INTERNATIONAL STANDARD

ISO 22581

First edition
2021-03

Surface chemical analysis — Near real-time information from the X-ray photoelectron spectroscopy survey scan — Rules for identification of, and correction for, surface contamination by carbon-containing compounds

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Analyse chimique des surfaces — Informations en temps quasi réel issues du balayage d'ensemble par spectroscopie photoélectronique à rayonnement X (XPS) — Règles portant sur l'identification et la correction d'une contamination des surfaces par des composés contenant du carbone

ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/01d6566e-1ac0-4659-a52a-59c79c045c6d/iso-22581-2021

Reference number
ISO 22581:2021(E)

© ISO 2021

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59c79c045c6d/iso-22581-2021

COPYRIGHT PROTECTED DOCUMENT

© ISO 2021

All rights reserved. Unless otherwise specified, or required in the context of its implementation, 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
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword ..... **iv**
Introduction ..... **v**
1 Scope **1**
2 Normative references **1**
3 Terms and definitions **1**
4 Symbols and abbreviated terms **2**
5 Sample contamination **2**
5.1 General 2
5.2 Causes of contamination 2
5.3 Recognition of contamination 3
5.3.1 Construction of rules based on sample description 3
5.3.2 Rules for use of the sample history 4
5.3.3 Rules for use of peak positions 4
5.3.4 Rule to establish carbon type 6
5.3.5 Rules identifying C1s as arising from absorbed material in the form of a thin film 7
5.3.6 Achievement of the goal 9
6 Estimation of film thickness and correction for its impact **9**
6.1 Film thickness 9
6.2 Correction of substrate composition 10
Annex A (informative) **Flow diagrams for operation of rules** **11**
Bibliography **16**

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59c79c045c6d/iso-22581-2021

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.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 3, *Data management and treatment*.

ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59c79e014d6d/iso-22581-2021

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.

© ISO 2021 – 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- 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 analysis of materials' surfaces. The increasingly wide use of the technique makes the development of rule sets, that enable accurate information retrieval, highly important and this document helps to meet this need.

In many cases the surface for which a composition is desired will have accreted a film of contamination, frequently organic in nature and arising from adsorption of molecules from the atmosphere, from the exposure to a working or test environment, or from the spectrometer itself. This film attenuates the different regions of the spectrum to a different extent, depending on the kinetic energy of the electron emitted in that region. Thus correction and removal of this influence is necessary for the desired surface composition of the substrate to be achieved. The procedure to be described enables recognition of the presence of carbon-containing contamination, an estimate of its thickness, and the removal of its influence on the measured surface composition. It is thus an integral part of data reduction in quantitative evaluation of the XPS Survey Scan. This could be automated within a data system and would be an essential first step in provision of a means for automatic retrieval of information from the survey scan for a number of technologies dependent on surface analysis.

All procedures described are intended to be based only on an XPS survey scan obtained in the fashion recommended in the conclusions of the IUVSTA Workshops 22[9] and 34[10]: they can be carried out in a manner which does not require intervention by an expert spectroscopist and could be adopted in an automated data system.

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59c79c045c6d/iso-22581-2021

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59c79c045c6d/iso-22581-2021

Surface chemical analysis — Near real-time information from the X-ray photoelectron spectroscopy survey scan — Rules for identification of, and correction for, surface contamination by carbon-containing compounds

1 Scope

This document is provided to assist in the surface analysis of thin films on materials which are not thought to contain carbon compounds as intended components but for which a C1s peak is observed in the survey spectrum. The films can be those generated on metals and alloys by aerobic or electrochemical oxidation or be those deposited on inert substrates. The procedure described is not suitable for discontinuous deposits of particles on a substrate. With this exception, a simple procedure is provided for identifying the C1s signal from carbon-containing surface contamination. When the C1s peak is identified as arising from an adventitious over-layer the composition derived from the survey spectrum can be corrected for its influence. Recommended procedures are provided in the form of simple Rules structured in the 'If – Then' format with the intention that the information they embody might be utilised by automated procedures in data-systems. The rules provided utilize only information retrieved from the XPS survey scan.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

2 Normative references

There are no normative references in this document.

ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59c79c045c6d/iso-22581-2021

3 Terms and definitions

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

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 http://www.electropedia.org/

3.1
region
part of the fully accessible photo-excited spectrum chosen for acquisition in a detail, i.e. 'narrow', scan

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.

