NPL REPORT COAM(A)6

REPORT

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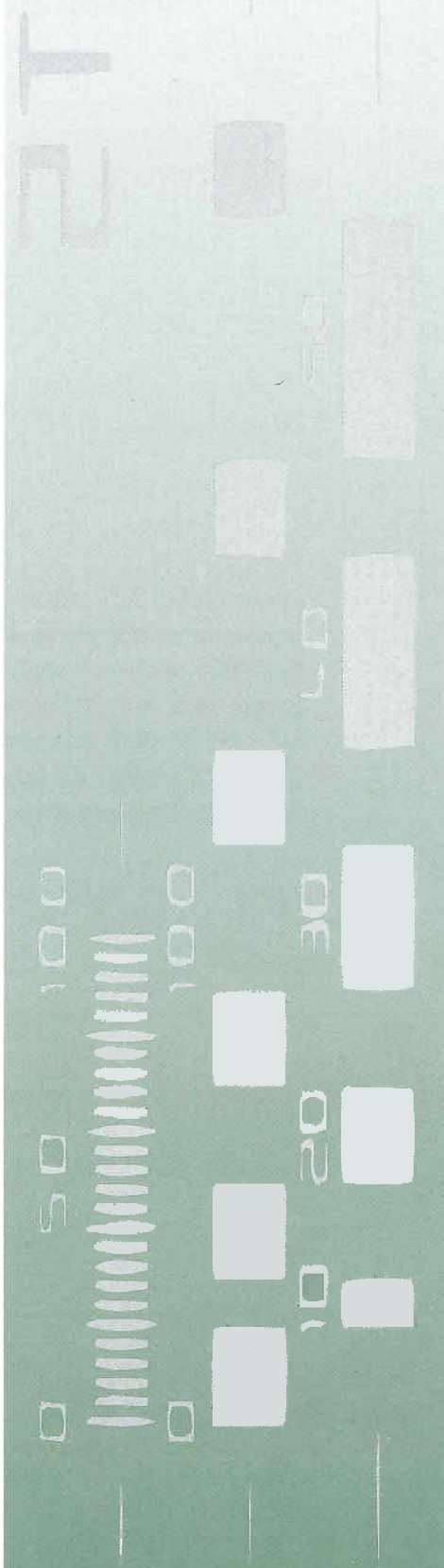

NPL National Physical Laboratory

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VAMAS 2002: Static ToF SIMS Inter-laboratory Study - Protocol For Analysis

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ABSTRACT

This report describes the protocol for analysis in the VAMAS 2002, static ToF SIMS inter-laboratory study. Procedures for setting the primary ion beam, mass analyser, ion detector and charge compensation are provided to ensure the equivalence of data between different instruments and analyser types. Three reference materials are supplied for this study, polycarbonate on silicon, a thin layer of polystyrene oligomers on silver and bulk PTFE. No sample preparation is required by the user and specific guidance is given on sample handling. Forms for reporting the data are provided in Appendix B together with the preferred data media and format.

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Approved on behalf of Managing Director, NPL,
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CONTENTS

1 INTRODUCTION

The first VAMAS static SIMS inter-laboratory study was conducted by NPL in 1996[1,2]. That study included 21 static SIMS instruments from 18 laboratories with a wide variety of spectrometer types, including quadrupole, magnetic sector and three time-of-flight designs. Results indicated that, whilst repeatabilities could be as good as 1%, they were on average only 10%. For each instrument a relative instrument spectral response (RISR)[1] was calculated. Using this RISR, the equivalence of data between all the different instruments was improved by a factor of 4.

Since that time, a new generation of time-of-flight instruments has been manufactured. These instruments have been found to be very powerful and reliable and so now dominate static SIMS analyses. In the first study, a few of these instruments were included but they were new and operators were still learning how best to use them. This second study is restricted to these time-of-flight instruments. This will improve the quality, validity and relevance of the results.

The objectives of this inter-laboratory study, for the new generation of instruments, are: (i) to determine the repeatability of instruments, (ii) to determine the reproducibility of results between different laboratories, (iii) to evaluate variations in spectral response between different generic types of SIMS instruments, (iv) to establish the effectiveness of charge neutralisation and (v) to check for electron beam damage. Optionally, instrument compatibility with G-SIMS[3] may also be tested.

2 PROPOSED METHOD

In this work, positive and negative ion spectra are measured for three reference samples to be analysed without further sample preparation. The analytical conditions are chosen by the analyst to be within a range to minimise sample damage during analysis and provide good signal to noise. The digital data are then sent to NPL for analysis. The three reference materials are, a thin spin cast polycarbonate (PC) film on a silicon wafer, a thin layer of polystyrene oligomers on polycrystalline silver (PS) and PTFE. The PTFE is supplied as a full reel of tape and the others are 1 cm × 1 cm pieces, each supplied in separate Fluoroware containers. PTFE is a bulk insulator and will require charge neutralisation. This is the same PTFE as was used in the first study[1,2] and allows cross-checking with those data. The other two materials are conducting and no charge neutralisation is required. Tests at NPL show that these surfaces are more reliable than the previous samples, especially where in-house cleaning had to be used. The present samples are all to be analysed in the "as received" condition with no in-house cleaning.

The spectrometer should be operated under conditions which give the most stable performance. For the optimum intercomparison, a common set of operating conditions is needed, however due to the variety of instruments available, no single set of conditions can do this. Instead we give general conditions for guidance to make things as common as possible.

3 INSTRUMENT OPERATING CONDITIONS

3.1. ION BEAM

The ion beam should be centred in the acceptance area of the mass spectrometer. If you can, first centre all the alignments for the mass analyser and then increase the raster area to image the entire mass analyser acceptance area. Using the ion beam controls, centre the imaged area in the mass analyser acceptance area. In some cases the maximum field of view may not be large enough to observe the acceptance area. If it is restricted by the software, it is sometimes possible to change the calibration scaling or "sensitivity" to access a larger raster area and then return to the calibrated conditions after centring. A recommended ion beam raster area for this work is 200 μm × 200 μm. If your system has dynamic emittance matching and you can turn it off, please do so. This may give slightly poorer mass resolution but should improve repeatability and reproducibility.

