# IUVSTA Workshop "XPS: From Spectra to Results – Towards an Expert System"
# St Malo, France, 21 – 26 April 2002

# Draft Report from Theme Group A – Instrument and Sample Characterisation

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## (1) Experts for Group A

The experts participating in Theme A were:

| No and Name | Country | | No and Name | Country |
|---|---|---|---|---|
| 1. D. R. Baer | US | | 2. A Benoit | F |
| 3. C Blomfield | UK | | 4. A Carrick | UK |
| 5. P. J. Cumpson | UK | | 6. U Gelius | S |
| 7. J T Grant | US | | 8. M Green | G |
| 9. S Mähl | G | | 10. K Robinson | UK |
| 11. M P Seah | UK | | 12. A Tanaka | J |
| 13. W Unger | G | | | |

## (2) Workshop Program Headings:

The Workshop Theme headings were:

A Instrument and specimen characterization
B Experimental objectives
C Wide-scan interpretation - trial composition and structure
D Protocols for narrow scans, instrument setup, and data acquisition
E Reduction of narrow-scan data - chemical state and morphology analysis
F Reduction of narrow-scan data – quantification

## (3) The suggested outline for Theme A: Instrument and sample characterization from Ced Powell

It is envisaged that the expert system would conduct an interview with the user on the following topics to be discussed by Theme A:

(1) How to ensure that the ***instrument*** is performing reliably (supplemental to maker's instructions).

(a) Calibration status of BE scale (by reference to the control chart established through ISO 15472).
(b) Determination of instrumental transmission function, and subsequent checks that it has not changed.
(c) Linearity of instrumental intensity scale.
(d) Knowledge of the spatial resolution and acceptance area of the analyzer.

Note: it is only through satisfactory calibrations, etc. that spectral and BE and spectral data can be meaningfully compared.

(2) User's knowledge of the ***sample*** (metal, ceramic, semiconductor, polymer, etc.), compatibility of sample with instrument vacuum (and possible need for pumping over an extended period of time), and sample history.

## (4) Purpose of the expert system

(1) to guide the user in the efficient acquisition of XPS data appropriate for solution of problems
(2) to assist the user in the interpretation and reduction of the XPS data.

The expert system modules could operate on a PC or be available in future data systems of XPS instruments.

The expert system needs to

- have existing knowledge of the sample in a structured manner
- have access to all previous analyses also in a structured way
- be able to set up appropriate experiments on an associated instrument and be able to suggest procedures for this when 'off line'

- advise the operator about the likely direction the analysis will take, its duration (cost) and the quality and type of conclusions that will be drawn (as the experiment proceeds this will be updated).

## (5) Items to be covered

The list of items to be covered by Theme A follows:

### (5.a) Existing Knowledge of the Sample

1a) Sample descriptors
1b) How the sample arrived at the analyst
1c) Sample cleaning and handling
1d) Prior analysis/ use of several methods

Some of these can be obtained from data files by the computer but many will need interpretative input from the analyst.

### (5.b) Ensuring that the Instrument is Performing Reliably – Calibrations

2a) System health check
2b) Mechanical
2c) Sample holder
2d) Vacuum
2e) Performance check
2f) Optimum settings
2g) System configuration
2h) Energy calibration
2i) Intensity repeatability and intensity/energy response function (IERF)
2j) Linearity test
2k) Spatial resolution
2l) Charge compensation
2m) Depth resolution
2n) Depth

Most of this should be part of regular calibration/monitoring and the computer should already have the necessary details. For the experiment in hand, it will know the ***correct settings for detectability, imaging, chemical state, charge compensation***, etc. It will also know if it is ***up to the job*** or to advise management to a) send the work out or b) buy a new instrument. Of course, in different laboratories the ES computer and the data capture computer may or may not be the same item. If they are not, there will need to be well defined, standard interfaces between control and ES at relevant hardware and software levels.

If the analyst ***decides not to use*** the computer's suggestion, it should log that and start to offer the new option but reminding the analyst that it is doing it under sufferance.

The computer will also know which ***previous similar samples*** were analysed and the extent to which the instrument was then in calibration. This is critical for ***data mining***. By

considering ***historical data***, the computer can propose an experiment, conduct an analysis of the data and obtain better quality results than an analysis in isolation. The recorded data then need to have the analysis and data processing, as well as the ancilliary information, in relevant ***data fields***, so that interrogation may proceed. If the data processing is done separately, this may need linking so that a proper ***audit trail*** is available.

## (6) Existing Knowledge of the Sample

It is important to categorise the existing knowledge of the sample in a structured way that is computer searchable. What is important here depends on theme area "B".

