Journal of Chromatography, 92 (1974) 267–279

CHROM. 7258

CATHODOLUMINESCENCE AND STATIONARY PHASE DISTRIBUTION: EXPERIMENTS WITH DIATOMITE SUPPORTS

M. DE METS and M. VERPLANKEN

Rijksuniversiteit Gent, Laboratorium voor Elektronenmicroscopie, St. Pietersnieuwstraat 41, B-9000 Gent (Belgium)

(Received December 10th, 1973)

SUMMARY

The stationary phase distribution on diatomite supports was controlled using the cathodoluminescence mode of operation of the scanning electron microscope. Benzylbiphenyl was loaded on Gas-Chrom P and Chromosorb P. Phase accumulation was present, independent of the loading technique used, and conditioning did not change this pattern.

INTRODUCTION

It is still uncertain whether or not a stationary phase is distributed on a diatomaceous support as a thin uniform film. A uniform distribution is considered as the ideal loading, resulting in a large surface area of the stationary phase, as required for the rapid exchange of a solute between the stationary and mobile phases. For a given stationary phase and support, column performances are optimal when this ideal distribution is achieved as completely as possible, assuming that the other parameters such as the amount of phase loading, the loading method, the column filling technique and the operating conditions of the gas chromatograph are also optimized.

Indirect measurements of the pore sizes of diatomite supports have been made using the mercury intrusion method. Also, data obtained from adsorption isotherms of gases at low temperatures can provide useful information. The former method was used to study the pore size distribution of a support with increasing phase loading[1,2], and it was concluded that a progressive filling of pores with increasing diameter occurs when the percentage of the phase is increased. Giddings[3] has also claimed that these small amounts of stationary phase, which presumably occupy the fine pores of the support, are connected through thin bridges of liquid. Such links, however, are not very important in solute transport, the open surfaces of the cavities being the sites of exchange. This is an elegant model for a number of chromatographic techniques and practical equations can be derived using this supposition. However, no direct evidence is available to support this model.

Attempts to control the distribution of the stationary phase on a support in

a direct manner using the secondary electron emission mode of operation of the scanning electron microscope (SEM)[4–7] were not convincing. Micrographs of the same area of a loaded (30% Carbowax) and bare surface of Chromosorb P show, in fact, that the pores of the unloaded support appear to be of a smaller size than after loading[5].

A possible approach to this problem is to use the cathodoluminescence of an organic substance distributed as a stationary phase on a support (cathodoluminescence is the emission of light by a specimen following absorption of irradiation from an electron beam). The cathodoluminescent properties in the SEM of a number of organic compounds have been investigated[8,9]. Benzylbiphenyl (BBP) was used as the stationary phase (temperature range 80–140°). It has a sufficient cathodoluminescence efficiency and the beam effect (*i.e.*, the decrease in luminescence yield after the specimen has been scanned by the electron beam for a given time) is negligible up to magnifications of *ca.* 5000×. We have used the cathodoluminescent properties of this compound to control its distribution on diatomite supports.

EXPERIMENTAL

A 20% (w/w) loading of BBP was applied on Gas-Chrom P, 80–100 mesh, using three different loading techniques: (a) pan loading, in which the stationary phase is dissolved in just sufficient methylene chloride to wet the support and the solvent is evaporated slowly with mild heating and shaking; (b) rotating evaporator loading, in which the stationary phase is dissolved in methylene chloride and added to the support and the solvent is evaporated *in vacuo* in a rotating evaporator with mild heating; and (c) funnel loading, in which, to obtain a 20% loading, 5 ml of an 11% solution of BBP is added to 1 g of Gas-Chrom P. The percentage of this solution is calculated using the equation[10]

$$\% \text{ solution} = \% \text{ loading} \times A$$

where $A = 0.55$ for Gas-Chrom P. After reducing the pressure for a few minutes, the flask is left for about 15 min and the slurry is then filtered on to a sintered glass filter under a moderate vacuum.

Loaded supports obtained by these methods were further air-dried overnight. Small glass columns were filled with these materials and conditioning was performed at 140° for 48 h. The loaded supports were observed before and after conditioning in a Cambridge Mark 2A scanning electron microscope using both the secondary electron emission and cathodoluminescence modes. Pairs of micrographs of a given particle surface were recorded in both modes of operation at 30-kV high tension using a beam current of *ca.* 175 μA. The photomultiplier for the detection of the emitted photons was a Type 6255B (EMI Electronics, Hayes Great Britain). No metal or any conducting coating was applied on to the particles prior to examination in the SEM, because such a layer would decrease the luminescence efficiency.

Chromosorb P was loaded with 20% BBP using the rotating evaporator method. This column material was observed under the same operating conditions of the SEM as described for Gas-Chrom P.

RESULTS

Hundreds of loaded Gas-Chrom P particles were examined before and after conditioning and results for the three loading techniques are shown in Figs. 1–19. General views at a relatively low magnification are presented together with more detailed records, illustrating some particular aspects of phase distribution on typical surfaces of particles. In all the figures, part a is the secondary electron (SE) emission and part b the cathodoluminescence (CL) micrograph. White areas on the SE micrographs are due to an excessive charging effect at that site. Therefore, micrographs of convenient quality were difficult to obtain. Qualitatively better results were obtained using a 10-kV high tension but the cathodoluminescence signal was too noisy under these working conditions of the SEM. Hence a 30-kV high tension was used for all experiments because it is more important to obtain CL images of good quality in this type of investigation.

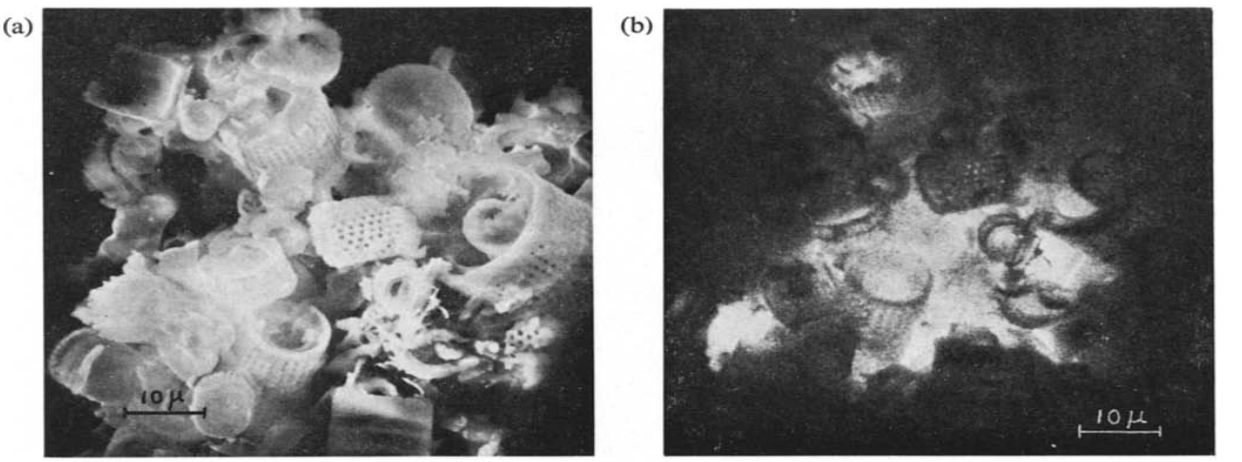

Fig. 1. 80–100 mesh Gas-Chrom P + 20% BBP (w/w). Pan loading, not conditioned. (a) SE; (b) CL. Magnification, 850×.