A maximum ion fluence of 1×10^{16} ions/m^2 is recommended. The total number of ions should be adjusted using the pulsed current or acquisition time to give a good signal to noise ratio. The ion beam current should be sufficiently low (i) to avoid non-linearity in the counting circuits, and (ii) to avoid saturation of the time-to-digital converter (TDC) in ToF spectrometers. The requirements for fluence are given generically by Eq (A.2) in Appendix A with illustrative numbers. For example, a 0.5 pA pulsed beam and a 200 μm square raster would require 128 s acquisition time. This beam would need to be defocused to a diameter greater than 3.1 μm for a 128 × 128 pixel display. If it can only be defocused to 1 μm, a 256 × 256 pixel display must be used or the local fluence on a pixel will be exceeded by more than a factor of 2. The number of frames acquired should be kept above 20, as described in Eq (A.4), so that the final frame, which most likely will not be a full frame, represents only a small fraction of the data.

For good statistics, we require the average spectrum over the whole analysis area. There is therefore no need to acquire images with high spatial resolution. In fact, high spatial resolution is a disadvantage, since, as we have noted, a finely focussed ion beam may exceed the ion fluence limit and cause unwanted sample damage. During a digital raster scan, an over-focused ion beam will drill a matrix of small holes. For this reason a large diameter defocused beam should be used as discussed above. The precise minimum beam size depends on your system but can be evaluated using Eq (A.1) in Appendix A.

The ion beam current density should be measured using a suitable Faraday cup. If your system does not have one, a simple but accurate device may be made as discussed in ref (4) using a drilled hole, aligned to the ion beam, with a depth more than 5 times the diameter. Alternatively, the raster area may be calculated from a calibrated grid and the pulsed current measured with an electrometer with a +10 V bias on the sample holder.

Use your preferred ion source and energy for spectroscopic analysis. Our preference for ion source is for least fragmentation, in decreasing order: Cs, Xe, Ga and Ar. Molecular beams such as SF_5^+ are excellent for static SIMS but currently only have a small, but growing, user base. Figure 1 illustrates an equivalence of primary ion mass and energy in terms of fragmentation, after ref (3).

3.2 MASS SPECTROMETER

In general, the spectrometer should be operated in the condition which gives the most stable and repeatable performance with good, high mass sensitivity. A suggested method for deflector alignment, if required, is as follows. With the primary ion beam centred in the analysis area, reduce the raster area to 50 μm × 50 μm square. The analyser deflectors should now be systematically adjusted, one set at a time, to maximise the mass resolution. This alignment process will need to be iterated by the number of analyser deflector pairs. The analysis area may move over the sample during this process and it will be necessary to re-centre the image using the primary ion beam controls.

It is recommended to use an energy acceptance of at least 50 eV, which is the default for TRIFT designs. This results in much improved repeatability with only a small degradation in mass resolution of approximately 5%. For reflectron instruments, the reflector potential should be adjusted to +50 V and –50 V above the sample surface potential for positive and negative ion polarities, respectively. This is straightforward for the conducting samples. For insulating samples this is more complex because the sample is a dielectric and the extraction field penetrates into the material bulk[5].

A systematic method for determining the surface potential, in order to set the reflector voltage, is required. The effect of reflector voltage on the peak intensity of the CF_2^+ ion from PTFE is shown in Fig 2. As the reflector voltage is made more positive the peaks move down the apparent mass scale simply because the ions are reflected earlier and their flight time is reduced. The reflector potential at which the ion signal begins to increase rapidly is approximately equal to the sample potential. In the example of Fig 2, the sample potential is approximately –79 volts. As the reflector voltage is increased positively, more of the secondary ion energy distribution is reflected to the detector and the signal rises to a plateau. The reflector voltage which gives an ion signal of half the maximum peak intensity, V_T, is accurately and quickly measured. Adding a further 50 volts gives a value for the reflector voltage, V_R, which may be set in a reproducible way. Here the half maximum intensity occurs at -75 volts and so we use a reflector voltage of -25 volts.

The repetition rates of the spectrometer should be set to give a mass range for each reference material shown in Table 1. Illustrative values for repetition frequencies and cycle times are also provided based on an ION-TOF IV spectrometer with a 2 keV pass energy.

Table 1 – Maximum mass needed with example repetition rates and cycle times for an ION-TOF IV instrument operated at 2 keV pass energy

Reference material and polarity	Max mass needed	Max rate, kHz	Min cycle time, μs
PC +	850	10000	100
PC -	850	10000	100
PS +	4000	4750	210
PS -	850	10000	100
PTFE +	1100	9050	110
PTFE -	850	10000	100

3.3 CHARGE COMPENSATION

Charge compensation is necessary only for the PTFE sample. For the other samples, the electron source should be turned off to prevent unnecessary electron beam damage (on computerised acquisition systems it is easy to forget to "un-check" the electron gun). A detailed study of electron beam damage[6] provides recommendations which are presented in a one page summary[7]. Participants in this study should either read the summary which may be accessed using the web page link below, or ref (6), in order to be able to set their electron flood neutraliser sufficiently low in current not to cause electron damage but sufficiently high to be effective. The settings here are quite critical.
http://www.npl.co.uk/npl/cmmt/sis/lowenergyfloodgundamage.pdf

3.4 ION DETECTOR

A detailed study of ion detection efficiencies for microchannel plates[8] provides recommended operating conditions which are presented in a one page summary[9]. Participants in this study may be interested to read the summary which may be accessed using the web page link below, or to read ref (8). For the best quality of measurement, you should set the impact energy of the detected ions at the detector surface to be as high as possible. Use 20 keV, if that is available, or as high an energy as you can reliably use.
http://www.npl.co.uk/npl/cmmt/sis/iondetectionefficiency.pdf

4 SAMPLE PREPARATION AND SAMPLE HANDLING

Static SIMS is, of course, very sensitive to trace contaminations and it is vital, therefore, that the samples are kept clean and are analysed as soon as possible after the Fluoroware containers are opened. Samples should only be handled at their edge using cleaned metal tweezers held using powderless polyethylene gloves. Vinyl gloves, often used in clean rooms, are coated with a release agent from the moulding process, and should not be used. The release agent is very mobile and quickly contaminates the samples. This will lead to poor measurement repeatability and poor quality data.

