Evaluating an Analytical TEM with the NIOX™ Test Specimen
Product No. 650

NiO Film Thickness **t** = 65nm nominal, C film thickness ≈25nm, Mo-grid thickness ≈25µm (200 mesh)

This specimen consists of a thin film of NiO deposited onto amorphous carbon and supported by a 200-mesh molybdenum grid. It allows diagnostic measurements on a TEM, as listed below.

CALIBRATION OF TEM CAMERA LENGTH AND OBJECTIVE-APERTURE ANGLE

The NiO film is a fine-grained polycrystal and gives a diffraction pattern consisting of sharp rings. Since NiO has the NaCl cubic crystal structure, the interplanar spacing d_{hkl} corresponding to each ring (Miller indices h,k,l) is $a/(h^2+k^2+l^2)^{1/2}$ with a = 0.417nm. For the first six rings:

h k l	d_{hkl}(nm)	D_{hkl}/D_{111}	Intensity
111	0.2408	1.000	strong
200	0.2085	1.155	strong
220	0.1474	1.634	strong
311	0.1257	1.915	medium
222	0.1204	2.000	medium
400	0.1043	2.31	weak

Bragg's law and the definition of camera length L give: $\lambda/d_{hkl} = \theta = D_{hkl}/2L$, where θ is the scattering angle in radians and D_{hkl} the ring diameter corresponding to the *hkl* ring, so that:

$$d_{hkl}\, D_{hkl} = 2\,\lambda L$$

Here, λ is the electron wavelength, obtainable from TEM textbooks or from the table below:

E_0(keV)→	80	100	120	150	200	300	400
λ (nm) →	0.00418	0.00370	0.00335	0.00296	0.00251	0.00197	0.00164

The product $d_{hkl}D_{hkl}$ can be calculated for several rings and should be nearly constant; its average value, divided by 2 λ, is the camera length L. Alternatively, D_{hkl} plotted against d_{hkl} should give a straight line, whose slope (2λL) provides a value of camera length.

Any systematic variation in the product $d_{hkl}D_{hkl}$ indicates barrel or pincushion distortion in the diffraction pattern. A difference in the diameter of a particular diffraction ring, measured in two perpendicular directions, indicates axial astigmatism of the pattern. On some microscopes, this astigmatism can be corrected by intermediate-lens stigmators whose controls are adjusted to make the rings as nearly circular as possible.

An objective aperture can be calibrated in terms of the limited scattering angle ß (for quantitative EELS) by inserting it during the recording of a diffraction pattern, whose camera length (in mm) is L. If D_{ap} is the diameter (in mm) of the outline of the aperture, ß (in mrad) = 500(D_{ap}/L).

EDX MEASUREMENTS

The test specimen may be inserted with **either** the film or the grid side upwards (inside the TEM). In the latter case, X-rays generated by scattered electrons striking a grid bar are minimized but care should be taken that the detector elevation angle and/or specimen tilt towards the detector are large enough, so that there is no shadowing of the detector by the grid. Use the microscope X and Y shifts to **roughly center** the specimen about the optic axis. Record an EDX spectrum from a clean area of film which is close to the **center of a grid square**, using a condenser aperture in the range 20-57μm diameter and a 20-200nm diameter focused probe. The spectrum should show characteristic peaks at energies of 851 eV (Ni-Lα), 2.29 keV (Mo- Lα), 7.47 keV (Ni-Kα), 8.26 keV (Ni-Kß) and 17.42 keV (Mo-Kα). A light-element detector should also reveal peaks at 525 eV (O-K) and 227 eV (C-K).

Calibration of the energy scale

The energy axis of the EDX spectrum can be calibrated using two of the above peaks, for example the Ni-Kα (7.47keV) peak and either the Ni-Lα (851eV) or the O-K (525eV) peak.

Energy resolution and peak shape

The detector resolution Δ(Mn) is usually defined in terms of the width of a Mn Kα peak. However, the Ni-Kα peak is close in energy and its full width at half maximum FWHM(Ni) can provide an estimate of resolution:

$$\Delta(Mn) \approx 0.926\ FWHM(Ni)$$

The factor of 0.926 makes allowance for the change in peak width with energy, based on measurements from several detectors [1]. For a light-element detector, the width FWHM(Ox) of the O-K peak is typically a factor of 1.6 lower than FWHM(Ni). For these measurements, the spectrum should be recorded at a low count rate (small fractional deadtime) and sufficient acquisition time to give good statistics. For accuracy, use an energy dispersion of no more than 10 eV/channel and subtract an estimate of the background level from the total counts/channel when evaluating peak height and half-height.

