



RESEARCH ARTICLE | NOVEMBER 25 2024

Following the propagation of erroneous x-ray photoelectron spectroscopy peak fitting through the literature. A genealogical approach

Special Collection: [Reproducibility Challenges and Solutions II with a Focus on Surface and Interface Analysis](#)

B. Maxwell Clark ; George H. Major ; Joshua W. Pinder; Daniel E. Austin ; Donald R. Baer ; Mark C. Biesinger ; Christopher D. Easton ; Sarah L. Harmer ; Alberto Herrera-Gomez ; Anthony E. Hughes ; William M. Skinner ; Matthew R. Linford 



J. Vac. Sci. Technol. A 42, 063213 (2024)
<https://doi.org/10.1116/6.0004093>



Articles You May Be Interested In

Site-Specific X-ray Photoelectron Spectroscopy: A New Method To Measure Partial Density of Valence States

AIP Conference Proceedings (August 2003)

Practical guide for x-ray photoelectron spectroscopy: Applications to the study of catalysts

J. Vac. Sci. Technol. A (March 2020)

Pyroshock data acquisition—historical developments using piezoelectric accelerometers and other transducers

J Acoust Soc Am (May 2002)



 Advance your science and career as a member of  [LEARN MORE >](#)

Following the propagation of erroneous x-ray photoelectron spectroscopy peak fitting through the literature. A genealogical approach

Cite as: J. Vac. Sci. Technol. A 42, 063213 (2024); doi: 10.1116/6.0004093

Submitted: 19 September 2024 · Accepted: 23 October 2024 ·

Published Online: 25 November 2024



B. Maxwell Clark,¹  George H. Major,²  Joshua W. Pinder,¹ Daniel E. Austin,¹  Donald R. Baer,³ 
Mark C. Biesinger,⁴  Christopher D. Easton,⁵  Sarah L. Harmer,⁶  Alberto Herrera-Gomez,⁷ 
Anthony E. Hughes,⁸  William M. Skinner,⁹  and Matthew R. Linford¹ 

AFFILIATIONS

¹Department of Chemistry and Biochemistry, Brigham Young University, C100 BNSN, Provo, Utah 84602

²Texas Instruments, Lehi, Utah 84043

³Pacific Northwest National Laboratory, Richland, Washington 99354

⁴Surface Science Western, University of Western Ontario, 999 Collipe Circle, London, Ontario N6G 0J3, Canada

⁵CSIRO Manufacturing, Ian Wark Laboratories, Clayton, Victoria 31685, Australia

⁶Flinders Microscopy and Microanalysis, College of Science and Engineering, Flinders University, Adelaide, South Australia 5001, Australia

⁷CINVESTAV–Unidad Querétaro, Querétaro 76230, Mexico

⁸CSIRO, Minerals Resources, Private Bag 33, Clayton, Victoria 3168, Australia

⁹ARC Centre of Excellence for Enabling Eco-Beneficiation of Minerals, University of South Australia, UniSA STEM, Future Industries Institute, Mawson Lakes, South Australia 5095, Australia

Note: This paper is part of the Special Topic Collection: Reproducibility Challenges and Solutions II with a Focus on Surface and Interface Analysis.

ABSTRACT

This study considers how poor x-ray photoelectron spectroscopy (XPS) peak fitting in the scientific literature is both affected by previous precedent and affects future published work. It focuses on a highly cited paper (the “Subject” paper) from a respected journal that contains incorrect S 2p peak fits. This paper was studied in a genealogical fashion vis-à-vis the XPS peak fitting in its “child,” “parent,” “grandparent,” and “great-grandparent” papers. Interestingly, precedents were not followed to a high degree between parent and child papers. However, in many cases, even when the authors of a study did not follow the incorrect precedent that they cited, they still incorrectly fit their data. Thus, not necessarily for good reasons, the effects of poor XPS peak fits on future generations of papers may be less than some experts had expected or feared. In many cases, older papers appear to contain better XPS peak fitting than newer ones.

Published under an exclusive license by the AVS. <https://doi.org/10.1116/6.0004093>

I. INTRODUCTION

In one of his *annus mirabilis* papers, for which he ultimately received the Nobel Prize, Einstein explained the photoelectric effect.¹ Along with blackbody radiation and the spectra of materials, e.g., the line spectra of gases, the photoelectric effect was a problem that, at that time, physics had not resolved. The solutions to these problems ultimately led to our understanding of the atom

and quantum mechanics. When first introduced to undergraduates in science classes, the photoelectric effect is usually discussed in the context of clean metal surfaces, often under vacuum, their work functions, and sample irradiation with ultraviolet light. With more energy than ultraviolet light, x-ray photons eject core electrons from solids via the photoelectric effect. Einstein’s explanation applies equally well for ultraviolet light and x rays. The kinetic

energies of photoelectrons depend on the energies of the photons that excite them.

