

## Loss of chromatographic resolution in the vacuum line of a gas chromatograph mass spectrometer (GC-MS) system

The tandem operation of a gas chromatograph with a mass spectrometer has rapidly emerged as a powerful analytical method. Numerous references pertaining to the development or the application of such systems can be found in recent bibliographies on gas chromatography<sup>1,2</sup> and a recent review on mass spectrometry<sup>3</sup>. Instruments which combine both a gas chromatograph and mass spectrometer in a single unit are already commercially available from two companies (LKB-Instrument AB, Stockholm, Sweden and Perkin-Elmer, Norwalk, Conn.). Other companies which produce mass spectrometers offer specially designed models and optional accessories to facilitate tandem operation with gas chromatographs.

A variety of interface devices<sup>4-9</sup> and methods<sup>10-13</sup> have been developed to facilitate the interconnection of gas chromatographs to mass spectrometers and achieve enrichment of the sample to carrier gas ratio. Other specific problems such as scan rate considerations<sup>14</sup>, obtaining high resolution mass spectra<sup>4,5,9,15</sup>, the effect of column bleed<sup>16</sup> and change of sample concentration during the recording of the mass spectra of gas chromatographic peaks<sup>10</sup>, have been studied with considerable detail. When the column outlet is directly connected to the inlet of the mass spectrometer, the total column effluent enters in the vacuum line and loss of chromatographic resolution may occur because part of the column is maintained at low pressures and very high linear velocities of the carrier gas. This aspect of the "total effluent" mode of operation was first discussed by VARADI AND ETTRE<sup>17</sup> and was later more thoroughly investigated by TERANISHI *et al.*<sup>18</sup>. These workers dealt only with capillary columns because the vacuum system of a mass spectrometer cannot tolerate the total column effluent issuing from packed columns without the use of interface devices. When the column outlet is kept at atmospheric pressure and only a fraction of the effluent is allowed to leak into the mass spectrometer or when an interface device is used, no loss of resolution should occur if the vacuum line of the mass spectrometer and the interface device can maintain the chromatographic resolution. HENNEBERG<sup>9</sup> showed that this is feasible but expressed the opinion that only some of the interface systems described in the literature can meet this requirement. In addition, we suspected that dead volumes or unswept pockets present in the vacuum line of the mass spectrometer may cause loss of resolution in much the same way as dead volumes cause loss of resolution in the gas chromatograph. Dead volumes in the vacuum line of the mass spectrometer are bound to occur, particularly when general purpose mass spectrometers are being modified for interconnection to gas chromatographs. It was our intention to use a modified general purpose mass spectrometer. We therefore investigated the effect of dead volumes in the vacuum system of the mass spectrometer.

### *Experimental*

*Apparatus.* A Hitachi-Perkin Elmer model RMU-6D all-glass inlet mass spectrometer was modified for interconnection with a gas chromatograph using an interface accessory kit modelled after the helium separator described by WATSON AND BIEMANN<sup>4,5</sup> which was made available by the Perkin Elmer Corporation. We assembled a gas chromatograph-mass spectrometer (GC-MS) system using an

Aerograph model 660 gas chromatograph, a microvolume stream splitter, a flame ionization detection (FID) system, a 5 ft. heated capillary (0.01 in. I.D.) which connects the stream splitter to the mass spectrometer, a helium separator, a mass spectrometer equipped with a total ion monitoring (TIM) electrode and a Keithley model 610B electrometer (used in conjunction with the TIM electrode) as schematically shown in Fig. 1. A Welch, Duo-Seal model 1405 H vacuum pump (not shown in Fig. 1) was used in conjunction with the helium separator. The helium separator was first connected to the inlet system of the mass spectrometer at a point which was half-way between the pinhole leak and the ion source (Fig. 2 a). After a series of experiments the interconnection between the helium separator and the inlet of the mass spectrometer was made as close as possible to the pinhole leak (Fig. 2 b).

