

Average Matrix Relative Sensitivity Factors (AMRSFs) for X-ray Photoelectron Spectroscopy (XPS)

These tables and plots contain AMRSFs for XPS calculated for the total peak area for all core levels with greater than 17 eV binding energy for both Mg and Al K α X-rays for instruments operated at the magic angle where, classically the effect of the dipole anisotropy parameter, β , is removed. At the magic angle, the angle between the incident photon beam and the detected photoelectrons is 54.7°. The background to, and use of, AMRSFs, I_i^{Av} , is discussed by Seah, Gilmore and Spencer [1] and also in ISO 18118 [2]. For homogeneous solids, the atomic fraction of element A, X_A , is given by

$$X_A = \frac{I_{\text{Am}} / I_A^{\text{Av}}}{\sum_i I_{im} / I_i^{\text{Av}}} \quad (1)$$

where the I_{im} are the measured peak area intensities for the element i in the sample m .

These AMRSFs are based on theory and are thus for use with spectrometers for which the intensity/energy response function is calibrated [3] or otherwise known [4]. They are unlikely to be as accurate, for quantification, as properly determined experimental sensitivity factors, measured on the instrument with the correct settings for which they are intended to be used [2].

It should be noted that these AMRSFs are thought to be valid for all systems, irrespective of the chemical state, but are only valid for a correct measure of the peak areas. The most correct general background to remove for homogeneous solids is Tougaard's background [5]. It is very common to use Shirley's background [6] but this does not give intensities that either agree with Tougaard's background or with theory [7]. These AMRSFs are not for use with Shirley's background.

The calculations of the AMRSFs use the procedure of Seah, Gilmore and Spencer [1] in which the AMRSFs, for the core level X in the element A, are given by:

$$I_{AX}^{\text{Av}} = n_{AX_i} \sigma_{AX_i}(hv) N_{\text{Av}} Q_{\text{Av}} \lambda_{\text{Av}}(E_{AX_i}) \quad (2)$$

where n_{AX_i} is the population of the level X_i , $\sigma_{AX_i}(hv)$ is photoionisation cross section for each electron in the core level X_i in the element A for X-ray photoelectrons of energy $h\nu$, N_{Av} is the atomic density of the average matrix, Q_{Av} is a term allowing for the reduction in overall escape probability of electrons from the average solid arising from elastic scattering, $\lambda_{\text{Av}}(E_{AX})$ is the inelastic mean free path (IMFP) for the Auger electrons with average energy E_{AX_i} in the average matrix.

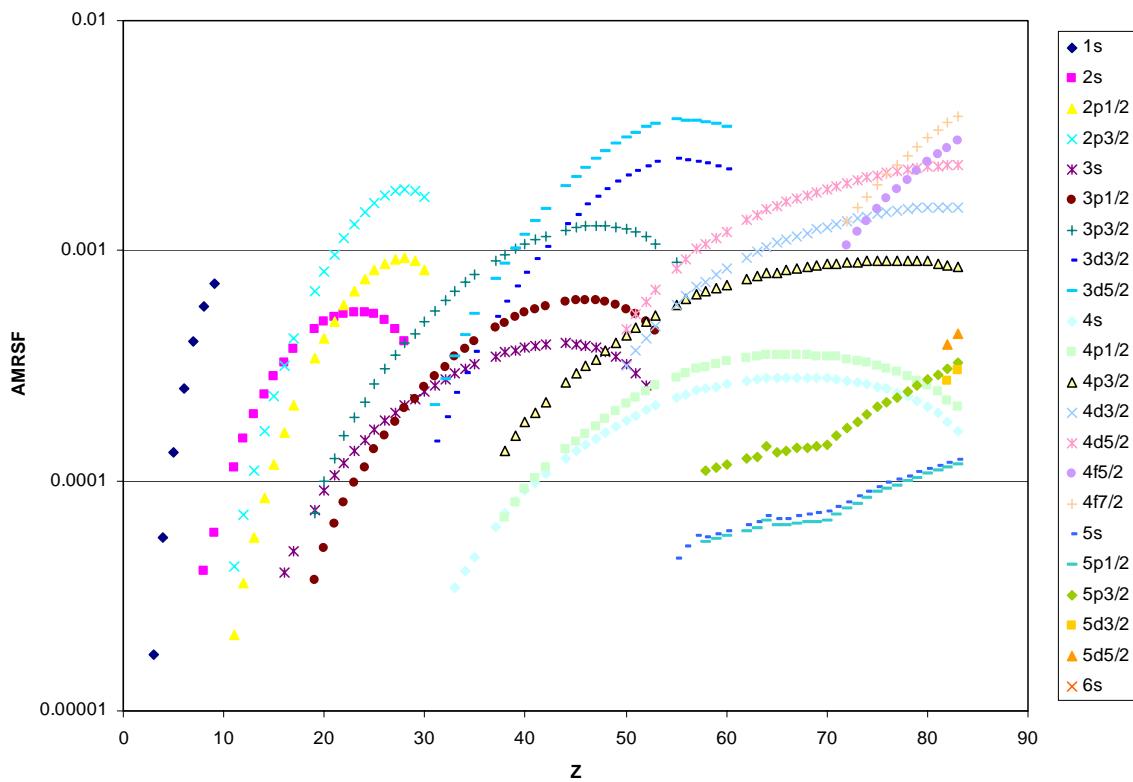
The contributions of N_{Av} , Q_{Av} and $\lambda_{\text{Av}}(E_{AX})$ are discussed in the document for AES AMRSFs and are the same here. The photoelectron cross sections used here are those of Scofield which have been found to be in good agreement with measurements.

