Journal of Chromatography, 77 (1973) 299–307

CHROM. 6489

ON THE UNEXPECTED BEHAVIOR OF A COMMON GAS CHROMATOGRAPHIC PHASE*

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(Received November 20th, 1972)

SUMMARY

Carbowax 20M was coated on Chromosorb W, heat-treated at 280°, and exhaustively extracted. The remaining support performed chromatographically in a manner similar to highly efficient, well deactivated gas–liquid chromatographic packings, even though the non-extractable polymer film was too thin to permit reliable combustion analysis. This phase was well suited for the analysis of polar compounds, producing symmetric, sharp peaks with very short retention times. A strong surface effect was evident, which could be utilized for otherwise difficult separations.

INTRODUCTION

Some time ago, we attempted, in a sequel to our earlier studies on support-bonded silicones[1], to combine the bonding abilities of silicones with the chromatographic properties of various polyethylene glycols. Typically, Carbowax 400 was reacted with an excess of methyltrichlorosilane, coated on to a suitably treated[1] Chromosorb support, the excess of silane removed under vacuum and the phase polymerized in a fluidized bed of humid nitrogen at elevated temperatures.

There was evidence of limited success, *e.g.*, this particular phase contained a few per cent of ignitable yet unextractable material, it showed low bleed at 250° and it gave reasonably good gas chromatograms with hydrocarbon and alcohol test mixtures. (For comparison: Carbowax 400 alone has a recommended maximum working temperature of 100° [2], and the polymer from methyltrichlorosilane alone is very heat-stable but yields extremely poor chromatography[3].) However, the "mixed" polymers finally did not quite measure up either to the support-bonded silicones or to

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* Part of this research is a contribution from the Missouri Agricultural Experiment Station, Journal Series No. 6565, supported by the Environmental Trace Substances Center, by NSF Grant GP-18616, and by EPA Grant R-801050 and presented at the IUPAC International Congress on Analytical Chemistry, Kyoto, Japan, April, 1972.

the conventional polyethylene glycols in chromatographic use, and the project was terminated.

While it was still on to in progress, however, we stumbled on to an interesting phenomenon. Chromosorb, which had been coated with Carbowaxes and was subsequently heated to various temperatures, could not be completely stripped of its apparent GLC capabilities by exhaustive extractions with either methanol or benzene. The further investigation of this somewhat unexpected effect is reported in this paper.

EXPERIMENTAL

Preparation of the packing

A diatomaceous earth support, in this study Chromosorb W or Celite 545, is acid-washed in a Soxhlet apparatus (Kontes Model K-585100) with hydrochloric acid at boiling temperature. This treatment is continued until new portions of HCl, hot or cold, remain free from yellow hue after several hours of extraction. The support is then washed to neutrality with distilled water, rinsed with acetone, dried and coated with 6% Carbowax 20M by the usual technique of rotary evaporation. Care is taken to ensure an even coating, similar to the preparation of GLC packings. The dried support is freed from fines with a stream of nitrogen and filled into a 40 cm × 3 cm I.D. Pyrex tube with Clearfit joints, connected to a supply of highly purified nitrogen. The tube is placed into a furnace and swept with a fast stream of nitrogen at ambient temperature to ensure that all oxygen has been purged from the support. Then the nitrogen stream is reduced to a minimum (the tube exit is connected to a capillary submerged in water such that a slow succession of bubbles can be observed) and the temperature raised within 3–4 h to the desired value, usually 260–280°. This temperature is maintained overnight and in the morning the phase is allowed to cool under nitrogen, ready to be filled into glass or paper thimbles for exhaustive extraction. The standard procedure calls for the use of methanol, for 1–2 days in the Goldfisch, or 4 days to 1 week in the Soxhlet extractor.