The ratio of full width at tenth maximum (FWTM) to FWHM provides a measure of peak shape, and is typically about 2.0 at the Ni-Kα peak (for an ideal Gaussian peak, the ratio would be 1.83). Larger values may indicate peak tailing, due to incomplete charge collection for example.

Test for shadowing of the detector by the specimen holder or by grid bars

Keeping the beam near the center of a grid square, record spectra with the specimen tilted towards the EDX detector through angles of $\theta = 30°$ (if permitted by the polepiece design), 20°, 10° and 0°. Since the projected thickness of the specimen is proportional to $1/\cos\theta$, there should be a small ($\approx$15%) decrease in signal as θ is reduced. A more substantial decrease suggests shadowing of the detector by a grid bar or the edge of the specimen holder. Subsequent measurements should be based on spectra recorded at the lowest angle which avoids this shadowing.

Measurements of stray electrons and X-rays in the TEM column

From the EDX spectrum, measure the Ni-Kα/Mo-Kα count ratio R(Ni/Mo). A simple way of doing this is to integrate the total number of counts T within a 600eV energy window centered about each peak and make allowance for the background B under the peak by taking B as the sum of the counts within two 300eV windows on either side, where the background is flat. Then:

$$R(\text{Ni/Mo}) = [T(\text{Ni-K}\alpha)-B(\text{Ni-K}\alpha)]/[T(\text{Mo-K}\alpha)-B(\text{Mo-K}\alpha)]$$

High R(Ni/Mo) denotes a "clean" column; values are typically in the range 3 to 7 for a modern conventional TEM [1]. Note that the value of R may be misleading if molybdenum condenser apertures are used; such apertures can usually be identified from the presence of a Mo-Kα peak in the spectrum recorded with no TEM specimen.

Predominant character of the column radiation

Measure the Mo-Kα/Mo-L intensity ratio $R_{K/L}$, making an allowance for the background under the Mo-Kα and Mo-L peaks. If X-rays are the main source of column radiation, $R_{K/L}$ will have a high value, of the order of 100. If high-energy stray electrons are predominant, $R_{K/L}$ is much lower, typically in the range 1 to 10; measurements with electrons directly incident on a grid bar gave the following values (for a takeoff angle of 30°):

E_0(keV) $\rightarrow$	80	100	120	140	160	180	200
$R_{K/L}$ **for Incident Electrons**	1.6	2.6	3.9	5.3	6.9	7.6	8.6

$R_{K/L}$ decreases slightly as the specimen is tilted towards the detector (increasing takeoff angle.)

Total EDX background

In addition to bremsstrahlung X-rays produced by the incident probe, the background beneath a characteristic peak contains contributions from column X-rays and electrons outside the probe, and from the EDX electronics. Peak/background ratio is a measure of the overall "cleanliness" of the EDX system and was defined by Fiori [2] as total number of *characteristic* counts in a particular peak divided by the number of *background* counts in a 10eV region at the center of the peak. If the background $\mathbf{B}$(Ni-Kα) is integrated over 600 eV, rather than 10 eV as specified in the definition, the Fiori peak/background ratio at the Ni-Kα peak is:

$$P/B_{10} = 60[\mathbf{T}(\text{Ni-Kα})-\mathbf{B}(\text{Ni-Kα})]/[\mathbf{B}(\text{Ni-Kα})]$$

For 100-200kV accelerating voltage, P/B_{10} should be at least 1000, with modern instruments giving a value closer to 3000 [1]. At 300 keV, values as large as 6000 have been measured [7]. Theoretical values, calculated assuming a bremsstrahlung background given by a modified Bethe-Heitler formula [8] and parameterized Ni-K ionization cross sections [9], are listed below:

E_0(keV) $\rightarrow$	100	200	300	400
P/B_{10} $\rightarrow$	4460	6250	7340	8170

Low values of P/B_{10} can result from stray column radiation generating bremsstrahlen in thick regions of the specimen (e.g. grid bars) or the specimen holder, from the EDX system electronics or from ground loops.

