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ELECTRON-IMPACT MASS SPECTROMETRY OF NON-VOLATILE SUBSTANCES BY FAST HEATING

Daniel DESSORT, Alain VAN DORSSELAER, Song Jiu TIAN and Guy VINCENDON

Centre de Neurochimie du CNRS
5, Rue Blaise Pascal - 67084 STRASBOURG - France

Abstract Electron impact mass spectra of labile substances of low volatility can be obtained by introduction near the electron beam on a metal filament quickly heated at an optimal temperature, quasi-molecular ions (M+1) are observed No modification of the mass spectrometer is required

During the last ten years, significant progress has been achieved in the mass spectrometry of non-volatile and/or thermally unstable substances Various technical features were associated with fast heating of the sample, and it was impossible to disentangle the relative importance of the various factors Thus, Beuhler et al used chemical ionization (C I) and a rapidly heated Teflon support to obtain mass spectra of underivatized peptides, the sample being directly exposed to the ion plasma (1,2) Later, Hunt et al showed that, in field desorption/chemical ionization (F D /C I), rapid heating to a "best emitter temperature" (B.E T), first defined by stepwise heating, reduced thermal decomposition (3). Anderson et al used "balistic heating" of the sample (up to 1100°C in 0 1 sec) on a tungsten wire exposed to the ion plasma, underivatized peptides thus gave proton transfer mass spectra (4) Similarly, Arpino and Devant established that C I mass spectra of labile substances could be obtained by rapid heating on a tungsten wire directly exposed to the ion plasma (5) Daves, summarizing these methods in 1979, emphasized the constant rôle of rapid heating; however, all these results have been obtained by C.I., which usually produces few significant fragments, and by introducing the sample directly into the ion plasma of the C I source (6).

In fact, electron impact (E I) mass spectra can also be obtained by flash heating to 1100°C in the absence of a reactant gas, as has been shown by Anderson et al (7). However, this technique is of limited use, as the spectrum can be observed only transiently, during a fraction of a second, which requires photographic recording and therefore a Mattauch-Herzog geometry

We have now shown that it is possible to obtain excellent E I. spectra of various substances of low volatility by fast heating (∼ 0.1 sec) of the sample but only to about 200-500°C on a conventional desorption/chemical ionization (D/C.I.) probe in the absence of a reactant gas The substance (∼ 1 microgram) was deposited as a solution on metal filament of the D/C I. probe, after the solvent was evaporated, the sample was introduced into the ion source of a Finnigan 4000/INCOS quadrupole instrument, two experimental factors had to be optimized initially by trial and error : the position of the wire with respect to the ion beam (8), and the heating current, to obtain the best emitter temperature (3) At this temperature the compound was instantly volatilized. The scanning rate was about 1 a m u / msec , the source temperature 120°C and the electron energy 70 e V Under these conditions, excellent and reproducible E.I spectra, exhibiting pseudo-molecular ion, were obtained during about 1 sec., which is enough to register the complete spectrum Figures 1-8 show typical results, with important quasi-molecular (M+1) peaks as well as informative fragmentation patterns For Leucine-Enkephalin deposited on a tungsten filament (20 mm leng and 0 0035 inch diameter) the best emitter current was 600mA. With permethylated gramicidin-A (Fig. 8), the fragments observed are characteristic of the primary structure up to the limit of the quadrupole instrument (1024 a.m u), thus, this substance of M W 2174 was indeed well vaporized and ionized. In the mass range indicated, its spectrum is identical with the one obtained by Tian et al (9) using the gold wire technique described by Constantin et al (10,11)

Our results now suggest that the efficiency of this gold wire technique may lie, at least partly, in the fast heating of the support, due to its high thermal conductivity, when the geometry of the ion source is favorable. In fact, the gold wire technique was not operative with the Finnigan instrument, probably because of the different design of the ion source.

Anderson et al. (3) had used tungsten, rhenium or molybdenum supports for their flash heating Similarly, we have shown that the E.I. mass spectra obtained by our method are practically identical with platinum, tungsten, or more simply stainless steel filaments.