The calculated results are given in Tables I and II for Mg and Al X-rays, respectively, as shown in Figure 1(a) and (b). Tables III and IV show the AMRSFs ratioed to C as unity. These data are slightly different from those published in reference [1] where, for comparison with experiment, a $\sec\alpha$ term was included in equation (1) and, in the plots there, often adjacent peaks were combined.

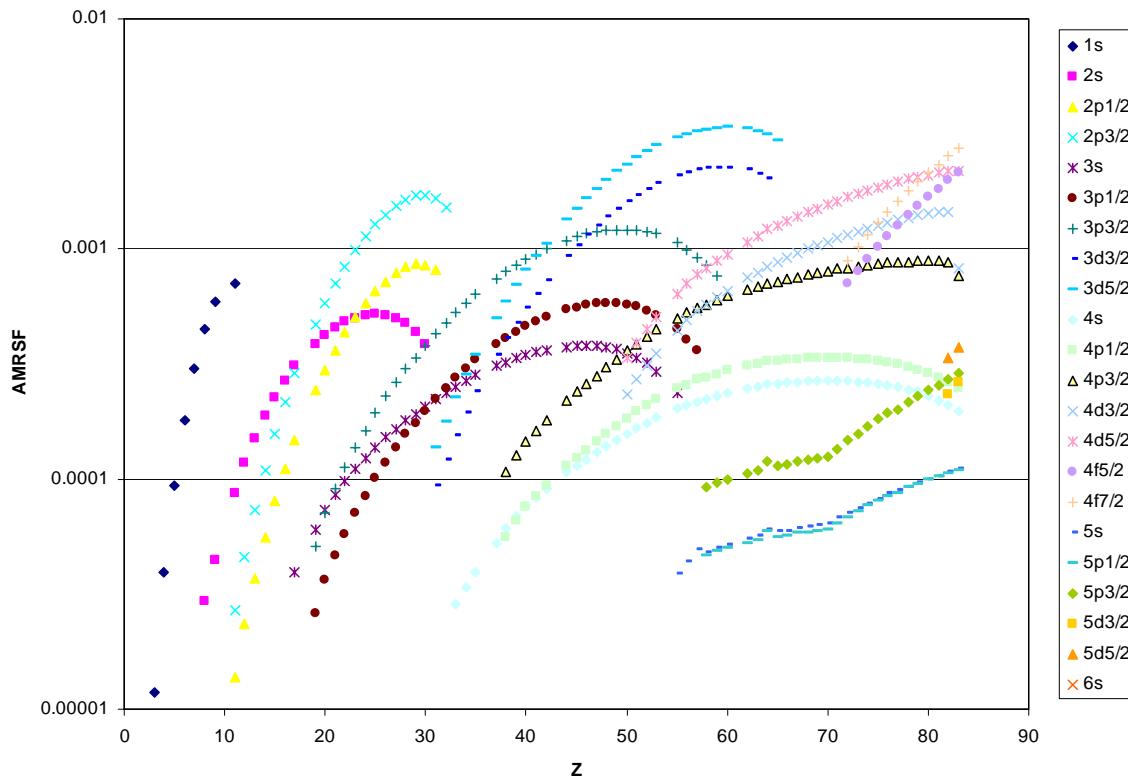
For work at angles, γ , between the incident X-rays and the detected photo-emitted electrons, other than the magic angle, an angular anisotropy needs to be considered. For homogeneous solids within the dipole approximation, the angular distribution is given by an added factor, $G(\gamma)$, on the right of Eq. (2) where, for angles of emission less than 60° from the surface normal [8],

