

can be fed to the mass spectrometer separated according to their mobility, ions of selected mobilities can be fragmented by this method in suitable mass spectrometers, allowing measurement of fragment ion spectra of ion species separated according to their mobility and mass.

[0029] These methods result in a surprisingly good mobility resolution which, according to all current knowledge on mobility separation principles, would not be expected. According to initial, still very rough experiments, the mobility resolution is in the region of better than $R_{mob}=35$; much higher mobility resolutions seem achievable. Also surprisingly, gas jets produced by pressure differences of below a few tens of pascals or lower can be used advantageously.

[0030] The ion guides here serve to canalize the ions to the field maximum of the potential barrier in such a way that their lateral spread is limited. For higher potential barriers, i.e. for stronger opposing fields, a stronger lateral guidance of the ions to the field barrier can be achieved by increasing the RF voltage at the ion guide synchronously with the potential barrier. Instead of increasing the RF voltage, its frequency can be decreased.

[0031] Some mass spectrometers already contain ion funnels or other suitable ion guides and also differential pumping systems, so it is possible to implement such a measuring station for ion mobilities in these mass spectrometers without much development effort.

[0032] The field barrier can be either a DC barrier or the barrier of a pseudopotential. The barrier can be increased or decreased continuously or incrementally to acquire the integrals over the mobility spectra.

[0033] The ion guide can be a multipole rod system, a system of diaphragms with apertures, or an ion funnel, all operated with RF voltages. But it can also be an ion-optical lens system to which only DC voltages are applied. In order to hinder the gas jet as little as possible, the pole rods or diaphragms can have special shapes which conduct the gas outside the gas jet as efficiently as possible to the pumps without disturbing the gas jet between nozzle and field barrier.

[0034] The methods and apparatus according to the invention achieve an unexpectedly good mobility resolution. One reason for the high mobility resolution is probably that the gas jet in the vicinity of the field barrier has the same velocity everywhere, i.e. it does not have a parabolic velocity profile as in publication WO 2004/109741 A2. A favorable design of the field barrier in the radial direction also contributes to the high mobility resolution. A further reason is the almost complete absence of diffusion broadening of the ion signals. Any diffusion of ions inside the gas before the barrier has no effect. After crossing the barrier, the now sorted ions should be fed as quickly as possible to the ion detector or the mass analyzer in order to keep the diffusion low. The temperature of the adiabatically cooled gas jet is very low in the critical region of the barrier and from there to the ion detector or mass spectrometer, which greatly reduces the diffusion.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] FIG. 1 schematically represents an ion mobility spectrometer according to this invention, with an electrospray ion source (1, 2) outside the vacuum system, an inlet capillary (3) for curtain gas and ions, two ion funnels (5, 8), an ion detector (21) and a differential pumping system (22, 23, 24). Passing the nozzle (6) at the end of the first ion funnel (5), the gas expands adiabatically into the vacuum chamber (7) of the second pumping stage, forming the gas jet (27). The apertures

of the diaphragms of the second ion funnel (8) have skimmers which guide the impinging gas of the outer regions of the gas jet (27) to the outside in order to maintain an unhindered gas jet inside the ion funnel (8). The ions are canalized inside the gas jet (27) by the second ion funnel (8) and transmitted virtually without any losses to the field barrier at the ring diaphragm (9). The ions are propelled by the gas jet (27). To acquire mobility spectra, the DC electric potential at the ring diaphragm (9) at the end of the second ion funnel (8) is increased continuously or incrementally, resulting in more and more ions from the ion current of the ion source being repelled due to their then excessive mobility, and thus filtered out. The integral of the mobility spectrum of the ions under investigation is thus measured at the detector (21). Differentiation provides the mobility spectrum.

[0036] FIG. 2 is a schematic representation of an orthogonal time-of-flight mass spectrometer (OTOF) with an electrospray ion source which contains the mobility spectrometer elements shown in FIG. 1. With the OTOF, mobility spectra for the individual ion species can be measured.

[0037] FIG. 3 shows the curves of the integral ion currents for a mixture of the doubly charged ions of bradykinin and angiotensin II, and the singly charged ions of the peptide Gly-Arg-Gly-Asp-Ser, plotted against the voltage at the ring diaphragm (9) of FIG. 2. The ion currents were extracted from a series of mass spectra which were acquired by incrementally increasing the potential barrier at the ring diaphragm (9).

[0038] FIG. 4 was derived by differentiating the integral curves from FIG. 3, and shows the mobility spectra of these three ion species. Despite the coarse incremental steps selected for the potential barrier and despite little optimization work, the mobility resolution is in the medium range above $R_{mob}=35$. The singly charged peptide exhibits a mixture of two different conformational forms, which differ in their mobility.

[0039] FIG. 5 shows the mobility spectra of a series of polyethylene glycoles (PEG 400), which differ not only in their mass, but also in increasing collision cross sections of the molecules and thus in their mobilities. The ions in the maximum of the distribution have a mass of 437 daltons.

[0040] FIG. 6 presents a rough scheme of a most simple ion mobility spectrometer. The arrangement (1, 2) symbolizes a usual electrospray unit comprising spray capillary, housing, curtain gas supply, and electrode arrangement to draw a large part of the ions into the nozzle (6) which is used here instead of an entrance capillary. Nozzle (6) is a tiny Laval nozzle with only a few micrometers diameter at the narrowest part, sucking a few liters of curtain gas per minute and generating a supersonic jet (27) directed into the pump chamber (23), where the overwhelming part of the jet is completely absorbed by a turbomolecular pump. At the exit of the Laval nozzle (6), all molecules of the jet have the same velocity. A voltage at the ring electrode (28) generates a field barrier directly at the exit of nozzle (6). The field barrier holds back all ions in the curtain gas not having sufficiently low mobility, and these ions are necessarily discharged at the inner surfaces of the Laval nozzle (6). The passing ions (34) are accelerated by a second ring electrode (37) towards the detector system, comprising a conversion dynode (35) and a channeltron plate secondary electron multiplier (21). The ions (34) generate electrons at the conversion dynode (35), and the electrons (36) are accelerated towards the detector (21).

[0041] FIG. 7 exhibits another simple arrangement for an ion mobility spectrometer according to this invention without