Notes

CHROM. 6182

A simple device for analogue recording of the abundance of selected ions from a combined gas chromatograph – mass spectrometer

Combined gas chromatography–mass spectrometry (GC–MS) has been widely used for qualitative analysis because of the unique combination of a high efficiency separation system with a very sensitive technique for structure elucidation. In quantitative analysis the potential of the mass spectrometer as a sensitive and specific detector for a gas chromatograph has long been recognised and in this application the mass spectrometer is tuned to monitor one ion which is characteristic of the compound to be measured. This potential, however, has not been exploited, partly because of the expense of GC–MS installation and partly because of the variability of the mass spectrometer sensitivity. The first obstacle has not yet been overcome though a mass spectrometer, for the single duty of a GC detector, can be obtained relatively cheaply. The second problem can be largely overcome by use of a suitable internal standard in quantitative measurements. Several approaches have been made to the problems in the last few years[1–3] and acceptable accuracy and precision have been obtained. The internal standard can give rise to the same prominent ion as the compound to be measured[3] and then tuning to one ion only is necessary. Alternatively, a deuterated compound can be used as the standard[1,2] and this necessitates following two ions as the gas chromatogram develops. There exists also a need to measure two or more compounds in one GC run; this may involve four tuned ions when two internal standards are used.

A device for sampling up to three ion signals separately was described by SWEELEY *et al.*[4] in 1966. This worked by switching the accelerating voltage of the mass spectrometer between pre-set values and thereby bringing pre-determined ions to focus at the collector slit successively. The stepped signal is fed to the UV recorder where a record is obtained. The problem with this record of the signal is that the amplifiers have to maintain relatively wide band width to cope with the jumps in the signal. This means that little noise can be filtered out and the record is difficult to interpret especially when three or more ions are considered, because inflections have to be detected.

A device has been described[5] which separates the individual signals into separate channels. This device depends on sophisticated sample-and-hold circuitry with rapid sampling and is expensive. For some time we have been using a simple circuit which achieves the separation into ion channels but without rapid switching, which means that a parametric amplifier with relatively slow response can be used with consequent increase in sensitivity.

Experimental

Simple switching in synchronism with the accelerating voltage changes is

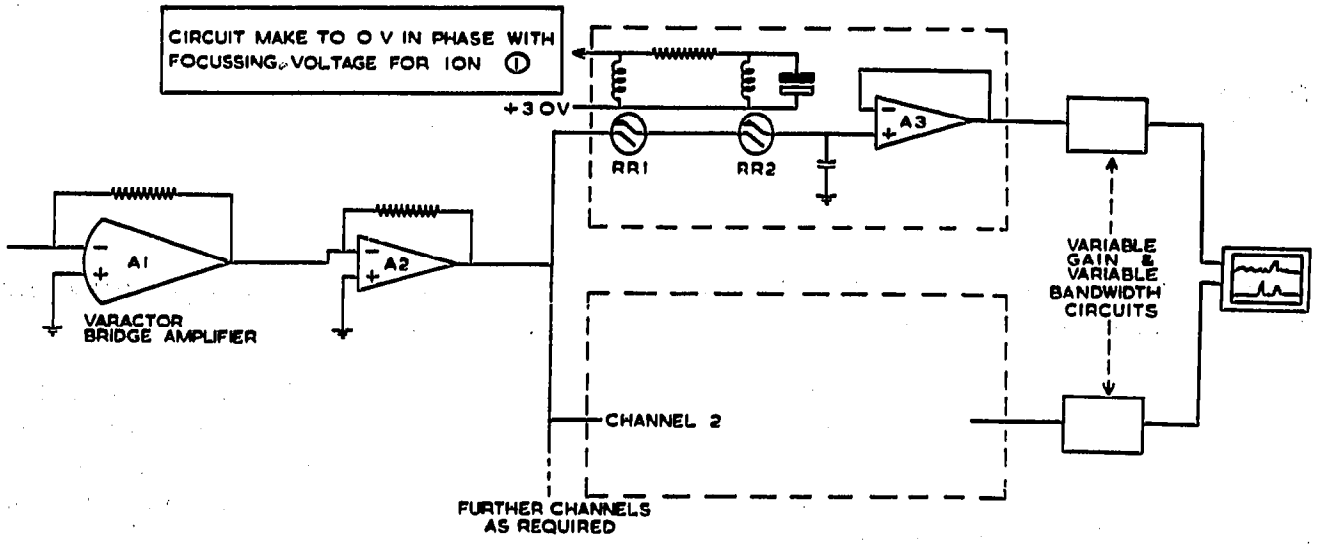

Fig. 1. Circuit diagram of analogue read-out device. A1 Varactor bridge amplifier (Analogue Devices 310J); A2, R.S. Components type 741; A3 F.E.T. amplifier R.S. Components FETOPA 30-533.

