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**Surface chemical analysis — X-ray  
photoelectron and Auger electron  
spectrometers — Linearity of intensity  
scale**

*Analyse chimique des surfaces — Spectromètres de photoélectrons X  
et d'électrons Auger — Linéarité de l'échelle d'intensité*

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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.

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

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## Introduction

Quantitative analysis of materials at surfaces by Auger electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS), requires measurements of the spectral intensities. Non-linearities in the respective instrument intensity scales, unless corrected, lead directly to errors in the amounts of material determined. In general, intensity scales are linear at very low count rates but become progressively non-linear as the count rates rise. Measurements of intensity rely on the measurement system delivering an intensity signal which is 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 non-linear. It is rare for non-linearities below 1 % to be treated as significant. The intensity scale non-linearity may exceed 1 % for count rates which exceed 5 % of the maximum permissible count rate<sup>[1,2]</sup>. For many instruments, the non-linearity behaviour will not vary significantly from month to month, provided the detection system is correctly set. For these instruments, the count rate may 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. In this International Standard, two simple relationships are described, involving a parameter known as the detector system dead time, to make this correction. For some instruments, the non-linearity may not be predictable or described by any simple relationship. For these instruments, this International Standard allows the extent of the non-linearity to be measured and a maximum count rate for an acceptable limit of divergence from linearity to be defined. This limit of divergence from linearity is set by the user appropriately for the analyses to be conducted.

In this International Standard, two methods for measuring the linearity are provided. The first is based on the principle that the spectrometer output is proportional to the electron beam current in AES or the X-ray beam flux in XPS<sup>[1]</sup>. This is the simplest method and may be conducted in instruments where the beam current or flux may be set at 30 or more approximately evenly spaced intervals up to the level required to generate the maximum count rate for which this International Standard is to be used. In some XPS instruments, this is not possible and the X-ray flux may only be set at one of two or more (but less than 30) pre-defined levels. For these instruments, the first method cannot be realized and a second method is given<sup>[2]</sup>.

This International Standard should be used when characterising a new spectrometer so that it may be operated in an appropriate count rate range. It is repeated after any substantive modification to the detection circuits, or after the multiplier voltage has been increased (since the previous test with this International Standard) by one-third of the range of increase provided by the manufacturer, or after replacement of the electron multiplier(s) or at intervals of approximately 12 months.

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# Surface chemical analysis — X-ray photoelectron and Auger electron spectrometers — Linearity of intensity scale

## 1 Scope

This International Standard specifies two methods for determining the maximum count rate for an acceptable limit of divergence from linearity of the intensity scale of Auger and X-ray photoelectron spectrometers. It also includes methods to correct for intensity non-linearities so that a higher maximum count rate can be employed for those spectrometers for which the relevant correction equations have been shown to be valid.

## 2 Normative reference

The following referenced documents are indispensable for the application 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 18115, *Surface chemical analysis — Vocabulary*

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## 3 Symbols

ISO 21270:2004

$E_{\text{Cu}}$	measured energy value for the $\text{Cu L}_{3\text{M}}$ peak
$E_j$	energy value for the $j$ th energy channel
$I_i$	measure of the $i$ th flux value of beam current in AES or X-ray anode emission current in XPS
$k$	a constant
$M_{\text{H}}(E_j)$	corrected count rate for the high-intensity X-ray spectrum at energy $E_j$
$M_i$	corrected count rate for the $i$ th flux value
$M_{\text{L}}(E_j)$	corrected count rate for the low-intensity X-ray spectrum at energy $E_j$
$N_{\text{H}}(E_j)$	measured count rate for the high-intensity X-ray spectrum at energy $E_j$
$N_i$	measured count rate for the $i$ th flux value
$N_{\text{L}}(E_j)$	measured count rate for the low-intensity X-ray spectrum at energy $E_j$
$N_{\text{max}}$	maximum count rate for which the system is to be used and for which the system remains within the acceptable limits of divergence from linearity given by $k(1 \pm \delta)$
$\pm \delta$	fractional limits to the linearity
$\tau_{\text{e}}$	extended dead time
$\tau_{\text{n}}$	non-extended dead time

## 4 Outline of the methods

Two methods are available to evaluate the instrument intensity linearity. For AES instruments, and for XPS instruments in which 30 or more approximately evenly spaced and known increments in the X-ray flux are available, a general method is described. This is called the method of varying the source flux. For XPS instruments with two or more but less than 30 settings available for the X-ray flux, this is not possible and a second method is given. This second method is called the spectrum ratio method.

