Designation: E 902 – 94 (Reapproved 1999)

Standard Practice for Checking the Operating Characteristics of X-Ray Photoelectron Spectrometers[1]

This standard is issued under the fixed designation E 902; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers a procedure for checking some of the operating characteristics of an X-ray photoelectron spectrometer. Tests herein provide checks of the following instrument characteristics: X-ray photoelectron spectroscopy (XPS) signal intensity, background, energy resolution, short-term voltage stability, transmission, and energy scale linearity. It is meant for spectrometers with digital storage of counts in energy channels.

1.2 *Limitations*—This practice is meant to augment, and not to replace, the calibration procedures recommended by the manufacturer of the spectrometer. This practice is also not meant to be used as a means of comparison between X-ray photoelectron spectrometers, but only as a self-consistent check of the operating characteristics of an individual spectrometer.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 673 Terminology Relating to Surface Analysis[2]

E 1015 Practice for Reporting Spectra in X-ray Photoelectron Spectroscopy[3]

E 1078 Guide for Specimen Handling in Auger Electron Spectroscopy, X-ray Photoelectron Spectroscopy, and Secondary Ion Mass Spectrometry[2]

3. Terminology

3.1 *Definitions*—Terms used in X-ray photoelectron spectroscopy are defined in Terminology E 673.

3.2 Additionally, the following terms and abbreviations are used throughout this practice:

c = counts
ch = channel
cps = counts per second
eV = electron volts
i = number of data channels acquired for the peak of interest
n = number of channels
no. = number of
S/B = signal-to-background ratio
sc = span
Δx = step size, eV, between successive data channels
A = peak area above background, mm^2
B = background height, mm
H = maximum peak height above background, mm
I_A = peak area intensity above background, c-eV/s
I_H = maximum signal intensity above background, cps
P = peak position on the binding energy scale, eV
FWHM = full width at half maximum

4. Significance and Use

4.1 This practice should first be used to establish the operating characteristics of a particular X-ray photoelectron spectrometer at a time when the spectrometer performance is known to be optimum. Hence, the spectrometer settings in Section 5 and the expected performance figures given in Section 7 are to be taken only as guides, to be supplanted by the behavior of the user's actual spectrometer.

4.2 Subsequently, this practice should be used as a routine check, performed at frequent intervals with the same instrument settings, and the results compared with those obtained in 4.1. Significant deviation from optimum performance may indicate that the spectrometer requires recalibration or other maintenance.

4.3 Typical analysis settings should be used with this practice. The use of settings not specified by this practice is left to the discretion of the user, however, the settings should be recorded in accordance with Practice E 1015 and the same settings should be used consistently whenever this practice is repeated, so that the results obtained will be directly comparable to previous results.

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[1] This practice is under the jurisdiction of ASTM Committee E-42 on Surface Analysis and is the direct responsibility of Subcommittee E42.03 on Auger Electron Spectroscopy and XPS.

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[2] *Annual Book of ASTM Standards*, Vol 03.06.

[3] Discontinued. See 1994 *Annual Book of ASTM Standards*, Vol 03.06.

5. Procedure

5.1 Obtain a clear copper specimen (~99.9 % purity) with a smooth, flat surface; a foil is preferred. This specimen should be larger than the analysis area of the spectrometer (the analysis area being defined as either the area viewed by the analyzer or the area of illumination of the X-ray beam, whichever is smaller). The three recommended cleaning methods are as follows: (*1*) Etch the specimen in a 1-M HCl solution for 5 min with constant stirring or ultrasonic agitation, followed by a rinse in distilled water; (*2*) clean the specimen with metal polish, or (*3*) abrade the specimen with No. 600 silicon carbide in a nitrogen atmosphere, taking care that the technique is carefully reproduced each time.

5.1.1 The choice of cleaning method will depend on the specimen dimensions, ease of handling, and availability of the necessary cleaning supplies.

5.1.2 After cleaning the specimen by one of these three methods, rinse the specimen in ethanol or a similar solvent.

5.1.3 Guide E 1078 recommends additional specimen handling precautions that may be required.

5.2 Mount the copper specimen at the usual specimen position in the spectrometer, and in electrical contact with the specimen holder.

