RESEARCH ARTICLE

XPS quantification with universal inelastic electron scattering cross section including intrinsic excitations

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In X-ray excited photoelectron emission (XPS), the shape and intensity of photoelectron peaks are strongly affected by extrinsic excitations due to electron transport out of the surface. It is also influenced by intrinsic excitations due to the sudden creation of the static core hole. In order to approximately determine the primary excitation spectrum of the considered transition corrected for both extrinsic and intrinsic excitations, we developed in a previous work [E. Gnacadja, N. Pauly, S. Tougaard, Surf. Interface Anal. 52 (2020) 413] a universal analytical expression for the energy loss cross section including extrinsic and intrinsic excitations. We apply the present universal cross section to test to what extent these primary excitations spectra can be used for XPS quantification based on peak area ratios. The procedure is applied to the study of three sets of polycrystalline alloys ($Cu_{0.75}Au_{0.25}$, $Cu_{0.50}Au_{0.50}$, and $Cu_{0.25}Au_{0.75}$) and to three metal oxides (HfO_2, ZrO_2, and Cu_2O). We show that although the individual peaks are very different from those obtained with the classical universal Tougaard cross section, the determined quantitative compositions are equivalent (but not better). This implies that the relative contribution from intrinsic excitations is roughly the same for all peaks for a given sample and they therefore cancel out when peak area ratios are considered.

KEYWORDS
intrinsic excitations, photoelectron spectroscopy, quantification, universal cross section, XPS

1 | INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is currently the most widely used non-invasive technique for surface analysis (i.e., on the nanometer depth scale).[1] XPS spectra consist of the energy distribution of emitted photoelectrons after excitation by X-ray absorption and electron transport out of the solid, and the quantitative analysis of such spectra allows to characterize the chemical and compositional properties of solid surfaces as well as to determine their electronic structure. Moreover, the availability of commercial equipment as well as its operation facility make XPS the primary method of characterization in the development of nanotechnologies.[2]

However, the quantification procedure, based on the measurement of the peak areas in the spectrum, is complicated by the inelastic scattering events the photoelectrons undergo during their transport

to the detector. Indeed, the XPS spectrum can be seen as the addition of the contributions from electrons that have undergone an increasing number of energy loss events. The zero-energy loss event, that is, the primary excitation spectrum, of a particular peak is thus obtained after the subtraction of intensity corresponding to all energy losses experienced by the electrons after their initial excitation.

The energy loss processes responsible for this inelastic background have two possible origins, denoted extrinsic and intrinsic excitations.[3–5] Extrinsic excitations[3–5] take place during the photoelectron transport out of the surface. Extrinsic excitations occurring inside the medium are referred to as bulk (or volume) excitations while those occurring for an electron moving in a shallow region in the medium and in the vacuum are called surface excitations (note that such strict separation between surface and bulk processes is not exactly valid because the effects interfere[6]). Intrinsic excitations

originate from interactions with the static core hole created during photoexcitation of the core electron. As for the extrinsic processes, the intrinsic losses are also divided into bulk and surface terms. Moreover, intrinsic excitations are also responsible[7] for the asymmetric peak characteristic of metals (the so-called Doniach-Sunjic line shape).[8]

Several methods are used to subtract this inelastic background from the initial spectrum. Among these, Shirley,[9] Tougaard,[10] and straight line[11] methods are in practice the most commonly used procedures. Comparisons of results obtained from these methods were done in various studies. We note, for instance, that Tougaard and Jansson[12] conclude that the Tougaard method is more accurate for quantification than the other ones and that it gives peak intensities that are probably at least as correct as the theoretical parameters needed for quantification.

Among these various methods, only the Tougaard method is based on a solid physical basis.[13] Indeed, while Shirley and linear procedures are largely empirical, Tougaard considers that the XPS spectrum can be seen as the addition of the contributions from electrons that have undergone an increasing number of energy loss events. Thus, the background can be evaluated from a convolution of the spectrum with the energy-differential inelastic electron scattering cross sections K characterizing the probability of losing some energy due to an inelastic interaction.[10] To model the K function, Tougaard takes into account only bulk extrinsic excitations through his well-known eponymous universal cross section.[14] This procedure removes the extrinsic energy loss and determines a primary spectrum that still includes the intrinsic excitations. This is the spectrum that in principle should be used in quantification analysis because the effect of the intrinsic excitations is generally included in the theoretical sensitivity factors used for quantification[15]; see, for instance, the well-known XPS MULTIQUANT software.[16]