X-ray photoelectron spectroscopy (XPS)^{2–5} is a surface analytical technique that is based on the photoelectric effect. In XPS, the kinetic energies of photoelectrons are measured and used to determine the binding energies of the elements in materials. In general, these binding energies identify both the elements present at a surface and their chemical states. Conventional XPS is very surface sensitive because the photoelectrons it generates can only travel short distances (up to a few nanometers) in solids before suffering inelastic losses. XPS has become the most widely used method for chemically analyzing surfaces.⁶ For example, it is frequently used to analyze catalysts.⁷ XPS is now available in multiple modes, including in angle resolved,⁸ depth profiling,^{9–11} imaging,^{10,11} operando,¹² near ambient pressure (NAP-XPS),^{13,14} low temperature,¹⁵ and hard XPS (HAXPES).¹⁶ It is closely related to ultraviolet photoelectron spectroscopy (UPS)¹⁷ and electron-stimulated Auger electron spectroscopy (AES).¹⁸

In spite of the considerable success and widespread use of XPS, there are concerns surrounding the acquisition, analysis, and reporting of some of the XPS data in the scientific literature.^{19–22} A previous effort to understand this issue examined the quality of the XPS peak fitting in a few hundred papers in three reputable journals.¹⁹ This study suggested that as much as 40% of the XPS peak fitting in the literature is wrong and that another ~40% is questionable. Another study evaluated the extent to which XPS instrumental and data fitting parameters are reported in the literature.²³ In many papers, key instrumental parameters are not reported. For example, in some cases, the type of spectrometer used is not even mentioned. Because of these concerns, multiple researchers have wondered how poor-quality XPS data acquisition, analysis, and reporting might affect future acquisition, analysis, and reporting of XPS data.¹⁹ To what degree is poor-quality work propagated? Will substandard peak fitting affect subsequent generations of papers to the point that the XPS literature will cease to be useful? In this paper, we take a genealogical approach to this problem, relating a well-known, problematic paper (the “Subject” paper) to the papers it cited (its “Parents”) and to those that cited it (its “Children”). We also examine the papers that were cited by the parent papers (“Grandparent” papers) and those that were cited by the grandparent papers (“Great-grandparent” papers). This approach allows a “family tree” to be constructed for a paper. An analysis of the quality of the XPS peak fitting in the children, parent, grandparent, and great-grandparent papers of a subject paper may provide some insight into how XPS data analysis in a paper affects subsequent generations of papers. Interestingly, the propagation of errors in the literature was less than may have been expected. However, in many cases, even though the authors of a study did not follow a poor precedent in a paper that they cited, they still incorrectly fit their XPS data. Finally, this analysis of the literature suggests that the XPS peak fitting in the past was better than it is now.

Sulfur is an important element in many contexts, and, accordingly, the XPS of sulfur is of interest to many practitioners of the technique.²⁴ Indeed, sulfur is one of the most common elements analyzed by XPS.²⁰ Sulfur is common in many ores and minerals, e.g., galena, which is PbS. Such sulfides are often only sparingly soluble in water (very low K_{sp} values). Sulfur is an important

element in organic chemistry where it shows up in various functional groups, including in thiols, disulfides, sulfonates, sulfoxides, and sulfones. It plays a useful role in bioconjugate chemistry. For example, thiols react with maleimides in a Michael-type reaction, thiols may be protected as thioacetates, and sulfonate groups are used to increase the water-solubility of NHS-esters and other reagents.²⁵ Two fundamental amino acids contain sulfur: methionine and cysteine. XPS spectra of sulfur are frequently reported, but often poorly analyzed, in battery research, where guidance of this fitting has previously been reported.²⁶ The focus of this work is on some S 2p spectra in a paper that have become quite well-known among XPS experts as examples of incorrect peak fitting.^{27–29} While other XPS narrow scans, e.g., C 1s and F 1s, were also shown in this paper, the fitted S 2p spectra in this paper have received the most attention. Of course, photoemission from *p* orbitals is somewhat complicated by spin-orbit splitting. However, these signals often exhibit less Lorentzian character than photoemission from *s* orbitals, which appear as singlets. It is sometimes challenging to determine where a peak begins and ends when it has substantial Lorentzian character. Thus, S 2p peaks are often easier to fit and integrate. Consequently, and also because of their slightly higher atomic sensitivity factor, the S 2p signal is usually preferred in XPS analyses over the S 2s signal. However, in a few cases, it may be best to avoid the S 2p peaks. For example, they may overlap with other signals, e.g., the plasmons of reduced/metallic silicon.

