

OVERVIEW

- PURPOSE**
- Removal of background ions in oa-TOF MS.
- METHOD**
- Fast gating of the axial ion beam synchronised to the orthogonal push out pulse.
- RESULTS**
- Principle of operation discussed.
 - Removal of low m/z ions using modified GC-MS oa TOF demonstrated.
 - Effect on resolution and calibration illustrated.

INTRODUCTION

The generation of unwanted, high intensity background ions is common to many ionisation modes. Examples include:

- Solvent ions in API.
- GC carrier gas, air, water in EI.
- Reagent ions in CI.
- Matrix ions in FAB, LSIMS and MALDI.
- Plasma support gas in ICP.

For orthogonal acceleration time-of-flight (oa-TOF) instruments, particularly those utilising a micro channel plate detectors (MCP), attenuation of these large ion currents is desirable to preserve detector efficiency and life-time.

INSTRUMENTATION

All results were obtained using a Waters Micromass GCT-TOF mass spectrometer. The transfer optics were modified to include a deflection lens capable of gating the axial ion beam prior to orthogonal acceleration.

The control electronics were modified to allow the voltage applied to this lens to be pulsed on and off in a predetermined relationship with respect to the firing of the orthogonal acceleration pulse.

Figure 1 is a schematic of the GCT showing the position of the ion gate and function when CLOSED.

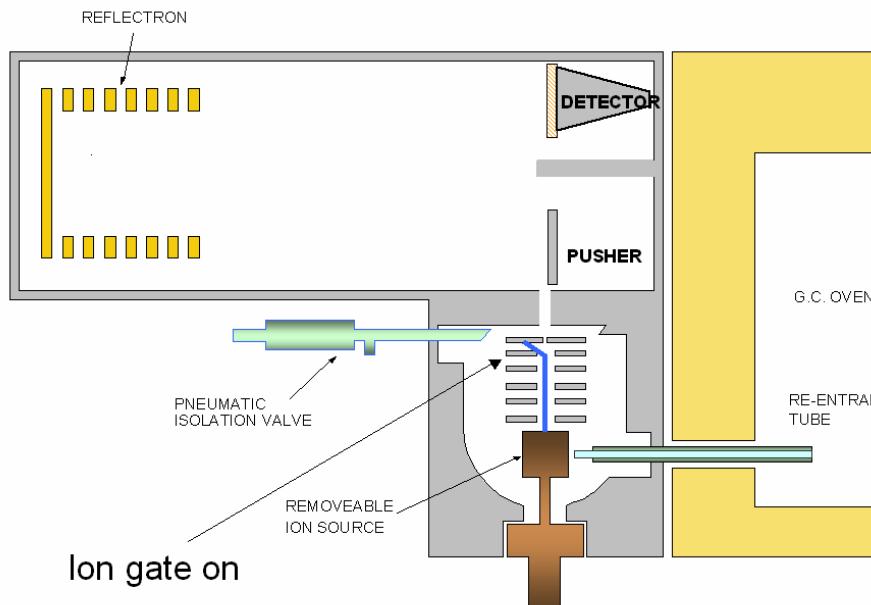


Figure 1. Schematic of GCT with ion gate closed

METHOD -LOW M/Z CUT OFF

Figure 2. Shows a schematic of the source, ion gate, pusher electrode and detector regions. The position of ions for m/z values, M₁, M₂, and M₃, are shown at time T = 0, when the ion gate has just been closed. Where M₁<M₂<M₃ and M₃ = the maximum m/z value corresponding to one cycle of operation of the oa TOF.