3.2
survey scan
scan or series of scans across the major part of the photo-electron spectrum excited by a given X-ray source

3.3
goal
achievement of an objective which is part of the process of the interpretation of a spectrum

Note 1 to entry: For example, the completion of a quantitative analysis can be thought of as the achievement of a goal.

© ISO 2021 – All rights reserved

4 Symbols and abbreviated terms

a — maximum value (cps) above a line drawn at constant intensity from a point on the linear region of the energy-loss background following the C1s peak

b — interval (eV) between the point on the linear background chosen as a reference in the measurement of ‘a’ and the position of the value (eV) at which ‘a’ is measured. It is anticipated that the interval will be of the order of 30eV

$C_{contamination}$ — atomic fraction of carbon in the contamination layer

$d_{contamination}$ — thickness of the contamination layer

D parameter — separation, in eV, of the maximum and deepest minimum peaks in the differential of the C KVV Auger peak

E — electron kinetic energy in eV of the peak to be corrected for overlayer contamination

$I_{z,measured}$ — measured intensity of the peak corresponding to element Z

$I_{z,corrected}$ — corrected intensity of the peak corresponding to element Z

IUVSTA — International Union for Vacuum Science, Technique and Applications

k — Shirley scattering factor

iTeh STANDARD PREVIEW
(standards.iteh.ai)

L_C — attenuation length of C1s electrons in the contamination layer.

L_z — attenuation length of electrons in the contamination layer corresponding to element Z

θ — angle of emission of the detected electrons with respect to the surface normal

ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59cf79c045c6d/iso-22581-2021

QUASES — Quantitative Analysis of Surface Electron Spectra

SESSA — Simulation of Electron Spectra for Surface Analysis

XPS — X-ray photoelectron spectroscopy

5 Sample contamination

5.1 General

The C1s peak is frequently observed in the XP spectrum of material samples that are not thought to include carbon in their composition. In a small number of cases, the peak is an important indicator of an unexpected surface composition, e.g. the surface film on Aluminium-Lithium alloys that have been exposed to air will often include lithium carbonate. However, in most cases, the C1s peak is an indicator of the presence of an adsorbed film of organic compounds, normally referred to as a contamination layer. Contamination may consist of an aliphatic chain having a polar end group which strongly adsorbs to many surfaces. The film so formed can strongly attenuate the intended signal arising from the substrate under investigation. Because of this, some analysts are tempted to remove the film by brief use of a conventional monatomic ion gun. This procedure will greatly enhance the spectrum intensity but only at the expense of serious and irrecoverable changes to the surface chemistry.

5.2 Causes of contamination

The sources of such contamination are widespread: surfactant molecules will be picked up from the meniscus film of aqueous media during the course of electrochemical or other test procedures; the air itself contains a wide variety of easily and strongly adsorbed molecules in the form of softening agents used in laundry activities, personal care products, or petrochemical compounds released from transport

 © ISO 2021 – All rights reserved

vehicles; or films can be generated from the packaging used to convey samples to the laboratory (especially when plasticizing agents have been used in manufacture of the 'plastic' bags often used for transport). Adsorption can occur within the spectrometer from contamination of the vacuum by vapour from the diffusion or oil pumps or from vapours released from prior examination of other samples, or even in cases of technological samples, from the analysed sample itself. Adsorption of contaminants is influenced by the hydrophobic/hydrophilic character of the surface, or in aqueous media, by the electropotential of the surface and so differing materials may have differing susceptibilities to the formation of a contaminant layer.

It should be noted that the presence and composition of a contaminating surface film can be obtained using ARXPS (angle-resolved XPS) but this degree of detail may not be available, either because of a lack of suitable equipment or because of a constraint on the time available for such a study.

5.3 Recognition of contamination

The correct identification of a given C1s peaks as being derived from and indicative of the presence of a thin film of adsorbed organic compounds is important. The ubiquitous character of a contamination film has given rise to the advice that its C1s peak can be used as a reference peak (nominally 285 eV) for correction of any electrostatic charging (see ISO 19318); it is important that it is not confused with an actual component of the material surface; and it is important that it is recognised as having the characteristics of a surface film since it is only in this case that the whole spectrum can be corrected for the consequential attenuation. Recognition is based on a mix of probabilities that a contamination is present; that it is not anticipated to be present in the material sample; and that it has the characteristics of a surface film. The means to assess that these attributes are associated with the C1s peak are outlined in the following paragraphs. Each single identifier of an attribute is given in Table 1 in the form of 'If – Then' statements which can be utilised for computer-based, near real-time correction of the XP spectrum for the effect of a contamination film.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

