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Methods/Protocols

Design of a Sample Transfer Holder to Enable Air-Free X-ray Photoelectron Spectroscopy

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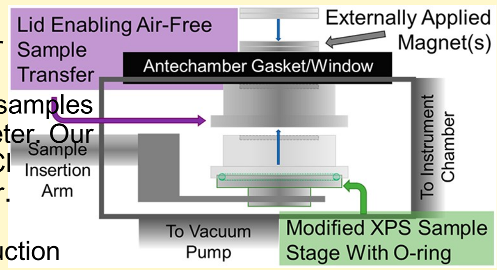
ABSTRACT: Surface analysis of air-sensitive samples is difficult without controlled-environment sample transfer tubes or expensive vacuum transfer suitcases. Through the use of vacuum sealing and commercial magnets, we demonstrate a concept for a sample holder that can be used to transfer samples from an inert environment directly into an X-ray photoelectron spectrometer. Our results show the efficacy of the holder through analysis of an air-sensitive CuCl powder, where oxidation was not observed when using the sample holder. This method offers a simple, low-cost alternative to enable routine air-free measurements in instrumentation with vacuum-controlled sample introduction chambers. Our aim with this report is to share the design so that this sample holder can be made anywhere where there is access to a basic machine shop.



INTRODUCTION

When dealing with the analysis of material surfaces, it is vital to be able to ensure that the surface being analyzed is as accurate to the in operando surface or product as possible. This can be difficult for lab situations in which there is not a system in place for samples to be transferred into an instrument via vacuum transfer suitcase or where an instrument is not directly attached to an environmentally controlled system such as a glovebox. In order to allow for air-free sample transfer into an X-ray photoelectron spectroscopy (XPS) instrument, we have designed a sample transfer holder (Figure 1) which can maintain an inert sample environment for an extended period of time using a negative pressure seal and magnetic release once inside the instrument entrance chamber and under vacuum.

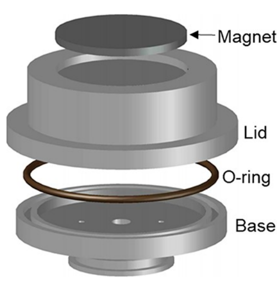


Figure 1. Graphic of the air-free XPS sample transfer holder, to scale without sample clips, clip screws, or the bleed screw visible. The base and lid are Al, the O-ring is Viton, and the magnet is a 1.26 in. neodymium disc magnet that is press-fit into the lid. Additional schematics can be found in Figure 2 and the Supporting Information.

The surface-sensitive nature of the XPS technique means any changes in surface chemistry due to oxidation or hydration upon exposure to ambient air are detrimental to collecting accurate and impactful data. Such changes have been reported when investigating battery materials,[1−3] nanoparticles,[4−6] bare metal surfaces,[7,8] nitrides,[9,10] and more.[11−14] Due to this, researchers employ a variety of techniques in order to maintain air-free environments. These include vacuum suitcases, vacuum transfer lines, direct attachment of instrumentation to inert environment chambers,[15] commercial transfer vessels flowing Ar over the sample during transfer,[16] use of glovebags placed over instrument entrance chambers,[2] or depositing a thin coating such as Al that can be removed via sputtering or measurements can be made through.[10] While all of these techniques are effective, each has its shortcomings.

It is not always possible for a lab, in particular an academic lab or anywhere where the XPS instrument is shared between a variety of users for numerous applications, to have the instrument in direct contact with a glovebox or system where samples are synthesized and prepared. Also, while vacuum transfer suitcases are very effective, they often need to be custom ordered directly from the instrument manufacturer (Thermo or Physical Electronics) or specialty manufacturer (UHV Transfer Systems, Inc.) and can be costly. Additionally, if there is a desire to have multiple samples prepared

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simultaneously or across various laboratories, as is often the case in a university setting, the need for several devices arises, and the costs only multiply.

