Samarium thin films molecular plated from *N,N*-dimethylformamide characterized by XPS

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Characterization of samarium thin films molecular plated from *N,N*-Dimethylformamide (DMF) solutions onto stainless steel substrates, with either mirror-like or brushed finishes, was carried out using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer. Survey scans of the two specimens showed the presence of samarium, carbon, and oxygen with minor amounts of sodium. High-resolution spectra were then taken of the Sm 3*d*, O 1*s*, and C 1*s* regions. The chemical compositions of the two samples were found to be very similar, with the key difference being the relative amounts of two carbon species. Spectra from the survey and narrow high-resolution scans of the Sm 3*d*, O 1*s*, and C 1*s* regions are reported herein.

Keywords: samarium, thin film, electrodeposition, molecular plating

Acccession#: 01483, 01484

Technique: XPS

Host Material: Molecular Sm thin film

Instrument: Thermo Scientific K-Alpha

Major Elements in Spectra: Sm, C, O

Minor Elements in Spectra: Na

Published Spectra: 8

Spectra in Electronic Record: 8

Spectral Category: comparison

INTRODUCTION

Oak Ridge National Laboratory's (ORNL) Radiochemical Engineering Development Center (REDC) produces actinide thin films for a variety of scientific programs around the world.[1-4] The Californium Rare Isotope Breeder Upgrade (CARIBU) program at Argonne National Laboratory utilizes a ^{252}Cf thin film as a fission fragment source produced at REDC to provide the Argonne Tandem Linac Accelerator System (ATLAS) with beams of neutron-rich nuclei. In order to achieve a high fission fragment flux for the experiments run under the CARIBU program, the ^{252}Cf films must be as thin and uniform as possible to minimize the self-attenuation of fission fragments in the thin film itself. A slight increase in thickness can lead to dramatically reduced fission fragment fluxes.[3] It is important to understand how current actinide thin film production techniques can be optimized to yield high-purity thin films with the desired morphologies. The most recent CARIBU sources have been produced by molecular plating californium from ammonium acetate solutions.[1-4] Previous work at ORNL using samarium as a surrogate for californium showed that molecular plating from ammonium acetate produced depositions with thicknesses of roughly 5 µm and only ~50% area coverages of the substrate.[3] Characterization of the samarium thin films using an X-ray photoelectron spectrometer (XPS) gave evidence that the depositions were composed of samarium acetate rather than pure samarium oxide/hydroxide, which the literature suggests the samarium should deposit as.[3,4]

N,N-Dimethylformamide (DMF) was recently investigated as an alternative molecular plating solvent by Vascon *et al*.[5,6] They reported that DMF produced higher quality lanthanide thin films in terms of morphology compared with typical molecular plating solvents. They also noted that the surface roughness of the deposition substrates had a noticeable effect on the morphology of the thin films produced. For these reasons, it was of interest to investigate DMF as a potential molecular plating solvent for CARIBU source production. Although the effect DMF had on the morphology of deposition was investigated by Vascon, whether the elemental and chemical composition were also impacted by the surface roughness was not. XPS measurements were performed to answer this question.

Initial studies were conducted with samarium as a surrogate for californium since it is nonradioactive and easier to handle. Samarium itself has applications as a component of magnetic, catalytic, and optical materials. It is also an important element in the nuclear fuel cycle since it is a major fission product and neutron poison.

Two different surface finishes, mirror-like (#8 finish) and brushed (#4 finish), were utilized for thin film molecular plating with DMF to evaluate the effect of surface finish on the morphology and chemical composition of the depositions.

XPS results from the samarium molecular plating in DMF exhibited noticeable differences in surface composition for the two surfaces. Specifically, the relative amounts of different carbon species were different. Although the two samples both had carbon peaks at ~285 eV (C-to C-bond) and ~290 eV (carbonate-type C bond), the mirror-like finish sample had a significantly higher peak at ~285 eV compared with its peak at ~290 eV. The brushed finish sample had the opposite effect with the peak at ~290 eV being of higher intensity than the one at

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~285 eV. It was also found that the mirror-like finish sample had higher ratios of carbon to samarium for total carbon as well as each peak. It then appeared that the mirror-like finish produces samarium thin films with higher amounts of trapped solvent and/or degradation products.

The survey scans for both samples confirm the major elemental constituents present are samarium, carbon, and oxygen along with minor amounts of sodium. The sodium trace contamination could arise from a variety of sources, such as generally handling, the hydrochloric acid solutions that are used to dissolve the $SmCl_3$ prior to the molecular plating. The samarium is added to the DMF solution in the form of $SmCl_3$ dissolved in dilute hydrochloric acid.

The Sm 3*d* regions for both samples show that the samarium is deposited as Sm(III). The C 1*s* regions for both samples have a carbonate-type carbon peak. and carbon-to-carbon-type peak. The carbonate-type carbon is likely from chemisorbed species from the DMF and/or solvent degradation products. Similar results have been seen by Vascon *et al.*[5,6] The XPS results suggest that the physisorbed and chemisorbed carbon-containing species are more stable on the mirror-like-finish substrate than the brushed-finish substrate. The binding energies of the O 1*s* peaks for both samples are consistent with oxygen being present in O/C-type to metal-type bonds and/or metal-to-hydroxide bonds.

