

## Gas-Solid Chromatographic Separation of Atmospheric Gases on Activated Alumina

SEPARATION of oxygen, nitrogen and carbon dioxide by gas-solid chromatography has been accomplished on multiple columns of different adsorbents<sup>1,2</sup>. Greene *et al.*<sup>3</sup> almost achieved this separation on activated charcoal, but resolution of oxygen and nitrogen with this adsorbent was incomplete.

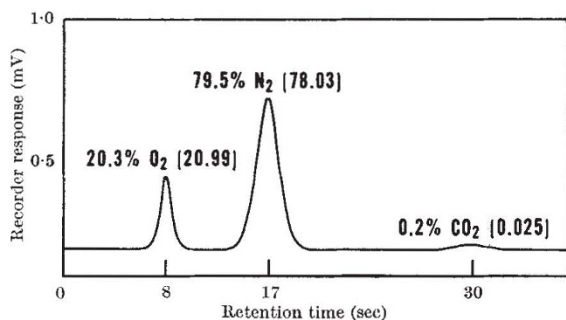


Fig. 1. Chromatogram of air gases from an alumina column purged with carbon dioxide. Figures in parentheses are values for the composition of dry air. Instrument: Beckman GC-4 Column, 4 ft.  $\times$  1/8 in. aluminium packed with 60/80 mesh P-20 'Microtek' alumina (activated by passing helium carrier through it for 1 h while at 350° C sample size, 15  $\mu$ l. injected by way of sampling valve; carrier, helium, at 30 c.c./min; detector, thermal conductivity, operated at 25° C, 235 m.amp; attenuation,  $\times$  5; chart speed, 12 in./min.

Fig. 1 is a chromatogram of air gases from a single 4-ft. column of 'Microtek' alumina operated isothermally at 0° C. Because alumina at low temperatures tends to adsorb carbon dioxide irreversibly<sup>4</sup>, the column was first purged with that gas for 1 h at 0° C to reduce adsorbent activity. Peak area percentages for both oxygen and nitrogen are in close agreement with the known composition of air. The somewhat high value for carbon dioxide probably resulted from dry ice used during the experiment. Column purge with carbon dioxide is necessary and important to its quantitative elution from alumina. Analysis of pure nitrogen, after the carbon dioxide purge, indicated no carbon dioxide displacement—only the nitrogen peak eluted. To ensure carbon dioxide peaks of reproducible area, it was necessary to carry out the purge often—preferably once every 3 h for about 15 min. Any gradual loss of carbon dioxide during column use would be shown by a slow rise in the chromatogram baseline. This was not observed when the purge was carried out regularly. Because irreversible adsorption effects are strong enough to remove carbon dioxide from air mixtures if purging is neglected, a carbon dioxide "peak" from a saturated column operated isothermally can only appear when carbon dioxide is introduced in amounts that exceed the adsorbed saturation concentration.

Although the Beckman GC-4 chromatograph was equipped with a low-temperature accessory for oven cooling, this attachment was not used. Instead, to check amenability of the separation technique to instruments of less refinement, dry ice in a paper cup was placed in the oven. The oven atmosphere was cooled as the airstream from the circulating fan was continuously passed over the surface of the dry ice. Inlet and exhaust ports, feed lines, and the detector compartment were operated at room temperature to maximize detector sensitivity<sup>5</sup>. Air samples of 15  $\mu$ l. were routed to the column through a gas sampling valve, although chromatograms could be exactly duplicated by syringe injections of equivalent volumes.

Activated alumina offers a convenient means by which air gases can be analysed. Its use allows the analyst to operate his instrument under the best possible conditions

of flow and temperature and also results in fast, reproducible chromatograms.

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<sup>1</sup> Jay, B. E., and Wilson, R. H., *J. App. Physiol.*, **15**, 298 (1960).

<sup>2</sup> Anon, *Aerograph Res. Not.*, 7 (spring issue, 1960).

<sup>3</sup> Greene, S. A., Moberg, M. L., and Wilson, E. M., *Anal. Chem.*, **28**, 1369 (1956).

<sup>4</sup> Hoffmann, R. L., and Evans, C. D., presented at winter meeting of Amer. Chem. Soc., Phoenix, Arizona, January 1966 (abstract No. 5a), *Anal. Chem.* (in the press).

