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HIGH-PERFORMANCE GAS CHROMATOGRAPH–MASS SPECTROMETER INTERFACING: INVESTIGATION AND OPTIMIZATION OF FLOW AND TEMPERATURE

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SUMMARY

A new version of an open-split type of gas chromatograph–mass spectrometer interface with a glass restriction has been developed, with particular emphasis upon the use of glass capillary columns. A flow of scavenger gas is provided in the interface, which at low flow-rates avoids "dead volume tailing" of large peaks and which at high flow-rates dilutes peaks that are too strong. The influence of both the interface and the ion source on chromatographic performance has been investigated with high-polarity and low-volatility test compounds. The interface proved to be effective but adsorption, mainly in the ion source, restricts the range of applications in modern high-temperature gas chromatography. Experiments with a platinum capillary as a restriction and experience in producing and mounting glass capillaries in the new interface favour the use of glass restrictions.

INTRODUCTION

Recent progress in gas chromatography with glass capillary columns[1] and the availability of new mass spectrometers with a high pumping capacity has led to the need for an improvement in the performance of the ion source and the interface of a gas chromatograph–mass spectrometer (GC–MS) system.

The open-split connection (OSC)[2,3] has been found to be a suitable means for the interfacing of chromatographic systems to mass spectrometers. The advantage of this type of column connection is that the interface is open to atmospheric pressure, so that sealing problems are reduced, valves are unnecessary in the vacuum region and column changing is easy. In addition, the atmospheric pressure at the end of the column allows one to reproduce easily previous or optimized chromatographic separations. Experience with the previous equipment and a new investigation of performance led to changes in the interface and the ion source.

INSTRUMENTAL

The GC–MS system is shown schematically in Fig. 1. Normally, a glass capillary is used as a restriction, but a platinum capillary can also be used. The heated

guide tube provides a uniform temperature over its full length, which can be examined at any point with a movable thermocouple. The graphite seal is the same as was used by us to connect glass capillaries to GC equipment[4].

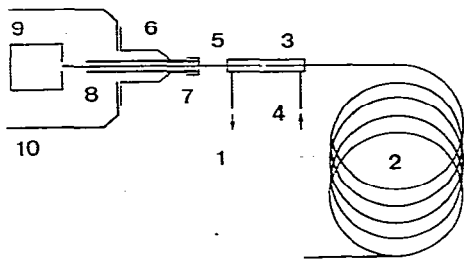

Fig. 1. Schematic diagram of the GC–MS system. 1 = Interface (heating facilities omitted); 2 = column; 3 = splitting device; 4 = scavenger gas flow; 5 = capillary restriction; 6 = connection flange; 7 = graphite seal; 8 = heated guide tube; 9 = ion source; 10 = source housing.

The mass spectrometer (Varian-MAT 311A) was equipped with 200 l/sec turbomolecular pumps. No deterioration of mass spectral peak profiles was observed with a 12 ml/min flow of helium into the mass spectrometer at a resolution of 2000. However, the sensitivity of the base peak of *n*-decane decreased by 20–30% and the molecular peak by 50%.

As a compromise between this decrease in sensitivity and the increase in the yield with increasing flow-rate into the mass spectrometer (see below), we use restrictions 20 cm long and of 0.1 or 0.11 mm I.D., the former for long columns for separations at higher efficiency (1–3 ml/min flow of helium) and the latter for shorter columns (3–6 ml/min).

The simple splitting device described earlier[2,3] is inadequate for today's performance requirements. With a higher flow-rate into the mass spectrometer giving a higher yield from the OSC, this flow-rate can be greater than the effluent flow-rate when longer columns are used. In this instance, the old construction cannot completely avoid the ingress of undesirable amounts of air into the mass spectrometer. In addition, the old equipment for the solvent peak dilution needed to be improved.

