INTERNATIONAL STANDARD

ISO
17974

First edition
2002-10-01

Surface chemical analysis — High-resolution Auger electron spectrometers — Calibration of energy scales for elemental and chemical-state analysis

Analyse chimique des surfaces — Spectromètres d'électrons Auger à haute résolution — Étalonnage des échelles d'énergie pour l'analyse élémentaire et de l'état chimique

© ISO 2002

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 17974:2002
https://standards.iteh.ai/catalog/standards/sist/d87d8fde-7ec1-46c2-bd17-
a20bc19fc981/iso-17974-2002

Contents

Page

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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 International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 17974 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 7, *X-ray photoelectron spectroscopy*.

iTeh STANDARD PREVIEW

(standards.iteh.ai)

ISO 17974:2002
https://standards.iteh.ai/catalog/standards/sist/d87d8fde-7ec1-46c2-bd17-
a20bc19fc981/iso-17974-2002

Introduction

Auger electron spectroscopy (AES) is used extensively for the surface analysis of materials. Elements in the sample (with the exception of hydrogen and helium) are identified from comparisons of the kinetic energies of their Auger electron peaks (determined from the measured spectra) with tabulations of those energies for the different elements or with handbooks of spectra. Information on the chemical state of such elements can be derived from the chemical shifts of measured Auger electron features with respect to those for reference states. Identification of chemical states is based on measurements of chemical shifts with accuracies in the range down to 0,1 eV, making necessary individual measurements having and reference sources available with, the appropriate accuracies. Calibrations of the kinetic energy scales of AES instruments are therefore required, often with an uncertainty of $\leqslant$ 0,3 eV.

The method for calibrating kinetic energy scales specified in this International Standard uses metallic samples of pure copper (Cu), and either aluminium (Al) or gold (Au), and is applicable to Auger electron spectrometers measuring direct spectra with relative resolutions of 0,2 % or better. It is valid for the kinetic energy range 0 eV to 2 250 eV if gold is used, and 0 eV to 1 550 eV if aluminium is used.

Traditionally, kinetic energies of Auger electrons have been referenced to the vacuum level, and this reference is still used by many analysts. However, the vacuum level is ill-defined and can vary from instrument to instrument over a range of 0,5 eV. Although use of the vacuum level reference procedure will generally not cause ambiguity in elemental identification, it may cause uncertainty in measurements at high resolution relating to chemical states. Because of this, instruments designed for both Auger electron spectroscopy and X-ray photoelectron spectroscopy reference the kinetic energies to the Fermi level, giving values typically 4,5 eV higher than those referenced to the vacuum level. For the purposes of this International Standard, the kinetic energies are referenced to the Fermi level.

AES instruments calibrated for providing analyses within the scope of ISO 17025 [1] as well as for other purposes may need a statement of the estimated calibration uncertainty. These instruments are in calibration for kinetic energy measurements within certain defined tolerance limits $\pm \delta$. The value of δ is not defined in this International Standard since it will depend on the application and design of the AES instrument. The value of δ is selected by the user, based on experience in the use of this International Standard, the calibration stability of the instrument, the uncertainty required for kinetic energy measurements in the intended applications of the instrument and the effort incurred in conducting the calibration. This International Standard provides information by which a suitable value of δ may be chosen. Typically, δ is $\geqslant$ 0,2 eV and greater than about four times the repeatability standard deviation, σ_R.

For an instrument to be in calibration, the divergence from the reference kinetic energy values plus the expanded calibration uncertainty for a confidence level of 95 %, when added to the instrumental drift with time, must not exceed the chosen tolerance limits. Before it becomes likely that the instrument is out of calibration, it needs to be recalibrated: a calibration measurement made and action taken to reduce the difference between the measured and reference values. This difference may not necessarily be reduced to zero, but will normally come down to a small fraction of the tolerance limits required for the analytical work.

This International Standard does not address all possible defects of instruments, since the required tests would be very time consuming and would need both specialist knowledge and equipment. However, it does address the basic and common problems in the calibration of the kinetic energy scales of AES instruments.

