



Full Length Article

Assessing the robustness of adventitious carbon for charge referencing (correction) purposes in XPS analysis: Insights from a multi-user facility data review

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ABSTRACT

An assessment of X-ray photoelectron spectroscopy (XPS) results from 1237 samples submitted to a multi-user facility from a five year period investigates the usage and effectiveness of common charge referencing methodologies for insulating samples. Carbon 1s (C 1s) starting peak-fitting routines for common graphitic-like materials and for adventitious carbon (AdC) are presented. An average adventitious carbon (AdC) C 1s binding energy of 284.91 eV (Std. Dev. 0.25 eV) was found for 117 samples that also contained a secondary charge reference possibility. With an understanding of the limits and possible issues with using AdC for charge referencing purposes and by incorporating other methodologies (Auger parameter, checks for data self-consistency, well-established peak-fitting routines) it was found that using AdC C 1s for charge referencing gave satisfactory and meaningful results in 95% of the 522 cases assessed. Differential charging is a common issue including in studies assessing AdC binding energies. This work demonstrates that electrical isolation (floating) of mixed insulating/semi-conducting/conducting samples significantly improves outcomes by mitigating differential charging issues.

1. Introduction

X-ray photoelectron spectroscopy (XPS) analysis of insulating materials is complicated by the need to use a charge correction method to compensate for the action of the electron flood gun and other charge neutralization devices. The effects of sample charging in XPS have been discussed at length elsewhere [1–4].

While there are a number of charge correction procedures available to the XPS analyst, the use of adventitious carbon (AdC) is in many cases, the only option available. AdC is generally considered to be a thin overlayer of mainly hydrocarbon (aliphatic with some small amounts of singly and doubly bound oxygen functionality) material that accumulates on air exposed sample surfaces. The source of this carbon has been debated. It does not appear to be graphitic in nature and in most modern high vacuum systems, vacuum oils are not readily present (as they have been in the past) [5–8]. Over time, there have been a number of publications that have evaluated and/or expressed concern about the use of AdC for charge referencing in XPS [4,6,9,10], including recent strong protestations of its use [11–14]. While acknowledging valid concerns,

there is a noted lack of possible effective alternative charge referencing procedures for insulating samples, and so its use continues.

From my years of XPS analysis of a large variety of samples, it has been my perception that the number of times where I have noted a complete failure of the AdC charge referencing method is minimal. What do I mean by this? A failure, from my perspective, would be to not be able to elucidate a reasonable assignment of the chemical states or species present within a sample. This does not mean that the method is perfect or without error, what it means is that by using it in conjunction with other methods and with an understanding of its limits and associated error that one can still obtain meaningful results.

This paper is an evaluation of XPS analysis results taken over a five-year period from a diverse set of 1237 samples submitted to our multi-user facility. The data-driven approach [15] used in this work leverages data acquired from a multitude of project types and varied clientele and combines material science data (XPS data) with information science techniques (methods/workflows, evaluations/standardized methodologies etc.) [16]. This evaluation has been undertaken to see what insights can be made about the types of samples submitted, types of charge

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correction procedures used (where needed), commonly associated problems, and standardized solutions used. One focus will be on samples using AdC for charge referencing, as this has been an area of greatest contention in the literature. This includes standardized fitting parameters and an evaluation of the variation in C 1s functional groups seen for AdC. The use of sample electrical isolation techniques to minimize sample differential charging effects is also explored.

2. Experimental

2.1. Dataset

An analysis was taken of high-resolution XPS data acquired at Surface Science Western (SSW) at The University of Western Ontario (Western University) over a five-year period from January 1, 2017, to December 31, 2021. Data analysed were from 1237 samples submitted for analysis to SSW by academic users at Western University, twelve additional Canadian universities, and a mix of industrial clients from across North America (Fig. 1). University departments and faculties requesting SSW's XPS services include Chemistry, Biochemistry, Physics, Earth Sciences, Materials Science, Anthropology, Dentistry, and Medicine, as well as Engineering departments such as Chemical, Biochemical, Materials, Mechanical, Biomedical, Civil and Environmental. SSW's industrial clients are from multiple sectors including automotive, energy, mining, environmental, electronics, medical, aerospace, defence, and general manufacturing. On a yearly basis, SSW works with between 175 and 200 separate small, medium and large companies. Over this five-year period, approximately 60% of our industrial clients were from Ontario, 15% from the rest of Canada, 22% from the United States (approximately 68% of these are from Michigan, Ohio, New York, California, Texas, and Indiana) and 3% from international clients. All these metrics are presented to illustrate the diversity of sources and types of samples that have been analysed in this dataset. The collected metadata is included in the [supplementary information](#) section.

2.2. Sample classification

All samples received, including sample details and analysis requirements, are logged in and tracked using a custom database. Additionally, external university and industrial client analyses follow our ISO 9001:2015 (up to 2020) and ISO 17025:2017 (2021) sample submission, handling, and tracking procedures. Generally, sample details (e.g., type

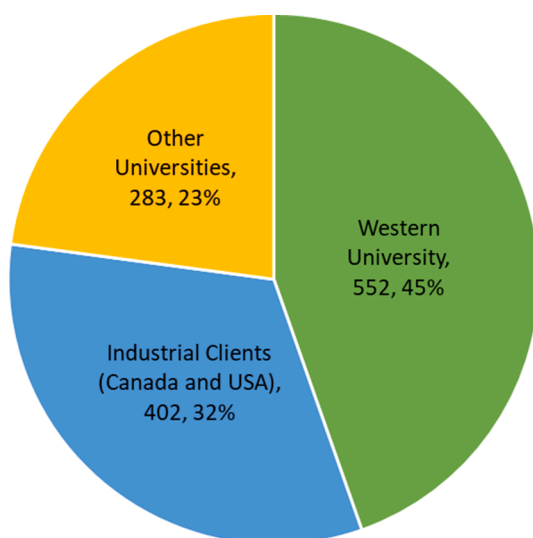


Fig. 1. Source of 1237 samples analysed over 5-year period (January 1, 2017, to December 31, 2021).

of sample, possible chemistries), analysis requirements (e.g., what results are needed, what species could be expected), handling issues (e.g., toxic materials, air/water sensitivities, heat, or X-ray degradation possibilities) et cetera are discussed with the clients prior to analyses being undertaken. These types of client communications are essential to successful analyses. For this dataset, samples were catalogued by type of sample and by conducting/insulating properties. Fig. 2 shows a broadly characterized percentage breakdown of the types of samples analyzed. Note that many samples can fall into multiple categories. For example, some metals/metal oxides could also be described as thin films, and some powder/nano inorganic samples could also contain graphite or graphene components etc. Samples were also broadly assessed as being conducting, insulating, or a mix of conducting and insulating (or semi-conductive) components (Fig. 3). For consistency, only samples where all sample analysis and data processing (curve-fitting) that was carried out by the author are included in this dataset.

2.3. Sample mounting

Where possible, fully conductive samples were mounted on the sample holder with conductive clips or using a conductive copper tape, providing good sample electrical contact with the holder. Samples that were deemed to have the possibility of containing both conducting (or semi-conducting) and insulating components were mounted so that they were electrically isolated from the holder (sometimes referred to as "floating the sample"). Benefits of this isolation technique are discussed in Baer et al. [4]. Within this dataset, 1143 (93%) of the samples were either fully insulating by nature or were electrically isolated during sample mounting (issues with samples where isolating was not done due to sample constraints discussed later). Sample isolation was generally either done by mounting the sample on a glass slide or, in the case of powders, on a non-conductive double sided adhesive tape. As a note of caution, choice of tape used is critical as we have found that there are some that are heavily contaminated with silicone release agent. Testing of any adhesives used for XPS is highly recommended, including testing of specific rolls of the same brand.