In the new splitting device, shown schematically in Fig. 2, a glass tube of I.D. 1.0–1.2 mm forms the splitting volume. The column and the restriction, with outer diameters of 0.7–0.8 mm, are mounted tightly on this tube with graphite seal , as mentioned already. The two tubes entering from the side allow the introduction of an additional flow of helium (F_3 in Fig. 2).

With this splitting device the three interesting cases of operation, $F_1 > F_2$, $F_1 < F_2$ and the dilution of solvent peaks, can be handled successfully. A small flow-rate of scavenger gas, F_S (about 0.5 ml/min), along the two capillaries inside the splitting volume avoids the tailing effects that are observed when solvent peaks or major components are passing the splitting region. This is important for the analysis of trace components eluted immediately after very large peaks.

Flow conditions and yields from the splitting device

The yield from the interface is determined generally by the ratio of the flow-

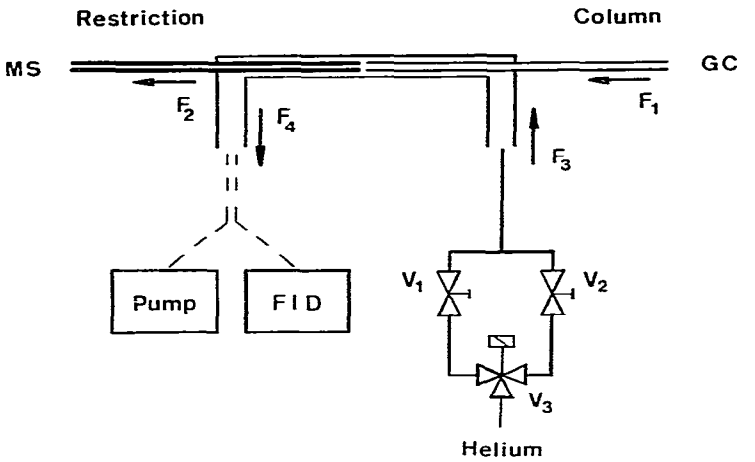

Fig. 2. Schematic diagram of the splitting device (above) and connections to the splitting device (below). V_1, V_2 = Adjustable valves for low (dead volume) and high (dilution) flow-rate of scavenger gas; V_3 = magnetic valve, push-button operated.

rate F_2 into the restriction to the flow-rate passing by the restriction. For the three different cases the following relationships hold:

(1) If F_1 is greater than or equal to F_2, and $F_S = F_3$ is the flow-rate of scavenger gas in the right-hand side of the splitting volume, the yield is

$$Y = F_2/(F_1 + F_S)$$

(2) If F_2 is greater than F_1, then the missing amount of helium of $F_2 - F_1$ has to be added to $F_1 + F_S$, which gives a yield of

$$Y = F_2/(F_2 + F_S)$$

In this instance F_3 has to be adjusted to $F_2 - F_1 + F_S$ to obtain a flow-rate F_S of scavenger gas in the left-hand side of the splitting volume. With temperature programming at a constant pressure drop, F_3 must be adjusted according to the smallest flow-rate F_1 at the end of the temperature programme.

For small F_S the resulting yields from an OSC are approximately $Y = F_2/F_1$ if $F_1 > F_2$, and 100% for $F_2 > F_1$. Using capillary columns and a mass spectrometer with a good pumping system, these yields can be better than values obtained with separators (30–90%). Even with packed columns operated at low carrier gas flow-rates (10–15 ml/min) the yields are good.

(3) For the reduction of peaks that are too intense, F_S is chosen to be much higher than F_1 and F_2 so that F_2/F_S is the resulting yield or F_S/F_2 the reduction factor. Values of 100–500 guarantee adequate protection of the mass spectrometer and are easily attained without any changes in the chromatogram. By means of this technique the peak is considerably reduced, but still observable, so that a sharp "heart cut" of a large peak can be achieved.