We are now exploring the mechanisms operating in the formation of the (M+1) ions, and the extension of this method to various mass spectrometers

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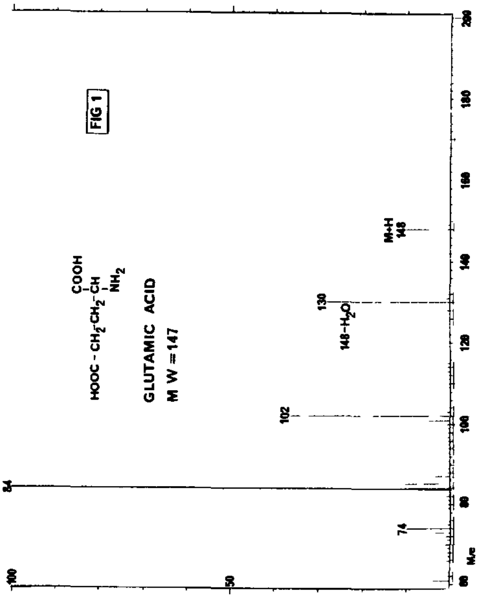
FIG 1

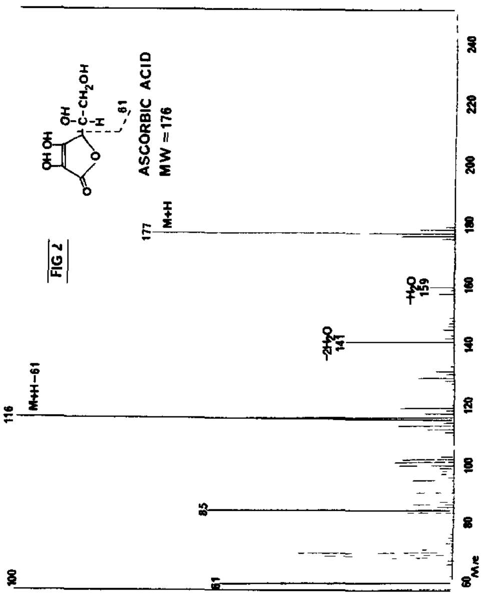
FIG 2