For many flat polymeric and coating samples, a copper tape masking technique was used to improve charge neutralization of the samples. With this technique, copper tape is used to surround a small area of the surface (generally a 5–10 mm square area) for analysis. Care is taken to press the tape flat onto the sample surface. Note that for this technique, one does not necessarily electrically connect the sample to the holder with tape, while it is not an issue for fully insulating samples, care should be taken for the sample to remain electrically isolated for mixed metal/oxide films and other mixed conductive/insulating samples. In some cases within this dataset, it was only understood that the sample was fully conductive after the analysis was taken and they may have been initially treated as mixed conducting/insulating samples and electrically isolated.

2.4. Instrumental

Prior to December 2018, the XPS analyses were carried out with both Kratos AXIS Ultra and Kratos AXIS Nova spectrometers (Kratos Analytical, Manchester, UK) using a monochromatic Al K α source (15 mA, 14 kV). From December 2018 onwards, analyses were carried out using a Kratos AXIS Supra spectrometer using a monochromatic Al K α source (15 mA, 15 kV). For all instruments the work functions are calibrated to give an Au 4f_{7/2} metallic gold binding energy (B.E.) of 83.96 eV. The spectrometer dispersion was adjusted to give a B.E. of 932.62 eV for metallic Cu 2p_{3/2} [17]. Our ISO process specifies that instrument calibration is within ± 0.025 eV of these values and that routine maintenance, instrument checks and calibrations are carried out at specific intervals. Instrument base pressure for all instruments was 1×10^{-9} Torr or better. The Ultra and Nova instrument analysis chambers are pumped using ion pumps while the Supra instrument analysis chamber is

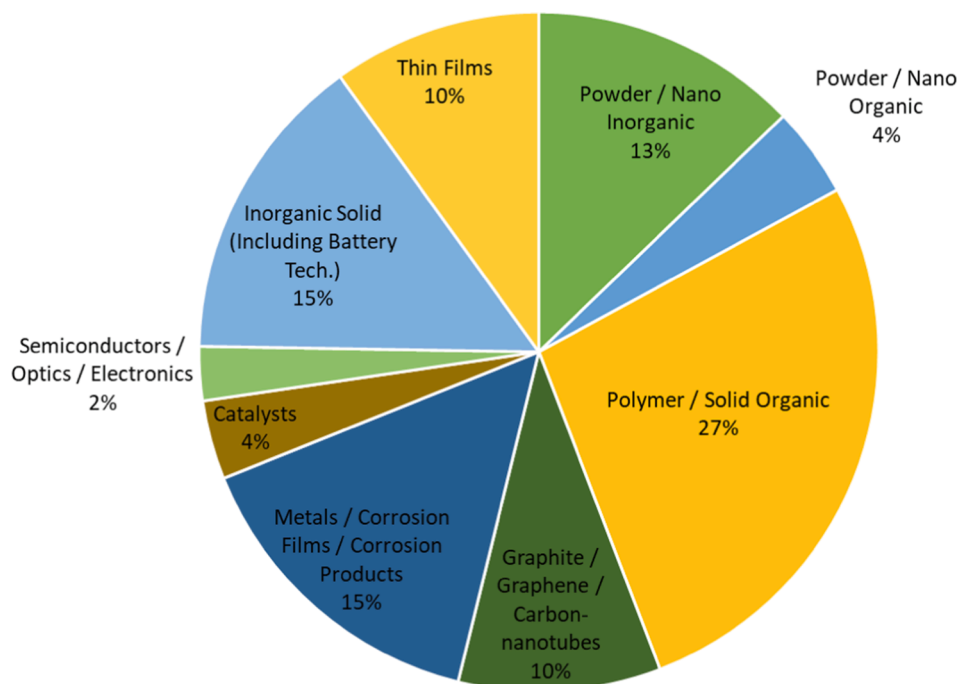


Fig. 2. General classification of sample types from 5-year period. Note that some samples may be classified in multiple ways.

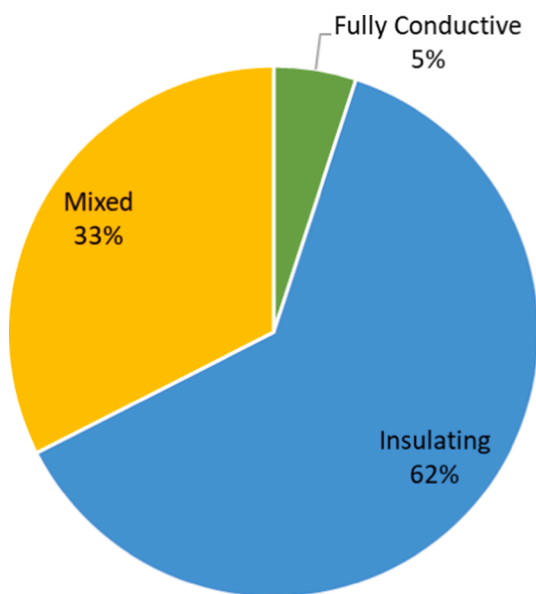


Fig. 3. Percentage of samples identified as conductive, insulating, or mixed conductive and insulating.

pumped using a turbomolecular pump backed by a two-stage rotary vane pump. The introduction chambers for all instruments are pumped using turbomolecular pumps backed by two-stage rotary vane pumps.

For most analyses, high-resolution spectra were obtained using an analysis area of $\approx 300 \times 700 \mu\text{m}$ and a 20 eV pass energy. This pass energy corresponds to a Ag $3d_{5/2}$ FWHM of 0.55 eV. In some instances where improved resolution was deemed necessary, a 10 eV pass energy was used. When low counts were noted due to low levels of a specific element of interest or during small spot analysis, a pass energy of 40 eV was used. All analyses were taken using a 90° electron take-off angle.

The Kratos charge neutralizer system was used for analyses as needed (insulating, mixed conducting/insulating and electrically isolated samples). The Kratos charge neutralizing system uses a coaxial low energy

electron source within the field of the magnetic lens. The energy resolution of this system for insulating materials is demonstrated by data showing FWHM of <0.68 eV on the ester component in polyethylene terephthalate (PET). Charge neutralization was deemed to have been fully achieved by monitoring the C 1s signal for many samples. A sharp main peak with no lower binding energy structure is generally expected. Spectra were analyzed using CasaXPS software [18] (version 2.3.14). A standard Shirley background is used for all sample spectra shown in this work.

3. Results and discussion

3.1. Charge reference assessment

Fig. 4 presents the number of times different charge referencing procedures were used for the 1237 samples from the five-year period. During the data review an assessment of the effectiveness of each procedure was carried out on a sample-by-sample basis. Any data issues and anomalies were noted and will be discussed in the following sections. A successful outcome for each sample analysis would generally be a satisfactory assessment of the chemistries present using a variety of tools available including:

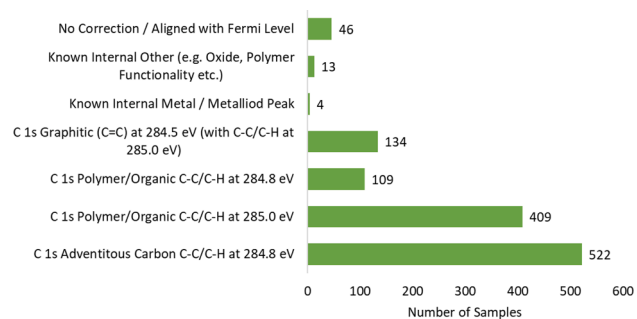


Fig. 4. Charge reference used for the 1237 samples analysed over the five-year period.

- (a) binding energies of specific peaks
- (b) Auger parameter data (where available)
- (c) curve-fitting routines of complex peak shapes (both core line and Auger spectra) including spin-orbit doublets, peak asymmetries, multiplet splitting, satellite structures, and spectral overlaps
- (d) checks of internal self-consistency within the data including:
 - (i) high-resolution data for different elements show same chemistries (e.g., O 1s spectrum show lattice oxide is present matching assessment of NiO in the Ni 2p spectrum).
 - (ii) stoichiometry assessed from survey scan data matches chemistries from high resolution data

During the sample analysis phase, anytime issues were noted (e.g., differential charging, insufficient charge neutralization, etc.) samples were rerun as needed to obtain results that fit the parameters above. For this dataset, full data analysis was carried out by this author with assignments of chemistries made. In a very small number of cases, peak assignments may not be fully attempted as confidentiality issues prevented sharing of needed sample information. In no case would data be released to our clients (academic or industrial) that would be deemed unacceptable for publication. As a further check on data quality, an in-house peer review is carried out prior to release of all data and reports to our industrial clients.

