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Surface chemical analysis — Secondary-ion mass spectrometry — Calibration of the mass scale for a time-of-flight secondary-ion mass spectrometer

Analyse chimique des surfaces — Spectrométrie de masse des ions secondaires — Étalonnage de l'échelle de masse pour un spectromètre de masse des ions secondaires à temps de vol

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Foreword

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Introduction

Secondary-ion mass spectrometry (SIMS) 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 repeatability and constancy (Reference [2] in the Bibliography). An increasing requirement is for the identification of the chemical composition of complex molecules from accurate measurements of the mass of the secondary ions. The relative mass accuracy to do this and to distinguish between molecules that contain different chemical constituents, but are of the same nominal mass (rounded to the nearest integer mass), is thus an important parameter. A relative mass accuracy of better than 10 ppm is required to distinguish between C_2H_4 (28,031 30 u) and Si (27,976 92 u) in a parent ion with total mass up to 1 000 u, and between CH_2 (14,015 65 u) and N (14,003 07 u) in parent ions with total mass up to 300 u. However, in a recent interlaboratory study (Reference [3] in the Bibliography), the average fractional mass accuracy was found to be 150 ppm. This is significantly worse than is required for unambiguous identification of ions. A detailed study (Reference [4] in the Bibliography) shows that the key factors degrading the accuracy include the large kinetic energy distribution of secondary ions, non-optimized instrument parameters and extrapolation of the mass scale calibration.

This International Standard describes a simple method, using locally sourced material, to optimize the instrumental parameters, as well as a procedure to ensure that accurate calibration of the mass scale is achieved within a selectable uncertainty.

Surface chemical analysis — Secondary-ion mass spectrometry — Calibration of the mass scale for a time-of-flight secondary-ion mass spectrometer

1 Scope

This International Standard specifies a method to optimize the mass calibration accuracy in time-of-flight SIMS instruments used for general analytical purposes. It is only applicable to time-of-flight instruments but is not restricted to any particular instrument design. Guidance is provided for some of the instrumental parameters that can be optimized using this procedure and the types of generic peaks suitable to calibrate the mass scale for optimum mass accuracy.

2 Symbols and abbreviated terms

2.1 Symbols

m	mass of interest
m_1	calibration mass 1
m_2	calibration mass 2
ΔM	mass accuracy (u)
M_P	measured peak mass (u)
M_T	true mass (u)
$U(m)$	mass uncertainty for a mass m, arising from calibration
U_1	uncertainty in the accurate mass measurement of m_1
U_2	uncertainty in the accurate mass measurement of m_2
U_0	average uncertainty in an accurate mass measurement
V_R	reflector or acceptance voltage (V)
W	relative mass accuracy
x	number of carbon atoms
y	number of hydrogen atoms
$\sigma(\Delta M)$	standard deviation of the mass accuracy for a number of peaks
σ_M	average of the standard deviations of ΔM for each of the four $\mathrm{C}_x\mathrm{H}_y^+$ cascades with 4, 6, 7 and 8 carbon atoms

2.2 Abbreviated terms

MEMS	micro-electromechanical system
PC	polycarbonate
ppm	parts per million
r/min	revolutions per minute
SIMS	secondary-ion mass spectrometry
THF	tetrahydrofuran
ToF	time of flight

3 Outline of method

Here, the method is outlined so that the detailed procedure, given in Clause 4, may be understood in context. Firstly, to optimize a time-of-flight mass spectrometer using this procedure, obtain a thin film of PC on a conducting substrate (silicon). The optimization procedure is achieved by carrying out the procedures in 4.3 to 4.5 iteratively; it uses 19 specific C_xH_y peaks in the polycarbonate (PC) positive-ion mass spectrum. In 4.6, a general calibration procedure is given which provides the rules by which calibrations for inorganics and organics may be incorporated. This leads to a new generic set of ions for mass calibration that can improve the mass accuracy from some often used calibrations by a factor of 5. 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. Therefore, the procedure has two parts, optimization and calibration. Subclauses 4.1 to 4.5 are only required as part of the regular maintenance of the instrument as defined by the testing laboratory. Subclause 4.6 is required for all calibrations of the mass scale. This is summarized in the flowchart in Figure 1.

