Surface mass spectrometry of organics and nano-objects
Part I - Watching chemistry in hi-definition with secondary ion mass spectrometry

www.npl.co.uk/nanoanalysis

Ian Gilmore, National Physical Laboratory (NPL), UK
Overview

1. Instrument optimisation and practical analysis
2. Interpretation, identification and informatics
3. Analysis of nano-objects
Damage of organics by primary ions (atomic)

STATIC SIMS dose limit for PTFE

- A 10% change = $0.035 \times 10^{17}$ ions per m$^2$
- A 1% change = $0.0035 \times 10^{17}$ ions per m$^2$

ISG & MPS, SIA. 24 (1996) 746
Table 3. Values of $R$, $S$, $r$ and $s$ for PET using 4 keV argon ions

<table>
<thead>
<tr>
<th>Mass (amu)</th>
<th>$S$ (counts)</th>
<th>$s$ (x10^{-17} m$^2$)</th>
<th>$R$ (counts)</th>
<th>$r$ (x10^{-17} m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>3525</td>
<td>0.72</td>
<td>13609</td>
<td>0.13</td>
</tr>
<tr>
<td>76</td>
<td>8681</td>
<td>0.88</td>
<td>64969</td>
<td>0.29</td>
</tr>
<tr>
<td>91</td>
<td>1938</td>
<td>0.57</td>
<td>12433</td>
<td>0.21</td>
</tr>
<tr>
<td>104</td>
<td>2553</td>
<td>1.44</td>
<td>41941</td>
<td>0.38</td>
</tr>
<tr>
<td>149</td>
<td>-21538</td>
<td>0.94</td>
<td>22216</td>
<td>0.35</td>
</tr>
<tr>
<td>193</td>
<td>-12414</td>
<td>1.36</td>
<td>6351</td>
<td>0.44</td>
</tr>
</tbody>
</table>
• Probability of producing fragment

\[ P = P_A P_B (1 - P_c) \]

• Fraction of whole A bonds decays as

\[ \exp (-N P_A \theta t) \]

\[ P(t) = \text{Probability that C is unbroken} \times \]

• Breaking unbroken A and B bonds

+ Breaking A bond given B broken

+ Breaking B bond given A broken

• The Intensity \( I(t) \) is given by

\[ I(t) = Q e^{-Nq \tau} + R e^{-Nr \tau} - S e^{-Nst} \quad (1) \]

ISG & MPS, SIA. 24 (1996) 746
• Fragments that grow in intensity require bonds broken at two or more points
• Polymer fragments that have a low initial intensity are likely to be larger than the diameter of the damage area, $\theta$
• Fragments attached by multiple bonds start progressively weaker but grow more and more strongly
Electron beam damage or organics

• Typical TOF-SIMS instruments deliver $1.9 \times 10^{20}$ electrons/m$^2$ causing relative intensities to change by a factor of 4.

• Maximum electron dose for SSIMS = $6 \times 10^{18}$ electrons/m$^2$ [=600 x ion limit].

Detector efficiency

Fig. 1. Schematic of the ion detection system used in this TOF SIMS spectrometer.

Effect of MCP voltage, $V_C$

Fig. 2. Positive ion SIMS spectra of Ag cationised PS oligomers at 20 kV post-acceleration voltage with detector voltages, $V_C$, of (a) 650 V and (b) 950 V.

How to set $V$ correctly

\[ V = V_T + 29.1 + 0.0572 \, m \]  

(3)

Effect of ion energy on detection efficiency (post acceleration, $V_D$)
\[ \gamma = A v \left( 1 - \left( \frac{1}{1 + \left( \frac{v}{v_0} \right)^n} \right)^{1/n} \right) \]
Detection efficiencies vary strongly for different detector voltages and masses.

A high post acceleration voltage reduces these effects considerably.

A procedure to set the detector has been established.

Linearity in SIMS is becoming more acute due to cluster ion beams, high resolution imaging and advanced data analysis e.g. multivariate methods.

