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DETECTION OF SMALL VARIATIONS IN SHAPE BETWEEN TWO CHROMATOGRAPHIC PEAKS

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SUMMARY

The detection of an impurity in a visually single peak by means of the "Distribution Function Method" necessitates a thorough control of every parameter which influences the shape of a peak. In particular, the heights of the peaks compared must be as equal as possible when the chromatographic response is not a linear function of the injected concentration.

The Distribution Function Method can also be used for the determination of the region in which the chromatographic response is linear.

INTRODUCTION

From the recording of a chromatographic peak, one can estimate characteristic quantities such as retention time, peak width or peak area. The shape of the profile, independent of the value of the parameters of position (time base) or scale (peak height, peak width) may also be worth considering. Then it is important to have a criterion that makes it possible to decide whether two peak profiles that are visually similar have the same shape or not. The distribution function method (DFM)[1] gives such a criterion: its mathematical treatment[2], simulated results[3,4] and experimental results[5] have been published. These results concern the main application of the method: the detection, under a visually single peak, of a secondary peak that corresponds to contamination of a few percent of the main peak and that constitutes with the main peak a strongly overlapped doublet (resolution *ca.* 0.25).

The DFM is particularly suitable for studying the problem of strong overlapping, to which the classical methods of deconvolution[6,7], slope analysis[8] and moments[9] are inapplicable. In this application, the detection of an impurity is based on the difference in shape observed between a peak produced by a pure sample and another peak produced by an impure sample; of course, the detection is valid if the only cause of the variation in shape is the presence of an impurity. In particular, the heights of two peaks to be compared were always equal. In fact, for certain chromatographic measurements, the response of the chromatograph can be assumed to be a

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linear function of the concentration injected over a fairly wide range. However, in the problem of detecting very small variations in shape, this range may be very much reduced. The aim of this paper is to point out the influence of variations in peak height on the peak shape by means of some experimental results.

THE DFM PRINCIPLE

The comparison of the shapes of two peak profiles $f(t)$ and $g(t)$ is made by a comparison of their normalized integrals (distribution functions) $F(t)$ and $G(t)$. Resolving the equation

$$F(t) = G(t')$$

for a series of points (t', t) gives a curve $t = \varphi(t')$; if f and g have the same shape, *i.e.*, if there is a relationship such as $g(t) = kf[(t-d)/a]$, the curve $t = \varphi(t')$ is a straight line. The mean deviation, Δ, of the curve from linearity is a measure of the difference in shape between the two profiles.

DETECTION OF DOUBLE PEAKS

Fig. 1 gives an example of the difference in shape, Δ, created by the 1 and 2% contamination of *n*-hexane with *n*-heptane (resolution *ca.* 0.25) for a signal-to-noise ratio of *ca.* 300. Each point represents the mean of ten measurements of the shape difference between a pure peak and another pure peak or a contaminated peak. The standard deviation of Δ calculated from the ten measurements is represented by the length of an upwards or downwards arrow. In this example, the detection of an impurity of 1% is obvious, assuming that the only cause of the variation in shape is such a contamination. In particular, the heights of all the peaks were equal. The following results emphasize this important point.

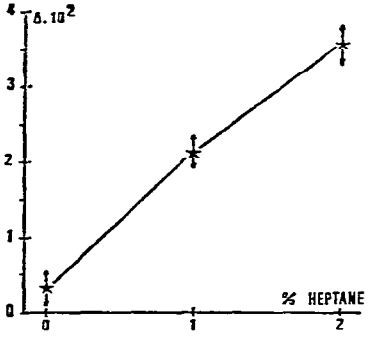

Fig. 1. Effect of contamination of *n*-hexane by *n*-heptane on peak shape. •, Mean value of 10 determinations; ↑, standard deviation. Unit of Δ: half width of the pure peak.

LINEARITY OF THE MEASUREMENT DEVICE

Ideally, the response of a chromatograph is proportional to the concentration of a component in the sample. In order to check this hypothesis, Fig. 2 was constructed. The ordinates represent the difference in shape, Δ, between two pure peaks of *n*-hexane eluted under the same conditions; one has a height H (as in the preceding example) and the other a height $H+\Delta H$. The difference in shape is plotted against the relative varation of height, $\Delta H/H$. From Fig. 2, one can make two observations:

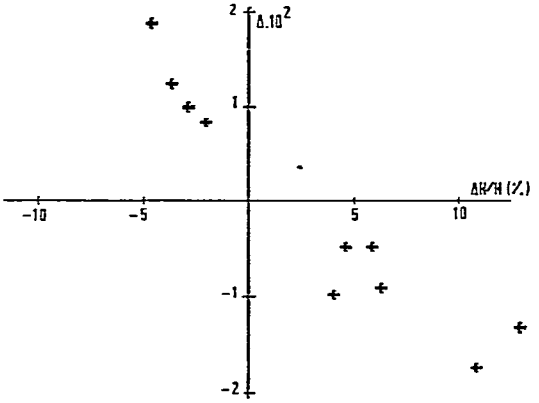

Fig. 2. Differences in shape between a peak of *n*-hexane with height H and other peaks of *n*-hexane with height $H + \Delta H$ *versus* the relative difference $\Delta H/H$. H corresponds to an injection of 0.5 μl.

(1) In comparison with Fig. 1, a slight variation in height (of a few pecent) may produce a shape difference masking a contamination of 1 or 2%.

(2) The DFM can be used to check the linearity of the response of the instrument around a given value of the concentration injected. In a more precise manner, the maximum variation of height (*i.e.*, concentration) consistent with an admissible variation in shape may be determinated by a statistical study using the DFM.

REFERENCES

1 H. Rix, *Thèse d'État es Sciences*, IMAN, Université de Nice, 1980.
2 H. Rix and J. P. Malengé, *IEEE Trans. Syst. Man Cybern.*, 2 (1980) 90.
3 H. Rix and J. P. Malengé, *Chromatographia*, 9 (1976) 554.
4 H. Rix and J. P. Malengé, *Colloque National sur le Traitement du Signal et ses Applications, Nice, 1977.*
5 H. Rix and J. P. Malengé, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 4 (1980) 172.
6 D. W. Krimse and A. W. Westerberg, *Anal. Chem.*, 43 (1971) 1035.
7 E. Grushka and G. C. Monacelli, *Anal. Chem.*, 44 (1972) 484.
8 E. Grushka, *Anal. Chem.*, 44 (1972) 1733.
9 E. Grushka, M. N. Myers and J. C. Giddings, *Anal. Chem.*, 42 (1970) 21.