Surface Science Spectra

RESEARCH ARTICLE | NOVEMBER 01 2024

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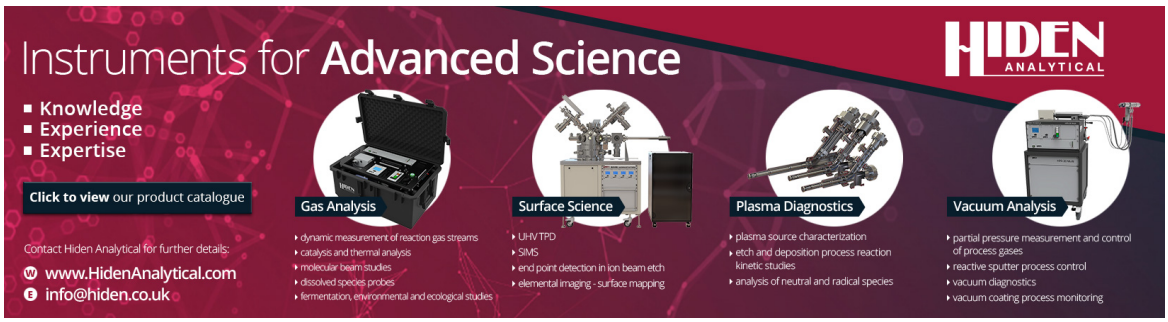
Surf. Sci. Spectra 31, 024008 (2024)
https://doi.org/10.1116/6.0003999



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Core-level spectra of metallic lanthanides: Holmium (Ho)

Cite as: Surf. Sci. Spectra **31**, 024008 (2024); doi: 10.1116/6.0003999
Submitted: 21 August 2024 · Accepted: 15 October 2024 ·
Published Online: 1 November 2024

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ABSTRACT

The core-level spectra for the lanthanide metal, holmium, are presented, including the typically unreported Ho 3*d* peaks. The spectra exhibit multiplet splitting that must be included for accurate quantification of the metallic state. Given the complexity of the spectra due to overlapping Auger structure and background determination, modified sensitivity factors are suggested for some regions, together with recommended background integration limits and shape.

Accession#: 01968
Technique: XPS and XAES
Specimen: Ho
Instrument: Thermo K-Alpha$^+$
Major Elements in Spectra: Ho
Minor Elements in Spectra: None
Published Spectra: 7
Spectral Category: Comparison

INTRODUCTION

The rare earth metal holmium (Ho) is the 11th element in the lanthanide series, with the ground-state electronic configuration [Xe] $4f^{11}$ $6s^2$. Given the reactive nature of metallic lanthanides, they have not been as widely studied as their compounds, with the majority of published data mostly limited to non-monochromatic sources (Ref. 1). Like dysprosium, its neighboring element, holmium exhibits multiplet splitting (Ref. 2) arising from the coupling of the core-hole generated in the low-lying 4*d* orbital with the partly filled 4*f* orbital yielding a final state of the form $4d^9 4f^n$. Despite being a relatively uncommon element presented to most surface analysts, holmium and its compounds find use in diverse fields including optical spectrometer calibration (Ref. 3) and data storage (Ref. 4).

Given its electropositive nature, metallic holmium slowly oxidizes in air to form a native oxide and can react with water to form holmium(III) hydroxide. Such affinity extends also to the halides, forming the respective trihalide. As previously noted (Refs. 2 and 5), maintaining a clean surface for lanthanides to record core-level spectra is difficult. Within this paper, the spectra for clean Ho are presented, which were obtained by light argon sputtering (30 s) between acquisitions. The often-unreported Ho 3*d* peaks are also presented. It is hoped the reported binding energies, modified sensitivity factors, where applicable, and enhanced resolution for the multiplet spitting over those in Refs. 1, 6, and 7 are an aid to improve any analysis on such materials in the future.