### (6.a) Sample descriptors - ISO 14975: "Surface chemical analysis – Information formats" gives:

- **the basic composition and elements from the identifiers** [with examples of entries]:

  *host_material* = In Ga As or ultra-thin metal layer on a thick $SiO_2$ layer on Si [a generic text description]
  *IUPAC_chemical_name* = polyethylene
  *chemical_abstracts_registry_number* = 9002-88-4
  *host_material_composition* = C2H4 [text of principal elements]
  *bulk_purity* = 99.5mass%
  *known_impurities* = O_0.3mass%, N_0.1mass%
  *structure* = crystal type and orientation, fracture surface, phase information, crystal size, crystal texture, layering, particulates, etc

- **and the form**:

  *homogeneity* = homogeneous, inhomogeneous or unknown
  *crystallinity* = amorphous, or single crystal (100), or poly or unknown.
  *material family* = metal, inorganic, organic, polymer, semi, bio, composite, super conductive, etc
  *special material class* = rod, sheet, single film, multi film, sintered, wafer, powder, fibre, etc
  *ex-situ prepara*tion = polished, cleaved, FIB, powder compact, acetone degrease, etc

The **form** should also include the sample roughness. This may be in terms of the rms roughness or in terms of the distribution of the tilts of the local surface planes about the average surface or in terms of selected classes, which may affect the

- geometry for analysis
- charge neutralisation
- quantification
- resolution attainable

The classes of roughness could be, for example:

wafer flatness < 1 nm
polished metals < 1 μm
flat < 100 μm
rough > 100 μm

We may see that there are selected classes one should also categorise which would **map across other ISO standards**. For instance, for sample **charge neutralisation**, one needs to know if the sample is a conductor or insulator and also the liabilty to degrade. Degradation may be deduced from the *material family* although some inorganic salts (e.g. oxidants, explosives, etc) may degrade.

- **stability** - is the sample stable in vacuum?
  does it have known stability problems? is it explosive, photo- or electron sensitive?
  is it likely to degrade during analysis?

- **health hazard** - assessment etc for regulatory or other health hazard to personnel or for contamination of the instrument

**(6.b) How the sample arrived at the analyst**

This may affect the analysis. Important information is given in **ISO(Draft) 18117: "Surface chemical analysis – Handling of specimens prior to analysis"**:

- **contamination -** has the sample been:
  **cleaned** by
  - a solution likely to remove the surface or alter it, such as Decon 80
  - a solution to remove hydrocarbon such as isopropyl alcohol
  - a solution to remove water soluble inorganic compounds
  - a method likely to remove particulates
  - a physical method likely to remove specific parts of the surface

  **coated** to reduce charging
  **covered** with colloidal metal for charge referencing

  [Subsequent to the workshop, Dr. G. Speranza proposed that it could be useful in some applications to select a solvent for surface cleaning which contained an element that could be tracked by XPS. For example, the chlorine photoelectron signal could be used to quantify the amount of residual solvent on an organic chlorine-free sample following cleaning with trichlorethylene.]

- **transportation**: in what did the sample arrive?
  - argon sealed container
  - vacuum vessel
  - glass
  - Fluoroware
  - plastic bag
  - handkerchief
  - immersed in oil or other liquid

**ISO 18117**, in draft, contains information about the way samples should be supplied to meet certain requirements. Table 1 from that standard illustrates this:

**Table 1 – Minimum handling methods and sample containers for different popular categories of information sought**

| Information sought | | Handling method | | Sample container | |
|---|---|---|---|---|---|
| **Clause** | **Information** | **Clause** | **Method** | **Clause** | **Container** |
| 4.7.1 | Specimens at analysis are to be as close to original condition as possible. | 6.5.1 | Clean non-magnetic, uncoated stainless steel or specialty tools only, handled using latex, powder-free, silicone-free gloves. | 7.3.1<br>7.3.2 | Two flat samples, face-to-face, sealed with PTFE tape. Ar or $N_2$ glove box or vacuum transfer vessel. |
| 4.7.2<br>4.7.3<br>4.7.4 | Hydrocarbon and molecular analysis (e.g. static SIMS and XPS analyses). | 6.5.2 | Clean non-magnetic, uncoated stainless steel tweezers or grippers only, handled using latex, powder-free, silicone-free gloves. | 7.3.3<br>7.3.4<br>7.3.5<br>7.3.6<br>7.3.7 | Clean glass with glass or clean Al foil stopper. High quality polypropylene wafer holder (N.B. avoid polyethylene spider inserts). |
| 4.7.5<br>4.7.6<br>4.7.7 | Other surface adsorbed layers. | 6.5.3<br>6.5.4 | Powder-free, silicone-free, latex gloves holding sample by edge. Powder-free polyethylene disposable gloves holding sample by edge. | 7.3.8<br>7.3.9<br>7.3.10 | Clean Al foil. Polyethylene box or bag. |
| 4.7.8<br>4.7.9<br>4.7.10<br>4.7.11 | Buried interfaces, fracture specimens. | 6.5.5<br>6.5.6 | Clean tools, hand held (no gloves). Acid-free, lint-free paper to hold specimen by edge. | 7.3.11 | Acid-free, lint-free, paper. |

### (6.c) Sample Cleaning and Handling

Depending on the experiment to be done by *theme group B*, the data may indicate that a good solvent or water wash is needed before analysis [Procedure needed]. Reducing the contamination may lead to greater ease of interpretation, better signal quality and, in depth profiles, may lead to better depth resolution. Cleaning may lead to longer instrument life.

