Journal of Chromatography, 185 (1979) 73–78

CHROM. 12,167

STUDIES OF OPEN-TUBULAR MICRO-CAPILLARY LIQUID CHROMATOGRAPHY

IV. SODA-LIME GLASS COLUMNS TREATED WITH ALKALINE SOLUTION

D.ISHII, T. TSUDA* and T. TAKEUCHI

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya-shi 464 (Japan)

SUMMARY

A soda-lime glass capillary treated with an alkaline solution was used as an adsorbent column for the separation of aromatic amines and phthalates in the normal-phase mode. The best adsorbent column for open-tubular micro-capillary liquid chromatography was made by treatment with 1 *N* sodium hydroxide solution at 25–54° for 2 days.

INTRODUCTION

Open-tubular liquid chromatography is now in the development stage[1–6]. Theoretical calculation requires a column with an inner diameter of 8–16 μm owing to the low diffusion coefficients in the liquid phase (about one ten thousandth of that in the gas phase), if the linear velocity in liquid chromatography (LC) is set at one tenth of that in gas chromatography (GC)[3,6]. Recent experiments have shown that some of the better columns, with inner diameters of 30–60 μm, give sufficiently good separations for the potential ability of microcapillary LC to be considered[3–6]. We have proposed open-tubular microcapillary columns which have physically coated or chemically bonded stationary phases[3–5]. In this paper we describe developments of the work of Nota *et al.*[1], a modified glass capillary column having been obtained by treatment with an alkaline solution behaves like a solid absorbent column.

Alkaline solutions have been used as cleaning, etching and modifying reagents for glass surfaces. For example, to improve the wetting of a glass surface, aqueous solutions of sodium hydroxide have been used in capillary GC[7] and LC[5]. Further Mohnke and Saffert[8] discovered that treating a glass capillary with ammonia solution for 70 h at 170° produced a layer of SiO_2 of thickness 20 μm on the glass surface, which could be seen clearly. The capillary obtained in this manner worked as

* Present address: Laboratory of Analytical Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya-shi 466, Japan

an efficient adsorbent column for hydrogen isotope separations at low temperature in capillary GC. The procedure employed for making the capillary column was very simple. Bruner and Cartoni[7] used a soft-glass capillary for the separation of low-boiling hydrocarbons in capillary GC, the capillary being treated with 20% sodium hydroxide solution, instead of ammonia solution, for 6 h at 100°. The capillary column, which had an internal layer of activated silica (about 10 μm thick), gave good separations of oxygen isotopes in capillary GC[9].

Nota *et al.*[1] first applied this method in capillary LC using soft-glass capillaries, for example I.D. 0.26 mm and length 5 m, treated with 2.5 *N* sodium hydroxide solution at 100° for 2–8 h. They achieved the separation of amino acid derivatives by using this column and a typical separation required about 5 h. Although they used a capillary column of large I.D. and their results were not very good, they were enough to suggest the potential ability of an adsorbent column in capillary LC.

We have applied this method to a micro soda-lime glass capillary with an inner diameter of about 50 μm, about one-fifth of that of Nota *et al.* column, and examined the alkaline solutions, concentrations, treating temperature and time period which give the most efficient adsorbent column.

EXPERIMENTAL

The composition of the original glass tube was SiO_2 72%, Na_2O 12.4%, CaO 11.4%, Al_2O_3 2.4%, K_2O 1.4%, SO_3 0.28% and Fe_2O_3 0.05%. A capillary tube was obtained by using an ordinary glass drawing machine, and its coiling diameter was about 11 cm. The capillary tube for the column, *ca.* 50 μm I.D., 0.6 mm O.D. and 3–8 m length, was filled with alkaline solutions and kept in an oven at various temperatures from 2 h to 6 days. Then it was washed with methanol until neutral, dichloromethane (*ca.* 100 μl) and *n*-hexane. *n*-Hexane was used as eluent in most instances. Sodium, lithium and potassium hydroxide were used as alkaline solutions at concentrations from 0.1 to 5 *N* and at temperatures from 3 to 74°.