SPECIMEN DESCRIPTION (ACCESSION #01483, 1 of 2)

Host Material: Molecular Sm thin film on mirror-like stainless steel

CAS Registry #: unknown

Host Material Characteristics: homogeneous; solid; unknown crystallinity; unknown conductivity; inorganic compound; Thin Film

Chemical Name: Sm_2O_3

Source: Molecular-plated thin film

Host Composition: Sm_2O_3 thin film, as deposited

Form: Thin film deposited onto stainless steel substrate with a mirror-like finish

Structure: unknown

History & Significance: Samarium was molecular plated as a thin film onto stainless steel substrates from a DMF solution containing 0.444 mM $SmCl_3$. Stainless steel plates with two different surface finishes, either mirror like or brushed, were used as the cathode and deposition substrate material. A constant current of 0.7 mA cm^{-2} was applied for 15 minutes. A platinum plate was used as the anode. The deposition solution was removed from the electrochemical cell immediately after the deposition was completed. The electrochemical cell was then rinsed twice with DMF. The deposition substrate was then removed, stored in a petri dish, and allowed to dry in a fume hood.

As Received Condition: As deposited onto a stainless steel plate. The sample was stored in a petri dish under ambient conditions.

Analyzed Region: 400 μm × 400 μm

Ex Situ Preparation/Mounting: The specimen was examined with a scanning electron microscope prior to analysis.

In Situ Preparation: none

Charge Control: Dual-beam low-energy electron/ion source was used for charge neutralization (Thermo Scientific FG-03). The ion gun current was 150 microamperes, and the voltage was 45 volts.

Temp. During Analysis: 300K

Pressure During Analysis: $<2 \times 10^{-5}$ Pa

Pre-analysis Beam Exposure: 0s.

SPECIMEN DESCRIPTION (ACCESSION #01484, 2 of 2)

Host Material: Molecular Sm thin film on brushed stainless steel

CAS Registry #: unknown

Host Material Characteristics: homogeneous; solid; unknown crystallinity; unknown conductivity; inorganic compound; Thin Film

Chemical Name: Sm_2O_3

Source: Molecular-plated thin film

Host Composition: Sm_2O_3 thin film, as deposited

Form: Thin film deposited onto stainless steel substrate with a brushed finish

Structure: unknown

History & Significance: Samarium was molecular plated as a thin film onto stainless steel substrates from a DMF solution containing 0.444 mM $SmCl_3$. Stainless steel plates with two different surface finishes, either mirror like or brushed, were used as the cathode and deposition substrate material. A constant current of 0.7 mA cm^{-2} was applied for 15 minutes. A platinum plate was used as the anode. The deposition solution was removed from the electrochemical cell immediately after the deposition was completed. The electrochemical cell was then rinsed twice with DMF. The deposition substrate was then removed, stored in a petri dish, and allowed to dry in a fume hood.

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Temp. During Analysis: 300K

Pressure During Analysis: $<2 \times 10^{-5}$ Pa

Pre-analysis Beam Exposure: 0s.

INSTRUMENT DESCRIPTION

Manufacturer and Model: Thermo Scientific K-Alpha XPS

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): N=-1

Excitation Source Window: 0.25 m Rowland circle monochromator with micro-focused x-ray source

Excitation Source: Al K_α monochromatic

Source Energy: 1486.68 eV

Source Strength: 72 W

Source Beam Size: 5 μm × 5 μm

Signal Mode: analog direct

■*Geometry*

Incident Angle: 0 °

Source-to-Analyzer Angle: 45 °

Emission Angle: 45 °

Specimen Azimuthal Angle: 0 °

Acceptance Angle from Analyzer Axis: 0 °

Analyzer Angular Acceptance Width: 45 ° x 0 °

■*Ion Gun*

Manufacturer and Model: Thermo Scientific EX-06

Energy: 1000 eV

Current: 10 mA

Current Measurement Method: Faraday cup

Sputtering Species: Ar

Spot Size (unrastered): 400 μm

Comment: The ion gun was utilized to clean the surfaces of the calibration standards.

DATA ANALYSIS METHOD

Energy Scale Correction: The sample was not charging, and no energy-scale correction was needed.

Recommended Energy Scale Shift: 0

Peak Shape and Background Method: Thermo Avantage software version 4.61 was used to carry out the background subtraction using the Shirley function as well as the determinations of the peak positions and full width at half maximum (FWHM) values. The peaks were fitted using Gaussians.

Quantitation Method: The atomic concentrations were calculated using the Al Scofield sensitivity factors in the Thermo Avantage software version 4.61.

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SPECTRAL FEATURES TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
01483-02	C 1*s*	284.9	2.2	27937	1.000	23.1	C-to-C type
01483-02	C 1*s*	289.9	2.2	19959	1.000	16.5	Carbonate type
01483-03	O 1*s*	531.8	2.2	151088	2.930	48.9	O/C type
01483-04	Na 1*s*	1071.8	3.8	18201	8.520	3.3	Residual Na
01483-04	Sm 3$d_{5/2}$	1083.4	4.2	208817	40.370	8.2	Sm(III)
01483-04	Sm 3$d_{3/2}$	1110.7	…	…	…	…	Sm(III)
01484-02	C 1*s*	285.2	2.1	11834	1.000	11.3	C-to-C type
01484-02	C 1*s*	290.1	2.0	20393	1.000	19.6	Carbonate type
01484-03	O 1*s*	531.8	2.0	150635	2.930	56.4	O/C type
01484-04	Na 1*s*	1072.0	0.7	2687	8.520	0.6	Residual Na
01484-04	Sm 3$d_{5/2}$	1083.8	4.1	265388	40.370	12.11	Sm(III)
01484-04	Sm 3$d_{3/2}$	1110.7	…	…	…	…	Sm(III)

