

# Testing and validating the improved estimation of the spectrometer-transmission function with UNIFIT 2022

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Recent developments of X-ray photoelectron spectroscopy using excitation energies different from the usual lab-sources Mg K $\alpha$  and Al K $\alpha$ , thus covering larger and different kinetic energy ranges, require more flexible approaches for determining the transmission function than the well-established ones using reference spectra. Therefore, the approach using quantified peak areas (QPA) was refined allowing a more precise estimation of the transmission function. This refinement was tested by comparing the results obtained with the new version with former calculations. Furthermore, the obtained transmission function was validated by comparing the results with a transmission function using the reference spectrum of polyethylene. Additionally, an ionic liquid was used as reference for estimating the transmission function at the energy-resolved HE-SGM beamline at BESSY II. Comparison between the measured and stoichiometric composition shows that a transmission function was determined, which allows a reasonable quantification.

## KEYWORDS

photoelectron spectroscopy, quantification, software UNIFIT 2022, synchrotron radiation, transmission function IERF

## 1 | INTRODUCTION

Quantitative analysis of the composition in the analysis area is one of the main aims of X-ray photoelectron spectroscopy (XPS).<sup>1</sup> Three approaches are common to achieve reliable quantitative results: The use (i) of experimentally determined relative sensitivity factors,<sup>2,3</sup> (ii) of specific reference samples or (iii) of theoretically derived sensitivity factors.<sup>4</sup> For all these methods, reliable transmission functions of the spectrometer are crucial for comparing measurements from different instruments.<sup>5</sup> In spite of the efforts in the last years, the quantification is still challenging even for homogeneous materials.<sup>6</sup> One reason is that no standards exist for a consistent procedure of the determination of the spectrometer transmission function.

Seah presented a first approach using reference spectra of the three noble metals Cu, Ag and Au.<sup>7</sup> This procedure needs spectra obtained under the same conditions (source, step width, number of

points, etc.) as the reference spectra, and hereby, it is limited to the non-monochromatic Al K $\alpha$ /Mg K $\alpha$  and the monochromatic Al K $\alpha$  sources, which are the most popular ones. Recently, this approach was modified and low-density polyethylene (LDPE) as reference material was used, which is much easier to handle and to clean than the three noble metals.<sup>8</sup> Furthermore, the reference spectra of LDPE can be described by a mathematical function, which can be used as a noise-free reference spectrum for the calibration of other XPS instruments. Recently, the suitability of this approach was shown in Versailles Project on Advanced Materials and Standards interlaboratory study.<sup>9</sup> In another approach, a typical photoelectron peak of a monoatomic sample was measured during the sample was biased with different voltage (sample-biasing method).<sup>10</sup> Recently, a correction function was introduced, which enhances the result of this method.<sup>11</sup>

Some years before these recent developments, Hesse et al. have implemented two different methods for the determination of the

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transmission function into the software package UNIFIT. The so-called survey-spectra approach (SSA) uses the reference spectra from the National Physical Laboratory (NPL) and estimates the transmission function by fitting a model function in such way that the reference and measured spectra have a good accordance. Because we have a large number of measuring points with respect to the number of fit parameters, the nonlinear Marquardt–Levenberg algorithm is used for the optimization of the fit parameters. But not all measured survey spectra are suitable, for example, internal scattering can influence the background of the survey spectra depending on the lens mode in state-of-the-art spectrometers. Therefore, an additional approach was proposed using quantified peak areas (QPA) of specified peaks, for example, from Ge, Cu, Ag and Au.<sup>12</sup> In this approach, the areas of different peaks of these elements are determined normalized with the inelastic mean free pathway and the cross sections of the photoelectrons. These normalized areas are used for the determination of the transmission function. Thereby, the ratios of the normalized areas are compared with the stoichiometric ratios. Using elements like pure Cu, Ag and Au, the ratio is one; otherwise the ideal stoichiometric composition has to be used. Hereby, it must be ensured that this ideal composition agrees with the real composition, which is not trivial. The disadvantage of this latter approach is that significantly less data points are available for the fitting of the transmission function than with a method using nearly the whole survey spectrum (SSA). On those conditions, the typical fitting methods (e.g., Gauss–Newton algorithm, gradient algorithm or a combination of both) cannot be used for the estimation of the fit parameters. A new optimization procedure was developed and presented.<sup>12</sup> Anyway, it must be noted that a wide range of the energy region is covered by the chosen peaks. A comparison showed that similar results were obtained with both approaches for standard experimental laboratory conditions.<sup>12</sup> This shows the reliability of this approach. Additionally, this QPA method is much more flexible in terms of excitation energies (resulting in other and larger kinetic energy ranges), spectrometer modes (using more complex lens arrangements) and reference materials that enhance the usefulness for the determination of the transmission function. It can be applied for different spectrometer modes, at synchrotron sources and with other suitable reference materials like ionic liquids.<sup>12–14</sup>

