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Surface chemical analysis — Secondary ion mass spectrometry — Linearity of intensity scale in single ion counting time-of-flight mass analysers

Analyse chimique des surfaces — Spectrométrie de masse des ions secondaires — Linéarité de l'échelle d'intensité des analyseurs de masse à temps de vol pour comptage des ions individuels

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 6, *Secondary ion mass spectrometry*.

This second edition cancels and replaces the first edition (ISO 17862:2013), which has been technically revised.

The main changes are as follows:

— the procedure has been simplified by removing the informative background (including Annexes B to D);

— all figures have been fixed to adhere with ISO standards.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

For the quantitative analysis of materials using secondary ion mass spectrometry (SIMS), measurements are made of the spectral intensities. Nonlinearity in the instrument intensity scale, unless corrected, leads directly to errors in the relative amounts of material determined at surfaces and in-depth profiles. In general, intensity scales are linear at very low count rates, or more correctly low counts per pulse, but become progressively nonlinear as the count rates rise. Measurements of intensity rely on the measurement system delivering an intensity signal fixed in proportion to the intensity being measured. In counting systems, this proportionality is expected to be unity. If this proportionality varies with the signal level or counting rate, the measurement system is said to be nonlinear. It is rare for nonlinearities below 1 % to be treated as significant. The intensity scale nonlinearity can exceed 1 % for count rates that exceed 5 % of the maximum permissible count rate[2]. For many instruments, the nonlinearity behaviour will not vary significantly from month-to-month, provided the detection system is correctly set. For these instruments, the count rate can be corrected, using the relevant relationship, so that the corrected intensity is then linear for a greatly extended fraction of the maximum obtainable count rate. This correction to the intensity scale might or might not already be available in the instrument's data capture or processing computer. In this document, a simple test of linearity is provided for the intensity lost in systems in which secondary ions arrive at a detector based on a microchannel plate or scintillator and photomultiplier followed by a time-to-digital converter. If this test is shown to be valid, a correction is provided that, for suitable instruments, can extend the intensity scale by up to a factor of more than 50. For some instruments, the nonlinearity cannot be predictable nor described by any simple relationship. For these instruments, this document allows the extent of the nonlinearity to be measured and a maximum count rate for an acceptable limit of divergence from linearity to be defined. In some cases, adjustments to the instrumental settings can improve the situation so that the required correction is then valid. The limit of divergence from linearity is set by the user appropriately for the analyses to be conducted.

Although there are a number of causes of nonlinearities in TOF-SIMS instrumentation, the most significant is intensity saturation caused by the effective dead-time of the detector system. This arises since only one secondary ion count per primary ion pulse can be detected within a dead-time interval τ, regardless of the actual number of secondary ions arriving at the detector. Nonlinearity can also be aggravated by unwanted background in the spectra.

This document provides, and can only provide, a correction to the dead-time nonlinearity for a somewhat ideal situation and not for all cases. Nevertheless, the significantly enhanced dynamic range or rate of working can be very important. Suggestions are included to optimize the instrument to provide the best measurement capability and to diagnose simple instrumental defects such as detector faults, e.g. a low detector efficiency or a detector not providing single ion counting. Then, a dead-time Poissonian correction is established to correct the measured counts within certain limits set by the analyst. This establishes an upper value for c_M, the count per pulse, either before or after correction. This upper limit is generally applicable to peaks where the signal is constant with both time and spatial distribution, where there is only one peak within the dead-time interval, and where the background intensities are negligible (these conditions are not always satisfied in practice). This is explored and explained in detail in Reference [2]. The results from applying this document relate to a “best-case scenario” and the linearity achievable with Formula (1) can be lower in real cases where it is not practical to use a wide peak integration limit of ± the dead-time. More advanced dead-time correction routines should be sought in these cases and their effectiveness can be tested using the methodology here.

This document requires technical skills that may go beyond everyday operation and should be used when characterizing a new spectrometer so that it can be operated in an appropriate intensity range. It should then be repeated after any substantive modification to the detection circuits, after replacement of the microchannel plate (MCP), or at approximately 1 year intervals.

Surface chemical analysis — Secondary ion mass spectrometry — Linearity of intensity scale in single ion counting time-of-flight mass analysers

1 Scope

This document specifies a method for determining the maximum count rate for an acceptable limit of divergence from linearity of the intensity scale in single ion counting time-of-flight (TOF) secondary ion mass spectrometers using a test based on isotopic ratios in spectra from poly(tetrafluoroethylene) (PTFE). It also includes a method to correct for intensity nonlinearity arising from intensity lost from a microchannel plate (MCP) or scintillator and photomultiplier followed by a time-to-digital converter (TDC) detection system caused by secondary ions arriving during its dead-time. The correction can increase the intensity range for 95 % linearity by a factor of up to more than 50 so that a higher maximum count rate can be employed for those spectrometers for which the relevant correction formulae have been shown to be valid.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 13084, *Surface chemical analysis — Secondary ion mass spectrometry — Calibration of the mass scale for a time-of-flight secondary ion mass spectrometer*

3 Terms, definitions, symbols and abbreviated terms

3.1 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

3.2 Symbols

The term intensity is used below and elsewhere. This refers to a measurement of peak area in the spectrum.

c_M	measured counts per pulse intensity
c_P	corrected counts per pulse intensity
F_M	shorthand for $F_M(i,j)$
$F_M(i,j)$	ratio of measured intensities for the ith $^{12}C_xF_y^+$ and $^{13}C^{12}C_{x-1}F_y^+$ secondary ions in Table 1
F_P	shorthand for $F_P(i,j)$

