Average Matrix Relative Sensitivity Factors (AMRSFs) for Auger Electron Spectroscopy (AES)

These tables and plots contain AMRSFs for AES calculated for the total peak area for the K, L, M and N shells for both 5 keV and 10 keV electron beam energies at 30º incidence angle. The background to, and use of, AMRSFs, I_i^{Av}, is discussed by Seah and Gilmore [1] and also in ISO 18118 [2]. For homogeneous solids, the atomic fraction of element A, X_{A}, is given by

$$X_{\mathrm{A}} = \frac{I_{\mathrm{Am}} / I_{\mathrm{A}}^{\mathrm{Av}}}{\sum_i I_{i\mathrm{m}} / I_i^{\mathrm{Av}}} \qquad (1)$$

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 in XPS to use Shirley's background [6] but this does not give intensities that either agree with Tougaard's background or with the theory for XPS intensities [7] These AMRSFs are not for use with Shirley's background. It is also very common to differentiate spectra but then the relative sensitivity factors become dependent on the analyser resolution, the differentiating function and the chemical state of the elements concerned [8].

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

$$I_{\mathrm{AX}}^{\mathrm{Av}} = \gamma_{\mathrm{AX}} \sec\alpha \; N_{\mathrm{Av}} \; Q_{\mathrm{Av}} \, \lambda_{\mathrm{Av}}(E_{\mathrm{AX}}) \sum_{\mathrm{i}} n_{\mathrm{AX_i}} \sigma_{\mathrm{AX}_i}(E_{\mathrm{o}}) \; [1 + r_{\mathrm{Av}} \; (E_{\mathrm{AX_i}}, E_{\mathrm{o}}, \alpha) \,] \qquad (2)$$

where γ_{AX} is the probability that the ionised core level X in element A is filled with the ejection of an Auger electron, α is the angle of incidence of the electron beam from the surface normal, 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, $\lambda_{\mathrm{Av}}(E_{\mathrm{AX}})$ is the inelastic mean free path (IMFP) for the Auger electrons with average energy E_{AX} in the average matrix, $\sigma_{\mathrm{AX}i}(E_{\mathrm{o}})$ is Casnati, Tatari and Baraldi's ionisation cross section for the core level X_i in the element A for electrons of energy E_{o}, $n_{\mathrm{AX}i}$ is the population of the level X_i, and $r_{\mathrm{Av}}(E_{\mathrm{AX_i}}, E_{\mathrm{o}}, \alpha)$ is the additional ionisation of the core level X_i arising from backscattered energetic electrons.

In this work, the parameter γ_{AX} allows for the competing process of X-ray emission where

$$\gamma_{AX} = 1 - \frac{Z^4}{Z^4 + Z_o{}^4} \tag{3}$$

and Z_o = 32.4 for X = K, 89.4 for X = L, 155.9 for X = M and 300 for X = N [9]. The angle α is 30º. In reference [10],

$$N_{Av} = 5.20 \times 10^{28} \text{ atoms m}^{-3} \tag{4}$$

and [11]

$$Q_{Av} = (1-\omega)^{0.5} \left[0.091 + 0.923 \left(\frac{1+1.908}{1+1.908(1-\omega)^{0.5}} \right) \right] \tag{5}$$

and where, for the average matrix,

$$\omega = 0.3 \tag{6}$$

Thus,

$$Q_{Av} = 0.9411 \tag{7}$$

The inelastic mean free path, $\lambda_{Av}(E_{AX})$, is taken from the TPP-2M formula [12]

$$\lambda_A(E) = \frac{10^{-10} E}{E_p^2[\beta \ln(\gamma E) - (C/E) + (D/E^2)]} \tag{8}$$

where

$$E_p = 28.8 \left(\rho N_v / A\right)^{0.5} \text{ in eV} \tag{9}$$

$$\beta = -0.10 + 0.944 \left(E_p^2 + E_g^2\right)^{-0.5} + 0.069 \ \rho^{0.1} \tag{10}$$

$$\gamma = 0.191 \rho^{-0.50} \tag{11}$$

$$C = 1.97 - 0.91W \tag{12}$$

$$D = 53.4 - 20.8W \tag{13}$$

$$W = \rho N_v / A \tag{14}$$

In these equations, ρ is the density (in g cm^{-3}), N_v is the number of valence electrons per atom and A is the atomic weight. For metals, the value of E_g, the band gap, is zero.