In published work[11],[12],[13] it was shown that the identification and characterisation of a contamination layer is reached by setting a goal, defined by an object, 'Carbon_Contamination', having the value 'Yes'. The achievement of this goal marks the end of a stage in the analysis and enables further interpretation of the spectrum. It should be noted that analysts who are experts in reviewing the XPS survey spectrum will recognise the C1s peak on many materials for what it is – contamination. For them, this document will give some guidance in answering the client who asks 'how do you know'. For non-experts it will give some assurance that they may safely assume the carbon peak to be generated by contamination but for those designing machine-assisted interpretation of a survey spectrum the analysis set out here is essential. A useful discussion of the suggested methodology, and possible pitfalls have been given by Vegh[14] and an example of its actual use in near real-time surface analysis has been given by Lea et al[15].

ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59c79c045c6d/iso-22581-2021

To reach the goal with 100 % certainty, it shall be established:

— that a photoelectron peak for carbon is present in the spectrum;

— that it is not expected for carbon to be part of the sample material, i.e. it is adventitious in character;

— that it has certain characteristics of contamination carbon;

— that it has an impact on the spectrum consistent with it being present in a thin surface layer;

— that its presence is part of a reaction layer formed by interaction with the environment.

5.3.1 Construction of rules based on sample description

The methodology outlined in this document is intended for use in real, or near real-time interpretation of the survey scan in XPS analysis of a surface. It is further assumed that the survey scan has been acquired by the method recommended by IUVSTA Workshop 34, i.e. over a range set to include the C KVV Auger peak and with a step size of ≤0,4 eV[9].

Once the survey scan is completed, the first Rule comes into operation, but this does require that a peak in the expected location of the C1s can be identified. If the C1s peak is to be found automatically, then

© ISO 2021 – All rights reserved

any specimen charging shall be small or otherwise known so that its effect on the apparent energy of the peak can be compensated. In the event that there are no obvious conflicts with the binding energy of the C1s peak, then the value of an object, Carbon_1s, can be given the value Yes, or default to No, according to whether there is a peak at a binding energy of 285 eV ± 0,4 eV. The rules used in this document are given in Table 1 and are discussed individually in the following paragraphs.

If Carbon_1s is Yes and Carbon_Sample is No then Carbon_Contamination_1 is Yes 1).

Rule 1 merely expresses what is obvious, that if C1s is identified in the spectrum then the element carbon will contribute to the overall analysis of the material, even if this is not expected by the sample provider. There is thus a possibility that a contamination film is present on the surface.

This rule is also used to stop the automated procedure, i.e. if carbon is expected to be present in the sample then it will not be possible to establish whether there is a contamination layer without interactive examination of the spectra by the analyst.

An important indicator of the presence of a contamination film comes from prior knowledge of the expected composition and the history of the sample. This information will be supplied by the owner of the material to be analysed and is discussed in more detail in the following paragraph. However, this knowledge is encapsulated in Rule 2:

If Sample is Aqueous_Exposed or Air_Exposed or Spectrometer_Unbaked then Carbon_Contamination_2 is Yes (2). These two Rules illustrate the use of Objects, such as Carbon_Sample, or Carbon_Contamination that can take values of Yes, or left at the default value of No. Carbon_Contamination is an example of an Object that can be given values from the operation of two or more rules. To record these values a ‘counter’, N, has been concatenated to the Object, i.e. Carbon_Contamination_N so as to be able to group these values, enable consensus to be reached, and set the value of the un-concatenated Object, Carbon_Contamination to Yes or defaulted to No. Objects typically take the values Yes or No, according to whether or not they are satisfied by the operation of a Rule or Rules. The Objects used in this document are defined in Table 2.