Non-linearities are principally caused by single ion counting detector with dead time $\tau$

- Max 1 count per primary ion pulse within $\tau$
- Dead time correction can be applied if $\tau$ is constant, peak width $< \tau$ and peak is not preceded by another peak within $\tau$ [1]
- Correction required for 95% linearity if $I_m$ exceeds 0.1 counts for pulse

$$\frac{I_c}{N} = -\ln \left( 1 - \frac{I_m}{N} \right)$$

Linearity results – Effects of detector dead time

\[ \tau = 65.6 \text{ ns} \]

- \( \tau \) is constant wrt. intensity, within the range commonly used in SIMS
- \( \tau \) is fairly constant for each impact event – small spread in recovery times
- Single ion counting assumption closely obeyed
- Peak integration limit set to peak centroid \( \pm \tau \) for the purpose of this study
Results

Excellent fit with theory:
With dead time correction, > 95% linearity can be achieved at 0.9998 counts per pulse

Deviation at high intensities: 95% linearity achieved up to a maximum of 0.50 counts per pulse

Deviation at low intensities:
Long acquisition times – increase in dark counts background reduces $^{12}$C/$^{13}$C ratios
Factors affecting linearity and dead time correction

1. Application of dead time correction

\[ \frac{I_c}{N} = -\ln\left(1 - \frac{I_m}{N}\right) \]

- Inhomogeneous intensities
- Poor charge compensation
- Inhomogeneous samples

Pixel-by-pixel correction recommended


Guidance plots given. Channel-by-channel correction* useful
Factors affecting linearity and dead time correction

2. Poor detector efficiency

- For incorrectly adjusted systems, non-linearities can arise when the detector efficiency becomes a function of ion intensity
- $^{12}$C/$^{13}$C isotopic ratio increases drastically at lower MCP voltages and higher discriminator voltages – detection efficiency reduced for weak $^{13}$C peaks

Important to optimise efficiency by correct setting of MCP and discriminator voltages

**Linearity of the intensity scale**

Single ion counting – maximum 1 count per pulse within dead time interval $\tau$

![Normalized intensity (log scale)](image)

1. **Recommendations from VAMAS study**
   - Apply dead time correction if the measured peak intensity > 0.1 counts per ion pulse.
   - Simple equation is affected by narrower integration limits, multiple peaks within $\tau$ or strong background intensities. More sophisticated correction can be helpful [2].
   - Pixel-by-pixel & scan-by-scan correction is recommended for images & depth profiles, respectively.
   - Important to optimise the detector efficiency e.g. MCP and discriminator voltages [1].

Calibration of the mass scale in a time-of-flight spectrometer

A reflectron, to compensate for a range of secondary ion energies

This consists of lens to focus the beam into the detector.

These are accelerated away from the surface with an electric field into a time-of-flight mass spectrometer.

F M Green, I S Gilmore & M P Seah, JASMS 17 (2006) 514
Accurate mass scale calibration is essential for correct identification.

An accuracy, $\Delta M$, < 10 ppm is required for unique identification.

Results from an interlaboratory study of 32 instruments, using local calibration procedures, shows the average mass accuracy of irgafos, at 647 u, is $-150$ ppm.

ISO identifies as a top issue for analysts.

F M Green, I S Gilmore & M P Seah, JASMS 17 (2006) 514
Characterisation of single stage reflectron – Chromatic aberration

- \( E_{\text{max}} \) for both atomic and molecular ions is < \( \text{min of } E_{\text{tof}} \),
- Ions with lower kinetic energies will have higher relative mass.
TOF-SIMS: Energy Compensation

Single Stage Reflectron

- First order time compensation
- Effect of the accelerating section has to be approximated
- If grids are used: max. transmission \(~80\%\) for 90\% transmission grids
- Mass resolution achieved: \(>10k\)

Slide from B. Schueler, Physical Electronics
2. Characterisation of single stage reflectron – Chromatic aberration

- A single stage reflection is modelled using SIMION.
- Parabolic spread in arrival times from first order focusing.
- Minimum moves to higher energies as $V_R$ increases.
3. Optimising parameters – using PC

- $\Delta M$ is poorest for high reflector voltages as expected from theory.