Surface chemical analysis — High-resolution Auger electron spectrometers — Calibration of energy scales for elemental and chemical-state analysis

1 Scope

This International Standard specifies a method for calibrating the kinetic energy scales of Auger electron spectrometers used for elemental and chemical state analysis at surfaces. It also specifies a calibration schedule for testing the kinetic energy scale linearity at one intermediate energy, for confirming the uncertainty of the scale calibration at one low and one high kinetic energy value, for correcting for small drifts of that scale and for defining the expanded uncertainty of the calibration of the kinetic energy scale with a confidence level of 95 % (this uncertainty includes contributions for behaviours observed in interlaboratory studies but does not cover all possible defects).

It is applicable only to those instruments incorporating an ion gun for sputter cleaning. It is not applicable to instruments with kinetic energy scale errors significantly non-linear with energy. Neither it is applicable to those instruments operated at relative resolutions poorer than 0,2 % in the constant $\Delta E/E$ mode or 1,5 eV in the constant ΔE mode, those requiring tolerance limits of $\pm$ 0,05 eV or less, nor to those with an electron gun that cannot be operated in the energy range 5 keV to 10 keV. It does not provide a full calibration check for confirming the energy measured at each addressable point on the energy scale, this being performed according to the manufacturer's recommendations.

2 Normative reference

The following normative document contains provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the normative document indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 18115, *Surface chemical analysis — Vocabulary*

3 Terms and definitions

For the purposes of this International Standard, the terms and definitions given in ISO 18115 apply.

4 Symbols and abbreviated terms

The following symbols and abbreviated terms are used throughout this International Standard (see also annex B)

AES Auger electron spectroscopy

A Analyser retardation factor

a Measured energy scaling error

b Measured zero offset error, in electronvolts

c Coefficient of R

d Coefficient of R^2

E_{corr} Corrected result for kinetic energy corresponding to given E_{meas}, in electronvolts

E_{elem} Kinetic energy of a frequently measured element at which the indicated kinetic energy scale is set, after calibration, to read correctly, in electronvolts

E_{meas} A measured kinetic energy, in electronvolts

$E_{meas,n}$ Average measured kinetic energy for peak n, in electronvolts

$E_{meas,ni}$ One of a set of measurements of kinetic energy for peak n, in electronvolts

$E_{ref,n}$ Reference values for position of peak n on kinetic energy scale, in electronvolts

$E_{ref,n}^o$ Reference kinetic energy of peak n

FWHM Full width at half maximum peak intensity above background, in electronvolts

i Index of spectrum for the seven repeat measurements of a peak

j Number of repeat measurements for new peak

k Number of repeat measurements for Cu $M_{2,3}$VV, Cu L_3VV, and Au $M_5M_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks in repeatability and linearity determinations

m Number of repeat measurements for Cu $M_{2,3}$VV and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks in regular calibrations

n Designation of peak identifier

R Relative resolution of a spectrometer, expressed as percentage

t_x Student's t values for x degrees of freedom of two-sided distribution for confidence level of 95 %

U_{95} Total uncertainty of calibrated energy scale at confidence level of 95 %, in electronvolts

$U_{95}^c(E)$ Uncertainty at confidence level of 95 % arising from calibration using Cu $M_{2,3}$VV and Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$ peaks at kinetic energy, E, assuming perfect scale linearity, in electronvolts

U_{95}^l Uncertainty of ε_2 at confidence level of 95 %, in electronvolts

U_{95}^{cl} Uncertainty of calibration at confidence level of 95 %, in the absence of a linearity error

Δ_n Offset energy, given by average measured kinetic energy for calibration peak minus reference kinetic energy, in electronvolts, for $n = 1, 2, 3, 4$

ΔE_{corr} Correction added to E_{meas} after calibration to provide corrected kinetic energy result

$\Delta\phi$ Average of Δ_1 and Δ_4

δ Value for tolerance limit of energy calibration at confidence level of 95 % (set by the analyst), in electronvolts

ε_2 Measured scale linearity error at Cu L_3VV peak, in electronvolts

σ_R Maximum of σ_{R1}, σ_{R2}, and σ_{R3} or σ_{R4}

σ_{Rn} Repeatability standard deviation for nth peak

σ_{Rnew} Repeatability standard deviation for new peak, in electronvolts

See annex B for a list of symbols used only in that annex.

5 Outline of method

Calibration of an Auger electron spectrometer using this International Standard is performed by obtaining and preparing copper and gold or aluminium reference foils in order to measure the kinetic energies of selected Auger electron peaks. These reference materials are chosen as they provide Auger electron peaks near the high and low kinetic energy limits used in practical analysis. For kinetic energy scale linearity tests, an intermediate energy peak is used. These peaks are well established for this purpose and the relevant reference data exist.