We have recently calculated[17] an analytical "universal" inelastic electron single scattering cross section for XPS (called here "Intrinsic-Extrinsic-Universal [IEU] cross section"). This IEU cross section models both extrinsic and intrinsic excitations (as well as their interference) of the emitted photoelectrons for transition metals and their oxides. We have shown that this IEU cross section allows to remove both extrinsic and intrinsic excitations with good accuracy for Au and Cu and with reasonable accuracy for CuO.[17] This obviously opened for a clearer quantitative interpretation of the remaining structures but did not necessarily provide more accurate peak areas for quantitative composition analysis. It is precisely the goal of the present paper to study to what extent the primary excitation spectra, $F(E)$, obtained with the IEU cross section might affect the accuracy of XPS quantification based on peak area ratios.

It is important to be aware of limitations of the IEU cross section that we briefly mention here: First, it must be noted that the IEU cross section is calculated for homogeneous materials at normal exit angle. The importance of intrinsic-relative to extrinsic-excitations varies with angle and is also expected to be larger for excitations close to the surface. Therefore, the IEU cross section may be less accurate for XPS from a thin surface layer. The cross section should as a result

not be considered to be highly accurate but rather it is a semi empirical alternative that may prove to be useful in quantification as tested here. The present background may also prove useful in peak fitting procedures where various types of empirical backgrounds are currently being used. Also note that in quantification analysis, the effect of the intrinsic excitations is generally included in the theoretical sensitivity factors and should therefore in principle be included in the peak areas. Indeed, the $F(E)$ spectrum obtained by subtracting both extrinsic and intrinsic excitations can be compared with theoretical calculations of the photoexcitation spectrum for an isolated atom or molecule where the many body effect of the core hole is ignored as discussed in Section 2. Consequently, strictly speaking, it cannot be used for quantitative analysis.[5] We show in this work to what extent it is true.

In the following sections we first summarize how the IEU cross section was calculated. Then we show quantification results for three sets of polycrystalline alloys ($Cu_{0.75}Au_{0.25}$, $Cu_{0.50}Au_{0.50}$, and $Cu_{0.25}Au_{0.75}$) and for three metal oxides (HfO_2, ZrO_2, and Cu_2O) using both this IEU cross section and also the classical Tougaard universal cross section. Finally, we compare and discuss the results.

2 | INTRINSIC-EXTRINSIC-UNIVERSAL CROSS SECTION

The effective characteristic inelastic electron single scattering cross section K_{sc}^{XPS} (including both extrinsic and intrinsic excitations) for a given material in a XPS experiment can be determined from the dielectric response model developed in Simonsen et al.[6] This model includes energy losses due to the effects of the bulk, of the shallow surface, of the static core hole created during the photoionization process, and of excitations in the vacuum after the photoelectron has left the surface, as well as interference between these effects. Shake-up peaks are not taken into account for the calculation of K_{sc}^{XPS}. Shake-up peaks are thus included in $F(E)$, and we note that they can be calculated within the charge transfer multiplet model implemented in the software CTM4XAS (Charge Transfer Multiplet program for X-ray Absorption Spectroscopy).[18] CuO spectra corrected by the present model was found to be in excellent agreement with CTM4XAS first principle calculations.[19] It should however be noted that there is a considerable ambiguity in the literature concerning the way to interpret these shake-up peaks.[20]

The model is based on a dielectric response description of the interaction of the fields set up by the moving photoelectron (here denoted extrinsic excitations) and by the suddenly created core hole (here denoted intrinsic excitations). It has been described in detail in Simonsen et al,[6] and its validity has been experimentally demonstrated in Yubero and Tougaard,[21] for instance, and the determined primary spectra were found to be in good quantitative agreement with first principle quantum mechanical calculations.[19,30] It has been implemented into a user-friendly software package, namely, QUEELS-XPS, which is freely available.[22,23]