II. EXPERIMENT

A. General methodology

The Subject paper²⁷ analyzed in this work appeared in a prestigious journal, and it has been well cited, receiving over 1500 citations. The incorrect S 2p fits in the Subject paper are in two figures that show simpler and more complex peak envelopes, where the more complex peak envelope suggests multiple underlying chemical states. The errors in these fits are regarded as classic in XPS data fitting.²⁹ For example, spin-orbit splitting is not considered in these fits, which is a major error (see also the more detailed critique of these fits below). Figure 1 shows reproductions of the S 2p XPS spectra in the Subject paper. Each citation in the Subject paper that contained XPS data or dealt with XPS was designated as a parent paper. Similarly, the XPS-related/containing papers that the parent papers cited were designated as grandparent papers, and the XPS-related/containing papers that the grandparent papers cited were designated as great-grandparent papers. Because the Subject paper has been cited many times, it was not practical to consider grandchildren papers. Furthermore, only the children papers that presented and analyzed/fitted S 2p spectra were considered. That is, only papers that dealt with XPS were considered in the family tree. After creating the family tree, each paper in it was evaluated by experienced XPS analysts according to the rubric in Fig. 2, which is from a study by Major *et al.*²⁰ Papers in the family tree that did not contain an S 2p analysis, but otherwise dealt with XPS in some way, were not assigned a color. To determine whether the papers in successive generations had affected each other, their S 2p peak fits were compared and ranked as highly similar, moderately similar, or bearing little similarity.

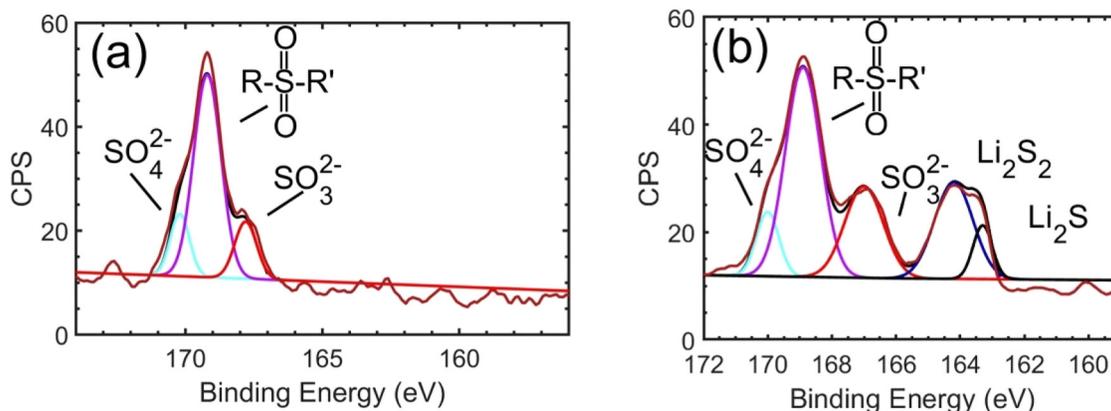


FIG. 1. Examples of the fitted sulfur 2p spectra in the Subject paper. Multiple errors appear, as described in the text, which include the omission of spin-orbit doublets and inconsistent peak widths.

B. Brief critique of the S 2p analyses in the Subject paper

The following is a brief critique of the S 2p analyses in the Subject paper. Both major and minor fitting errors are present.²⁹

Major errors include:

- Lack of spin-orbit splitting. Doublets ($2p^{3/2}$ and $2p^{1/2}$ peaks) in their appropriate 2:1 ratios, respectively, should be used to represent each chemical state in the material.
- Inconsistent and widely varying peak widths/full widths at half maximum (FWHMs).
- Questionable assignments of the peaks to chemical species or oxidation states. The assignments in the Subject paper are inconsistent with reference studies and prior knowledge.

Intermediate errors include:

- Backgrounds that cut through and then extend above the data on the high and low binding energy sides of the peak envelopes.

Less significant errors include:

- Relatively large range of peak binding energy positions or fit components that are assigned as the same chemical states and should have well defined positions.
- The truncation (lack of extended background) on the high binding energy side of Fig. 1(b). It would also be preferable to have a little more extended background on the high binding energy side of Fig. 1(a).

Three positive aspects to these XPS data and accompanying analysis are as follows:

- The signals are not overly noisy. The signal-to-noise ratios in the data are good. The peak envelopes are reasonably well defined.
- The sum of the fit components is shown, which reveals the closeness of the sum of the fit components to the peak envelope. Residuals of fits, which perform a similar function, can also be used to graphically show the goodness of a fit.

- The data are plotted correctly in the sense that binding energy increases to the left.

C. Methodology for evaluating the S 2p spectra in the family tree of the Subject paper

The committee of XPS scientists that evaluated the spectra in this study was composed of most of the authors on this paper, which included: Baer, Biesinger, Clark, Easton, Harmer, Herrera-Gomez, Hughes, Linford, Major, and Skinner. Each committee member was provided the fitted S 2p XPS spectrum or spectra from each paper under consideration in this work (from a literature search from June 2023) and asked to evaluate the quality of these fits independently of the other committee members according to the scheme in Fig. 2. In one case, three committee members (Linford, Major, and Clark) worked together to perform these initial evaluations. This approach of using multiple, separate groups or individuals was employed to minimize bias from other committee members and to give each member (or small group) of