Portions of all phases produced in this study were weighed, ignited (*i.e.*, kept at 1000° for 3 h in air), and re-weighed in order to establish the loss of organic polymer. "Blanks" were subjected to treatments resembling as closely as possible those of the prepared phases. The extracted supports were repeatedly sent to two commercial firms for elemental analysis, accompanied by notes of caution on the possible absorption of water and CO_2 by these materials.

Other investigations

A large batch of 6% Carbowax 20M on Chromosorb was prepared and divided into portions, which were heat-treated at various temperatures to demonstrate thermally effected differences.

In a special study, the separation of the butyl ester derivatives of citric acid and nitrilotriacetic acid served to demonstrate the changes in resolution and retention as the packing was produced: first the regularly loaded phase, then the same phase after heat treatment, and finally the exhaustively extracted packing.

The Carbowax 20M obtained from extracting the heat-treated support was compared to the original Carbowax 20M by infrared spectroscopy and gel perme-

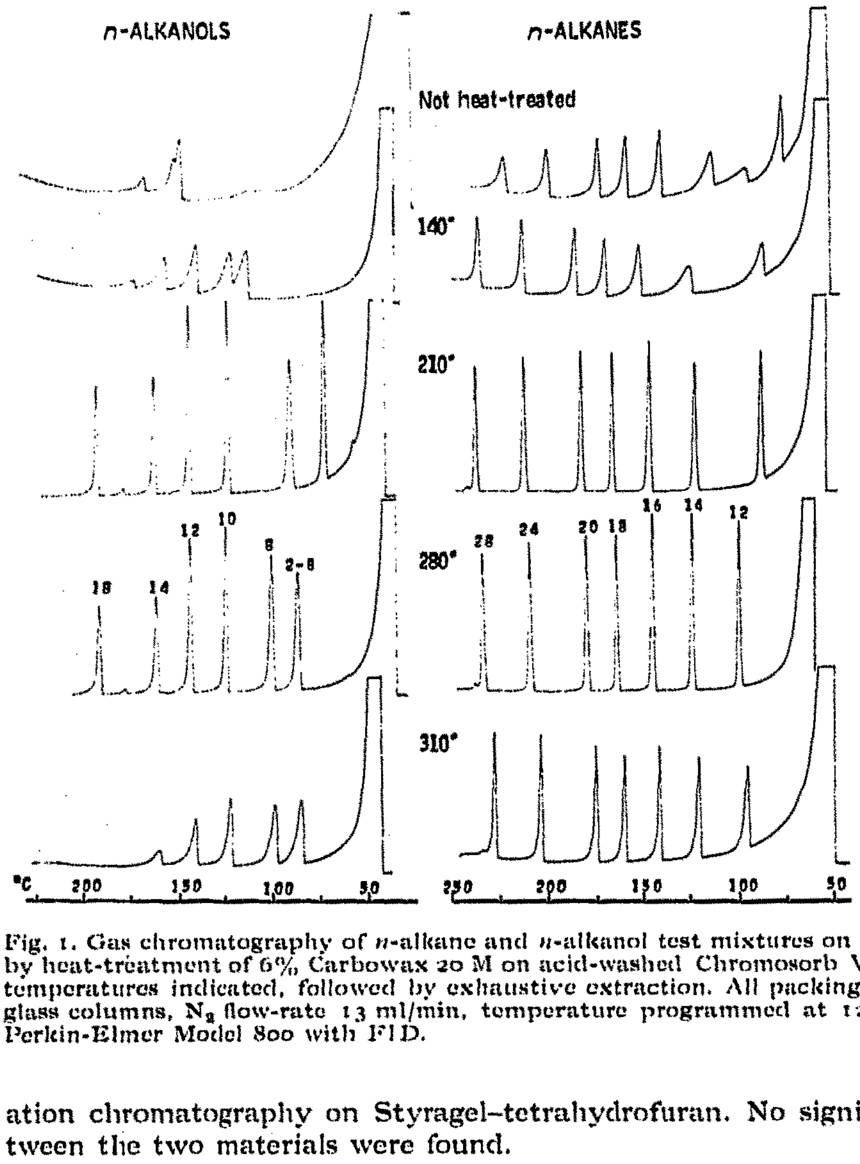


Fig. 1. Gas chromatography of *n*-alkane and *n*-alkanol test mixtures on various phases, obtained by heat-treatment of 6% Carbowax 20 M on acid-washed Chromosorb W, 100–120 mesh, at the temperatures indicated, followed by exhaustive extraction. All packings in 50 cm × 4 mm I.D. glass columns, N_2 flow-rate 13 ml/min, temperature programmed at 12°/min from 40 to 250°. Perkin-Elmer Model 800 with FID.

ation chromatography on Styragel–tetrahydrofuran. No significant differences between the two materials were found.

RESULTS AND DISCUSSION