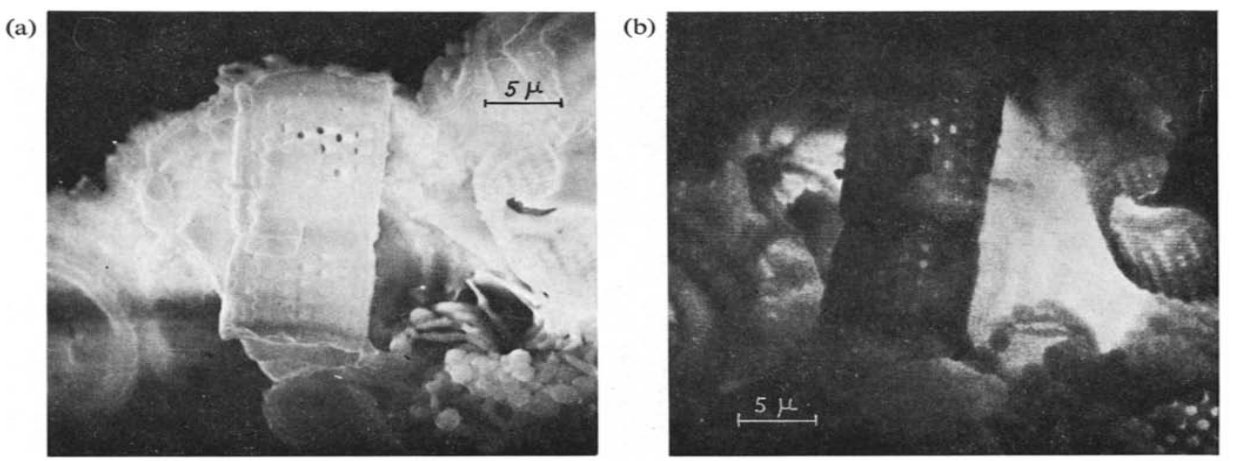

Fig. 2. Same as Fig. 1. Magnification, 1600×.

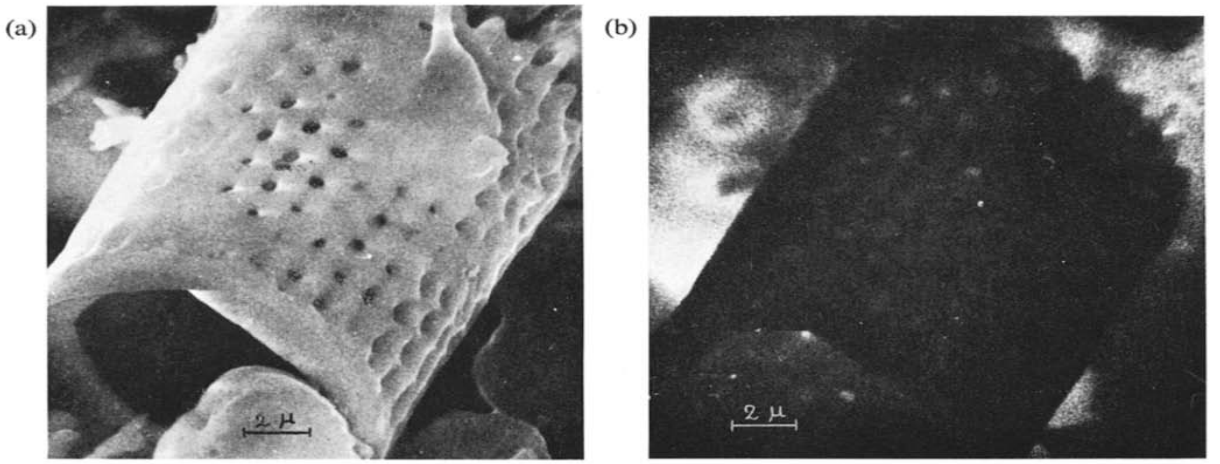

Fig. 3. Same as Fig. 1. Magnification, 3500×.

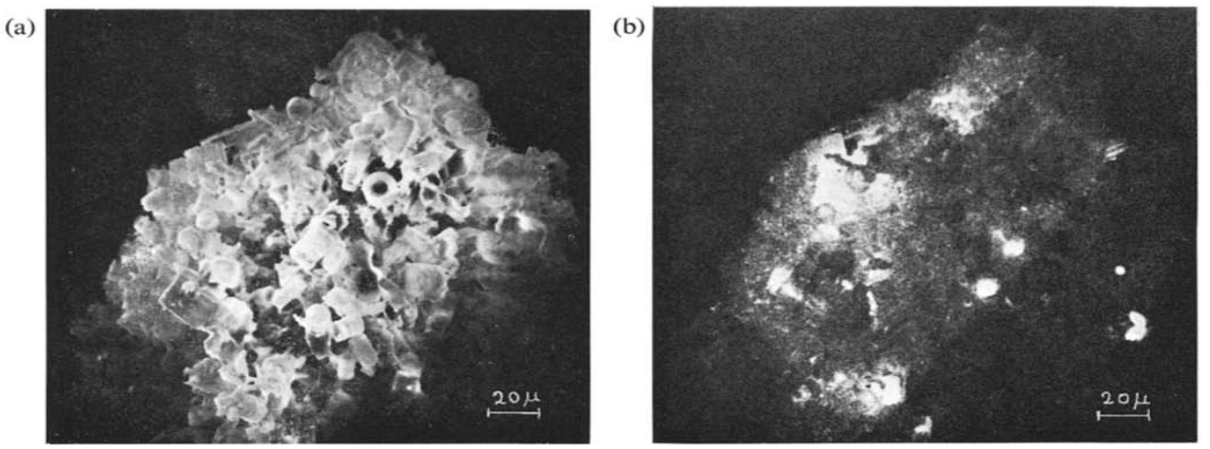

Fig. 4. 80–100 mesh Gas-Chrom P + 20% BBP (w/w). Pan loading, after conditioning. (a) SE; (b) CL. Magnification, 275×.