- **instrument health** system contamination of the sample by:
  - oil
  - sputter deposit of insulating films
  - charging of fragments of sample
  - wear of moving parts by hard or insulating powder fragments

### (6.d) Prior analysis/ Use of Several Methods

The sample history includes prior analysis of the sample and, if so,

- if coatings have been deposited
- if there has been radiation which may contaminate or remove the surface
- if there has been any contact, e.g. a stylus, which may remove or deposit surface layers.

If there is a need to use several methods, the choice of which method to use first is important and depends on:

- analyses on *different samples* – do the quickest and cheapest first to inform the other methods
- analyses on *different regions of the same sample* – use any involving sputtering last and those in air first
- analyses on the *same regions of the same sample* – use any involving sputtering last but presently needs a case by case consideration.

Other likely methods:

**Form** – Scanning electron microscopy (SEM), Atomic force microscopy (AFM), stylus profilometry
**Surface composition** – Auger electron spectroscopy (AES), Secondary ion mass spectrometry (SIMS)
**Optical measurements** – microscopy, Fourier transform infra-red spectroscopy (FTIR)
**Bulk composition** – Electron probe microanalysis (EPMA), Laser ion mass analysis (LIMA).

## (7) Ensuring that the Instrument is Performing Reliably - Calibration

The following topics need to be covered, either by calibration within the due date or at the time of analysis:

**(7.a) System health check** - reference sample of Au for:

- X-ray source efficiency – advise remaining life
- X-ray ghosts – advise on problems in interpretation
- X-ray window damage – warning to replace, high backgrounds and contamination
- detector setting – adjust or signal levels will drift and quantification will be in error - advise on remaining life
- overall performance check
- internal scattering – higher pass energy and narrower slits?

**(7.b) Mechanical** - Sample stage X, Y and Z movements as well as tilt, etc – tilt needs to be defined from the spectrometer axis. A 1% error in thickness requires an effective tilt angle at $60^o$ known to $0.3^o$. The system needs to be able to check with the input data that the experiment required is feasible – it may advise, for example, that ARXPS is not possible as the sample is too large.

**(7.c) Sample holder** – calibration of any effects of the sample holder, cell type, sample temperature setting – any controlled heating or adventitious heating from ion flux or X-ray gun

**(7.d) Vacuum -** For reactive samples or sputter depth profiling, the vacuum quality and the sputtering gas purity need to be verified.

**(7.e) Performance check -** Performance versus energy resolution, spatial resolution and depth resolution – the system will have settings for the best achievable but the analyst may

need good repeatability, rather than the limits of performance – i.e. good signal levels at modest resolution.

**(7.f) Optimum settings** - sensitivity versus energy resolution (may not need the best energy resolution but adequate and giving the best accuracy or best precision, depending on requirement – three basic settings

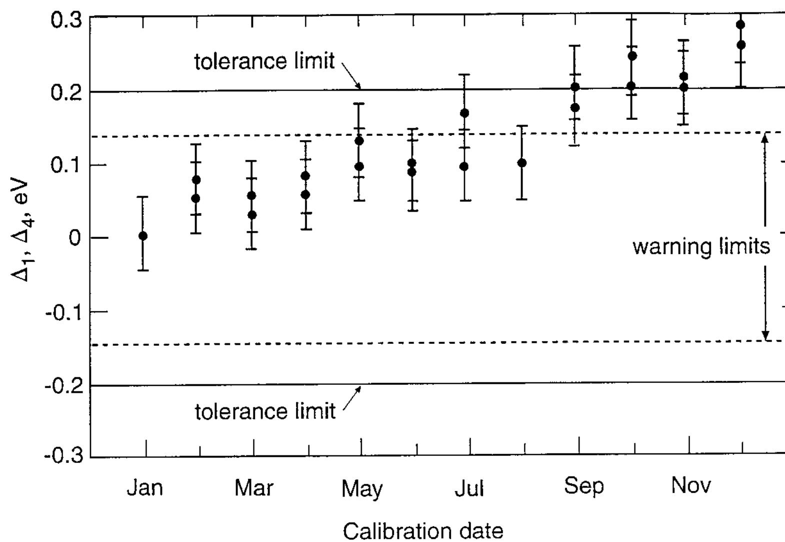
- chemical state – better resolution but not necessarily the best
- quantification – medium resolution
- detectability – poorer resolution