$F_P(i,j)$	ratio of corrected intensities for the ith $^{12}\mathrm{C}_x\mathrm{F}_y^+$ and $^{13}\mathrm{C}^{12}\mathrm{C}_{x\text{-}1}\mathrm{F}_y^+$ secondary ions in Table 1
i	index number for ion pair listed in Table 1
$i_{\max}$	highest primary ion current used for the saturation analysis
I_M	integrated measured secondary ion intensity of a specified SIMS peak
$I_M(\mathrm{X})$	integrated measured secondary ion intensity of the SIMS fragment X
I_P	integrated corrected secondary ion intensity of a specified SIMS peak
$I_P(\mathrm{X})$	integrated corrected secondary ion intensity of the SIMS fragment X
j	index number for spectrum in the measurement series
k	index number for setting the different primary ion currents
L_P	shorthand for $L_P(i,j)$
$L_P(i,j)$	ratio of $F_P(i,j)$ to the product $\alpha(i)$ and $\beta(i)$
L_M	shorthand for $L_M(i,j)$
$L_M(i,j)$	ratio of $F_M(i,j)$ to the product $\alpha(i)$ and $\beta(i)$
L_M^T	theoretical ratio of measured and corrected intensities per pulse
n	number of raster frames used to generate each SIMS intensity
N	total number of primary pulses used to generate the SIMS spectrum
R	length of the raster side used to generate each SIMS intensity
V_E	mass analyser desired energy acceptance, in eV
V_R	mass analyser reflector voltage referred to the sample potential
V_T	mass analyser reflector voltage referred to the sample potential for a secondary ion intensity to fall to half the maximum intensity
$\alpha(i)$	expected isotope ratio of the ith $^{12}\mathrm{C}_x\mathrm{F}_y^+$ and $^{13}\mathrm{C}^{12}\mathrm{C}_{x\text{-}1}\mathrm{F}_y^+$ secondary ions in Table 1
$\beta(i)$	scaling factor to correct $\alpha(i)$ for the measured data, found by fitting
τ	detection system dead-time
x	number of ^{13}C or ^{12}C atoms in the characteristic PTFE secondary ion
y	number of F atoms in the characteristic PTFE secondary ion
	Symbols used in Annex A
A	peak intensity of a selected peak (counts)
c	secondary ion counts per primary ion pulse (counts)
d	beam diameter (m)
e	charge on the electron (C)

F	pulse repetition rate or frequency (s−1)
iP	pulsed ion beam current (A) (i.e. the time-averaged current with pulsing on)
I	DC ion beam current (ions/s) (i.e. the current with the pulsing off)
J	total ion fluence (ions/m2)
M	number of pixels along a line of the raster
P	total number of primary ion pulses in the acquisition time T (no units)
Q	total number of incident ions
R	raster size (m)
T	total spectrum acquisition time (s)
w	pulse width (s)

3.3 Abbreviated terms

For the purposes of this document, the following abbreviated terms apply.

MCP	microchannel plate
PTFE	poly(tetrafluoroethylene)
SIMS	secondary ion mass spectrometry
TDC	time-to-digital converter
ToF	time-of-flight

4 Outline of method

The method is outlined by the flow chart shown in Figure 1. In this method, secondary ion spectra are measured for PTFE tape analysed in the “as received” condition with no in-house cleaning and no further sample preparation as described from 5.1 to 5.3. The analytical conditions are chosen by the analyst as described in 5.4 to provide secondary ion intensities per pulse in the linear and nonlinear ranges of detector ion counting. This is established using 16 test spectra for a test sample to define the correct range of primary ion beam current settings and 16 data spectra are then measured for the analysis sample to provide data for the linearity establishment. In order to ensure that the instrument is operating in the best condition for linearity, considerations for setting the ion beam, the mass analyser, the charge compensation, and the ion detection system are described from 5.5.2 to 5.5.5. PTFE is a bulk insulator and requires charge neutralization.

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

The acquisition of data is described in 5.5 and details of the peaks to be measured are given in Table 1. The behaviour expected is described in 5.6 with relevant formulae. If the linearity is adequate, either for the data directly or for the data after correction using the instrument's data capture computer, the work is complete until, through changes to the instrument or the passage of time, a repeat of this document is required. If the linearity is inadequate, and if the instrument follows the predicted behaviour, a correction can be made as described in 5.6.5 which can extend the linear range by a factor of more than 50. The work is now complete until, through changes to the instrument or the passage of time, a repeat of this document is required.