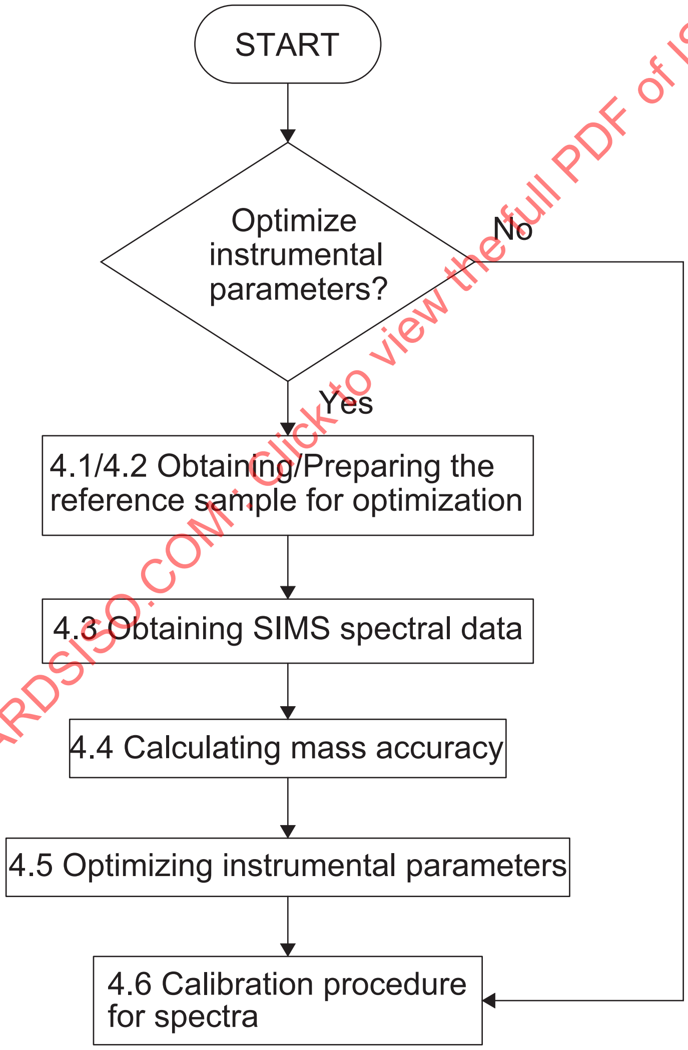


Figure 1 — Flowchart of sequence of operations of the method

4 Method for improving mass accuracy

4.1 Obtaining the reference sample for optimization

A sample of thin (10 to 100 nm) PC on a flat conducting substrate (e.g. silicon wafer) shall either be obtained or prepared, as described at 4.2.

4.2 Preparation of polycarbonate sample

4.2.1 Instructions for the preparation of a PC reference sample are provided. This method can give sample-to-sample repeatability in ToF SIMS spectra of better than 1,9 % [2]. To prepare such a sample for static SIMS analysis requires a clean working environment. To reduce surface contamination, clean glassware, tweezers and powderless gloves shall be used. The equipment required is a 1 ml glass pipette, a 100 ml glass-stoppered measuring flask and a device for spin casting. If a device for spin casting is not available, droplet deposition of the PC solution may be used. However, this will give poor repeatability, which will need to be carefully taken into account during spectral analysis.

4.2.2 Using poly(bisphenol A carbonate), abbreviated to PC, weigh out 100 mg on a clean piece of aluminium foil. Introduce the PC into the 100 ml, glass-stoppered measuring flask, add tetrahydrofuran (THF) of analytical reagent quality, to the 100 ml level line. Shake the flask to mix the PC and allow time to dissolve it completely. This produces a 1 mg/ml solution of PC in THF. The aluminium foil shall be freshly unrolled and the shiny surface used. Ensure that the THF is anhydrous. Otherwise, streaks will appear from water when spin coating as described in 4.2.3. The shelf life of freshly prepared stock solution shall be no more than one month owing to water take-up.

NOTE 1 It does not matter if the PC contains low levels of additives such as Irgafos.

NOTE 2 It does not matter if the final PC/THF solution concentration varies by ±20 %.

4.2.3 Use a conveniently sized (1 cm by 1 cm) piece of silicon, or another flat or polished conducting substrate, and clean it overnight by soaking in propan-2-ol (isopropyl alcohol). Ultrasonically clean the substrate in fresh propan-2-ol and dry. If an ultrasonic bath is not available, just rinse the sample in fresh propan-2-ol. Mount the substrate on the spin casting device. Pipette approximately 0,2 ml of the PC solution onto the substrate and spin cast at 4 000 r/min for 25 s. Samples may be prepared by depositing the PC solution using a 5 ml pipette onto the silicon surface then air drying under ambient conditions. However, this method will result in an uneven PC film, so care shall be taken when comparing spectra, as peak intensities will vary.

