Journal of Chromatography, 112 (1975) 343–352

CHROM. 8535

SPECIAL TECHNIQUES IN THE COMBINATION OF GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

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SUMMARY

On the basis of a new open split-type connection of a gas chromatograph and a mass spectrometer, particularly suitable for glass capillary columns, procedures are described for decreasing a peak concentration that is too high by dilution and increasing a maximum peak concentration that is too low by trapping and subsequent evaporation.

On-line hydrogenation in a glass capillary reactor with palladium as catalyst and its analytical application is described.

A low-cost quadrupole mass spectrometer as an independent detector has been mounted inside a mass spectrometer. The resulting possibilities and advantages are discussed.

INTRODUCTION

The combination of gas chromatography (GC), mass spectrometry (MS) and a computer is one of the most powerful tools in analytical chemistry. The effective utilization of the expensive equipment involved is essential, so that all parts and techniques should be optimized with regard to versatility and reliable performance.

At present, some problems remain that have not been solved satisfactorily, for example the connection of the column to the ion source. More or less complicated and critical parts such as valves and separators are involved, and problems arise with columns, adaptation to different types of column and gas flow-rates and the maintenance of good separations.

Another problem is the recording of a sensitive chromatogram with a good base-line. In the cyclic scanning mode used in connection with computers, the signals should not be distorted or interrupted while measuring spectra. Special difficulties arise while using chemical ionization, where measurements have to be made with discrimination of the vast amounts of reactant gas.

Moreover, even when a good spectrum has been obtained, additional information is often needed for the identification of the compounds, because only a few classes of compounds can be identified from their mass spectra alone. In this instance, retention data (*e.g.*, index increments) or data from suitable derivatization methods can help.

As a contribution to these problems, in this paper we describe three developments made in the last 2 years that have improved the overall reliability of the complicated instrumentation and the quality of the results.

(1) The open split-type connection avoids most of the well known difficulties in connecting a gas chromatograph to a mass spectrometer. We described the principle and construction recently[1] and in this paper we give two special applications of the modified device: dilution of peaks that have too high a concentration and trapping of broad peaks with subsequent rapid evaporation to increase the maximum concentration.

(2) The technique of on-line hydrogenation, which gives much additional information for the identification of hydrocarbons, has been improved by using glass capillaries prepared with the catalyst as reactor and a hydrogen–helium mixture as carrier gas.

(3) The use of a very simple quadrupole mass spectrometer as a detector for the chromatogram inside the spectrometer seems suitable for the demands of combined GC–MS.

THE OPEN SPLIT-TYPE CONNECTION OF GC AND MS

A simple and reliable construction for connecting GC columns to a mass spectrometer has recently been described[1], based on an open split as the connecting element. This construction is suitable for all types of columns, especially for glass capillary columns.

Fig. 1 shows a scheme of the connecting device, which has been slightly modified so as to perform peak trapping between the column and the mass spectrometer. The inlet line to the mass spectrometer is a platinum capillary (90 cm long, 0.15 mm I.D.). The mass spectrometer end is positioned a few millimetres in front of the entrance to the ionization region and the outer end is located inside the splitting device in the gas chromatograph.

The splitting device (Fig. 1) is a short open tube into which the outer end of

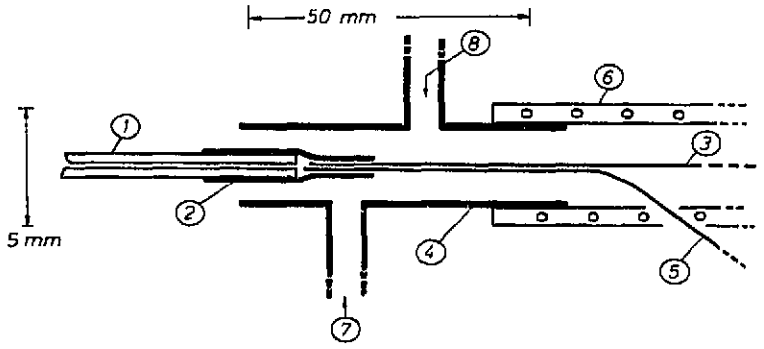

Fig. 1. The splitting device. 1, End of the capillary column; 2, PTFE shrinkable tubing; 3, mass spectrometer inlet capillary; 4, mantle tubing (protects the inlet capillary, holds the column end and carries the flushing helium); 5, scavenger gas for peak dilution; 6, heated tube to the mass spectrometer, holding the inlet capillary; 7, inlet for flushing helium; 8, inlet for cooling gas.