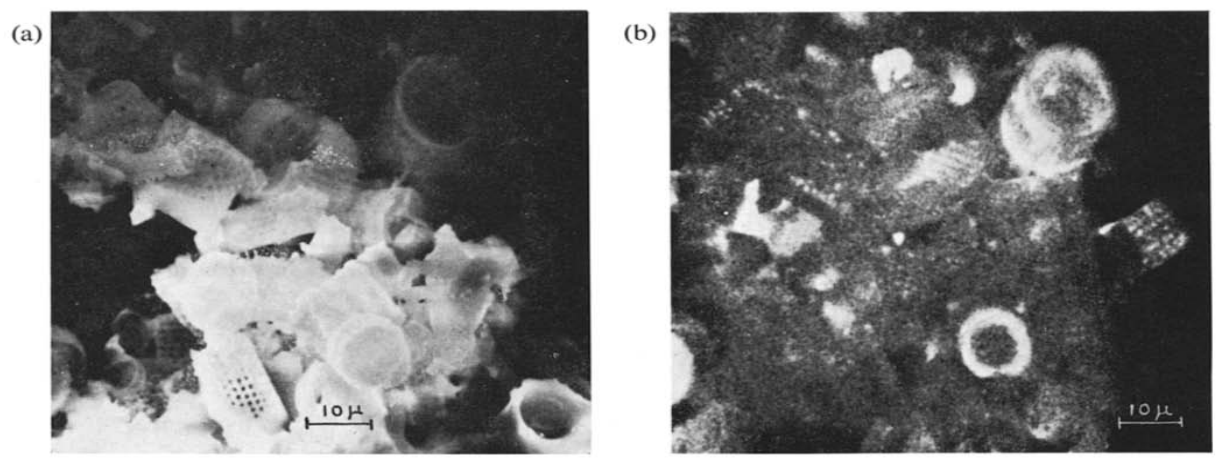

Fig. 5. Same as Fig. 4. Magnification, 700×.

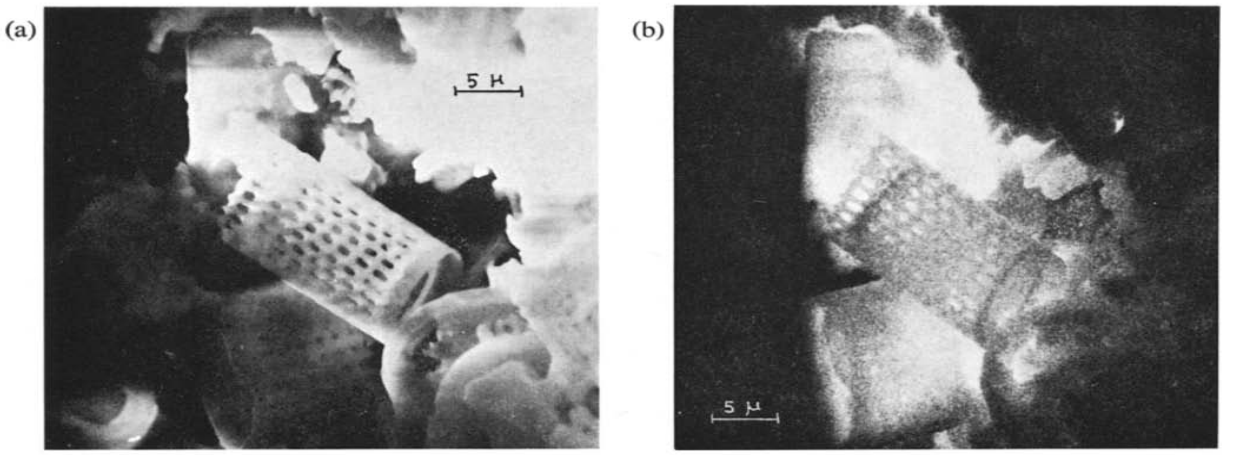

Fig. 6. Same as Fig. 4. Magnification, 1400×.

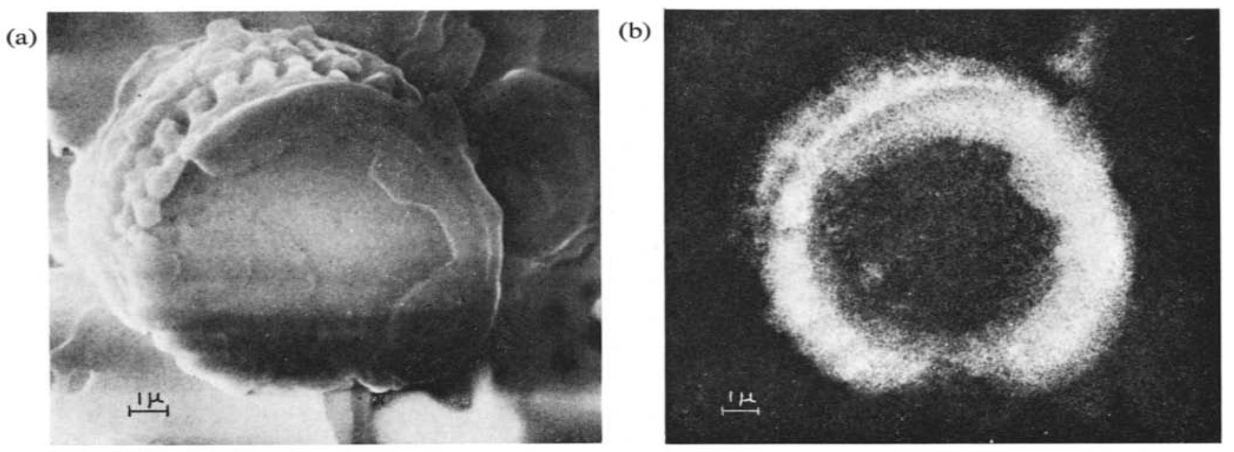

Fig. 7. Same as Fig. 4. Magnification, 4000×.

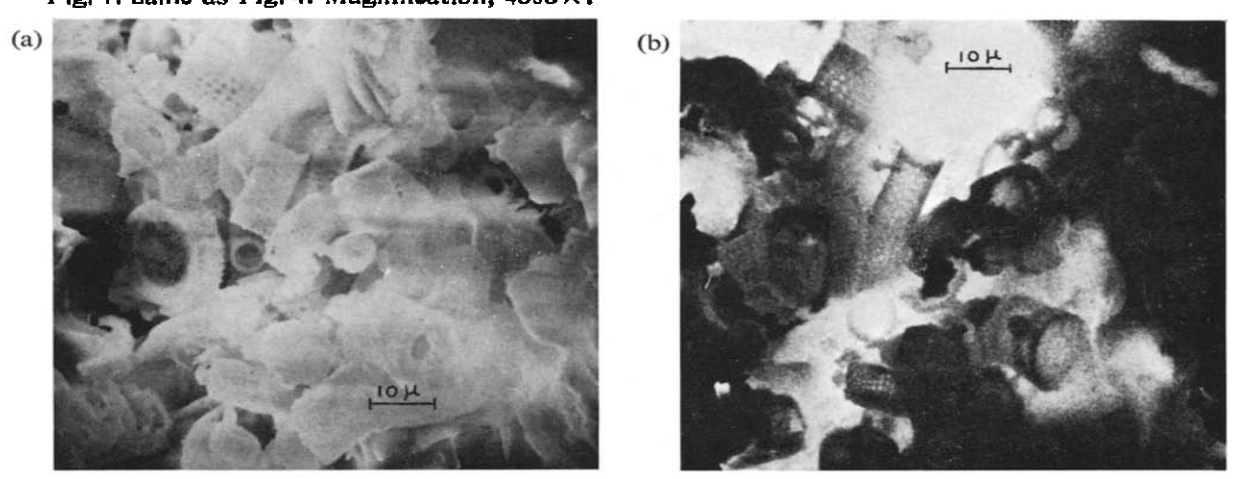

Fig. 8. 80–100 mesh Gas-Chrom P + 20% BBP (w/w). Rotating evaporator loading, not conditioned. (a) SE; (b) CL. Magnification, 700×.

