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The Development of a High-Speed Detector for Time of Flight Mass Spectrometry

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Introduction

- Time of Flight Mass Spectroscopy has become the most widely used technique for identifying very large organic molecules. This technique has become the method of choice for most drug discovery and polymer applications.

- The Time of Flight technique is frequently chosen because it is the only technique capable of the high mass sensitivity needed for many substances.

- Recently, table top RGA, ICPMS, GC and LCMS instruments have emerged.

Introduction (Continued)

- The Time-Of-Flight mass spectrometry technique is an old technique which has seen a resurgence in popularity due to cost reductions in electronics and the advent of high temporal resolution detectors.
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- The availability of high temporal resolution detectors has enabled shorter flight tubes to be used, which lead to smaller vacuum systems and lower overall instrument costs.

Introduction (Continued)

- In the operation of a typical MALDI TOF Instrument, analyte molecules, dispersed among matrix material are ionized by a nitrogen laser. (Figure 1)
- The resultant ions are held (delayed extraction) and then ejected down a flight tube through the application of high voltage pulses.
- Mass separation occurs during the flight (typically 1 meter) to the detector, with the lower mass ions arriving first, followed by progressively larger mass ones.
- Upon arrival at the detector, the electron multiplier will produce a charge pulse corresponding to the arrival time of each ion. (Figure 2)
- A high-speed digitizer is then used to record the arrival times of the ions, from which the mass of the ion can be determined.
- Three types of electron multipliers have been historically used in TOF-MS. Single Channel Electron multipliers (SEM), Discrete Dynodes (DD), and Microchannel Plate (MCP) based. Single Channel Electron Multipliers are not used in modern instruments because of limitations in temporal resolution (20-30 ns FWHM) and dynamic range. Discrete dynode electron multipliers exhibit good dynamic range but are used in moderate and low-resolution applications because of relatively poor pulse widths (Typically 6-10 ns FWHM). MCP based detectors are used in high resolution applications because they provide the highest (650 ps) temporal resolution, however they are limited in dynamic range to about 20 mhz/cm2 of active area.

