

Consideration of Parameters for Coupling Gas Chromatographs to Mass Spectrometers

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Presented at the Fifth International Symposium on Advances in Chromatography held in Las Vegas, Nevada, January 20-23, 1969.

The coupling of gas chromatographs to mass spectrometers has become almost universal so that nearly every make and model of mass spectrometer features fast scan capability and a means of attaching a gas chromatographic column inlet. An inherent incompatibility, however, has existed between the requirement for reduced pressure in the spectrometer ion source and the relatively large volumes of carrier gas needed to elute the chromatography column. Two approaches have been developed, both receiving rather wide acceptance in recent years, which attempt to overcome this difficulty. One method utilizes the low flow rate characteristic of small capillary columns (1-6) and the other some type of molecular separator (7-12) to concentrate the eluates in the effluent carrier gas. Although successful where applicable, both methods suffer serious disadvantages when complex mixtures such as flavor isolates, smokes, air pollutants, etc., having a high dilution factor and containing small amounts of components are to be analyzed. The capillary columns are restricted to small sample sizes whereas molecular separators have poor recovery ratios, frequently losing more than 90% of the sample to the differential pumping system. In either case the presence of small amounts of components, especially in unknown samples, may go undetected or the mass spectrum may not be sufficiently intense to permit identification. For those investigators who must deal with small amounts of sample, with components at low concentration levels, and with component types that require optimum separability, an improved performance of the gas chromatography - mass spectrometer system is needed. This paper describes the utilization of support coated open tubular columns to meet this requirement.

Experimental

The performance of a gas chromatographic inlet was evaluated on several mass spectrometers of differ-

ent types. The following mass spectrometers were used: Consolidated ElectroDynamics Corporation Model 21-110B double focussing, high resolution mass spectrometer, Bendix Model 14-101 time of flight mass spectrometer, Electronics Associates, Inc., Model 300 quadrupole mass spectrometer and Perkin Elmer Corporation, Model 270 double focussing mass spectrometer. Spectra from the CEC high resolution mass spectrometer were recorded at resolving powers greater than one part per ten thousand on a photoplate and on a direct writing recording oscillograph at fast scan speeds. All other spectra were obtained at low resolution and recorded on a recording oscillograph. Visible displays of spectra on an oscilloscope were available

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on both the time of flight and quadrupole mass spectrometers. Detection of component elution from the gas chromatograph was by a recording of mass spectrometer total ion current. Although the mode of total ion current measurement was different for each type of mass spectrometer, in all cases helium ion defocussing was employed to reduce standing current and enhance component sensitivity. All spectra were adequate for component identification.

The gas chromatographic inlet consisted of a heated septum injection device especially constructed to provide narrow band injection and a support coated open tubular column connected to the spectrometer inlet through a capillary flow restrictor. The SCOT columns used were 50 ft x 0.02 in. procured from the Perkin Elmer Corporation and the capillary restrictor was made from a six inch piece of 0.02 capillary tubing which was crimped over about two inches of its length in an arbitrary fashion with a flow of helium passing through until the ion source pressure was reduced to a desirable level ($\sim 1 \times 10^{-5}$ Torr). The entire inlet system was transferred to the various mass spectrometers and its performance evaluated.

Results and Discussions

The main requirement for coupling a gas chromatography column to a mass spectrometer ion source is to reduce ion source pressure due to helium to a range in which ionization efficiency is unimpaired and which is unfavorable for ion-molecule reactions due to collisions with the carrier gas. The large body of experience with coupling of gas chromatographs to mass spectrometers (1-12) as well as previous special (13, 14) studies directed to the selection of the optimum ion source pressure range has shown that the pressure should be less than 10^{-4} Torr and preferably in the range 1×10^{-5} to 3×10^{-5} Torr. Commonly employed 100 ft x 0.01 inch capillary columns normally provide a pressure in this range whereas molecular separators are usually employed in conjunction with a needle valve or a restrictor. In this investigation a capillary restrictor was chosen to limit ion source pressure since it provided better reproducibility than a needle valve in observing the effects of the various operational parameters of the various ion sources from spectrometer to spectrometer used in the study.

In early phases of the investigation the effect of spectrometer ion source pumping speed was investigated, but it was found that a change in pumping speed was without effect provided it was high enough to maintain a flow rate in the ion source consistent with maintaining the flow rate in the column needed to achieve separation. The effect of ion source flow rate was reported in a previous investigation (14) of the direct coupling of a multichannel open tubular column especially devised for use with a mass spectrometer. As with multichannel columns flow rates in the ion source were also shown to be optimum for SCOT columns in the range 0.5 to 2 ml/min.

The results of the earlier study (14) showed that a chromatographic column having suitable operational characteristics could be directly coupled to the spec-

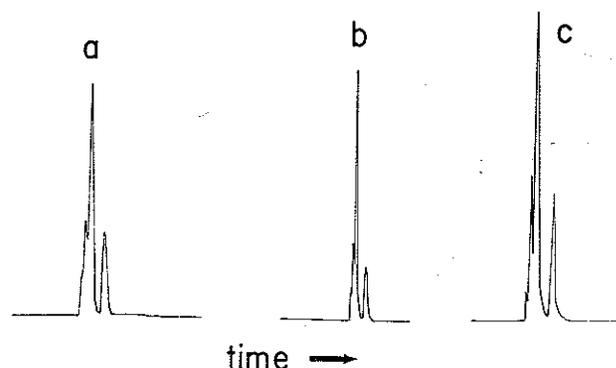


Figure 1. Comparison of the separation of hexane isomers on the same SCOT column, a) in a Barber Colman series 5000 modular gas chromatograph with FID detector, b) coupled to a Perkin Elmer Model 270 mass spectrometer through a glass frit separator, and c) coupled directly to an EAI QUAD 300 mass spectrometer. Chromatograms in b) and c) are recordings of spectrometer total ion current. Column, 50 ft x 0.02 in., Carbowax 1540; Temperature, ambient. Sample size, 0.05 μ l; Flow rates, a) 2 ml/min, b) 8 ml/min, c) 2 ml/min; Ion source pressure, b) 5×10^{-7} torr, c) 1×10^{-5} torr.

trometer without a splitter and yet have sufficient capacity to handle samples containing small amounts of components. The multichannel open tubular columns lacked the desired resolving power and efficiency. It appeared, however, that the characteristics of support coated open tubular columns might be well suited to the requirements for a generalized type of chromatographic inlet for a mass spectrometer. Several such columns, employing a variety of stationary phases and a variety of mixtures for separation and analysis have been operated with the four spectrometers employed in this study. The columns were directly coupled to the CEC high resolution spectrometer and to the Bendix and EAI spectrometers. Performance was nearly identical on all the instruments. The column was coupled to the Perkin-Elmer spectrometer through the glass frit type separator which is the standard interface supplied with the spectrometer for coupling chromatographic columns. Performance of the column through the separator was comparable to that when directly coupled to the other spectrometers, but required a somewhat larger sample for the same response.

A comparison is shown in Figure 1 of typical column performance in a conventional gas chromatograph and when coupled to a mass spectrometer directly and through a separator. The sample is reagent "nano-grade" hexane which contains four close boiling isomers and was chosen to demonstrate the relative resolving power of the column. It is seen that direct coupling of the column to the spectrometer provides separations which are wholly comparable to those obtained with a separator or in a chromatograph.

Manuscript received November 4, 1968

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