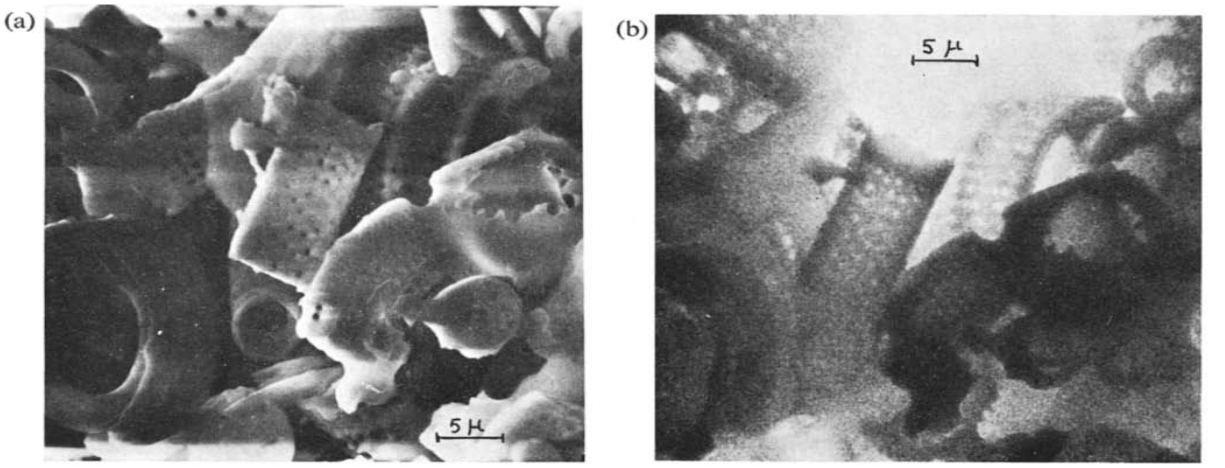

Fig. 9. Same as Fig. 8. Magnification, 1400×.

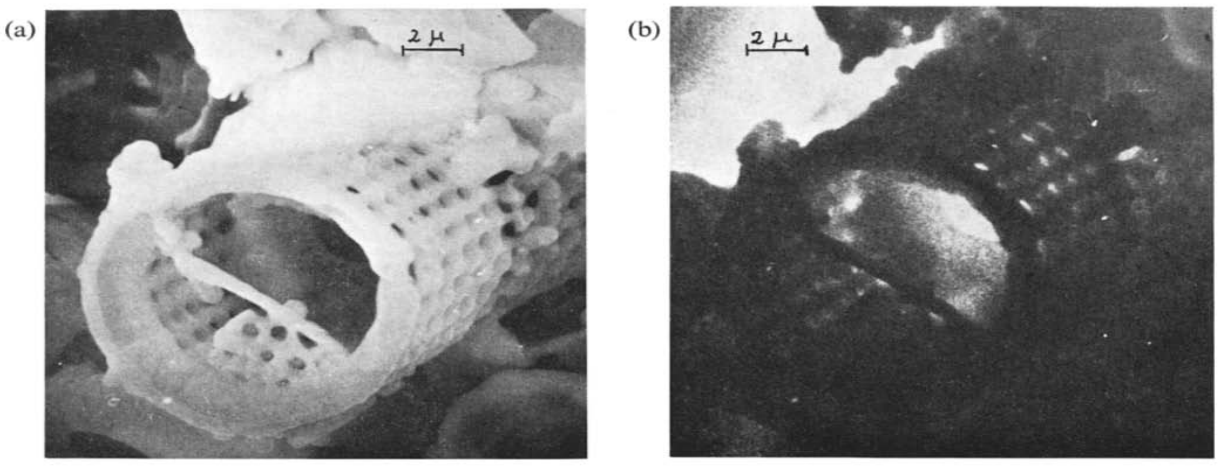

Fig. 10. Same as Fig. 8. Magnification, 2750×.

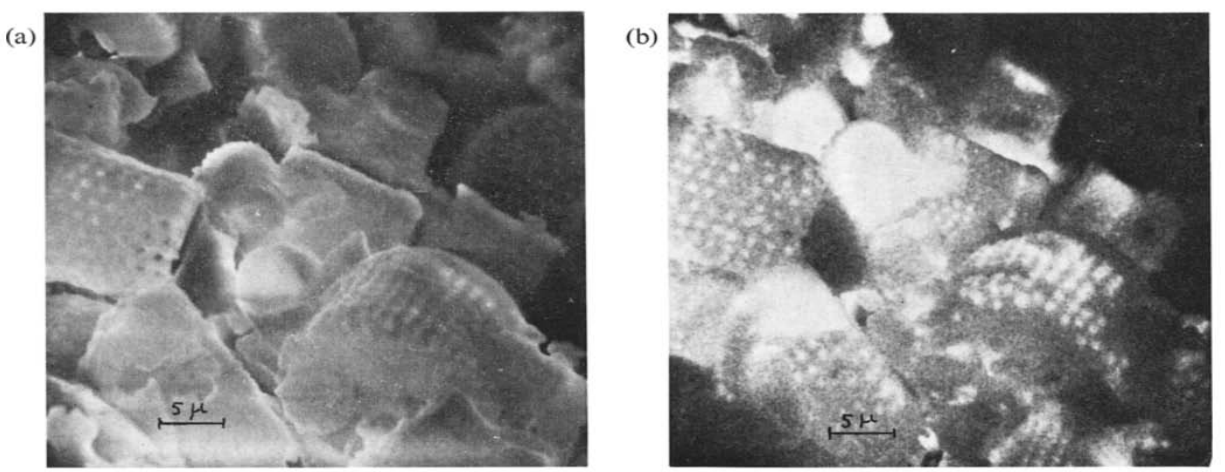

Fig. 11. 80–100 mesh Gas-Chrom P + 20% BBP (w/w). Rotating evaporator loading, after conditioning. (a) SE; (b) CL. Magnification, 1400×.

