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Oxygen-induced next-nearest neighbour effects on the C_{1s}-levels in polymer XPS-spectra

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This letter reports the results of *ab initio* quantum chemical calculations on the C_{1s} core levels of model systems for a number of oxygen containing polymers. Conformational effects were studied. SCF calculations have been carried out with STO-3G and 4-31G basis sets, and Koopmans' theorem was applied to obtain the core-level binding energies. To evaluate the performance of the procedure ΔSCF calculations were carried out on polyacrylic acid. The existence of oxygen-induced secondary substituent effects in the XPS-(ESCA-)spectra is discussed. A comparison with semi-empirical CNDO/2 results from Clark and Thomas has been made.

Key words: Polymers — XPS — ESCA — *Ab initio* — Oxygen

Introduction

In some recent publications [1–3] we have presented *ab initio* calculated values for shifts in core-level XPS-spectra of some model substances for polymers. The binding energies (BE's) were obtained by applying Koopmans' theorem [4]. Calculations on oxygen containing polymers only involved polyacrylic acid (PAA) and polymethylmethacrylate (PMMA). We have shown in that work that a theoretical basis exists for an oxygen-induced secondary substituent effect on the carbon C_{1s}-levels. This has helped us to improve the interpretation of the experimental spectra.

In the present work we present calculated results on a series of oxygen containing polymers. Furthermore, ΔSCF (self consistent field) calculations have been carried out in order to improve over data obtained using Koopmans' theorem. Effects of the conformation on the XPS-shifts will be discussed.

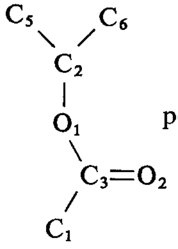
Calculational procedure

Calculations have been carried out using the CADPAC [6] *ab initio* program package. For the polymer model compounds full geometry optimisations were performed and stopped when the maximum and rms (root mean square) displacements were less than 0.06 and 0.04 Hartree/Bohr(radian). Strengthening the conditions one order of magnitude did not affect any of the conclusions.

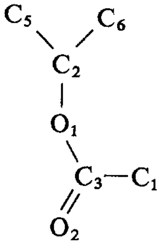
BE's were obtained by applying Koopmans' theorem. Since the relaxation of the electron cloud is then neglected, ΔSCF calculations[1] have been performed on a model compound resembling PAA. The open-shell calculations did not converge easily, which does not seem uncommon [7, 8]. The correct combination of damping factors and canonicalisation factors had to be found in combination with large negative level shifters to ensure convergence. Moreover, in many cases different parameter settings were necessary for different atoms in the same molecule and for different basis sets.

Calculations using Koopmans' theorem

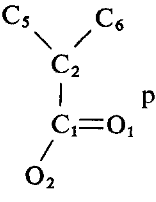
Using Koopmans' theorem we have calculated BE's for the following model compounds that stand for the denoted polymers (hydrogen atoms have been omitted from the pictures for reasons of clarity; in the following all model compounds will be named by the abbreviated polymer name).



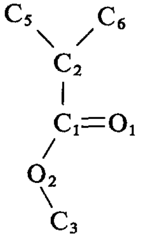
polyvinylacetate (PVAC) conformation I



polyvinylacetate (PVAC) conformation II



polyacrylic acid (PAA)



polymethylacrylate (PMA)

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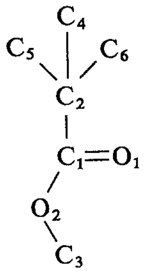
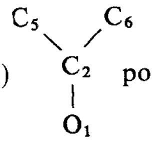
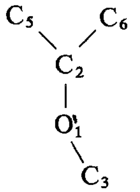
[1] In a ΔSCF calculation the BE is calculated as the difference between the total energy of the neutral molecule and the energy of the ionised species, i.e. a 1s hole-state



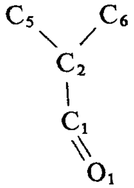
polymethylmethacrylate (PMMA)



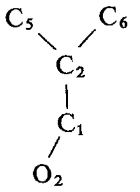
polyvinylalcohol (PVA)



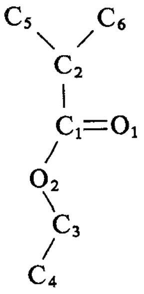
polyvinylmethylether (PVME)



polyacrolein (PAL)



polyvinylmethanol (PVM)



polyethylacrylate (PEA)