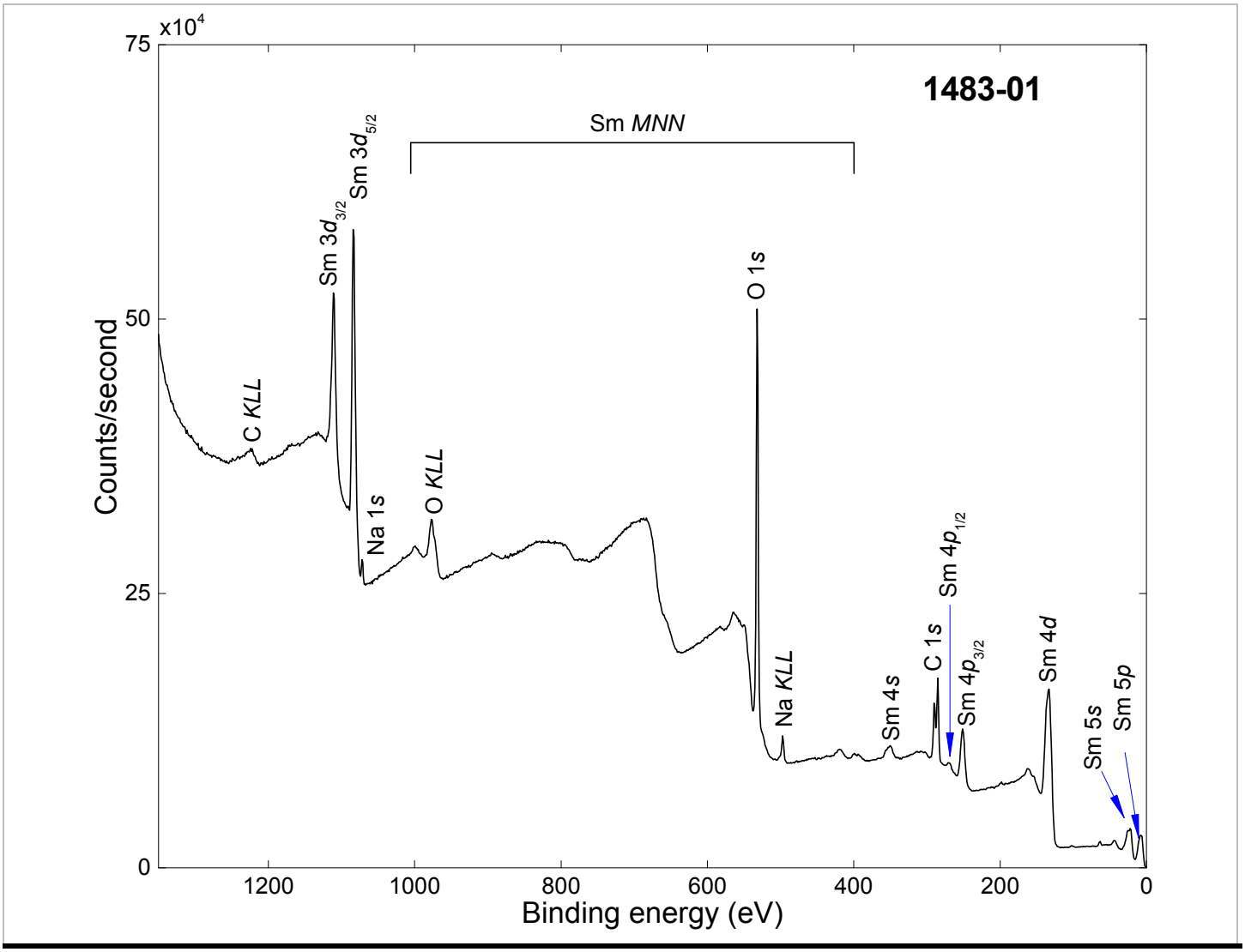
ANALYZER CALIBRATION TABLE

Spectrum ID #	Element/ Transition	Peak Energy (eV)	Peak Width FWHM (eV)	Peak Area (eV x cts/s)	Sensitivity Factor	Concentration (at. %)	Peak Assignment
…	Ag 3$d_{5/2}$	368.2	0.92	818043	11.054	>95%	...
…	Cu 2$p_{3/2}$	932.6	1.08	1049700	15.425	>95%	...
…	Au 4$f_{7/2}$	83.9	1.02	529237	8.839	>95%	...

