

Invited Paper

Development of a Standards Base for Static SIMS

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Reliability and confidence in static SIMS have grown enormously since 2000. This is demonstrated by the growing uptake of the technique in industry both for quality control and supporting innovation in a wide range of sectors from aerospace to health care and medical devices. The development of a firm measurement base has been an essential part of this growth. International Standards ensure that this measurement base is then accessible to all in clear documented procedures, ideally suited for use in accreditation and quality control systems such as ISO 17025 (General requirements for the competence of testing and calibration laboratories). ISO standards for Secondary ion mass spectrometry are developed in Technical Committee TC 201 on Surface chemical analysis in Sub-Committee 6 on SIMS. Only recently has this committee started the development of standards for static SIMS. The development of a measurement base for static SIMS and the pre-normative research developed through three VAMAS interlaboratory studies is reviewed and the progress in the development of International Standards is reported.

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1. Introduction

Static secondary ion mass spectrometry (SSIMS) is growing strongly in both industry and academia for the characterisation and understanding of molecular and organic surfaces, which are key to many advances in biotechnology, nanotechnology, pharmaceuticals and other emerging technologies. Concomitantly, there is a growing realisation of the need for a standards base so that results are valid, repeatable and comparable between instruments and institutions.

A key platform for this success has been the underpinning metrology developed and validated in three interlaboratory studies conducted under the auspices of VAMAS (The Versailles Project on Advanced Materials and Standards). These interlaboratory studies have networked over 50 laboratories worldwide. The studies have focused on (i) a survey of issues [1], (ii) repeatability and reproducibility [2,3] and (iii) repeatability and constancy of the relative intensity scale and mass scale calibration [3,4]. This paper reviews the development of the metrology and the interlaboratory studies that have led to the establishment of a measurement base for static SIMS and how this is now leading into robust International Standards.

An ISO survey of analysts needs for standards has been conducted so that effort can be focused where the needs are highest. This allowed a prioritised action plan for standards to be developed including:

- (i) A procedure for repeatability and constancy of the relative intensity scale.
- (ii) A procedure for the mass calibration for TOF spectrometers.
- (iii) A procedure to define the fluence limit to avoid damage for molecular groups.
- (iv) A procedure to evaluate the linearity of the intensity scale and for setting the detector.
- (v) A procedure for relative quantification.
- (vi) A guide to multivariate analysis of spectra, images and data reduction.
- (vii) A procedure for depth profiling of organic/polymeric layers

In the following we will see how this action plan is being addressed and how far the development of standards has progressed.

2. Underpinning Metrology

Effective standards are built on a robust science base. Key to this is the underpinning metrology of the technique and the instrumentation. In Fig 1, a typical static SIMS instrument is illustrated with six core metrology components. These are discussed in more detail in the following with sub-heading numbers relating to the figure.

2.1 Ion beam damage

A decade ago, ion beam damage in polymers was a major issue with significant discrepancy in the literature. A major obstacle to understanding the effects was inadequate charge stabilization leading to poor repeatability. At NPL a novel charge stabilization system was developed that bathed the sample in low energy electrons [7]. This provided outstanding stability allowing very high repeatability in the study of secondary ion intensities with increasing primary ion dose for polymer systems. A simple bond-breaking model was developed that accurately described the observed damage effects [8]. Using this model, Figure 2 shows how secondary ion intensities for large fragments with single attachment, fragments requiring two bonds to be broken and fragments with multiple attachment evolve with increasing primary ion