SPECIMEN DESCRIPTION (ACCESSION # 01968)

Specimen: Holmium, Ho
CAS Registry #: 7440-60-0
Specimen Characteristics: Homogeneous; solid; polycrystalline; conductor; metal; other
Chemical Name: Holmium
Source: Alfa Aesar
Composition: Ho
Form: Solid dendrite, approximately 40 × 20 mm^2
Structure: Ho

History and Significance: Distilled dendrites 99.9% (REO) grade material obtained from Alfa Aesar.
As Received Condition: Received as distilled metallic dendrites of varying sizes.
Analyzed Region: Elliptical region approximately $400 \times 600\,\mu$m within the approximate center of the etched area.
***Ex Situ* Preparation/Mounting:** Given its malleability, a suitable sized dendrite was sandwiched between aluminum foil and pressed flat using a small sample press to a pressure of 1 tonne. The flattened sample was subsequently polished using isopropyl alcohol and SiC paper (grit size $7\,\mu$m) to obtain a visibly smooth and shiny surface. After further rinsing with alcohol and drying under nitrogen, the sample was attached to a metallic sample plate using copper clips before insertion into the spectrometer load lock.
***In Situ* Preparation:** Argon ion sputtering
Charge Control: None
Temp. During Analysis: 298 K
Pressure During Analysis: 3.31×10^{-7} Pa
Pre-analysis Beam Exposure: 30 s

INSTRUMENT DESCRIPTION

Manufacturer and Model: Thermo Fisher Scientific K-Alpha$^+$
Analyzer Type: Spherical sector
Detector: Multichannel resistive plate
Number of Detector Elements: 128

INSTRUMENT PARAMETERS COMMON TO ALL SPECTRA

Spectrometer

Analyzer Mode: Constant pass energy
Throughput ($T = E^N$): Calculated from a polynomial fit to a plot of log[peak area/(PE*XSF)] versus log(KE/PE), where PE is the pass energy, KE is the kinetic energy, and XSF is the relative sensitivity factor (Ref. 8).
Excitation Source Window: No window
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Beam Size: $600 \times 400\,\mu$m^2
Signal Mode: Multichannel direct

Geometry

Incident Angle: 60°
Source-to-Analyzer Angle: 60°
Emission Angle: 0°
Specimen Azimuthal Angle: 0°
Acceptance Angle from Analyzer Axis: 0°
Analyzer Angular Acceptance Width: 30° × 30 °

Ion Gun

Manufacturer and Model: Thermo Scientific MAGCIS
Energy: 4000 eV
Current: 6 mA
Current Measurement Method: Faraday cup
Sputtering Species and Charge: Ar^+
Spot Size (unrastered): 50 μm
Raster Size: $2000 \times 1000\,\mu$m^2
Incident Angle: 58°
Polar Angle: 58°
Azimuthal Angle: 90°
Comment: The ion gun was used to clean the as-introduced sample for 600 s. Prior to recording of each region, the sample was sputtered for a further 30 s to remove any adsorbed species arising from the chamber background gases.

DATA ANALYSIS METHOD

Energy Scale Correction: None as the sample is conductive and in direct contact with the sample holder.
Recommended Energy Scale Shift: 0
Peak Shape and Background Method: A Shirley background is used for all regions, with the exception of Ho 5*p* and 4*s* where a linear background is more appropriate. Recommended background start and end points are ±0.2 eV.
Ho 4*f*: 2.1–14.5 eV
Ho $5p_{3/2}$: 19.0–28.0 eV
Ho 5*p*: 19.0–35.0 eV
Ho 5*s*: 44.5–65.5 eV
Ho 4*d*: 157.2–197.5 eV
Ho 4*p*: Overlap with the Auger structure, not amenable for quantification with Al radiation.
Ho 4*s*: 426.4–448.8 eV
Ho $3d_{5/2}$: 1346.8–1365.6 eV
Ho $3d_{3/2}$: 1386.8–1402.0 eV
Quantitation Method: Data analysis was performed using CasaXPS performed in CasaXPS V2.3.26 rev1.2Y, using a Shirley background unless otherwise specified. Electron escape depth correction was performed using the TPP-2M equation within CasaXPS and peak areas corrected using Scofield sensitivity factors. Modified sensitivity factors were used for Ho 5*p* and 4*d* levels as noted in the comments on the spectral features table.