In the first method, the spectrometer must be fitted with an inert gas ion sputtering gun for cleaning samples. The intensity scale linearity measurements are then conducted using a sputter cleaned pure copper sample. In the second method, this sample or, if there is no ion gun, a stainless steel sample or sample holder is used. The selection of these samples is described in 6.1 and their preparation in 6.2 and 6.3. Next, the spectrometer settings are selected in 6.4 and the instrument operated as described in 6.5.

In the first method, described in 6.6, the spectrometer is set to detect the count rate at the Cu L<sub>3</sub>VV Auger electron peak. That count rate is then determined as a function of the electron beam current or as a function of the X-ray flux for 30 or more approximately evenly spaced increments in the X-ray flux. From these data, as described in 6.7, a plot of the quotient of the measured count rate and the beam current in AES, or of the quotient of the measured count rate and the X-ray flux in XPS, versus the measured count rate allows the linearity range and any relevant correction to be determined.

In the second method, described in 6.8 and to be used for those XPS instruments in which 30 settable values of X-ray flux are not available, widescan spectra are recorded for a high and a low X-ray source emission current. From these data, as described in 6.9, a plot of the quotient of the count rates of these two spectra, for each energy channel, versus the count rate for that channel in the high emission current spectrum, allows the linearity range and any relevant correction to the count rates to be determined.

Finally, 6.10 summarizes the data to be recorded.

## 5 When to use this International Standard

This International Standard shall be used when characterising a new spectrometer so that it may be operated in an appropriate count rate range. It shall then be repeated after any substantive modification to the detection circuits, after the multiplier voltage has been increased by one third of the range of increase (since the previous test with this standard) provided by the manufacturer, after replacement of the electron multiplier(s) or at intervals of approximately 12 months.

## 6 Procedure for evaluating the intensity linearity

### 6.1 The samples

For the method of varying the source flux, AES or XPS instruments may be used if they incorporate an inert gas ion gun for cleaning samples. For this method, use a polycrystalline Cu sample of at least 99,8 % purity and proceed to 6.2. The second method, the spectrum ratio method, is only applicable to XPS instruments. For this second method, either use a polycrystalline Cu sample of at least 99,8 % purity or a stainless-steel sample or sample holder. If the instrument does not incorporate an inert gas ion gun, the stainless-steel sample or sample holder shall be used. Proceed to 6.3.

NOTE 1 For convenience, copper in the form of a foil typically of an area 10 mm by 10 mm, and 0,1 mm to 0,2 mm thick, is used.

NOTE 2 If stainless steel is to be used, either a foil 10 mm by 10 mm, and 0,1 mm to 0,2 mm thick, or a sample holder, or some other form may be chosen, as convenient.

## 6.2 Preparing the copper sample

**6.2.1** If the sample appears to need cleaning, a short dip in 1 % nitric acid may be used followed by a rapid rinse in distilled water.

**6.2.2** Mount the sample on a sample holder using fixing screws or other metallic means to ensure electrical contact. Do not use adhesive tape.

**6.2.3** Achieve ultra-high vacuum and clean the sample by ion sputtering to reduce the oxygen and carbon contamination until the heights of the respective signals are each less than 2 % of the height of the most intense metal peak in a survey spectrum. Record a survey (widescan) spectrum to ensure that the only significant peaks are those of Cu. The quality of vacuum necessary here is such that the oxygen and carbon peak heights shall not exceed 3 % of the heights of the most intense metal peaks by the time you have reached completion of the data acquisition in 6.6 or 6.8 or at the end of the working day (whichever is the earlier).

NOTE 1 Inert gas ion sputtering conditions that have been found suitable for cleaning are 1 min of a 30  $\mu$ A beam of 5 keV argon ions covering 1 cm<sup>2</sup> of the sample.

NOTE 2 Example AES and XPS spectra for Cu may be found in bibliography references [3] to [6].

**6.2.1** Try to conduct all relevant parts of this International Standard in one working day. If more than one day is required, confirm the cleanness of the samples at the start of each day's work. Now proceed to 6.4.

## 6.3 Preparing the stainless-steel sample or sample holder

**6.3.1** Wash the stainless-steel sample or sample holder in distilled water and then in ethanol to remove handling contaminants. If a sample is to be used, it is mounted on a sample holder using fixing screws or other metallic means to ensure electrical contact. Adhesive tape shall not be used.

NOTE Example XPS spectra for air-contaminated stainless steel may be found in bibliography references [2], [7] and [8].