Flowing inert gas throughout sample transfer or the use of a glovebag system is imperfect and can be inconvenient, despite being more readily available to most users. Lastly, air-free sputter coating may not be accessible for many users (because of the same challenges in sample transfer from a glovebox), and concerns arise over altering the analyte properties both upon deposition of the protective coatings through the sputtering process and during the removal of these coatings in the instrument.

Taking all of this into account, we have developed a system that consists of relatively inexpensive, readily sourced materials, can be reproducibly manufactured, is user-friendly, is reusable, and once manufactured, requires no special equipment, significant maintenance, or special training to use. Furthermore, while the design and specifications reported here are specific to our particular XPS instrument specifications (Physical Electronics ESCA 5800), we hope the core concept behind the holder's function can be extended to numerous applications and instruments. In theory, most systems that employ a low-pressure antechamber could use the fundamental design principals we report here to make a comparable negative-pressure air-free sample transfer holder. Potential modifications are further discussed in the Troubleshooting and Modification section. This could minimize the barrier for people who need to make this kind of measurement, enabling measurements of air-sensitive samples for a broader participation.

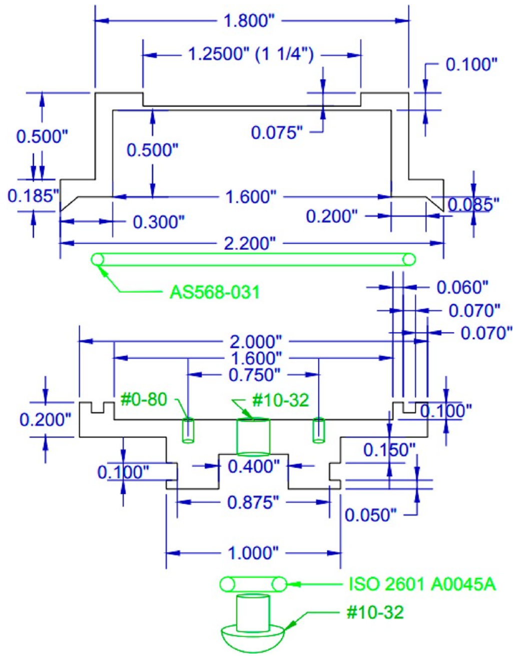

Figure 2. Schematic showing the dimensions of the machined air-free XPS sample transfer holder cap and base. Not shown is the neodymium disc magnet (1.26 in. diameter), press-fit into the upper cut-out of the sample holder. Listed in green are the O-rings and screws listed in the materials section, as well as the screw holes tapped into the base. Full schematic with all labeled peripherals can be found in the Supporting Information and Figure S1.

MATERIALS

The air-free XPS holder was milled on a lathe from 2.25 in. aluminum 6061-T65 round stock (McMaster-Carr) to the specifications detailed in Figure 2. Further details on the design and specifications can be found in the Supporting Information in Figure S1 and an accessible CAD file (available from https://sites.chem.colostate.edu/prietolab/publications.html, under the appropriate reference). The main holder O-ring located between the base and lid (standard O-ring size AS568-031), the bleed screw O-ring located between the base and bleed screw (standard O-ring size ISO 3601 A0045A), the bleed screw (U.S. standard no. 10-32 × 0.5 in. button head screw), and the sample clip holder screws (U.S. standard no. 0-80 × 0.125 in. socket head cap screws) were all purchased from local hardware supply stores. The 1.26 in. Ni−Cu−Ni triple coated neodymium disc magnets for the holder cap were purchased through amazon.com and are ~0.08 in. thick. This type of magnet is commercially available through online retailers and craft/home-goods stores. The seller claimed the magnets to be N52 NdFeB, but no verification tests were done nor manufacturing information provided with the purchase. The copper(I) chloride (CuCl anhydrous beads, ≥99.99%) was purchased from Sigma-Aldrich and was ground in an agate mortar and pestle under inert conditions in a N_2-filled glovebox. The CuCl powder was adhered to the air-free XPS holder via carbon tape (Ted Pella) as shown in Figure S2.