3.2. No correction/aligned with Fermi level (FL)

The number of fully conductive samples analyzed is quite small at approximately 5% of the total sample set. In our facility, requests for analyses of pure metals and single crystals have been minimal over this timeframe, as have requests for acquisition of valence band spectra for Fermi level (FL) analysis. Conductive materials analyzed include Pt-Au and Pt-Ni alloys (after sputter cleaning), graphitic materials, very thin metal oxide films (Ni, Cu, Fe, Mn, Ag, Sn, Cd, Zn), and a small number of semiconductor materials (Ge, Si). For many of these metal and semiconductor samples an assessment of the position of the AdC C 1s peak was possible and is included in the data presented in that section.

3.3. Known internal component

In a small number of cases (17) charge referencing was made to a known component within the samples such as a metallic peak, a specific metal oxide or sulfide, or known polymer functional group. Reasons include low amounts of carbon on the surface (either not present or due to sample sputter cleaning), interferences from unknown organic chemistries with no clear C 1s C-C/C-H peak, or just preference in certain instances to reference to a well-established internal reference peak that is part of the sample. Some examples used include metallic Au film surfaces, S 2p_{3/2} peak for MoS₂, and N 1s for N in an aromatic ring. In one sample from the entire sample set, an internal component of the sample was used for referencing as it was clear that AdC was not in good electrical contact with the sample and could not be used as a charge reference. This was a mixed insulating/conductive sample that could not be electrically isolated for analysis (Li battery research sample with stringent sample preparation and handling requirements).

3.4. Graphitic/Graphene/Carbon nanotube (C=C)

Materials of a graphitic nature (e.g., graphite, graphene, carbon nanotubes etc.) will have a C 1s main peak, attributed to C=C, which can be used as a charge reference set to 284.5 eV. An average of values for graphite from 21 references from the NIST database [19] is 284.46 eV with a standard deviation of 0.14 eV. Note that the well characterized value of 284.5 eV for graphitic carbon is also a strong indicator that this value is not appropriate as a value to use for AdC charge referencing. While these types of samples are generally conductive and if they can be mounted in a manner (in electrical contact with the sample stage) to

take advantage of this one should do so. However, many of these types of samples come to us as a small volume of powders or flakes which are very difficult to mount. Usually, we mount these on a double-sided adhesive which works well but electrically isolates the sample. Oxidation of these types of samples (e.g., graphene oxide) or their functionalization (e.g., functionalized CNTs) can result in them behaving less conductively or as a mixed conductive/insulating material. Samples where these materials are mixed with other conducting or insulating compounds can also result in a mixed conductive/insulating sample. For most of these types of samples we now electrically isolate the sample and charge reference to C 1s at 284.5 eV for the graphitic (C=C) peak. In a minor number of cases, where the main elements of interest were not related to carbon (e.g., metal oxides or other inorganic species), a charge reference of the C=C peak to 284.3 eV (subsequently placing the aliphatic (C-C, C-H) peak at 284.8 eV) was used.

Table 1 presents general fitting parameters for graphitic, graphene and carbon nanotube type materials. These starting fitting parameters include the main peak asymmetry (defined using an asymmetric Lorentzian (LA) line shape [20,21]) and π to π^* shake-up satellite from a pure graphite standard sample. These fitting parameters are similar to the approach taken by Morgan (Fig. 5, Table 2), [22] Moieni et al. (Table 1), [23] and Gengenbach et al. [24]. It is always best to run your own standard (pure graphite, graphene, CNT etc.) to get fitting parameters appropriate for your sample type, instrument and conditions used. Slight differences in the main peak asymmetry and differing shake-up satellite position, shape and intensities are possible for differing classes of graphitic materials. See for example from Morgan [22] where HOPG and nano-onion C 1s spectra show peak-shape differences, likely due to hydrogenation of the sample. However, with this caveat stated, the parameters used based on a graphite standard have worked very well for variety of samples (134) analyzed in this five-year survey. Fig. 5 (A) presents the standard graphite spectrum used to obtain the parameters presented in Table 1. The spectra from Fig. 5 (B, C and D) show the use of these fitting parameters from Table 1 to effectively model a variety of graphitic component containing materials.

3.5. Polymers or organic materials

A total of 518 polymer and organic materials were analyzed over the five-year period. For most of these samples (409) the main C 1s peak for aliphatic carbon (C-C, C-H) was charge referenced to 285.0 eV to match the referencing used in the seminal work of Graham Beamson and David Briggs in their book "High Resolution XPS of Organic Polymers, The Scienta ESCA300 Database" [25]. This work has been foundational for all that conduct XPS on polymeric and organic materials. Every serious XPS facility should have a copy readily available for its users (now available via SurfaceSpectra Inc.).

A smaller portion of polymeric and organic material samples (109) used a charge reference of 284.8 eV for the aliphatic C 1s peak. When this reference was used it was generally because the focus of the analysis was to characterize elements not associated with the organic material (i.e., not C, N, O) for which 284.8 eV is a more common charge reference. As the carbon used for referencing is integral to the sample (as opposed to only on the surface for AdC), in only one instance were issues noted when using this reference in this survey. In two similar samples, where Ni(OH)₂ was present as a species of interest within an organic matrix, the binding energy envelope fitting parameters [26] for Ni(OH)₂ needed to be set at approximately 0.2 eV higher than normal to allow for a satisfactory fitting of the Ni 2p envelope.

3.6. Adventitious carbon (AdC)

522 of the 1237 samples from this five-year period were charge referenced to the main line of the C 1s spectrum for aliphatic carbon from adventitious carbon (AdC) set to 284.8 eV. Note that one must be clear about stating that it is actually adventitious carbon that is being

Table 1
General fitting parameters for graphitic/graphene/carbon nanotube type materials.

Species	Peak Identifier	Starting Position (eV)	Common Range (eV)	FWHM (eV)	Lineshape	Area Constraint	Notes
C=C	A	284.5		0.4–0.8 eV	LA(1,2,2,5,5) #		Peak defined here by pure graphite sample
C–C, C–H	B	A + 0.5	A + 0.3 to A + 0.5	0.9–1.3 (tip to 1.5)	GL(30) ##		In most relatively pure graphitic based systems not a lot of this peak should be expected
C–OH, C–O–C	C	A + 2.0	A + 1.8 to A + 2.2	B*1	GL(30)		
C=O	D	A + 3.5	A + 3.3 to A + 3.5	B*1	GL(30)		
O–C=O	E	A + 4.5	A + 4.3 to A + 4.8	B*1	GL(30)		
π to π^* Sat.	F	A + 6.41		2.7	GL(30)	A*0.06963	Position, FWHM and area constraints can change depending on starting material (e.g. graphite vs CNT) - use values from appropriate reference sample

Nomenclature for CasaXPS - define in other software using pure graphite/graphene or CNT sample related your specimens.
Gaussian/Lorentzian product formula, GL(30) is 30% Lorentzian 70% Gaussian.

referenced for a sample. It must not be graphitic, polymeric or an organic material that is part of the sample itself. This ambiguity about the source of carbon used for charge referencing is a major part of the confusion surrounding AdC's use as a charge reference in the literature.