The average IMFP function is not determined by averaging the TPP-2M parameters but by evaluating $\lambda_i(E)$, averaging these and fitting this average with Equations (8) to (14) to give the parameters to generate $\lambda_{Av}(E)$. Thus [1],

$$N_v(\lambda_{Av}) = 4.684 \quad (15)$$

$$\rho\ (\lambda_{Av}) = 6.767\ \text{g cm}^{-3} \quad (16)$$

$$A(\lambda_{Av}) = 137.51 \quad (17)$$

$$E_p = 13.827\ \text{eV} \quad (18)$$

$$\beta(\lambda_{Av}) = 0.0518 \quad (19)$$

$$\gamma = 0.0734 \quad (20)$$

$$C = 1.7602 \quad (21)$$

$$D = 48.606 \quad (22)$$

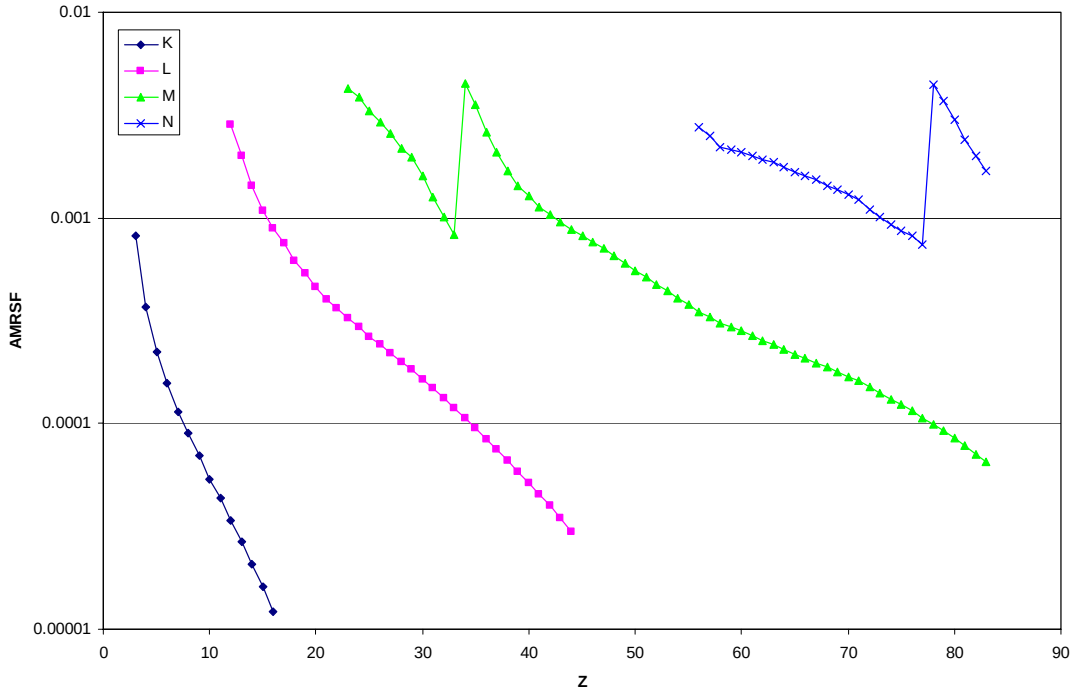
$$W = 0.2305 \quad (23)$$

The sum over the core level ionisation cross sections is made with Casnati, Tatari and Baraldi's formula [13], which have been found to be in good agreement with measurements, and the backscattering with Shimizu's fitted relation at 30º. For the use of backscattering in Shimizu's equations [1]:

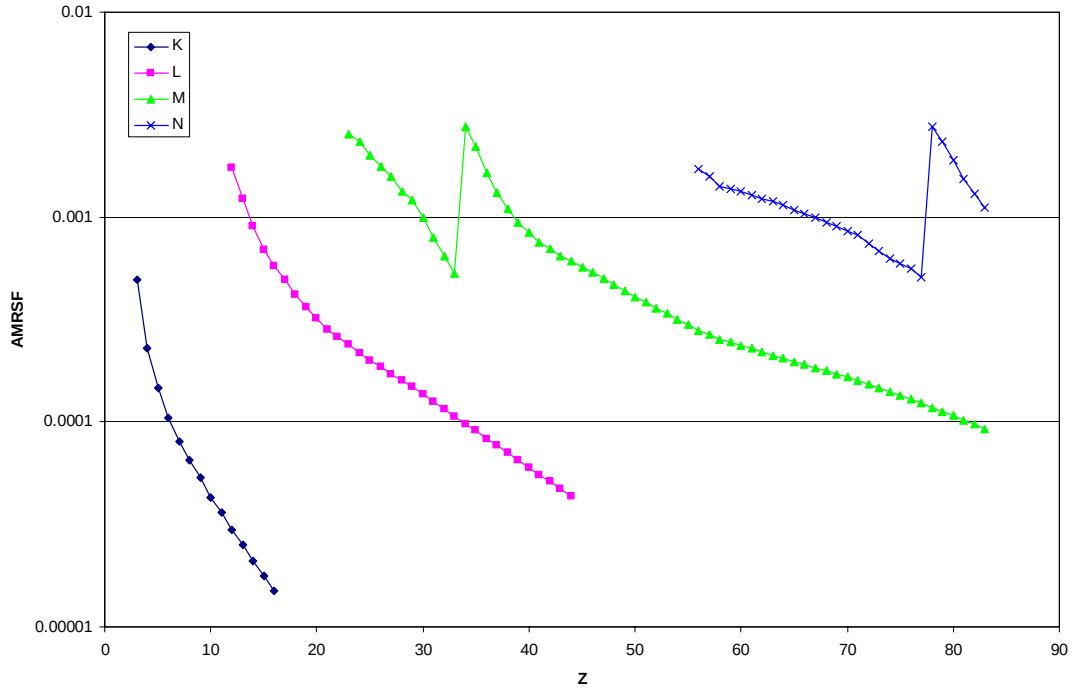
$$Z(r_{Av}) = 40.57 \quad (24)$$

The calculated results are given in Tables I and II for 5 keV and 10 keV electron beams, respectively, as shown in Figure 1(a) and (b). Tables III and IV show the AMRSFs ratioed to Ag as unity.

For work at 0º and 45º, the backscattering term and secα need changing. For Tables III and IV the backscattering changes the AMRSFs. Within the approximations discussed above, the ratio of the backscattering term $[1 + r_{Av}\ (E_{AX_i}, E_o, \alpha)\ ]$ for 0º and 45º to that at 30º for 5 keV and 10 keV electron beams is shown in Fig 2. The effect is simple to incorporate but is small and in many circumstances may be ignored.



(a) 5000 eV



(b) 1000 eV

Figure 1 - The AMRSFs for K, L, M and N shell peaks areas in sr^{-1} units for 5 keV and 10 keV beams incident at 30º.