5.3 Use an ion sputter gun to clean the specimen until the C1s and O1s peak heights above background are each less than or equal to 10 % of the Cu 3p peak height above background. If sputtering is not available, the intensities of the C1s and O1s peaks may exceed 10 % of the Cu 3p peak; in this case, record the C1s and O1s peak heights above background.

5.4 Set and record the anode material, excitation potential, emission current, any leakage current, anode height (if adjustable), specimen tilt, and the pass energy or slit widths. Use typical analysis settings. For all spectra, choose at least ten data channels per electron volt and adjust the time per point and number of sweeps to meet the counting criteria noted in 5.5-5.7. Record these settings in a manner consistent with Practice E 1015 and use them exactly the same way each time the spectrometer is checked.

5.5 Acquire and store the photoelectron spectrum of the Cu 2p doublet between 963 and 923 eV, with enough scans to collect at least 10 000 counts at the peak maximum.

5.6 Acquire and store the photoelectron spectrum of the Cu 3p doublet between 86 and 66-eV binding energy, with enough scans to collect at least 5000 counts at the peak maximum.

5.7 If using Mg X-rays, acquire and store the spectrum of the Cu $L_3M_{4,5}M_{4,5}$ Auger line between 340 and 330 eV (Note 1) on the binding energy scale. If using Al X-rays, acquire and store the spectrum of the Auger line between 573 and 563 eV on the binding energy scale (Note 1). In either case, acquire enough scans to collect at least 10 000 counts at the peak maximum.

NOTE 1—For instruments where the minimum scan width is larger than recommended, use the minimum allowable scan width. For instruments where the energy interval cannot be set up in integer steps, use the closest allowed energy.

6. Treatment of Data

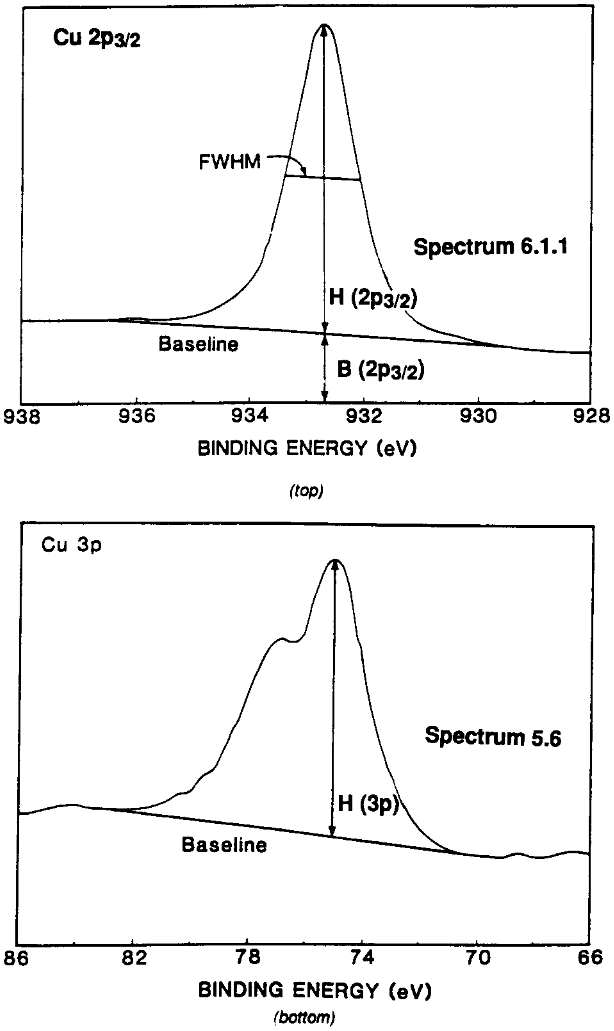
6.1 Print or plot the spectra as obtained in 5.5-5.7. In addition:

6.1.1 Print or plot the Cu $2p_{3/2}$ line between 938 and 928-eV binding energy.

6.1.2 Print or plot the Cu $3p_{3/2}$ line between 78.5 and 73.5-eV binding energy.

6.2 *For Spectra* 5.6 *and* 6.1.1—If a computer can be used to measure the peak and background, fit the background with a linear baseline, as shown in Fig. 1, and record I_H and the endpoints. If a linear background fit is not available, an alternate background shape (for example, an integral background) may be used, however, this background may change the signal intensity. Whichever background shape is chosen, the same background shape and endpoints should be used whenever this practice is repeated. Also measure B (Note 2) for each spectrum, as shown in Fig. 1.