PROCEDURE

The transfer holder is used to prevent exposure to the atmosphere between an inert glovebox environment and an XPS instrument. In order to do this, the holder is first pumped into the glovebox with the cap and base separated and the bleed screw loosened, which is done to ensure there were no trapped gases and allow for all surfaces to be exposed for the pumping and purging process. The sample of interest can then be placed on the holder and affixed by either copper clips or using conductive adhesives. For the preliminary results presented here, a two-sided carbon tape was used. The adhesive was attached to the base of the sample transfer holder prior to pumping and purging into the box in order to remove as much adsorbed oxygen and water as possible. Prior to attaching the sample of interest, the bleed screw is tightened until flush with the base sample surface.

To test for holder efficacy, the sample analyzed consisted of CuCl, freshly ground in an agate mortar and pestle. A reactive Cu(I) species was used for the test due to the clear transition from Cu(I) to Cu(II) seen in the XPS spectra.[17,18] Once the ground CuCl is placed onto the adhesive, the holder cap is placed on the base, ensuring the O-ring is properly seated in the base groove and the lid is seated flush on the O-ring. When aligned properly, the transfer holder is put into the glovebox antechamber. The antechamber is then pumped down slowly, pulling as much trapped gas from the holder as possible. The antechamber is then refilled with N_2, creating a vacuum seal due to the negative pressure within the holder relative to the N_2 environment. Repressurizing the antechamber with N_2 instead of atmospheric air serves a dual purpose: first, it allows the transfer holder to be re-entered into the glovebox where the quality of the seal can be evaluated without risking exposure to the atmosphere. The seal is tested by attempting to pull apart the base and the lid, which will not readily happen given a good seal. Second, repressurizing with N_2 minimizes the possibility of contamination due to gas getting into the

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transfer holder while the negative-pressure seal is being established. Once the negative-pressure seal is established and tested, the transfer holder can be removed from the glovebox directly, at which point the sample will remain free from atmospheric contamination and can be stored for extended periods of time or brought directly to the instrument.

To release the seal of the transfer holder for subsequent analysis of the sample, the holder is placed into the entrance chamber of the instrument, which is then pulled down to high vacuum as is standard for the instrument. As the vacuum of the instrument is higher than the vacuum of the glovebox antechamber, the negative-pressure seal previously established is overcome. The lid is then lifted from the base using magnets external to the sample introduction chamber as seen in Figure 3A. This results in the separation of the lid, where it hangs

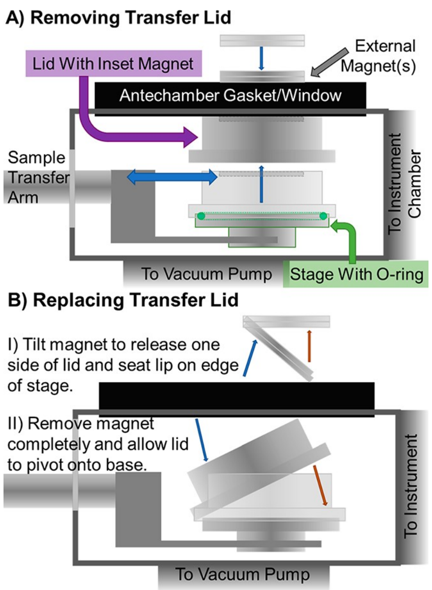

Figure 3. Cross sectional representation of the sample transfer holder in the instrument antechamber showing the basic operating principle. (A) Following evacuation of the antechamber, magnets are applied to the window, causing the lid to lift off the base and remain suspended. This allows the sample transfer arm to pass under the lid and the sample to be inserted into the instrument. (B) Following analysis and sample removal, the lid can be returned to the base to prevent air exposure upon removal. This is done by (I) tilting the external magnet at an angle where one side of the lid falls to the sample stage and the other is held at the window. (II) Once the lid is in the correct location, the magnet is lifted completely, allowing the sample to pivot onto the base and seat properly.

suspended by the magnets, allowing the pristine material to pass underneath and be introduced into the instrument for analysis as depicted by the blue, two-sided arrow in Figure 3A.

