C.2.

ANALYTICAL APPLICATIONS OF X-RAY

PHOTOELECTRON SPECTROSCOPY

bу

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ABSTRACT

The surface-specific analytical technique of X-ray photoelectron spectroscopy (XPS) is described, and was used to study various geochemical materials and organic compounds.

Variation of surface pyrite density with coal particle size $(53-250\mu m)$ in a typical Canadian coal (Minto) provided some interesting data- it is very likely that as coal is crushed, one eventually reaches a particle size where the surface pyrite/carbon ratio maximizes. It is this parameter that is examined here, and correlations were found between (i) surface pyrite concentration, (ii) surface pyrite/sulfate ratio, and (iii) oxidized and non-oxidized sulfur with particle size. This is information which should find useful application in coal cleaning technology. For non-oxidized coal, we find the area of exposed pyrite on the coal surface is approximately inversely proportional to coal particle However, for oxidized coal the appearance of curves radius. depends on the oxidation times, but there is a particle size which exhibits maximum surface pyrite relative to 1/radius, corresponding the intercept point of the two linear to segments (low and higher values of 1/R) for the non-oxidized coal (fig. 3.9), and which is evidently that we will call the "characteristic" size of constituent pyrite.

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sulfur peaks from major sulfur constituents XPS other than sulfate in sediment recovered from Mahoney Lake (south-central British Columbia, Canada) show a surprisingly periodic variation in sulfur 2p binding energy (BE), and hence molecular structure, with sediment age. The pattern ceases at a core depth of about 3.2 meters, where a major deposit of fine sandy sediment occurs just below ash deposition (2.6m) from a major eruption of Mount Mazama. Oregon, approximately 6500 year ago, which led to the formation of Crater Lake. Sedimental sulfur exists mainly as sulfate; however, there is a pronounced increase in amount of the lower BE sulfur species relative to sulfate toward The "reduced" species also shows a trend lower depths. towards slightly higher oxidation level at lower depths. We are able to suggest the probable chemical forms in which the sulfur species exist, which is of interest 'to biologists working on sulfur transformation studies in lakes.

BE's for nitrogen 1s and sulfur 2p in the metal 3/2chelates of dibenzyldithiocarbamic acid M(DBDTC)_n for n=2, M=Cu(II) and Zn(II), and for n=3, M=Bi(III), have been measured. The nature of the spectral peaks and core BE's indicates that the nitrogen atom in the DBDTC is not intramolecularly bound with the metal as had been previously suggested. The relatively high BE's for the nitrogen 1s orbitals indicate planar geometry for the coordinated ligands, and the form $\left\{ {}^{b}S_{2}C \cdots {}^{b+}NR_{2} \right\}$ to reasonably represent their structure, which agrees with previous infrared studies.

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CHAPTER ONE

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

1.1: INTRODUCTION

a) Historical

One of the earliest references to the importance of the relationship between the surface composition of solid materials and its effect on the materials' properties, appeared in the illuminated manuscript "De Proprietatibus Rerum" (The Properties of Things) of 1250 AD:

"When a plate of gold shall be bonded with a plate of silver, or joined thereto, it is necessary to beware of three things, of dust, of wind, and of moisture: for if any come between the gold and silver they may not be joined together ...".

It remains a fact that the manner in which any solid surface interacts with its environment, or with any other solid surface, is determined by the precise nature of the specimen surface. Although bulk and surface compositions may be related, to a greater or lesser degree, it is generally accepted that the nature of a solid surface is influenced more by sample environment than the bulk.

Compositional, chemical state and molecular bonding information about the topmost atomic layers of solid specimens (metals, organic and inorganic chemicals, polymers and powders, fibres and films) is therefore crucial if we are to understand how they behave when placed in a particular environment. XPS is an excellent technique for supplying such information, and it has many applications in areas of science and technology where solid surfaces or interfaces are involved.

... As an analytical technique, XPS has its foundations in the pioneering work of Siegbahn and co-workers in Sweden during the 1950's. However, the history of the field goes back to the time of Heinrich Hertz , who in 1887 noticed that the maximum length of the spark of an induction coil is increased by illuminating the gap with ultraviolet light. had, in fact, produce photoelectrons between the gap He electrodes. In 1905, Einstein showed that the kinetic energy of the photoelectrons is equal to the quantum energy of the radiation minus the electron binding energy (BE) and the "work function" of the solid. This was called the "photoelectric effect". By reducing the X-ray wavelength it. was possible to investigate the ionization of inner electron shells. This was first called X-ray absorption-edge spectroscopy, and in 1920, Bergengren related the positions of X-

ray absorption-edges to oxidation states of atoms in various materials.

Ιt became clear that not only could later one profitably examine the absorption of X-rays in the direction of the X-ray beam, but also photoelectrons ejected at right angles to it. Siegbahn found that BE's of atomic electrons could be sufficiently affected by the chemical environment of that atom to produce a measureable shift in the photoelectron spectrum. termed the "chemical This was Realising that shift". any tool capable of readily differentiating between chemical states of the same element enormous potential in chemical analysis, Siegbahn had designated the new spectroscopy as Electron Spectroscopy for Chemical Analysis, or "ESCA", but it is more usually referred to as "XPS", or X-ray Photoelectron Spectroscopy.

For many years, XPS remained primarily an academic research technique, simply because of the expensive instrumentation required, and the necessity of taking extreme care in its application and interpretation. The advent of modern commercial spectrometers, however, has enabled spectroscopists to improve their understanding and of the technique to the point where it is a major use contributor in industrial analysis and problem solving, as well as in pure research.

b) Basic Principles

The basic photoionization process promotes an electron to the free electron level (fig.1.1). XPS, like UPS (ultraviolet Photoelectron Spectroscopy), is based on the same photoelectric effect, but employs soft X-rays to remove core rather than valence shell electrons . In the basic XPS experiment, a small (< 2 cm) sample surface is illuminated with X-rays, generally A1 K α (1486.60 eV) or Mg K α (1253.60 eV), -11 under high vacuum (10 torr). Ultra-high vacuum (10 -10 torr) is desirable when gas absorption on the surface is а factor, to ensure that surfaces once cleaned will remain free from contamination. High vacuum also ensures that photoelectrons emitted will have a sufficiently long mean free path to survive energy analysis to the detector .

In the XPS of solids, the sample is placed on a metal If the sample is metallic, there are two conductors probe. in contact and their Fermi levels will adjust to coincidence. If the sample is non-metallic, a sufficient number of free charge carriers are usually present in the sample for it to adjust to the thermodynamic equilibrium state and so again the Fermi levels will coincide. Figure 1.1 relates the BE, work functions, etc. relative to the Fermi level of the materials. If there is any difference in the work functions



- E = Energy
- E_T = Recoil Energy

 ϕ_{sp} = Work Function of Spectrometer

• Work Function of Sample

- CB = Conduction Band
- VB = Valence Band

FEL = Free Electron Level

E _ Energy of Exciting X-radiation

- KE ' = Kinetic Energy of Photoelectrons Before Entering the Monochromator
- KE = Kinetic Energy of Photoelectrons After Entering the Monochromator
- BE = Binding Energy of Core Level Electron Ejected

Figure 1.1: The Energy Levels Involved in XPS

of the spectrometer and samples, i.e. the energy required to move an electron from the Fermi level to free electron level, the result of the formation of a common Fermi level is to make the energy difference between the sample and the probe equal to the difference in their work functions.

Photoionization takes place in the sample surface. In the absence of electrical contact between the sample and the probe, the resultant photoelectrons have a kinetic energy KE' related to the X-ray energy hy by the Einstein relation:

$$KE' = h\vartheta - BE - \phi_s - E_r$$

where ϕ_s is the sample work function, and E_r is the recoil energy, resulting from conservation of momentum in the ejected electron parent-ion system. This equation can readily be understood by examining figure 1.1 again. In a real system with electrical contact between the spectrometer and the sample we have an additional term, the contact potential, V_c :

$$KE = hv - BE - \phi - E - V_{c}$$

where KE is slightly different from KE'. As already discussed, V_{c} is the difference between the work functions of the probe ϕ_{sp} and the sample. Thus we have, on substitut-ing for V_{c} and ϕ_{s} :

$$KE = hv - BE - \phi_{sp} - E_r$$

In practice the recoil energy is extremely small ($\langle \langle 1 eV \rangle$) and can be neglected. For Mg K α radiation, which is used in our laboratory, the maximum recoil energy is less than 0.1 eV, and E_r varies directly with X-ray energy and inversely with the mass of the parent atom . Moreover, the use of the level as a BE reference zero allows the Fermi same work function correction to be applied to all measurements, i.e. is constant for a given spectrometer. The above considerations lead to the simple relationship:

$$KE = hv - BE - \phi_{sp}$$

KE is well defined and any uncertainty in the determination of BE is due to the natural width of the level from which the electron has been ejected and to the width of the 9 incident X-ray line . In practice instrumental broadening will add to this (see below).

In XPS emission of photoelectrons with well-defined KE's results in photoelectron spectra -in effect direct images of the atomic energy levels if Koopmans' Theorem (KT) were true (see section 1.2c). Table 1.1 shows the variations of electron BE's with atomic number. The core of the constituent elements of a compound lines are characteristically atomic and their ordering does not depend chemical environment, which makes line assignment very оп Thus, information on electrons' BE's within a sample. easy . allows qualitative elemental analysis. Electron BE's within

