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AN X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) STUDY OF ACTIVATED CARBONS IMPREGNATED WITH SOME ORGANOCOPPER COMPLEXES (U)

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ABSTRACT

Five organocopper complexes were impregnated on an activated carbon surface, and the surface composition of the resulting impregnated carbon investigated by X-ray photoelectron spectroscopy (XPS). From surface composition, and the high-resolution C(1s) and Cu($2p^{3/2}$) XPS spectra, the ratios of O/Cu, N/Cu, F/Cu and C/Cu could be calculated. It was found that three of the complexes were either unstable or decomposed on the carbon surface. This evidence could only be obtained by XPS technique, and the analytical method employed in this report.

RÉSUMÉ

Cinq complexes organocuivre ont été imprégnés à la surface du charbon activé, et la composition de la surface du charbon imprégné a été examinee par spectroscopie photoélectron au Rayon X (XPS). De la surface de composition, et du spectre XPS à haute résolution du Carbone (1s) et du Cu($2p^{3/2}$), le rapport de O/Cu, N/Cu, F/Cu et du C/Cu a pu être calculé. Il a été trouvé que trois de ces complexes étaient soit instables ou décomposés à la surface du charbon. Cette évidence a pu être déterminée seulement par la technique XPS et la méthode analytique employée dans ce rapport.

EXECUTIVE SUMMARY

In the search for novel chemical impregnants for activated carbon, carbon is impregnated with chemicals, and the performance of the impregnated carbon against chemical warfare agents evaluated. Without proper spectroscopic techniques, it is impossible to ascertain whether the impregnant is the active species involved in the removal of the toxic chemical warfare agents. In this report, the technique of X-ray photoelectron spectroscopy (XPS) was employed in the elucidation of the species which actually resided on the carbon surface. Five organometallic complexes containing copper were used as impregnants. For two complexes, the XPS spectra were similar for the complex and in the impregnated form. In addition, the surface composition and high-resolution XPS spectra revealed that the complex is the same in the free form and in the impregnated form. The other three complexes showed different XPS spectra for the free complex form and the impregnated form - indicating that the complex was either unstable or was decomposing on the carbon surface. This observation was again supported from surface composition and high-resolution XPS spectra. Thus XPS technique has been demonstrated as a very useful tool in the elucidation of the nature and structure of the impregnated species on the carbon surface.

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1.0 INTRODUCTION

In an earlier report (1), the preparation and characterization of a series of organometallic complexes containing transition metals were described. These transition metal complexes were being considered as chemical impregnants to be loaded onto activated carbon in the removal of toxic gases and vapors in the breathing air. In the early attempt, only copper, chromium and silver were considered as the central metal atoms because they are the three metal impregnants employed in the current adsorbent, the ASC/T carbon. The T in ASC/T stands for triethylenediamine (TEDA), a tertiary amine which not only imparts extra chemical activity in the removal of cyanogen chloride, but also prolongs the shelf-life of the carbon. Thus in the initial consideration, only transition metal complexes containing metals such as copper, chromium and silver, and a ligand such as triethylenediamine were studied. The premise is that since there exists sufficient data on the performance of the ASC/T carbon, the performance of the carbon impregnated with organometallic complexes formed between TEDA and one of these three transition metals could easily be correlated to the database on ASC/T carbon.

It was found that (1) while the preparation of the complexes containing transition metal salts and TEDA was straight forward, most of these complexes were insoluble in any solvents. This poses a problem in impregnating these complexes onto the carbon surface. The preparation of ASC/T carbon involved using an aqueous ammoniacal solution as a carrier into which all impregnants (except TEDA) were dissolved. Without a suitable carrier, and with the inherent low vapor pressure of these complexes (i.e. limiting impregnation by sublimation), it is almost impossible to impregnate these complexes onto the carbon surface. From experimental results (1), a class of complexes containing transition metal and TEDA was found, namely, the complex of the type $Cu(hfac)_2 \cdot (TEDA)$, (hfac = hexafluoroacetylacetonate, or 1,1,1,5,5,5-hexafluoropentane-2,4-dionate), which is soluble in chlorinated hydrocarbons; thus the complex could be impregnated onto the carbon surface using chloroform as a carrier. Similarly, other complexes (not containing TEDA) were also tried as chemical impregnants on the carbon surface.

In this report, five complexes, $Cu(acetate)_2 \cdot 1/2(TEDA)$, $Cu(hfac)_2 \cdot (TEDA)$, $Cu(acac)_2$, $Cu(hfac) \cdot (1,5\text{-}COD)$ and $Cu(dmg)_2$ (the abbreviation will be explained in Section 2.1.2) were impregnated on the carbon surface and the resulting surface studied by X-ray photoelectron spectroscopy (XPS).

2.0 EXPERIMENTAL

2.1 MATERIAL

2.1.1 Carbon Substrate

A BPL carbon, Lot 973-YB procured from Calgon Carbon Corporation, Pittsburgh, PA, USA was used as the base carbon. The physical properties of this carbon are summarized in Table 1.

TABLE 1

Physical Properties of Calgon ASC Feed Stock Lot No. 973-YB

BET Surface Area (N_2 at 77°K)	1165 m^2/g
Dubinin Micropore Volume (N_2 at 77°K)	0.49 mL/g
Porosimetry:	
Bulk Density	0.72 g/mL
Apparent Density	1.15 g/mL
Macropore Volume	0.31 mL/g
Mesopore Volume	0.20 mL/g
External Surface Area	127 m^2/g

2.1.2 Copper Complexes

Five organometallic complexes containing copper were studied in this report:

(i) $Cu(acetate)_2 \cdot 1/2(TEDA)$

(ii) $Cu(hfac)_2 \cdot TEDA)$

(iii) $Cu(acac)_2$ acac = acetylacetonate

(iv) $Cu(hfac) \cdot (1,5\text{-}COD)$ 1,5-COD = 1,5-cyclooctadiene

(v) $Cu(dmg)_2$ dmg = dimethylglyoxime

The synthetic routes to these complexes have been described (1), and will not be repeated here. All five complexes were synthesized at DREO using known methods.

2.2 IMPREGNATING PROCEDURES

Two impregnating procedures were employed in loading these five complexes onto the carbon surface. They are summarized below.

2.2.1 Cu(acac)$_2$, Cu(hfac)·(1,5-COD) and Cu(hfac)$_2$·(TEDA)

Typically 20.0 g of Cu(acac)$_2$ was dissolved in 400 mL of chloroform to give an opaque blue liquid with a density of 1.39 g/mL. This was added in a slow stream through Tygon tubing onto 250.5 g of BPL carbon, using part of a Rotavap apparatus as shown in Figure 1A. Time of delivery was typically 25-30 minutes and the carbon appeared wet after the addition of the solution. The condenser was then fitted back onto the Rotavap as shown in Figure 1B, and the solvent was removed at 40°C under reduced pressure. No blue residue was observed inside the round bottom flask containing the carbon, indicating the absence of impregnants on the carbon outer surface. The impregnated carbon was then placed inside a Fisher Forced Draft Oven at 65°C to dry for 16-24 hours.

2.2.2 Cu(acetate)$_2$·1/2(TEDA) and Cu(dmg)$_2$

Typically 15.68 g of Cu(acetate)·1/2(TEDA) was dissolved in a solution containing 210 mL of distilled water and 140 mL of ammonium hydroxide, giving a clear navy blue solution with a density of 0.97 g/mL. This solution was then added slowly to 250.54 g of BPL carbon using the apparatus described in a previous report (2). After the addition of the impregnating solution, the wet carbon was scooped up and spread onto a Fisher Spectra/Mesh, a macroporous filter made of fluorocarbons (mesh opening: 420 microns, % open area = 36, thickness = 525 microns) and placed inside a Fisher Forced Draft Oven. The drying of the carbon was started at 80°C for 50 minutes, then 100°C for 20 minutes, 120°C for 20 minutes, 140°C for 10 minutes, 160°C for 20 minutes and 180°C for 40 minutes. The impregnated carbon appeared black and odor-free when it was cooled.

2.3 XPS STUDIES

All XPS studies were carried out at Surface Science Western, University of Western Ontario, London, Ontario with assistance of Prof. N.S. McIntyre. X-ray photoelectron spectra were measured with an SSX-100 spectrometer (Surface Science Laboratories, Sunnyvale, CA, USA). A monochromatized Al Kα x-ray source was used to excite photoelectrons from the surface. The exiting x-rays could be focused to a diameter of less than 200 microns, so that a certain amount of localized surface information could be obtained. For all XPS spectra reported here, the spot size is 600 microns.

3.0 RESULTS AND DISCUSSION

In order to demonstrate the difference(s) observed during the transition from an organocopper complex to an impregnated species on a carbon surface, each organocopper complex will be discussed separately.

3.1 $Cu(acac)_2$

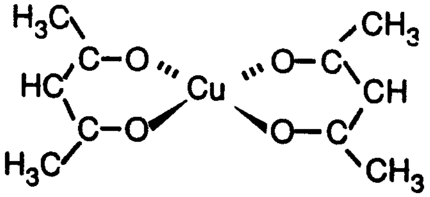
Figures 2 and 5 show the XPS spectra of $Cu(acac)_2$ as a free complex, and in the impregnated form on the carbon surface respectively. The surface compositions obtained with these two spectra at different sites are summarized in Table 2.

TABLE 2

Surface Composition (Atom %) of $Cu(acac)_2$ at Different Sites

Elements	Free Complex				Impregnant	
	Site 1	Site 2	Site 3	Site 4	Site 1	Site 2
$Cu(2p^{3/2})$	-	6.64	8.20	-	1.02	-
F(1s)	0.75	0.71	0.87	0.89	4.84	4.86
O(1s)	28.48	26.86	-	-	8.45	8.48
In(3d5)	0.16	0.15	0.18	0.18	0.07	0.07
C(1s)	63.75	64.73	79.92	80.90	84.15	84.38
Si(2p)	0.96	0.91	1.13	1.14	0.50	0.50
Cu(3p)	5.91	-	-	7.08	-	0.74
O(2s)	-	-	9.70	9.82	-	-
N(1s)	-	-	-	-	0.64	0.64
Cl(2p)	-	-	-	-	0.10	0.10
S(2p)	-	-	-	-	0.22	0.22
O/Cu	4.82	4.05	1.39	1.39	8.28	11.46
C/Cu	10.79	9.75	9.75	11.43	82.50	114.03

$Cu(acac)_2$ has the structure given as follows:



There are four oxygen and ten carbon atoms in the close vicinity of the central copper atom. Thus one would expect that the ratios of O/Cu and C/Cu would be 4 and 10 respectively. From the surface composition listed in Table 2 for the free complex, the ratios of O/Cu and C/Cu could be calculated and are shown in the bottom of table. While the values of C/Cu obtained were reasonably close to the theoretical values of 10, there were some anomalies with the O/Cu ratio. Two values were very close to the theoretical value of 4, but the values obtained for the other two sites were low (by half). Since the spot size is 600 microns, this anomaly cannot be explained by the angle of the XPS beam or the orientation of the $Cu(acac)_2$ crystal. This sample of $Cu(acac)_2$ crystals has been recrystallized and the presence of impurities can be ruled out.

For $Cu(acac)_2$ in the impregnated form, the O/Cu and C/Cu ratios were quite different from those of the free complex form. The C/Cu ratios were much higher because the copper species was residing on a carbon substrate, which increased the number of carbon atoms as immediate neighbours. The O/Cu ratios were higher also in the impregnated form than the free complex. One of the reasons for this may be due to the -OH groups already present on the carbon surface which increase the ratio of oxygen to carbon atom. Another reason is the presence of Cu_2O, a decomposition product arising from the reaction between $Cu(acac)_2$ and the carbon surface, catalysed by the functional groups on the surface, or atmospheric carbon dioxide and moisture. The explanation for this is given in the next paragraph when the high-resolution C(1s) spectra are presented.

The high resolution $Cu(2p^{3/2})$ XPS spectra of $Cu(acac)_2$ in the free and the impregnated form are shown in Figures 3 and 6 respectively. The sharp peak at the binding energy of 934 eV in Figure 3 characterizes the presence of Cu(II) species. However the same peak for the impregnated species was broad, and on expansion, as shown in Figure 6, can be deconvoluted into two species: Cu(I) and Cu(II) species. From surface composition analysis, there was actually a higher concentration of Cu(I) than Cu(II), the original impregnant. It has been mentioned in an earlier report (2) that fresh Whetlerite (a carbon which has been impregnated with an ammoniacal solution containing CrO_3, $(NH_4)_2CO_3$ and $CuCO_3 \cdot Cu(OH)_2$))

contained on the surface, a certain amount of crystallites of cuprous oxide in the size range of 5-20 nm. While the mechanism for this reaction, i.e. $Cu(acac)_2 \rightarrow Cu_2O$ is not immediately obvious, the presence of Cu(I) species definitely indicated some decomposition (and reduction) on the carbon surface.

The high resolution C(1s) XPS spectra of $Cu(acac)_2$ in the free complex and impregnated form on the carbon surface are shown in Figures 4 and 7. The assignment of the de-convoluted peaks between binding energies of 275 and 295 eV is given in Table 3.

TABLE 3

High Resolution C(1s) Peak Assignment of $Cu(acac)_2$

Free Complex			Impregnant		
Binding Energy (eV)	Area %	Assignment	Binding Energy (eV)	Area (%)	Assignment
283.24	7.9	?			
285.03	68.0	C-H carbon	284.37	57.1	Amorphous & sp^2 C
286.13	9.9	$^-O_2C-C^*H_2-CO$	285.64	28.0	$^-O_2C-C^*H_2-CO$
287.62	8.8	C=O or C-OH carbon	288.36	11.8	C=O carbon
289.08	5.4	C=O carbon	290.03	3.1	C=O carbon

It should be noted that organometallic complexes in general do not have a simple bonding arrangement, frequently they exist as coordination complexes which do not have distinct covalent or ionic bonding, but rather delocalized bonding. As a result, it is not simple to assign the C(1s) spectra, since it is not certain what chemical shifts the central metal atom will impose on the organic portion of the complex. This is further complicated by the fact that several of the complexes, such as Cu(hfac)·(1,5-COD) have two organic components. In the case of carbon impregnated with these organometallic complexes, the assignment is further complicated because the XPS spectrum obtained is a convolution of the spectrum from the untreated carbon itself and the organometallic complex.

For the $Cu(acac)_2$ complex, the peaks in the C(1s) XPS spectrum were what one would expect. For the impregnated form, the biggest peak belonged to amorphous carbon (i.e. the carbon substrate) at binding energy of 284.37 eV. The contributions from $^{-}$COO-C*H$_{2}$-CO at 285.64 eV and C=O at 288.36 eV become negligible compared to this peak.

3.2 Cu(acetate)2·1/2(TEDA)

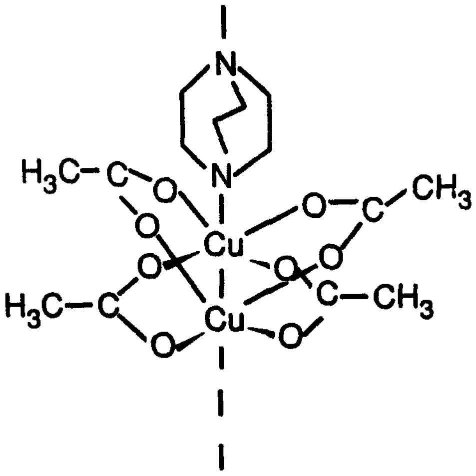
Figures 8 and 11 show the XPS spectra of Cu(acetate)$_2$·1/2(TEDA) as a complex, and as a chemical impregnant on the carbon surface respectively. The surface compositions obtained with these two spectra are summarized in Table 4.

TABLE 4

Surface Composition (Atom %) of Cu(acetate)$_2$·1/2(TEDA) at Three Different Sites

Elements	Free Complex			Impregnant		
	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
Cu($2p^{3/2}$)	7.13	-	-	0.92	-	-
F(1s)	2.84	2.88	3.32	7.49	7.49	7.97
O(1s)	27.39	27.73	-	7.23	7.24	-
In(3d5)	0.17	0.18	0.20	0.08	0.08	0.09
N(1s)	7.01	7.10	8.21	0.81	0.81	0.86
C(1s)	55.44	56.12	64.86	82.57	82.66	87.93
Na(1s)	-	-	-	0.10	0.10	0.10
Cu(3p)	-	6.00	6.93	-	0.81	0.86
O(2s)	-	-	16.48	-	-	1.32
S(2p)	-	-	-	0.32	0.32	0.34
Si(2p)	-	-	-	0.49	0.48	0.52
O/Cu	3.84	4.62	2.38	7.86	8.94	1.53
N/Cu	0.98	1.18	1.20	0.88	1.00	1.00
C/Cu	7.78	9.35	9.50	89.75	102.05	102.24

From this composition, the ratio of the atoms on the surface can be calculated. This yields, as shown in the bottom of Table 4, for the free complex a range of 2.38 to 4.62 for O/Cu, and 0.98 to 1.20 for N/Cu, and 7.78 to 9.50 for C/Cu, which is consistent with the structure of Cu(acetate)$_2$·1/2(TEDA) given as follows:



In this structure, there are four oxygen atoms, one nitrogen atom and up to ten carbon atoms (two carbons on each acetate ligand and six on the TEDA molecule) as closest neighbours.

For the impregnants, the range of these ratios varied: e.g. from 1.53 to 8.94 for O/Cu, 0.88 to 1.00 for N/Cu and 89.75 to 102.24 for C/Cu. The values of these ratios showed that:

(i) there was one nitrogen atom per copper atom, indicating that the TEDA molecule was still attached to the central copper atom;

(ii) the C/Cu ratios are large numbers because the impregnant is now residing on a carbon substrate with many carbon atom as close neighbours; and

(iii) the O/Cu ratio seemed to vary, however, given the presence of -OH groups and water on the carbon surface, this ratio seemed to fit the impregnated form on the carbon surface.

The high resolution copper, Cu($2p^{3/2}$) XPS spectra for Cu(acetate)$_2$·1/2(TEDA) as a complex, and in the impregnated form are shown in Figures 9 and 12 respectively. Both spectra showed a sharp peak at binding energy of 934 eV, indicating a Cu(II) species. The shake-up due to the paramagnetic species at about 945 eV is characteristic of the presence of copper.

The high resolution carbon C(1s) XPS spectra for the free complex and the impregnated form are shown in Figures 10 and 13. The assignment of the de-convoluted peaks between 283 and 291 eV for these two species is summarized in Table 5.

TABLE 5

High Resolution C(1s) Peak Assignment of Cu(acetate)$_2$·1/2(TEDA)

Free Complex			Impregnant		
Binding Energy (eV)	Area %	Assignment	Binding Energy (eV)	Area (%)	Assignment
284.40	7.7	CH_2=CH_2 carbon	284.22	62.8	amorphous & sp^2
285.25	56.7	C-H carbon	285.28	21.8	C-H carbon
286.44	18.6	C-N carbon	286.72	6.7	C-N carbon
288.99	17.1	carboxylate C	288.49	5.1	carboxylate C
			290.61	3.5	C=O carbon

For the Cu(acetate)$_2$·1/2(TEDA), the assignments of the peaks were very close to the literature values (3). From the impregnated form, the peak at 284.22 eV (amorphous sp^2 carbon) tended to obscure the rest of the convoluted spectra. This may be due to inherent weak signal arising from the impregnated organometallic complex, or the nonuniform distribution of the complex on the carbon surface.