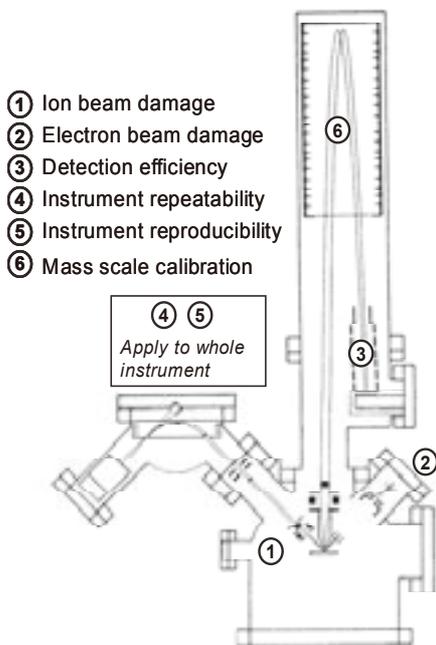


Figure 1. A metrology tour around a ToF-SIMS instrument identifying six underpinning metrologies enabling standardisation. Note that the metrology applies to all instrument designs not just the one illustrated, after Gilmore [5] and ref [6].

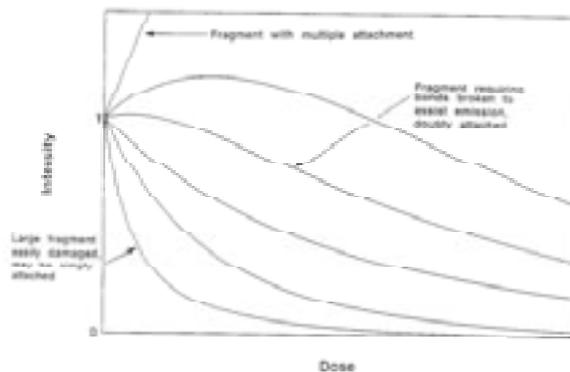


Figure 2. Summary damage plot showing general behaviours for different fragment types using a simple bond breaking model [8].

fluence.

More recently, it has been demonstrated for many materials that molecular ion intensities may be retained under sputtering by cluster ion beams. For those materials, the total integrated secondary ion intensity is therefore considerably larger leading to higher sensitivities as well as new possibilities for depth profiling of organic materials. The understanding of cluster ion sputtering is at an early stage but is developing rapidly. Cheng *et al.* [9] have developed a model based on the supply balance of sputtered material, damaged material and supply of fresh material that accurately describes the initial decay in molecular intensities to a steady-state or quasi-steady state. Recently, Shard *et al.* [10,11] have developed a model that may be applied to a wide range of materials

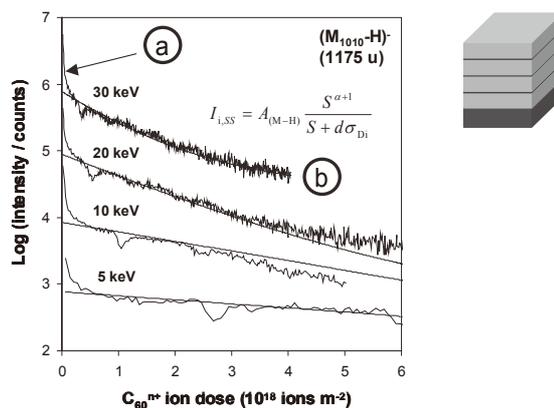


Figure 3. For many materials cluster ion beam sputtering retains the molecular intensity up to depths of several hundred nm. Models (a) Cheng *et al* [9] and (b) Shard *et al* [10,11] describe two key aspects of the damage curves. The intensity relates to the matrix shown in the inset and the intensity dips occur at the delta layers – see ref [11] for details.

where the sputtering yield volume is non-linear with ion dose as shown in Fig 3. This allows quantification of the amount of material in nanolayers to 10%. A fourth VAMAS interlaboratory study will commence in 2008 to evaluate the issues in organic depth profiling using a delta layer reference material.

2.2 Electron beam damage

Electron neutralisation is necessary for the analysis of insulating materials. Whilst ion beam damage has been a well recognised issue for many years the damage caused by electrons is often ignored. Whilst the electron energy is often only a few eV, typically many nA of current are used and the electron beam is effectively on for the entire acquisition time. Coupled with the fact that the electron beam illuminates a much larger area (typically 6 mm²) than the ion beam analysis area the accumulated electron beam dose is very large. In a detailed study [12] it was found that in a typical time-of-flight SIMS instrument, the electron fluence during spectrum acquisition would be around 1.9×10^{20} electrons/m². Analysis of the molecular fragmentation for PS, PVC, PMMA and PTFE, shows that an upper limit of 6×10^{18} electrons/m² can be defined before significant electron-induced damage is observed. After a fluence of 7.5×10^{20} electrons/m², the secondary ion intensities, for some materials, have changed by over a factor of two. From this study, Fig 4 provides clear guidance on setting the electron neutraliser to stay within acceptable limits for different ion current densities.