ACKNOWLEDGMENTS

This work was performed through the support of the EPSRC National Facility for x-ray photoelectron spectroscopy ("HarwellXPS," Nos. EP/Y023587/1, EP/Y023609/1, EP/Y023536/1, EP/Y023552/1, and EP/Y023544/1).

AUTHOR DECLARATIONS

Conflict of Interest

The author has no conflict to disclose.

Author Contributions

David J. Morgan: Conceptualization (equal); Data curation (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Project administration (equal); Resources (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are provided within the article and its supplementary material.

REFERENCES

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[6]*The Lawrence Berkeley National Laboratory X-Ray Data Handbook*, see https://xdb.lbl.gov/. Accessed 21 August 2024.
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[8]Thermo Scientific, *Avantage Version 6 Data Analysis Reference Manual* (Thermo Scientific, 2023).

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
01968-01	Ho 4*d*	…	…	6 233 982	12.00	100	Ho 4*d* with multiplet structure
01968-02	Valence	…	…	…	…	…	Valence, Ho 4*f*, Ho 5*p*
01968-02[a]	Ho 4*f*	…	…	222 852	3.10	…	…
01968-02[b]	Ho $4f_{7/2}$	5.2	…	…	…	…	…
01968-02[c]	Ho $5p_{3/2}$	23.6	…	57 531	0.836	…	…
01968-02	Ho $5p_{1/2}$	30.0	…	…	…	…	…
01968-03	Ho 5*s*	…	…	…	…	…	…
01968-04[d]	Ho 4*d*	…	…	1 428 000	19.50	…	Ho 4*d* with multiplet structure. See comments
01968-04	Ho $4d_{5/2}$	160.0	…	…	…	…	…
01968-05[e]	Ho 4*p*, Ho *MVV*	…	…	…	…	…	Ho 4*p*, Ho *MVV* Auger
01968-06[f]	Ho 4*s*	…	…	112 138	1.61	…	…
01968-07[g]	Ho 3*d*						Ho 3*d* with multiplet structure
01968-07	Ho $3d_{5/2}$	1351.9	…	4 589 956	56.60	…	…
01968-07	Ho $3d_{3/2}$	1392.4	…	3 261 383	39.19	…	…

Comment to Spectral Features Table:

[a]See peak shape and background discussion. The peak area includes peaks arising from both Ho $4f_{5/2}$ and multiplet splitting.

[b]The Ho $4f_{5/2}$ and multiplet splitting peak energies in eV, with relative percentages in parenthesis are 3.8 (0.23%). 5.2 (22.18%), 6.2 (16.64%), 8.6 (49.13%), 9.8 (8.53%), 11.0 (1.69%), and 12.5 (1.6%). For simplicity of fitting, Ho $4f_{5/2}$ peak is not defined explicitly. Reference 1 reports the value to be 9 ± 0.2 eV, while the x-ray data handbook (Ref. 6) reports the value to be 8.6 eV.

[c]Peak shows structure at both higher and lower energy sides of the peak maxima reported. Fitting in CasaXPS using a LA(1.53,243) Voigt-like shape reveals peaks at the reported binding energies, with the relative percentages in parenthesis: 22.5 (6.19%), 23.6 (85.43%), and 25.7 (8.38%). Note the sensitivity factor is the total value published by Scofield (Ref. 7), using the $5p_{3/2}$ value of 0.562 gives approximately a 30% error; the reason for this discrepancy is unknown at this juncture. If the total 5*p* peak is to be used, a modified sensitivity factor of 1.13 is recommended.

[d]For the region quoted in the peak shape and background discussion, a modified sensitivity factor of 19.5 is used as opposed to the Scofield value of 12. Peak includes Ho $4d_{3/2}$ and multiplet splitting. Peak binding energies determined, with the relative peak percentages in parenthesis from fitting in CasaXPS using an LA(1.53,243) line shape, are 16.0 (7.64%), 162.1 (11.35%), 165.4 (17.87%), 168.8 (1.75%), 173.8 (50.85%), and 188.5 (10.53%).