NOTE 1 It is not essential what substrate is used, as long as it is conducting. Silicon has been found to give good-quality films.

NOTE 2 Using this procedure, the film thickness will be approximately 10 nm. The absolute thickness is not critical.

4.3 Obtaining the SIMS spectral data

4.3.1 Insert the PC sample inside the chamber of the SIMS instrument.

4.3.2 Operate the instrument in accordance with the manufacturer's or local documented instructions. The instrument shall have fully cooled following any bakeout. Ensure that the operation is within the manufacturer's recommended ranges for the ion-beam current, counting rates and any other parameter specified by the manufacturer. Check that the detector multiplier settings are correctly adjusted.

4.3.3 Select the normal analytical settings and acquisition time. For ToF instruments, select a repetition rate that gives a maximum mass of at least 800 u. If the total counts in the $C_9H_{11}O$ peak are less than 10 000, increase the acquisition time to ensure that this peak contains more than 10 000 counts. This may not be possible if the signal is too weak and it is not possible to achieve 10 000 counts within a reasonable time. To ensure that the maximum ion fluence (1×10^{16} ions/m^2) is not exceeded, an enlarged raster area may be required. The acquisition time finally chosen will be a compromise between the data quality and the duration of the work. Record the parameters set. Ensure that the detector is not saturated using the manufacturer's or local documented instructions. This may be achieved by reducing the number of primary ions per pulse.

NOTE For details of acquiring high-quality SIMS spectra with good repeatability and constancy, refer to ISO 23830[1].

4.4 Calculating mass accuracy

4.4.1 Instrument manufacturers' software may provide the calculation of the peak position automatically; it is often sufficient to use this to obtain a value of M_o. A more accurate and reliable method for measurement of the mass of the peak in the spectra, M_o, can be used. An asymmetric Gaussian function, G_A, can be used to fit to the signal intensity versus the mass position, M_P, and the fitting used to calculate the peak position, M_o. Where M_o is the peak centre, M_P is the peak mass and G_o is a scaling term, G_A, the fit to signal intensity, is given by

$$G_\mathrm{A} = G_\mathrm{o} \exp\left(\frac{-(M_\mathrm{P}-M_\mathrm{o})^2}{2[\sigma-\alpha(M_\mathrm{P}-M_\mathrm{o})]^2}\right) \tag{1}$$

and

$$\sigma = \frac{\mathrm{FWHM}(\alpha=0)}{2\sqrt{2\ln 2}} \tag{2}$$

where

FWHM($\alpha = 0$) is the full width at half-maximum of the base Gaussian width for $\alpha = 0$. The term α gives the asymmetry, and for $\alpha = 0$ the function is pure Gaussian.

For each peak, fit Equation (1). Only use those intensities above 50 % of the maximum intensity to avoid interference from neighbouring peaks. You should calibrate using the peak position method you intend to use for accurate mass identification in your work.

NOTE An asymmetric Gaussian function gives a good fit to a wide range of peak shapes, whereas the mean value can lead to significant errors for asymmetric peaks. Typically, the asymmetric Gaussian function is an excellent description of the peak down to 15 % of the maximum intensity, although the fitting, here, only covers to 50 %.

4.4.2 The mass accuracy, ΔM, is defined as the difference between the measured peak mass, M_P, and the true mass, M_T

$$\Delta M = M_\mathrm{P} - M_\mathrm{T} \tag{3}$$

and the relative mass accuracy, W, is given by

$$W = \frac{\Delta M}{M_\mathrm{T}} \tag{4}$$

In the text that follows, W will be given in parts per million.

4.4.3 Figure 2 shows ΔM for a range of hydrocarbon peaks of polycarbonate in an unoptimized instrument. ΔM varies widely along the mass range for ions with different fragmentation. This illustrates an instrument with modest mass scale accuracy.

In Figure 2 the peaks marked with an arrow are used to calibrate the spectra. The circumscribed symbols denote the mass peaks used to measure σ_M. Here the asymmetric Gaussian function is used.