2.3 Ion detection efficiency

Of course for mass spectrometries, the ion detection efficiency and optimal setting of the detector are of critical importance. The detection efficiency of a microchannel plate (MCP) for high mass ions was modelled to describe the ion induced electron emission followed by amplification in the channel [13]. The model gives an excellent description of the data and shows how the efficiency falls away as the mass increases or the ion impact energy reduces. At a mass of 10,000 u, the detection efficiency for 20 keV ions is 80%, falling to 25% for 10 keV ions, as shown in Fig 5. If the post-acceleration voltage is set to 20 kV, approximately unity detection efficiency may be achieved for masses up to 4000 u.

That study [13] also developed a simple method for

repeatable setting of the detector voltage regularly, using an accurate and simple procedure.

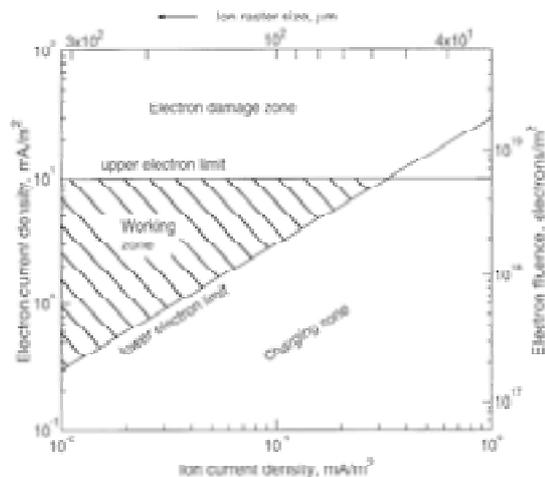


Figure 4. Map of parameters that define the conditions to acquire spectra without charging and with low electron beam damage [12]. The horizontal line gives the upper fluence limit for damage and refers to the right hand ordinate. The fluence scale and the dimension of the square raster are calculated for a 100 s acquisition time with a 1 pA ion beam current, respectively. The diagonal line is the lower limit for charging.

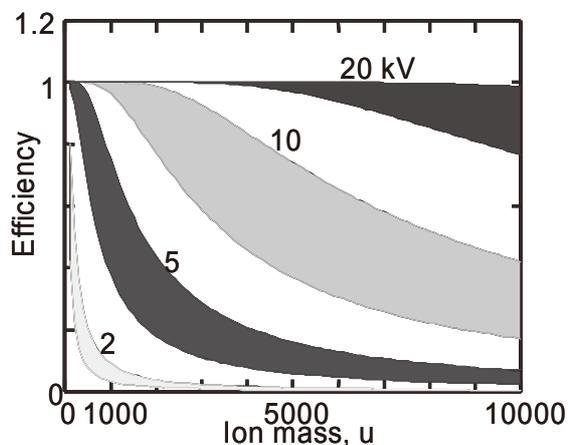


Figure 5. Detection efficiency bands for different secondary ion compositions for post-acceleration voltages of 2, 5, 10 and 20 kV; metal clusters are at the top of each band and organic ions at the bottom [13].