See Figure 1 for a flowchart showing the general structure of the work and the sequence of procedures.

The initial steps are given in 6.1 to 6.5. For the first calibration it is assumed that there has been no characterization of the spectrometer behaviour for the chosen instrument settings. Thus, in accordance with 6.7, measurements are made of the kinetic energies of the Cu $M_{2,3}VV$ and Cu L_3VV, and either Au $M_5N_{6,7}N_{6,7}$ or Al $KL_{2,3}L_{2,3}$, peaks in a sequence repeated seven times. These data give the repeatability standard deviation, σ_R, of the kinetic energy of a peak. This repeatability has contributions from the stability of the spectrometer electronic supplies, from the sensitivity of the measured peak energy to the sample position and from the statistical noise at the peak. In the procedure, conditions are defined to ensure that the statistical noise is relatively small. The other two contributions may vary with the measured kinetic energy, and so σ_R is defined as the greatest of the values obtained for the three peaks used. The value of σ_R may depend on the sample positioning procedure. In 6.7.1, the use of a consistent sample positioning procedure is required and the final calibration is only valid for samples positioned using this positioning procedure.

The Au $M_5N_{6,7}N_{6,7}$ peak is weak, especially at 5 keV beam energy, and reference values for the peak energy are available only for incident beam energies of 5 keV and 10 keV. Thus, for instruments in which the signal-to-noise ratio is poor, or which cannot scan above 2 000 eV kinetic energy or do not operate at 5 keV or 10 keV beam energies, the Al $KL_{2,3}L_{2,3}$ peak is available as an alternative. Using the Au $M_5N_{6,7}N_{6,7}$ peak allows the calibration to cover the kinetic energy scale from 0 eV to 2 250 eV, whereas with Al $KL_{2,3}L_{2,3}$ the upper limit is restricted to 1 550 eV.

Studies of spectrometers show that, in general, any measured error in the peak energies varies approximately linearly with the peak kinetic energy. The equations presented in this International Standard are valid only for this most common situation and are based on the principle that the difference between the measured kinetic energies and the reference kinetic energies are both small and are linearly, or close to linearly, dependent on the kinetic energy. This linearity may fail if the instrument is defective and so a test is specified in 6.7 and 6.10 for confirming the closeness to linearity at an intermediate energy. For convenience, this test involves the Cu L_3VV peak.