(a) PC and PS

The PC and PS samples are provided face down in separate small Fluoroware containers with a concave base. Do not remove the samples until you are ready to analyse them. The containers are opened by rotating the cap clockwise. Remove the wafer using clean metal tweezers and mount it on the sample holder. Use a clamp mounting, not adhesive tape. For the PC sample, the correct side to analyse has a smooth mirror-like finish and the reverse side is matt (lapped). The thin layer of PS is on one side of the silver only, the reverse side has a set of deep parallel scratches.

(b) PTFE

The PTFE is provided as a reel of tape. Remove and discard the first 20 cm of material from the reel and then cut appropriately sized samples from the subsequent material with clean scissors. As the reel is unwound, a fresh surface of PTFE is exposed, it is this surface that should be

analysed. If you hold a strip of tape to the light, you may occasionally notice a thicker region approximately 2 mm by 1.5 mm. We have always avoided these regions in case they modify the neutralisation conditions. Please discard any samples with such regions. The samples should then be mounted on the sample holder to produce a flat even surface. Friction by clamping should be used to hold the sample in place. Do not use any adhesive tape.

5 DATA ACQUISITION

Static SIMS analyses are to be made for each material and, if time and resources permit, conditions are given to generate G-SIMS spectra. A flow chart for the work is given in Fig 3. Figures 4, 5 and 6 show spectra from these reference materials, for both positive and negative ions.

(a) Static SIMS repeatability

The order of analysis shall be (i) PC, (ii) PS and (iii) PTFE using positive and negative ion detection each time before moving to the next sample. For the PC and PS, the electron flood must be turned off. It must be used only for the PTFE.

A fresh area of material should be analysed each time with a total fluence of less than 1×10^{16} ions/m^2 (1×10^{12} ions/cm^2). Acquire five positive ion spectra and five negative ion spectra, each spectrum being for a separate sample or region of each of the three materials giving 30 spectra in total. Fig 7 shows a schematic of a 4 x 4 array of measurement positions, for a sample holder with an 8 mm × 8 mm square aperture. All analysis areas should be at distances greater than 1.5 mm from the edge of the sample holder. For a square raster of side R the recommended repeat distance (centre to centre) is 2.5 R. With the recommended raster area R = 200 μm, the minimum gap between each raster is 500 μm. For the PTFE, the first area analysed is that nearest to the electron gun. The order of analysis then works in the direction away from the electron gun. Use the same instrument operating conditions for each sample.

Notes

1 Both the PS and PTFE material have high secondary ion emissions and care should be taken to avoid saturation of the detector. This is achieved by reducing the number of primary ions per pulse. For this study we recommend a maximum of 150 ions per pulse which is equivalent to 0.24 pA pulsed current with a repetition rate of 10 KHz.

2 If, for your instrument, there is insufficient PC or PS reference material to acquire a full set of positive and negative secondary ion data then omit the negative data.

(b) G-SIMS study

G-SIMS[3] is a new method developed at NPL to provide much simpler spectra with parent fragments which give easier and direct interpretation. A detailed account is given in ref (3) and a one page summary[10] may be accessed on our web page using the link below. The amount of molecular fragmentation for beams of different mass, species and energy is shown in Fig 1 in terms of the coefficient β. High values of β depict low fragmentation conditions such as Xe, Cs

or SF_5 at 10 keV and low values represent high fragmentation such as Ar or Ga at 10 keV. To calculate a G-SIMS spectrum, two spectra for positive secondary ions are required, one for low and one for high fragmentation conditions. One of these spectra, hopefully the low fragmentation condition, has already been recorded in part (a) of this study. Now acquire a further 5 positive secondary ion spectra from different regions of the PC sample with either a complementary ion beam species or energy which gives good separation on the β axis of Fig 1. For example, if in part (a) Cs at 10 keV was used then, for part (b), Ar at 10 keV would be a good choice. Note, in this study 5 spectra repeats are required to assess repeatability. For G-SIMS, generally, only two spectra are required. A summary of applications of G-SIMS to crystallisable organics[11] with recommended operating procedures may be accessed on our web page using the link below. NPL will compute the G-SIMS spectrum for you from your data.
http://www.npl.co.uk/npl/cmmt/sis/gsimsofcrystallisableorganics.pdf

6 AFTER ANALYSIS

When all analyses are complete, return the PC and PS samples to their containers. The small PTFE sample cut from the reel may be scrapped. Please retain the other samples and the PTFE reel in case we find any anomalies in your data. When we have reviewed your data we shall either request some further work or the return of the samples.

7 DATA REPORTING FORMAT

All data should be mass calibrated using your local procedures. Record the calibration mass peaks in Table B.1 in Appendix B on page 12. In decreasing order of preference, the preferred digital data formats are:

(1) ISO 14976: Surface chemical analysis – Data transfer format with the static SIMS information format.
(2) ION-TOF or PHI data format.
(3) Two column ASCII format as shown in Table 2 below.
(4) A simple binary format – with details of structure supplied.

Data compression should be used with formats (1) and (2) above. The recommended software is WinZip V8. Identify the software and version used in the reporting form in Appendix B.

Table 2 - Format for ASCII data

Column 1	Column 2
Mass (amu)	Intensity (counts)

The preferred data media are, in decreasing order of preference:

(1) CD-ROM (PC-readable)
(2) E-mailed.
(3) ZIP100 or ZIP250 disks.

If you cannot use any of these systems then contact the author for advice.

ACKNOWLEDGEMENTS

The authors are grateful to Professor Dr A Benninghoven and Dr S Bryan for helpful comments. This work forms part of the Valid Analytical Measurement programme supported by the United Kingdom Department of Trade and Industry.

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5. I S Gilmore in "ToF-SIMS: Surface Analysis by Mass Spectrometry" Edited by J. C. Vickerman and D. Briggs, SurfaceSpectra and IM publications, 2001.