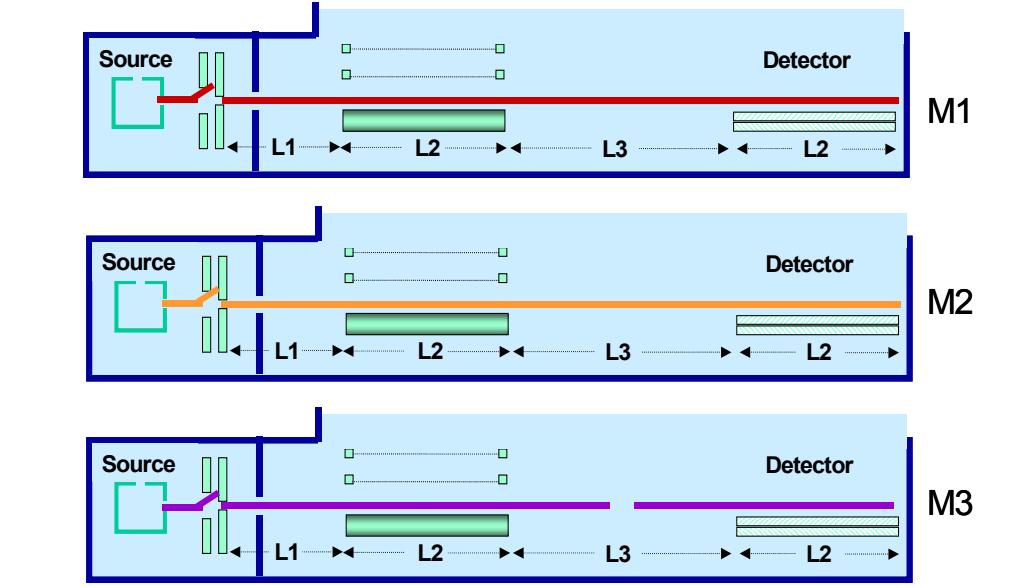


Figure 2. Low m/z cut off . T = 0 ion gate CLOSED

Figure 3. Shows the position of the ions at time T = dt when voltage is applied to the orthogonal acceleration electrode.

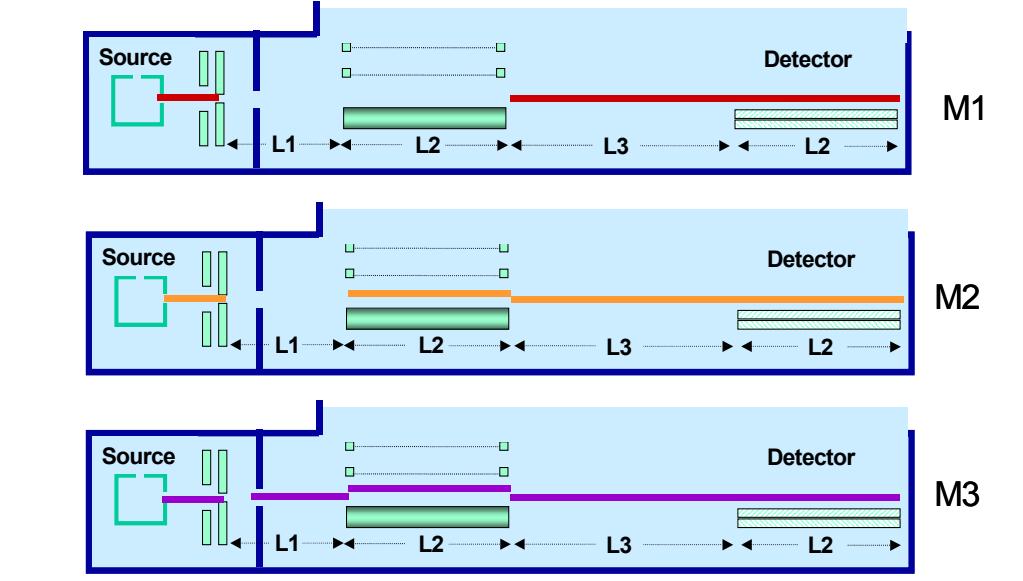


Figure 3. Low m/z cut off . T = dt ion gate OPEN

L = distance travelled after time T = dt. The transmission for each m/z range is shown in Table 1.

m/z	L	Result
Less than M ₁	Greater than (L ₁ +L ₂)	No ions accelerated into TOF
M ₁	(L ₁ +L ₂)	No ions accelerated into TOF
Between M ₁ and M ₂	Less than (L ₁ +L ₂) Greater than L ₁	Some ions accelerated into TOF
M ₂	L ₁	All ion accelerated into TOF
Greater than M ₂	Less than L ₁	All ion accelerated into TOF

Table 1.