Scanning electron micrographs of the glass surfaces were taken by using a JSM-T20 instrument (JEOL, Tokyo, Japan). For checking the chromatographic behaviour, a test sample mixture of α-, β-, N-phenyl-α- and N-phenyl-β-napthylamine and aniline in isooctane was used, the amount injected being *ca.* 10 ng with *n*-hexane as eluent and detection at 235 nm.

RESULTS AND DISCUSSION

Scanning electron micrographs of the soda-lime glass surface treated with alkaline solutions are shown in Fig. 1. Fig. 1A is a wide view and shows a uniform pattern of the aggregates deposited on the glass surface. Fig. 1B is a plane figure, and Fig. 1C was taken at a large magnification. The size of the aggregates is about 1 μm wide and 0.5 μm high. Mohnke and Saffert[8] obtained larger aggregates (about 20 μm high) by treating soft glass with alkaline solutions, and Bocola *et al.*[9] obtained a height of about 10 μm. The present method of treating a soda-lime glass capillary with alkaline solutions is mild compared with their procedures. The ratio of the inner diameter of the capillary tube to the height of aggregates in the present work is nearly one tenth of that in the others, *i.e.*, in the present work the ratio is about

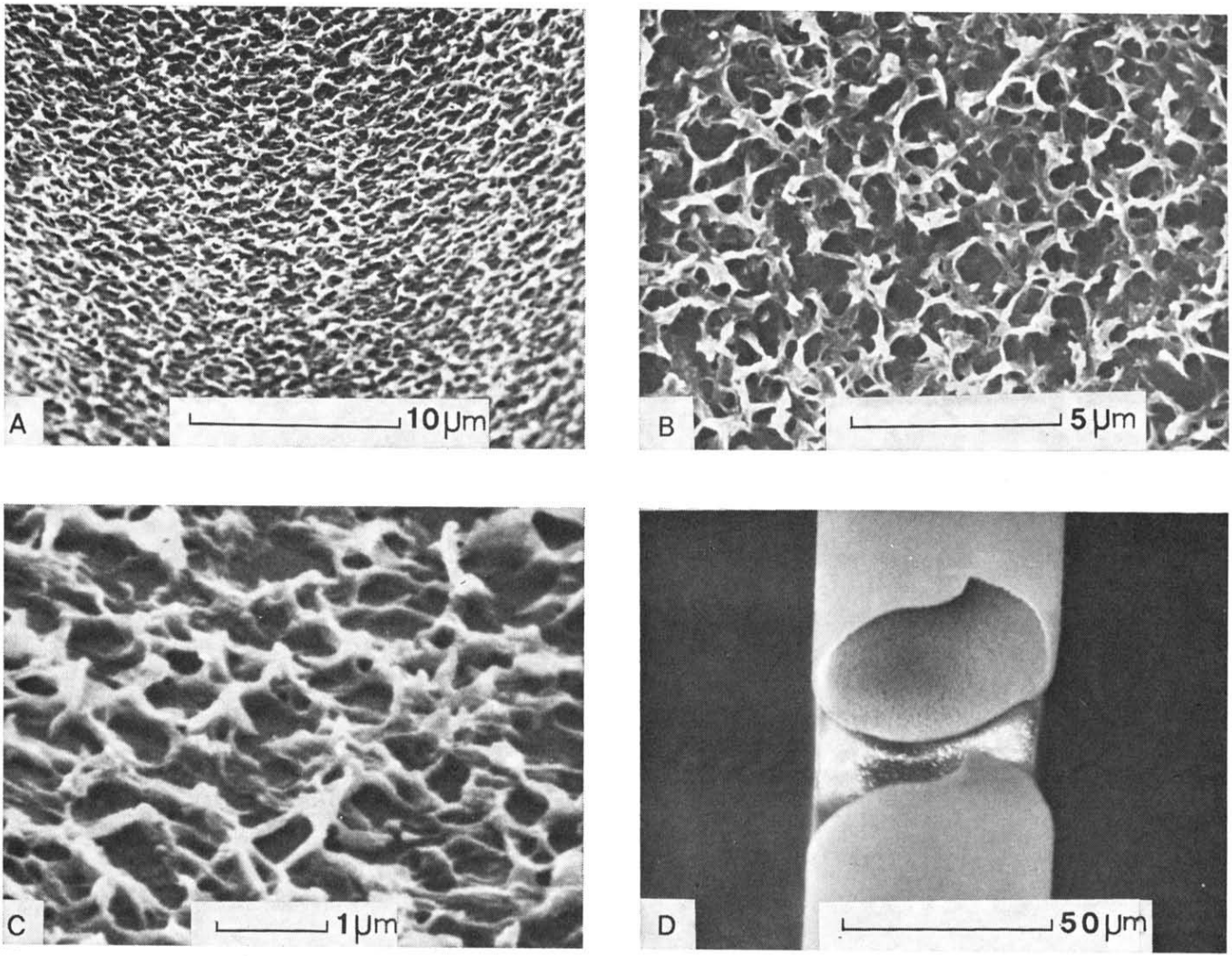
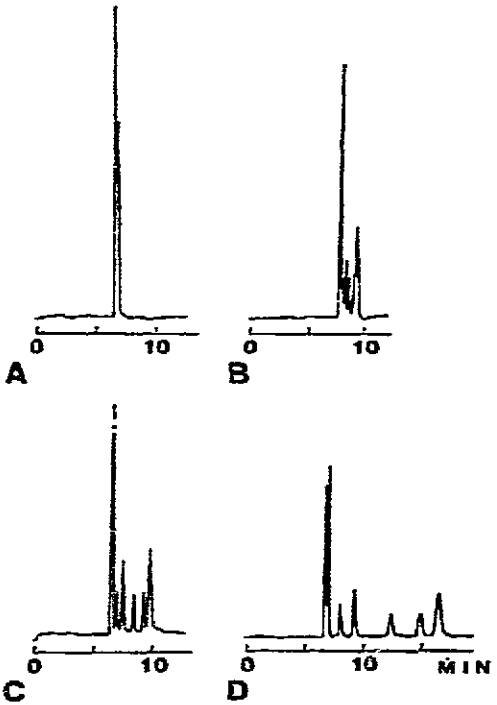