$$G_A(\gamma) = 1 + \frac{1}{2}(0.69\beta_{AX_i})(\frac{3}{2}\sin^2\gamma - 1) \quad (3)$$

where β_{AX_i} is the angular anisotropy parameter for the level X_i in the element A. Equation (3) includes the effects of elastic scattering in the 0.69 appropriate for the average matrix. Figure 2 shows how this term affects the intensities for scattering angles, γ , in the range 45° to 90° . For scattering angles in the range 90° to 180° , use $180^\circ - \gamma$. In Fig 2, the β values are from 0.5 to 2. For all s levels, $\beta = 2$. For the other angles, the values are taken from Reilman *et al* [9]. These are given at intervals of 5 in Z and so a simple linear interpolation has been used for the plots of b for relevant levels for Mg and Al K α X-rays in Figs. 3 (a) and (b), respectively. For angles other than the magic angle, the effects of Figs 2 and 3 need to be included.



(a) Mg K α X-rays



(b) Al K α X-rays

Figure 1 - The AMRSFs for all core levels with binding energies greater than 17 eV for Mg and Al K α X-rays.

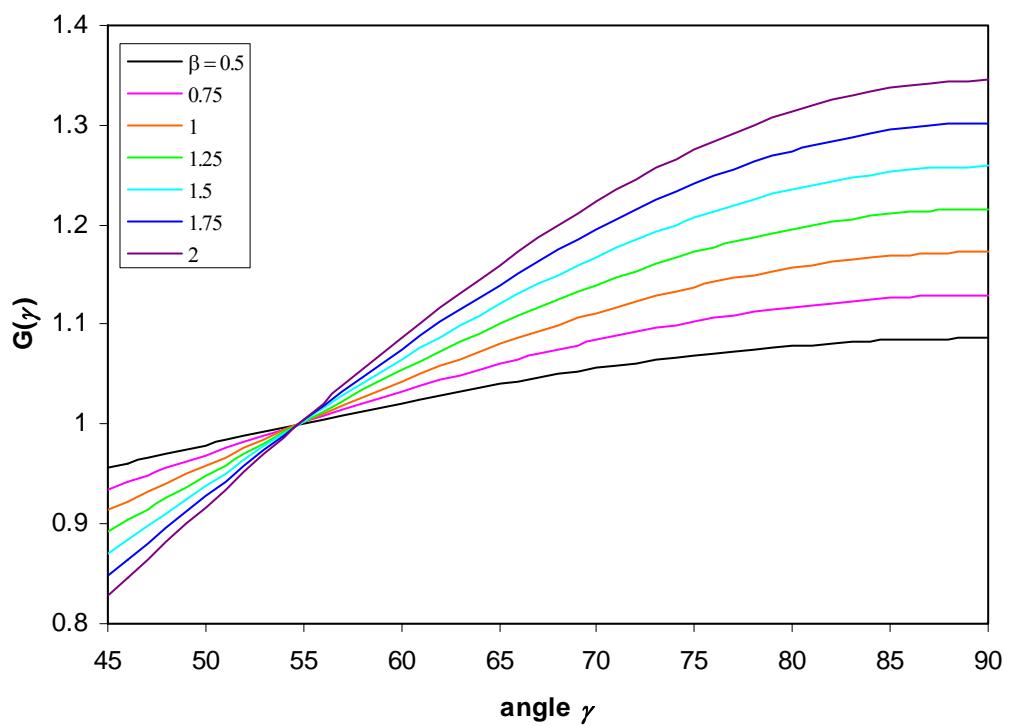
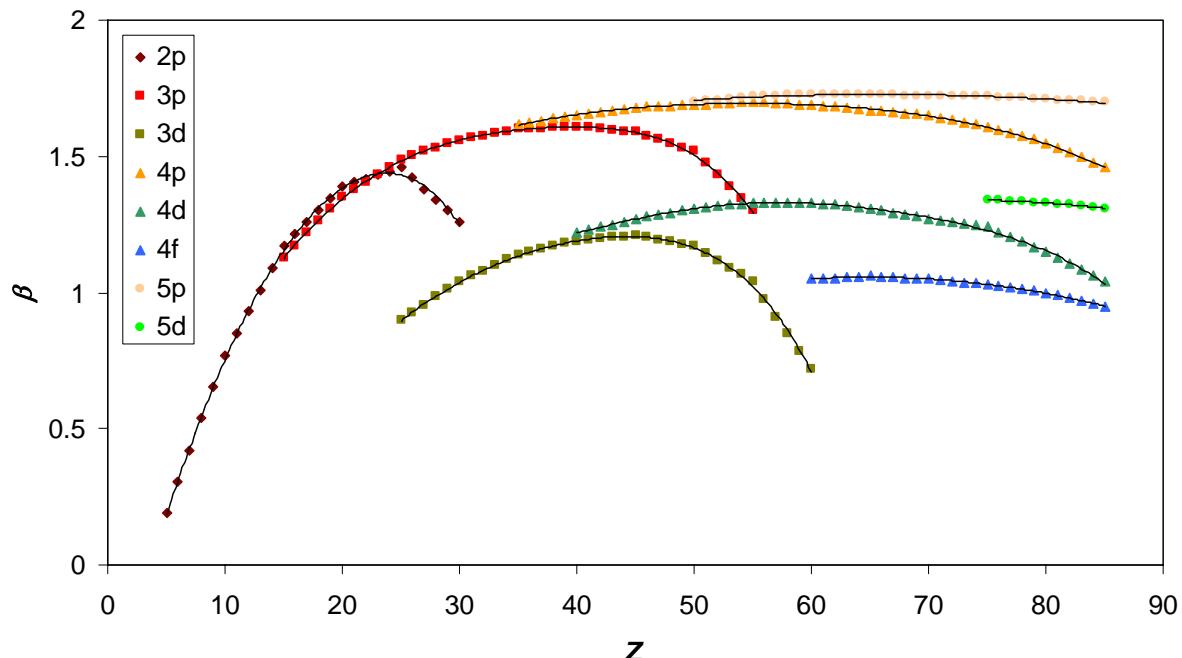
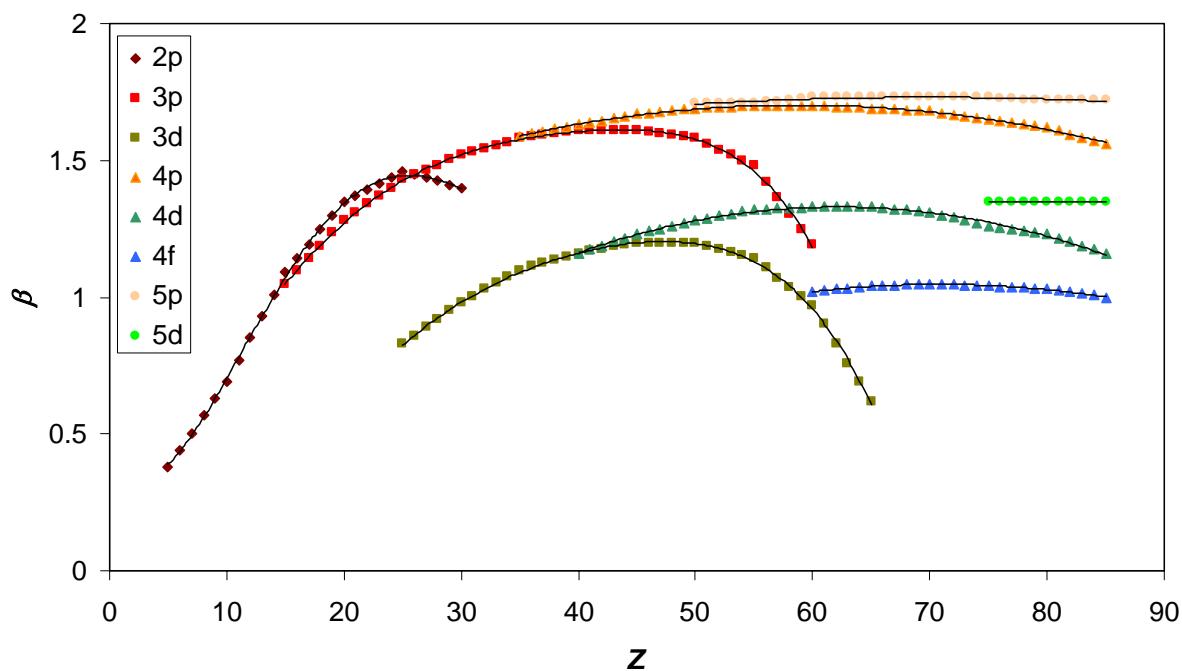


