

Enargite by XPS

Marzia Fantauzzi, Davide Atzei, Stefania Da Pelo, Bernhard Elsener, Franco Frau et al.

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Enargite by XPS

Marzia Fantauzzi and Davide Atzei

Department of Inorganic and Analytical Chemistry, University of Cagliari, Cittadella Universitaria Monserrato, Cagliari 09100, Italy

Stefania Da Pelo

Department of Earth Sciences, University of Cagliari, via Trentino 51, Cagliari 09127, Italy

Bernhard Elsener

Department of Inorganic and Analytical Chemistry, University of Cagliari, Cittadella Universitaria Monserrato, Cagliari 09100, Italy

Franco Frau and Piero Franco Lattanzi

Department of Earth Sciences, University of Cagliari, via Trentino 51, Cagliari 09127, Italy

Antonella Rossi

Department of Inorganic and Analytical Chemistry, University of Cagliari, Cittadella Universitaria di Monserrato, Cagliari, Cagliari 09100, Italy

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X-ray photoelectron spectroscopy was used for characterizing the enargite surface. Freshly cleaved samples were analyzed at liquid nitrogen temperature. Enargite is a copper arsenic sulfide of formula Cu_3AsS_4 ; it is used as a minor ore of copper. Enargite is a potential source of arsenic and may create environmental problems through the release of toxic elements upon oxidation. © 2004 American Vacuum Society. [DOI: 10.1116/11.20030801]

Keywords: *x-ray photoelectron spectroscopy; Enargite*

PACS: 82.80.Pv, 91.60.-x

SPECIMEN DESCRIPTION (Accession #00782)

Host Material: Natural enargite (Cu_3AsS_4)

Host Material Characteristics: homogeneous; solid; unknown crystallinity; semiconductor; inorganic compound

Chemical Name: copper arsenic sulfide

Host Composition: Cu_3AsS_4

Form: crystal

History & Significance: The sample is a mineral extracted from mines in Furtei (CA, Italy).

As Received Condition: The sample was received as crystal.

Analyzed Region: flat surface in the "as received" condition (Refs. 1 and 2)

Ex Situ Preparation/Mounting: The sample was mounted as crystal on double sided adhesive tape.

In Situ Preparation: none

Charge Control: Sample charging was constant during analysis. Energy shift was compensated by referencing all the spectra to a C 1s signal taken at 285.0 eV.

Temp. During Analysis: 77.4 K

Pressure During Analysis: $<5 \times 10^{-8}$ Pa

SPECIMEN DESCRIPTION (Accession #00783)

Host Material: Synthetic enargite

Host Material Characteristics: homogeneous; solid; unknown crystallinity; semiconductor; inorganic compound

Accession #s 00782, 00783

Technique: XPS

Host Material: #00782: Natural enargite (Cu_3AsS_4); #00783: Synthetic enargite

Instrument: Vacuum Generators Ltd, East Greenstead, UK Escalab Mark II with upgrade to Escalab 200

Major Elements in Spectrum: Cu, As, S, C, O

Minor Elements in Spectrum: none

Printed Spectra: 8

Spectra in Electronic Record: 20

Spectral Category: comparison

Chemical Name: copper arsenic sulfide

Host Composition: Cu_3AsS_4

Form: powder

History & Significance: The sample is synthetic enargite. It was synthesized at high temperature (500 °C) in sealed silica tubes under vacuum.

As Received Condition: not specified

Analyzed Region: not specified

Ex Situ Preparation/Mounting: The sample was mounted as powder on double sided adhesive tape (Refs. 1 and 2).

In Situ Preparation: not specified

Charge Control: Sample charging was constant during analysis. Energy shift was compensated by referencing all the spectra to a C 1s signal taken at 285.0 eV.

Temp. During Analysis: 77.4 K

Pressure During Analysis: $<5 \times 10^{-8}$ Pa

INSTRUMENT DESCRIPTION

Manufacturer and Model: Vacuum Generators Ltd., East Greenstead, UK Escalab Mark II with upgrade to Escalab 200

Analyzer Type: spherical sector

Detector: Channeltron

Number of Detector Elements: 5

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

■ Spectrometer

Analyzer Mode: constant pass energy

Throughput ($T=E^N$): $N=-0.5$

Excitation Source Window: Al window, foil thickness 1.0 μm

Excitation Source: Al K_{α}

Source Energy: 1486.6 eV

Source Strength: 300 W

Source Beam Size: 12.5 mm \times 12.5 mm

Analyzer Width: 2000 μm \times 5000 μm

Signal Mode: V/F analog

Number of Scans: 1

■ Geometry

Incident Angle: 49°

Source to Analyzer Angle: 49°

Emission Angle: 0°

Specimen Azimuthal Angle: 40°

Acceptance Angle from Analyzer Axis: 0°

Analyzer Angular Acceptance Width: 4° \times 8° at 886 eV

■ Ion Gun

Manufacturer and Model: VG scientific AG 21

Energy: 4000 eV

Current: 0.180

Current Measurement Method: biased stage

Sputtering Species: Ar

Incident Angle: 48°

Polar Angle: 53°

Azimuthal Angle: 85°

Comment: The analyzed area was etched to remove contamination and the oxide layer. Sputtering was performed by back-filling the chamber.