In Figs. 1 and 2 the calculated Koopmans' values for the C_{1s} and O_{1s} BE's have been depicted. The oxygen-induced primary shift of the C_{1s} levels is somewhat larger for doubly bonded than for singly bonded O-atoms, roughly 1.6 eV (compare PVAL, PVME, PAL and PVM). The shift due to two attached oxygen atoms, one doubly and one singly bonded, is close to twice as large (approx. 3.0 eV). All calculated values of the C_{1s} binding energies deviate from the experimental values to approximately the same extent. For these systems the difference between BE's of both oxygen O_{1s} levels is hardly informative; the shift is nearly constant and depends primarily on geometry [1].

In Table 1 we have collected calculated data on PMMA. The experimental data were obtained at our laboratory. In order to study the effect of truncating the main chain, data for PMMA are given for a structure in which an additional carbon-atom is attached to both the C_5 and the C_6 atoms so as to better represent the main chain (this structure will be called PMMAEXT) as well as for the structure shown above. Furthermore, calculated data are given for PMMA with strengthened convergence conditions (maximum and rms displacements less than 0.006 and 0.004 Hartree/Bohr(radian) respectively). Neither the extension of the

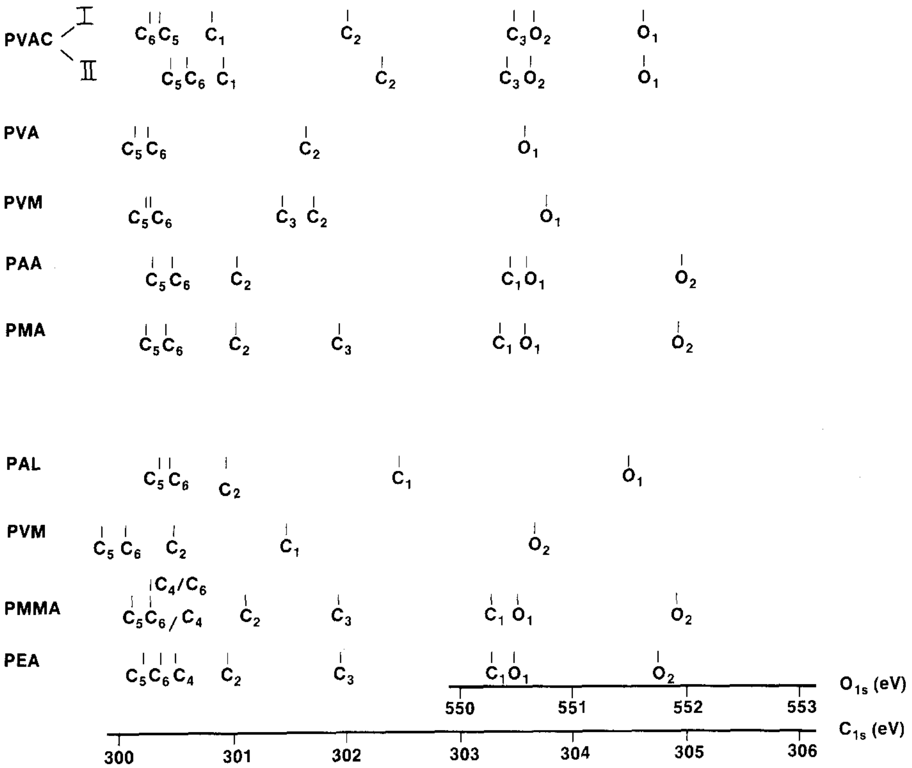


Fig. 1. Koopmans' values for the O_{1s} and C_{1s} binding energies calculated with a STO-3G basis set