Figure 2 – Dependence of $G(\gamma)$ on γ for $0.5 \leq \beta \leq 2$.



(a) Mg K α X-rays



(b) Al K α X-rays

Figure 3 – Values of β as a function of Z for relevant core levels for (a) Mg and (b) Al, K α X-rays.

- [1] M P Seah, I S Gilmore and S J Spencer, *J. Electron Spectrosc.* **120** 93-111 (2001).
- [2] ISO 18118:2004 - Surface chemical analysis - Auger electron spectroscopy and X-ray photoelectron spectroscopy - Guide to the use of experimentally determined relative

sensitivity factors for the quantitative analysis of homogeneous materials, ISO, Geneva (see also S Tanuma, *Surface and Interface Analysis* **38** 178-180 (2006)).

- [3] <http://www.npl.co.uk/nanoanalysis/a1calib.html>.
- [4] M P Seah, *J. Electron Spectrosc.* **71** 191-204 (1995).
- [5] S Tougaard, *Surface and Interface Analysis* **11**, 453-472 (1988).
- [6] D A Shirley, *Phys. Rev. B* **5**, 4709 (1972).
- [7] M P Seah and I S Gilmore, *Phys. Rev. B* **73** 174113 (2006)
- [8] M P Seah, *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, Eds D Briggs and J T Grant, SurfaceSpectra Ltd/I M Publications 2003, pp 345-375, Chapter 13, Quantification in AES and XPS.
- [9] R F Reilman, A Msezane and S T Manson, *J. Electron Spectrosc.* **8** 389-394 (1976).

