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Estimation of the Charging Effect Observed in the XPS Study of Thin Films of Inorganic Compounds

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X-ray Photoelectron Spectroscopy (XPS) is a useful tool for the study of inorganic complexes. The power of the technique lies mainly in the correlation between chemical shifts and oxidation states [1]. From XPS data the estimation of the effective charge on atoms in various complexes becomes possible. This provides a more accurate description of the electron distribution in molecules than the oxidation state [2].

The procedure of calibration of the energy scale in XPS often still is controversial. For conducting materials, the Fermi level constitutes the most reliable reference. This method cannot be used for insulators. It also has been shown [3] that for powder materials, the use of the Cls peak from the mounting tape is not satisfactory for calibration [3]. The Cls line from pump-oil deposits is often used as reference [4, 5]. However, for instruments equiped with dry vacuum pumps, the Cls signal originating from the contaminant can be so weak that it is impossible to determine the binding energy accurately. Furthermore the contribution from the contaminant to the Cls signal can be difficult to distinguish from other contributions (other C atoms belonging to the material under investigation). The gold decoration technique has been used by many investigators. This calibration procedure has some serious limitations. The evaporated gold can react with the compounds studied when those contain cyanide or halide [4, 6]. Influence of the thickness of the gold layer also has been reported [7]. A flood gun can be used to neutralize the positive charging. Yet it is rather difficult to determine when charge neutralization has occurred. Most samples can become negatively charged when the treatment is prolonged beyond the point of neutralization. A spectral line of known binding energy which can therefore be used as charge reference line would be ideal. The use of this method is illustrated by the work of B. Folkenson and R. Larsson [2]. Unfortunately this internal referencing is not always possible. Furthermore, this always includes the assumption that the binding energy of the selected level does not change for various complexes.

In this communication we want to suggest a convenient way to estimate the charging effect in such a way that correction can be applied to the measured values. The aim of the exercise is not the suppression of the charging but rather a reliable and easy estimation of the effect.

Results and Discussion

A convenient method to prepare soluble inorganic compounds for introduction in the spectrometer is the crystallisation of a thin film on a gold plate. This method has the advantage of reducing the charging effect, though it does not suppress it completely. The charging in this condition depends very much on the film thickness and varies with the nature of the compound.

A very complete study of the charging effect has been published by Ebel and Ebel [8]. They showed that at a constant X-ray tube voltage, V, the charging is dependent on the tube current, i, according to eqn. (1) where V_{ch} is the mean charging potential.

$$V_{ch} = \frac{ABi}{1 + Bi} \tag{1}$$

A and B are constants and different for each sample.

In practice A and B are unknown and V_{ch} is what has to be determined.

Furthermore, the true binding energy is given by eqn. (2)

$$E_b^t = E_b^o - V_{ch} \tag{2}$$

where E_b^o is the observed binding energy and E_b^t is the true binding energy. At large values of i the observed binding energy V_{ch} becomes constant. It approaches the true binding energy for i tending to zero. It is for small values of i that the variations of V_{ch} are the largest.

The method we should like to suggest for the estimation of the charging occurring at the surface of thin films of inorganic compounds therefore is to select the electronic level with the highest intensity to follow the variation of his binding energy (BE) as a function of the X-ray tube current (i).

A plot of the various binding energies observed as a function of i can be obtained. The value of the binding energy for i = 0 then has to be extrapolated. We tested two techniques of extrapolation. The first one is based on an interpolation polynomial. A polynomial of degree 4 was sufficient, in our case, and the procedure could be carried out on a micro computer of the type HP3354A. The second technique is based

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TABLE I. B.E. of Cl_{2p} Levels Uncorrected and Corrected for Charging Effect on this Film of UCl_4L_2 Complexes.

	uncorrected Cl_{2p} B.E. (eV)	corrected Cl_{2p} B.E. (eV)	charging (eV)
L = tpao	198.6	198.6	0.0
pva	198.9	198.5	0.4
tdpo	199.3	198.5	0.8
bmse	197.8	197.8	0.0

on the Marquardt method [9]. It uses the NONLINEAR program from the SPSS package [10]. For this technique, eqn. (2) is used explicitly and the programme determines the best set of constants A and B of eqn. (1) and E_b^t of eqn. (2). In our study, the values obtained for E_b^t by both techniques never differed by more than 0.05 eV which is very satisfactory.

As an example of the use of our method of evaluation of the charging effect on thin films on inorganic compounds, we report some results on a study of UCl_4L_2 complexes. For the complexes UCl_4-tpao$_2$, UCl_4pva$_2$, UCl_4tdpo$_2$ and UCl_4bmse$_2$, (where tpao = triphenyl arsine oxide, pva = NN-dimethylpivaloylamide, tdpo = tris(dimethylamido) phosphine oxide and bmse = bis(dimethylsulfonyl)ethane) the Cl was thought to be suitable as internal standard. Initially it was believed that the B.E. of the Cl_{2p} levels would not be much affected by the other ligands. However, experimental results showed that the B.E. of the $Cl_{2p3/2}$ in the various complexes differed significantly. When the charging of the thin films is taken into account the results become quite different. This is illustrated in Table I. The value obtained for the UCl_4bmse$_2$ complex is clearly different from the three other complexes. It is not the goal of this communication to discuss this point which will be dealed with in a following paper devoted to a full analysis of the results obtained for these complexes. It appears that when a correction for the charging effect is applied, compounds which can be expected to show similar Cl_{2p} B.E. actually do so. It also appears that using the Cl as internal standard is justified for these type of complexes.

The main advantage of the described method is that it can easily be carried out on any type of material and is applicable to any instrument. It does not require special preparation of the sample and is rather fast. Its main limitation, on the other hand, resides in the difficulty of working with low intensities. This can often be minimized by an appropriate choice of the level used for carrying out the study.

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