New Developments of Laser Desorption Ionization Mass Spectrometry in Natural Products Research

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Résumé en anglais	Mass spectrometry (MS) represents an indispensable tool for the structural identification of natural products (NPs) and is one of the major focus areas of analytical chemistry research. The technique has long been used to obtain molecular weights and further molecular formulae. In the past, former ionization sources such as electronic impact (EI) limited MS analysis to predominately volatile, polar, and thermostable compounds. However, the development of soft ionization techniques such as electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and laser desorption/ionization (LDI) have gradually extended the scope of MS analysis to a much wider range of chemical entities. Moreover, the hyphenation of liquid and gas chromatography with MS (LC-MS, GC-MS) has provided a most powerful tool for the analysis of complex mixtures and NPs. In fact, LC-MS is often considered as a method of first choice particularly when studying complex mixtures of small molecules. On the other hand, recent developments in matrix-assisted laser desorption/ionization (MALDI) and LDI may provide useful supplements and potential alternatives to this approach. Both methods share similar, though slightly different ionization mechanisms. While MALDI uses small molecules comprising strong UV chromophores (matrices) to transfer laser energy to the sample material, LDI targets compounds that can be directly ionized by laser irradiation without any matrix support. Moreover, certain compounds showing LDI properties may also work as MALDI matrices. With regard to NPs research, MALDI and LDI may help overcoming certain limitations encountered in LC-MS such as the indispensable use of buffer solutions when analyzing alkaloids. Moreover, as (MA)LDI hardly requires any sample conditioning, analysis time can be significantly shortened. With all this in mind, the subsequent article will highlight some interesting MALDI and LDI applications, which focus on the detection of NPs in complex mixtures. This includes the use of specifically adapted matrices for the selective detection of alkaloids (i), the study of the inherent LDI and matrix properties of phenolic compounds (ii) as well of evaluation on the reproducibility of LDI signal patterns (iii). Eventually, a statistical approach toward LDI profiling, which may provide a future tool for quality control of large sample batches will be presented (iv).
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