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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

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National foreword

This British Standard is the UK implementation of ISO 18554:2016.

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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

Reference number
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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
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Foreword

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

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.

INTERNATIONAL STANDARD **ISO 18554:2016(E)**

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

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

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

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
$d_{\text{contamination}}$	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)
$I_{Z,\text{corrected}}$	intensity of a given photoelectron peak after correction for the formation of a layer of contamination
$I_{Z,\text{measured}}$	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

$I_{t,Z}$	intensity of a given element or state measured after a period of X-ray exposure, $t_{\mathrm{m},Z}$
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
$t_{\mathrm{m},Z}$	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 $t_{\mathrm{m},Z}$ 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.

4.1 Causes of degradation

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.

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]

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.

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, $t_{\mathrm{m},Z}$, 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 $t_{\mathrm{m},Z}$, 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

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.

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.

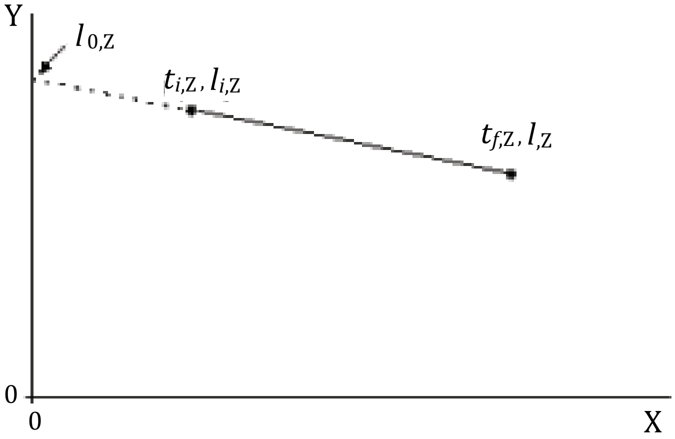
4.3.7 Deduce the undegraded intensity

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

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

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

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, $t_{\mathrm{m},Z}$, may be used in Formula (1).



Key

X exposure time, t

Y intensity

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 $I_{0,Z}$

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

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

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).

Organic polymers may give evidence of degradation by changes of parameters characteristic of the polymer and measurable by XPS. The parameters used by Reference [7] are atomic ratios, the area ratio of C 1s shake-up peaks to the main peak for unsaturated hydrocarbons or the FWHM of the C 1s peak for saturated hydrocarbons. These parameters were used in establishing degradation measures for their Scienta ESCA300 instrument and their degradation index, DI, is proportional to the parameter A_Z defined here. In a VAMAS inter-laboratory comparison (Project A5) on the degradation of polymers, the relationship between the degradation rate and X-ray source flux in XPS was investigated by Reference [10]. An example of the use of the Beamson and Briggs Degradation Index can be found in Reference [11] together with a suggested method for recording the X-ray flux.

NOTE Measured over longer periods, it will be found that the degradation is not linear with time and might follow, for instance, an exponential decay. Examples are given in Annex B. The data at longer times can provide useful information about the degradation process but do not improve the accuracy of the evaluation of $I_{0,Z}$ compared with Formula (2).

A_Z values for the same material will differ with the instrument settings and might differ from laboratory to laboratory. However, the relative values of A_Z for different materials should be approximately constant. Data from Reference [6] should be proportional to A_Z values.

4.4 Assessing the likelihood of degradation

4.4.1 Determining the value of A_Z

The parameter A_Z in Formula (1) can be used to compare instruments for a given sample, or to compare samples for a given instrument, or to modify settings to minimize degradation, as given in Formula (3):

$$A_Z = \left(I_{f,Z} - I_{i,Z}\right) / \left(t_{f,Z} - t_{i,Z}\right) \tag{3}$$

For example, a cast layer deposited from PVC dissolved in tetrahydrofuran may be used for comparison purposes in setting up an instrument to minimize degradation but it should be noted that all PVC products behave differently. A comparison of data from two laboratories is given in Annex B.

4.5 Reporting degradation

When degradation is observed, it shall be reported. The following formats are recommended.

