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**VAMAS TWA 2, 2019 — SUB-PROJECT A27:
“INTENSITY CALIBRATION FOR XPS INSTRUMENTS USING LOW-
DENSITY POLY(ETHYLENE)” — PROTOCOL FOR ANALYSIS**

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VAMAS TWA 2, 2019: INTENSITY CALIBRATION FOR XPS INSTRUMENTS USING LOW-DENSITY POLY(ETHYLENE) – PROTOCOL FOR ANALYSIS

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ABSTRACT

This report outlines the analysis protocol for an interlaboratory study conducted under the auspices of VAMAS TWA 2 (Surface Chemical Analysis) for the intensity calibration for XPS instruments using polyethylene. The protocol involves the use of low-density poly(ethylene), prepared using a clean scalpel to remove surface oxygen, as a secondary calibration standard. For monochromated Al $K\alpha$ sources, the acquired spectrum is used in conjunction with a mathematically-generated poly(ethylene) reference spectrum to determine a representative transmission function. A rational function is then fitted to produce a noise-free continuous transmission function description which can be used to intensity-correct spectra from other materials. Participants will also acquire a spectrum from sputter-cleaned gold for validation purposes. This report will guide VAMAS participants through the sample preparation, calibration process, and reporting of their results. For non-monochromated sources, the study will enable an assessment of whether poly(ethylene) could also be used as a secondary calibration standard.

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Approved on behalf of NPLML by
Andrew J. Pollard, Science Area Leader, Surface Technology Group.

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1 INTRODUCTION

X-ray Photoelectron Spectroscopy (XPS) is a highly surface sensitive, ultra-high vacuum technique capable of quantitatively measuring the elemental composition and the chemical state of a material's surface. Accurate and precise analysis of photoelectron spectra relies on a well-calibrated spectrometer, both in the kinetic energy scale and the intensity scale. For this study, only the intensity calibration is considered. Photoelectron analysers rely on electrostatic and magnetic lens systems to guide electrons into the deflection hemispheres via the entrance plane and retard their velocities to match the chosen pass energy. The efficiency at which the lens system samples photoelectrons at different kinetic energies is known as the analyser's *transmission function* $T(E)$, and this function changes for different acquisition modes, pass energies, X-ray spot sizes, and aperture settings. To obtain accurate intensities, and hence elemental compositions, from an XPS spectrum without the use of reference materials, the data must be $T(E)$ corrected.

The purpose of this inter-laboratory study is to assess the validity of a new intensity calibration method for determining a spectrometer's $T(E)$ using low-density poly(ethylene) (LDPE) as a cheap and easy-to-prepare alternative to gold, silver, and copper calibration standards. In contrast to these calibration standards, LDPE does not require ion sputtering to decontaminate the surface and is insensitive to hydrocarbon contamination; a clean oxygen-free surface can be obtained by scraping the surface of the LDPE with a clean metal scalpel. A LDPE spectrum contains far fewer photoelectron and Auger peaks than other metal calibration standards making it simple enough to be described by a mathematical function. This means that a nearly continuous noise-free reference spectrum can be obtained. The potential issue arises from the need for longer acquisition times and therefore the necessity for dark noise removal due to LDPEs low photoelectron yield.

The $T(E)$ calculated from this protocol will be used to correct a sputter-cleaned gold spectrum from the same spectrometer, and this corrected spectrum will be compared against spectra from other laboratories and traceable reference spectra of gold, taking into account the instrument's geometry. The variance between these $T(E)$ corrected spectra will be assessed to determine whether the LDPE secondary standard intensity calibration qualifies as a suitable $T(E)$ correction method.

2 CONTACTS & TIMETABLE

This VAMAS interlaboratory study is being coordinated by the National Physical Laboratory, UK under the auspices of VAMAS TWA 2 (Surface Chemical Analysis). Your contacts for this study are Benjamin Reed (benjamin.reed@npl.co.uk) and Alexander Shard (alex.shard@npl.co.uk). If any part of this protocol is unclear or you obtain unexpected results, please contact us immediately.

You should complete the analysis for this work by 1st August 2019. If you are unable to do so and require extra time, please inform Benjamin Reed or Alexander Shard.

3 THIS PACKAGE

This package contains this protocol, a LDPE sample, a gold foil, and a clean scalpel. The LDPE and gold are contained in 1" polypropylene wafer trays. Upon receipt of this package, please inform NPL that you have received it and that all items are accounted for. There is also a 'notice to customs' which should inform you if the samples have been handled by customs / postal staff.

☐

I have e-mailed NPL to confirm that all is okay with the sample(s) on: / / 2019

4 SAMPLES

Low-density poly(ethylene) (LDPE) is a thermoplastic with general formula $(C_2H_4)_n$. LDPE is used in applications mostly pertaining to containers, packaging, and tubing due to its excellent chemical resistance, flexibility, and toughness. Importantly, it is easy to handle and not toxic or harmful. In this XPS study, LDPEs simple chemical structure results in a spectrum with few peaks and an easily described inelastic background.