Typical MALDI Time of Flight Mass Spectrometer Operation

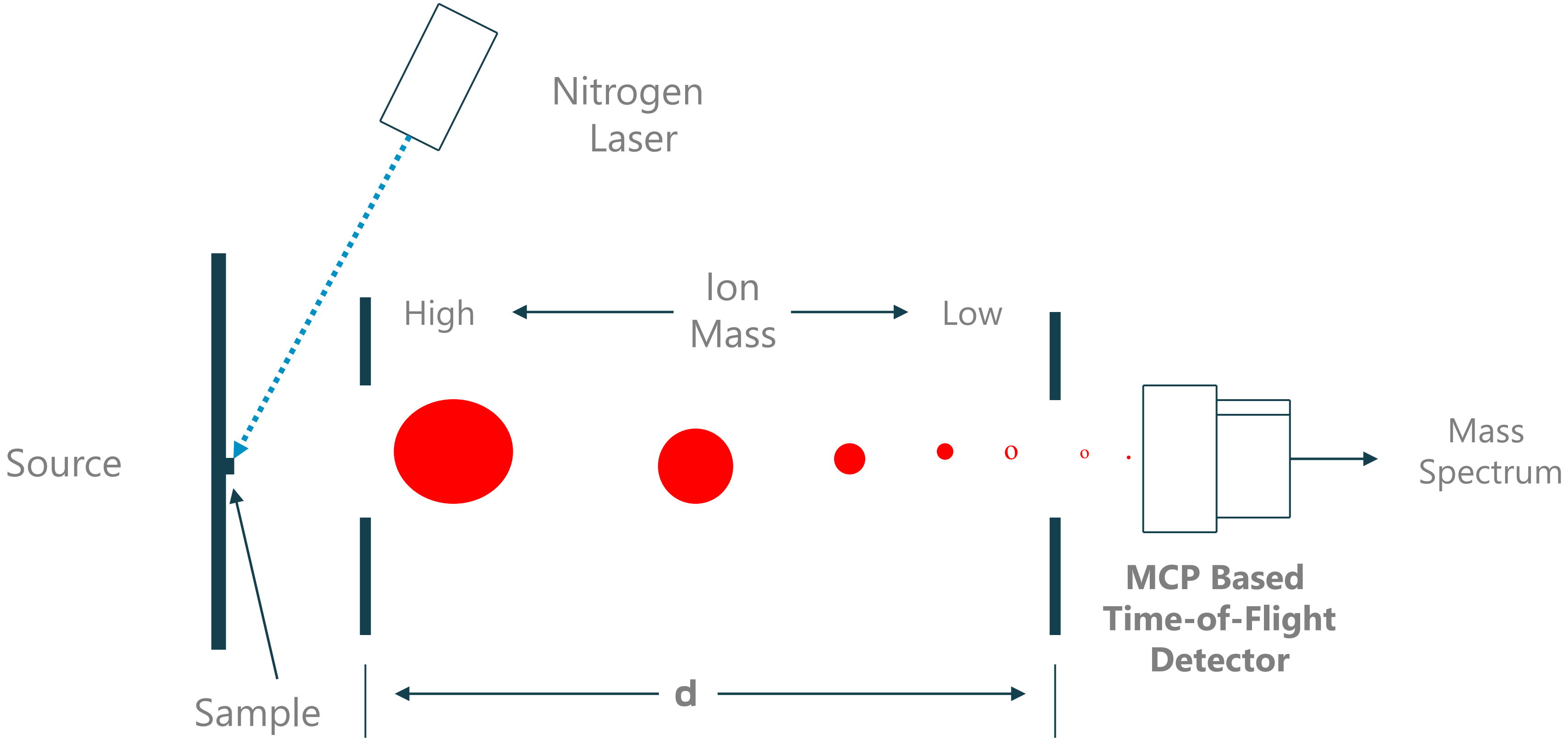

Figure 1

Polymer Sample Polyethylene Glycol

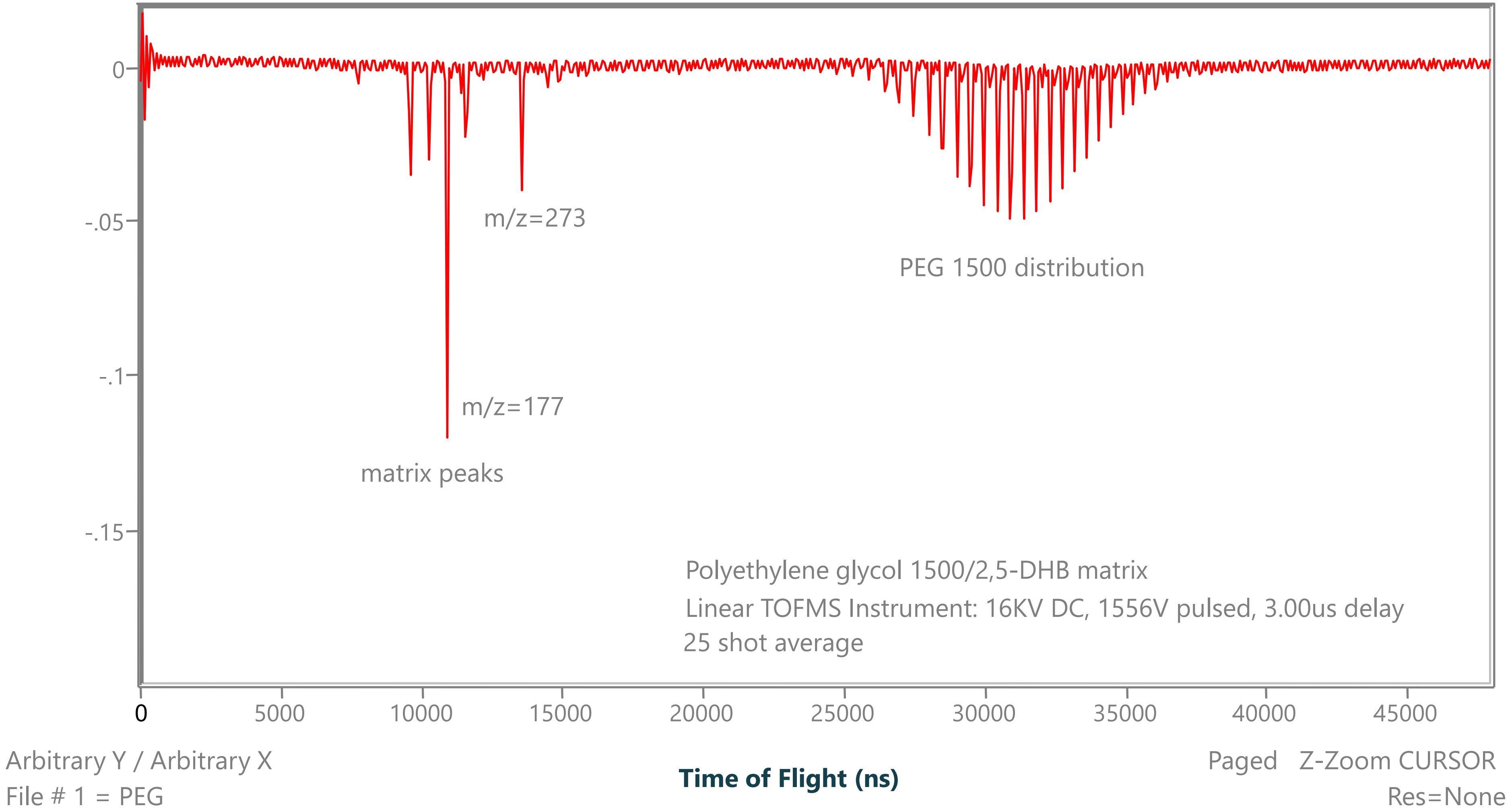

Figure 2

Development History

- The First Time of Flight Detectors were introduced in the late 1960s, were discrete dynode multipliers and single channel electron multipliers known as Channeltrons™. Channeltrons ™ became the detector of choice because of their stable performance.

- These devices had relatively poor temporal resolution by today's standards with pulse widths ranging from 20 – 50 ns.

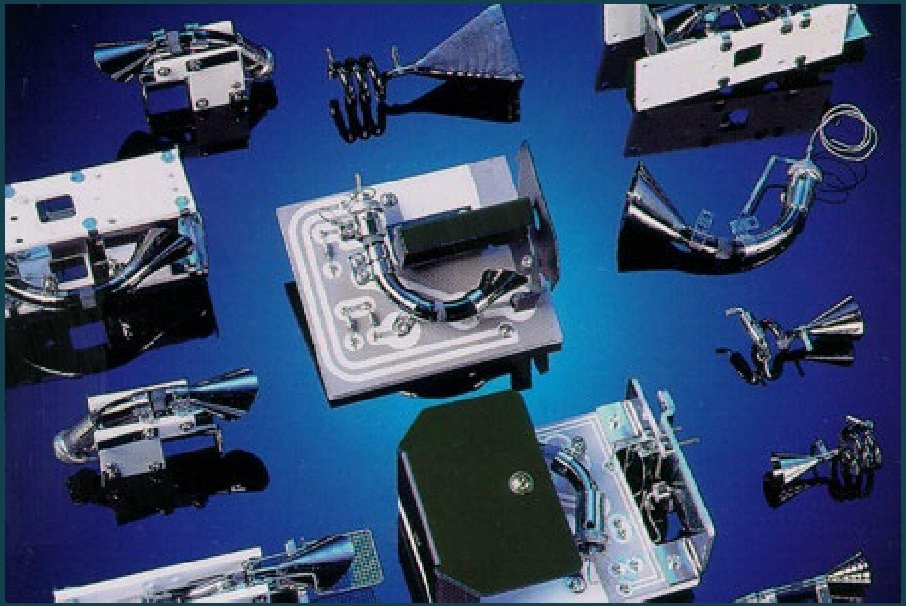

Figure 3

Development History

Figure 4

- TOF and FTDs were Detectors utilizing microchannel plates were commercialized in 1976.
- These devices incorporated microchannel plates with 25 micron pores and as a result had temporal resolutions of about 2 ns.
- Although very bulky, these devices were the first to incorporate 50 ohm impedance matched anode technology which resulted in diminished signal ringing.