The only input in the calculations is the dielectric function, depicted via its energy loss function (ELF) $Im\{-1/\epsilon(\mathbf{k},\omega)\}$, where $\epsilon(\mathbf{k},\omega)$ is the dielectric function of the material, $\hbar\omega$ is the energy lost, and $\hbar k$ is the momentum transferred from the primary electron to electrons in the solid. To evaluate this ELF, we consider as a model the expansion in Drude-Lindhard type oscillators[24]

$$Im\left\{-\frac{1}{\epsilon(\mathbf{k},\omega)}\right\} = \sum_{i=1}^{n} \frac{A_i \hbar\gamma_i \hbar\omega}{(\hbar^2\omega_{0ik}^2 - \hbar^2\omega^2)^2 + \hbar^2\gamma_i^2\hbar^2\omega^2}\theta(\hbar\omega - E_G) \quad (1)$$

with the dispersion relation:

$$\hbar\omega_{0ik} = \hbar\omega_{0i} + \alpha_i\frac{\hbar^2 k^2}{2m}. \quad (2)$$

Here, A_i, $\hbar\gamma_i$, $\hbar\omega_{0ik}$, and α_i are the strength, width, energy, and dispersion of the ith oscillator, respectively, and the step function $\theta(\hbar\omega - E_G)$ is included to describe the effect of the energy band gap E_G present in semiconductors and insulators.

Thus, it is necessary to know the ELF to obtain K_{sc}^{XPS} for a given material. This ELF can be obtained from various sources (Palik's compilation of optical data,[25] reflection electron energy loss spectroscopy [REELS],[26,27] or density functional theory [DFT][28]). However, Palik's data are quite limited, REELS equipment is not always available, and DFT calculations are usually complex and require input parameters that are not available for many materials. Moreover, it is almost impossible to obtain an accurate ELF for non homogeneous materials.

In consequence, the use for routine analysis of ELF data to obtain a scattering cross section allowing to obtain the primary excitation spectrum $F(E)$ from an XPS spectrum is not practical. This is why we determined[17] a "universal" inelastic electron single scattering cross section for XPS (namely, the IEU cross section), $A(T)$ (where T is the lost energy), in the form:

$$A(T) = \frac{BT}{(C+T^2)^2} + \frac{a_1}{a_2 + T^{a_3}}. \quad (3)$$

The first term of Equation (3) was selected to be similar to Tougaard's universal inelastic scattering cross section[10,14] because it principally represents extrinsic excitations. However, as the present IEU cross section takes into account extrinsic/intrinsic excitations plus interference effect, there is no particular reason to have constants B and C equal to those obtained by Tougaard for his universal cross section. The second term is very similar to the photoemission cross section derived by Doniach and Sunjic[8] for transition metals and accounts for the asymmetric tail of the line shapes. The a_2 constant avoids the singularity at $T=0$ and thus accounts for the finite lifetime of the core hole. For insulators and semiconductors, the energy band gap has to be specified and taken into account when using $A(T)$ ($A(T)=0$ for $T \le E_G$).

In order to obtain the constants in Equation (3), the normalized cross sections $\lambda^{XPS}(E)K_{sc}^{XPS}(E,T)$ were calculated with QUEELS-XPS for various transition metals and various primary energies E. $\lambda^{XPS}(E)$ is the

inelastic mean free path of a given photoelectron at energy E, related to the energy loss cross section K_{sc}^{XPS} by

$$\lambda^{XPS}(E) = \frac{1}{\int_\epsilon K_{sc}^{XPS}(E,T)dT}. \quad (4)$$

As noted earlier,[6,17] $K_{sc}^{XPS}(E,T)$ diverges for $T \to 0$. As a result, a minimum value of ϵ must be chosen in Equation (4) (we also note that $T=0$ is not allowed in the QUEELS-XPS software). In previous works,[19,29–31] we found that $\epsilon = 0.2$ eV allows to obtain a sufficient accuracy in all our calculations. We use the same value in the present work. It was checked that the normalized cross sections $\lambda^{XPS}(E)K_{sc}^{XPS}(E,T)$ were to a good approximation independent of the initial energy E and could then be averaged over all transition metals and all primary energies to give the mean normalized cross section $(\lambda^{XPS}(E)K_{sc}^{XPS}(E,T))_{mean}$ that has been is fitted to Equation (3) to determine the best values of the constants B, C, a_1, a_2, a_3 (values given in Table 1). All details of this procedure are available in Gnacadja et al.[17] Note that in Gnacadja et al,[17] the values of a_2 and a_3 are interchanged. The correct values are those shown in Table 1.

