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VAMAS 2006: Static SIMS Interlaboratory Study for Intensity Repeatability, Mass Scale Accuracy and Relative Quantification - Protocol For Analysis

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VAMAS 2006: Static SIMS Interlaboratory Study for Intensity Repeatability, Mass Scale Accuracy and Relative Quantification - Protocol For Analysis

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ABSTRACT

This report describes the protocol for analysis in the VAMAS 2006 static SIMS interlaboratory 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, bulk PTFE, polycarbonate on silicon and a thin layer of Irganox 1010 on silicon. No sample preparation is required by the user and specific guidance is given on sample handling. Forms for reporting the data are provided at http://www.npl.co.uk/nanoanalysis/interlaboratory2006.html.

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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 have 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. Based on the progress for these studies a new draft ISO standard CD 23830[4] for measuring repeatability and constancy of the relative intensity scale is being developed.

There is growing need for repeatable measurements and for instruments to be operated to give constancy. For example, in an analysis to distinguish between 'good' and 'bad' samples the analyst needs to know if the differences are statistically significant. In this study, based on the draft ISO standard ISO CD 23830, we evaluate the repeatability and constancy of the relative intensity scale. In a recent ISO survey of needs for standardisation in static SIMS a procedure for relative quantification and for calibration of the mass scale in TOF-SIMS ranked amongst the top needs. Thus, in this study we begin the development of relative quantification as well as evaluating methods for the mass scale calibration for TOF-SIMS instruments. The objectives of this interlaboratory study are therefore: (i) to determine the repeatability and constancy of the relative intensity scale, (ii) to evaluate the accuracy of the mass scale calibration for different generic types of TOF SIMS instruments and (iii) to evaluate the current capability of relative quantification using SSIMS.

2 TIME TABLE

You should complete the analysis for this work by 31st July 2006. If you cannot do so and need extra time please inform felicia.green@npl.co.uk.

3 THIS PACKAGE

This package contains this protocol, ISO CD 23830, one reel of PTFE tape, one sample in a fluoroware container and another sample in a sealed light-tight black plastic bag. 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 e-mailed NPL that all is OK with the samples on / / 2006

4 OUTLINE OF PROPOSED METHOD

In this work, secondary 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 ratios. A spreadsheet is provided (http://www.npl.co.uk/nanoanalysis/interlaboratory2006.html) to calculate repeatability and constancy according to ISO CD 23830 as well as for repeatability data. The digital data are then sent to NPL for further analysis. The three reference materials are PTFE, a thin spin-cast polycarbonate (PC) film on a silicon wafer and a patterned thin layer with different amounts of Irganox 1010 on a silicon wafer. The PTFE is supplied as a full reel of tape and the others are 1 cm × 1 cm pieces. PTFE is a bulk insulator and will require charge neutralisation. The PTFE is to determine repeatability and constancy of the relative intensity scale. The other two materials are conducting and no charge neutralisation is required. The PC is supplied in a Fluoroware container. The Irganox sample is supplied in a Fluoroware container within a black bag. Please keep the Irganox sample inside the black bag until you are ready to analyse the sample. Store the samples out of direct heat and direct light in a normal laboratory environment. 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 that 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.

5 INSTRUMENT OPERATING CONDITIONS

5.1 ION BEAM

The ion beam should be centred in the acceptance area of the mass spectrometer, if you can do this. 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 the software restricts it, 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. Appendix A is helpful here. The total number of ions should be adjusted using the ion beam 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 (note: this is especially important for PTFE which exhibits high ion yields). 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 (5). Alternatively, the raster area may be calculated from an image of a calibrated grid and the ion beam current measured using a drilled hole aligned with the ion beam, with a depth 5 times more than the diameter.

Use your preferred ion source and energy for spectroscopic analysis. Our preference for ion source is for consistency and least fragmentation, in decreasing order: Bi or Au, Cs, Xe and Ar. Cluster beams such as Au_5^+ and C_{60}^+ are excellent for static SIMS but for comparability here we would prefer, if possible, single atomic primary ions to be used.

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 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 for reflection instruments. For TRIFT instruments we recommend using the wider energy slit giving an energy acceptance of 240 eV and also recommend setting the contrast diaphragm to the "out" position. This results in much improved repeatability with only a small degradation in mass resolution and optimisation of the energy compensation[6]. For reflection 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[7]. This is discussed below.

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. 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.