- The sample showed evidence of degradation during analysis in the form of a decrease in the intensity of element P and an increase of intensity for element Q by x% and y%, respectively, over the period of analysis. The reported compositions are those calculated using intensities corrected using linear extrapolations to the start of X-ray exposure as described in Annex B. The maximum values for x% and y%, suitable for linear extrapolation, should not exceed 30 %.
- The sample showed evidence of degradation during analysis in the form of a decrease in the relative abundance of chemical state (Xn) by x% over the period of analysis. The reported compositions are those corrected using linear extrapolations to the start of X-ray exposure as described in Annex B.

4.6 Suggested procedures for minimising degradation

When degradation is suspected, an attempt should be made to use an adjacent region of the sample surface to set up the acquisition parameters, such as X-ray intensity, detector settings, and sample angle or height. Once these parameters are established, the sample can be moved to a new, unexposed part of the sample and the acquisition started; use the time at which the sample was moved to this new position as time zero. Note that with unmonochromated sources, regions of the sample holder within 15 mm can be exposed to heat, electrons, and X-rays from the source.

If acquisition needs to be suspended for any period of time, it can be advantageous to switch off the X-ray source. Note the time at this point in the acquisition sequence and again note the time when the flux is re-established. Only the cumulative times when the sample is exposed to X-rays are used in this

International Standard. The use of flood guns can cause damage if not turned off when the X-ray flux is interrupted and hence, these should be switched off whenever possible.

Degradation may be reduced by use of a monochromated source because of the removal of the Bremsstrahlung component of the radiation[12][13] but any gain may be offset by the need to use a flood gun to control charging. In interlaboratory studies, the degradation rates were found to be generally lower for monochromated systems.[4][5] However, the VAMAS inter-laboratory comparison covering 40 instruments[10] revealed that independent of the use of a monochromator, the degradation depends on the individual instrument used. The observed degradation may also be reduced by using more normal emission where the layer from which materials are lost may comprise a smaller fraction of the layer analysed.[5]

4.7 Influence of contamination

4.7.1 Contamination formation during spectrum acquisition

A layer of surface contamination might form during acquisition if the spectrometer has not been baked after air exposure or if porous samples have been analysed, or if the sample itself is a source of organic vapour. In such cases, an increase in the C 1s intensity can be observed during the period of analysis. Increasing thickness of this layer will cause the signal intensities from peaks, arising from elements in the substrate, to decrease in a manner that might be confused with degradation. It should be noted, however, that attenuation arising from a contaminant layer increases from high to low kinetic energies across the width of the spectrum. These changes are not characteristic of X-ray degradation.

As an example, a level of contamination giving a value of 20 atomic% for the C 1s peak is equivalent to a layer of 0,55 nm in thickness (assuming that the usual RSF values are used to quantify an otherwise isotropic layer). Such a layer will attenuate the peak intensity of Fe2p by 4 % and Ni2p by 8 %. A means for correction for the influence of contamination is given in Annex C.

4.7.2 Reporting contamination

When a correction for contamination is applied, it shall be reported. The following formats are recommended.

- A contamination layer was present on the surface (or was formed on the surface during analysis) and attenuated the signals from the underlying material that was the subject of analysis. The thickness of the underlying material has been estimated on the assumption that contamination was mainly in the form of an adsorbed layer of organic molecules.
- The estimated thickness of contamination is given in this report together with the composition determined after the influence of that contamination has been removed.

Annex A
(informative)

Materials reported to degrade during analysis

AgCl

Carbon fibre[13]

Catalysts (e.g. Pt/Al_2O_3)

Chromium (VI) salts (e.g. CrO_3, K_2CrO_4)

Copper (II) salts (e.g. CuO, $CuBr_2$, $CuCl_2$, CuF_2, $CuSO_4$, $CuCO_3$)[1],[4]

Iron salts [e.g. Fe (II) cyanide compounds, Fe (III) cyanide compounds]

Gold oxide[2]

$NaClO_4$, $NaClO_3$[14]

Nitrates

Nitrocellulose[15]-[18]

Organic polymers and materials[15]-[27]

Organometallics

Oxylates[28]

Paper

Platinum oxide[2]

Poly(methyl methacrylate) (PMMA)[25]

Poly(ethylene terephthalate) (PET)[26]

Poly(tetra-fluoro ethylene) (PTFE)[28]

Poly(vinyl chloride) (PVC)[10],[24]