Finally, the IEU cross section, $A(T)$, could be used to determine an approximate $F(E)$ for a wide range of materials without any knowledge of their exact composition and thus opens for a clearer interpretation of the remaining structures.[7,19,29,30] The full K_{sc}^{XPS} cross section allows to obtain general insight in the fundamental photoelectron excitation process and the electronic structure of the atom in its local chemical environment.[7,19,29–31] The purpose of $A(T)$ is to provide a practical method to easily obtain approximately similar information.

3 | QUANTIFICATION

The next step is to determine to what extent the present $F(E)$ obtained with the IEU cross section applies to XPS quantification and possibly enhances the accuracy of quantification based on peak area ratios. To proceed to this analysis, we have chosen on the one hand samples for which the quantification was already accurately performed in the past,[12] namely, three sets of polycrystalline alloys ($Cu_{0.75}Au_{0.25}$, $Cu_{0.50}Au_{0.50}$, and $Cu_{0.25}Au_{0.75}$) and on the other hand three metal oxides (HfO_2, ZrO_2 and Cu_2O), all samples being thick. For the latter, experimental conditions are given in previous studies[32–34] for hafnium oxide, zirconium oxide, and copper oxide, respectively. All data were corrected for the electron analyzer transmission function, and we proceed to an analysis up to an energy loss

**TABLE 1** Parameters of the Intrinsic-Extrinsic-Universal (IEU) cross section

B	C	a_1	a_2	a_3
2192.8	1643.1	0.082	0.0695	0.8217

of 100 eV below each peak. Up to this limit, the agreement between data and fits is quite good but IEU is not recommended for use at much larger energy loss. For the oxides, we compare quantification results obtained using the true K_{sc}^{XPS} cross section obtained with QUEELS-XPS, the IEU cross section proposed in Gnacadja et al,[17] and also the classical Tougaard universal cross section. We precise that we consider $E_G(HfO_2, ZrO_2, Cu_2O) = 5.5, 4.5, 2.1$ eV when using the K_{sc}^{XPS} and IEU cross sections. For the metallic samples, the K_{sc}^{XPS} cross

section is not used because the ELF of the composite material is not known.

Figures 1 and 2 show, as an example, results of the background subtraction procedure for Hf 4p and O 1s of HfO_2 using the Tougaard universal cross section, the IEU cross section, and the true K_{sc}^{XPS} cross section calculated with QUEELS-XPS. In Figure 2, we note the presence of the Hf 4s peak with a binding energy of about 538 eV.[35] Even though the intensity of this peak is quite small, it can influence our

