
**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

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

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 \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 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*

<https://standards.iteh.ai/catalog/standards/sist/4ff7f3c0-aa59-4217-aca8-bb704e3d14ce/iso-17862-2022>

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 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

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/m ²)
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.

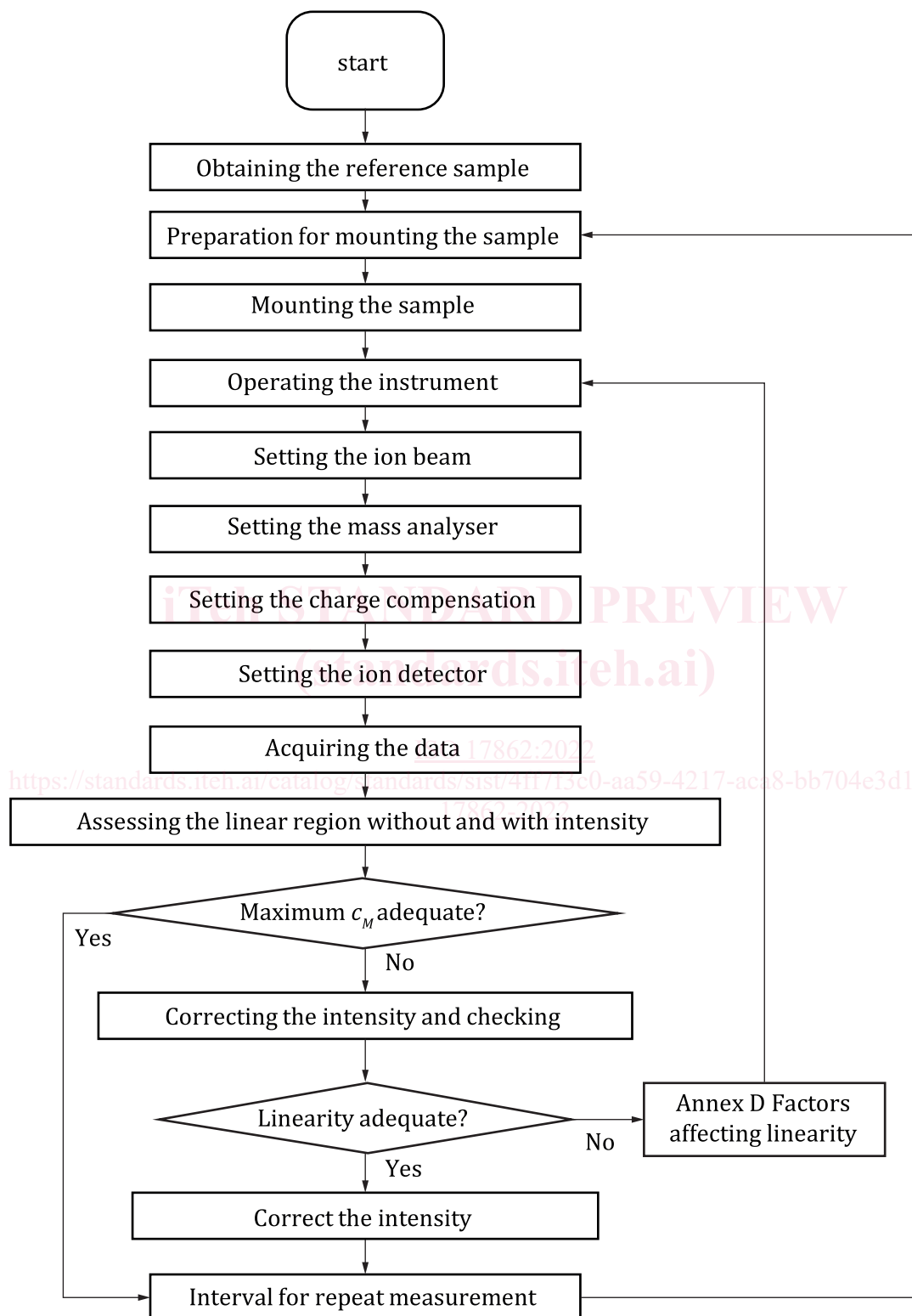


Figure 1 — Flow chart of the work

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).