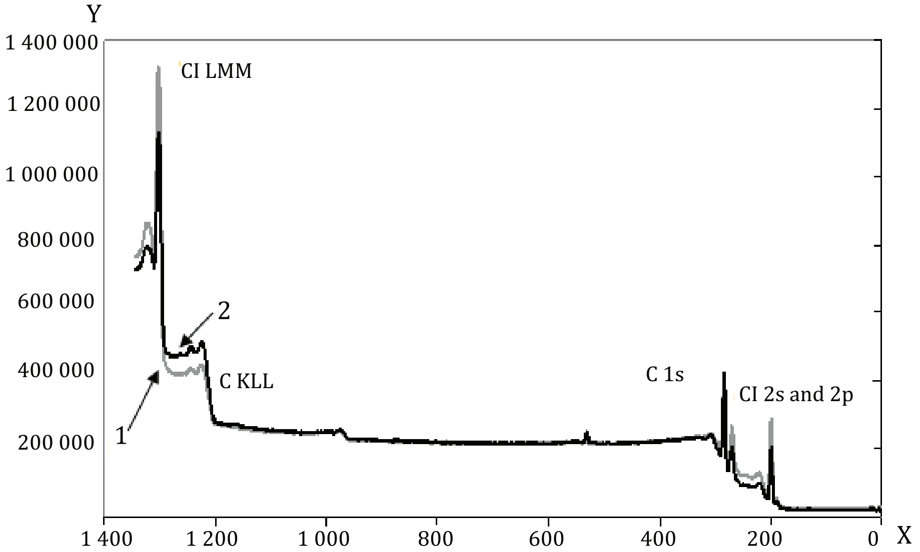
Vanadium and Manganese salts

Annex B
(informative)

Examples of degradation

B.1 Recognizing degradation

Degradation is most readily recognized by comparison of two scans that have had different periods of exposure to the X-rays or other source of exciting radiation. When degradation is suspected to be occurring during acquisition, the initial survey scan should be compared with a final survey scan made before ceasing acquisition. The differences may appear quite slight, as shown in Figure B.1. If degradation has taken the form of the loss of one or more elements, this can be detected by a change in an elemental composition, obtained using peak windows within the survey scan.



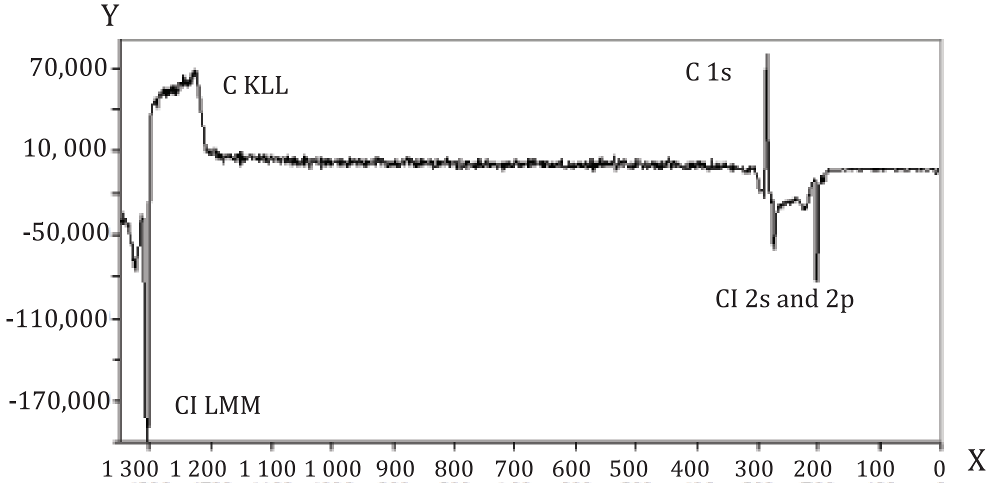
Key

1 initial
2 final
X binding energy (eV)
Y intensity (counts)

NOTE The final scan was taken after 70 min exposure to AlKα un-monochromatized X-rays (data courtesy of Surface Analysis Laboratory, University of Surrey).