Table 2 presents common fitting parameters for AdC. A single peak (Gaussian (70 %) – Lorentzian (30 %)), ascribed to alkyl type carbon (C–C, C–H), is fit to the main peak of the C 1s spectrum. A second peak is added that is constrained to be 1.5 eV above the main peak, and of equal FWHM to the main peak. This higher B.E. peak is ascribed to alcohol (C–OH) and/or ester (C–O–C) functionality. Additional components at higher B.E., C=O, 2.8–3.0 eV above the main peak, and O=C=O, at 3.8–4.3 eV above the main peak are also usually added, again constrained to have the same FWHM as the main peak. The peak ascribed to O=C=O shows the most variation between differing samples. Intensity ranges from nil to a well-defined peak with sufficient resolution to necessitate removing its FWHM constraint to the C–C, C–H main peak. Its position also can move noticeably. A summary of the binding energy positions used in its fitting for AdC in this survey is presented in Fig. 6. Fig. 7 presents a series of typical spectra for AdC on a variety of sample surfaces. For the majority of samples, the standard fitting starting position of A + 4.0 eV (where A is the main C–C, C–H peak) for the O=C=O peak is sufficient, and the fitting wouldn't normally be changed for smaller shifts of ~0.1 eV. In approximately 30% of the assessed samples, excluding samples where O=C=O was not noted or where overlap with carbonate species from within the samples precluded accurate positional assessment (note carbonate species are not normally associated with AdC), this peak was at or around A + 4.3 eV. In a smaller group (~10%), this peak was at a lower binding energy around A + 3.8 eV. Changes in the type and amount of oxygen containing moieties depending on substrate analyzed are also noted by others [9,10]. While these results indicate that the nature of the functionality associated with AdC does vary somewhat, these changes shouldn't play much of a role in the positioning of the main aliphatic peak used for charge referencing.

In 117 samples where AdC was used for charge referencing, a possible secondary internal charge reference was also available, generally from a metallic peak (Au, Pt, Cu, Ag, Ni, Fe, Co, Cr, Nb, Pd, Zn, Al, Cd), other conductive or semiconductive species (Si(0), Se(0), Ge(0)), or well defined component (Mo 3d_{5/2} or S 2p_{3/2} peak for MoS₂, Fermi level). These secondary references were used to assess the deviation of the aliphatic C 1s signal for AdC from the 284.8 eV standard value used. Included in these 117 sample results are some fully conductive samples where an assessment of the peak position for AdC could be made (as noted in *No Correction/Aligned with Fermi Level* section). Results of this assessment are presented in Fig. 8. The average deviation from the reference 284.8 eV value obtained is +0.11 eV, with a standard deviation of 0.25 eV. This corresponds to an AdC C 1s value of 284.91 eV (standard deviation 0.25 eV). The median value for these 117 samples is +0.16 eV, or 284.96 eV. It should be noted that some of the error associated with these values will come from the error associated with the binding energy values used for the secondary references as not all, particularly the more obscure metals, are as well characterized as others. Where available, binding energies of metal standards taken on instruments within our laboratory under similar analysis conditions were used [26–29].

The B.E. values and standard deviations found here align well with some of the previous estimates in the literature. Swift [6] lists several studies showing errors ranging from ±0.1 eV to ±0.4 eV. “Newer” studies (late 1970's) range from ±0.1 to ±0.3 eV. “Older” studies (late 1960's to early 1970's) were in the ±0.4 eV range - however, reproducibility and resolution of the spectrometers of the time may have played a role. Barr's [5] work from 1995 states that error in using adventitious carbon is ±0.2 eV. Our work [7] in 2002 also suggested error in the ±0.2 eV to ±0.3 eV range.

Crist's [9] 36 old native oxides surface on metals showed the AdC C 1s at 285.4 eV with a standard deviation of 0.55 eV. The same samples

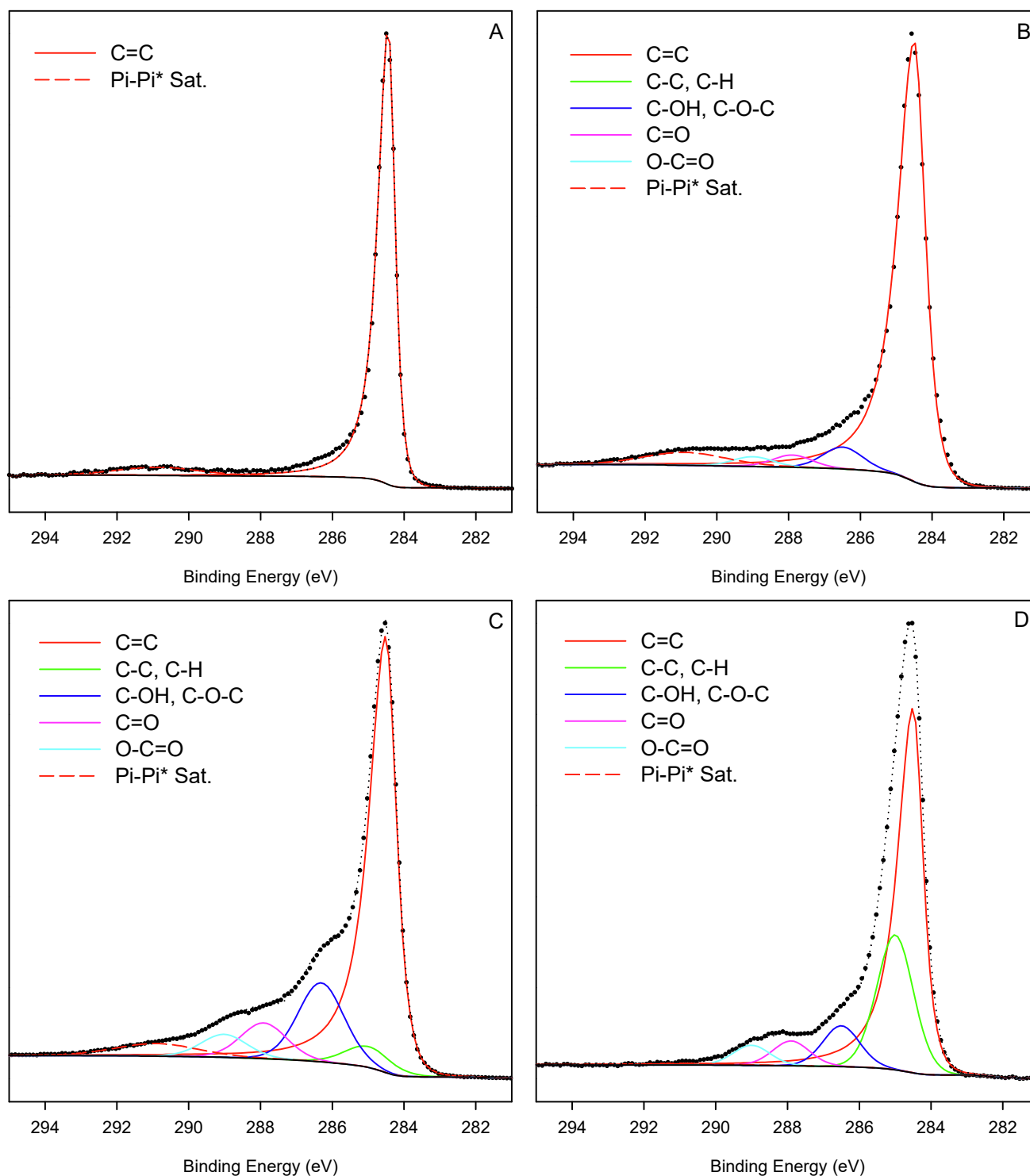


Fig. 5. Examples of curve-fitting of graphitic type systems using the parameters from [Table 1](#). A) pure graphite, B) carbon nanotube-based material modified in caustic solution, C) oxidized graphene and D) acid modified graphene and organic compound mixture.

after ion etching and 10 h in UHV showed an AdC C 1s mean of 284.9 eV with a standard deviation of 0.56 eV. Crist asserts that “Based on these statistics, the 284.9 eV value, which is free from any native oxide effects, is probably the more reliable number to be assigned to the hydrocarbon moiety. The high 285.4 eV number from native oxides is probably due to unexpected charging effects or surface dipole moments, neither of which have been studied.”