It is not recommended that one should prevent access of "large peaks" to the

mass spectrometer by evacuating the splitting region during the appearance of the peak: the peak profile cannot be observed, the retention times of subsequent peaks are shortened and these peaks may even be pumped away completely. The connection of a pump to the splitting volume by suitable valves, however, has the advantage that the mass spectrometer can be kept free of helium for measurements not using the sample inlet of the gas chromatograph.

A device is being constructed and tested for the connection of a flame-ionization detector (FID) to F_4 in order to record a perfect chromatogram in parallel. This is of importance, especially in chemical ionization mass spectrometry, where the mass spectrometer cannot generate a continous trace of the chromatogram.

The ion source

High sensitivity is required from ion sources in GC–MS systems considering the problems of trace analysis. Further, the ion source should not affect the quality of the preceding chromatographic separation.

The ionization chamber of an ion source normally operates under molecular flow conditions, *i.e.*, the molecules undergo a certain number of wall collisions. Irreversible adsorption of a sample molecule does not influence the peak profile or retention time, but results in a decrease in sensitivity (see 1,4-butanediol in Fig. 5C). Temporary adsorption causes peak distortion phenomena such as tailing, peak broadening and/or shifts of peak maxima (see Figs. 3D and 6C). Adsorption of low-volatile and strongly polar compounds can obviously be minimized by increasing the usual operating temperatures (250°). However, in addition to technical problems and difficulties with decomposable components, this is not recommended because the intensities of the important ions in the upper part of the spectrum, and of the molecular ion in particular, will decrease.

We measured different temperatures for the elements forming the walls of the ionization chamber. The drawing plates and the pusher electrode were found to be at a temperature 80° lower than that of the block which bears the heater and the temperature-sensing element. By installation of additional heaters we achieved a uniform temperature over the whole ionization chamber. In the following experiments the source temperature T_S refers to this modified source.

Although the restriction is a part of the interface, the further end of it is in contact with the ion source, and therefore has the same temperature as the source. The viscous flow inside the restriction changes to molecular flow at its vacuum end. Therefore, this end of the restriction has to be considered as part of the ion source in a discussion of the influence of ion source and interface temperatures.

An increase in sensitivity by reducing the apertures of the ionization chamber was rejected because the resulting pressure increase increases the number of wall collisions, which is not recommended for components of low volatility and/or high polarity.

RESULTS AND DISCUSSION

The GC part of the whole system was run under optimal conditions for each test mixture. Starting at sufficiently high values, the temperature of the ion source or interface was decreased stepwise until clearly recognizable effects of peak broadening,

tailing and/or shifts appeared. By this method the influence of the interface and ion source could be studied separately using test compounds that are not too problematical, so that effects due to insufficient column performance and sampling techniques during a longer series of experiments could be excluded. To allow for an optimal assessment of peak shape and tailing, mass chromatograms are recorded instead of total ionization chromatograms. In the following experiments untreated glass (Duran) capillaries were used as restrictions.

The chromatograms in Fig. 3 were measured with a mixture containing C_{20}, C_{22}, ..., C_{34} *n*-alkanes in equal amounts, dissolved in *n*-dodecane. Chromatogram A, obtained at high temperatures of the ion source (T_S) and interface (T_I), shows no tailing or discrimination of the higher *n*-alkanes: when corrected for response (on