[e]The Ho 4*p* peaks are not resolved due to overlap with the Ho *MVV* Auger. The 4*p* binding energies reported in Ref. 6 are 308.2 and 343.5 for the $4p_{3/2}$ and $4p_{1/2}$ peaks, respectively.

[f]Weak signal and low photoionization cross section precludes an accurate determination of the binding energy, and hence, this region is not recommended for quantification. Reference 6 reports the binding energy as 432.4 eV, with the caveat it has undergone corrections from previously reported values.

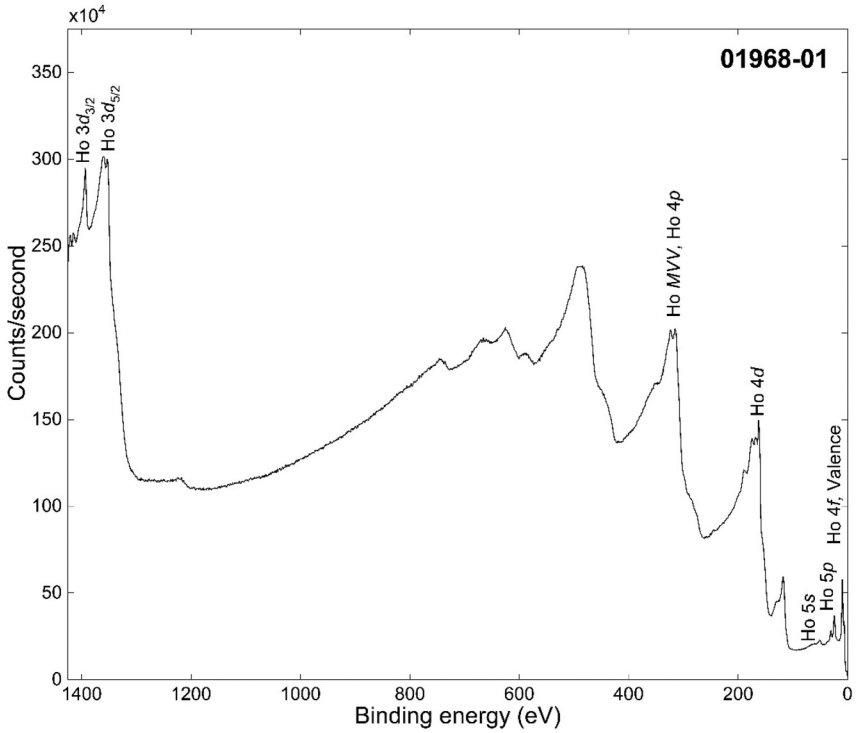
[g]The Ho 3*d* region is not recommended for quantification due to the large background and potential overlap with Auger structures in compounds. It is, however, noted that there may be use in these peaks in determining depth distributions of Ho by comparison with the lower binding energy levels, such as Ho 4*d*. The peak positions for the $3d_{5/2}$ and $3d_{3/2}$ peaks are the recorded peak maxima.