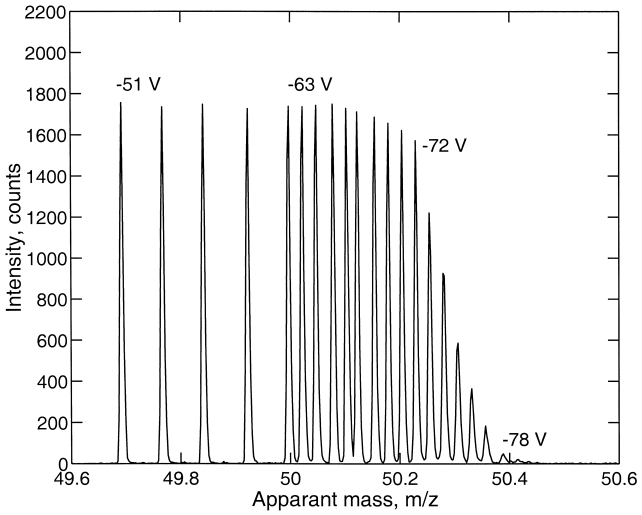

Fig 1 The effect of reflector voltage on the CF_2^+ peak intensity from PTFE.

For time of flight instruments, 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, u	Max rate, Hz	Min cycle time, μs
PTFE +	850	10000	100
PC +	850	10000	100
PC -	850	10000	100
Irganox -	1300	8350	120

5.3 CHARGE COMPENSATION

Charge compensation is necessary only for the PTFE sample. For the other samples, the electron source shall 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[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. The settings here are quite critical. Appendix B gives a

method to align the electron beam that is suitable for use with instruments that can image and display a total ion intensity image in real time.

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]. 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. Participants in this study should either read the summary, which may be accessed using the web page for reference (11), or ref (10).

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 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.

6.1 PTFE

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.

6.2 PC AND IRGANOX

The PC and Irganox samples are provided face down in separate small Fluoroware containers with a concave bottom. The Irganox sample is also in a light-tight black bag to reduce degradation from UV light. 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. The correct side to analyse has a smooth mirror-like finish and the reverse side is matt (lapped). The Irganox sample has a limited shelf life for quantification and needs to be analysed **after** the 7th June 2006 and **before** the 6th July 2006 to be within acceptable limits for quantification. Once analysed the Irganox sample needs to be returned to NPL. When mounting the Irganox sample it is important to note where the "X" scratched on the back of the sample is, so that results can be related to the four quadrants, each with different amounts of Irganox as shown in Fig 2. The reason for this is described in the next section.

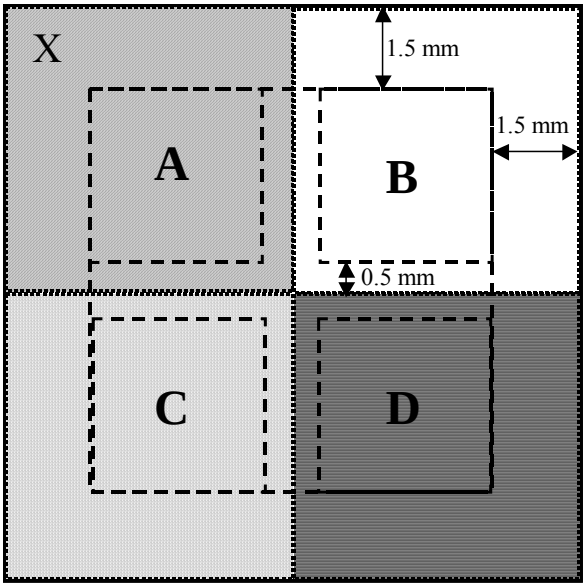

Fig 2 Irganox sample patterned with four quadrants each with different amounts of Irganox. Acquire spectra in the zones denoted by a letter within the dashed perimeter lines. Do not analyse within 1.5 mm of the edge of the sample holder or within 0.5 mm of the boundary of a quadrant. The symbol "X" denotes an "X" scratched on the reverse side of the samples for correct registration of the quadrant letters. This is the position of the scratch under the sample as viewed from the top. Note that the quadrants are depicted here by a different density of shading (you cannot see visually any differences between the quadrants on the sample), this does not necessarily correspond with the amount of material!

7 DATA ACQUISITION

Static SIMS analyses are to be made for each material and, if time and resources permit, conditions are given to evaluate accuracy of mass scale calibration for PC. A flow chart for the work is given in Fig 3. To help, reference spectra for each material are shown in Fig 4. These are also available on the NPL website as digital files in ISO 14976 format (http://www.npl.co.uk/nanoanalysis/interlaboratory2006.html) and may be viewed using a free eViewer available at http://www.npl.co.uk/nanoanalysis/eviewerindex.html.