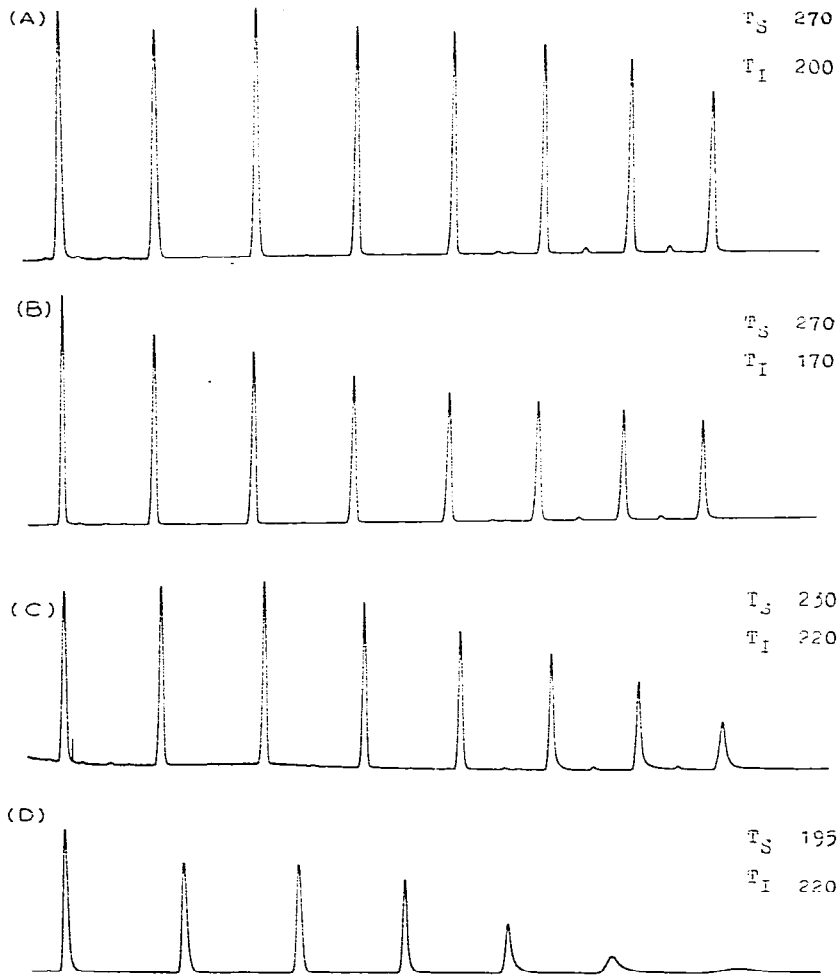

Fig. 3. Discrimination of higher boiling components at different temperatures of the ion source (T_S) and interface (T_I). First peak C_{20}; last peak C_{34} in A, B and C and C_{32} in D. Mass chromatograms (*m/e* 57) of a mixture of *n*-alkanes (equal amounts). Column, 10 m × 0.27 mm I.D., OV-1, programmed from 80 to 250° at 6°/min.

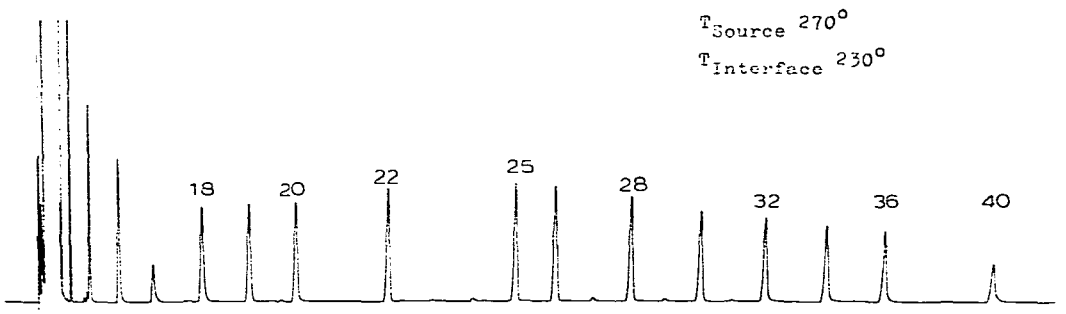

Fig. 4. Mass spectrum (*m/e* 57) of a mixture of *n*-alkanes up to C_{40}. Column, 10 m × 0.27 mm I.D., OV-1, programmed from 80 to 280° at 6°/min.

m/e 57 being approximately inversely proportional to the molecular weight) the areas are about equal.