	ELECTRON BINDING ENERGIES (CV)															
	15173 K	23.113 L1	2 2	L_{11}^{2}	Se in Mi	3.00 Ma	3p3/3 Mill	M3/3 M17	3d _{3/3} Му	40,1/2 N1	401/1 Nii	403/3 Nati	4d3/3 Nev	4d _{1,3} Ny	M3/3 Nvi	4(7/3 Nys
1 He 2 He 3 Be 5 B	14 22 55 11 14															
60 70 90 10	284 39919 5321 6861 867	341 31 45														
11 Na 12 Mg 13 Al 14 Si 15 P	10721 13051 15601 18391 21491	63) 89) 118) 149) 189)	74 100 136	11 12 73 99 135												
165 17 Ci 18 A 19 K 20 Ca	24721 28231 3203	2293 2703 3203 3773 4383	165 202 247 297 350	164 200 245 294 347	16 18 23 34 44	11 24										
21 Sc 22 Ti 23 V 24 Cr 25 Ma		5003 5643 6283 6953 7693	407 461 520 584 652	402 455 513 575 641	54 59 56 74	1111 111 11										
26 Fe 27 Co 28 Ni 29 Cu 30 Zn		846 ³ 926 ³ 1008 ³ 1096 ³ 1194	723 794 872 951 1044	710 779 855 931 1021	95 101 112 120 137	34 4 7 8										
31 Ga 32 Ge 33 As 34 Se 35 Br		1298 14134 1527 1654 1782'	1143 1249 1359 1476 1596 '	1116 1217 1323 1436 1550'	158 181 204 232 257	107 129 147 164 189	103 122 141 162 182	18 29 41 57 70	6 9	27						
36 Kr 37 Rb 38 Sr 39 Y 40 Zr		1921	1727	1675	289* 322 358 395 431	223 248 280 313 345	214 239 269 301 331	81 112 135 160 183	111 133 158 180	24 20 34 46 52	222					
41 Nb 42 Mo 43 Tc 44 Ru 45 Rh					469 505 544* 585 627	379 410 445 483 521	363 393 425 461 496	208 230 257 284 312	205 227 253 279 307	58 62 68* 75 81	15944					
46 Pd 47 Ag 48 Cd 49 In 50 Sn					670 717 770 826 884	559 602 651 702 757	531 571 617 664 715	340 373 411 451 494	335 367 404 443 485	86 95 108 122 137	62 51 67 77 89	' 56				
51 Sb 52 Te 53 I 54 Xe 55 Ca					944 1006 1072 1145* 1217	812 870 931 999 1065	766 819 875 937 998	537 582 631 685* 740	528 572 620 672 726	152 168 186 208* 231	99 110 123 147 172	162	32 40 50 63*	77		
56 Ba 57 La 58 Ce 59 Pr 60 Nd					1293 1362 1435 1511 1576	1137 1205 1273 1338 1403	1063 1124 1186 1243 1298	796 849 902 951 1000	781 832 884 931 978	253 271 290 305 316	192 206 224 237 244	180 192 208 218 225	93 99 111 114 118	90		
61 Pm 62 Sm 63 Eu 64 Gd 65 Tb					1650* 1724 1800 1881 1968	1472* 1542 1614 1689 1768	1357* 1421 1481 1544 1612	1052* 1107 1161 1218 1276	1027* 1081 1131 1186 1242	331* 347 360 376 398	255* 267 284 289 311	237° 249 257 271 286	121 130 134 141	•		
66 Dy 67 Ho 68 Er 69 Tm 70 Yb					2047 2128 2207 2307 2397	1842 1923 2006 2090 2172	1676 1741 1812 1885 1949	1332 1391 1453 1515 1576	1295 1351 1409 1468 1527	416 436 449 472 487	332 343 366 386 396	293 306 320 337 343	154 161 177 180 197	168 184		
71 Lu 72 Hf 73 Ta 74 W 75 Re					2491 2601 2708 2820 2932	2264 2365 246912 257513 268213	2024 2108 219413 228132 236733	1640 1716 179313 187213 194913	1589 1662 173513 181013 188313	506 538 566 595 625	410 437 465 492 \$18	359 380 405 426 445	205 224 242 259 274	195 214 230 246 260	1917 2717 3717 4717	1817 2517 3417 4517
76 Os 77 Ir 78 Pi 79 Au 80 Hg					3049 3174 3298 ²⁰ 3425 ¹³ 3562	279213 290913 302720 315013 3279	245813 255113 264630 274313 284713	203113 211613 220220 229113 238513	196013 204113 212130 220613 229513	655 690 724 ²⁰ 759 800	547 577 60835 644 677	469 495 51920 546 571	290 312 33130 352 379	273 295 31420 334 360	5217 6317 7420 8717 10317	5017 6017 7027 8317 9917
81 TI 82 Pb 83 Bi 84 Po 85 Al			;		3704 3851 399 913 4149 4317*	341613 355413 369712 3854 4008	295712 306713 317712 3302 3426	248513 258613 268813 2798 2909	239013 248413 258013 2683 2787	846 894 93913 995 1042*	722 764 80613 851 886	609 645 67913 705 740	407 435 46413 500 533	386 413 44013 473 507*	12217 14317 16317 184 210	11817 13817 15817
86 Rn 87 Fr 88 Ra 89 Ac 90 Th										1097* 1153* 1208* 1269* 1330**	929 980 1058 1080 116819	768 810 879 890 96813	567 603 636 675 71413	541° 577 603 639° 67713	238 268 299 319 344 13	3 3513
91 Pa 92 U 93 Np 94 Pu 95 Am										1387 144214 150128 1558 1617	1224 127314 132816 1377 1412	1007 104514 108718 1120 1136*	743 78014 81718 84916 879	708 73814 77315 80115 828	371 392 4151 422 440	360 381 4041#

Table 1.1: Orbital Ionization Potentials for Different Atoms *

any one element are far from fixed (fig.1.2), and variations (of up to 10 eV) may occur, depending on molecular environment. These so called "chemical shifts" may be used to provide valuable information on chemical 11 bonding.

After photoionization, the ion will revert to the ground state either by releasing a photon (X-rav fluorescence) or by electron (Auger) emission. In the former case the vacant orbital may be filled by an electron from an outer orbital and the energy emitted as an X-ray, while in the latter an electron from an outer orbital drops into the 10 primary hole, and other electron(s) are ejected (fig 1.3) . As an example of Auger terminology, KL L indicates that I III the primary vacancy occurred in the K shell, the $L_{_{T}}$ electron underwent a transition to fill the primary vacancy and a electron was ejected. The three processes are represented in the following equations:

> Photoionization: $M + hv(1) \longrightarrow M + e(1)$

X-ray Fluorescence: +* + +M - M + hv(2)Auger Emission: +* ++ -M - ---- M + e(2)

Relaxation Processes

where hv(1) is the exciting radiation.

Compound	E,	∆E,
Nitrogen		
CrN	396.6	0.0
VN	397.2	0.6
P ₃ N ₅	397.8	1.2
C,H,N	398.0	1.4
BN	398.2	1.6
C.H,CN	398.4	1.8
KSCN	398.5	1.9
NaN*NN*	399.3	2.7
(CONH ₁) ₂	400.0	3.4
Na ₂ (ON [•] NO ₂)	400.9	4.3
C.H.N	401.1	4.5
(C,H,),NCI	401.1	4.5
NaN ₂ O ₇	401.3	4.7
S.N.	402.1	5.5
NHOHCI	402.1	5.5
(CH.).NB.H.	402.2	5.6
(CH ₁),NO	402.2	5.6
Na(NN [•] N)	403.7	7.1
Na.(ONNºO.)	403.9	73
NaNO.	404 1	75
C.H.NO.	405 1	85
PNO CHLCONH.	405.9	0.5
$f_{rant}[Co(e_n), (NO_n), IN^{\bullet}O_n]$	406.8	10.2
NaN ^o .	407.4	10.2
Carbon	407.4	10.0
	201.0	-40
	201.0	_11
WC	201.7	-2.1
C (maphite)	2840	
C.H.CH.NH.	285 0	-0.7
C+H.COOH	285.0	0.0
С.Н.	285.0	0.0
KCN	285.0	0.0
	205.0	0.0
CHOR HIGH	787 7	27
Oxygen	407.2	4 4 -
5-5		
	530.3	0.0
(C.H.).PO	531 3	10
Na.SO.	531 9	16
FeSO.	532.5	2.2
C.H.O.SO.*	532.5	2.2
SOF.	533.0	2.7
ANO.	533.0	27
SOC1.	533.6	3.3
C.H.O.*SO.	534 1	3.7
~J0~J P.~ J		



Figure 1.2:

Electron Binding Energies for Some N-, C-O- and S- Containing Compounds



RELAXATION



Figure 1.3: Auger and X-ray Fluorescence Relaxation

The relative probabilities of Auger and X-ray emission are given in figure 1.4. Auger processes are dominant in light elements, which is an indication of the difficulty of X-ray fluorescence techniques in this area and the value of the XPS method. Auger electron spectroscopy (AES) is a surface analytical technique in its own right, and further information can be found in references 12-16.



Figure 1.4: Probability of Auger Electron Emission and X-ray Fluorescence as Function of Atomic Number

1.2: THE SURFACE ANALYTICAL TECHNIQUE OF XPS

a) Sampling Depth

The average sampling depth (depth from which photo-7 electrons may escape without inelastic scattering) from a solid is considerably less than the penetration depth of the exciting rediation. Table 1.2 gives typical penetration depths of photons, electrons, and ions in the energy range commonly used for surface analysis. A photon-in/ photon-out technique will clearly not normally be surface specific and either the beam-in or the beam-out must involve electrons or ions.

escape depth of a particle such as an electron The or ion depends on the energy of the photoelectron and the matrix environment through which it travels to the 17,18 ; the relationship surface of the escape depth οf 15 electrons versus KE is given in figure 1.5 . Notably, very low and high energy electrons have relatively large escape depths, the former of little use in analytical applications since thev mostly result from inelastic collisions. Electrons having energies of about 100 eV have the lowest escape depths, and so spectroscopy involving high energy or low energy electrons will likely not be surface specific. In XPS, however, the photoelectrons are usually in the 100-1000eV range, from depths of <10-20 Å, i.e. the first two or three molecular layers. For this reason, XPS is classified



Figure 1.5: Relationship Between Electron Escape Depth in Solids and Kinetic Energy

INCIDENT SPECIES	ENERGY(eV)	PENETRATION DEPTH(Å)					
PHOTON	1000	>10000					
ELECTRON	1000	20 10					
ION	1000						

TABLE 1.2 Penetration Depths of Particles into a Typical Solid Surface as a surface spectroscopy. Comprehensive data on experimentally determined escape depths are contained in reference 17. It is possible to use the variation in escape depths with kinetic energies to distinguish between elements which 19 are present on the surface . In section 1.2d, the effect of sampling depth on quantitative surface analysis will be discussed.

XPS must take surface impurities and constudies taminants into account. Contamination layer(s) usually comprise species adsorbed from the atmosphere, through handling, or orginating from the vacuum system. It is obviously highly desirable to have ultra-high vacuum and a sample preparation chamber in which samples may be cleaned prior to analysis. In our case, vacuum is achieved using extremely low vapour-pressure oil diffusion pumps in conjunction with the usual rotary backing pumps. The diffusion pump oils used in the Varian IEE-15 system are Convalex-10 and Neovac-SY which are polyphenyl ether and alkylated diphenyl ether, respectively.

b) <u>Calibration</u> of the <u>Binding</u> Energy Scale

In order to realize the potential of XPS fully, accurate calibration of the spectral energy scale is essential, since different chemical environments usually

cause only small (typically 1/10 to a few eV) shifts in peak position. Generally speaking, BE's are accurate to +0.2 eV in our measurements; however, having a solid sample makes calibration difficult in the following sense- the BE zero for a solid is arbitrarily set at the Fermi level, the highest electronic energy level that is occupied by an electron in conductors at room temperature, whereas for a is defined with respect to the ejected free molecule it electron at rest at infinity . Therefore, it is a natural choice for conductors to be used as standards, because in principle, any would define the Fermi level.