LDPE samples should be stored in a dark, clean, and dust-free environment. LDPE can be stored for years without degradation, although long-term oxidation does occur on the surface. A standard solvent rinse (i.e. acetone, isopropanol, methanol / deionized water rinse) is not recommended because, despite LDPEs compatibility with these solvents, they may leave residues on the surface or cause the LDPE to swell. The samples should be analysed as soon as convenient and before the deadline stated in Section 2.

To prepare the sample for analysis, mount the LDPE onto the spectrometer sample stage or stub. If required, the sample can be cut down to a smaller size using a clean pair of scissors. A fresh surface of LDPE is prepared using a clean flat-bladed metal scalpel; firmly scrape the surface of the LDPE several times until the surface turns from shiny to matte. Also ensure that the direction of last few scrapes are parallel to the monochromator-sample-analyser plane to reduce the X-ray shadowing effect of any directional topography induced by the cleaning process. Always make sure to scrape away from yourself to avoid injury.

Immediately place the sample into the XPS load lock and begin pumping down. Move the sample into the UHV analysis chamber as soon as possible. If sample preparation is performed correctly, the O 1s signal in XPS should be below the detection limit which is less than 0.03 at%.

A gold sample should also be prepared for XPS analysis using whatever methods your lab has to ensure a clean contaminant-free surface, preferably ion sputtering *in-vacuo*. The analysis should be performed in a manner that prevents cross-contamination between the gold and LDPE samples. For example, avoid sputtering the gold before completing the LDPE analysis.

5 INSTRUMENT OPERATING CONDITIONS

5.1 XPS ANALYSIS OF POLY(ETHYLENE)

The complete intensity calibration procedure is suitable for spectrometers which use a monochromatic Al K α X-ray source. The anode, monochromator, sample, and analyser entrance should be in the same plane and the angle between the incident X-rays and the emitted photoelectrons should be close to the magic angle (i.e. 54.7°). For other instruments, the complete calibration procedure may not be applicable, and it is part of the interlaboratory study to identify the range of applicability and whether modifications to the procedure will extend that range. If your instrument does not meet these criteria, please proceed as described below, but note that there may be issues and discrepancies in the data processing. Provided that the data are collected and reported as described in the document, they are still useful and will be analysed at NPL.

The selected area of analysis for XPS on the LDPE should be free of contaminants, most notably oxygen. A LDPE sample prepared according to Section 4 will not have any surface oxygen or foreign contaminants present across the entire PE surface. Figure 2 in Section 6.1.1 shows an example of survey scans for a properly prepared LDPE surface and an unacceptable surface respectively. If the selected analysis area shows no evidence of an O 1s, O KLL peak, or other contaminating elements, then it is appropriate to continue with XPS analysis.

5.2 XPS ANALYSIS OF GOLD

A survey spectrum of contaminant-free gold should also be acquired. The transmission function of a spectrometer can change over time, so it is important that this gold spectrum is acquired around the same time as the LDPE spectra. Preferably on the same day.

The data should be reported as raw intensities in counts per second without transmission function correction. The energy scale should be in kinetic energy. Feel free to apply this procedure to as many lens modes and pass energies as you wish, but we do ask, as a minimum, that you provide data for a high pass energy (i.e. typical survey scan pass energy) with a fully open entrance slit/aperture.

5.3 CHARGE COMPENSATION

LDPE is an insulator and therefore sample charging is expected. To ensure the correct background shape, charge neutralisation must be used. Figure 1 shows the C 1s peak before and after charge compensation using an electron flood gun has been applied.