Where

$$M_1 := \frac{V \cdot \delta t^2}{5184(L_1 + L_2)^2} \quad (1)$$

$$M_2 := \frac{V \cdot \delta t^2}{5184 \cdot L_1^2} \quad (2)$$

The transmission (Tr) for ions M of m/z between M₁ and M₂ is given by

$$Tr := 1 - \frac{1}{L_2} \cdot \left(\frac{\delta t}{72} \sqrt{\frac{V}{M}} - L_1 \right)$$

V = Axial ion energy (electron volts)

L₁ and L₂ = distance (meters)

dt = Time (usec)

EXPERIMENTAL CONDITIONS

Heptacosa (PFTBA) was continuously introduced into GCT via the septum inlet in El+ ionisation mode.

L₁ = 101 mm

L₂ = 30 mm

L₃ = 71 mm

Axial energy = 43 eV

For dt = 9.0 usec, M₁ = 39 daltons, M₂ = 66 daltons

RESULTS

Figure 4. Shows the spectrum produced with and without operation of the ion gate. Background ions from air (m/z 28, 32 and 40 are attenuated).

Figure 5. Shows the theoretical and measured relative transmission of ions for m/z range 10–140 da. Good correlation between experimental and calculated transmission is demonstrated.

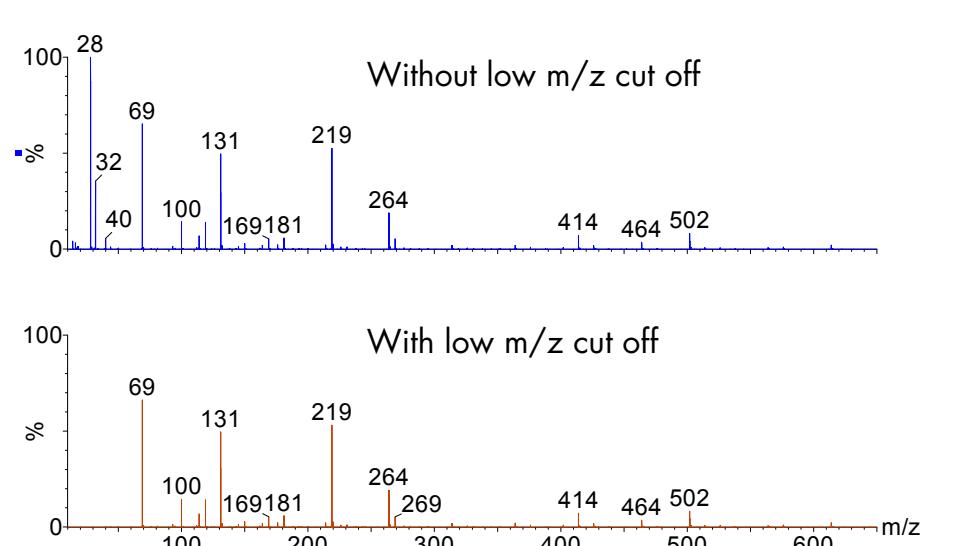


Figure 4. PFTBA. Low m/z cut off operation.