Table I – Calculated AMRSFs for Mg X-rays

Table II – Calculated AMRSFs for Al X-rays

Level	1s	2s	2p _{1/2}	2p _{3/2}	3s	3p _{1/2}	3p _{3/2}	3d _{3/2}	3d _{5/2}	4s	4p _{1/2}	4p _{3/2}	4d _{5/2}	4f _{5/2}	4f _{7/2}	5s	5p _{1/2}	5p _{3/2}	5d _{1/2}	5d _{3/2}					
Z = 1																									
2																									
3	0.0000118																								
4	0.0000392																								
5	0.0000936																								
6	0.000181																								
7	0.000302																								
8	0.000446	0.0000297																							
9	0.000591	0.0000442																							
10																									
11	0.000711	0.0000872	0.0000138	0.0000271																					
12		0.000117	0.0000234	0.0000460																					
13		0.000151	0.0000372	0.0000732																					
14		0.000188	0.0000559	0.000110																					
15		0.000227	0.0000802	0.000157																					
16		0.000269	0.000111	0.000217																					
17		0.000309	0.000148	0.000289	0.0000392																				
18																									
19		0.000387	0.000243	0.000474	0.0000601	0.0000260	0.0000506																		
20		0.000423	0.000298	0.000583	0.0000733	0.0000363	0.0000707																		
21		0.000454	0.000363	0.000706	0.0000854	0.0000465	0.0000902																		
22		0.000481	0.000432	0.000842	0.0000979	0.0000580	0.000113																		
23		0.000502	0.000500	0.000984	0.000111	0.0000711	0.000138																		
24		0.000517	0.000581	0.000113	0.00022	0.0000836	0.000162																		
25		0.000520	0.000652	0.000127	0.000138	0.0001010	0.000195																		
26		0.000518	0.000723	0.000141	0.000152	0.000118	0.000229																		
27		0.000502	0.000784	0.000154	0.000166	0.000137	0.000263																		
28		0.000475	0.000832	0.000164	0.000179	0.000156	0.000301																		
29		0.000437	0.000663	0.000171	0.000192	0.000174	0.000335																		
30		0.000383	0.000856	0.000171	0.000206	0.000198	0.000380																		
31		0.000817	0.000166	0.000221	0.000222	0.000427	0.0000937	0.000136																	
32		0.00152	0.000238	0.000247	0.000478	0.000122	0.000177																		
33			0.000252	0.000274	0.0000531	0.000155	0.000226	0.0000287																	
34			0.000268	0.000302	0.000583	0.000194	0.000282	0.0000339																	
35			0.000282	0.000331	0.000640	0.000239	0.000346	0.0000393																	
36																									
37						0.000310	0.000384	0.000747	0.0000346	0.000502	0.0000529														
38						0.000322	0.000409	0.000800	0.0000409	0.000594	0.0000610	0.0000561	0.000108												
39						0.000334	0.000435	0.000853	0.0000478	0.000694	0.0000687	0.0000656	0.000126												
40						0.000345	0.000460	0.000900	0.0000554	0.0008807	0.0000764	0.0000752	0.000145												
41						0.000355	0.000484	0.000952	0.0000637	0.000927	0.0000833	0.0000836	0.000161												
42						0.000364	0.000507	0.000100	0.000728	0.00106	0.0000910	0.0000934	0.000181												
43							0.000375	0.000544	0.000109	0.000926	0.000135	0.000107	0.000114	0.000219											