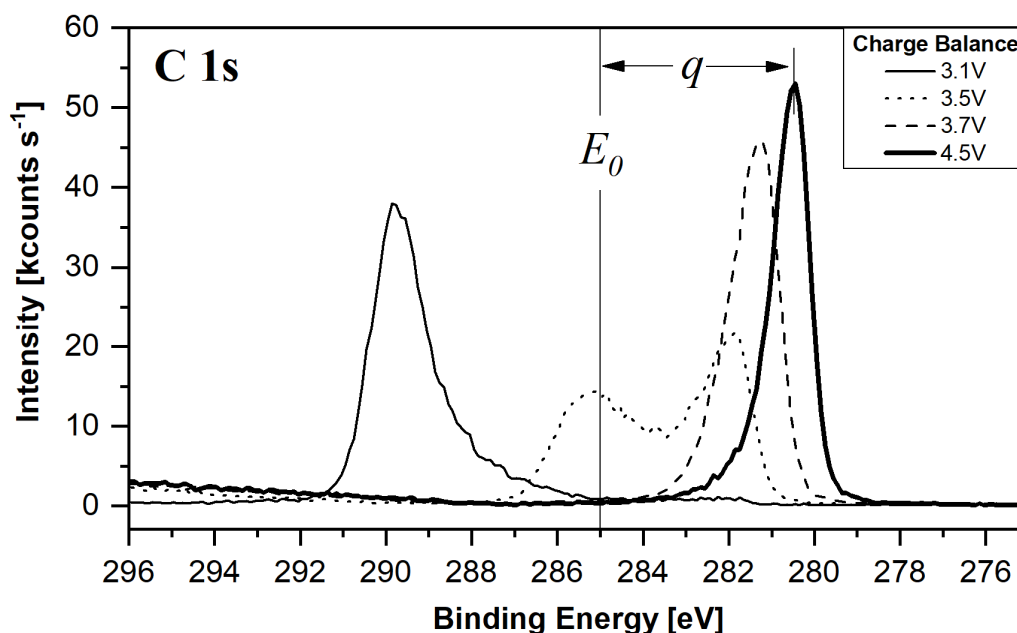


Figure 1. C1s peak measured from a polyethylene sample for different charge compensation parameters. The bold line shows the correct line shape for the C 1s peak. The peak may be offset by q from E_0 , which is the charge reference energy of C 1s that minimises the residual between the mathematically generated LDPE spectrum and the acquired LDPE spectrum (see Section 6.3.1.).

6 DATA ACQUISITION AND ANALYSIS

In general, the objectives of this study are:

- (1) Acquire oxygen-free LDPE survey spectra and combine into a single low-noise spectrum.
- (2) Acquire a contaminant-free gold spectrum.
- (3) Divide the acquired LDPE spectrum by the reference LDPE spectrum to obtain a representation of the spectrometer's transmission function, $Q(E)$.
- (4) Extrapolate $Q(E)$ to higher kinetic energies for fitting.
- (5) Fit a rational function to $Q(E)$ to obtain a continuous, noise-free $T(E)$.

6.1 ACQUISITION

6.1.1 LDPE Spectra

Without turning the X-rays on, acquire a survey spectrum from 180 eV to 1500 eV (1280 eV for Mg $K\alpha$ sources) kinetic energy. With the sample well out of the way of the analysis position, switch on the X-ray source and allow at least half an hour for the instrument to equilibrate. During this time, run several spectra in the high kinetic energy region above the X-ray source energy to determine the spectrometer's dark noise count rate. Make sure that the sample and sample holder is not in the X-ray beam during the dark noise acquisition, especially if you are operating a non-monochromated X-ray source. Now move the sample into the analysis position and optimise the sample height and charge compensation settings (see Section 5.2). The C 1s peak should be a single peak with the maximum count rate between 1200 eV and 1206 eV kinetic energy (967 eV to 973 eV for Mg $K\alpha$ sources).

Once a suitable analysis area has been chosen, acquire a survey scan from 180 eV to 1500 eV kinetic energy using a high pass energy. Make sure that no elements other than carbon are detectable. If you observe any contaminating species and are unable to find an analysis region devoid of contaminants, remove the sample from the system, repeat the sample preparation outlined in Section 5 and start again. Figure 2 provides example XPS survey scans that illustrate an acceptable and an unacceptable sample surface condition. Change the spectrometer settings to the lens mode and pass energy that requires calibration and allow at least five minutes for the instrument to equilibrate.

Acquire an initial survey spectrum from 180 eV to 1500 eV (1280 eV for Mg $K\alpha$ sources) kinetic energy. The low count rate region between the C 1s peak and the valence band will require acquisition times 30 to 40 times greater than the rest of the spectrum, so also acquire at least 30 spectra between 1195 eV and 1500 eV (960 eV to 1280 eV for Mg $K\alpha$ sources) using the same step size and dwell time as the initial survey. If possible, ensure that the start energy in the scan has the same kinetic energy as one of the data points in the initial survey spectrum. Acquire a final survey spectrum from 180 eV to 1500 eV (1280 eV for Mg $K\alpha$ sources) kinetic energy. It is recommended that a step size of approximately 1 eV is used.

At the end of the LDPE acquisition stage, the following datasets should be saved:

1. Survey spectrum with X-ray source OFF
2. High Kinetic Energy Spectra with X-ray source ON
3. Initial Survey
4. High KE Region (multiple acquisitions)
5. Final Survey

This acquisition procedure should be repeated on a fresh area of the sample for every operating mode of the instrument that needs to be calibrated. There should be the five datasets listed above for every lens mode and pass energy that needs to be calibrated. The data should be exported without transmission function correction and the intensity should be stated in counts per second.