2.4 Instrument repeatability

The second VAMAS interlaboratory study built on this underpinning metrology to provide guidance for analysts on setting the ToF-SIMS instrument operating conditions. This study focused on the repeatability and reproducibility of spectra, which are of paramount importance for

analysts. The repeatability was calculated using the N_{ij} method; for each respondee, the j_0 repeat spectra for a given ion polarity and material are formed into a matrix of ion intensities, I_{ij} , where i is the index of the relevant characteristic peak of i_0 peaks and j is the index of the individual repeat spectrum. We then calculate the average intensity \bar{I}_i of each mass peak

$$\bar{I}_i = \sum_{j=1}^{j_0} I_{ij} / j_0 \quad (1)$$

and divide each intensity I_{ij} by the relevant average \bar{I}_i to evaluate the power P_{ij} in each peak.

$$P_{ij} = I_{ij} / \bar{I}_i \quad (2)$$

The average power \bar{P}_j in the spectrum, which depends on the beam current etc, is given by:

$$\bar{P}_j = \sum_{i=1}^{i_0} P_{ij} / i_0 \quad (3)$$

This average power is now removed from the spectrum by forming the normalised intensities N_{ij} :

$$N_{ij} = P_{ij} / \bar{P}_j \quad (4)$$

Normalisation using this method removes relative intensities of the i different mass peaks and any drift in beam current between the j spectra. Values for each element in the resulting matrix of normalised intensities, N_{ij} , are around unity, with an average value for each spectrum of unity. The repeatability is expressed by the average of the standard deviations of N_{ij} for each mass and is shown in Fig 6 for the three reference materials PC, PS and PTFE for positive ions. Over 80% of instruments have better than 2% repeatability with the best instruments achieving 1% repeatability. This is a factor of 10 improvement on the first interlaboratory study, conducted 6 years earlier, and demonstrates an excellent level of control that has helped boost confidence in the technique.

2.5 Instrument reproducibility

The comparability and equivalence of spectra between instruments is essential to allow data acquired on different generic instruments to be related, and for more effective use of library data. To show how the spectral response from one instrument compares to that of another the Relative Instrument Spectral Response (RISR) method

was developed [1,2]. This uses data from the second

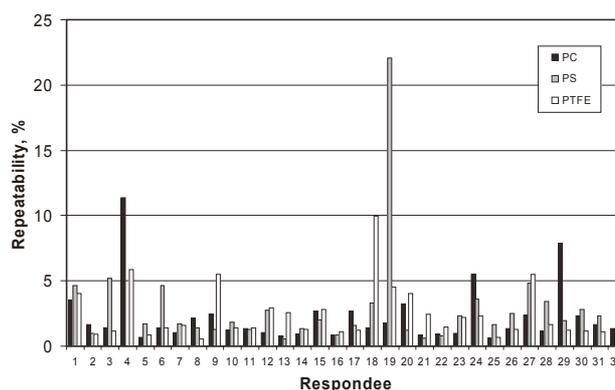


Figure 6. The positive ion repeatability from PC, PS and PTFE reference materials for 32 instruments [2].

interlaboratory study to generate a normalised average spectrum from the best performing instruments (the control set). The RISR is then found from the ratio of the normalised spectral intensities to the normalised average spectrum. The normalisation uses an approach similar to equation (3) which removes differences in ion beam current, acquisition time and overall spectrometer efficiency. An example RISR is shown in Fig 7 for instrument 3 for PTFE [2] together with the RISR function (red line) which is a fit to the RISR values for key fragments shown in green.

The RISR approach improves comparability of spectra by a factor of up to 33 and allows the identification of contamination, charge stabilisation problems and incorrectly functioning ion detectors to be identified. This provides the basis for monitoring the constancy of the relative intensity scale discussed later.

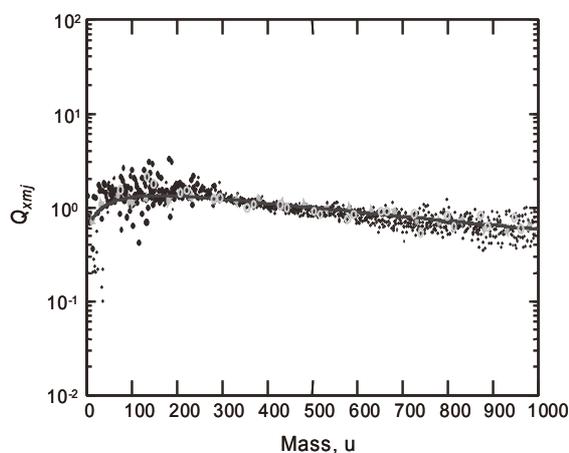


Figure 7. Example RISR for instrument 3 for PTFE. Solid line is the RISR function (see text), characteristic fragment ions are denoted by a star symbol [2].

