

APPLICATIONS OF FIELD IONIZATION MASS SPECTROMETRY IN THE ANALYSIS OF ORGANIC MIXTURES

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The advantages of using the data provided from field ionization (FI) as a complement to that obtained from electron-impact ionization (EI) in the mass spectral study of organic compounds have been well described.¹ Recently the combinations of FI mass spectrometry with on-line data acquisition² and with gas chromatography³ have been reported, and applications of high resolution FI/MS have also been described.^{2,4} We have now applied all of these techniques routinely in the study of mixtures of organic compounds and find that the results obtained, when supplemented with those obtained by EI/MS, provided an extremely powerful method for the analysis of crude mixtures.

For example, we have used these techniques to examine a crude mixture of alkaloids obtained from the seeds of Erythrina princeps^{5,6} Fig. 1 shows the FI spectrum of the mixture and, since the pure alkaloids show no significant fragment ions in their FI spectra, all the peaks present represent molecular ions. Examinations of the group of molecular ions at high resolving power enabled accurate mass measurements of the major ions by the peak matching method, using the molecular ion of erysodine plus erysovine (m/e 299 $C_{18}H_{21}NO_3$) as an internal standard (Table 1).

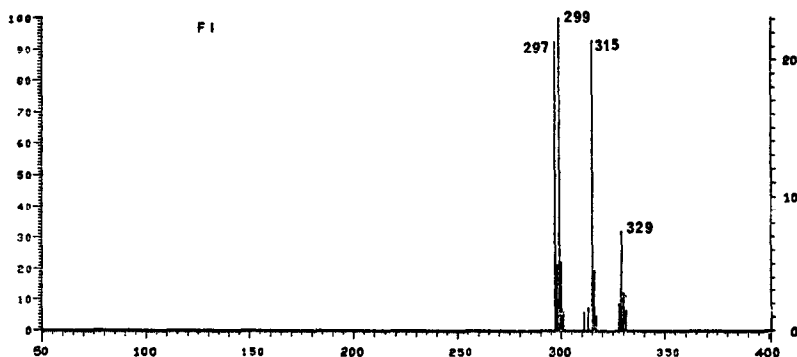


Fig. 1 FI spectrum of the alkaloids from E. princeps.

Table 1 High Resolution Mass Measurements (R.P. 6000)

FOUND	CALCULATED	MOLECULAR FORMULA
297.140	297.136	$C_{18}H_{19}NO_3$
315.145	315.147	$C_{18}H_{21}NO_4$
329.157	329.163	$C_{19}H_{23}NO_4$

After derivatization as trimethylsilylethers, the same alkaloid mixture was examined by GC/MS using both EI and FI, and the total ion current monitor traces obtained using both ionization methods were virtually identical (Fig. 2). Pure components such as A, B and C each gave rise to single molecular ion peak by FI, while composite peaks such as E gave more than one ion (Fig. 3) indicating the molecular weights and approximate relative proportions of each constituent. Examinations of the FI spectra in combination with EI spectra enabled tentative structural assignments to be made for the components of the mixture (Table 2).

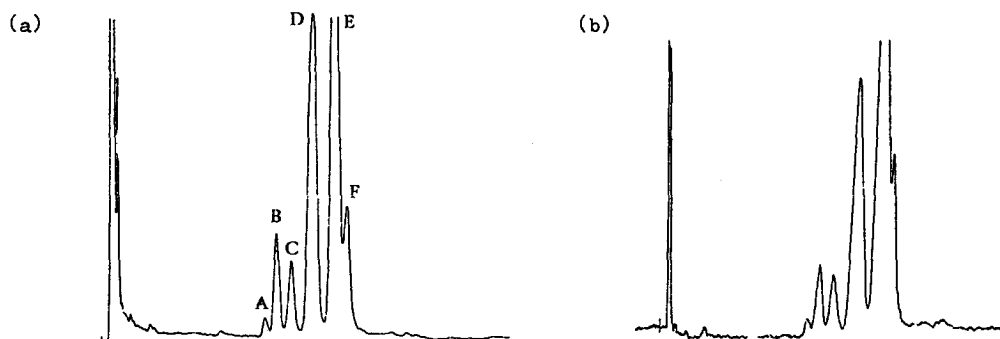


Fig. 2 a) EI and b) FI total ion current monitor traces of the TMS derivatives of the alkaloids from E. princeps