ANALYZER CALIBRATION TABLE

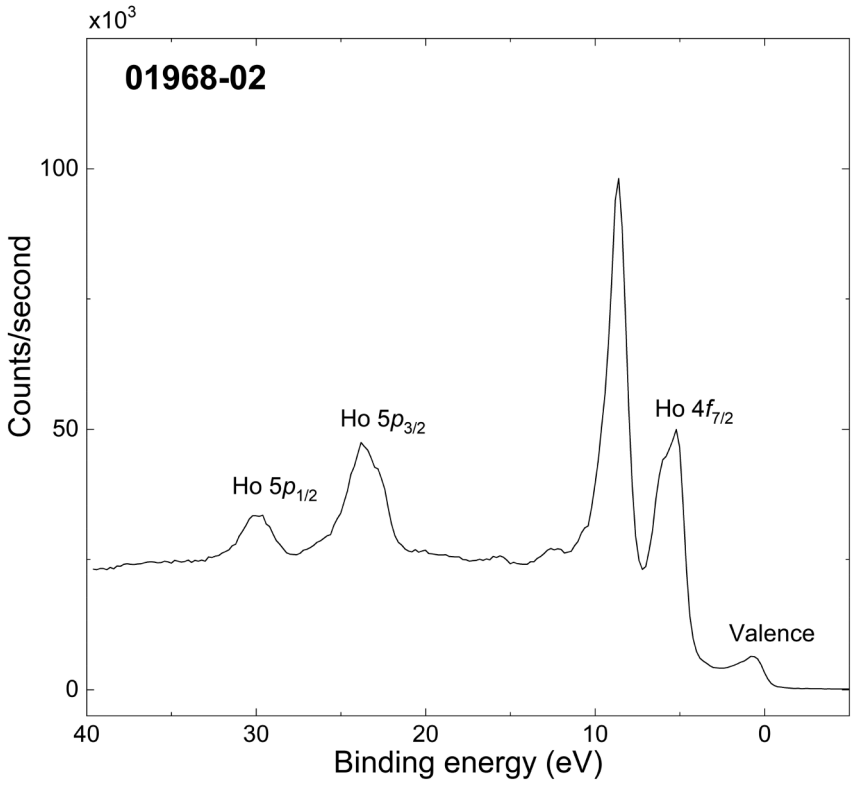
Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV × cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
…	Au $4f_{7/2}$	83.99	0.78	1 252 439	9.58	100	Gold metal
…	Ag $3d_{5/2}$	368.28	0.61	1 676 008	7.38	100	Silver metal
…	Cu $2p_{3/2}$	932.67	0.86	2 867 973	16.73	100	Copper metal

GUIDE TO FIGURES

Spectrum (Accession) #	Spectral Region	Voltage Shift	Multiplier	Baseline	Comment #
01968-01	Survey	0	1	0	…
01968-02	Valence, Ho 4*f*, Ho 5*p*	0	1	0	…
01968-03	Ho 5*s*	0	1	0	…
01968-04	Ho 4*d*	0	1	0	…
01968-05	Ho 4*p*, Ho *MVV*	0	1	0	…
01968-06	Ho 4*s*	0	1	0	…
01968-07	Ho 3*d*	0	1	0	…

