

CHROM. 10,365

## Note

---

### Influence of silanol groups on the bonding of Carbowax 20M

MAREK M. DANIEWSKI\* and WALTER A. AUE\*\*

*5637 Life Sciences Building, Dalhousie University, Halifax, Nova Scotia (Canada)*

(Received June 24th, 1977)

Non-extractable thin layers of Carbowax 20M can be formed on diatomaceous earth surfaces by heat treatment of a thick polymer layer followed by exhaustive extraction<sup>1</sup>. It was suggested that multipoint chemisorption involving the silanol groups of the surface and the ether oxygens of the polymer could have contributed to the resistance to extraction (ref. 2, *cf.* ref. 3).

However, some subsequent attempts to demonstrate differences between regular and dehydrated supports and between “dry” and “moist” synthesis conditions failed; *i.e.* all products gave the same satisfactory chromatographic performance. Since very small amounts of water are difficult to exclude and could have caused the failure to observe differences, these results were not considered final at the time.

Recently, we developed an alternative method to produce bonded layers<sup>4</sup>, which happens to allow better control of trace amounts of water. The initial attempt was therefore repeated.

## EXPERIMENTAL

Chromosorb W, 100–120 mesh, was cleaned as previously described<sup>5</sup>, then heated for 12 h at 850° and allowed to cool in a stream of dry nitrogen (pre-purified grade, dried over molecular sieve 5A and freed of residual water and oxygen by passage through a heated scavenger cartridge (Supelco, Bellefonte, Pa., U.S.A.)). This treatment would be expected to remove sorbed water and all but a few isolated silanol groups.

The coating solvent, hexadecane, and the extracting solvent, toluene, were high-purity products kept over anhydrous sodium sulphate. The coating apparatus, swept by dry nitrogen, was heated prior to the reaction with a heat gun to remove water adsorbed on the glass. All steps were done under dry nitrogen, with exposure to the atmosphere during transfer being kept to a minimum. The extraction time with toluene, in a special, high-efficiency apparatus swept by nitrogen<sup>6</sup>, was 20 h.

The experiment was repeated once; then a similar experiment was performed which started with regular Chromosorb (cleaned and dried in vacuum overnight at 160°, but not further heated). Also, no special precautions were taken this time to dry the glassware.

---

\* Present address: Polish Academy of Science, Warsaw, Poland.

\*\* To whom correspondence should be addressed.