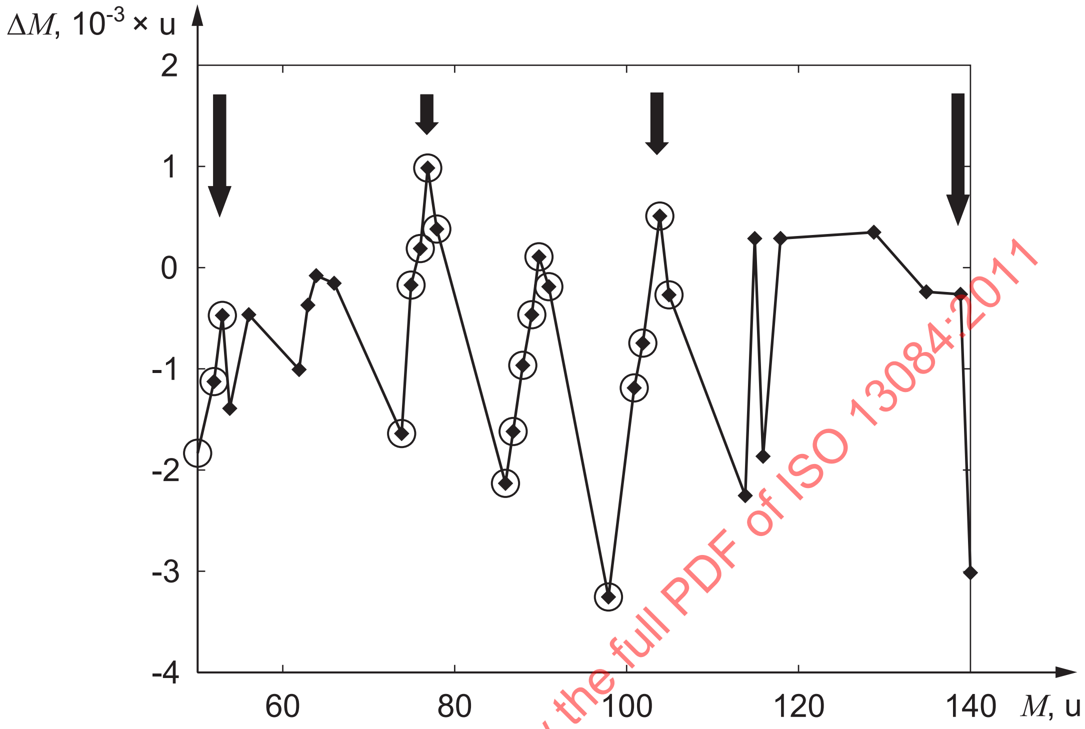


Figure 2 — Mass accuracy, ΔM, for hydrocarbon peaks from PC positive-ion spectra with a reflector voltage, $V_R = 60$ V

To provide a statistical measure of the divergence of ΔM from 0, select the peaks for the four well-defined $C_xH_y^+$ cascades with $x = 4$, 6, 7 and 8, respectively, identified in Figure 2 by the circumscribed data points and detailed in Table 1.

Table 1 — Peaks identified in Figure 1 used to calculate σ_M

x value	Ion	True mass, u
4	C_4H_2	50,015 65
4	C_4H_4	52,031 30
4	C_4H_5	53,039 13
6	C_6H_2	74,015 65
6	C_6H_3	75,023 48
6	C_6H_4	76,031 30
6	C_6H_5	77,039 13
6	C_6H_6	78,046 95
7	C_7H_2	86,015 65
7	C_7H_3	87,023 48
7	C_7H_4	88,031 30

Table 1 (*continued*)

x value	Ion	True mass, u
7	C_7H_5	89,039 13
7	C_7H_6	90,046 95
7	C_7H_7	91,054 78
8	C_8H_2	98,015 65
8	C_8H_5	101,039 10
8	C_8H_6	102,047 00
8	C_8H_8	104,062 60
8	C_8H_9	105,070 40

Measure ΔM for each peak using Equation (3) and calculate the four standard deviations for $\sigma_{C_xH_y}(\Delta M)$, $x = 4$, 6, 7 and 8. The formula to calculate $\sigma_{C_xH_y}(\Delta M)$ is exampled for $x = 6$ in Equation (5).

$$\sigma_{C_6H_y}(\Delta M) = \sqrt{\frac{\sum_{y=2}^{6}\left(\Delta M_{C_6H_y} - \overline{\Delta M_{C_6H_y}}\right)^2}{4}} \tag{5}$$

Finally, calculate, σ_M, the average of the standard deviations of ΔM for each of the four $C_xH_y^+$ cascades defined in Table 1 using:

$$\sigma_M = \frac{1}{4}\left[\sigma_{C_4H_y}(\Delta M) + \sigma_{C_6H_y}(\Delta M) + \sigma_{C_7H_y}(\Delta M) + \sigma_{C_8H_y}(\Delta M)\right] \tag{6}$$