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 5 shows a schematic of a 4 x 4 array of measurement positions, for a sample holder with an 8 mm × 8 mm square aperture, suitable for use with PTFE and PC. A separate arrangement is required for the patterned Irganox sample as shown in Fig 2. 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. Use the same instrument operating conditions for each sample unless otherwise stated. Record relevant information in the electronic reporting form supplied. We now give specific guidance for each of the three objectives of this study defined earlier.

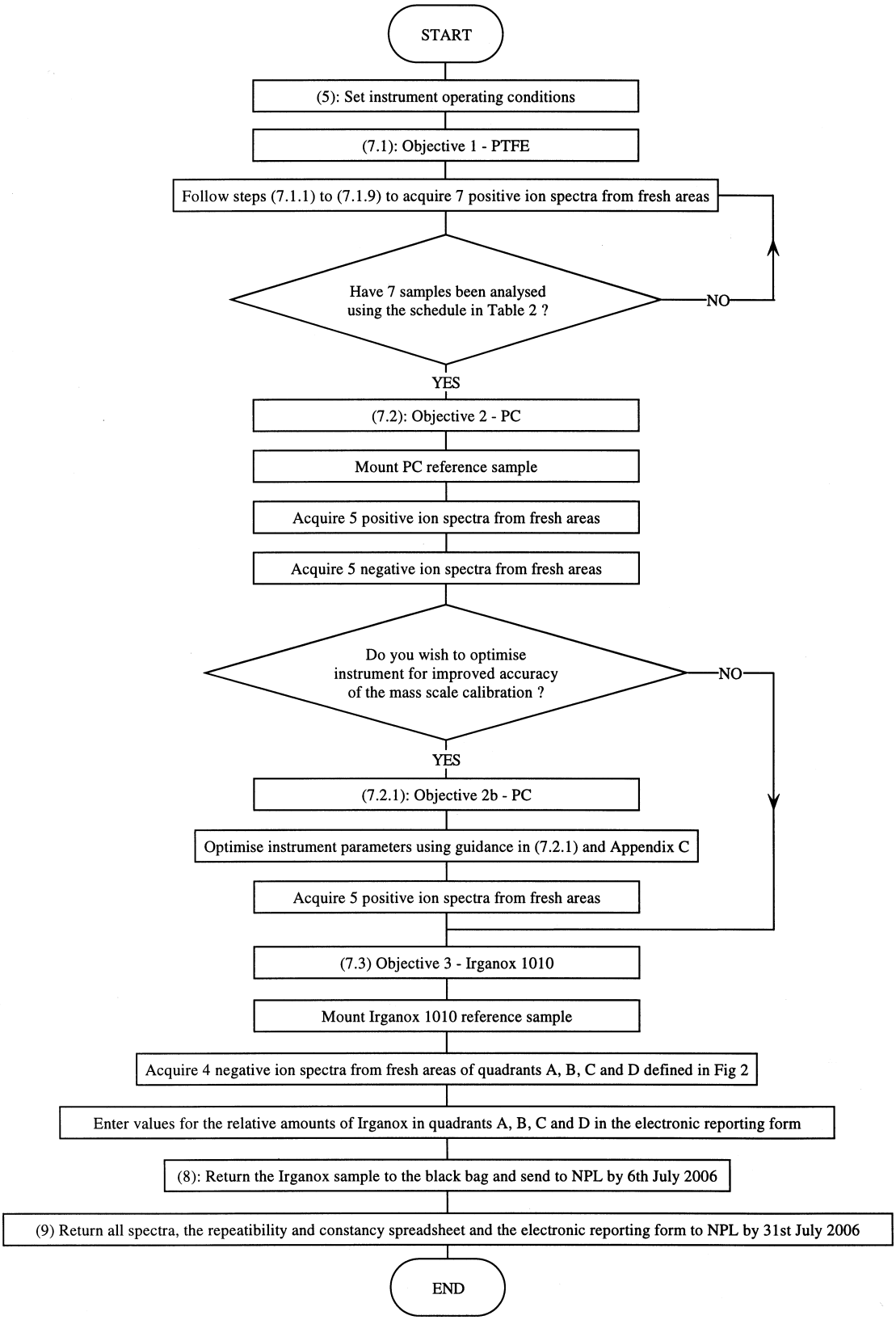

Fig 3 Flow chart of the work. The numbers in parentheses refer to sections in the text.