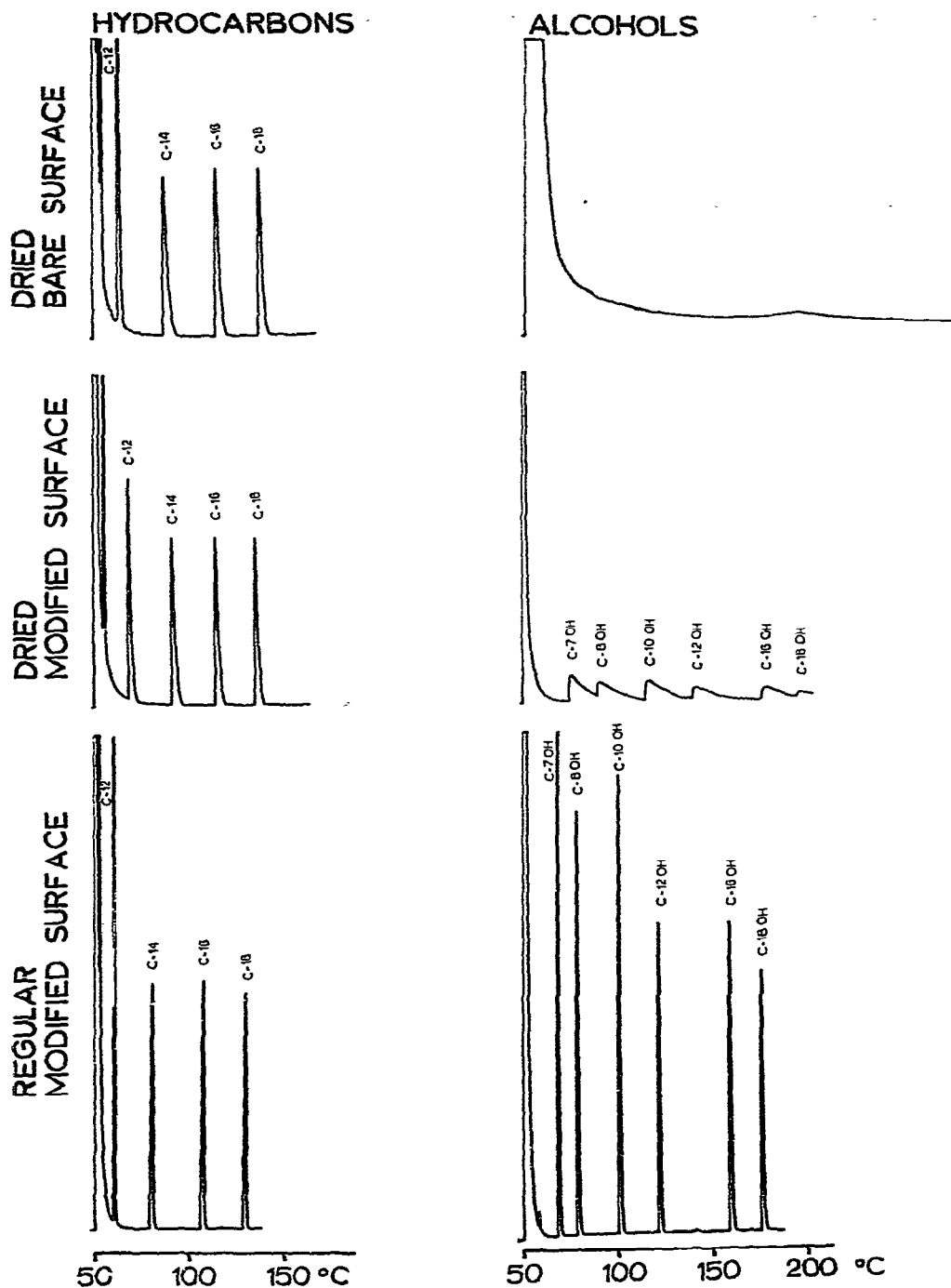


Fig. 1. Gas chromatograms of straight-chain hydrocarbons and primary alcohols as listed by carbon number. Upper chromatograms: on bare Chromosorb W RW, 100-120 mesh, heated 12 h at 850° under nitrogen. Middle chromatograms: on the same material coated with Carbowax 20M in refluxing hexadecane and extracted for 20 h with toluene, all under anhydrous conditions. Lower chromatograms: on Chromosorb W RW 100-120 mesh, not heat-treated, coated with Carbowax 20M in refluxing hexadecane and extracted for 20 h with toluene. Conditions: 1 m × 1.8-2.0 mm I.D. glass columns; flame-ionization detection; nitrogen flow-rate *ca.* 30 ml/min; temperature programme 6°/min.

## RESULTS AND DISCUSSION

Fig. 1 summarizes the results by way of some typical chromatograms. The upper two originated from bare, specially purified Chromosorb W after treatment at 850°, and were obtained only to define the starting material. The two chromatograms in the middle show the results of the attempt to bond Carbowax 20M at "dry" conditions onto a support essentially free of silanol groups. The attempt failed in this as well as in the repeated experiment. Though the presence of some small portion of the polymer is noticeable, the amount is far less than necessary for good chromatography.

Such chromatography is shown, for comparison, in the lower two chromatograms, which originate from the synthesis having been performed with "regular" Chromosorb and without special exclusion of moisture.

Thus, it appears that a drastic decrease in number and type of silanol groups (and the loss of sorbed water) from the diatomaceous earth surface can indeed be detrimental to the successful "bonding" of Carbowax 20M; however, this adverse effect can be noticed only under the most extreme conditions.

## ACKNOWLEDGEMENTS

This study was supported by NRC grant A-9604, AC grant EMR 7401 and DRB grant 9502-04.

## REFERENCES

- 1 W. A. Aue, C. R. Hastings and S. Kapila, *J. Chromatogr.*, 77 (1973) 299.
- 2 W. A. Aue and D. R. Younker, *J. Chromatogr.*, 88, (1974) 7.
- 3 R. K. Iler, *The Colloid Chemistry of Silica and Silicates*, Cornell University Press, Ithaca, N.Y., 1955, p. 58; as cited in M. Uihlein and I. Halász, *J. Chromatogr.*, 80 (1973) 1.
- 4 M. M. Daniewski and W. A. Aue, *J. Chromatogr.*, in press.
- 5 W. A. Aue, M. M. Daniewski, E. E. Pickett and P. R. McCullough, *J. Chromatogr.* 111, (1975) 37.
- 6 W. A. Aue, M. M. Daniewski, J. Müller and J. P. Laba, *Anal. Chem.*, 49 (1977) 1465.