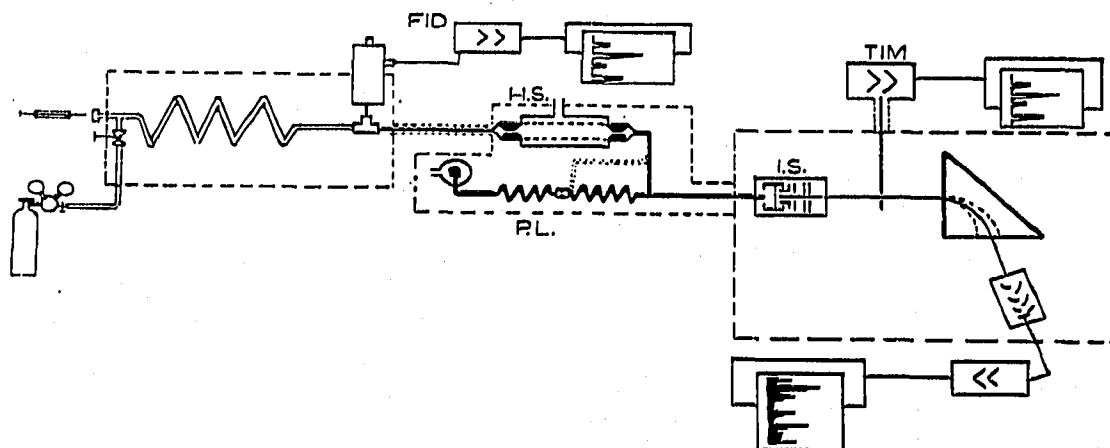


Fig. 1. Layout of the GC-MS system (schematic). FID = Flame ionization detection system; H.S. = helium separator; P.L. = pinhole leak; I.S. = ion source; TIM = total ion monitor.

**Procedure.** The GC-MS system was operated as a FID-TIM dual channel system. The FID system was used to record the chromatographic resolution at the outlet of the column and the TIM system to record the chromatographic resolution at the ion source of the mass spectrometer. The column effluent reaches the stream splitter at the rate of 30 ml/min. When kept at 200° the interconnecting capillary allowed about 10 ml/min of helium to be drawn off into the helium separator (according to the specifications). This means that the column effluent was split in a 2:1 ratio with 20 ml/min flowing to the flame. The pressure of the high vacuum section of the mass spectrometer was kept between  $3 \cdot 10^{-6}$  to  $5 \cdot 10^{-6}$  torr (the reading of the ion gauge). Total ion monitor (TIM) and flame ionization (FI) chromatograms were simultaneously recorded during each chromatographic run, and the percent loss of chromatographic resolution in the vacuum line of the mass spectrometer was calculated by comparing the resolution between corresponding pairs of peaks appearing in the chromatograms obtained before and after changing the point of connection of the helium separator.

#### Results and discussion

The FI and the TIM chromatograms obtained with the GC-MS system while the helium separator was connected to the mass spectrometer at a point midway

