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Note

Peak squarer for square-top runs in gas–liquid chromatography–mass spectrometry

Some factors affecting gas–liquid chromatographic output to a mass spectrometer

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A gas chromatographic peak usually approximates a gaussian curve (Fig. 1a). This is not particularly suitable for introduction into a mass spectrometer. The concentration of substance should be constant while the mass spectrum is scanned, *i.e.* for 5–10 sec, so that the peak shape required is more or less that shown in Fig. 1b (*cf.* ref. 1). Ideally, peak shape should also allow warning of the appearance of a peak, it should provide a signal for scan triggering, it should not terminate too abruptly, and it should allow some exclusion of initial and final fractions which might contain impurities. It should therefore be of the form shown in Fig. 1c. A peak of almost ideal form taken from a gas chromatogram run with a peak squarer is shown in Fig. 1d.

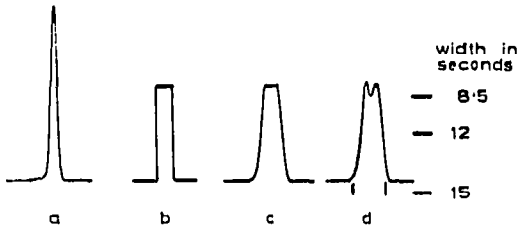

Fig. 1. Peak shape in GLC. (a) Standard gaussian peaks; (b) semi-ideal peak for GLC–MS; (c) ideal GLC–MS peak; (d) a square-top peak from a gas chromatogram produced using a peak squarer.

The peak squarer is a very simple device, but little or no attention seems to have been given to the advantages of its use in gas–liquid chromatography–mass spectrometry (GLC–MS). The present paper is concerned with the application of the peak squarer to a GLC output and with appropriate GLC operating conditions. In its simplest form the peak squarer divides the GLC column output into two equal streams. It applies a delay to one stream and then recombines them. When the delay corresponds to the peak width at half height this will give a square-top peak of ideal form. When resolution is less important, as in the use of a GLC column as an inlet

device for single substances, it may be worthwhile dividing the column output into three streams. The recombined peak will be broader with steeper sides.

METHODS AND CONSTRUCTION

The peak squarer used here is made up of inlet and outlet T-pieces, a delay tube (1.6 mm O.D. steel tube, approx. 200–300 mm long) and two flow resistors (0.5 mm I.D. steel tube), one in each arm of the divided flow. The flow through the two arms of the divided circuit is balanced, using soap bubble flow meters, by varying the resistors. The volume of the delay tube is adjusted to give the desired separation of the two component peaks. Since the main resistance in the device is due to the two flow resistors, the separate flows remain balanced at different temperatures. In practice it is convenient to divide the flow resistor for the delay arm in two and use the halves as connections to allow interchange of delay tubes of different volumes. The peak squarer requires peaks of constant width (in ml of gas flow), as produced by a temperature-programmed GLC run, and changes in peak width may require adjustment of the gas flow-rate.

For sensitive materials the peak squarer could be made of glass. It would also be better made with smaller components, machined rather than soldered, to minimise irregularities and contact time. The present simple model does not, however, contribute significantly to peak broadening (in a Varian 1400 with 25-m and 50-m columns). The peak squarer is assembled with PTFE sleeves as couplings and PTFE adaptor sleeves on the capillary resistors so that they fit the same PTFE couplings as the 1.6-mm-O.D. tubing. The resistors are pushed into the 1.6-mm tubing to give rigidity and to minimise volume. The PTFE sleeves are also used for coupling the capillary columns to the injection system and to the peak squarer and the detector. They have been used here for this purpose for a number of years and have proved very satisfactory.

All injections into the GLC system are made by direct injection into a 1.6-mm stainless-steel tube. This is much simpler than a splitter system, less wasteful and makes no significant practical contribution to peak broadening.

It is necessary to maintain the end of the capillary column above atmospheric pressure to prevent air being sucked in through the PTFE connections but this is needed anyway to provide suitable flow conditions in the capillary column and for connection of a flame detector (when required).

DISCUSSION

A mass spectrometer requires a GLC input in the form of a series of substance plugs of uniform concentration (within each peak) that are 5–10 sec long (depending on the scan time chosen). A gaussian input can only give a reasonably constant substance concentration at the expense of time, inefficient use of substance and a poorer ratio of substance to background. If the GLC peaks are made narrow, the concentration will vary considerably during the scan and there is a risk of misplacing the MS scan on the peak or of missing the peak altogether. A capillary column output is excellently suited to a mass spectrometer because of its high resolution and low gas flow but has the disadvantage of poor (gaussian) peak shape. This can be cor-

rected by using a square-top mass spectrometer input to give material plugs with the required shape.