Fig. 1. Scanning electron micrographs of soda-lime glass treated with 1 *N* sodium hydroxide solution for 2 days at room temperature (A, B and C) or at 64° (D). A, magnification ×3500 and angle 60°; B, magnification ×7500 and angle 0°; C, magnification ×20,000 and angle 60°; D, magnification ×7500 and angle 30°.

1:100 and in the others it is about 1:10 to 1:30. Mohnke and Saffert showed one photograph of a cross-section of the capillary but it was not clear enough to confirm whether the aggregates were like narrow needle whiskers or flat. Fig. 1 here shows that the deposits are flat and low, and also that the aggregates are aligned in a cross-striped pattern. This pattern is different from whiskers, which are like narrow needles, on glass capillaries which were grown using fluoro-ether[10] or hydrofluoric acid[11]. Although previous workers suggested that the aggregates grown by treating soft glass with an alkaline solution consisted of active silica[9], no data for elemental analysis of the aggregates were given. From the viewpoint of chromatographic behaviour, the present adsorbent capillary is nearly identical with silica gel[7–9]. For example, an eluent that contained a small proportion of methanol or acetonitrile gave retention volumes of samples that were very different from those obtained by using pure *n*-hexane as the eluent. Hence the adsorbent could be a kind of silica gel.

As the treatment of soda-lime glass with lithium, sodium or potassium hydroxide solution gave almost identical aggregates with respect to both chromatographic behaviour and microscopic appearance, most of the experiments were carried with sodium hydroxide solution.