02 December 2024 13:40:51

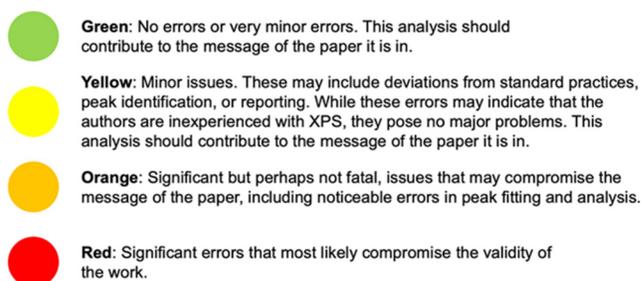


FIG. 2. Scheme used for rating each paper in this work, reproduced from the 2020 paper of Major *et al.* That is, reprinted with permission from Major *et al.*, *J. Vac. Sci. Technol. A* **38**, 061204 (2020). Copyright 2020 American Vacuum Society.

the committee equal representation. The independent ratings of the committee members were then sent to Clark, who organized/compiled them, and the committee then met in an electronic video call to discuss the fit(s) in each paper. In this meeting, which was directed by Clark, the average of the initial ratings and any initial outlier ratings were shown to the committee at the start of the discussion about a fit, the committee discussed any differences in ratings and/or any other concerns with the fits, and a final rating was decided upon once a consensus was reached. For about half of the papers, the committee's initial ratings of the papers did not change. For the other half, the ratings were downgraded roughly 2/3 of the time and upgraded the remainder of the time. In all these cases, only a single paper's rating changed by more than one category. Ratings often changed because a particular committee member possessed specific prior knowledge about the class of samples in an analysis.

The similarities between analyses in successive generations of papers were determined by Clark, Major, and Linford based on the following criteria: inclusion of spin-orbit splitting, whether the appropriate 2:1 peak area ratio for spin-orbit doublets was used when spin-orbit splitting was employed, whether peak widths were consistent throughout the fit, whether appropriate chemical states

had been assigned, the order in which chemical states were assigned over the binding energy range (including whether they were correct or not), the energy range of the background used, and the general handling of the baseline. This evaluation was done independently of the committee and had no bearing on the ratings presented in Fig. 3. Successive papers were judged to be highly similar if their analyses were obviously similar in multiple ways, moderately similar if there was enough similarity to suggest that a given paper had been influenced to some degree by the parent paper it cited, and lacking any significant similarity if the analyses were considerably different per the criteria just mentioned.

III. RESULTS AND DISCUSSION

A family tree for our Subject paper is presented in Fig. 3. It shows the ratings of the S 2p fits in the papers in the tree and also the degree to which the fit in a paper resembles the fits in its parent and children papers. Because of the huge number of papers that have cited the Subject paper, only child papers of the Subject paper that show S 2p peak fittings are displayed. In contrast, all the parent, grandparent, and great-grandparent papers of the Subject paper that either mention XPS, while not showing S