3.3 Cu(hfac)$_2$·(TEDA)

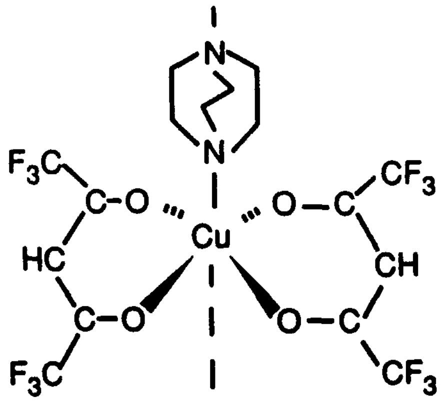
Figures 14 and 17 show the XPS spectra of Cu(hfac)$_2$·(TEDA) as a free complex, and as an impregnant on the carbon surface respectively. The surface compositions obtained with these two spectra are summarized in Table 6.

TABLE 6

Surface Composition (Atom %) of $Cu(hfac)_2 \cdot (TEDA)$ at Different Sites

Elements	Free Complex			Impregnant	
	Site 1	Site 2	Site 3	Site 1	Site 2
$Cu(2p^{3/2})$	-	2.94	-	1.37	-
F(1s)	30.09	29.81	31.97	10.31	10.28
O(1s)	12.59	13.57	-	6.90	6.77
In(3d5)	0.31	0.29	0.31	0.07	0.07
N(1s)	3.59	3.44	3.69	0.61	0.61
C(1s)	49.54	48.47	51.97	79.80	79.61
Na(1s)	0.37	0.57	0.01	-	-
Cu(3p)	2.56	-	2.63	-	1.73
O(2s)	-	-	7.84	-	-
S(2p)	-	-	-	0.16	0.16
Si(2p)	0.32	0.30	0.33	0.77	0.77
Cl(2p)	0.63	0.61	0.65	-	-
O/Cu	4.92	4.62	2.98	5.04	3.91
N/Cu	1.40	1.17	1.40	0.45	0.35
C/Cu	19.35	16.49	19.76	58.25	46.02
F/Cu	11.75	10.14	12.16	7.53	5.94

The ratios O/Cu, N/Cu and C/Cu calculated from this surface composition are listed in the bottom of Table 4. As a free complex, $Cu(hfac)_2 \cdot (TEDA)$ has a structure given below:



It should be observed that the ratios obtained were consistent with the structure above. There are four adjacent oxygen atoms (on the acetylacetone framework), one to two nitrogen atoms, sixteen carbon atoms (as shown in th structure) and twelve fluorine atoms neighbouring very close to the central copper atom. Depending on the angle of the XPS beam, all the carbons on the hexafluoroacetylacetonate, and the three carbon atoms bonded to the nitrogen on the TEDA molecule can all be observed, i.e. 16 to 22 carbon atoms.

For the impregnated species, although the O/Cu ratio (approximately 4) was similar to the ratio obtained for the free complex, the rest of the calculated ratios were significantly different. Both the N/Cu and F/Cu ratios had decreased in value. However, if there were still four oxygen atoms surrounding the copper atom, this may imply that the hexafluoroacetylacetonato ligands were still intact. The carbon surface was opaque (i.e. absorbing infrared radiation), otherwise Fourier Transform Infrared (FTIR) spectroscopy would be the best candidate to determine if the complex is still intact in the impregnant form by looking at the Cu-N bonding.

The high resolution Cu($2p^{3/2}$) XPS spectra for Cu(hfac)$_2$·(TEDA) as free complex, and in the impregnant form are shown in Figures 15 and 18 respectively. Both spectra showed a sharp peak at binding energy of 934 eV, indicating the presence of Cu(II) species only.

The high resolution C(1s) XPS spectra for the free form and impregnated form of Cu(hfac)$_2$·(TEDA) are shown in Figures 16 and 19. The assignment of the deconvoluted C(1s) spectra is summarized in Table 7.

TABLE 7

High Resolution C(1s) Peak Assignment of Cu(hfac)$_2$·(TEDA)

Free Complex			Impregnant		
Binding Energy (eV)	Area %	Assignment	Binding Energy (eV)	Area (%)	Assignment
			284.28	65.4	Amorphous & sp^2 carbon
284.99	69.2	C-H carbon	285.45	21.6	C-H carbon
286.66	19.4	$^-O_2CC^*H_2CO$ carbon	286.86	8.0	$^-O_2CC^*H_2CO$ carbon
288.49	11.4	C=O	288.68	4.9	C=O carbon
293	Note 1	CF_3			

Note 1: Not measured.

The C(1s) spectrum of Cu(hfac)$_2$·(TEDA) was what one would expect. The peak at bonding energy of 293 eV was not "peaked-fit" in the original spectrum. This peak indicated the presence of $-CF_3$ group. It was at high bonding energy and was missed in the original observation. The peak at 286.66 eV may also include the contribution of C-N carbons. For the complex in the impregnated form, the C(1s) spectrum was quite similar, except:

(i) the huge peak corresponded to amorphous sp^2 graphitized carbon at 284.28 eV, arising from the carbon substrate; and

(ii) the absence of the CF_3 peak at 293 eV.

The second point was puzzling, however it was attributed to artifacts in the spectrum because the presence of fluorine was ascertained in the original XPS spectrum shown in Figure 17.

3.4 Cu(hfac)·(1,5-COD)

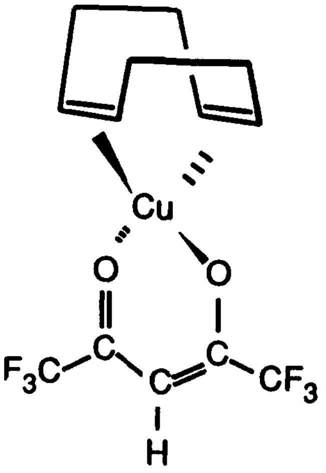
The XPS spectra of Cu(hfac)·(1,5-COD) in the free and impregnated form (on carbon) are shown in Figures 20 and 23. The surface compositions in these two spectra are summarized in Table 8.

TABLE 8

Surface Composition (Atom %) of Cu(hfac)·(1,5-COD) at Different Sites

Elements	Free Complex		Impregnant		
	Site 1	Site 2	Site 1	Site 2	Site 3
Cu($2p^{3/2}$)	8.31	-	-	20.58	-
F(1s)	32.14	31.52	6.42	5.95	6.78
O(1s)	19.11	18.74	24.90	24.23	-
C(1s)	40.04	39.28	47.80	48.49	55.19
Cl(2p)	-	-	0.65	0.75	0.86
Cu(3p)	-	10.10	20.23	-	13.30
O(2s)	-	-	-	-	13.30
In(3d5)	0.39	0.39	-	-	-
O/Cu	2.30	1.86	1.23	1.18	1.00
C/Cu	4.82	3.89	2.36	2.36	4.15
F/Cu	3.87	3.12	0.32	0.29	0.51

The ratios of O/Cu, C/Cu and F/Cu calculated from these compositions are shown in the bottom of Table 8. The complex Cu(hfac)·(1,5-COD) has the following structure:



In this structure, the central copper atom has for neighbours, two oxygen atoms, six fluorine atoms and four immediate carbon atoms (i.e. the four carbons on the 1,5-cyclooctadiene molecule which are donating electrons to the copper; those carbons on the hexafluoroacetylacetonato ligand are separated by one oxygen atom and not the closest neighbours). Thus the theoretical ratios of O/Cu, C/Cu and F/Cu would be 2, 4 and 6 respectively. While the calculated O/Cu ratio was close enough to the theoretical values, the calculated C/Cu and F/Cu ratio were much lower than the theoretical value. Previous experience in this laboratory (1) has indicated that Cu(hfac)·(1,5-COD) decomposes after exposure to atmosphere in 2 days. This may explain why these ratios (calculated and theoretical) were different because the complex was decomposing.

For the impregnated form, the calculated ratios of O/Cu, C/Cu and F/Cu were more different from the theoretical values, and also quite different from the calculated ratios of the free complex form. As explained in the last paragraph, this discrepancy most likely arises from the complex Cu(hfac)·(1,5-COD) decomposing on the carbon surface.

The high-resolution $Cu(2p^{3/2})$ XPS spectra of Cu(hfac)·(1,5-COD) as a free complex and in the impregnated form are shown in Figures 21 and 24 respectively. The copper peaks in these spectra were broader, compared to other high-resolution Cu XPS spectra presented earlier. Although the copper peak was not de-convoluted, one can observe a major peak at about 932-933 eV, and a shoulder at about 934-935 eV, indicating the presence of both Cu(I) and Cu(II) species (as in $Cu(acac)_2$ case).

The high resolution C(1s) XPS spectra of Cu(hfac)·(1,5-COD) in the complex and the impregnated form are shown in Figures 22 and 25 respectively. The assignment of the deconvoluted peaks in these spectra are given in Table 9.

Although it has been suggested in the earlier paragraphs that the Cu(hfac)·(1,5-COD) is unstable, and that the impregnated form may be decomposing very rapidly on the carbon surface the C(1s) XPS spectra for both complex and the impregnated form were remarkably similar. The C(1s) spectrum of the free complex was what one would expect, except for the absence of the peak corresponding to C=C signal at around 284.3 eV. This peak may be observed by the C-H peak at 284.92 eV. At 293 eV, the peak corresponding to CF_3 was observed. The huge peak corresponding to amorphous sp_2 carbon (at 284.31 eV) dominated the C(1s) spectrum for the impregnated species. The sp^2 carbons in 1,5-cyclooctadiene should appear at around 284 eV, but obviously it is obscured by the peak from the carbon substrate. The lack of substantial C-H (hydrocarbon) contribution to the spectrum of the impregnated carbon (at ca. 285 eV) supported the idea that the complex was not well distributed in the area of analysis.

TABLE 9

High Resolution C(1s) Peak Assignment of Cu(hfac)·(1,5-COD)

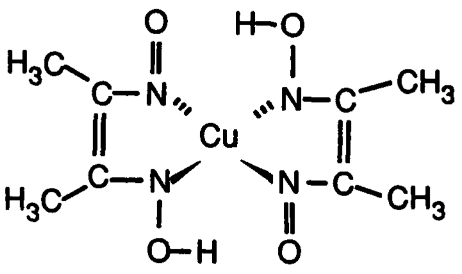
Free Complex			Impregnant		
Binding Energy (eV)	Area %	Assignment	Binding Energy (eV)	Area (%)	Assignment
			284.31	68.3	amorphous & sp^2 C
284.92	74.6	C-H' carbon	285.32	22.8	C-H carbon
286.57	13.9	$O_2C-C^*H_2CO$ carbon	286.88	5.0	$^-O_2C-C^*H_2-CO$ carbon
288.48	11.5	C=O carbon	288.87	3.9	C=O carbon
293	Note 1	CF_3 carbon			

Note 1: Not measured.

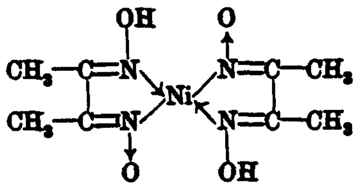
3.5 Cu(dmg)$_2$

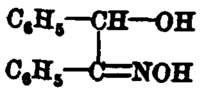
Figures 26 and 29 show the XPS spectra of Cu(dmg)$_2$ as a complex and in the impregnated form respectively. While there is always a shift in the baseline for XPS spectrum at high binding energies, the spectrum for Cu(dmg)$_2$ complex showed very strong shifts and also some unknown peaks, which have never been observed before. The surface composition obtained from these two spectra are summarized in Table 10.

The ratios of C/Cu, N/Cu and O/Cu can then be calculated, and the computed values are given in the bottom of Table 10. The structure of Cu(dmg)$_2$ is given below:



Thus, there are four nitrogen atoms, four oxygen atoms and eight carbon atoms as the closest neighbours. This gives rise to theoretical N/Cu, O/Cu and C/Cu as 4, 4 and 8 respectively. However, this is only the case for the calculated ratios as shown in the bottom of Table 10 for both the free complex and the impregnated form. While it is well known that Ni(dmg)$_2$ and cupron complex of copper with structures of:





cupron

are stable species (4), it is not certain that Cu(dmg)$_2$ is stable. If that is the case, then it will explain why the calculated ratios of the free complex and the impregnated form are so different from the theoretical ones.

TABLE 10

Surface Composition (Atom %) of Cu(dmg)$_2$ at Different Sites

Elements	Free Complex	Impregnant Form	
		Site 1	Site 2
Cu(2p$^{3/2}$)	12.41	1.20	-
O(1s)	7.33	7.85	7.86
N(1s)	15.67	1.51	1.51
C(1s)	64.58	83.74	83.87
F(1s)	-	5.14	5.15
In(3d5)	-	0.06	0.06
Cl(2p)	-	0.12	0.12
Cu(3p)	-	-	1.05
S(2p)	-	0.23	0.23
Si(2p)	-	0.17	0.17
C/Cu	5.20	69.78	79.88
N/Cu	1.26	1.26	1.44
O/Cu	0.59	6.54	7.49

The high-resolution Cu(1s) XPS spectra of $Cu(dmg)_2$ in the free complex and impregnated form are shown in Figures 27 and 30. Both peaks are broad, and for the copper peak in Figure 27 (free complex), there is evidence for presence of impurities at the high energy side of the peak, at around 936-938 eV. These impurity peaks were not as pronounced in the impregnated form (Figure 30). It is obvious that some decomposition has taken place.

The high-resolution C(1s) XPS spectra of $Cu(dmg)_2$ in the free complex and impregnated form are shown in Figures 28 and 31. The assignment of the de-convoluted peaks in these spectra are given in Table 11.

TABLE 11

High-Resolution C(1s) Peak Assignment of $Cu(dmg)_2$

Free Complex			Impregnant		
Binding Energy (eV)	Area %	Assignment	Binding Energy (eV)	Area (%)	Assignment
282.74	9.6	?			
283.38	4.2	?	284.34	63.4	amorphous & sp^2 C
285.20	78.0	CH carbon	285.50	21.0	C-H carbon
286.43	8.2	C-NOH carbon			
			287.38	7.8	?
			289.23	3.0	?
			290.72	4.8	?

The assignment of the peaks in the C(1s) spectrum for the free complex was difficult. At bonding energies of 282.74 and 283.38 eV, the only possible species were carbide species, which was impossible in the present context. The other possibility was that the C(1s) spectrum was undergoing some differential charging and these two peaks were artifacts.

The binding energies of all the peaks appearing in both spectra were quite different, indicating significant transitions from the complex to the impregnated form. Furthermore, with the suspicion that the complex $Cu(dmg)_2$ may be decomposing, thus the high resolution C(1s) peak may look different.

4.0 CONCLUSIONS AND RECOMMENDATIONS

(a) It is apparent that three complexes $Cu(acac)_2$, $Cu(hfac)\cdot(1,5\text{-}COD)$ and $Cu(dmg)_2$ are not stable by themselves or when impregnated on the activated carbon surface.

(b) X-ray photoelectron spectroscopy (XPS) is a powerful spectroscopic technique in the investigation of carbon surface, and in the observation of changes which occur to chemicals upon impregnation on the carbon surface.

(c) In the investigation of a novel impregnant, it is important to determine the active impregnated species on the carbon surface, instead of simply evaluating the performance of the impregnated carbon against chemical warfare agents. Using a hypothetical case: activated carbon impregnated with $Cu(acac)_2$ may be very effective in removing some toxic chemicals in air, however, $Cu(acac)_2$ itself may not be the active species involved, because it has been shown in this report that $Cu(acac)_2$ is not the impregnated species observed by XPS. Thus the chemical activity (in removing toxic chemicals) most likely arises from the decomposed product(s) of $Cu(acac)_2$.

(d) As a continuation of (c), after the determination of the active species on the impregnated carbon, the mechanism of the toxic chemical removal could then be elucidated. This would then lead to improvement of the impregnated carbon, or a more cost-effective way to produce the carbon.

(e) Another corollary arising from (c) is that if it is determined from XPS that the chemical impregnant decomposed on the carbon surface, then product improvement projects could be initiated to improve the impregnating procedure so that the decomposition process can be inhibited or slowed down.

5.0 REFERENCES

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3. J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Data for Use in X-ray Photoelectron Spectroscopy, published by Perkin-Elmer Corporation, Minn, USA (1992); D. Briggs and M.P. Seah, Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, J. Wiley and Sons, NY (1983).

4. A.I. Vogel, A Textbook of Quantitative Inorganic Analysis, 2nd Edition, Longmans, UK (1960).

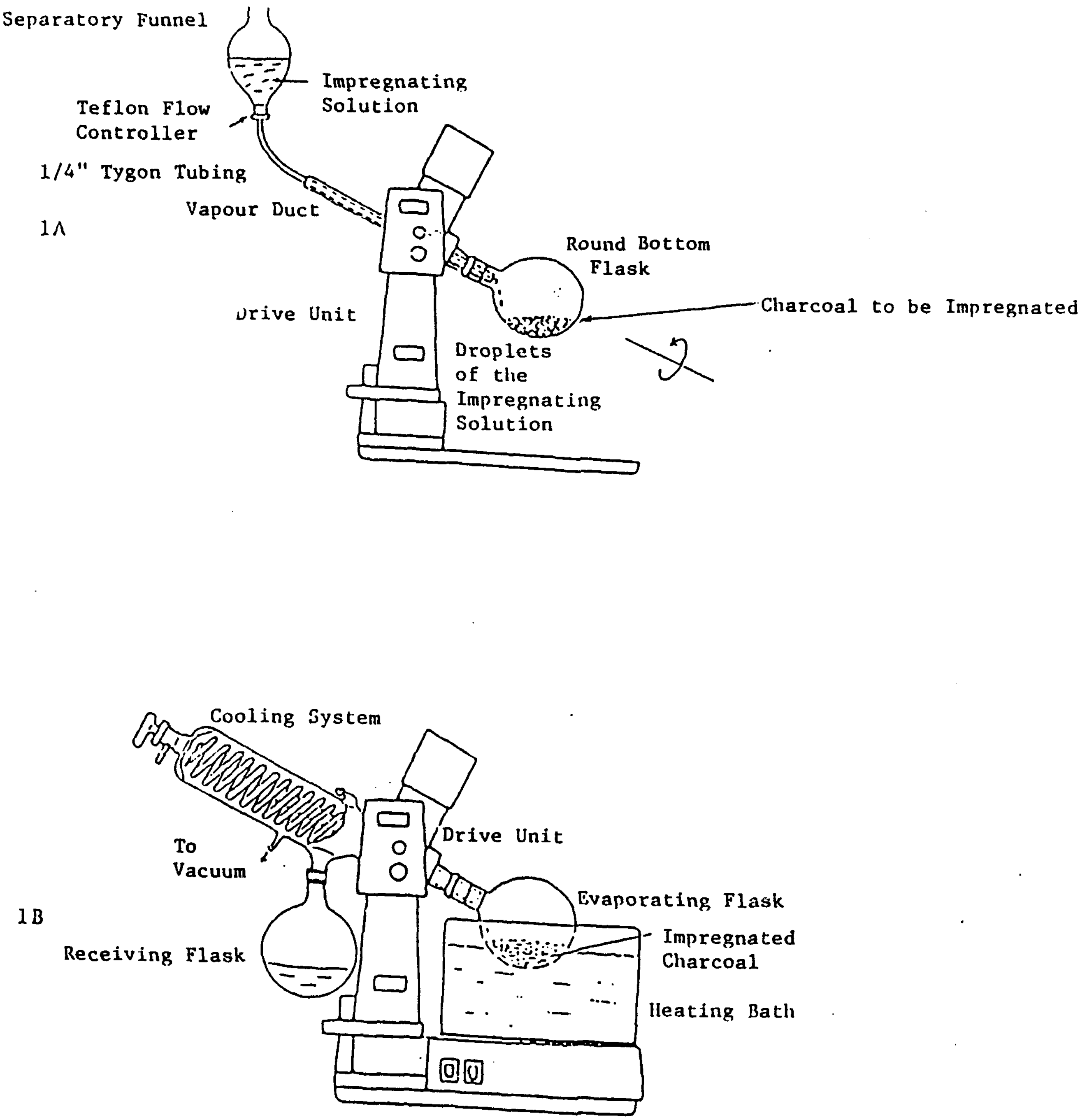


Figure 1: Set-up of a Special Impregnation Apparatus.