DATA ANALYSIS METHOD

Energy Scale Correction: Calibration of the energy scale was performed according to Ref. 3. For charging correction, C 1s was taken at 285.00 eV.

Recommended Energy-Scale Shift: For all Accession #00782, -1.4 eV; for all Accession #00783, -3.6 eV

Peak Shape and Background Method: Shirley–Sherwood background subtraction, line shape mixed product Gaussian–Lorentzian functions with exponential tails in some cases

Quantitation Method: Surface analysis was based on the areas of the photoelectron peaks using the following equation: $C_i = (I_i/S_i)[\sum_j (I_j/S_j)]^{-1}$, where C_i is the atomic percentage of element i , I_i is the intensity of the photoelectron signal (i.e., the peak area) after subtraction of a nonlinear background, and S_i is the atomic sensitivity calculated using the photoionization cross section of Scofield (Ref. 4), corrected for the angular asymmetry function and for the asymmetry parameter (Ref. 5).

REFERENCES

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4. J. H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* **8**, 129 (1976).
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SPECTRAL FEATURES TABLE

Spectrum ID #	Element/Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
00782-02 ^a	Cu 2p _{3/2}	932.2	1.44	32183	1.44	28	...
00782-03 ^a	As 3d	43.5	1.63	1590	0.17	12.0	...
00782-04 ^a	S 2p	162.1	2.10	7082	0.15	60	...
00783-02 ^b	Cu 2p _{3/2}	932.7	1.43	46068	1.44	33	...
00783-03 ^b	As 3d	43.5	1.64	1855	0.17	12	...
00783-04 ^b	S 2p	162.6	2.44	7929	0.15	55	...

^a Natural Enargite

^b Synthetic Enargite

Comment to Spectral Features Table: The composition listed in item I-6 does not include carbon and oxygen because the concentration is calculated taking into account the attenuation of the emitted electrons due to the presence of the outermost layer constituted of C and O. C and O do not belong to enargite but only to the surface contamination of the sample. Including C and O in the calculation would imply the wrong assumption of homogeneity of the sample.

Footnote to Spectrum 00783-04: Two *s2p* signals were revealed in detailed sulfur spectra. The more intense signal at 162.5 eV can be assigned to sulfur in the sulfide chemical state (formal oxidation state -2). The weak signal at 164.3 eV was assigned to a species with a higher oxidation state.

ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV-cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
00786-01	Ag $3d_{5/2}$	368.10	1.10	1341501
00784-01	Au $4f_{7/2}$	83.93	1.28	982980
00785-01	Cu $2p_{3/2}$	932.67	1.41	2426632
00785-02	Cu <i>LMM</i>	567.96	1.16	380987