FIGURE 1 Results of the background subtraction procedure for Hf 4p of HfO$_2$: Raw data (dash-dotted line), spectra obtained with use of the Tougaard universal cross section (dashed line), with the IEU cross section (solid line) and with the true K_{sc}^{XPS} cross section (dotted line). The inset shows an expansion of the energy loss close to the Hf 4p3/2 peak
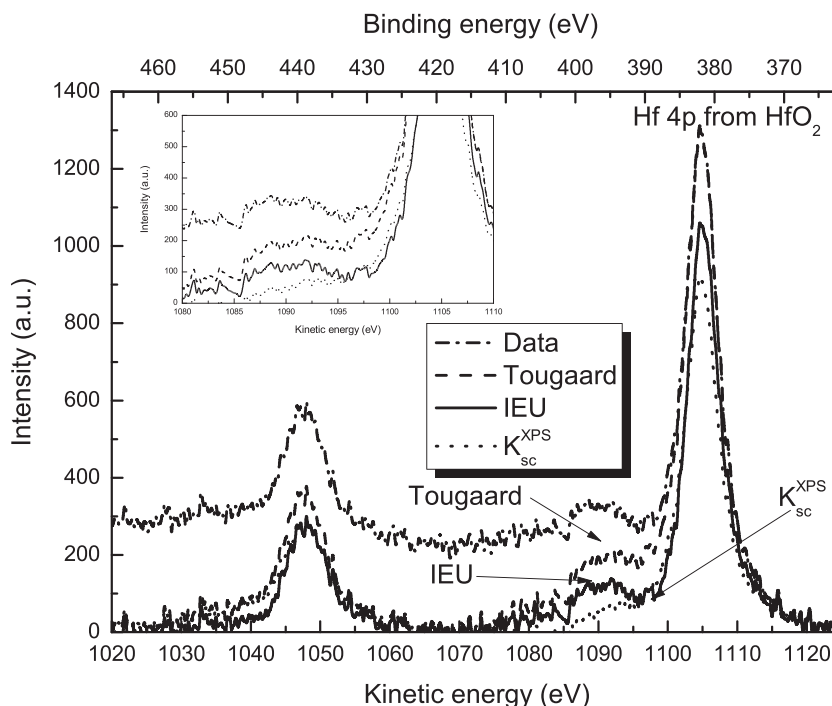
FIGURE 2 Results of the background subtraction procedure for O 1s of HfO$_2$: Raw data (dash-dotted line), spectra obtained with use of the Tougaard universal cross section (dashed line), with the IEU cross section (solid line) and with the true K_{sc}^{XPS} cross section (dotted line). The inset shows an expansion of the energy loss close to the peak
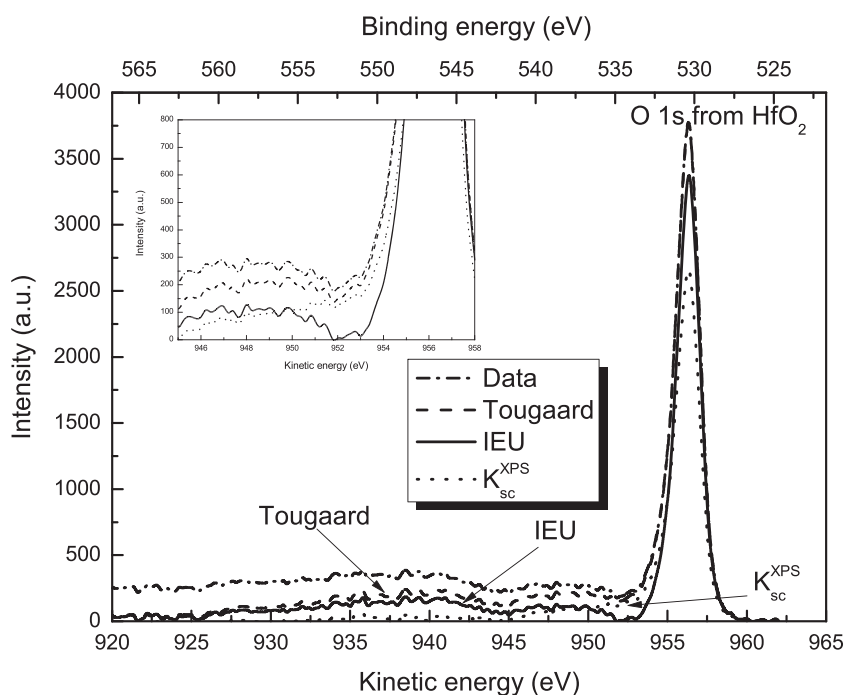
HfO_2	Hf (%)	O (%)	ZrO_2	Zr (%)	O (%)	Cu_2O	Cu (%)	O (%)
Tougaard	33.9	66.1	Tougaard	31.7	68.3	Tougaard	67.8	32.2
IEU	34.9	65.1	IEU	31.3	68.7	IEU	63.1	36.9
K_{sc}^{XPS}	34.4	65.6	K_{sc}^{XPS}	32.7	67.3	K_{sc}^{XPS}	65.7	34.3

TABLE 2 Results of the quantification for HfO_2, ZrO_2, and Cu_2O, using the universal Tougaard, IEU, and K_{sc}^{XPS} cross sections

$Cu_{75}Au_{25}$	Cu (%)	Au (%)	$Cu_{50}Au_{50}$	Cu (%)	Au (%)	$Cu_{25}Au_{75}$	Cu (%)	Au (%)
Tougaard	71.5	28.5	Tougaard	46.8	53.2	Tougaard	26.6	73.4
IEU	69.9	30.1	IEU	49.5	50.5	IEU	24.9	75.1

TABLE 3 Results of the quantification for $Cu_{75}Au_{25}$, $Cu_{50}Au_{50}$, and $Cu_{25}Au_{75}$, using the universal Tougaard and IEU cross sections

quantification calculations. However, as we are mainly interested in the relative comparison between results obtained from the various background subtraction methods, its effect is considered to be negligible.

