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VAMAS project A3(d) Static SIMS Interlaboratory Study – Part I: Linearity of the intensity scale – Protocol for analysis

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Division of Quality of Life

ABSTRACT

This report describes the protocol for analysis in the VAMAS project A3(d) static SIMS interlaboratory study – Part I: Linearity of the intensity scale. Procedures for setting the primary ion beam, mass analyser, ion detector and charge compensation are provided to assist users in obtaining repeatable results. A reference material of bulk PTFE is supplied for this study. No sample preparation is required by the user and specific guidance is given on sample handling. A spreadsheet is provided for the reporting and analysis of the data.

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Approved on behalf of the Managing Director, NPL
by Dr M Sene, Director, Quality of Life Division.

CONTENTS

1 INTRODUCTION

Static SIMS (SSIMS) is a powerful technique for the analysis of organic and molecular surfaces. Over the last decade, instrumentation has improved significantly so that modern instruments now have very high reliability. The first VAMAS static SIMS interlaboratory study was conducted by NPL in 1996[1,2]. Results indicated that, whilst repeatabilities could be as good as 1%, they were on average only 10%. In the second interlaboratory study[3] repeatabilities had improved significantly so that over 84% of instruments exhibited excellent intensity repeatabilities of better than 1.9%. It was also demonstrated that the comparability of relative ion intensities between different instrument designs can be better than 4% when using the Relative Instrument Spectral Response (RISR)[3]; the RISR method improves comparability by a factor of up to 33. In the third interlaboratory study[4], the repeatability and constancy of instruments was evaluated based on the draft ISO standard, ISO 23830 "static SIMS repeatability and constancy of the relative intensity scale". This shows that 50% of instruments had a constancy of better than 5%. For the identification of complex organic molecules, an accurate mass scale calibration is essential and this study was used in the development of ISO 23830.

Over recent years the use of cluster primary ion beams for the analysis of organic materials has grown enormously. This is because of the large increase in molecular ion yields and the ability to depth profile organic material. In this fourth interlaboratory study, the aim of part I is to measure the linearity of the intensity scale and evaluate dead-time correction procedures and the aim of part II is to relate experimental conditions of organic depth profiling to the (dose-dependent) sputtering yield. This study is not limited to cluster primary ions.

This report is only for part I, a separate protocol of analysis for part II is given in NPL Report AS 32 (2009).

2 TIME TABLE

You should complete the analysis for this work by 30th June 2009. If you cannot do so and need extra time please inform joanna.lee@npl.co.uk.

3 THIS PACKAGE

This package contains this protocol and one reel of PTFE tape for part I of the interlaboratory study and a separate protocol and sample for part II (organic depth profiling). Inspect the packaging to check if it has been opened by customs and if the integrity of the samples has been compromised. If you are in doubt, contact NPL. Please notify us that everything is received in order.

☐ I have emailed NPL that all is OK with the sample on / / 2009

4 OUTLINE OF PROPOSED METHOD

In this work, secondary ion spectra are measured for the PTFE reference sample to be analysed without further sample preparation. The analytical conditions are chosen by the analyst to provide secondary ion intensities per pulse in the linear and non-linear range of detector ion counting. This is established using 16 test spectra for a test sample and the 16 data spectra are measured for the analysis sample. This study is only applicable to time-of-flight instruments operating in single ion counting mode. A spreadsheet is provided to report the data and evaluate the detector linearity. The digital spectral data are then sent to NPL for further analysis. The PTFE is supplied as a full reel of tape. It is a bulk insulator and will require charge neutralisation. The PTFE is to be analysed in the "as received" condition with no in-house cleaning.

The spectrometer should be operated under conditions that give the most stable performance. It is recommended that analysts use ISO 23830 to confirm the repeatability of their instrument. The protocol described here is closely aligned with ISO 23830 and those using that standard will already be familiar with much of the procedure given here. 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 operating conditions as consistent as possible.

5 INSTRUMENT OPERATING CONDITIONS

5.1 ION BEAM

In this study, the primary ion current is varied to provide secondary ion intensities per pulse that range from minimal detector saturation to high detector saturation. A measurement of the ion beam current is not required since isotope ratios are used. High mass resolution is not necessary for this study. The mass peaks simply need to have a width smaller than the dead-time and this is usually easily satisfied.