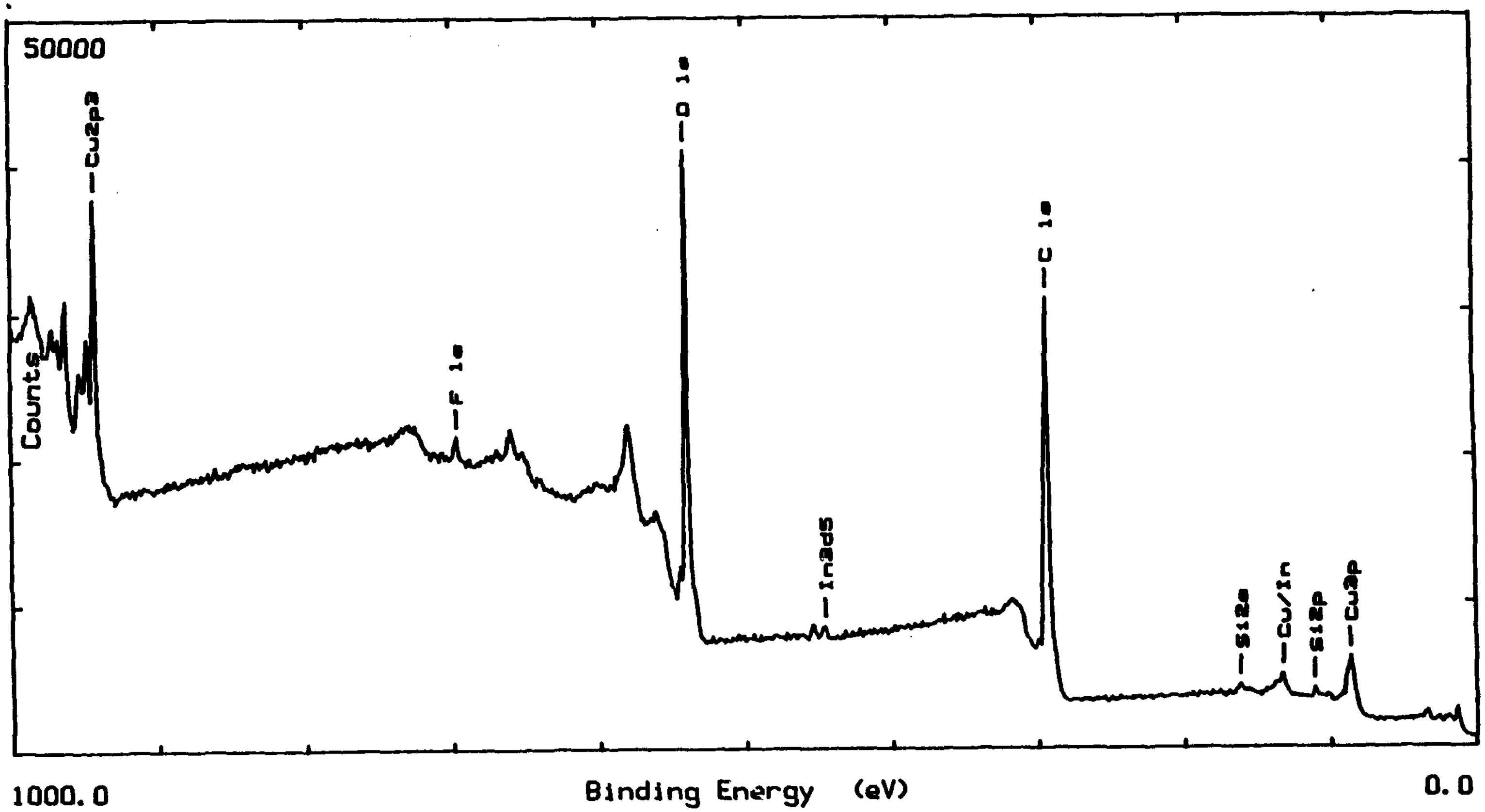


Figure 2: XPS Spectrum of Cu(acac)$_2$.

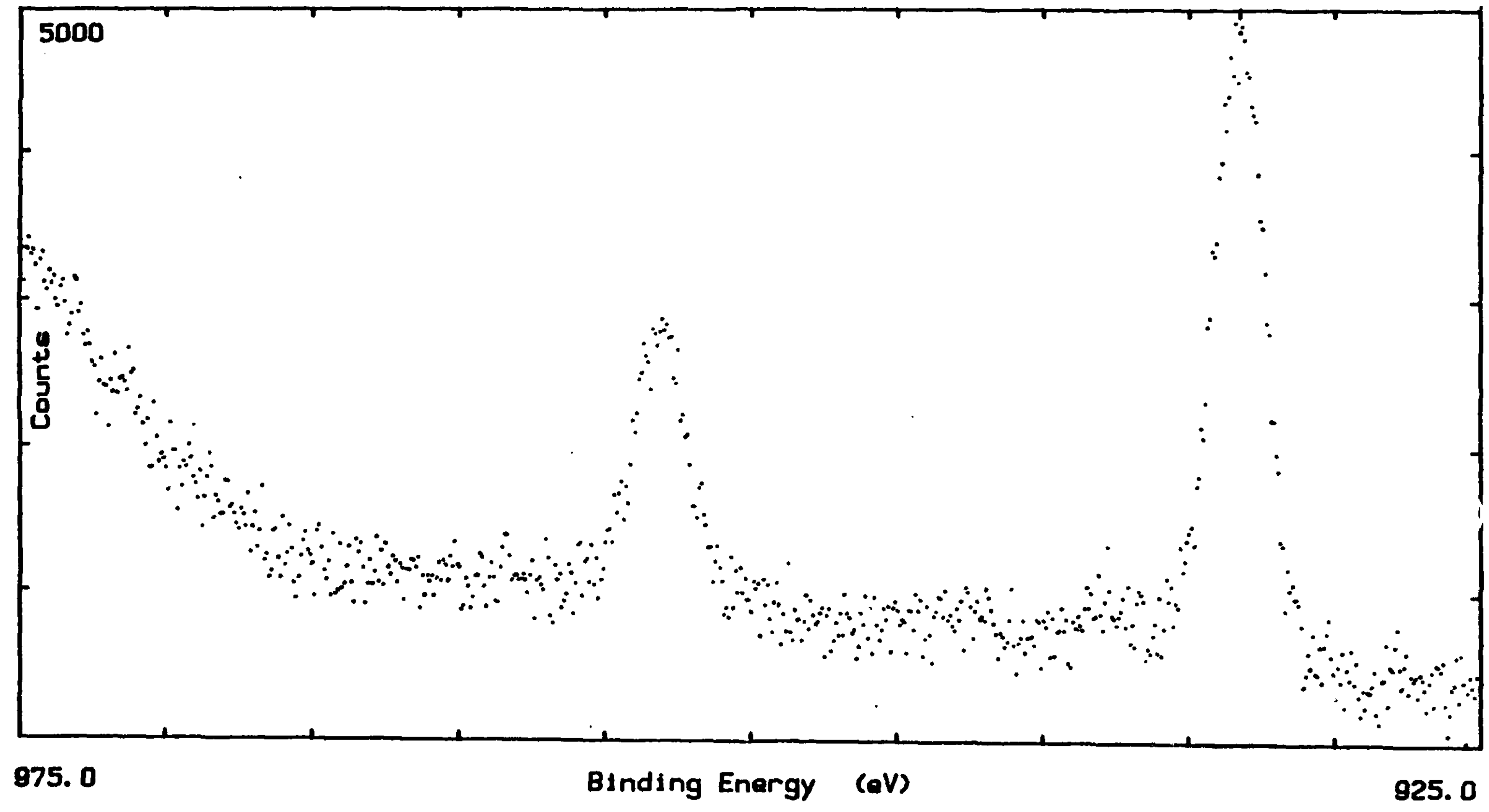


Figure 3: High Resolution Cu($2p^{3/2}$) XPS Spectrum ofCu(acac)$_2$.

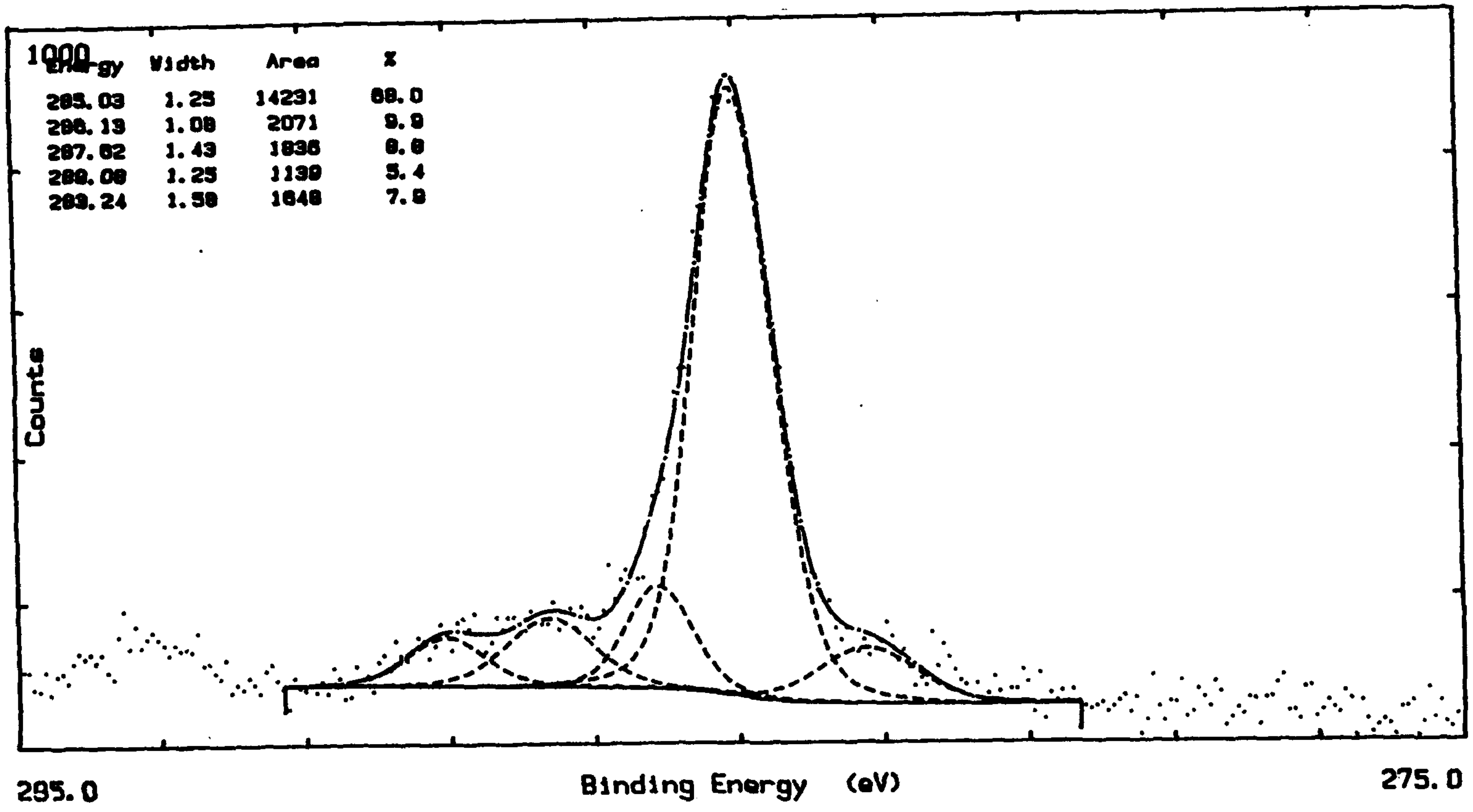


Figure 4: High Resolution C(1s) XPS Spectrum ofCu(acac)$_2$.

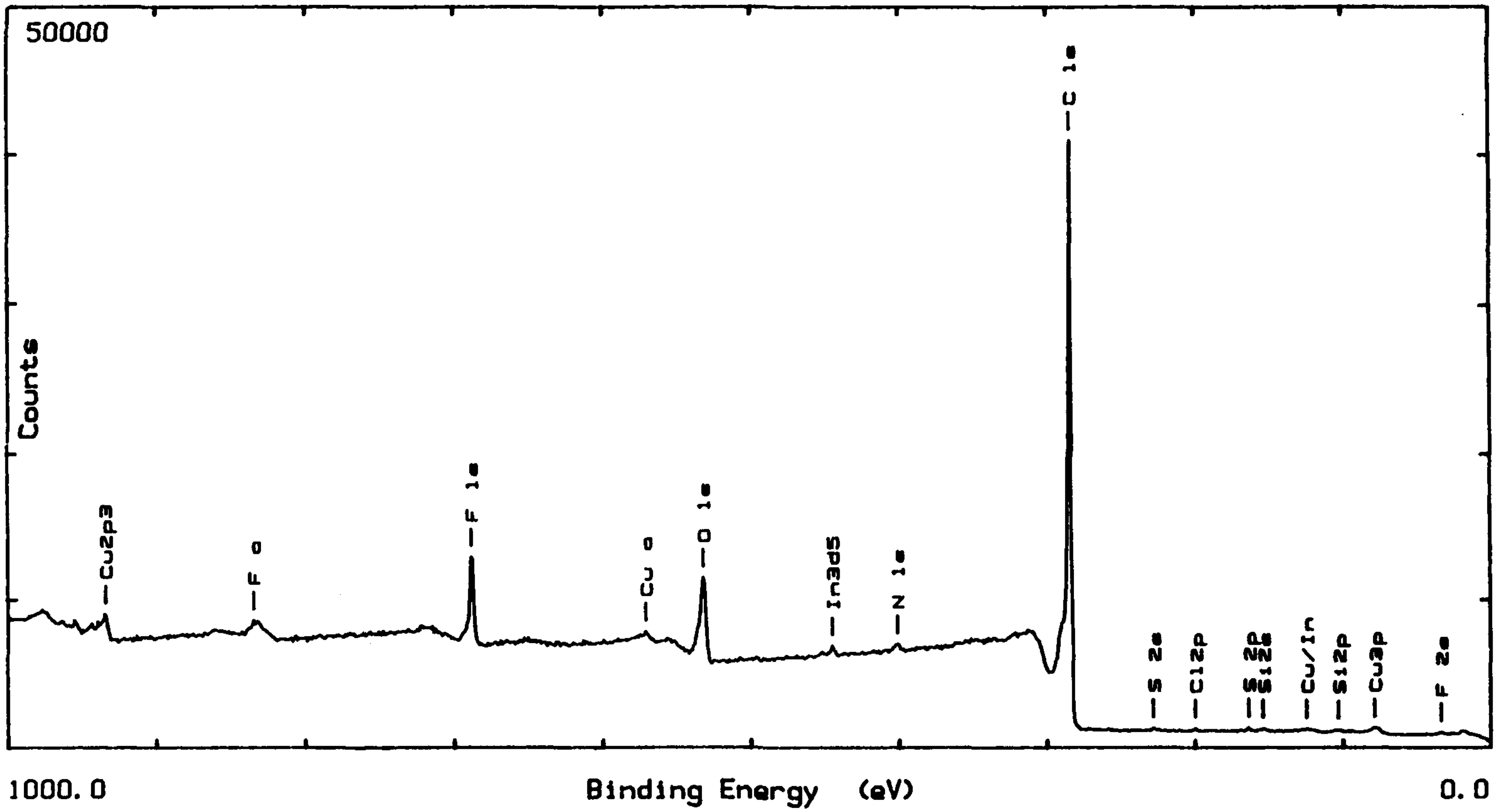


Figure 5: XPS Spectrum of $Cu(acac)_2$ Impregnated on BPL Carbon.

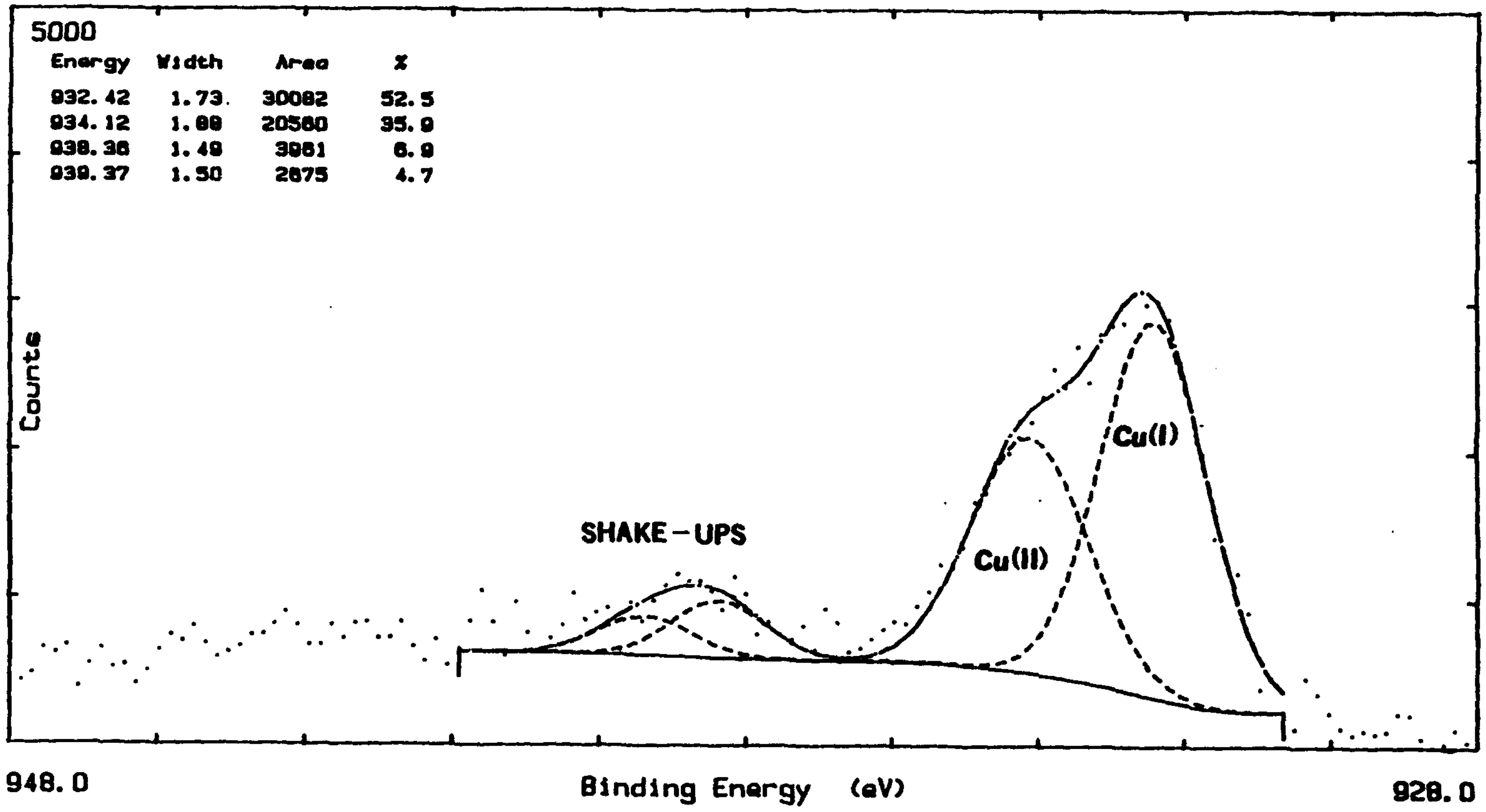


Figure 6: High Resolution Cu($2p^{3/2}$) XPS Spectrum of Cu(acac)$_2$ Impregnated on BPL Carbon.

