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Atmospheric pressure MALDI

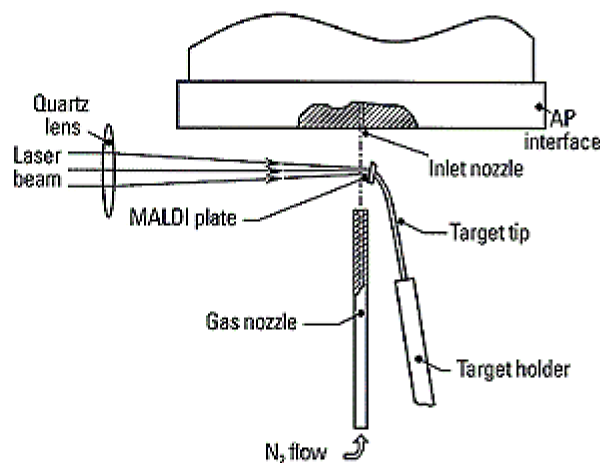
Electrospray ionization (ESI) and MALDI are not usually interchangeable—ESI is carried out at atmospheric pressure, whereas MALDI sources operate under a vacuum. As a result, two different mass spectrometers are needed to perform ESI and MALDI MS analyses. But that may soon be a thing of the past.

In the February 15 issue of *Analytical Chemistry* (pp 652–657), Alma L. Burlingame, Victor V. Laiko, and Michael A. Baldwin of the University of California–San Francisco describe a new ionization source for MS that combines MALDI and atmospheric pressure ionization. Although the source can operate without auxiliary gas flow, the sensitivity and stability are enhanced when ion transfer from atmospheric pressure to the high vacuum region is pneumatically assisted by a stream of nitrogen.

The atmospheric pressure (AP) MALDI source can be used with any mass spectrometer that has an atmospheric pressure interface; however, for biopolymer applications, the researchers chose to interface it with a commercially available orthogonal acceleration time-of-flight (oaTOF) system because of its high sensitivity and extended mass scale. A pneumatically assisted ESI source was simply replaced with the home-built AP MALDI source, says Burlingame. The ESI and AP MALDI sources are readily interchangeable and can be switched in a matter of minutes, he says.

For complex mixtures, such as a protein digest, it may be necessary to use both ESI and MALDI to find all of the components. “The components you see in MALDI are dependent to a large extent on the matrix you select,” says Burlingame. “In ESI, if you don’t separate the mixture, you tend to see a suite of components, some of which overlap with MALDI, some of which do not. By using both techniques, you have a higher probability of finding all the components,” he says.

AP MALDI and conventional vacuum MALDI have many similarities—they use the same matrixes, the same matrix-to-analyte proportions, and the same sample preparation procedures. But how does their performance compare? It turns out that AP MALDI is a softer ionization technique than vacuum MALDI, says Burlingame. And that might be a long-term advantage, he says. “Using [AP MALDI] we were able to see sulfated material in the positive ion mode. You can see sulfate in the negative ion mode with other instruments, but it is always eliminated in the positive mode,” he explains. This could be good news for researchers interested in labile protein and carbohydrate posttranslational modifications. “There are a lot of labile structures that people do not bother with because they tend to fall off no matter what you do. Sulfate is just one example. [AP MALDI] may play a significant role in that area,” he says.



Pneumatically assisted, atmospheric pressure MALDI source.

As a soft ionization technique, AP MALDI has the potential to produce intact protein molecular ions. However, in actuality, the softness causes abnormally high levels of analyte–matrix cluster ions. The extent of cluster ion formation depends on the chemical nature of the analyte. Heavier analyte molecules, such as proteins, produce stronger cluster ions, resulting in decreased sensitivity. According to the researchers, it may be possible to eliminate cluster ions by trying other matrixes commonly used in vacuum MALDI or by searching for new matrixes specific to AP MALDI.

One of the major limitations of AP MALDI in its current setup is low ion-transfer efficiency. To compensate for the loss of ions at the interface, more sample is consumed than in vacuum MALDI. But Burlingame is optimistic that the ion-transfer efficiency can be improved. Newer oaTOF mass spectrometers with more powerful pumping systems, which would allow larger nozzle and skimmer orifices, have already hit the market. The ion-transfer efficiency might be substantially improved by interfacing AP MALDI with one of these newer systems, he says.

Although AP MALDI consumes nearly all of the analyte, this may not be so bad because it lends itself to automation. Rather than

focusing the laser beam on a particular spot, as is done in vacuum MALDI, the laser beam could be rastered across the entire sample. Multiple matrix crystals would contribute to the final spectrum, making it relatively independent of sample preparation. With high-throughput sample handling and analysis becoming more and more essential in biological MS, especially for areas such as proteomics, this could turn out to be a real advantage. *Britt Erickson*

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