A Combined Field Ionisation/Electron Impact Ion Source for High Molecular Weight Samples of Low Volatility

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A new combined field ionisation/electron impact ion source is described which can be used in connection with a direct inlet probe. The distance between the electron beam and the wire emitter is only one mm, so that the vapour of the sample reaches both ionizing zones. The vapour passes the ion source as a quasi molecular beam. Results obtained with this source will be given.

1. Construction of the source

1964 Beckey reported about a combined field ionisation/electron impact ion source\(^1\) the commercial version of which is shown in Fig. 1\(^2\). The vapour to be analyzed enters the source via an inlet line. However such inlet is suitable only for samples of not too low volatility. For the qualitative analysis of organic compounds of very low volatility evaporation out of an oven (direct inlet) in the immediate neighborhood of the ionization region is required. On principle, there are two possibilities to solve this problem for a combined field ionisation/electron impact ion source:

a) One uses the arrangement with two separate ionization regions as shown in Fig. 1. Then one must have two separate direct inlet systems, or one must make the direct inlet probe with the vacuum lock or the ion source movable.

b) The second possibility is to make the ionization region for field ionization to coincide with the one for electron impact ionization. Then one direct inlet only will suffice. This second possibility is the more elegant and more efficient. But some ion optical problems have to be solved.

We have realized this second possibility. The respective ion source is shown in Fig. 2. Electron beam and wire emitter are nearly at the same spot so that the vapour beam out of the oven can be ionized in both operating modes.

The first plate in the ion source functions in case of electron impact ionization as draw-out plate for the ions. In case of field ionization, a voltage of 6 to 10 kV is applied for generation of the required high electrical field.

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2. Measuring results

The stability of the ion current can be seen from Fig. 3: recorded is the ion current of the molecular peak of the cholesterol. The constancy is of the order of 1 per cent.

Fig. 3. Constancy of the ion current.

The maximum obtainable current is about $10^{-11}$ amps at the ion collector with field ionization.

A new direct inlet probe has been used for this measurements about which has been reported elsewhere $^3$. The mass spectrometer used was an ATLAS CH 4.

Fig. 4 a shows a spectrum of the d-ribose with a predominant molecular and m + 1 peak. It is well known that the electron impact spectrum (Fig. 4 b)

shows virtually no molecular peak, even at very low evaporation temperatures. The spectrum of Fig. 4 a is very similar to the one published by BECKEY $^1$.

Another typical example is tetradecanol (Fig. 5).

The molecular ion is very unstable: a small excess energy suffices to cause fragmentation. With electron impact ionization practically no molecular peak can be observed. Field ionization where no energy transfer to the molecule occurs again produces a very high molecular peak.

This example demonstrates also the possibility of differentiating between thermal decomposition of the sample and electron impact fragmentation if one uses exactly the same evaporation conditions in both ionizing modes: when there is a molecular peak in the field ionization spectrum, then thermal decomposition has necessarily not occurred, and the eventual absence of the molecular ion in the electron impact spectrum can only be due to unimolecular fragmentation as in the case of tetradecanol.

d-ribose and tetradecanol both represent compounds with very unstable molecular ions. In Fig. 6 the electron impact and field ionization spectra of the morphine molecule are shown. Because the molecular ion is rather stable in this case, both spectra differ not too much.

The spectra of an unstable high molecular weight compound, the cardenolid glycoside somalin are given in Fig. 7. The sample was again evaporated out of the oven in the immediate vicinity of the wire.

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Fig. 6. Upper part of the mass spectra of morphine: (a) field ionization, (b) electron impact ionization (70 eV).

emitter. For field ionization (Fig. 7 a) the molecular peak is by far the highest. The isotope peaks are not plotted because the resolution did not suffice for separation with field ionization. As well known there is a larger initial energy spread for field ionization than for electron impact ionization; thus, with single focusing instruments the resolution is limited to about 300. Double focusing instruments will show no reduction of resolution. Plotted in Fig. 7 b is a spectrum recorded with the same ion source but using electron impact ionization: the molecular is very small. Fig. 7 c shows a negative ion spectrum peak taken recently by ARDENNE, STEINFELDER and TÜMMLER 4 with an electron attachment ion source. Here, also, the molecular peak dominates but not as strongly as in the case of field ionization.