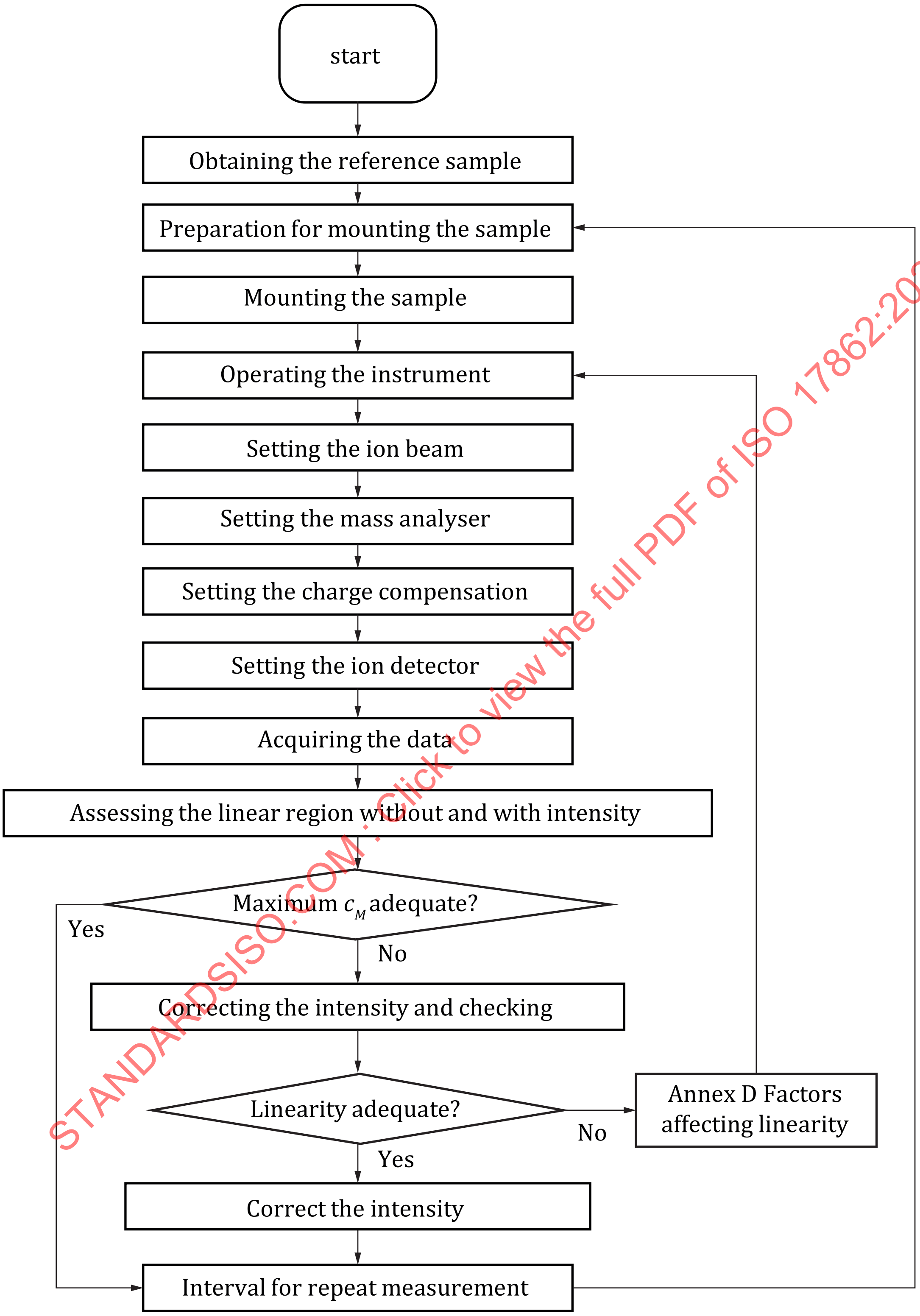


Figure 1 — Flow chart of the work

5 Procedure for evaluating the intensity linearity

5.1 Obtaining the reference sample

For the calibration of ToF-SIMS, spectrometers obtain a new roll of PTFE tape of the type used for domestic plumbing. Label and keep this roll with your reference samples.

NOTE The PTFE is usually in the form of a roll of tape of length 12 m, width 12 mm, and approximately 0,075 mm thick and is often sold for domestic plumbing.

5.2 Preparation for mounting the sample

Samples shall only be handled with clean, uncoated stainless steel tweezers. Any fingerprints on the sample shall be avoided.

NOTE This document uses the intensity ratio of natural ^{12}C and ^{13}C isotopes to determine the linearity. For the isotope ratio method to be successful, it is important that the isotope peaks can be measured without any significant background from peak interferences. Since most ToF-SIMS instruments do not have sufficient resolution to completely separate between a fragment with ^{13}C and the peak interference with ^{12}CH, it is important to have no hydrogen in the reference material and a low surface energy so that hydrocarbon contamination is minimized. PTFE has both crucial attributes and, importantly, is very easy to obtain and use.

5.3 Mounting the sample

5.3.1 To manipulate the samples, the gloves are used to hold the tweezers and not the sample. Avoid any wiping materials, sometimes used to handle samples, as they can result in unwanted contamination of the sample surface. Unnecessary contact of the sample with the gloves shall be avoided. Sample mounts and other materials used to hold samples shall be cleaned regularly whenever there is a possibility of cross-contamination of samples. The use of tapes containing silicones and other mobile species shall be avoided[3].

5.3.2 Remove and discard the first 20 cm of the material from the roll obtained in 5.1 and then cut appropriately sized samples from the subsequent material with clean scissors. As the roll 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.

NOTE 1 Common mounting systems include metal plates with holes of various sizes and metal grids. The grid often helps if severe charging is experienced.

NOTE 2 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.

A repeat of this document is required in Clause 6. For this, a fresh sample is required and for consistency, the sample should be from the same roll.

5.4 Operating the instrument

5.4.1 General

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 ion beam current, counting rates, spectrometer scan rate, and any other parameter specified by the manufacturer. Check that the detector multiplier settings are correctly adjusted (see 5.4.5).

5.4.2 Setting the ion beam

5.4.2.1 In this document, the primary ion current is to be varied to provide secondary ion intensities per primary ion pulse that range from the linear regime to highly nonlinear regime. If many ion sources are available, use the one generating the highest intensities for the $^{12}CF_3^+$ peak from PTFE. It does not matter if it is an atomic primary ion or a cluster primary ion, so long as the beam current can be adjusted to give a large range of secondary ion intensities and detector saturation as discussed in 5.5.4. The ion beam should be set according to the method specified in Annex A.

5.4.2.2 In setting the primary ion beam to provide a range of currents on the target sample, it is important that the following conditions are satisfied.

a) The pulse width and peak shape do not change drastically at different current settings.

b) The peak width is much smaller than the dead-time of the detector (determined following 5.5.10 but is usually approximately 50 ns).

c) The selected C_xF_y peaks (see Table 1) do not suffer from mass interference.

5.4.2.3 The ion beam should be centred in the acceptance area of the mass spectrometer as well as possible using specific standard procedures of the instrument.

5.4.2.4 A maximum ion fluence of 1×10^{16} ions/m^2 is recommended for each measurement. A typical ion beam raster area for this work is 200 µm × 200 µm but can be increased to 400 µm × 400 µm to satisfy the fluence requirements given generically by Formula (A.2) with illustrative numbers and where *R* is the length of the raster side. For example, a 0,5 pA pulsed beam and a 200 µm square raster requires 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 shall be used or the local fluence maximum on a pixel will be exceeded by more than a factor of 2. 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 is required. The precise minimum beam size depends on the instrument used but can be evaluated using Formula (A.1).

5.4.2.5 The number of frames acquired, *n*, should be kept above 20, as described in Formula (A.4), so that the final frame, which most likely will not be a full frame, represents only a small fraction of the data. It is recommended that a random raster pattern is used to minimize local sample charging, if available.

5.4.2.6 For good statistics, the integrated spectrum over the whole analysis area is required.

5.4.3 Setting the mass analyser

5.4.3.1 Choose the spectrometer operating settings which provide high intensities and for which the linearity is to be determined. Select settings to measure positive secondary ions.

