



## Transmission function calibration of an angular resolved analyzer for X-ray photoemission spectroscopy: Theory vs experiment



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### ABSTRACT

In order to achieve the most accurate quantification results in an X-ray photoelectron spectroscopy (XPS) experiment, a fine calibration of the analyzer response is required. In this work an experimental characterization of a modern angle-resolved analyzer, carried out with a unfocused and a highly collimated synchrotron source, is shown. The transmission function is extrapolated from the discrepancy between experimental and theoretically predicted XPS peak areas; the influence of different sensitivity factors and of the escape depth correction on the expected values is also discussed. The analyzer response and the theoretical approach are then tested against energy dispersive XPS measurements (EDXPS). These results are finally compared with TF calculated on the basis of an high accuracy electron ray tracing code, also described in this work.

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### 1. Introduction

While in standard X-ray photoelectron spectroscopy (XPS) the element detection limit can be better [1] than 0.1%, the practical accuracy for relative elemental quantification is generally considered to be [2] 7–10%. As a results, a careful XPS analysis must often rely either on comparison with reference samples, whose surface preparation and compositions have to be validated by other techniques, or on specific sensitivity factors deduced by previous experiment carried out with the same instrumentation and similar data treatment. In order to obtain a resolution better than 10%, an accurate control over many photoemission analysis details must be carried out. The factors that limit the XPS accuracy can be summarized into four groups: (i) data collection and analysis (data noise, background removal, area extrapolation or peak-fitting routines); (ii) specimen preparation (contamination, photoelectron diffraction effects in crystals, charge compensation in insulators, surface roughness); (iii) XPS theory (cross sections or sensitivity factors, escape depth correction, inelastic and elastic scattering effects);

(iv) instrumental parameters (X-ray source, analyzer configuration and response calibration function). An extensive review of quantitative XPS resolution can be found at this reference [2].

While the accuracy enhancement related to the data quality can be systematically improved, for instance through larger acquisition time, the theoretical details and instrumentation parameters may introduce large errors in the relative elemental quantification. In particular, the analyzer transmission function (TF) [3], which defines the detector sensitivity at different electron kinetic energies, is often neglected in quantification calculations, assuming to be counterbalanced by the electron escape depth (ED) correction [4] (due to the total number of photoelectrons emitted from the sample at different kinetic energies). However, it should be pointed out that while the escape depth correction is a sample characteristic, the transmission function depends [5] on the analyzer working parameters (i.e. pass energy, entrance slit and acquisition mode, e.g. with or without angular dispersion) as well as on the X-ray source spot size and sample dimensions. As a result, the quantification carried out on spectra collected, for instance, at different pass energy could give different results on the same sample, if the TF is not properly considered.

Usually, two classes of methods can be adopted in order to experimentally evaluate an analyzer transmission function. The first method, named Survey Spectra Adaptation (SSA) [6], requires

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to compare a survey spectrum collected on a defined material with reference data measured with a calibrated spectrometer (“calibration by reference”). Typically, this procedure is performed on clean gold or silver sample spectra collected with standard X-ray source (Mg or Al anode). In a SSA procedure, both the main XPS peaks and the loss background are considered. Although this method could be very accurate, it can be applied only through reliable reference spectra, measured with the same X-ray source energy, with a similar experimental geometry and total resolution; as will be shown in this work, the response of modern angle-resolved analyzer can be rather sensitive to the photoelectron emission area (defined by sample and source focus size).

Another experimental approach is to compare the intensities of various peak of the same element to theoretical values, i.e. a “calibration by theory”; this method is also known as Quantification Peak Adaptation (QPA, ref. [5] and refs. therein). The relative discrepancies between the measured and predicted peak areas are then interpolated with a model parametric TF function, usually given by an exponential decay with a polynomial background. Since each XPS peak is related to a single kinetic energy value, QPA must be performed on spectra taken from various reference sample and/or with different photon energies, in order to better fill the required energy range. In this method, the knowledge of sensitivity factors or cross sections is needed and the accuracy is limited by the number of XPS peaks being considered; however, depending on the type of calculation and the parameter databases, QPA could be applied for any photon energies, analyzer geometries and sample size.

Recent developments in photoemission spectroscopy have been boosted either by third generation synchrotron light sources or by pulsed laser sources combined with a plentiful of choices in detector technology [7–10]. The result is the availability of a wide range of photon energies from few eV up to hard X-rays, photon beam polarizations from linear to circular, and time-resolved experiments. A reliable calibration procedure is thus mandatory in order to reach a suitable accuracy in photoemission experiments.

