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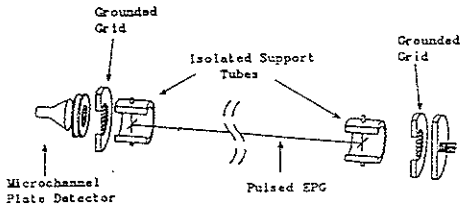
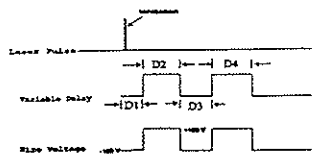
Time of flight mass spectrometry (TOF-MS) has come to the forefront of high-mass analysis due to the high sensitivity and extended mass range offered by the instruments.[1-3] These techniques have shown superb sensitivity for sample sizes within the range of a few hundred attomoles,[3,4] and the mass range of TOF-MS is theoretically unlimited.[5] Although the high sensitivity and mass range of MALDI-TOF provide strong arguments for its use, the spectra are complicated by the high-intensity background peaks that result from the matrix which limit both the 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.[2,6] 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 electrode 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 composed of low-mass ions (m/z<300), and because the time scale of the experiment is in the microsecond range, early saturation of the detector occurs frequently, resulting in a reduced capacity to detect high-mass ions.[2]

One approach to selective elimination of low molecular weight matrix ions was demonstrated by use of a bipolar pulsed EPG.[7] The ability to apply pulsed positive and negative voltages on the EPG allows one to combine the deflection 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 an elliptical, spiraling orbit about the EPG 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.





The mechanism and selectivity of the ion elimination can be described on the basis of ion motion about the EPG derived by Oakey and Macfarlane.[8] A particle injected into the potential field of a centrally located EPG will have a velocity with vector components parallel and perpendicular to the ion axis. The perpendicular component of the ion's velocity, vp, results in an eccentric spiral motion around the EPG. Ions trapped by the radial electric field are transported to the detector by the velocity component parallel to the ion axis. It is important to note that the parallel component of the velocity is unchanged by the radial electric fields and therefore does not alter the time of flight of the ion. When the polarity of the EPG is made positive to create a repulsive electric field, the ions are accelerated toward the flight tube walls. Ions are therefore eliminated by collision with the walls of the flight tube. If the polarity of the applied voltage is changed to create an attractive electric field (i.e., negative) prior to collision with the flight tube, the ion will by recaptured into a stable orbit. This ability to recapture and detect deflected ions results in a highly selective ion elimination technique. This technique was shown to be an effective method of selected reduction of unwanted background peaks and provides an increase in both dynamic range and sensitivity.[9]

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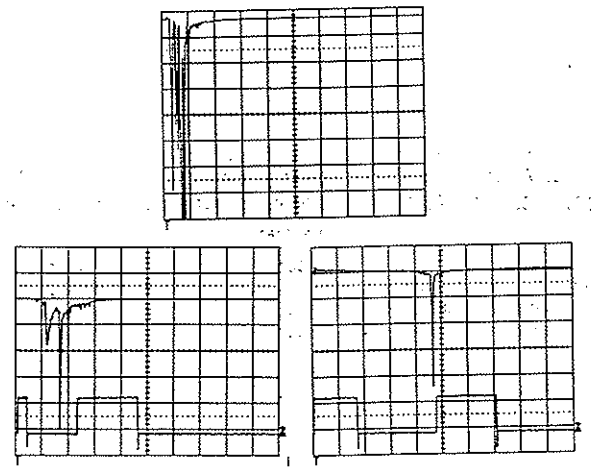

The work presented here demonstrates the effects of the addition of a second pulse to the pulsing sequence to allow for ion isolation. This allows the EPG to be used as a band-pass filter for the ions. Ion isolation using an EPG permits a method of selecting specific ions for structural analysis. Because the EPG has no field vectors along the flight axis, ion selection does not effect the TOF of the selected ions. However, presently the resolution of the second pulse is fairly low because the initial pulse gives the ions a radial velocity distribution. If coherency could be induced in the ions prior to the second pulse, the resolution of this technique would increase dramatically.

Literature Cited

(1) Karas, M.; Bahr, U.; Ingendoh, A.; Hillenkamp, F. *Angew. Chem., Int. Ed. Engl.* 1989, 28, 760.
(2) Beavis, R.; Chait, B. *Rapid Commun. Mass Spectrom.* 1989, 3, 233-237.
(3) Beavis, R.; Chait, B. *Anal. Chem.* 1990, 62, 1838.
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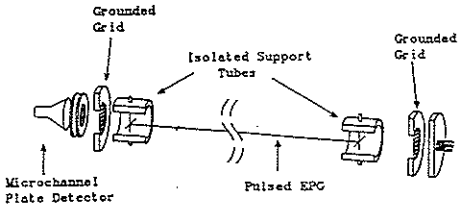

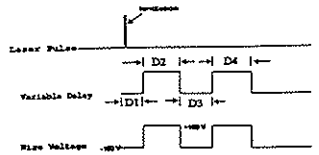

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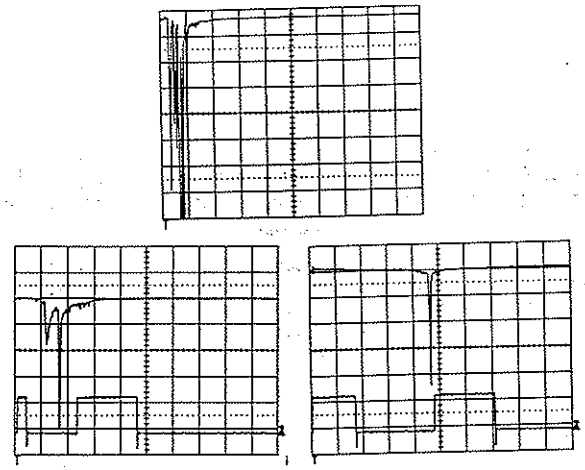

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