Figure B.1 — Survey scans for PVC dissolved in tetrahydrofuran and deposited as a film on aluminium

If quantitative analyses are not required, it may be more convenient to subtract the initial spectrum from the final spectrum or to determine the ratio of the final spectrum to the initial spectrum at each energy channel. In the event of element loss, in the latter approach, a downward pointing peak will be obtained in the appropriate region. Examples for PVC are given in Figure B.2 and Figure B.3. In some cases, the build-up of contamination will give the appearance of degradation and, in this case, the peaks for all elements, with the exception of carbon, will be negative. Both Figure B.2 and Figure B.3 enable the reduction in Cl, and a concomitant increase in one of the C 1s components, to be recognized. The ratio plot has the benefit of showing directly the fractional changes in intensity, matching the requirement that the linear correction will give a poor estimate of the corrected intensity, $I_{0,Z}$, if the change in any intensity exceeds 30 %.



Key

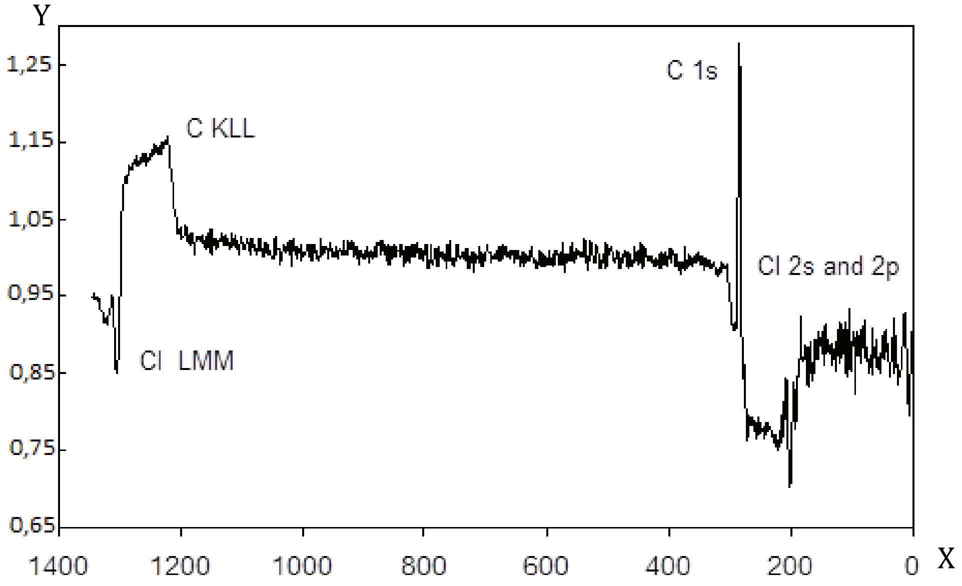
X binding energy (eV)

Y counts (final - initial)

NOTE 1 Downward pointing peaks are those that have lost intensity.

NOTE 2 Data for PVC as in Figure B.1.

Figure B.2 — Result of spectrum subtraction



Key

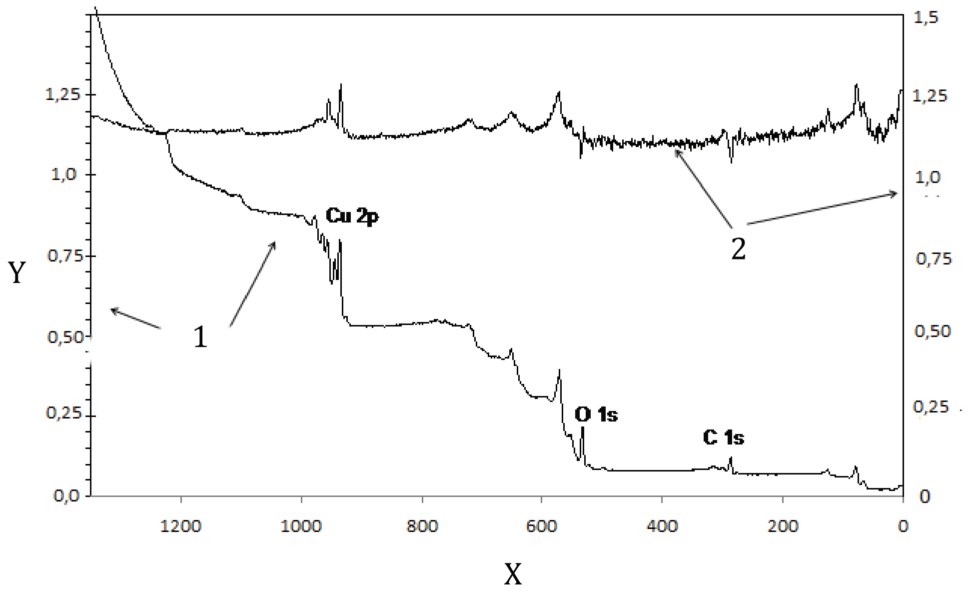
X binding energy (eV)