This latter point is of great importance due to the developments in the last years. For achieving best signal-noise ratios and maximum lateral resolutions, the electro-optic lens systems of the spectrometers have become more and more sophisticated. This positive development has led to more complex transmission function, which complicates the approximation of the transmission function to the reference spectra. Furthermore, other excitation sources than the usual Al K $\alpha$  or Mg K $\alpha$  X-ray sources, especially in the hard X-ray energy region, has become more popular.<sup>15</sup> Especially, the introduction of lab-based HAXPES (Hard-Energy X-ray photoelectron spectroscopy) spectrometer will lead to a further dissemination of such instrumentation.<sup>16,17</sup> First efforts were done to use sputter cleaned gold as reference material for a lab-based instruments using an Ga K $\alpha$  source.<sup>18</sup> This approach leads to reliable quantification results, but the obtained

reference spectra are limited to spectrometers of the same type. Therefore, the need of easy, reliable and flexible procedures for the determination of the transmission functions remains, especially for synchrotron radiation sources with different excitation energies and, thus, different resulting kinetic energy ranges.

To meet this need, the QPA method has been significantly improved, carefully tested and implemented into UNIFIT 2022. As the former software packages, it can be used for any spectrometer modes, every excitation energy and every suitable reference material, for example, noble metals or ionic liquids. By increasing the number of useable fit parameters from seven in the previous version to now eight more complex transmission functions can be handled, which takes into account the development of more complex electron optics for the spectrometers in the last years. Furthermore, one vital point is the increase in flexibility within the fitting routine. While before only four sweeps with predefined accuracies and one cycle could be used, now maximum five sweeps and in addition a variable number between 1 and 99 of cycles can be defined. Thereby, every new cycle uses the optimum values found with the former cycle. With that extended minimization procedure, a better minimum of the sum of the squared deviations (SSD) can be found, especially with regard to undesired local minima. A break error value can be chosen to find an optimum between accuracy and calculation time. Thereby, a certain uncertainty can be fixed without increasing the calculation time to unrealistic values needing a few days. Therefore, the calculation time and the accuracy are compared between UNIFIT 2004 and the new version UNIFIT 2022 in the result section. For the practical use, considerable progress has been achieved in the visualisation of the results which allow an intuitive comparison between the measured transmission at the energies of the used peaks and the fitted function. Thus, a quick check of the quality of the fit for the transmission function is possible and the progress of the procedure can be followed more easily. Summarizing, all these achievements allow a more accurate estimation of the transmission function at the same time or faster as before, which is a great advantage for the practical use of the software. Further information is given in the Supporting Information S1.

In order to test the improvements, UNIFIT 2022 was used to determine the transmission functions of

1. Synthetic test functions,
2. Real data measured with the spectrometer ESCAL 220 iXL and comparison with results using the former version of the QPA method,
3. Real data measured using the spectrometer Kratos Axis Ultra to test a low number of input peak pairs,
4. Real data recorded with the Scienta R3000 spectrometer at the BESSY beamline HESGM.

The beamline in the last study is suitable for kinetic energies between 50 and 750 eV with excitation energies between 150 and 850 eV. Next to the transmission of the spectrometer, the intensity characteristics of the beamline and certain beam parameters must be considered. Due to these challenges, usual procedures for the

estimation of the transmission function using the survey spectra are not feasible. We have developed a procedure to determine the transmission function of the spectrometer using different excitation energies. As test material, an ionic liquid was used, which had been checked earlier for its suitability.<sup>14</sup> The possibilities but also the limits of this approach will be discussed.