**(7.g) System configuration** for different basic types of experiment

- survey scan
- low level detection or discrimination for quality control
- samples that degrade
- insulators
- samples requiring Auger parameter (need for bremsstrahlung)

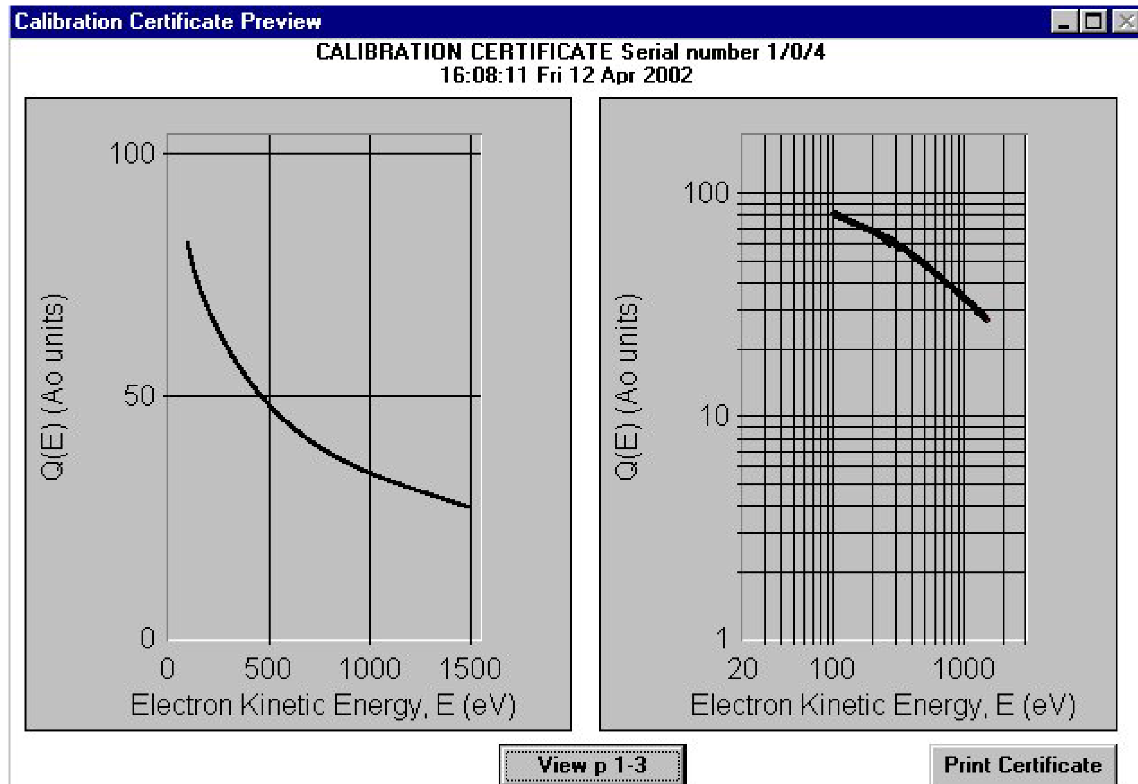
**(7.h) Energy calibration – ISO 15472: "Surface chemical analysis – XPS – Calibration of energy scales"**, needs to be used with reference samples of Au and Cu, to enable the calibrations to be made – users need to know what tolerance, $\pm\delta$, they require for their work for, say, quantitative analysis ($\delta_Q$) and for chemical state analysis ($\delta_{CS}$) if these are done with different conditions. The calibration needs a control chart and call up log. Ideally the instrument does this automatically.

The tolerance $\delta_{CS}$ will depend on the instrument capability and the time that the analyst has to do the work. Results are generally limited by drift:



**(7.i) Intensity repeatability and intensity/energy response function (IERF) - ISO 24237: "Surface chemical analysis – XPS – Repeatability and constancy of the intensity scale"** using Cu enables the intensity repeatability and constancy to be tracked for each mode used. This is essential for consistent quantification. The NPL system for calibrating the IERFs of spectrometers, http://www.npl.co.uk/npl/cmmt/sis/x1calib.html, also does this as well as diagnoses sample–to-sample repeatability, ghosts and cross-talk of the anodes, internal scattering, etc, automatically.