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Development History

- In 1994, the AP Time of Flight Detector was introduced.
- This compact detector was less than one inch tall, maximizing the flight tube length.
- By reducing the pore size to 5 um the temporal resolution of the detector was improved to 800 ps with a rise time of just under 400 ps.
- The detector design enabled end users to refurbish the detector in minutes by simply replacing the cartridge containing the microchannel plates.
- A bakeable version was introduced in 2000, allowing rapid system degassing

Figure 6

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Development History

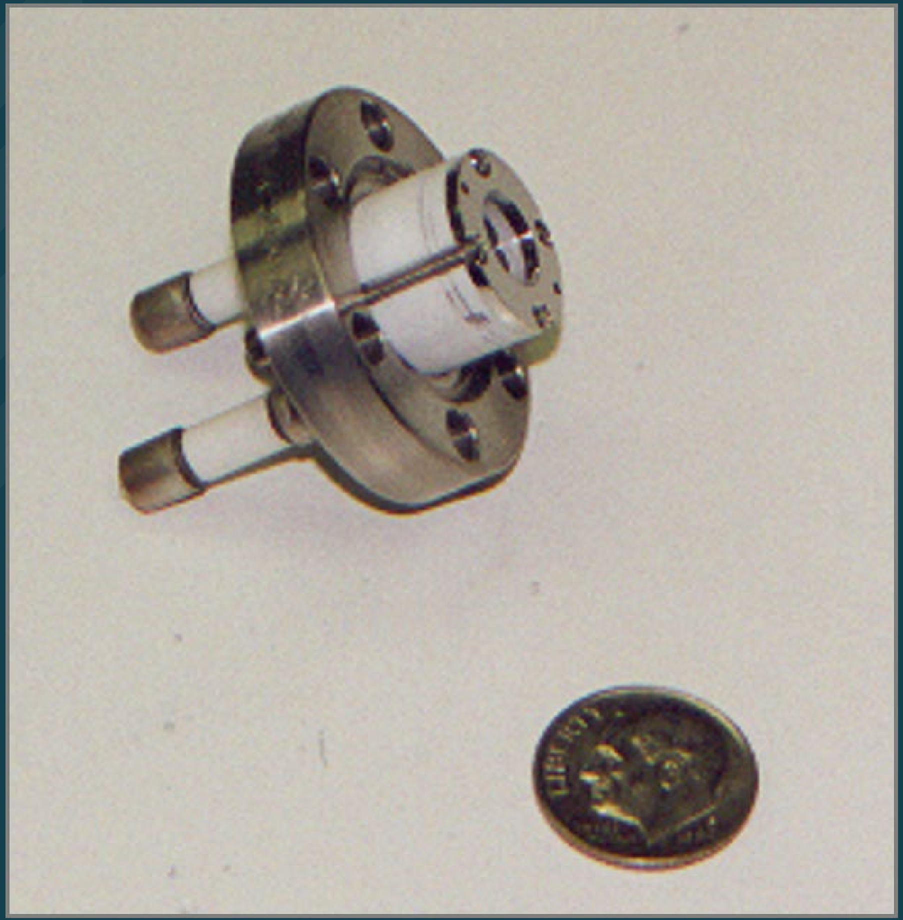

Figure 7

- In 1997, the Mini Time of Flight Detector was introduced.
- This miniature detector was developed for portable instruments. Featuring the same pore size microchannel plates as the AP TOF (5 um), the temporal resolution of the detector was improved to 800 ps with a rise time of just under 400 ps.

Development History

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Figure 7

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Discussion

- Improving the temporal resolution of the ion detector will enable resolution of lost peaks (Figure 8)
- The temporal resolution of a microchannel plate (Figure 9) based detector is ultimately determined by the electron transit time (Figure 10) through the channel and the anode impedance.
- The electron transit time of a microchannel plate can be decreased by shortening the channel length. To maintain proper operating conditions, the channel diameters must be reduced proportionally.