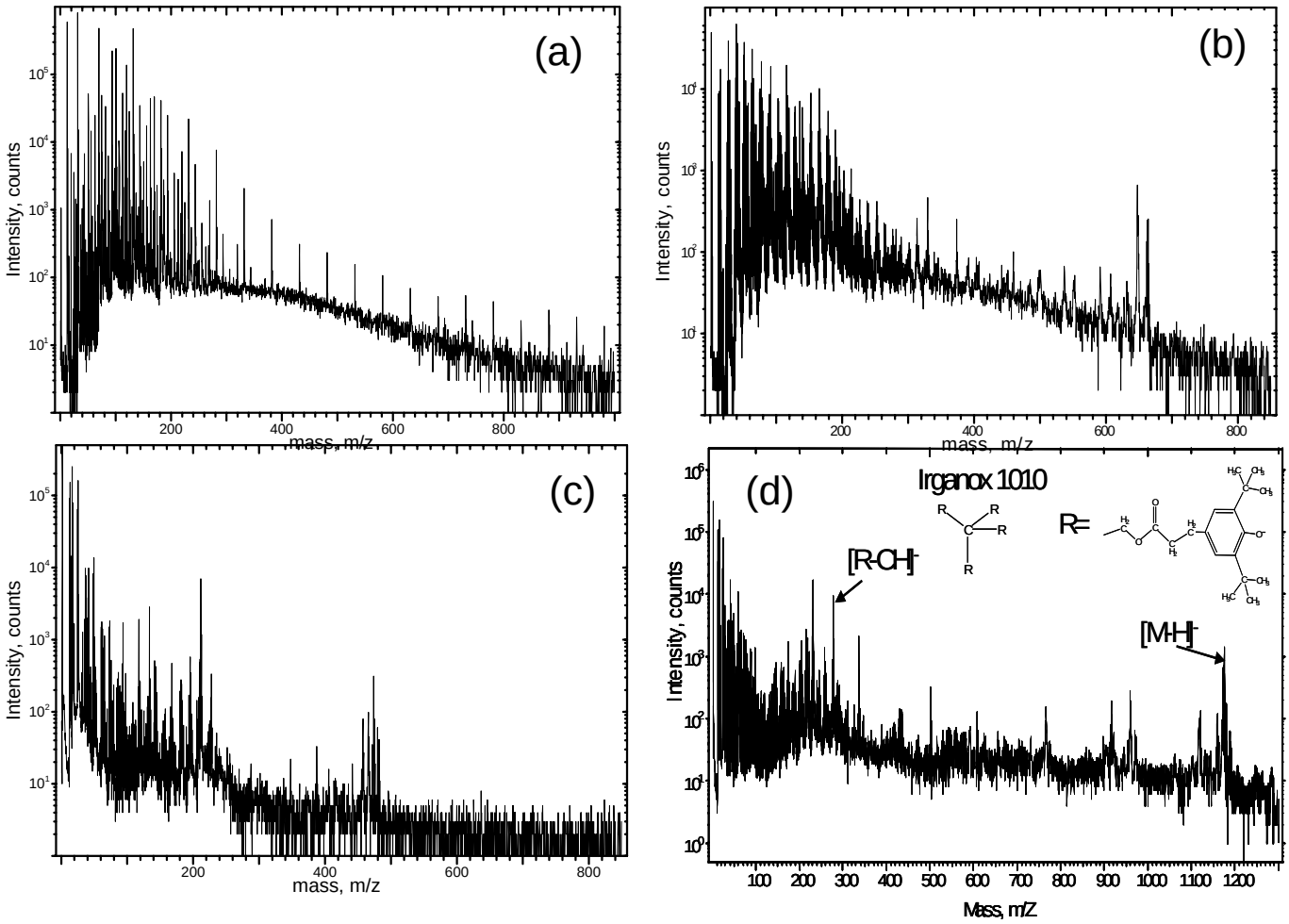

Fig 4 Static SIMS spectrum using the recommended conditions in Appendix A for (a) PTFE positive ions, (b) PC positive ions, (c) PC negative ions and (d) Irganox 1010 negative ions.