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7. I S Gilmore and M P Seah, NPL website, http://www.npl.co.uk/npl/cmmt/sis/lowenergyfloodgundamage.pdf

8. I S Gilmore and M P Seah, Int. J. Mass Spectrom. **202** (2000) 217.

9. I S Gilmore and M P Seah, NPL website, http://www.npl.co.uk/npl/cmmt/sis/iondetectionefficiency.pdf

10. I S Gilmore and M P Seah, NPL website, http://www.npl.co.uk/npl/cmmt/sis/gsims.pdf

11. I S Gilmore and M P Seah, NPL website, http://www.npl.co.uk/npl/cmmt/sis/gsimsofcrystallisableorganics.pdf

APPENDIX A

COMPUTATION OF SETTINGS FOR ANALYSIS

(1) Symbols

d = beam diameter (m)
e = charge on the electron (C)
i = pulsed ion beam current (A) [i.e. the time averaged current with pulsing on]
n = number of complete raster frames
w = pulse width (s)
F = pulse repetition rate or frequency (s^{-1})
I = DC ion beam current (ions/s) [i.e. the current with the pulsing off]
J = total ion fluence (ions/m^2)
N = No of pixels along a line of the raster
Q = total number of incident ions
R = raster size (m)
T = total spectrum acquisition time (s)

(2) Computation

(a) Condition that the beam is sufficiently defocused

$$d > 2R/N \tag{A.1}$$

(b) Total dose

$$J = \frac{iT}{eR^2} \tag{A.2}$$

for some instruments, i, is not known and the DC current, I, is recorded instead, then

$$J = \frac{FIwT}{eR^2} \tag{A.3}$$

(c) Number of frames

The number of complete frames, n, in the acquisition is

$$n = \frac{JeR^2F}{iN^2} \tag{A.4}$$

We recommend that the ion beam current and/or the acquisition time are adjusted so that $n > 20$.

(3) Example values for static SIMS

For a reasonable quality spectrum we may need $Q = 4 \times 10^8$ incident ions. Then, if the maximum dose is to be less than 10^{16} ions/m^2 (J), we find from Eq (A.2)

$$R \geq 200\text{ì m} \tag{A.5}$$

To ensure that mass resolution is not too degraded R=200 μm is recommended. If better counting statistics are required, especially for the PC sample, R will need to be increased. This may be at the cost of reduced mass resolution. For a 128 x 128 raster, from Eq (A.1)

$$d \geq 3.1\,\mu\text{m} \tag{A.6}$$

If you cannot defocus to this extent, N must be increased. Typically, many systems use a 0.5 pA pulsed ion beam current (i), a repetition rate of 10 KHz (F) , a square raster of 128 pixels (N), then for our recommended conditions, where J = 1 x 10^{16} ions/m^2 and R =200 μm:

then

$$T = 128\,\text{s} \tag{A.7}$$

and

$$n = 78 \tag{A.8}$$

APPENDIX B

FORMS FOR REPORTING

NPL STATIC SIMS INTERLABORATORY STUDY

Documentation to Accompany Data

This form is to be completed by the analyst.

Name: _____ Signature: _____

Address: _____ Date: _____
_____
_____
_____

Tel: _____
Fax: _____
E-mail _____

INSTRUMENT

Manufacturer _____
Model _____
Description _____
_____
_____
_____

REFERENCE MATERIAL NUMBERS

PC _____
PS _____
PTFE _____

ION SOURCE

Primary ion species _____(a) for SIMS_____ (b) extra for G-SIMS_____
Energy at sample (keV) _____(a) for SIMS_____ (b) extra for G-SIMS_____
Beam size (μm) (*d*) _____(a) for SIMS_____ (b) extra for G-SIMS_____
Ion beam angle from sample normal (deg) (a) for SIMS_____ (b) extra for G-SIMS_____
Raster length x direction (on sample) (μm) (*R*)_____
Raster length y direction (on sample) (μm) (*R*)_____
Number of pixels in x-raster (*N*) _____
Number of pixels in y-raster (*N*) _____

MASS SPECTROMETER

Extraction potential (Volts) ----------
Sample potential (Volts) ----------
Analyser angle from surface normal (deg) ----------
Analyser acceptance cone semi-angle (deg) ----------
Analyser acceptance energy (eV) ----------
Analyser slit or other details ----------

DETECTOR

Type (single MCP, chevron stack) ----------
Post-acceleration (kV) ----------
Voltage across detector (kV) ----------
Dead time (ns) ----------

CHARGE COMPENSATION

Electron beam energy at sample (eV) ----------
Electron beam angle from surface normal (deg) ----------
Electron pulsed beam current (nA) ----------
Pulse length and timing details ----------

DATA FILES

Format ----------
Ordinate (Counts, counts/s, counts/amu) ----------

Table B.1 - Spectral Information

Sample	PC		PS		PTFE	
Ions detected	+	-	+	-	+	-
Spectrum file name(s)						
Start mass / end mass						
Time bin size, ns						
Ion beam pulsed current (i) (pA)						
Repetition rate (F) (Hz)						
Acquisition time in seconds (T)						
Total ions/m^2 for (J)						
Calibration masses and peak label i.e. CH_3						
Other data, observations.						

CAPTIONS

Fig 1 Unified cascade gradient plot for Ar^+, Ga^+, Xe^+, Cs^+ and SF_5^+ for energies between 4keV and 25 keV for PS, after ref (3).

Fig 2 The effect of reflector voltage on the CF_2^+ peak intensity from PTFE. The recommended operating potential, +50 V, for this study is marked.

Fig 3 Flow chart of the work

Fig 4 Static SIMS spectra of PC, using the recommended conditions in Appendix A, (a) positive ions, (b) negative ions.

Fig 5 Static SIMS spectra of PS, using the recommended conditions in Appendix A, (a) positive ions, (b) negative ions.

Fig 6 Static SIMS spectra of PTFE, using the recommended conditions in Appendix A, (a) positive ions, (b) negative ions.

Fig 7 Schematic of 4 x 4 array of measurement positions for a sample holder with a square aperture of side 8 mm. A zone 1.5 mm from the perimeter is identified where data should not be acquired.

