

AP MALDI Performance on a Hybrid Quadrupole – Linear Ion Trap (QqLIT) Instrument

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AP MALDI¹ is a technique that has gained increased acceptance over the past few years. Although the mechanism of ion formation differs from that of electrospray, the principals for ion transport from atmosphere to vacuum are similar. AP MALDI generates ions and matrix clusters within the atmospheric pressure ion source. Matrix clusters contribute to background and contamination, so it is desirable to efficiently desolvate ions prior to transport into the vacuum system of a mass spectrometer. A nanoflow electrospray atmosphere – vacuum interface has been modified for sampling ions generated with an AP MALDI ion source. The particle discriminator interface (PDI)² is ideally suited for this application because it provides multiple stages of desolvation and unwanted residual particle removal as shown in Figure 1.

Optimization of the PDI for MALDI ions requires the laminar flow chamber to be elongated so that its entrance can be positioned in close proximity to the sample target plate. In order to keep the chamber as short as possible (3.3 cm), the source optics flange was redesigned. With the new configuration, the distance between the target plate and laminar flow chamber entrance was approximately 3 mm.

The inner diameter of the laminar flow chamber was increased from 1 mm to 2 mm to more efficiently capture the plume generated from the target surface. With this configuration, the optimum temperature was approximately 200° C for the heated chamber. A cool nitrogen bath gas was used to prevent target plate heating with this configuration. Target plate heating by a hot curtain gas was detrimental to performance, resulting in thermal degradation of some samples.

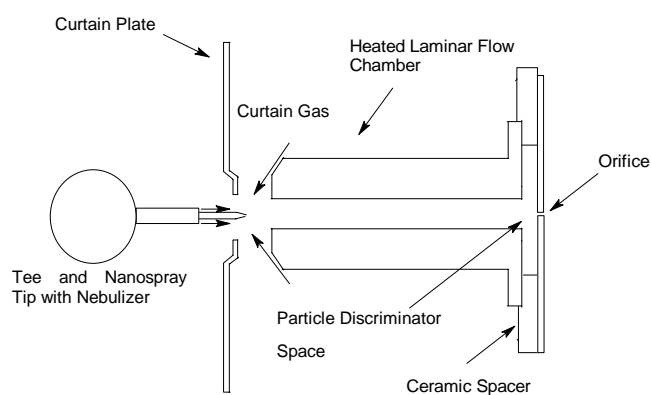


Figure 1. Particle Discriminator Interface

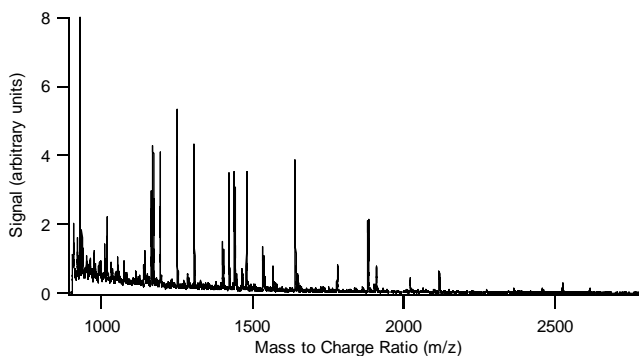


Figure 2. 1 Minute Acquisition of Data for 5 fmol BSA Digest

The AP MALDI source was operated using a 10 Hz nitrogen LASER with a 200 μm optical fiber. Figure 2 shows average data acquired for a 5 fmol deposit of bovine serum albumin (BSA) digest. These data correspond to a 1 minute acquisition with the sum of approximately 92 measurements. The LASER repetition rate was 10 Hz and the trap fill time was 150 ms, corresponding to approximately 1 pulse per trap fill. Figure 2 shows many of the known peptides from BSA digests, including m/z 927.5, 1163.6, 1168.5, 1193.6, 1249.6, 1283.7, 1305.7, 1420.7, 1439.8, 1479.8, 1534.7, 1577.8, 1639.9, 1881.9, 1908.9, 2020.9, 2116.8, and 2459.2. With this system, it was possible to generate MS data at the subfemtomole level for a variety of protein digests.

One of the key advantages with an AP MALDI system based upon the 4000 QTRAP is the ability to generate MS/MS data at low levels. The QqLIT design of this instrument makes it possible to fill the linear ion trap selectively with fragment ions of a given m/z. This translates directly into very low limits of detection in MS/MS mode. Table 1 shows MASCOT search results generated for MS/MS of a single 500 amol deposit of bovine catalase digest.

Peptide Ion (m/z)	Score	Rank
1046.5	18	1
1119.6	22	1
1407.6	14	1
1479.7	16	1

Table 1. MASCOT search results for MS/MS of 500 amol bovine catalase digest.

As shown in Table 1, a series of MS/MS experiments generated from a single sample spot resulted in successful identification of 4 peptides, with a total score of 70 and 8% sequence coverage at the 500 amol level. These data were acquired over the course of approximately 8 – 10 minutes, and the limitation to identification of more peptides was sample depletion in the target spot.

The AP MALDI source provides rapid interchangeability between MALDI and nanoflow ESI on this system. Conversion time from one source to the other is on the order of 10 minutes, making it feasible to utilize the complementary nature of the 2 ion sources to improve sequence coverage for digests.

References:

1. Laiko VV, Baldwin MA, Burlingame AL, *Anal. Chem.*, **2000**, 72, 652-657.
2. Schneider BB, Baranov VI, Javaheri H, Covey TR, *J. Am. Soc. Mass Spectrom.*, 2003, 14, 1236-1246.