The heat-treatments of Carbowax-coated Chromosorb, followed by exhaustive extractions, resulted in a series of efficient chromatographic packings. As shown in Fig. 1 with examples selected from a large number of chromatograms, the efficiency improved with the temperature of the treatment up to 260 or 280°; at higher temperatures the Carbowax 20M apparently started to deteriorate. Fig. 2 shows the chromatography of *n*-alkanes and alkanols in a more common 5-ft. column.

What happens in the heat-treatment is by no means clear. One of several pos-

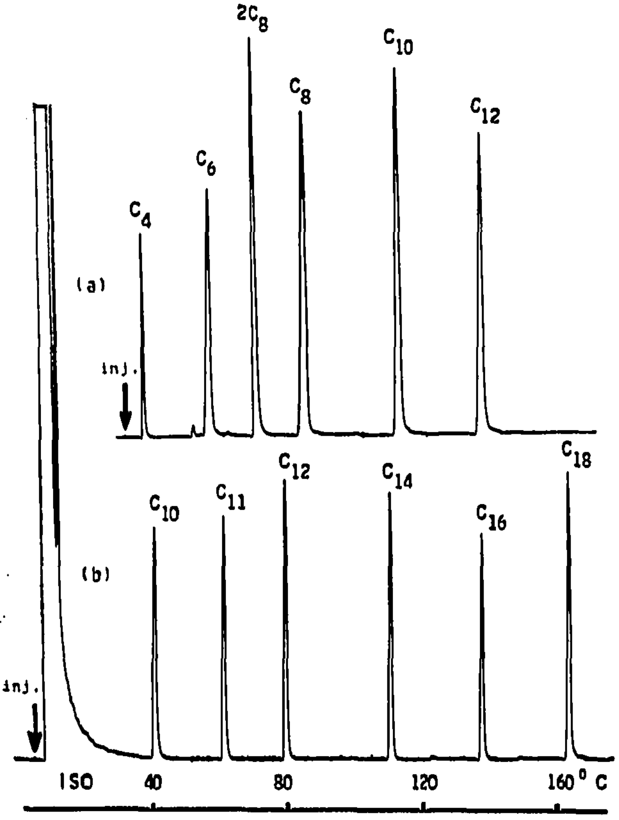


Fig. 2. Gas chromatography of (a) *n*-alkanols ($2C_8$ = 2-octanol) and (b) *n*-alkanes on a phase derived from 6% Carbowax 20 M on 100–120 mesh, acid-washed Chromosorb W by heat-treatment at 280° and exhaustive extraction. 5 ft. × 4 mm I.D. Pyrex U-tube, programmed from 40 to 180° at 6°/min, N_2 flow-rate 60 ml/min, Mikrotek Model MT 220 with FID.

sible assumptions is that the high temperature allows the polymer chains contacting the surface to rearrange physically (in competition with each other) to a minimum potential energy configuration. This configuration, ideally, would involve an optimal number of contact points and a steric arrangement equivalent to maximal total intermolecular bond strength between a particular polymer chain and the silicic surface. The difficulty in achieving this configuration increases with the chain length of the polymer, as shown, for instance, by KISELEV *et al.*[4] with polyethylene glycols of different molecular weights on carbon black. A "stretched-out", long polymer chain that has wriggled to a position involving a large number of (hydrogen and various types of Van der Waals) bonds to the surface may be non-extractable even in protracted continuous extractions (compare ref. 5).