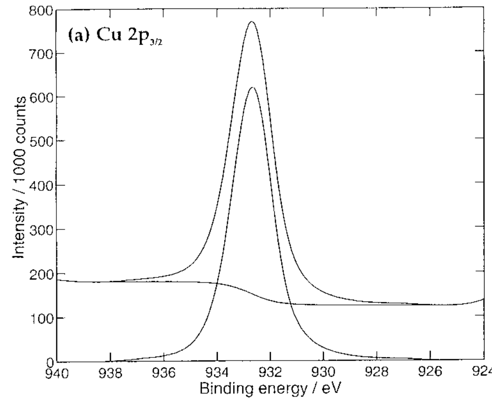
This also gives the IERF as an analytical function and graphical output:



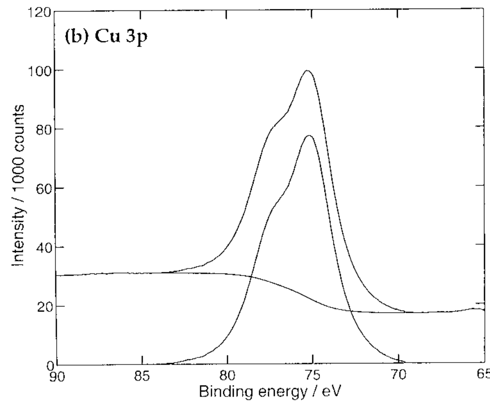

From a knowledge of the **repeatability** one can provide optimum conditions for the **detection** of any element at any level.

**Intensity repeatability and intensity/energy response function (IERF) - ISO 24237: "Surface chemical analysis – XPS – Repeatability and constancy of the intensity scale"**
ISO 24237 uses the Cu $2p_{3/2}$ and 3p peaks with specified minimum signal levels:

Cu $2p_{3/2}$




Cu 3p




Example calculated and measured repeatabilities for the conditions of the standard are:

**Table 1 — Calculated RSDs [%] for the Cu $2p_{3/2}$ and 3p peaks for intensities required and for the number of points to average, *t*, at the end points**

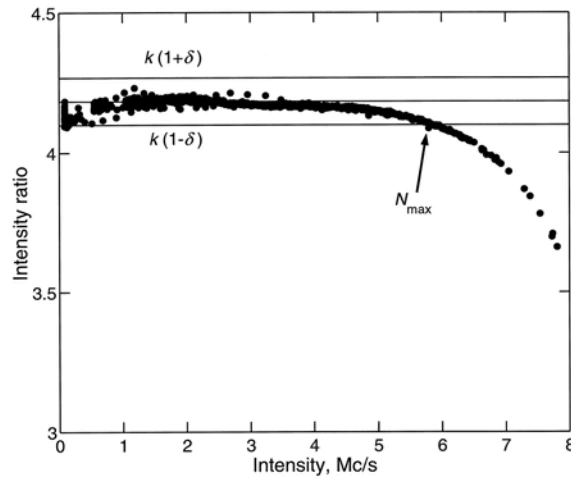
| Peak parameter | *t* | | |
|---|---|---|---|
| | 1 | 3 | 11 |
| $2p_{3/2}$ | 0.19% | 0.11% | 0.06% |
| 3p | 0.58% | 0.34% | 0.19% |
| ratio $3p/2p_{3/2}$ | 0.61% | 0.36% | 0.20% |

**Table 2 — The Measured RSDs**

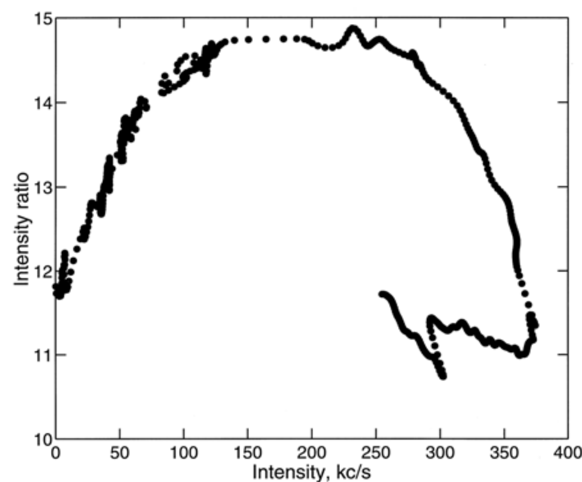
| Peak parameter | *t* | | |
|---|---|---|---|
| | 1 | 3 | 11 |
| $2p_{3/2}$ | 0.17% | 0.13% | 0.18% |
| 3p | 0.65% | 0.33% | 0.12% |
| ratio $3p/2p_{3/2}$ | 0.78% | 0.40% | 0.24% |

**(7.j) Linearity test – ISO 21270: "Surface chemical analysis – X-ray photoelectron and Auger electron spectrometers – Linearity of intensity scale"**, allows the linearity to be defined, relevant corrections to be applied and maximum counting rate established for a given, chosen, linearity level

Two examples of the method show, in one case, how to correct for dead time so that the 2% linearity limit of 1.5 Mc/s is raised to 6 Mc/s but, in the other that the 2% limit is hit at 12 kc/s, with no possibility of correction.




Ratio data, corrected for dead time, at source emission currents of 20 mA and 5 mA, showing the ±2% acceptability limits of divergence from linearity.