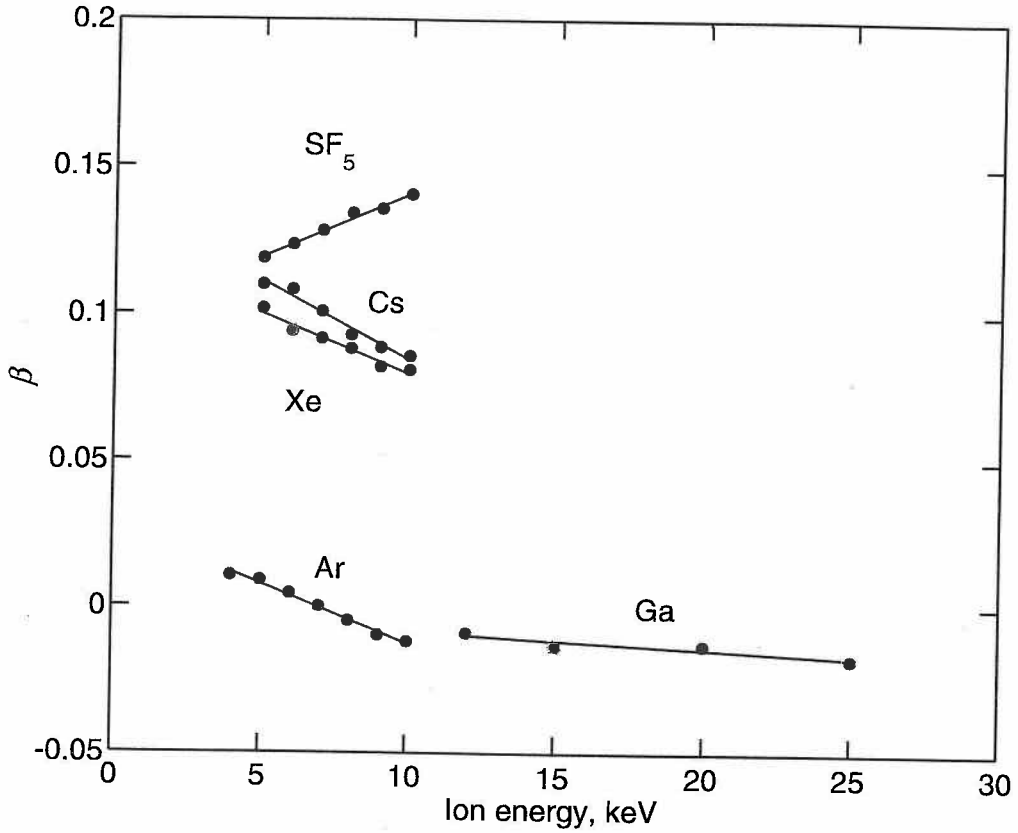

Fig 1 Unified cascade gradient plot for Ar^+, Ga^+, Xe^+, Cs^+ and SF_5^+ for energies between 4keV and 25 keV for PS, after ref (3).

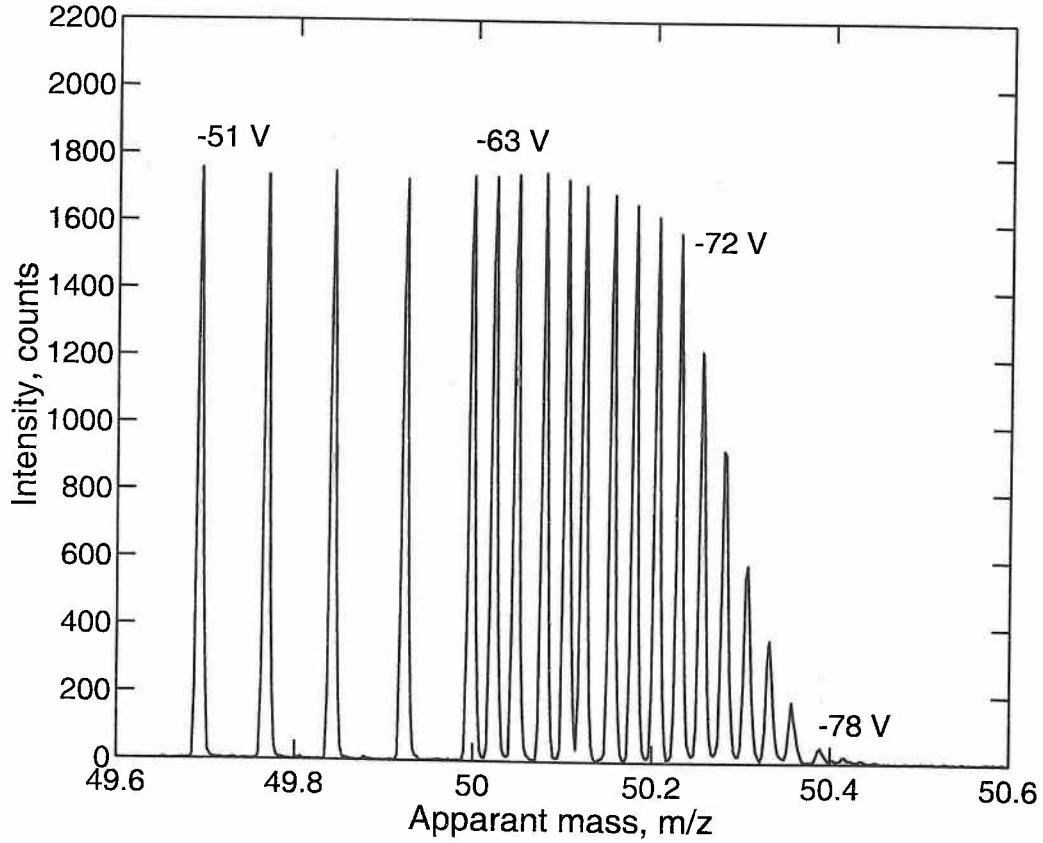

Fig 2 The effect of reflector voltage on the CF_2^+ peak intensity from PTFE. The recommended operating potential, +50 V, for this study is marked.