In any case, if one considers the chromatographic capabilities of the packing, it is obvious that some Carbowax must have remained on the Chromosorb. We were not able to remove this residue by weeks of continuous extraction with methanol and/or benzene in Soxhlet or Goldfisch equipment.

Carbowax 20M differs from other polyethylene glycols—Union Carbide describes it as follows: "Polyethylene Glycol Compound 20M has a molecular weight of 15,000 to 20,000. It is prepared by joining together two 7,500 molecular weight alpha-hydro-omega-hydroxy-poly(oxyethylene) molecules with a diepoxide[6]". "It is non-hygroscopic and somewhat more flexible than the other solid polyethylene glycols[7]". Further information appears to be proprietory and non-accessible. Whether there exists a significant influence of the diepoxide moiety on chromatographic performance has not been ascertained; however, some caution in comparing Carbowax 20M with some of the other, well characterized polyethylene glycols[8] may be in order.

Other polyethylene glycols of various molecular weights, purchased from different suppliers, gave effects similar to those obtained from Carbowax 20M, although the latter remained the material of choice. Polymers of higher molecular weight were generally preferable, possibly because higher temperatures could be used in the heat-treatment.

Whether the chromatographically active layer is still identical with Carbowax 20M in structure (although not in behavior) has not been determined. However, IR and gel permeation chromatographic analysis of materials extracted showed no difference to the original Carbowax 20M. The effects of the heat-treatment can be noticed in Fig. 1 to occur much below the recommended maximum GLC temperature of 250°. These findings suggest that no gross chemical changes have taken place. It is also unlikely that our inability to remove the polymer completely from the support was due to a condensation reaction between surface silanol groups and terminal polymer hydroxyl groups (similar to HALÁSZ AND SEBESTIAN's brushes[9] or other condensation products of alcohols and silicic materials (for a review, see ref. 10), since long-term exposure to boiling methanol was involved in the extraction.

How thick the polymer layer is, which remains after the extraction is a most intriguing question. We think of it as nominally monomolecular, with no precise evidence to corroborate the claim. Our own ignition analyses indicated various loads, usually smaller than 0.2%. The commercial elemental analyses gave similarly ambiguous results. A special quadruplicate analysis of one batch, performed with special precautions against CO_2 and H_2O absorption, gave carbon values of 0.15, 0.12, 0.00 and 0.03% (Peninsular Chemical Research, Inc., Gainesville, Fla., U.S.A.). A monolayer calculated from the Van der Waals dimensions of the monomer unit[4] would represent a 0.06% load.

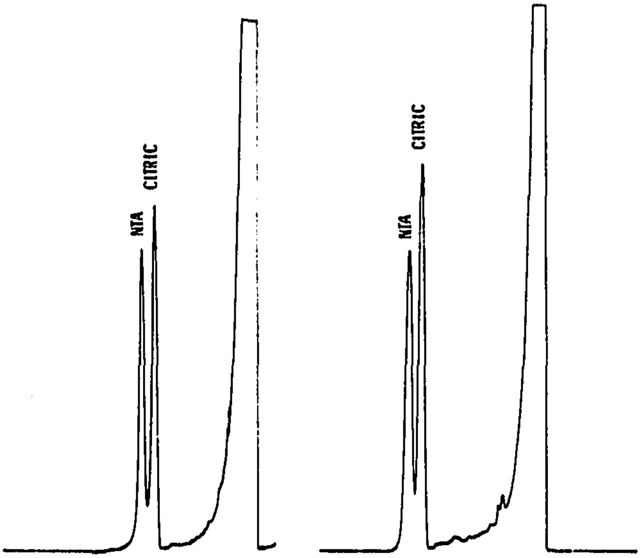
Both methods, ignition and elemental analysis, are apparently working at their lower limits. Either they would have to be adapted to the particular requirements of these samples, or supports with larger surface areas would have to be used in order to define closer the actual polymer load. Even if this number were known, there are several reasons why it would be difficult to arrive at a valid conclusion about the thickness of the layer. First, the surface area of the support used is 1.3 m^2/g (Micromeritics Instrument Corp., Norcross, Ga., U.S.A.). This value corresponds to B.E.T. adsorption of nitrogen, and not all of the surface thus measured may be accessible to the polymer.