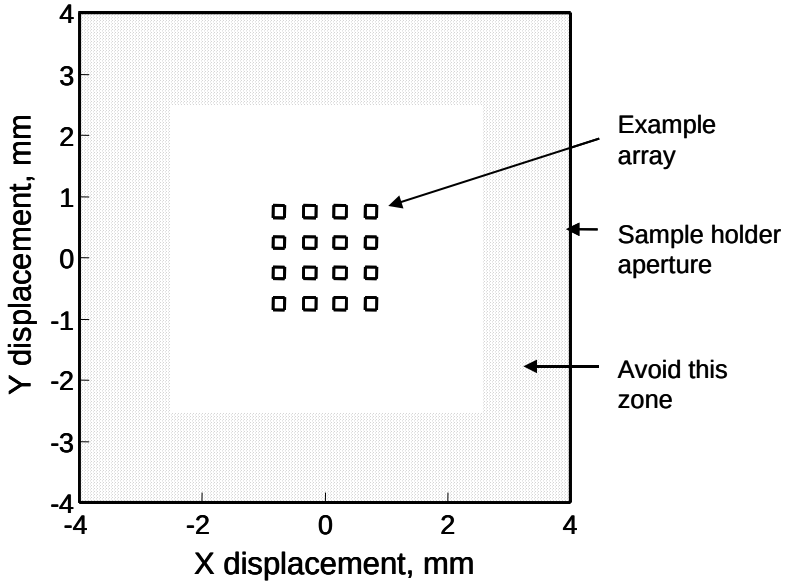

Fig 5 Schematic of 4 x 4 array of measurement positions suitable for use with PTFE or PC reference materials, for a sample holder with a square aperture of side 8 mm. A zone 1.5 mm from the perimeter is identified where data should not be acquired.

7.1 OBJECTIVE 1: STATIC SIMS REPEATABILITY AND CONSTANCY OF THE RELATIVE INTENSITY SCALE - PTFE

The following method is based on the draft standard ISO CD 23830. That standard is enclosed in the package for information only, you do not have to read it! In order to conduct the measurements for constancy in a reasonable time scale of approximately two weeks, 7 fresh samples need to be analysed at time periods defined in Table 2. Follow steps 7.1.1 to 7.1.9 for each of 7 samples using the schedule defined in Table 2.

Table 2 – Repeatability and constancy schedule.

Sample number	Day	Comment
1, 2	1	Load and analyse these at the same time if you have a sample holder that takes more than one sample.
3	1	On the same day, remove the sample holder from the instrument. Discard samples 1 and 2 and mount sample 3.
4	2	
5	~4	Approximate date – schedule at your convenience.
6	~8	
7	~15	

7.1.1 Mount a PTFE sample as described in 6.1.

7.1.2 Switch on charge neutralisation.

7.1.3 Ensure that the primary ion beam current is not so high that detector saturation occurs leading to non-linearity in the intensity scale. The PTFE material has 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 TOF systems in 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.

7.1.4 Select the settings chosen in section 5 and an acquisition time defined by equation (A.2) or equation (A.3) for your choice of beam current and raster size to keep below the maximum dose of $< 1 \times 10^{16}$ ions/m^2. For ToF instruments, select a repetition rate that gives a maximum mass of at least 850 u. For scanning mass spectrometers such as quadrupole and magnetic sector mass spectrometers record only the mass peaks selected in Table 3, in descending order of mass.

Table 3 — Values of the mass for each fragment to be recorded in the various situations.

Index, *i*	**Fragment**	**Use***	**Mass, u**
1	CF_2	b	49.9968
2	CF_3	a	68.9952
3	C_3F_3	b	92.9952
4	C_2F_5	b	118.9920
5	C_3F_5	a	130.9920
6	C_4F_6	b	161.9904

7	C_4F_7	a	180.9888
8	C_5F_7	a	192.9888
9	C_5F_9	a	230.9856
10	C_7F_{13}	c	330.9792
11	C_8F_{15}	c	380.9760
12	$C_{14}F_{27}$	c	680.9569
13	$C_{15}F_{29}$	c	730.9537
***Key** a - for intensity repeatability b - as "a" and used for mass calibration c - used only for constancy of the relative intensity scale.			

7.1.5 Acquire seven positive ion spectra on the same sample. A fresh area of material shall be analysed with a total fluence of less than 1 x 10^{16} ions m^{-2} (1 x 10^{12} ions cm^{-2}) each time.

7.1.6 For ToF spectrometers, calibrate the mass scale for each spectrum using the exact masses of the peaks labelled "b" in Table 3. For other spectrometers, confirm that the mass of the maximum intensity for each peak is within ±0.1 u of the exact mass. If the mass peaks are outside this range, recalibrate the instrument using a documented procedure.

7.1.7 To ensure maximum linearity of the intensity scale use the dead time correction procedure provided by the instrument manufacturer or other locally documented procedures.

7.1.8 For each of the 7 measurements of each mass peak sum the dead time corrected intensities within the mass limits ±0.5 u of the mass position defined in Table 3. For high mass resolution instruments, the mass interval between the limits may be reduced. Keep a record of these limits and use them for all subsequent measurements in this standard. Record the peak areas, I_{ij}, for the 13 mass peaks and the 7 spectra in the spreadsheet provided. For high mass resolution instruments using gallium primary ions, avoid including Ga^+ (68.9256 u) in the CF_3^+ peak.