the platinum inlet capillary is introduced, so that the effluent from the column flows past the entrance of the capillary. The end of the inlet capillary is always at atmospheric pressure, independent of the flow-rate of the carrier gas. For a column with an I.D. greater than 0.5 mm, the last few centimetres of the empty part of the column can act as guiding tube; for a glass capillary column, as in Fig. 1, a 3-cm length of a PTFE shrinkable tubing is fixed on the column in order to guide the effluent along the inlet capillary. Fig. 2 shows the splitting device with a glass capillary column connected.

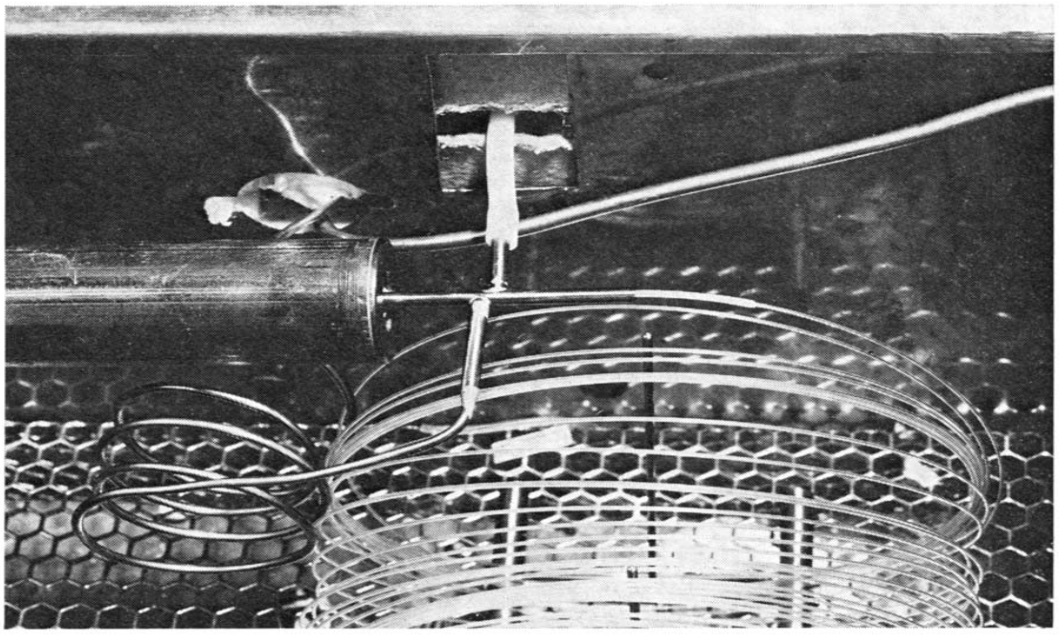

Fig. 2. Splitting device with a glass capillary column connected. The mantle tubing is in the slid-back position, used to shrink the PTFE and insert the inlet capillary.

The yield of sample reaching the mass spectrometer is given by the ratio of the flow-rate of effluent through the inlet capillary to that through the column. The theoretical value was confirmed by measurements at column flow-rates between 1 and 6.5 ml/min of helium and was found to be independent of the position of the end of the inlet capillary inside the PTFE tubing. The use of the PTFE tubing never caused disturbances such as adsorption or contributions to the background, even at high temperatures.

The flow resistance of the inlet capillary has to be adjusted so as to allow for the amount of helium that can be accepted by the mass spectrometer under suitable operating conditions (in our work, with a Varian-MAT CH4 instrument, about 1 ml/min of helium at 250°).

