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Electron Probe Microanalysis of U and U-alloys… How Hard Can It Be?

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Electron probe microanalysis of pure metals and simple alloys should be relatively trivial. However, Uranium metal and its alloys pose some additional problems compared to many other materials. For example, its high atomic number (Z=92) means that it produces a large number of characteristic x-ray lines, ranging in energy from <1 KeV to >100 KeV. Whilst the large number of lines potentially gives a large choice for analysis the K-lines are inaccessible to conventional EPMA and the L-lines can only be efficiently excited at relatively high accelerating voltages (>25kV). The necessary correction factors for the more accessible M-lines are poorly constrained, in particular for pairings with low element numbers such as O and C.

The choice of reference material for U is also not trivial. The very high affinity of U metal for O can form a 10 - 20nm thick oxide layer within minutes of polishing, making the metal unsuitable for calibration. U has a wide range of possible oxidation states, from UO to U_3O_8. Where stoichiometric UO_2 can be found it is frequently in the form of sintered powder. Even high pressure sintered UO_2 powders retain a significant level of micro-porosity, making it less than ideal for calibration. Synthetically grown UO_2, if it can be found, is far superior but still produces consistently high analysis totals for U-metal (Figure 1). Measurement of and correction for the ubiquitous oxide layer on the U metal surface can recover closer to 100% totals at 15kV and above. At voltages below this, though, the oxide corrected analyses rapidly deviate from 100% and produce even poorer analysis totals than without correction for the oxide layer below 10kV.

The Pouchou and Pichoir[1] EPMA method for the determination of mass attenuation coefficients (MACs) was used to measure the compound MACs for both U and O in UO_2. The resulting values show good agreement with the FFAST[2] and MAC30[3] database values, as shown in tables 1 and 2. Assuming the FFAST database values for O Kα and U Mα by O values for U Mα and O Kα by U were calculated and again showed good agreement with the existing database values (tables 1 and 2). Using the calculated MAC values failed to correct the very poor low voltage analyses. Comparison of EPMA measured U Mα k-ratios on U metal against GMRFilm[4], DTSA-II[5] and PENEPMA[6] calculated k-ratios for both metallic U and UO_2 on U indicate that the measured samples behave more like metallic U than oxidised U at low accelerating voltages. Possible explanations are that i) the models for all three programs produce similar erroneous results at low accelerating voltages, or ii) U appears to be less oxidised towards the surface.

The large number of possible U x-ray lines also produces a high probability of interferences: Analysis of C in U is complicated by the presence of an obscure U N6-O4[7] line which is not reported in many software peak overlap tools. This, in combination with its proximity to the C Ka peak position, means that this overlap can easily be mistaken for a ~3.5eV shift in the C Kα peak position. At the vitreous C peak position the U line can account for ~40% of the measured C Kα signal (Figure 2). If the 'shifted' peak position is used this increases to ~60% and is therefore the source of a very large potential error in C analysis. A U N6-O5 line, indicated to be 100x more intense than the N6-O4 line, is not seen in

measured spectra. However, the electron shell and orbital populations indicate that the O5 orbital should not be occupied if the U atom is not in an excited state, precluding the fluorescence of this line [8].

References:

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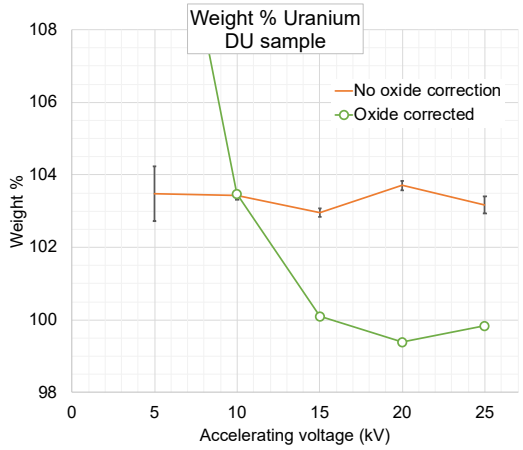

Figure 1. Comparison of analysis totals on a pure U-metal sample, both with and without correction for the surface oxide on the sample.

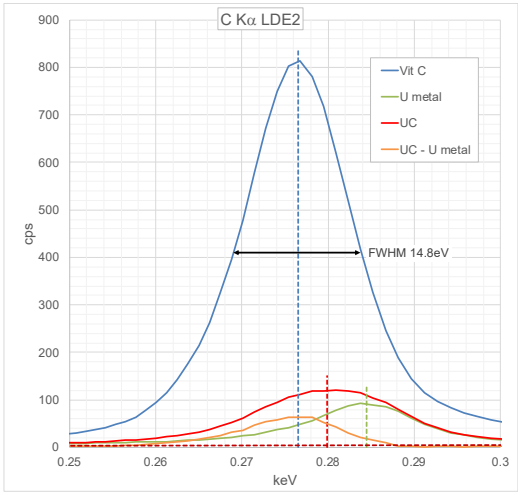

Figure 2. Comparison of x-ray spectra in the region of the C Ka peak from vitreous C, U metal, and UC samples, and a calculated residual C Kα peak after subtraction of the U metal peak from the UC spectrum.

O Kα by	FFAST	MAC30	P&P
U	7498.270	11399.210	9168.164
O	1120.430	1180.630	*1120.430*
UO_2	6742.423	10188.206	8214.427

Table 1. Database and calculated MAC values for O Ka absorbed by U, O and UO_2.

U Mα by	FFAST	MAC30	P&P
U	638.870	720.830	996.839
O	174.870	183.070	*174.870*
UO_2	583.881	657.100	899.428

Table 2. Database and calculated MAC values for U Ma absorbed by U, O and UO_2.

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