7.1.9 Review the seven values of each of the peak area intensities for the 13 mass peaks for any systematic changes with time through their order of acquisition. Such systematics may indicate an inadequate warm-up period, change in the laboratory temperature, inadequate detector voltage or other source of drift. If this appears to be the case, take appropriate action (for example increase the warm-up period) and repeat steps 7.1.1 to 7.1.8.

The spreadsheet [repeatabilityandconstancyspreadsheet.xls] available at the website http://www.npl.co.uk/nanoanalysis/interlaboratory2006.html, will automatically calculate the repeatability and plot the control charts for constancy. This does all the work given in equations (5) through to (15) in the ISO CD23830.

7.2 OBJECTIVE 2: EVALUATE THE ACCURACY OF THE MASS SCALE CALIBRATION - PC

Acquire five positive ion spectra and five negative ion spectra, each spectrum being for a separate region of PC giving 10 spectra in total. Calibrate the mass scale using your normal procedure. In addition, calibrate the positive ion spectra using the mass peaks in Table 4 and save the spectra with new data file names. Record this in the electronic reporting form. If, for your instrument, there is insufficient PC reference material to acquire a full set of positive and negative secondary ion data then omit the negative data.

Table 4 – Calibration peaks

Sample	Calibration ions	Calibration mass, u
PC +ve	$C_4H_5^+$	53.03913
	$C_6H_5^+$	77.03919
	$C_8H_9^+$	105.07040
	$C_9H_{11}O^+$	135.08099

7.2.1 OBJECTIVE 2b: OPTIMISING INSTRUMENT FOR IMPROVED ACCURACY OF THE MASS SCALE CALIBRATION -PC

This option is only applicable to time of flight instruments. A method to optimise the accuracy of the instrument operating conditions to improve the mass scale calibration is given in reference (6) and in a one page summary in reference (12), which is available at http://www.npl.co.uk/nanoanalysis/tofsimsmassscale.pdf. For reflection instruments we recommend a reflection voltage of 20 V. For TRIFT instruments we recommend setting the energy slit to the 50 eV setting and put the contrast diaphragm in the "out" position. We also recommend optimising the analyser focussing lens and deflector settings. A method to do this is given in Appendix C. Record the optimised parameters in the electronic reporting form. Acquire 5 positive ion spectra from fresh areas, as earlier. Calibrate the mass scale using the calibration ions identified in Table 4.

7.3 OBJECTIVE 3: EVALUATE CAPABILITY OF SSIMS FOR RELATIVE QUANTIFICATION – IRGANOX 1010

The Irganox sample has four quadrants with different amounts of Irganox. The sample is illustrated in Fig 2, where quadrants are labelled A, B, C and D. The quadrant “A” may be identified by a small “X” scratched on the reverse side of the sample. Be careful to note which quadrant is “A” before mounting the sample. Acquire four negative ion spectra from each of the four quadrants, A, B, C and D, giving 16 spectra in total. Ensure that no spectra are closer than 0.5 mm to the boundary of another quadrant or 1.5 mm from the edge of the sample holder. Record spectral information in the electronic reporting form. Use your preferred method to derive relative quantification for the amount of Irganox in the four quadrants. Document this method in the electronic reporting form. If you can, provide an estimate of the uncertainty of these values. If you have a scanning mass spectrometer such as a quadrupole or magnetic sector mass analyser you can inspect the reference spectrum at http://www.npl.co.uk/nanoanalysis/interlaboratory2006.html to select peaks within the mass range of your spectrometer.

8 AFTER ANALYSIS

When all analyses are complete, return the PC and Irganox samples to their containers. The small PTFE sample cut from the reel may be scrapped. The Irganox container shall then be returned to the black plastic bag and resealed by folding over the open end and stapling to secure (as it was sent). Return the Irganox sample to NPL by courier using the original packaging. Please retain the PC sample and the PTFE reel in case we find any anomalies in your data. A check list is provided in the electronic reporting form.

9 DATA REPORTING FORMAT

The preferred method for returning 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 DOUBTS

If you are unsure of anything please contact Felicia Green, email: felicia.green@npl.co.uk.