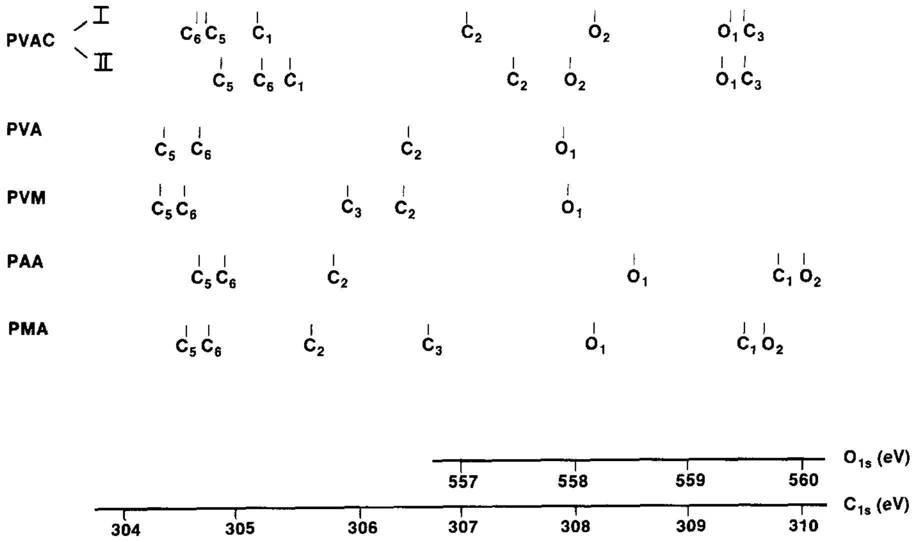


Fig. 2. Koopmans' values for the O_{1s} and C_{1s} binding energies calculated with a 4-31G basis set

Table 1. Calculated and experimental C_{1s} and O_{1s} binding energies (BE) and shifts (ΔBE) for PMMA as obtained from SCF-calculations employing the STO-3G basis set. All values are in eV. The shifts of the C_1 and C_2 atoms have been calculated relative to the average BE of the main chain C_5 and C_6 atoms. The structure of the PMMA model compound is that of a monomerunit of the true PMMA polymer including one additional carbon atom in the main chain, PMMAEXT includes two more main chain carbon atoms in order to eliminate possible end effects of terminating the chain. The experimental data were obtained at our laboratory. These differ slightly from previously published data [1] due to the fact that the present data were obtained from a large number of observations (24 in total)

Calculated total energy (Hartree)	PMMA STO-3G GRADTOL 2 −379.046102		PMMAEXT STO-3G GRADTOL 2 −456.158419		PMMAEXT STO-3G GRADTOL 3 −456.159096		Experimental —	
	BE	ΔBE	BE	ΔBE	BE	ΔBE	BE	ΔBE
O_2	551.90	1.40	551.85	1.52	551.87	1.48	533.48	1.59
O_1	550.50	0	550.33	0	550.39	0	531.89	0
C_1	303.27	3.16	303.13	3.00	303.16	3.09	288.57	3.97
C_3	301.92	1.81	301.91	1.78	301.92	1.85	286.45	1.85
C_2	301.09	0.98	301.09	0.96	301.04	0.97	285.38	0.78
C_6	300.27	0.16	300.35	0.22	300.32	0.25	284.60[a]	0
C_4	300.27	0.16	300.18	0.05	300.16	0.09	284.60[a]	0
C_5	300.11	0	300.13	0	300.07	0	284.60[a]	0

[a] The position of the C_5-peak was set equal to 284.60 eV, which is a well-known reference value [10]

chain nor the tightening of the convergence criteria gave rise to different or additional conclusions.

It can be seen from Figs. 1 and 2 that all systems that could in principle exhibit a secondary shift due to the two carboxylic oxygen atoms do so; this applies to the C_1 atom in PVAC and the C_2 atom in PAL, PAA, PVM, PMA, PMMA and PEA. The secondary shift due to a single oxygen atom is small (~0.4 eV) but will certainly influence the line-width; in particular in the solid state even with most advanced apparatus it is impossible to resolve the lines. The STO-3G (Fig. 1) and 4-31G (Fig. 2) results only differ quantitatively.