At lower temperatures of the ion source (Fig. 3C and D), increasing discrimination, peak broadening (symmetrical) and higher retentions are observed, indicating reversible adsorption on the walls of the ion source. On the other hand, a very low interface temperature (B) leads to only small discrimination. In Fig. 4 the mass chromatogram of an *n*-alkane mixture is shown with C_{40} (boiling point 540°) as the component of lowest volatility. This spectrum and that in Fig. 3A are of the same quality as those obtained with the same column directly connected to an FID.

Measurements with a mixture containing the polar compounds 1,6-diaminohexane and 1,4-butanediol (Fig. 5) again do not reveal any interface problems. Only a slightly increased tailing is observed at 110°. At low ion source temperatures, however, irreversible adsorption of the diol occurs without distortion of the peak profile,

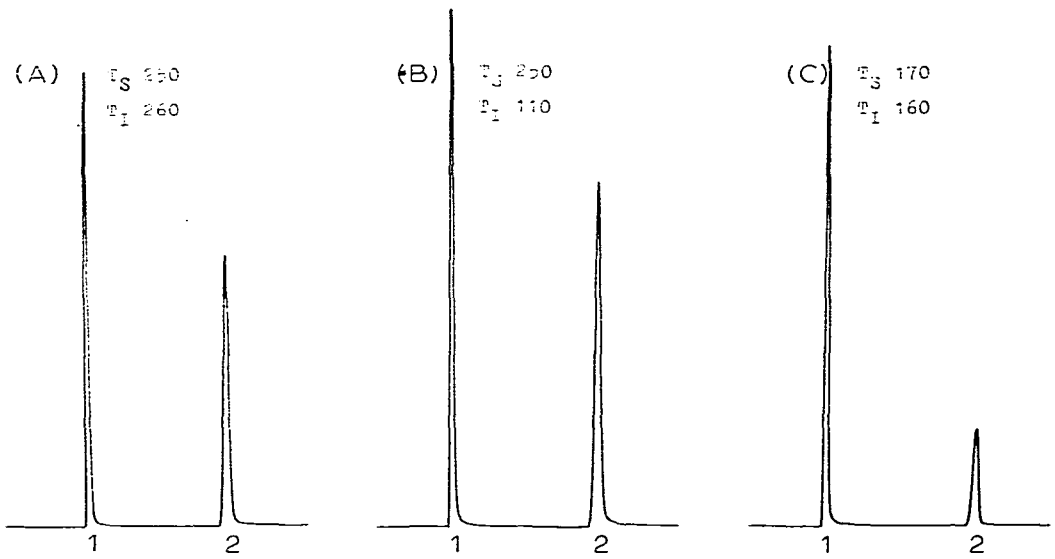

Fig. 5. Influence of different temperatures of the ion source (T_S) and interface (T_I) on polar compounds. Mass chromatograms of a mixture of 1,6-diaminohexane (peak 1, *m/e* 30) and 1,4-butanediol (peak 2, *m/e* 31). Column, 23 m × 0.27 mm I.D., Marlophen, 160°.

differing from the results with the *n*-alkanes. Similar results (Fig. 6) were obtained with a third mixture, consisting of phthalic anhydride, 1-oxo-1,3-dihydrobenzo[*c*]furan and benzoic acid. With the interface at 110°, all three components began to exhibit slight tailing. At an ion source temperature of 180° peak broadening was observed, especially for the peak of benzoic acid, but its area was relatively unaffected. The FID chromatogram of the mixture is of exactly the same standard as that in Fig. 6A.

