
**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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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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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).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 6, *Secondary ion mass spectrometry*.

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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.^[1] 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 can or cannot already be available in the instrument's data capture or processing computer. In this International Standard, 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 International Standard 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 exacerbated by unwanted background in the spectra.

This International Standard 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 [1]. The results from applying this International Standard 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 \pm 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 International Standard 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 six monthly intervals.

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

1 Scope

This International Standard 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. This International Standard can also be used to confirm the validity of instruments in which the dead-time correction is already made but in which further increases can or cannot be possible.

2 Symbols and abbreviations

2.1 Abbreviated terms

For the purposes of this International Standard, the following abbreviations are used:

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

2.2 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 i th $^{12}\text{C}_x\text{F}_y^+$ and $^{13}\text{C}^{12}\text{C}_{x-1}\text{F}_y^+$ secondary ions in Table 1
F_P	shorthand for $F_P(i,j)$
$F_P(i,j)$	ratio of corrected intensities for the i th $^{12}\text{C}_x\text{F}_y^+$ and $^{13}\text{C}^{12}\text{C}_{x-1}\text{F}_y^+$ 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
$I_M(X)$	integrated measured secondary ion intensity of the SIMS fragment X
I_P	integrated corrected secondary ion intensity of a specified SIMS peak
$I_P(X)$	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 i th $^{12}\text{C}_x\text{F}_y^+$ and $^{13}\text{C}^{12}\text{C}_{x-1}\text{F}_y^+$ 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

3 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 [4.1](#) to [4.3](#). The analytical conditions are chosen by the analyst as described in [4.4](#) 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 [4.5.2](#) to [4.5.5](#). PTFE is a bulk insulator and requires charge neutralization.

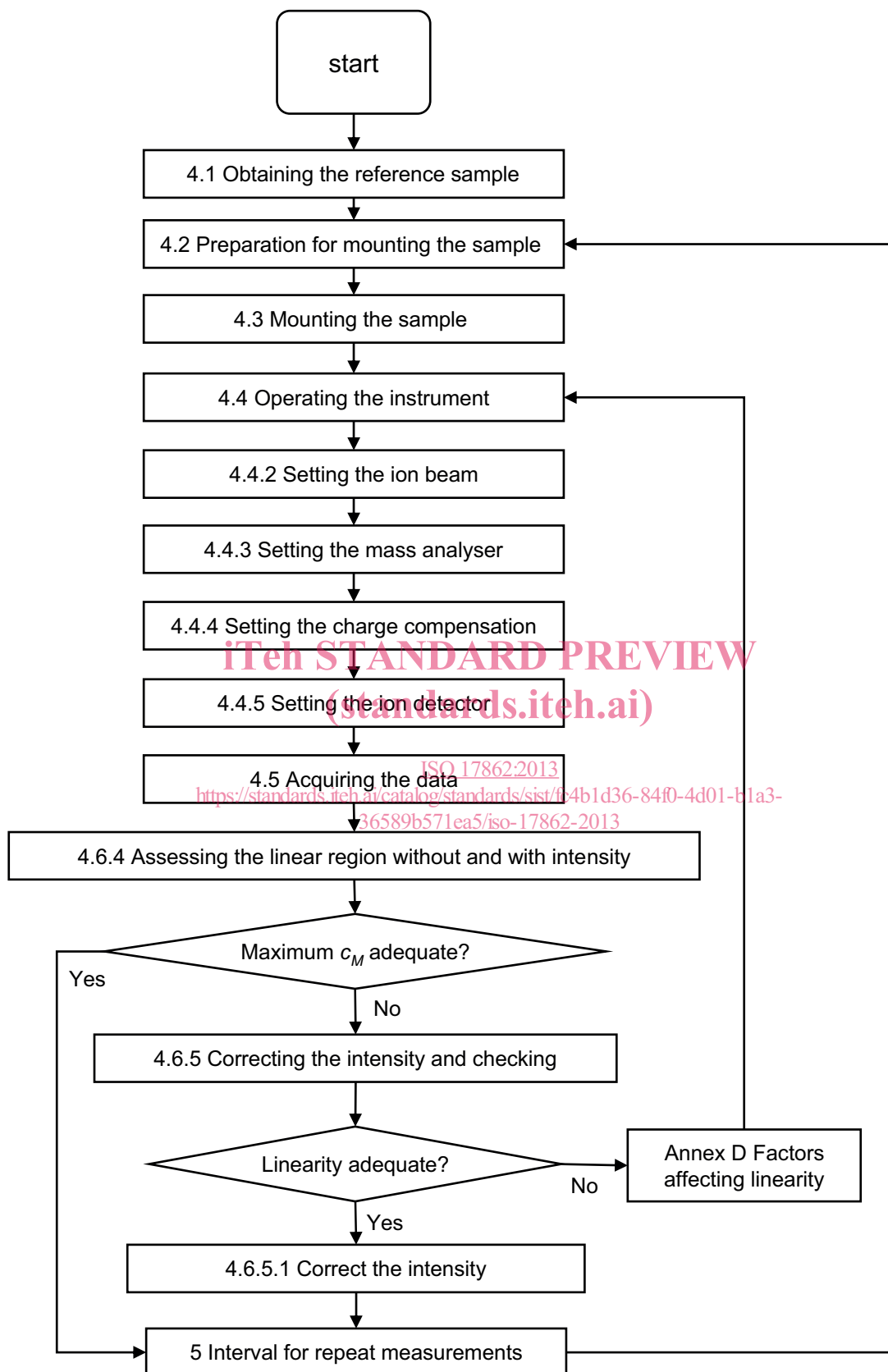
The spectrometer should be operated under conditions that give the most stable performance. It is recommended that analysts use ISO 23830[2] to confirm the repeatability of their instrument. The protocol described in this International Standard is closely aligned with that in ISO 23830 and those using that International Standard are already familiar with much of the procedure given here.