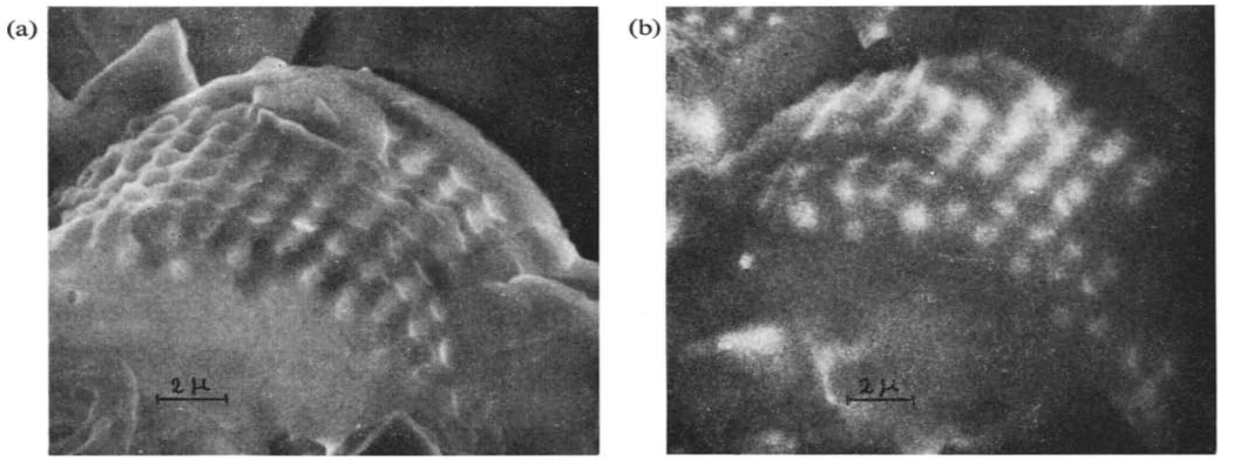

Fig. 12. Same as Fig. 11. Magnification, 3600×.

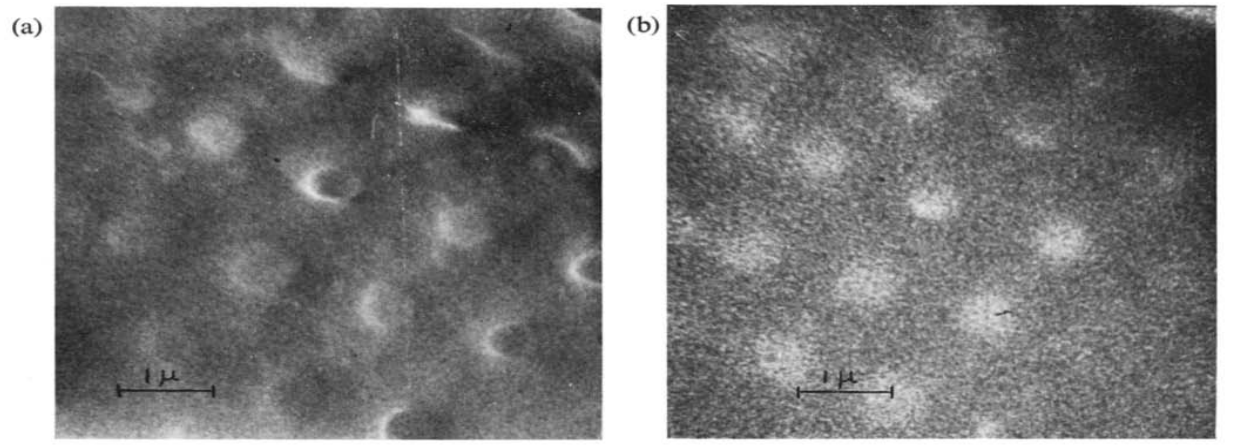

Fig. 13. Same as Fig. 11. Magnification, 10,000×.

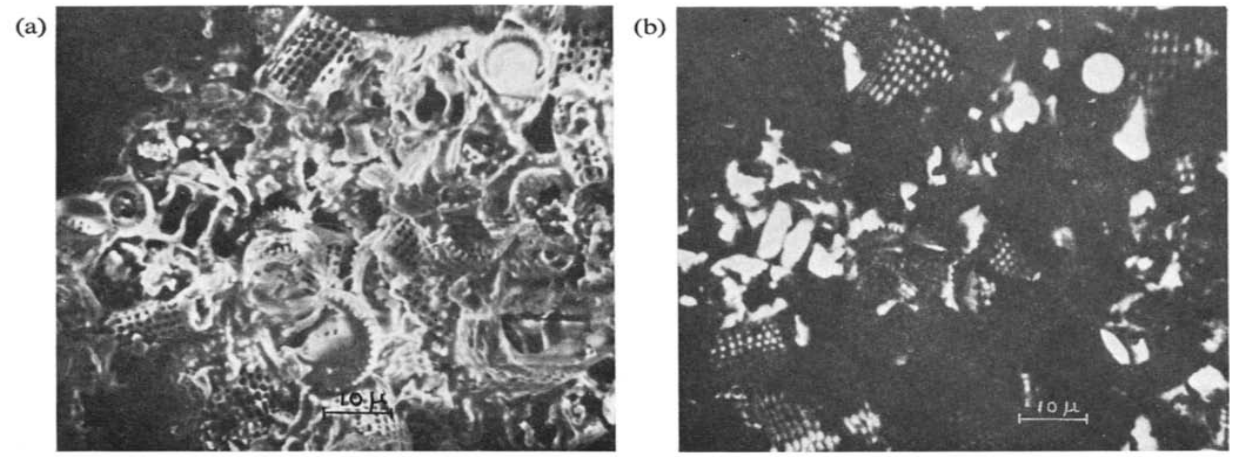

Fig. 14. 80–100 mesh Gas-Chrom P + 20% BBP (w/w). Funnel loading, not conditioned. (a) SE; (b) CL. Magnification, 720×.

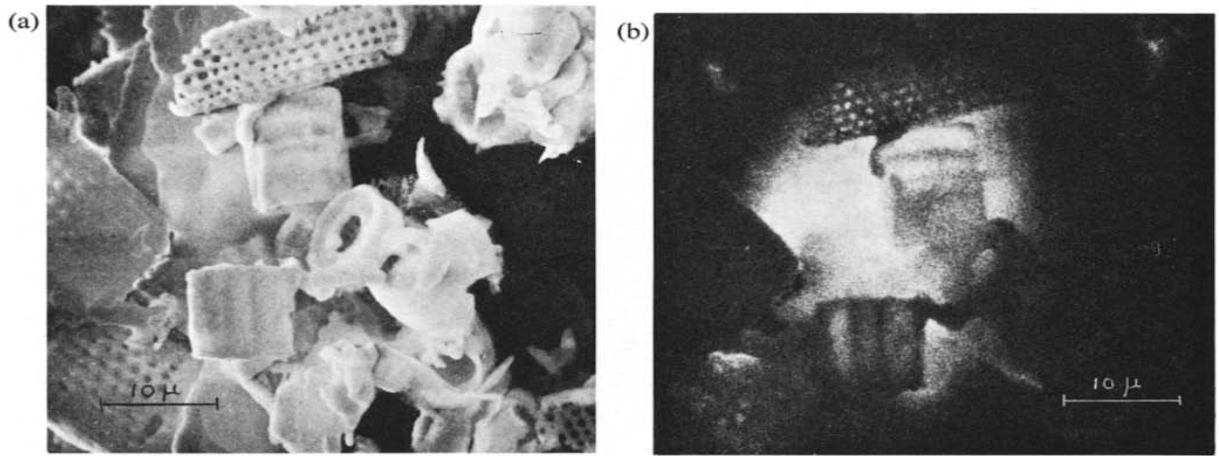

Fig. 15. Same as Fig. 14. Magnification, 1250×.