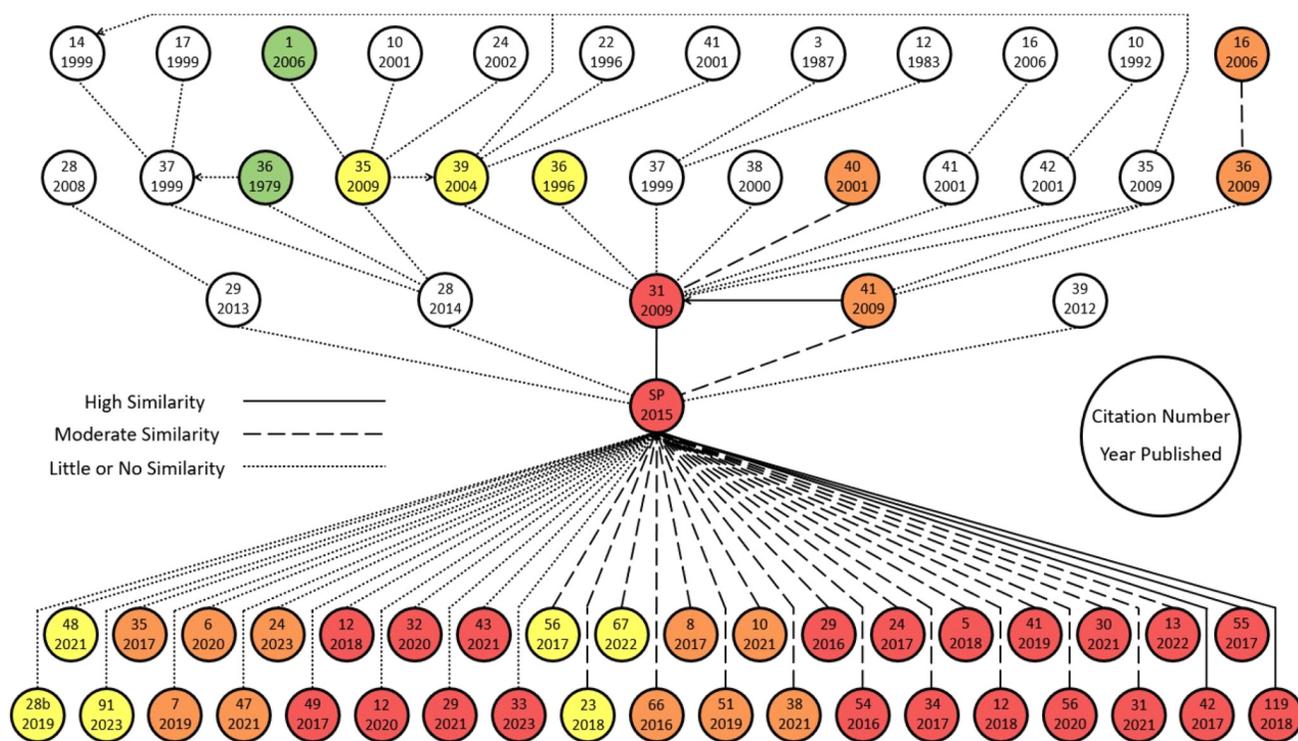


FIG. 3. “Family tree” for the Subject paper (SP) considered in this study. The great-grandparent, grandparent, and parent papers are on the top three rows of this figure, the Subject paper is in the center of the figure, and the children papers are listed on the bottom two rows of the figure. The green, yellow, orange, and red colors in this figure indicate the rankings of the papers (see Fig. 2). Open/white circles indicate papers with XPS analyses but no S 2p data. As indicated in the legend, the type of line between the circles/papers indicates their degree of similarity. The “Year Published” and the “Citation Number” in a circle refer to the year that a paper was published and the reference number in that paper for a parent. To preserve privacy, the majority of the papers referred to in this figure were not cited. Finally, an arrow between two papers points toward the paper that was cited by the other paper.

2p data (black circles), or that show S 2p data (colored circles) are displayed.

In Fig. 3, we first note the overall lack of quality of the S 2p analyses across all the generations. Only 11 of the 48 papers that show S 2p fits in Fig. 3 received favorable (“green” or “yellow”) rankings, where 2 papers (4%) were rated “green,” and 9 papers (19%) were rated “yellow.” Of the remaining papers, 14 were “orange” (29%) and 23 were “red” (48%). These results are in reasonable agreement with a previous review of the XPS peak fitting in the literature.²⁰ This previous study found that, among all peak fitted XPS spectra, ~20% were of good quality (“green” and “yellow”), while the remainder were questionable or believed to be wrong (~40% “orange” and ~40% “red”). The previous study also considered fits of S 2p spectra. Among the 51 papers considered, 30% were “green” or “yellow,” ~30% were “orange,” and ~40% were “red.” These results are reasonably close to those found here.

While the sample size of our survey is limited, Fig. 3 suggests that the S 2p fits in the parent, grandparent, and great-grandparent papers of the Subject paper are of higher quality than those in its child papers. Indeed, 5 of the 10 (50%) S 2p fits in the parent, grandparent, and great-grandparent papers were “green” or “yellow” (2 were “green” and 3 were “yellow”), while only 17% of the 36 child papers received one of these favorable rankings. Furthermore, only 1 of the 10 (10%) parent, grandparent, and great-grandparent papers of the Subject paper received a “red” ranking, while 21 of the child papers did (58%). These rankings appear to correlate with the year these studies were published. The average year that the parent, grandparent, and great-grandparent papers were published was 2003 ± 9 , while the average year that the child papers that contained S 2p fits were published was 2019 ± 2 . XPS experts have observed that the quality of XPS peak fitting in the literature has decreased with time. Indeed, in the past, most XPS analyses came out of research groups that were dedicated to XPS and/or surface science, while, more recently, XPS has increasingly been employed by researchers with other expertise.²² Thus, while the precedents cited by, and that appeared to have affected, the Subject paper were not perfect, there is some suggestion that this work is quite a bit better than much of what is being generated today. We hope, in the future, to review the peak fitting in a larger number of papers that were published in the past, including papers that had excellent precedents, to shed further light on the propagation of erroneous peak fitting.

As just noted, Fig. 3 indicates that it is likely that the XPS peak fitting in the past was, on average, better than that being performed today. However, there is a tendency in science to favor and cite more recent research over older research. Figure 3 suggests that this preference may not always be justified. Paradoxically, in another field, organic chemistry, reactions reported in the literature more than a century ago often prove to be more reliable than those reported in the recent literature. [This opinion was presented by Professor Gerald Dyker from the Ruhr University Bochum (Germany) in his YouTube lectures on organic chemistry^{30,31} and confirmed in a private conversation with the organic chemist Paul B. Savage from Brigham Young University (Provo, UT).] In general, with the limited analytical methods and apparatuses available in the past, only organic reactions that proceeded in high yield, produced products that could be nicely isolated on relatively

large scales by bulk purification methods, and could be analyzed by chemical analysis/derivatization could be well studied. Furthermore, most of these reactions yielded fairly small molecules, so the overall changes in these molecules were comparatively large. The tools needed to study more subtle outcomes simply were not available. Today, organic chemists synthesize very large and complex molecules and observe very small changes in them, e.g., in their stereochemistry. The analysis and discussion of Fig. 3 above similarly suggests that, if one is not an expert in XPS, it may also be better to look for precedents to one’s peak fitting in the earlier literature (before 2010 or even before 2000) than in more recent papers. The year 2010 appears to have been a transitional year in XPS, with noticeably fewer papers beyond that year being published in “surface” journals, which implies that fewer of the authors, reviewers, and editors of these papers were surface scientists. However, the decline in the fraction of XPS-containing papers appearing in surface journals was already taking place by 2010.²⁰