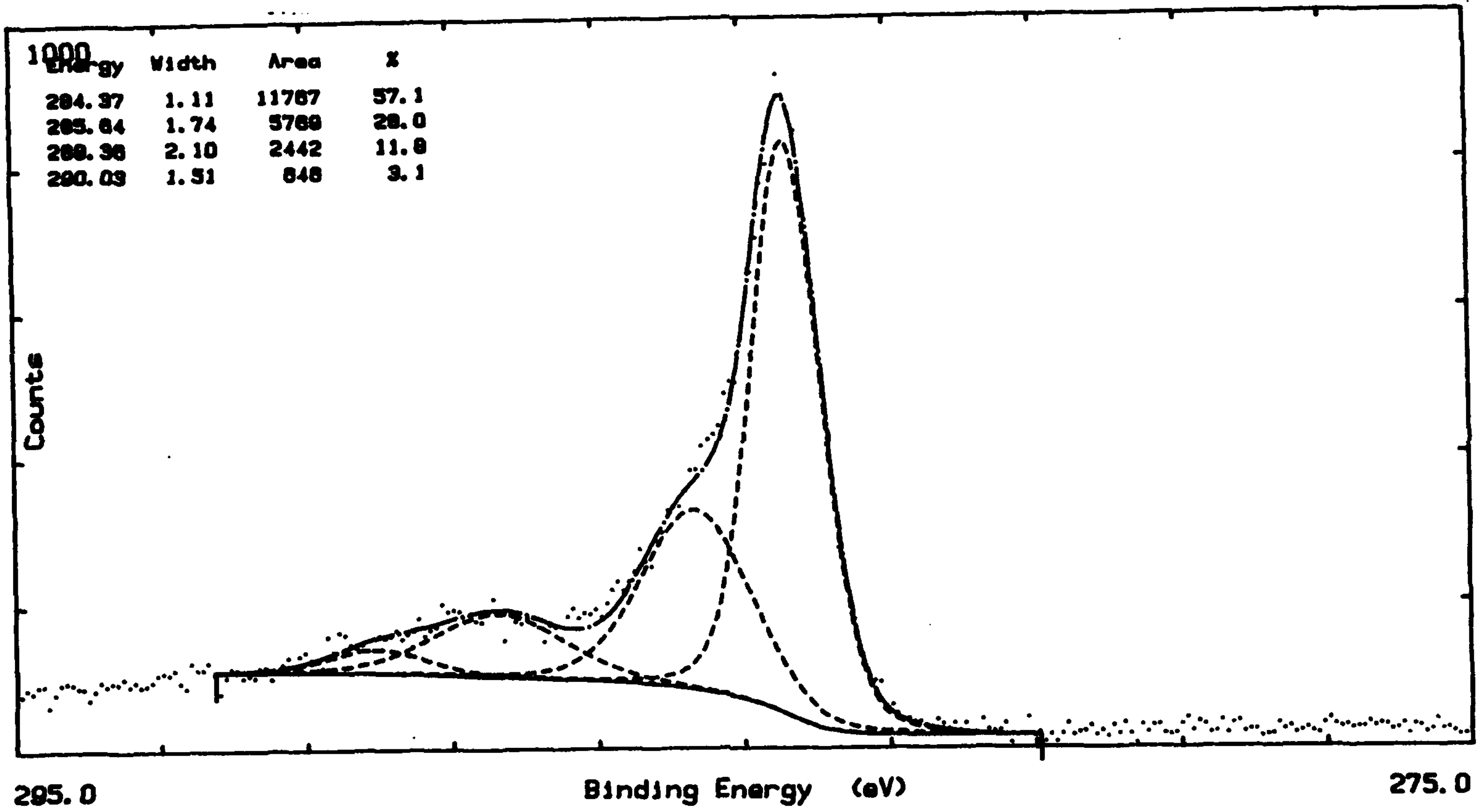


Figure 7: High Resolution C(1s) Spectrum of $Cu(acac)_2$ Impregnated on BPL Carbon.

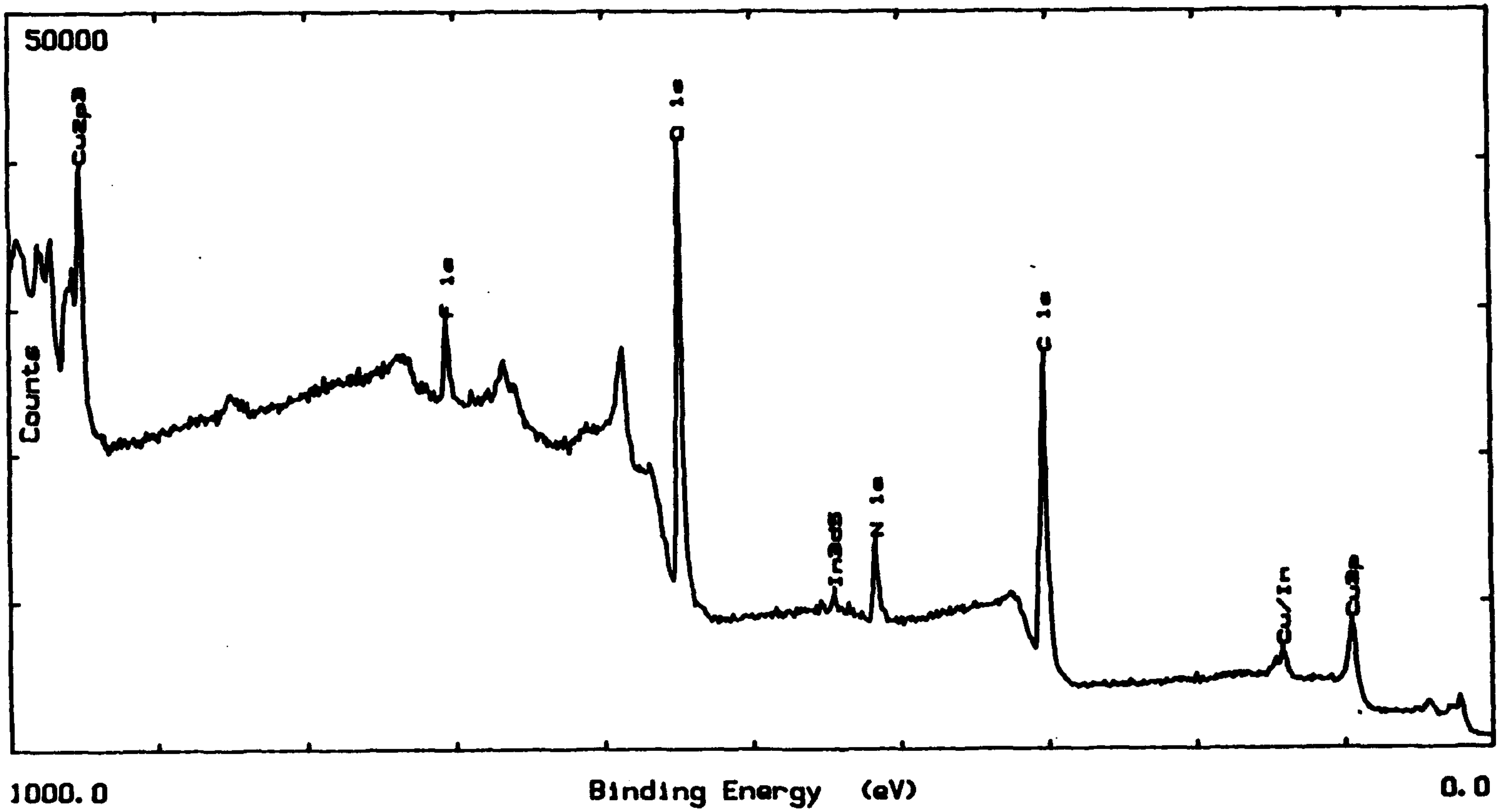


Figure 8: XPS Spectrum of Cu(acetate)$_2$·1/2(TEDA).

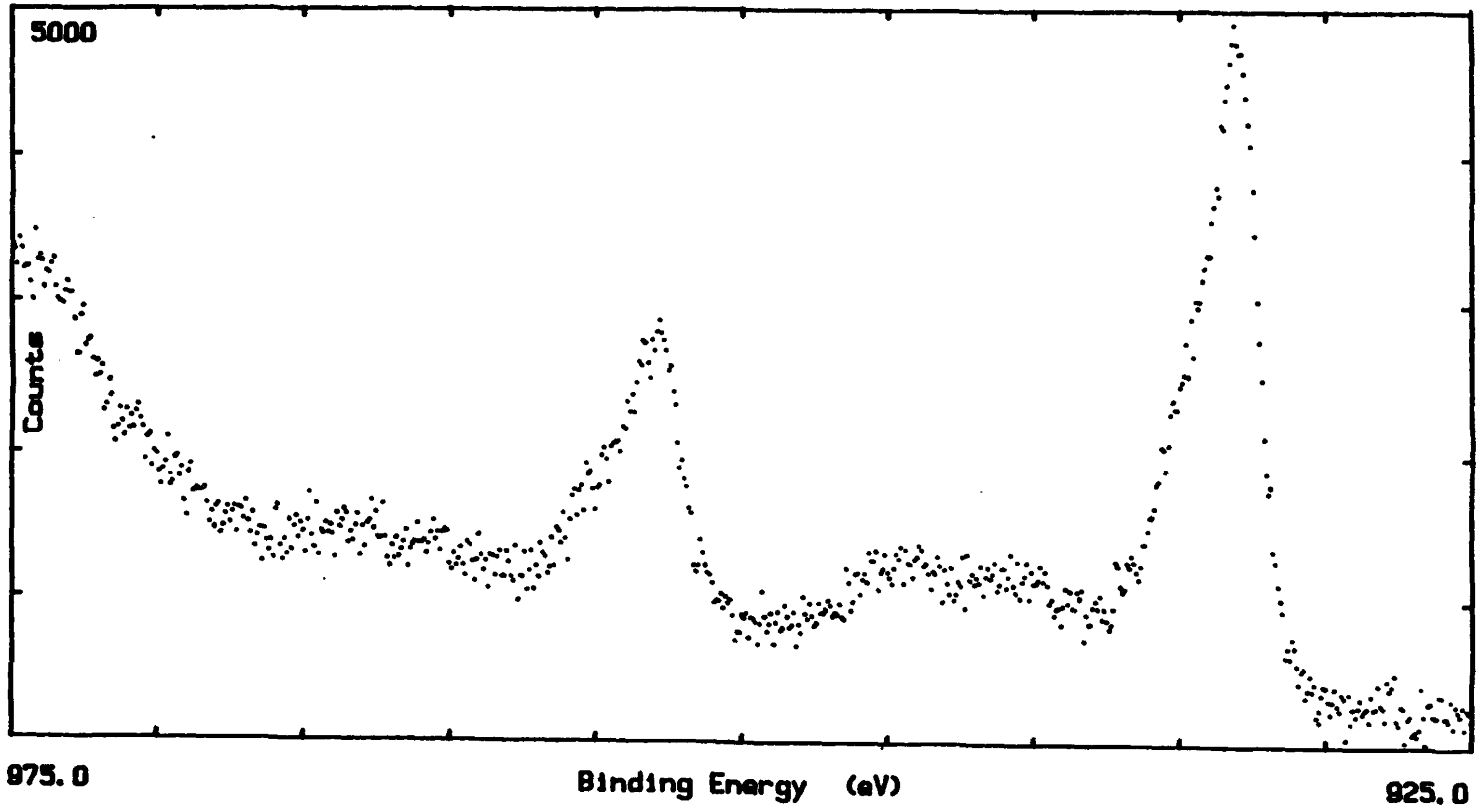


Figure 9: High Resolution Cu($2p^{3/2}$) XPS Spectrum of Cu(acetate)$_2$·1/2(TEDA).

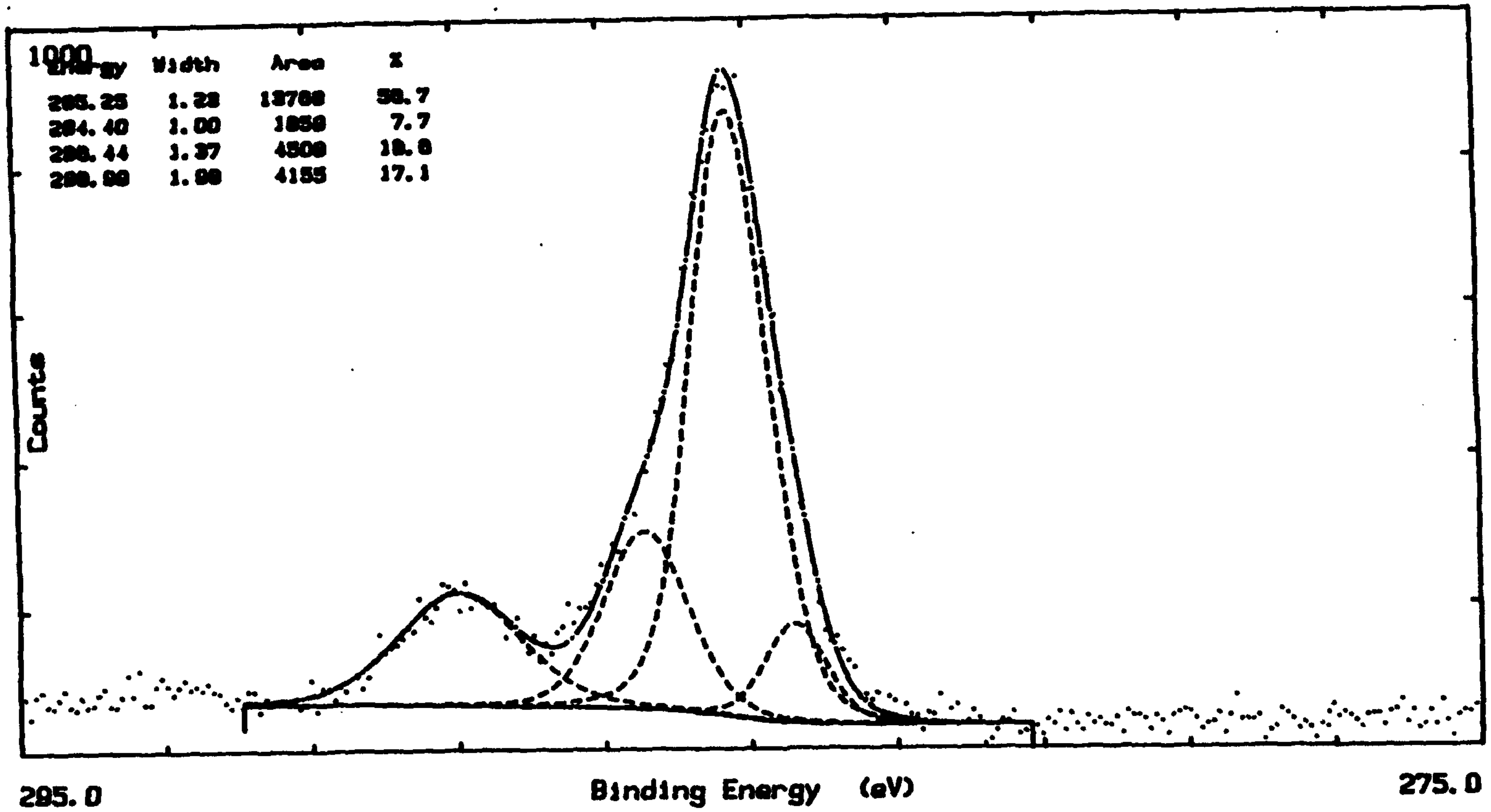


Figure 10: High Resolution C(1s) XPS Spectrum of Cu(acetate)$_2$·1/2(TEDA).

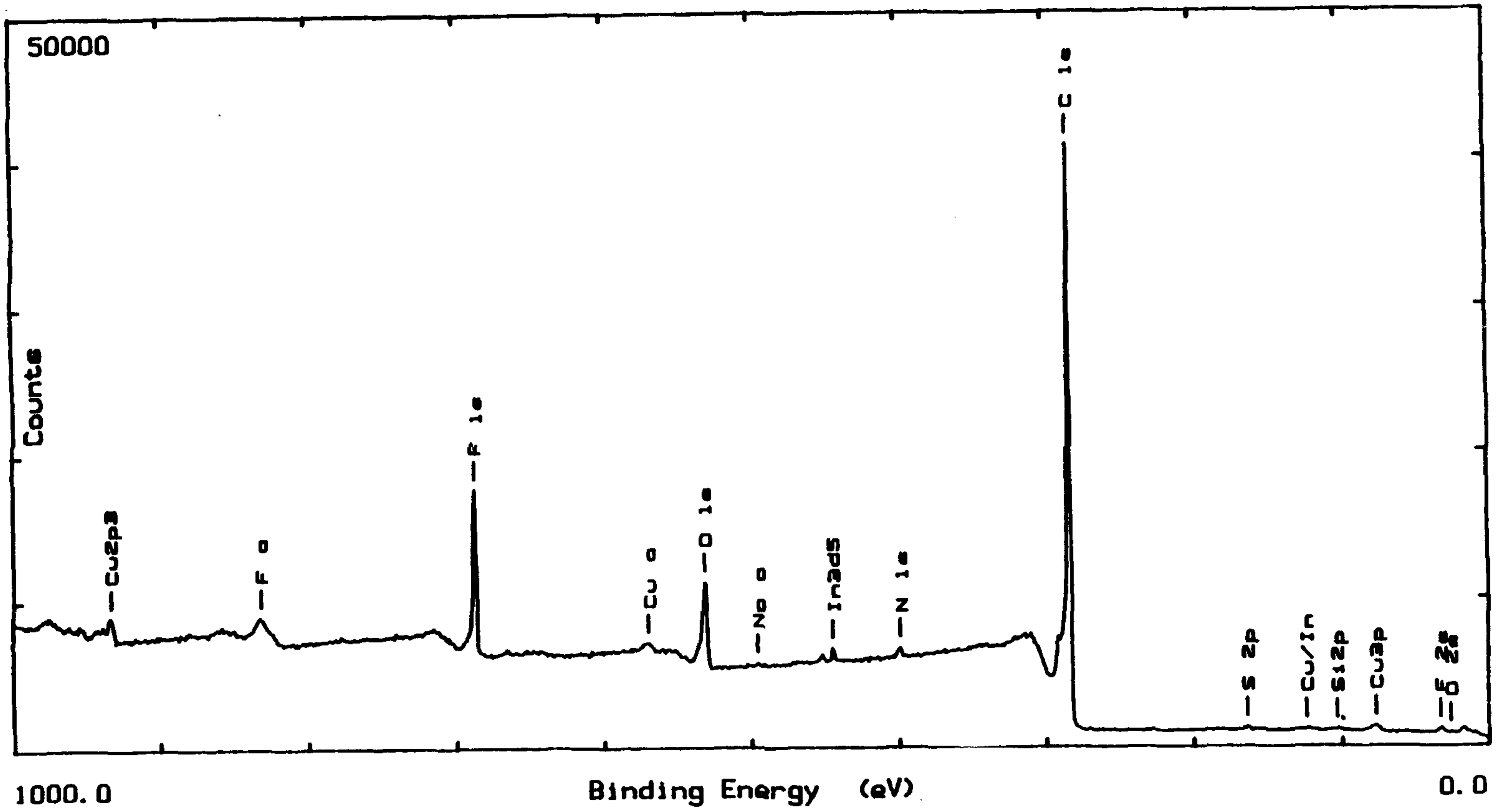


Figure 11: XPS Spectrum of Cu(acetate)$_2$·1/2(TEDA) Impregnated on BPL Carbon.