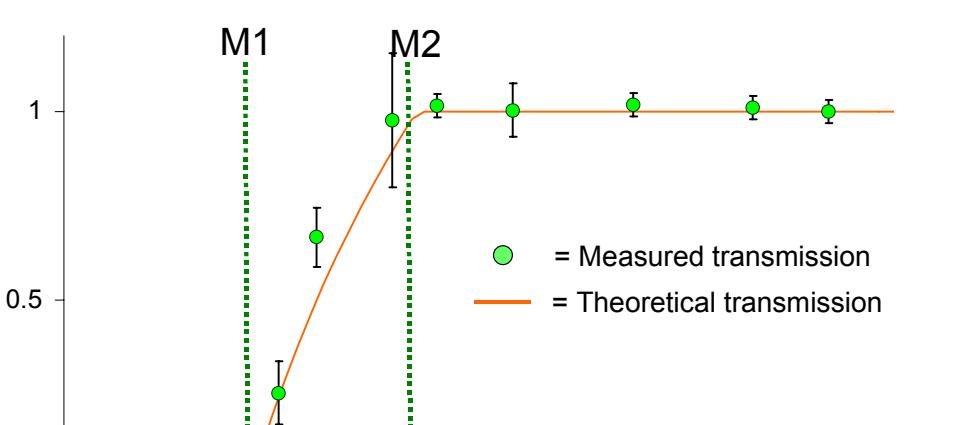


Figure 5. PFTBA. Measured and theoretical transmission.

RESOLUTION AND CALIBRATION

The GCT operates at high resolution (>7000 FWHM) giving exact mass measurement to within 5ppm.

To maintain mass accuracy it is important that there is minimal distortion in resolution and calibration during ion gate operation.

Figure 6. Shows the mass resolution in gated operation as a percentage of that in non-gated operation. For m/z > M₂ (full transmission) no distortion in resolution is observed.

Figure 7. Shows calibration curves relating observed to expected mass values (assuming a simple linear relationship between time and square root of mass). There is no significant change in these curves when the ion gate is in operation.

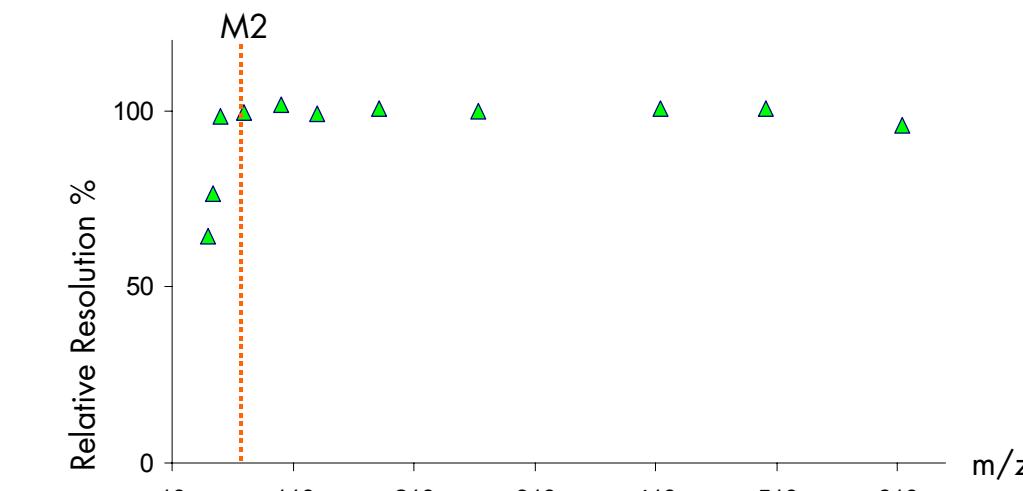


Figure 6. Resolution in gated and non-gated operation.

