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Letter to the Editor

Specific surface area of GLC column packings as a function of stationary phase volume

Sir,

From the title of the recent paper "Evaluation of changes in the specific surface area of sorbents based on the volume of stationary phase in gas–liquid chromatography" by Berezkin *et al.*[1], one would expect to find some theoretical or experimental information about the dependence of the specific surface area of the sorbent on the volume of the stationary phase. It becomes evident later in the paper that the authors concentrated on the pore volume distribution according to their diameters in the GC solid supports. Nevertheless, I am afraid that the paper suffers from the following two defects.

(1) According to the authors' assumptions, eqn. 4, written as

$$S = S_\varepsilon$$

is incorrect, because

$$S = S^+ - S_L$$

where S is the surface area of the sorbent per gram of the support, S^+ is the specific surface area of the non-coated support and S_L is the surface area of the pores filled with the stationary phase per gram of the support. It follows that the surface area of the pores per gram of support, S_ε, will be equal to S_L. Hence eqn. 4 must be written as

$$S_L = S_\varepsilon$$

(2) The authors have proposed that eqn. 6:

$$V_L = V_\varepsilon = \omega\delta - v$$

is a satisfactory approximation of the dependence of pore volumes on their diameters. Following the development of eqn. 7, one can see that its final form:

$$S = S^+ - 4\ \ln[(V_L/v) + 1]$$

is questionable, because it follows from eqn. 6 that

$$\mathrm{d}V_\varepsilon = \mathrm{d}V_L = \omega \mathrm{d}\delta$$

and

$$4\int_{\delta_{\text{min.}}}^{\delta} (1/\delta)\mathrm{d}V_\varepsilon = 4\int_{\delta_{\text{min.}}}^{\delta} (1/\delta)\mathrm{d}\delta = 4\omega\ \ln(\delta/\delta_{\text{min.}})$$

Then, expressing δ and $\delta_{\mathrm{min.}}$ from eqn. 6 as $\delta = (V_L + v)/\omega$ and $\delta_{\mathrm{min.}} = (V_{L\,\mathrm{min.}} + v)/\omega$, respectively, where $V_{L\mathrm{min.}}$ is the volume of the pores with diameters $\delta \leqslant \delta_{\mathrm{min.}}$, it follows that eqn. 7 must be presented in the form

$$S = S^{+} - 4\omega \ln[(V_L + v)/(V_{L\,\mathrm{min.}} + v)]$$

If one accepts that the absence of the constant ω in eqn. 7 is the result of a misprint, it could not explain the absence of the term $V_{L\,\mathrm{min.}}$. Obviously, the value of $V_{L\,\mathrm{min.}}$ is limited by the end of the interval in which eqn. 6 is approximately valid. In the case of higher support loadings, the authors have found that eqn. 6 is valid for $V_L > 0.1$ ml/g or even for $V_L > 0.05$ ml/g. Accepting that $V_{L\,\mathrm{min.}} = 0.05$ ml/g and taking for Chromosorb W $v = 3.77 \cdot 10^{-3}$ ml/g (which is the highest value of v according to the data in Table I), one can see that $V_{L\,\mathrm{min.}} > v$. Hence, $V_{L\,\mathrm{min.}}$ cannot be neglected in obtaining the final form of eqn. 7, as it probably was by the authors. Further, it is clear that the derived equations 8, 11 and 12 will be incorrect.

In conclusion, it is difficult to accept that the long procedure proposed for the evaluation of the pore volume distribution according to pore diameters will find any practical application. This information can be obtained much more easily from the results of porosimetric measurements, such results being more exact and more reliable. It is more interesting practically to obtain an equation that describes the surface area of the sorbent as a function of the volume of stationary phase coated on the support.

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1 V. G. Berezkin, D. Kouřilová, M. Krejčí and V. N. Fateeva, *J. Chromatogr.*, 78 (1973) 261.