Second, the use of bulk density for the calculation of thin-film thickness is hardly permissible. In bulk, polyethylene glycol chains form helices, with oxygen atoms pointed toward the axis and methylene groups at the periphery (theoretical density 1.33 at 20°), with numerous voids between them. (For a comprehensive discussion of 1,2-epoxide polymers, see ref. 11). In a "monomolecular" film, however, one could expect to find the oxygen atoms extended toward the diatom surface, for maximal interaction. In this state, bulk properties are obviously of little value. For instance, the melting-points of "thin" films of liquids on chromatographic supports are different from those of "thick" films[12], and so, one assumes, would be their "densities", not to mention their chromatographic behaviors.

Third, a polymer molecule may be adsorbed on to the surface only for a certain average chain length, the remainder participating in a second or third layer. When the material is used in liquid chromatography, this remainder might simply be sticking out with various degrees of coiling, depending on the nature of the mobile phase.

One could expand on several other aspects of uncertainty in the calculation of dimensions at adsorbent–polymer–gas interfaces, even leaving aside the obvious problem of inhomogeneous polymer distribution on the macro- or micro-structure of the adsorbent particles. Our best estimate, at the moment, is that the thickness of the polymer layers is lower than 15 Å. This value presumes chromatography which is strongly influenced by the solid support. Literature values vary, but one generally assumes that a liquid phase thickness of 30 Å represents a limit of sorts below which the influence of the support can become evident through a rise in retention time and an increase in peak broadness and asymmetry[13]. Our packings do show a strong influence of the support (or perhaps the oriented first layer of Carbowax 20M), but most of the compounds tested, including polar compounds, yield sharp, symmetrical peaks.

The experimental section describes the synthesis using a 6% original load. The same procedure has been used with 1% and 0.5% original loads and the results were

