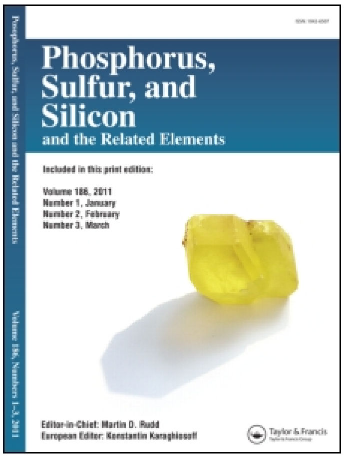

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Fast Atom Bombardment Mass Spectrometry of Organophosphorus Compounds

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Fast Atom Bombardment Mass Spectrometry of Organophosphorus Compounds

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Fast atom bombardment mass spectrometry has been applied to a range of ionic, zwitterionic, and thermally labile organophosphorus compounds and has been shown to be a potentially valuable aid to identification and characterisation. Results are presented for the positive ion spectra of quasiphosphonium salts, aminophosphonic, aminophosphonous, and aminophosphinic acids, phosphonopeptides, and a number of heat sensitive derivatives. The quasiphosphonium intermediates derived from alkyl esters of phosphorus (III) acids and halogeno compounds generally show base peaks corresponding to the phosphonium ion which fragments to give the protonated form of the Arbuzov product. Strong characteristic peaks are also obtained from various phosphonic and phosphinic derivatives. α- and ω-aminoalkanephosphonic acids and their guanidino analogues give base peaks corresponding to $[M+H]^+$ ions and show simple fragmentations arising mainly from the loss of HPO_3 and H_3PO_3. Phosphonous derivatives give peaks corresponding to $[M+H]^+$ and $[2M+H]^+$ with the base peak apparently resulting from the elimination of HPO_3 from the dimeric structure. Elimination of H_3PO_2 is also indicated. Examples of phosphonopeptides are also shown to give base peaks at $[M+H]^+$ and to exhibit characteristic fragmentations that are of potential value as aids to identification. Fast atom bombardment mass spectra have also been recorded for a number of pesticidal phosphorodithioates, their principal metabolites, and some related esters. Although $[M+H]^+$ peaks are clearly present in all cases, the intensity is variable and fragmentations are generally more complex than those obtained for the compounds referred to above. O,O-Diethyl phosphorodithioates, for example, frequently give rise to $(EtO)_2PS^+$, which fragments further by stepwise elimination of ethylene as is also observed in electron impact mass spectrometry. We are grateful to SERC for support of this work and for FAB mass spectrometry facilities at the Physico-Chemical Measurements Unit, Harwell.