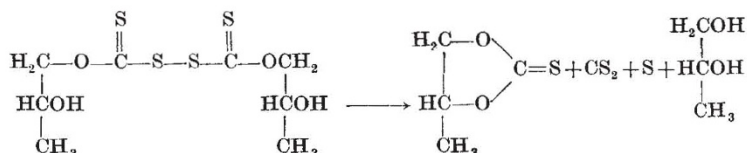
<sup>5</sup> Hoffmann, R. L., and Evans, C. D., *J. Gas Chromatog.*, **4** (5), 198 (1966).

## Rearrangement of Bis(o-thiocarbonyl) Disulphides

IN recent work<sup>1</sup> we showed that *bis*(1,2-*o*-isopropylidene-3-*o*-thiocarbonyl- $\alpha$ -D-glucofuranose) disulphide rearranged on standing in basic organic solvents to give equimolar amounts of carbon disulphide, elemental sulphur, 1,2-*o*-isopropylidene- $\alpha$ -D-glucofuranose, and 1,2-*o*-isopropylidene- $\alpha$ -D-glucofuranose 5,6-thionocarbonate. That work has now been extended to an investigation of *bis*(*o*-thiocarbonyl) disulphide derivatives (referred to as xanthides) of 1,2-, 1,3-, 1,4-, 1,5-, and 1,6-dihydroxy alkanes.

The monoxanthates of the diols were prepared by treating the diol compound or its dioxane solution with 1 molar equivalent of sodium hydroxide (5 N) and excess carbon disulphide. The corresponding xanthides were prepared by treating the xanthates with iodine solution.

The monoxanthide of 1,2-propanediol on standing either at 25° C for 3 days or in anhydrous pyridine at 25° C for 3 h rearranged to yield equimolar amounts of 1,2-propanediol, 1,2-propane thionocarbonate, carbon disulphide, and elemental sulphur.



The thionocarbonate was recovered as an oil. Analysis showed a sulphur content of 27.6 per cent; the sulphur content calculated for  $\text{C}_4\text{H}_6\text{O}_2\text{S}$  is 27.1. The ultra-violet spectrum showed  $\lambda_{\text{max}}^{\text{MeOH}}$  234 m $\mu$  ( $\epsilon$  13,800). The extinction coefficient of 1,2-*o*-isopropylidene- $\alpha$ -D-glucofuranose 5,6-thionocarbonate at 234 m $\mu$  was 15,700.

The monoxanthide of 2,2-dimethyl-1,3-propanediol (I) was recovered in an overall yield of 43 per cent as a yellowish crystalline compound, m.p. 103–106°;  $\lambda_{\text{max}}^{\text{MeOH}}$  240 m $\mu$  ( $\epsilon$  20,000), 285 m $\mu$  ( $\epsilon$  11,400). Analysis showed: carbon, 39.2; hydrogen, 6.1; sulphur, 36.0. The values calculated for  $\text{C}_{12}\text{H}_{22}\text{O}_4\text{S}_4$  are: carbon, 40.2; hydrogen, 6.1; sulphur, 35.7. When (I) was allowed to stand in anhydrous pyridine at 45° C for 4 h, equimolar amounts of carbon disulphide, elemental sulphur, and the cyclic thionocarbonate derivative (II) of 2,2-dimethyl-1,3-propanediol were identified. Compound II was crystalline, m.p. 101°.  $\lambda_{\text{max}}^{\text{MeOH}}$  244 m $\mu$  ( $\epsilon$  14,500) and its structure was formulated on the following basis: elemental analysis gave the empirical formula  $\text{C}_6\text{H}_{10}\text{O}_2\text{S}$ . Found: carbon, 49.5; hydrogen, 6.9; sulphur, 21.7; molecular weight, 138 (vapour pressure osmometry in acetone); calculated for  $\text{C}_6\text{H}_{10}\text{O}_2\text{S}$ : carbon, 49.3; hydrogen, 6.9; sulphur, 21.9; molecular weight, 146. The infra-red spectrum showed no hydroxyl absorption. The presence of a C=S group was shown by a positive iodine-sodium azide test<sup>2</sup> and by