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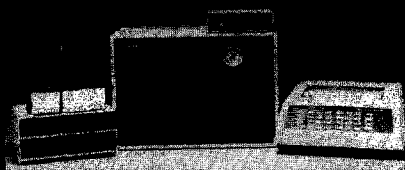
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niques have been used, however, where the aim is to enhance the production of molecular ions from larger, nonvolatile compounds. Such techniques are characterized by desorption of the sample within the source, in combination with a "soft" ionization method.

Schulten et al. (72) have used *laser-assisted field desorption* for the mass spectral analysis of chlorophyll-a. A 10^4 -W/cm² argon ion laser, with the beam focused on a 10- μ m activated emitter, replaces conventional emitter current heating. Higher sensitivity and longer emitter wire life are the results.

In the strictest sense, *chemical ionization* involves the use of a reagent gas at high pressure (e.g., 1–4 torr of isobutane) containing reagent ions produced by EI. Using that definition, *laser desorption chemical ionization* mass spectra of several steroid glucuronides have been obtained (58). The method has the further advantage that collisions of the sample molecules in the high-pressure source extend the analysis time following a short (10-ns) laser pulse to several milliseconds, so that rapid accelerating voltage scanning can be accomplished on sector instruments (58). Reagent ions can, however, be produced from the solid phase. Cooks et al. deposited samples doped with ammonium chloride on silver foils for laser desorption. The spectra yielded mainly $(M + Ag)^+$ ions, while the vaporization of ammonia in the source has a similar effect in extending the analysis time (73). In the negative-ion mode, Hercules et al. (74) have used reagent compounds containing the nitro group to produce $(M - H + O)^-$ ions of several aromatic compounds. In the most general sense, cationization of any kind might be viewed as laser desorption chemical ionization, particularly in those cases where a gas phase ion-molecule process can be invoked (65). The combination techniques are important in view of the abundance of neutral species that are desorbed, and one can expect to see additions of other reagent materials to enhance their ionization in future work.

Summary

As analytical methods, many of the laser-MS techniques described here might be considered as still in the development-demonstration stage, which is of course an exciting one.

The multiphoton techniques, using small molecules for which there is already a wealth of spectroscopic information, are more easily understood perhaps than the desorption methods, where secondary ion yield studies for laser and particle beams have not yet fully described the desorption of very