not sufficient, for when a voltage change is made to change the ion in tune, the effect is similar to a very rapid voltage scan from the first ion to the second. If a large ion is present between the two selected ions, this will be focussed momentarily and give rise to a spike. The circuit (Fig. 1) shown suppresses the signal during the switching to channel 1 by means of the damped relay RR2. When the change from channel 1 to channel 2 is required, it is essential to cult the signal to channel 1 instantaneously or a change in the signal will be experienced. This is achieved by relay RR1, in series with RR2, and with no damping. The signal in each channel

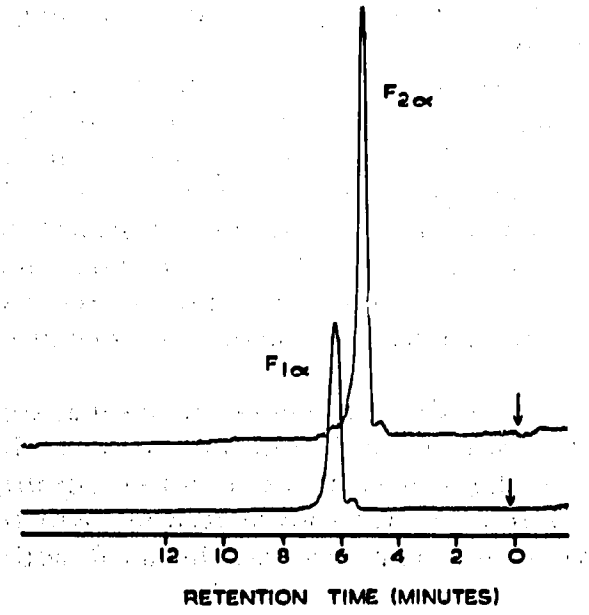

Fig. 2. Analysis of prostaglandin $F_{2\alpha}$ using prostaglandin $F_{1\alpha}$ as internal standard. The derivatives are the methyl ester, butyl boronate and TMS ethers of the respective prostaglandins. Prostaglandin $F_{2\alpha}$ is recorded at m/e 435 and prostaglandin $F_{1\alpha}$ is recorded at m/e 437.

is fed to a holding amplifier and can then be fed to variable gain circuits and filter circuits. After the relays, each channel is completely independent of the others. This allows ions of different abundance in a spectrum to be displayed with equal prominence.

If relatively high rise levels are experienced in the signal from the multiplier, extra damping can be added by inserting a resistor immediately after the pair of relays.

The device described operates in conjunction with any peak switching or "accelerating voltage alternator" system and the power to operate the relays is provided from such a unit, alternatively, if no such power is available, a contact closure in the peak switching system could be used to supply an 18V signal in phase with the switching of the accelerating voltage.

Discussion

The effect of this circuitry is to turn the mass spectrometer into two, three or more separate and specific GC detectors which operate simultaneously; an example is shown in Fig. 2 of a GC determination of prostaglandin $F_{2\alpha}$(PG $F_{2\alpha}$) using PG $F_{1\alpha}$ as the internal standard. The methyl ester, butyl boronate and TMS ethers of both compounds are used and this derivative gives a prominent ion at *m/e* 435 for PG $F_{2\alpha}$ and *m/e* 437 for PG $F_{1\alpha}$. Although these compounds are not completely separated on the column used, the individual ion traces are distinct and only a small contribution is made by the isotope peak of PG $F_{2\alpha}$ at *m/e* 437, no contribution is made by the PG $F_{1\alpha}$ to the signal at *m/e* 435. Using this technique less than 1 ng of PG $F_{2\alpha}$ can be quantitated.

The channel separating device described provides an analogue signal from each ion independently. Because of its cheapness and simplicity this device could be used to adapt low-cost mass spectrometers to "slave" detectors for gas chromatographs. With automatic solid injection there is no need to turn down the accelerating voltage or otherwise provide for the solvent peak, and the GC–MS system can be allowed to analyse thirty samples for two or more components without operator intervention.

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1 B. SAMUELSSON, B. M. HAMBERG AND C. C. SWEELEY, *Anal. Biochem.*, 38 (1970) 301.
2 L. SIEKMANN, H. O. HOPPEN AND H. BREUER, *Z. Anal. Chem.*, 252 (1970) 294.
3 R. W. KELLY, *J. Chromatogr.*, 54 (1971) 345.
4 C. C. SWEELEY, W. H. ELLIOT, I. FRIES AND R. RYHAGE, *Anal. Chem.*, 38 (1966) 1549.
5 C. G. HAMMAR AND R. HESSLING, *Anal. Chem.*, 43 (1971) 298.

Received April 17th, 1972