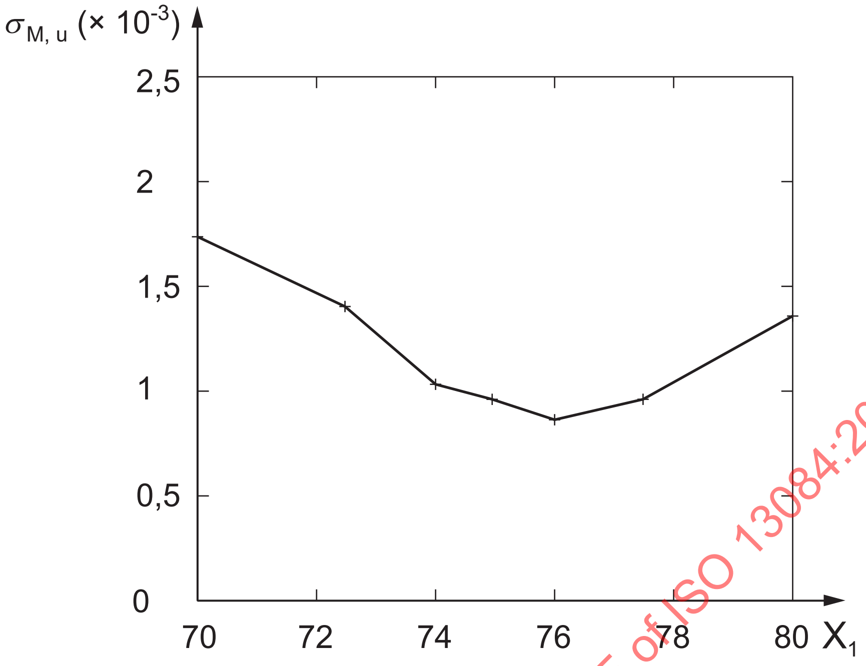
where for $x = 4$, 6, 7 and 8, $\sigma_{C_xH_y}(\Delta M)$ is the standard deviation for the $C_xH_y^+$ cascade.

NOTE Some care might be needed to take into account the lifetime of molecules and the changes this has on the mass accuracy. For the molecules used here, and shown in Table 1, there is no noticeable effect of the lifetimes of the molecules on the mass accuracy.

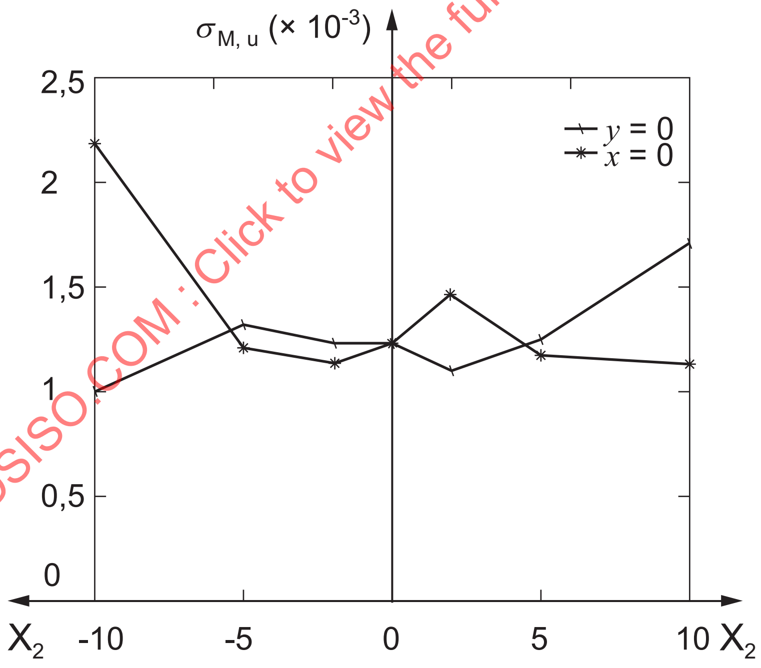
4.5 Optimizing instrumental parameters

The measure σ_M is now used to optimize the instrument operating parameters. For improved mass accuracy, the value of σ_M needs to be minimized. This is illustrated with examples here, for a reflection instrument, for optimization of the lens settings and optimization of the analyser deflector X and Y plates, as shown in Figure 3. It is simple to locate the optimum lens setting from the minimum of the curve in Figure 3 a) giving a lens setting of 76 %. Similarly, it is clear that the optimum setting 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 optimize other parameters, such as energy slit values, contrast diaphragms, pass energy and extraction potential. Optimize these by conducting, iteratively, the procedures in 4.3 to 4.5 for a range of analyser settings, to obtain graphs similar to those in Figure 3. These can be used to decide which analyser settings will minimize σ_M and hence give an optimum mass accuracy. Use guidance from the instrument operator's manual or the instrument manufacturers, to choose suitable variations in analyser settings.