For further details relating to the introduction and extraction of a sample using PHI mounts, refer to the electronic Supporting Information, relevant instrument operators guide,[19] site-specific standard operating procedures (SOPs), or RBD instruments instruction brochure.[20] The Supporting Information also contains optical images of the holder and chamber (Figure S2) and a complete description of the procedure for using the air-free holder along with graphics demonstrating each step (Figure S3).

Upon completion of analysis, resealing the lid is possible by simply returning the sample holder base to the original position and carefully removing the magnets holding the lid in place as shown in Figure 3B. Dropping the lid onto the base allows it to reseat, and the vacuum environment in the XPS sample antechamber is used to re-establish the negative pressure seal (now even stronger) when exposed to ambient pressure. The sample can then be transferred back to the glovebox, where it can be opened by breaking the seal by using the bleed screw found on the bottom. Through this process, an air-free environment can be maintained repeatedly for a sample going between inert-atmosphere testing and XPS analysis.

SAFETY

The primary safety concerns for using this air-free XPS sample transfer holder are those found when working with vacuums, gloveboxes, and X-ray equipment. This includes being aware of all chemicals present in your workspace, ensuring the sample holder is properly cleaned between all uses (so as to avoid cross-contamination between samples), and having proper training completed through your institution and lab for working with X-ray and glovebox equipment. The primary safety concern more specific to the holder is being aware of pinch-points that occur when working with magnets. In order to make the sample holder, it is recommended that a professional machinist complete the work, but if being completed by an amateur, there are many safety concerns associated with operating machining equipment and proper training and precautions are required. While not shown in the holder schematics, creating a very slight bevel (rounding) on all corners helps to minimize the possibility of cuts when working with the holder.

TROUBLESHOOTING AND MODIFICATION

Multiple iterations of the sample holder were designed, built, and tested before coming to this final design. The lower portion of the base (bottom 0.3 in.) cannot be altered significantly due to how the sample holder is seated and held in the instrument.[20] Similarly, the dimensions of the base overall are limited due to the instrument entrance chamber. The lip around the base was designed to contain the O-ring and elevate the lid slightly relative to the sample stage surface, assisting in the magnetic release of the lid, but was not raised farther to ensure no interference with the incident X-ray beam or any instrument detectors. The lid height was optimized to get the magnet close enough to the entrance chamber window that it could be lifted using external magnets, while being short enough to allow the lid to travel far enough to get past the arm used for inserting the sample stage into the instrument (see Figure 3). The weight of the lid needed to be light enough to be lifted by the magnets, and the transfer holder overall needed to be light enough to not bend or otherwise damage the pronged arm used to insert the sample into the chamber.

The O-ring groove is located in the base in order to keep the O-ring in place throughout sample movement and manipulation both when entering the chamber and when moving the stage in the instrument. The angled bevel (0.085 in. depth) was added to the lid to aid in reseating the lid following analysis, as well as it prevents the lid from shifting when pumping down in the glovebox antechamber, as a higher internal pressure regime is reached in the transfer holder during that process. Pumping down the antechamber slowly and refilling quickly was found to create the best negative-pressure seal on the holder. At times the lid can stick to the

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base and have trouble releasing in the entrance chamber, but the use of additional external magnets can help it to release in those cases. These cases can be minimized by ensuring the O-rings are clean and in good condition, with minimal exposure to solvents or grease, as well as through minimizing the time the sample is left under negative pressure in the holder.

The bleed screw was designed with an O-ring in the base as it provides a very stable seal with the O-ring being contained on the sides by the base and establishing a seal between the button-head screw and the base. A different design was successfully tested using a flat-head screw with the base being carefully counter sunk, creating a direct seal between the screw and the holder base. While both designs work, the tolerances are much tighter for the second option, and therefore the machining skill required is lessened and long-term stability is increased through using the O-ring design. Lastly, each holder lid was custom fit to the attached magnet, as the magnets had poor tolerances, and were press-fit into the lid tops in order to prevent the use of any adhesives that could outgas, dry, or otherwise fail through prolonged use in a chemistry lab.