If the linearity test is adequate, an energy scale correction may be derived using the simple regular calibration procedure given in 6.11. Exactly how the kinetic energy scale is corrected depends on practical details of the instrument being calibrated and so a number of strategies are given in 6.12. The analyst also needs to consider the uncertainty with which the peak kinetic energies need to be measured. Table 1 shows values of some of the typical parameters, defined in this International Standard, which lead to illustrative tolerance limits of $\pm$ 0,2 eV and $\pm$ 0,3 eV at a confidence level of 95 %. Note the importance of the allowable drift between calibrations in Table 1. Thus, as shown in Figure 1, the calibration interval is determined from measurements of the instrument drift as given in 6.14. The regular calibration is then made at the appropriate calibration interval to maintain the instrument kinetic energy scale within the required tolerance limits.
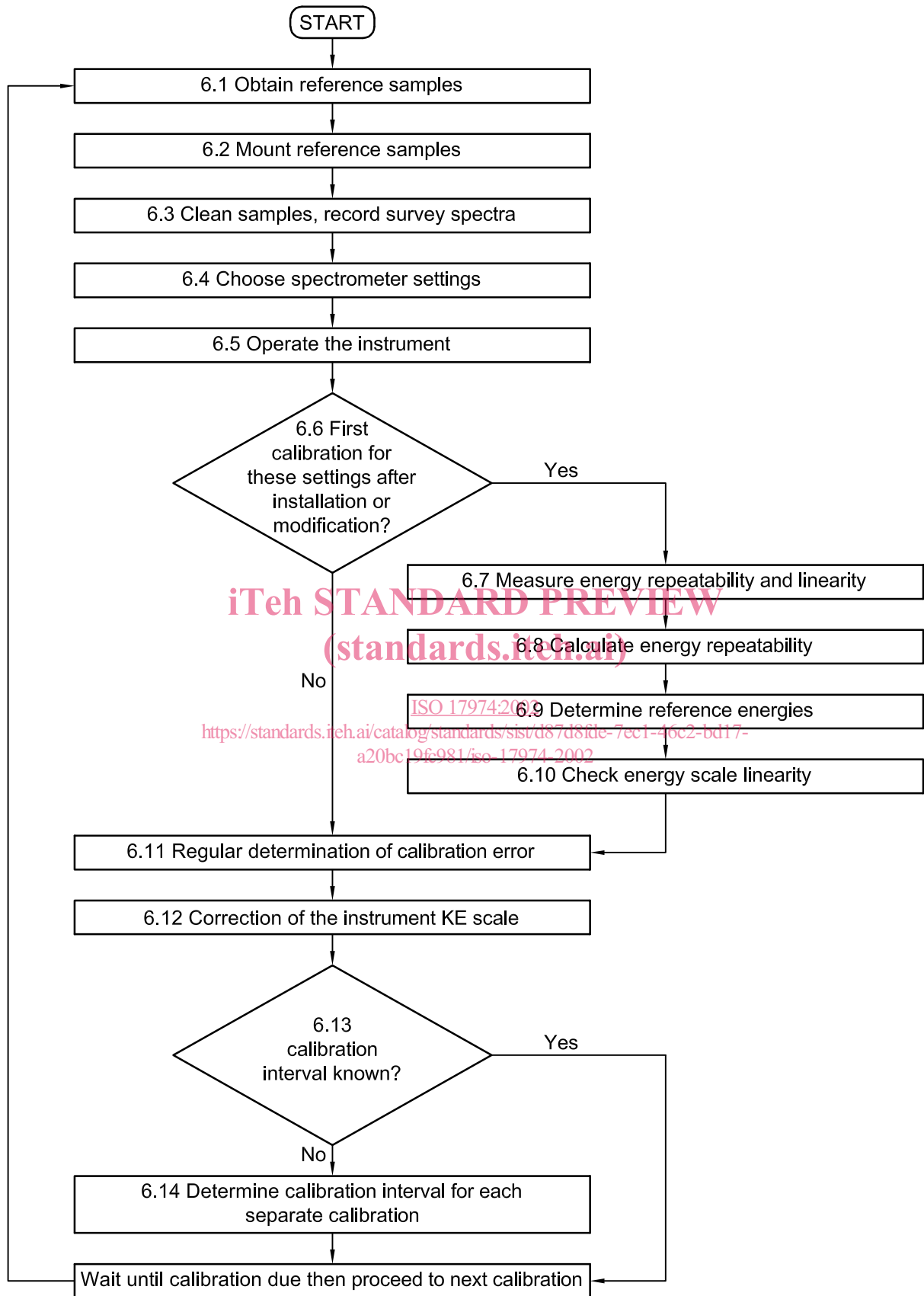
NOTE   The numbers refer to the corresponding subclauses of this International Standard.

Figure 1 — Flowchart of sequence of operations of method

Table 1 — Illustrative contributions to error budget for kinetic energy scale calibration

Item	Symbol	Calculated from	Examples — If high accuracy required		Examples — If lower accuracy required		Comment
Tolerance limits, eV	$\pm \delta$	User's choice	$\pm 0,2$		$\pm 0,3$		User's choice dictated by accuracy required and number of spectra there is time to acquire in regular calibrations
Repeatability standard deviation, eV	σ_R	Equation (1)	0,050		0,050		Characteristic of spectrometer measured at first calibration (see 6.7)
Number of times, each pair of spectra is acquired	m	User's choice $m = 1$ or 2	$m = 1$	$m = 2$	$m = 1$	$m = 2$	
Uncertainty of calibration measurements, eV	U_{95}^{cl}	Equation (12) or (13)	0,185	0,130	0,185	0,130	
Measure of scale non-linearity, eV	ε_2	Equation (5) or (6)	0,050	0,050	0,050	0,050	Characteristic of spectrometer measured at first calibration (see 6.7)
Uncertainty of energy scale after calibration, eV	U_{95}	Equation (11)	0,192	0,139	0,192	0,139	
Maximum allowable drift between calibrations, eV	$\pm (\delta - U_{95})$	δ and U_{95}	$\pm 0,008$	$\pm 0,061$	$\pm 0,108$	$\pm 0,161$	Define drift allowable before danger of exceeding the chosen limits $\pm \delta$ eV
Maximum calibration interval (for an illustrative instrument that exhibits a steady drift rate of 0,025 eV per month), months	—	See 6.14	0,3	2,4	4,3	6,4	Choose convenient interval below this maximum, and less than four months, with safety margin for any erratic behaviour
Choice of calibration interval, months	—	User's choice, based on observed drift behaviour	Option impractical	1	3	4	