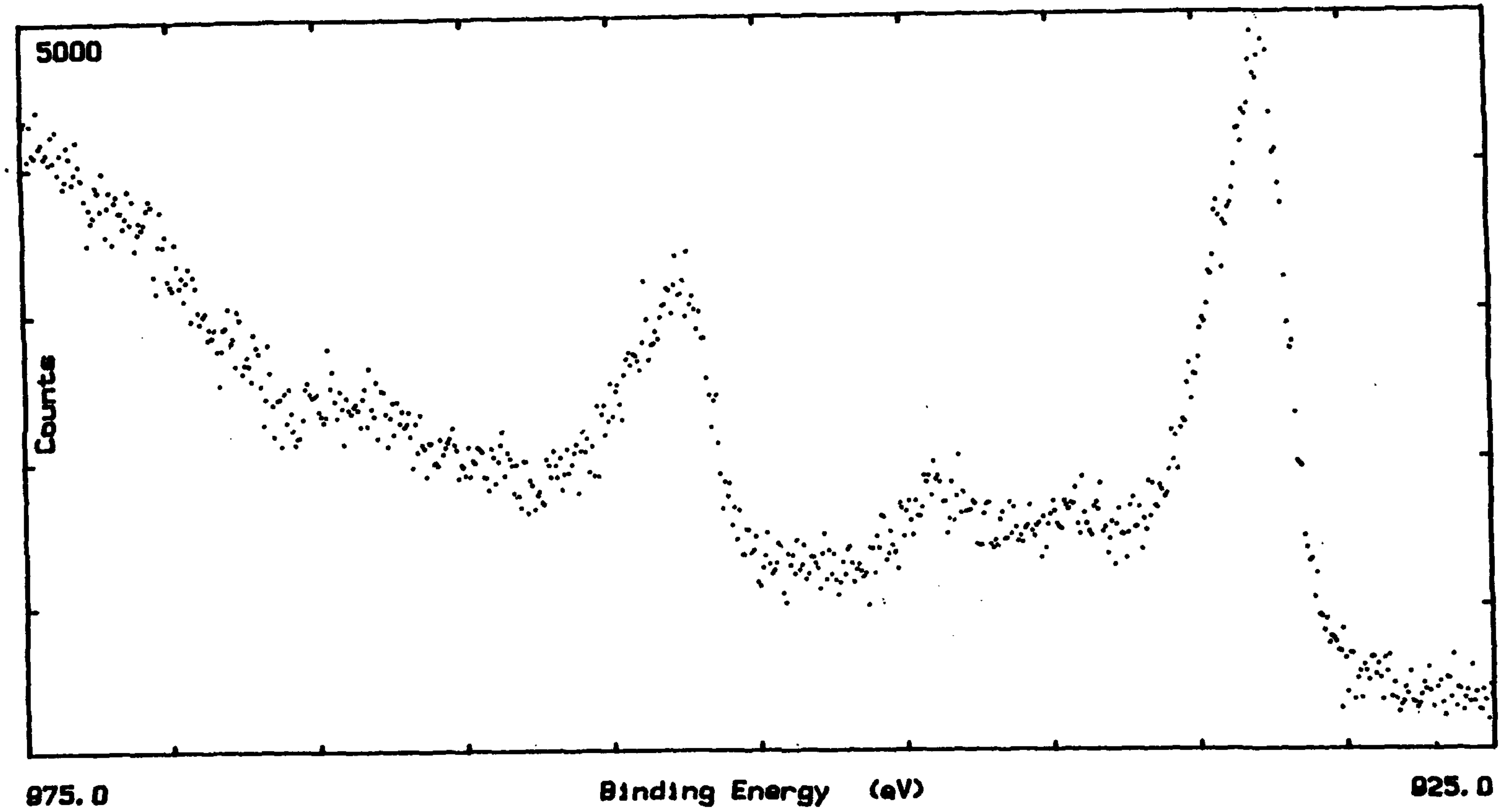


Figure 12: High Resolution Cu($2p^{2/3}$) XPS Spectrum of Cu(acetate)$_2$·(TEDA) Impregnated on BPL Carbon.

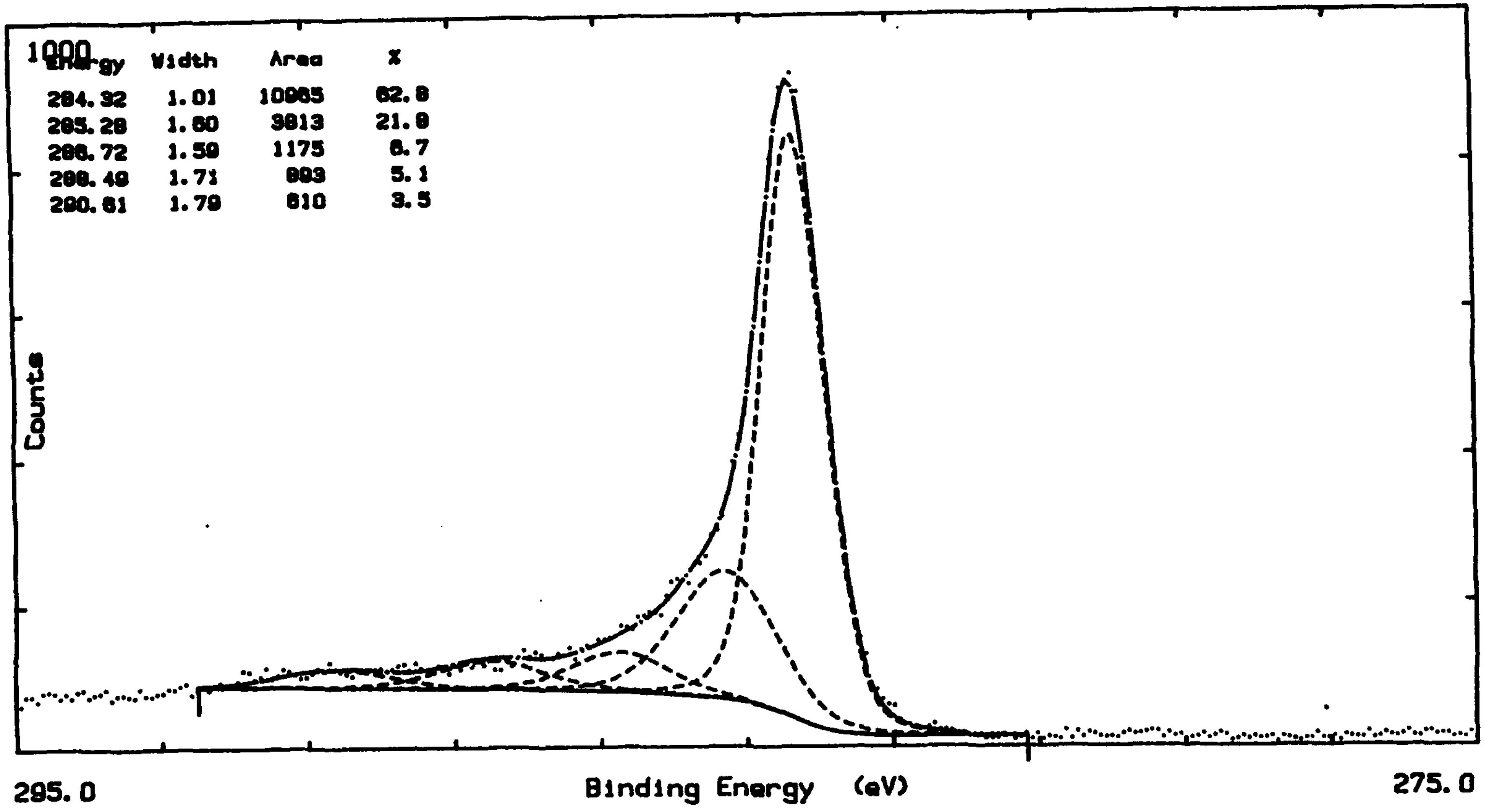


Figure 13: High Resolution C(1s) Spectrum of Cu(acetate)$_2$·(TEDA) Impregnated on BPL Carbon.

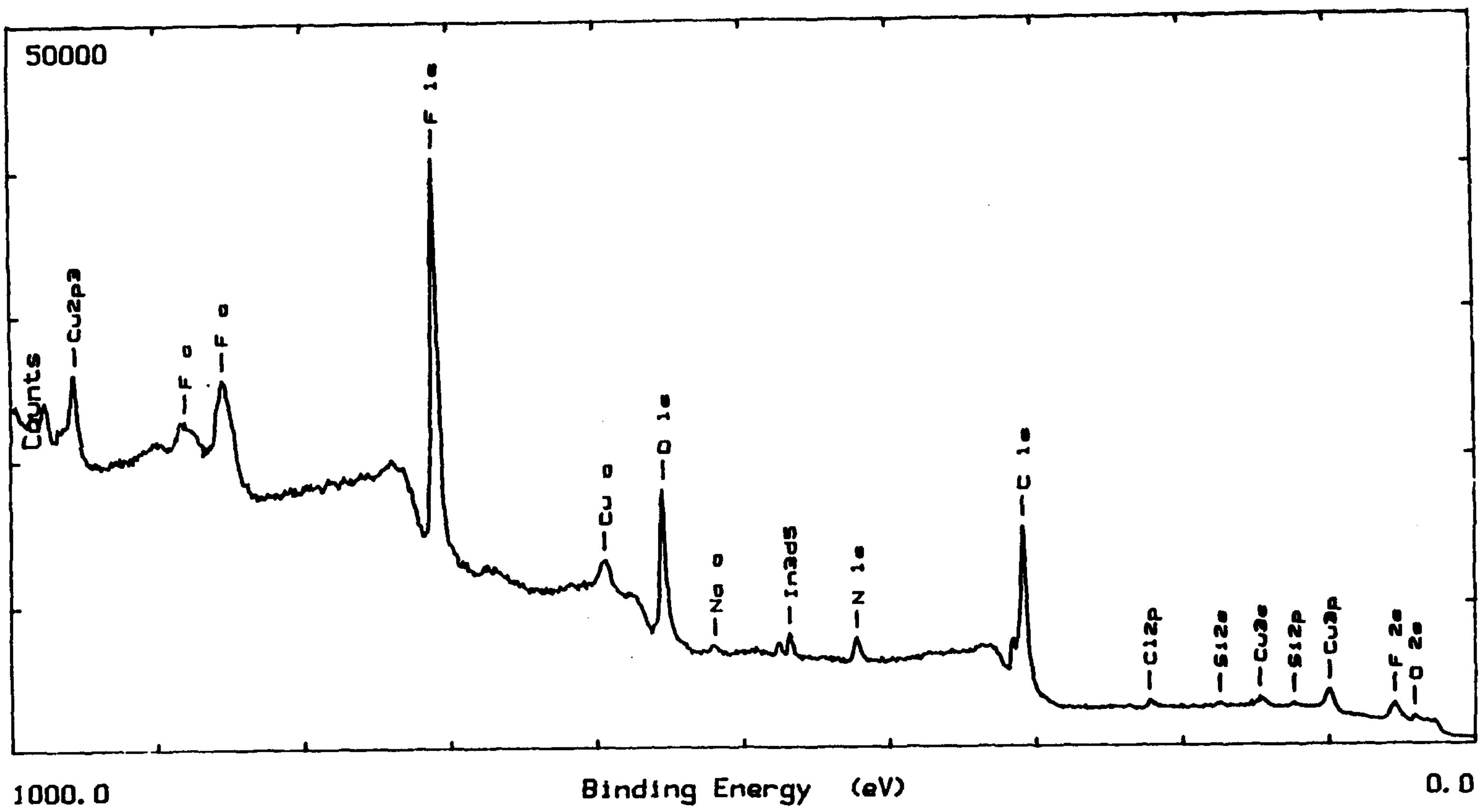


Figure 14: XPS Spectrum of $Cu(hfac)_2 \cdot (TEDA)$.

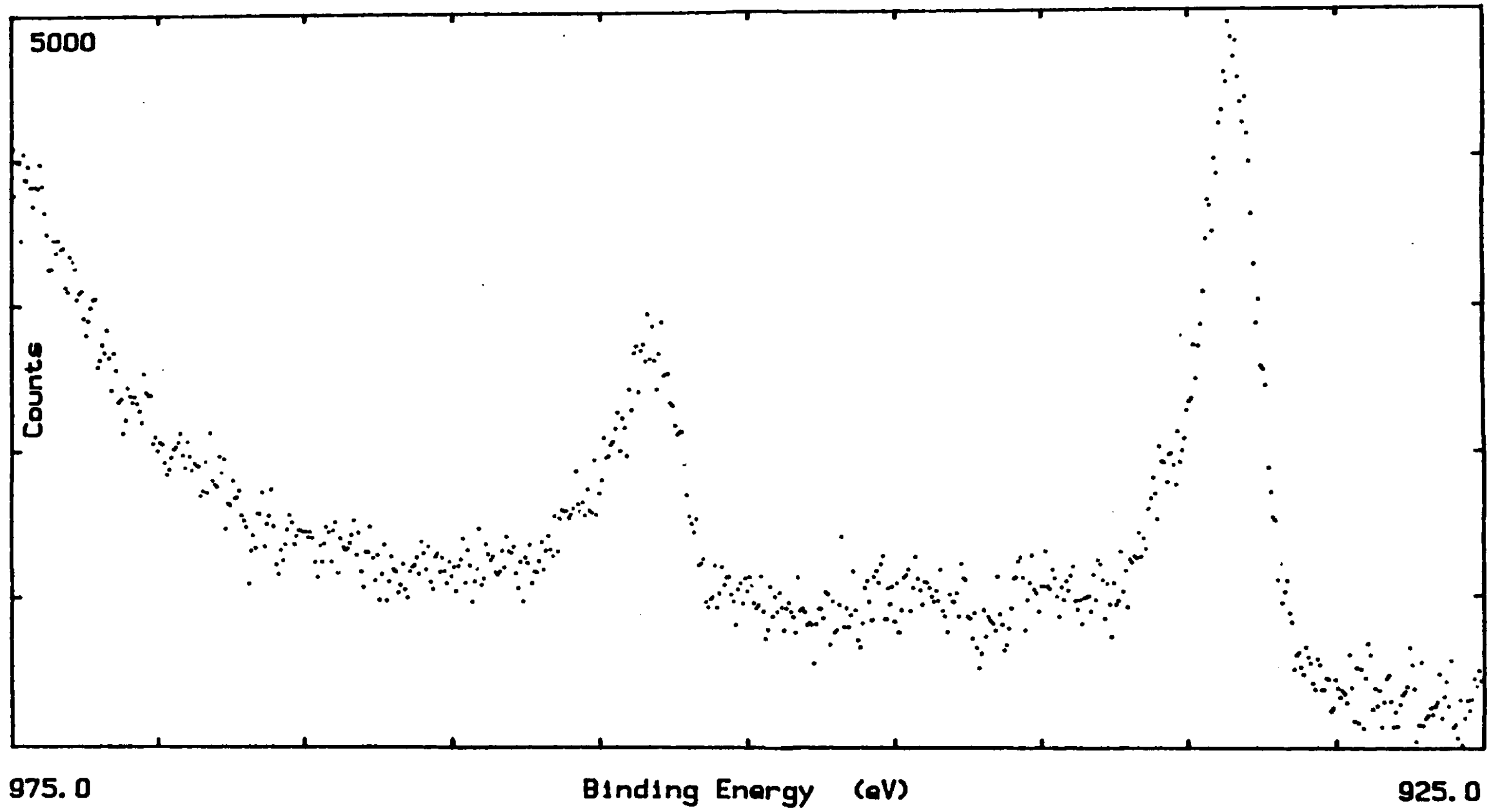


Figure 15: High Resolution Cu($2p^{3/2}$) XPS Spectrum of Cu(hfac)$_2$·(TEDA).

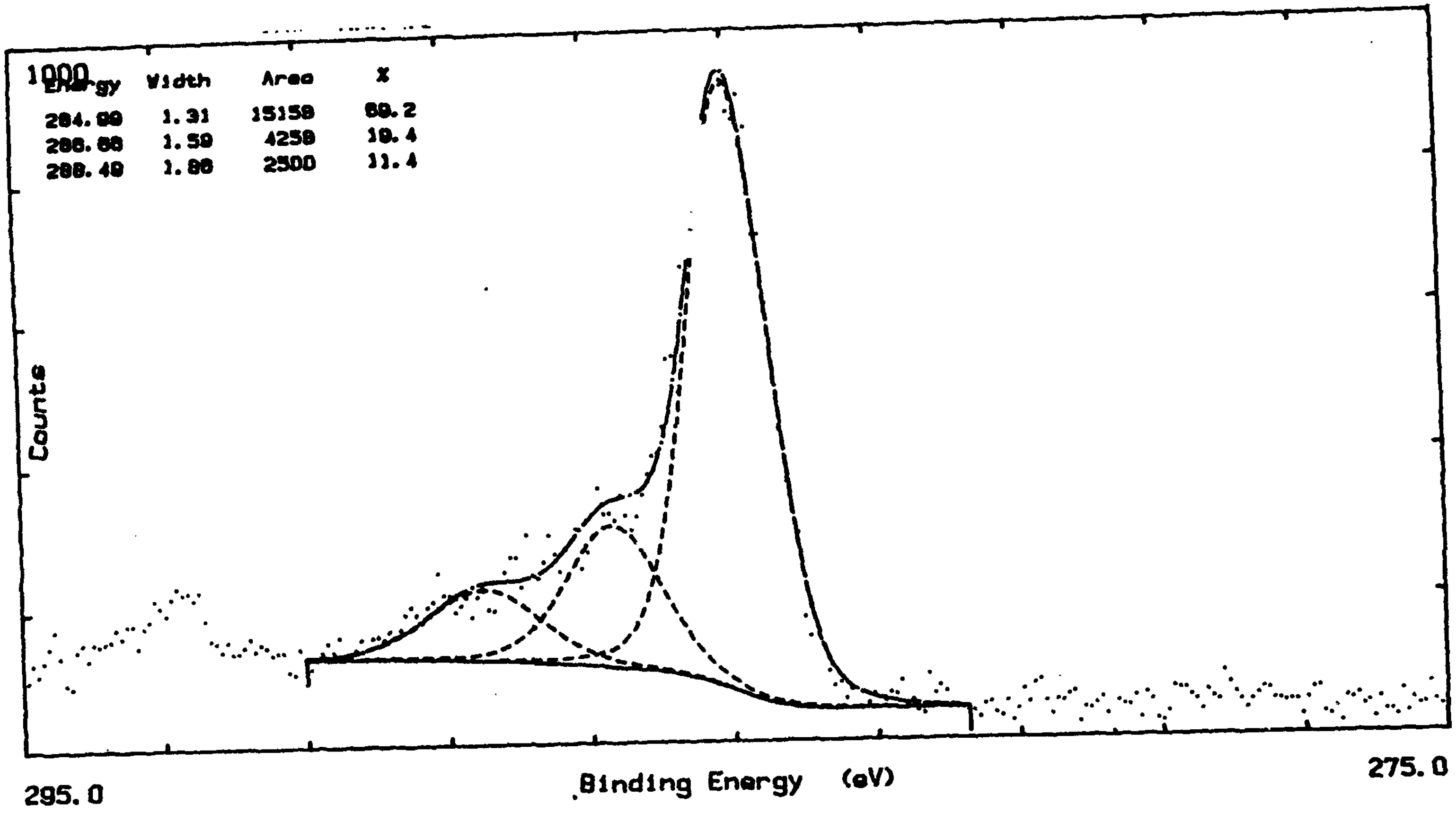


Figure 16: High Resolution C(1s) XPS Spectrum of Cu(hfac)$_2$·(TEDA).