- $\Delta M$ varies by $4.3 \times 10^{-3}$ u over only a few mass units.

- A simple procedure is required to optimise instrumental parameters.

- We define $\sigma_M$ as the average of the scatters of $\Delta M$ for each of the four $C_xH_y$ cascades circumscribed.
Uncertainty in the measured peak position leads to extrapolation error beyond the mass calibration range.

Over a fragmentation series (e.g. C\textsubscript{x}H\textsubscript{y}), the increase in kinetic energy results in a negative mass difference.

The calibration uncertainty rises rapidly outside the calibration mass interval.

Hydrogen is not recommended as a calibration ion.

Use a mass around 12 to 30 u and at a mass ≥ 55% of the masses requiring identification.

For the analysis of organic molecules, do not include atomic ions in the mass calibration.

For molecular analysis of minimally degraded fragments, use peaks for similarly minimally degraded entities as calibration peaks.
Repeatability and constancy of the relative intensity scale

- Mass spectra integrated to 1 amu width bins.
- Repeatability calculated using the $N_{ij}$ method gives the one sigma scatter about the average for each characteristic mass peak.

\[
\bar{I}_i = \sum_j I_{ij} / j_0 \quad (1)
\]

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

\[
\bar{P}_j = \sum_i P_{ij} / i_0 \quad (3)
\]

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

ISG & MPS, SIA 23 (1995) 191
• Repeatability improved by a factor of 10 between first and second interlaboratory study. Now, excellent repeatabilities with over 84% instruments better than 1.9%.
• PTFE excellent material for measuring repeatability, readily available and no need for cleaning.

Divide each spectrum by the “power” so that all average around unity.

Form an average spectrum, $A_i$, from those instruments exhibiting the best control for each material; 7, 8, 13, 14, 16, 17, 21, 22 and 30.
RISR – identifies instrument problems

PC, Instrument 10

- Contamination
- Background noise

PTFE, Instrument 15

- Charge compensation problem

PS, Instrument 19

- Detector fault

Ion mass, amu

Background noise
Contamination
Charge compensation problem
Detector fault
tolerance limits set for 10% drift.

Instrument first out of calibration in Jan 05 and should, have been recalibrated in July 04.
5 Affect of topography

**Conducting samples**
- Drug coated stent (A G Shard)
- Etched silicon (J L S Lee)

**Insulating samples**
- Aerosols (C Font Palma et al)
- Human hair (I W Fletcher)
- Paper (P Fardim et al)
- Textile fibres (I W Fletcher)
1. Conducting fibres – Topographic field effects

ION-TOF TOF-SIMS IV, 1.5 mm extraction gap, 2000 V extractor voltage

Total ion image (Gold wire $D=125\,\mu m$)

Effect of distortion of extraction field:
1. Significant intensity in thin central region only
2. Substrate signals ‘shadowed’ in vicinity of wire

Reducing extractor voltage

Recommendation 1.
For conducting samples, reduce topographic effects by reducing extractor voltage to minimum 500 V
Topographic field effects:

- **Reduce** with lower extractor voltage
- **Increase** disproportionally with diameter of wire
- **Increase** for poorly mounted samples

**Recommendation 2**: Mount conducting samples in good contact with a flat conductive substrate

- Typically only ions from top ±15° of wire can be detected
- Observable area is larger Au than Au$_3$ and organics – ion kinetic energy on emission affects trajectory
- Could affect data interpretation

Primary ion beam scattering

Si$^+ + C_2H_4^+$ image

Primary ions with incidence angle $>55^\circ$ can be scattered by the target

Substrate signals recorded at location of the wire

Recommendation 3: Use high mass resolution image to diagnose effects caused by primary ion scattering