NOTE   The uncertainties are for a confidence level of 95 %. The examples illustrate the effect of user choices on the uncertainty of calibration and the required interval between recalibrations.

In this International Standard, measurements are given to establish the uncertainty of the calibration at a confidence level of 95 %, directly after the calibration. The error of the kinetic energy scale will generally increase with time and, during the interval between calibrations, must not exceed the tolerance limits of $\pm \delta$ chosen by the analyst to define the quality of their measurements. Completing a table such as in Table 1 will assist the user in defining a suitable value for δ. If the user has little or no idea of the capability of his or her instrument, if the manufacturer's data give no assistance and if there is no clear idea of the requirements, start with Table 1 with δ set at 0,2 eV. Go through the procedure specified, filling in the rows, and finally check if this value of δ is feasible for the instrument being used. If not, review the operating procedures and either reduce one or more of the terms contributing to U_{95} or increase the value of δ to one that is acceptable.

It is important to note that δ is the tolerance limit for the accuracy of the calibration of the instrumental energy scale. Subsequent energy measurements can have uncertainties greater than δ as a result of peak breadth, poor counting statistics, peak synthesis or charging effects. For guidance on reporting the uncertainty of subsequent measurements, see annex D.

6 Procedure for calibrating the energy scale

6.1 Obtaining reference samples

For the calibration of Auger electron spectrometers able to scan to at least 2 050 eV and with beam energies of 5 keV or 10 keV available, use samples of Cu and of Au. For other instruments use Cu and Al. The samples shall be polycrystalline and of at least 99,8 % purity metals which, for convenience, are usually in the form of foils typically of an area 10 mm by 10 mm and 0,1 to 0,2 mm thick.

If the samples appear to need cleaning, a short dip in 1 % nitric acid may be used for Cu with subsequent rinsing in distilled water. If the Cu sample has been stored in the air for more than a few days, the dip in nitric acid will make the sample cleaning (see 6.3) much easier.

6.2 Mounting samples

Mount the samples of Cu and Au or Al on the sample holder or on separate sample holders, as appropriate, using fixing screws or other metallic means to ensure electrical contact: do not use double-sided adhesive tape.

6.3 Cleaning samples

Achieve ultra-high vacuum and clean the samples by ion sputtering to reduce the contamination until the heights of the oxygen and carbon Auger electron peaks are each less than 2 % of the height of the most intense metal peak in each survey spectrum. Record a survey (widescan) spectrum for each of the samples to ensure that the only significant peaks are those of the required pure elements. 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 completion of the procedure in accordance with 6.11 or at the end of the working day, whichever is the earlier.

All relevant procedures of this International Standard should be completed in one working day. If more than one day is required, the cleanness of the samples shall be confirmed at the start of each day's work.

NOTE 1   Inert gas ion sputtering conditions that have been found suitable for cleaning are 1 min of a 30 µA beam of 5 keV argon ions covering 1 cm^2 of the sample.

NOTE 2   Contamination effects are generally least for Au and greatest for Al.

See Figure 2 for example AES survey spectra.

6.4 Choosing spectrometer settings for energy calibration

Choose the combination of spectrometer operating settings for which the energy calibration is required. Repeat the calibration procedure in accordance with 6.4 to 6.14 for each combination of analyser settings of pass energy, retardation ratio, slits, lens settings etc., for which a calibration is required. Record the values of these settings in the spectrometer calibration log.

NOTE   The designs of spectrometers and their circuits vary and a spectrometer calibration made for one combination of lens settings, slits and pass energy will not necessarily be valid for any other combination of lens settings, slits and pass energy. Many spectroscopists make measurements under one optimum combination of analyser settings so that only this combination of settings needs calibration. Any calibration made is only valid for the combination of settings used.