The acquisition of data is described in 4.5 and details of the peaks to be measured are given in Table 1. The behaviour expected is described in 4.6 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 International Standard is required. If the linearity is inadequate, and if the instrument follows the predicted behaviour, a correction can be made as described in 4.6.5 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 International Standard is required. Finally, if the linearity is inadequate and if the instrument does not follow the predicted behaviour, annexes are provided to indicate how to improve the matters. These can improve the linearity range to the extent that this is possible with the equipment being used. This can or cannot be the full range expected for ideal equipment but should lead to some improvement.

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NOTE The numbers refer to the relevant subclauses.

Figure 1 — Flow chart of the work

4 Procedure for evaluating the intensity linearity

4.1 Obtaining the reference sample

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

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

4.2 Preparation for mounting the sample

Samples shall only be handled with clean, uncoated stainless steel tweezers held using powderless polyethylene gloves. Vinyl gloves, often used in clean rooms, are coated with a release agent from the moulding process and shall not be used. The release agent is very mobile and quickly contaminates the samples. This leads to poor measurement repeatability and poor quality data.

NOTE This International Standard 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}C , 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 of these crucial attributes and, importantly, is very easy to obtain and use.

In selecting gloves, care should be taken to avoid those with talc, silicone compounds, or similar contaminants. "Powder-free" gloves have no talc. Coated stainless steel or other tweezers can cause unwanted contamination.

4.3 Mounting the sample

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4.3.1 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]

4.3.2 Remove and discard the first 20 cm of the material from the reel obtained in [4.1](#) and then cut appropriately sized samples from the subsequent material with clean scissors. As the reel is unwound, a fresh surface of PTFE is exposed and it is this surface that is analysed. Do not clean the sample. Mount samples on the sample holder to produce a flat, even surface using a mechanical clamping or fixing method. Do not use adhesive tape. Ensure that the reverse side of the sample is against a conducting surface, electrically connected to the sample holder. The PTFE shall not be placed over a hole.

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 International Standard is required later in [Clause 5](#). For this, a fresh sample is required and for consistency, the sample should be from the same reel.

4.4 Operating the instrument

4.4.1 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 4.4.5). In some instruments, the issue of count rate nonlinearity is dealt with by providing the user with a warning that a certain count rate should not be exceeded. This can limit the count rate to below, say 0,1 counts per pulse. It can be possible to correct the nonlinearity to significantly higher count rates using the present procedure such that a much higher dynamic range is possible, enabling the work of a higher quality to be achieved in a shorter analytical time. Doing so can require this warning to be ignored. If the warning is ignored, ensure by checking in the instrument manual or by contact with the manufacturer that it is safe to do this.

4.4.2 Setting the ion beam

4.4.2.1 In this International Standard, 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. A measurement of the ion beam current is not required since ^{12}C and ^{13}C isotope ratios are used. If many ion sources are available, use the one generating the highest intensities for the $^{12}\text{CF}_3^+$ 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 4.5.4.

4.4.2.2 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 4.5.10 but is usually ~ 50 ns).
- (c) The selected C_xF_y peaks (Table 1) do not suffer from mass interference.

The primary ion current can be easily adjusted by altering the alignment of the ion beam through the internal apertures of the ion beam column using deflection voltages. Other methods can cause changes to the pulse timing or mass calibration.

4.4.2.3 The ion beam should be centred in the acceptance area of the mass spectrometer as well as possible. To do this, first, centre all the alignments for the mass analyser and then increase the ion beam raster area to image the entire mass analyser acceptance area. Using the ion beam controls, centre the mass analyser acceptance area in the imaged area. In some cases, the maximum field of view cannot be large enough to observe the acceptance area. If the software restricts it, it can be possible to change the calibration scaling or "sensitivity" to access a larger raster area and then return to the calibrated conditions after centring.

4.4.2.4 A maximum ion fluence of 1×10^{16} ions/m² is recommended for each measurement. A typical ion beam raster area for this work is $200 \mu\text{m} \times 200 \mu\text{m}$ but can be increased to $400 \mu\text{m} \times 400 \mu\text{m}$ 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 $200 \mu\text{m}$ square raster requires 128 s acquisition time. This beam would need to be defocused to a diameter greater than $3,1 \mu\text{m}$ for a 128×128 pixel display. If it can only be defocused to $1 \mu\text{m}$, 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).