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In the past 30 years, mass spectrometry (MS) has undergone a spectacular development, in terms of both its technological innovation and its extent of application. On-line liquid chromatography–mass spectrometry (LC–MS) has become a routine analytical tool, important in many application areas. The introduction of electrospray ionization (ESI) and matrix-assisted laser desorption/ionization (MALDI) has enabled the MS analysis of highly polar and large molecules, including biomacromolecules. MS is based on the generation of gas-phase analyte ions, the separation of these ions according to their