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-95c79c045c6d/iso-22581-2021

5.3.2 Rules for use of the sample history

The most likely source of carbon contamination arises from initial collection of the sample, its subsequent handling and the conditions of transport. Little can be done to ameliorate contamination arising during collection; for example, electrodes are likely to pick up contamination as they are removed through the meniscus layer of the electrolyte and many samples of technological interest will suffer from similar problems during collection. Transport of the sample in plastic bags is also endemic, and clear instructions need to be issued to clients of a user laboratory. Thus the history of the sample can help in establishing an opinion that the carbon observed in the spectrum is a contamination film; thus building on knowledge that contamination will arise from exposure to the environment. In one-to-one discussions between analyst and client, the history can be recorded but such 'surgery' type interviews are time consuming and expensive. Thus, a succinct means of establishing relevant history is necessary for an automatic appraisal of the survey scan. An ideal description of the sample might include the question: 'has the sample been exposed to unfiltered air or other gaseous atmosphere or to an aqueous environment? A yes or no answer is all that is required to set a value for Carbon_contamination_2. This will be recorded as one piece of evidence by Rule 2, given in Table 1. A suggested route giving a sequence by which the following rules might be applied is given in Annex A.

5.3.3 Rules for use of peak positions

Knowledge of the sample type and its history suggests that information might be gained from regions other than that of the C1s peak. If the O1s peak is likely to be present in the acquired spectrum, then its position will show less variation with composition than that of C1s peak[9]. Thus the interval between the O1s peak and that of the C1s peak can be used to suggest that the carbon is in the form of aliphatic carbon and thus has the characteristics of contamination. If a thin film, such as that on a metallic surface sample is known to have been exposed to air, then it is likely that an oxide is present, or alternatively, exposure to aqueous environments is likely to have generated a hydroxide component. The carbon 1s – oxygen 1s peak separation can be determined automatically and is therefore useful in automatic

 © ISO 2021 – All rights reserved

retrieval of information: a value of 245 eV ± 0,4 eV corresponds to the separation of contamination carbon and the oxide peak for many metals; hydroxides will give a value of 246,5 eV ± 0,4 eV and the oxygen of organic compounds or bound water gives a value of about 247,5 eV ± 0,4 eV. Values outside these ranges should flag a query and may indicate that the C1s is primarily associated with a carbonate, a fluorocarbon or even a carbide. Rule 3 embodies the means for establishing whether, or not, this identifier is satisfied. If 'Yes' then this represents an independent means as identifying a C1s peak as likely to have arisen from contamination. An illustration of the required measurement is given in Figure 1.

Table 1 — Rules to indicate the presence of surface contamination and to correct for its influence

Rule Number	Rule
Note	All values of Carbon_Contamination_N are set to the default value of No
1	If Carbon_Sample is No and Carbon_1s is Yes then Carbon_Contamination_1 is Yes
2	If Sample is Aqueous_Exposed or Air_Exposed or Spectrometer_Unbaked then Carbon_Contamination_2 is Yes
3	If Oxygen_1s is Yes and Oxygen_1s-Carbon_1s energy separation >244,6 eV and <247, eV then Carbon_Contamination_3 is Yes
4	If Carbon is_1s Yes then Carbon_KVV_KE is 263,6eV
5	If Carbon_D >15eV and Carbon_D<20eV then Carbon_Contamination_4 is Yes
6	If Carbon_Shirley_k is >0,01 then Carbon_Contamination_5 is Yes
7	If Carbon_Background_Slope >= 0 then Carbon_Contamination_6 is Yes

iTeh STANDARD PREVIEW
(standards.iteh.ai)
ISO 22581:2021
https://standards.iteh.ai/catalog/standards/sist/0fd6566e-1ac0-4659-a52a-59c79c045e6d/iso-22581-2021

Table 2 — Objects used in the rules

Object	**Possible values** (For objects with a value of Yes or No, the starting default value is No)	
Carbon_Sample	Yes/No	Sample Description
Carbon_1s	Yes/No	Survey scan
Carbon_Contamination_1	Yes/No	Rule 1
Sample	Aqueous_Exposed; Air_Exposed;	Sample description
Carbon_Contamination_2	Yes/No	Rule 2
Carbon_BE	C1s BE in eV	Survey spectrum
Carbon_Contamination_3	Yes/No	According to Rule 3
Carbon_KVV_KE	263,6 eV ± 0,4eV in kinetic energy	Rule 4
Carbon_D	Value in eV	Peak maximum – Peak Minimum in differentiated peak at Carbon_KVV_KE region of survey scan
Carbon_Contamination_4	Yes/No	Rule 5
Carbon_Shirley_k	Value, Fraction of Peak area	Integration constant for Integral of C1s peak in survey scan
Carbon_Contamination_5	Yes/No	Rule 6
Carbon_Background_Slope	Value, counts/kinetic energy	Linear approximation to slope of background on the high BE side C1s

© ISO 2021 – All rights reserved