13 Ambient Mass Spectrometry

Learning Objectives

- Ion formation under ambient conditions
- Interfaces for ambient mass spectrometry
- Screening techniques for rapid quality control and safety applications
- Real time examination of samples during physical manipulation

All methods for the generation of ions for mass spectrometry described up to this point require the analyte for ionization to be presented either directly under high vacuum (EI, CI, FI, FD) or contained in a sort of solution from which ions are to be extracted into or generated in the gas phase (FAB, LDI, MALDI). Even the atmospheric pressure ionization techniques employ processes that create ions from dilute (solid) solutions of the sample (ESI, APCI, APPI, AP-MALDI). This chapter deals with the manifold methods and interfaces which are allowing to overcome these limitations, and which have developed at a breathtaking pace within the short time since the publication of the first edition of this book.

Desorption electrospray ionization (DESI) [1] was introduced at the end of 2004, and direct analysis in real time (DART) [2] soon after in 2005. The apparent potential of both DESI and DART in high-throughput applications soon led to the development of some “derivatives” with the intention to broaden the field of applications or to adapt the underlying methodology to specific analytical needs. Now, the repertoire of methods includes variations of the DESI theme such as desorption sonic spray ionization (DeSSI) [3], later renamed easy sonic spray ionization (EASI) [4] or extractive electrospray ionization (EESI) [5,6]. Then, there are the DESI analogs of APCI and APPI, i.e., desorption atmospheric-pressure chemical ionization (DAPCI) [7,8] and desorption atmospheric pressure photoionization (DAPPI) [9].

All these methods have one important characteristic in common: they direct a stream of ionizing or at least ion-desorbing fluid medium onto a sample surface from which analyte ions are withdrawn and transported through air into the mass analyzer via a standard API interface. The beauty of this approach lies in the fact that a sample needs just to be exposed to the ionizing medium under ambient conditions. In other words, DESI, DART and those numerous related methods enable the detection of surface materials like waxes, alkaloids, flavors, or pesticides from plants as well as explosives, pharmaceuticals, or drugs of abuse from luggage or banknotes. These and many more analytical applications are readily accessible by...
plainly exposing the corresponding items to the ionization region of the interface – even without harm to living organisms [10]. This reduced need for sample pre-treatment is key to the success of ambient MS. In ambient MS, samples are accessible to observation and may even be subjected to some kind of processing, either mechanical manipulations or chemical treatments, while mass spectra are continuously being measured. Recently, a fieldable ion trap mass spectrometer for use with commercial DESI and DART ion sources has been constructed [11].

**Note:** Although the features of DESI and DART are in many ways superior and “revolutionary”, one should be aware of intrinsic limitations. The detection of a compound largely depends on the matrix, e.g., whether it is on or eventually in skin, fruit, bark, stone etc. This also results in a lack of quantification abilities. However, also no other single ionization method, especially when used under just one set of conditions, can deliver ions of all constituents of a complex sample. Nonetheless, DESI, DART and related methods can deliver a wealth of chemical information with unprecedented ease.

### 13.1 Desorption Electrospray Ionization

The novel feature of desorption electrospray ionization (DESI) is that it allows ambient MS without sample preparation or sample pre-treatment. Furthermore, “ambient” means here not only the mere operation at atmospheric pressure, e.g., as is the case with AP-MALDI, but the operation in a freely accessible open space in front of the atmospheric pressure interface [12]. DESI is applicable to solids, liquid samples, frozen solutions, and to loosely surface-bound species like adsorbed gases. It can detect low-molecular-weight organic compounds as well as comparatively large biomolecules. The material presented to DESI may be a single compound suitably prepared on a sample target analogous to LDI or it can be a complex biological material like tissue, blood, whole leaves, or fruit [13].

**Note:** Although it appears that the results of DESI analyses are almost instantaneously available, DESI spectra tend to require more thorough examination than standard ESI spectra in order to draw the right analytical conclusions.

#### 13.1.1 Experimental Setup for DESI

In a standard ESI experiment the spray capillary is set to high voltage in respect to a counter electrode that is essentially represented by the atmospheric pressure entrance of the interface. Sample ions are already contained in the solution that is supplied to the sprayer (Chap. 12). For desorption electrospray, only a solvent or solvent mixture is sprayed under strong pneumatic assistance onto a surface at an impact angle $\alpha$. Driven by the high-velocity gas stream, the highly charged microdroplets receive sufficient kinetic energy to be forced onto the sample surface.