Polyethylene Glycol

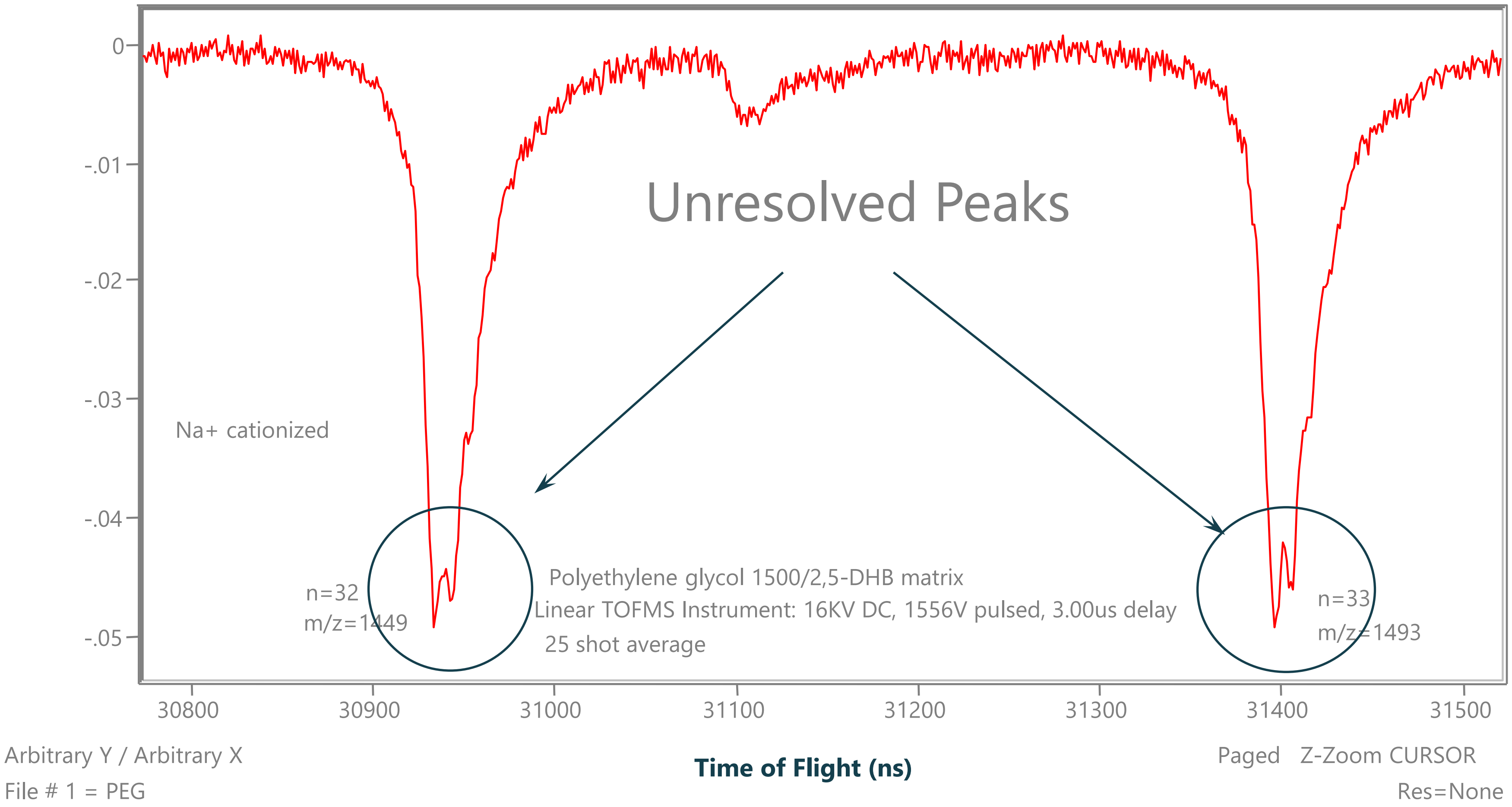


Figure 8

Microchannel Plate Configurations

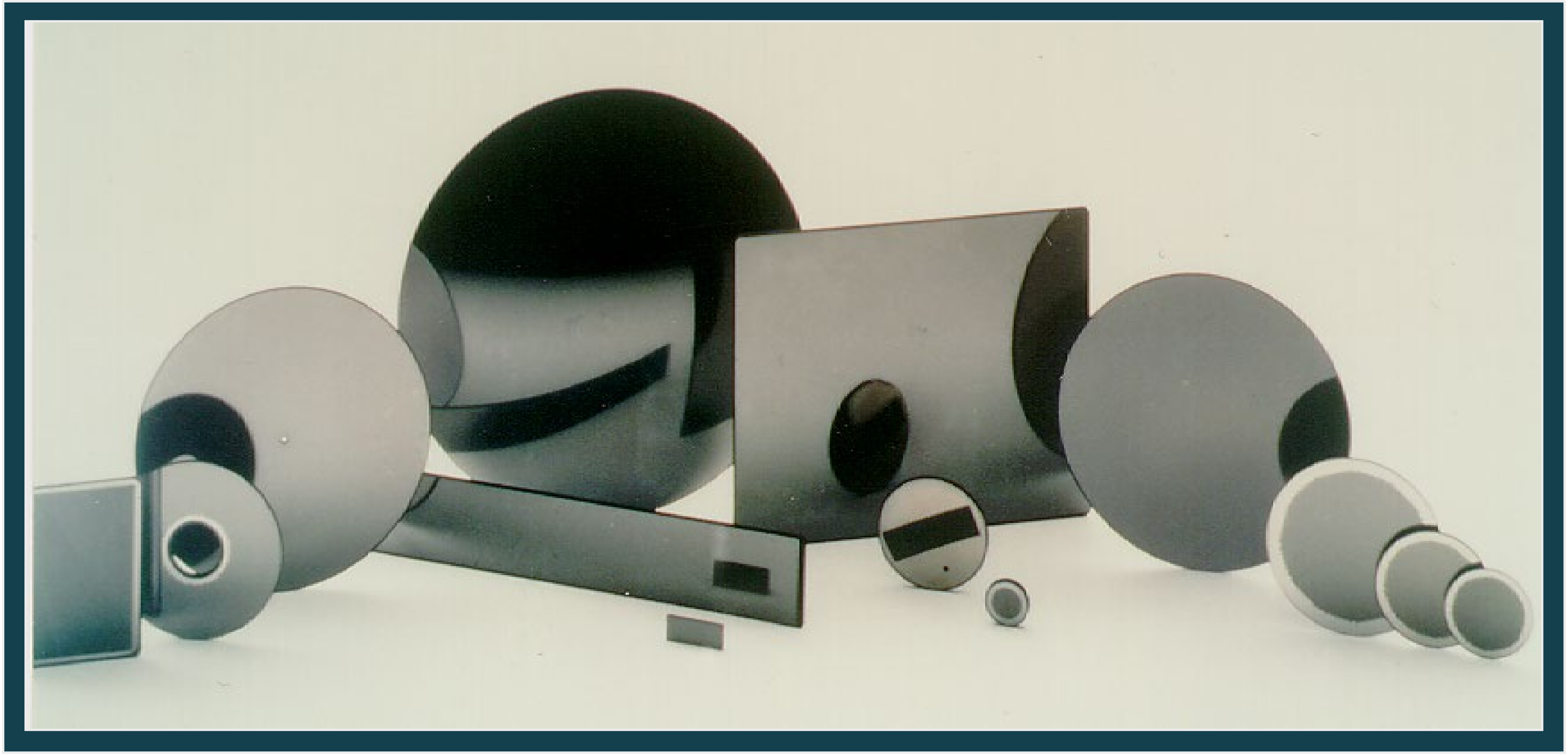
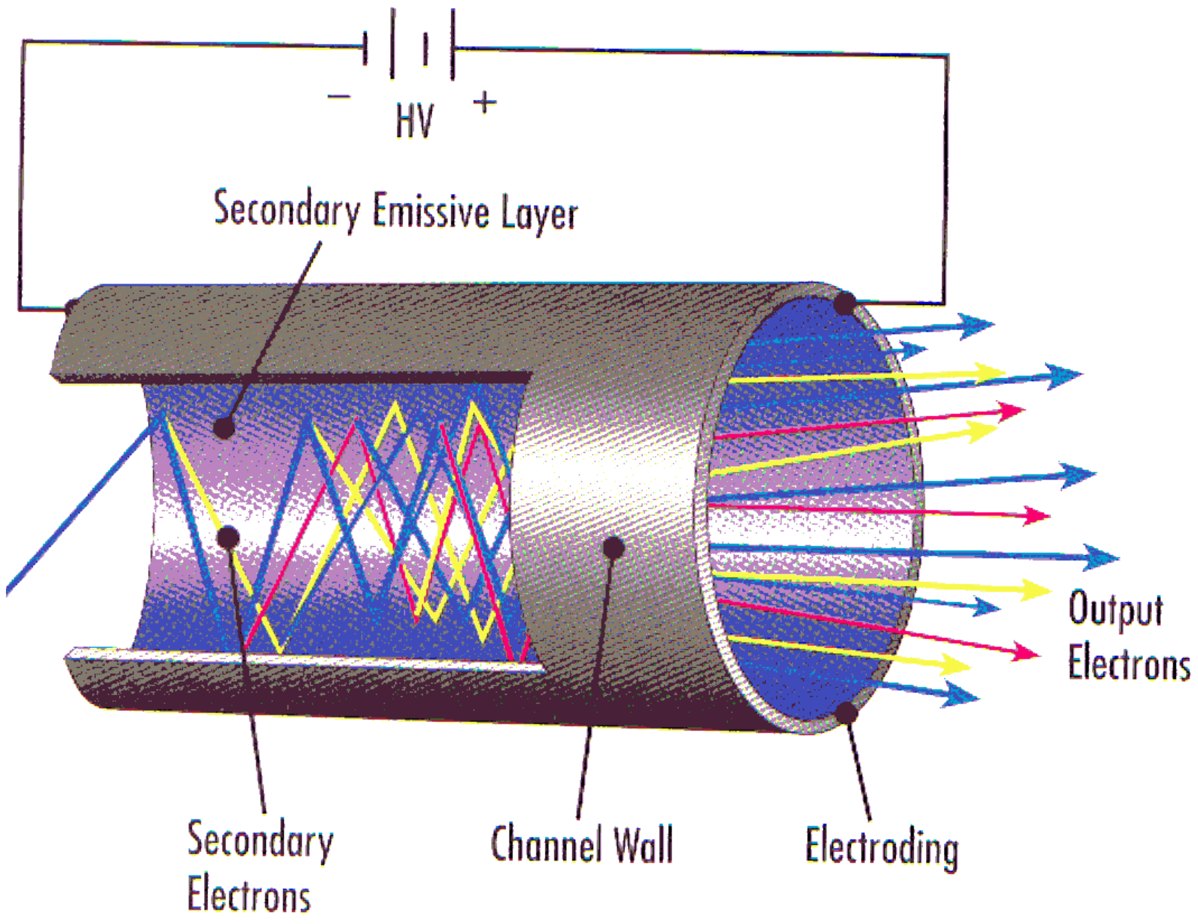