Considerations for Holder Modification and Adaptation to Alternate Systems. The hope is that this simple design can be used not necessarily as a blueprint for reproduction but as a basis for developing similar holders for other XPS instruments and even non-XPS instrumentation. The fundamental negative pressure sealed lid concept and magnetic release have several necessary or preferred requirements. First, the required components for making an analogous system include (1) the low pressure sample entrance chamber (sample must pass from a chamber into the instrument in order to allow separation from the lid so it does not interfere with taking measurements), (2) the ability to add a gasket/O-ring to the sample holder stage or lid if using a bonded gasket, and (3) the design of a lid with a magnet to accompany the stage. When designing the lid, important considerations must include the lid's ability to clear the sample insertion arm or other apparatus, while still being tall and light enough to interact with an external magnet and remain suspended.

Those are the true fundamentals behind this design, but there are other considerations as well. Generally, there should not be a need to modify the stage at the point where it attaches or interacts with the instrument. Ideally the sample stage would be a flat, solid surface, with the only moving part or potential leak point being a bleed screw. For the instrument, it is beneficial to have a sample chamber with a window/ability to view to view the sample stage but not necessary (remounting would be less precise). Also, our system is ideal as the sample sits horizontally, so the lid is lifted straight up and set straight down, allowing for reseating after analysis. Given the bevel-lipped lid design, it is possible to use the holder in an angled sample port (up to ~50° tilt based on benchtop tests), but postanalysis resealing would likely be an issue at steep angles. One remedy would be to give the lid a step down around the base instead of or prior to a bevel, which would presumably allow the sample to be tilted to ~90° depending on fit, but this would not allow for reseating postanalysis. There are cases where this design simply fails to be applied to other instrumentation as reported here. These instances include most situations where the sample is put directly into an instrument (no antechamber), most fully automated systems that the authors have considered, systems where the antechamber is not conducive to through-wall magnetic interactions, and instances where a sample is not mounted upright (could still work in theory without a magnet and the lid simply falling off, but that would likely be detrimental to the instrument).

CHARACTERIZATION

X-ray photoelectron spectroscopy measurements were performed using a Physical Electronics ESCA 5800 system equipped with a monochromatic Al Kα source (E = 1486.6 eV). Survey scans were performed using a pass energy of 187.85 eV and a step size of 1.6 eV/step. High resolution scans were performed using a pass energy of 23.5 eV and a step size of 0.10 eV/step. A neutralizer (15 μA emission, 1.70 V bias, 40.0 V extractor) was employed to mitigate charging effects. Data analysis was performed using Multipak version 9.3.0.3. Background fitting was performed using the iterated Shirley method, and peaks were smoothed using SG5 smoothing.

DISCUSSION

X-ray photoelectron measurements demonstrate the efficacy of the air-free XPS sample transfer holder. Due to its sensitivity to oxidation upon exposure to atmospheric oxygen, as well as the clear transition between Cu^{+} and Cu^{2+} signals in the XPS, CuCl was chosen as the sensor to test the air-free nature of the holder.[17] Initial assessment of CuCl as purchased showed a slight presence of Cu^{2+}, so the sample was ground in a N_2 glovebox in order to expose the fresh CuCl surface for analysis. To assess the initial purity of the ground CuCl, samples were transferred from the box to the instrument using the transfer holder, and XPS measurements (Figure 4A and Figure S4) identified environments due to only Cu^{+} and Cl^{-} (in addition to C from the carbon tape used to adhere the CuCl powder to