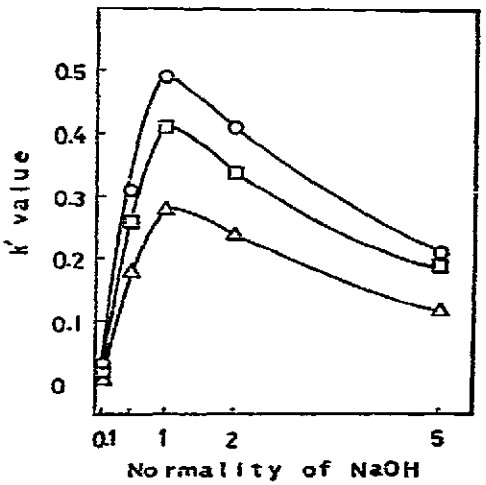
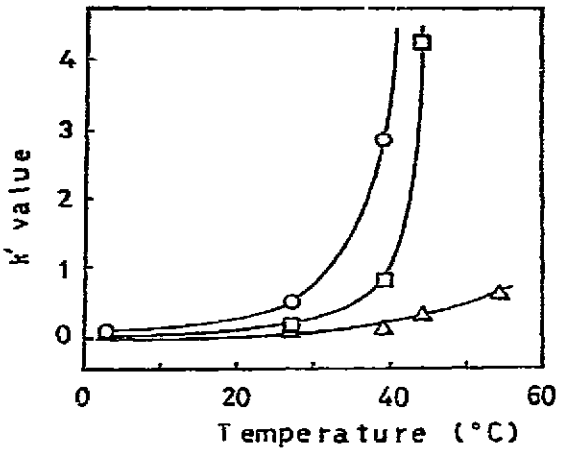


Fig. 2. Effect of treatment period on separation. A, 2 h; B, 1 day; C, 2 days; D, 6 days. Column, glass capillary treated with 1 *N* sodium hydroxide solution at 27°; eluent, *n*-hexane; flow-rate, 1.7 μl/min; sample, aromatic amines.

Fig. 3. Effect of concentration of sodium hydroxide solution on *k'* values. Column, glass capillary treated with aqueous sodium hydroxide solution of different concentration for 2 days at 27°; eluent, *n*-hexane. Sample: ○, β-naphthylamine; □, α-naphthylamine; △, aniline.

The experimental conditions that produced adsorbents that gave the best chromatographic separations were examined. An increase in the period of treatment with 1 *N* sodium hydroxide solution at 27° increased the *k'* value of the test sample as shown in Fig. 2, with a linear relation in the range from 2 h to 6 days. A longer treatment period resulted in a higher density of the adsorbent. A treatment period of 6 days does not cause any problems, such as clogging up. Fig. 3 shows the effect of the concentration of sodium hydroxide solution on *k'* values; a 1 *N* solution gave the largest *k'* value.

Fig. 4 shows the effect of temperature on *k'* values. At a low treatment temperature, such as 3°, the deposited adsorbents were small and sparse on the glass surface. At about 20–44°, the pattern of the adsorbent was striped and each lump of the adsorbent formed on the glass base independently. Above 54°, the adsorbent formed a layer. At temperatures over 60° the adsorbent became a thick layer and was not retained well on the glass base. The scanning electron micrograph of a capillary that was treated at 64° for 2 days is shown in Fig. 1D. The adsorbent layer formed is very thick, being nearly 2–5 μm. This layer became detached from priginal glass capillary base and formed a tube. In Fig. 1D only the bare adsorbent tube is shown (in other words, there is no inner wall of the glass capillary). The chromatogram obtained by using this column showed very poor resolution and the peaks showed severe tailing. Although a higher treatment temperature gives larger *k'* values, for the chromatographic separation the most favourable capillary is that



