Journal of Chromatography, 198 (1980) 176–179
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 12,981

Note

Gas chromatographic stationary phases analysed by capillary gas chromatography

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(Received May 30th, 1980)

Two fundamental advances have recently broadened the range of application of capillary gas chromatography (GC) to include far less volatile and far more delicate samples. One type of progress is based on the greatly increased inertness and thermostability of persilylated glass capillary columns[1–4]. Independently, the recently introduced fused silica columns[5,6] offer a progress in the same direction. However, the potential of these columns would not become effective, at least for certain classes of sample, as the substances to be analysed would be destroyed during injection. Consequently, the new columns exhibit their full power only when operated with an appropriate sampling technique, which is on-column injection[7–10].

ANALYSIS OF CARBOWAX

The situation may be illustrated by the fact that many classical stationary phases can now be partly or fully analysed by GC. Fig. 1 shows the complete separation of Carbowax 400, with a molecular weight distribution from 266 to 662 and a maximum at 442. However, this separation is based on non-vaporizing transfer of the sample solution into the column. Regular injection into a hot (400°C) vaporizer almost totally pyrolyses the sample, producing a large number of low-molecular-weight fragments (see the early section of the upper chromatogram). As expected, the heavier components of Carbowax are most affected, while the lighter ones partly survive vaporization. Gradually reducing the vaporizer temperature does reduce the extent of pyrolysis. Simultaneously, however, an increasing proportion of the heavier components remains in the insufficiently heated syringe needle. Thus, they become increasingly discriminated by insufficient volatility, instead of by pyrolytic destruction.

ANALYSIS OF POLYMETAPHENYL ETHER

Fig. 2 shows two further stationary phases, the complete separation of which presents no problem. These phases are unique (other examples are squalane and C_{87}) in the sense that they represent almost pure substances, at most including isomers of one basic structure (OS 124). The two chromatograms demonstrate the weakness of the phases OS-124 and OS-138, which is excessive volatility. Unfortunately, the non-volatile high-molecular-weight phase PMPE hardly contributes to practical capillary

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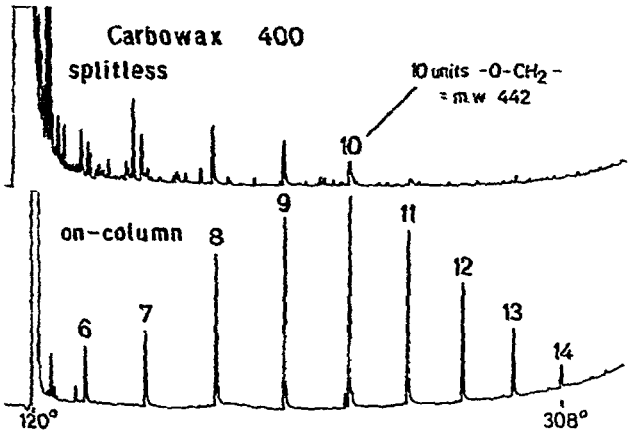

Fig. 1. Analysis of Carbowax 400 dissolved 1:10,000 in toluene. Column: Pyrex, 15 m × 0.31 mm I.D., persilylated, 0.15-μm OV-73. Conditions: carrier gas, hydrogen, 0.6 bar; sample size, 2 μl; temperature, programmed at 6°C/min from 120 to 380°C. Splitless injection: injection at 90°C, splitless period 40 sec, vaporizer temperature 400°C, rapid heating to 120°C. On-column injection: injection at 110°C, secondary cooling, immediate heating to 120°C. Carlo Erba Model 4160 chromatograph. Vaporizing injection pyrolyses (hot vaporizer) or insufficiently vaporizes (cold vaporizer) particularly the heavy components. On-column injection avoids both problems perfectly.