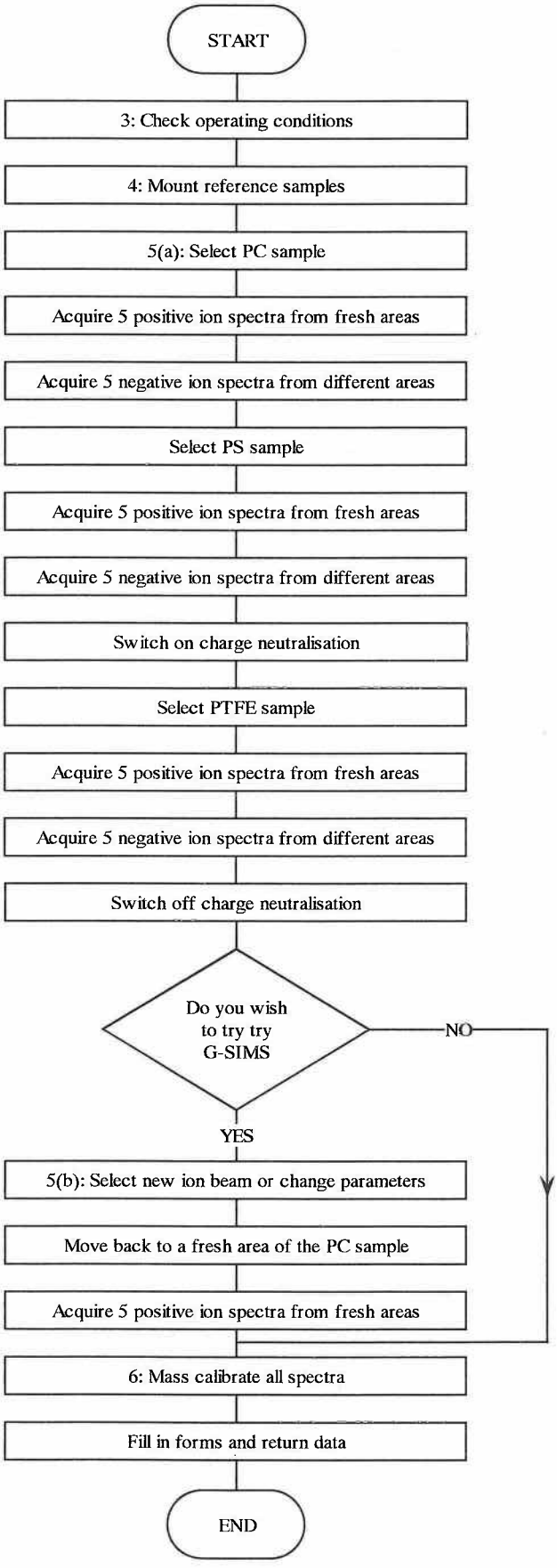

Fig 3 Flow chart of the work

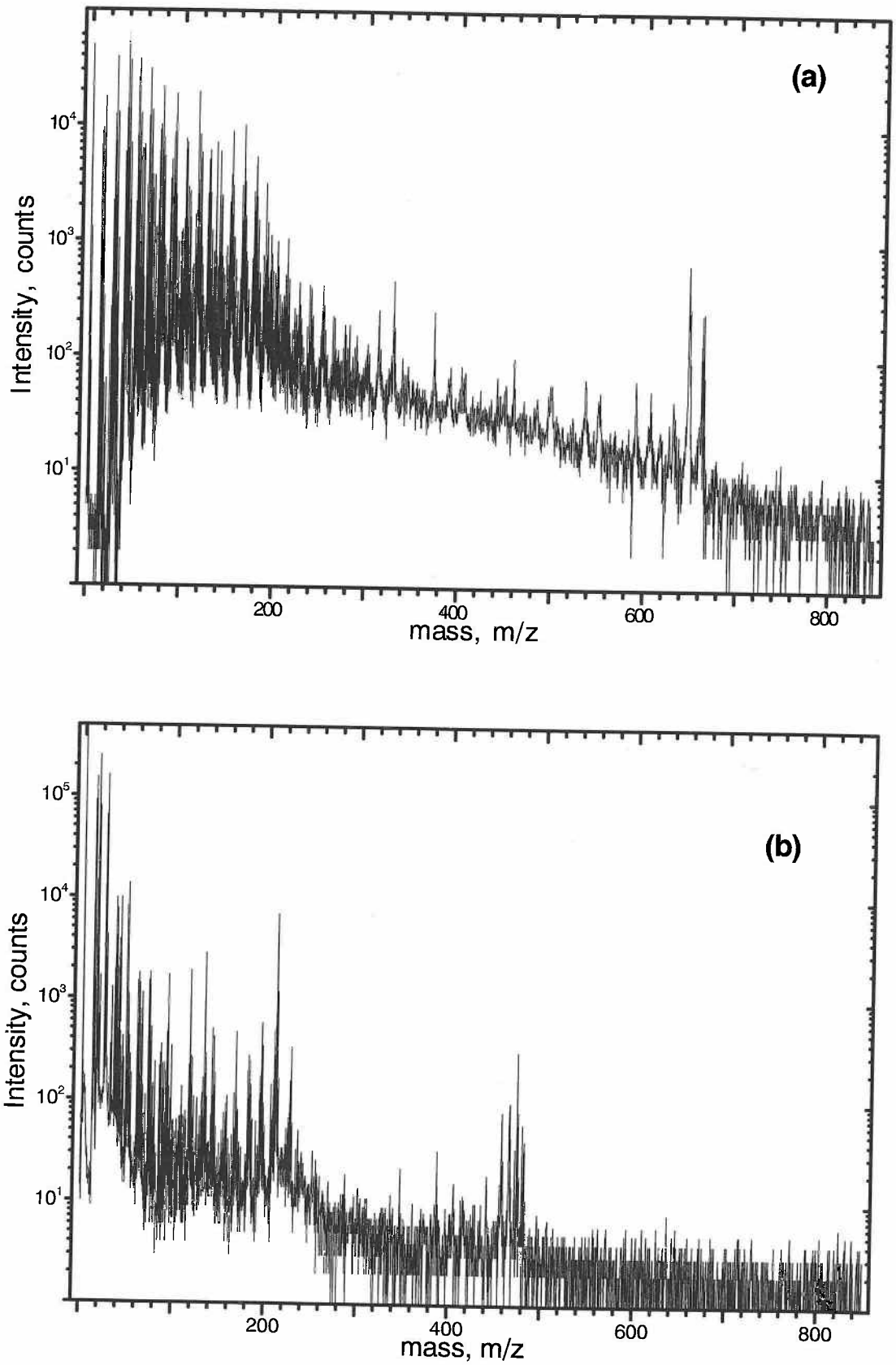

Fig 4 Static SIMS spectra of PC, using the recommended conditions in Appendix A, (a) positive ions, (b) negative ions.