Regional time-of-flight spectra for H$^+$ peak

Before sputter cleaning

After in-situ sputter cleaning

Time of flight, µs

Intensity, counts
Conducting samples – Reducing effects of topography

- Minimum extractor voltage of 500 V
- Use of extraction delay

**SIMION modelling**

**Recommended Region**
- **A**: Upper limit extraction delay for useful peak shape
- **B**: Maximum delay required for basic mass calibration

**Recommendation 4**: For conducting samples, extraction delay reduces effects of topography – summary plot provided
2. Insulating fibres – Experimental set up

- PET fibre (diameter 100 µm) mounted onto Si wafer
- Surface potential varies throughout sample surface
- Recommended reflector voltage is +20 V higher than potential at fibre sides
- Topographic field effects limit regions from which secondary ions can be detected

**Recommendation 5:** For insulating samples, use a larger reflector voltage to maximise the acceptance of secondary ions
Effects of electron current

- Typically insulating samples are **negatively charged** by incident electrons.
- This *reduces* topographic field effects in *positive* ion mode.
- But *increases* topographic field effects in *negative* ion mode!
Effects of electron current

- Charge compensation significantly affects image obtained using SIMS!
- At large electron currents, electrons are deflected by the negatively charged sample. This causes accumulated damage on the substrate!

**Recommendation 6:** For insulating samples, careful control of electron current is required to obtain repeatable images and minimise sample damage.
Reducing differential charging

**Recommendation 7:** Differential charging of the sample can be reduced via a lower electron energy.

<table>
<thead>
<tr>
<th>Positive ions</th>
<th>Negative ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 eV</td>
<td>Negative ions</td>
</tr>
<tr>
<td>15 eV</td>
<td>25 eV</td>
</tr>
<tr>
<td>15 eV</td>
<td>15 eV</td>
</tr>
</tbody>
</table>

**Recommendation 8:** Mount insulating samples onto insulating substrates to improve repeatability of images for different charge compensation settings.

Mounting onto insulating (glass) substrate
**Conclusions and recommendations**

### Conducting samples
- Analyse samples in an orientation that minimises geometrical distortions
- Use high mass resolution image to diagnose primary ion scattering
- Mount samples in good contact with a flat conductive substrate
- Reduce topographic effects by reducing extractor voltage to a minimum of 500 V
- Extraction delay reduces effects of topography – use summary plot provided

---

### Insulating samples
- Mount samples in good contact with a flat insulating substrate
- Use a larger reflector voltage to maximise the acceptance of fibre secondary ions
- Careful control of electron current is required to obtain repeatable images and minimise sample damage
- Use a lower electron energy to reduce differential charging of the sample

---


*J. L. S. Lee et al, SIA (2011) Early View DOI 10.1002/sia.3833*
Standardisation and traceability

Measurements made in Industry

ISO TC 201
Surface chemical analysis (Terminology, XPS, AES, SIMS, SPM etc)

ISO TC 229
Nanotechnologies
*Terminology, *Measurement & Characterisation
*HSE

VAMAS – Versailles Project on Advanced Materials and Standards
– Pre-normative studies (TWA 2 for Surface Analysis)

CIPM - Nation-to-Nation intercomparability and traceability is established legally (CCQM for Surface Analysis)
Objective: To produce, by coordinated effort, the reference procedures, reference data, and reference materials necessary to establish standards for surface chemical analysis (SCA)

Quantifiable, Repeatable, Reliable and Meaningful Results

Normative (ISO)

Pre-Normative (VAMAS)

Metrology and Fundamental Science
1. Repeatability and Constancy of the Relative Intensity Scale (ISO 23830).

2. Calibration of the mass scale for a time of flight secondary ion mass spectrometer (ISO 13084).

3. Linearity of intensity scale in single ion counting time-of-flight mass analysers (ISO NWI)