Australian Government
Australian Radiation Protection and Nuclear Safety Agency

Isotopic Ratios of Uranium in Uranium Salts and Pitchblende

David Urban

Technical Report Series No. 160

Australian Government
Australian Radiation Protection and Nuclear Safety Agency

Isotopic Ratios of Uranium in Uranium Salts and Pitchblende

David Urban

Technical Report 160
ISSN 0157-1400
July 2012

619 Lower Plenty Road
Yallambie VIC 3085
Telephone: +61 3 9433 2211
Fax: +61 3 9432 1835

Notice

Australian Radiation Protection and Nuclear Safety Agency 2012

ISSN: 0157-1400

Creative Commons

ARPANSA
619 Lower Plenty Road
YALLAMBIE VIC 3085

Tel: 1800 022 333 (Freecall) or +61 3 9433 2211
Email: info@arpansa.gov.au
Website: www.arpansa.gov.au

Disclaimer

Acknowledgements

The author is indebted to Sandra Sdraulig, Liesel Green and Stephen Long from the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) for their invaluable contributions and support in the development of this paper. Technical support and supervision in the radiochemistry laboratory during sample preparation and analysis was provided by both Sandra Sdraulig and Liesel Green. Stephen Long provided invaluable technical support in the interpretation of alpha spectra for result calculation purposes.

Abstract

An investigation was conducted to ascertain if high resolution alpha spectrometry could be used to effectively determine the isotopic ratios ($^{234}U/^{238}U$ and $^{235}U/^{238}U$) of a group of uranium salt samples. The aim of this characterisation was to use the ratios as a means of discriminating between these samples. A sample of pitchblende was analysed and used for quality control purposes.

The determined uranium mass percentages and ratios in the pitchblende sample were in agreement, within experimental uncertainty, with published values. However, it was found that the experimental uncertainty for ^{235}U was significantly higher than that for ^{234}U and ^{238}U. The pitchblende sample could be easily discriminated from the salt samples by using both the $^{234}U/^{238}U$ and $^{235}U/^{238}U$ ratios. When attempting to distinguish between the salt samples, the $^{234}U/^{238}U$ ratio was more reliable than the $^{235}U/^{238}U$ ratio. This was because the difference between salt samples for the $^{235}U/^{238}U$ ratio was not sufficiently large enough to overcome the higher experimental uncertainty. Statistical analysis showed that there was no difference between the ratios within some of the salt samples so discrimination was not possible.

During the course of the pitchblende analysis, different digestion procedures were evaluated in order to determine the best recovery of the uranium within the ore. It was found that microwave digestion techniques were successful in attaining near to or total recovery of the uranium within the ore and would be the most appropriate method of quantitative analysis.

Contents

1. Introduction

High resolution alpha spectrometry is a conventional method used for the quantification of alpha emitting radionuclides such as uranium, plutonium, americium, and polonium. The application of alpha spectroscopy, if sufficiently accurate and reproducible, could be used to characterise the uranium isotopic abundance in unknown orphan uranium salts. Expressed as either mass percentages or isotopic ratios, this may then be used to determine the manufacturer, manufacturing batch and date, or custodian of the salt by cross referencing the results with any archived records containing this information.

This analysis also offered an opportunity to investigate the best digestion method for the determination of uranium in the pitchblende matrix. The information gained could then be used to assist in the analysis of other environmental samples.

2. Methods and Materials

The uranium isotopic mass percentages of ^{234}U, ^{235}U and ^{238}U were calculated after their alpha activities were determined in various samples of uranium salts and in a sample of pitchblende.

The results for the isotopic mass percentages in the pitchblende sample, a natural uranium containing ore, should agree with the known natural abundance of these isotopes. Therefore, this analysis offered a convenient means of quality control with regard to accuracy. The results were expressed as both individual mass percentages and ratios in terms of ^{234}U/^{238}U and ^{235}U/^{238}U.

The samples analysed were part of the inventory at the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) and were identified by their unique Radiation Source Identification Number (RSIN).

The activities of the uranium isotopes were determined for each of the uranium salts and for the pitchblende ore sample. These activities, measured by high resolution alpha spectroscopy, were then used to derive the mass percentages and ratios of the uranium isotopes. A maximum activity of 0.3 Bq of uranium was chosen in order to minimise chamber contamination from radioactive decay daughter products. This activity provided a measurable and well resolved signal with a reasonably low level of uncertainty.

The mass of sample required for this activity was very small (in the 10s of micrograms) and impractical to accurately weigh on a balance. Therefore, a much larger mass of sample was digested and subsequently diluted to the desired activity concentration. In each case an appropriate dilution was determined based on the mass weighed for each salt. Digestions of the raw salt samples were carried out in triplicate.

