INTERNATIONAL STANDARD

ISO 18554

First edition
2016-03-15

Surface chemical analysis — Electron spectroscopies — Procedures for identifying, estimating and correcting for unintended degradation by X-rays in a material undergoing analysis by X-ray photoelectron spectroscopy

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Analyse chimique des surfaces — Spectroscopie d'électrons — Procédures pour l'identification, l'estimation et la correction de la dégradation involontaire par rayons X pendant une analyse de matériau par spectroscopie de photoélectrons par rayons X

ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-4f3c-9f37-7b2db366e2a1/iso-18554-2016

Reference number
ISO 18554:2016(E)

© ISO 2016

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-4f3c-9f37-7b2db366e2a1/iso-18554-2016

COPYRIGHT PROTECTED DOCUMENT

© ISO 2016, Published in Switzerland

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized otherwise in any form or by any means, electronic or mechanical, including photocopying, or posting on the internet or an intranet, without prior written permission. Permission can be requested from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

 © ISO 2016 – All rights reserved

Contents

Page

Foreword ..... **iv**

Introduction ..... **v**

1 Scope **1**

2 Terms and definitions **1**

3 Symbols and abbreviated terms **1**

4 Sample degradation **2**

4.1 Causes of degradation 2

4.2 Sample degradation 3

4.3 Measurements for identifying, and correcting for, degradation 3

4.3.1 Recognition of degradation 3

4.3.2 The first survey scan 3

4.3.3 The detail scans 4

4.3.4 The final survey scan 4

4.3.5 Inverting the order of acquisition for unstable compounds 4

4.3.6 Check for degradation 4

4.3.7 Deduce the undegraded intensity 4

4.4 Assessing the likelihood of degradation 6

4.4.1 Determining the value of A_Z 6

4.5 Reporting degradation 6

4.6 Suggested procedures for minimising degradation 6

4.7 Influence of contamination 7

4.7.1 Contamination formation during spectrum acquisition 7

4.7.2 Reporting contamination 7

Annex A (informative) **Materials reported to degrade during analysis** **8**

Annex B (informative) **Examples of degradation** **9**

Annex C (informative) **Compensation for formation of a contamination layer** **14**

Bibliography **16**

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-4f3c-9f37-
792d5506c2a1/iso-18554-2016

© ISO 2016 – All rights reserved

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 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.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

The committee responsible for this document is ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *Electron spectroscopies*.

ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-4f3c-9f37-7b2db366e2a1/iso-18554-2016

 © ISO 2016 – All rights reserved

Introduction

The basis of X-ray photoelectron spectroscopy is irradiation of a sample surface by soft X-rays and examination of the excited emission in the form of photo-electrons and Auger electrons. In its most widely used mode, the X-ray flux is of low intensity and spread over a large area. Thus, the technique is generally regarded as one of the least destructive of the available "beam" techniques used for the surface chemical analysis of materials. However, since the time of its inception as a technique for surface analysis, there have been reports of changes in composition arising during the course of analysis.[1]-[4] These reports indicated that, for some materials, a form of degradation during analysis needs to be taken into account and, where possible, a correction made. This International Standard addresses these issues and describes a method by which the extent of degradation can be estimated and a suitable correction obtained.

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-4f3c-9f37-7b2db366e2a1/iso-18554-2016

© ISO 2016 – All rights reserved

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-4f3c-9f37-7b2db366e2a1/iso-18554-2016

Surface chemical analysis — Electron spectroscopies — Procedures for identifying, estimating and correcting for unintended degradation by X-rays in a material undergoing analysis by X-ray photoelectron spectroscopy

1 Scope

This International Standard provides a simple procedure for identifying, estimating and correcting for unintended degradation in the elemental composition or chemical state of a material which occurs as a result of X-radiation during the time that a specimen material is exposed to the X-rays used in X-ray photoelectron spectroscopy (XPS).

This International Standard does not address comparisons between different types of material nor does it address the mechanisms, depth, or chemical nature of the degradation that occurs. The correction procedure proposed is only valid if the changes are caused by the X-rays and result in less than a 30 % reduction or increase in intensity of a chosen photoelectron peak from the sample material.

2 Terms and definitions

iTeh STANDARD PREVIEW
(standards.iteh.ai)

For the purposes of this document, the following terms and definitions apply.

2.1
region
part of the photo-excited spectrum chosen for detailed acquisition and analysis

ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-415c-9137-7b2db366e2a1/iso-18554-2016

Note 1 to entry: The region may be chosen because it contains a major or minor peak of a given element or to represent the shape or slope of a background within that energy range, e.g. a detail scan.

Note 2 to entry: This usage of region is not to be confused with the area of analysis.