The main advantages of the open split-type connection of GC and MS can be summarized as follows: atmospheric pressure at the end of the column; maintenance

of chromatographic resolution; versatility with respect to column types and flow-rates; rapid and safe changing of columns; and very high reliability. More details were given in our previous paper[1]. For certain types of analyses, special modes of usage are described, and they are implemented in the splitting device without affecting its simplicity.

PEAK DILUTION

By means of a scavenger flow into the splitting region (see Figs. 1 and 3), the effluent can be diluted to a certain extent so that the mass spectrometer receives only a certain proportion (flow-rate into the mass spectrometer divided by the sum of the effluent and scavenger flow-rates) of the sample, an effect that is equivalent to peak cutting. This is important when large amounts of solvents or major components of the sample are involved. For instance, the introduction of large amounts of silylating agents into the mass spectrometer, which may cause isolation problems in the ion source, should be avoided.

Fig. 4 shows an example of peak dilution, demonstrating the effect of reducing the concentration of a peak and the rapid response (a few tenths of a second) to switching on and off the flow of scavenger gas.

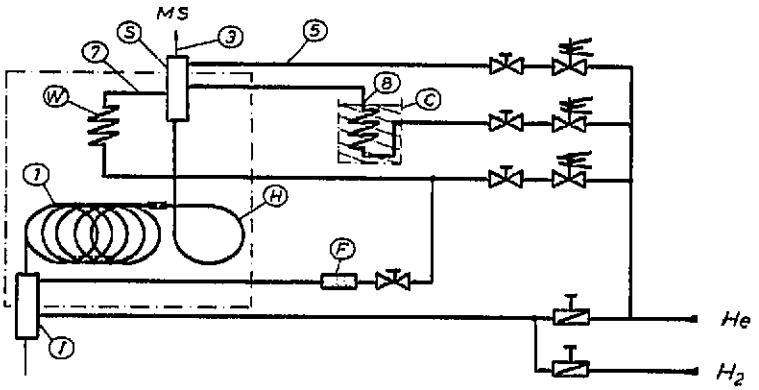

Fig. 3. Flow diagram of the gas chromatograph. I, Injection part; S, splitting device; H, hydrogenation catalyst tube; F, filter for the injection split flow; the purified helium is used to flush the splitting region; W, warm-up coil for flushing helium. Numbers as in Fig. 1.

PEAK TRAPPING

At the end of isothermal chromatograms or in chromatograms with a restricted application of temperature programming, broad peaks may occur. Such peaks can represent a sufficient amount of sample but too low a maximum concentration for a good mass spectrum, either absolute or relative to the background spectrum, to be obtained. By trapping such a peak followed by rapid evaporation into the mass spectrometer, the maximum concentration can be increased.

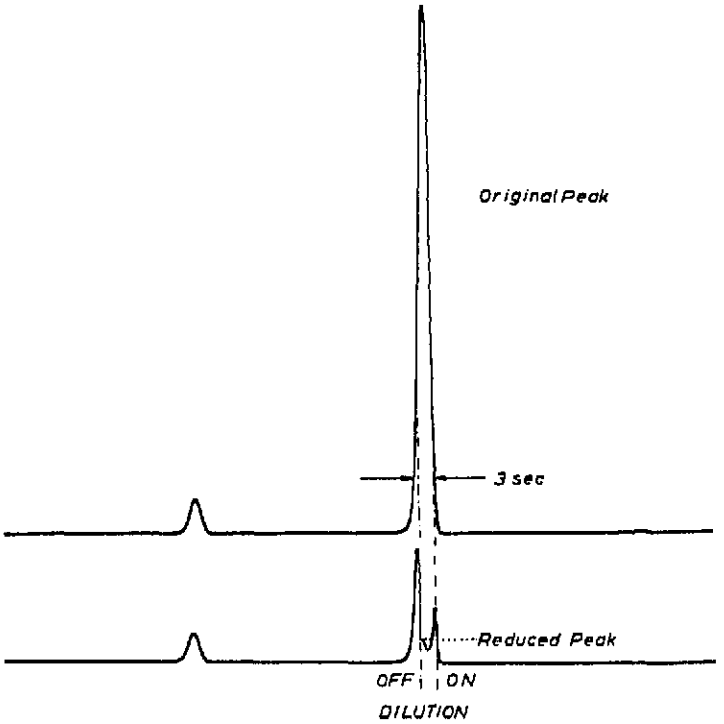

Fig. 4. Example of peak dilution, carried out at beginning and end of a narrow peak, demonstrating the short time constants of the procedure.