The ion beam should be centred in the acceptance area of the mass spectrometer, if possible. First centre all the alignments for the mass analyser and then increase the ion beam raster area to image the entire mass analyser acceptance area. Using the ion beam controls, centre the mass analyser acceptance area in the imaged area. In some cases the maximum field of view may not be large enough to observe the acceptance area. If the software restricts it, it may be possible to change the calibration scaling or “sensitivity” to access a larger raster area and then return to the calibrated conditions after centring.

A maximum ion fluence of 1×10^{16} ions/m^2 is recommended. Appendix A is helpful here. A typical ion beam raster area for this work is 200 μm × 200 μm but may be increased to 400 μm × 400 μm to satisfy the fluence requirements. 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. . It is recommended that a random raster pattern is used, if available.

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 local 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.

Use your preferred ion source and energy for spectroscopic analysis. It does not matter if it is an atomic primary ion or a cluster primary ion, so long as the beam current can be adjusted to give a large range of secondary ion intensities and detector saturation as discussed in 7.2.

5.2 MASS SPECTROMETER

In general, the spectrometer should be operated in the condition that gives the most stable and repeatable performance with good, high mass sensitivity. A suggested method for analyser deflector alignment, if required, is as follows. With the primary ion beam centred in the analysis area on the PTFE sample, 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.

For reflection instruments, 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 1. 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 1, the sample potential is approximately –79 volts (this arises from the extractor pulsing on when the flood gun is off and depends on the sample thickness and dielectric constant). 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 20 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 -55 volts.

The reflector potential may need adjustment to ensure that strong metastable peaks do not overlap the weaker ^{13}C isotopic peaks identified later in Table 1. An energy acceptance of 20 eV (reflector voltage of –55 V) for a 2 keV pass energy for an ION-TOF IV instrument is convenient.

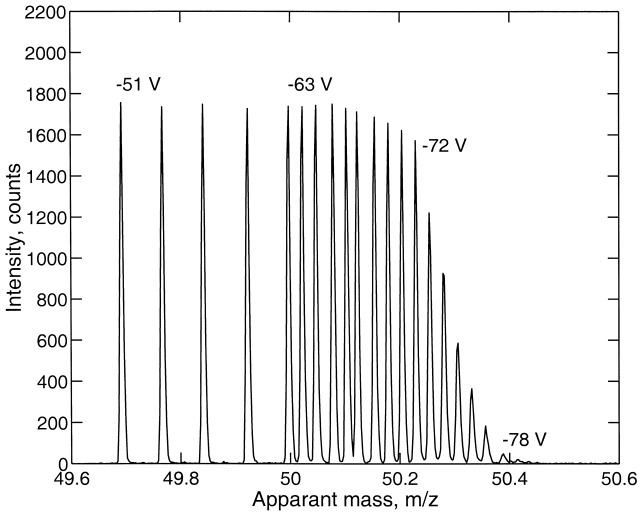

Fig 1 The effect of reflector voltage on the CF_2^+ peak intensity from PTFE.

5.3 CHARGE COMPENSATION

Charge compensation is necessary for this study. A detailed study of electron beam damage[8] provides recommendations which are presented in a one page summary[9]. Participants in this study should either read the summary, which may be accessed using the web page for reference (9), or ref (8), 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.

5.4 ION DETECTOR

A detailed study of ion detection efficiencies for microchannel plates[10] provides recommended operating conditions which are presented in a one page summary[11]. Use the detector post acceleration voltage that is normal for your work. Set the voltage of the microchannel plate using your usual procedures; guidance is given in references (10) and (11).

6 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. 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.

The PTFE is provided as a reel of tape. Remove and discard the first 20 cm of material 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 and it is this surface that is analysed. Do not clean the sample. Mount samples on the sample holder to produce a flat even surface using a mechanical clamping or fixing method. Do not use adhesive tape. Ensure that the reverse side of the sample is against a conducting surface, electrically connected to the sample holder. The PTFE shall not be placed over a hole. The presence of a hole under the sample leads to poor mass resolution and repeatability in systems that use high extraction fields such as time-of-flight and magnetic sector systems.