## 2 | EXPERIMENTAL

The measurements were performed at the spectrometer ESCALAB 220 iXL with six different settings, using the standard spectra Au 4f, Au 4d, Au 4p<sub>3/2</sub>, Ag 3d, Ag 3p<sub>3/2</sub>, Cu 3p, Cu 2p<sub>3/2</sub>, Ge 3d and Ge 2p<sub>3/2</sub> excited with Al K $\alpha$  and Mg K $\alpha$  radiation. At a Kratos Axis Ultra DLD, sputtered Au, Ag and Cu foil was used for estimating the transmission function. For the excitation, the monochromatic Al K $\alpha$  source was used. The synchrotron radiation measurements were carried out with the Scienta R 3000 electron spectrometer at the end station of the High-Energy-Spherical Grating Monochromator (HE SGM) dipole magnet beam line at BESSY II (Berlin, Germany) at the ionic liquid 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide Solarpur<sup>®</sup> as reference sample, which was purchased by Merck. Further details are described in the Supporting Information S2.

## 3 | TEST OF THE METHOD

Before using the improved fit method, it was validated and the best conditions for obtaining reliable fits, the behaviour of the convergence, the calculation time and the correctness of the calculated fit parameters were evaluated. Therefore, two transmission-test functions and the corresponding perfect data set of 10 peak pairs were generated. The first one simulates calibration measurements of reference elements (e.g., Au, Cu and Ag). The second test simulates a calibration measurement of a reference compound (e.g., ionic liquids ILs). The procedures and the results are described in the Supporting Information S3.

The aim of these tests with synthetic data was to validate the algorithm and to find the best strategies for fitting. As criterion for the quality of a fit, the sum of squared standard deviation (SSD) was chosen. This criterion considers the whole energy range and fails, if the deviations are located only at some peak pairs in a small binding energy range. For identifying such local deviations, the visualization of the input parameters helps. Herewith, the difference between the input values and the estimated transmission function can be easily seen and regions of kinetic energies with strong deviations located. Therefore, a visual inspection of the fitted transmission with the input parameter is recommended. Thereby, it must be kept in mind that different parameters of the transmission function can lead to functions with a similar course or shape. For standard laboratory configuration, six free fit parameters, three sweeps and three cycles led to results with an acceptable accuracy in a reasonable calculation time. Furthermore, it is recommended to start the fitting with different parameters.

## 4 | ESTIMATION OF $T(E)$ USING REAL DATA

In order to demonstrate the advantages of the improved method in praxis and to validate the results with other approaches, a calculation of  $T(E)$  functions using real measurements were carried out. Measurements with laboratory spectrometers (ESCALAB 220 iXL and Kratos Axis Ultra) and the SCIENTA R3000 electron spectrometer, installed on the HE-SGM beamline at the BESSY II Synchrotron, were used.

We recommend using the same photoionization cross sections and inelastic mean free pathways for the estimation of the transmission functions like for the quantitative analysis. In principle, all cross sections and mean free pathways or effective attenuation length can be used. For all measurements, it was ensured that the electron detector was operated within its linear range. Especially, for the measurements with the noble metal foils, the detector settings were adapted.