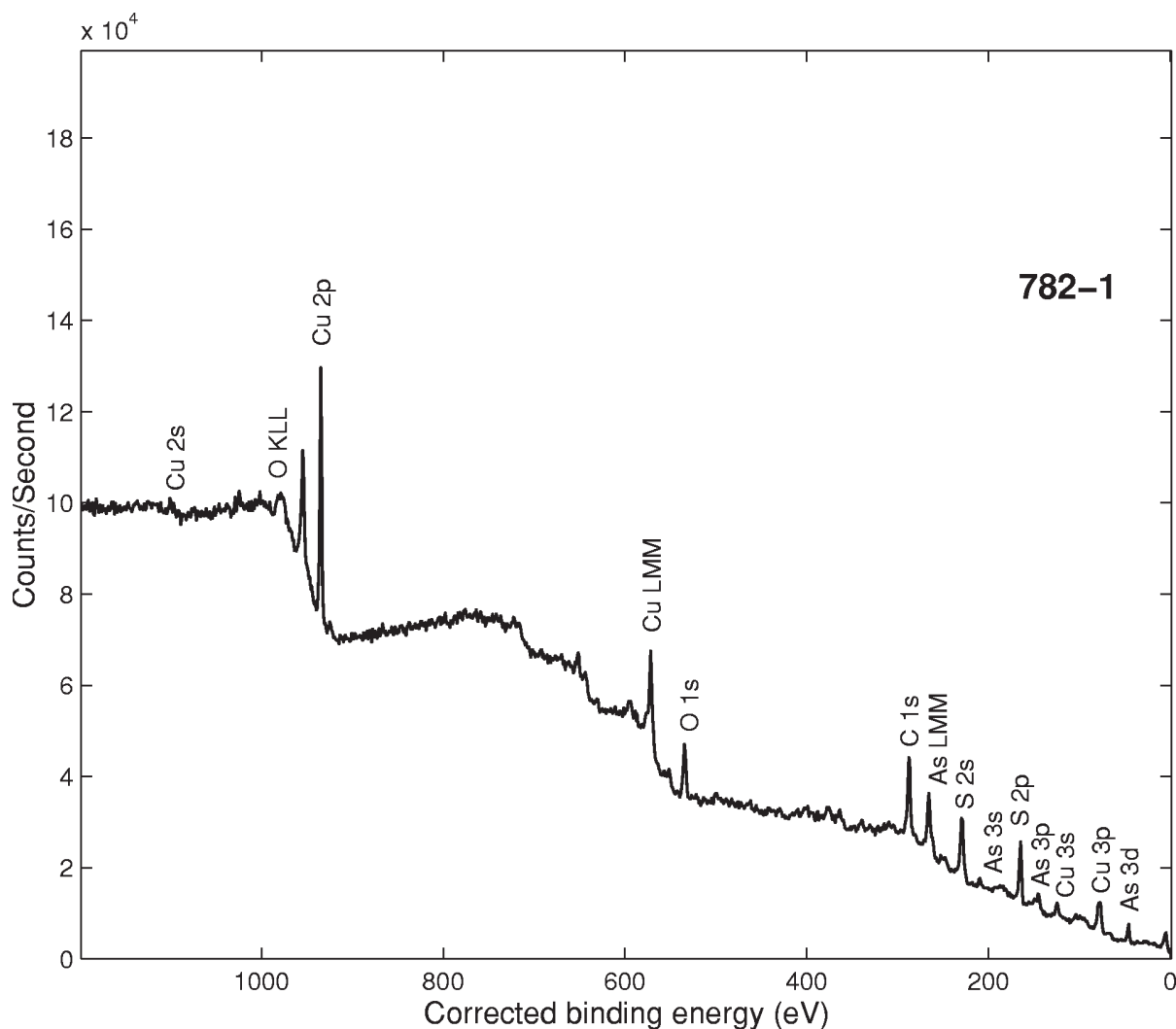
GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift*	Multiplier	Baseline	Comment #
782-1	Survey	+1.4	1	0	
782-2	Cu $2p$	+1.4	1	0	
782-3	As $3d$	+1.4	1	0	
782-4	S $2p$	+1.4	1	0	
783-1	Survey	+3.6	1	0	
783-2	Cu $2p$	+3.6	1	0	
783-3	As $3d$	+3.6	1	0	
783-4	S $2p$	+3.6	1	0	
782-5 [NP]**	Cu <i>LMM</i>	+1.4	1	0	
782-6 [NP]	As <i>LMM</i>	+1.4	1	0	
782-7 [NP]	C $1s$	+1.4	1	0	
782-8 [NP]	O $1s$	+1.4	1	0	
783-5 [NP]	Cu <i>LMM</i>	+3.6	1	0	
783-6 [NP]	As <i>LMM</i>	+3.6	1	0	
783-7 [NP]	C $1s$	+3.6	1	0	
783-8 [NP]	O $1s$	+3.6	1	0	
784-1 [NP]	Au $4f$	0	1	0	1
785-1 [NP]	Cu $2p$	0	1	0	1
785-2 [NP]	Cu <i>LMM</i>	0	1	0	1
786-1 [NP]	Ag $3d$	0	1	0	1

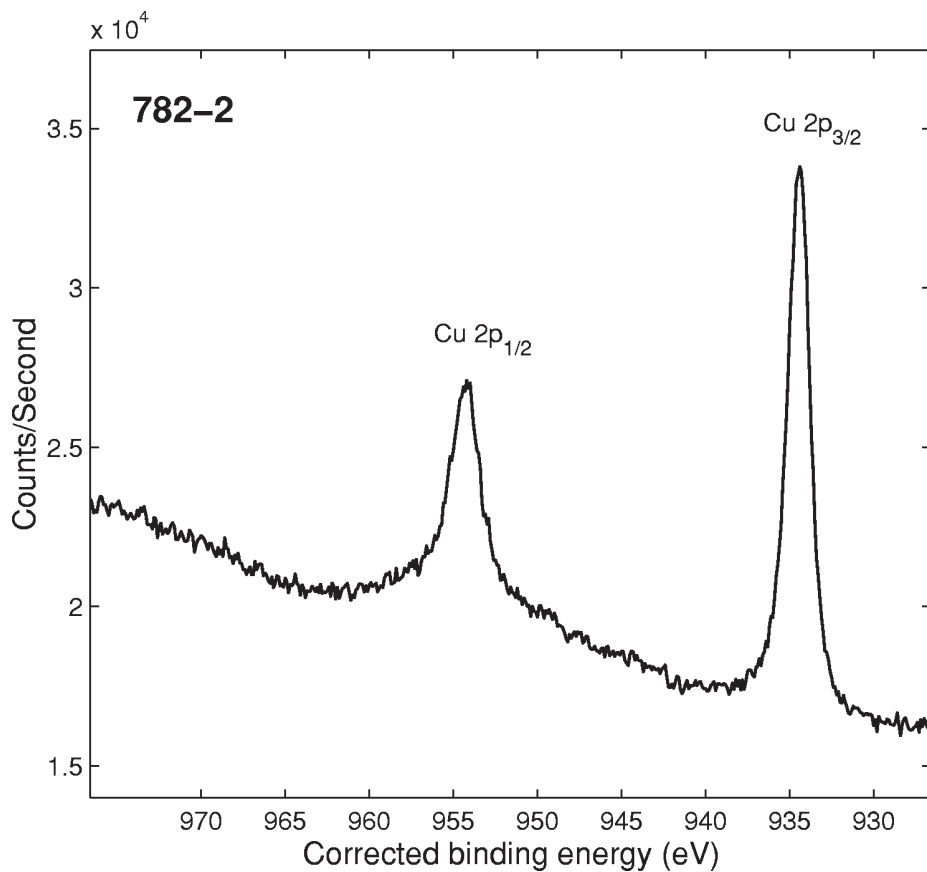
* Voltage shift of the archived (as-measured) spectrum relative to the printed figure. The figure reflects the recommended energy scale correction due to a calibration correction, sample charging, flood gun, or other phenomenon.