2.2
time zero
time at which the X-rays start to irradiate the sample

3 Symbols and abbreviated terms

Symbol	Meaning
A_Z	deduced linear rate of change of $I_{t,Z}$ as a result of degradation for a given element or state
C	atomic fraction of contamination carbon from the quantification computation
$d_{\mathrm{contamination}}$	thickness of a contamination layer on the surface of the sample
DI	degradation index
E	kinetic energy, in eV, of the detected electrons
FWHM	full width at half maximum (intensity)
$I_{Z,\mathrm{corrected}}$	intensity of a given photoelectron peak after correction for the formation of a layer of contamination
$I_{Z,\mathrm{measured}}$	measured intensity of a given photoelectron peak that is influenced by the presence of a layer of contamination
$I_{0,Z}$	undegraded photoelectron intensity of a given element or state, Z
$I_{f,\mathrm{S}}$	final photoelectron intensity of a given element in the survey spectrum
$I_{i,\mathrm{S}}$	initial photoelectron intensity of a given element in the survey spectrum

© ISO 2016 – All rights reserved

$I_{t,Z}$	intensity of a given element or state measured after a period of X-ray exposure, $t_{m,Z}$
L_c	attenuation length of detected electrons in the contamination layer
PTI	photo threshold index
PVC	poly(vinyl chloride)
θ	angle of emission of the detected electrons from the surface normal
$t_{i,Z}$	elapsed time of exposure to X-rays at the start of data collection for a particular element, Z
$t_{f,Z}$	elapsed time of exposure to X-rays at the termination of data collection for a given element, Z
$t_{m,Z}$	mean time of X-ray exposure for a given element or state, Z
t_0	time at which the sample was first exposed to X-rays
$t_{i,S}$	mean time at which the initial survey scan was acquired
$t_{f,S}$	mean time at which the final survey scan was acquired
XPS	X-ray photoelectron spectroscopy

NOTE $t_{m,Z}$ may be the same for all elements if, for example, the scans for individual elements are acquired in a pseudo-parallel mode, but can be very different for each element if element regions are acquired serially, i.e. in turn, after the previous one has been completed.

4 Sample degradation

Reports of sample degradation during acquisition of a photoelectron spectrum are widespread and affect most, if not all, classes of materials under certain circumstances. A list of materials reported to degrade under XPS analysis is provided for information in Annex A.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

4.1 Causes of degradation

ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/4051777b-19ee-4f3a-9f37-7b2dfa266e2a/iso-18554-2016

Sample degradation in the course of analysis by XPS occurs, mainly, because of bonding changes in the sample caused by the X-ray beam through the direct interaction with the X-rays (characteristic X-rays or bremsstrahlung) or the electrons emitted from un-monochromated sources or the photoelectrons. It will occur when the sample is exposed to the X-ray beam before analysis and in the period between survey or detail scans, as well as in the scans themselves; it does not occur solely during data acquisition. Degradation can occur also through heating, especially from twin anode sources which are close to the sample and emit heat. These anodes operate close to 100 °C and are often as close as 5 mm to the sample stage, covering a large solid angle.

Minor damage can occur from exposure of samples to the vacuum of the instrument and in other cases from exposure to the low-energy secondary electron flux within the spectrometer chamber. The former is outside the scope of this International Standard while damage from secondary electrons is likely to be a concomitant factor of the X-ray flux and does not need to be treated as an independent factor.

Degradation also arises from electron flood guns which may have to be run at high current to neutralize focused monochromated X-ray sources or may be set at an unnecessarily high value by default. Low-energy ions used for charge neutralization, also, can have a deleterious effect. Such devices may be on for some time before analysis starts. Control of some or all of these factors can be helpful in reducing degradation; however, the procedure recommended in this International Standard considers only changes that occur once the sample is exposed to the X-rays (defined as time zero in the procedure described below).[3][4][5][6]

Material will also be removed from the surface during ion-etching; this is intentional but unintended changes in chemical state may result. Ion-beam sputtering is outside the scope of this International Standard but some concepts relating to chemical degradation may be helpful in understanding the phenomenon.

© ISO 2016 – All rights reserved

4.2 Sample degradation

Sample degradation is said to have occurred whenever there is a measurable change in the spectrum of a sample after a period of exposure to the X-ray flux. This change typically arises from a change in the atomic fraction or chemical state of one or more elements, giving rise to a relative shift in peak positions or to a change in intensity of one of more peaks and thus a change in the measured constitution of the sample. A good description of the overall effects of a photon beam has been given by Reference [5].

