

Notes

CHROM. 6322

Reaction of Chromosorb 102 with oxygen

Chromosorb 102 and the similar Porapak Q are microporous polymer column packings widely used for the gas chromatographic analysis of a large number of compounds¹⁻³. Amines are not suitable for analysis with these types of columns, owing to a specific interaction between the free vinyl groups on the surface of the polymer and the free pair of electrons on the nitrogen⁴. Recently, TROWELL⁵ also found some problems when analyzing NO₂- and NO-containing mixtures. In this note we report some effects found when a Chromosorb 102 column was used with commercial oxygen-containing nitrogen as the carrier gas. Oxygen adsorbed on the surface of the packing apparently reacts with the surface at high temperatures, depolymerizing part of it to produce carbonylic compounds.

Experimental

A Varian-Aerograph 1860 dual-column gas chromatograph with thermal and flame ionization detectors was used. A diversion of the carrier gas flow was inserted between the columns and the detectors, together with a cold trap, in order to condense the products formed during the passage of the carrier gas through the columns.

The columns were 2 m × ¼ in. I.D. glass tubing, packed with 100-120 mesh Chromosorb 102 (Johns-Manville). Some experiments were performed with aluminium and copper tubing, as well as a commercial 1/8 in. stainless-steel Porapak Q column from Perkin-Elmer Ltd. The results obtained with all these columns were identical. Matheson Prepurified Grade argon (99.998%) and locally available nitrogen and compressed air were used as carrier gases.

A Perkin-Elmer 621 infrared spectrophotometer was used to examine column packings before and after experiments. Pellets were made after grinding the products and mixing them with KBr, the pellets being compressed at 20,000 p.s.i. for 1 h. Some infrared spectra were also taken of the vapour phase produced by heating Chromosorb 102 in the bottom of a high-temperature gas cell.

Results and discussion

The first problems with this column packing arose when trying to use it for temperature-programmed analyses of reaction mixtures of fluorocarbon plus atomic oxygen. Recurrent extraneous peaks appeared when the oven temperature was increased to above 100°. These experiments were carried out with commercial nitrogen as carrier gas. When the experiments were repeated in a glass column, it was noticed that after heating for 24 h at 175-200°, (a) the column turned brown, (b) white crystals began to deposit at the far end of the column and in the trap at room temperature and (c) when bubbling the outcoming gas into a solution of 2,4-dinitrophenyl-

hydrazine a yellow precipitate was observed, indicating the presence of some relatively volatile carbonyl compounds in the carrier gas.

The melting-point of the white crystals was in the range 60–105°, and elemental analysis did not show any nitrogen present in the crystals. These solids were identified as a mixture of aromatic ketones by using the Friedel–Crafts test and reaction with 2,4-dinitrophenylhydrazine. Thin-layer chromatography of the 2,4-dinitrophenylhydrazones showed that the solid was composed of at least seven different carbonyl compounds.

The use of argon as carrier gas did not present any of these problems, but when air was passed through the column the same effects were observed as with the commercial nitrogen.

Infrared analysis of the white solid deposited in the trap showed peaks at 1680, 1600 and 1580 cm^{-1} . The first peak is typical of aromatic ketones and the latter two of aromatic rings. In Fig. 1, the IR spectra of unused Chromosorb 102 and the brown product after heating at 200° in a column with commercial nitrogen as carrier gas are shown.

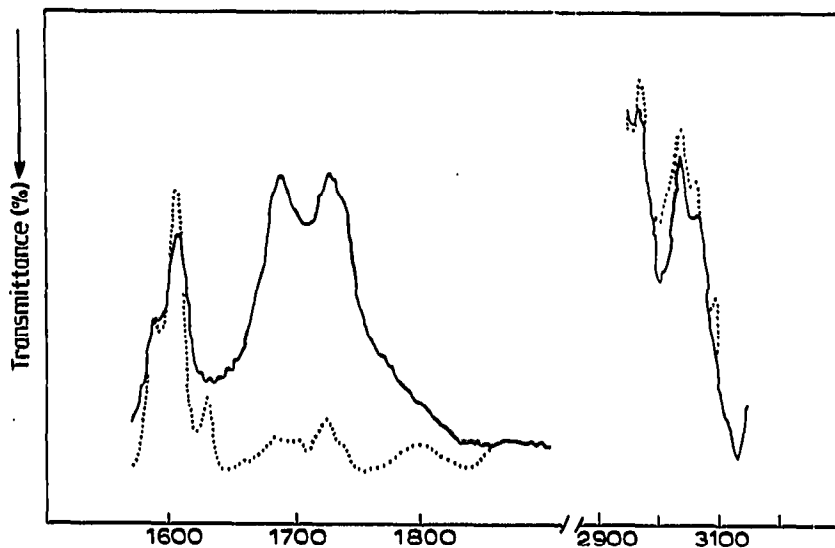


Fig. 1. Spectra of Chromosorb 102 before (dotted line) and after (solid line) heating at 200° for 24 h in an oxygen-containing nitrogen flow.

The presence of conjugated carbonyls at 1682 cm^{-1} , as well as the disappearance of the vinylic C–H band at 3080 cm^{-1} , can be clearly seen. When a sample of Chromosorb 102 was heated at 225° in a previously evacuated oven, the presence of a product in the gas phase could be detected by IR spectroscopy, its spectra being similar to that of the carbonyl compounds found as solids behind the columns. When the oven was evacuated and the heating process repeated several times, the concentration of these products decreased until complete disappearance.

From these results, it seems that the oxygen adsorbed on the polymer reacts with Chromosorb 102 (or Porapak Q) to form carbonyl compounds on the surface that induce depolymerization and oxidation of the column packing. The reaction can be assumed to be initiated by a specific adsorption of oxygen on the surface vinyl groups followed by oxidation of the carbon atom nearest to the aromatic ring. An alternative

mechanism could involve the catalyzed formation of NO_2 followed by nitration of the aromatic portion of the polymer, as suggested by TROWELL⁵.

These studies have indicated that great care has to be taken when selecting the carrier gas to be used with this type of column, especially when analyses have to be performed with temperature programming. The small amounts of oxygen adsorbed during handling of the packing are not sufficient to degrade the polymer, and the products are formed in such small amounts that they are easily eliminated by the conditioning process.

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