44							0.000380	0.000559	0.000113	0.000103	0.000150	0.000115	0.000124	0.000240											
45							0.000380	0.000570	0.000116	0.000115	0.000166	0.000122	0.000133	0.000258											
46							0.000379	0.000579	0.000119	0.000126	0.000183	0.000131	0.000145	0.000281											
47							0.000374	0.000581	0.000121	0.000133	0.000200	0.000140	0.000157	0.000307											
48							0.000366	0.000578	0.000121	0.000149	0.000217	0.000148	0.000170	0.000332											
49							0.000353	0.000571	0.000121	0.000161	0.000234	0.000158	0.000183	0.000361	0.000234	0.000336									
50							0.000338	0.000560	0.000121	0.000172	0.000250	0.000167	0.000196	0.000387	0.000271	0.000389									
51							0.000319	0.000542	0.000119	0.000183	0.000266	0.000176	0.000209	0.000417	0.000312	0.000448									
52							0.000294	0.000518	0.000116	0.000193	0.000281	0.000185	0.000222	0.000446	0.000352	0.000508									
53								0.000235	0.000446	0.000106	0.000209	0.000305	0.000203	0.000247	0.000501	0.000441	0.000636								
54								0.000404	0.000992	0.000214	0.000314	0.000209	0.000257	0.000528	0.000488	0.000793	0.000114								
55								0.000360	0.000924	0.000220	0.000324	0.000208	0.000270	0.000559	0.000541	0.000780									
56								0.000847	0.000224	0.000331	0.000224	0.000224	0.000277	0.000577	0.000572	0.000824									
57								0.000769	0.000226	0.000336	0.000239	0.000229	0.000286	0.000600	0.000617	0.000887									
58								0.000220	0.000322	0.000193	0.000267	0.000236	0.000296	0.000624	0.000660	0.000951									
59								0.000213	0.000326	0.000194	0.000273	0.000268	0.000303	0.000647	0.000654	0.000937									
60								0.000202	0.000313	0.000195	0.000258	0.000258	0.000313	0.000670	0.000680	0.000973									
61									0.000294	0.000329	0.000196	0.000278	0.000273	0.000328	0.000723	0.000880	0.00126								
62									0.000220	0.000324	0.000197	0.000272	0.000272	0.000312	0.000667	0.000749	0.00108								
63									0.000213	0.000326	0.000198	0.000275	0.000275	0.000318	0.000667	0.000793	0.00114								
64									0.000202	0.000313	0.000199	0.000258	0.000258	0.000321	0.000710	0.000844	0.00122								
65										0.000294	0.000329	0.000199	0.000273	0.000273	0.000328	0.000723	0.000880	0.00126							
66										0.000262	0.000326	0.000231	0.000331	0.000331	0.000344	0.000921	0.00132								
67										0.000263	0.000333	0.000232	0.000344	0.000344	0.000351	0.000924	0.00132								
68										0.000266	0.000335	0.000235	0.000345	0.000345	0.000355	0.000999	0.00144								
69										0.000266	0.000338	0.000236	0.000348	0.000348	0.000358	0.000962	0.00138								
70										0.000269	0.000343	0.000237	0.000350	0.000350	0.000368	0.000989	0.00145								
71										0.000269	0.000343	0.000238	0.000351	0.000351	0.000369	0.000989	0.00146								
72										0.000266	0.000347	0.000239	0.000351	0.000351	0.000368	0.0009890	0.00147								
73										0.000265	0.000333	0.000240	0.000349	0.000349	0.000369	0.0009802	0.00148								
74										0.000262	0.000330	0.000241	0.000351	0.000351	0.000369	0.0009804	0.00149								
75										0.000259	0.000326	0.000242	0.000347	0.000347	0.000365	0									