7 DATA ACQUISITION

A flow chart for the work is given in Fig 2. The reference spectrum for PTFE is available as a digital file in ISO 14976 format at:
http://resource.npl.co.uk/docs/science_technology/nanotechnology/ssims/ptfe_pos.zip
and may be viewed using a free eViewer available at:
http://www.npl.co.uk/nanoanalysis/eviewerindex.html

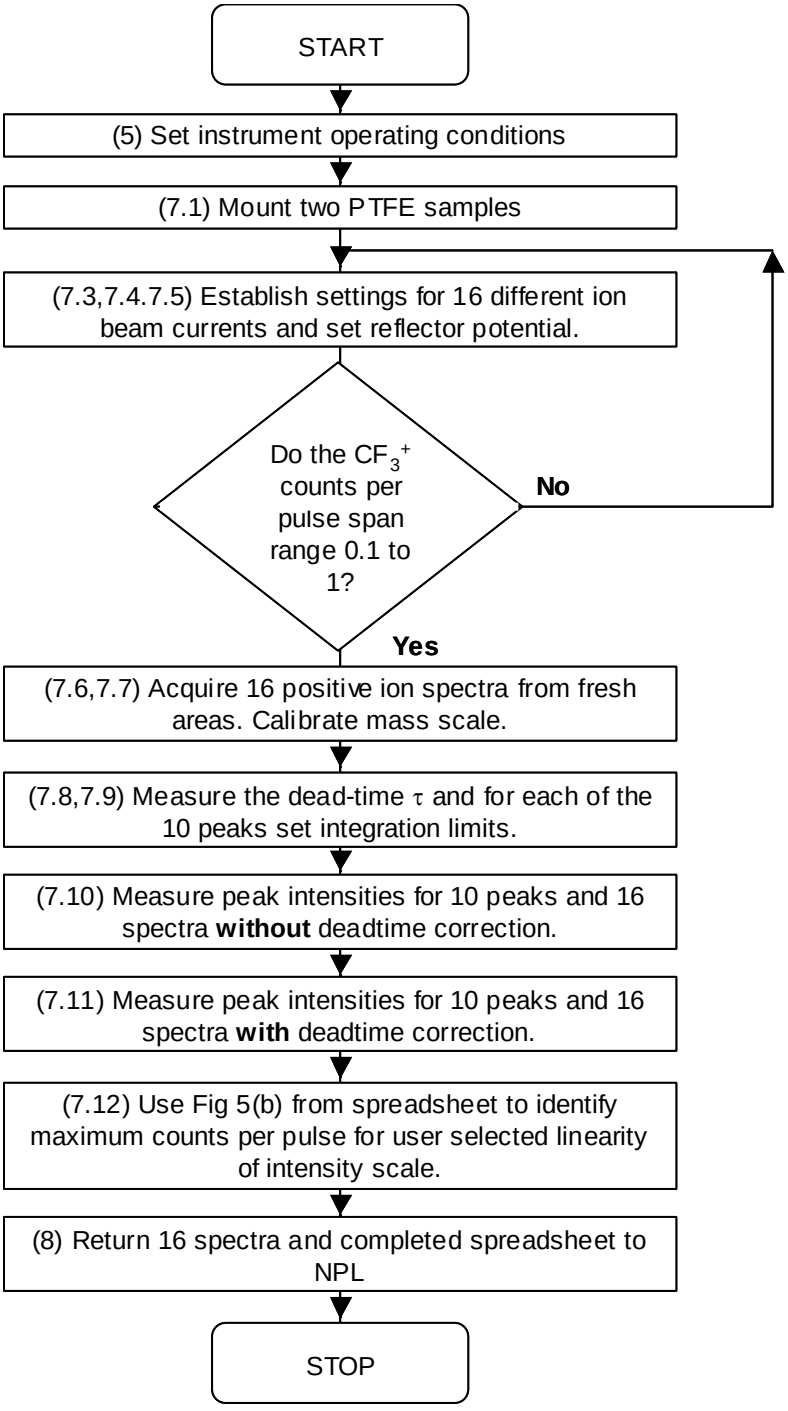

Fig 2 Flow chart of the work. The numbers in parentheses refer to sections in the text.

A fresh area of material should be analysed each time with a total fluence of less than 1 x 10^{16} ions/m^2 (1 x 10^{12} ions/cm^2). Fig. 3 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. Record relevant information in the electronic reporting form supplied.