For this procedure, the first few centimetres of the inlet capillary inside the mantle tubing are cooled (see Figs. 1 and 3). The subsequent heating process takes place normally by simply stopping the flow of coolant gas. The heat capacity of the capillary, oven and flushing helium provides a sufficient increase in temperature for components that do not have too low a vapour pressure.

Fig. 5 shows the improvement in the concentration profiles of peak 4 of a mixture of underivatized steroids. In this instance, the heating of the trap part of the inlet capillary was supported by an additional flow of helium through the warm-up coil inside the oven (see Fig. 3). The heating rate of the trap part has to be adjusted to the scanning conditions of the mass spectrometer; the resulting width of the peak should be about two cycles of a repetitively scanning spectrometer.

When the peak to be trapped is followed immediately by another during the period of heating, the scavenger gas is switched on (dilution mode) so as to prevent mixing of the two components.

ON-LINE HYDROGENATION

Hydrogenation of the compounds after their separation, but before their entry into the mass spectrometer, was proposed in 1962[2] and has been used by us since 1968[3]. This technique is extremely helpful, especially in the analysis of hydrocarbon

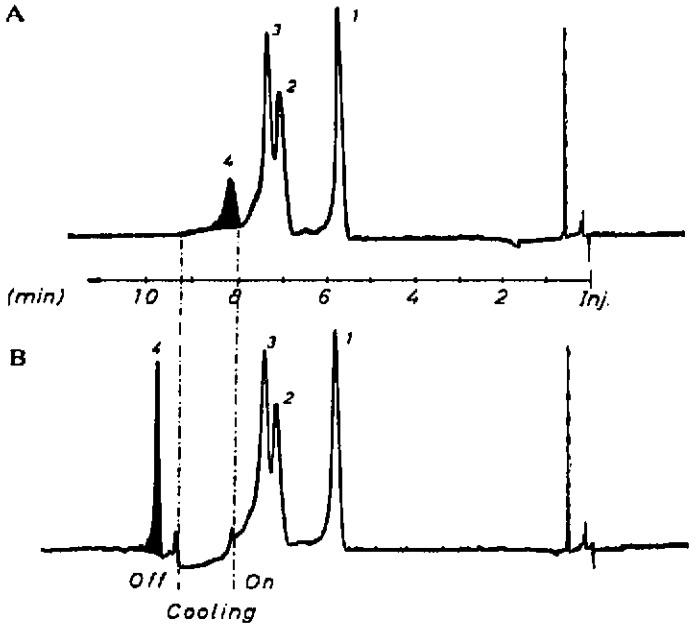

Fig. 5. Peak trapping. A, Chromatogram of cholesterol (1), campesterol (2), stigmasterol (3) and β-sitosterol (4). Column: 20-m Carbowax 20M; 250°; helium at 1.8 atm as carrier gas. B, Same mixture, peak 4 trapped and heated rapidly into the mass spectrometer. The maximum concentration is increased by a factor of 4.

mixtures. It permits the determination of double bond equivalents by comparison of the spectra of the original and the hydrogenated components. If the hydrogenated compound can be identified, the carbon skeleton is known and only the positions of double bonds remain to be determined. This simplification in many instances permits complete identification to be made from the mass spectrum and/or retention index increments.

As a simple example, the identification of two components (peaks 1 and 2 in Fig. 7) is described. The sample originated from the reaction[4] of isoprene with a 3-methyl-but-2-enylmagnesium halide. The main reaction in this instance is the addition of the metal to one double bond of isoprene.