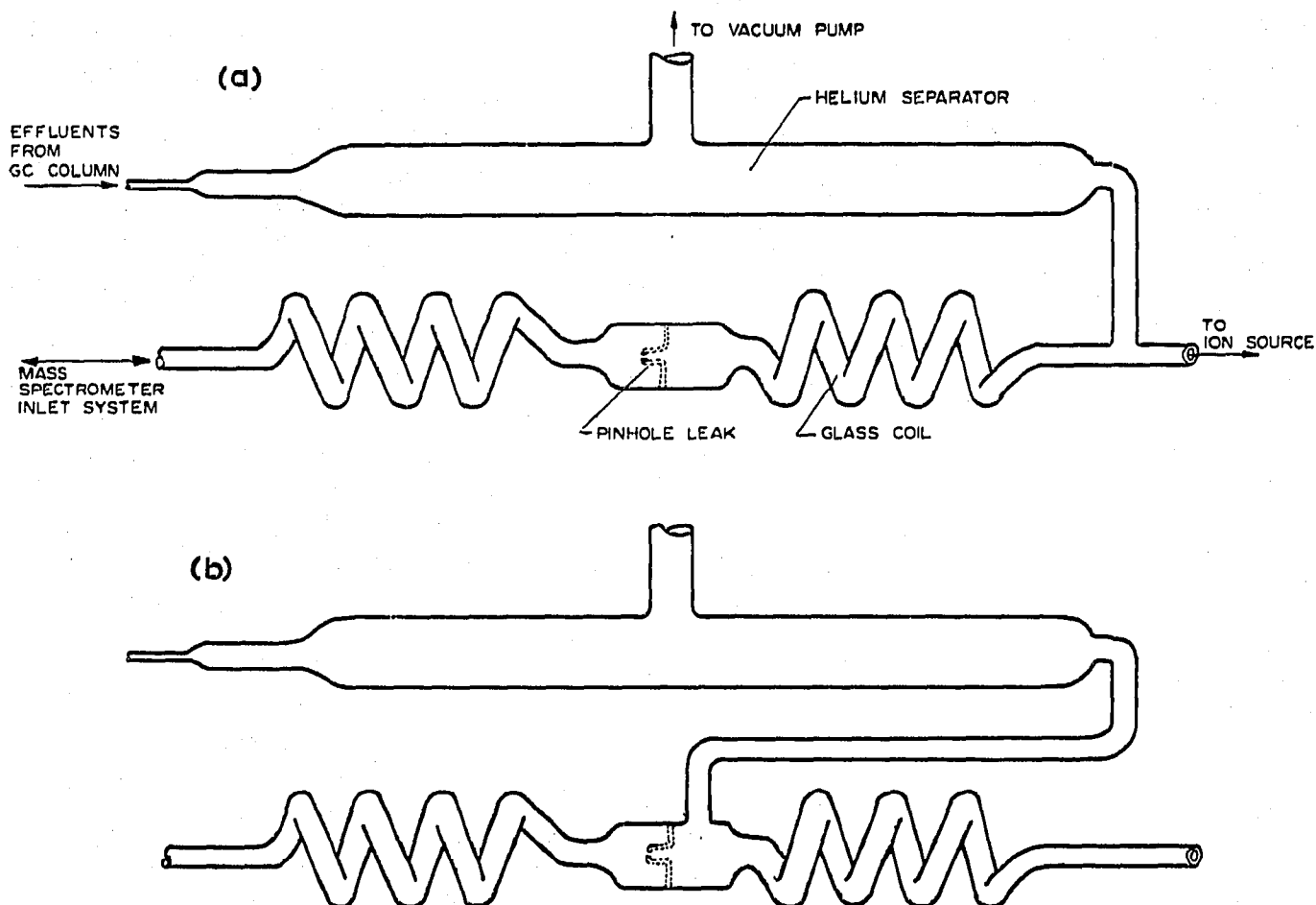


Fig. 2. Helium separator hook-up to the inlet system of the mass spectrometer: (a) close to the ion source; (b) close to the pinhole leak.

between the pinhole leak and the ion source (Fig. 2a), shows loss of resolution in the TIM chromatogram of 53 % between peaks 2 and 3 and 42 % between peaks 10 and 11 (Fig. 3), as compared to the resolution between these peaks observed in the FI chromatogram. The original point of interconnection between the helium separator and the mass spectrometer (Fig. 2a) was the shortest possible. However, with this arrangement the volume between the pinhole leak and the point of connection represents an "unswept pocket" which causes the observed loss of resolution.

The FI and TIM chromatograms obtained with the GC-MS system while the helium separator was connected next to the pinhole leak (Fig. 2b), showed no loss of resolution between peaks 30 and 31 (Fig. 4). However, some trace constituents appearing on the shoulder of larger peaks which are detected in the FI chromatogram are not seen in the TIM chromatogram indicating that in the case of small peaks following large ones loss of resolution still takes place. This is probably due to some hold-up by the sintered glass helium separator. With the point of interconnection between the helium separator and the mass spectrometer positioned next to the pinhole leak an extra volume of 20 ml and extra length of 40 cm were added to the path of the gases to the ion source. A comparison of the resolution in the TIM chromatograms relative to the FI chromatograms obtained before and after the

change of the point of interconnection shows that the presence of unswept volumes in the high vacuum line of the mass spectrometer causes serious loss of chromatographic resolution whereas extra volume has little or no effect on the resolution. It seems possible to assume that the shape and dimensions of an unswept pocket are more critical than its total volume. As a "peak" enters the vacuum system the pressure rises and the vapors of the substance rapidly diffuse into the unswept pockets. The speed of pumping the substance away from these pockets depends largely on their shape and dimensions.