We now make the following additional observations about the Subject paper and those in its family tree. These observations relate to the similarities of the S 2p fits in the various parent and child paper combinations and the quality of the peak fitting in child papers compared to in their parent papers.

- The poor S 2p fit in the Subject paper appears to have originated in one of its parent papers.²⁸ Poor literature precedent can affect future scientific work.
- However, in Fig. 3, there are only 5 examples out of 47 possibilities, 11%, of the S 2p fits in parent and children papers, that are highly similar to each other. Furthermore, 22 incidences, 47%, of the fits in parent and children papers were moderately similar to each other, where it is possible, but not certain, that a precedent was followed, and 20 incidences, 43%, where the fits in parent and children papers bear little resemblance to each other, suggesting that the precedents that were cited had little or no effect on the fit that was performed.
- Interestingly, 16 of the 37 children papers (43%) of the Subject paper showed some *improvement* (“yellow” or “orange” ratings) over the Subject paper, which was “red,” where the 6 of these papers that received “yellow” rankings showed noticeably better fits than the Subject paper.
- Only three of the S 2p fits in the children papers (8%) of the Subject paper were highly similar to the S 2p fit in the Subject paper.
- 21 of the 37 children papers (57%) received “red” rankings. Thus, even when the bad precedents in the Subject paper were not followed, researchers appeared to apply other poor practices to incorrectly fit their XPS data.

Addressing the propagation of erroneous analyses in XPS, and in other analytical methods, is a daunting task that does not have a single remedy. One previous (and, in our opinion, very good) suggestion is that journals use specialized reviewers to focus specifically on the results of a particular characterization technique.^{22,32} This suggestion would probably eliminate most of the gross errors that are appearing in the literature. However, there are challenges with this idea. The pool of willing reviewers is already stretched thin, and while the proposed specialized reviewers would review smaller

parts of papers, the number of papers they might review could be large. Furthermore, more than 50 surface and analytical techniques are regularly used by scientists,²² and many surface and materials studies employ and report data from 5–10 characterization methods. It would be challenging to develop and maintain a pool of specialized reviewers that would have to cover so many techniques and so many papers, where a fairly large number of reviewers might be needed for many papers. Nevertheless, this idea may be viable and helpful for the more commonly used analytical methods such as XPS. At least for now, the burden of collecting good data and interpreting it correctly still rests largely with the authors of studies. They need either to develop a sufficiently high level of skill with a method to be able to collect and interpret the data from it at a reasonable level or to collaborate with an individual that possesses this skill.

In conclusion, while XPS-containing precedents were cited in some cases, the majority of the children papers in Fig. 3 did not closely follow the precedent in the Subject paper that they cited. Accordingly, while literature precedents do play some role in XPS peak fitting, this role may not be extremely significant. These results are also consistent with the idea that, in a number of cases, papers that are cited in the literature are not carefully read.^{33,34}

IV. CONCLUSIONS

Many XPS experts have been concerned that poor XPS peak fitting in papers will propagate throughout the scientific literature and diminish its usefulness. This study shows that erroneous XPS peak fitting precedents can and do propagate. However, the findings of this study also suggest that the propagation of poor XPS peak fits may be less than some may have suspected. The number of peak fits in parent and children papers in Fig. 3 that are highly similar is low; i.e., the peak fits in most parent and children papers in Fig. 3 show moderate to little or no similarity. Thus, many researchers appear not to follow poor precedents. However, this conclusion may be less positive for the community than it may initially appear. While not following the poor precedents that they cited, many papers still contain erroneous peak fits that may affect future analyses. Some current XPS users may simply not be following any precedents or are relying on analyses in more recent papers in application-specific journals, e.g., on energy research, rather than on older work in surface science journals, effectively ignoring established methodology. A quick survey of the papers from this study confirms that only a few are from surface-focused journals, supporting this conclusion. Again, initial indications of this study are that researchers with little experience in XPS are better off following precedents established in older, rather than in more recent, papers. Researchers that are unsure how to collect, report, and fit their XPS data should refer to the many books,^{2,7,15,35,36} guides,^{4,9–14,21,29,37–53} reference spectra, and websites^{54–60} that have been written and maintained by experts.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