The knowledge of TF became crucial while performing complex synchrotron experiments. In fact, preliminary to a synchrotron experiment, the sample preparation and characterization is quite often carried out on the basis of fixed-energy anode sources in a standard XPS setup. However, the soft X-ray energies of a typical synchrotron end-station are in general lower (high photon fluxes are usually available for photon energies below about 1000 eV), thus leading to photoemission peaks with lower kinetic energy. A quantitative comparison can thus be difficult. Without considering TF, the spectra collected from the same samples can lead to quite different quantifications, even if prepared in identical way. As it is shown in this work, energy-dependent cross-section alone cannot account properly of the peak intensity variation in different set-up; most importantly, the TF of the same analyzer can be nearly flat or vary up to the 300% in an XPS survey, according to the experimental parameters.

In this work, a full characterization of the TF of a modern analyzer (Scienta R3000) is carried out within the framework of QPA method. The TF has been evaluated for a standard XPS setup equipped with a non monochromatic source and for a synchrotron beamline with a focused X-ray source. In the latter case, the TF evaluation has been also carried out by collecting the intensity of the same peaks in a wide range of photon energy, thus resulting in an higher accuracy; this technique is also known as energy dispersive XPS (EDXPS).

The experimental TF are then compared to the theoretical calculation predictions based on the electronic lens design of the analyzer, using a proprietary electron optical code here modified in order to take into account both large sources and the relatively poor optical properties associated with large solid angles.

## 2. Experimental details

The analyzer characterized in this work is a Scienta R3000 in the XPS-UPS-ARPES configuration, which allows simultaneous collection of ARPES (Angle Resolved Photoelectron Spectroscopy) spectra in maximum of a  $\pm 10^\circ$  angular dispersion range.

The Scienta R3000 is a 135 mm hemispherical analyzer equipped with an electrostatic lens system with an acceptance angle of  $\pm 15^\circ$ . In the standard configuration, the analyzer operates in constant analyzer energy mode using pass energies between 2 and 200 eV for a kinetic energy range of 0.5–1500 eV. The spectrometer is equipped with six pairs of slits, resulting in six different aperture/slit combinations. The slit height is defined to be in the radial direction of the hemisphere, hence in the energy dispersive direction. In each pair, the slit and aperture heights are matched in order to maximize the product of acceptance angle and slit height at a given resolution [11]. In a modern hemispherical energy analyzer large angles in the non-energy dispersive direction, i.e. along the slit direction, do not deteriorate the energy resolution [12].

The analyzer is equipped with a 40 mm diameter MCP and CCD detector covering 12% of the pass energy (EP) and can operate in both transmission and angular mode [11,12]. In the transmission mode the spectrometer lens elements are set to maximize the intensity while preserving the spatial information with a magnification of  $5\times$  and moderate resolution on the sub mm scale. The transmission mode gives good intensity from both small and spread out X-ray spot sizes. In the angular mode the lens elements are set so that electrons emitted in different directions are refocused onto different points of the detector; to preserve high performance of the angular information a small source spot sizes ( $< 1$  mm along the slit direction) is thus suggested. Each of these analyzer modes is related to a different transmission function.

The first measurements have been carried out with a standard XPS setup at the Surface Science and Spectroscopy Lab of the Università Cattolica (Brescia, Italy); the X-ray source is a non-monochromatic PsP dual-anode (Mg and Al), providing a photon energy of 1486.6 eV and 1253.6 eV. In this case, the source spot size on the sample is larger than the sample itself (8 mm  $\times$  8 mm). Total resolution was about 1.0 eV for the Al  $k_\alpha$  and 0.8 eV for the Mg  $k_\alpha$  source. In order to provide the maximum effect of the TF, the analyzer entrance slit have been kept at the largest aperture (3.0 mm). The angle between the analyzer and the source axis is  $62^\circ$ : thus geometry has been taken into account in the theoretical model.

The second set of data has been collected at the BACH beamline of ELETTRA synchrotron at Trieste; the available photon energy range span from 1600 to 35 eV, both in linear and circular polarization. The smallest spot size was 250  $\mu\text{m} \times 20 \mu\text{m}$  and the analyzer slit aperture was 0.8 mm. The analyzer-source angle was  $60^\circ$ . In this case, the R3000 has been tuned in order to reach a wider kinetic energy range (2000 eV) and a slightly larger angular dispersion (A21 instead than A20). These modification are not expected to induce variation in the TF as compared to the standard analyzer.

Specimen of pure, polycrystalline Au and Cu have been prepared for the calibration. Single crystals should be avoided both in QPA and SSA, because of possible photoelectron diffraction effects. A slice of standard Cu vacuum gasket 99.99% pure could be used for this purpose. In both cases, samples have been cleaned in-vacuum with  $\text{Ar}^+$  sputtering and annealing cycles and the pass energy was set to 100 eV.

## 3. Theoretical details

### 3.1. XPS peak intensity

As will be shown in the Section 4, in a reliable TF “calibration by theory” method, the peak quantification can not be based solely on

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