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HIGH-TEMPERATURE GAS–LIQUID CHROMATOGRAPHY WITH A DENDRITIC SALT SUPPORT

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SUMMARY

Dendritic salt has been evaluated as an inert support for high-temperature gas–liquid chromatography. Lightly loaded columns, of a thermally stable sulfone polymer, on this support are suitable for the rapid separation of heavy hydrocarbons and for other organic materials.

INTRODUCTION

For some time, our laboratory has worked in the area of column technology for gas–liquid chromatography (GLC). One of our previous reports[1] indicated that dendritic sodium chloride was a useful inert support material. We noted that tailing, loss by adsorption, or reaction of polar compounds did not occur with this support. Recently, Thizon *et al.*[2] have confirmed the inert behavior of dendritic salt.

Because of our interest in the separation and analysis of the heavy hydrocarbons in crude petroleum and in refined petroleum products, we synthesized and evaluated a special polyphenylether sulfone[2] for use at temperatures as high as 400°. This sulfone, in packed and in open tubular columns, has proven useful[3,4] for the separation and analysis of lipids, drugs, pesticides, and other high molecular weight compounds. Subsequently, we have continued to study the performance of the sulfone, at temperatures of 200° to 400°, for the analysis of hydrocarbons. The results obtained for the sulfone columns, on ordinary silicious supports, have been quite satisfactory. However, we have detected certain problems which occur on prolonged use of our columns at 350° to 400°. First of all, organo-silyl groups on silane-treated silicas tend to decompose and column bleed as well as silicious deposits on connecting pieces and on portions of the flame detector have been noted. This problem is particularly acute if gas chromatography–mass spectrometry equipment is employed. Silicon is a bad contaminant in such systems. In addition, if untreated silicas are employed, some adsorption of aromatic hydrocarbons is noted particularly when lightly loaded (0.5–1 %) sulfone columns are evaluated. Although we do not ordinarily work with polar materials, such as alcohols, amines, or aldehydes, we have observed difficulty in obtaining symmetrical peaks with lightly loaded sulfone columns on untreated silica supports.

Therefore, we decided to prepare some lightly loaded sulfone columns with

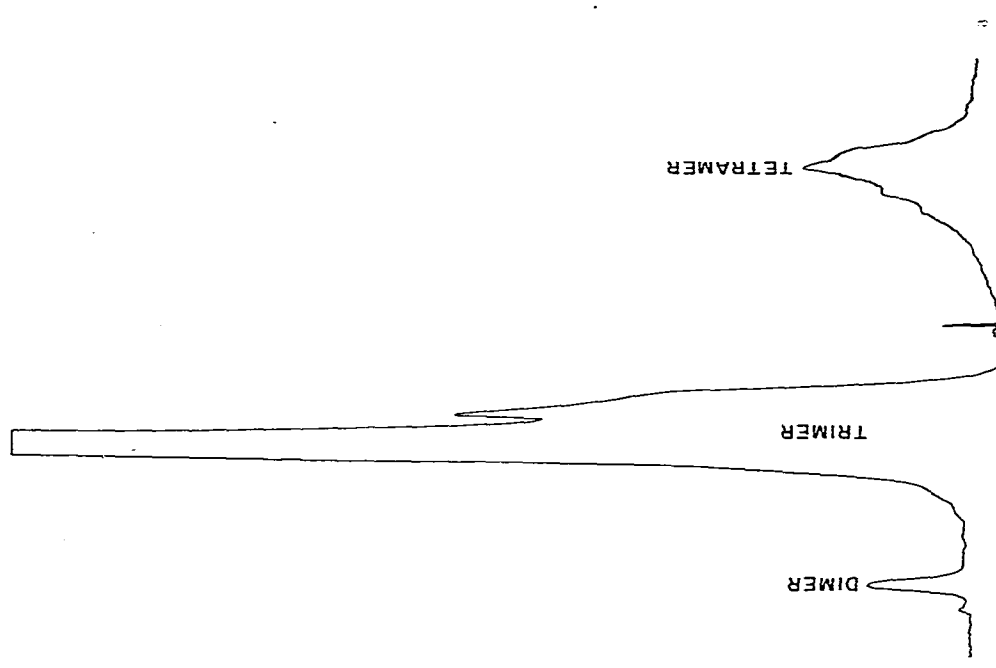


Fig. 2. Separation of commercial octene trimer.