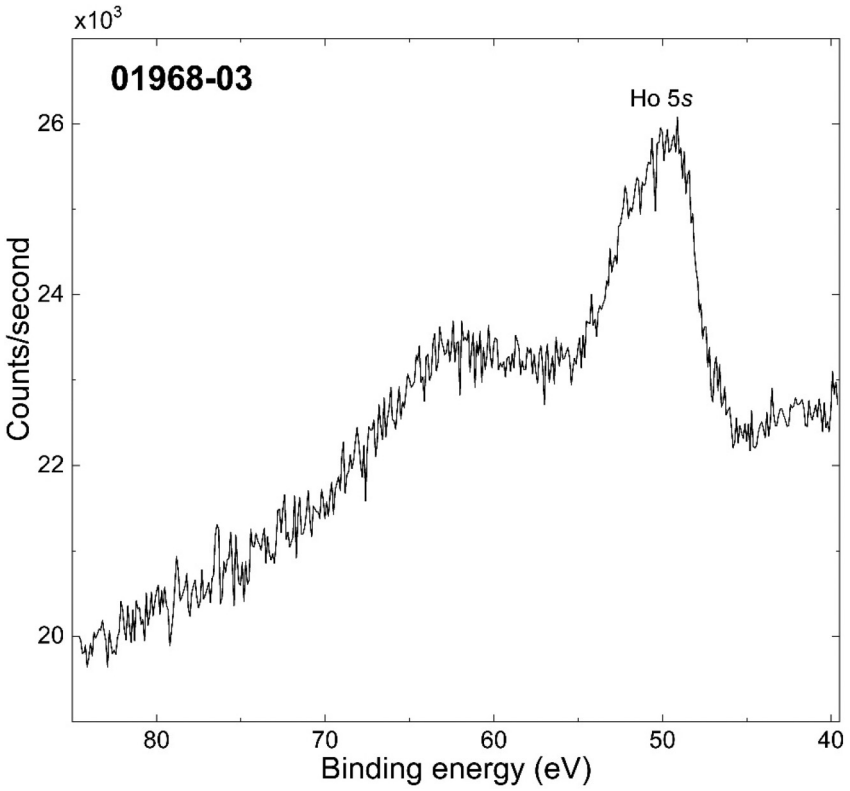


Accession #:	01968-01
■ Specimen:	Ho
■ Technique:	XPS
■ Spectral Region:	Survey
Instrument:	Thermo Fisher Scientific K-Alpha$^+$
Excitation Source:	Al K_α monochromatic
Source Energy:	1486.6 eV
Source Strength:	72 W
Source Size:	0.6 × 0.4 mm^2
Analyzer Type:	Spherical sector analyzer
Incident Angle:	60°
Emission Angle:	0°
Analyzer Pass Energy:	200 eV
Analyzer Resolution:	1.5 eV
Total Signal Accumulation Time:	86 s
Total Elapsed Time:	116 s
Number of Scans:	6
Effective Detector Width:	27.1 eV
Comments:	Spectra collected immediately after cleaning. Note the feature around 1210 eV is not due to a C *KVV* Auger as indicated by the absence of carbon in high resolution spectra.



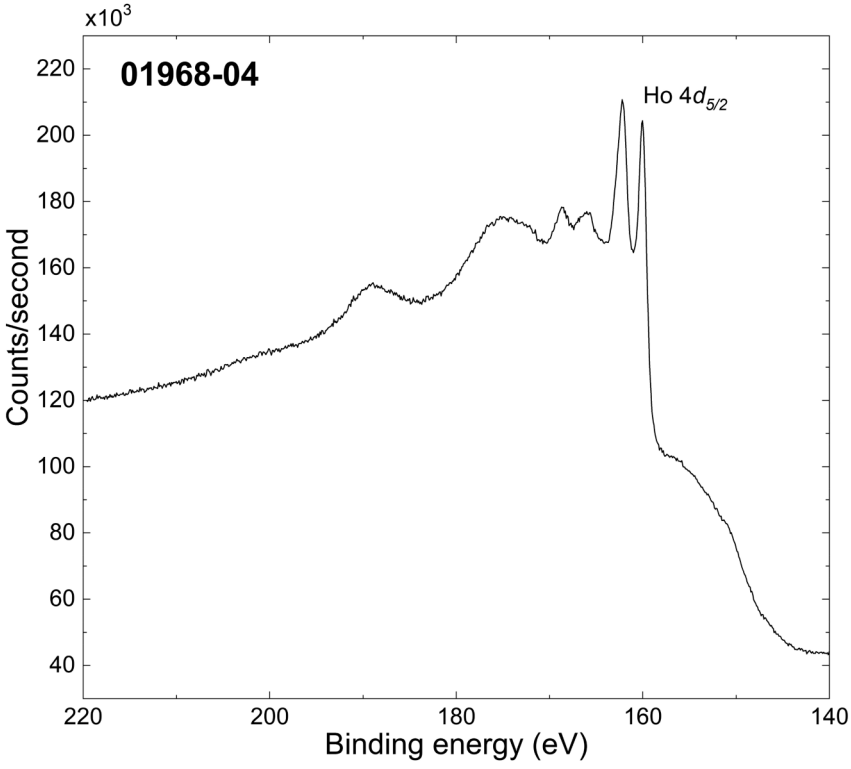
■ **Accession #:** 01968-02
■ **Specimen:** Ho
■ **Technique:** XPS
■ **Spectral Region:** Valence, Ho 4*f*, Ho 5*p*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.2 eV
Total Signal Accumulation Time: 112 s
Total Elapsed Time: 258 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s sputter after collection of the prior spectrum to minimize any oxidation. Total elapsed time includes previous scans and sputtering time. The 4*f* level exhibits multiplet structure.