Greczynski and Hultman’s work [10,12] on AdC on magnetron sputtered thin films of metals, nitrides, carbides, borides, oxides and

oxynitrides has shown a large AdC C 1s range of 284.08–286.74 eV. Substrates were mainly Si (001) (with some on Al₂O₃ or steel as well as a few pure metal samples) and film thicknesses were between 80 and 2560 nm. These 89 samples, mounted with good conductivity to the spectrometer and showing the Fermi level cut-off at 0 eV for all samples, were air exposed at ambient conditions for several weeks to a few years. The authors state “It seems that the fact the AdC is not an inherent part of the analyzed sample and as such may not remain in proper electrical contact by establishing a common Fermi level across the interface” [12].

Table 2
Adventitious carbon (AdC) C 1s curve-fitting parameters.

Species	Peak Identifier	Starting Position (eV)	Common Range (eV)	FWHM (eV)	Constraints	Lineshape	Notes
C—C—H	A	284.8		0.7–1.5		GL(30) #/ #	
C—OH, C—O—C	B	A + 1.5	A + 1.3 to A + 1.7	A*1		GL(30)	1.2–1.3 eV FWHM is common, narrower main peak may indicate polymeric material
C=O	C	A + 3.0	A + 2.8 to A + 3.0	A*1		GL(30)	
O—C=O	D	A + 4.0	A + 3.8 to A + 4.3	A*1		GL(30)	See Fig. 6 for position distribution, if peak-shape is well defined remove FWHM constraint

Gaussian/Lorentzian product formula, GL(30) is 30% Lorentzian 70% Gaussian.

What is not considered is that the various oxide, hydroxide or hydrated oxide films of varying thicknesses formed on these weeks to years long air exposed samples is adding (layered) differential charging issues into this dataset. From the supplemental data¹² an average AdC C 1s value of 285.23 eV was found with a standard deviation of 0.58 eV. The higher average B.E. value, standard deviation and larger range is very similar to that seen for Crist's old native oxides (ave. 285.4 eV, standard deviation 0.55 eV, range 284.5–286.7 eV, all samples in good electrical contact with the spectrometer) – data for which Crist states suffers from differential charging effects.

The amount that differential charging, in particular for layered materials containing conductive, semiconductive and insulating layers, has caused variability in the AdC C 1s value in these and other works is worth considering. It should also be noted that a key tenet on the use of AdC as a charge referencing mechanism is that there will be vacuum level alignment between AdC and the sample, something that differential charging can disrupt. The extensive use of electrical isolation of samples within this present dataset, and the subsequent low standard deviation value and smaller range for AdC found in this work, suggests its use is beneficial. To further illustrate the issue with thin oxide films causing differential charging the reader is referred to examples in reference 4 sections B2 and D4, which describes and shows the variation in positioning of thin film oxide peaks in relation to the metallic peak for specimens conducting to the spectrometer with the charge neutralizer both off and on and compared to the same sample isolated from ground (floating, C/N on). The position of the AdC C 1s peak, which is in contact with the oxide film, will naturally shift along with the position of the oxide peaks in relation to the metallic substrate (and FL cut-off). This also lends support for the extensive use of electrical isolation for samples where any component of the sample is insulating in nature.

To further illustrate this issue, reference 14 presents a series of spectra taken at 0.1 mm steps across a Au foil/Al foil (with a significant oxide film) interface with the foils in good contact with each other and with the sample stage. These results show a splitting of the AdC C 1s peak going from the Au to Al foil surface, with the AdC C 1s on Au at 285.0 eV and on Al at 286.6 eV (FL at 0 eV for all spectra). The authors suggest that this result “should terminally disqualify the charge referencing method based on the C 1s peak of AdC, and refute the deep-

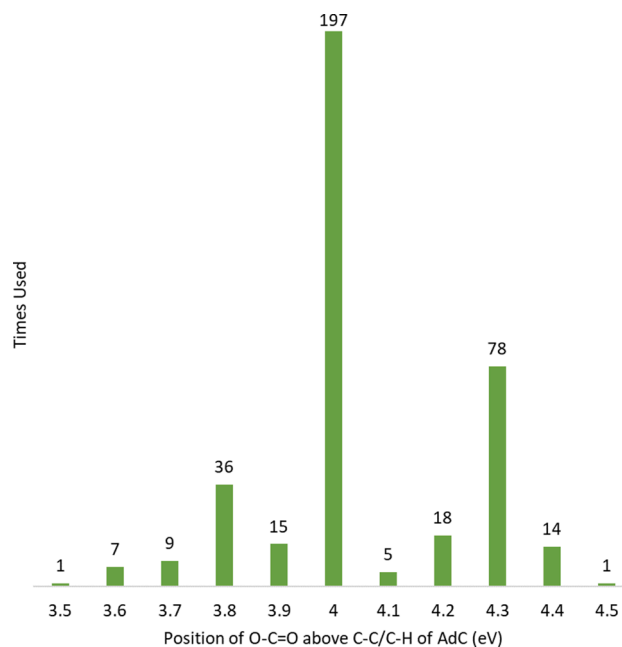


Fig. 6. Position of the O=C=O peak above the main line of C—C, C—H for adventitious carbon (AdC).

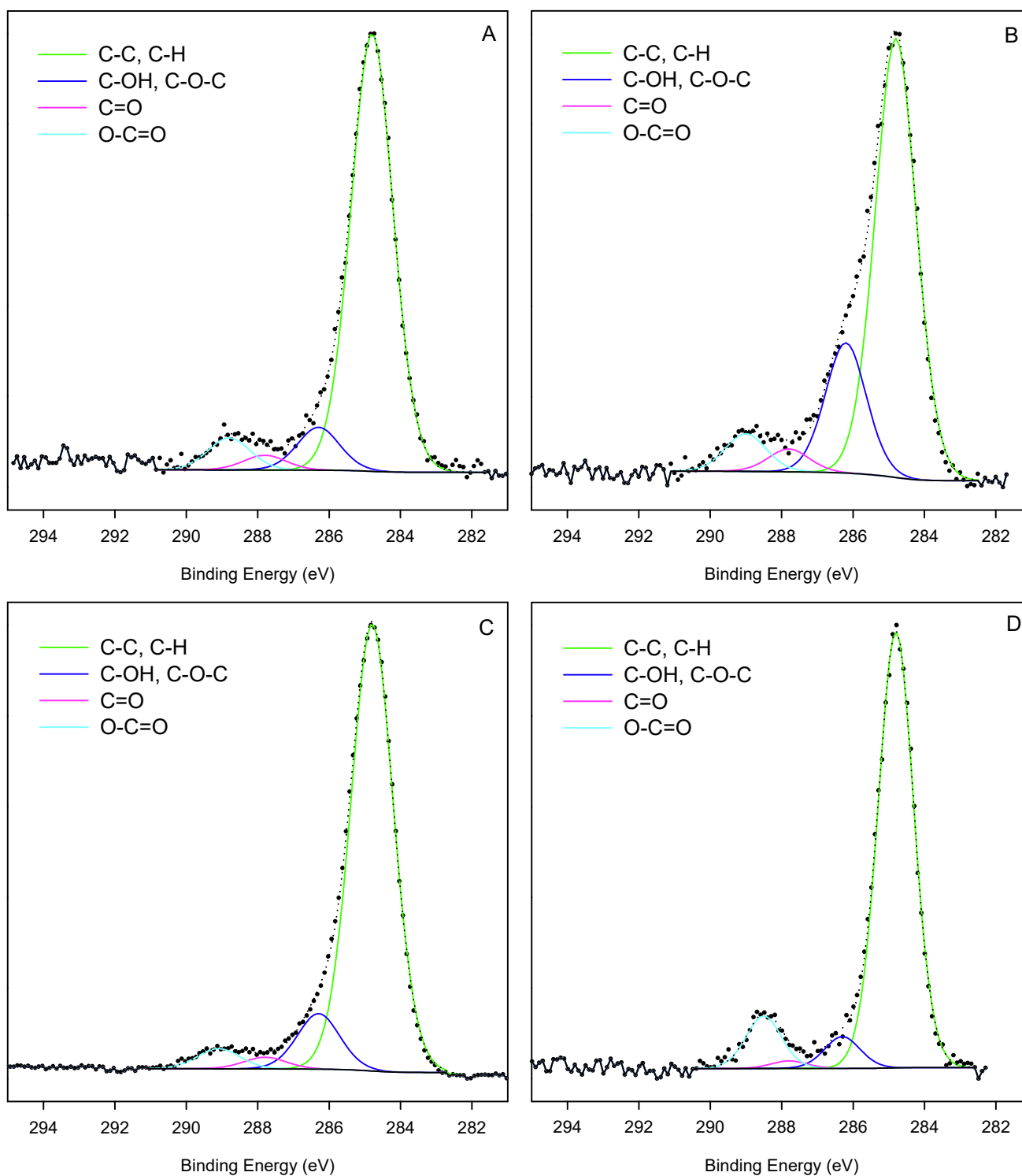


Fig. 7. Examples of curve-fitting of adventitious carbon (AdC) using the parameters from [Table 2](#). A) an oxidized cadmium and molybdenum disulfide containing surface, B) tin oxide film with iodine and phosphorus containing components, C) mixed copper and aluminum oxides thick film and D) lithium sulfide and phosphorus containing material.