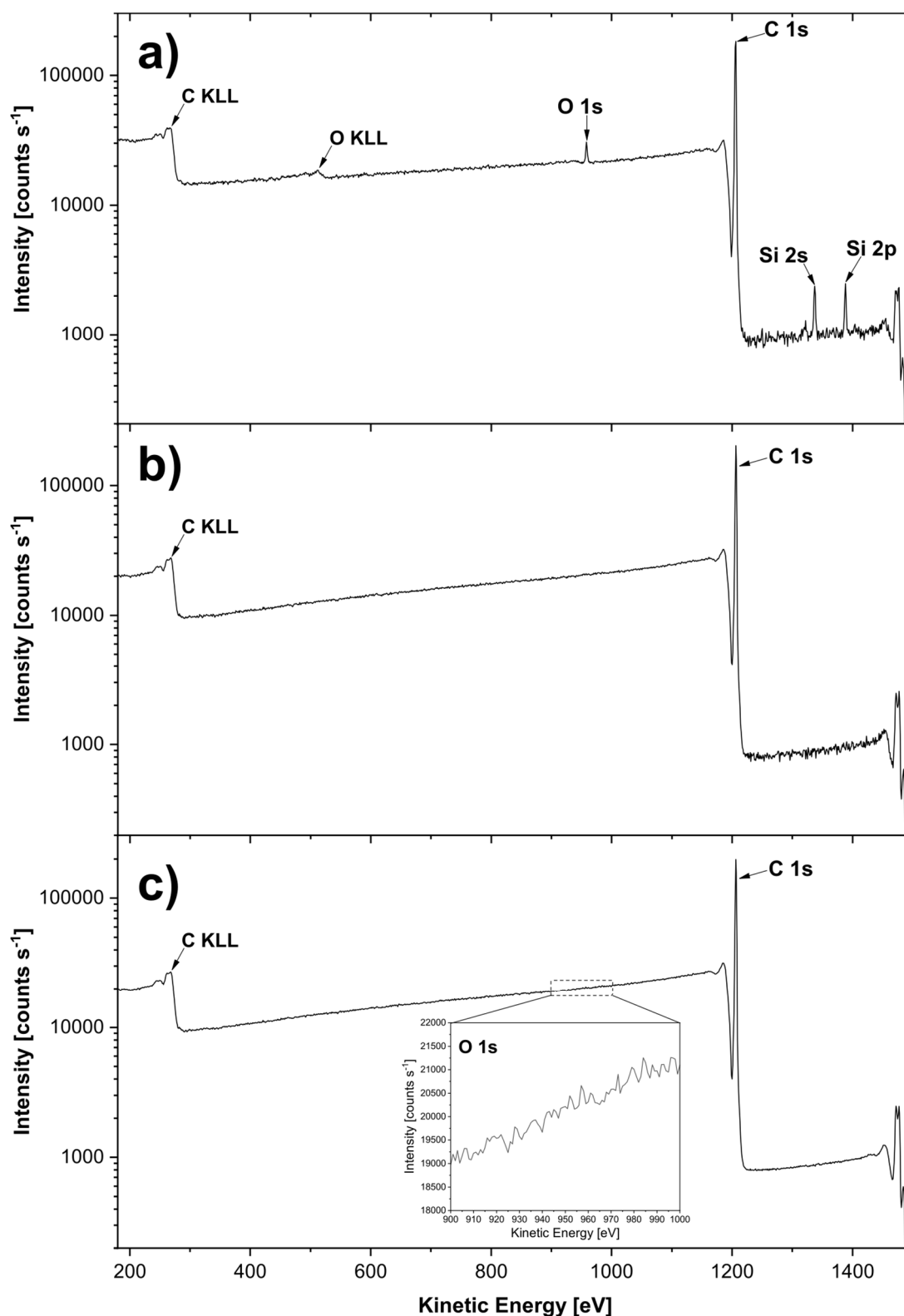


Figure 2. A comparison between (a) a bad survey scan, (b) a good survey scan, and (c) the average combined spectra (see Section 6.2). The acceptable scans (b, c) show no evidence of contaminating whereas the bad scan (a) has oxygen and silicon contaminants which impart a significant change in the background, especially in the low kinetic region near the C KLL feature.

6.1.2 Gold Spectrum

For each lens mode and pass energy that LDPE spectra were acquired, a corresponding gold spectrum should also be obtained. Load the gold sample into the spectrometer and use ion sputtering to remove all surface contaminants. Move the sample into the analysis position and optimise the sample height to obtain the maximum count rate in the Au 4f peak (~84 eV binding energy). Acquire a spectrum over a kinetic energy range between 180 eV and 1500 eV. The data should be exported without transmission function correction and the intensity should be stated in counts per second.

6.2 COMBINING LDPE SPECTRA

Organic materials are known to degrade under X-ray illumination, which possibly affects the intensity of the inelastic background. In the case of LDPE, little-to-no change is expected because even if chemical damage occurs, the loss of hydrogen should not strongly affect the spectrum. Nevertheless, the effects of sample damage and spectrometer performance with time, for each lens mode and pass energy, should be tested.

For each lens mode / pass energy, take the final survey scan and divide it by the initial survey scan. Plot this intensity ratio (final : initial) against kinetic energy to produce a plot similar to Figure 3. From this plot, any changes in the acquisition conditions can be diagnosed. In Figure 3, there is a systemic reduction in intensity between 2% and 3%. Figure 3 also illustrates that the region with kinetic energies higher than the C 1s peak has a much larger noise, justifying the longer acquisitions times demanded in Section 6.1 for this region of the spectrum.