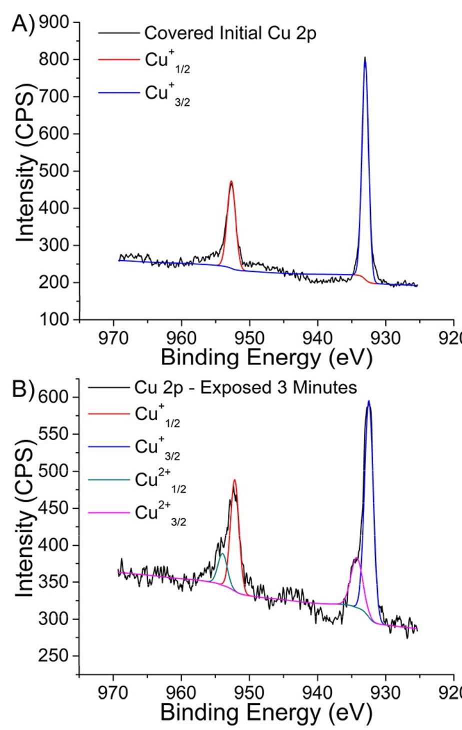

Figure 4. High resolution Cu 2p XPS scans with a calculated fit depicted for (A) CuCl transferred using the designed holder and (B) CuCl transferred not using the holder, resulting in approximately 3 min of ambient air exposure.

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the holder), which are shown in Figure S4. This indicates not only the purity of the starting material but also the ability of the holder to maintain an air-free environment, as no Cu^{2+} peaks were observed.

To the contrary, a comparable sample of ground CuCl was measured under the same conditions and transferred in the same amount of time, though without the use of the air-free transfer holder. Though the time this sample spent in air was only about 3 min, oxidation is readily observable (Figure 4B). An approximately 3 min time of exposure was used because that is the time it takes to quickly transfer the sample from the lab glovebox used to the XPS instrument chamber (which, in our case, involves going down one flight of stairs).

To demonstrate the effectiveness of the holder in maintaining an air-free environment, the covered sample was removed from the instrument and the sealed holder was kept out on a benchtop in the atmosphere for 24 h before being measured again. This process was repeated another 24 h later (for a total of 48 h in the atmosphere after the initial scan). These spectra also show the lack of a Cu^{2+} environment (Figure 5A). Finally, after maintaining the air-free environment in the atmosphere for another 72 h (120 h total in atmosphere), the seal was broken, the lid was removed, and the sample was controllably exposed to ambient conditions for 30 min. The multiple day long experiments were conducted to test the limits of the holder and demonstrate that there is not a slow leak of air being hidden by a 3 min test, but rather a truly robust system, capable of repeated openings, transfers, and analyses, all while maintaining an air-free environment.

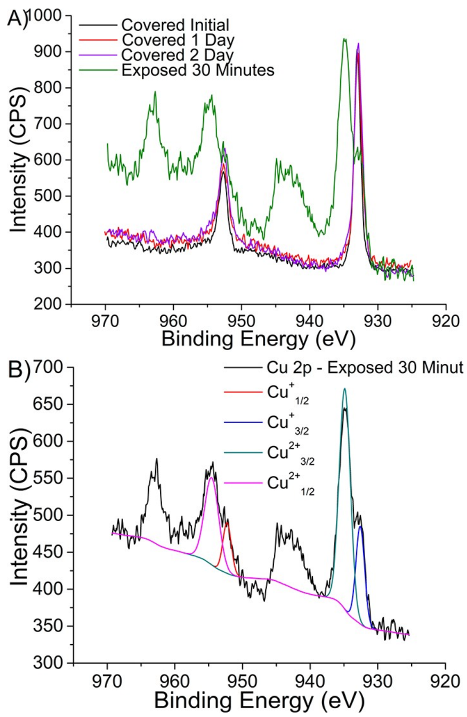

Figure 5. (A) Cu 2p spectra of the CuCl sample as a function of time in the atmosphere in the holder and following air exposure. Despite several days in the holder in air, CuCl only exhibits peaks due to Cu^{+}. However, after 30 min of air exposure, Cu^{2+} peaks and shakeup peaks are readily observable. (B) Cu 2p spectra of the 30 min air-exposed CuCl showing the fitting of the Cu^{+} and Cu^{2+} peaks.