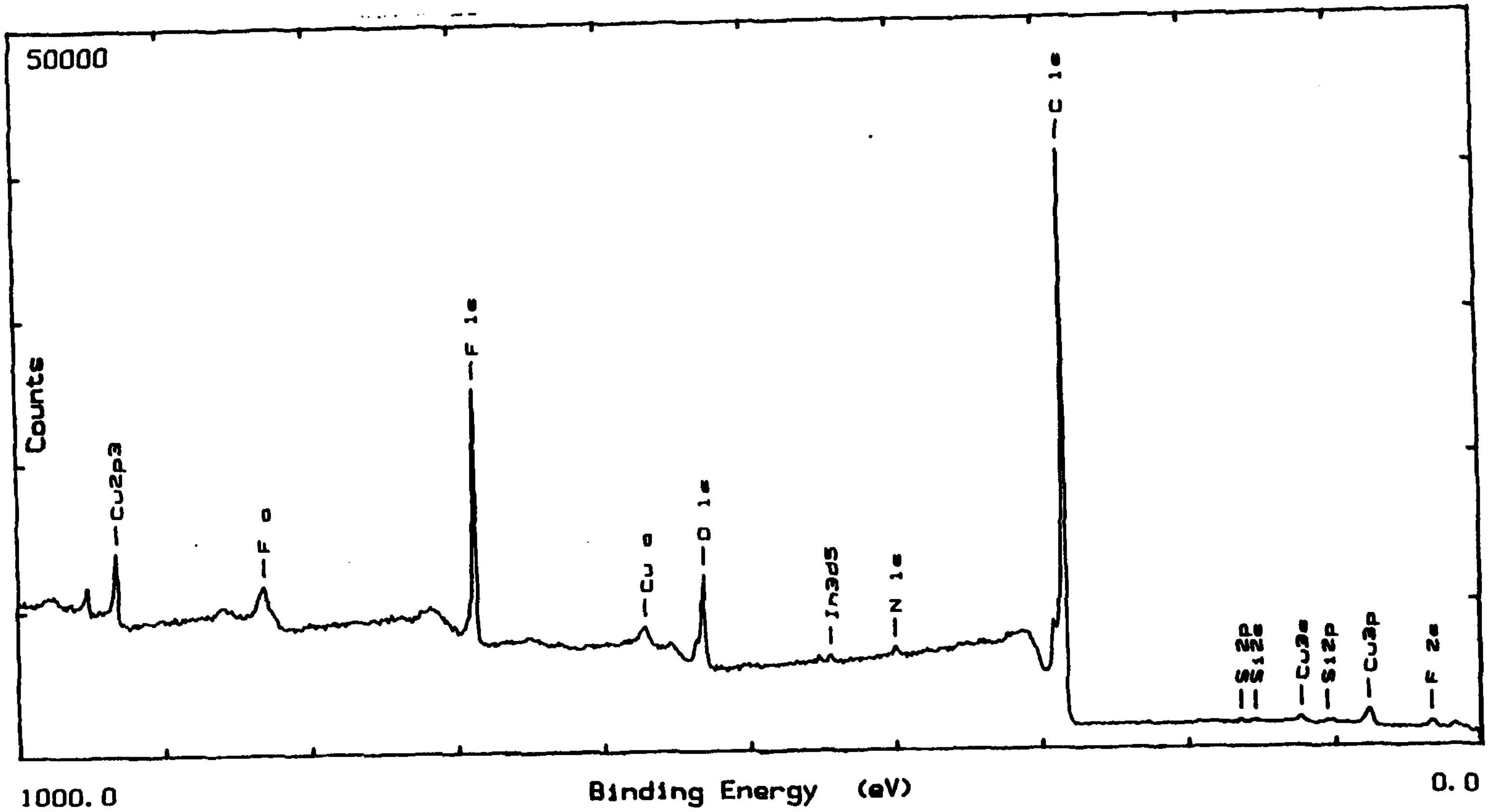


Figure 17: XPS Spectrum of Cu(hfac)$_2$·(TEDA) Impregnated on BPL Carbon.

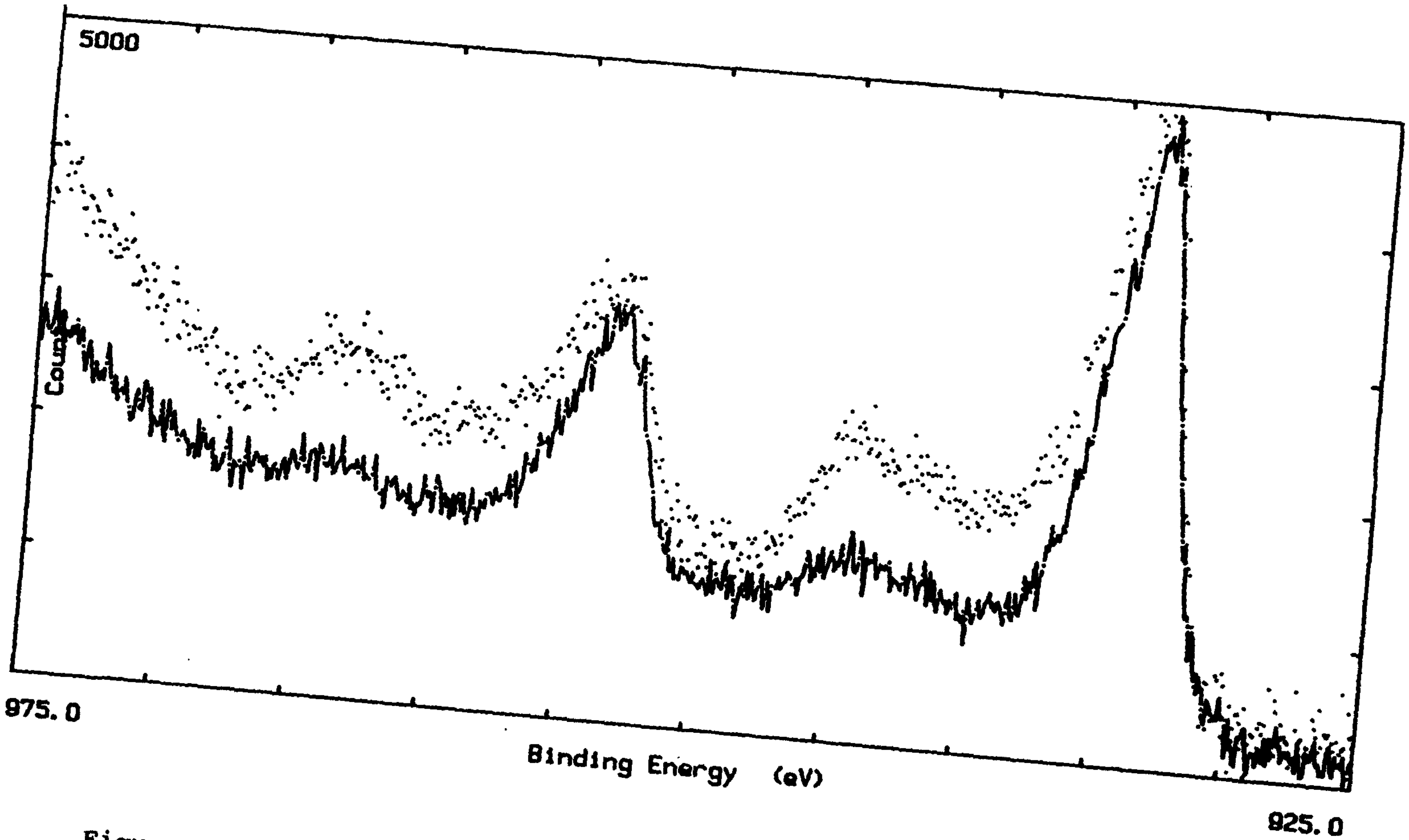
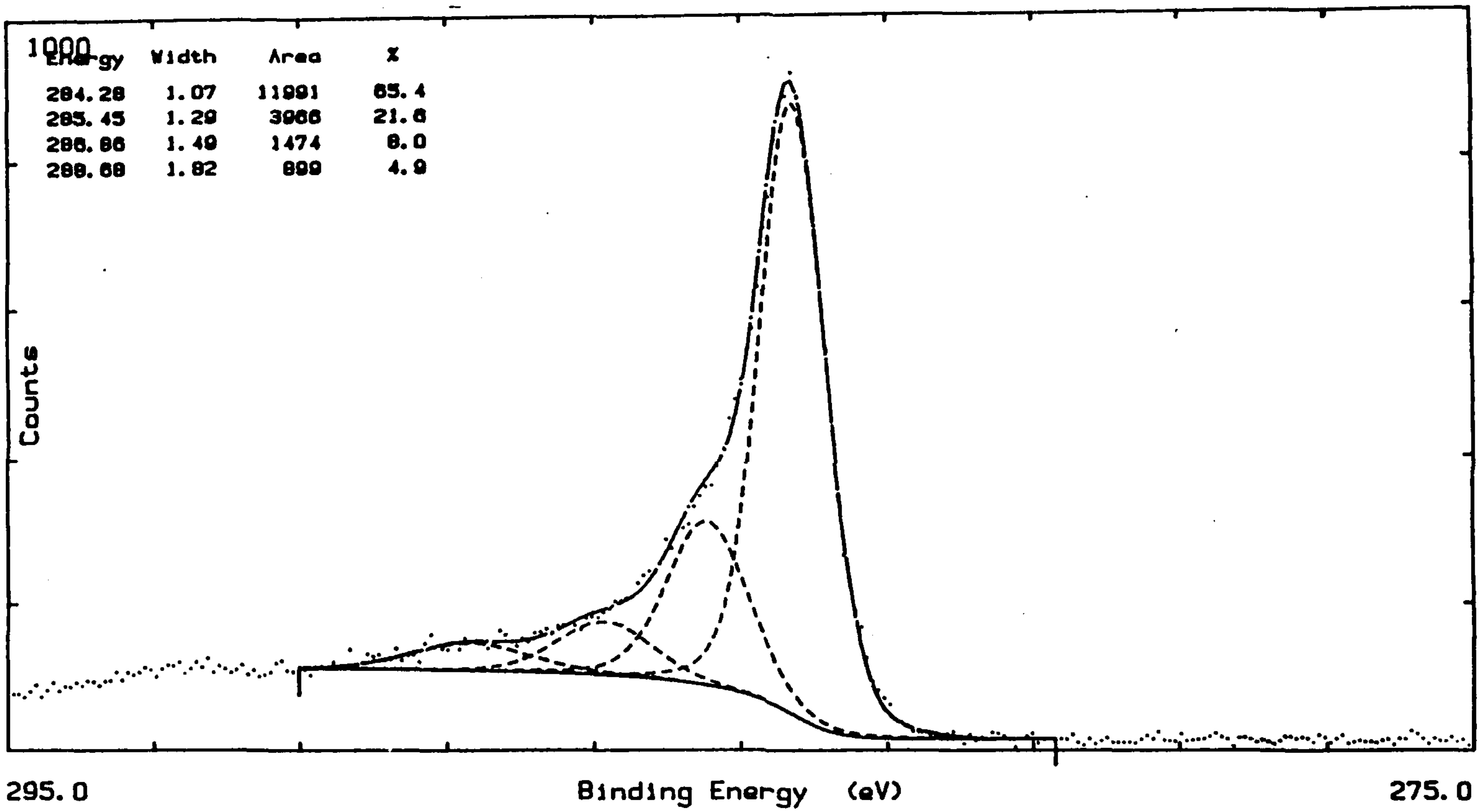


Figure 18: High Resolution Cu($2p^{3/2}$) XPS Spectrum of Cu(hfac)$_2$·(TEDA) Impregnated on BPL Carbon.



Energy	Width	Area	%
284.28	1.07	11991	65.4
285.45	1.29	3966	21.6
286.86	1.49	1474	8.0
288.68	1.82	899	4.9

Figure 19: High Resolution C(1s) Spectrum of Cu(hfac)$_2$·(TEDA) Impregnated on BPL Carbon.

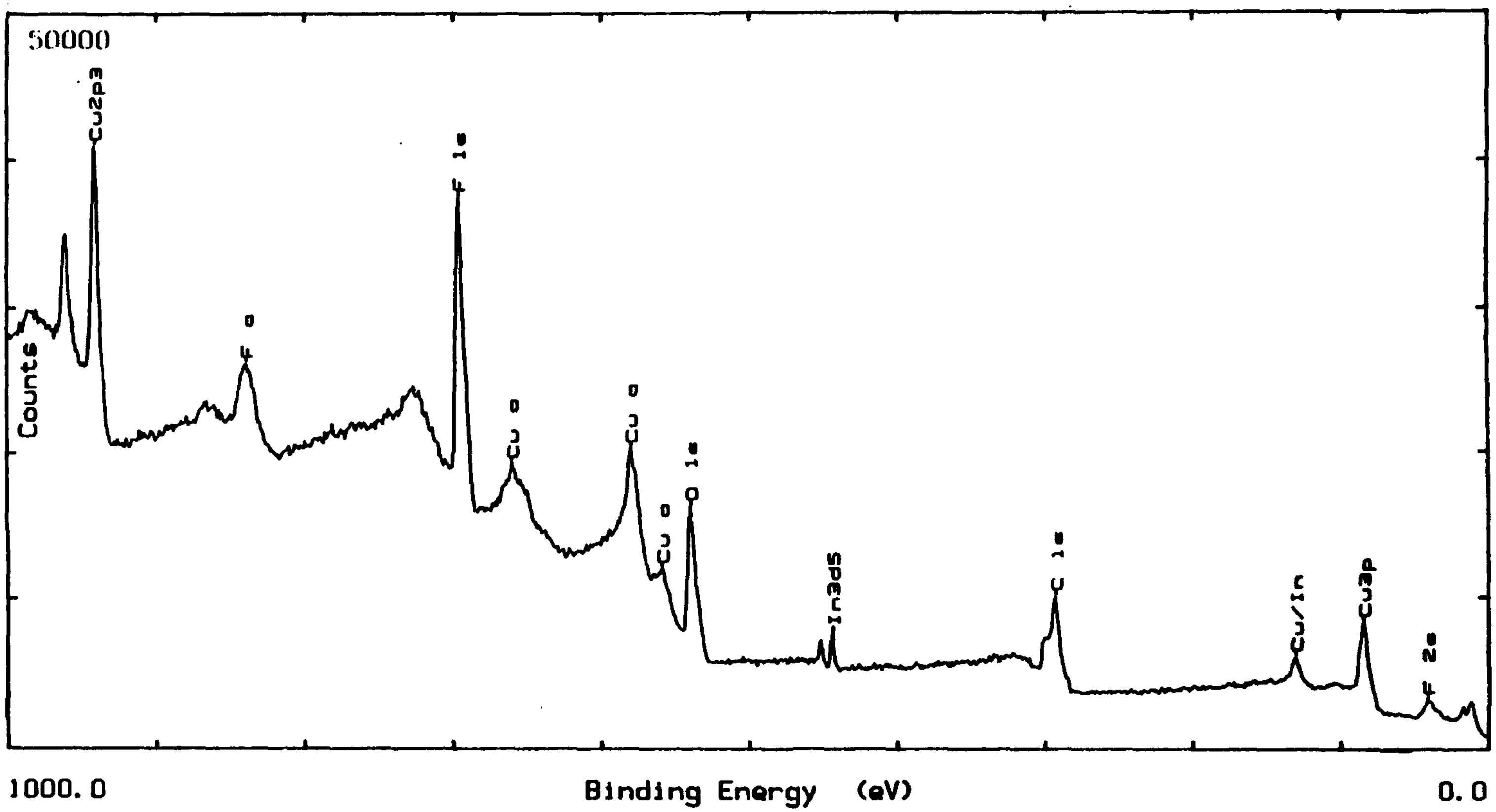


Figure 20: XPS Spectrum of Cu(hfac)·(1,5-COD).

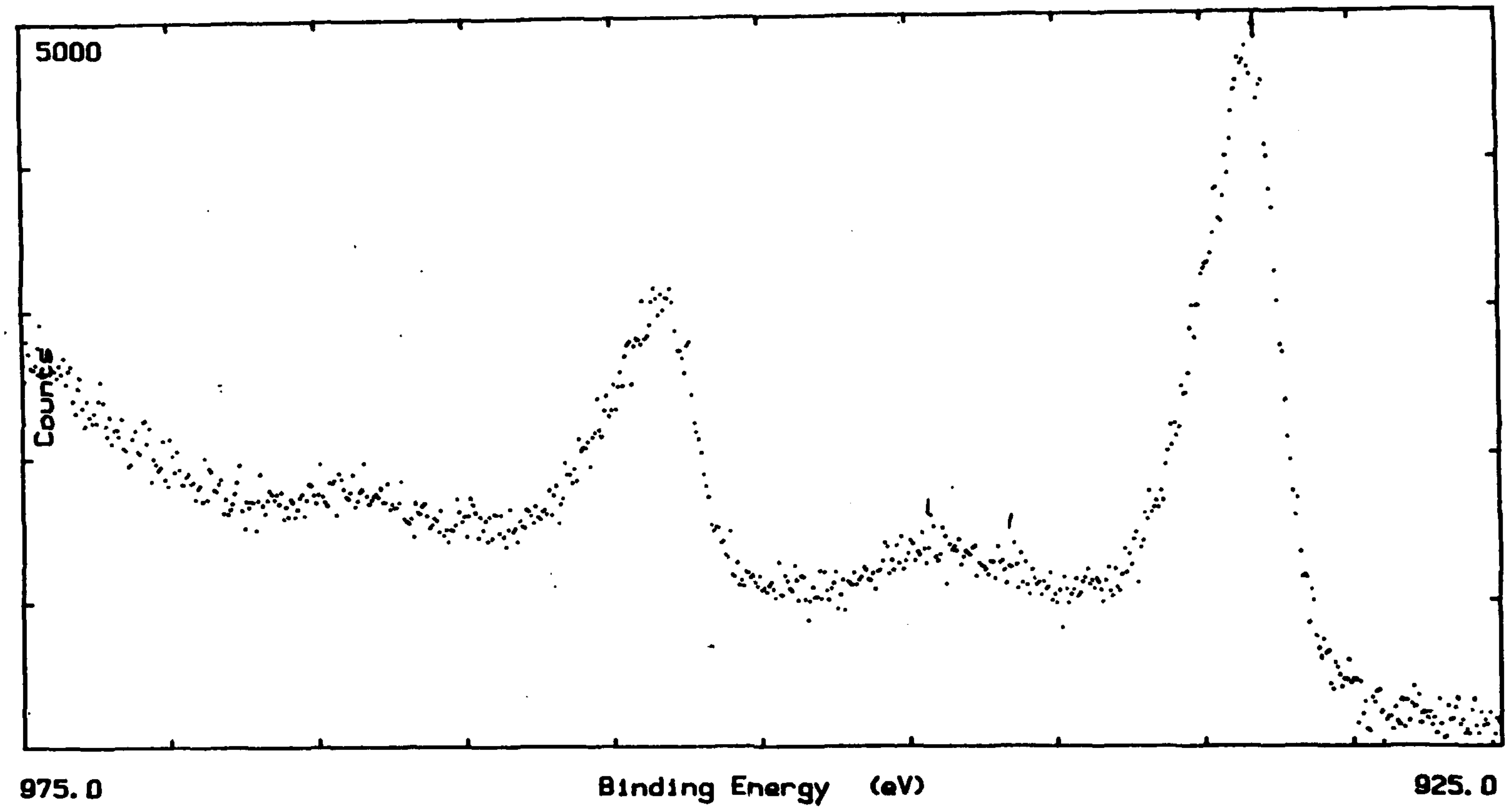


Figure 21: High Resolution Cu($2p^{3/2}$) XPS Spectrum of Cu(hfac)·(1,5-COD).