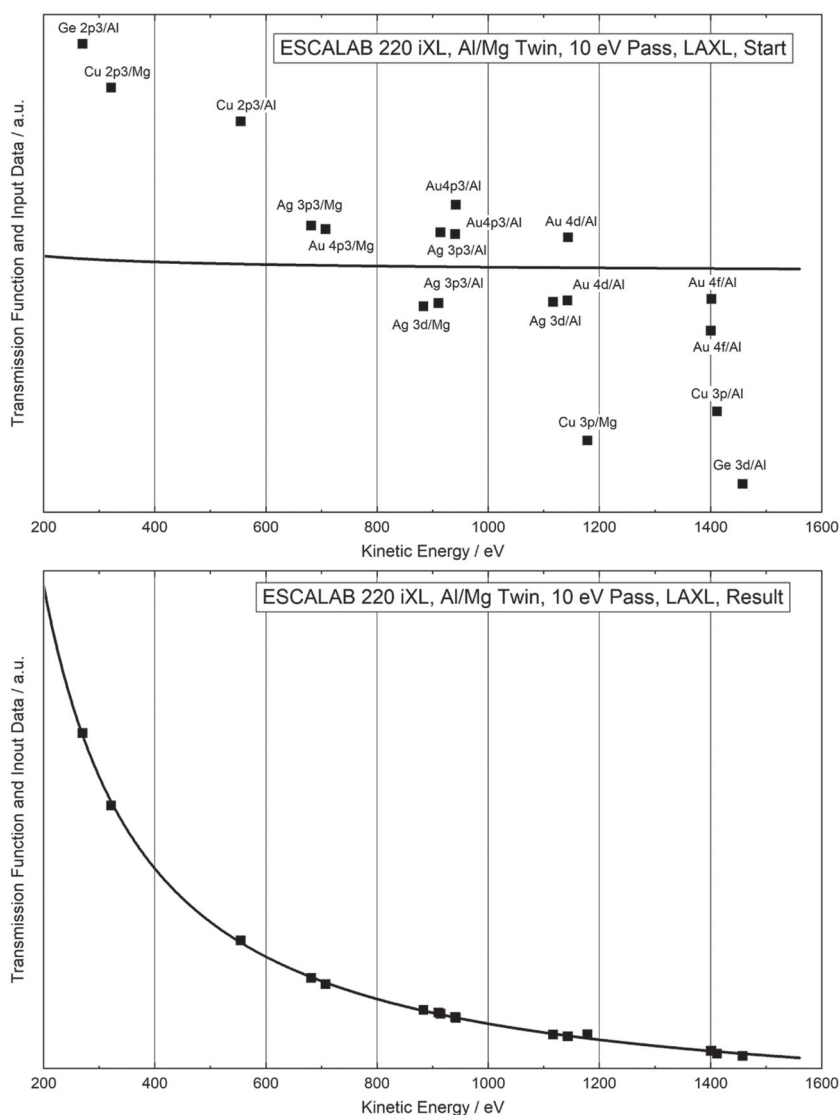
### 4.1 | Laboratory spectrometers

#### 4.1.1 | Spectrometer ESCALAB 220 iXL

The method QPA has been successfully applied since several years.<sup>12</sup> Six data sets were recorded with the spectrometer ESCALAB 220 iXL, twin anode, 50 and 10 eV pass energies and three lens modes (LAE, LAXL, SAE 150). The experimental conditions, the peak area estimation and the calculation of the transmission function were described. The parameters of the different lens settings are given in tab. 3 of the publication introducing the QPA method.<sup>12</sup>

The results with UNIFIT 2004 were extracted from tab. 5(a), 5(b), 6(a) and 6(b) of this former publication.<sup>12</sup> There, only the three parameters  $a_0$ ,  $b_1$  and  $b_2$  of the model function  $T(E)$  were fitted; four sweeps and one cycle were supported. The new calculation with UNIFIT 2022 was performed with five parameters ( $a_0$ ,  $a_1$ ,  $a_2$ ,  $b_1$  and  $b_2$ ) (Tables S8 and S9) and three sweeps and cycles were defined. For the comparison of the new estimated  $T(E)$  functions using the software UNIFIT 2022 with respect to the results using UNIFIT 2004, the same input data set was used. The following peaks with Al/Mg Twin excitation were used: Au 4f, Au 4d, Au 4p<sub>3/2</sub>, Ag 3d, Ag 3p<sub>3/2</sub>, Cu 3p, Cu 2p<sub>3/2</sub>, Ge 3d, Ge 3p<sub>3/2</sub>. The input values and the estimated transmission function after fitting for an exemplary setting are presented in Figure 1. Other estimated transmission functions are provided in the Supporting Information (Figures S4 and S5).

For comparing the result obtained with UNIFIT 2022 with UNIFIT 2004, the quantification was performed with the used peak pairs using the different transmission functions. Although the  $T(E)$  calculations with UNIFIT 2004 were already good, nearly all new calculations of  $T(E)$  gave better results. The comparison of the errors of the different quantifications for the different settings shows this observation (Figure 2, details are in Tables S10a–S10c).