The pitchblende samples were digested in triplicate for each of four different digestion procedures. This was done in order to determine the most effective digestion procedure for extracting the uranium out of the pitchblende matrix. The salt samples and pitchblende were weighed into specimen containers and transferred with water into digestion beakers.

2.1 Digestion Procedures

2.1.1 Uranium salts

The uranium salts were digested using concentrated nitric acid that was added to the beakers containing the transferred salt in water. The solution was then evaporated to dryness on a hotplate. The addition and evaporation of HNO_3 was repeated twice more before the residue was dissolved in water with gentle heating.

2.1.2 Pitchblende

The pitchblende sample was digested using four different procedures in order to investigate the recovery of the uranium content:

1. The pitchblende was digested in concentrated HNO_3 using the same procedure as for the uranium salts.

2. The pitchblende was digested using a 3:1 mixture of concentrated HNO_3:HCl, and evaporated to dryness on a hotplate. This was repeated twice before the residue was dissolved in water.

3. The pitchblende was transferred to a Teflon® TFM vessel, and digested in a temperature controlled microwave with a rise from room temperature to 200°C for 10 minutes in a solution containing a 2:1 mixture of concentrated HNO_3:HCl. The digestion was then continued at 200°C for a further 15 minutes (Milestone 2005a). The resulting solution was allowed to cool to room temperature.

4. The pitchblende was transferred to a Teflon® TFM vessel, and digested by temperature controlled microwave heating in a number of steps. First the sample was digested to a temperature of 160°C for 8 minutes in a solution of 1.5 mL concentrated HF, 5 mL of concentrated HCl and 8 mL of HNO_3. The digestion was then continued with a temperature rise to 210°C for a further 5 minutes and a further 20 minutes at 210°C. After cooling 1 mL of concentrated HF and 5 mL of 5% H_3BO_3 were added and the solution was digested further in a temperature rise to 160°C for 8 minutes and a further 10 minutes at 160°C (Milestone 2005b; 2005c).

After each digestion, the resulting solution was transferred to plastic bottles using deionised water as a rinse. Based on the mass of sample digested the solution was then appropriately diluted to achieve the desired 0.3 Bq activity concentration. To maintain consistency, the results for the isotopic ratios in the pitchblende obtained using procedure 1, the same procedure used for the salt digestions, were used for comparison with the salt samples.

2.2 Sample Purification

Appropriate volumes were sub-sampled from the bottles containing digestates and transferred to pre-weighed 50 mL beakers. Concentrated HNO_3 was then added and the mixture was evaporated to dryness on a hotplate. The resulting residue was dissolved in 3 M HNO_3-1 M $Al(NO_3)_3$ and then passed through a column packed with UTEVA® resin preconditioned with 3M HNO3. Sequential rinses of 3 M HNO_3, 9 M HCl, and 5 M HCl-0.05 M oxalic acid were used to remove all radionuclide impurities. The uranium remaining was eluted using 0.01 M HCl and prepared for electrodeposition.

2.3 Electrodeposition and alpha spectrometry

Concentrated HNO_3 was added to the eluent and the solution was evaporated to dryness. 5% $NaHSO_4$ in 9 M H_2SO_4, and HNO_3 were then added and the evaporation process was repeated. The residue was then dissolved in an electrolyte solution and the uranium was electrodeposited onto a stainless steel disk. The disks were measured for 24 hours by high resolution alpha spectrometry to determine the alpha activities of ^{234}U, ^{235}U and ^{238}U.

No uranium tracer was used in the analysis as it was only necessary to measure the activity of each isotope for the purposes of this investigation. This is possible because the efficiency of the detectors is independent of the alpha energy being measured. After the alpha activities were determined, the results were converted to masses using the specific activity for each uranium isotope (IAEA 2011). The derived masses for each isotope were then summed to give the total uranium mass. Each isotopic mass was then divided by this total to give an isotopic mass percentage and isotopic ratios.

3. Results and Discussion

The results for the calculated mass percentages and mass ratios of the uranium in the salts and pitchblende samples are tabulated in Appendix A. The figures show reasonably consistent results for the derived mass percentages. The largest variability is observed in the mass percentages of ^{235}U and the smallest in the mass percentages of ^{238}U. As a result, all calculated mass ratios of ^{235}U/^{238}U show a consistently larger uncertainty than the ratios determined for ^{234}U/^{238}U.