Figure 9

Microchannel Plate Cross Section



Incident Ions

Figure 10

Objectives

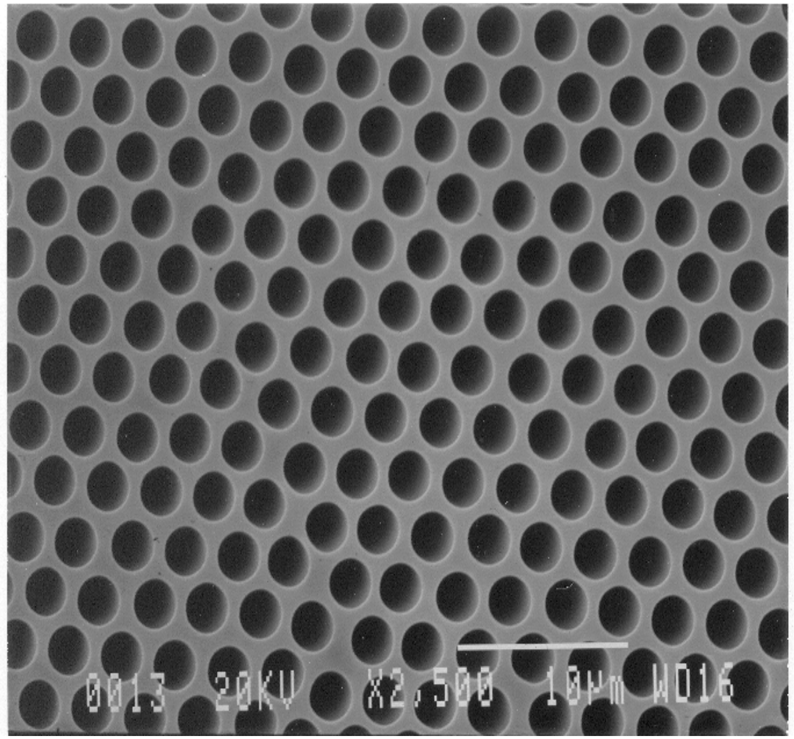
- The primary objective of this development project was to significantly increase the temporal resolution of the conventional Time of Flight Mass Spectrometer Detector.

- In order to increase the temporal resolution, the MCP pore size must be significantly reduced. Reengineering the fabrication process was necessary in order to overcome obstacles materials fiber draw, wafer grind and polish, activation and test.

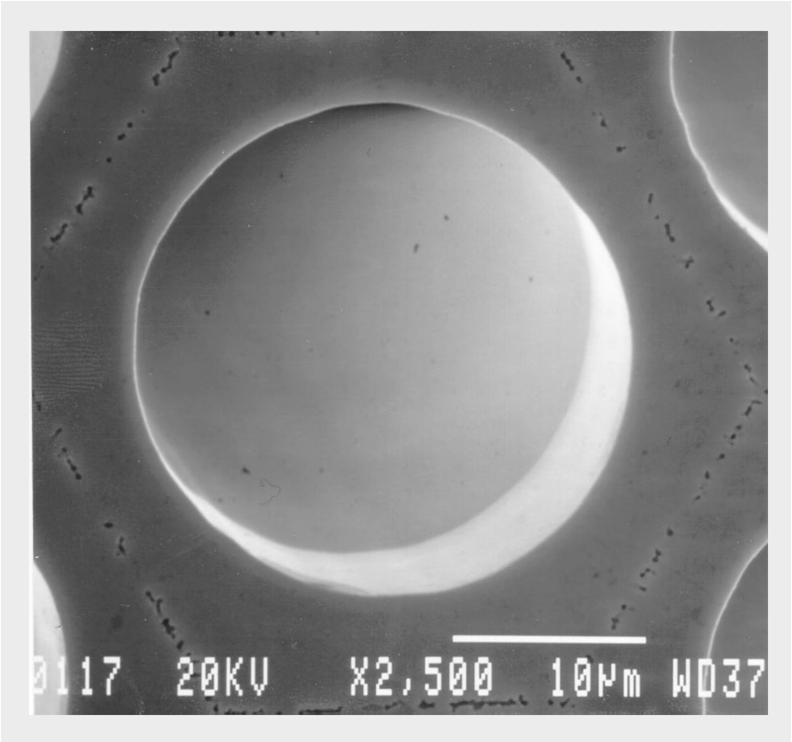
Experimental Method

- Microchannel Plates are fabricated by a series of fiber draw operations involving a two-glass system.
- Precision alterations were made to the draw parameters resulting in the successful fabrication of 18mm active diameter format MCPs with 2.3 µm (Figure 11) channel diameters.
- Interdiffusion obstacles were overcome by the development of a new process.
- New grinding and polishing techniques were developed in order to produce microchannel plates as thin as 80 microns.
- A cartridge assembly (Figure 12) containing two microchannel plates, a grounded mesh and an output biasing system was developed in order to accommodate the thin microchannel plates.