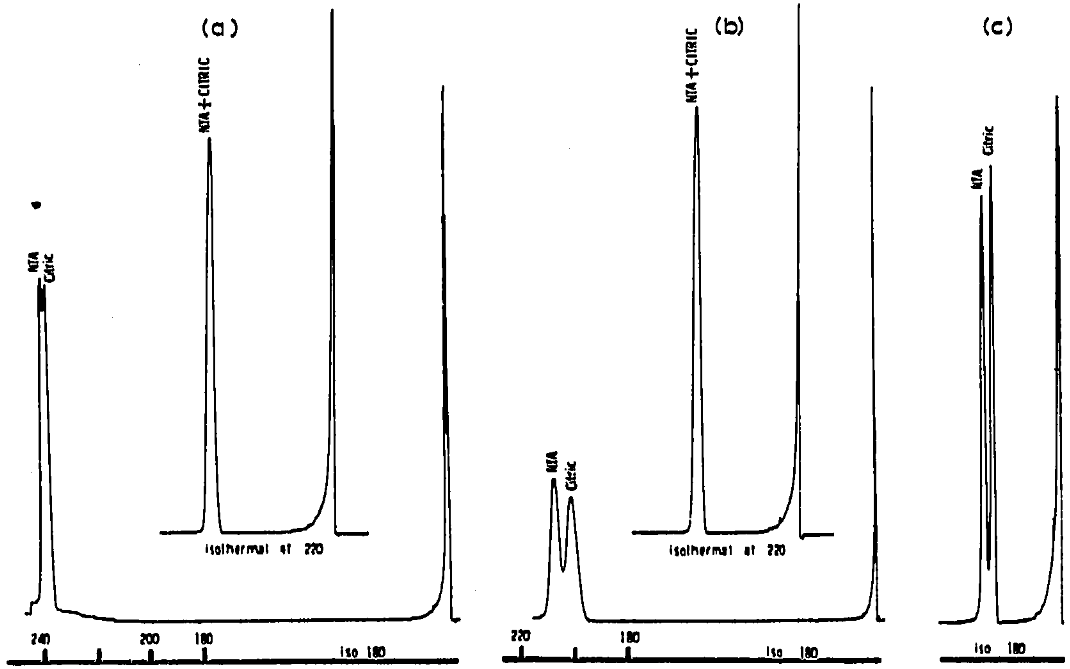


6% original load 0.5% original load

Fig. 3. Gas chromatography of *n*-butyl ester derivatives of nitrilotriacetic and citric acids[18] on heat-treated packing. Left: 6% original load, extracted; right: 0.5% original load, non extracted. Carbowax 20M on Chromosorb W, 100–120 mesh. 5 ft. × 4 mm I.D. Pyrex U-tube, 183° isothermal, N_2 flow-rate 60 ml/min, Mikrotek Model MT 220 with FID.

comparable. Fig. 3 shows the chromatography of the *n*-butyl esters of citric and nitrilotriacetic acids, a difficult but important chromatographic separation, on extracted support derived from 6% and non-extracted support from 0.5% original loads of Carbowax 20M.

The separation of these two acid derivatives is not due to the bulk properties of Carbowax 20M, *i.e.*, to its role as a common liquid phase. This is pointed out by Fig. 4, in which the same separation is shown along the path of synthesis: before heat-treatment, after heat-treatment and after extraction. Both isothermal and programmed runs are shown in this example, which also illustrates the considerable decrease in retention time/temperature.



Before heat-treatment, 5.8% load
After heat-treatment, 4.8% load
After extraction

Fig. 4. Isothermal and temperature-programmed separations of the *n*-butyl ester derivatives of nitrilotriacetic and citric acids, on phases representative of the stages of packing preparation. All in 5.5 ft. × 4 mm I.D. Pyrex columns, nitrogen flow-rate approx. 60 ml/min, Mikrotek Model MT-220 with FID. Packings are (a) 5.8% (by ignition) Carbowax 20M on Chromosorb W, acid-washed, 100–120 mesh; (b) same as (a), but heat-treated overnight at 280° under nitrogen. 4.8% load by ignition analysis. (c) same as (b), but exhaustively extracted with methanol. Uncertain load ($\approx$0.2%).

The separation is apparently due to the surface, about which we know very little. One could theorize that the chromatograms shown in Figs. 1–4 arise from adsorption equilibria on an "ideal" or "homogeneous" surface, *i.e.*, one where adhesion operates within a small range of bond strengths. Using the concept of gas-solid chromatography on a "monomolecular" layer appears to be possible once the layer thickness is comparable to the range of surface forces. On the other hand, Figs. 1–3 conform better to the mental image one has of gas–liquid rather than of gas–solid chromatography.

There is no doubt that other workers must have observed at least part of the described chromatographic, if not extractive, effects. To wit, the familiar "no-flow conditioning" of packed columns for GLC is similar to our heat-treatment. Various polar substances, including polymers, have often been added to stationary liquid phases in order to reduce solute decomposition or peak asymmetry (*e.g.*, ref. 14). Polyethylene glycol served this purpose (*e.g.*, refs. 13 and 15), among other applications to produce "monolayers" on activated carbon for gas–solid chromatographic studies[4]. A variety of other polar substances can be coated on to adsorbents, either from solution or from the gas phase, as discussed in a review of molecular adsorption chromatography by KISELEV[16]. The very successful use of vapor-phase deposition of polyether-type material for the improvement of column performance in GLC has been described by IVES AND GIUFFRIDA[17], who used the bleed originating from Carbowax 20M for deactivating coated Chromosorb W.

