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Selective Background Suppression Using a Pulsed Bipolar Electrostatic Particle Guide

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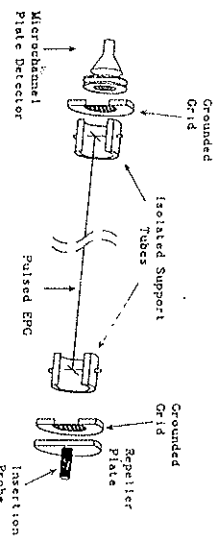
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Time of flight mass spectrometry (TOF-MS) has come to the forefront in high mass analysis due to the high sensitivity and extended mass range that characterize the instruments (1, 2, 3). Although the sensitivity and mass range are strong arguments for the use of MALDI-TOF, the spectra are complicated by the high intensity background peaks resulting from the matrix. This high intensity background results in both limitations in resolution and detector response, reducing the effectiveness of the technique for high molecular weight biomolecule analysis.

Microchannel plate (MCP) detectors are ideally suited for high sensitivity applications due to the rapid response coupled with a very high gain (2, 4). However, these same characteristics make the MCP detectors susceptible to saturation resulting from the low mass ion component in the MALDI spectrum. An individual channel of the microchannel plate array becomes saturated following generation of the electron cascade and a recovery of up to several milliseconds is required before the channel is restored to an active state. Because a large component of the ion flux in MALDI is comprised of low mass ions ($m/z < 300$), early saturation of the detector occurs frequently, resulting in a reduced capacity to detect high mass ions (2).

An alternate approach to background reduction has been based on an electrostatic particle guide (EPG). The EPG is an isolated wire electrode that spans the length of the flight tube, creating a potential field in the center which effectively "guides" ions to the detector (5, 6). The ability to apply pulsed positive and negative voltages on the EPG allows one to combine the deflection capability of pulsed plates with the transport capability of an EPG that traverses the full length of the flight region. The bipolar pulsed EPG not only deflects undesired ions away from the detector, but recaptures divergent high molecular weight ions into a spiral orbit back toward the detector. This mode of operation permits the selective elimination of low mass ions by operating the bipolar pulsed EPG as a high pass filter.

Mass spectra were obtained on a prototype MALDI-TOF mass spectrometer built at the University of Northern Iowa. The electrostatic particle guide consisted of a 0.25 mm diameter stainless steel wire suspended down the center of the flight tube (Figure 1). The wire (180 cm long) was supported by cross-hair wires anchored in a small section of an isolated 76 cm diameter tube located 10 cm downstream from the ion source and terminated 5 cm prior to a grounded grid. The cross-hair support for the EPG near the ion source was moved 5mm off axis to introduce a small component of angular velocity into the ion trajectories to reduce ion loss by collision with the wire. A second meshable repeller grid was maintained at a ground potential (relative to the flight tube) so both parent and metastable ions were detected. The wire voltages were controlled by a R. M. Jordan 1040 Remote Pulsing Circuit that permitted voltage swings between +100 V and -100 V. Detection of the extracted ions was accomplished using a Comstock CP625/M microchannel plate detector with chevron



geometry at the end of a 2 meter flight tube.

The time required to eliminate an ion by collision with the flight tube can be calculated based on the flight time for an ion released from rest in an electric field between two concentric conducting cylinders of radii a and b (where $b > a$)

$$t = \frac{r}{v} \sqrt{\frac{2m}{eV_0} \ln\left(\frac{b}{a}\right)} \int_0^{\theta} \sigma^2 d\theta$$

Based on this equation, the elimination flight time is proportional to the square root of the mass of the ion in a constant system. Therefore, an empirical proportionality constant, k, for mass and time can be derived.

$$\frac{m}{t} = k \cdot t^2$$

The selectivity of the elimination, $\Delta m/z$, can be derived as the range of masses (m_1, m_2) affected during Δt

$$\Delta \frac{m}{z} = 2k(\Delta t) \sqrt{\frac{m}{zk} + k(\Delta t)^2}$$

For the system used with $k=2.1 \text{ amu}/\mu\text{s}^2$ and a $\Delta t=170 \text{ ns}$, elimination of ions of $m/z=300$ would result in a $\Delta m/z$ of approximately 15 amu. This selectivity adequately eliminates competing background noise from sample ion detection.

The selectivity of the fast pulsing circuitry also permits a "notched" ion elimination technique capable of ejecting unwanted ions from any point in the mass spectrum. This allows versatility when analyzing samples that produce a closely knit mass spectrum where ions of interest can be masked by other nearby background ions. By notching out a portion of the unwanted mass spectrum before a peak of interest, the signal to noise ratio for that peak can be improved by reducing the detector saturation that would have occurred without ejection.

These improvements afforded by rapid bipolar pulsing permits an enhancement of the dynamic range of MCP detection for TOF mass spectrometry. This will expand the utility of TOF mass spectrometry for the analysis of high molecular weight biomolecule analysis.

Literature Cited:

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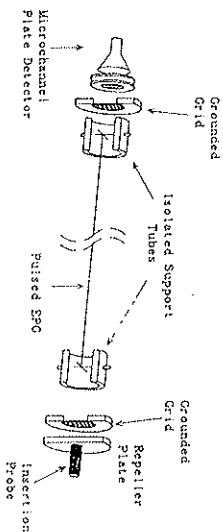
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