Ratio measurements for a different spectrometer, not corrected for dead time, at source emission currents of 200 mA and 25 mA.

**(7.k) Spatial resolution** for analysis - **ISO 19319: "Surface chemical analysis – AES and XPS – Determination of lateral resolution, analysis area, and sample area viewed by the analyser"** provides details of many methods for both aligning spectrometers and for evaluating the spatial resolution. Analysts need the sensitivity versus spatial resolution to set the optimum information content for selected area/image analysis

**(7.l) Charge compensation** for insulators - **ISO 19318: "Surface chemical analysis – X-ray photoelectron spectroscopy – Reporting of methods used for charge control and charge correction"** provides details of many methods, e.g:

**Methods of charge control** [we need to know about stability and conductivity for these]

- *Electron Flood Gun*
- *Ultraviolet Flood Lamp*
- *Specimen heating*
- *Electrical Connection*
  - *Grounding and enhanced conduction path*
  - *Isolation from ground*
  - *Biasing*
- *Low-Energy Ion Source*

**Methods of charge correction**

- *Adventitious Hydrocarbon Referencing* [contamination source?]
- *Gold Deposition*
- *Implantation with Inert Gases*
- *Internal Referencing* [do we know an element in the surface layer in a known state?]
- *Substrate Referencing* [is this a thin film on a known substrate?]

We also need advice concerning if these methods work directly or with special settings for:

- flat samples
- powders
- degradable samples

**(7.m) Depth resolution** – evaluate requirements for depth resolution versus speed of profiling, optimise settings and calibration of the sputtered area for
– choice of ion beam energy and angle of incidence for best depth resolution or for fastest profile or compromise
- calibration of alignment and sputtered area for each energy needed
- sample rotation speed

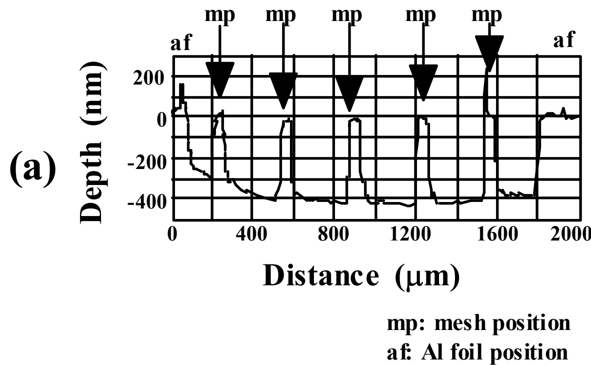
**ISO 20341: "Surface chemical analysis SIMS – Method for estimating depth resolution parameters with multiple delta-layer reference materials**" provides a useful description of the constituent parts of the resolution function. CRMs BCR 261 [$Ta_2O_5$ on Ta] and NIST 2135 [Ni/Cr multilayers] allow helpful characterisation.

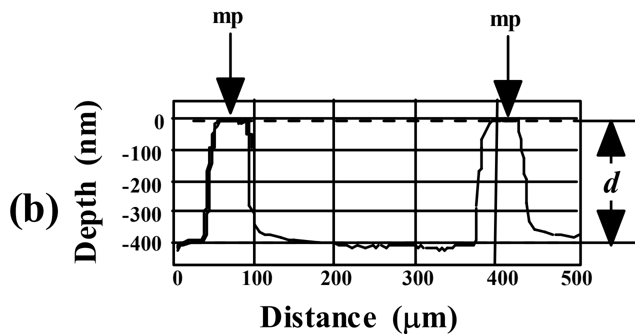
**(7.n) Depth – ISOTR 15969: "Surface chemical analysis – Sputter depth profiling – Measurement of sputtered depth"** provides details of many methods

**Annex A: Survey of typical applications and uncertainties of the different methods**

| Sub-clause | Method / Tech | Typical application | | Uncertainty | |
|---|---|---|---|---|---|
| | | **Depth, nm** | **Material / Remarks** | **nm** | **%** |
| 4.1.2 | Stylus | 100 − 10 000 | Hard | 5 | 1−5 |
| | AFM | 2 − 700 | Hard | 2 | 2 |
| 4.1.3 | Optical interf | 200 − 5 000 | Polished, reflective | 10 | 0,2−5 |
| | Confocal laser | 10 − 500 000 | Non transparent | 10 | 2 |
| 4.2.2 | RM | 2 − 500 | – | 2 | 2 |
| 4.2.3 | Angle lapping | 100 − 50 000 | Hard | 5 | 1−5 |
| | Crater edge | 20 − 10 000 | – | 2 | 1−10 |
| | Ball cratering | 500 − 50 000 | Hard, layered structures, thick films | 20-dep on interf roughness | 3−7 |
| 4.2.3 | XTEM | 10 − 1 000 | – | 0,2 | 1 |
| | Cross section SEM | 10 − 300 000 | Change in at no., contamination problems | 5–10 | 2 |
| 4.2.3 | RBS | 100 − 30 000 | – | 5–20 | 5–20 |
| 4.2.3 | EPMA and EDS | 5 – 1000 | – | 2–20 | 5 |
| 4.2.3 | XRF | 100 – 100 000 | – | 10–10 000 | 10 |
| 4.2.3 | GIXR | 1 − 1 000 | – | 0,1 | 1 |
| 4.2.3 | Ellipsometry | 1 – 5 | Non transparent | 0,1–1 | 1 |
| | | 1 – 10 000 | Transparent | 0,1–1 | 1 |
| 4.2.3 | Chemical analysis | 10 – 100 000 | – | 1–10 | 5–10 |