If one is bombarding a surface with charged particles or charged particles are emitted from a surface, sample charging may occur. This is a significant problem in all such spectroscopic techniques involving electrons or ions for example, sample charging can distort spectra and shift the location of peaks on the energy scale, the extent depending on the nature of the sample. For insulators, charging effects can be quite severe, while in conductors they are relatively small. Fortunately, the surface conductivity of most samples is much greater than the bulk conductivity, and so an even charge distribution builds up on the surface to a steady state value . In XPS there are frequently stray electrons in the vicinity of the sample which also help to reduce sample charge, especially in our spectrometer, in which electrons are ejected from the aluminum film between the X-ray source and sample. Because

of this conducting cloud the sample will assume a potential $$^{\rm 8}$$ very close to that of the film .

For insulators, there are two possible approaches to the calibration problem: one may attempt to prevent charge from building up on the sample or one can measure the magnitude of the charge and apply a correction. The first approach almost always employs stray electrons (as mentioned using an electron "flood gun" _ -that above) or by is а source of low energy (thermal) electrons from a heated filament. The second approach is to employ calibration material (internal or external) that effectively monitors surface charge and changes the spectrometer work function in the computer program to compensate. Using internal calibrants, when a series of related compounds is being examined, one signal from a common element in the compounds is chosen and all other signals are measured relative to it, which works quite satisfactorily. Also, an intimate mixture of sample with various inert materials of known BE such as graphite (our preference), metal oxides, and potassium 21.22 salts for can be used calibration purposes. Rationale of this internal procedure is that the surface charge produces a field around the sample which affects the KE of all photoelectrons, and hence all peaks experience the same shift. Use of external calibrants relies on the calibrant and sample being charged to the same extent. The peak of a graphite sample and the adhesive "scotch" С 1s

23 tape or the 4f peak of metallic gold are excellent 7/2,5/2 external calibrants. Table 1.3 summarizes some of the difficulties caused by sample charging.

c) <u>Chemical Shifts</u>

When atoms are brought close together to form molecules, the orbitals of individual atoms are perturbed and may then be represented by molecular orbitals (MO's). Since valenceshell electrons are directly involved in bonding, they are very sensitive to substituent and other structural effects, but because the MO's they occupy are generally multi-centred, it is not usually possible to identify the individual component atoms of a molecule from its valence-shell photo-Moreover, different types of valenceelectron spectrum. shell orbitals have very similar energies, resulting in adjacent bands in photoelectron overlap of spectra. However, inner core orbitals do retain their atomic identity to a greater extent, which allows XPS to provide a viable elemental analysis.

Notwithstanding the above comments, core electrons do suffer small changes in BE as their environment is changed. This may be explained by regarding individual atoms in a molecule as spheres of differing potentials. Inside each charged sphere the atomic potential, set up by charge shift to or from its surface to the neighbouring atom(s), is

PROBLEMS IN XPS:

DISTORTION OF SPECTRA Shifts of Peak Location Movement on Surface

EXTENT OF PROBLEM: INSULATORS > SEMICONDUCTORS > CONDUCTORS

COMPENSATION: SURFACE CONDUCTION STRAY ELECTRONS CALIBRATION FLOOD-GUN

Table 1.3: Difficulties Caused by Sample Charging

constant, according to classical electrostatics. The result of this change in atomic potential is a shift of the whole energy level system of any atom by a inner small 24,25 These changes or "chemical shifts" amount . due to electrostatic interaction allow useful structural deductions to be made from XPS spectra.

The application of XPS to the solution of structural problems can be simplified by developing methods for predicting reasonably accurate BE values for any particular structural formula one might propose for a given compound. These methods will not be described in detail here as quantitative chemical shift analysis has not been attempted in the work described in this thesis.

is important to mention Koopmans' Theorem (KT), It а factor usually involved in molecular orbital calculations 26-28 based on semi-empirical and empirical methods This 29 relates orbital energies theorem with the ionization energy obtained from photoelectron spectra, and is a useful approximation bridging experimental data and theoretical calculations. The theorem assumes that the molecular orbitals are unaltered ionization (frozen by orbital aproximation), thus the BE's calculated using KT usually differ from the actual experimental BE's. The most important limitation is the neglect of correlation energy between the neutral molecule and the ion -this should make the calculated

ionization energy too small. The further approximation that the electron interactions are exactly the same in the ion and molecule, which is manifestly not true, as the electrons in the ions can always attain a more stable state than the defined by their motions in the molecule, should give a one calculated ionization energy that is too high. In general, the cancellation of errors in using KT due to neglect of both correlation energy and electron interactions enables theorem to effect a good approximation for many small the molecules; however, there is substantial evidence which shows that use of KT is not justified where relativistic effects 30,31 (electron correlation and relaxation) are important The most accurate calculation is the "exact" Hartree-Fock SCF (self consistent field) methods; these have a serious disadvantage with regard to the size of computations involved.

In spite of these problems, good correlations between experimental chemical shifts and theoretical estimates of them, and therefore of the atomic potential, have been 32obtained . The simplest model is provided by the electro-33,34static point charge potential which relates the chemical shift, ΔE , of the atom to several factors:

$$\Delta E(i) = kq(i) + V + 1$$

where q(i) is the charge difference on an atom i between the molecule under consideration and a reference molecule, and V

is the interatomic effective potential, or molecular potential found from:

$$V = \sum_{j \neq i} q(i)/R_{ij}$$

The parameter k and 1 of the equation are constants determined by a least squares plot to fit the experimental data characterizing the type of chemical compound. The atomic charge can be estimated by Pauling's procedure . or 36 by CNDO (Complete Neglect of Differential Overlap) methods It is also possible to determine "group shift" parameters in which chemical shifts are represented by the sum of parameters characteristic of the atom(s) or substituent groups attached to the atom under consideration

d) <u>Interpretation</u> of <u>Data</u>

XPS is one of the most useful surface techniques to emerge into widespread use in the last decade. Providing the exciting energy is high enough, core level spectra can be obtained for all elements of the periodic table except H and He, and the BE's of these core levels are sufficiently unique for their unambiguous assignment (cf. table 1.1). Since the BE of an atom within the molecule reflects its environment, it should be possible to construct correlation tables (cf. fig.1.2) which would serve to identify the oxidation condition of an atom within a molecule and thereby help to identify its immediate environment.

When a photoelectron spectrum from the sample of interest has been obtained, analysis may be carried out at one or more of several levels of interpretation, where the degree of complexity of the task increases with the level of sophistication. At the lowest level, identification and assignment of the photoelectron peaks in the spectrum allow a qualitative analysis to be carried out. The analysis may be made quantitative to a fairly high degree of accuracy by measurement of relative photoelectron peak intensities or areas. Since the intensity of a core level peak from species X in the spectrum is proportional to the surface concentration of the species (where surface, here, means the top 2 nm less of the solid), it is possible to arrive at a value or for the surface concentration of X, providing the relevant sensitivity factors are known. Details of this procedure will be discussed later.

XPS sensitivity (in bulk terms) is only about 0.1 atom % for elements with average cross-sections; however, its surface specificity puts it in a much higher class as a 37 analytical tool . Sophisticated spectrum deconvolution is 8 necessary to obtain high resolution spectra in some cases , and from these the absolute BE's of the core levels can be measured (to within 0.1 eV), and the presence of any fine structure detected (such as multiplet splitting, shake-up etc). Knowledge of the core level BE and fine structure

permits more rigorous assignments of the features to be made, since it is possible to distinguish more easily between different oxidation states of an element, or even to infer the presence of particular chemical species such as the various form of pyrite (further information may be found in references 10, 39 and 40).

The intensity of a peak derived from a given orbital is proportional to photon flux, orbital occupancy and the photoionization cross-section of the orbital (see table 1.4) . The cross-section varies in a complex way with a number of factors such as the shape, size and number of nodes of the orbital and the energy of the ionization radiation . Peak intensity may also be affected by other processes which take place, such as "shake-up" and "shake-off" . In the former, electron is excited to a higher level an within the molecules at an expenditure of E^*eV , resulting in a peak $\mathbf{E}^{\star}\mathbf{eV}$ above the main ionization peak. A "shake-off" process is one in which a second electron is ejected, giving rise to double ionization.

Notwithstanding these difficulties, Wendt et al. and 43,44 Swingle have used a simplified expression relating measured photoelectron intensity to fundamental parameters, for an infinitely thick sample:

$$I(j) = K\gamma(j)N(j) / S(j)$$

. .

where I(j) is the peak intensity corresponding to photo-

	1+1/2	2=1/2	201/2	203/2	3+1/2	301/2	3p3/2	343/2	345/2	41/2	⁴ P1/2	4p3/2	4d3/2	4d5/2	4/5/2	4/7/2	5=1/2	501/2	5p3/2	5-13/2	3d 5/2	5/5/2	517/2	6-1/2	6p1/2	6ø3/2
1 H 2 He 3 Li 4 Be 5 B	0.0002 0.0089 0.059 0.200 0.492	0.0008 0.007 0.022																						<u> </u>	<u>-</u> -	
6 C 7 N 8 O 9 F 10 Ne	1.00 1.78 2.85 4.26 5.95	0.047 0.084 0.134 0.199 0.277	0.0006 0.0025 0.0073 0.0178 0.0381	0.0012 0.0049 0.0145 0.0352 0.0751																						
11 Ne 12 Mg 13 Al 14 Si 15 P	7.99	0.390 0.325 0.681 0.855 1.05	0.0714 0.121 0.193 0.292 0.422	0.141 0.239 0.380 0.573 0.828	0.0059 0.0261 0.0485 0.0726 0.0998	0.0012 0.0050 0.0129	0.0023 0.0097 0.0253																			
16 S 17 Cl 18 Ar 19 K 20 Ca		1.25 1.48 1.71 1.96 2.21	0.590 0.810 1.06 1.37 1.74	1.155 1.564 2.07 2.67 3.39	0.130 0.163 0.199 0.249 0.305	0.0269 0.0493 0.0503 0.122 0,169	0.0527 0.0963 0.161 0.238 0.330			0.006 0.023									×							
21 Se 22 Ti 23 V 24 Cr 25 Mn		2.46 2.72 2.98 3.23 3.45	2.18 2.68 3.26 3.92 4.63	4.24 5.22 6.33 7.60 8.99	0.356 0.408 0.462 0.511 0.575	0.216 0.268 0.326 0.382 0.460	0.420 0.521 0.633 0.740 0.892	0.002 0.006 0.014 0.030 0.048	0.003 0.009 0.021 0.044 0.071	0.027 0.031 0.034 0.014 0.040	, , , ,															
26 Fe 27 Co 28 Ni 29 Cu 30 Zn		3.70 3.92 4.16 4.38 4.55	8.43 6.28 7.18 8.18 9.29	10.5 12.2 13.9 15.9 18.0	0.634 0.693 0.753 0.805 0.873	0.535 0.616 0.701 0.779 0.882	1.04 1.19 1.36 1.50 1.70	0.079 0.122 0.181 0.268 0.365	0.116 0.179 0.26* 0.390 0.532	0.043 0.945 0.048 0.019 0.052																
31 Gn 32 Ge 33 As 34 Se 35 Br			10.6	20.5 21.2	0.943 1.02 1.10 1.18 1.26	0.993 1.11 1.24 1.37 1.50	1.92 2.15 2.40 2.65 2.92	0.485 0.631 0.602 1.00 1.24	0.708 0.920 1.17 1.46 1.80	0.074 0.094 0.114 0.134 0.156	0.006 0.018 0.037 0.064 0.100	0.011 0.034 0.071 0.123 0.191													·	
36 Kr 37 Rb 38 Sr 39 Y 40 Zr					1.35 1.43 1.52 1.61 1.70	1.64 1.79 1.93 2.08 2.24	3.20 3.48 3.78 4.09 4.40	1.50 1.81 2.15 2.54 2.97	2.19 2.63 3.14 3.70 4.33	0.178 0.209 0.242 0.273 0.303	0.144 0.187 0.230 0.268 0.307	0.276 0.361 0.445 0.521 0.596	0.013 0.035	0.019 0.051			0.006 0.021 0.025 0.029									·
41 NB 42 Mo 43 Tc 44 Ru 45 Rh					1.79 1.89 1.98 2.07 2.15	2.39 2.54 2.69 2.84 2.98	4.71 5.03 5.36 5.68 6.00	3.45 3.97 4.54 6.17 5.84	5.01 5.77 6.60 7.51 \$.48	0.333 0.364 0.397 0.429 0.463	0.340 0.379 0.419 0.460 0.501	0.661 0.739 0.818 0.899 0.981	0.082 0.130 0.192 0.269 0.365	0.118 0.187 0.276 0.387 0.524			0.013 0.014 0.015 0.016 0.016								·	