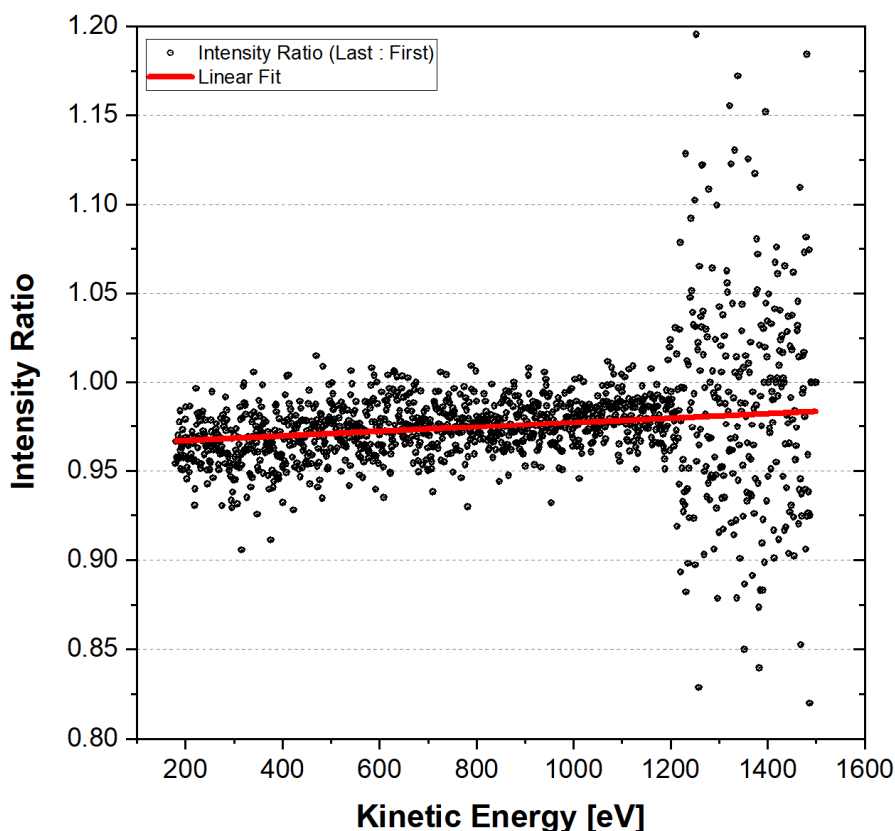


Figure 3. XPS Survey of fresh LDPE divided by survey taken after 3 hours of X-ray exposure. The systematic shift of 0.02 - 0.03 is attributed to changes in the MCP condition over time. Your Final:Initial ratio should be flat, but systematic shifts from unity are acceptable as long as they are not greater than 5%.

Combine the spectra numbers 3 to 5 (excluding the dark noise spectrum) into a single spectrum in counts per second against kinetic energy for each lens mode / aperture size / pass energy. To do this, take the average of all the spectra at each kinetic energy remembering that there are only two spectra to combine at low kinetic energy, but more than 30 at high kinetic energy. Determine the average dark noise as the average value of spectrum 1 in counts per second. Now subtract the average dark noise counts per second across the combined spectrum to obtain I , the dark noise corrected average spectrum of poly(ethylene)

If the spectrum is generated using monochromatic Al $K\alpha$ X-rays, proceed to Section 6.3. Otherwise proceed to Section 7 and 8.

6.3 ANALYSIS: DETERMINING THE TRANSMISSION FUNCTION

6.3.1 Generating the LDPE Reference Spectra

To generate the LDPE reference spectrum, a mathematical description containing six components is used. Three of these components account for the steps in the inelastic background at the valence band, the C 1s peak, and the C KLL peak. The other three components are Gaussian peaks, two of which describe the C KLL features and the third describes long-range variations in intensity apparent in the background between the C 1s and C KLL peaks. Equation (1) is the summation of these six components which form the reference LDPE spectrum, I_{ref} .

$$I_{ref} = \sum_{i=1}^3 \left(\left\{ b_i \left[\exp\left(\frac{\varepsilon}{c_i}\right) + d_i \right] \left[1 - \Phi\left(\frac{\varepsilon - e_i}{5}\right) \right] \right\} + \left\{ f_i \phi\left(\frac{\varepsilon - g_i}{h_i}\right) \right\} \right) \quad (1)$$

The constants of equation (1) are b_i to h_i and are required to reproduce the LDPE reference spectrum for a typical instrument geometry. These constants have been determined by fitting equation (1) to a LDPE reference spectrum calibrated to the NPL metrology spectrometer and are listed in table 1. DO NOT use equation (1) to fit your data, as this will not be I_{ref} . In equation (1), the capital phi Φ is a cumulative normal distribution with mean e_i and a standard deviation of 5 eV. The lower-case phi ϕ is a normal distribution (normalised Gaussian) with a mean g_i and a standard deviation h_i . The independent variable in equation (1) represents the charge corrected kinetic energies of the electrons, ε , which is calculated by:

$$\varepsilon = E + q \quad (2)$$

where E is the electron kinetic energy, and q is a variable static charge correction. For now, set $q = 0$ but later it will be adjusted to correct for charge compensation and reduce the residual between I and I_{ref} .