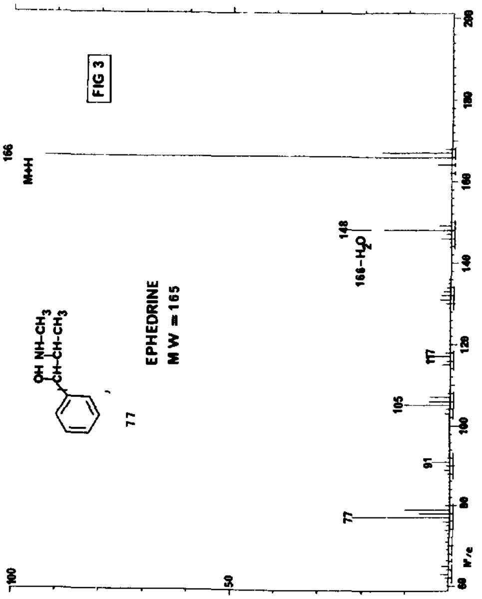
FIG 3

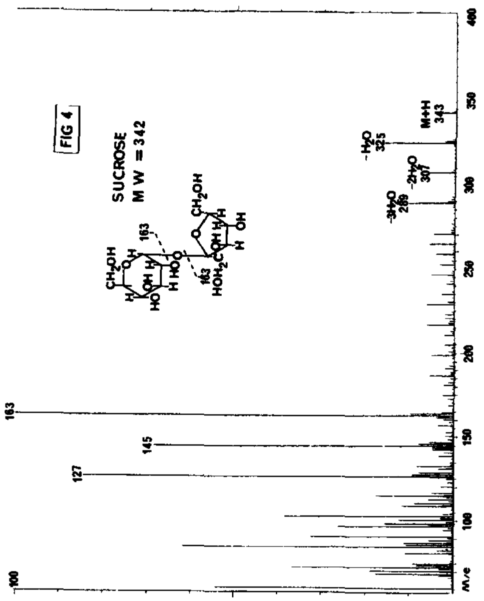
FIG 4

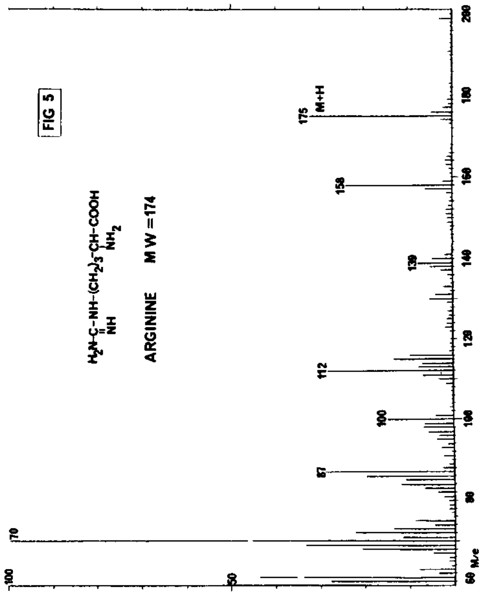

FIG 5

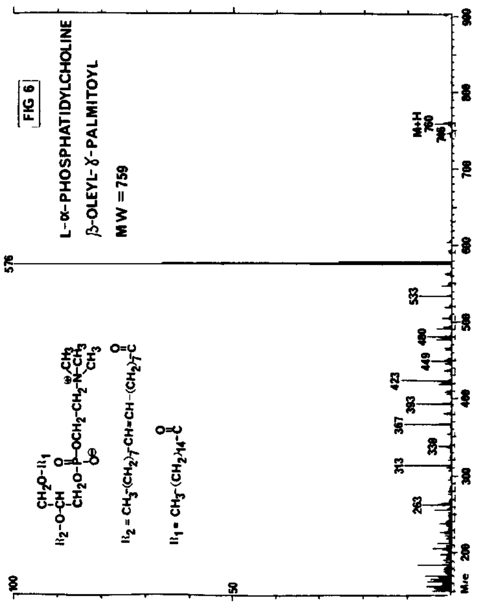

FIG 6

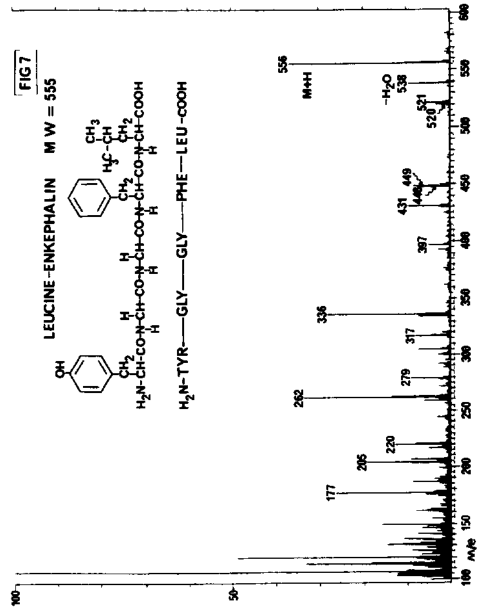

FIG 7

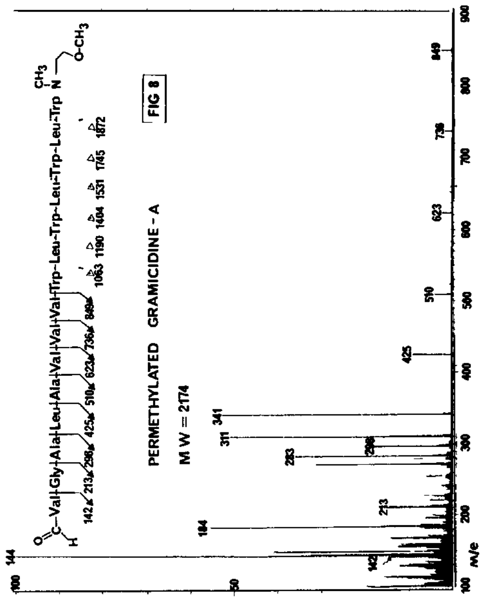

FIG 8

(Received in UK 18 January 1982)