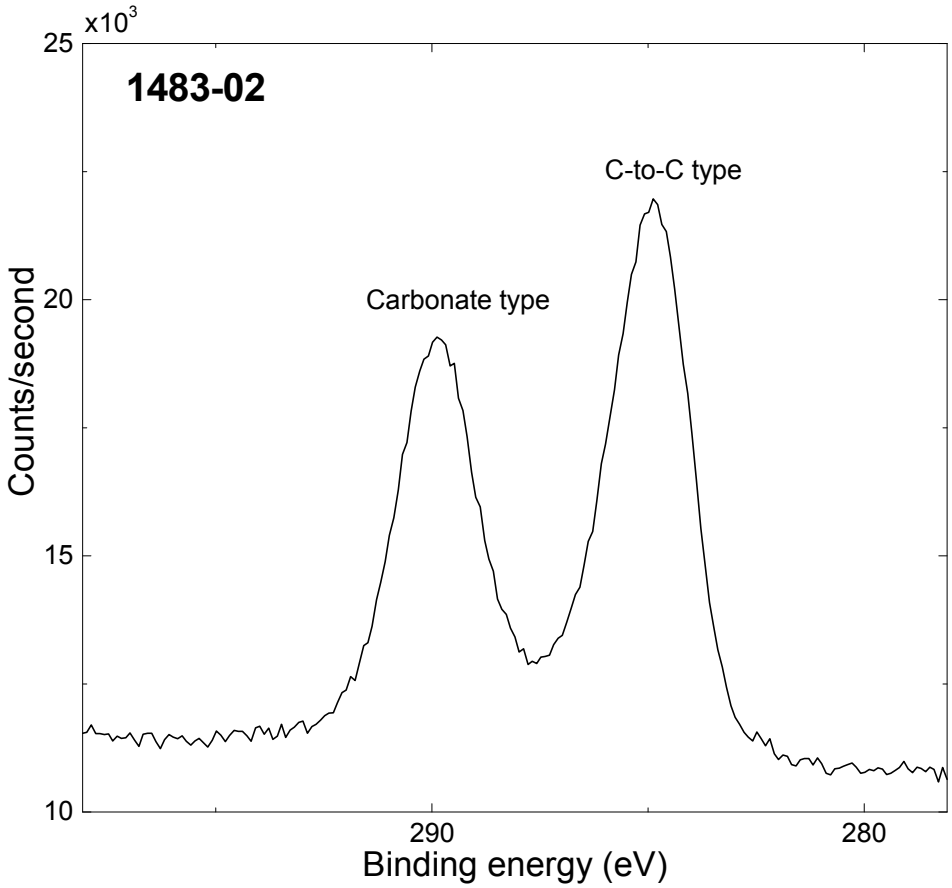
GUIDE TO FIGURES					
Spectrum (Accession) #	**Spectral Region**	**Voltage Shift***	**Multiplier**	**Baseline**	**Comment #**
01483-01	survey	0	1	0	1
01483-02	C 1*s*	0	1	0	2
01483-03	O 1*s*	0	1	0	3
01483-04	Sm 3$d_{5/2}$, Sm 3$d_{3/2}$, Na 1*s*	0	1	0	4
01484-01	survey	0	1	0	5
01484-02	C 1*s*	0	1	0	6
01484-03	O 1*s*	0	1	0	7
01484-04	Sm 3$d_{5/2}$, Sm 3$d_{3/2}$, Na 1*s*	0	1	0	8

*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.

1. Survey scan of Sm thin film molecular plated onto mirror-like-finish stainless steel substrate.
2. High resolution scan of C 1*s* region. Two different types of carbon are present. The peak at ~285 eV is C-to-C type carbon whereas the peak at ~290 eV is likely carbonate-type carbon. The carbonate-type carbon is likely from physisorbed and chemisorbed DMF solvent.
3. High resolution scan of the O 1*s* region. The binding energies of the O 1*s* peak is consistent with oxygen being present in O/C-type to metal-type bonds and/or metal-to-hydroxide bonds.
4. High resolution scan of the Sm 3*d* region. Only Sm(III) is present given the positions of the Sm 3$d_{5/2}$ and 3$d_{3/2}$ peaks. The shoulder at higher binding energy of the Sm 3$d_{5/2}$ peak is likely due to a charge transfer effect.[7]
5. Survey scan of Sm thin film molecular plated onto brushed-finish stainless steel substrate.
6. High resolution scan of C 1*s* region. Two different types of carbon are present. The peak at ~285 eV is C-to-C type carbon whereas the peak at ~290 eV is likely carbonate-type carbon. The carbonate-type carbon is likely from physisorbed and chemisorbed DMF solvent.
7. High resolution scan of the O 1*s* region. The binding energies of the O 1*s* peak is consistent with oxygen being present in O/C-type to metal-type bonds and/or metal-to-hydroxide bonds.
8. High resolution scan of the Sm 3*d* region. Only Sm(III) is present given the positions of the Sm 3$d_{5/2}$ and 3$d_{3/2}$ peaks. The shoulder at higher binding energy of the Sm 3$d_{5/2}$ peak is likely due to a charge transfer effect.[7]



Accession #	01483-01
Host Material	Molecular Sm thin film
Technique	XPS
Spectral Region	survey
Instrument	Thermo Fisher K-Alpha XPS
Excitation Source	Al K_α monochromatic
Source Energy	1486.68 eV
Source Strength	72 W
Source Size	0.005 mm x 0.005 mm
Analyzer Type	spherical sector analyzer
Incident Angle	0˚
Emission Angle	45˚
Analyzer Pass Energy	200 eV
Analyzer Resolution	0.86 eV
Total Signal Accumulation Time	680.5 s
Total Elapsed Time	831 s
Number of Scans	10
Effective Detector Width	1 eV