In Fig. 3 the BE's for PAA have been depicted with the side-group (COOH) rotated with respect to the main chain. The zero-degree angle of rotation is the situation for which the atoms $C_1C_2C_5O_1O_2$ lie in a plane. One set of calculations were begun in this optimised conformation. The side-group was then rotated by a fixed angle and an SCF calculation performed. The second set involved the reoptimisation of the geometry of the molecule, except for the angle of rotation of the side-group, which was kept fixed. The results show that BE's from both fixed geometry and reoptimised structures show the same trend (except for a peculiar deviation at 60°). Whereas the C_1, C_2, O_1 and O_2 BE's are essentially angle-independent, the C_5 and C_6 BE's are angle dependent. They show behaviour that could easily lead to line-broadening in the experimental spectra. Since experimental spectra of compounds like those under study here are usually studied

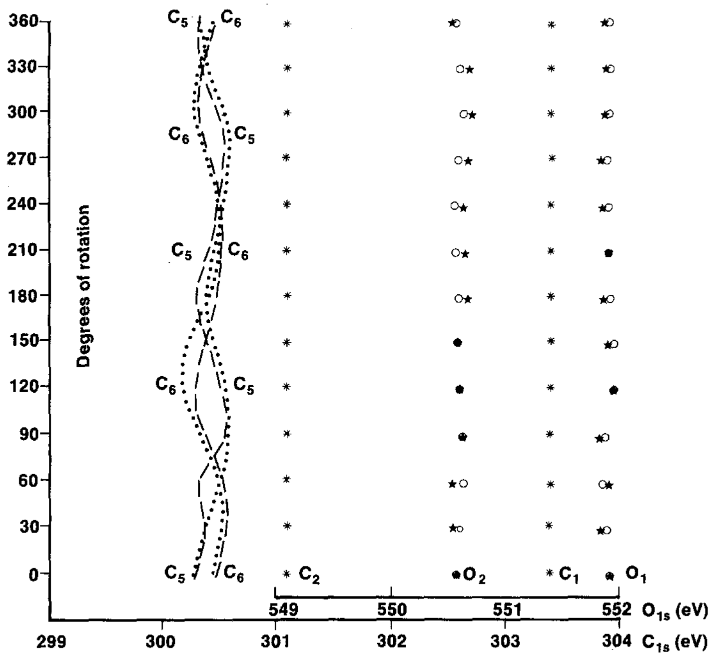


Fig. 3. Calculated Koopmans' values for the C_{1s} and O_{1s} binding energies using an STO-3G basis set for polyacrylic acid. The angle indicated along the y-axis relates to the orientation of the COOH side-group with respect to the main chain carbon skeleton. The zero-degree angle corresponds to the situation in which the atoms $C_1C_2C_5O_1O_2$ lie in a plane. The *dotted line* and the *open circles* represent data on conformations that were obtained by starting with the zero-angle optimised geometry followed by rotation of the side-group over a fixed angle. The *broken line* and *stars* for the oxygens result from calculations in which the whole geometry of the molecule was reoptimised except for the angle of rotation of the side-group with respect to the main chain

in the solid state one has to consider whether solid state interactions can compete with the energy difference between the different rotational conformers. The energy difference between the highest and lowest energy structures is 10.0 kJ/mol for the fixed geometry calculations, and 9.6 kJ/mol for the reoptimised calculations. As a consequence, it is expected that rotational conformations other than that of lowest energy one are found in the solid state leading to an apparent line-broadening or a small shift.

ΔSCF calculations

In order to improve over the Koopmans' values ΔSCF calculations of type STO-3G//STO-4G and 4-31G//STO-4G were carried out on PAA. The results are compiled in Table 2. Concerning the O_{1s}-shifts we have noted elsewhere [1] that these are primarily geometry dependent. These calculated values are comparable to the experimental values (1.6 ± 0.1 eV). For the STO-3G//STO-4G calculation the secondary shift of the C_2 atom has vanished, in contrast to all values (STO-3G up to DZP quality basis sets) obtained using Koopmans' theorem (see

Table 2. Calculated and experimental C_{1s} and O_{1s} binding energies (BE) and shifts (ΔBE) for PAA as obtained from ΔSCF-calculations. All values are in eV. The shifts of the C_1 and C_2 atoms have been calculated relative to the average BE of the main chain C_5 and C_6 atoms. The experimental data were obtained at our laboratory

Calculated total energy (Hartree)	STO-3G//STO-4G −301.910517		4-31G//STO-4G −305.406979		Experimental	
	BE	ΔBE	BE	ΔBE	BE	ΔBE
O_2	540.42	2.0	540.91	1.8	533.4	1.4
O_1	538.40	0	539.07	0	532.0	0
C_1	294.41	4.1	297.44	5.5	288.8	4.2
C_2	290.22	−0.1	292.74	0.8	285.1	0.5
C_6	290.41	0.1	292.10	0.2	284.6[a]	0
C_5	290.30	0	291.88	0	284.6[a]	0