rooted notion that the same chemical state gives rise to peaks at well-defined BE values.” However, if one duplicates this experiment with the Au and Al foils electrically isolated and using the instrument charge neutralizer, no splitting of the AdC C 1s main peak is found moving from the Au to Al foil. [Fig. 9](#) presents the C 1s spectra obtained after charge correction to FL (or to Au 4f_{7/2} peak at 83.95 eV – matching results). The C1s peak in this work is at 285.18 eV (Std. Dev. 0.08 eV) if referenced to FL or 285.10 eV (Std. Dev. 0.03 eV) if referenced to Au 4f_{7/2}. See

[supplementary information \(S1-S5\)](#) for Au 4f_{7/2}, Al 2p, O 1s and valence band spectra. Additionally, the Al 2p for the oxide film is at 74.8 eV in this work which is in line with accepted values. This compares to ~76 eV in reference 14, which again suggests significant charging of the oxide film. An analysis of an Al foil only area on the floated sample gave an AdC C 1s value of 285.8 eV when corrected to the (now Al metal only) Fermi level. The uncorrected C 1s peak is still in a similar position to the mixed Au/Al C 1s spectra.

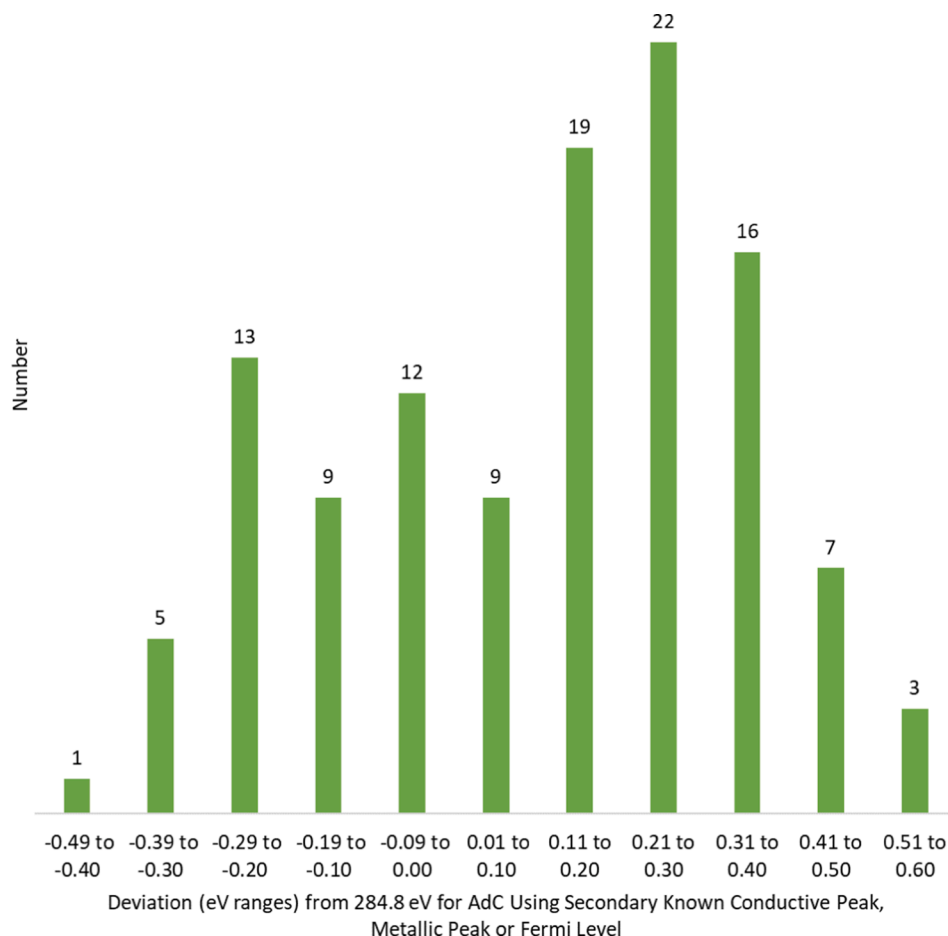


Fig. 8. Deviation (eV ranges) from 284.8 eV for AdC using a secondary known conductive peak, metallic peak or Fermi level for 117 random samples. Data mean is +0.11 eV with a standard deviation of 0.25 eV. Data median is +0.16 eV.

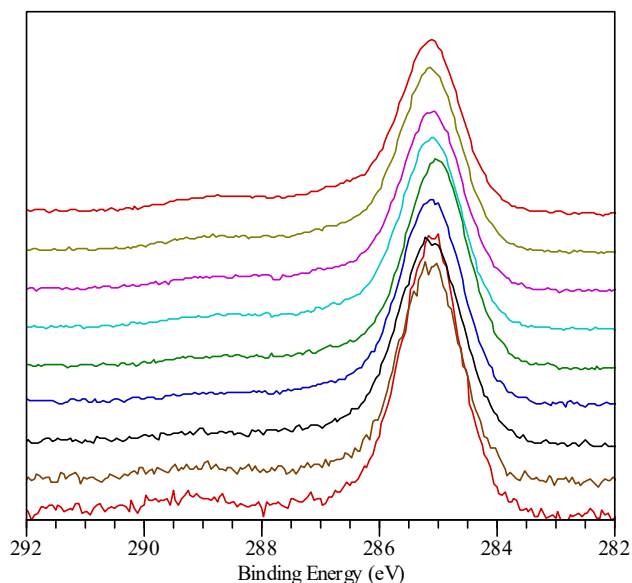


Fig. 9. C 1s spectra (corrected to FL) recorded from adjacent Au to Al foil samples (electrically isolated on a glass slide) as a function of lateral position, which varies from mostly Au foil (top) to mostly Al foil (bottom) in steps of 0.1 mm.

As this shows, though helpful in many cases one should not assume that the electrical isolation method is without issue. The various insulating, semi-conductive and conductive layers or domains in a sample may still reach differing steady state conditions under the influx of charge neutralization electrons and outflow of photoelectrons. This work may also suggest that assessing the C 1s B.E. value of AdC on layered systems of oxidized conductive metal surfaces may not be the best way to assess its true B.E. position.

If we return to the current dataset, one note of mention is that the analyses of powder samples were generally quite successful. For powder samples the surface of individual particles is fully covered with AdC. As such, AdC will be found within the bulk of the material as well as its outer analyzer facing surface i.e., AdC is more evenly distributed throughout the powder sample.

Incorporation of carbon species within older oxide films may also influence the position of AdC C 1s in relation to the metal FL. For example, a freshly polished Al metal surface, cleaned and air exposed for one hour gave an AdC C 1s position of 286.2 eV, compared to the old oxide film above at 285.8 eV and a separate old Al sample (Al boat weighing holder) also at 285.8 eV (all samples electrically isolated). The reader is referred to the introduction section of Baer et al. [4] for an in-depth survey of the many charging and conductivity complexities that are possible for nonuniform multi-material samples.

While most analyses in this dataset that used AdC for charge referencing provided a chemically meaningful, self-consistent and reasonable result based on user input and expectations, there were still instances where issues with the changing values (range) of the AdC C 1s peak required modification in peak-fitting routines used. These are described below.