2.6 Calibration of the Mass Scale

After the basic issues of repeatability and reproducibility, the highest priority for analysts in the ISO survey is calibration of the mass scale for ToF SIMS. The urgency of this requirement is highlighted in results from the second interlaboratory study [3], which showed that calibration accuracy for large molecules (647 u) was typically -150 ppm. This is a factor of 10 poorer than is useful for identification of organic molecules.

A detailed metrological study of the factors affecting the calibration of the mass scale has been conducted [14]. The effect of the ion kinetic energy, emission angle and other instrumental operating parameters on the measured peak position are determined. This shows clearly why molecular and atomic ions have different relative peak positions and the need for an aperture to restrict ions at large emission angles. These data provide the basis for a coherent procedure for optimising the settings for accurate mass calibration and rules by which calibrations for inorganics and organics may be incorporated. This leads to a new generic set of ions for mass calibration that improves the mass accuracy in our interlaboratory study by a factor of 5. A calibration protocol is developed which gives a relative mass accuracy of better than 11.5 ppm for masses up to 140 u. The effects of extrapolation beyond the calibration range are discussed and a recommended procedure is given to ensure that accurate mass is achieved within a selectable uncertainty for large molecules, as shown in Fig 8.

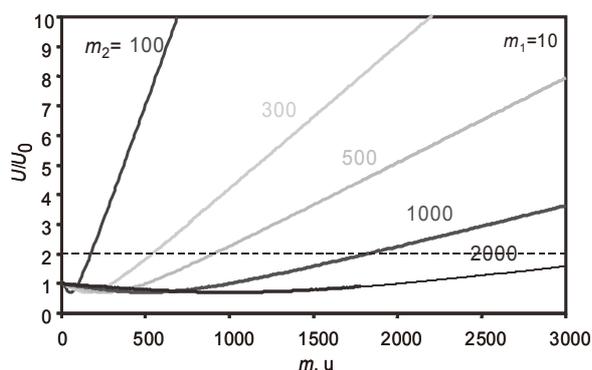


Figure 8. Relative uncertainties, U/U_0 , using two calibration mass peaks illustrating the effect of extrapolation as a function of the given mass peak, m , up to 3500 u with $m_1=10$ and with separate curves for m_2 set at 100, 300, 500, 1000 and 2000 u [14].

For establishing a mass scale for accurate mass measurement of molecules the following are recommended: (1) using the procedure described in ref [14] to optimise the instrument parameters, (2) calibration using ions that have low degradation or fragmentation from the original parent structure, these may be identified using G-SIMS [15,16], (3) for the analysis of molecules, do not include atomic ions, (4) not including hydrogen in a final calibration and (5) selecting a mass range of calibration ions to give the required accuracy for large molecules using Figure 8 as a guide.

3. Development of International Standards

The underpinning metrology surveyed above has provided a robust base to begin the development of ISO standards. For static SIMS this is conducted in ISO TC 201 Surface Chemical Analysis and a rapidly growing number of experts are now participating in developing static SIMS standards. The first standard developed ISO 22048:2004 [17] provided a supplementary information format to the popular standard data transfer format for surface chemical analysis ISO 14976:1998 [18]. This enables time-of-flight data with mass scale calibration information to be freely exchanged between different users and software systems. In the following we summarise the standards that are currently under development.