The hydrogenated species in both instances are 3,3,6-trimethylheptane (spectra B1 and B2 in Fig. 6), as derived from fragmentation rules for isoalkanes[5]. One of the two double bonds of the original diolefin is in the 1-position, because of the absence of an (M — ethyl) fragment (see spectra A1 and A2 in Fig. 6). From the three alternatives that remain for the second double bond, one (the ene-4) was ruled out by knowledge of the reaction and the other two can easily be assigned because of the characteristically differing patterns of the two spectra. These results were confirmed by the NMR spectra.

The hydrogenation catalyst tube

In the first few years of application of on-line hydrogenation, we used platinum on Embacel packed into a metal tube of 20 or 50 cm length and about 1 mm I.D. with

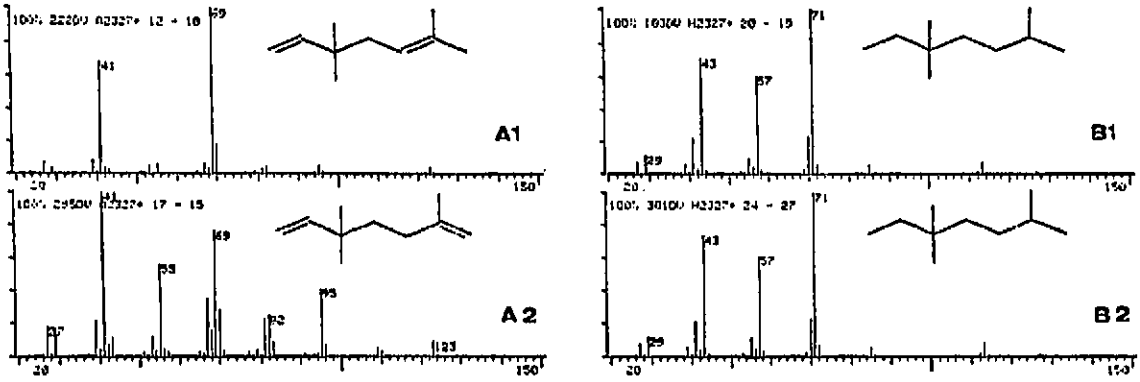

Fig. 6. Mass spectra of peaks 1 and 2 (see Fig. 7) of the original (A) and hydrogenated (B) compounds.

hydrogen as the carrier gas. A disadvantage of these conditions was the deterioration of separation owing to tailing caused by adsorption of the sample in the catalyst tube.

For 2 years we have used as the hydrogenation reactor 30- or 60-cm lengths of glass capillary that contain about 0.2–0.6 mg of palladium deposited on the inner wall. The preparation is carried out as follows. A 20% solution of bis(π-allyl)palladium[6] in benzene was passed through a 50-m × 0.3 mm I.D. glass capillary tube that had been etched with hydrochloric acid. After blowing out the excess of solution, the solvent is removed and the metal complex decomposed in a flow of hydrogen. The decomposition of the complex can be followed by the colour change from light brown to grey. By-products of the decomposition reaction are removed by heating the column under a flow of hydrogen at 260°. By this procedure, active palladium is deposited on the walls.

For hydrogenation experiments, one or two turns of the catalyst tube are broken from the originally prepared capillary and mounted in the oven, the connection with the column and that with the splitting device being effected with PTFE shrinkable tubing. If the catalyst tube has become inactive (this normally occurs after a few days or sometimes a few weeks), it is replaced with a fresh piece broken from the supply. The activity is tested with an actual analytical sample or by measuring a test mixture that consists of compounds that have characteristic differences in their ease of hydrogenation.

Sometimes the catalyst tube is mounted between the injection block and the column so that hydrogenation is carried out on-line before separation. With this arrangement, the identification of the different skeletons of the saturated compounds can be supported by their retention index increments.

The capillary reactors described contain the same amount of catalyst metal as the previous type, but their hydrogenation activity is greater. Also, the tailing produced by the reactor is negligible compared with that in previously used packed reactors (see chromatograms A and B in Fig. 7).