The starting curve-fitting routines [26–28,30] used for the elucidation of transition metal oxide/hydroxide and other species typically start with a binding energy window of the reference B.E. of ± 0.1 – 0.2 eV. For example, in a Ni metal/oxide containing system, if the main $2p_{3/2}$ peak for NiO is set at 853.7 eV, with all the other peaks used to mimic the entire peak shape of NiO constrained to be at set positions from this main peak, a binding energy window of ± 0.1 eV is generally used in the starting fitting conditions (i.e., a peak range of 853.8–853.6 eV). These curve-fitting routines rely on a combination of peak-shape and binding energy positioning. In instances where the C 1s deviates more than 0.1 eV from 284.8 eV, the binding energy fitting window (constraints) for all components in the system (NiO, Ni(OH)₂, NiCr₂O₄ etc.) are expanded to allow for this shift. In this manner the entire peak-shape (multiplet and satellite structures), not just peak binding energies, ensure a proper fitting process. In this dataset there were 14 instances where the \pm value of the envelope had to be expanded to accommodate the range in AdC C 1s values and it was almost exclusively to a higher binding energy window (i.e., the actual value for AdC C 1s was higher than 284.8 eV). In peak-fitting routines with standard spectra with more structure in the peak-shapes for various species (e.g., Ni $2p_{3/2}$, Cr $2p_{3/2}$, Mn $2p_{3/2}$, Co $2p_{3/2}$, Cu LMM) we are very confident that this process works based on cross-checks of other high-resolution peaks and stoichiometry from survey scan data. Fitting of the unique shapes caused by multiplet splitting and various satellite features of the species present becomes more important than absolute BE accuracy. Where standard spectra have significant overlap and have more similar peak-shapes, such as for Fe $2p_{3/2}$, more uncertainty is present. An alternative here is to constrain BE positions of all species against one another. So peak A for Fe₂O₃ is referenced to the starting main peaks for Fe₃O₄ and FeOOH etc. Peak A is then allowed to move freely to fit envelope with all species. In general, the additional shift to a higher binding energy, if needed, was in the range of $+0.2$ to $+0.5$ eV (general range/error of AdC) for these types of systems.

In five cases, the addition of silicone, silicon oxide or aluminum oxide components, either as a contaminant or as a component of the material, caused a differential shifting of peaks in a Ni metal/oxide/hydroxide system. AdC C 1s positioning at 284.8 eV would give satisfactory results for the Si 2p or Al 2p (and others) peak position but poor agreement with acceptable NiO or Ni(OH)₂ Ni $2p_{3/2}$, peak positions. Shifts of $+0.5$ to $+2.5$ eV were needed and the effect would worsen with increasing Si or Al component amount, likely suggesting a differential charging issue even with electrical isolation applied to these samples.

In seven samples, mild to moderate differential charging was noted, with one case showing severe differential charging (and considered an analysis failure). In these samples, electrical isolation was either not possible due to 1) sample size constraints (e.g., too big to isolate properly), 2) small, delicate samples that could not be mounted on adhesive as they needed to be kept pristine for other analyses, or 3) samples that we only had one chance to mount and analyze (e.g., air/water sensitive samples loaded into the instrument via an attached glove box). In any other case where differential charging was found during their initial analysis, samples were remounted using the electrical isolation technique. In most cases, this approach eliminated the differential charging issue and successful outcomes were achieved.

4. Conclusions

This dataset illustrates the various XPS charge neutralization strategies used for a large, diverse set of samples and has assessed the merits and problems found for each. For 117 samples that relied upon AdC for charge correction purposes and where a possible secondary check of B.E. referencing was available, a AdC C 1s average value of 284.91 eV with a standard deviation of 0.25 eV was found.

One of the main questions assessed is when it comes to using AdC as a charge reference, and considering the lack of alternatives for a large subset of samples, is it good enough? This survey and the results

obtained would suggest the answer is a “qualified yes”. Noted accommodations or failures of the AdC charge referencing method were found for 26 out of 522 samples for a success rate of 95%. There are of course caveats and points worth reiterating:

1. It must be AdC that you are analysing. Graphitic material, polymers, samples with complex organic components, carbon from silicone contamination et cetera are not the same as AdC and should be treated differently (e.g., graphitic C is at 284.5 eV).
2. One must choose and report on a consistent B.E. value for AdC. Our group has been using 284.8 eV for 20+ years so most of our internally generated reference material spectra use this. A case could be made to go back to using 285.0 eV – for consistency with polymeric referencing of Beamson and Briggs [25] One could also make the case to use 284.9 eV – like the data in this survey and the data of Crist [9] suggests is the average value for AdC. However, the wide range noted in the literature survey by Greczynski and Hultman [10] of 284.0 eV to 285.6 eV is completely unacceptable and, as they point out, “contradicts the very notion of a B.E. reference”. In this respect, consistency in the literature is part of a larger issue being addressed by recent efforts [9,31–33].
3. If a secondary check of B.E. positions is available, use it to confirm your results, report that you have done so, and that it confirms that AdC is working satisfactorily.
4. A range of between ± 0.2 eV to ± 0.3 eV is in most cases sufficient for many chemical state analyses, especially if a reasonable amount of background knowledge of the sample is known by the analyst.
5. For studies where monitoring B.E. shifts similar to or smaller than the error associated with AdC usage are needed – careful thought on how to carry out this study will be necessary e.g., some specific species peak integral to the sample will be needed, or using thin films to make conductive etc. The use of AdC will not be appropriate in this case.
6. The XPS community needs to embrace the use of the Auger parameter which is free of charging issues. This is something our [29,30,34] and other [35–37] groups are advocating for and have had good success with.
7. Look for self-consistency within the dataset. High-resolution data for different elements need to show similar chemistries and the stoichiometry assessed from survey scan data much match the chemistries from the high-resolution data.
8. Publications should strive for data transparency and include access to spectral datasets beyond just the specific spectra or element of interest presented in the main text. Show all data (in supplementary info or as a link to data) so that the readers may draw their own conclusions on data quality, effectiveness of charge correction method, presence or absence of differential charging issues etc.
9. The biggest issue for consistent analysis of samples is managing differential charging. Some of the problems associated with “using adventitious carbon as charge correction” are, as has been shown here, more likely to be a differential charging issue. The extensive use of sample electrical isolation (floating) in this dataset has shown its usefulness in alleviating this issue. However, caution is still warranted when using this with mixed conductive/insulating samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apsusc.2022.153681>.

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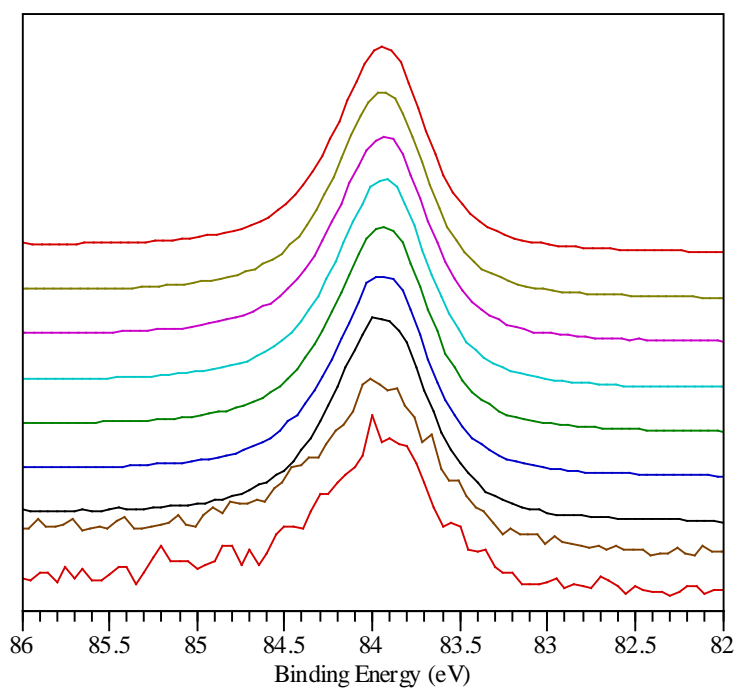


Figure S1. Au 4f_{7/2} spectra recorded from adjacent Au to Al foil samples (electrically isolated on a glass slide) as a function of lateral position, which varies from mostly Au foil (top) to mostly Al foil (bottom) in steps of 0.1 mm.