Estimate of EDX detector solid angle

For this test, the EDX spectrum must be recorded for a known lifetime (τ seconds) and with a known probe current of $\mathbf{I}$ picoamps. The probe current can be measured by connecting a picoammeter to:
(a) a Faraday cup, as incorporated into some analytical specimen holders, *or*
(b) an electrically isolated TEM screen, if the meter reading is multiplied by a factor of 1.3 to allow for backscattering from the screen, *or*
(c) the electrically-isolated flight tube of a serial- or parallel-recording energy-loss spectrometer, with the spectrometer power supply off.

Assuming negligible absorption of Ni-Kα photons in the specimen and the detector window, the collection solid angle of the EDX detector (in sterad) is given by:

$$\Omega = 4\pi\eta \approx C_1 \cos ծ \; [\mathbf{T}(\text{Ni-Kα})-\mathbf{B}(\text{Ni-Kα})]/(\text{t } \tau \text{ } \mathbf{I})$$

where η is the geometrical photon-collection efficiency, ծ is the specimen-tilt angle and $\mathbf{t}$ is the NiO film thickness in nm on page 1. C_1 is a coefficient which takes into account the Ni-K ionization cross section, fluorescence yield and fraction (0.88) of emitted K-radiation within the Kα peak [1]; it depends on the incident-electron energy E_0 as follows:

E_0(keV) $\rightarrow$	80	100	120	200	300	400
C_1 $\rightarrow$	2.6	2.9	3.2	4.0	4.8	5.3

Collection efficiency at low photon energy

In the case of a light-element EDX detector, the total-absorption factor f_{tot} for O-K X-rays (in the specimen, detector window, front coating and dead layer of the detector) is:

$$f_{tot} = \eta(Ox)/\eta = C_2 [\mathbf{T}(Ox)-\mathbf{B}(Ox)]/[\mathbf{T}(Ni\text{-}K\alpha)-\mathbf{B}(Ni\text{-}K\alpha)]$$

where the coefficient C_2 is a ratio of oxygen-K and Ni-K cross sections and fluorescence yields:

$E_0(keV)$ $\rightarrow$	80	100	120	200	300	400
$C_2 \rightarrow$	1.49	1.56	1.59	1.68	1.70	1.72

Note that f_{tot} does not require a measurement of beam current; typical values are 0.3 [1]. The absorption factor f_{det} for the detector alone can be estimated as:

$$f_{det} = f_{tot} / f_{spec}$$

if allowance is made for the fractional absorption f_{spec} of oxygen X-rays within the specimen, typically ≈ 0.9 but given approximately by:

$$f_{spec} \approx \exp(-\mu L \approx \exp \frac{-t/2}{367 \sin(\theta + \varnothing)}$$

where t is the specimen thickness in nm, σ is the specimen tilt towards the detector and $\varnothing$ is the detector elevation angle above the horizontal plane.

Check for contamination or icing of the detector

Both hydrocarbon and ice buildup on the detector (or its protective window) will decrease the collection efficiency for Ni-Lα (870eV) photons and increase the Ni-Kα/ Ni-Lα ratio, defined by:

$$R(K/L) = [\mathbf{T}(Ni\text{-}K\alpha)-\mathbf{B}(Ni\text{-}K\alpha)]/[\mathbf{T}(Ni\text{-}L\alpha)-\mathbf{B}(Ni\text{-}L\alpha)]$$

Ice is relatively ineffective at reducing the O-K signal because the photon energy (525eV) is below the O K-absorption edge (535eV). Therefore the Ni-Kα/O-K ratio, measured as:

$$R(Ni/O) = [\mathbf{T}(Ni\text{-}K\alpha)-\mathbf{B}(Ni\text{-}K\alpha)]/[\mathbf{T}(O\text{-}K)-\mathbf{B}(O\text{-}K)]$$

is more affected by carbonaceous layers. If $R_0(K/L)$ and $R_0(Ni/O)$ are the values of these ratios measured for a *clean* detector (soon after installation or after thermal treatment of the detector), while $R_t(K/L)$ and $R_t(Ni/O)$ are the values measured *for the same specimen tilt* when ice and/or carbon contamination is present, the thickness $\mathbf{t}$[ice] and $\mathbf{t}$[C] of ice and carbon are given **in nm** by:

$$\mathbf{t}[ice] \approx 1850 \ln[R_t(K/L)/R_0(K/L)] - 532 \ln[R_t(Ni/O)/R_0(Ni/O)]$$

$$\mathbf{t}[C] \approx 485 \ln[R_t(Ni/O)/R_0(Ni/O)] - 87 \ln[R_t(K/L)/R_0(K/L)]$$

