Field Desorption Mass Spectrometry. A Microanalytical Tool for Environmental Research, Biochemistry, and Medicine*

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With 12 Figures

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Mass spectrometry is a very sensitive, highly specific, and rapid analytical technique. With sample sizes in the microgram to picogram range it is possible to determine nominal or precise molecular weights and also to obtain structural information from the pattern of the fragment ions present in the mass spectrum. Because of these capabilities the mass spectrometric approach is frequently able to provide the decisive data in problems where other analytical methods fail to yield an unambiguous result.

The most severe limitation to the broad application of mass spectrometry in environmental research, biochemistry, and medicine is the requirement that the compound to be analysed should be convertible into free gaseous ions which can survive for the time interval between formation and detection, i.e. for the order of microseconds. In the classical electron impact (EI) mass spectrometric technique the substance must be vaporized under high-vacuum conditions into the ionization source of the mass spectrometer, where it is ionized by electron impact. This procedure produces good yields of positively charged ions but polar and thermally unstable compounds undergo thermal decomposition during the evaporation process or show intense fragmentation of the molecular ions.

generated. Consequently the analytically important molecular ions appear with low relative intensity in the mass spectrum or are even completely absent. Therefore, the development of new ionization techniques has always aimed at the generation of spectra showing few but structurally significant fragment ions and high relative intensities of molecular ions.

One approach to this end is ionization in the gas phase by more gentle processes such as low-energy electron impact, field ionization (FI), chemical ionization, and electron attachment. Another approach is direct ionization from the condensed phase, as has been achieved by field desorption (FD), electrohydrodynamic ionization, plasma desorption, and secondary-ion mass spectrometry.

Among these novel developments, FD-mass spectrometry is the technique which has found the most widespread application. The following is a description of the principles, practice, and application of field desorption mass spectrometry.

**Principles and Experimental Technique**

In field ionization as well as in field desorption the generation of positively charged ions occurs at an anode in an extremely high electric field of some $10^7$ V/cm. Achieving field strengths of this order requires surfaces having extremely small radii of curvature and a potential drop of some kV/mm. If the compound to be ionized reaches the field anode through the gas phase the technique is called field ionization. If the compound is directly applied to the field anode and therefore the sample supply during the measurement is maintained from the emitter surface, the ionization process is called field desorption. Fig. 1 shows schematically the set-up of the emitter and the counter-electrode in a field desorption ion source.

An ideal FD emitter should have a large surface area for the deposition of the sample as well as a large number of centres of high field strength for the production of ions. Very thin tungsten wires (10 μm diameter) covered with carbon microneedles have so far proved the best solution to this problem. Usually, the carbon microneedles are produced in a special high-temperature activation process. Fig. 2 shows the surface of such a high-temperature activated FD emitter at high magnification.

The positive ions are generated either by loss of an electron — leading to [M]$^+$ ions — or by attachment of a cation [Cat]$^+$ — leading to [M + Cat]$^+$ ions. These cations are preferably protons or metal cations such as alkali metal ions. With increasing polarity