By allowing narrower peaks to be used, this gives increased sensitivity, efficiency and speed with a decrease in background contamination and thus enhances the advantages of the capillary column. It should also facilitate direct connection of a capillary column to a mass spectrometer (*cf.* ref. 2) with elimination of the need for a molecule separator with its attendant problems.

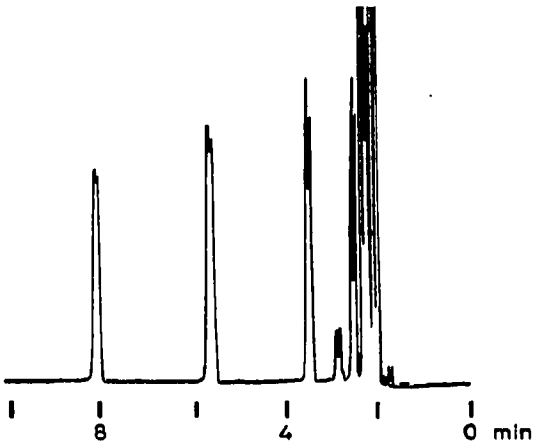

Fig. 2. A square-top GLC run. This shows a mixture of *n*-heptane, *n*-octane and *n*-nonane in a hexane solvent run with the peak squarer fitted and no splitter. Column: OV-101, 25 m × 0.5 mm I.D. stainless steel; programmed from 3 min at 8°/min; gas flow-rate, nitrogen, 29 cm/sec. The *n*-alkane peaks are 5–6 sec wide at the top.

A typical square-top chromatogram is shown in Fig. 2. The initial peaks have not reached the width specified by the temperature programme rate and the chromatogram shows the gradual coalescence of the two halves as they broaden to the width corresponding to the delay at which the peak squarer is set.

A square-top input is more convenient in operation since it gives peaks of similar form with a definite triggering point for the MS scan at the beginning of the peak plateau. The triggering point uncertainty in a gaussian input can be largely eliminated by placing a flame detector in parallel with and a few seconds in advance of the mass spectrometer signal. While a flame detector is very easily incorporated into the system and is in fact desirable for both modes of operation in order to obtain a gaussian record and to allow the mass spectrometer to be isolated from unnecessary chromatogram background, it does not bypass the other advantages of the square-top input.

A square-top input to the mass spectrometer implies a trading of formal resolution for advantages in the mass spectrometer scan. However, while the width at half height is doubled (on combining two peaks separated by the half-height width), the base width will increase only by 50%. In practice, for several reasons, the square top is wider than the separation between the two component peaks and the base width increase seems to be slightly less than 50%. In any case it is only the main

part of the peak where the scan is to be placed that is of interest. For peaks that appear as shoulders on larger peaks, the outer half will be resolved just as well as in an ordinary GLC run, even though the inner half may be swamped.

To simplify the GLC system as much as possible for GLC–MS operation, all column and peak squarer couplings have been made with PTFE sleeves. Experience over several years indicates that these are in every way superior to screw connections except for high temperatures and high and low pressures (which are not relevant in ordinary capillary column operation). They give flexibility and speed in assembly and can be used up to at least 250°. Care is needed above 200° to prevent tensions in the column pulling the couplings open. To avoid the sample losses of a splitter system and the unnecessary complications, the inlet system used here has been simplified to a plain steel tube (1.6 mm O.D., 1.0 mm I.D.). Direct injection of the material contained in the needle of a 10-μl syringe or between air plugs gives very narrow peaks. At a carrier gas velocity of 21 cm/sec (25-m column of Fig. 2; column at 70°) the first significant peak of a hexane solvent mixture is 1.0 sec wide at half height and shows no trailing. In the injection tube this corresponds to a length of 5 cm so that the entire peak and presumably the entire injected sample is contained within a plug less than 10 cm in length (injection tube length: 20 cm).

Special procedures have been described for the production of narrower peaks on injection[3]. However, these have no application here since the present injection system gives a peak width that is negligible relative to the width of the temperature programme peaks required and to the peak broadening of an isothermal column. The chromatogram of Fig. 2 could of course be run much more slowly and by no means utilizes the resolution potential of the column.

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