** [NP] signifies not published; digital spectra are archived in SSS database but not reproduced in the printed journal.

1. Calibration spectrum



Accession #	00782-01
Host Material	Natural enargite (Cu ₃ AsS ₄)
Technique	XPS
Spectral Region	survey
Instrument	Vacuum Generators Ltd., East Greenstead, UK Escalab Mark II with upgrade to Escalab 200
Excitation Source	Al K _α
Source Energy	1486.6 eV
Source Strength	300 W
Source Size	12.5 mm × 12.5 mm
Analyzer Type	spherical sector
Incident Angle	49°
Emission Angle	0°
Analyzer Pass Energy	50 eV
Analyzer Resolution	1.12 eV
Total Signal Accumulation Time	140.10 s
Total Elapsed Time	140.10 s
Number of Scans	1
Effective Detector Width	1.0 eV



■ **Accession #:** 00782-02
 ■ **Host Material:** Natural enargite (Cu_3AsS_4)
 ■ **Technique:** XPS
 ■ **Spectral Region:** Cu 2p

Instrument: Vacuum Generators Ltd., East Greenstead, UK
 Escalab Mark II with upgrade to Escalab 200

Excitation Source: Al K_α
 Source Energy: 1486.6 eV
 Source Strength: 300 W
 Source Size: 12.5 mm \times 12.5 mm
 Incident Angle: 49°

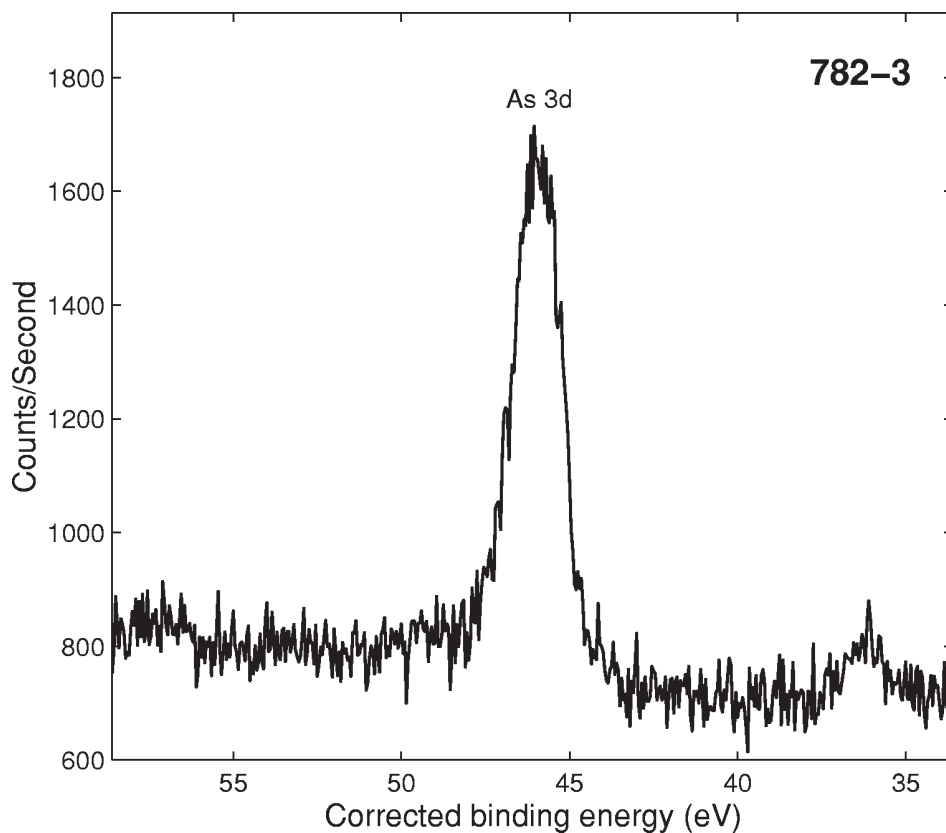
Analyzer Type: spherical sector
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 1.12 eV
 Emission Angle: 0°