**ISO 22335: "Surface chemical analysis – Depth profiling – Measurement of sputtering rate, mesh replica method with the use of mechanical stylus profiler"** provides details of one method for depth.




Analysts need calibrations of **sputtered depth**, **optimisation of sputtering** with regard to sample position; angle of incidence, ion type, energy and gas flow rate, minimum area sputtered consistent with the depth measurement and depth resolution they require. Other methods use a Faraday cup and a **CRM or RM** such as $Ta_2O_5$ or $SiO_2$.

**(7.o) Software** – It is assumed here that the software has all the necessary functions and that these have been validated [software has been found with significant faults – see JES 95 (1998) 71-93]. The software will set up experiments correctly, identify all elements in the spectrum and then quantify them correctly, as discussed in the other theme areas.

**(8) Calibration Matrix**

The following calibrations are needed to obtain meaningful data or to optimise the instrument for the best data in the time available. The ticks show the calibrations required for different applications.

| Parameter | ISO | Chemical state | Low level Detection | Quant-ification | Layer thickness | Nano-structure |
|---|---|---|---|---|---|---|
| **BE** | **15472** | XX | | X | | X |
| **Intensity (I) repeatability & constancy** | **24237** | | XX | XX | X | X |
| **I/E response function** | **NPL** | | | XX | X | XX |
| **Linearity** | **21270** | X | | XX | X | XX |
| **Energy resolution versus intensity** | own procedure | X | XX | X | X | X |
| **Ion gun & Sputter rate** | **15969 22335 CRM BCR261** | | | | XX | XX |
| **Depth resolution** | **CRM BCR261 NIST2135** | | | | XX | XX |
| **Spatial resolution** | **19319 18156** | | | | X | XX |
| **Sample Stage** | own procedure | | X | X | XX | X |

**X = generally important, XX = generally very important**

**(9) Summary of ISO standards**

Details of the ISO standards and technical reports (TRs) referred to in this theme follow. Those with a date are currently available from ISO. The drafts (D = draft) are in progress.

**ISO 14975:2000**: "Surface chemical analysis – Information formats"

**ISO(D) 18117**: "Surface chemical analysis – Handling of specimens prior to analysis"

**ISO 15472:2001**: "Surface chemical analysis – XPS – Calibration of energy scales"

**ISO(D) 24236**: "Surface chemical analysis – XPS – Repeatability and constancy of the intensity scale"

**ISO(D) 21270**: "Surface chemical analysis – X-ray photoelectron and Auger electron spectrometers – Linearity of intensity scale"

**ISO TR(D) 19319**: "Surface chemical analysis – AES and XPS – Determination of lateral resolution, analysis area, and sample area viewed by the analyser" (ISO Technical Report)

**ISO(D) 18156**: "Surface chemical analysis – AES and XPS – Determination of lateral resolution"

**ISO(D) 19318**: "Surface chemical analysis – X-ray photoelectron spectroscopy – Reporting of methods used for charge control and charge correction"

**ISO TR 15969:2002**: "Surface chemical analysis – Sputter depth profiling – Measurement of sputtered depth" (technical report)

**ISO(D) 20341**: "Surface chemical analysis SIMS – Method for estimating depth resolution parameters with multiple delta-layer reference materials"

**ISO(D) 22335**: "Surface chemical analysis – Depth profiling – Measurement of sputtering rate, mesh replica method with the use of mechanical stylus profiler"

## (10) Issues discussed in detail in Theme A

Important to have efficient interrogation of the analyst without requesting too much information

1) Gain as much information of the sample as easily as possible.

a) Is this sample:
- one of a set?
- one sample but similar to previous samples?
- one isolated sample?

b) Sample description minimum set requires

items for analysis
- elements
- form
- stability

items for charge neutralisation
- conductivity

items for contamination
- hazards
- transport and history

c) How did samples arrive?
- prehistory
- transport

d) Sample cleaning and handling
- inspect, simple wash if hydrocarbons or particulates need removal

e) Prior analysis
- information on the sample
- loss of required information

f) Order of analysis
- same or different regions of sample

2) Calibrations are all required but *tolerances* need to be decided by user allowing for time and equipment capability

3) All items need updates from the output from other themes

## (11) Theme A, CONCLUSIONS

**(11.a)** The Expert System needs to **operate at different levels**: at least an administrator and a user level. There will be many forms of the expert system at different levels of integration. One may envisage (a) a paper-based ISO-type guide, (b) a computer-based equivalent with a question and answer basis, (c) a computer-based system interrogating the data-capture computer, and (d) a fully integrated system.