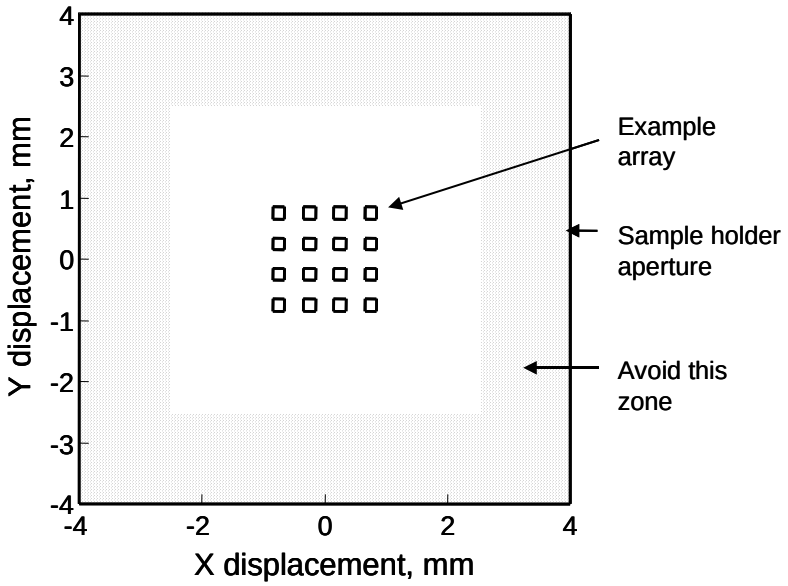

Fig 3 Schematic of 4 x 4 array of measurement positions for a sample holder with a square aperture of side 8 mm. A zone 1.5 mm from the perimeter is identified where data should not be acquired.

This procedure has been developed to be closely compatible with ISO 23830[(4)] "Static SIMS repeatability and constancy of the relative intensity scale". You may wish to use this standard prior to this study to confirm your repeatability.

7.1 Mount two PTFE samples as described in 6. One will be for setting the range of primary ion currents required (**test sample**), the other for the analysis (**analysis sample**).

7.2 Switch on the charge neutralisation.

7.3 From the **test sample**, acquire a positive ion spectrum using the primary ion current that would normally be used for analytical conditions. Establish 16 settings of the primary ion current that provide spectra which, at the highest current, i_{max}, give ion intensities that lead to total saturation of the detector. The remaining 15 currents each at approximately $(k/16)i_{max}$, where k = 1 to 15, should produce a saturated detector and an unsaturated detector. Example spectra, covering this range, for the CF_3^+ peak are shown in Fig. 4 (the spectra here are normalised to a constant intensity for the $^{13}CF_3^+$ peak). It is not too critical if the ion beam current drifts during the experiments as intensity ratios to isotopic peaks are used.

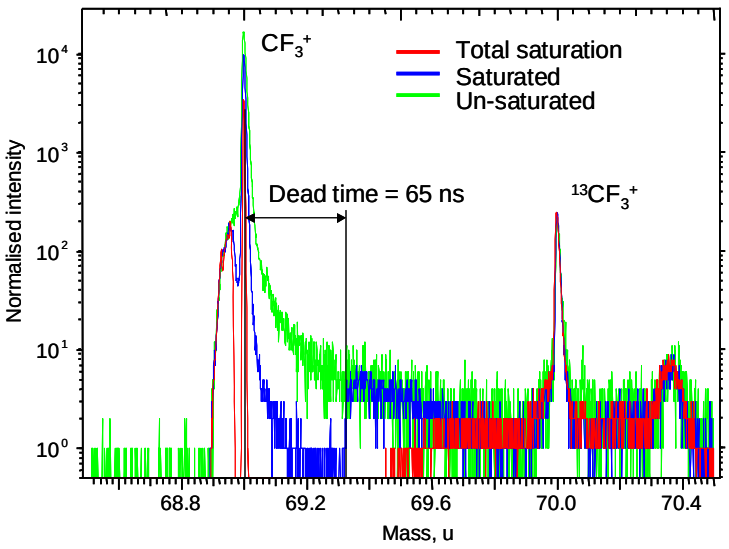

Fig 4 Example spectra showing detail of the CF_3^+ and $^{13}CF_3^+$ peaks with total saturation of the detector, saturation of the detector and un-saturated detector. The peak intensities are normalised to the $^{13}CF_3^+$ for display.