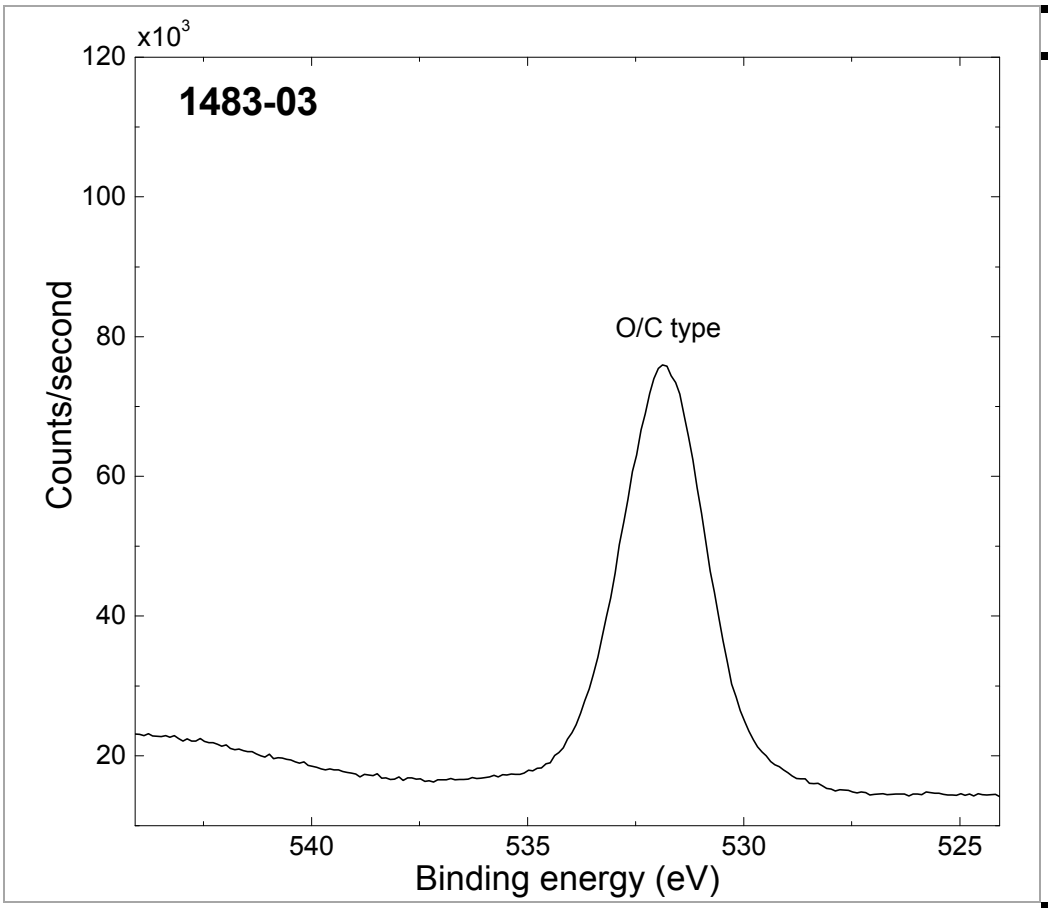
■ **Accession #:** 01483-02

■ **Host Material:** Molecular Sm thin film

■ **Technique:** XPS

■ **Spectral Region:** C 1*s*

Instrument: Thermo Fisher K-alpha XPS
Excitation Source: Al K_α monochromatic
Source Energy: 1486.68 eV
Source Strength: 72 W
Source Size: 0.005 mm x 0.005 mm
Analyzer Type: spherical sector
Incident Angle: 0 °
Emission Angle: 45 °
Analyzer Pass Energy 50 eV
Analyzer Resolution: 0.01 eV
Total Signal Accumulation Time: 201 s
Total Elapsed Time: 291 s
Number of Scans: 20
Effective Detector Width: 0.1 eV