[a] The position of the C_5-peak was set equal to 284.60 eV, which is a well-known reference value [10]

Figs. 1, 2 and [1]). However, upon employing the 4-31G basis a value close to that deduced from experiment is obtained. Overall it thus seems that ΔSCF results are, for the molecules under study here, no better than Koopmans' values. One may only suspect that, as for the Koopmans' values [1], larger basis sets (DZP and larger) do improve the agreement between theory and experiment. Presumably the neglect of electron correlation causes the poor behaviour of the ΔSCF-method here. When open-shell Møller-Plesset routines become available this might be verified.

Comparison with semi-empirical CNDO/2 calculations

In order to evaluate the possible use of a semi-empirical method we have considered the work of Clark and Thomas [5] who have performed calculations on a similar series of compounds. They employed the semi-empirical CNDO/2 method [8] in connection with the charge-potential model [9]. The CNDO/2 calculated charge distribution is inserted in an expression relating the BE of a particular atom to the atomic charge distribution in the molecule. The relation (Eq. 3 of [5]) involves the fitting of two parameters: a reference binding energy and one other constant.

Clark and Thomas rounded off their values for the BE's to the nearest 0.5 eV (see Table 5 of [5]). The large primary shift exhibited by the carboxylic oxygen atoms on the carboxylic C-atom is found to be, relative to the main chain BE, 3.4 ± 0.1 eV, which is similar as in our STO-nG calculations using Koopmans' theorem (experimental value is 4.0 eV). Peculiar features in the results are observed. An example is given by the data on poly-n-laurylacrylate and poly-octadecylacrylate. It is remarkable that in the former there is one more type of C-atom (referring to the C_{1s} BE) in the ester carbon chain than there is in the latter. This indicates that subtle effects such as the secondary substituent effect can not be obtained reliably by such a method. This is confirmed by further inspection of the results: only the main chain C-atom of PMMA (to which the side-group is attached) seems to show a shift that could be the secondary substituent effect. No such shift is apparent for PAA, PMA, PBA (poly-n-butylacrylate) and several other acrylates. This is unlikely to be due to rounding errors, but rather to a deficiency of the method in accounting for such subtle effects as the secondary shift. On the other hand even small basis set *ab initio* to use semi-empirical calculations for the geometry-optimisation, since it is much faster than an *ab initio* optimisation, then perform a single point *ab initio* calculation.

Further calculations on nitrogen and sulfur containing systems

In order to investigate the influence of nitrogen and sulfur atoms on the oxygen-induced shift of the C_{1s} binding energies the following set of model compounds was studied.

$C_2{-}C_1{-}C_3{-}C_4$	butane ($R{-}CH_3$)
$C_2{-}C_1{-}C_3{-}C_4OOH$	propanecarbonic acid ($R{-}COOH$)
$C_2{-}C_1{-}C_3{-}NH_2$	aminopropane ($R{-}NH_2$)
$C_2{-}C_1{-}C_3{-}NO_2$	nitropropane ($R{-}NO_2$)
$C_2{-}C_1{-}C_3{-}SH$	propanethiol ($R{-}SH$)
$C_2{-}C_1{-}C_3{-}SO_3H$	propanesulfonic acid ($R{-}SO_3H$)

The results of the calculations are collected in Table 3. The carboxylic group of the carbonic acid induces both primary and secondary shifts on the C_{1s} levels of

Table 3. Calculated 1s binding energies for some propane derivatives. All data are obtained by applying Koopmans' theorem on fully optimised structures employing a STO-3G basis set. The data between brackets for the nitrogen-containing systems refer to data calculated with a 4-31G basis. The starting butane conformation was trans

	$R{-}CH_3$		$R{-}COOH$		$R{-}NH_2$		$R{-}NO_2$	
C_2	300.08	0	300.46	0	300.20	0	300.89	0
					(304.45	0)	(305.32	0)
C_1	300.23	0.15	300.80	0.34	300.37	0.17	301.38	0.49
					(304.65	0.20)	(305.73	0.41)
C_3	300.24	0.14	301.16	0.70	301.10	0.90	302.78	1.89
					(305.31	0.86)	307.33	2.01
C_4	300.12	0.04	303.48	3.02	—	—	—	—
N	—	—	—	—	415.20	—	424.42	—
					(421.13)		(430.42)	