The peaks to record intensities for are given in Table 1. For the low ion beam currents it may be necessary to increase the acquisition time so that the weakest peaks (the isotopes) have > 1000 counts. The weakest peak is likely to be the $^{13}CCF_5^+$ peak.

Table 1 — Values of the mass for each fragment and corresponding isotope fragment to be recorded for different primary ion beam currents.

Fragment	Mass, u	Isotope Fragment	Mass, u
CF	30.9984	^{13}CF	32.0018
CF_3	68.9952	$^{13}CF_3$	69.9986
C_3F_3	92.9952	$^{13}CC_2F_3$	93.9986
C_2F_5	118.9920	$^{13}CCF_5$	119.9954
C_3F_5	130.9920	$^{13}CC_2F_5$	131.9954

7.4 For the analysis of linearity of the intensity scale later, it is the counts per primary ion pulse, *c*, that is important rather than the total ion counts. Use Eq (A.5) or Eq (A.6) to confirm that the selected primary ion currents provide a range of values of *c*, for the CF_3^+ peak, between approximately 0.1 and 0.99 counts per pulse. If this is not the case, adjust the primary ion beam current until the condition is satisfied.

7.5 Check that there are no major metastable peak overlaps with the peaks in Table 1. If there are, adjust the reflector voltage.

7.6 Move to the **analysis sample**. For each of the 16 settings of primary ion current determined at 7.3, acquire a positive ion spectrum from a fresh area of sample. Select the acquisition time to ensure the counts for the $^{13}CCF_5^+$ peak are greater than 1000 and the maximum dose is < 1 x 10^{16} ions/m^2.

7.7 Calibrate the mass scale for each spectrum.

7.8 Measure the dead-time, τ, of the spectrometer from an overlay plot of the CF_3^+ peak. If your software allows, it is helpful to normalise the spectra to the peak height of the $^{13}CF_3^+$ peak. Identify a spectrum similar to the one labelled "saturated" in Fig. 4. Here, the signal is reduced after the peak but does not go to zero and after some time, τ, recovers. Measure the value of τ. It is usually possible in the software to switch between a mass scale, a time scale and sometimes a channel number. To convert from channel number to time, simply multiply by the instrument channel width (usually around 200 ps). In this example τ = 65 ns. Record the value of τ in the spreadsheet.

7.9 Integration limits are now set for measuring the peak intensities. This is normally done by establishing a peak list in the instrument analysis software. For each peak in Table 1 identify the masses equivalent to τ ns less than and τ ns more than the peak centre. Set these as the peak integration limits. Some weak metastable peaks and metastable background intensity will be included in the integration. This generally does not matter as they are relatively weak. **It is important that the intensity is summed for at least τ ns after the peak.**

7.10 Measure the intensities of the 10 peaks for the 16 spectra **without** any software dead-time correction. Enter these and the number of primary ion pulses in each spectrum in the spreadsheet.

7.11 Measure the intensities of the 10 peaks **with** instrument analysis software dead-time correction (if available). Enter these and the number of primary ion pulses in each spectrum in the spreadsheet.

7.12 Enter the software version in the spreadsheet.

7.13 The spreadsheet will automatically calculate the detector efficiency and the corrected detector efficiency as a function of the number of measured counts per pulse at the detector. These are shown in Figures 5(a) and (b) respectively. If you experience difficulties, send the data to NPL. The theoretical curve in Fig 5(a) is calculated from reference (13).