Total Signal Accumulation Time: 90.10 s

Total Elapsed Time: 90.10 s

Number of Scans: 1

Effective Detector Width: 0.04 eV



■ **Accession #:** 00782-03
 ■ **Host Material:** Natural enargite (Cu_3AsS_4)
 ■ **Technique:** XPS
 ■ **Spectral Region:** As 3d

Instrument: Vacuum Generators Ltd., East Greenstead, UK
 Escalab Mark II with upgrade to Escalab 200

Excitation Source: Al K_α
 Source Energy: 1486.6 eV
 Source Strength: 300 W
 Source Size: 12.5 mm \times 12.5 mm
 Incident Angle: 49°

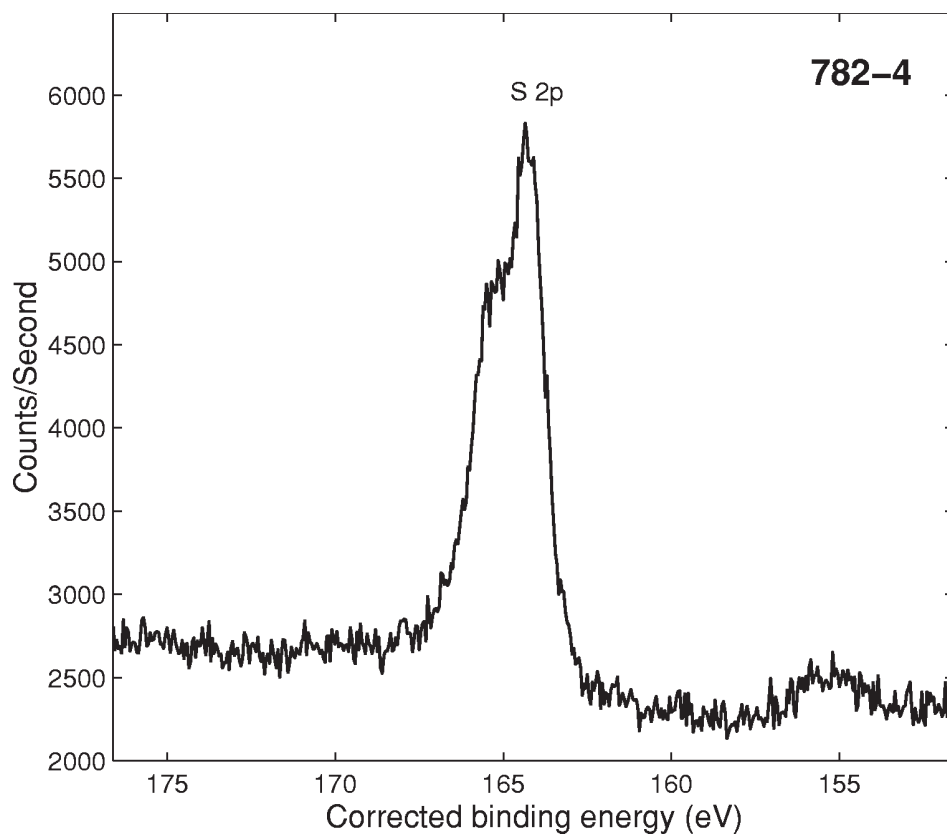
Analyzer Type: spherical sector
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 1.12 eV
 Emission Angle: 0°

Total Signal Accumulation Time: 150.30 s

Total Elapsed Time: 150.30 s

Number of Scans: 3

Effective Detector Width: 0.4 eV



- Accession #: 00782-04
- Host Material: Natural enargite (Cu_3AsS_4)
- Technique: XPS
- Spectral Region: S 2p

Instrument: Vacuum Generators Ltd., East Greenstead, UK
Escalab Mark II with upgrade to Escalab 200