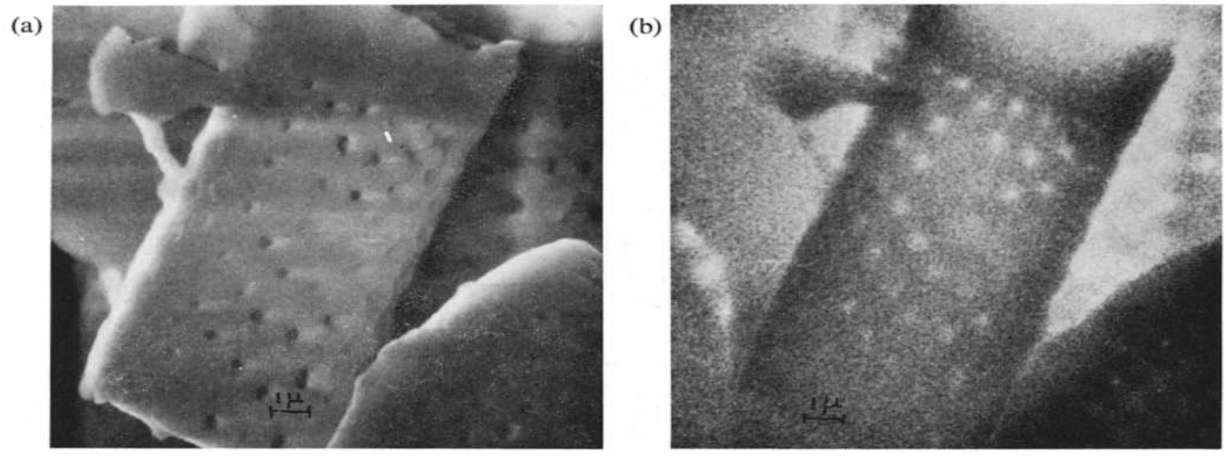

Fig. 16. Same as Fig. 14. Magnification, 4000×.

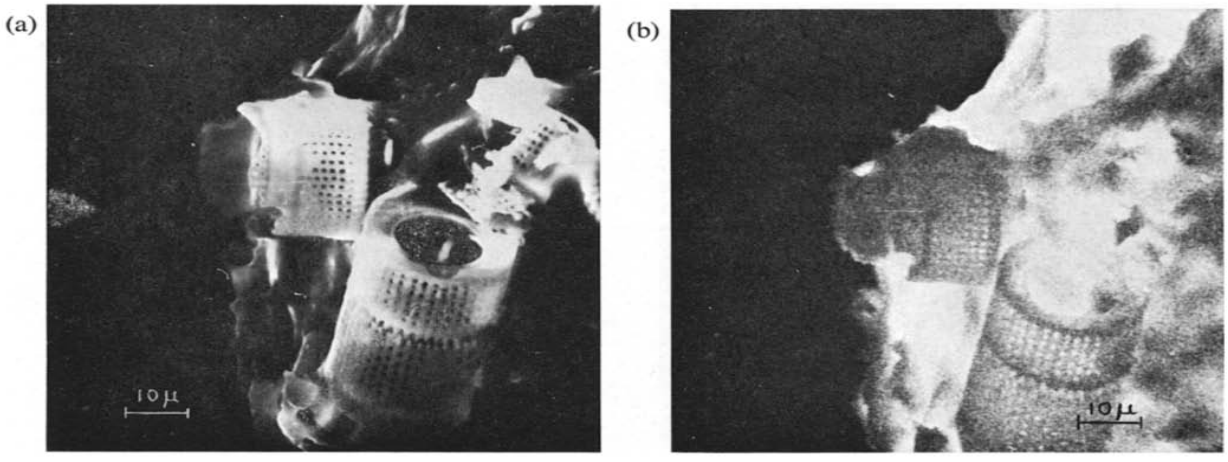

Fig. 17. 80–100 mesh Gas-Chrom P + 20% BBP (w/w). Funnel loading, after conditioning. (a) SE; (b) CL. Magnification, 650×.

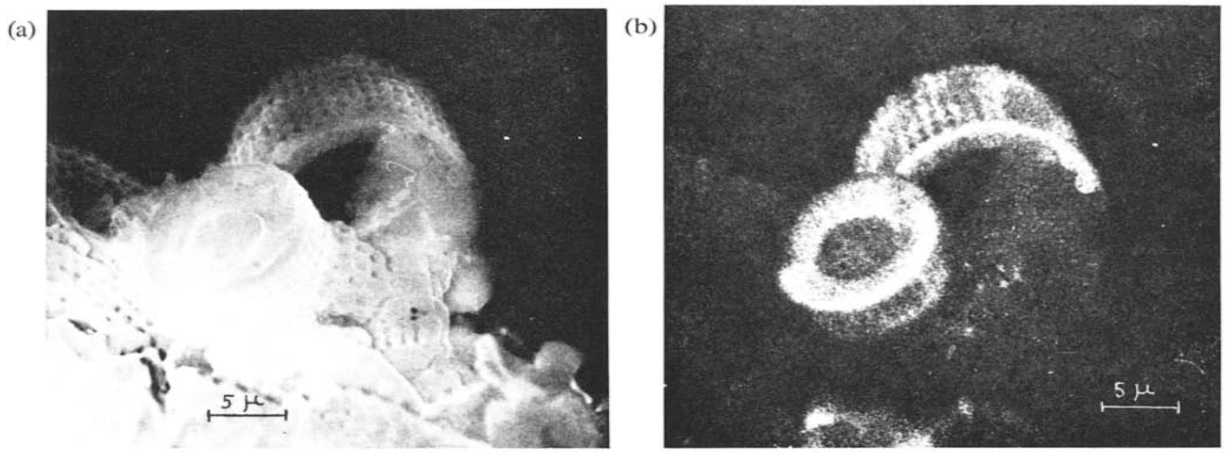

Fig. 18. Same as Fig. 17. Magnification, 1600×.