■ **Accession #:** 01483-03

■ **Host Material:** Molecular Sm thin film

■ **Technique:** XPS

■ **Spectral Region:** O 1*s*

Instrument: Thermo Fisher K-alpha XPS

Excitation Source: Al K_α monochromatic

Source Energy: 1486.68 eV

Source Strength: 72 W

Source Size: 0.005 mm x 0.005 mm

Analyzer Type: spherical sector

Incident Angle: 0 °

Emission Angle: 45 °

Analyzer Pass Energy 50 eV

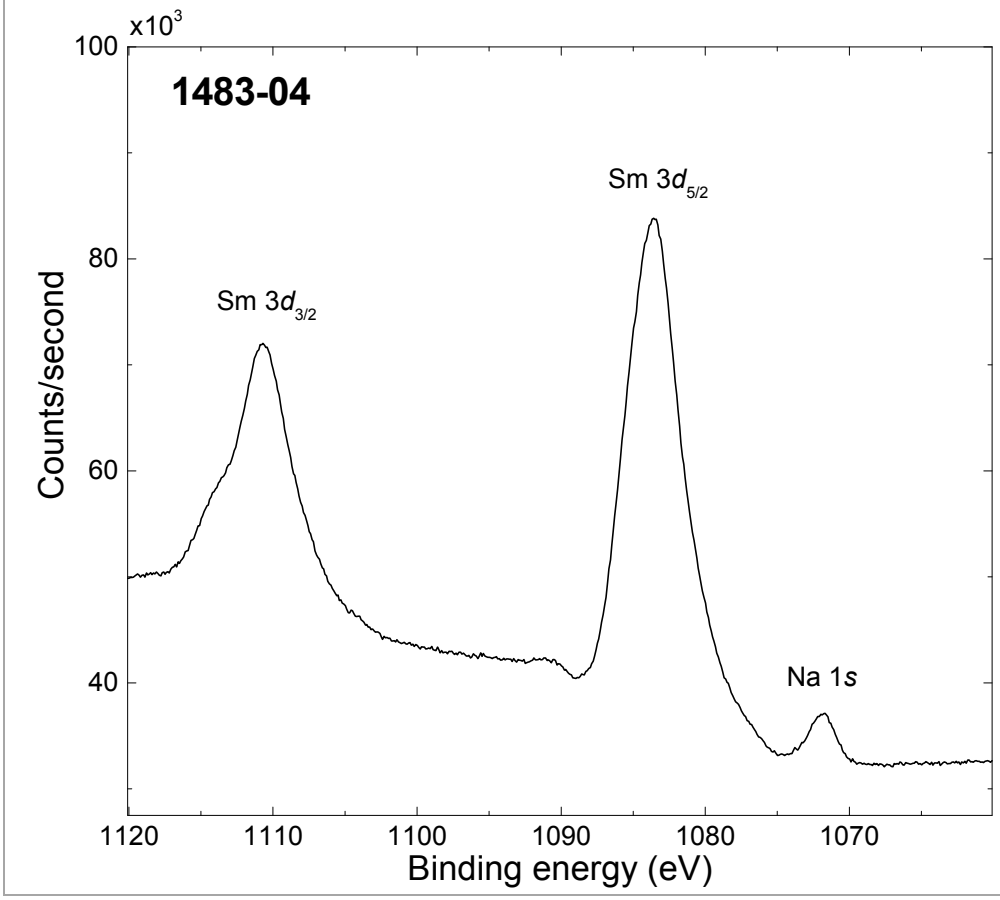
Analyzer Resolution: 0.01 eV

Total Signal Accumulation Time: 100.5 s

Total Elapsed Time: 145 s

Number of Scans: 10

Effective Detector Width: 0.1 eV



■ **Accession #:** 01483-04

■ **Host Material:** Molecular Sm thin film

■ **Technique:** XPS

■ **Spectral Region:** Sm $3d_{5/2}$, Sm $3d_{3/2}$, Na 1*s*

Instrument: Thermo Fisher K-alpha XPS

Excitation Source: Al K_α monochromatic

Source Energy: 1486.68 eV

Source Strength: 72 W