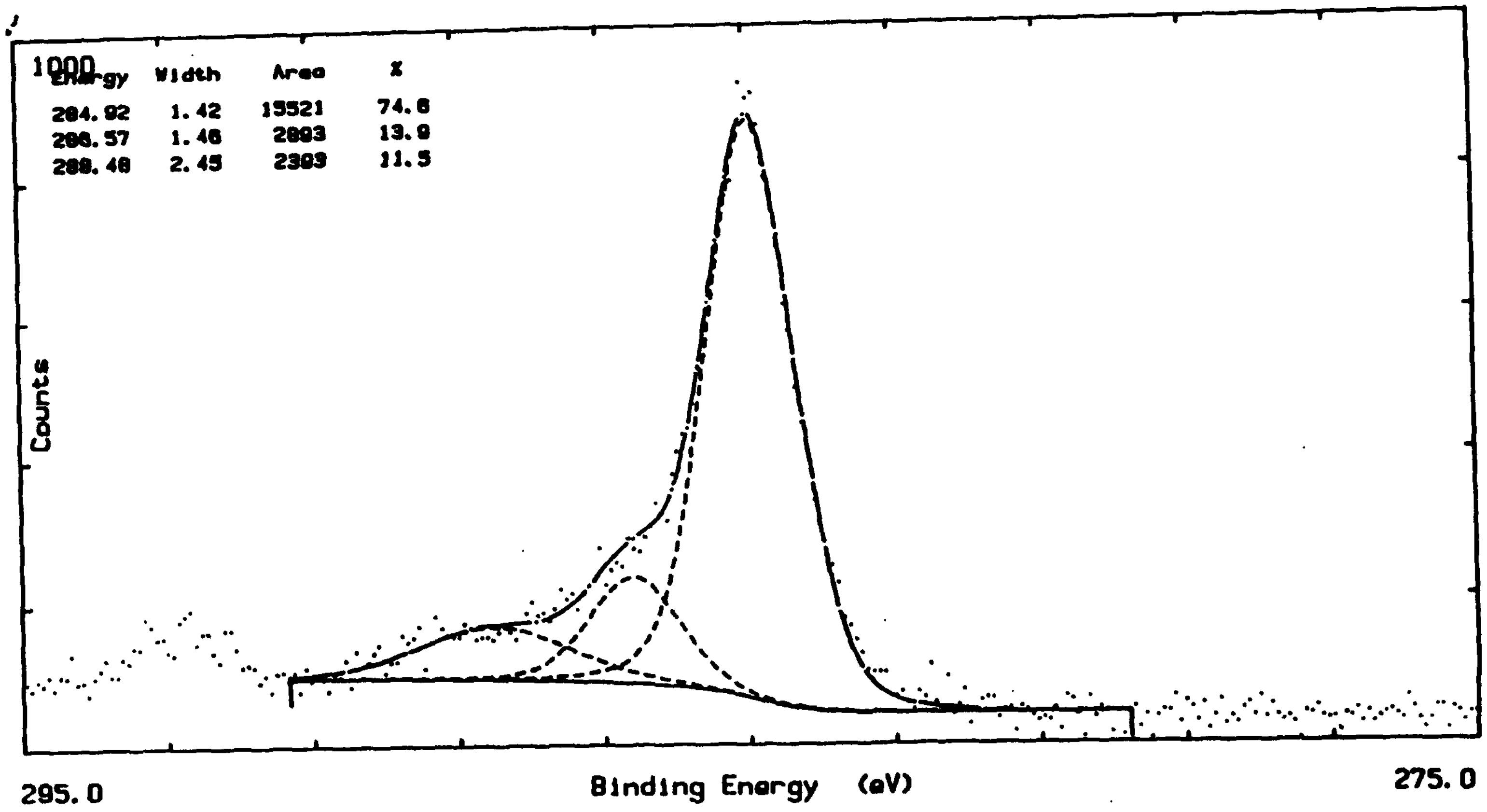


Figure 22: High Resolution C(1s) XPS Spectrum of Cu(hfac)·(1,5-COD).

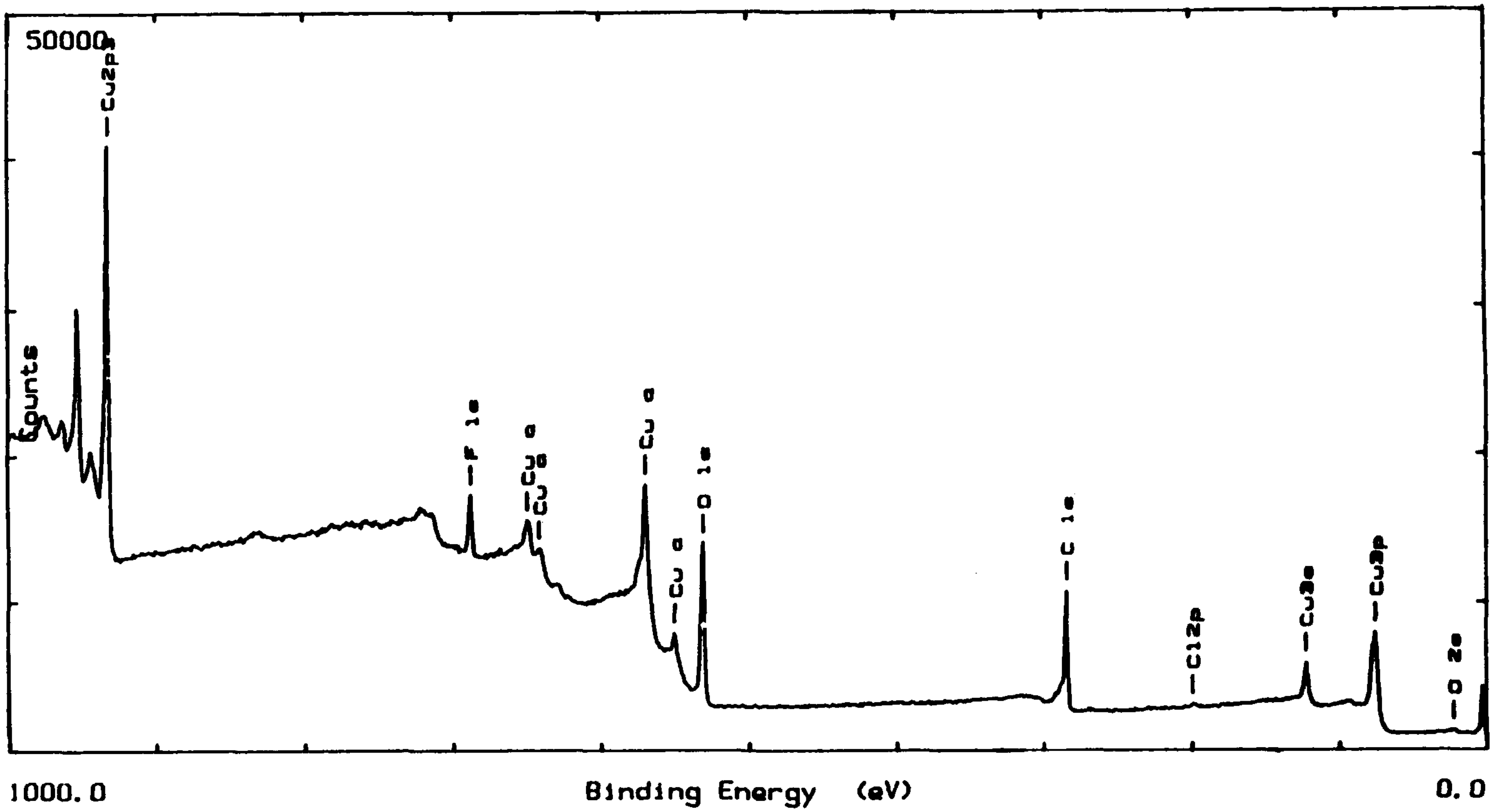


Figure 23: XPS Spectrum of Cu(hfac)·(1,5-COD) Impregnated on BPL Carbon.

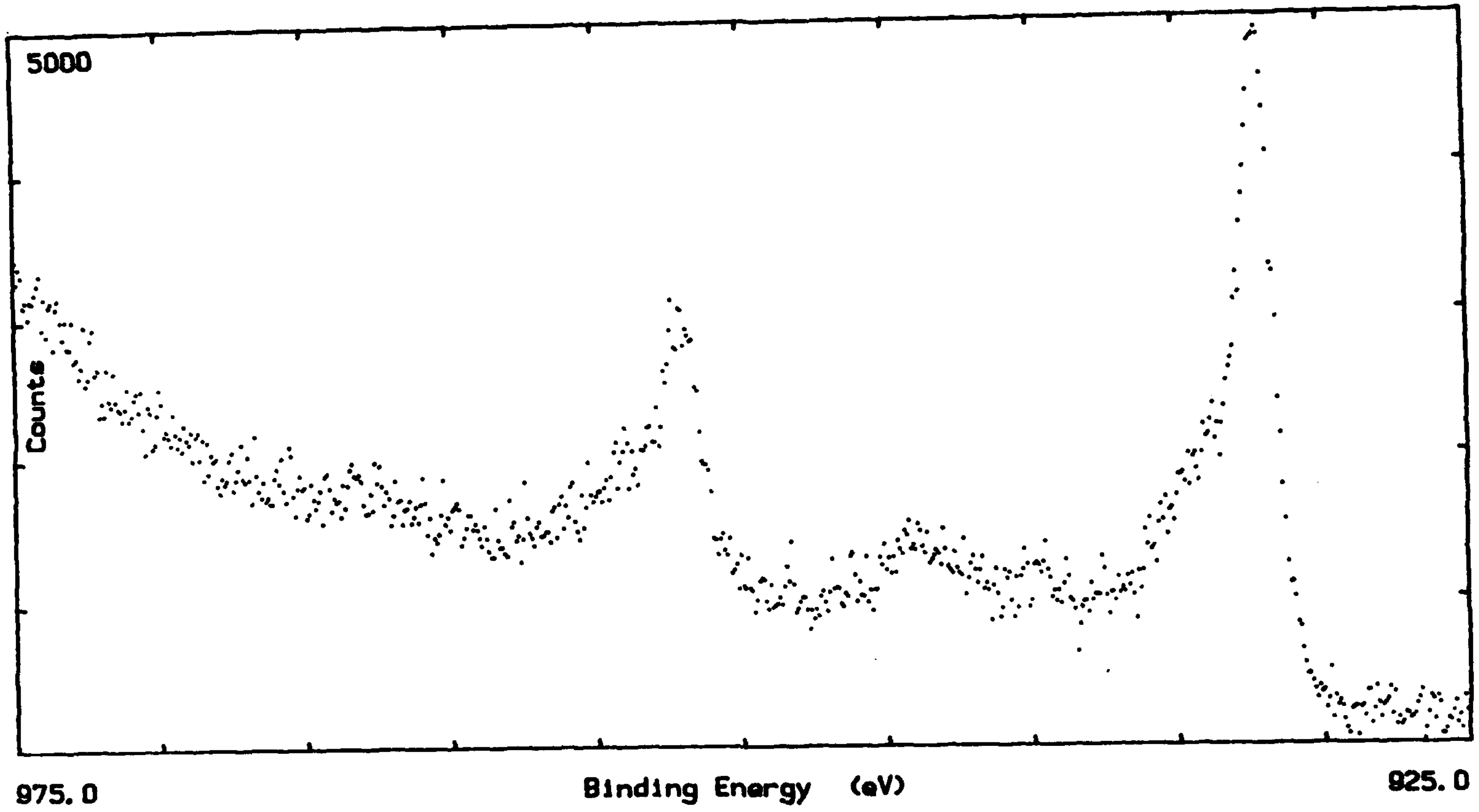


Figure 24: High Resolution Cu(2p$^{3/2}$) XPS Spectrum of Cu(hfac)·(1,5-COD) Impregnated on BPL carbon.

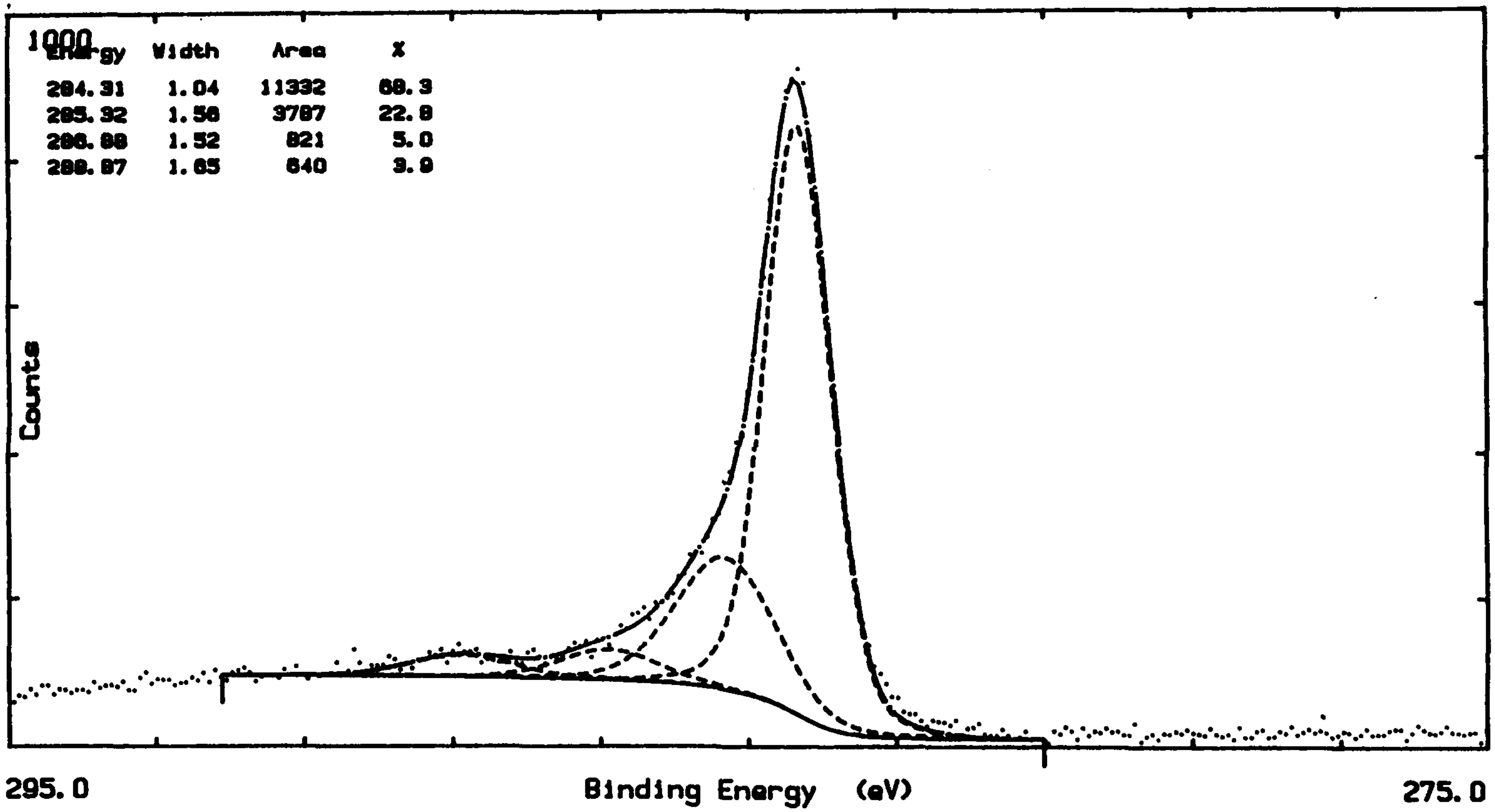


Figure 25: High Resolution C(1s) Spectrum of Cu(hfac)·(1,5-COD) Impregnated on BPL carbon.

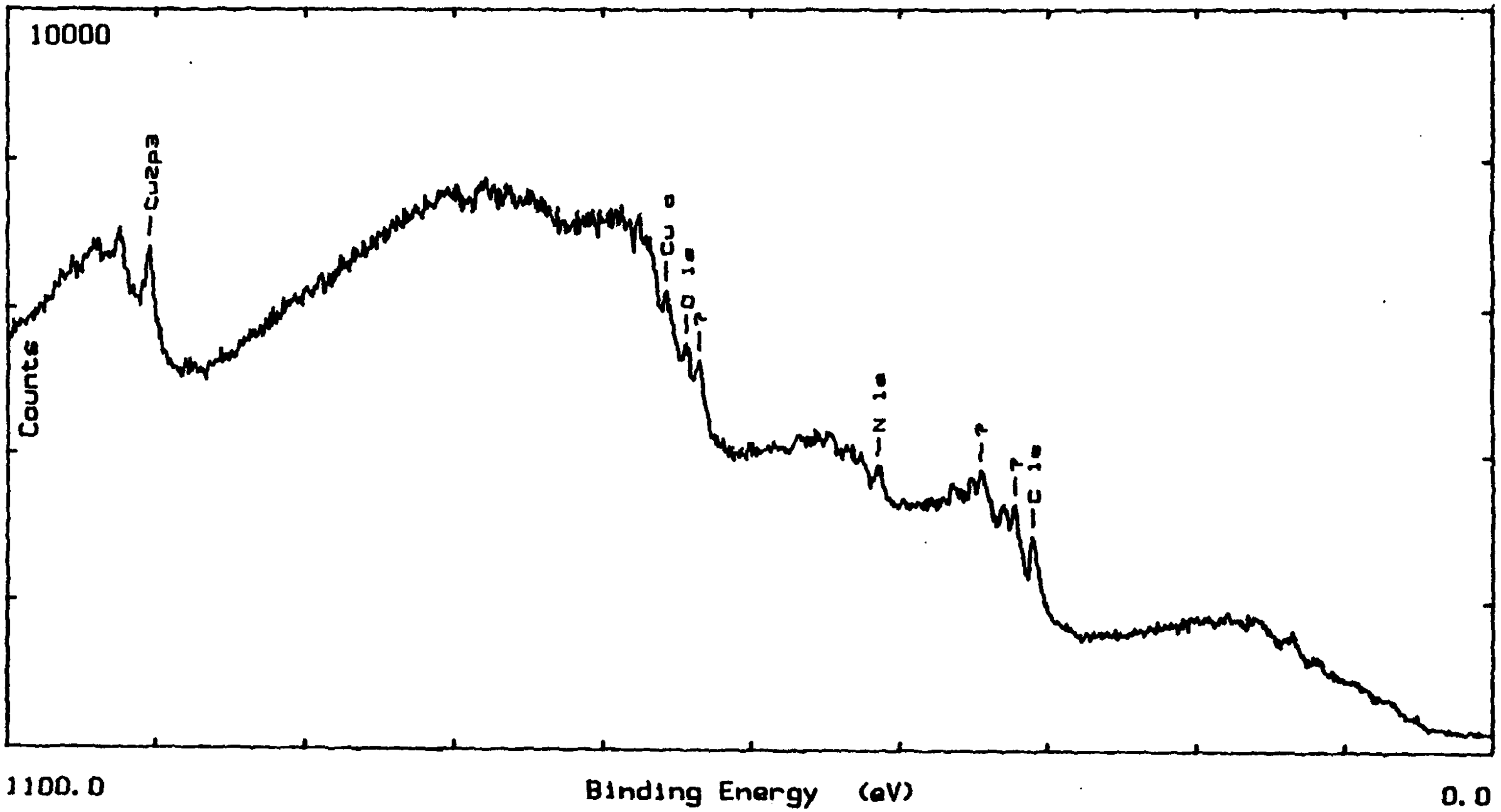


Figure 26: XPS Spectrum of $Cu(dmg)_2$.