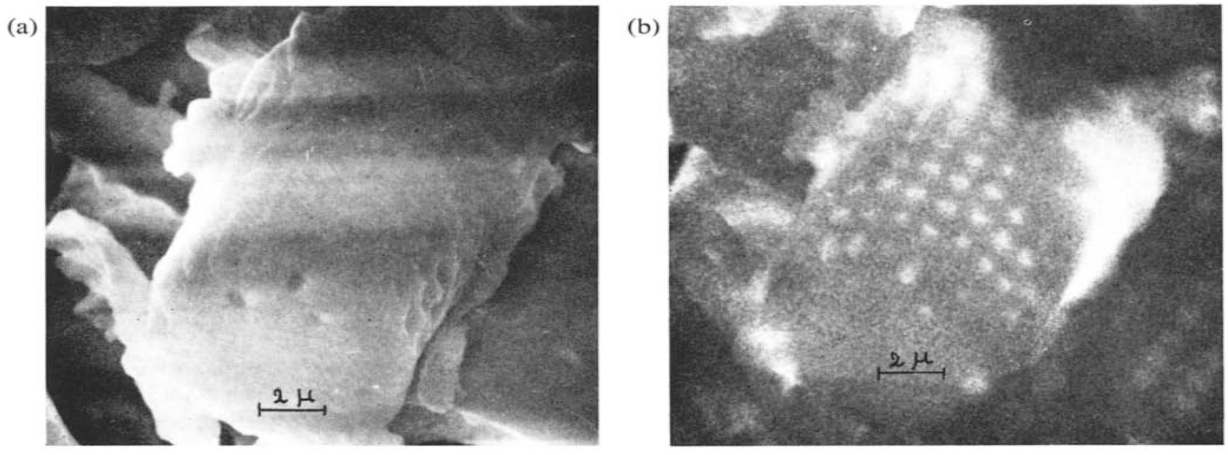

Fig. 19. Same as Fig. 17. Magnification, 3500×.

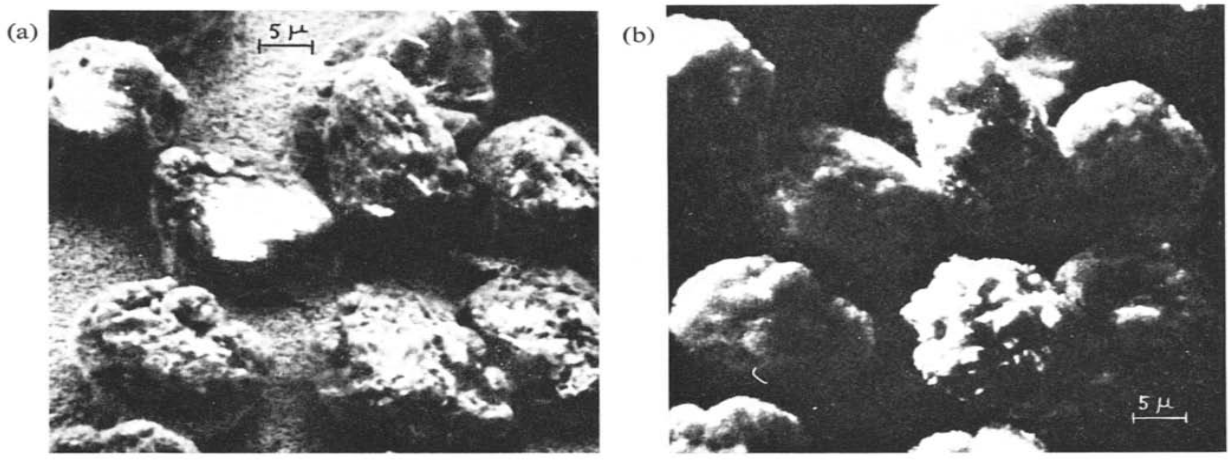

Fig. 20. 80–100 mesh Chromosorb P + 20% BBP (w/w). Rotating evaporator loading. (a) SE; (b) CL. Magnification, 1100×.

Figs. 20 and 21 are micrographs of non-conditioned Chromosorb P, 80–100 mesh, loaded with 20% BBP. Fig. 22 is a high-magnification photograph of a bare Chromosorb P particle area, illustrating pores of *ca.* 0.1 μm diameter.

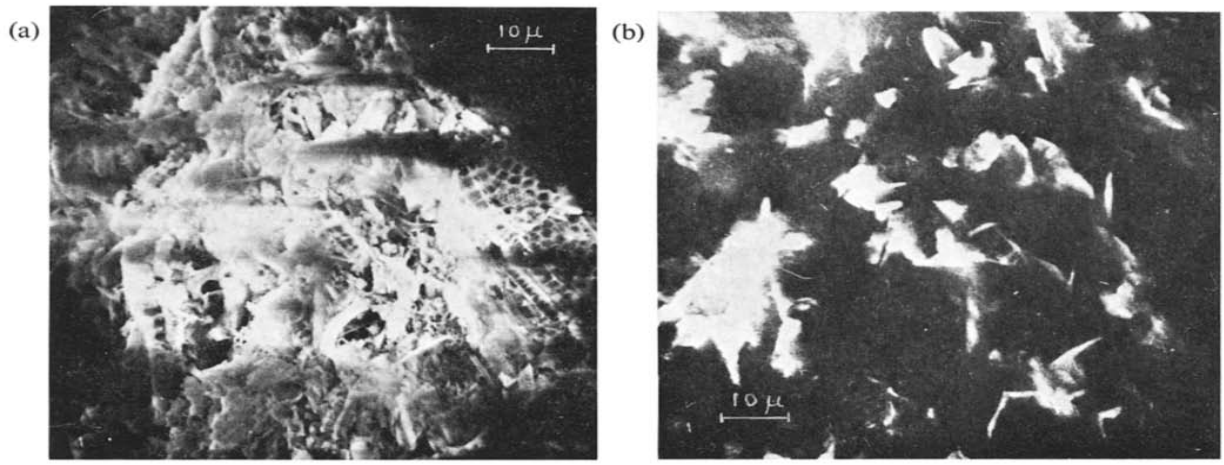

Fig. 21. Same as Fig. 20. Magnification, 700×.

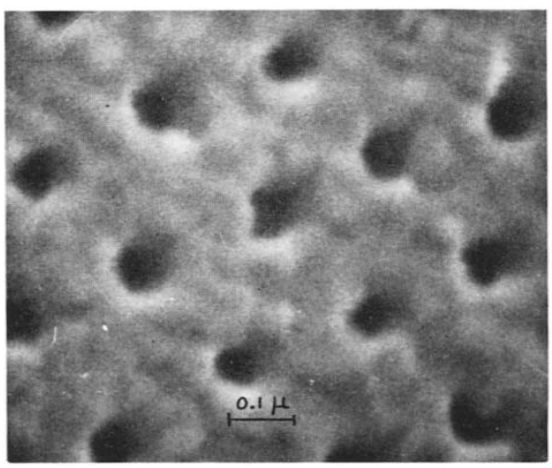

Fig. 22. High-magnification SE micrograph of bare Chromosorb P. Bores of *ca.* 0.1 μm are the smallest pores found so far in gas chromatographic supports of the diatomite type using the SEM. Magnification, 70,000×.

DISCUSSION

Cathodoluminescence of organic compounds is similar to the fluorescence of such materials excited with short-wave light, and also to the basic principle of scintillation techniques. Photons are emitted during decay of electrons from the lowest excited state to the ground-state following excitation by energetic irradiation. In cathodoluminescence, this excitation is provided by the electron beam in the microscope. The excitation of π-electrons of polyunsaturated organic molecules is ener-

getically more favourable than that of σ-electrons, so that cathodoluminescence occurs mainly during the decay of such excited π-electron systems. Therefore, aromatic and conjugated unsaturated aliphatic compounds are potential cathodoluminescent substances. A more complete review of these principles has been presented elsewhere[9].