These equations assume that the layer thicknesses are insufficient to appreciably absorb the higher-energy Ni-Kα X-rays, that the hydrocarbon layer is predominantly carbon and that the linear absorption coefficients (in cm^{-1}) are 1022 (at 525 eV) and 5696 (at 870 eV) for ice 21720 (at 525 eV) and 6240 (at 870 eV) for carbon [4]. The magnitudes of $\mathbf{t}$[ice] and $\mathbf{t}$[C] give an indication of the severity of the contamination problem; their ratio may indicate a possible remedy [6].

EELS MEASUREMENTS

Energy-axis calibration

The NiO specimen can be used for E-axis calibration in electron energy-loss spectroscopy. The oxygen K-edge occurs at 533 eV and the nickel L-edge at 854 eV if measured at the point of maximum slope; the energy separation (321 eV) can therefore be used to calibrate the energy dispersion, without need to record the low-loss region. Alternatively, the position of the first (white-line) maximum at the nickel L-edge can be taken as 853.2eV relative to the zero-loss peak.

Test of elemental quantification procedure

A measurement of the areas I_L^{Ni} and I_K^{O} under the nickel-L and oxygen-K edges provides a measure of the Ni/O atomic ratio and a test of EELS quantification procedure. The energy-loss spectrum should be recorded with known values of incident energy E_0 and collection semiangle β. If the spectrum is acquired in TEM image mode (an image of the specimen on the viewing screen), the value of β is determined by an objective aperture, which can be calibrated by reference to the diffraction pattern as described below. Power-law backgrounds can be fitted over regions (about 100eV wide) preceding the edge and the core-loss intensity (above background) integrated over an energy range Δ (conveniently taken as 100 eV) directly following each edge. The nickel/oxygen ratio should be close to unity, as determined from:

$$\frac{[Ni]}{[O]} \approx \frac{I_L^{Ni}}{I_K^{O}} \frac{\sigma_K^{O}(\beta, \Delta, E_0)}{\sigma_L^{Ni}(\beta, \Delta, E_0)}$$

where the nickel-L and oxygen-K cross sections can be calculated using a hydrogenic model [5]. Measurements in four laboratories have given Ni/O atomic ratios in the range 0.92 to 1.06 [1].

[1] J. C. Bennett and R. F. Egerton, NiO Test Specimens for Analytical Electron Microscopy: Round Robin Results. J. Microsc. Soc. Amer. (1995)
[2] S. M. Zemyan and D. B. Williams. Standard Performance Criteria for Analytical Electron Microscopy. Journal of Microscopy 174 (1994) 1-14.

[3] R. F. Egerton and S. C. Cheng, Characterization of an Analytical Electron Microscope with a NiO Test Specimen. Ultramicroscopy 55 (1994) 43-54.

[4] K. Wong and R. F. Egerton, The Performance of Analytical Electron Microscopes and EDX Systems. Proc. 53rd Ann. Meet. Microsc. Soc. Amer. (1995)

[5] R. F. Egerton, EELS in the Electron Microscope (Plenum, New York, 1986).

[6] P. Hovington, G. L'Esperance, E. Baril and M. Rigaud, A Standard Procedure for the Modeling of the Decrease in Detection Efficiency with Time for Low-Energy EDS Spectra. Microbeam Analysis 2 (1993) 277-288.

[7] C. E. Lyman, private communication.

[8] J. N. Chapman, C.C. Gray, B.W. Robertson and W.A.P. Nicholson, X-ray Production in Thin Films by Electrons with Energies between 40 and 100 keV. X-ray Spectrometry 12 (1983) 153-162.

[9] N. J. Zaluzek, K- and L-shell Cross Sections for X-ray Microanalysis in an AEM. Analytical Electron Microscopy – 1984 (ed. D. B. Williams and D. C. Joy, San Francisco Press, 1984) 279-284.

Disclaimer

The NIOX test specimen is intended for diagnostic measurements on a TEM. Its purpose is to assist the user in the setup and evaluation of such an instrument. The specimen is not intended as a calibration standard and no warranty is provided in terms of performance or accuracy of the test specimen.

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