NOTE The optimization procedure aims to reduce the scatter seen in Figure 2. The scatter is characterized by the σ_M value; a reduction of σ_M is a reduction in that scatter. An example of the possible improvement in scatter is shown in Figure 3 as a reduction in σ_M. The overall improvement will depend on the instrumental parameters that can be changed.



a) **Lens settings**



b) **Analyser deflector X and Y settings**

Key

X_1 lens setting, in %

X_2 analyser deflector X and Y settings

Figure 3 — Change in σ_M for different lens settings and analyser deflector X and Y settings

4.6 Calibration procedure

4.6.1 The mass calibration in ToF SIMS spectra is conducted in the spectrum itself, rather than the instrument being calibrated. In the measured spectrum, only peaks that you are confident in correctly identifying, shall be used as calibration peaks.

NOTE Incorrectly identified peaks will lead to inaccuracies in the mass scale calibration; however, ensuring correct identification of peaks will negate this.

4.6.2 For samples exhibiting a roughness or edge height of over 1 µm, the mass resolution and mass scale calibration accuracy will be degraded. If the topography is structured (for example a MEMS device) rather than random (abraded surface), the mass calibration should be restricted to zones of similar sample height.

4.6.3 The true mass of the calibrant peaks shall be calculated using the identified molecular formula and a standard look-up table of atomic masses. Isotopic mass values, rather than average mass values, shall be used. In mass spectrometry, the ion is measured and therefore the mass of the electron ($5{,}49 \times 10^{-4}$ u) times the number of ionization charges should be subtracted or added for positive and negative ions respectively, for the relevant level of accuracy.

NOTE For the example C_4H_5O: from a periodic table of isotope masses the commonest carbon (C) isotope is 12 and it has a mass of 12,000 000 u; similarly the mass of H = 1,007825 u and the mass of O = 15,994 915 u. Therefore the true mass of the molecule $C_4H_5O = 4 \times 12\ \text{u} + 5 \times 1{,}007\ 825\ \text{u} + 15{,}994\ 915\ \text{u} = 69{,}034\ 040\ \text{u}$.

4.6.4 It is common practice to use hydrogen as the first mass in the calibration. This is very useful as it is easy to identify without a calibrated mass scale and may be used to establish a first calibration. However, for accurate calibration of the mass scale, hydrogen is not recommended.

NOTE The uncertainty of the mass measurement of hydrogen is significantly greater than average. Part of the reason for this arises since the trajectory of hydrogen is affected more strongly by stray magnetic fields than heavier ions (often observed as a displacement of the ion image), thus adding to the uncertainty in the measured transit time and hence the deduced mass value.

4.6.5 For molecular analysis of minimally degraded fragments, use peaks for similarly minimally degraded entities as calibration peaks. That is: calibrate using ions that have low degradation or fragmentation from the original parent structure. Do not include atomic ions in the mass calibration. Avoid metastable ions.

NOTE 1 Minimally degraded ions can be identified using G-SIMS (Reference [5] in the Bibliography).

NOTE 2 Atomic ions have large kinetic energies, which lead to large values of ΔM compared with organic ions. This biases the calibration. This arises since most mass spectrometers do not have full energy compensation.

NOTE 3 Metastable ions can be identified by their broad peak shape.

4.6.6 Calibrate using a first mass m_1 within, or as close as possible to, the mass range 12 to 30 u and a second mass m_2 with as high a mass as is conveniently available. For identification of large molecules of mass m, include a mass $m_2 \geq 0{,}55\ m$ in the calibration ions. Some care may be needed to take into account the lifetime of molecules and the changes this has on the mass accuracy. The use of molecules with large peak widths that may indicate short lifetimes should be avoided.

NOTE The requirement to use widely separated masses in the calibration, with $m_2 \geq 0{,}55\ m$, is explained in Annex A.

4.6.7 Add several further intermediate calibration masses; five calibrant ions are sufficient.

NOTE Using several measures generally improves the quality of the calibration.