ACKNOWLEDGEMENTS

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REFERENCES

1. I S Gilmore and M P Seah, Surf. Interface Anal. **29** (2000) 624.
2. I S Gilmore and M P Seah, NPL Report CMMT(D)14, 1996.
3. I S Gilmore, M P Seah and F M Green, *Surf. Interface Anal.* 2005, 37, 651.
4. ISO CD 23830 – Surface chemical analysis – Secondary ion mass spectrometry – Repeatability and constancy of the relative intensity scale in static secondary ion mass spectrometry.
5. I S Gilmore and M P Seah, Surf. Interface Anal. **23** (1995) 248.
6. F M Green, I S Gilmore and M P Seah, J. Am. Soc. Mass. Spectrum., 2006, **17**, 4, 514.
7. I S Gilmore in "ToF-SIMS: Surface Analysis by Mass Spectrometry" Edited by J. C. Vickerman and D. Briggs, SurfaceSpectra and IM publications, 2001.
8. I S Gilmore and M P Seah, Appl. Surf. Sci. **187** (2002) 89.
9. I S Gilmore and M P Seah, NPL website, http://www.npl.co.uk/nanoanalysis/lowenergyfloodgundamage.pdf
10. I S Gilmore and M P Seah, Int. J. Mass Spectrom. **202** (2000) 217.
11. I S Gilmore and M P Seah, NPL website, http://www.npl.co.uk/nanoanalysis/iondetectionefficiency.pdf
12. F M Green, I S Gilmore and M P Seah, NPL website http://www.npl.co.uk/nanoanalysis/tofsimsmassscale.pdf

APPENDIX A

COMPUTATION OF RASTER, CURRENT AND NUMBER OF FRAMES 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

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

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 $n > 20$.

(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)

$$R \geq 200\,\mu\text{m} \tag{A.5}$$

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

STATIC SIMS: ELECTRON FLOOD GUN ALIGNMENT PROCEDURE FOR ORGANIC MATERIALS

Alignment of the low energy electron flood gun is critical for good repeatability and constancy of the relative intensity source. If high electron currents (> 1 μA) are required to achieve charge compensation it is likely that the electron beam is out of alignment. The following gives a simple procedure to align the electron beam using the PTFE tape supplied. It involves using the primary ion beam to image the area and observing the effect of the electron gun alignment on the changes to the total ion intensity image.

1. Set up the instrument as described in ISO CD 23830.

2. Warm up the electron flood gun at the usual filament settings for > 15 minutes.

3. With the electron gun turned on and with normal settings, raster the primary ion beam over a small area ~10 μm x 10 μm. The small area for the primary ion beam would maximise the charging in the absence of the electron flood gun. Reduce the electron beam current until the sample just begins to charge, seen as a rapid drop in the intensity of the positive secondary ion image.

4. Adjust the electron gun alignment, using either orthogonal screw sets on the source or deflector plates depending on your system, to reduce the observed charging (observed by an increase in the intensity of the positive ion image).

5. Maximise the raster area to 100 μm x 100 μm or greater. The previous small raster will show up as a small dark patch that gradually disappears as the charging is reduced over the area. If the sample is still charging go back to step 4. When the charging is minimised continue to step 6.

6. Set the primary ion beam raster back to the small area 10 μm x 10 μm. Decrease the electron gun filament current and repeat steps 4 and 5. Continue this until no further improvement can be made.

7. Increase the electron current so that charge compensation is achieved and electron induced damage is not too severe. We find an electron current of 500 nA is suitable.

APPENDIX C

OPTIMISING THE INSTRUMENT FOR IMPROVED ACURACY OF THE MASS SCALE CALIBRATION

(1) Symbols

ΔM = mass accuracy (u)
M_P = measured peak mass (u)
M_T = true mass (u)
V_R = reflector or acceptance voltage (V)
x = number of carbon atoms
y = number of hydrogen atoms

(2) Optimal settings

Below we outline a procedure for optimising your instrument for improved accuracy of the mass scale. For further details please see reference 6 which is presented in a one page summary in reference (12).

(3) Optimising your instrument

We define the mass accuracy, ΔM, as the difference between the measured peak mass, M_P, and the true mass M_T

$$\Delta M = M_P - M_T \qquad \text{(B.1)}$$

The figure below shows ΔM for a range of hydrocarbon peaks of polycarbonate, as can be seen ΔM varies widely along the mass range. A wide range in ΔM for ions with different fragmentation has a major effect on the accuracy of the mass scale calibration. Ideally, we would like ΔM to be a flat line through zero!