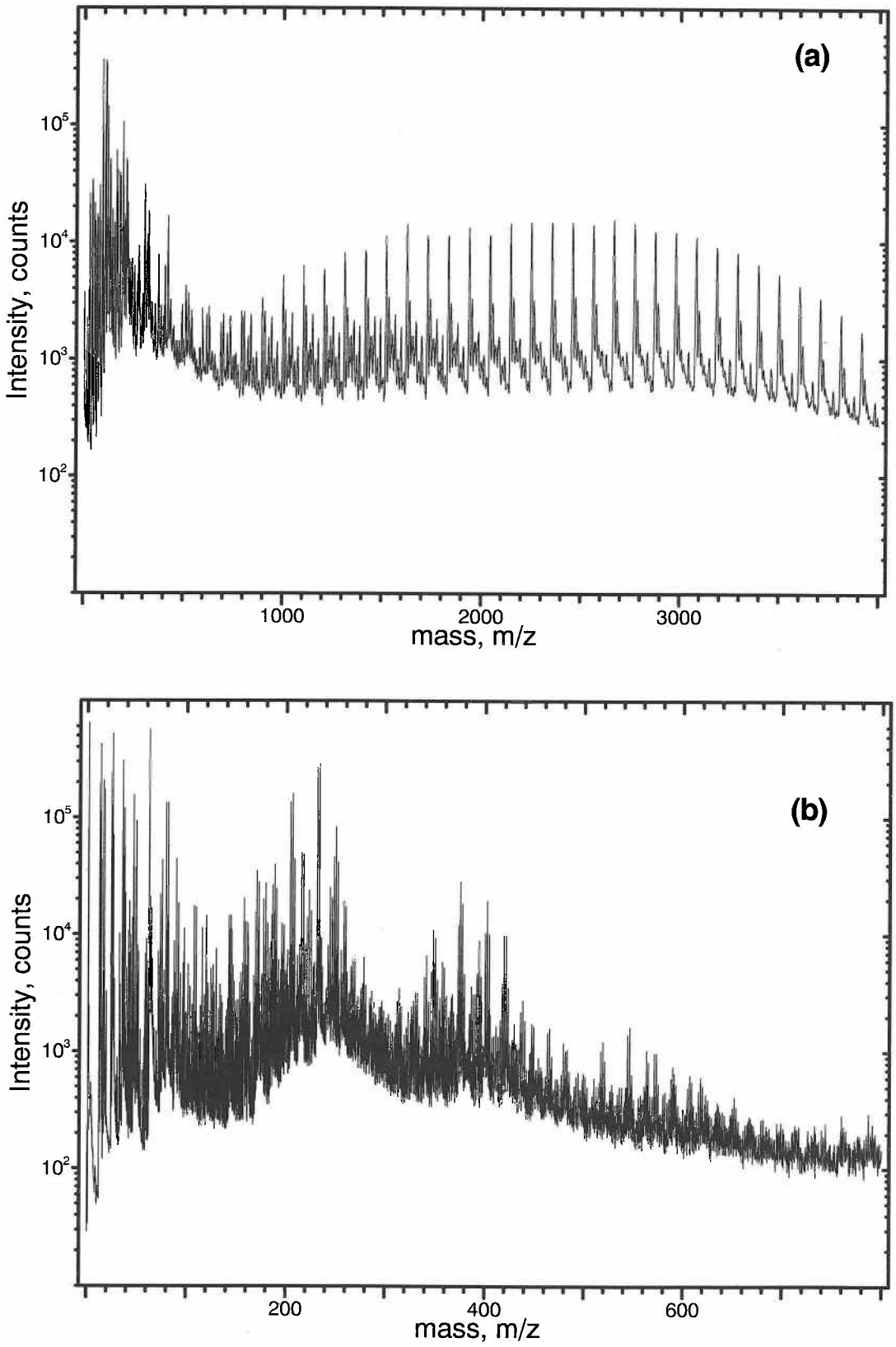

Fig 5 Static SIMS spectra of PS, using the recommended conditions in Appendix A, (a) positive ions, (b) negative ions.