Excitation Source: Al K_α

Source Energy: 1486.6 eV

Source Strength: 300 W

Source Size: 12.5 mm \times 12.5 mm

Incident Angle: 49°

Analyzer Type: spherical sector

Analyzer Pass Energy: 20 eV

Analyzer Resolution: 1.12 eV

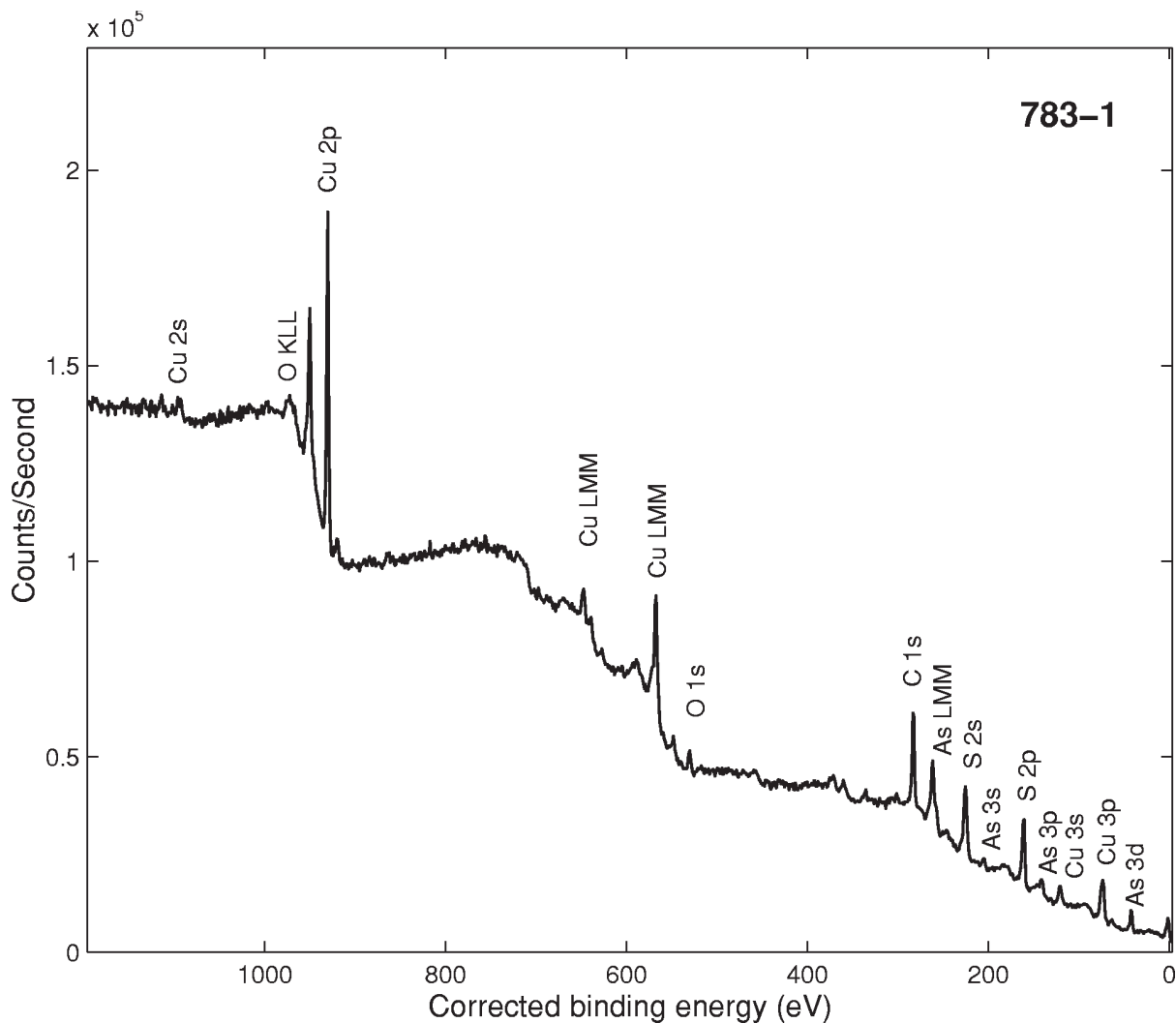
Emission Angle: 0°

Total Signal Accumulation Time: 150.30 s

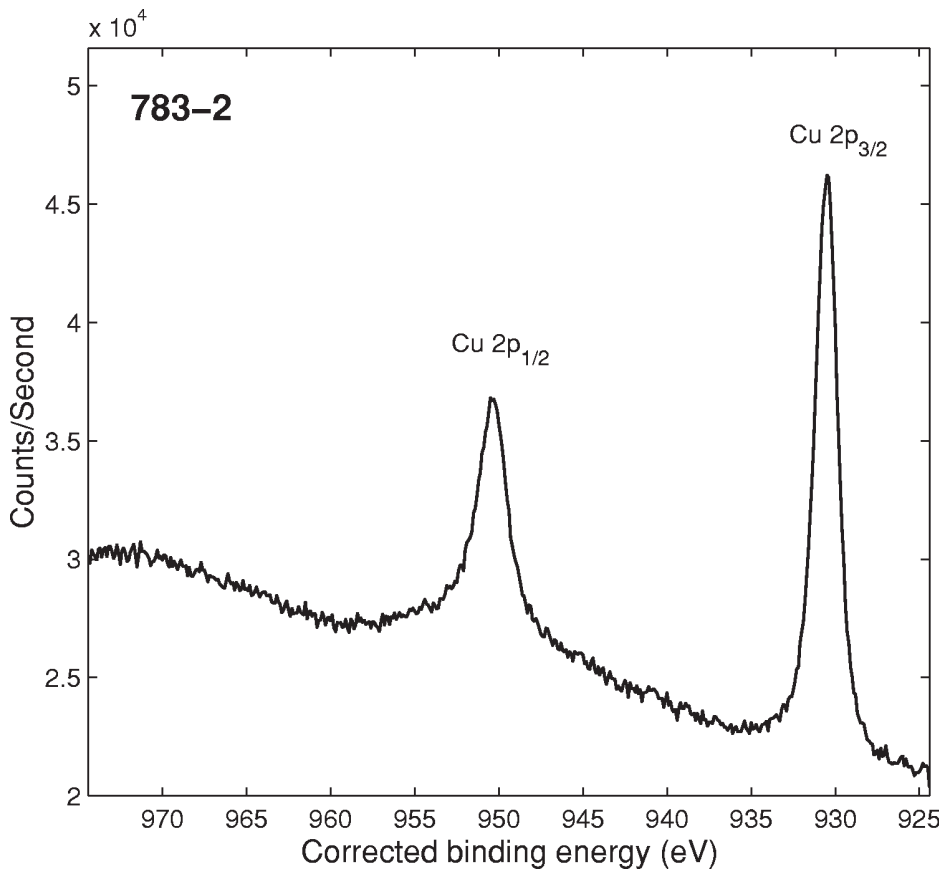
Total Elapsed Time: 150.30 s

Number of Scans: 3

Effective Detector Width: 0.4 eV

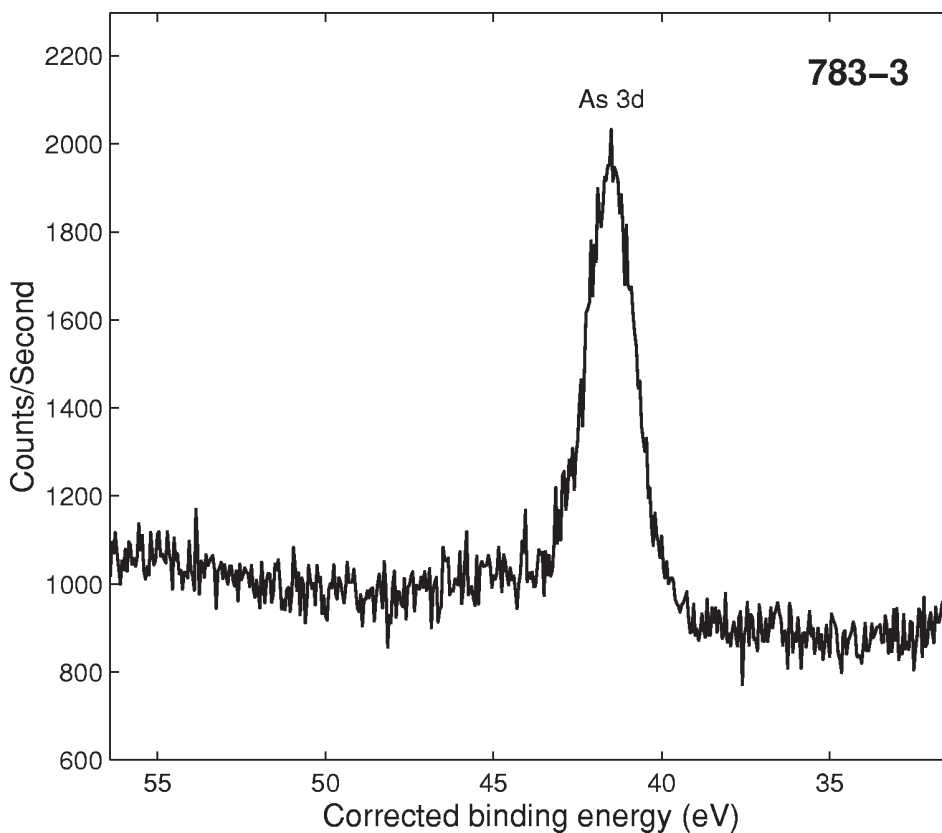


Accession #	00783-01
Host Material	Synthetic enargite
Technique	XPS
Spectral Region	survey
Instrument	Vacuum Generators Ltd., East Greenstead, UK Escalab Mark II with upgrade to Escalab 200
Excitation Source	Al K_{α}
Source Energy	1486.6 eV
Source Strength	300 W
Source Size	12.5 mm × 12.5 mm
Analyzer Type	spherical sector
Incident Angle	49°
Emission Angle	0°
Analyzer Pass Energy	50 eV
Analyzer Resolution	1.12 eV
Total Signal Accumulation Time	140.10 s
Total Elapsed Time	140.10 s
Number of Scans	1
Effective Detector Width	1 eV