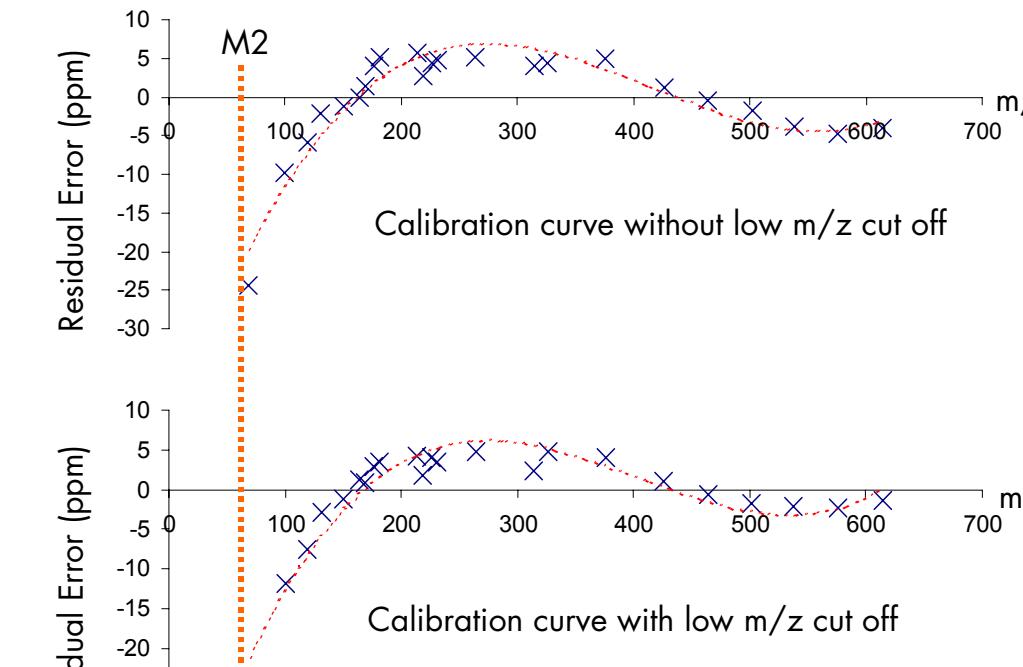


Figure 7. Effect of ion gate on mass calibration curve.

METHOD—HIGH M/Z CUT OFF

By changing the relationship between opening the ion gate and applying voltage to the orthogonal acceleration electrode the system may be set to allow only ions below a set m/z value to be transmitted into the TOF analyser. High mass cut off operation. Figure 8. Shows a schematic of the source, pusher and detector regions.

The position of ions for m/z values, M₁, M₂, and M₃, are shown at the time T=0 when the gate has just been opened. Where M₁<M₂<M₃

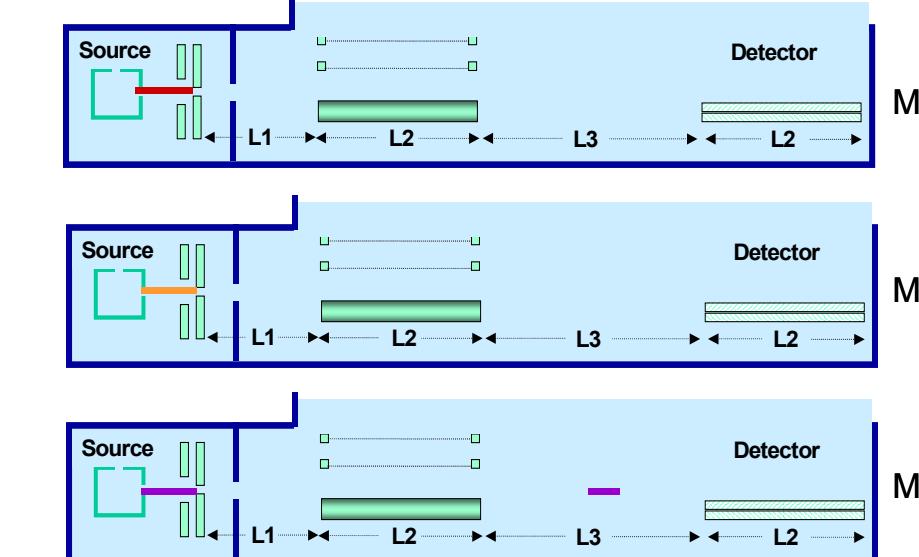


Figure 8. High m/z cut off . T = 0 ion gate OPEN.

Figure 9. Shows the position of the ions at time T = dt when voltage is applied to the orthogonal acceleration electrode.