The change in chemical state can be due to photo-excited reduction of an ion, such as occurs when Cu(ll) is chemically reduced to Cu(l). Sometimes, but not always, this can be accompanied by oxidation of another element in the near-surface region. An example is given in Annex B. The change in composition can arise, particularly in organic compounds, through the breaking of chemical bonds and the subsequent diffusion and escape of low-molecular weight species generated as a result. Some relative rates of degradation are given by Reference [6], e.g. using their degradation index, DI, which is proportional to the parameter, A, defined in this International Standard. Polypropylene has a DI value of 5 and polyethylene has a DI of 10; these are examples of various forms of degradation, including bond breaking, radical formation and cross-linking. Poly(vinyl chloride), which has been used to assess degradation rates has a DI of 25 on this scale. An example of the loss of Cl from a poly(vinyl chloride) blend is described in Annex B.

Although the degradation noticed in the X-ray photoelectron spectrum concerns only the outermost 10 nm, the X-rays penetrate to much greater depths and damage is not confined to the escape depth of photoelectrons. Thus, material lost from the surface layers may be compensated by material diffusing from deeper within the sample. This behaviour can give a dynamic plateau in the degradation of observed composition or chemical state. An illustration is given in Annex B. In the period prior to establishment of the plateau, an approximately linear rate of degradation is normally observed and the procedure recommended in this International Standard applies a correction by means of a linear extrapolation. Near-surface degradation may be particularly important in analysis of monolayer films because of disruption to the bond required for attachment to the substrate.[7][8]

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-4f3c-9f37-7b2d0366e2a1/iso-18554-2016

4.3 Measurements for identifying, and correcting for, degradation

4.3.1 Recognition of degradation

Recognition of degradation is based primarily on a comparison of the first and final scan in the acquisition sequence. For the majority of samples, this is most easily done by comparison of the survey scans taken at the commencement and closure of analysis. Examples of methods by which the scans can be compared are given in Annex B. Since degradation is dependent on the total dose of X-rays, it is necessary to record the time of exposure throughout data acquisition. The following procedure is recommended for a simple identification and correction of the effects of X-ray induced degradation with a minimum of effort rather than a detailed study of that degradation.

4.3.2 The first survey scan

Set up the spectrometer for XPS analysis using your usual method and note the time at which the specimen is first exposed to X-rays. Record this as “time zero”, t_0. Record a survey spectrum (a 0,4 eV step interval is recommended[9]), noting the time at which the acquisition is started and finished. It is recommended that any exposure of the sample to direct X-ray flux, electron irradiation from electron flood guns, low energy ions used for charge neutralization, or heat from X-ray anodes is kept as short as possible prior to acquisition of this scan. The mean exposure time for the first survey scan, $t_{i,S}$, is the difference between the average of the start and finish times of the initial survey scan and time zero, t_0.

© ISO 2016 – All rights reserved

4.3.3 The detail scans

Record relevant detail scan spectra using your usual operating conditions, noting the times at which the spectra are started and finished.

a) Procedure for acquisitions recorded individually in a serial mode.

If each detail scan region is recorded individually (serially), use the mean time derived from the start, $t_{i,Z}$, and finish times $t_{f,Z}$, relative to time zero, for the acquisition of each individual element or component peak. The mean exposure time for each detail scan, $t_{m,Z}$, is the difference between the average of the start and finish times of the given acquisition and time zero, t_0.

b) Procedure for acquisitions recorded in an interlaced mode (pseudo parallel).

If the detail scans are derived in an interlaced mode (pseudo-parallel), use the mean value of start time of the series, relative to t_0, and the finish of the series, relative to t_0, as $t_{m,Z}$, the mean exposure time for the measurement. Pseudo-parallel acquisition is the recommended mode of use since the acquisition of each chosen region of the spectrum will have been made for the same exposure time. Record this set of intensities and associated mean exposure time to X-rays.

In the event that a signal-to-noise criterion is used to terminate acquisition of individual elements or peaks in a parallel scan mode, then note shall be taken of the time at which the scan is terminated and the exposure time calculated from the start and finish times for that region of the spectrum.

4.3.4 The final survey scan

iTeh STANDARD PREVIEW

Repeat the survey spectrum at the end of the acquisition sequence using the same instrumental settings as used for the first survey scan at 4.3.2. Note the time for the start and finish of this acquisition. The mean exposure time for the final survey scan, $t_{f,S}$, is the difference between the average of the start and finish times of the final survey scan and time zero.

(standards.iteh.ai)
ISO 18554:2016
https://standards.iteh.ai/catalog/standards/sist/d951777d-18ee-4f3c-9f37-7b2db306e2a7/iso-18554-2016

4.3.5 Inverting the order of acquisition for unstable compounds

For organic and other unstable compounds (see Annex A), it may be advantageous to substitute a detail scan through the carbon 1s region, or other detail region as appropriate, for the first survey scan at 4.3.2 in the above procedure. If a survey scan is required, record this detail scan first. Use a detail scan through the same region, instead of a survey scan, to terminate the acquisition as 4.3.4.