Source Size: 0.005 mm x 0.005 mm

Analyzer Type: spherical sector

Incident Angle: 0 °

Emission Angle: 45 °

Analyzer Pass Energy 50 eV

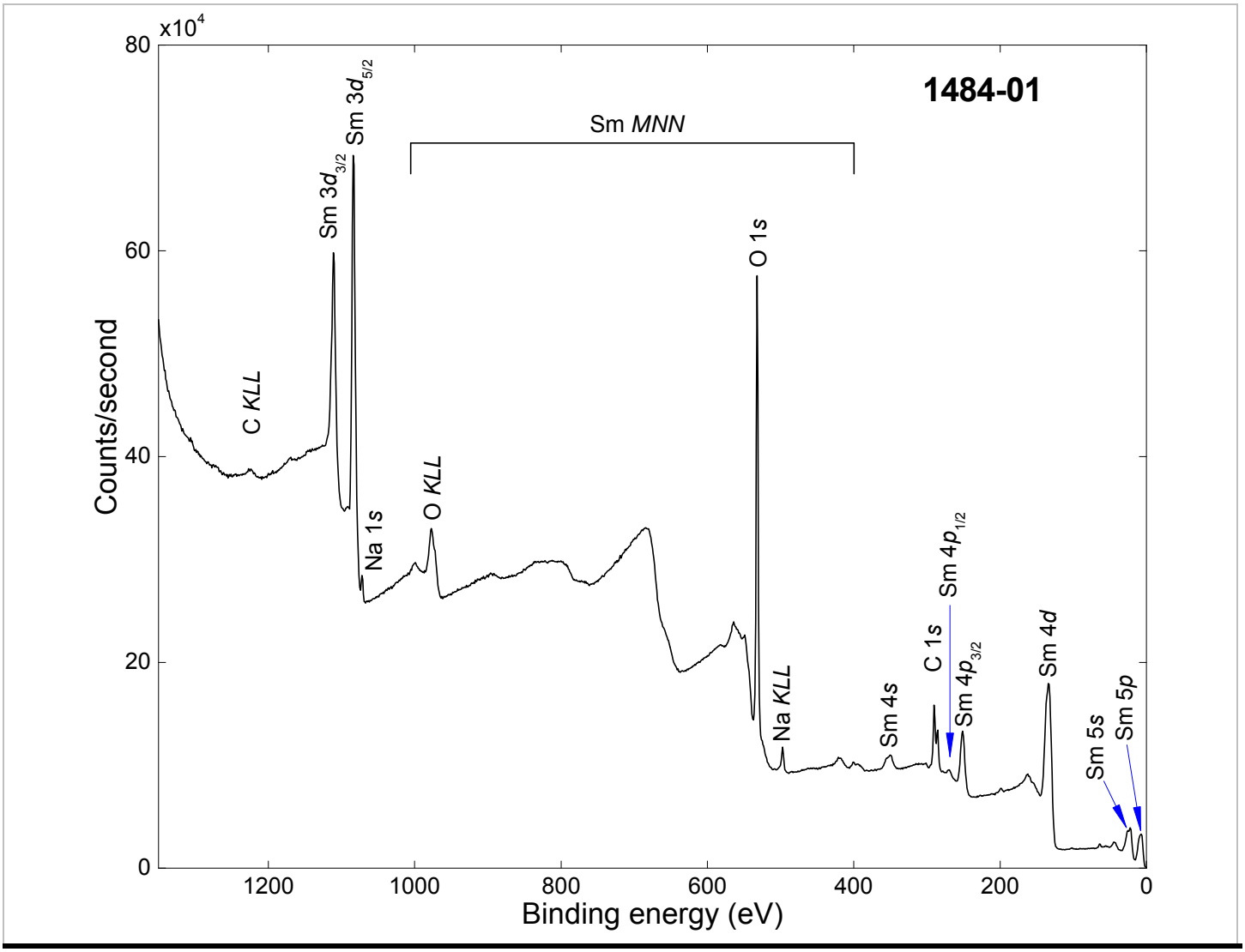
Analyzer Resolution: 0.01 eV

Total Signal Accumulation Time: 901.5 s

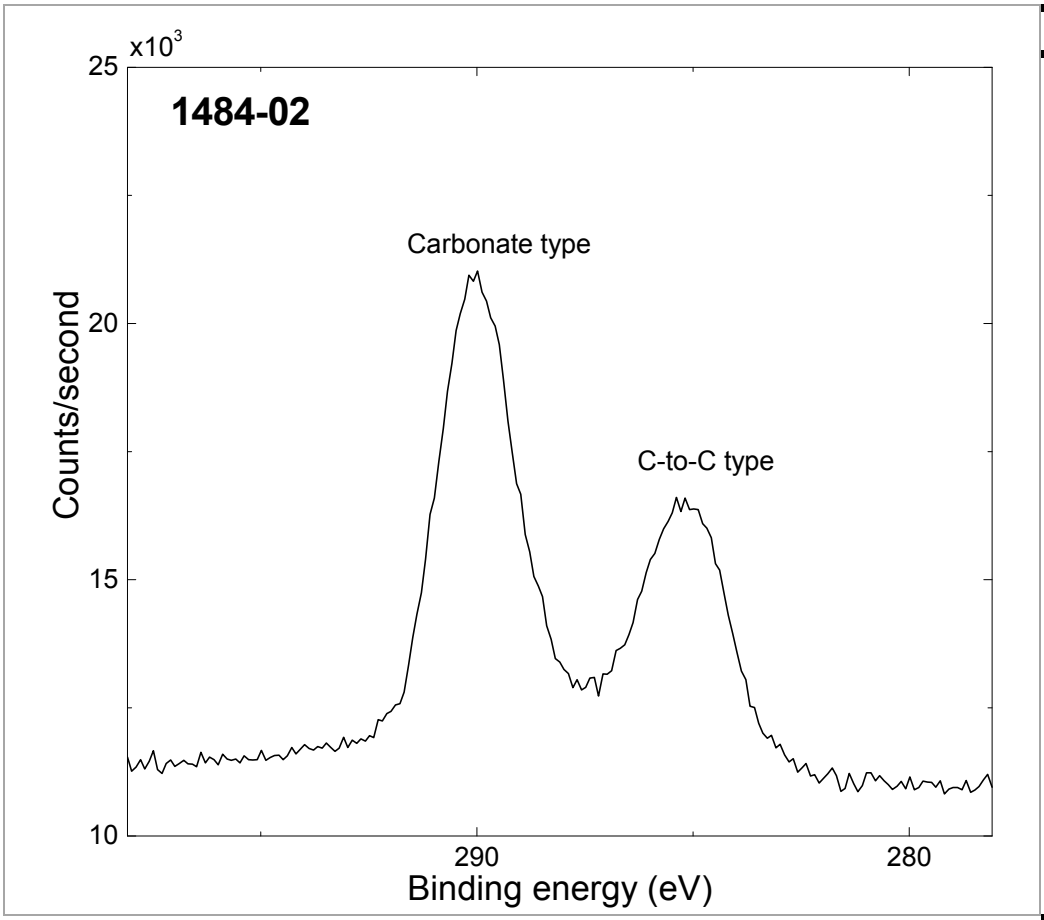
Total Elapsed Time: 1080 s

Number of Scans: 30

Effective Detector Width: 0.1 eV



Accession #	01484-01
Host Material	Molecular Sm thin film
Technique	XPS
Spectral Region	survey
Instrument	Thermo Fisher K-Alpha XPS
Excitation Source	Al K_α monochromatic
Source Energy	1486.68 eV
Source Strength	72 W
Source Size	0.005 mm x 0.005 mm
Analyzer Type	spherical sector analyzer
Incident Angle	0˚
Emission Angle	45˚
Analyzer Pass Energy	200 eV
Analyzer Resolution	0.86 eV
Total Signal Accumulation Time	680.5 s
Total Elapsed Time	831 s
Number of Scans	10
Effective Detector Width	1 eV



