INTRODUCTION
Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry (MALDI-Tof MS) is one of the most sensitive mass spectrometric techniques for the analysis of biomolecules. The limit of detection of a MALDI system is determined by two factors. The absolute sensitivity of the hardware and the preparation of the sample. Of these factors the sample preparation is usually the limiting factor.

EXPERIMENTAL
The sensitivity of the Waters® Micromass® MALDI micro MX™ mass spectrometer was tested in reflectron and linear mode, with positive and negative polarity.

Sensitivity reflectron mode
Sample: Glu-fibrinopeptide B at concentrations of 2 and 20 fmol/µL for positive and negative ion mode respectively made up in 0.1% trifluoroacetic acid (TFA).
Matrix: Purified α-cyano-4-hydroxy cinnamic acid matrix was obtained from Waters (186002331). The matrix was prepared at 2 mg/mL in 1:1 acetonitrile:aqueous 0.1% TFA. Samples were mixed 1:1 with matrix and 1 µL was spotted directly onto the target plate and allowed to air dry prior to analysis.
The final amount of sample per spot was 1 fmol for positive ion mode and 10 fmol for negative ion mode.

Data acquisition: Six separate acquisitions in positive and negative mode.

Sensitivity linear mode
Sample: Glu-fibrinopeptide B at concentrations of 20 and 100 fmol/µL for positive and negative ion mode respectively made up in 0.1% TFA.
Matrix: The same method and matrix were used as in reflectron mode.
Data acquisition: Six separate acquisitions in positive and negative mode.
Final amount of sample per spot was 10 fmol for positive ion mode and 50 fmol for negative ion mode.

Data Processing
20 spectra (100 laser shots) were combined and background subtracted (polynomial order 15, subtraction 10 %). The baseline was magnified by factor 5 over the m/z range 1590 - 1650.

RESULTS
The mass spectra obtained are shown in Figures 1a)-1d). In all cases a section of the baseline is magnified to be compared to the monoisotopic Glu-fibrinopeptide B peak. In all experiments performed the MALDI micro MX easily surpassed the instrument sensitivity specifications of a Signal:Noise ratio of 5:1 (Table 1).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Polarity</th>
<th>Average S/N ratio (six acquisitions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>negative</td>
<td>39:1</td>
</tr>
<tr>
<td>Linear</td>
<td>positive</td>
<td>41:1</td>
</tr>
<tr>
<td>Reflecton</td>
<td>negative</td>
<td>26:1</td>
</tr>
<tr>
<td>Reflecton</td>
<td>positive</td>
<td>16:1</td>
</tr>
</tbody>
</table>

Table 1. Summary of the sensitivity experiments, showing Tof analyzer mode, polarity mode and average S/N ratio.
Figure 1. a) 50 fmol Glu-fibrinopeptide B on target measured in linear mode (negative), b) 10 fmol Glu-fibrinopeptide B on target measured in linear mode (positive), c) 10 fmol Glu-fibrinopeptide B on target measured in reflectron mode (negative), d) 1 fmol Glu-fibrinopeptide B on target measured in reflectron mode (positive).

CONCLUSION

• These data easily surpass the sensitivity specifications of the instrument in both linear and reflectron mode, and in positive and negative mode.
• The average S/N ratio in reflectron positive mode was 16:1 (specification is 5:1).
• The average S/N ratio in reflectron negative mode was 26:1 (specification is 5:1).
• The average S/N ratio in linear positive mode was 41:1 (specification is 5:1).
• The average S/N ratio in linear positive mode was 39:1 (specification is 5:1).