The most likely cause for the lower precision in the determinations of ^{235}U mass percentages was due to random errors that occurred during the alpha measurement. When the alpha spectrum was examined a 'tailing' of the peak regions of interest (ROIs) for the uranium isotopes was observed. In order for the alpha particles generated by the decay of the uranium isotopes to be counted at their discrete energies, they would have to be emitted and reach the detector unimpeded during the counting. Complex interactions with either the electrodeposited sample or the detector window may have lead to energy losses in some of the emitted alpha particles. This effect is not easily quantifiable and thus corrections were not made for all peak regions.

A spectrum demonstrating this effect is shown in Figure 1.1. From the spectrum the tailing from the energies of both ^{234}U and ^{238}U can clearly be seen. It can be observed that the tailing contributions from the ROI for ^{234}U between 4625 keV and 4825 keV interfered with the resolution in the ROIs for ^{235}U. This was especially evident in the 4446 - 2646 keV ROI for ^{235}U.

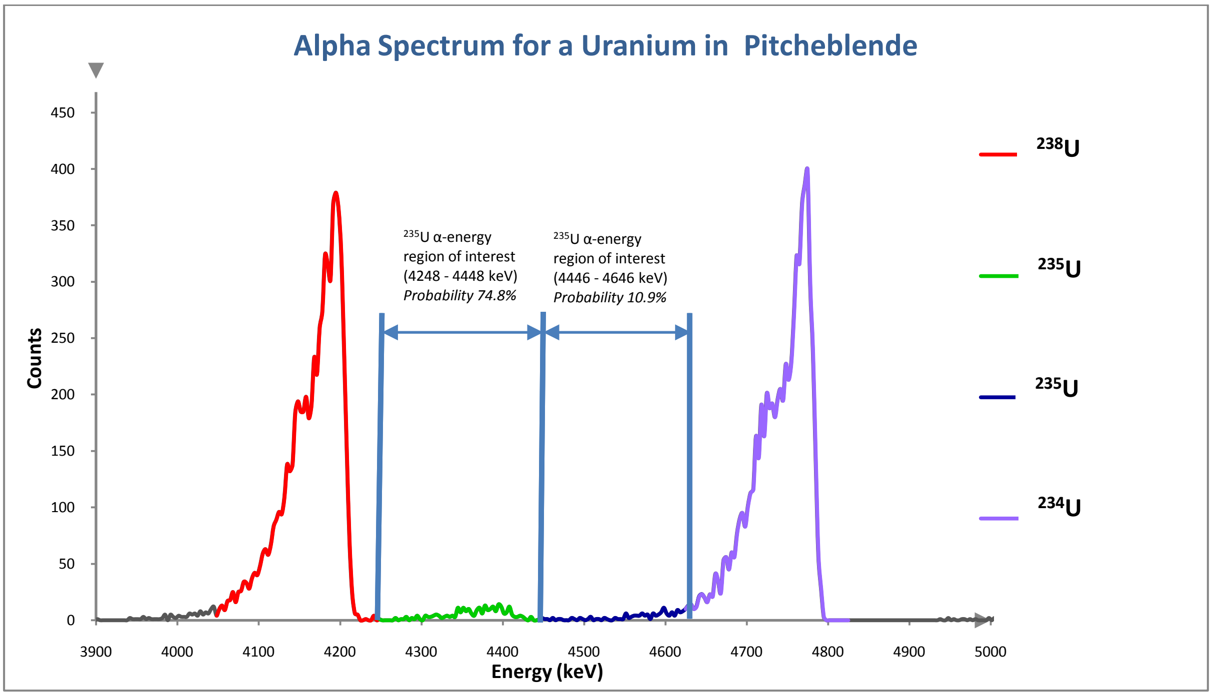

Figure 1.1 Alpha Spectrum for natural uranium sample showing the effects of 'tailing' from the peak regions of interest (ROIs).

The uncertainty in the activity of ^{235}U was enhanced by the fact that its much lower relative activity in both the salts and pitchblende samples resulted in a much lower count rate for this isotope. This could not be solved by using more sample mass to increase the activity of ^{235}U as this would have increased the uncertainty contributions from the tailing energy.

The combination of these factors contributed to a positive bias in the measured activity, and therefore calculated mass, for ^{235}U. One corrective measure that was taken to improve the precision of the ^{235}U determinations was to discount the activity contribution in the 4446 - 4646 keV ROI and use only the contribution from the 4248 - 4448 keV ROI for the determination. This helped to reduce the positive bias caused by the tailing contributions from ^{234}U. The latter region showed less evidence of interference.

The pitchblende analysis was used as a means of quality control to determine the accuracy the analysis. It would be reasonable to assume that the uranium abundances within this sample would agree with published values for the naturally occurring uranium. It can be seen from Table 1.1 that the results for the natural uranium contained in the pitchblende ore showed no statistical difference with published values.