3.1 ISO DIS 23830 Repeatability and Constancy of the Relative Intensity Scale in static SIMS

The underpinning metrology together with the comprehensive VAMAS interlaboratory studies have provided an excellent method for measurement of the repeatability and constancy of the relative intensity scale based on PTFE as a reference material. PTFE in the form of domestic plumber's tape is readily available and a fresh surface is exposed as the reel is unwound. This has been shown to provide contamination-free spectra with high repeatability in three VAMAS interlaboratory studies [1-4]. Repeatability is measured using the N_{ij} method discussed earlier for 9 well defined peaks and for 7 repeat measurements. The standard provides a clear procedure for mounting the sample, choosing spectrometer settings, operating the instrument and the calculation of repeatability and the associated uncertainty. The constancy is defined by two ratios A_1/A_2 and A_3/A_2 where A_1 , A_2 and A_3 are the average intensities of the C_3F_3 and C_2F_5 peaks,

C_5F_9 and C_7F_{13} peaks and $C_{14}F_{27}$ and $C_{15}F_{29}$ peaks. These ratios allow any tipping of the RISR shown in Fig 7 at around 100 u and 700 u relative to 281 u. Control charts for both A_1/A_2 and A_3/A_2 may then be constructed allowing the constancy of the relative intensity scale to be monitored. This provides key information required to demonstrate compliance to ISO 17025. An easy-to-use Excel spreadsheet, based on the standard, is available for download from the NPL website [19]. This has recently been validated in the third VAMAS interlaboratory study and an example control chart for the A_1/A_2 ratio is shown in Fig 9 for instrument 15. This demonstrates excellent constancy over a two week period [4].

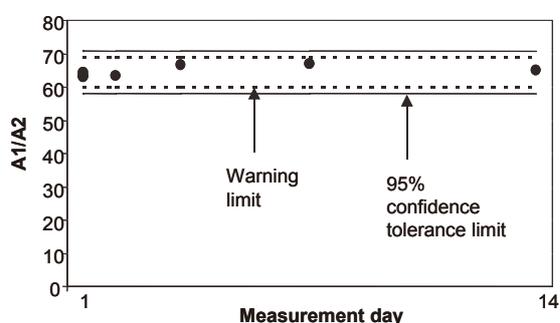


Figure 9. Control chart for A_1/A_2 for instrument 15 [4].

3.2 NWI Calibration of the Mass Scale for ToF-SIMS

A new ISO standard is being developed based on the underpinning metrology discussed earlier in section 2.6 and recently validated in the third VAMAS interlaboratory study [3,4]. The standard provides a clear procedure for optimising instrument parameters and a calibration procedure. Results from the VAMAS study and a detailed study show that this improves the accuracy, typically, by a factor of 10. This is a major improvement for analysts.

3.3 A Guide for the use of Multivariate Analysis and SIMS

Multivariate methods are very valuable for the analysis of complex mass spectra and especially for image data sets which may have $>10^6$ peak intensities. Unfortunately, the literature is laden with confusing terminology and jargon. Furthermore there are many different methods and procedures and it is unclear for analysts which method (e.g. PCA or MCR) is most suited to a particular application or requirement and what the effects are of

following different procedures such as normalisation and scaling. Recently, ISO 18115 vocabulary [20] has been updated with definitions for key multivariate terms. This has now provided a common language to start to develop the fundamental understanding of the different methods and procedures, for example in ref [21]. Prof B Tyler is leading the development of a guide for the use of multivariate analysis in SIMS. This will include [22] PCA, MCR, PLS and DFA as well as data preprocessing procedures including binning, peak integration, normalization, mean centering, scaling and transformation.

4. Conclusions

A robust standards base for static SIMS is being developed based on rigorous underpinning metrology combined with development and validation in three VAMAS interlaboratory studies. Consultation with analysts both from industry and academia has led to a clear action plan of standards development. Excellent progress is being made with one standard on repeatability and constancy of the relative intensity scale soon to be published and a standard for mass scale calibration and a guide for multivariate analysis well underway. A fourth VAMAS interlaboratory study will be conducted in 2008 to study organic depth profiling using a novel organic delta layer and also the linearity of the intensity scale, which is of increasing importance with new cluster ion beams. The continued integration of underpinning metrology with interlaboratory studies will allow the development of standards to prosper.

5. Acknowledgements

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