t

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Table 1.4: Photoelectric Cross-sections Relative to C ls Level for Mg Ka (1253.60 eV) Radiation
													<u> </u>													
	141/2	241/2	2p1/2	203/2	3+1/2	3p1/2	303/2	3d3/2	3d 5/2	4+1/2 4	P1/2	403/2	41312	4/3/2	41512	417/2	5-1/2	5p1/2	5p3/2	5rf 3/2	543/2	M8/2	5/7/2	6-1/2	621/2	6P3/2
46 Pd 47 Ag 48 Cd 49 In 50 Sn					2.24 2.33 2.40 2.48 2.54	3.12 3.25 3.39 3.51 3.62	6.33 6.64 6.96 7.27 7.58	6.58 7.36 8.22 9.13 10.1	9.54 10.7 11.9 13.2 14.6	0.494 0 0.531 0 0.571 0 0.611 0 0.653 0	.538 .586 .636 .689 .743	1.06 1.15 1.26 1.37 1.48	0.495 0.616 0.747 0.893 1.05	0.707 0.884 1.07 1.29 1.51			0.018 0.046 0.063 0.076	0.00% 0.017	0.011 0.031			-				
51 Sb 52 Te 53 l 54 Xe 55 Cs					2.60 2.67 2.75 2.83 2.84	3.71 3.79 3.87 3.95 4.04	7,86 8,14 8,37 8,64 8,94	11.1 12.2 13.3 14.5 15.8	16.1 17.7 19.3 21.1 22.9	0.696 0 0.741 0 0.785 0 0.831 0 0.877 1	.799 .856 .913 .971 .03	1.60 1.73 1.86 1.99 2.12	1.22 1.40 1.58 1.78 1.99	1.76 2.01 2.29 2.57 2.88			0.090 0.104 0.117 0.132 0.152	0.033 0.054 0.080 0.112 0.140	0.063 0.104 0.156 0.218 0.278					0.005		
56 Ba 57 La 58 Ce 59 Pr 60 Nd						4.10 4.06	9,26 9.52 9.67 9.75	17.0 18.2 19.7 21.1 22.6	24.8 26.5 28.6 30.7 32.9	0.924 1 0.971 1 1.00 1 1.04 1 1.07 1	.09 .15 .18 .22 .26	2,26 2,40 2,49 2,59 2,70	2.21 2.44 2.58 2.76 2.95	3.20 3.53 3.74 4.00 4.28	0.069 0.126 0.200	0.088 0.161 0.257	0.174 0.193 0.189 0.196 0.202	0.166 0.189 0.180 0.186 0.191	0.334 0.382 0.365 0.378 0.390	0.019	0.027			0.017 0.021 0.018 0.018 0.018		
61 Pm 4 62 Sm 63 Eu 64 Gd 65 Tb								24.3 26.1 28.2 24.3	35.3 37.9 40.9 43.4 20.8	1.10 1 1.14 1 1.17 1 1.20 1 1.22 1	.30 .34 .37 .41 .43	2.81 2.91 3.01 3.13 3.21	3.14 3.33 3.51 3.73 3.88	4.55 4.82 5.09 5.41 5.61	0.296 0.416 0.562 0.693 0.949	0.378 0.531 0.718 0.687 1.21	0.208 0.213 0.219 0.235 0.228	0.196 0.201 0.205 0.223 0.211	0.400 0.412 0.422 0.465 0.440	0.032	0.031			0.018 0.019 0.019 0.022 0.019		
66 Dy 67 Ho 68 Er 69 Tm 70 Yb										1.25 1 1.27 1 1.29 1 1.31 1 1.32 1	.45 .47 .49 .50 .51	3.30 3.39 3.48 3.56 3.64	4.05 4.22 4.39 4.56 4.72	5.67 6.13 6.37 6.62 6.85	1.20 1.49 1.82 2.20 2.63	1.52 1.89 2.31 2.78 3.33	0.232 0.237 0.240 0.244 0.244	0.214 0.216 0.219 0.220 0.222	0.449 0.457 0.464 0.471 0.478					6.019 0.019 0.019 0.019		
71 Lu 72 Hf 73 Te 74 W 75 Re										1.34 1 1.36 1 1.38 1 1.39 1 1.41 1	.52 .53 .54 .55	3.73 3.83 3.93 4.03 4.13	4.91 -5.10 5.29 5.48 5.67	7.13 7.42 7.15 8.01 8.30	3.05 3.50 3.99 4.92 5.08	3.87 4.45 8.08 8.75 6.46	0.261 0.271 0.290 0.306 0.321	0.237 0.252 0.268 0.283 0.299	0.519 0.562 0.606 0.651 0.697	0.021 0.054 0.098 0.152 0.217	0.029 0.074 0.136 0.212 0.303			0.023 0.026 0.029 0.031		
76 Os 77 îr 78 Pt 79 Au 80 Hg										1.42 1 1.43 1 1.44 1 1.45 1 1.45 1	.55 .55 .54 .53 .52	4.24 4,34 4.45 4.55 4.65	5.86 6.05 6.24 6.42 6.60	8.60 8.90 9.20 9.50 9.79	5.67 6.30 6.97 7.68 8.43	7.22 8.03 8.87 9.79 10.8	0.337 0.350 0.366 0.380 0.397	0.314 0.324 0.340 0.353 0.368	0.743 0.774 0.825 0.877 0.935	0.293 0.431 0.508 0.619 0.707	0.410 0.593 0.709 0.865 0.997			0.033 0.017 0.017 0.017		
81 TI 82 Pb 83 Bi										1.46 1 1.46 1 1.44 1	1.50 1.47 1.45	4.75 4.86 4.96	6,78 6,94 7,11	10.1 10.4 10.6	9.22 10.0 10.9	11.8 12.8 14.0	0.413 0.430 0.446	0.383 0.398 0.412	0.996 1.06 1.12	0.804 0.900 0.997	1.14 1.29 1.44			0.051 0.059 0.068	0.004 0.011 0.021	0.008 0.023 0.046

Table 1.4 (cont.)

electron j, γ (j) is the emissivity of atom j (approximated by the atomic photoelectric cross-section), N(j) is the number of these atoms per cubic centimeter, K is an instrument response function dependent on the KE of the photoelectron and S(j) is the total photoelectron scattering coefficient in cm⁻¹.

Electron scattering accounts for surface sensitivity of XPS, and S(j) is inversely related to the inelastic mean free path or escape depth, Å (as mention in section 1.2a). Moreover Å vs KE plots show that in the region of interest for XPS, $\overset{\circ}{A}$ is approximately a function of E (see fig 5), which also explains why S (or \tilde{A}) may not be the same for each component (j) of a surface, because Å for an electron determined by its KE. The KE of a photoelectron is is in function of the BE which, of course, will turn a be different for each component. The K term varies approximately as E^{-1} for instruments employing fixed analyzer transmission energies (as in our spectrometer), or as E for those employing fixed retardation ratios of emitted electron KE to analyzer pass energies. The former type of instrument tends to be more common and, since both K and S(j) are inversely proportional to KE in this case, some degree of cancellation results in the previous equation, and I(j) will correlate 41.45-47 reasonably well with $\gamma(j)$ and N(j)

The concentration distribution of a measured species as

a function of depth can seriously affect quantitative surface measurements, because the concentration of the species can vary from the outermost surface layer into the bulk, i.e. N(j) will vary with different surface layers. In order to investigate the variation of composition with depth, the sample may be etched using an ion beam, thereby enabling the establishment of a composition depth 18,48 profile

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CHAPTER TWO

INSTRUMENTATION

2.1 INTRODUCTION

Ιn XPS spectrometer an X-ray flux irradiates ап the target sample and the ejected photoelectrons enter an electron analyzer to be subsequently detected. Since the number of ionization events is so small (typically 10 /sec), pulse counting techniques must be used. Pulses are counted and recorded in a manner suitable for data analysis. An XPS spectrometer should have resolution sufficient to reveal the influence of the chemical surroundings upon the energy levels, and sensitivity as high as possible; however, as in many forms of spectroscopy, a compromise must be reached since the two requirements conflict.

A Varian IEE-15 ("Induced Electron Emission") solid phase X-ray photoelectron spectrometer was used in the work described in this thesis. The spectrometer was extensively upgraded as part of this work, and now functions as well if not better than when new. In this chapter the spectrometer will be described in some detail. A brief description of 1,2 the spectrometer has also appeared elsewhere

2.2: THE VARIAN IEE-15 SPECTROMETER

a) General Considerations

A block diagram of the IEE spectrometer, illustrating the main components, is shown in figure 2.1. The spectrometer system contains an X-ray source, a vacuum system, an electrostatic electron analyzer, a Varian 620/i computer, an IEE/computer interface with ASR33 teletypewriter, an X-Y recorder, and an oscilloscope for spectral display.