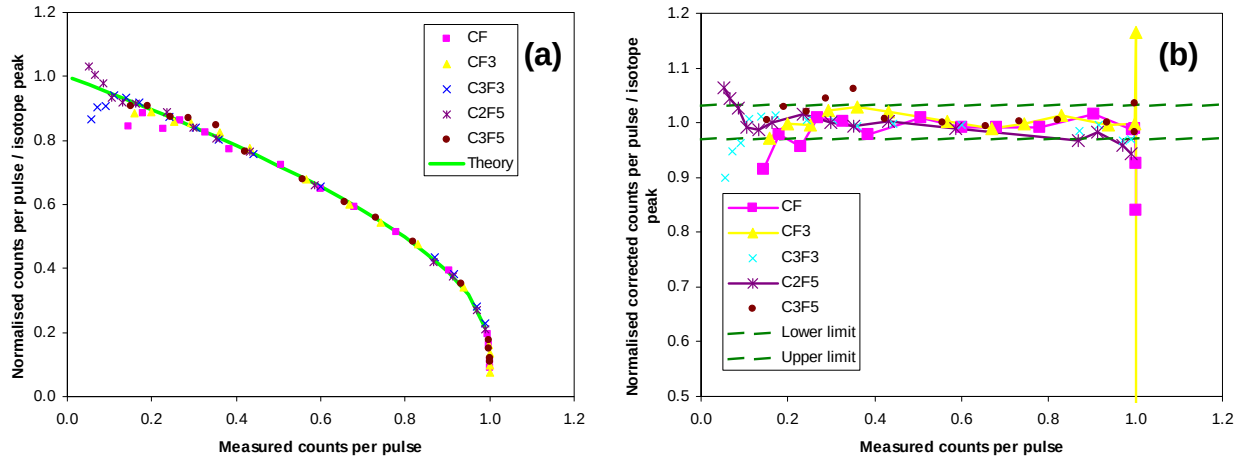

Fig 5 Detector efficiency for CF^+, CF_3^+, $C_3F_3^+$, $C_2F_5^+$ and $C_3F_5^+$, calculated from the normalised intensity ratio with the corresponding isotope peak, versus counts per pulse for (a) uncorrected data with a constant scaling factor to the theoretical efficiency (green line) from reference (13) and (b) data with instrument software dead-time correction and upper and lower limits for linearity of the intensity scale.

7.14 From Figure 5(b), select the operating limits that you wish the intensity scale to be linear over, for example ± 3% and enter this in the spreadsheet. The limits are shown as dashed lines. The maximum number of counts per pulse in a peak (integrated over the dead-time) is given by the value at which the detector response is outside of these limits. In this example a maximum of 0.95 counts per pulse gives a linearity of ± 3%.

NOTE: At low measured counts per pulse (approximately 0.2) the data are rather scattered owing to low counts in the isotope peaks and the increasing effect of background signals. These data are not necessary for setting the linearity of the intensity scale and should be ignored.

8 AFTER ANALYSIS

When all analyses are complete, return the completed spreadsheet and the original 16 spectral data files by email to NPL (joanna.lee@npl.co.uk). Please retain the PTFE reel in case we find any anomalies in your data. A check list is provided in the spreadsheet form.

9 DATA REPORTING FORMAT

The preferred method for returning spectral data and forms is by email, alternately use a CD ROM. The preferred digital data formats are, in decreasing order of preference:

(1) ISO 14976: Surface chemical analysis – Data transfer format with the static SIMS information format. Compress the files using WinZip.
(2) ION-TOF or ULVAC-PHI data format.
(3) Two column ASCII format with the first and second columns being mass and intensity respectively.

10 ANY QUESTIONS

If you are unsure of anything please contact Joanna Lee, email: joanna.lee@npl.co.uk.

ACKNOWLEDGEMENTS

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APPENDIX A

COMPUTATION OF RASTER, CURRENT, NUMBER OF FRAMES FOR ANALYSIS AND COUNTS PER PULSE

(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 = number of pixels along a line of the raster
Q = total number of incident ions
R = raster size (m)
T = total spectrum acquisition time (s)
c = secondary ion counts per primary ion pulse (counts)
A = peak intensity of a selected peak (counts)
P = total number of primary ion pulses in the acquisition time T (no units)

(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

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

For non-pulsed instruments such as magnetic sector and quadrupole based systems use equation (A.2) but with the pulsed current, i, substituted with the non-pulsed current, I.

(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 $n > 20$.

(d) Counts per primary ion pulse

$$c = \frac{A}{P} \tag{A.5}$$

if the total number of pulses is not given by the software use

$$c = \frac{A}{FT} \tag{A.6}$$

(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)

$$R \geq 200\,\mu\text{m} \tag{A.7}$$

To ensure that mass resolution is not too degraded R=200 μm is recommended. If better counting statistics are required, 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)

$$d \geq 3.1\,\mu\text{m} \tag{A.8}$$

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

$$T = 128\,\text{s} \tag{A.9}$$

and

$$n = 78 \tag{A.10}$$