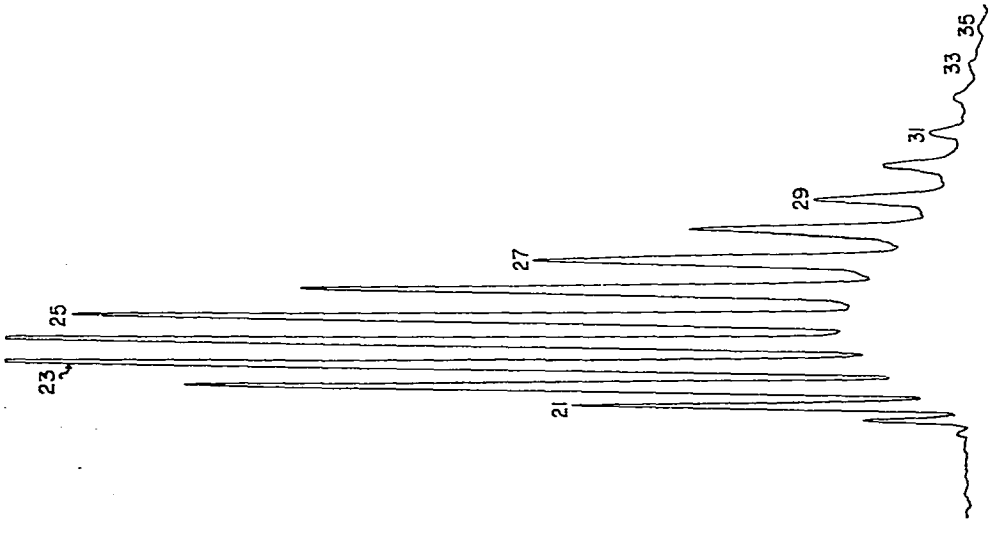


Fig. 1. Separation of paraffin hydrocarbons, identified by carbon number.

the dendritic salt support, and to begin an evaluation of these columns for the separation of hydrocarbons and also for some polar materials. The techniques employed, the results obtained, and a discussion are presented below.

EXPERIMENTAL

Equipment

A Barber-Colman Series 5000 gas chromatograph equipped with a hydrogen flame ionization detector was used in this study.

Reagents and materials

Dendritic sodium chloride was obtained as a sample from the Morton Salt Company (Chicago, Ill., U.S.A.). Poly-S 179 was obtained from Applied Science Labs. (State College, Pennsylvania, U.S.A.). Chloroform, used to prepare the column packings, was procured from Matheson, Coleman & Bell (East Rutherford, N.J., U.S.A.).

The metal columns used in this study were prepared from Type 304 stainless steel, 0.125 in. O.D. × 0.062 in. I.D. from Handy & Harman (Norristown, Pa., U.S.A.). All columns were 2 m in length.

Poly-S 179 was coated onto the dendritic sodium chloride from chloroform solution. Packings with 0.5 and 1.0% Poly-S 179 were prepared and evaluated. The columns were conditioned by programming from ambient temperature to 350° at 0.5°/min. The final temperature was maintained until the baselines had stabilized.