**6.3.2** Achieve the system working pressure and, if possible, leave the sample in the vacuum overnight to allow the desorption of contaminants to stabilize.

## 6.4 Choosing the spectrometer settings for which the intensity linearity measurement is required

Choose the spectrometer operating settings for which the intensity linearity measurement is required. The procedure from 6.4 to 6.10 shall be repeated for each combination of spectrometer settings of pass energy, retardation ratio, slits, lens settings etc for which a linearity measurement is required. Record the values of these settings in the spectrometer log.

NOTE The designs of spectrometers and their circuits vary and a spectrometer linearity measurement for one combination of lens settings, slits and pass energy will not necessarily be valid for any other setting of the lens, slits and pass energy. Many spectroscopists make accurate measurements under one optimum set of conditions and then only that set of analyser conditions needs a linearity assessment. Any result is only valid for the combination of settings used, although the designs of some of the simpler instruments do lead to linearity results that are consistent for all settings.

## 6.5 Operating the instrument

**6.5.1** Operate the instrument in accordance with the manufacturer's or locally defined documented instructions. The instrument shall have fully cooled following any bakeout. Ensure that the operation is within the manufacturer's recommended ranges for source power (for XPS), primary beam current (for AES), counting rates, spectrometer scan rate and any other parameter specified by the manufacturer. Check that the detector multiplier settings are correctly adjusted. For multidetector systems, ensure that any necessary optimizations or checks described by the manufacturer are conducted prior to this assessment.

NOTE Incorrect detector settings may lead to an excessive non-linearity of the intensity scale, the behaviour of which may vary from day to day and from sample to sample. It is particularly important that the multiplier voltage is correctly set<sup>[9]</sup> as this voltage generally needs to be increased during the multiplier life<sup>[10]</sup>. It is also important that the counting electronics discriminator is correctly set.

**6.5.2** For AES instruments, and for XPS instruments in which 30 or more approximately evenly spaced and known increments in the X-ray flux are available, use the method of varying the source flux, described in 6.6. For XPS instruments with two or more but less than 30 settings available for the X-ray flux, proceed directly to the spectrum ratio method, described in 6.8.

**6.6 Measurement of the intensity scale linearity by varying the source flux**

**6.6.1** Using the sputter-cleaned Cu sample, identify the Cu L<sub>3</sub>VV Auger electron peak. Use a low beam current or X-ray flux and measure and record the energy of the peak maximum,  $E_{Cu}$ , to a precision of 0,1 eV.

NOTE The kinetic energy of the Cu L<sub>3</sub>VV peak for spectrometers with energy resolutions better than 1 eV is 918,69 eV<sup>[11,12]</sup> when referenced to the Fermi level or approximately 914,2 eV when referenced to the vacuum level. The binding energy equivalent values for XPS are 334,91 eV using Mg X-rays and 567,92 eV using Al X-rays.

**6.6.2** Record a spectrum of the top of the peak from approximately 0,5 eV below the energy of the peak maximum to approximately 0,5 eV above that maximum with energy increments of approximately 0,1 eV and acquisition times of at least 1 s per channel or sufficient time to record more than 100 000 counts for the channel corresponding to the energy of the peak maximum intensity. Record the spectrum for each of 30 values of the primary electron beam current for AES or of the X-ray flux for XPS. These 30 values of current or flux are to be approximately evenly spaced between 5 % of the maximum flux and the maximum flux with which you intend to work for the instrument with the settings chosen in 6.4. The values of the current or flux are changed using the controls of the electron gun or X-ray source and during these measurements no other changes shall be made. For AES, the beam shall be rastered over an area of 25 µm by 25 µm and the current shall be measured using a Faraday cup with a calibrated current-measuring instrument. As the beam current is varied, the beam diameter shall be kept smaller than 25 µm. For XPS, the flux cannot usually be measured directly but is often proportional to the X-ray source filament emission current for a constant source anode voltage. Either measure the flux by an appropriate means or record the source emission values whilst maintaining a constant anode voltage.

NOTE The acquisition time may be set using one or more scans as appropriate.

**6.7 Determination of the intensity scale linearity by varying the source flux**

**6.7.1** Determine the 30 values of the measured count rates,  $N_i$ , at the energy  $E_{Cu}$  identified in 6.6.1 for the 30 values of the beam current or anode emission current,  $I_i$ . Evaluate the 30 values of  $N_i/I_i$ . On a plot of  $N_i/I_i$  as ordinate versus  $N_i$  as abscissa, as shown in Figure 1, extrapolate the data for  $N_i/I_i$  to  $N_i = 0$  and denote this value  $k$ . On this plot draw horizontal lines of ordinate values  $k(1 + \delta)$  and  $k(1 - \delta)$  where  $\pm \delta$  are the fractional acceptable limits of divergence of the intensity scale from linearity. The range of  $N_i$  from zero to  $N_{max}$ , over which the  $N_i/I_i$  data are within the bounds of  $k(1 \pm \delta)$ , defines the maximum measured count rate,  $N_{max}$ , for which the intensity scale is linear within the fractional limits  $\pm \delta$ .