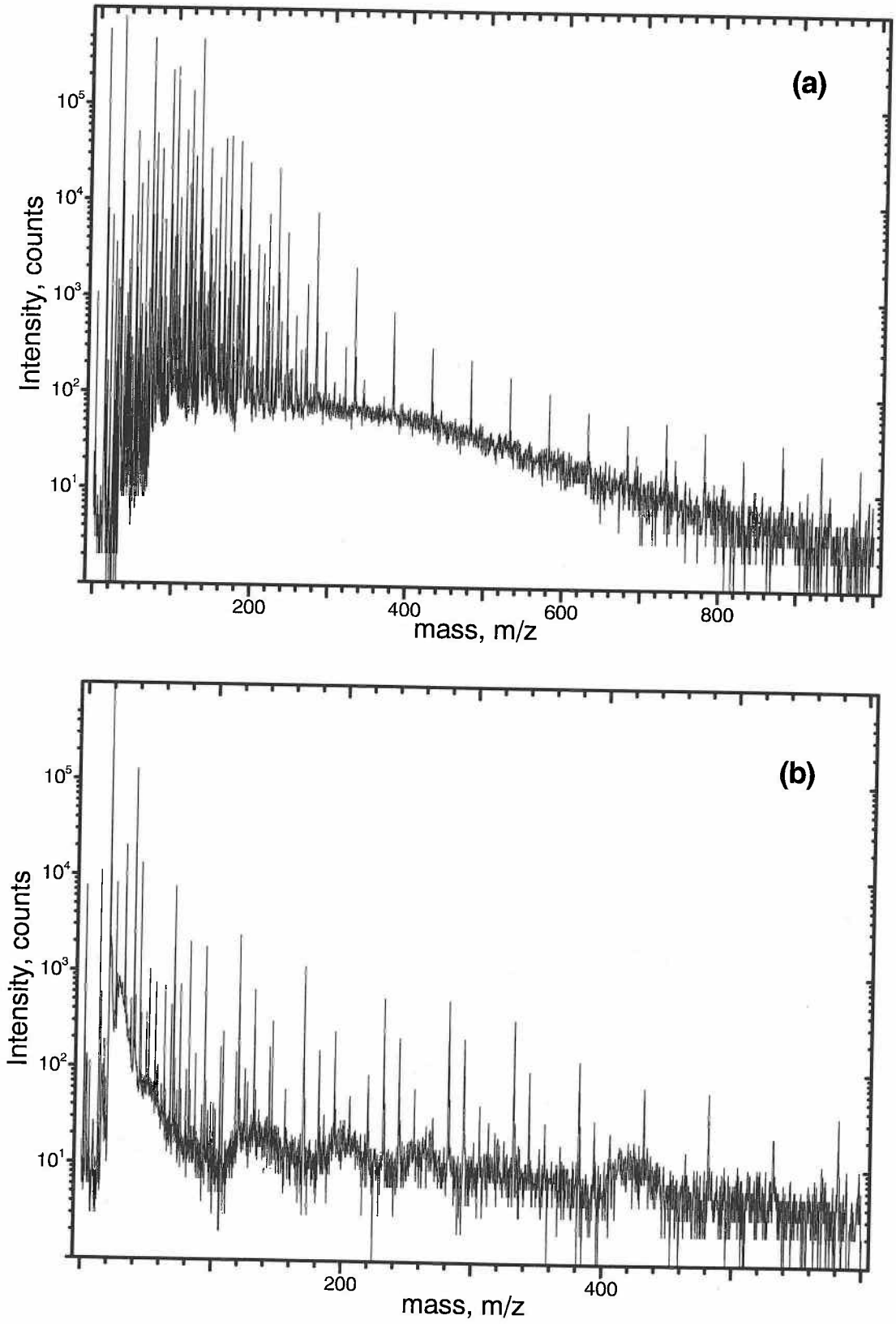

Fig 6 Static SIMS spectra of PTFE, using the recommended conditions in Appendix A, (a) positive ions, (b) negative ions.

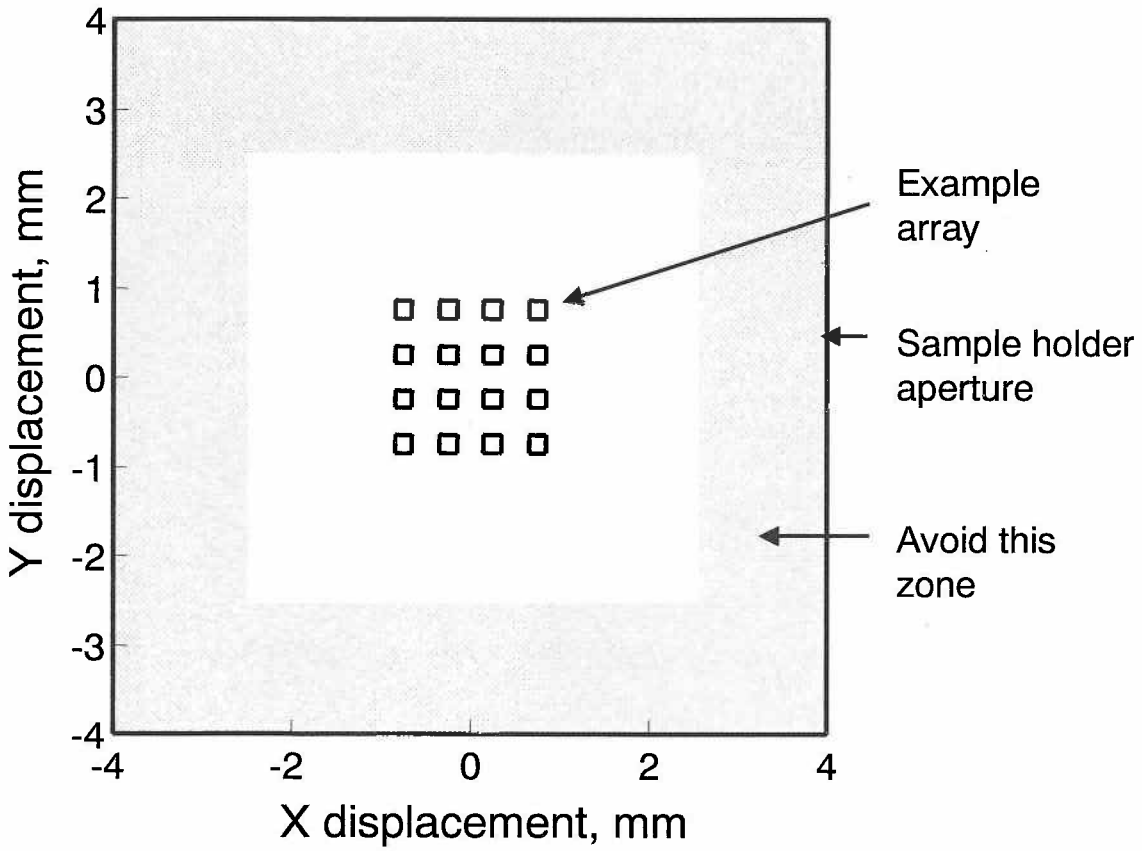

Fig 7 Schematic of 4 x 4 array of measurement positions for a sample holder with a square aperture of side 8 mm. A zone 1.5 mm from the perimeter is identified where data should not be acquired.