Comparison between experimental and published data for natural uranium isotopic abundance			
% isotopic mass source	^{234}U	^{235}U	^{238}U
Firestone (1999)	0.0055	0.7200	99.2745
uncertainty (k=1)	0.00025	0.0006	0.003
Experimental	0.00523	0.740	99.255
uncertainty (k=1)	0.000060	0.018	0.018
u-test	**1.03**	**1.13**	**1.10**

Table 1.1 u-Test for comparison of experimental determination of isotopic ratios in pitchblende with published values.

The uncertainty for the measured activity of both ^{234}U and ^{238}U was relatively low. The activity of these isotopes is relatively high, both being equal in natural uranium samples. As expected, the uncertainty in the ^{235}U was relatively high due to the previously discussed analytical errors. Also, as the individual mass percentages were derived from the activity of each isotope using their sum as the total activity within the sample, the variation in the measured activity for ^{235}U resulted in the same variation being reflected in the derived mass percentage for ^{238}U. As the mass percentage for

^{238}U is so large, this had negligible impact on the derived uncertainty. However, this calculation method meant that the positive bias in the derived ^{235}U mass percentage had the flow on effect of negatively biasing the derived results for both ^{234}U and ^{238}U. The extent of this bias was insignificant for ^{234}U because of its small mass percentage contribution and high activity. These observations are consistent with the results obtained on the pitchblende samples where the ratio ^{234}U/^{238}U was lower and the ratio ^{235}U/^{238}U was higher than the expected values.

It would be reasonable to assume that the same analytical biases occurred during the analysis of the uranium salt samples. Despite this the analysis and derivations for the ratios ^{234}U/^{238}U and ^{235}U/^{238}U showed reasonable repeatability. The results for the calculated mass percentages and ratios of the uranium salts are shown in Appendix A. The grey points in Figures 1.2 and 1.3 illustrate the variability in the calculated ratios for all samples analysed. From this it can be seen that the pitchblende sample can be easily distinguished from any of the salt samples. This shows that all the salt samples analysed were not consistent with a state of natural isotopic equilibrium for uranium. The red point on the plots shows the ^{234}U/^{238}U and ^{235}U/^{238}U ratios derived from the published values of the uranium isotopic abundances. From this it is evident that the experimental results fall well within the uncertainties of the published ^{234}U/^{238}U ratio and vice versa for the ^{235}U/^{238}U ratio. The precision of the results is shown by the 95% confidence interval uncertainty (k=2) ranges depicted by the error bars associated with each point.