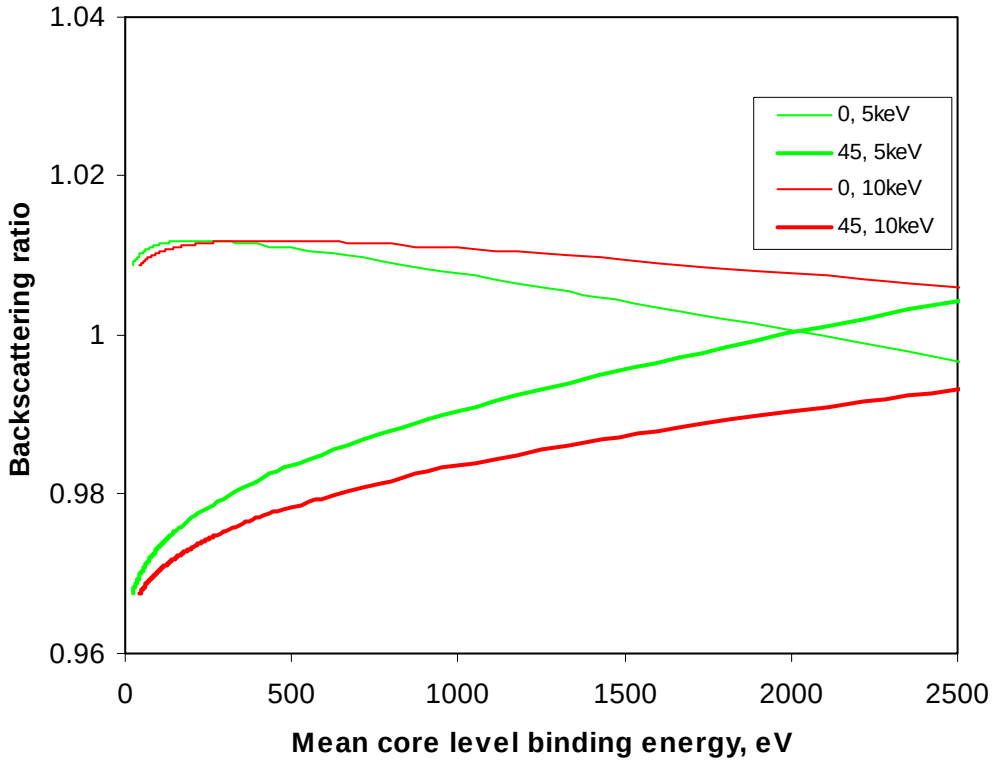


Figure 2 – Ratio of the term $[1 + r_{\mathrm{Av}}\,(E_{\mathrm{AX_i}}, E_{\mathrm{o}}, \alpha)\,]$ **for 0º and for 45º to that at 30º to scale the AMRSFs for work at 0º and 45º.**

[1] M P Seah and I S Gilmore, *Surface and Interface Analysis* **26** 908-929 (1998).

[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 (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, I S Gilmore, H E Bishop and G Lorang, *Surface and Interface Analysis* **26** 701-722 (1998).

[9] M P Seah and I S Gilmore, *J. Vacuum Sci. Technolog*. A **14** 1401-1407 (1996).

[10] M P Seah, I S Gilmore and S J Spencer, *J. Electron Spectrosc*. **120** 93-111 (2001).

[11] M P Seah and I S Gilmore, *Surface and Interface Analysis* **31** 835-846 (2001).

[12] S Tanuma, C J Powell and D R Penn, *Surface and Interface Analysis* **21** 165-176 (1994).

[13] M P Seah and I S Gilmore, *Surface and Interface Analysis* **26** 815-824 (1998).

Table I – Calculated AMRSFs for 5 keV electron beam

Level	K	L	M	N
Z = 1				
2				
3	0.000815			
4	0.000367			
5	0.000224			
6	0.000156			
7	0.000115			
8	0.0000893			
9	0.0000701			
10	0.0000536			
11	0.0000432			
12	0.0000339	0.00286		
13	0.0000266	0.00200		
14	0.0000208	0.00144		
15	0.0000160	0.00108		
16	0.0000122	0.000890		
17		0.000755		
18		0.000623		
19		0.000535		
20		0.000461		
21		0.000403		
22		0.000361		
23		0.000326	0.00424	
24		0.000294	0.00386	
25		0.000265	0.00331	
26		0.000241	0.00291	
27		0.000219	0.00258	
28		0.000200	0.00218	
29		0.000182	0.00198	
30		0.000164	0.00161	
31		0.000148	0.00126	
32		0.000132	0.00101	
33		0.000119	0.000833	
34		0.000106	0.00449	
35		0.0000950	0.00357	
36		0.0000842	0.00263	
37		0.0000750	0.00208	
38		0.0000664	0.00170	
39		0.0000586	0.00144	
40		0.0000517	0.00127	
41		0.0000454	0.00114	
42		0.0000398	0.00104	