Most of the constituent parts of the spectrometer (Xray anode, electron multiplier, ion and electron sources) will operate only in high vacuum. Moreover, as mentioned before, the high surface sensitivity of XPS requires as good vacuum as possible in order to maintain a clean sample even at 10 surface. However torr, exposure to high а vacuum system for 1 h will approximate monolayer coverage . Fortunately, if the sample is not susceptible to degradation by small amounts of residual gases such as oxygen, water, vacuum pump fluid vapours, a vacuum in the range of 10 --8 10 torr may be tolerated. The normal background pressure in the present IEE spectrometer is about 1x10 torr, and is by employing two pumping systems and baking maintained the chambers. Since a bakeable valve is used to separate the sample preparation (inlet) chamber from the analyzer chamber, regions are pumped separately by oil these two diffusion (285 L/sec for the former and 1500 L/sec pumps for the



Figure 2.1:

Block Diagram of the Varian Spectrometer

IEE-15

XPS

latter), fitted with baffles and water cold traps to minimize backstreaming of pump oil into the system. Each diffusion pump is backed by a rotary pump, and in addition, a liquid nitrogen-cooled trap is fitted before each chamber to condense water and pump oil vapors, the two major potential Moreover, the sample can be changed without contaminants. affecting conditions in the analyzer. The vacuum lock through which sample transferral takes place must not be - 5 opened until the preparation chamber is below 10 torr. otherwise rupture of the delicate aluminum foil window $(7\mu m)$ would occur. This thin window is used to separate the X-ray tube and sample; moreover, it also prevents low energy radiation from causing undesirable effects in the sample, and scattered electrons from the X-ray gun reaching the sample . As mentioned previously, low energy electrons from inside of the window serve to neutralize sample the charging.

fraction of the photoelectrons produced Α from the sample pass through the annular entrance slit into the spherical analyzer, essentially two concentric spheres with a potential difference between them. The electron image of the entrance slit is at the annular exit slit, electrons passing through being focussed on the aperture of a berillium-copper electron multiplier (see fig.2.2). Typically, a positive voltage is applied to the sample so that initial photoelectrons are retarded to 100 eV upon passing through the entrance slit. The geometry of the



Figure 2.2: Schematic of the IEE-15 Spectrometer Analyzer retarded region does not appear to be critical as long as electrons entering the analyzer originate from a11 а strongly irradiated portion of sample surface. However, the photoelectrons' paths are constrained to prevent second order aberrations from degrading the resolution of the Therefore, given resolution, analyzer. at а the photoelectrons' transmission is limited by the slit-width and second order angular aberrations. The effect of angular aberration is most easily visualized as in the case of throwing a ball in a uniform gravitational field. The ball will travel the maximum horizontal distance when it is launched at 45°. If S is the distance thrown, and S_0 is the maximum distance then:

$$S - S_o = -2S_o (\Theta - \widetilde{\Pi}/4)^2$$

 S_0 is a first order focal point with second order aberrations. This is a general expression valid for focussing of charged 1,2 particles in electric and magnetic fields.

XPS spectrum is generated by varying the voltage An applied to the sample, with respect to the analyzer entrance slit. This has the advantage that the analyzer deflection voltages remain fixed and the resolution of the analyzer remains constant throughout a scan. One can improve the analyzer resolution by reducing the energy at which the electrons are analyzed. Nominally, electrons are analyzed at an energy of 100 eV, and with the spectrometer designed

for 1% resolution , we commonly obtain a total spectrometer doublet of ~1.7 eV full width resolution for the Au 4f 7/2,5/2 (including the Mg K α radiation linewidth of half maximum about 0.7 eV, figure 2.3). With an X-ray power output of 280 watts, an electron count rate of >10,000 counts/sec can obtained at this peak maximum. In order to obtain be а perfect registry of the image of the annular entrance slit onto the annular exit slit, it is necessary to use an electrostatic octopole focus corrector to adjust the position and shape of the final electron image (see fig. 2.2).

In summary, the spectrometer has the following features:

1. Spherical analyzer

6

2. Electron retardation between sample and analyzer

3. Electronically variable resolution

4. Annular source and detector slits

5. Annular X-ray tube (to be discussed in the next section)

6. Octopole focus adjustment

 Cylindrical electron filter between analyzer and detector

Since electron paths are influenced by magnetic fields, is necessary that the electron trajectory be determined it the field of the analyzer, and so only by earth's the magnetic field (~ 500 mG) in the vicinity of an electron must be nullified. This may be done by using spectrometer or ferromagnetic shielding Helmholtz coils materials ;



BINDING ENERGY (eV)

Figure 2.3: XPS Spectrum of the 4f Gold Doublet 7/2,5/2

however, a basic Helmholtz system compensates only for static and not for varying magnetic fields. In practice, fluctuations in field can be observed in the 2-10 mG region depending upon time of day and day of the week. Therefore the electrostatic analyzer used in the IEE spectrometer is shielded by a double layer of mu-metal, about 1 foot in diameter and 4 feet high, which reduces the earth's magnetic field to ~0.3 mG at the spectrometer center.

b) The X-ray Source

An ideal X-ray source should provides an intense. constant level of sample radiation. The simplest type for in XPS is one which utilizes characteristic emission use lines from an anode bombarded by high energy electrons. The energies of these lines are dependent only on the anode material. In addition to these characteristic lines, a continuous spectrum dependent upon the primary electron energy (Bremsstrählung) is also produced from the X-ray increases the background level tube. which of the photoelectron spectrum. However, a more serious problem concerns X-ray satellite lines. The most commonly used X – ray lines in XPS are the Al and Mg K $\alpha_{1,2}$ emission lines, which have linewidths of 0.85 eV and 0.7 eV and energies of 1486.60 eV and 1253.60 eV respectively. The $K\alpha_{1,2}$ line is essentially an unresolved doublet resulting from 2 p 3/2, 1/2

to ls transitions; however, lines resulting from similar 10 transitions within multiply ionized atoms $(K\alpha_3, K\alpha_4)$ and from valence band to 1s transition (K β) are also present. In the case of Al (and Mg) there are two satellites about 10 eV the high energy side of the main X-ray line which are produced by transitions involving the K hole of a doubly ionized atom. In XPS spectra these K_{α}^{α} and K_{α}^{α} satellites can interfere and obscure weak peaks. As mentioned before, one of the primary limitions on instrumental resolution is the X-ray bandwidth; the narrower this is the more accurate be the information obtained. Hence, when considering will the choice of a suitable X-ray line, linewidth is always a major consideration, the other being the energy itself since this determines the actual atomic orbitals which can be ionized.

Recently, there has been considerable interest in the use of X-ray sources other than the traditional Mg and Al K α , since alternation of source energies would increase the flexibility of the technique. Obviously harder X-ray sources deeper core levels accessible; however, although make more photoelectron peaks would by obtained, the X-ray linewidth increases so there is some reduction in accuracy in determinating peak positions. Some characteristic X-ray energies and linewidths of the sources that have been used in XPS 7.11 are given in table 2.1. These represent a wide range of energies available to photoeject core electrons of most elements of interest. The comparative broadness of the X-

Line	Be	Υ	Zr	Nb	Мо	Ru	Rh	С	Ti	Ti	O	Cr
	K	Μζ	Mζ	Mζ	Мζ	Μζ	Mζ	К	Li	La	K	La
Energy (eV)	108.9	132.3	151.4	171.4	192.3	236.9	260.1	278	395.3	452.2	524.9	572.8
Width (eV)	5.0	0.47	0.77		1.53	2.49	4.0	6	3	3	4	3
Line	Ne Ka	Ni La	Cu La	Zn La	Na Ka	Mg Ka	Al Ka	Zr La	Ti Ka	Cr Ka	Cu Ka	
Energy (eV)	849	851.5	929.7 1	1011.7 1	1041.0 1	1253.61	1486.6	2042	4510	5417	8048	
Width (eV)	0.3	2.5	3.8	2.0	0.42	0.7	0.85	1.7	2.0	2.1	2.6	

Table 2.1: Some X-ray Lines Used in XPS

ray sources, together with their attendant satellites (K α and $K\beta$ is undesirable, because they overlap with other features in the spectrum. In modern commercial instruments, the source is often monochromatized using a quartz crystal diffraction grating to yield a narrow X-ray line devoid of Typically the Al K α line may be reduced from satellites. 0.85 to 0.6 eV FWHM. The X-ray flux is usually somewhat reduced. As a result, the monochromated source is used only in circumstances where sufficient benefit is derived from its narrow linewidth to offset the reduction in sensitivity. Synchrotron radiation is also available and gives high count rates. This radiation is produced by electrons accelerated in a ring under static magnetic field conditions, yielding a 12 tunable continuous radiation of high intensity Obviously synchrotron facility is large and expensive, but many successful XPS experiments have been done at Stanford, Madison, etc.

X-ray source used in this study is shown in The fig. 2.4. Electrons produced by thermionic emission from a hot annular tungsten filament (0.18mm diameter) strike the anode of the annular X-ray tube, creating Mg K α X-radiation at a photon energy of 1253.60 eV. Several supports are provided so the filament does not distort upon heating. The anode is copper, vacuum-coated with approximately 0.3 cm of high-The X-ray tube is maintained at $\sim 2 \times 10$ grade magnesium. torr under typical operating conditions in order to prevent voltage breakdown, and to increase filament lifetime.



Figure 2.4: The X-ray Tube Assembly

Disadvantages in the traditional X-ray design are that fast elastically scattered electrons from the anode can strike the aluminum window, and the line-of-sight design results in contamination of the anode by evaporation of the filament material. The latter factor clearly results in attentuation of X-ray flux and introduces impurity lines. The former generate Al K α X-rays and can secondary electrons in the window which may then irradiate the sample. presence of Al K α is a disadvantage if an Mg anode The is secondary electrons can cause in use; also sample degradation . Fortunately some of these electrons can Ъe thermalized to reduce sample charging (mentioned above). Τo bypass such problems a positive potential (7-10 kV)is applied to the anode while the filament, maintained at ground potential, is placed out of direct line-of-sight of 13 anode . The positive potential ensures that scattered the electrons are drawn back towards the anode and do not strike the window. Since the anode cannot "see" the cathode, a cylindrical stainless steel shield between the anode tubing and the filament is introduced to focus the electron beam onto the face of the anode.

To prevent destruction of the aluminum window and the anode itself by overheating, the X-ray tube is water-cooled using electrically insulated pipes, and the anode itself is insulated from ground by ceramic/metal seals. Anode potentials between 7 to 10 kV give efficient production of

characteristic radiation from Mg -operation of the X-ray gun below 5 kV is avoided since space charge around the filament would limit the electron current.

c) <u>The Sample</u>

In principle, any type of sample, including gases and 14 liquids , may be studied by XPS. However, the instrumental design of the IEE-15 spectrometer restricts us to low vapour torr) solids. The sample is inserted through pressure (<10 vacuum lock and its temperature can be cooled by liquid а nitrogen flowing in the interior of the probe. Use of such permits a wide range of materials a. probe to be investigated. The sample size must be of diameter <1cm; however, the spectrometer can accommodate three samples simultaneously on the sample holder. The sample must not. 15.16 of course, decompose under high vacuum

Methods of sample mounting are numerous, and are often dictated by the nature of the sample itself. Bulk solid samples may be held in a clip. Powdered samples are finely ground (pestle/mortar) and spread on single-sided adhesive "scotch" tape attached to the probe with sticky side out. This method is widely used but leads to a longer recovery time for the pressure in the sample chamber because of outgassing of the adhesive tape. Either method can be used for fibre samples. It is worth noting, with regard to the sample insertion mechanism, that if a cooled probe is being used a teflon 'O'ring contracts and may cause undesirable movement of the probe, possibly causing loss of vacuum.

d) Data Collection

An intrinsic problem in this type of spectrometer is the low signal/background (S/B) count ratio. The background is mainly due to the continuum radiation produced by deceleration of the primary electrons on hitting the X-ray target (Bremsstrahlung radiation). The ratio may be improved by X-ray monochromatization but this option is not available for the Varian instrument.