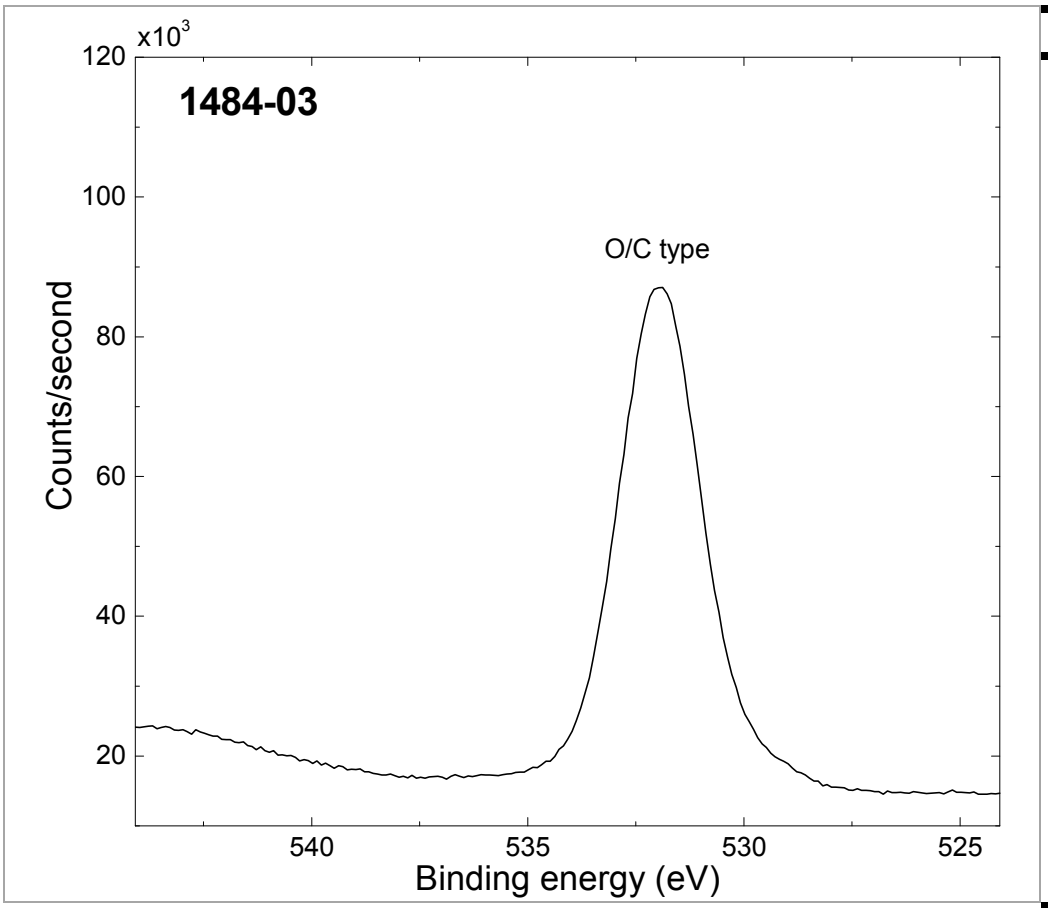
■ **Accession #:** 01484-02

■ **Host Material:** Molecular Sm thin film

■ **Technique:** XPS

■ **Spectral Region:** C 1*s*

Instrument: Thermo Fisher K-alpha XPS
Excitation Source: Al K_α monochromatic
Source Energy: 1486.68 eV
Source Strength: 72 W
Source Size: 0.005 mm x 0.005 mm
Analyzer Type: spherical sector
Incident Angle: 0 °
Emission Angle: 45 °
Analyzer Pass Energy 50 eV
Analyzer Resolution: 0.01 eV
Total Signal Accumulation Time: 201 s
Total Elapsed Time: 291 s
Number of Scans: 20
Effective Detector Width: 0.1 eV



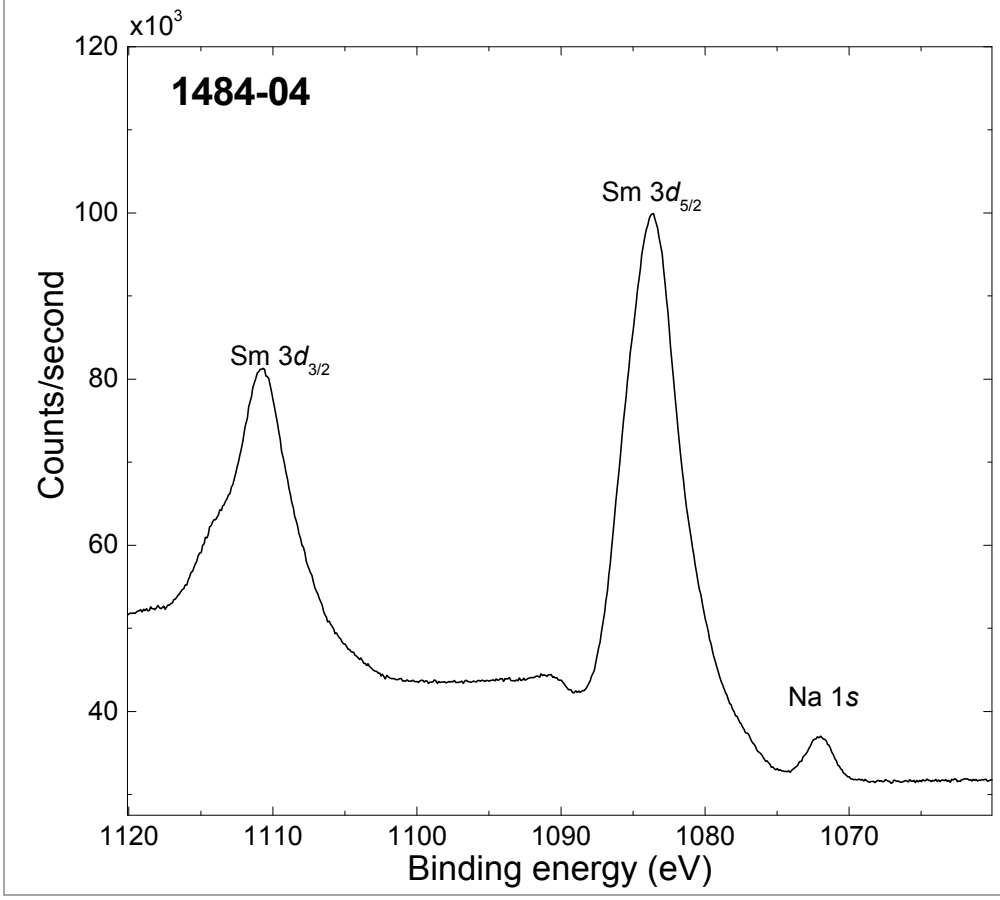
■ **Accession #:** 01484-03

■ **Host Material:** Molecular Sm thin film

■ **Technique:** XPS

■ **Spectral Region:** O 1*s*

Instrument: Thermo Fisher K-alpha XPS
Excitation Source: Al K_α monochromatic
Source Energy: 1486.68 eV
Source Strength: 72 W
Source Size: 0.005 mm x 0.005 mm
Analyzer Type: spherical sector
Incident Angle: 0 °
Emission Angle: 45 °
Analyzer Pass Energy 50 eV
Analyzer Resolution: 0.01 eV
Total Signal Accumulation Time: 100.5 s
Total Elapsed Time: 145 s
Number of Scans: 10
Effective Detector Width: 0.1 eV



■ **Accession #:** 01484-04

■ **Host Material:** Molecular Sm thin film

■ **Technique:** XPS

■ **Spectral Region:** Sm $3d_{5/2}$, Sm $3d_{3/2}$, Na $1s$

Instrument: Thermo Fisher K-alpha XPS

Excitation Source: Al K_α monochromatic

Source Energy: 1486.68 eV

Source Strength: 72 W

Source Size: 0.005 mm x 0.005 mm

Analyzer Type: spherical sector

Incident Angle: 0 °

Emission Angle: 45 °

Analyzer Pass Energy 50 eV

Analyzer Resolution: 0.01 eV

Total Signal Accumulation Time: 901.5 s

Total Elapsed Time: 1082 s

Number of Scans: 30

Effective Detector Width: 0.1 eV