Y spectrum ratio (final - initial)

NOTE 1 Downward pointing peaks are those that have decreased in intensity during X-ray exposure.

NOTE 2 Data for PVC as in Figure B.1.

Figure B.3 — Ratio plot



Key

1	initial survey scan
2	ratio, final/initial
X	binding energy (eV)
Y	counts × 10^{-6}

NOTE Data courtesy of Surface Analysis Laboratory, University of Surrey.

Figure B.4 — Example of change in chemical state: Ratio plot for “as received” copper sample (right scale) and initial spectrum (left scale)

Figure B.4 illustrates the degree of complexity that might arise as a result of degradation. During analysis of the “as received” surface of a copper foil, Cu(II) satellites were clearly apparent in the initial survey scan. These diminished with time as the reduction of Cu(II) to Cu(I) took place under the influence of the X-ray beam. The ratio of the survey scans shows that this reduction is accompanied by a reduction (downward pointing peaks) in both the O 1s and the C 1s peaks. The overall intensity of the survey scan increased indicating that the contamination layer has been partially eliminated by the oxidation of the organic molecules that it contained. In the course of these changes, the Cu(I) 2p peaks have been enhanced in intensity (upward pointing peaks).

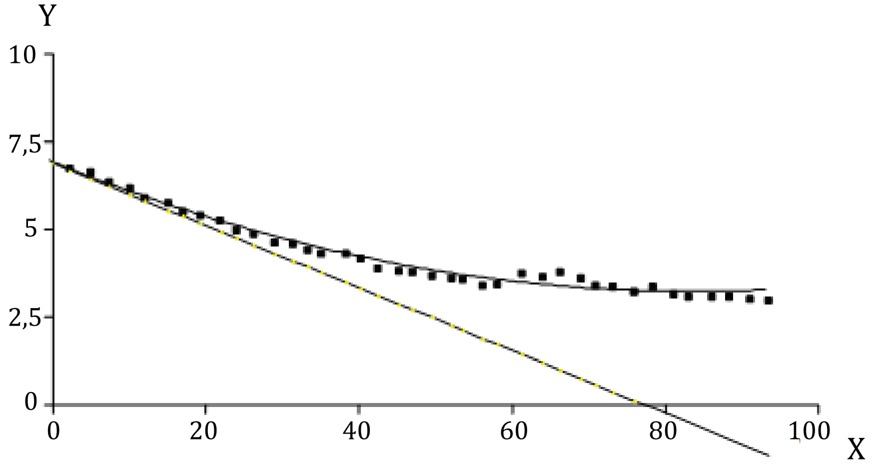
B.2 Correcting for degradation

The influence of degradation can be corrected in quantification by extrapolation of all peak intensities to time zero.

The data set for degradation of a commercial PVC blend is shown in Figure B.5. The decrease in the Cl atomic fraction with time can be fitted to a quadratic polynomial, giving an intercept of 6,89 atomic% for the value after zero exposure time. The Cl atomic fraction measured after the first survey scan was 6,68 atomic%. Generally, such an extensive data set would not be available and with fewer data, a linear extrapolation can be satisfactory. The straight line, as a tangent to the quadratic curve at exposure time zero, is shown on Figure B.5. The straight line extrapolation obtained using the first and ninth points (an interval that might correspond to a typical analysis) are given in Figure B.6. These results show that a linear extrapolation is satisfactory if the atomic fraction of the measured element has not fallen below 70 % of the earliest measurement. A degradation rate corresponding to the decrease in atomic fraction for a given element over a certain time can be expressed as atomic%/min and may be obtained from the slope of the linear fit.