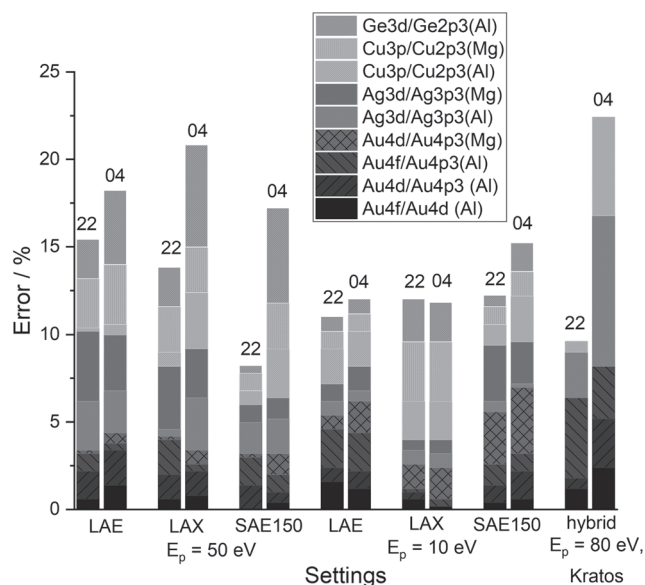
**FIGURE 1** Input values (squares) and  $T(E)$  start function before (on top) and after (below) the fit with the start parameters of Table S8, (solid line), spectrometer: ESCALAB 220 iXL, pass energy: 10 eV, lens mode: LAXL

#### 4.1.2 | Spectrometer Kratos Axis Ultra

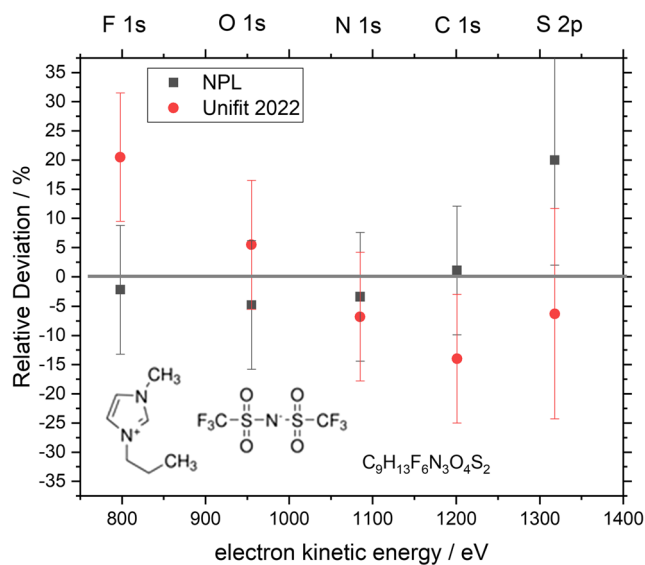
For the estimation of the transmission function  $T(E)$ , sputtered Au, Ag and Cu foil were used as reference samples. The excitation source was Al K $\alpha$ ; the lens mode was set to hybrid; no aperture was adjusted (slot mode with the spot size of  $300 \times 700 \mu\text{m}^2$ ). These are typical conditions for recording survey spectra, which are used for the quantification. Thus, the following peaks can be used for the analysis: Au 4f, Au 4d, Au 4p $_{3/2}$ , Ag 3d, Ag 3p $_{3/2}$ , Cu 3p and Cu3p $_{3/2}$ . The areas of these peaks were determined after subtraction of a modified Tougaard background.<sup>19</sup> The areas were normalized by Scofield photoionization cross sections and the inelastic mean free paths (IMFPs) with an energy-dependent power-law dependence derived from the TPP formula.<sup>20</sup> Then, the measured results for the peak pairs were compared with the theoretical ratio of one as performed for the measurements at the different setting of the ESCALAB. The transmission function obtained with UNIFIT 2022 is compared in Figure S6 together with the one estimated with UNIFIT 2004. Although only five peak pairs were used for the estimation of  $T(E)$ , the new algorithm

of UNIFIT 2022 has led to a SSD which is comparable with the results obtained with more points for the ESCALAB 220iXL (see Figure 2, further details in Tables S12 and S13). The error is minor compared to the estimation with UNIFIT 2004.

In the next step, the transmission function obtained with UNIFIT 2022 was compared with the one obtained with LDPE as reference material and recently validated by an interlaboratory comparison.<sup>8,9</sup> Therefore, quantitative results obtained for the ionic liquid 1-propyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide Solarpur<sup>®</sup> with both transmission function were compared with the stoichiometric values of the ionic liquid. The peak areas for the quantification were obtained as described before. For the 1s levels an uncertainty of 5% was estimated due to the calculated Scofield values, for the S 2p level an uncertainty of 15% indicated.<sup>6</sup> For the IMFPs an uncertainty of minimum 10% was reported.<sup>21,22</sup> Although the deviations from the stoichiometric values vary for the both transmission functions depending on the photoelectron peaks, there are in the range of the uncertainties. Therefore, both approaches led to reasonable results (Figure 3).