Several significant differences in the spectra are readily apparent when comparing the unexposed material to the same sample after removing the lid (Figure 5A). First and foremost, the appearance of shake up peaks is indicative of the presence of paramagnetic Cu^{2+}, demonstrating that the CuCl readily oxidizes in air. Also, the major signal observed in the Cu 2p scan indexes to Cu^{2+} instead of the intrinsic Cu^{+} associated with the native CuCl. Despite the short time of exposure (30 min), the majority of the CuCl oxidizes, which is consistent with the reactivity of CuCl in air and demonstrates the ability of the holder to remain air-free (since the spectra between exposure to air versus containment in the air-free holder are markedly different).

This becomes even more apparent when these peaks are fit (Figure 4A,B and Figure 5B). For the covered sample (Figure 4A), there are two peaks indicative of the presence of only Cu^{+}. The Cu $2p_{1/2}$ peak has a binding energy of 952.7 eV while the Cu $2p_{3/2}$ peak is at 933.0 eV, with a peak separation of 19.7 eV. Similarly, for the sample exposed to air for 30 min (Figure 5B), the same Cu^{+} environments can be observed, indicating that the CuCl has not fully oxidized in this amount of time. Here, the Cu^{+} $2p_{1/2}$ peak has a binding energy of 952.3 eV and the Cu^{+} $2p_{3/2}$ peak is at 932.6 eV, with the same peak separation. Additionally, a Cu^{2+} environment can be observed with Cu^{2+} $2p_{1/2}$ exhibiting a binding energy of 954.6 eV while Cu^{2+} $2p_{3/2}$ is at 934.9 eV with the same separation energy. A comparison of the air-free sample, 3 min exposed sample, and 30 min exposed sample qualitatively demonstrating these changes can be found in Figure S5.

Slight changes in the absolute binding energy of the Cu^{+} peaks are attributed to ambiguity in the signal-to-noise ratio of the exposed sample as well as uncertainty in the consistency of the carbon signal that spectra were shifted to. Further, due to the paramagnetic nature of Cu^{2+}, shakeup peaks very clearly indicate the presence of the oxidized copper species.

CONCLUSIONS

The XPS data collected on the CuCl samples clearly demonstrate the efficacy of the air-free XPS sample transfer holder. It is shown that the holder is free of air, and this air-free environment can be maintained for extended periods of time and can be used to transfer a sample under inert conditions without contamination by the ambient environment both to-and-from the instrument repeatedly. The final exposure to air results in the rapid oxidation of the CuCl, which demonstrates that there is nothing preventing the oxidation of this species other than the presence of the holder. Through the use of the negative-pressure sealed holder with in-instrument magnetic release, we have presented an opportunity for a sample to be sealed and resealed under vacuum (a condition met in many XPS and inert sample analysis systems). This technique has the potential to avoid the costly infrastructure necessary for inert sample transfer lines or vacuum transfer suitcases, allowing a low-cost alternative for the surface analysis of reactive or unstable species.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.0c01895.

(1) Image showing what is contained in the CAD file, (2) optical images of the instrument antechamber,

holder in the antechamber and sample mounting, (3) schematic representation and discussion of holder operation and procedures, (4) XPS survey spectra and an initial spectra of Cu 2p, Cl 2p, and C 1s, and (5) comparison of the XPS Cu 2p spectra at multiple exposure times (PDF)

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Author Contributions

The manuscript was written by J.D.S. and D.B.A. J.D.S. designed the holder, and D.B.A. performed the XPS oxidation experiments. A.L.P. assisted with drafting and editing the manuscript. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

The editable CAD file may be accessed and downloaded from https://sites.chem.colostate.edu/prietolab/publications.html, under the appropriate reference.

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ABBREVIATIONS

XPS, X-ray photoelectron spectroscopy; CuCl, copper(I) chloride; eV, electronvolt; CPS, counts per second

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