	$R{-}SH$		$R{-}SO_3H$	
C_2	300.48	0	300.47	0
C_1	300.87	0.39	300.75	0.28
C_3	301.74	1.26	301.39	0.92

both the C_4 and C_3 carbon atoms. The amine group exhibits a primary shift on the nearest neighbour carbon atom of about 0.9 eV (experimental value typically 0.6 eV [11]). The nitro group exhibits a primary shift of 1.89 eV (experimental value is 1.8 eV [11]) which is for the greater part due to the oxygen atoms (compare with the amine group). As far as the N_{1s} levels are concerned the calculated absolute BE's are usually larger than the experimental values when Koopmans' theorem is applied, but the relative values are in good agreement: calculated differences for N_{1s} Be's between amine and nitro group are 8.2 eV (STO-3G) and 9.3 eV (4–31G), whereas experimental values are in the range 6–8 eV [11]. The primary shift of the sulfon group on the C_{1s} level of the C_3 carbon is relatively small (0.92 eV; experimental value is around 0.4 eV measured in polysulphone [11]). However, the calculated induced shift of the thiol group is larger.

Thus it can be concluded, both from the calculations and from the experimental values, that the sulfur does not transfer much of the influence of attached atoms (such as the three oxygens) to the nearest neighbour carbon atom. By way of contrast for oxygens attached to a nitrogen and oxygens directly attached to the carbon chain result in a marked difference between the oxygen-containing and the oxygen-free situation with regard to the induced shifts on the C_{1s} levels.

Conclusions

The secondary shift induced by oxygen atoms has been recovered both from SCF calculations with consecutive applications of Koopmans' theorem and from ΔSCF calculations. For the molecules under study the ΔSCF method does not seem to determine shifts in binding energy of the C_{1s}-levels any better than Koopmans' theorem does. It would be interesting to see the effects of electron correlation on the results. True quantitative agreement with experiment can only be expected with large (better than DZP) basis sets and/or ΔSCF calculations incorporating electron correlation.

Conformational changes, in particular the rotation of the side-group, result in a shift of the BE's of the main chain carbon atoms. This implies that in particular amorphous polymers will show a broadening (and possibly a shift) of the main chain C_{1s} XPS lines.

Semi-empirical calculations at the CNDO/2 level show primary shifts that are not in better agreement with experiment than our STO-3G results. Secondary shifts were only found systematically with *ab initio* techniques, even when using small basis sets. Thus semi-empirical techniques are not a good alternative for the more time-consuming *ab initio* method, since extended parametrisation will weaken the power of the models involved.

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References

1. Pijpers AP, Meier RJ (1987) J Elec Spectr Rel Phen 43:131
2. Meier RJ (1987) Chem Phys Lett 138:471
3. Meier RJ (1988) J Mol Struct Theochem, in press
4. Koopmans TA (1933) Physica 1:104
5. Clark DT, Thomas HR (1978) J Pol Sci, Pol Chem Ed 16:791
6. Amos RD: The Cambridge Analytical Derivatives Package (CADPAC), CCP1/84/4, Computational Science Group, Science and Engineering Research Council, Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, UK
7. Heaton MM, El-Talbi MR (1986) J Chem Phys 85:7198
8. Pople JA, Beveridge DL (1970) Approximate molecular orbital theory. McGraw-Hill, New York
9. Siegbahn K, Nordling C, Johansson G, Hedman J, Hedén PF, Hamrin K, Gelius U, Bergmark T, Werme LO, Manne R, Baer Y (1969) ESCA applied to free molecules. North-Holland, Amsterdam
10. Wagner CD, Riggs WM, Davis LE, Moulder JF, Muilenbos GE (eds) (1979) Handbook of X-ray photoelectron spectroscopy. Perkin-Elmer, Eden-Prairie, p 17
11. Briggs D, Seah MP (1983) Practical surface analysis by Auger and X-ray photoelectron spectroscopy. Wiley, Chichester