

# Comment on Spectrometer Calibration in Electron Spectroscopy

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During the history of electron spectroscopy a lot of work were made on the problem of the energy calibration of electron spectrometers. The most precise determination of the binding energies of the calibration lines of the best standards Ag, Cu and Au metals was made extensively in metrology laboratories from many point of view in a traceable way and the atomic standards with methodical suggestions were established [1,2,3]. Although a lot of details of the problems have been solved, but some problems are remained. One of the questions is, whether the given binding energy values of the calibration lines of the above mentioned atomic standards are how near to the real binding energy values. This problem is a challenge for the analysts and the manufacturers of the instruments as well. At first one needs to use the same standards and the same methods in every laboratory for the line position determination to compare the results reached in different laboratories.

The absolute traceable line positions are very suitable for the usage of the so called relative energy calibration, which is generally applied in a usual laboratory. In this case f. e. the knowledge of the electron spectrometer work function not a problem. The knowledge of the spectrometer work function only important to get the real binding energy values. For the measurements of the spectrometer work function one should analyse a specimen which was made of the same material as the spectrometer. Then it is necessary to measure another specimen which has a known work function measured with an independent method and the specimen in the same conditions as in the case of the measurement by electron spectroscopic method. The same conditions means that, in optimal case, both work function measurements should be carried out, as much as possible, in the same vacuum environment as is used during the electron spectroscopic measurements. Then from the difference of the secondary electron edges in the electron spectra, that is from the so called zero-kinetic energy edges one can conclude for the work function of the spectrometer. After this one can correct the binding energies, if this problem solved in a metrology laboratory. By the help of the atomic reference standards the real binding energy values can be measured even in an average laboratory with the relative energy calibration method.

At any laboratory even in that case if one measures only relative energies, f.e. chemical shifts of the electron lines belonging to different chemical states of an element in different materials, the calibration of the electron spectrometers should be checked time to time. If one experiences any alteration from the usual value it should be adjusted, for example set up the zero position of the

power supply giving the voltage for the electron spectrometer electrodes to correct for aging of the electronic parts of it. Any drift, even long range one during months or years, is important. The most difficult problem is to save the conditions of the instruments in the metrology laboratory, because its references (voltage reference, temperature reference) have to be kept in very stable conditions. In such a case even the spectrometer work function must be constant. In an UHV or XHV chamber the conditions are very hopeful to minimize or eliminate the changes of the contact potentials depending on the manufacturers technology as well.

In the case of long range energy shifts, which were experienced in the case of a home built double pass CMA[4], the question was arisen. Which part of the instrument was drifted, aged? Which type of effects caused the shift happened to be in the offset value of the binding energy scale in the relative energy calibration method. The changes of the offset values were experienced in the Constant Analyser Energy (CAE) mode at different pass energies. The offset values in the kinetic energy scale were increasing during time a) 0.51 eV, b) 0.11 eV at 50 eV; a) not measured, b) 0.16 eV at 130 eV and a) 0.46 eV, b) 0.01 eV at 200 eV pass energies in a few months (the a. and b. values are differences for the same period, respectively)[5]. The specimen conditions, X-ray flux, and the power supply of the analyser with the voltage divider were the same. Similar drifts can be experienced with a new HSA spectrometer<sup>5</sup> in Fixed Retardation Ratio (FRR) mode, although the type of the power supply and the voltage divider are different. The similarity is the material of the spectrometer, an aluminium-magnesium-silicon alloy. But these drifts allow to measure reliable binding energies with 0.05 eV error by the help of the relative binding energy calibration method. For the detailed study of the origin of such drifts one needs to use a Digital Voltmeter (DVM), which is calibrated to the national voltage standard. In this way one can adjust the electronics to eliminate any drift comparable with the spectrometer work function changes and the measurement of the work function can be carried out. But for this aim one needs to use an additional specimen made of the material of the spectrometer (as it was mentioned above), in this way any change of the conditions (f. e. the outgassing) of the electrodes of the spectrometer can be monitored. The possibility of the set up of the zero point of the power supply is very important.

The mentioned energy range is the usual XPS-XAES range up to 1.5 keV. But for the less usual energy range up to 10 keV similar problems should be solved, amongst them the relativistic effects should be corrected [6,7,8,9,10,11] in the determination of the line positions, especially in that cases when the retardation not high enough. The relativistic effects, as the work function of the spectrometer, have to be taken into account, not only in the case of the high energy measurements, but even in the low energy (1 keV) measurements when one does not use any retardation. For the higher energy range the errors of the experimental binding energy values are near to 0.5 eV. For a more precise determination of the line positions monochromatic excitation line would be important, which probably can be reached with hard X-rays choosing the respective monochromators constructed with the multilayer technique, but for such aims X-ray sources are necessary with very high brightness. Such type of possibilities would be useful for metrology aim as well. But for simple laboratory usage probably the precision and the accuracy of the determination of the line

positions will be a bit poorer than in the low energy range (below 1.5 keV), not only because of the high natural widths of the excitation X-ray lines, but sometimes the high natural widths of the studied high binding energy inner shell lines as well. The study of such high energy lines may be interesting to know more on layers/interfaces just below the top surface without the destruction of the layers. The high energy calibration (up to 7 keV) of the above mentioned home built HSA5 are demonstrated by the help of Al, W, Mo, Ag, Cu X-ray tubes, which are used for the XPS-XAES studies using Cu target as a well established atomic standard.

For the mentioned high energy range studies may be a new technique, Surface Electron Tomography (SET) [12] will also be a new possibility, especially in the multiple angular detection mode. In such cases new problems are arisen, namely the energy calibration of the different angular channels angle by angle.

From the point of view of the measurements of the real binding energy values, not only the background structure of the spectra is important in the accurate determination of the photo- and Auger electron line positions, but the better and better knowledge of the spectrometer function as well. The mentioned two problems influence the precise calibration procedures of electron spectrometers and in this way encourage the development and the usage of precise mathematical models as much as possible in simple analytical forms, as for example a background correction formula.<sup>13</sup> For the study of background problems the production of the atomic standards in situ in the form of ultra thin layers is also very helpful, especially in XHV chambers [12].

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