Table 1. Parameters to recreate I_{ref} using equation (1)

<i>i</i>	1	2	3
Values for step functions			
Feature	C KLL	C 1s	Valence
Intensity, b_i [I_x]	2.04	0.638	0.0204
Decay energy, c_i [eV]	276	423	450
Constant, d_i	0	3.37	0
Position, e_i [eV]	264	1201	1485
Values for the normal distributions representing peaks			
Peak	C KLL (minor)	C KLL (major)	Broad peak
Area, f_i [$I_x \cdot \text{eV}$]	6.36	50	612
Position, g_i [eV]	242	264	685
Sigma width, h_i [eV]	4.0	4.9	228

6.3.2 Calculating $Q(\varepsilon)$ and static charge correction

Once I and I_{ref} have been produced, use equation (3), to obtain the ratio $Q(\varepsilon)$ which provides a visual representation of the spectrometer's *transmission function*.

$$Q(\varepsilon) = \frac{I}{I_{ref}} \quad (3)$$

The C 1s peak and the peaks in the valence band have not been considered in I_{ref} and so these regions will need to be removed before continuing. For consistency, please remove the regions with kinetic energy between 1150 eV to 1220 eV and greater than 1420 eV. The region between 200 eV and 300 eV is the C KLL feature which in $Q(E)$ deviates considerably. Up to this point $\varepsilon = E$ because q is set to zero and therefore the energy shift caused by sample charging has not yet been corrected. By adjusting q , the sharp feature due to C KLL can be reduced to a minimum. From this point forward, the static charge corrected kinetic energy ε will be used for our calculations.

Figure 4 gives an indication of what $Q(\varepsilon)$ may look like after q has been set correctly and which regions to omit from the subsequent analysis.

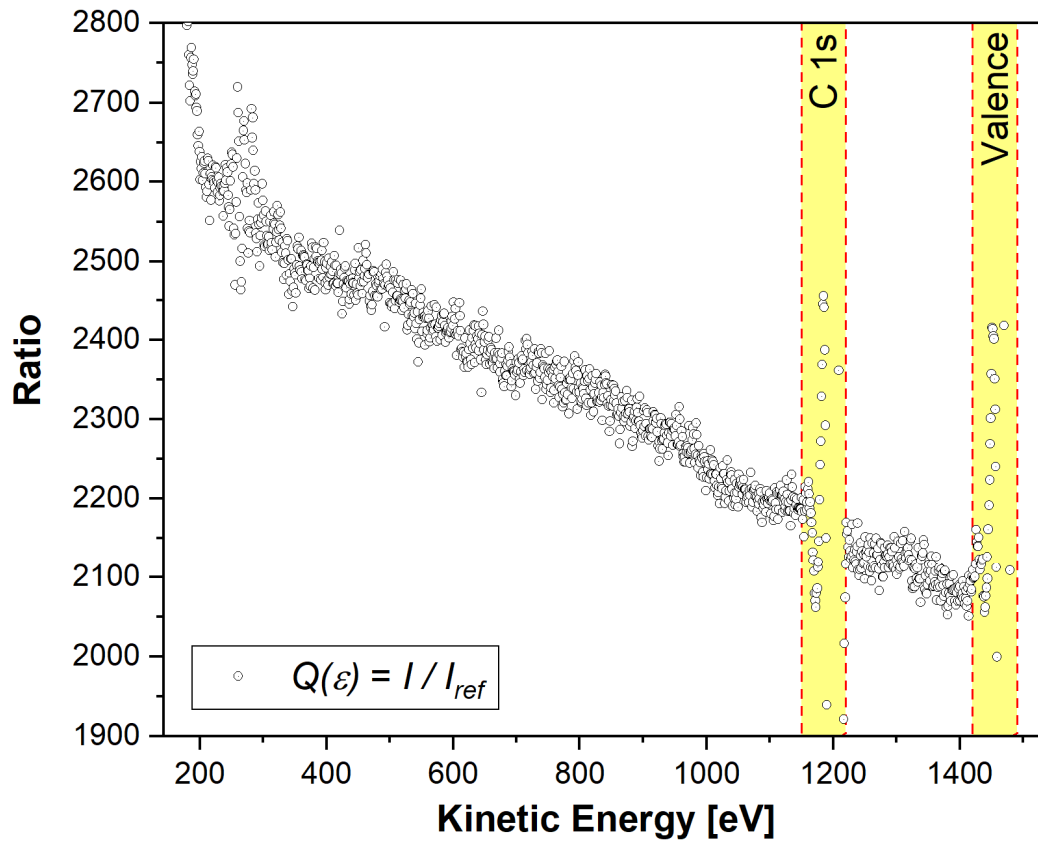


Figure 4. An example $Q(\varepsilon)$ ratio plot with the regions to omit clearly marked.

6.3.3 Extrapolating $Q(\varepsilon)$ to Higher Kinetic Energies

If the fitting procedure in Section 7.3.4 is implemented on $Q(\varepsilon)$ as calculated, then the fit beyond 1420 eV can diverge unrealistically from the true $T(E)$. Therefore, it is necessary to extrapolate the $Q(\varepsilon)$ beyond this point to at least 2000 eV kinetic energy using a power law. To do this, the logarithm of $Q(\varepsilon)$ is plotted against the logarithm of ε over the kinetic energy range 1220 eV to 1420 eV and linear regression provides a and n for equation 4.

$$X(\varepsilon) = a\varepsilon^n \quad (4)$$

Figure 5 demonstrates a fit to the $Q(\varepsilon)$ shown in Figure 4. Once a function describing the higher kinetic energy region has been calculated, extrapolate $Q(\varepsilon)$ to 2000 eV by appending values of X . It is sufficient to use eleven points between 1500 eV and 2000 eV with 50 eV separation. These would be spaced on the red line. The combination of $Q(\varepsilon)$ and the additional points calculated from equation (4) is $R(\varepsilon)$.