The computer is programmed to control most of the spectrometer functions. The program will time average up to 2000 channels of data in up to 10 discrete regions. Different combinations of number of channels, scan time (1-1000 sec), scan width (1-100 eV) and number of scans (1-999)allow optimum choice of parameters. Increase of source intensity will result in improving data only to a point, if increased source intensity does not induce even sample decomposition, since high source intensity is accompanied by real increase in background. The S/B ratio can be an improved by accumulation of data over a period of time with

multiple scanning. Random noise should cancel, while real signals reinforce. When the counting statistics are sufficiently good, accumulation of data may be terminated and the data stored for later use. This type of signal enhancement is particularly important when one is dealing with weak signals, such as from fractional monolayers on a surface. Moreover, the data may be smoothed by least squares 6 fitting to polynomials before being plotted.

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CHAPTER THREE

THE DEPENDENCY OF PYRITE OXIDATION IN COAL ON PARTICLE SIZE

3.1: INTRODUCTION

is a complex material of variable composition Coal on both the macroscopic and microscopic levels, and often contains significant quantities of sulfur in the form of associated minerals such as pyrites and /or sulfur in part of the coal organic combination as substance . The major elements present in coal are carbon, hydrogen and oxygen, with minor quantities of sulfur, silicon, nitrogen, aluminum. iron, calcium, magnesium, potassium, sodium and titanium. etc. Carbon is by far the major element present, and combined with smaller amounts of hydrogen and oxygen provides the structural integrity and most of the heat content and reducing power of the fuel. Despite the obvious structural complexities and composition variables, there has considerable speculation concerning the structure been of called a "typical coal molecule". be what might For 2 example, Sheer has proposed a complex structure (fig.3.1) in which aromatic and aliphatic units are linked together in the basic coal structure.



Figure 3.1: A Proposed Structure for Coal

Coal is а resource certain to be available to meet future energy demands for some considerable time; however, major cause of air pollution has been shown to the arise from combustion of fossil fuel to form sulfur oxides harmful to both industry and the ecosystem. Moreover, sulfur is a potential contributor to spontaneous combustion of coals in mines and stockpiles and the pollution of ground water flowing from or through coal mines . Generally, the higher the sulfur content the worse the problems, which has led to government legislation imposing stringent controls on coal utilization.

Certainly, a better understanding of the nature and distribution of sulfur-bearing minerals and organic sulfurcontaining functional groups and their concomitant chemistry have a desirable impact on coal preparation will processes the environmental acceptability of coal-derived energy. and ASTM practice is to analyze for various Current forms of 4.5 sulfur in coal such as organic, pyritic, and sulfatic Determination of organic sulfur is carried out by а subtraction technique, which, being indirect, tends to accumulate errors involved in the inorganic analyses (themselves somewhat unreliable and tedious) . Clearly, an instrumental method giving a direct quantitative indication of coal-associated sulfur would be most desirable.

Comparatively few XPS studies have been reported relat- 8-18 12-18 ing to geochemical materials and coal science ,

which is surprising since the properties of coal surfaces play such an important role in a number of coal utilization technologies. Flotation, coal-liquid mixing and coking all depend on the chemical nature of coal properties 18 surfaces . Since initial interaction of a solid with its via its surface, XPS has obvious environment occurs advantages.

Of the available methods for controlling sulfur oxide emissions, the physical removal of pyritic sulfur prior to combustion is the most technologically developed and cost-19 has been employed in our effective • XPS laboratory before , to study the sulfur atoms' molecular environment in various coals. Since XPS S 2p peaks from the probable coal-organic sulfide- or thiol- (R-S-R',-SH), disulfide-(R-S-S-R'), or thiophene- (R-I) type sulfur moieties 12,13 can be expected to overlap with the pyrite S 2p Deak 3/2 study suggested that surface pyrite could further be separated by oxidation to reveal and directly measure the 17 organic sulfur present . Coal-cleaning methods are normally capable of removing only pyrite, and not organically bonded since only pyrite may be oxidized to soluble sulfur. 12 sulfatic salt . Therefore, one of the important factors in pyrite elimination would appear to involve crushing the coal the point where surface pyrite maximizes, which our to experiments indicate it to do. We call this the "characteristic" size, and refer to it later.

3.2: EXPERIMENTAL

Experimental conditions are as described in Chapter 2.

Bu1k Minto coal samples as received from Chemical Engineering UBC were crushed very gently before sievescreening, to produce particles ranging from 53 to 250 µm in diameter, which were immediately placed inside а vacuum desiccator until analysis. Some samples were oxidized b v using the "Blue M" controlled temperature and humidity chamber, under 99+1 % relative humidity at 45 °C for two different intervals (3 and 15 h) to see if pyrite oxidation was time dependent. Table 3.1 indicates the appropriate settings of wet and dry bulb temperatures for a particular relative humidity. Samples were mounted on the XPS sample holder before oxidation and subsequent analysed in the The XPS S 2p IEE-15. and C ls peak heights were used to calculate the ratios of pyrite to sulfate, pyrite to carbon, and sulfate to carbon. BE's were accurate to ± 0.2 eV.

Relatively low X-ray intensities (280 watts) in exposures of about 1 h were used to minimize radiation damage, and in fact no evidence for sample deterioration was detected. For all coal samples, spectrometer settings were maintained constant in order to remove spectrometer

* Manufacturer: Blue M Electric Co., Blue Island, Illinois, USA

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12 14 16 18 20	94 95 95 95 96	89 90 90 90 91	84 84 85 86 87	78 79 91 82 82	73 74 76 78 78	68 69 71 73 74	63 65 67 69 70	58 00 62 65 65	53 55 58 61 62	48 81 54 57 88	38 41 45 49 51	30 33 37 42 44	21 24 29 35 36	12 16 21 27 30	4 10 14 20 23	7 13 17	6 11																	12 14 16 18 20
22 24 26 28 30	96 96 96 98 98 98	92 92 92 92 93	87 88 89 89 89	83 85 85 85 85	79 81 81 82 82	75 77 77 78 79	72 74 74 75 76	68 70 71 72 73	64 66 67 68 70	60 63 64 65 67	53 56 57 59 61	48 49 51 53 55	40 43 45 47 50	34 37 39 42 44	27 31 34 37 39	21 26 28 31 35	16 21 23 26 3 0	11 14 18 21 24	10 13 17 20	13 16	12													22 24 26 28 30
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52 54 56 58 60	97 97 97 97 98	94 95 95 95	92 92 92 93 93	89 90 90 90	87 87 87 85 85	84 85 85 85 85	82 82 83 83 83	79 90 90 90 80	77 78 78 79 79	75 76 76 77 77	70 71 72 72 73	66 67 68 68 69	62 63 64 65	59 59 60 61 62	55 56 57 57 58	51 52 53 54 55	48 49 50 51 52	44 45 46 47 48	41 42 43 44 45	38 39 40 42 43	35 36 3× 39 40	30 31 32 33 35	23 26 27 29 30	20 21 23 24 26	16 17 19 20 21	11 13 15 16 18	11 12 14	11						52 54 56 58 60
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82 84 86 88 90	98 98 98 98 98	96 96 96 96 97	94 94 95 95	92 92 92 93 93	90 90 91 91 91	88 88 89 89 89	86 86 87 87 87	84 85 85 85 85	83 83 83 83 84	81 81 82 82 82	77 78 78 78 78	74 74 75 75 76	71 71 72 72 73	68 68 69 69 69	65 65 66 67	62 62 63 63 64	59 59 60 60 61	56 57 57 58 58	54 54 53 53 56	51 52 52 53 53	49 49 50 51 51	44 45 45 46 47	40 40 41 42 42	36 37 37 38 39	32 33 34 34 35	29 29 30 31 32	25 26 27 28 28	22 23 24 25 26	20 20 21 22 23	17 18 19 19 20	15 16 16 17 18	12 13 14 15 16	10 11 12 13 14	82 84 85 88 90
92 94 96 98 100	98 99 99 99 99	97 97 97 97 97	95 95 95 95 95	93 93 93 93 93	91 91 91 92 92	89 89 90 90 90	87 88 88 88 88	86 86 86 86 86	84 84 85 85	82 83 83 83 83	79 79 80 80 80	76 76 76 77 77	73 73 74 74 74	70 70 70 71 71	67 67 68 68 69	64 65 65 65 66	61 62 63 63	50 59 60 60 60	56 57 57 58 58	54 54 55 55 56	52 52 53 53 54	47 48 49 49	43 44 45 45	39 40 41 41 42	36 36 37 38 38	32 33 34 34 35	29 30 31 31 32	26 27 28 28 29	24 24 25 26 26	21 22 22 23 24	19 19 20 21 22	16 17 18 19 19	14 15 16 16 17	92 94 95 98 100

Table 3.1: Centigrade Table of Relative Humidity

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variations from the analyses as much as possible. Moreover, all BE determinations were referenced to the C ls peak from graphite at 284 eV (fig. 3.2).

3.3: RESULTS AND DISCUSSION

Typical C ls and S 2p spectra from "3M" Scotch tape are shown in figure 3.3. This C ls BE is shifted from that of the carbon in coal or graphite, reflecting the different chemical environments of carbon in these materials. Carbon to study by XPS because of the is difficult high concentration of carbon present in the adhesive tape and the of contamination of sample possibility surfaces by hydrocarbon present in the pumping system. To minimize background carbon, the liquid nitrogen traps are kept filled at all times, the adhesive tape should be completely covered with sample, and all samples should be scanned for carbon at interval after the introduction the same time into the This procedure does permit a spectrometer. relative calibration procedure as illustrated in figure 3.4. Sulfur analysis normally should not present the same problems as carbon, since insufficient sulfur-containing species are present and able to affect the samples during the course of this work.

