

Field Desorption Mass Spectrometry

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A recent advance in the application of mass spectrometry to biomedical and environmental research has been the development of the field desorption ionization technique. Although its potential has not been fully realized, the simplicity of the field desorption (FD) spectra, and its applicability to a wide range of analytical problems that encompass a multitude of compounds from inorganic salts to polar metabolites has become its trademark. The growing use of this technique is amply demonstrated by the increasing number of publications, workshops, reviews, and books during the period 1971-78 (1-8, 16). In this brief report, the principles and analytical applications will be included for this important mass spectrometric technique.

Field desorption mass spectrometry's unique properties arise from the behavior of chemical compounds under high potential fields. When a high field is applied to an adsorbed organic layer on a metal surface, it experiences an electrostatic force similar to that on the plates of a charged condenser. If the metal surface (anode) has the proper geometry (sharp tip) and under high vacuum (10^{-8} torr), this force can be sufficient to eject particles as positive ions that can be analyzed via a mass spectrometer (Figure 1). This, in essence, is the basis for field desorption mass spectrometry. However, if the compound to be ionized reaches the anode via the gas phase instead of being surface applied, the process is called field ionization.

In comparison with other ionization techniques, the smaller amount of transferred energy in the FD process (~ 0.1 eV) increases the probability of detecting intact molecular ions. Thus, the salient feature of field desorption spectra is normally the predominance

of the molecular ion. Fragment ions can also be produced through thermal decomposition and field induced surface reactions.

Emitters

Early investigations by Müller on field ionization microscopy and Inghram and Gomer's subsequent work led H. D. Beckey to a systematic study of the parameters required for field desorption mass spectrometry of organic compounds (9-10). The intense electric fields (10^7 - 10^8 V/cm) necessary for field desorption are produced with positively charged emitters having at their surface multipoint needles of very great curvature (10^2 - 10^3 Å radii) on which an intense electric field is established.

Emitter Properties. It will be helpful in understanding the basis for obtaining field desorption spectra of organic compounds to consider the development and limitations of the emitters. Early in the development of this technique, several different emitter configurations were used such as thin metal blades, etched foils, and needle-sharp metal points (6). Sharp point emitters have the advantage over the other configurations in producing extremely high field strengths. The local microfield strength (F_0) at the tip of the microneedle, as defined by Speier et al. (11), is a function of the applied voltage (V), radius of curvature of the tip (r) as well as the distance to the counter electrode (d):

$$F_0 = V \left(\frac{1 - \alpha}{r \ln \frac{4d}{r}} + \frac{\alpha}{r} \right)$$

where α = shape factor = 0.006.

For an applied voltage of 5000 V and an electrode distance of ~ 2.3 mm,

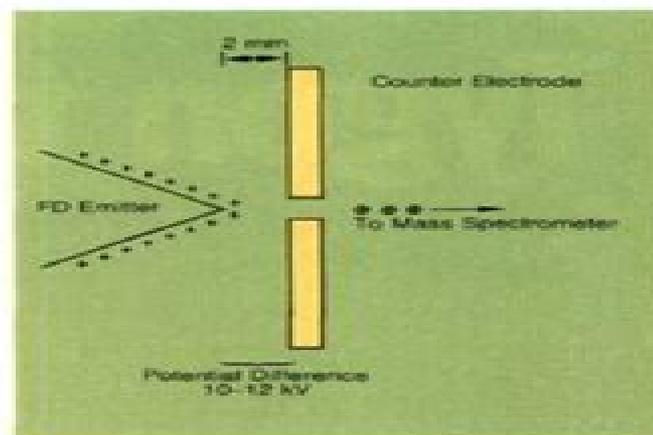


Figure 1. Simple model of field desorption microneedle ionization source

F_0 is 0.9 V/Å for a normally sharp tip of 10^3 Å radius. With increasing distance from the apex of the tip, the field strength decreases, but the area of equipotential field increases.

H. D. Beckey and colleagues (University of Bonn) have developed a procedure for growing multiple ("Christmas-tree") polymeric needles, using hexacarbonitrile, from the vapor phase on a fine tungsten wire (10 μ m) under the influence of high electric fields (12) (Figure 2). Subsequent in-situ high-temperature carbonization resulted in structurally strong carbonaceous needles with improved efficiency of ionization. Although similar dendritic needles of other types of materials such as permanganum, nickel, and other metals have been tried, these metal

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