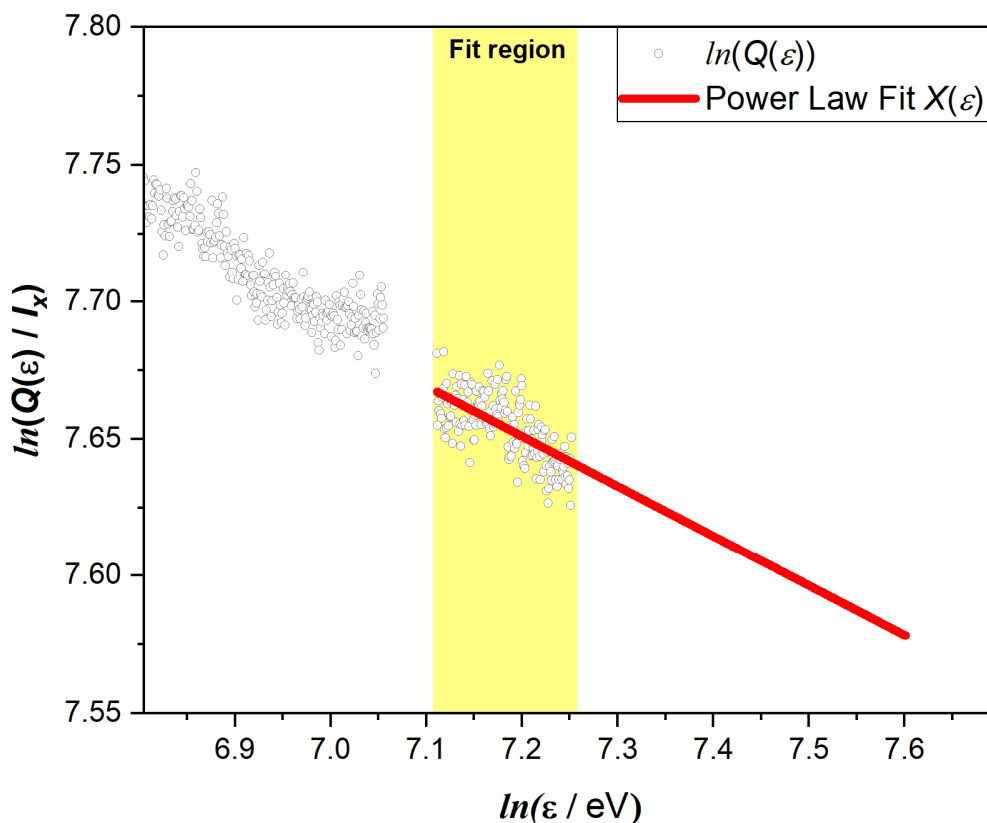


Figure 5. Extrapolation of $\ln(Q(\varepsilon))$ using a power law fit from 1220 eV to 1420 eV and extended out to 2000 eV.

6.3.4 Fitting the Transmission Function $T(\varepsilon)$ to $R(\varepsilon)$

As mentioned in Section 6.3.2, $Q(\varepsilon)$ is representation of the spectrometer's transmission function. For future $T(E)$ correction, a smooth description of $Q(\varepsilon)$ is required over the range of kinetic energies where typical XPS experiments are conducted. A functional form which describes a wide range of instruments provided in equation (5),

$$T(E) = \frac{r_0 + \sum_{m=1}^k r_m \left(\frac{E}{1000} - 1 \right)^m}{1 + \sum_{n=1}^l s_n \left(\frac{E}{1000} - 1 \right)^n} \quad (5)$$

where r_0 is the value of $T(1000 \text{ eV})$, and r_m and s_n are coefficients of polynomial series of degree k and l respectively. Fit $T(\varepsilon)$ to $R(\varepsilon)$. You may do this using any software, but you can also do it in the Excel spreadsheet sent to you as a participant in the study.

Using the Excel spreadsheet, ensure that the ‘Solver’ add-on in Excel is activated. The ‘Minimization Parameter’ is a root-sum-of-squares value derived from the residual of $T(\varepsilon) - Q(\varepsilon)$ and should be the target of the ‘Set Objective Cell’ field. The objective should be set to ‘minimise’. The ‘By Changing Variable Cells’ should be set to change the values of r_0 , r_m , and s_n up to $k = l = 4$. The ‘Make Unconstrained Variable Non-Negative’ option should be unticked; the solving method should be set to ‘GRG Non-linear’. Click ‘Solve’ to initiate the fit. Figure 6 shows what a successful fit may look like, with $T(E)$ plotted between 200 eV and 1600 eV, a range which encapsulates the needs of most experiments. If the fit does not converge or deviates widely from $Q(\varepsilon)$, try the fitting procedure again but only include the terms for $k = l = 1$ first, and then include higher-order terms in a second fitting attempt.