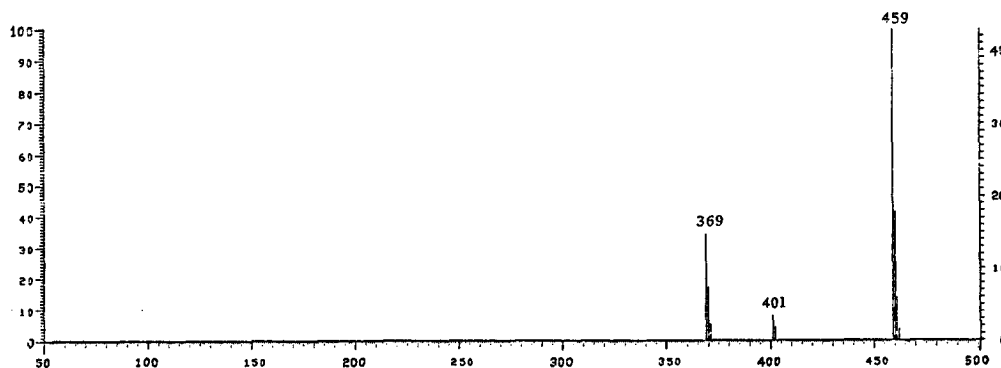
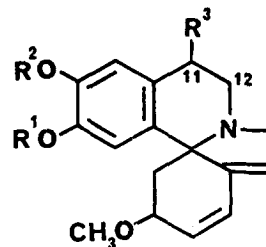


Fig. 3 FI spectrum of GC peak E (cf Fig. 2a)

Table 2 Structures tentatively assigned to the T.M.S. derivatives from E.princeps

G.C. Peak	Structure	Alkaloid
A	$R^1=R^2=TMS, R^3=H$	Erysopine
B	$R^1=Me, R^2=TMS, R^3=H$	Erysodine
C	$R^1=TMS, R^2=Me, R^3=H$	Erysovine
D	$R^1=Me, R^2=TMS, R^3=OTMS$ 11, 12 dehydro-B or C	New New
E	$R^1=TMS, R^2=Me, R^3=OTMS$ $R^1=Me, R^2=TMS, R^3=OMe$ 11, 12 dehydro-C or B	New New New
F	$R^1=TMS, R^2=Me, R^3=OMe$	New



Utilization of both EI and FI in the manner described enables an effective check to be made for possible decomposition on GC examination and of the homogeneity of GC peaks. More strikingly, the molecular weights of compounds which are amenable to GC/MS but give weak or insignificant molecular ions by EI can be readily and unambiguously ascertained by use of FI/GC/MS and Fig. 4 shows the EI and FI spectra recorded during combined GC/MS of a chemical degradation product of a naturally occurring terpene.⁷

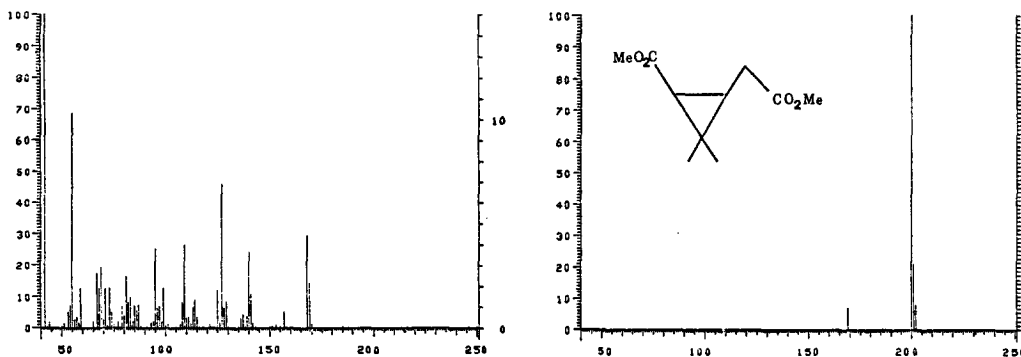


Fig. 4 EI and FI spectra of a terpene degradation product

Mass spectra were obtained in line diagram and mass list form (with background subtracted) using with a Varian 620i computer on line to a Varian CH5D mass spectrometer. FI measurements were carried out with a Varian combined EI/FI source using acetone activated emitters. Glass columns (3% OV1 or 3% OV17 on Gas Chrom Q) were used in the g.c. and coupling to the mass spectrometer was via a two-stage Watson-Biemann separator.

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