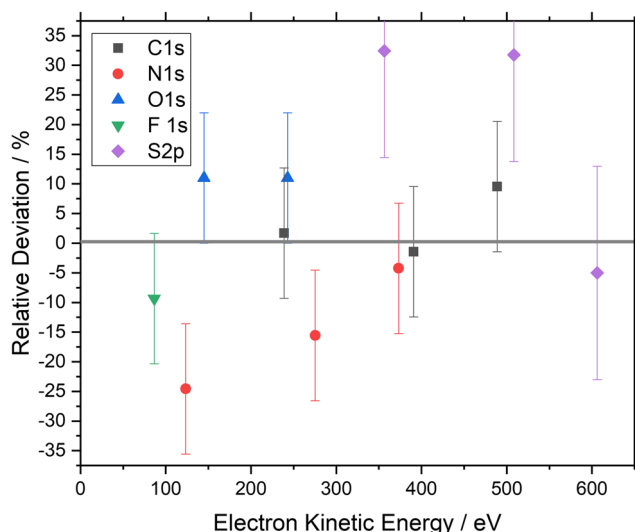
**FIGURE 2** Comparison between the errors of the quantification between UNIFIT 2022 and UNIFIT 2004



**FIGURE 3** The deviations between the stoichiometric and the measured amounts obtained at the Kratos spectrometer using a transmission function derived according to ref. 7 (denoted NPL) and one derived by UNIFIT 2022. Uncertainty ranges are shown. The inlet shows the structure of the ionic liquid used for these measurements.

## 4.2 | Synchrotron beamline

The estimation of the transmission function at a synchrotron beamline is challenging. Different excitation energies are possible with a different transmission of the radiation through the monochromator. Therefore, the well-established survey spectra approach or using the background is not practicable. Only the QPA approach using a suitable test material seems to be suitable and was applied successfully.<sup>14,23</sup> Hence, UNIFIT 2022 was applied at the HE-SGM beamline at BESSY.



**FIGURE 4** The deviations between the stoichiometric and the measured amounts at the different excitation energies. The different shapes of the points reflect the used photoelectron peaks. Uncertainties ranges are shown.

This beamline allows varying the excitation energy from 150 up to 850 eV and is optimized for organic compounds. Thus, 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide Solarpur<sup>®</sup> was used because with C, N, O and S, typical elements of organic compounds are present in this ionic liquid.

The suitability of ionic liquids for the determination of the transmission function was described several times.<sup>14,24–26</sup> Nevertheless, the homogeneous composition in region of the information depth and the stability of the ionic liquid under X-ray radiation was verified (see Supporting Information S5 with Tables S14 and S15).

The transmission function was estimated with suitable photoelectron pairs at excitation energies of 775, 677 and 525 eV (Table S16). It must be noted that only photoelectron pairs were used, which are measured at the same excitation energies at the same time. Therefore, effect of the transmission through the monochromator can be neglected. Nevertheless, the monochromator transmission was measured. The linear polarization of the synchrotron light and the source-to-sample angle of 45° in this experiment require an asymmetry correction of the photoionization cross sections. Hence, the asymmetry correction by Trzaskovskaya, Nefedov and Yarzhevsky were used.<sup>27</sup> Details about the asymmetry correction of the photoionization cross sections can be found in the Supporting Information S6 with Tables S18 and S19. With these data, the transmission function  $T(E)$  was obtained, as shown in Figure S7.