Microchannel Comparison



Two Micron Pore



25 Micron Pore

Figure 11

Results

- Microchannel plates with a pore sizeof 2.3 microns and an open Area ratio of 65% (Figure 11) were successfully fabricated.
- Single plate gains (figure 13)exceeded 10,000 and Chevron Gains (Figure 14) up to 10,000,000 were produced.
- Rise times approaching 200 ps with pulse widths of 400 ps (Figure 15) were achieved, improving by a factor of 2 the best performance previously available. (Figure 16)
- A self biasing cartridge, incorporating a grounded grid was developed for ease of handling the MCPs.

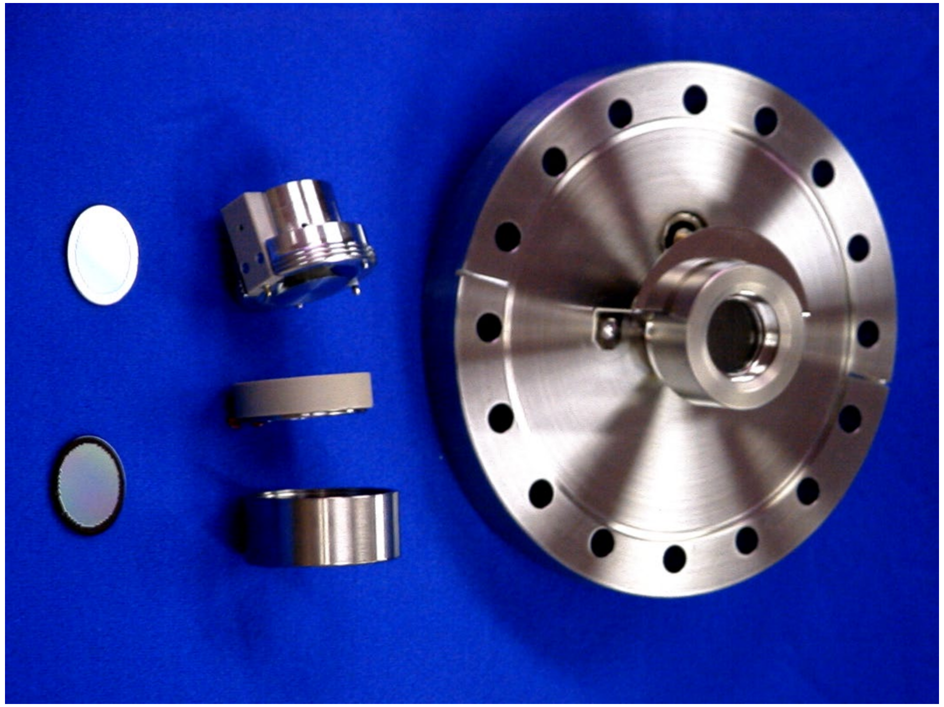


Figure 12

Results – Single MCP Gain

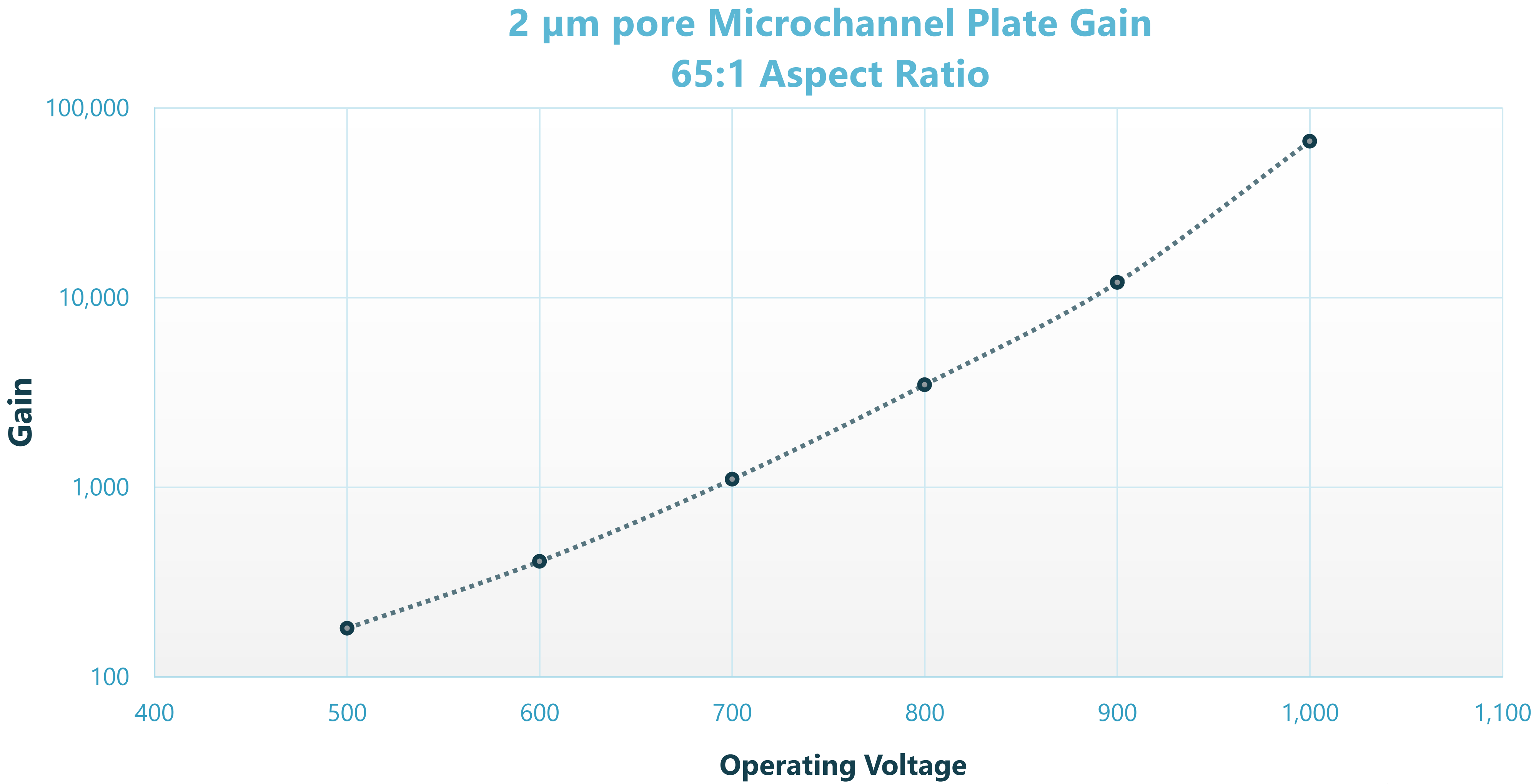


Figure 13

Results – Chevron Gain

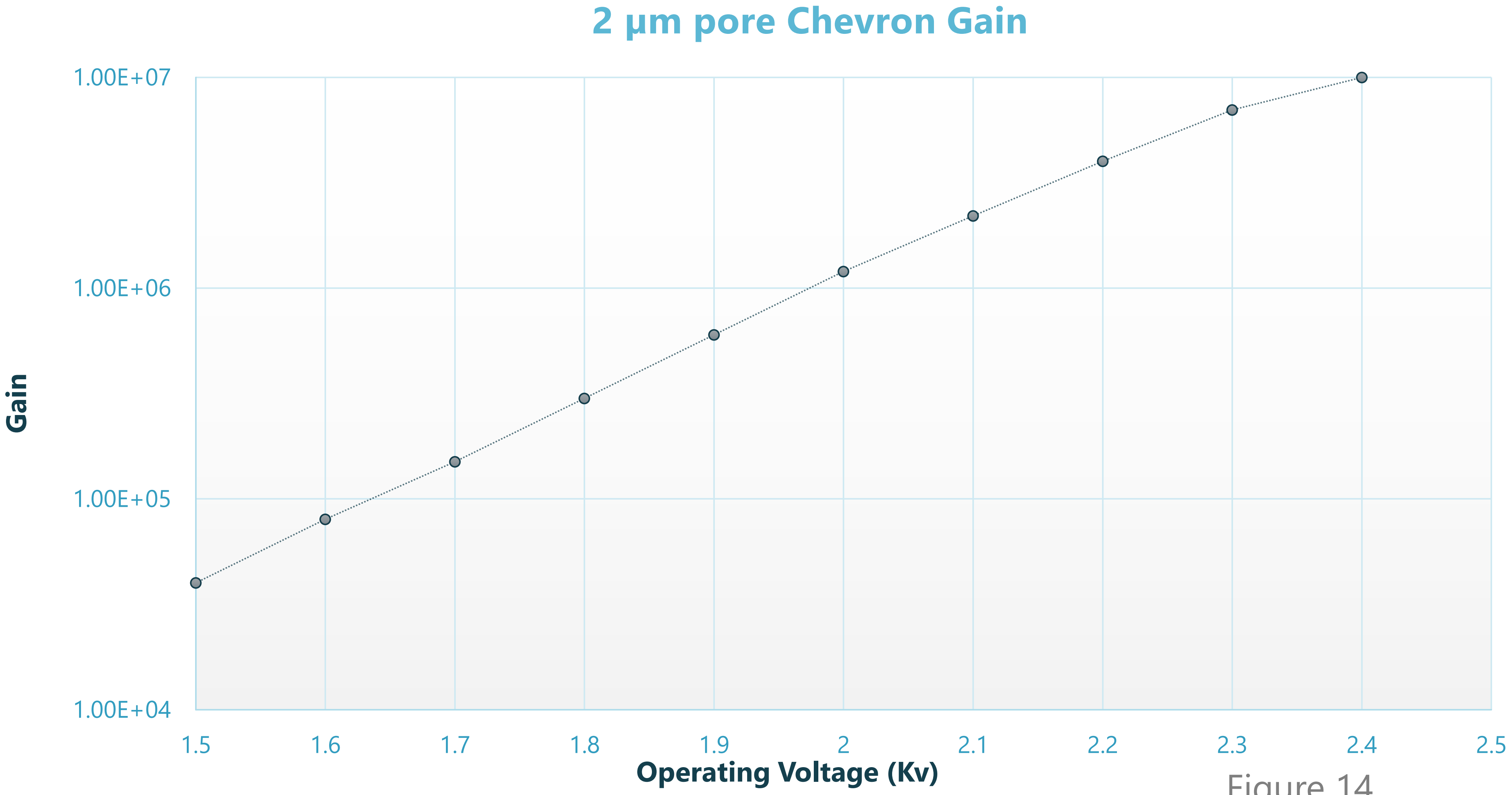
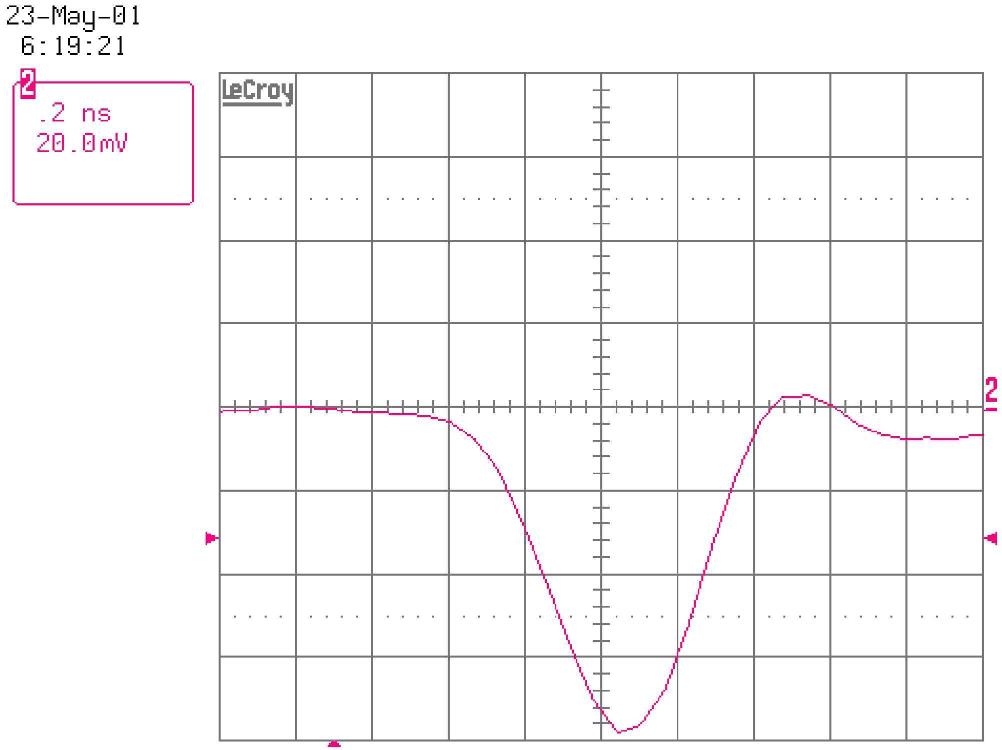
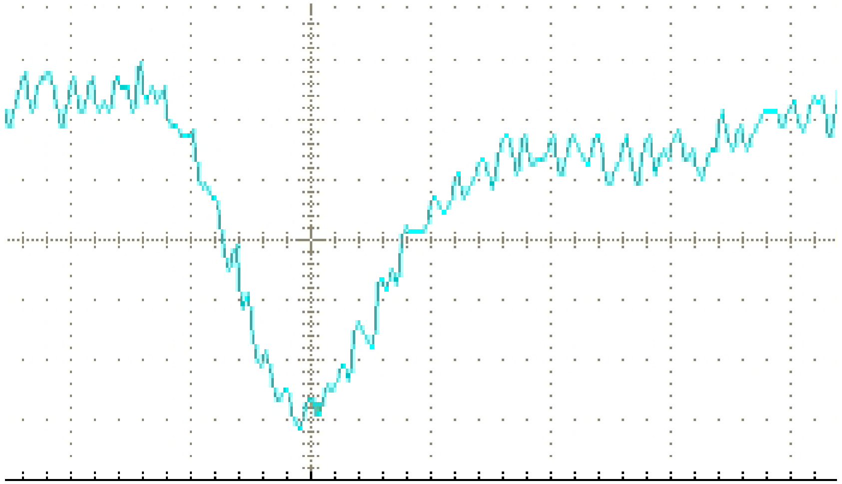