**(11.b**) The Expert System **development needs to be phased**. Start with simple, well-established aspects so that it moves forward in a visible and constructive way.

**(11.c) K.I.S.S**. [keep it simple, stupid]

**(11.d) Existing Knowledge of the Sample**

1a) Sample descriptors
1b) How the sample arrived at the analyst
1c) Sample cleaning and handling
1d) Prior analysis/ use of several methods

Though some ISO14975 items are not clearly defined, provided we list what needs to be in there, in free-form text, an intelligent programme can parse it. There are a number of items that need inclusion:

**Items of form** – these need to include the size and thickness of the sample. Classes of sample roughness, which need to be set-up so as to match the requirements of those dealing with charge neutralisation, quantification, etc in other theme areas.

**Form for analysis**: a description of the form also needs to be included in text or as an image, preferably both before and after an analysis. It also needs a log of areas exposed to radiation during analysis (Theme B?). Aspects of form can be captured as a digital image of the sample on the sample holder, so that specific areas that are analysed or irradiated are tracked and visual changes monitored. **As comprehensive an audit trail as practicable is required.**

**Stability** is an important descriptor, and here a procedure could be to analyse the most sensitive elements first in narrowscan, followed by the widescan. The narrowscans could be recorded as a "virtual depth-profile" (also a consideration for Theme B – and a potential rule). Degradation of samples is important, but is presently unknown as there is no single, coherent database. Therefore advice cannot be given from the existing fields. ISO18327 should be extended with an informative annex listing classes or materials and any knowledge of degradation. Classes which may degrade are: polymers, LB layers etc.

**(11.e) Prior Analysis/ Use of several methods**

If other analytical methods are used an ES should flag a warning that the surface may not be the original surface unless the technique is a low power optical inspection method. Prioritise analytical methods.

**(11.f) Ensuring that the Instrument is Performing Reliably – the calibration matrix**

| Parameter | ISO | Chemical state | Low level Detection | Quant-ification | Layer thickness | Nano-structure |
|---|---|---|---|---|---|---|
| **BE** | **15472** | XX | | X | | X |
| **Intensity (I) repeatability & constancy** | **24237** | | XX | XX | X | X |
| **I/E response function** | **NPL** | | | XX | X | XX |
| **Linearity** | **21270** | X | | XX | X | XX |
| **Energy resolution versus intensity** | own procedure | X | XX | X | X | X |
| **Ion gun & Sputter rate** | **15969 22335 CRM BCR261** | | | | XX | XX |
| **Depth resolution** | **CRM BCR261 NIST2135** | | | | XX | XX |
| **Spatial resolution** | **19319** | | | | X | XX |
| **Sample stage x, y and z; orientation of spectrometer, etc; and angular resolution for ARXPS** | own procedure | | X | X | XX | X |

**X = generally important, XX = generally very important**

The calibrations listed above were all considered to be essential. We should aim to recommend that these calibrations are dealt-with by the expert system at **three monthly intervals** scheduled into quiet time in instrument usage. In version 1 of the ES the **top five** items are seen as the most common priorities. The remaining four may be left to a later version. Linearity was seen as a **critical issue for CCD-based instruments**.

**(11.g) Performance Checks and Calibrations** – here for simplicity, a single reference sample of Ag is recommended for:

- X-ray source efficiency – advise remaining life
- X-ray window damage – warning to replace, high backgrounds and contamination
- detector setting – adjust or signal levels will drift and quantification will be in error - advise on remaining life
- internal scattering – higher pass energy and narrower slits?
- Performance versus energy, spatial and depth resolutions – the system will have settings for the best achievable but the analyst may need good repeatability, rather than the limits of performance – i.e. good signal levels at modest resolution.

**(11.h) Binding Energy Calibration**

At the same time as the BE calibration, when Au is being used, test for X-ray ghosts and cross talk.

**(11.i) Charge compensation** for insulators - **ISO 19318: "Surface chemical analysis – X-ray photoelectron spectroscopy – Reporting of methods used for charge control and charge correction"** provides details of many methods. However instruction is needed, perhaps in a new standard, to allow the user to check neutralisation and the stability of peaks with time, shifts with grounded or floating holders, etc. – part of Theme area B.