In glass inlet mass spectrometers, the presence of a glass spiral (Fig. 2) is desirable for relieving strain which can be tolerated with metal systems. In some systems described in the literature<sup>18-20</sup>, the shapes of the unswept pockets are cylindrical, which could explain why no loss of resolution was observed.

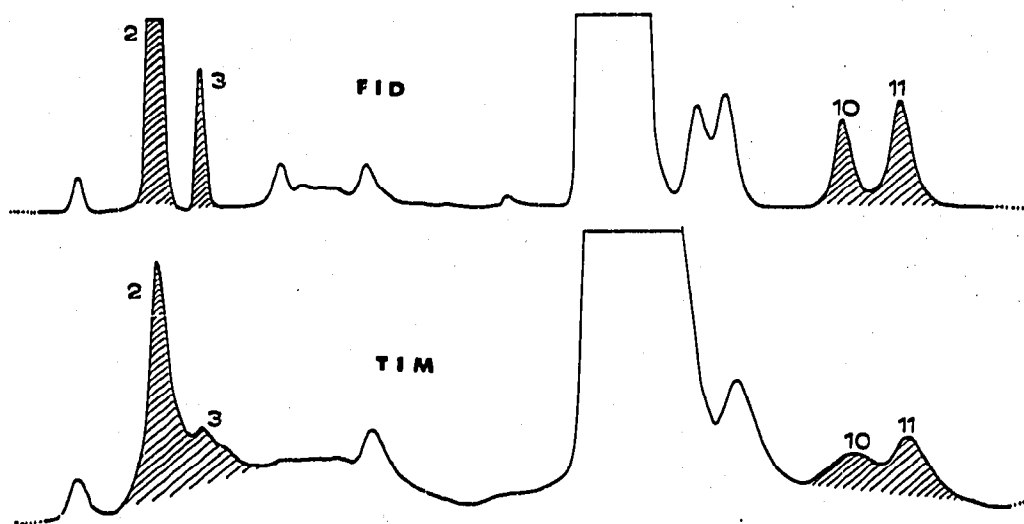


Fig. 3. Corresponding portions of FID and TIM chromatograms of fusel oil obtained with helium separator connected as shown in Fig. 2 a.

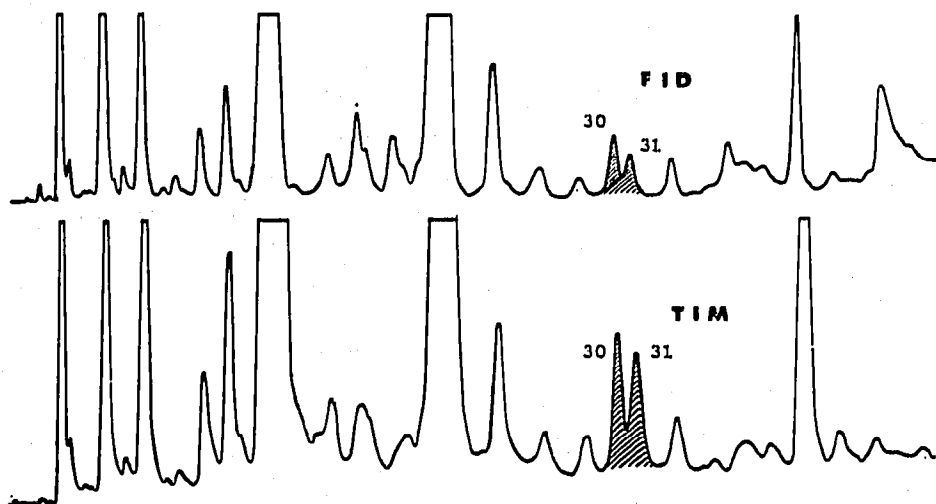


Fig. 4. Corresponding portions of FID and TIM chromatograms of fusel oil obtained with helium separator connected as shown in Fig. 2 b.

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*Midwest Research Institute, Kansas City, Mo. 64114 (U.S.A.)*

R. L. LEVY

*Department of Chemistry, University of Manitoba,  
Winnipeg (Canada)*

H. D. GESSER  
J. B. WESTMORE

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