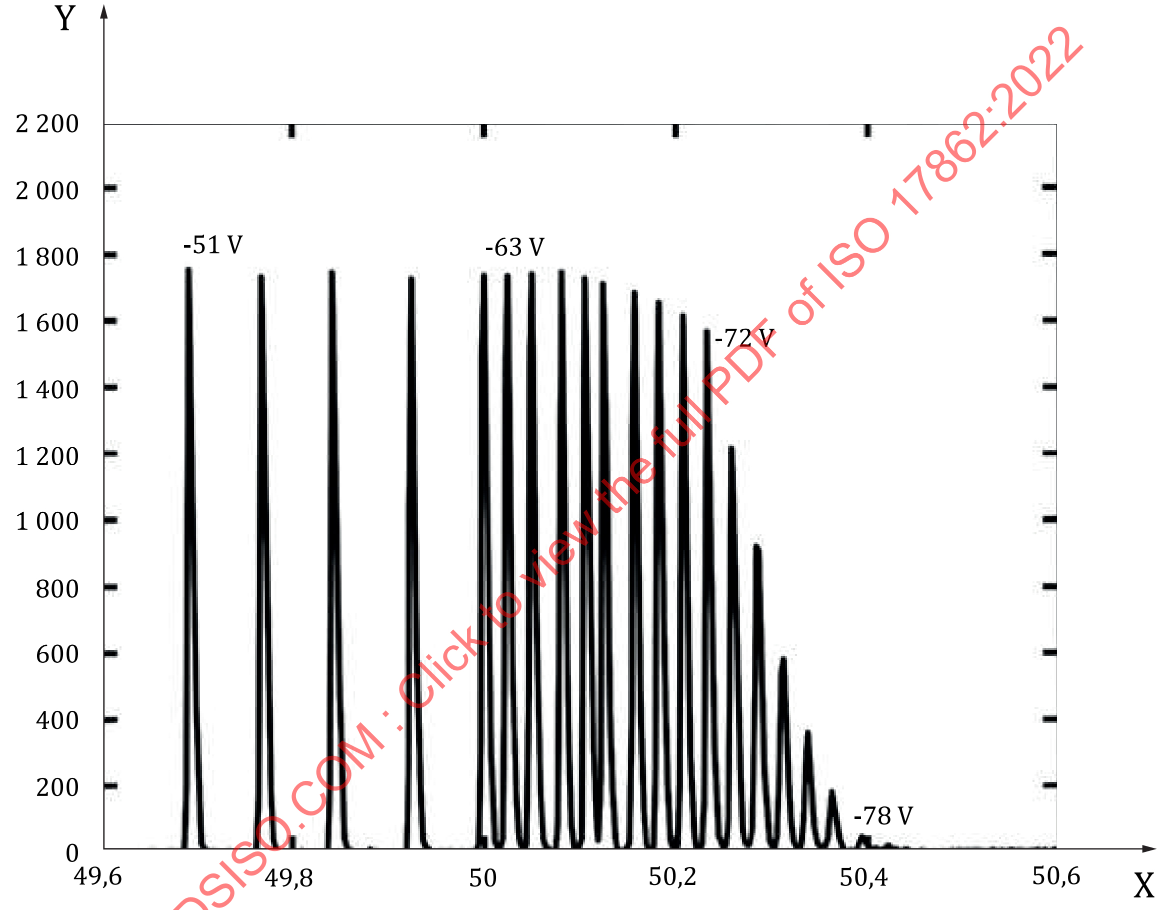
NOTE The consistency of the intensities varies with the combination of settings used. In general, the repeatability is best when using an energy acceptance of the mass analyser of 50 eV or more.

5.4.3.2 In general, the mass analyser should be operated in the condition that gives the most stable and repeatable performance with good, high mass sensitivity and optimal transmission. Ensure that charge compensation is switched on and is operating correctly. Ensure that the detector is set correctly according to local procedures.

5.4.3.3 For reflection instruments, the surface potential shall be adjusted to optimise transmission. In many instruments, the optimal surface potential is determined by simultaneously varying the relectron voltage, lens voltages and alignment plates. The effect of reflector voltage on the peak intensity of the

CF_2^+ ion from PTFE is shown in Figure 2. As the reflector voltage is made more positive, the peaks move down the apparent mass scale, 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.

5.4.3.4 After setting the reflector potential as that in 5.4.3.3, the reflector potential might need further minor adjustment to ensure that strong metastable peaks do not overlap the weaker ^{13}C isotopic peaks identified in Table 1.



Key

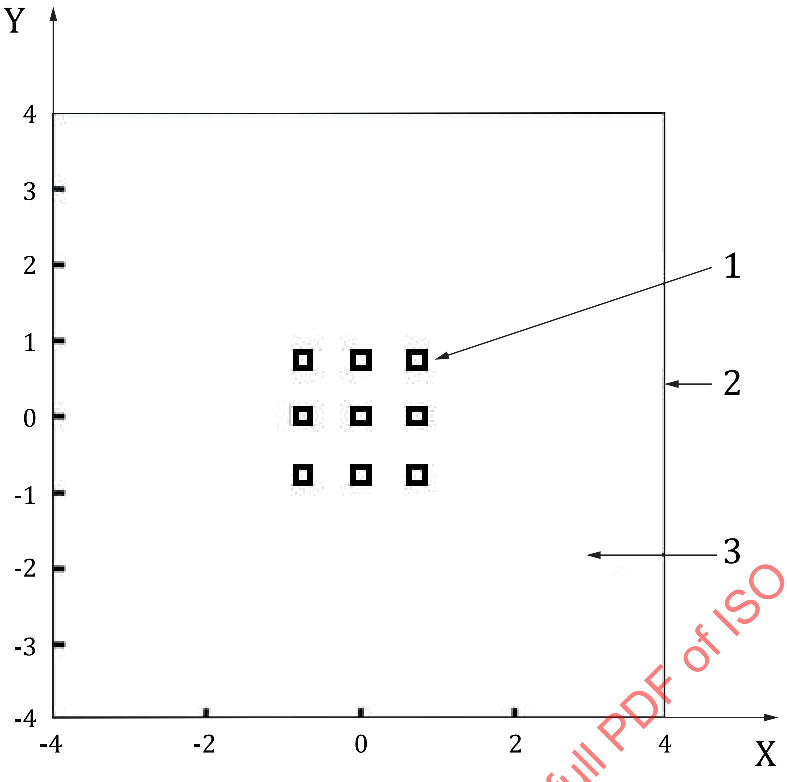
X apparent mass (u)