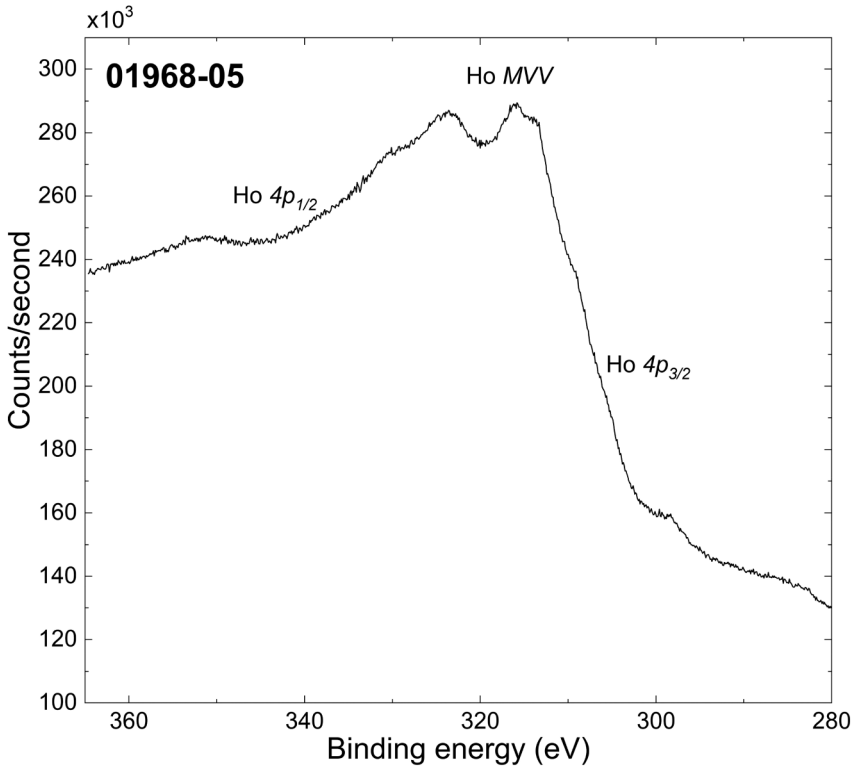
- **Accession #:** 01968-03
- **Specimen:** Ho
- **Technique:** XPS
- **Spectral Region:** Ho 5*s*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 277 s
Total Elapsed Time: 515 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s argon sputter after collection of the prior spectrum to minimize any oxidation.



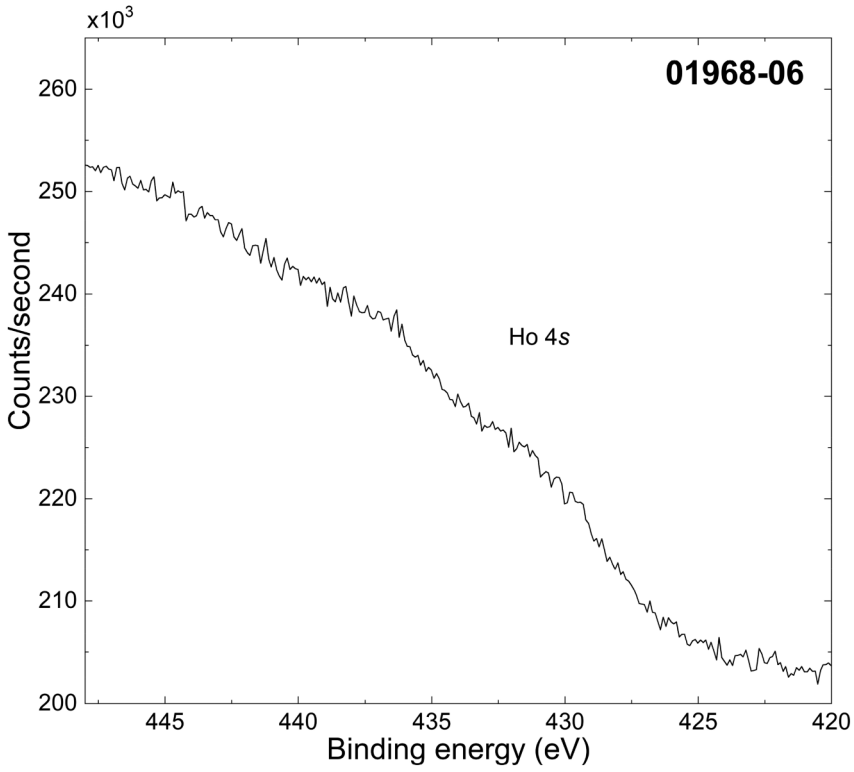
- **Accession #:** 01968-04
- **Specimen:** Ho
- **Technique:** XPS
- **Spectral Region:** Ho 4*d*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size:0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 400 s
Total Elapsed Time: 945 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s argon sputter after collection of the prior spectrum to minimize any oxidation.