Figures 1 and 2 show that the inelastic background is more efficiently removed when the K_{sc}^{XPS} and the IEU cross sections are used compared to the case in which the Tougaard universal cross section is considered because surface and intrinsic excitations are not taken into account in the Tougaard cross section. Moreover, if we observe the losses larger than about 10 eV, it is also clear that the use of K_{sc}^{XPS} removes not only the extrinsic excitations but also all intrinsic excitations, while the IEU cross section, being only an approximation, removes only partly the intrinsic excitations. These results correspond well to those obtained in Gnacadja et al.[17]

We also note an interesting feature concerning the HfO_2 results. As pointed out above, we identify the 538 eV binding energy peak (see Figure 2) as the Hf 4s contribution, but in other works (Ohtsu et al,[36] for instance), the Hf 4s and O 1s peaks are seen fully overlapped, implying that the structure at 538 eV is a plasmon contribution. The goal of is this work is not to study this question, but we note that, in Figure 1, the plasmon of Hf 4p is almost fully removed when the K_{sc}^{XPS} cross section is considered, while it is not case for the other cross sections. Indeed, the plasmon was identified in the ELF used for the calculation of K_{sc}^{XPS}, while the Tougaard and IEU cross sections do not take into account precise losses for each material. However, in Fig 2, the structure at 538 eV is not removed when K_{sc}^{XPS} is used, implying that it does not correspond to a plasmon.

Results of quantification using these three cross sections with the XPS MULTIQUANT software[16] are now shown in Tables 2 and 3. From these results, we observe that the variation between the results for all samples is smaller than 7%, but also that the difference compared with the stoichiometric value is also smaller than 7%. We note that the real composition of the materials may differ from the stoichiometric values in an unknown way. Thus, the most important result is the small relative variation observed when using the three cross sections. Indeed, no clear trend emerges from the results obtained with the different methods. Thus, even though the areas of the individual peaks are different, the ratio considered for the quantification is almost independent of the applied cross section. This implies that the relative contribution from intrinsic excitations is roughly the same for all peaks for a given sample and that they therefore cancel out when peak area ratios are considered. This may be expected because the intrinsic excitations are determined by the dielectric response of the medium (which is identical for the two peaks) to the suddenly created core hole.

These results imply that both the IEU and the K_{sc}^{XPS} cross sections can be used to provide quantitative ratios of peak areas for composition analysis and results are not significantly different from the ones obtained with the classical universal Tougaard cross section. On the other hand, the use of these two cross sections including extrinsic and intrinsic excitations allows to determine the primary excitation spectrum for a given transition which can directly be compared with theoretical calculations.[19,30] Note that knowledge of the ELF is necessary to calculate the K_{sc}^{XPS} cross section for a given material, which is not always straightforward. On the contrary, the IEU cross section allows to obtain an approximate $F(E)$ for a wide range of homogeneous materials.[17]

4 | CONCLUSION

This paper demonstrates that the analytical "universal" inelastic electron single scattering cross section for XPS, or IEU cross section, obtained in a previous work[17] can be used to provide peak areas for quantitative composition analysis even if a strict application of the theory would forbid it. The use of the IEU cross section does not change the accuracy of XPS quantification achieved with other well known procedure, as the Tougaard cross section, and gives an equivalent but not better result while providing the approximate primary excitation spectrum where both extrinsic and intrinsic losses are removed. This result implies that the IEU cross section might be used (this needs to be tested), as an alternative to the classical Tougaard universal cross section, for analysis of nanostructured materials. Note however that the relative importance of intrinsic/extrinsic excitations will vary with depth while the present IEU cross section is evaluated for homogeneous materials. Our results also imply that the relative contribution from intrinsic excitations (i.e., excitations caused by the core hole) is approximately the same for all peaks from a given sample. This might be expected because the intrinsic excitations are determined by the dielectric response of the medium to the suddenly created core hole.

In conclusion, the suggested IEU cross section is not considered to result in a highly accurate analysis. Rather, it is a semi empirical cross section that attempts to approximately remove both intrinsic and extrinsic excitations. It might be useful for XPS quantification and XPS peak fitting procedures where various backgrounds are currently being used.

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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