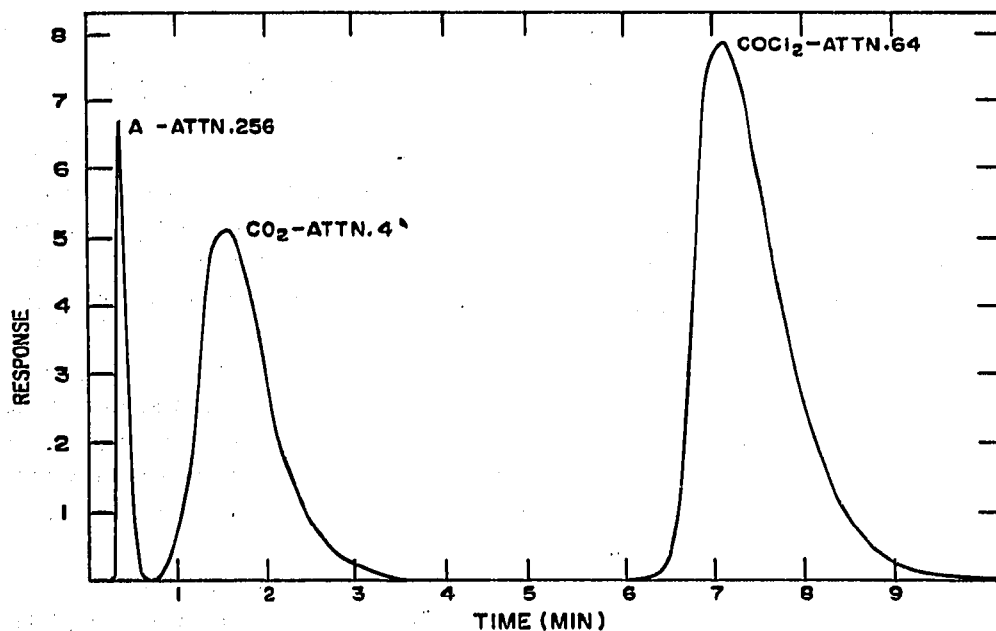


Fig. 2. Chromatogram of argon, carbon dioxide, and phosgene (sample volume 2.5 c.c.).

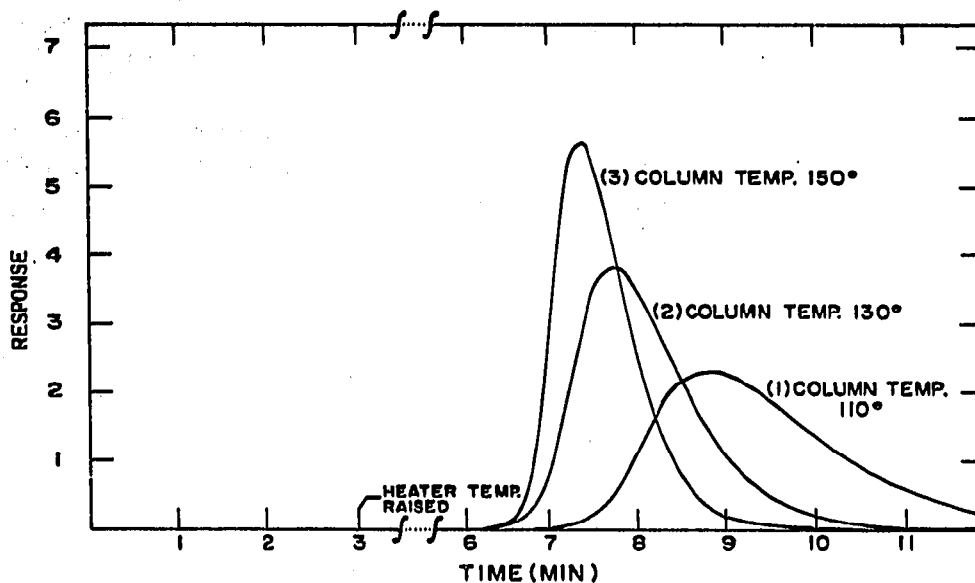


Fig. 3. Effect of column temperature on phosgene retention time (sample volume 1 c.c.; attn. 64).

phosgene by the method described resulted in poor resolution of the carbon dioxide and argon and also resulted in considerable tailing of the phosgene. As with the silica gel, a column long enough to separate carbon dioxide and argon resulted in extremely long retention times for phosgene.

The chromatograph used in this study is a Model 720 dual-column programmed-temperature gas chromatograph with nickel detector cell filaments manufactured by F & M Scientific Corporation. The column consists of 5 in. of F & M A-40 silica gel (30-60 mesh) in a 6-in. long \times 1/8-in. O.D. column. The silica gel was activated at 150° for 3 h in a stream of helium. The flow rate of the helium carrier gas was main-

tained at 20.5 std. c.c./min by a flow controller. The detector temperature was maintained at 45° with a bridge current of 190 mA. The chart speed used was 1 in./min. The column temperature could be held at any temperature up to 500° by an insulated oven with a heater and a blower to circulate the air.

The phosgene calibration data were obtained by injecting measured sample volumes into the chromatograph by means of a syringe. The column was held at 30° for the first 3 min after injecting the sample. The column temperature was then raised to 150° to elute the phosgene. This was done by setting the temperature control of the oven to 150°. About 2 min were required for the column temperature to reach 150°. A linear plot was made of sample volume *vs.* peak area, as determined by a disc integrator (see Fig. 1).

The carbon dioxide calibration curves were made in the normal way by injecting carbon dioxide samples into the chromatograph by means of a syringe. The column temperature was held at 30°.

A typical chromatogram is presented in Fig. 2 showing the analysis of a 2.5-c.c sample containing 33% argon, 2% carbon dioxide and 65% phosgene. Retention times for the argon, carbon dioxide and phosgene were approximately 20, 100 and 400 sec., respectively, for the conditions as described. (Chlorine, in similar mixtures, was eluted at about 270 sec with some interference with the phosgene peak. A 1-in. longer silica gel column should result in satisfactory resolution of chlorine.) Determination of concentrations was made from calibration curves for carbon dioxide and phosgene. The argon concentration was determined by the difference between the sample volume and the sum of the carbon dioxide and phosgene volumes.

Three sets of data taken at successive 2-week intervals were used to construct the phosgene calibration curve of Fig. 1. During each 2-week period about twelve samples, each containing at least 1 c.c. phosgene, were analyzed. Initially, it was suspected that the calibration might change with use due to the corrosive properties of phosgene, but the data show no such change. Minor differences between the data sets are probably the result of minor differences in the setting of the detector bridge current and carrier gas flow rate.

The calibration curve for phosgene shown in Fig. 1 appears to be linear for sample volume *vs.* area. The standard deviation of the residuals for the curve is 0.0177 c.c. or approximately 1.5% of the response.

Fig. 3 shows the effect of the column temperature on the phosgene peaks. Increasing the column temperature improves the sharpness and shape of the phosgene peak and reduces the retention time significantly.

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