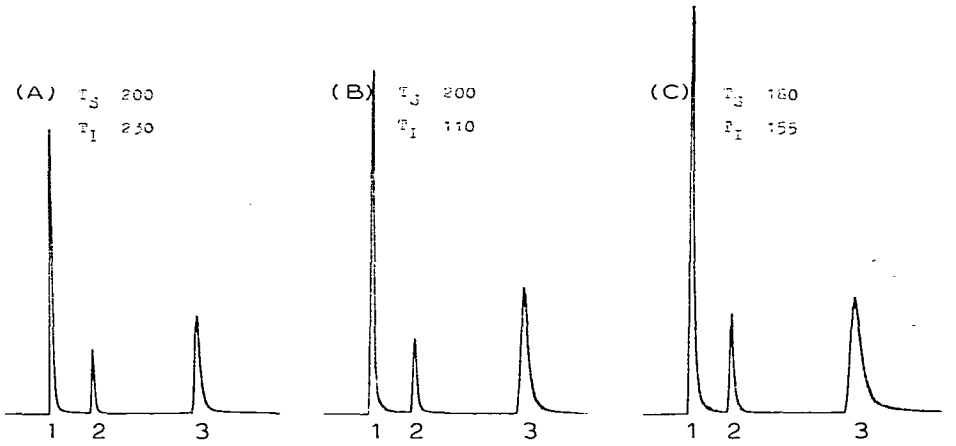

Fig. 6. Influence of different temperatures of the ion source (T_S) and interface (T_S) on a mixture of phthalic anhydride (1), 1-oxo-1,3-dihydrobenzo[*c*]furan (2) and benzoic acid (3). Mass chromatograms (*m/e* 50). Column, 40 m × 0.27 mm I.D., trimer acid, 160°.

These results show that the use of an untreated glass restriction does not affect the quality of the chromatograms, even at temperatures lower than that of the column itself. Nevertheless, it is not possible to realize fully the extension of the range of applications of high-temperature chromatography[1] in a GC–MS system, because the wall collisions in the regions of molecular flow are a limiting factor. It seems to be necessary to redesign ion sources for GC–MS work at higher temperatures.

Platinum capillaries have been used in different types of interfaces for many years[2,3,5–7]. Necessary procedures for the surface treatment of the capillaries have been described[7], and more recently a detailed investigation was carried out[8].

For a comparison with the behaviour of the glass restriction we repeated the same experiments with a 20-cm × 0.15 mm I.D. platinum capillary, which had been rinsed with a solvent and then heated under a flow of oxygen. No changes were observed except that the benzoic acid disappeared almost completely from the chromatogram (Fig. 7A). When the restriction was treated with the basic compound triethanolamine, a small part of the eluted acid could be detected, although with strong tailing (Fig. 7B). Slightly better results were obtained after treatment with "trimer acid" (Applied Science Labs., State College, Pa., U.S.A.), with the same compound as the stationary phase in the column (Fig. 7C).

Measurements of the same mixture in our previous GC–MS system[2,3] equipped with a 60-cm platinum capillary as a restriction gave results (Fig. 7D) comparable to those obtained with the glass restriction (the polygonal curve in Fig. 7D results from the fact that the mass spectrum was reconstructed from a series of spectra taken in a

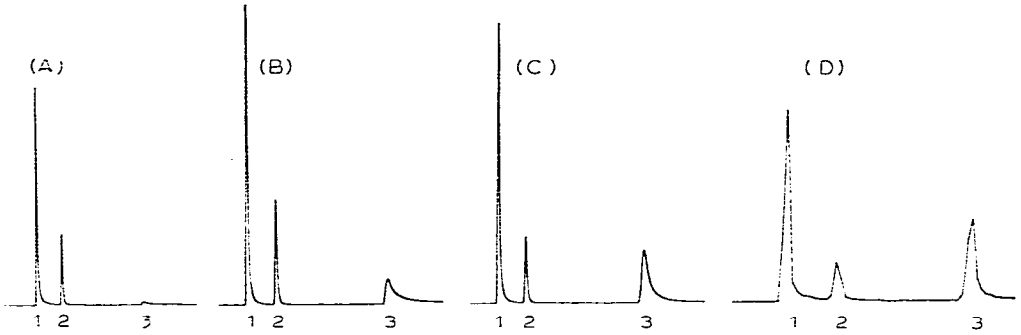

Fig. 7. Mass chromatograms (m/e 50) of the same mixture as in Fig. 6, with differently treated platinum capillaries as restrictions in the interface. Source and interface temperatures 250°. Column, 40 m × 0.27 mm I.D., trimer acid, 160°: (A), 20-cm long, untreated; (B), 20-cm long, treated with triethanolamine; (C), 20-cm long, treated with trimer acid; (D), 60-cm long, after several months of use with different polar and apolar columns, reconstructed from a series of spectra.