NOTE The  $N_i$  values are count rates and not total counts.

**6.7.2** In many systems, the value of  $N_{max}$  may be increased by correcting for known divergencies from linearity. This correction may be available through the software of the spectrometer data processing system or other available software. If you have such software or if you are interested in analysing the system behaviour, proceed to 6.7.3. If not, proceed directly to 6.10.

**6.7.3** For linear systems:

$$\frac{N_i}{I_i} = k \tag{1}$$

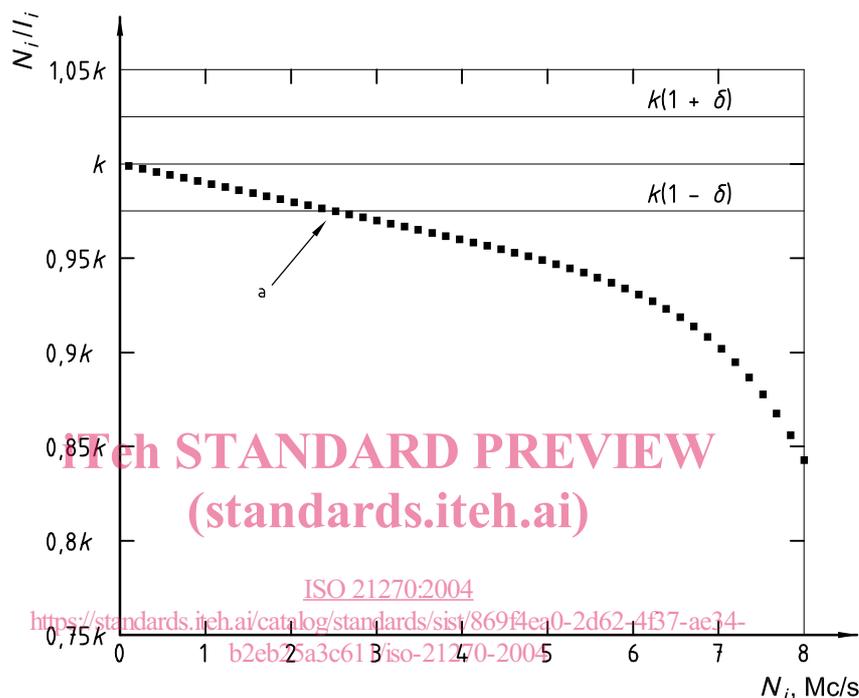
where  $k$  is a constant.

For systems involving a non-extended dead time,  $\tau_n$ :

$$\frac{N_i}{I_i} = k(1 - N_i\tau_n) \quad (2)$$

and for those with an extended dead time,  $\tau_e$ :

$$\frac{N_i}{I_i} = k \exp(-kI_i\tau_e) \quad (3)$$



a  $N_{\max}$

**Figure 1 — Illustration for  $N_i/I_i$  as a function of  $N_i$  showing the fractional acceptable limits of divergence of the intensity scale from linearity and the maximum measured count rate,  $N_{\max}$**

**6.7.4** Determine, from the data, which of Equations (1), (2) or (3) is valid, or, from other information, that a different relation is appropriate. Determine the range of validity of the equation used and evaluate the relevant dead time. Note the equation used and the value of the dead time in the instrument log.

NOTE 1 For values of  $N_i\tau_n$  or  $N_i\tau_e$  less than 0,128, the difference between Equations (2) and (3) give values of  $N_i$  which differ by less than 1 % for the same true count rate.

NOTE 2 The derivation of Equations (2) and (3) may be found in bibliography reference [13].

NOTE 3 Equations (2) and (3) are derived for single-channel detector systems but remain valid for detector systems comprising a set of single detectors where the overall system dead time is equal to that of the single detectors divided by the number of single detectors contributing to the signal [14].

NOTE 4 Non-extended dead times ranging from 24 ns [14] to 200 ns [1] have been reported for electron spectrometers used for AES and XPS.

NOTE 5 Bibliography references [1] and [2] show additional behaviours not conforming to Equations (1), (2) and (3).