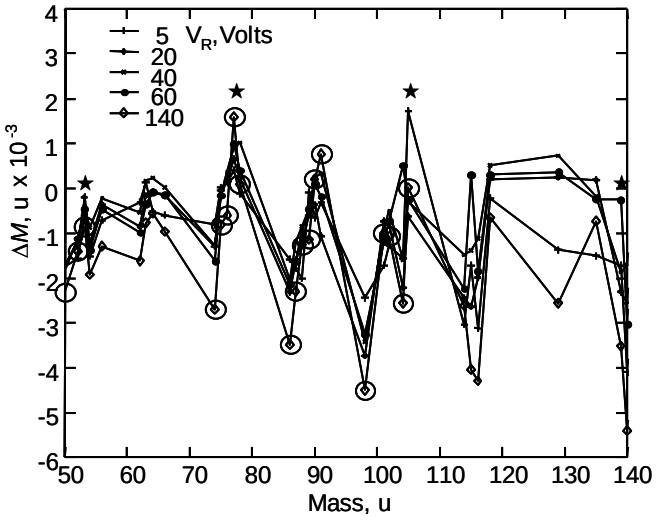

Fig B1 Mass accuracy, ΔM, for hydrocarbon peaks from PC positive ion spectra with V_R values of 5 V (+), 20 V (*), 40 V (x), 60 V (•) and 140 V (◊). The peaks denoted with a symbol (★) are used to calibrate the spectra. The circumscribed symbols denote the mass peaks used later to measure σ_M.

To provide a measure of the divergence from this we select four of the well-defined $C_xH_y^+$ cascades with x = 4, 6, 7 and 8 respectively, identified in the above figure by circumscribing the data point for the V_R = 140 V data set and detailed in the Table below.

Table B1 Selected ions for calculation of σ_M

Ion	True Mass, u	Ion	True Mass, u
C_4H_2	50.01565	C_7H_4	88.03130
C_4H_4	52.03130	C_7H_5	89.03913
C_4H_5	53.03913	C_7H_6	90.04695
C_6H_2	74.01565	C_7H_7	91.05478
C_6H_3	75.02348	C_8H_2	98.01565
C_6H_4	76.03130	C_8H_5	101.03910
C_6H_5	77.03913	C_8H_6	102.04700
C_6H_6	78.04695	C_8H_8	104.06260
C_7H_2	86.01565	C_8H_9	105.07040
C_7H_3	87.02348		

We now define σ_M as the average of the standard deviations of ΔM, $\sigma(\Delta M)$, for each of the four $C_xH_y^+$ cascades defined above.

$$\sigma_M = \frac{1}{4}\left[\sigma_{C_4H_y}(\Delta M) + \sigma_{C_6H_y}(\Delta M) + \sigma_{C_7H_y}(\Delta M) + \sigma_{C_8H_y}(\Delta M)\right] \qquad \text{(B.2)}$$

We may now use σ_M as a parameter to optimise operating parameters. For improved mass accuracy the value of σ_M needs to be minimised. Here we illustrate this with examples, for a reflection instrument, of optimisation of the lens settings and optimisation of the analyser deflector X and Y plates, as shown in Fig B2. It is simple to locate the optimum lens setting from the minimum of the curve in Fig B2 (a) giving a lens setting of 76 %. Similarly, it is clear that the optimum settings for the analyser deflector plates has a broad minimum, rising steeply at large deflections, centred approximately around a setting of 0 for both X and Y deflectors. It is therefore important that a suitable procedure is used to align the ion optical axis and the ion beam raster area**.** This method may be used to optimise other parameters such as energy slits, contrast diaphragms, pass energy and extraction potential.

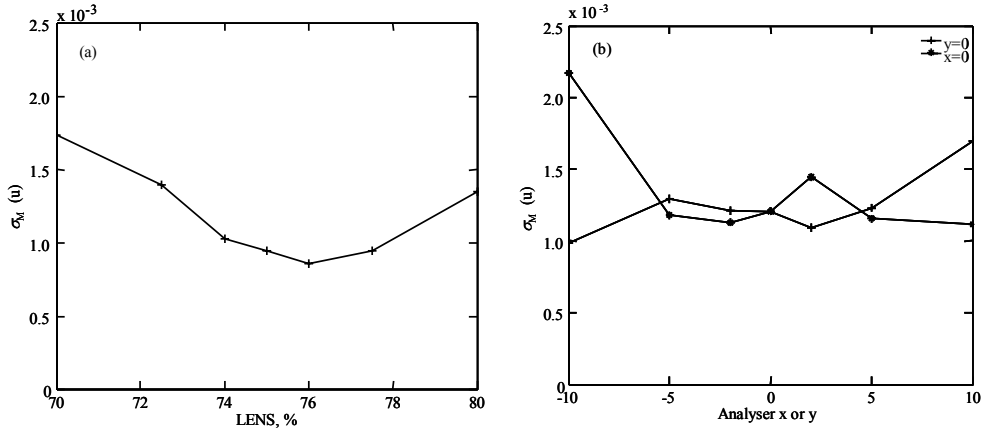

Fig B2 The change in σ_M for different (a) lens settings and (b) analyser deflector X and Y settings