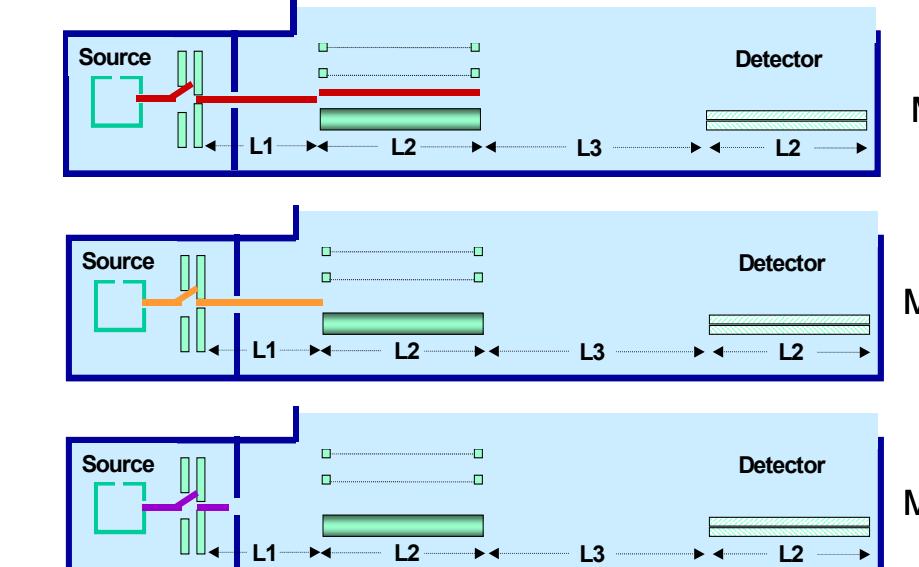


Figure 9. High m/z cut off . T = dt ion gate CLOSED.

L = distance travelled after time T = dt. The transmission for each m/z range is shown in Table 2.

m/z	L	Result
Less than M ₁	Greater than (L ₁ +L ₂)	All ions accelerated into TOF
M ₁	(L ₁ +L ₂)	All ions accelerated into TOF
Between M ₁ and M ₂	Less than (L ₁ +L ₂) Greater than L ₁	Some ions accelerated into TOF
M ₂	L ₁	No ion accelerated into TOF
Greater than M ₂	Less than L ₁	No ion accelerated into TOF

Table 2.

OTHER MODES OF OPERATION

The two modes of operation described may be combined to produce two further modes of operation.

1. Band-pass transmission mode.

The gate is set to be OPEN for a short period each cycle of operation of the oa TOF.

2. Band-pass cut off mode.

The gate is set to be CLOSED for a short period each cycle of operation of the oa TOF.

BAND-PASS TRANSMISSION

Figure 10 A. Shows the theoretical transmission vs m/z value for band-pass transmission mode using the ion gate to orthogonal acceleration pulse relationship shown in Figure 10 B.