B.3 Assessing and comparing instruments and settings

References [8] and [29] describe an index of degradation based on the time in minutes for a reduction of signal by 10 %. They call this the photo threshold index (PTI). The PTI is inversely proportional to the A_Z values described earlier and small PTI values indicate a high degradability. Their data for PVC are shown in Figure B.7. The square marker is their interpolated value for a 10 % reduction in initial measured signal. The PTI is 80 min, based on this point. The straight-line extrapolation based on this index gives a zero exposure time composition of 17,03 % whereas the quadratic gives 17,44 %. The straight line corresponding to the data not exceeding a 30 % reduction gives a similar intercept to that of the PTI. The PTI value for the data given in Figure B.5 is 10, indicating that the PVC blend used for the data in Figure B.5 was more easily damaged (or that the condition under which its spectrum was acquired was more damaging than that for the data in Figure B.7).



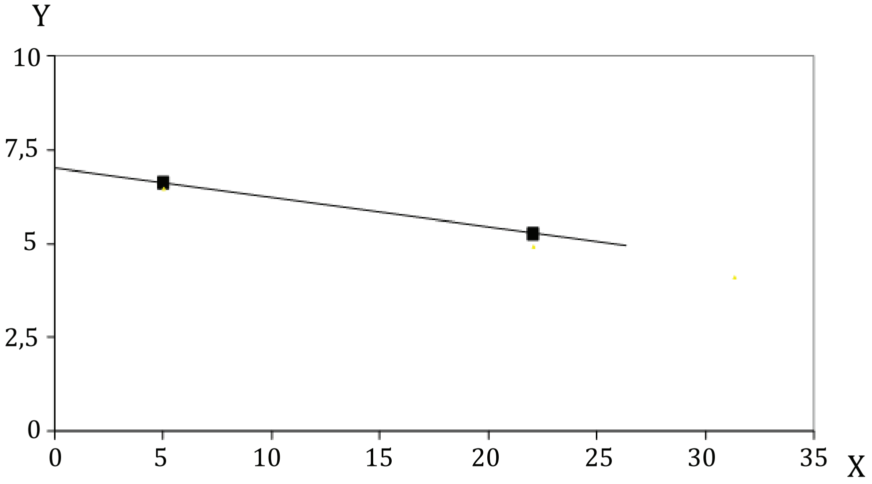
Key

X exposure time (minutes)

Y Cl concentration (atomic%)

NOTE The quadratic trend line is shown in heavy black. The thinner black line, showing the linear component of the quadratic, yields an intercept value of 6,89 atomic%; the first recorded measurement after 2 min gave 6,68 atomic% (data courtesy of Surface Analysis Laboratory, University of Surrey).

Figure B.5 — Chlorine atomic% as a function of X-ray exposure time for a commercial PVC blend



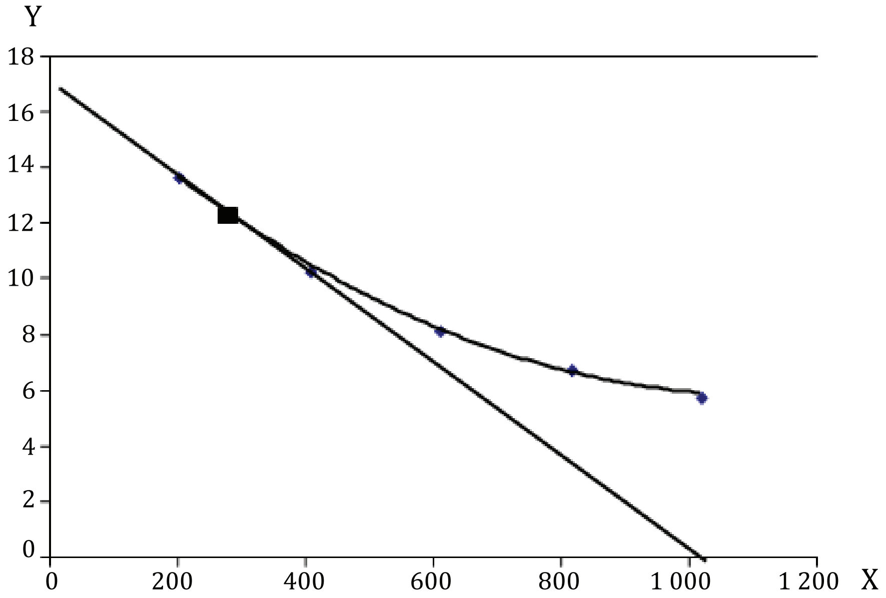
Key

X exposure time (minutes)

Y composition (atomic%)

NOTE Two points extracted from Figure B.5 showing the use of a linear approximation for chlorine atomic% as a function of X-ray exposure time. This approximation is unreliable once the peak intensity of a given element falls below 70 % of the first measurement.