Probably the most valuable aspect of the XPS technique is its ability to provide information on the electronic



Figure 3.2: XPS Spectrum of Carbon 1s/Graphite



BINDING ENERGY (eV)

Figure 3.3: Carbon 1s and Sulfur 2p XPS Spectra for '3M' Scotch Tape



Figure 3.4:

Correlation Between XPS C ls Peak Height and the % by Weight of Carbon Present in Sample (The error bar is the estimated maximum error)

environment of a surface atom (see reference 8). This will be valuable in studies relating to flotation mechanisms in reactions between solids and solvated species since the outermost atomic layers of the solid are primarily involved, and the coal flotation process is based on differences in 20 surface properties . Moreover, the S 2p peak provides a good indication of the S oxidation state, since the sulfur atomic electrons are particularly sensitive to their atomic environment. XPS is sensitive enough to be used to detect low level pyrite oxidation in coal at a very early stage, when oxygen incorporation is too low to be detected by conventional analysis.

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Washability tests must be conducted to determine the proper method and equipment needed in deep-cleaning; these involve stage crushing to release impurities and specific gravity fractionation to determine the quality and quantity 20.21 of the cleaned product Even though these tests • are extremely valuable in predicting washability, they are costly. We demonstrate here how XPS information can be used give maximum washing efficiency by indicating one of the to important conditions for pyrite elimination, the best size of coal particle to use.

XPS spectra of coal samples usually showed two S 2p 3/2 XPS peaks, with a separation averaging 5.5 eV. These are assigned to iron sulfides (163.5 eV) and iron sulfate (169.0

eV). Surface oxidation often arises during sample preparation (e.g. grinding); in fact several workers have related the effects of ester cross-linkage development 22 - 24during oxidation to deterioration of coking A slight • shoulder to the higher BE side of the main hydrocarbon XPS peak is characteristic of carbon singly bonded to 17,18 Referring to our XPS measurements, it appears oxygen • that our fresh coal was low in sulfatic sulfur (fig. 3.5), but significant amounts appear in weathered or oxidized samples (figs. 3.6 & 3.7). It appears, then, that surface oxidation is not significant when samples are prepared by crushing at ambient conditions, the S 2p spectra showing little or no sulfate (and the C ls peak no shoulder). In the process of crushing, there may well be a degree of preferential cleavage along the mineral planes which will reduce the amount of heat generated and hence surface oxidation.

As shown in figures 3.8 and 3.9, the pyrite/carbon ratio measured by XPS decreases as particle size increases, which is consistent with having relatively more pyrite dispersed over the coal surface in small coal particles than for large ones. Furthermore, relatively less photoelectrons will be ejected from S atoms in larger pyrite particles as compared to those escaping from small ones. Therefore, the pyrite/carbon intensity ratio is approximately inversely proportional to radius for non-oxidized samples. This has a possible implication that pyrite is finely dispersed or

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Figure 3.5: Carbon 1s and Sulfur 2p XPS Spectra of 3/2 Non-oxidized (fresh) Minto Coal Samples for Different Particle Size



Figure 3.6: Carbon 1s and Sulfur 2p XPS Spectra for 3/2 Minto Coal Samples of Different Particle Sizes After 3 h Oxidation



Figure 3.7: Carbon 1s and Sulfur 2p XPS Spectra for 3/2 Minto Coal Samples of Different Particle Sizes After 15 h Oxidation





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Figure 3.9: Minto Coal Pyrite/Carbon vs Particle Radius "The significance of the intercept point I is explained in the text, page 71". (The error bar is the estimated maximum error)

homogeneously distributed in Minto coal, since otherwise linearity in figure 3.8 will not be obtained. The above observation may also reflect the fracture mechanism of the 18 coal particles .

After the non-oxidized samples were exposed to humid air for some hours, the sulfate peak increased in intensity, the sulfide peak decreased (figs. 3.6 & 3.7). and The oxidation was performed under mild conditions (99+1 % relative humidity at 45 $^{\circ}$ C) since temperatures >75 $^{\circ}$ C could result in loss of S-containing molecules from the sample surface and deterioration of for instance, . coking 22-24 properties as mentioned above. during oxidation Figures 3.6 & 3.7 show no evidence of such deterioration. XPS results on pyrite oxidation after 3 and 15 h are shown in figures 3.10 & 3.11 where we see pyrite maximized and sulfate minimized at $53+3\mu$ m in radius. Note that prolonged exposure to humid air does not change this "characteristic" pyrite size for the coal we are using here. The same explanation can be applied to the rising portion of the curve as for non-oxidized coal. However, when one progressively approaches the smaller particle size, surface oxidation to be dominant, and the pyrite oxidizes rapidly to seems sulfate regardless of the particle size at which maximum pyrite surface concentration occurs. This is because at this stage one is crushing pyrite itself and surface oxidation will likely be approximately inversely dependent on radius,







Figure 3.11: Minto Coal Pyrite/SO₄ ; SO₄ /C; Pyrite/C vs 1/Particle Radius (After 15 h Oxidation) (For error estimation see table 3.2)

i.e. the smaller the pyrite particle size on the coal, the faster oxidation. the rate of Incidentally, this "characteristic" size also corresponds to the intercepts of the curve extremities (point I) for the non-oxidized coal pyrite/carbon versus particle radius curve in figure 3.9. The mathematical implications of this are by no means clear.

The results obtained may be applied as a partition apparatus for producing coal particles which are of optimum cleaning size since they are close to the same size as the pyrite clusters. This optimum size is almost certainly rankdependent, owing to variations in morphology, and mode of coal evolution arising from the geochemical environments in 5which the minerals were originally formed.

The determination of the intensity of XPS peaks is important if quantitative analysis is desired. However, it is often difficult to determine a "base" reference level in spectrum. Ιn this study, an appropriate base line а is formed by base line extrapolation. The base lines for a set of spectra from similar samples are approximately parallel, which improves the accuracy of our ratio values (i.e. the inelastically scattered electron spectrum and all the peak widths will be very similar). Table 3.2 summarizes the relative peak intensities of the fresh and oxidized coal samples.

			:	FR	ESH	THREE HOURS OXIDATION				FIFTEEN HOURS OXIDATION							
ſ	SIZE	RADIUS	RADIUS ⁻¹	Fe-S/C		Fe-S/C		Fe-S/S04 2-		so ₄ ²⁻ /c		Fe-S/C		Fe-S/S04 ²⁻		so ₄ ²⁻ /c	
L	(µm)	(mu)	(x10 - <u>µm</u> -1)	max	min	max	min	max	min	max	min	max	min	max	min	max	min
	53.0	26.5	3.77	.589	.572	.300	.292	.375	.363	.809	.796	.371	.356	.328	.314	1.14	1.12
L	61.0	30.5	3.28	.573	.544	.386	.373	.973	.940	.404	.395	.365	.358	.410	.402	.897	.884
	75.0	37.5	2.67	.513	.494	.396	.387	1.11	1.08	.361	.353	.458	.444	.515	.500	.896	.884
	90.0	45.0	2.22	.484	.460	.410	.400	1.38	1.32	.304	.295	.455	.445	.540	.523	.849	.838
	106.0	53.0	1.89	.458	.434	.436	.428	1.55	1.49	. 288	.280	.496	.482	.910	.872	.558	.534
	125.0	62.5	1.60	.439	.424	. 390	.382	1.35	1.30	.295	.288	.486	.475	.811	.790	.608	.594
Ł	150.0	75.0	1.33	.423	.397	.380	.372	1.24	1.20	.312	.303	.401	.392	.674	.656	.602	.591
	180.0	90.0	1.11	.414	.392	.355	.350	1.13	1.10	.319	.314	.395	.383	.562	.543	.710	.699
	208.0	104.0	0.96	.400	.386	.338	.329	.502	.487	.679	.670	.381	.371	.541	.526	.710	•698
	250.0	125.0	0.80	.401	.376	-	-	-	-	-	-	.344	.334	.333	.322	1.04	1.03

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Table 3.2: Ratios of XPS Peak Heights at Various Particle Sizes for Fresh and Oxidized Samples of Minto Coal It is believed that coal surface characterization obtained by XPS after various conditioning steps, and during flotation, could well allow both "chemical shift" analysis, and semi-quantitative analysis based on relative intensity measurements.

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CHAPTER FOUR

SULFUR SPECIATION IN LAKE SEDIMENT

4.1: INTRODUCTION

Various sulfur-containing compounds have long been known to be major pollutants in many industrialized parts of the world . Sulfur, an essential biological nutrient, is found in both organic and inorganic forms. In living material it is present primarily in its most reduced states, for example as -SH. When organic S-compounds are decomposed by bacteria, the initial product is generally the reduced form hydrogen sulphide. Since sulfate, as sulfuric 2.3 acid, is a major component of acidic precipitation а clear understanding of S dynamics and diagenesis in lakes is desirable since S transformations markedly affect this most F.5 acidification process

Mahoney Lake is a small hypersaline meromictic lake (20 m deep) located in southeast British Columbia, with the sediment being preserved much as it was laid down originally. The seasonal changes in its various 6.7 limnological features have been described , and it appears that sulfur in its many oxidation states plays a dominant

role in the chemical and biological processes occurring in this lake.

The elemental composition of the surface layers can be reasonably related to the origins of the sediments, because lake sediments and their interfaces with overlying water are 8,9 major sites for sulfur accumulation and transformation Moreover, geochemical reactions occur often only to a depth of a few atomic layers, thus an analytical technique with high surface sensitivity such as XPS is ideally suited to elemental composition as well as the chemical analyse the 10 - 12state(s) of molecules present which may bе of 13 geochemical and/or mineralogical interest

Although geologists have made ample use of Scanning Electron Microscopy-Energy Dispersive X-ray Analysis (SEM-EDX) and Electron Microprobe Analysis (EMA), such techniques are seldom able to identify unambiguously the phase(s) present, and so they are often only of value for preliminary 10 surveys of surfaces . Moreover, current ASTM practice to analyze various forms of sulfur is also somewhat unreliable and tedious (see Chapter three).

XPS has recently found application in several environ-14-17 mental studies and here we have attempted to characterize, in a general way, the distribution of the inorganic and organic S constituents in a core of Mahoney Lake sediments.

4.2: EXPERIMENTAL

Experimental conditions are as described in chapter 2.

The sediment sample upon receipted from Professor T.Northcote and his associates (Zoology Department UBC) was subdivided into many 10 cm sections to a depth of 455 cm, which were stored in a vacuum desiccator at about -15 °C until analysis. X-ray power of 320 watts was used, and no evidence of sample decomposition during analysis was seen. The electron BE's were standardized against the potassium 2p (294.0 eV) line 3/2 3/7 mixture of potassium chloride/sample. from а The measurements were repeated after exposure of the samples to air for two months, and no changes were seen.

4.3: RESULTS AND DISCUSSION

Sulfur can accumulate by decomposition of particulate or be derived by immobilization of soluble matter forms. 18 predominantly sulfate, from the water . All the XPS S spectra show two peaks- one representing sulfur atoms 2p in the sulphate ion and the second, sulfur in more reduced Some typical spectra are shown in figure 4.1. forms. The second peak, slightly broader, has a maximum value of ΒE



Figure 4.1: Sulfur 2p XPS Spectra of Some Mahoney 3/2 Lake Sediments (at indicated core sample depths)



Figure 4.1 (cont.)

which varies with sediment depth in a remarkably periodic way (fig. 4.2).