NOTE 2—Some data-processing software packages automatically suppress the background, either when the data is collected or when it is



(top)

(bottom)

NOTE 1—Spectral lines obtained in accordance with procedures in 5.6 (bottom) and 6.1.1 (top) illustrating the data treatments described in 7.1-7.3.

FIG. 1 Spectral Lines

displayed. The user should ensure that the background has not been altered before making the background measurement. Information about the treatment of backgrounds for a particular instrument can often be obtained by contacting the manufacturer of the software package or indirectly by comparison of computer-acquired data with analog data acquired with the same instrument settings over the same energy range.

6.2.1 If a computer cannot be used to establish the background, draw a linear background, as shown in Fig. 1 and record the energies above and below the peak maximum where the baseline intersects the data spectrum. Measure H, in millimetres, for each spectrum and make note of the counts per millimetre. Also measure B, in millimetres, for each spectrum (Note 2).

6.2.2 If possible, use peak fitting algorithms to measure and record P, in electronvolts, for each spectrum and the FWHM, in electronvolts, for spectrum 6.1.1, as shown in Fig. 1. For an accurate comparison to the standard binding energies of **(2)**, note that the Cu 3p doublet there is fit to a quadratic to the top 10 % of the most intense peak. It must be further noted that a curve fit or peak synthesis routine will likely yield results that differ slightly from that method. Whichever method is chosen, the same method should be used whenever this practice is repeated. If a peak fitting routine is not available, then accurately measure, compute, and record these values from the data outputs of spectra 5.6 and 6.1.1 as shown in Fig. 1.

7. Analysis of Data

7.1 Refer to Section 3 for definitions and abbreviations. For all peaks, record the signal intensity. If this information is not directly available, determine the signal intensity for each peak, j, using one of the following equations:

$$I_{H(j)} = \frac{H(j)\,[c/mm(j)]}{[s/sc(j)][no.\ sc(j)]} \tag{1}$$

or

$$I_{H(j)} = \frac{H(j)\,[c/mm(j)]}{[s/ch(j)]\,[no.\ ch/sc(j)]\,[no.\ sc(j)]} \tag{2}$$

7.2 Determine and record the signal-to-background ratio for the Cu $2p_{3/2}$ line from spectrum 6.1.1 and data treatment 6.2 by:

$$S/B = H(2p_{3/2})/B(2p_{3/2}) \tag{3}$$

For most instruments with conventional X-ray sources, this ratio is typically between 4.0 and 5.0. For spectrometers equipped with monochromatic X-ray sources, this value is expected to be higher. For an abraded sample, this ratio will be expected to be lower because of surface roughness and the effects of greater contamination. A low ratio may indicate detection of excessive stray electrons or insufficient counting speed by the detector.

7.3 The FWHM determined in 6.2.2 is a measure of instrumental resolution and checks for freedom from short-term fluctuations in the voltage supplies that determine the electron kinetic energy. Changes in the FWHM are indicative of a spectrometer that need maintenance or recalibration.

7.4 The area ratio can be used to determine the transmission ratio. The peak area intensity, I_A, for a given peak, j, can be computed by:

$$I_{A(j)} = \frac{A(j)\,[c/mm(j)]\,[eV/sc(j)]}{[s/sc(j)]\,[no.\ sc(j)]\,[mm/sc(j)]} \tag{4}$$

or

$$I_{A(j)} = \frac{A(j)\,[c/mm(j)]\,[eV/mm(j)]}{[s/sc(j)]\,[no.\ sc(j)]\,[no.\ ch/sc(j)]} \tag{5}$$

Record the ratio $I_{A(3p)}/I_{A(2p3/2)}$.

7.4.1 If a computer cannot be used to measure A(j) or $I_{A(j)}$, other methods may be used. One common algorithm utilizes the trapezoidal rule, which reduces to

$$I_{A(j)} = \Delta x \sum_{i=1}^{n} I_{H(i)} \tag{6}$$

where the two endpoints = zero intensity.

7.4.1.1 Whichever method is chosen, it should be used con-sistently, since different methods may give different results.

7.4.2 For an instrument with transmission varying as (kinetic energy)$^{-1}$, the value of $I_{A(3p)}/I_{A(2p3/2)}$ has been determined on several instruments to be approximately 0.1. This value appears to be higher for abraded samples. For instruments with transmission varying as (kinetic energy)$^{+1}$, the ratio will be between 0.7 and 1.0.