For validating this result, the relative composition of the ionic liquid obtained by using this transmission function was compared with the stoichiometric values (Figure 4). For the uncertainties, the same factors were regarded as for the validation of the transmission function of the Kratos spectrometer. Therefore, for the asymmetry corrected photoionization cross sections, an uncertainty of 5% for the 1s orbitals and of 15% for the S2p orbitals were assumed. As before, for

the IMFP, an uncertainty of 10% was estimated. Depending on the kinetic energy, the relative deviations scatter statistically. The scattering is for the most points in the range of  $\pm 20\%$ , which corresponds to the typical uncertainty for the quantification with theoretical cross sections. It must be noted that the asymmetry correction, which is necessary for the polarized synchrotron lights, should lead to a rather greater uncertainty of the theoretical cross sections. This impression is reinforced by the more systematic deviation of the results depending on the components and their orbitals. For example, the deviations for N 1s are always negative, whereas for O 1s are rather positive. For a more accurate quantification, the use of suitable reference materials is recommended, which allows to determine empirical sensitivity factors of the components which should be measured. It must be noted that these sensitivity factors are only valid for the specific measurement equipment including the transmission of the specific spectrometers. This hinders the use of these sensitivity factors for other systems and, herewith, hampers the reproducibility of these factors.

## 5 | CONCLUSIONS

A new and better algorithm to more precisely estimate the transmission function  $T(E)$  has been established, tested and implemented into UNIFIT 2022. It contains a reliable and a traceable method for estimating the transmission function  $T(E)$ , which can be used under different spectrometer settings, excitation conditions and calibration samples. In practical use, the most important new feature is to compare the used reference data points derived from the measured results with the estimated transmission function easily by showing both in one plot. This allows for a fast check of the defined start parameters as well as the quality of the estimated function.

Previously, it was shown that the survey spectra approach (SSA) using the survey spectra of clean Ag, Au and Cu and the quantitative peak approach (QPA) using the peak area of defined components led to comparable results.<sup>12</sup> The improvement due to the new features of UNIFIT 2022 could be shown in this manuscript by means of two laboratory experiments. Even with a rather low number of parameter it was possible to estimate reliable transmission functions which are comparable with well-established methods.

Finally, the applicability for synchrotron-based spectrometers was shown by the estimation of the transmission function for the spectrometer at the HE-SGM beamline at BESSY. Thereby, a well-defined ionic liquid was used as reference sample using theoretical cross sections and IMFPs for the determination of the normalized peak intensity. Satisfactory results were obtained which allows a first overview about the quantitative composition of the sample. It must be noted that with such approach only the spectrometer dependent transmission function was determined. For a reliable quantification at synchrotron light sources a careful beam intensity monitoring is necessary to detect any influences of the photon flux on the results which must be consider in the calculation of the amounts of each component (Table S18).

The procedure presented here offers a unique flexibility for the determination of the transmission function. Usually, Scofield

photoionization cross sections and an approach using the TPP-2M formula<sup>20</sup> are recommended for laboratory sources. The software package allows to use other cross sections like the ones of Trzhaskovskaya et al. which were used for the synchrotron application. Likewise, the cross sections calculated by Yeh and Lindau can be used.<sup>28</sup> Recently, theoretical cross section for HAXPES were published which can be adopted<sup>29-31</sup> Furthermore, the accuracy of the quantification can be increased by using effective attenuation lengths.<sup>32</sup> Like for the settings used for the estimation of the transmission functions, the photoionization cross sections and mean free paths used for the quantification are always a compromise between effort or time and the accuracy, which is needed for a reliable statement. In any case, the users should be aware of the uncertainties of the chosen approach for the quantification. We recommend using the same approach with same cross sections and mean free pathways for the estimation of the transmission functions, which are used for the quantifications of unknown compounds.

## ACKNOWLEDGEMENTS

The authors thank the BESSY II synchrotron radiation facility of the Helmholtz Center Berlin and its team for the allocation of beamtime at the HE-SGM beamline and for excellent support during the experiments. Furthermore, the authors acknowledge the support from Dr. A. Nefedov (Karlsruhe Institute of Technology, KIT) and Dr. Maria Brzhezinskaya (Helmholtz Center Berlin) for of the HE-SGM CRG. For the measurements at the Kratos Axis Ultra DLD, the authors thank Jörg Manfred Stockmann (BAM). Open Access funding enabled and organized by Projekt DEAL.

## DATA AVAILABILITY STATEMENT

The data are available at the authors on request.

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## SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

**How to cite this article:** Hesse R, Denecke R, Radnik J. Testing and validating the improved estimation of the spectrometer-transmission function with UNIFIT 2022. *Surf Interface Anal*. 2022;1-7. doi:[10.1002/sia.7131](https://doi.org/10.1002/sia.7131)