Y intensity (counts)

Figure 2 — The effect of reflector voltage on the CF_2^+ peak intensity from PTFE

5.5 Acquiring the data

5.5.1 Be prepared to analyse a fresh area of material each time with a total fluence of less than 1×10^{16} ions/m^2 (1×10^{12} ions/cm^2) from an array of 9 measurement positions as shown in Figure 3 (a minimum of 9 is required). Here, the example is for a sample holder with an 8 mm × 8 mm square aperture. All analysis areas should be at distances greater than 1,5 mm from the edge of the sample holder. For a square raster of side *R*, the recommended repeat distance (centre to centre) is 3,5 *R*. With the recommended raster area *R* = 200 µm, the minimum gap between each raster is 500 µm. Record these settings.



Key

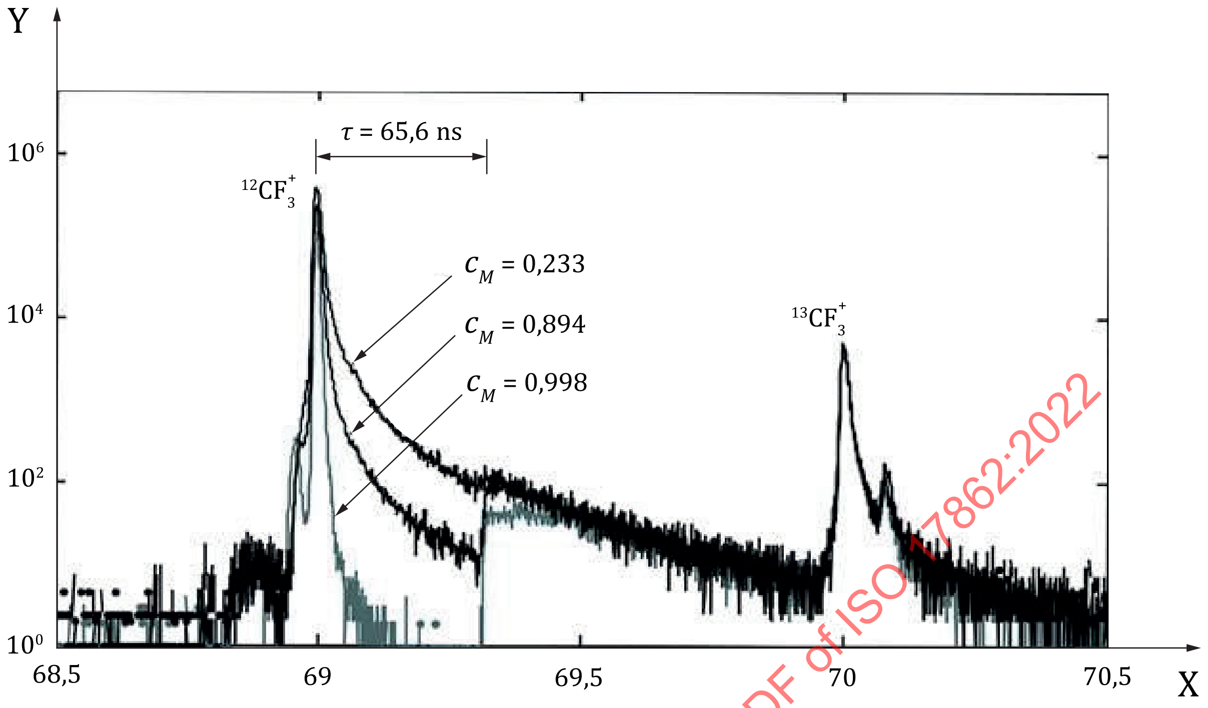
X	displacement (mm)
Y	displacement (mm)
1	example array
2	sample holder aperture
3	avoid this zone

Figure 3 — Schematic of 3 × 3 array of measurement positions for a sample holder with a square aperture of side 8 mm

5.5.2 Mount two PTFE samples as described in 5.3. One is for setting the range of primary ion currents required called the "test sample", the other, for the analysis using those settings, called the "analysis sample".

5.5.3 Switch on the charge neutralization.

5.5.4 From the test sample, acquire a positive ion spectrum using the primary ion current that would usually be used for analytical conditions. Next, establish 9 settings of the primary ion current that provide spectra that, at the highest current, i_{max}, give ion intensities that lead to strong saturation of the detector. The remaining 8 currents are each at approximately $(k/9)i_{max}$, where k = 1 to 8. Three example spectra for the CF_3^+ peak, covering this range, are shown in Figure 4. The spectra shown are normalized to a constant intensity for the $^{13}CF_3^+$ peak.



Key

X mass (u)

Y intensity (counts)

NOTE The line identifiers in the boxes show the integrated intensity of the $^{12}CF_3^+$ peak in units of c_M (secondary ion counts per primary ion pulse). The intensity of the most saturated (highest c) spectrum is presented in its measured counts on the logarithmic intensity scale, and the other spectra are normalized to the same $^{13}CF_3^+$ intensity. The dead-time, τ, of 65,6 ns is marked for the saturated peak.

Figure 4 — Details of the $^{12}CF_3^+$ peak and $^{13}CF_3^+$ peak for spectra obtained using a range of primary ion currents

5.5.5 The secondary ion peak intensities to record are given in Table 1. For the low ion beam currents, it might be necessary to increase the acquisition time so that the weakest peaks (i.e. those containing ^{13}C isotopes) have > 1 000 counts. The weakest peak is likely to be the $^{13}C^{12}CF_5^+$ peak.