B. Maxwell Clark: Conceptualization (lead); Formal analysis (lead); Investigation (lead); Methodology (lead); Supervision (equal); Writing – original draft (lead); Writing – review & editing (lead). **George H. Major:** Conceptualization (equal); Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (supporting). **Joshua W. Pinder:** Writing – original draft (supporting). **Daniel E. Austin:** Writing – original draft (equal). **Donald R. Baer:** Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Mark C. Biesinger:** Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Christopher D. Easton:** Formal analysis (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal); Writing – review & editing (equal). **Sarah L. Harmer:** Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Alberto Herrera-Gomez:** Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Anthony E. Hughes:** Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **William M. Skinner:** Formal analysis (equal); Investigation (equal); Writing – original draft (equal); Writing – review & editing (equal). **Matthew R. Linford:** Conceptualization (lead); Investigation (lead); Methodology (lead); Project administration (lead); Writing – original draft (lead); Writing – review & editing (lead).

DATA AVAILABILITY

Sufficient data to support the findings of this study are present in it. Other data that support the findings of this study are available from the corresponding author upon reasonable request. The data are not publicly available due to privacy concerns.

REFERENCES

- 1 A. Einstein, *Ann. Phys.* **322**, 132 (1905).
- 2 P. Van der Heide, *X-Ray Photoelectron Spectroscopy: An Introduction to Principles and Practices* (John Wiley, New York, 2011).
- 3 P. M. A. Sherwood, *Anal. Bioanal. Chem.* **405**, 2415 (2013).
- 4 F. A. Stevie and C. L. Donley, *J. Vac. Sci. Technol. A* **38**, 063204 (2020).
- 5 C. S. Fadley, *J. Electron Spectrosc. Relat. Phenom.* **178–179**, 2 (2010).
- 6 C. J. Powell, *Microsc. Today* **24**, 16 (2016).
- 7 S. Zafeirotos, *Applications of X-Ray Photoelectron Spectroscopy to Catalytic Studies* (World Scientific, Singapore, 2023).
- 8 C. S. Fadley, *Prog. Surf. Sci.* **16**, 275 (1984).
- 9 A. G. Shard and M. A. Baker, *J. Vac. Sci. Technol. A* **42**, 050801 (2024).
- 10 S. Tougaard, *J. Electron Spectrosc. Relat. Phenom.* **178–179**, 128 (2010).
- 11 S. Hajati and S. Tougaard, *Anal. Bioanal. Chem.* **396**, 2741 (2010).
- 12 S. Suzer, E. Strelcov, and A. Kolmakov, *Anal. Chem.* **93**, 13268 (2021).
- 13 M. Kjærøvik, K. Schwibbert, P. Dietrich, A. Thißen, and W. Unger, *Surf. Interface Anal.* **50**, 996 (2018).
- 14 D. I. Patel, S. Noack, C. D. Vacogne, H. Schlaad, S. Bahr, P. Dietrich, M. Meyer, A. Thißen, and M. R. Linford, *Surf. Sci. Spectra* **26**, 024004 (2019).
- 15 M. A. Isaacs, *Appl. Surf. Sci. Adv.* **18**, 100467 (2023).
- 16 J. Woicik, *Hard X-Ray Photoelectron Spectroscopy (HAXPES)* (Springer, New York, 2016); see: <https://doi.org/10.1007/978-3-319-24043-5>.