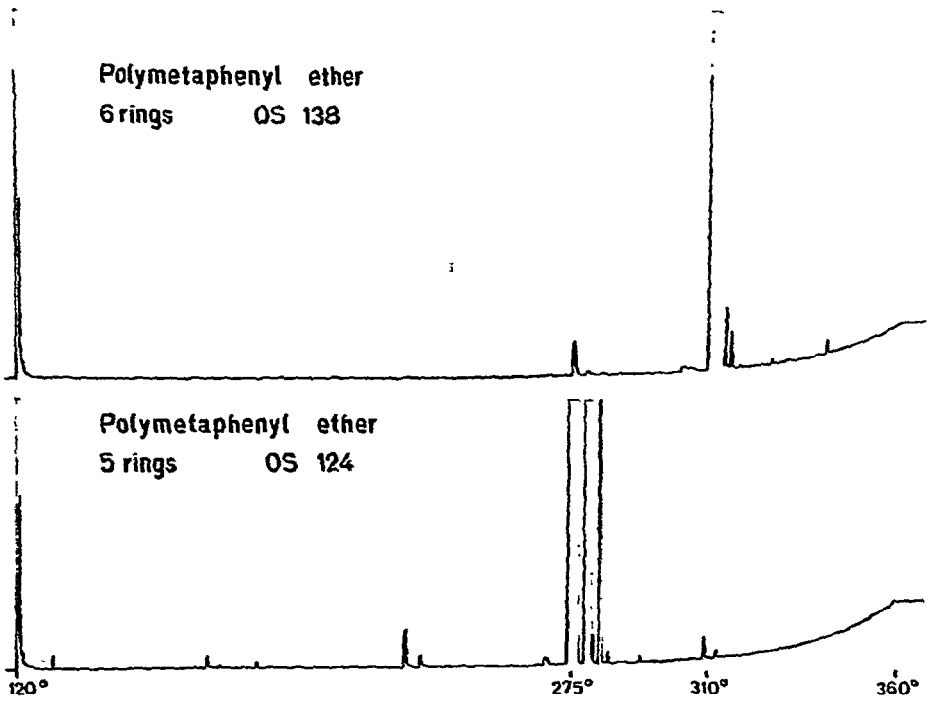

Fig. 2. Analysis of classical polymetaphenyl ether phases. Column and conditions as in Fig. 1. On-column injection. Both phases represent virtually pure substances, possibly consisting of a few isomers, with only trace amounts of by-products.

GC. The problem lies in the low solubility in all common solvents, thus precluding the production of high-quality coatings. It seems that a homologue with 10–12 rings might fill a gap, as the material is outstanding in thermal and catalytical stability.

ANALYSIS OF SOME DETERGENT PHASES

Fig. 3 shows the weakness of the Ucon phases, which is an excessively broad molecular weight distribution (the more popular Ucon HB 5100 shows a relative shift towards heavier components, but no significant difference). The broad peaks in the upper chromatogram should not be attributed to poor separation efficiency, but to the presence of several closely related isomers probably containing the same number of ethylene and propylene glycol units copolymerized in different sequences.

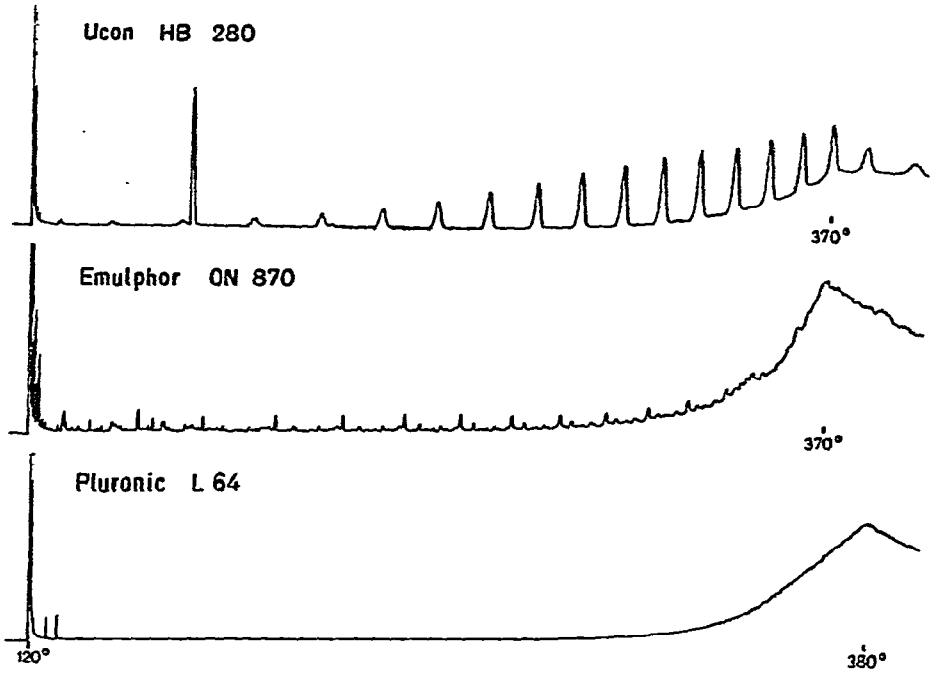

Fig. 3. Analysis of detergent phases. Column and conditions as in Fig. 1. On-column injection. Ucon HB 280 shows a very broad molecular weight distribution, with several isomers forming one peak. Emulphor contains no volatile component up to 370°C, but delivers the products of a constant degradation process. The Pluronic phase is free of both volatile components and decomposition products.

Emulphor ON 870 does not contain any component that would be eluted within the volatility range of our separation. This may be surprising to practical analysts familiar with the constant, considerable bleed rate exhibited by this phase. As the chromatogram shows, the source of this bleeding is not slow evaporation of low-molecular-weight components, but rather a constant breakdown producing the complete series of possible fragments.

Pluronics[11] are copolymers of ethylene and propylene oxide, like the Ucons. In contrast to the Ucons, they are made by block copolymerization. We recommended them because of their lower bleed rate in comparing with other polyglycol phases. Fig. 3 confirms our earlier observations. The relatively low bleed rate of Pluronics is obviously due to the absence of both low-molecular-weight components and a breakdown reaction. It must be added that Pluronics start to behave like Emulphor as soon as they have come in contact with very small amounts of oxygen at elevated temperature.

Note that all runs in Fig. 3 occurred under identical conditions, including the amount and concentration of the sample.

ACKNOWLEDGEMENT

This work was sponsored by F. J. Burrus & Cie, Boncourt, Switzerland.

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