Fast Atom Bombardment Quadrupole Mass Spectrometry

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Summary Fast atom bombardment quadrupole mass spectrometry (F.A.B.Q.M.S.) is shown to have considerable benefit for the production of structural mass spectral data from non-volatile organic compounds.

THE development of F.A.B.Q.M.S. has enabled structural mass spectral data to be obtained *directly* from *solid* organic compounds. The technique can therefore have considerable benefit in the mass spectral analysis of large non-volatile organic molecules, particularly those of biological interest.

The technique has been developed in this laboratory and is a modified form of static secondary ion mass spectrometry (S.S.I.M.S.), which has been applied to the analysis of organic compounds.[1-3] Ion beam bombardment leads to a build-up of charge on insulating samples and consequently the secondary ion mass spectrum is lost. This problem is usually circumvented in organic analysis by evaporating a *very thin* layer of the organic compound to be analysed on to a metallic substrate. However, if the layer is not very thin charging may continue to occur. Furthermore the technique results in short sample lifetime and spectral interference from the substrate. In F.A.B.Q.M.S. the primary ion beam of S.S.I.M.S. is replaced by a fast atom beam of Ar, generated by charge neutralisation of an Ar^+ ion beam. This prevents charge build up on the surface of the sample, and as a result analysis may be carried out directly on the solid compound in the form of a pellet, crystal, or powder.

In this study a preliminary investigation has been carried out using a series of amino-acids, typical of molecules of biological importance. Two typical F.A.B.M.S. spectra are shown in Figures 1 and 2 for L-histidine and L-arginine. They were obtained from the compounds in powder form. Attempts were made to obtain mass spectra using ion bombardment. There was an initial burst of secondary ions which died away rapidly to a very low and unstable level inconsistent with the recording of satisfactory spectra. One of the significant features of this type of mass spectrometry is the observation of a pseudo-molecular ion at an

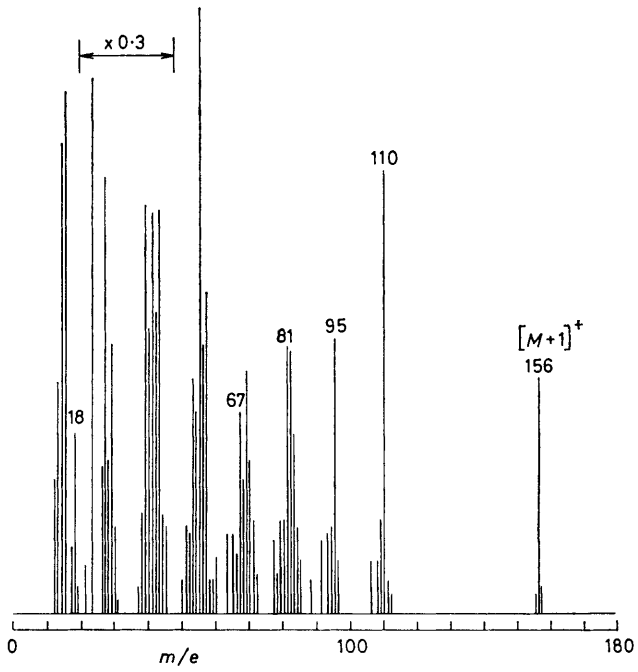

FIGURE 1. Spectrum of L-histidine obtained by fast atom bombardment of the solid.

m/e value of $M + 1$ (M = molecular weight). A similar species is obtained with chemical ionisation (C.I.) mass spectrometry; however, unlike C.I.M.S. a considerable amount of structural information is also available using F.A.B.Q.M.S. The most significant fragments in Figures 1 and 2 have been identified. The fragmentations seem to be simply derived from the molecular species, although plausible fragmentation pathways can be derived from the $[M + 1]^+$ ion.

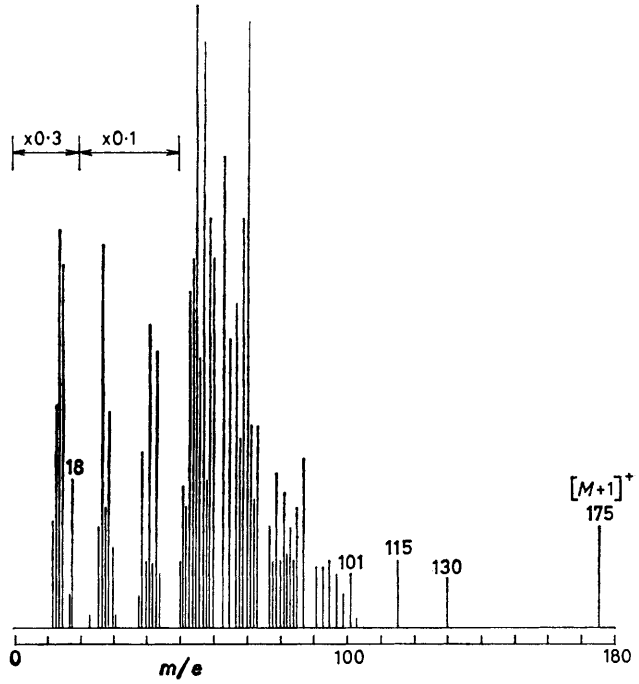

FIGURE 2. Spectrum of L-arginine obtained by fast atom bombardment of the solid.

It has been found that for all the amino-acids studied so far, the first major fragment peak occurs at an *m/e* value equivalent to that of the species $[M-COOH]^+$. Subsequent fragmentation usually involves the loss of the NH_2 group, followed by a systematic fragmentation of the molecule. In general for these amino-acids the relative intensity of the $[M + 1]^+$ peak is almost one third that of the $[M-COOH]^+$ species, which is often the most intense. This relative intensity is much higher than that usually obtained using conventional mass spectrometry techniques, and illustrates the potential importance of F.A.B.Q.M.S. as an analytical tool for this type of sample. A second feature of the spectra obtained so far is the presence of a peak with an *m/e* value of 18. This has been ascribed to the NH_4^+ ion, and may arise following further protonation of the $-NH_3^+$ group which exists in the ionic form of amino-acids. This protonation would result in the formation of the $[M + 1]^+$ species, as the resulting molecule would have an overall single positive charge. Protonation may occur *via* a similar mechanism to that recently proposed for the long-range proton transfer observed with steroidal diamines.[4] In our case the proton transfer may occur in the surface region as a consequence of the emission process.

The technique of F.A.B.M.S. was initially developed here by Vickerman, Bordoli, and Barber jointly using the present quadrupole mass spectrometer. A quadrupole analyser is not essential and Sedgwick and Barber describe elsewhere the exploitation of the technique with a double-focusing magnetic mass-spectrometer.

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