Figure B.6 — Example of degradation of the PVC blend



Key

X time (minutes)

Y composition (atomic%)

NOTE The PTI estimated for this data by interpolation of the time for a 10 % reduction in signal (square marker) is 80 min. This index gives a zero time value of 17,0 atomic% whereas a polynomial fit gives 17,4 atomic%.

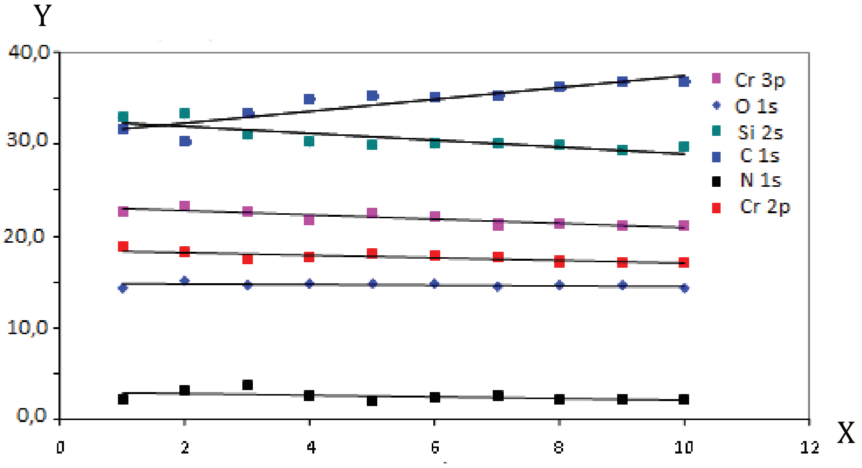
Figure B.7 — Use of the PTI for the degradation of PVC

Annex C
(informative)

Compensation for formation of a contamination layer

C.1 Correcting for surface contamination

Formation of a contaminant film during the data acquisition time can lead to reductions in peak intensities similar to those found in X-ray degradation. Film formation is often recognizable by an increase in the C 1s peak with an associated decrease in the intensity of all other peaks. In this manner, it differs from degradation, in which the reduction, or increase, in intensity affects only the peaks of the degraded compounds. An example of contamination formation in an unbaked system is given in Figure C.1.



Key

X scan number

Y concentration (atomic%)

NOTE The increase in the C 1s atomic composition arises from the formation of a contamination layer. This layer attenuates the signals from all of the substrate elements.

Figure C.1 — Composition (atomic%) derived from repetitive scans of a chromium silicide surface in an unbaked instrument

A method for correction of the substrate composition for the influence of contamination has been described by Reference [30]. Reference [31] has provided an evaluation of the utility of the method in his industrial laboratory.

The suggested procedure is as follows.

a) Estimate the thickness of the contamination layer, $d_{\text{contamination}}$, from the atomic fraction of contamination carbon, C. given by the usual quantification routine of the data processing softwares, as given in Formula (C.1):

$$d_{\text{contamination}} = -L_{\text{c}} \cos\theta \ln\left(1 - C\right) \tag{C.1}$$

where

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

L_c is the attenuation length of those electrons in the contamination layer.

NOTE Values of the attenuation length, L, in nm, for contamination layers may be calculated from Formula (C.2):

$$L = 0,00837\,E^{0,842} \tag{C.2}$$

where E is the electron kinetic energy, in eV.[32]

b) Correct the measured intensity of each recorded peak, as given in Formula (C.3):

$$I_{Z,\text{corrected}} = I_{Z,\text{measured}} \exp\left(d_{\text{contamination}} / L_Z \cos\theta\right) \tag{C.3}$$

c) Renormalize to a total composition of 100 atomic% (excluding carbon).

d) Report the corrected composition and the estimated thickness of the contamination layer.

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