4.3.6 Check for degradation

To check for degradation, compare the first and final survey scans or, for organic samples the first and last carbon 1s detail scans, and observe any changes. For insulators, small changes in the charging shifts can complicate this comparison and realignment against a peak common to both spectra can be necessary. The spectra may be compared using quantification, subtraction of spectra, division of spectra channel by channel, or by visual observation. Examples of the results of such procedures are given in Annex B.

4.3.7 Deduce the undegraded intensity

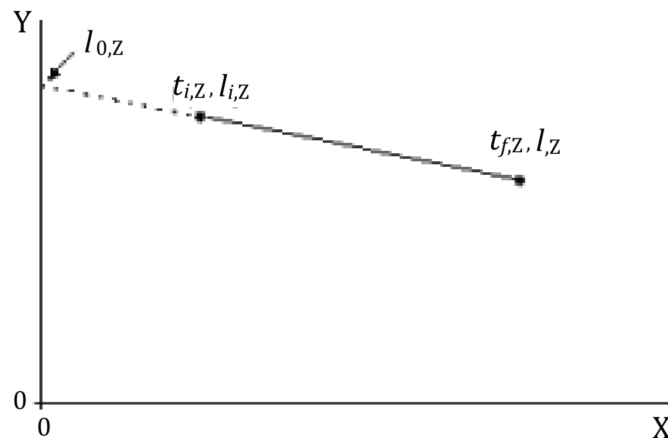
To deduce the undegraded intensity $I_{0,Z}$ for a peak that is degrading and exhibits intensity $I_{t,Z}$ at time of exposure $t_{m,Z}$, the following linear relationship given in Formula (1) is assumed for the rate of degradation:

$$I_{t,Z} = I_{0,Z} - A_Z t_{m,Z} \tag{1}$$

where A_Z is a constant for a given element and peak position that depends on the instrument, its settings and the sample.

 © ISO 2016 – All rights reserved

This relationship is shown in Figure 1. Be aware of the fact that during the necessary set-up time for the survey scan, the sample might already have degraded: thus, all times are those measured in real time from the onset of X-ray exposure (t_0) and are not the experimental acquisition times for a particular scan. This degradation is assumed to be linear with exposure time and thus, the mean exposure time at which the peak was acquired, $t_{m,Z}$, may be used in Formula (1).



Key

X exposure time, t

Y intensity

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Figure 1 — Schematic diagram illustrating a linear relationship between initial and final intensities, $I_{i,Z}$ and $I_{f,Z}$, for the corresponding average exposure times, $t_{i,Z}$ and $t_{f,Z}$, and extrapolation to time zero to give $I_{0,Z}$

ISO 18554:2016
7b2db366e2a1/iso-18554-2016

The undegraded intensity, $I_{0,Z}$, for a given element, Z, is thus given in Formula (2):

$$I_{0,Z} = \left(I_{i,Z} t_{f,Z} - I_{f,Z} t_{i,Z} \right) / \left(t_{f,Z} - t_{i,Z} \right) \quad (2)$$

where $t_{i,Z}$ and $t_{f,Z}$ are the initial and final mean exposure times at which the initial and final intensities, $I_{i,Z}$ and $I_{f,Z}$ were recorded.

These values may be based on individual regions of a survey scan (or on values from individual detail scans, obtained under identical conditions and at recorded times, for the elements concerned). This relation is valid for small changes in intensity resulting from degradation. Ensure that $I_{f,Z}/I_{i,Z} > 0,7$ or $I_{f,Z}/I_{i,Z} < 1,3$ for any intensity that is to be corrected.

Each peak intensity that is to be used in determining a composition should be corrected using a value of $I_{0,Z}$ determined for that peak. The corrected composition is then calculated in the usual manner using the individual values for each element. Note that in a multi-element compound or mixture, degradation can affect different elements in different ways. Thus, A_Z may take positive or negative values. It may be more convenient to use the compositions, expressed in atomic% instead of intensities in order to check for degradation. In this case, the procedure above may be followed, correcting the values contributing to the composition and finally renormalizing to 100 atomic%.

Detail scan spectra that contain two or more chemical states may be examined for degradation using spectra obtained at differing, known, times. The peak ratio or the peak subtraction method may be used. If there is evidence of change, then degradation involving a change in chemical state will have taken place. This can occur even if the overall composition of the sample, determined from comparisons of the survey scans in 4.3.2 and 4.3.4, show no change. To correct for a change in the chemical state, the intensities of the individual component peaks should be determined by peak fitting for each time of acquisition and the zero-time intensities for each chemical state calculated using Formula (2).

© ISO 2016 – All rights reserved