Level	K	L	M	N
Z = 43		0.0000345	0.000955	
44		0.0000298	0.000884	
45			0.000820	
46			0.000768	
47			0.000713	
48			0.000656	
49			0.000603	
50			0.000556	
51			0.000515	
52			0.000478	
53			0.000443	
54			0.000407	
55			0.000378	
56			0.000350	0.00274
57			0.000329	0.00250
58			0.000309	0.00222
59			0.000294	0.00216
60			0.000281	0.00210
61			0.000267	0.00200
62			0.000254	0.00191
63			0.000242	0.00186
64			0.000230	0.00177
65			0.000218	0.00168
66			0.000208	0.00160
67			0.000197	0.00153
68			0.000188	0.00144
69			0.000178	0.00136
70			0.000169	0.00129
71			0.000161	0.00123
72			0.000150	0.00110
73			0.000140	0.00101
74			0.000131	0.000930
75			0.000123	0.000867
76			0.000115	0.000814
77			0.000107	0.000740
78			0.0000994	0.00445
79			0.0000921	0.00370
80			0.0000849	0.00300
81			0.0000777	0.00241
82			0.0000711	0.00200
83			0.0000648	0.00170

Table II – Calculated AMRSFs for 10 keV electron beam

Level	K	L	M	N
Z = 1				
2				
3	0.000493			
4	0.000230			
5	0.000146			
6	0.000105			
7	0.0000804			
8	0.0000651			
9	0.0000532			
10	0.0000427			
11	0.0000361			
12	0.0000299	0.00173		
13	0.0000251	0.00123		
14	0.0000211	0.000900		
15	0.0000177	0.000688		
16	0.0000149	0.000576		
17		0.000497		
18		0.000417		
19		0.000365		
20		0.000320		
21		0.000284		
22		0.000259		
23		0.000238	0.00254	
24		0.000218	0.00232	
25		0.000200	0.00200	
26		0.000185	0.00176	
27		0.000172	0.00157	
28		0.000159	0.00134	
29		0.000149	0.00122	
30		0.000137	0.000998	
31		0.000126	0.000793	
32		0.000116	0.000643	
33		0.000107	0.000533	
34		0.0000980	0.00274	
35		0.0000905	0.00221	
36		0.0000830	0.00165	
37		0.0000766	0.00132	
38		0.0000705	0.00110	
39		0.0000649	0.000939	
40		0.0000599	0.000838	
41		0.0000553	0.000757	
42		0.0000512	0.000702	

Level	K	L	M	N
Z = 43		0.0000472	0.000649	
44		0.0000436	0.000606	
45			0.000569	
46			0.000538	
47			0.000505	
48			0.000470	
49			0.000438	
50			0.000408	
51			0.000383	
52			0.000360	
53			0.000338	
54			0.000316	
55			0.000297	
56			0.000279	0.00172
57			0.000266	0.00158
58			0.000254	0.00141
59			0.000245	0.00137
60			0.000237	0.00134
61			0.000228	0.00128
62			0.000220	0.00123
63			0.000212	0.00120
64			0.000204	0.00114
65			0.000197	0.00109
66			0.000190	0.00104
67			0.000184	0.000999
68			0.000178	0.000944
69			0.000171	0.000898
70			0.000166	0.000854
71			0.000160	0.000815
72			0.000153	0.000739
73			0.000146	0.000680
74			0.000140	0.000631
75			0.000135	0.000592
76			0.000129	0.000559
77			0.000123	0.000512
78			0.000118	0.00277
79			0.000113	0.00232
80			0.000107	0.00191
81			0.000102	0.00155
82			0.0000971	0.00130
83			0.0000924	0.00112