Once a suitable fit has been achieved, the $T(\varepsilon)$ fitting parameters can be used to reproduce your spectrometer’s transmission function $T(E)$ for any kinetic energy E for that pass energy and lens mode.

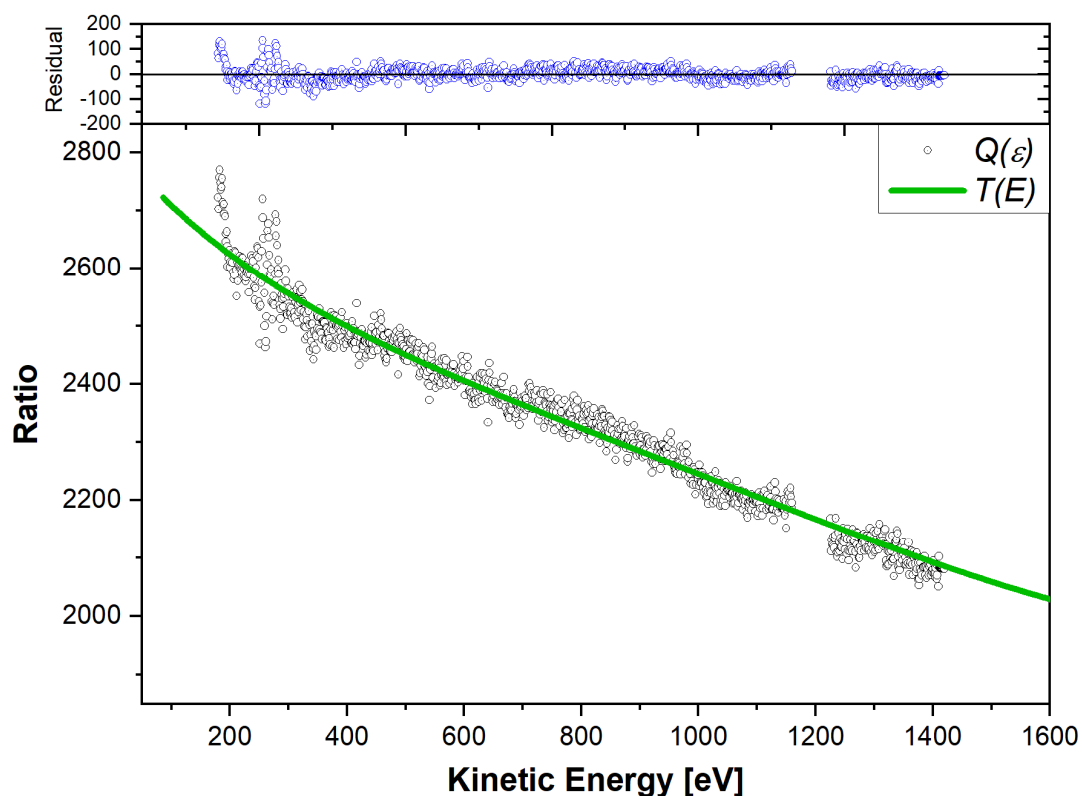


Figure 6. A correctly fitted transmission function $T(E)$ to $R(\varepsilon)$. The extrapolation procedure ensures that the higher kinetic end of $T(E)$ does not diverge significantly from the $Q(\varepsilon)$ data. This smooth continuous $T(E)$ can be reproduced in any data analysis software simply by re-calculating equation (5) using the fitting parameters. A corrected spectrum is then obtained by dividing the raw spectrum by $T(E)$.

7 AFTER ANALYSIS

When all analyses are complete, please return your results to NPL *via* email or an appropriate file exchange server at the earliest convenience in the format outlined in Section 8. The contents of the VAMAS package do not need to be sent back to NPL.

8 DATA REPORTING FORMAT

Provided with this protocol will be a MS Excel electronic reporting form which will have step-by-step instructions on how to use it. Please report your details, instrument geometry, data and acquisition parameters into this form. We ask that a new form is used for each transmission function you wish to calculate, i.e. for each data set. If you are sending back multiple data reporting forms, then please place them into a .zip folder and name them appropriately.

In the data reporting form, pages 2A and 2B are open sheets with no cell formatting. These spaces should be used to import the kinetic energy and intensity data from the five LDPE datasets and the gold dataset outlined in Section 6.1. For clarity, an example reporting form with model data already included will also be distributed.

Along with the reporting form, please return your raw data files in .vms format and note the filename of the dataset used in each reporting form. Please do not send instrument specific raw data files.

If you wish to send the data in an alternative format, please contact benjamin.reed@npl.co.uk. The preferred method of returning data and reporting forms is by e-mail.

9 CONFIDENTIALITY

The samples supplied in this VAMAS study are not certified reference materials. They are sent to you in confidence and if there are any issues with them upon arrival, we ask that you contact us. Please do not publish or present your results or any details of the analysis used in this study without consulting NPL first. If your laboratory does not want to be identified in our final report, please note this in your data reporting form and inform us by e-mail.

ACKNOWLEDGEMENTS

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