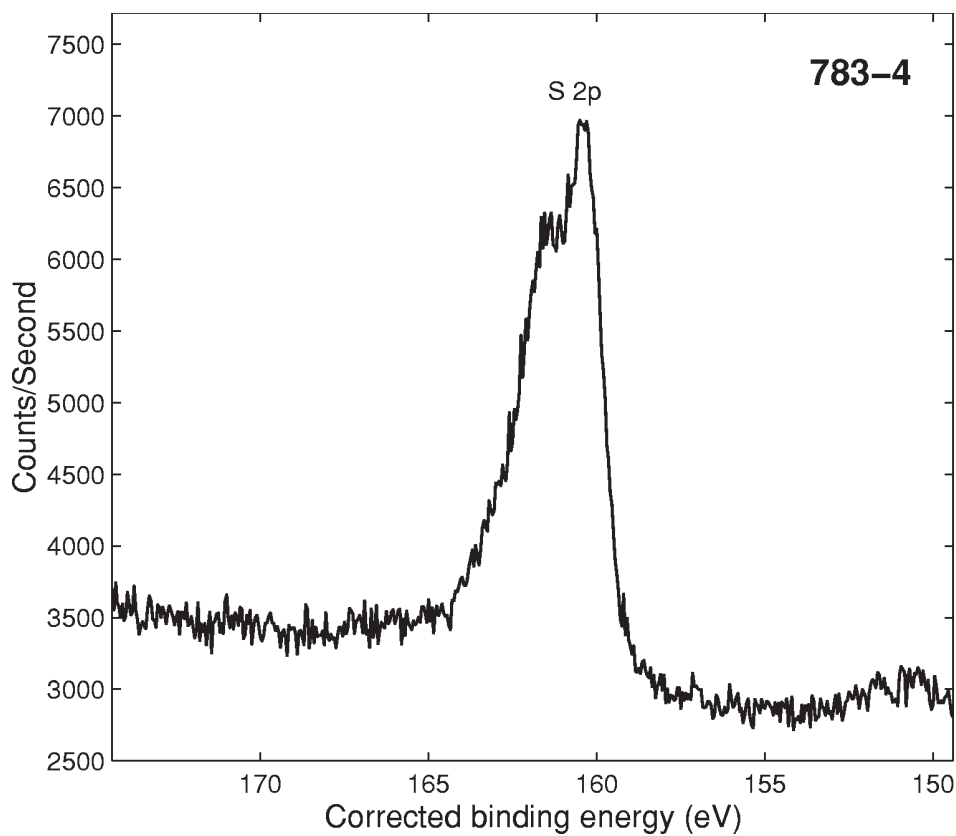
- **Accession #:** 00783-02
- **Host Material:** Synthetic enargite
- **Technique:** XPS
- **Spectral Region:** Cu 2p

Instrument: Vacuum Generators Ltd., East Greenstead, UK
 Escalab Mark II with upgrade to Escalab 200
 Excitation Source: Al K_{α}
 Source Energy: 1486.6 eV
 Source Strength: 300 W
 Source Size: 12.5 mm \times 12.5 mm
 Incident Angle: 49°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 1.12 eV
 Emission Angle: 0°
 Total Signal Accumulation Time: 90.10 s
 Total Elapsed Time: 90.10 s
 Number of Scans: 1
 Effective Detector Width: 0.4 eV



- **Accession #:** 00783-03
- **Host Material:** Synthetic enargite
- **Technique:** XPS
- **Spectral Region:** As 3d

Instrument: Vacuum Generators Ltd., East Greenstead, UK
 Escalab Mark II with upgrade to Escalab 200
 Excitation Source: Al K_{α}
 Source Energy: 1486.6 eV
 Source Strength: 300 W
 Source Size: 12.5 mm \times 12.5 mm
 Incident Angle: 49°
 Analyzer Type: spherical sector
 Analyzer Pass Energy: 20 eV
 Analyzer Resolution: 1.12 eV
 Emission Angle: 0°
 Total Signal Accumulation Time: 150.30 s
 Total Elapsed Time: 150.30 s
 Number of Scans: 3
 Effective Detector Width: 0.4 eV



- **Accession #:** 00783-04
- **Host Material:** Synthetic enargite
- **Technique:** XPS
- **Spectral Region:** S 2p

Instrument: Vacuum Generators Ltd., East Greenstead, UK
Escalab Mark II with upgrade to Escalab 200

Excitation Source: Al K_{α}

Source Energy: 1486.6 eV

Source Strength: 300 W

Source Size: 12.5 mm \times 12.5 mm

Incident Angle: 49°

Analyzer Type: spherical sector

Analyzer Pass Energy: 20 eV

Analyzer Resolution: 1.12 eV

Emission Angle: 0°

Total Signal Accumulation Time: 150.30 s

Total Elapsed Time: 150.30 s

Number of Scans: 3

Effective Detector Width: 0.4 eV

Comment: See footnote below the Spectral Features Table.