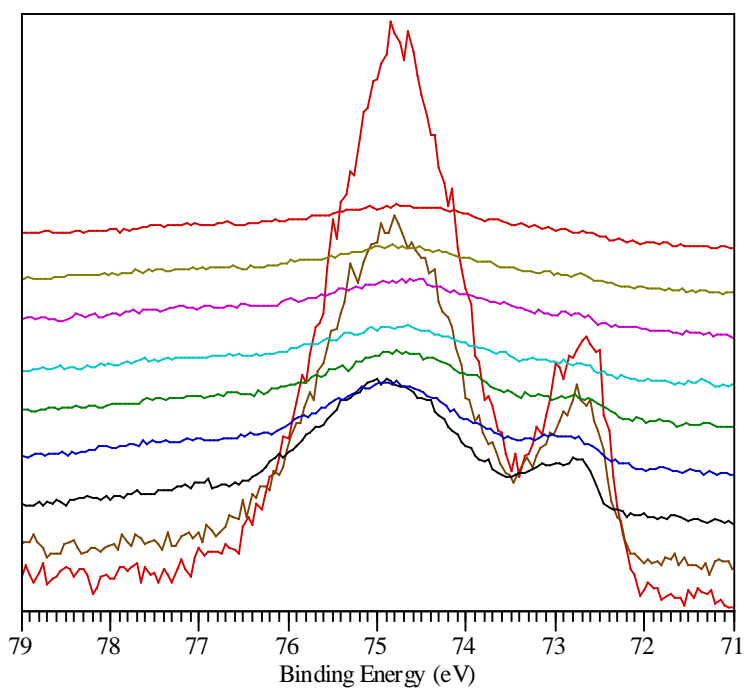


Figure S2. Al 2p spectra recorded from adjacent Au to Al foil samples (electrically isolated on a glass slide) as a function of lateral position, which varies from mostly Au foil (top) to mostly Al foil (bottom) in steps of 0.1 mm.

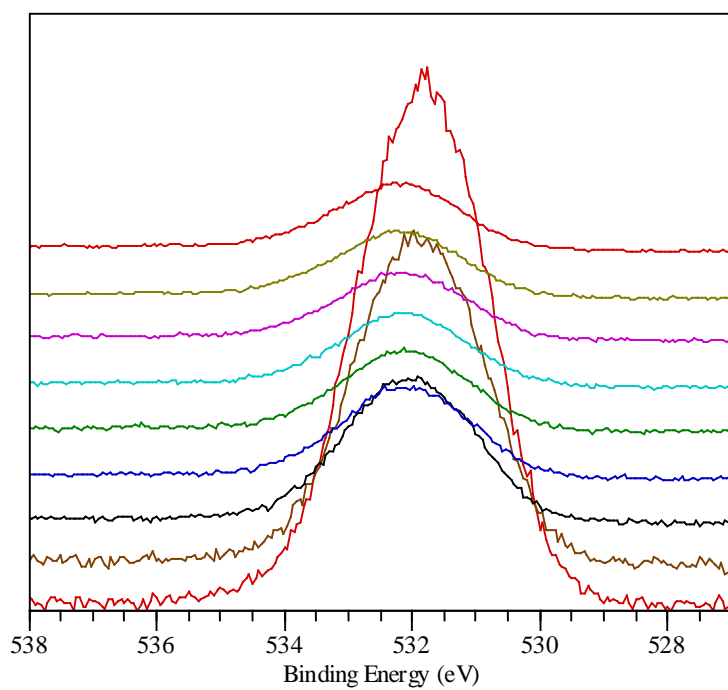


Figure S3. O 1s spectra recorded from adjacent Au to Al foil samples (electrically isolated on a glass slide) as a function of lateral position, which varies from mostly Au foil (top) to mostly Al foil (bottom) in steps of 0.1 mm.

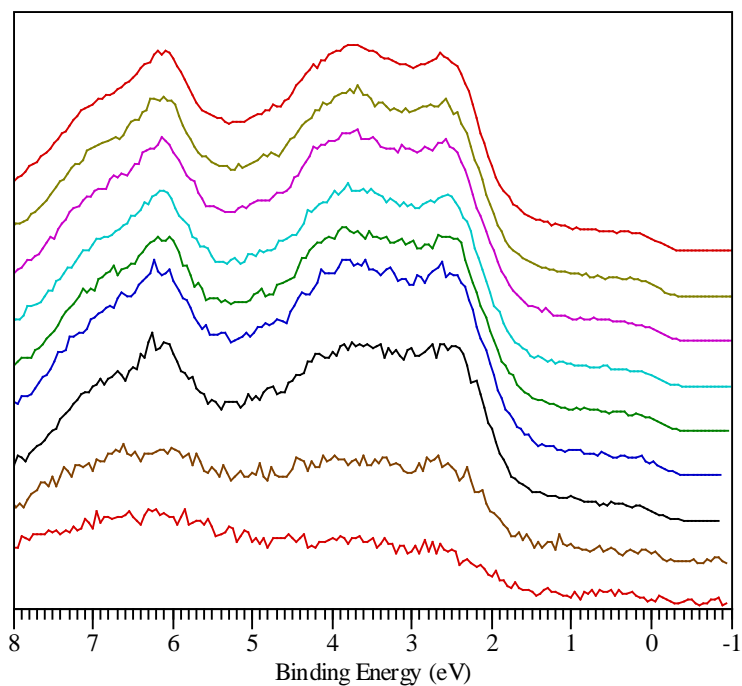


Figure S4. Valence band spectra recorded from adjacent Au to Al foil samples (electrically isolated on a glass slide) as a function of lateral position, which varies from mostly Au foil (top) to mostly Al foil (bottom) in steps of 0.1 mm.

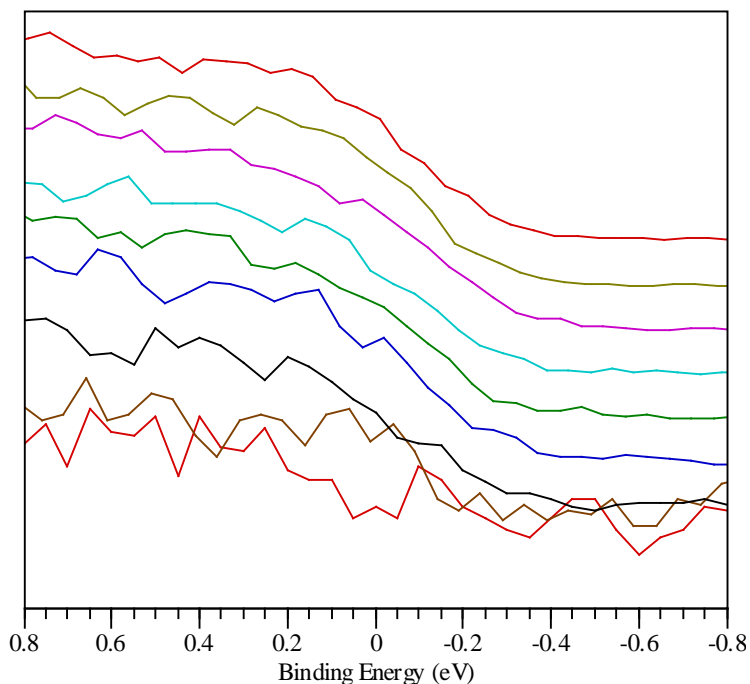


Figure S5. Valence band (expanded to show Fermi Edge) spectra recorded from adjacent Au to Al foil samples (electrically isolated on a glass slide) as a function of lateral position, which varies from mostly Au foil (top) to mostly Al foil (bottom) in steps of 0.1 mm.