The carrier gas in hydrogenation runs

The use of pure hydrogen as carrier gas leads to difficulties in combined GC–MS. Firstly, with a restriction of constant size, as we use in the open split-type ar-

rangement, one admits approximately double the flow of hydrogen compared with that of helium. If the split is optimized for helium, the ion source is overloaded when hydrogen is flowing and therefore the quality of the resulting spectra and the sensitivity of the mass spectrometer will decrease. Secondly, the recording of the chromatogram by total ionization is worse, because for discrimination against the carrier gas an electron energy of 12 eV must be used, instead of 20 eV with helium. As a result, the response for the eluted compounds is appreciably reduced and poor chromatograms are obtained.

We found that for on-line hydrogenation in the described catalyst tubes, a 2:1 helium–hydrogen mixture is satisfactory, so the above difficulties are greatly reduced. For instance, the electron energy of the total ionization source can be increased to 16 eV.

Fig. 7 shows parts of the chromatograms of a sample under normal measurement (A) and under hydrogenation conditions (B). The comparison shows that the separation is of the same quality, no severe additional tailing being introduced into the chromatogram under hydrogenation conditions, and the quality of the latter is appreciably lower but is sufficient for components of medium concentration in the mixture.

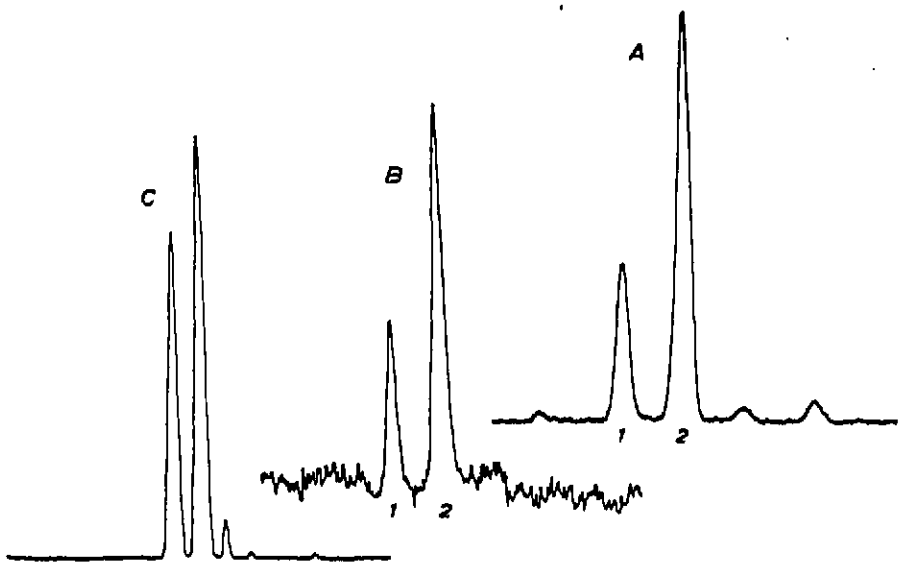

Fig. 7. Total ionization curves for part of the chromatogram of a mixture of branched decadienes. A, Normal GC–MS chromatogram with helium as carrier gas; total ionization source at 20 eV. B, Same sample as in A with on-line hydrogenation, a 2:1 He–H_2 mixture as carrier gas and total ionization source at 14 eV. C, Similar mixture of the same compounds on another column with on-line hydrogenation, 2:1 He–H_2 mixture as carrier gas and a QMG 111 quadrupole mass spectrometer as total ion detector; ions below *m/e* 10 suppressed.

Results of hydrogenation

The components remain in the tube for about 3–10 sec, calculated from the linear gas velocity of the carrier gas, adsorption times being neglected. The absolute

amounts of palladium metal and substance (per component) are of the same order of magnitude. Under these conditions, the following hydrogenation behaviour is observed:

(1) The degree of hydrogenation decreases as the temperature increases, probably because the residence times of the molecules on the catalyst metal decrease. In practice, an oven temperature chosen for the volatility range of a sample is a good compromise for hydrogenation.

(2) Sometimes an artefact can be observed; a small part of a component or a reaction product of it remains adsorbed, and is displaced by a following substance of higher polarity.

(3) As long as the catalyst is fully active, hydrocarbons are normally completely hydrogenated, including aromatic compounds and those which contain tetrasubstituted double bonds.