7.5 Table 1 which lists some high-accuracy measurements of the copper peak positions (Refs **1-3**).[4] Determine the energy separation between the Cu $2p_{3/2}$ and Cu 3p peaks. It should be 857.5 eV **(4)**. (See Note 3.) This measurement tests the linearity of the power supplies over a wide range of voltages.

NOTE 3—The specific accuracy of the measured Cu $2p_{3/2}$ and 3p peak separations and energies needed for calibration will depend upon the work to be undertaken. For routine work, most spectrometers may be calibrated to better than ±0.1 eV, remain stable for considerable periods of time, and tolerate some variation in sample position. Tighter limits may be achieved with greater difficulty and most spectrometers will not hold ±0.02 eV for long or for a wide variety of specimen types and mounting conditions.

7.6 Also determine the energy separation in the Cu 2p doublet from 5.5 (Note 4) (See Note 3.). It should be 19.80 eV **(4)**. This measurement tests the linearity of the scanning voltage scale.

NOTE 4—It is assumed that the data is acquired in the scanned mode, that is, that the detector is scanned through all energies in the spectrum. For some monochromator-equipped instruments, a clean gold specimen may be used, scanning between 90 and 80 eV. The separation in the Au 4f doublet should be 3.67 eV **(4)**.

7.7 Measure the binding energy of the copper 3p doublet. Compare this value with the 3p binding energy in Table 1. If the binding energies do not match, the offset of the X-ray

TABLE 1 Measured Peak Positions from Sputtered Copper[A]

Peak		Binding Energy, eV		
		Ref **(1)**	Ref **(2)**	Ref **(3)**
Cu $2p_{3/2}$	Al X rays	932.66 ± 0.06	932.67 ± 0.02	...
...	Mg X rays	...	932.66 ± 0.02	932.68 ± 0.07
Cu $L_3M_{4,5}M_{4,5}$	Al X rays	567.97 ± 0.04	567.96 ± 0.02	...
...	Mg X rays	...	334.94 ± 0.01	...
Cu $3p_{3/2}$	Al X rays	...	75.14 ± 0.02	...
...	Mg X rays	...	75.13 ± 0.02	...

[A] The stated uncertainties represent the sum of estimates of random error (one standard deviation) and possible systematic error.

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[4] The boldface numbers in parentheses refer to the references at the end of this practice.

power supplies may have to be adjusted. (For some systems, a change in the voltage offset may be accompanied by a change in the voltage linearity. In such a case, it may be necessary to repeat 7.5 and 7.7 until both conditions are met.) The spectrometer work function can also be used to change the apparent binding energy value. Citation of the specific values used for checking the binding-energy scale will permit convenient adjustment of the reported binding-energy data to a relevant standard when that is available.

8. Conclusion

8.1 Most values obtained in this practice will be characteristic of a particular spectrometer and serve to demonstrate whether the instrument is performing reproducibly. A few data have been provided as a guide to the values to be expected. No attempt has been made here to supply voltage checks or individualized tests that may be supplied by instrument manufacturers.

8.2 These tests are conducted with a single material and have the advantage that accurate placement and treatment of two specimens is unnecessary. For those who wish also to use the Au $4f_{7/2}$ peak to check their instrument, it must be emphasized that reproducible specimen positioning can have an influence on the determination of the relative binding energies measured for two specimens. The values of the Au $4f_{7/2}$ binding energy are reported in Table 2.

9. Keywords

9.1 spectrometer calibration; spectrometer characterization; X-ray photoelectron spectroscopy

TABLE 2 Measured Peak Positions from Sputtered Gold[A]

NOTE 1—The binding energy value for the Au $4f_{7/2}$ peak from Ref **(3)** is significantly larger than those of the other references.

Peak		Binding Energy, eV		
		Ref **(1)**	Ref **(2)**	Ref **(3)**
Au $4f_{7/2}$	Al X rays	83.98 ± 0.02	83.98 ± 0.02	...
...	Mg X rays	...	84.00 ± 0.01	84.28 ± 0.07

[A] The stated uncertainties represent the sum of estimates of random error (one standard deviation) and possible systemic error.

REFERENCES

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