Figure 14

Results – Temporal Resolution

Conventional Detector
2300 ps pulse width
1600 ps rise time





Two µm Pore TOF Detector
400 ps pulse width
209 ps rise time

Figure 15

Results – Pulse Width

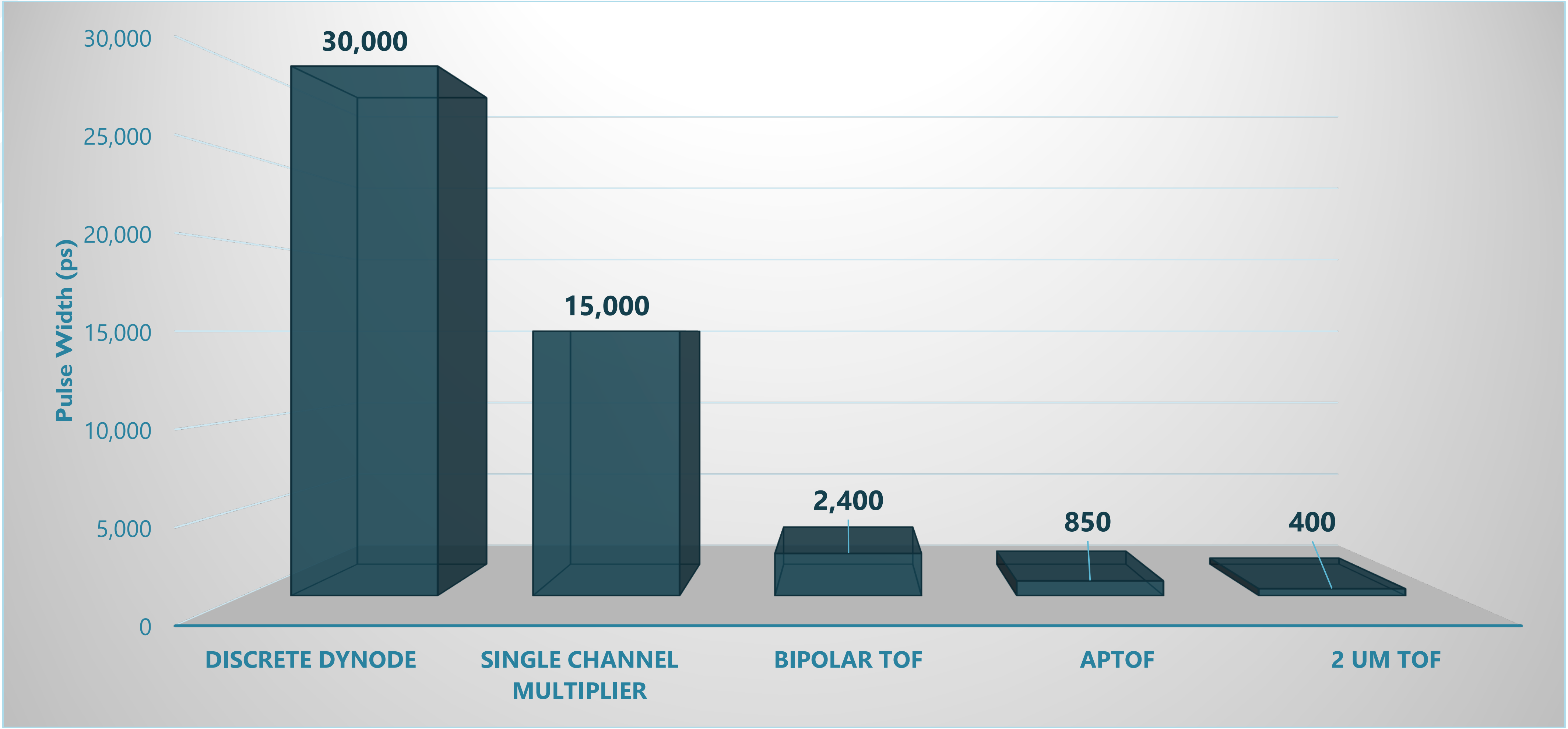


Figure 16

Conclusions

- A low profile, Time of Flight detector for Mass Spectrometry incorporating the smallest pore microchannel plates ever developed has been successfully produced.
- The temporal resolution of this detectors is over twice that of the best detector currently available.
- The availability of this detector can significantly reduce instrument size and cost, while improving mass resolution