Column preparation and evaluation

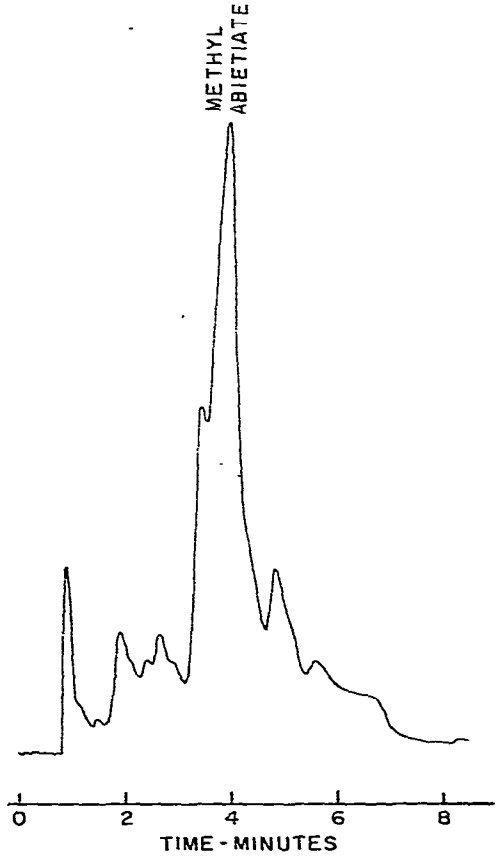
The dendritic salt was lightly crushed, screened to 80–100 mesh, and dried at 120°. The packing was added slowly, with vibration, to a cleaned section of stainless-steel tubing and the columns were conditioned as described above. These techniques have been adequate for our work with metal columns. However, those using glass columns may require and employ modified column packing preparation and/or column filling techniques. Dendritic salt is not particularly hygroscopic and is no more fragile than silicas. We will study methods for the removal of "fines" from dendritic salt packings in order to obtain better flow-rates and better column efficiency. Obviously, water or acid washing cannot be employed for removal of fines from dendritic salt. Volatile organic solvents will be evaluated for this purpose.

RESULTS AND DISCUSSION

Preliminary tests indicated that for high-temperature work, 0.5 or 1.0% of the sulfone provided good stability and adequate separating power in 1/8 in. × 2 m columns.

A commercial paraffin wax was separated, with a 1% sulfone column programmed from 225° to 350° at 15°/min. The chromatogram obtained is shown as Fig. 1. Under these conditions C_{35} was eluted in about 10 min. The same column was tested, with a programming rate of 10°/min, from 225° to 350° for the separation of an octene trimer preparation. Significant amounts of the dimer (C_{16}) and of the tetramer (C_{32}) are shown in the chromatogram (Fig. 2). Fig. 3, obtained with this

column programmed from 275° to 350 °C at 10°/min, demonstrates the separation of a complex methyl abietate mixture in approximately 8 min. A lightly loaded 0.5% column was tested at 200° for the separation of dimethylphthalate from N,N-diethyl-*m*-toluamide (Fig. 4).



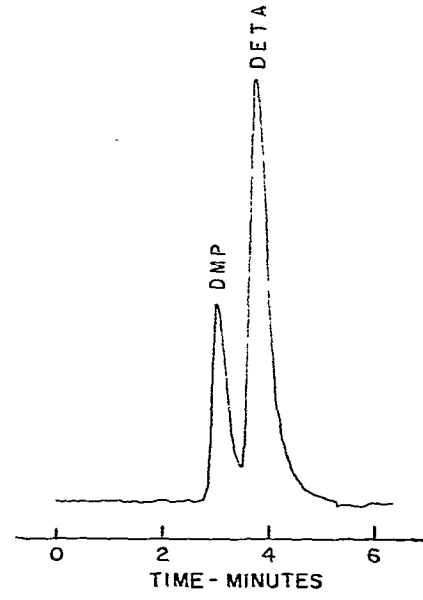


Fig. 3. Separation of commercial methyl abietate.

Fig. 4. Separation of dimethyl phthalate (DMP) and N,N-diethyl-*m*-toluamide (DETA).

The results obtained in this investigation indicate that dendritic salt is a useful support for GLC at elevated temperatures. The combination of this support with light loadings (0.5 to 1%) of a synthetic thermally stable sulfone (Poly-S 179) provides packings useful for the rapid separation of heavy hydrocarbons and of some "polar" materials.

Our preliminary tests were performed with stainless-steel columns. However, we expect to continue this evaluation with glass columns. The reaction of salt with metal columns is always a possibility, and we expect that glass columns will be more inert. Further, the visibility of the materials in glass systems should improve the reproducibility of the packing. The "noise" levels we have obtained, in clean systems,

with the salt support and the thermally stable sulfone have been very low and may, perhaps, be due to the ionization of the salt itself, rather than to the usual organic bleed which originates from the liquid phase or from the organic groups on silicious supports.

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