Table III – Calculated AMRSFs ratioed to C as unity for Mg X-rays

Level	1s	2s	2p _{1/2}	2p _{3/2}	3s	3p _{1/2}	3p _{3/2}	3d _{3/2}	3d _{5/2}	4s	4p _{1/2}	4p _{3/2}	4d _{3/2}	4d _{5/2}	4f _{5/2}	5s	5p _{1/2}	5p _{3/2}	5d _{1/2}	5d _{3/2}	
Z = 1																					
2	0.0697																				
3	0.226																				
4	0.528																				
5	1.00																				
6	1.61																				
7	2.29	0.161																			
8	2.87	0.237																			
10																					
11	0.456	0.0852	0.168																		
12	0.603	0.143	0.282																		
13	0.768	0.225	0.441																		
14	0.944	0.333	0.654																		
15	1.13	0.471	0.925																		
16	1.30	0.644	1.26	0.158																	
17	1.50	0.851	1.66	0.196																	
18																					
19	1.81	1.36	2.65	0.297	0.147	0.286															
20	1.94	1.65	3.22	0.361	0.203	0.395															
21	2.04	1.97	3.84	0.419	0.258	0.501															
22	2.11	2.31	4.51	0.478	0.319	0.620															
23	2.15	2.65	5.18	0.539	0.387	0.752															
24	2.15	2.98	5.83	0.593	0.453	0.877															
25	2.10	3.26	6.41	0.663	0.543	1.05															
26	1.98	3.50	6.91	0.727	0.629	1.22															
27	1.82	3.65	7.26	0.791	0.722	1.39															
28	1.61	3.68	7.35	0.853	0.817	1.58															
29	3.60	7.28	9.007	0.905	1.74																
30	3.29	6.77	9.73	1.02	1.96																
31				1.04	1.13	2.19	0.584	0.852													
32				1.10	1.24	2.42	0.754	1.10													
33				1.17	1.37	2.67	0.951	1.39	0.137												
34				1.23	1.49	2.90	1.17	1.71	0.161												
35				1.29	1.61	3.15	1.44	2.10	0.186												
36																					
37				1.39	1.84	3.60	2.05	2.98	0.250												
38				1.43	1.94	3.82	2.40	3.50	0.288	0.276	0.535										
39				1.47	2.03	4.04	2.78	4.06	0.323	0.321	0.624										
40				1.50	2.13	4.24	3.20	4.68	0.359	0.367	0.712										
41				1.53	2.21	4.42	3.65	5.32	0.391	0.405	0.787										
42				1.56	2.29	4.60	4.13	6.02	0.426	0.451	0.880										
43																					
44				1.57	2.39	4.89	5.17	7.54	0.498	0.545	1.06										
45				1.56	2.42	4.99	5.71	8.33	0.535	0.592	1.16										
46				1.54	2.43	5.08	6.29	9.16	0.569	0.634	1.25										
47				1.51	2.42	5.11	6.85	9.99	0.608	0.685	1.34										
48				1.45	2.39	5.10	7.40	10.8	0.648	0.742	1.47										
49				1.37	2.32	5.04	7.92	11.6	0.687	0.798	1.59										
50				1.27	2.22	4.93	8.41	12.3	0.727	0.854	1.70	1.26	1.81								
51				1.16	2.10	4.76	8.88	13.0	0.767	0.913	1.83	1.46	2.10								
52				1.04	1.95	4.56	9.29	13.6	0.807	0.970	1.96	1.66	2.39								
53				1.78	4.27	9.60	14.1	14.844	1.03	2.09	1.86	2.70									
54					3.55	9.93	14.7	0.913	1.12	2.32	2.30	3.34				0.183					
55						9.88	14.7	0.946	1.17	2.44	2.53	3.68				0.206					
56						9.73	14.5	0.981	1.22	2.57	2.79	4.03				0.230					
57						9.56	14.3	0.995	1.24	2.64	2.92	4.24				0.225	0.217	0.439			
58						9.30	14.1	1.02	1.28	2.73	3.13	4.54				0.233	0.224	0.454			
59						8.94	13.7	1.04	1.31	2.84	3.34	4.83				0.240	0.230	0.468			
60									1.08	1.36	2.99	3.73	5.39				0.253	0.241	0.495		
61									1.10	1.37	3.51	5.21	7.62				0.261	0.246	0.506		
62									1.11	1.40	3.16	4.14	6.01				0.280	0.268	0.559		
63									1.11	1.40	3.21	4.29	6.20				0.271	0.253	0.527		
64									1.12	1.40	3.28	4.46	6.46				0.271	0.256	0.537		
65									1.12	1.40	3.33	4.62	6.71				0.279	0.260	0.549		
66									1.12	1.39	3.38	4.76	6.94				0.281	0.262	0.554		
67									1.12	1.38	3.41	4.93	7.16				0.287	0.262	0.562		
68									1.11	1.38	3.47	5.03	7.38				0.290	0.266	0.573		
69									1.10	1.37	3.51	5.21	7.62				0.300	0.283	0.621		
70									1.08	1.34	3.54	5.34	7.83	4.21	5.36		0.322	0.301	0.671		
71									1.07	1.32	3.56	5.47	8.04	4.78	6.09	0.338	0.317	0.721			
72									1.04	1.29	3.58	5.59	8.25	5.38	6.85	0.355	0.334	0.775			
73									1.02	1.26	3.61	5.72	8.46	6.03	7.66	0.372	0.354	0.830			
74									0.995	1.23	3.62	5.84	8.68	6.70	8.53	0.389	0.368	0.879			
75									0.959	1.19	3.62	5.92	8.83	7.36	9.40	0.401	0.379	0.912			
76									0.927	1.14	3.62	6.01	8.99	8.09	10.3	0.417	0.397	0.976			
77									0.887	1.09	3.60	6.08	9.13	8.84	11.3	0.433	0.410	1.03			
78									0.835	1.04	3.58	6.11	9.21	9.61	12.3	0.447	0.425	1.10			
79									0.783	0.966	3.51	6.13	9.27	10.4	13.3	0.460	0.437	1.16			
80									0.719	0.893	3.45	6.11	9.32	11.1	14.3	0.475	0.453	1.22	1.08	1.55	
81									0.656	0.829	3.38	6.10	9.33	12.0	15.3	0.489	0.465	1.30	1.19	1.73	

Table IV – Calculated AMRSFs ratioed to C as unity for Al X-rays