Many sulfur-containing molecules have been studied by 19 XPS , and hence we are able to predict the most likely Scontaining species at the various depths, as indicated in figure 4.2. The S distribution in the sediment profile reflects the exchanges of sulfate among other inorganic and 20 organic S-constituents . We find a progressive decline of total sulphate concentration with sediment depth, to the point where at 400 cm the lower BE S represents about 40% of the total sulfur, (Whereas for example, at 35 cm depth it was only about 16 %).

Although organic sulfur compounds often lead to formation of hydrogen sulfide in water. it is of interest that Desulfovibrio bacteria can reduce SO_4^{2-} to H_2S by utilizing it in the oxidation of organic matter²¹:

$$SO_4^{2-} + 2(CH_2O) + 2H^+ \longrightarrow H_2S + 2CO_2 + 2H_2O$$

Bacterial generation of H_2S from sulfate ions, with subsequent formation of iron sulfides, has been clearly established in coastal lagoons and lakes/oceans in which salinities and sulphate contents are high and organic 22productivity is not dominant. Therefore, the major pathway for incorporation of S in sediment may well be through sulfate reduction and the formation of Fe-S compounds of low solubilities. For example, in a lake



SEDIMENT DEPTH (cm)

Figure 4.2: Sulfur 2p Binding Energies of the Pre-3/2 dominant "Lower Oxidation State" Sulfur Species in Mahoney Lake Sediments (The error bar is the estimated maximum error)

experimentally acidified with sulphuric acid, Fe-S compounds found to be concentrated at the sediment were surface process of pyrite formation originates as the result of The the reaction of dissolved hydrogen sulfide with fine-18 minerals. However, Berner grained iron noted that the substances which form by the reaction of iron minerals or dissolved ferrous ion with hydrogen sulfide under simulated sedimentary conditions in the laboratory are mainly noncrystalline Fe-S, and gregite (cubic-Fe S). None of these thermodynamically stable phases is under sedimentary conditions. Therefore the final transformation of these metastables (iron sulfides to pyrite) is believed to involve elemental with sulfur the reactions Moreover. incorporation of labelled aqueous SO_4^{2-} by organic matter observed to be bacterially mobilized has been and then recovered both ester- and carbon-bonded s. as The biodegradation of the S-containing amino acids cysteine, and methionine can result in production of volatile cystine S compounds such as methyl thiol organic and dimethyl disulfide; however, carbon-bonded sulfides and polysulfides are released as HS or possibly as mercaptans, which if hydrolyzed may also contribute further to pyrite 22 above processes would account formation The for the proncunced increase of organic/pyritic sulfur and loss of sulfate in the basal zone.

The fluctuations evident in figure 4.1 & 4.2 depend on 20 a complexity of abiotic, biotic and watershed factors and

may well prove to be a useful index in assessing various limnological processes, in which transformation and translocation of S in its many oxidation states play critical roles in the chemical and biological energetics of 4,5 lakes .

With our present instrumental resolution it is impossible to separate the contributions of the various organic S compounds to the 'reduced' peak at low BE. Also, signals from sulfur in certain Fe-S compounds (i.e. FeS, FeS₂, Fe₃₄), may be superposed, and so the average elemental compositions of the surface layers of the material as indicated here may deviate from those given by total analysis . However, the strength of XPS analysis is in providing data which reflects the origin and/or the history of the sediment samples, which have acted as centres for sulfur accumulation and transformation. The interpretation of these data is an ongoing project in conjunction with other analytical studies on N, O and P etc. in the sample core, in our laboratory and in the Zoology Department UBC.

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CHAPTER FIVE

THE BONDING OF DIBENZYLDITHIOCARBAMATE METAL COMPLEXES

5.1: INTRODUCTION

Dithiocarbamate metal chelates are used in a wide variety of chemical processes including rubber vulcanization and the production of agricultural fungicides and 1 pesticides. Soluble dithiocarbamate salts have found extensive application in the extraction of metal chelates from 2 acid solutions, and the chemical and physical properties of these complexes are of much interest, particularly the nature of the nitrogen-metal bonding.

3,4 5,6 Previous experimental data from NMR, IR and elect-7 8-12 ron spectroscopy, as well as XPS have indicated two possibilities for the bonding in these compounds:





TYPE I

TYPE II

Structure I illustrates the long-held view that the ligand stable four-membered chelate ring. forms a Early XPS studies supported this idea solely on the basis of the 8 - 11existence of only one broad sulphur 2p peak : however recent XPS studies on N 1s BE's in Cu(II)-, Pb(II)- and Sn(II)- diethyldithiocarbamate complexes by Cheng et al. suggested that there may exist an additional bond between N atom and the metal M (structure II) to the form a second four-membered ring, since they found the BE of the N to be approximately the same as that in the $1\,\mathrm{s}$ peak complexes formed between the ions of the alkaline earths 13 and EDTA (ethylenediaminetetraacetic acid), where the N atoms are certainly coordinated to the metal ion.

In order to clarify this issue, we extended the XPS studies to include the more thermally stable Cu(II), Zn(II) and Bi(III) dibenzyldithiocarbamate (DBDTC) compounds.

5.2: EXPERIMENTAL

a) Preparation of Metal-Dibenzyldithiocarbamate Chelate:

The metal {Cu(II) and Bi(III)} chelates were synthesized by the general procedure outlined for the 12 synthesis of diethyldithiocarbamic acids. Zinc-DBDTC was obtained from Eastman Kodak Chemical Company and was recrystallized using a 1:1 mixture of chloroform and

ethanol as solvent. The sodium salt of DBDTC was prepared from Zn-DBDTC by ion exchange, and the other chelates were 14 then synthesized from the sodium salt. The chelate precipitates were filtered, washed with water, dried in vacuum, and finally recrystallized from another chloroformethanol solvent.

b) Instrumental

The liquid nitrogen cooled probe was used in this study, to minimize sample decomposition. Since metal chelated dithiocarbamates powders are electrical insulators, all BE's were calibrated with reference to the potassium 2p peak (294.0 eV) from a 3/7 mixture of potassium 3/2 chloride/sample as an internal standard.

5.3: RESULTS AND DISCUSSION

The study of the structure of inorganic or organic complexes by XPS is often hampered by the decomposition of the compounds during measurement. We obtained N ls BE data on the dibenzyldithiocarbamate metal complexes containing Cu(II), Zn(II), and Bi(III), choosing benzyl compounds in preference to the less stable ethyl derivative compounds used in previous studies, -even so, with the lowest practical X-ray power and sample probe cooled by liquid nitrogen, the

hydrogen and sodium complexes decomposed in the spectrometer The data obtained from the remaining complexes are given in table 5.1, and the spectra are shown in figures 5.1 and 5.2.

Our results show that from Zn(II) to Bi(III) DBDTC the BE increases, but the N 1s BE remains essentially S 2p 3/2 opposed to the case of the similar molecules unchanged, as CuH2-EDTA and BiH-EDTA, where there is N-M bonding, and see a difference in N ls BE of approximately where we 2.0 eV. This is a strong indication that N is not bonded to the metal in the DBDTC complexes. Furthermore. the N 1sin the DBDTC complexes have a BE of about 1.0 electrons e۷ greater than "neutral" nitrogen in triphenylamine, which suggests that the N-C bond in $\left\{ \begin{array}{c} 8+\\ R\\ N \end{array} \right\}^{8+} CS = 1$ is polar, leading to local planarity , as has been previously observed in the 15.16 X-ray crystallography studies of diethyl complexes.

PEAK	SAMPLE	BINDING ENERGY (eV)	PEAK WIDTH (eV) FWHM				
N ls	Zn(DBDTC)	400.50	2.10				
	Cu(DBDTC)	400.55	2.16				
	CuH (EDTA)	400.20	2.85				
	Bi(DBDTC)	400.50	1.95				
	BiH(EDTA)	402.25	2.47				
S 2p	Zn(DBDTC)	162.20	2.75				
5/2	Cu(DBDTC)	162.20	2.61				
	Bi(DBDTC)	162.60	2.67				

Table 5.1: XPS Data on Some Dibenzyldithiocarbamates, $Cu(II)H_2$ -EDTA and Bi(III)H-EDTA



Figure 5.1: Nitrogen 1s XPS Spectra of Some Dibenzyldithiocarbamates, Cu(II)H_-EDTA and Bi(III)H-EDTA



Figure 5.2: Sulfur 2p XPS Spectra of Some Dibenzyl-3/2 dithiocarbamates

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SUMMARY

The minimal perturbing effect of the photoelectron makes X-ray photoelectron spectroscopy an excellent technique for surface analysis of almost any type of solid sample. The sample can take any shape or form, and often needs no special preparation prior to analysis.

High resolution XPS instruments are now commercially available, the use of which can lead to much improved information on chemical bonding in addition to basic elemental analysis.

The study on coal demonstrates how the XPS technique may bе used to study how the relationships between concentration ratios involving sulfur in pyrite and sulfate. and carbon, on coal surfaces are dependent оп particle size. It also gives information to improve sulfur elimination in coal cleaning processes, particularly flotation, that depend on differences in surface properties. This should have significant economic implications, for reduction instance in capital investment required for preparation plant equipment and operational costs relating to the flow variables of mineral dressing. Moreover, the results also reinforce the importance of XPS intensity ratios as a measure of element dispersion.

There are few studies which have considered the depth distribution of sulfur in sediments. The sulfur content in sedimental deposits from Mahoney Lake is primarily of two types at any particular depth, -sulfate, and a second, which is probably a mixture of several sulfur compounds in similar oxidation forms, which displays a remarkable cyclic variation of oxidation state (more properly, sulfur atom electronic environment) with depth beneath the lake bottom. The change in proportion of sulfur in SO_4^{2-} to S in other forms, with time (lake sediment depth in our case), most probably results from S exchange reactions in the lake itself. Moreover, portions of this sulfur pool are labile as reflected in temporal fluctuations.

Clearly, XPS has a great potential for studying sulfur dynamics in lakes, and hence to obtain information on the role of this element in limnetic nutrient cycles, as well as for identification of geologic surface structures. However to obtain accurate identification and quantification of such complex heterogeneous materials spectra of much higher resolution and sensitivity such as could be provided bv today's state-of-art instruments would be needed, especially when studying lakes of lower sulfur content than Mahoney.

In the DBDTC complexes studied, S 2p binding energies 3/2 are shown to vary with the oxidation state of the metal. The same change in oxidation state has no effect on the N ls

peak, -strong evidence that there is no metal-nitrogen interaction and consequently no intramolecular N-M bond, as had been previously thought to be the case.

XPS is now a well established surface analytical tool, finding widespread application in both fundamental research and industrial problem-solving. It is likely to become increasingly valuable as both our knowledge and understanding of surface chemistry increases, and the power of the technique becomes more widely recognized.