5-sec cycle). This platinum capillary had been deactivated during several months of use with different columns and samples. The photograph in Fig. 8 of the inner surface of a platinum capillary may indicate why the chromatographic performance of this type of capillary is so sensitive to any kind of "treatment".

Summarizing the results and experience with glass and platinum capillaries in GC–MS interfaces, we consider that glass is definitely to be preferred. Firstly, short

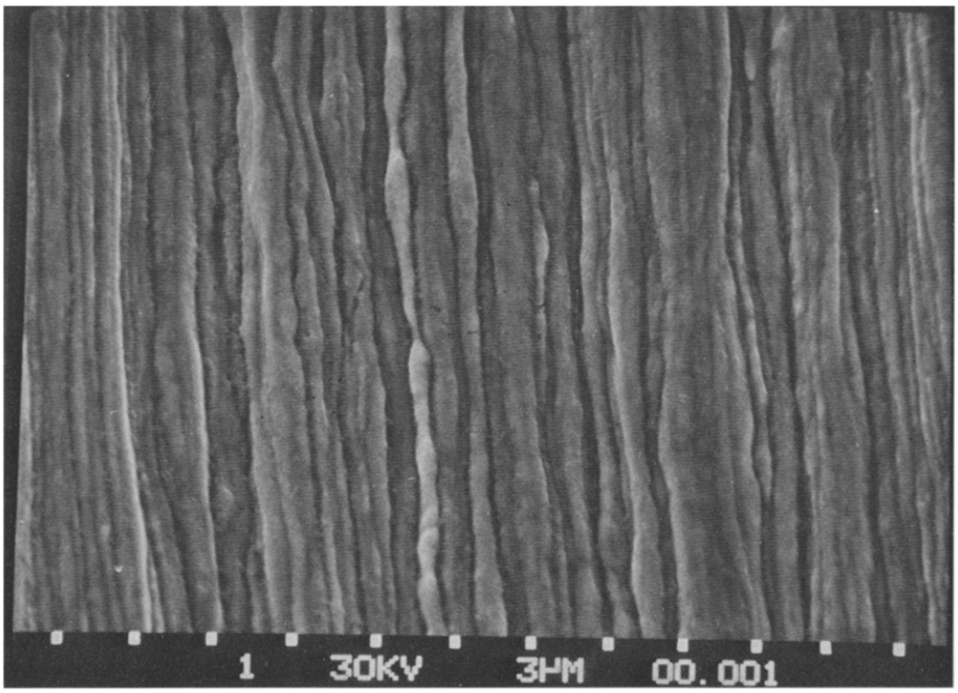

Fig. 8. Inner surface of a platinum capillary, 0.15 mm I.D. Photographed from a scanning electron microscope, scale 3 μm per division.

glass capillary restrictions can easily be produced with the required diameters by a drawing machine, the replacement of a contaminated or broken one is no problem and not expensive. Platinum capillaries with different specified geometries, on the other hand, cannot be bought. Secondly, in agreement with general remarks made by Grob[8], glass has superior chemical and chromatographic properties, which can be altered by simple surface treatment procedures; these are being thoroughly investigated at present in connection with the manufacture of glass capillary columns. However, glass can be used successfully even without any pre-treatment and maintains its performance under changing chromatographic conditions such as the nature of the stationary liquid, bleeding and temperature.

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