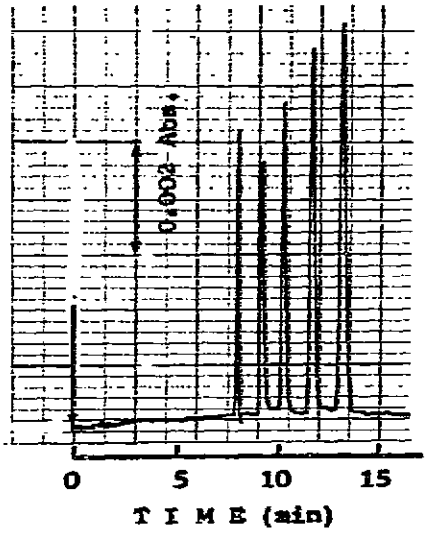


Fig. 4. Effect of treatment temperature on *k'* values. Column, glass capillary treated with 1 *N* sodium hydroxide solution for 2 days at different temperatures; eluent, *n*-hexane. Sample: ○, β-naphthylamine; □, N-phenyl-β-naphthylamine; △, N,N-diethylaniline.

Fig. 5. Separation of phthalates. Column, 575 cm × 43 μm I.D. glass capillary treated with 1 *N* sodium hydroxide solution for 2 days at 54°; eluent, *n*-hexane solution containing 0.07% of methanol and 5% of dichloromethane; flow-rate, 1.1 μl/min; sample, mixture of 4.2 ng of dioctyl, 4.0 ng of dibutyl, 4.7 ng of diethyl and 5.5 ng of dimethyl phthalate in isooctane, eluted in that order; wavelength, UV 235 nm.

treated below 54° for 2 days. This condition is also favourable for minimizing the clogging problems.

The best column was prepared by treatment with 1 *N* sodium hydroxide solution at 25–30° for 2–6 days or at 40–54° for 2 days. In the latter instance, if the capillary was treated for more than 2 days, clogging occurred.

A Pyrex glass capillary also was tried, but it gave poorer separations and lower retention volumes. Washing the adsorbent formed below 44° with 1 *N* hydrochloric acid changed the retention volume slightly, but similar washing of the adsorbent formed at above 54° made the layer detach from the glass base.

A typical example of a separation is shown in Fig. 5. The theoretical plate number of the last peak is about 10,000. The relationship between HETP and linear velocity between 0.4 and 2.7 cm/sec is linear. The amount of dimethyl phthalate does not effect the HETP up to 20 ng, but more than 20 ng causes tailing of the peak with $k' \approx 1$.

In this work, the adsorbent, which behaves like silica gel, was easily formed on the soda-lime glass surface. The adsorbent gave relatively good separations of aromatic amines, phthalates and phenols. As a result of treatment with sodium hydroxide solution, the surface area of the inner wall of the glass capillary would be much larger than that of the bare original wall. Although treatment of soda-lime glass with sodium hydroxide solution is not new, this work gives a clear view of the adsorbent formed with respect to both surface observations and chromatographic behaviour. There is some potential for obtaining columns that have different selectivities after chemical treatment of the surface, and studies of this aspect are in progress.

REFERENCES

1 G. Nota, G. Marino, V. Buonocore and A. Ballio, *J. Chromatogr.*, 46 (1970) 103.
2 T. Tsuda and M. Novotny, *Anal. Chem.*, 50 (1978) 632.
3 K. Hibi, D. Ishii, I. Fujishima, T. Takeuchi and T. Nakanishi, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 21.
4 T. Tsuda, K. Hibi, T. Nakanishi, T. Takeuchi and D. Ishii, *J. Chromatogr.*, 158 (1978) 227.
5 K. Hibi, T. Tsuda, T. Takeuchi, T. Nakanishi and D. Ishii, *J. Chromatogr.*, 175 (1979) 105.
6 D. Ishii, T. Tsuda, K. Hibi, T. Takeuchi and T. Nakanishi, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 371.
7 F. A. Bruner and G. P. Cartoni, *Anal. Chem.*, 36 (1964) 1522.
8 M. Mohnke and W. Saffert, in M. van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 216.
9 W. Bocola, F. Bruner and G. P. Cartoni, *Nature (London)*, 209 (1966) 200.
10 J. D. Schieke, N. R. Comius and V. Pretorius, *J. Chromatogr.*, 112 (1975) 97.
11 F. J. Onuska, M. E. Comba, T. Bistricki and R. T. Wilkinson, *J. Chromatogr.*, 142 (1977)117.