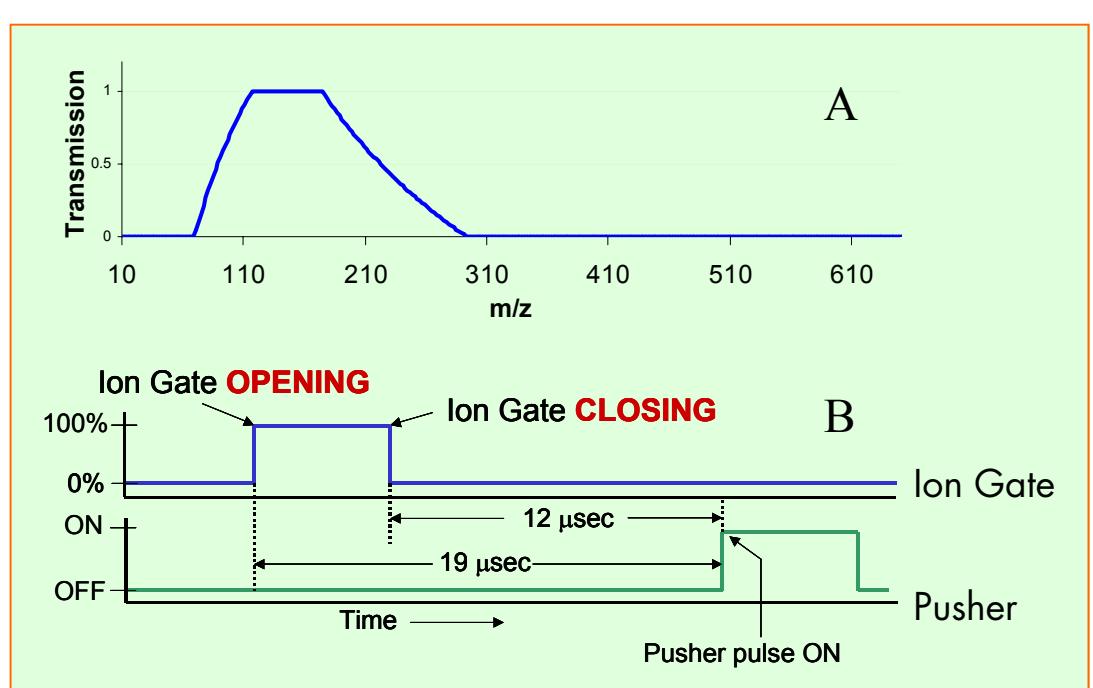


Figure 10. Band-pass transmission mode.

BAND-PASS CUT OFF

Figure 11 A. Shows the theoretical transmission vs m/z value for band-pass cut off mode using the ion gate to orthogonal acceleration pulse relationship shown in Figure 11 B.

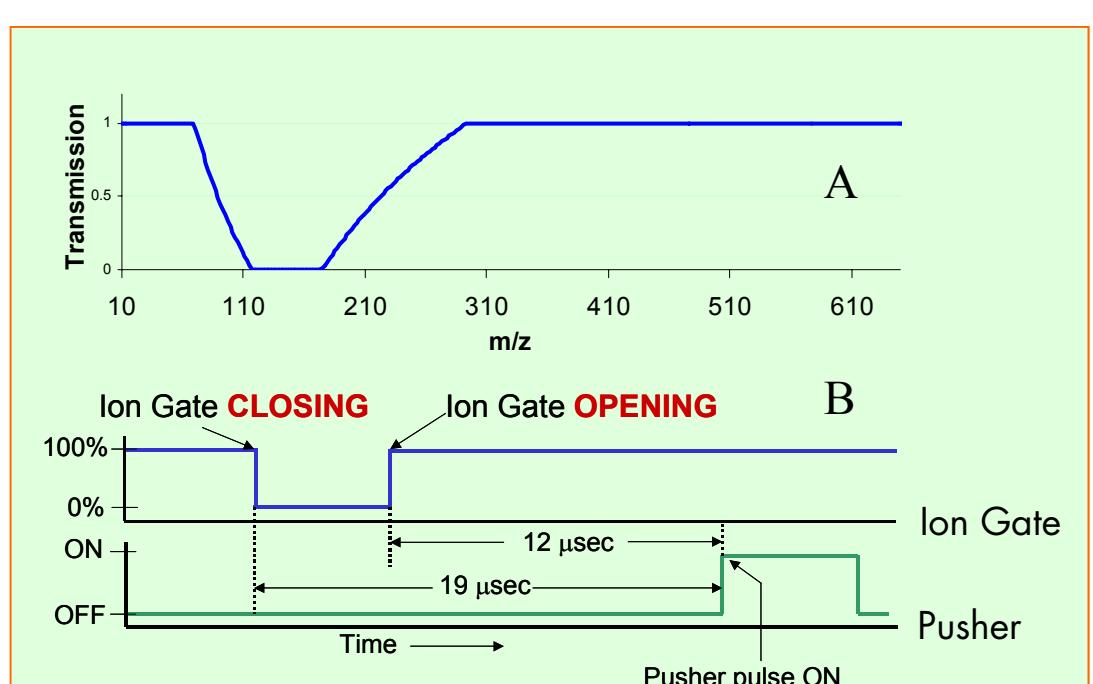


Figure 11. Band-pass cut off mode.

CONCLUSIONS

- Fast gating of the axial ion beam provides a simple efficient means of removing unwanted background ions.
- There is minimal effect on mass resolution and calibration.
- Exact mass measurement capability is not compromised.
- Low m/z cut off, high m/z cut off, band pass cut off and band pass transmission modes may be accommodated.