Table 1 — Characteristic PTFE isotopic secondary ion intensities to be measured, showing their exact masses and the expected isotope ratios $\alpha(i)$ calculated using the natural abundance of ^{13}C

i	$^{12}C_xF_y^+$ ion	Mass u	$^{13}C^{12}C_{x-1}F_y^+$ ion	Mass u	Expected isotope ratio $\alpha(i)$
1	$^{12}CF^+$	30,998 4	$^{13}CF^+$	32,001 8	92,46
2	$^{12}CF_3^+$	68,995 2	$^{13}CF_3^+$	69,998 6	92,46
3	$(^{12}C)_3F_3^+$	92,995 2	$^{13}C(^{12}C)_2F_3^+$	93,998 6	31,25
4	$(^{12}C)_2F_5^+$	118,992 0	$^{13}C^{12}CF_5^+$	119,995 4	45,45
5	$(^{12}C)_3F_5^+$	130,992 0	$^{13}C(^{12}C)_2F_5^+$	131,995 4	31,25

NOTE The expected isotope ratio varies with the number of carbon atoms in the secondary ion fragment. The natural abundance of ^{13}C is around 1,07 % of that of ^{12}C.

5.5.6 For the analysis of the linearity of the intensity scale in 5.6 it is the measured counts per primary ion pulse, c_M, that is important rather than the total ion counts. Use Formula (A.5) or (A.6) to confirm that the selected primary ion currents provide a range of values of c_M, for the CF_3^+ peak, between approximately 0,1 and 0,99 counts per pulse. If this is not the case, adjust the primary ion beam current and repeat 5.5.4 until the condition is satisfied.

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

5.5.8 Move to the analysis sample. For each of the 9 settings of primary ion current determined in 5.5.4, acquire a positive ion spectrum from a fresh area of sample. Select the acquisition time to ensure the counts for the $^{13}C(^{12}C)F_5^+$ peak exceed 1 000 and the maximum dose is < 1 × 10^{16} ions/m^2.

5.5.9 Calibrate the mass scale for each spectrum using the instrument calibration system or ISO 13084.

5.5.10 Measure the dead-time, τ, of the spectrometer from an overlay plot of the $^{12}CF_3^+$ peak. If your software allows, it is helpful to normalize the spectra to the peak height of the $^{13}CF_3^+$ peak. Identify a spectrum similar to the one labelled in Figure 4 with c_M value of 0,894. Here, the signal is reduced after the peak but does not go to zero and, after some time, τ, recovers. Measure the value of τ. It is usually possible, in the software, to switch between a mass scale, a time scale, and sometimes a channel number. To convert from channel number to time, simply multiply the channel number by the channel width (usually around 200 ps). In this example τ = 65,6 ns. Record the value of τ.

5.5.11 For some instruments, the background signal can be too low to determine the dead-time of the detector using the method in 5.5.10. If this is the case, proceed by using the manufacturer's specified dead-time value.

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

5.5.13 Measure the intensities of the 10 peaks listed in Table 1 for the 9 spectra without any software dead-time correction.

5.5.14 Measure the intensities of these 10 peaks with instrument analysis software dead-time correction, if available.

5.6 Checking the linearity

5.6.1 The relation of corrected and measured counts

For a single SIMS peak where the peak width is smaller than the dead-time τ (usually around 30 ns to 70 ns), and where the peak is not preceded by another peak within the time τ, the intensity correction simplifies to[4]

$$\frac{I_P}{N} = -\ln\left(1 - \frac{I_M}{N}\right) \tag{1}$$

or

$$c_P = -\ln(1 - c_M) \tag{2}$$

Note that with these assumptions, c_M has a maximum value of unity.

Since Formula (1) is not a function of the dead-time τ, it should properly be called a "Poissonian correction". However, to be consistent with common usage, in this International Standard, this is referred to as "dead-time correction". Formula (1) is deduced for a Poissonian flux in which I_M is the measured intensity and I_P is the true intensity. It scales the measured secondary ion count rate per pulse, c_M, so that the corrected count rate per pulse c_P is proportional to the actual number of secondary ions impinging the detector. It is routinely applied to SIMS data and has been demonstrated to be very successful for many data sets[4][5][6]. From Formula (1), dead-time correction is required to maintain 95 % linearity between the measured intensity and the true (corrected) intensity when the value of c_M exceeds 0,1.

NOTE Formula (1) is for an intensity measured under steady-state conditions in which the counts follow pure Poissonian statistics. If the intensity is summed or averaged over a period in which the beam is rastered, deviations can occur arising from one of many instrumental or sample related factors that affect the constancy of the signal. Examples include sample heterogeneity, charging, variation in instrumental sensitivity with position in the raster, beam current fluctuations and sample damage.

5.6.2 The measured ratios for isotopes

Calculate the linearity of the intensity scale as follows. Where applicable, the subscript M denotes quantities calculated using measured intensities and subscript P denotes quantities calculated using dead-time corrected intensities. The linearity, L, is defined such that L is exactly unity for an unsaturated spectrum, and $L < 1$ for a spectrum where the more intense $^{12}\mathrm{C}_x\mathrm{F}_y{}^+$ peak begins to saturate relative to the much weaker $^{13}\mathrm{C}^{12}\mathrm{C}_{x\text{-}1}\mathrm{F}_y{}^+$ peak. For measured peak intensities without dead-time correction, the theoretical linearity L_M^T assuming single ion counting theory[4] is from Formula (1).

$$L_M^T = \frac{I_M}{I_P} = \frac{c_M}{-\ln(1-c_M)} \tag{3}$$

Next are defined as the isotope ratios for measured intensities, F_M, and the isotope ratios for corrected intensities, F_P.

$$F_M = \frac{I_M(^{12}C_xF_y)}{I_M(^{13}C^{12}C_{x-1}F_y)} \tag{4}$$

$$F_P = \frac{I_P(^{12}C_xF_y)}{I_P(^{13}C^{12}C_{x-1}F_y)} \tag{5}$$

For each pair of isotope ions (index i, identified in Table 1) and each spectrum acquired (index j), the linearity before and after dead-time correction, L_M and L_P, are then calculated from F_M and F_P, as follows

$$L_M(i,j) = \frac{F_M(i,j)}{\alpha(i)\beta(i)} \tag{6}$$

$$L_P(i,j) = \frac{F_P(i,j)}{\alpha(i)\beta(i)} \tag{7}$$

Here, for each isotopic pair i, $\alpha(i)$ is the expected isotope ratio and $\beta(i)$ is a scaling factor that is determined by fitting.