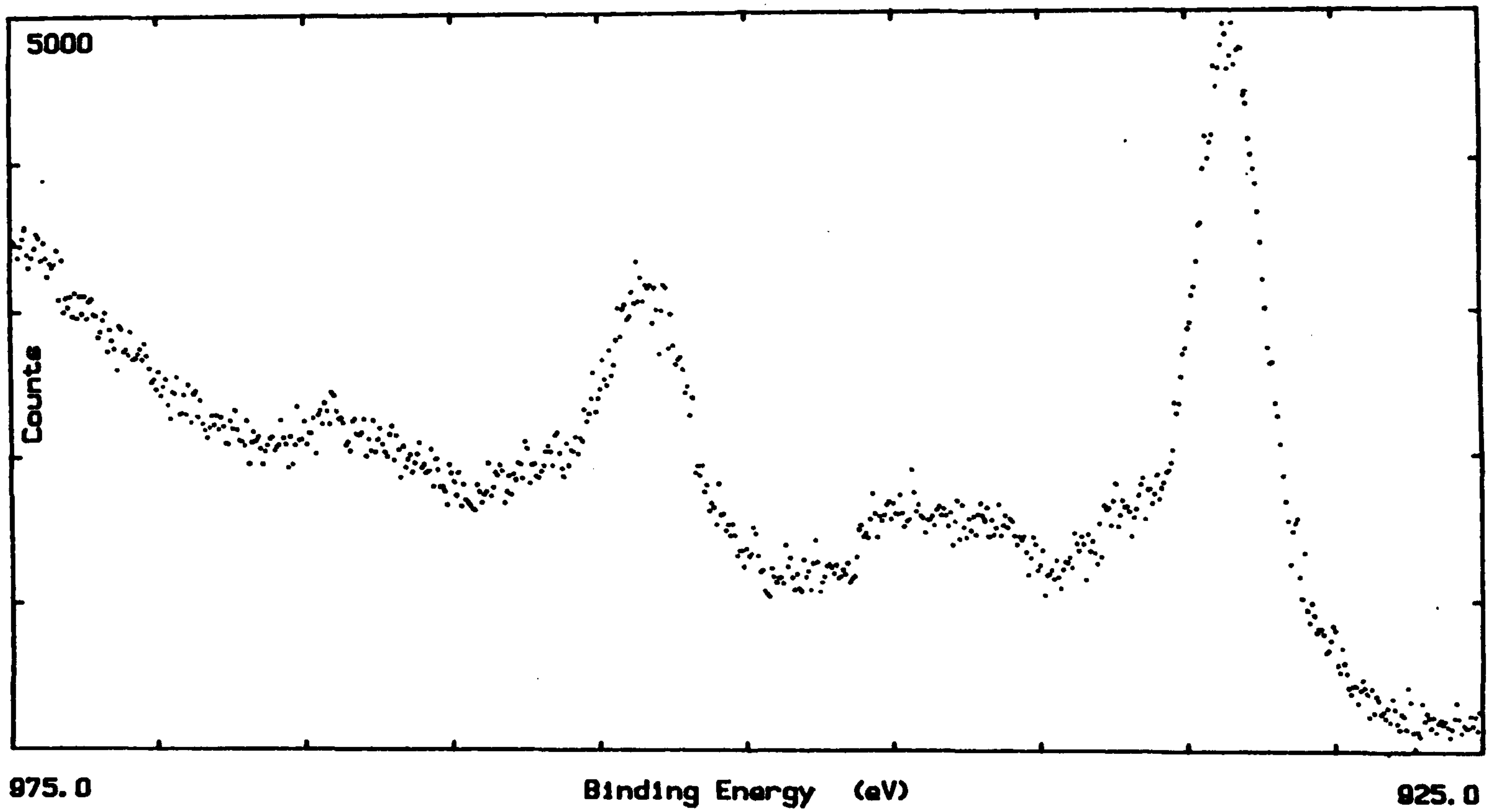


Figure 27: High Resolution Cu($2p^{3/2}$) XPS Spectrum of Cu(dmg)$_2$.

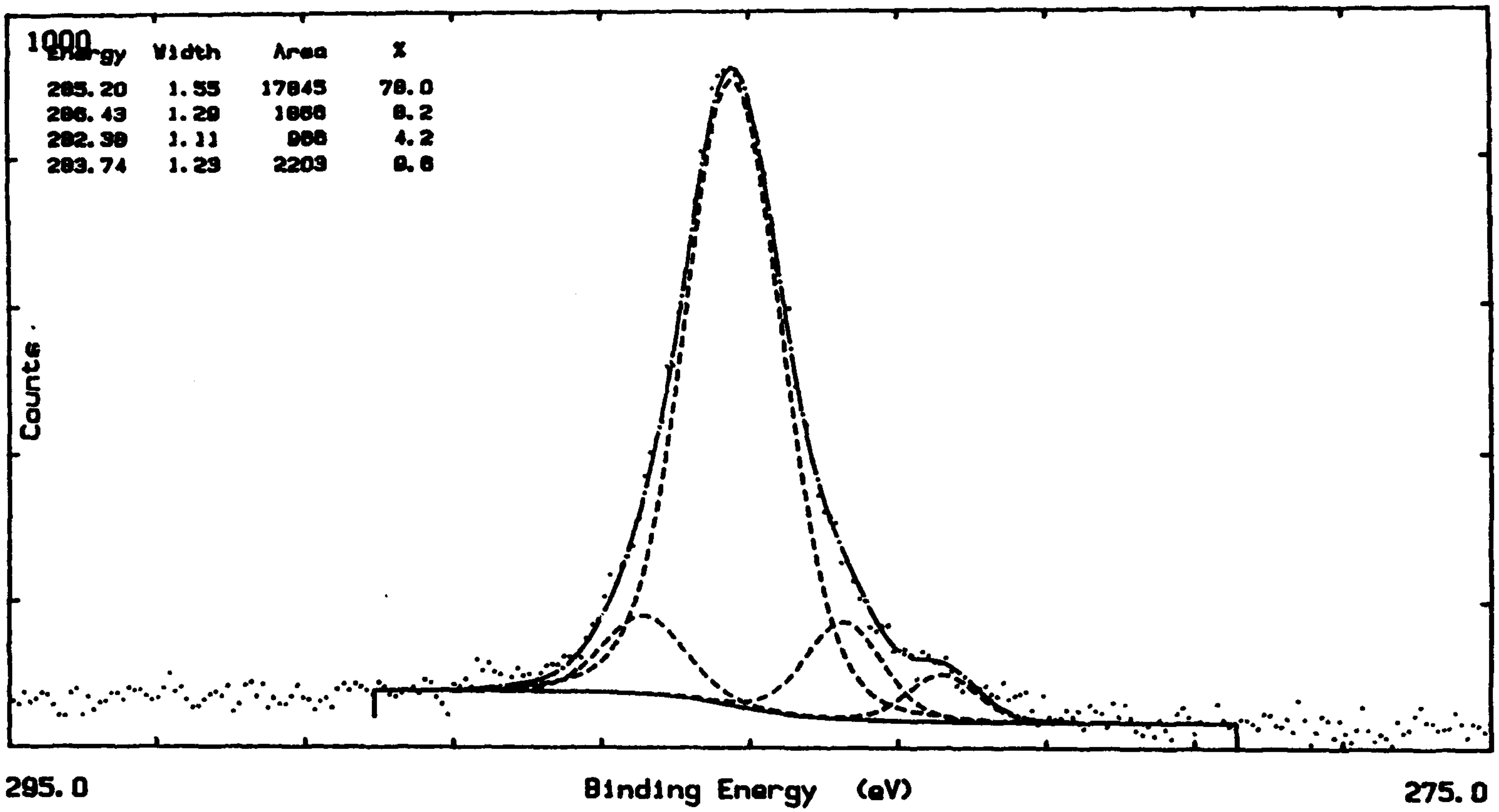


Figure 28: High Resolution C(1s) XPS Spectrum of $Cu(dmg)_2$.

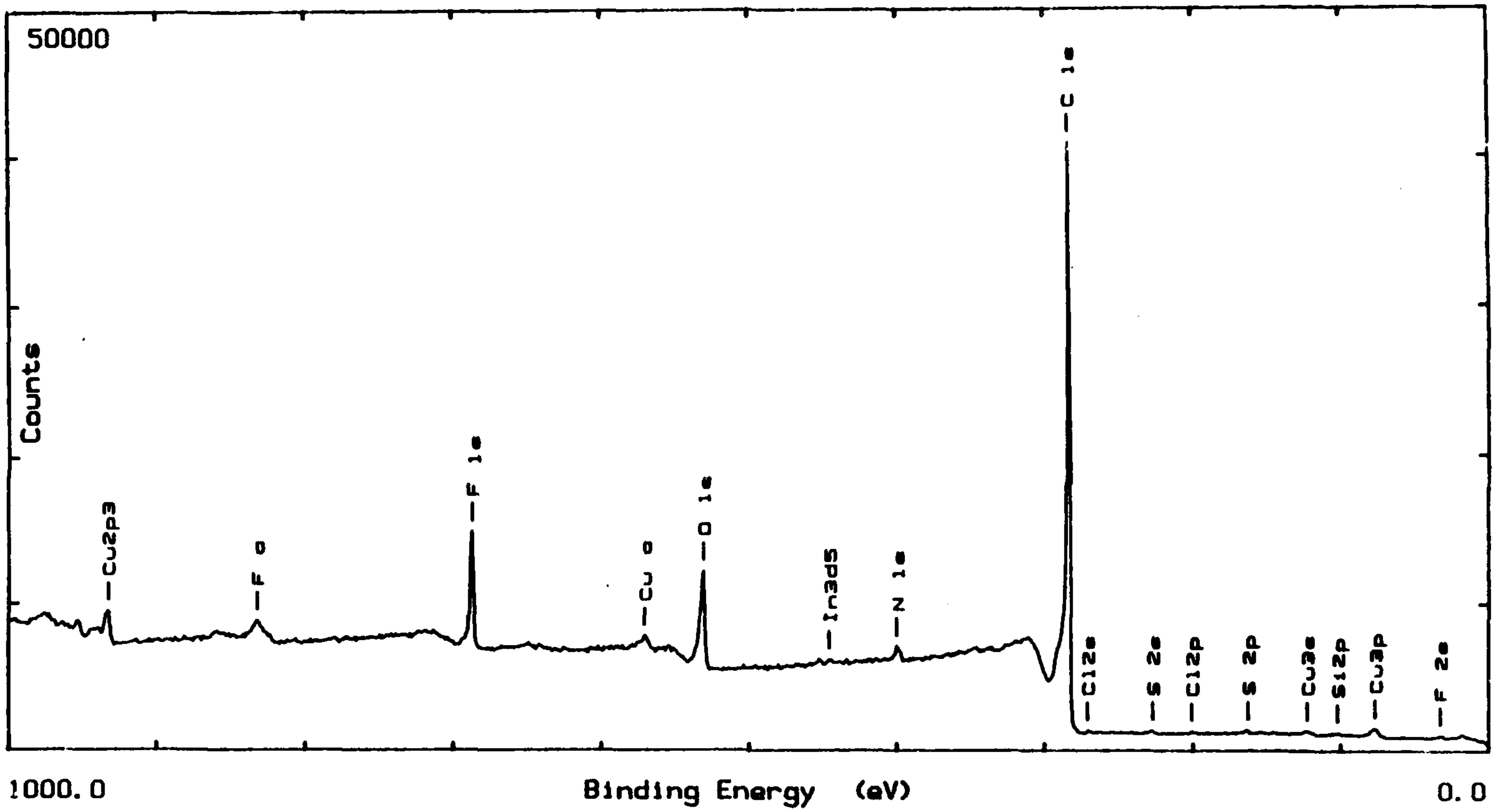


Figure 29: XPS Spectrum of Cu(dmg)$_2$ Impregnated on BPL Carbon.

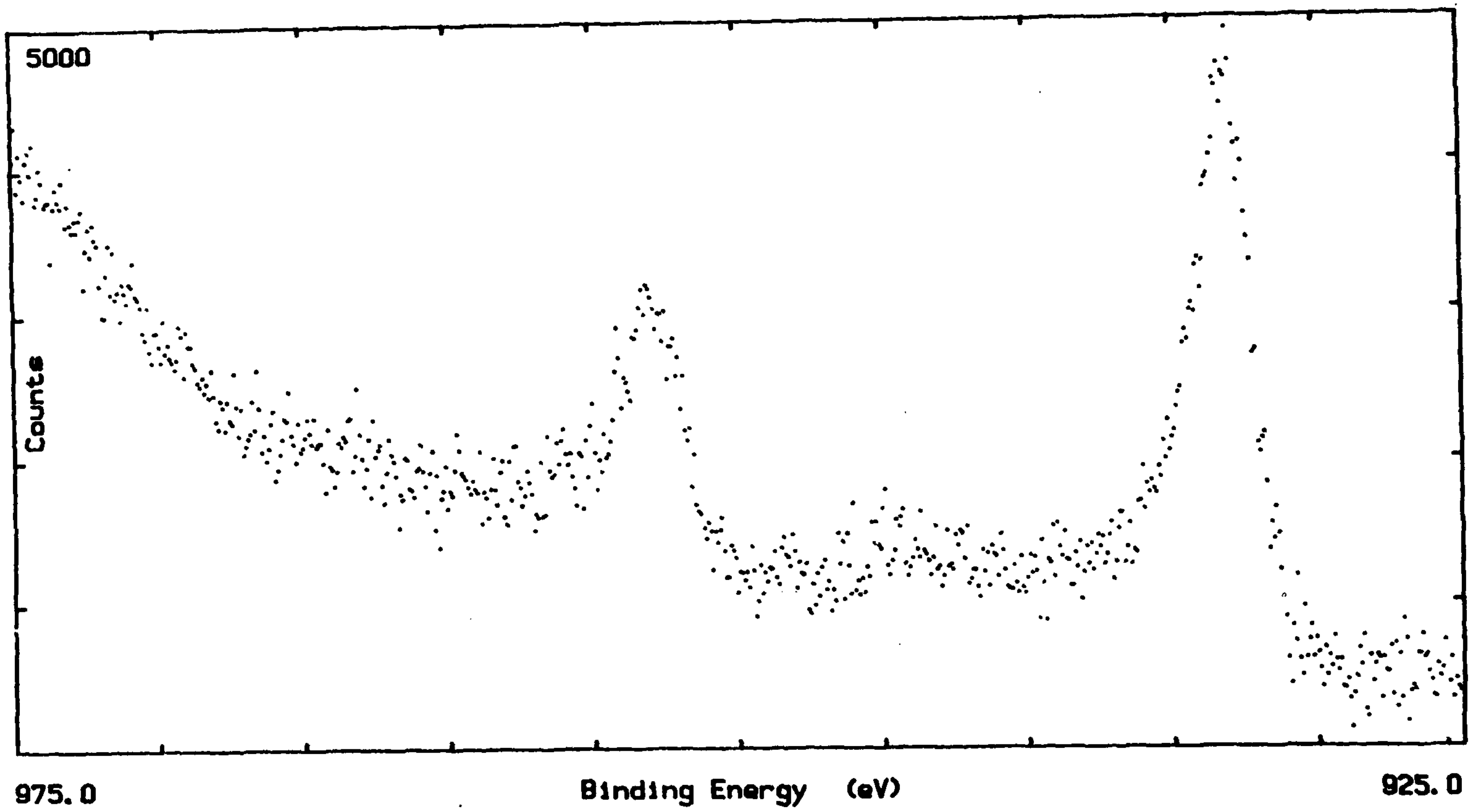


Figure 30: High Resolution Cu($2p^{3/2}$) XPS Spectrum of Cu($dmg)_2$ Impregnated on BPL Carbon.

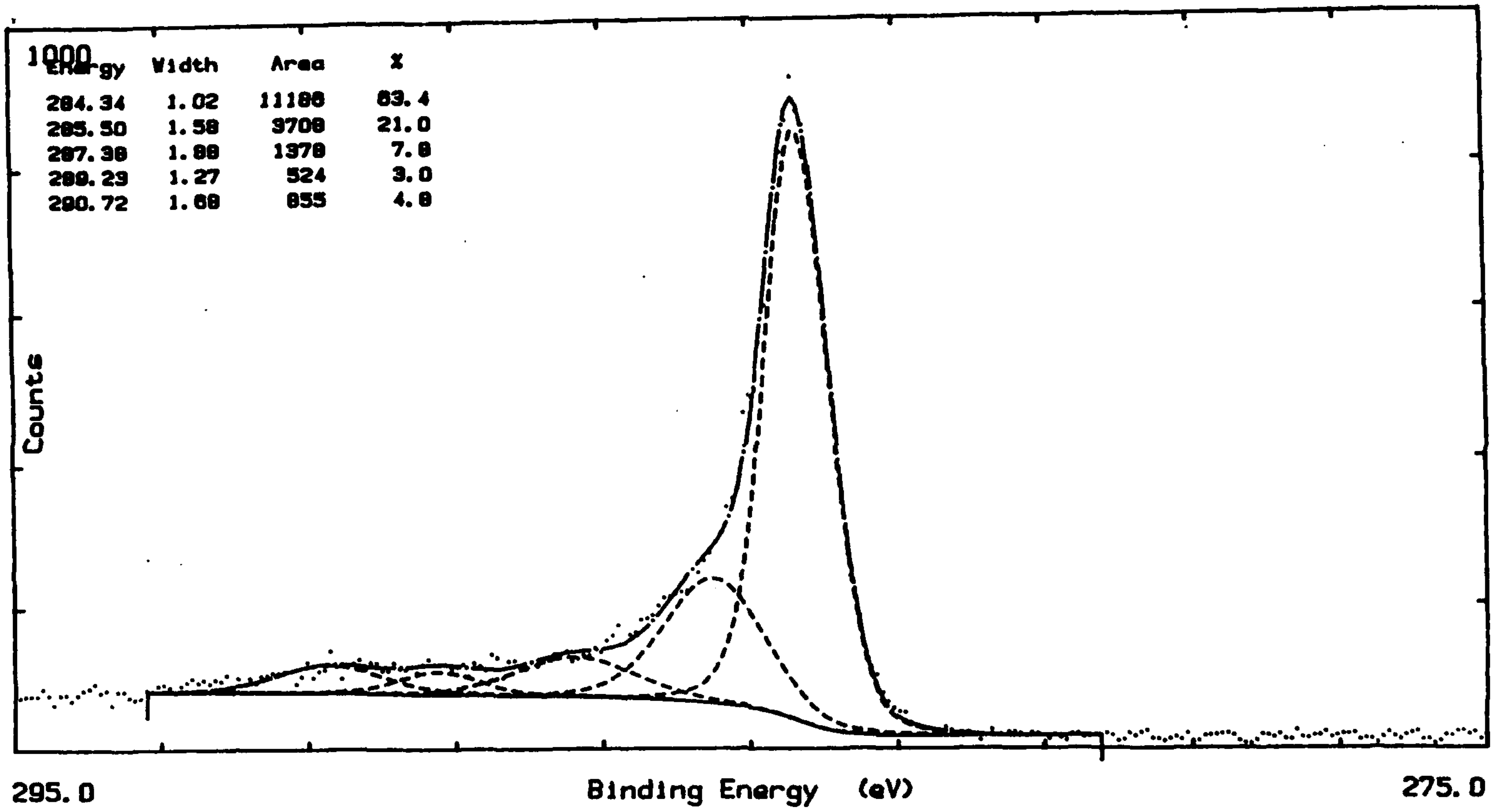


Figure 31: High Resolution C(1s) Spectrum of $Cu(dmg)_2$ Impregnated on BPL Carbon.

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Five organocopper complexes were impregnated on an activated carbon surface, and the surface composition of the resulting impregnated carbon investigated by X-ray photoelectron spectroscopy (XPS). From surface composition, and the high-resolution C(1s) and Cu($2p^{3/2}$) XPS spectra, the ratios of O/Cu, N/Cu, F/Cu and C/Cu could be calculated. It was found that three of the complexes were either unstable or decomposed on the carbon surface. This evidence could only be obtained by XPS technique, and the analytical method employed in this report.

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ACTIVATED CARBON
ORGANOCOPPER COMPLEXES
X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)