- ¹⁷J. E. Whitten, *Appl. Surf. Sci. Adv.* **13**, 100384 (2023).
- ¹⁸J. Wolstenholme, *Auger Electron Spectroscopy: Practical Application to Materials Analysis and Characterization of Surfaces, Interfaces, and Thin Films* (Momentum, New York, 2015).
- ¹⁹M. R. Linford *et al.*, *Microsc. Microanal.* **26**, 1 (2020).
- ²⁰G. H. Major *et al.*, *J. Vac. Sci. Technol. A* **38**, 061204 (2020).
- ²¹D. R. Baer, G. E. McGuire, K. Artyushkova, C. D. Easton, M. H. Engelhard, and A. G. Shard, *J. Vac. Sci. Technol. A* **39**, 021601 (2021).
- ²²G. H. Major *et al.*, *J. Vac. Sci. Technol. A* **41**, 038501 (2023).
- ²³G. H. Major, B. M. Clark, K. Cayabyab, N. Engel, C. D. Easton, J. Čechal, D. R. Baer, J. Terry, and M. R. Linford, *J. Vac. Sci. Technol. A* **41**, 043201 (2023).
- ²⁴Thermo Fisher Scientific, “X-Ray Photoelectron Spectroscopy Table of Elements”; see: <https://www.thermofisher.com/us/en/home/materials-science/learning-center/periodic-table/non-metal/sulfur.html>.
- ²⁵G. T. Hermanson, *Bioconjugate Techniques* (Academic, London, 2013).
- ²⁶V. Shutthanandan, M. Nandasiri, J. Zheng, M. Engelhard, W. Xu, S. Thevuthasan, and V. Murugesan, *J. Electron Spectrosc. Relat. Phenom.* **231**, 2 (2019).
- ²⁷W. Li, H. Yao, K. Yan, G. Zheng, Z. Liang, Y. Chiang, and Y. Cui, *Nat. Commun.* **6**, 7436 (2015).
- ²⁸D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C. S. Kelley, and J. Affinito, *J. Electrochem. Soc.* **156**, A694 (2009).
- ²⁹J. W. Pinder *et al.*, *Appl. Surf. Sci. Adv.* **19**, 100534 (2024).
- ³⁰G. Dyker, Vorlesung Organische Chemie 1; see: <https://www.youtube.com/playlist?list=PLE3EecBGydvSW1PpR0-r1sxdEXroxa-d>.
- ³¹G. Dyker, Vorlesung Organische Chemie 2; see: https://www.youtube.com/playlist?list=PLE3EecBGydvRuZPNsoUcerxtW6_oNIDPD.
- ³²D. R. Baer, J. F. Watts, A. Herrera-Gomez, and K. J. Gaskell, *Surf. Interface Anal.* **55**, 480 (2023).
- ³³L. Borrmann and H. D. Daniel, *J. Doc.* **64**, 45 (2008).
- ³⁴J. T. Evans, H. I. Nadjari, and S. A. Burchell, *JAMA* **263**, 1353 (1990).
- ³⁵J. F. Moulder, W. F. Stickle, P. E. Sobol, and K. D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Physical Electronics, Eden Prairie, MN, 1979).
- ³⁶D. Briggs and J. T. Grant, *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy* (IM and SurfaceSpectra, Manchester, 2003).
- ³⁷T. Conard, A. Vanleenhove, and P. van der Heide, *J. Vac. Sci. Technol. A* **38**, 033206 (2020).
- ³⁸D. R. Baer *et al.*, *J. Vac. Sci. Technol. A* **37**, 031401 (2019).
- ³⁹F. A. Stevie, R. Garcia, J. Shallenberger, J. G. Newman, and C. L. Donley, *J. Vac. Sci. Technol. A* **38**, 063202 (2020).
- ⁴⁰W. E. S. Unger, *J. Vac. Sci. Technol. A* **38**, 021201 (2020).
- ⁴¹S. Tougaard, *J. Vac. Sci. Technol. A* **39**, 011201 (2021).
- ⁴²J. Wolstenholme, *J. Vac. Sci. Technol. A* **38**, 043206 (2020).
- ⁴³D. R. Baerm *et al.*, *J. Vac. Sci. Technol. A* **38**, 031204 (2020).
- ⁴⁴A. G. Shard, *J. Vac. Sci. Technol. A* **38**, 041201 (2020).
- ⁴⁵M. H. Engelhard, D. R. Baer, A. Herrera-Gomez, and P. M. A. Sherwood, *J. Vac. Sci. Technol. A* **38**, 063203 (2020).
- ⁴⁶G. H. Major, N. Fairley, P. M. A. Sherwood, M. R. Linford, J. Terry, V. Fernandez, and K. Artyushkova, *J. Vac. Sci. Technol. A* **38**, 061203 (2020).
- ⁴⁷C. J. Powell, *J. Vac. Sci. Technol. A* **38**, 023209 (2020).
- ⁴⁸P. R. Davies and D. J. Morgan, *J. Vac. Sci. Technol. A* **38**, 033204 (2020).
- ⁴⁹S. A. Chambers, L. Wang, and D. R. Baer, *J. Vac. Sci. Technol. A* **38**, 061201 (2020).
- ⁵⁰N. Fairley *et al.*, *Appl. Surf. Sci. Adv.* **5**, 100112 (2021).
- ⁵¹G. Greczynski and L. Hultman, *J. Appl. Phys.* **132**, 011101 (2022).
- ⁵²G. Greczynski and L. Hultman, *Prog. Mater. Sci.* **107**, 100591 (2020).
- ⁵³M. C. Biesinger, *Appl. Surf. Sci.* **597**, 153681 (2022).
- ⁵⁴A. V. Naumkin, A. Kraut-Vass, S. W. Gaarenstroom, and C. J. Powell, NIST X-Ray Photoelectron Spectroscopy Database (SRD 20), version 5.0, National Institute of Standards and Technology; see: <https://srdata.nist.gov/xps/>.
- ⁵⁵SurfaceSpectra, XPS of Polymers Database; see: <https://surfacespectra.com/xps/>.
- ⁵⁶V. Crist, The International XPS Database; see: <https://xpsdatabase.net/>.
- ⁵⁷V. Crist, The XPS Library; see: <https://xpslibrary.com/>.
- ⁵⁸M. C. Biesinger, X-Ray Photoelectron Spectroscopy (XPS) Reference Pages; see: <https://www.xpsfitting.com/>.
- ⁵⁹RDATAA, XPS Oasis; see: <https://xpsoasis.org/>.
- ⁶⁰The National XPS Service, HarwellXPS; see: <https://www.harwellxps.guru/>.