NOTE 1 The true isotopic ratio of the sample does not need to be known since any difference is accounted in the β scaling parameter.

NOTE 2 The scaling factor β is necessary because experimental SIMS intensities might not accurately reflect the expected isotope ratio α for three reasons. First, α varies naturally depending on the source of the carbon. Second, the existence of background intensities, caused by metastable ions or contamination, can contribute differently to different isotopic peaks. Finally, the sputtering and ionization efficiencies are generally not constant for different isotopes of the same element and the degree of difference can vary with experimental conditions.

5.6.3 Fitting the data

For each pair of isotope ions *i*, $\beta(i)$ is calculated by the least squares fitting of L_M to the theoretical ratio L_M^T. Plot L_M from Formula (6) and L_M^T from Formula (3) versus c_M as shown in Figure 5 a). The fitting is carried out over the range of c_M where the data are in good agreement with the theory, thus, data with very low c_M are often excluded due to the low signal-to-noise ratio, and data with c_M approaching unity are often excluded as they can begin to deviate from the theory. The range of c_M used to calculate $\beta(i)$ is determined separately for each instrumental condition (if more than one is being studied) but this range is the same irrespective of the fragment *i*. For consistency, the same value of $\beta(i)$ is then used in the calculation of dead-time corrected linearity L_P shown in Figure 5 b).

NOTE 1 In using a constant value of $\beta(i)$, it is assumed that the fractional contribution of background intensities is different for each peak *i*, but for the same peak *i*, it is the same regardless of the spectrum *j*.

NOTE 2 In an interlaboratory study[2], $\beta(i)$ averaged 1,06 and, for all participants, was between 0,9 and 1,2.

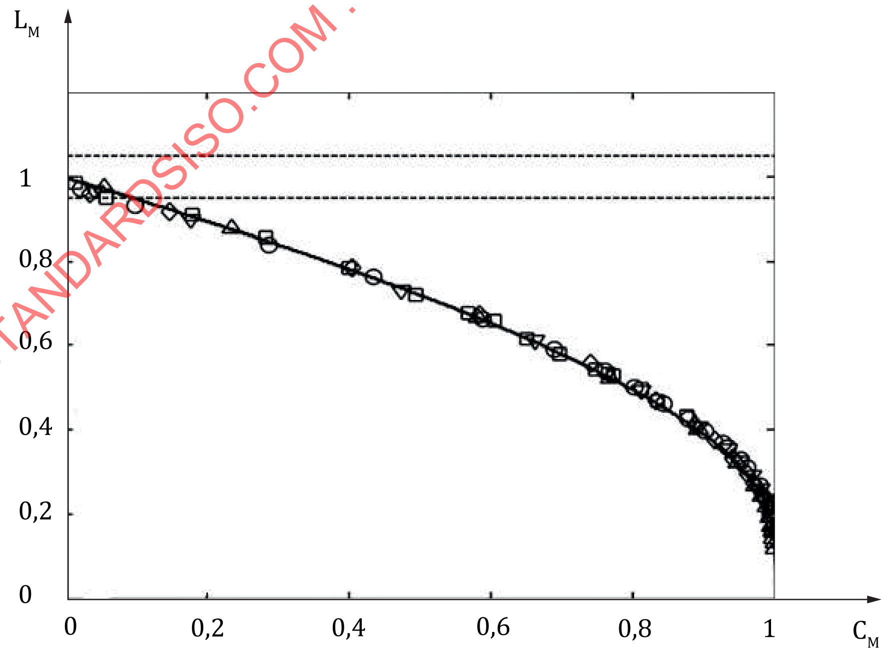
5.6.4 Assessing the linear region without and with any instrumental intensity correction

5.6.4.1 On a plot of L_M from Formula (6) versus c_M for assessment without the instrumental intensity correction, and L_M^T from Formula (3) versus c_M, draw horizontal bounds representing the linearity tolerance. Note the range of c_M acceptable within this tolerance.

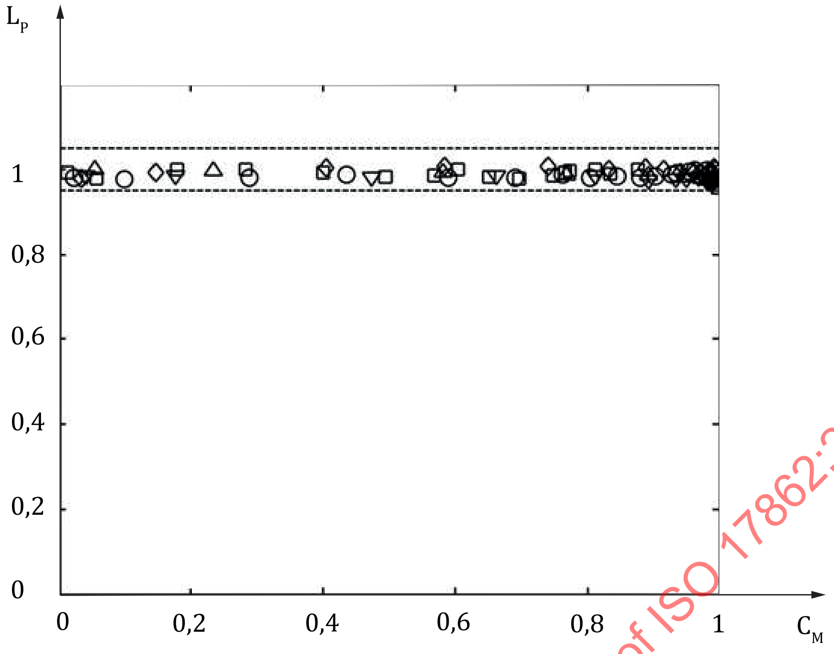
NOTE An example plot is shown in Figure 5 a) with the tolerance set at 95 %. The acceptable range is up to $c_M = 0{,}098$.

5.6.4.2 If the instrument has an intensity correction capability, plot the instrumental value of L_P versus c_M and draw horizontal bounds representing the linearity tolerance. Note the range of c_M acceptable within this tolerance.