BBP gives an acceptable cathodoluminescence yield and a negligible beam effect. The latter fact is very important because this beam effect becomes very tedious at higher magnifications and makes most of the cathodoluminescent organic materials useless at magnifications above *ca.* 1500×.

Stationary phase distribution patterns on diatomite supports have been investigated by Drew and Bens[5] using the secondary electron emission mode of the SEM. They examined a 30% loading of Carbowax or SE-30 on Chromosorb P. The loaded particles were coated with silver in order to improve the electrical and thermal conductivity, and a series of photographs were taken at different magnification settings. After removing the silver coating and the stationary phase, the particles were again coated with a thin layer of silver and the same areas were photographed. Drew and Bens[5] showed that holes in the bare particles appear to be smaller than after loading with a stationary phase. This is, of course, very annoying and no convincing explanation can be found for this phenomenon. On the other hand, they detected large amounts of stationary phase in certain particle areas, as shown by blurring of the fine details of the support.

Diatomite supports are obtained by calcination of raw diatomaceous earth with or without an alkaline flux at elevated temperatures. Gas-Chrom P is obtained by the former method and Chromosorb P by the latter. Cathodoluminescence observations of the distribution of BBP on both Gas-Chrom P and Chromosorb P show a very irregular and inhomogeneous pattern as far as the appearance of the outer surface of the particles is concerned. This aspect occurs with all three methods of stationary phase application on Gas-Chrom P and presumably also on Chromosorb P and other types of diatomite support.

It was thought that conditioning might have some influence on this distribution pattern. Although the same loaded particles were not observed before and after conditioning, the mean distribution was not changed drastically by this treatment. BBP is a solid at room temperature and the possibility of a more uniform distribution in the liquid state could not be excluded. To control this, stationary phase pools on particles were observed at room temperature and at 80° using the hot-stage feature of the SEM. No spreading of the liquid pools was observed at magnifications up to *ca.* 1500×. The examination conditions in the SEM do not fully meet the operating conditions of a gas chromatographic column as no mobile phase is moving over the particles. However, it seems likely that no important redistribution of the stationary liquid occurs during conditioning of the column. A similar conclusion was drawn by Drew and Bens[5] who found no significant changes in phase distribution on a sample of 30% Carbowax 20M on Chromosorb P removed from the end of a column which was operated for some time at 250°.

Another fact to be considered is the heterogeneous structure of diatomite supports. A capillary model is an oversimplified description of such materials, as demonstrated by examinations in the SEM[4–7]. The extremely irregular appearance of support particles also suggests that the probability of a uniform, smooth distribution

of stationary phase over the spikes, holes and planes of the particle units is very small. Therefore, it seems realistic to accept that a stationary phase accumulates preferentially at certain areas of the support, due to surface tension forces, for example.

Distribution patterns of commonly used stationary phases could not be observed using the cathodoluminescence mode of operation of the SEM because these stationary phases do not have cathodoluminescent properties. Therefore, the results obtained on BBP cannot be extended directly to other phases. It is likely, however, that most stationary phases are distributed in a similar manner to BBP.

Fig. 22 is an illustration of the smallest holes (diameter *ca.* 0.1 μm) that we have found so far in an unloaded diatomite support (Chromosorb P) using the secondary electron emission mode of the SEM. The absence of such small holes in supports calcined with an alkaline flux at elevated temperatures must be due to a smoothing effect of the latter treatment. Whether or not holes of this diameter are filled with the stationary phase unfortunately could not be established by cathodoluminescence. This is due partly to the insufficient luminescence yield of BBP and to the accompanying beam effect at high magnifications, and partly to the resolution limit of this mode of operation of the SEM.

Lower loadings of BBP on diatomaceous supports were not investigated. A 20% loading was chosen in view of the results of Drew and Bens[5], who found that even 30% Carbowax or SE-30 generally did not demonstrate an overloading of the support. It is unlikely that the distribution pattern of the stationary phase at lower loadings would be significantly different from that observed for 20% loadings, except that pools of stationary phase might be present in less distinct amounts.

No important differences in distribution pattern between the three loading methods were found. This does not imply that these methods are equivalent. A loading technique must also be evaluated by other parameters, such as the HETP of the column. Although hundreds of particles have been examined in the SEM for their stationary phase distribution, this is still only a small fraction of the total amount of particles present in a gas chromatographic column. Column performances are the result of a statistical average determined by a number of parameters, including stationary phase distribution, so that the individual features of phase distribution on particular support units must be neglected in view of the general aspect of the distribution on a large number of particles. It would be very misleading to specify a loading method based on such single observations. Therefore, the figures presented here should be considered as illustrations of distribution patterns and do not permit any classification of the loading techniques.

A general restriction on the use of the SEM is that only the outer surface of the specimen is observed, so that only the distribution of the stationary phase on the outside of the support particles can be examined and no direct information on the situation on the inside can be obtained. It is unlikely, however, that important distribution inequalities will exist between the outer and inner parts of the particles.

The present observations do not completely exclude the possibility that a very thin film of stationary phase exists over the particle units. The cathodoluminescence yield of BBP at a certain particle area is determined by the amount of this compound present at that particular site. There is a minimal amount of BBP, expressed as the film thickness, which can just be detected by the equipment; this detection limit is unknown. On the other hand, photon production does not increase continuously with increasing

film thickness, so that brighter areas indicate a larger amount of BBP but do not permit a fully quantitative measurement of the phase loading. However, as discussed above, an ideal distribution is unlikely in view of the heterogeneous structure of diatomite supports. Also, accumulation of stationary phase in very small cavities, as presumed by Giddings[3], could not be confirmed. Nevertheless, it is certain from the present observations that stationary phase pools of distinct volumes are present and such an accumulation must have an important influence on the exchange of solutes between the stationary and mobile phases and on the HETP of the column.

REFERENCES

1 W. J. Baker, E. H. Lee and R. F. Wall, in H. J. Noebels, R. F. Wall and N. Brenner (Editors), *Gas Chromatography*, Academic Press, New York, 1961, Ch. 3.
2 N. C. Saha and J. C. Giddings, *Anal. Chem.*, 37 (1965) 822.
3 J. C. Giddings, *Dynamics of Chromatography*, Part I, Marcel Dekker, New York, 1965, p. 138.
4 E. M. Bens and C. M. Drew, *Nature (London)*, 216 (1967) 1046.
5 C. M. Drew and E. M. Bens, in C. L. A. Harbourn (Editor), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, p. 3.
6 M. De Mets and A. Lagasse, *Chromatographia*, 2 (1969) 401.
7 M. De Mets and A. Lagasse, *J. Chromatogr. Sci.*, 8 (1970) 272.
8 M. De Mets and A. Lagasse, *J. Microscopy*, 94 (1971) 151.
9 M. De Mets, in M. A. Hayat (Editor), *Principles and Techniques of Scanning Electron Microscopy*, Vol. II, Van Nostrand-Reinhold, New York, in press.
10 H. M. McNair and E. J. Bonelli, *Basic Gas Chromatography*, Varian Aerograph, Walnut Creek, Calif., 1966, p. IV-21.