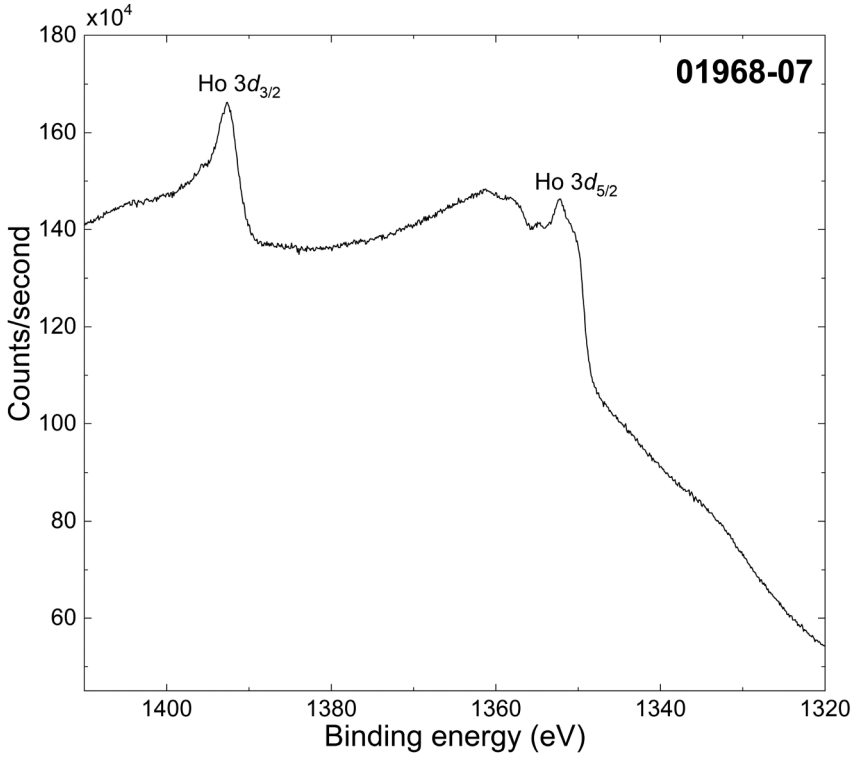
- **Accession #:** 01968-05
- **Specimen:** Ho
- **Technique:** XPS and XAES
- **Spectral Region:** Ho *MVV*, Ho 4*p*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 450 s
Total Elapsed Time: 1425 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s argon sputter after collection of the prior spectrum to minimize any oxidation. Note the Ho 4p peaks are not resolved due to overlap with the Auger structure. It is recommended to record the spectra over the range herein to ensure the absence of carbon as a peak in the survey spectra between 1210 and 1220 eV may be interpreted as a C KVV Auger.



- **Accession #:** 01968-06
- **Specimen:** Ho
- **Technique:** XPS
- **Spectral Region:** Ho 4*s*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 151 s
Total Elapsed Time: 1606 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s argon sputter after collection of the prior spectrum to minimize any oxidation.



- **Accession #:** 01968-07
- **Specimen:** Ho
- **Technique:** XPS
- **Spectral Region:** Ho 3*d*

Instrument: Thermo Fisher Scientific K-Alpha$^+$
Excitation Source: Al K_α monochromatic
Source Energy: 1486.6 eV
Source Strength: 72 W
Source Size: 0.6 × 0.4 mm^2
Analyzer Type: Spherical sector
Incident Angle: 60°
Emission Angle: 0°
Analyzer Pass Energy: 50 eV
Analyzer Resolution: 0.1 eV
Total Signal Accumulation Time: 98 s
Total Elapsed Time: 1734 s
Number of Scans: 10
Effective Detector Width: 6.8 eV
Comments: Spectra were collected after a 30 s argon sputter after collection of the prior spectrum to minimize any oxidation.