(4) Depending on the amount, condition and temperature of the catalyst, different functional groups can be attacked. Halogen is eliminated as HX and the resulting double bond may subsequently be hydrogenated. An unsaturated ketone, for instance, was, depending on the experimental conditions, converted into the saturated ketone, but under different conditions reacted to give a saturated alcohol and even the corresponding alkane. Three-membered rings can be opened to a certain degreee.

It is beyond the scope of this paper to describe such details and we are just beginning to study in a more systematic way the hydrogenation of different functional groups and their possible selectivities as a function of the type of catalyst and the experimental parameters.

A QUADRUPOLE MASS SPECTROMETER AS A TOTAL IONIZATION DETECTOR

An ideal detector inside the mass spectrometer should monitor the partial pressure of the eluting components only. This would be achieved by an additional total ionization measurement, where ions of lower masses that originate from hydrogen or helium (carrier gas) or even water, nitrogen, oxygen (main constituents of constant background) or isobutane (common reaction gas for chemical ionization) can be suppressed. The sensitivity should at least be sufficiently high that small peaks that still give a rapid scan spectrum are detected with a good signal to noise ratio.

These conditions are fulfilled by simple quadrupole mass spectrometers, manufactured as residual gas analyzers. We tested the performance of such a low-cost quadrupole (Balzers QMG 111, mass range up to 100) in a provisional experimental arrangement. We found the sensitivity and the prolonged stability to be sufficient for its use as a detector in our GC–MS combination.

In the resolution-off mode, the d.c. voltage of the mass filter is switched off and the amplitude of the HF voltage determines the lower limit of the mass range ("first mass") in which the intensity of all ions is measured as total ionization. In Fig. 8, the ion current is shown as function of the first mass for a few gases. The resulting curves represent the mass discrimination properties of the QMG 111 instrument in the resolution-off mode. It is demonstrated that the discrimination of the gases is possible without losing too much sensitivity for larger molecules, even for *n*-decane, which, as an *n*-alkane, exhibits most of its ions in the lower mass range.

Chromatogram C in Fig. 7 shows the quality of the base-line achieved for the

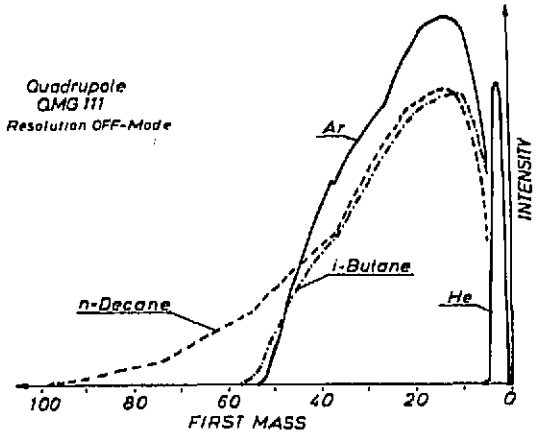

Fig. 8. Mass discrimination of the Balzers QMG 111 quadrupole mass spectrometer for several compounds, spectrometer operating in the resolution-off (total ionization) mode.

same amount of a sample similar to that in A and B under identical hydrogenation conditions (as a different column was used, the resolution is different).

Three other advantages of using such a detector should be mentioned:

(1) An independent mass spectrometer is available for leak detection in the event of malfunction of the main ion source.

(2) The quadrupole mass spectrometer can record a mass chromatogram simultaneously with a signal (spectra or mass chromatogram) from the main ion source.

(3) Coupled with a computer, combined GC–MS is operated with cyclic scanning and the changing magnet current produces a cyclic distortion of the total ionization signal (chromatogram). This distortion almost vanished in our work with the quadrupole spectrometer as a detector.

We are still attempting to optimize the conditions for maintaining the peak profile from the end of the column into the ion source of the quadrupole mass spectrometer by the use of special geometries for conducting the molecules, and a detailed description of the optimal mounting of the quadrupole can only be given in a future publication. At present, the quadrupole mass spectrometer is mounted on the flange at the ion source housing of the Varian-MAT CH4 instrument, where originally the pressure-monitoring ion source was located.

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