Table III – Calculated AMRSFs ratioed to Ag as unity for 5 keV electron beam

Level	K	L	M	N
Z = 1				
2				
3	1.14			
4	0.514			
5	0.314			
6	0.219			
7	0.161			
8	0.125			
9	0.0983			
10	0.0751			
11	0.0606			
12	0.0475	4.01		
13	0.0374	2.80		
14	0.0292	2.02		
15	0.0225	1.51		
16	0.0171	1.25		
17		1.06		
18		0.873		
19		0.751		
20		0.646		
21		0.565		
22		0.507		
23		0.457	5.95	
24		0.412	5.42	
25		0.372	4.64	
26		0.338	4.08	
27		0.308	3.62	
28		0.280	3.06	
29		0.256	2.77	
30		0.231	2.25	
31		0.207	1.77	
32		0.185	1.42	
33		0.166	1.17	
34		0.149	6.29	
35		0.133	5.00	
36		0.118	3.69	
37		0.105	2.92	
38		0.0931	2.39	
39		0.0822	2.02	
40		0.0725	1.78	
41		0.0637	1.59	
42		0.0558	1.47	

Level	K	L	M	N
Z = 43		0.0484	1.34	
44		0.0418	1.24	
45			1.15	
46			1.08	
47			1.00	
48			0.919	
49			0.846	
50			0.780	
51			0.722	
52			0.670	
53			0.621	
54			0.572	
55			0.530	
56			0.491	3.85
57			0.461	3.50
58			0.434	3.11
59			0.413	3.03
60			0.394	2.95
61			0.374	2.81
62			0.356	2.68
63			0.339	2.61
64			0.322	2.48
65			0.305	2.35
66			0.291	2.25
67			0.277	2.15
68			0.263	2.02
69			0.250	1.91
70			0.237	1.81
71			0.225	1.72
72			0.211	1.55
73			0.197	1.42
74			0.184	1.30
75			0.173	1.22
76			0.161	1.14
77			0.150	1.04
78			0.139	6.24
79			0.129	5.19
80			0.119	4.21
81			0.109	3.37
82			0.0997	2.80
83			0.0909	2.39

Table IV – Calculated AMRSFs ratioed to Ag as unity for 10 keV electron beam

Level	K	L	M	N
Z = 1				
2				
3	0.977			
4	0.456			
5	0.289			
6	0.209			
7	0.159			
8	0.129			
9	0.105			
10	0.0846			
11	0.0714			
12	0.0593	3.43		
13	0.0497	2.44		
14	0.0417	1.78		
15	0.0350	1.36		
16	0.0295	1.14		
17		0.984		
18		0.827		
19		0.723		
20		0.633		
21		0.563		
22		0.514		
23		0.471	5.03	
24		0.432	4.60	
25		0.397	3.96	
26		0.367	3.50	
27		0.341	3.12	
28		0.316	2.65	
29		0.294	2.41	
30		0.271	1.98	
31		0.250	1.57	
32		0.229	1.27	
33		0.211	1.06	
34		0.194	5.44	
35		0.179	4.37	
36		0.164	3.27	
37		0.152	2.63	
38		0.140	2.17	
39		0.129	1.86	
40		0.119	1.66	
41		0.110	1.50	
42		0.101	1.39	

Level	K	L	M	N
Z = 43		0.0935	1.29	
44		0.0864	1.20	
45			1.13	
46			1.07	
47			1.00	
48			0.931	
49			0.867	
50			0.809	
51			0.759	
52			0.713	
53			0.670	
54			0.626	
55			0.589	
56			0.554	3.41
57			0.527	3.12
58			0.503	2.79
59			0.485	2.72
60			0.469	2.65
61			0.451	2.54
62			0.435	2.43
63			0.420	2.37
64			0.405	2.26
65			0.390	2.15
66			0.377	2.07
67			0.365	1.98
68			0.352	1.87
69			0.340	1.78
70			0.329	1.69
71			0.317	1.61
72			0.303	1.47
73			0.290	1.35
74			0.278	1.25
75			0.267	1.17
76			0.255	1.11
77			0.244	1.01
78			0.234	5.48
79			0.223	4.60
80			0.213	3.78
81			0.202	3.06
82			0.192	2.58
83			0.183	2.22