Even in the light of the literature cited above, plus general knowledge on chemisorption, plus current concepts on the adhesion of long-chain polymers, the characteristics of the developed phase are still surprising. First, it has been impossible to extract the "monomolecular" polymer layer from the Chromosorb, even under very trying conditions. Second, the remaining phase had unusually good gas chromatographic properties—not only low bleed, short retention times and high selectivity (which could have been expected), but also excellent peak symmetry and resolution of highly polar compounds. It differs distinctly, in this respect, from other reported chromatographies on monolayers.

Whatever the processes or mechanisms may be, which are operative in the preparation and chromatographic use of this phase, its peculiar properties make it appear interesting in several respects. The analytical application of this packing in *gas* chromatography is undoubtedly the most obvious, but it is also likely that the phase can serve as a highly deactivated support for other stationary liquid phases. When coated on different porous particles, these unextractable polymer layers could conceivably serve either to deactivate rigid gels or to modify adsorbent surfaces in two techniques of *liquid* chromatography. Finally, it should be interesting to use this or a similar phase as an "ideal" surface in the study of interface phenomena.

ACKNOWLEDGEMENTS

We are grateful to J. M. AUGL for his lucid explanations of polymer adhesion, and to J. J. STRATTA for his help in obtaining non-proprietory information on Union Carbide's Carbowax 20M compound.

REFERENCES

1 W. A. AUE AND C. R. HASTINGS, *J. Chromatogr.*, 42 (1969) 319.
2 *Chromatography Catalog*, Supelco, Inc., Bellefonte, Pa., 1973.
3 C. R. HASTINGS, W. A. AUE AND J. M. AUGL, *J. Chromatogr.*, 53 (1970) 487.
4 A. V. KISELEV, N. V. KOVALEVA AND YU. S. NIKITIN, *J. Chromatogr.*, 58 (1971) 19.
5 R. R. STROMBERG, D. J. TUTAS AND E. PASSAGLIA, *J. Phys. Chem.*, 69 (1965) 3955.
6 J. J. STRATTA, Union Carbide, private communication.

7 *Carbowax Polyethylene Glycols*, Union Carbide Corporation, Interim Reprint F-4772F, 11/68-5M.
8 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 36 (1968) 489.
9 I. Halász and I. Sebestian, *Angew. Chem. Int. Ed.*, 8 (1969) 453.
10 H.-P. Boehm, *Angew. Chem.*, 78 (1966) 617.
11 F. W. Stone and J. J. Stratta, *Encyclopedia of Polymer Science and Technology*, Vol. 6, J. Wiley & Sons, New York, 1967, p. 103.
12 J. Serpinet, *J. Chromatogr.*, 68 (1972) 9.
13 C. L. Guillemin, M. Deleuil, S. Cirendini and J. Vermont, *Anal. Chem.*, 43 (1971) 2015.
14 M. B. Evans, *Chromatographia*, 4 (1971) 441.
15 A. A. Zhukhovitskii, M. L. Sazonov, M. Kh. Lunskii and V. Yusfin, *J. Chromatogr.*, 58 (1971) 87.
16 A. V. Kiselev, *J. Chromatogr.*, 49 (1970) 84.
17 N. F. Ives and L. Giuffrida, *J. Ass. Offic. Anal. Chem.*, 53 (1970) 973.
18 W. A. Aue, C. R. Hastings, K. O. Gerhardt, J. O. Pierce, II, H. H. Hill and R. F. Moseman, *J. Chromatogr.*, 72 (1972) 259.