NOTE An example plot is shown in Figure 5 b) where the lines are shown for 95 % linearity and the acceptable range is up to $c_M = 0{,}999\ 8$. However, in the uncorrected state, the maximum value of c_M is only 0,098 for this level of linearity.



a) Linearity L_M calculated using measured intensities



b) Intensity linearity L_P calculated using dead-time corrected intensities

Key

X	measured counts per pulse (C_M)	□	C_2F_5
Y	linearity (L_M, L_P)	∇	C_3F_5
C_M	measured counts per pulse	◊	CF
L_M, L_P	linearity	Δ	CF_3
○	C_3F_3	—	theory L^T_M

NOTE 1 The theoretical linearity L_M^T using single ion counting statistics is plotted as a solid line.

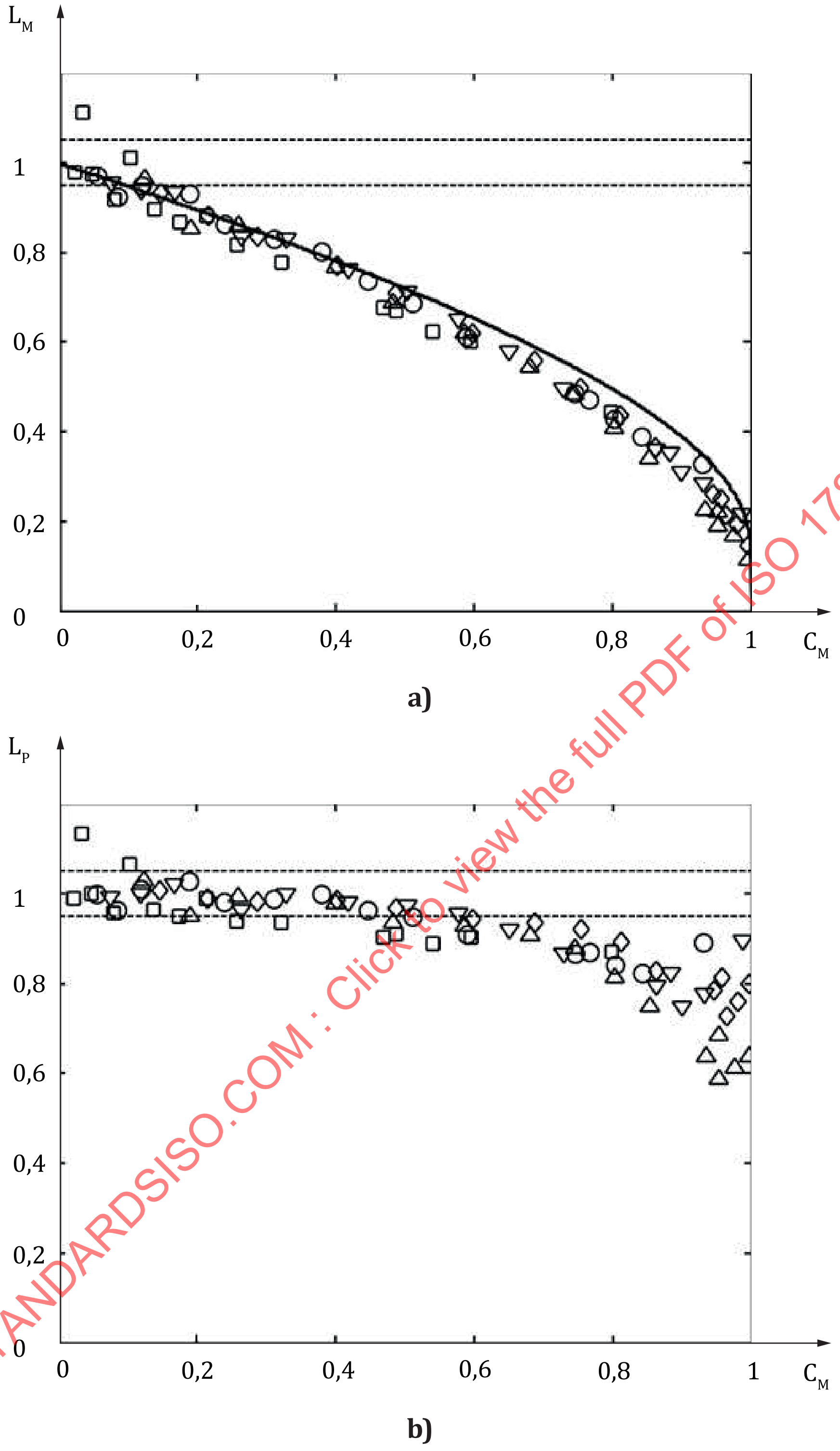
NOTE 2 The dashed lines show the limits for 95 % linearity for the corrected intensities[2].

Figure 5 — Example results showing the linearity plotted against the measured counts per pulse c_M of the $^{12}C_xF_y{}^+$ peak

5.6.4.3 If the value of c_M from 5.6.4.1 or 5.6.4.2 is adequate, go to Clause 6. If not, or if the instrumental correction software is to be compared with the correction available in this document to validate it, proceed to 5.6.5.

5.6.5 Correcting the intensity and checking the validity of any instrumental correction

5.6.5.1 The intensity is corrected using Formula (1) and is valid over the range for which L_M and L_M^T agree and the extent to which they agree. Figure 5 a) shows excellent agreement such that the useful measured counts per pulse c_M for 95 % linearity can be increased by a factor of 10. The corrected intensity at the highest limit is then 8,5 counts per pulse, showing an 85-fold improvement over the uncorrected result. Often, agreement between L_M and L_M^T is not this good as shown in Figure 6. In this case, the useful measured counts per pulse for 95 % linearity can only be increased by a factor of 4. The corrected intensity at the highest limit is then 0,5 counts per pulse, showing only a fivefold improvement over the uncorrected result.



a)

b)

Key

C_M	measured counts per pulse
L_M, L_P	linearity
◊	CF
Δ	CF_3
○	C_3F_3
_	theory $L^T{}_M$
□	C_2F_5
∇	C_3F_5

Figure 6 — Example results for a poorly adjusted instrument