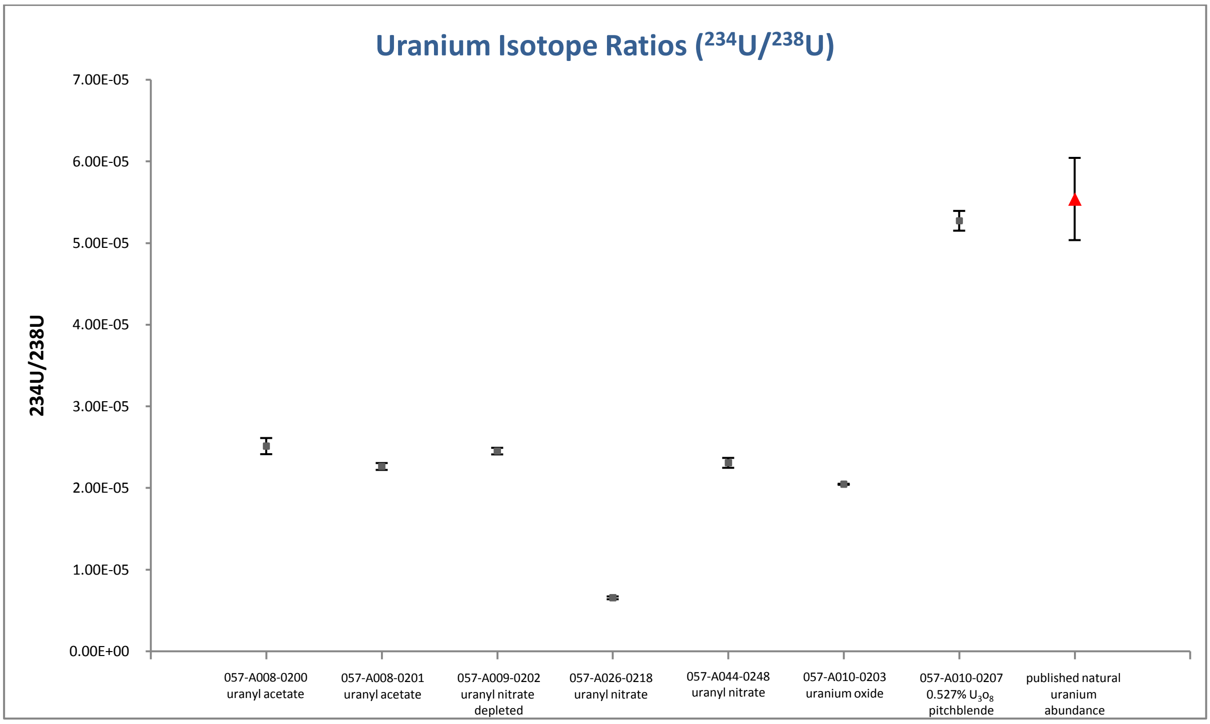

Figure 1.2 Plot of uranium isotope ratios (^{234}U/^{238}U).

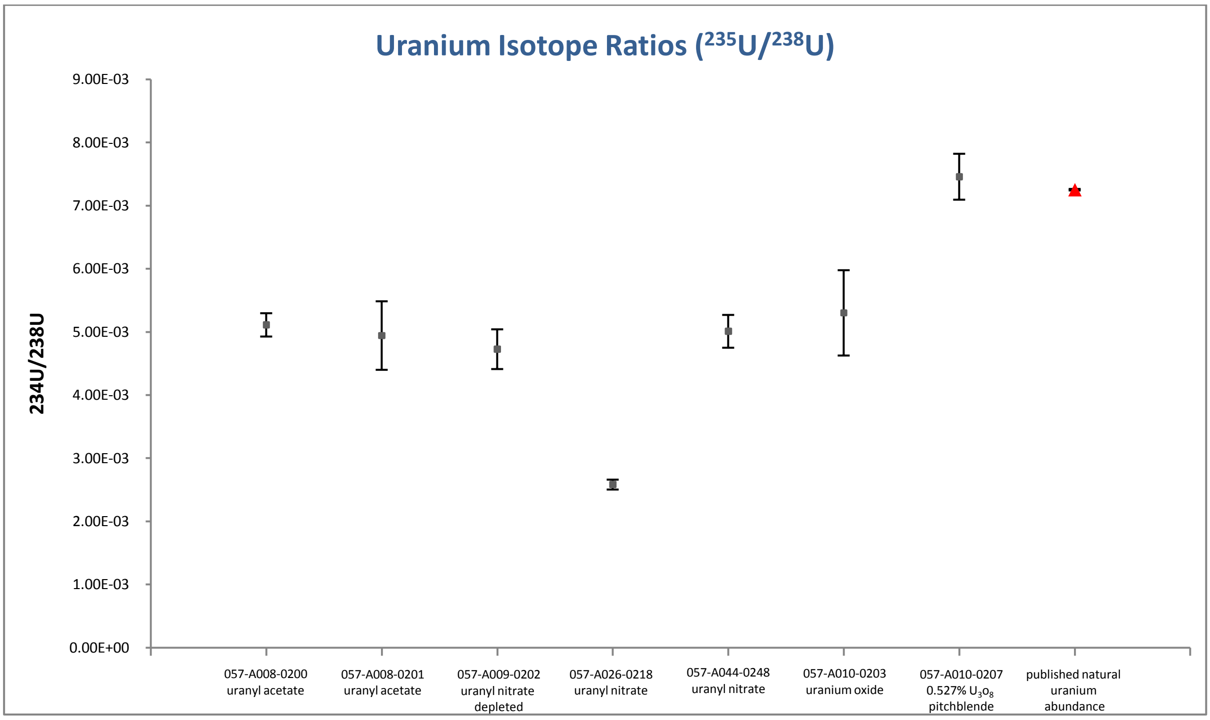

Figure 1.3 Plot of uranium isotope ratios ($^{235}U/^{238}U$).

Statistical analysis indicates that some of the salt samples could be distinguished from one another in terms of the $^{234}U/^{238}U$ ratio. The $^{235}U/^{238}U$ ratio showed less ability for discrimination. Tables 1.2 and 1.3 show the results for the u-tests applied to the salt samples. The bold numbers indicate a significant difference between the determined ratios.

u-test comparison between uranium salts for $^{234}U/^{238}U$						
	uranyl acetate 057-A008-0200	uranyl acetate 057-A008-0201	uranyl nitrate dep. 057-A009-0202	uranyl nitrate 057-A026-0218	uranyl nitrate 057-A044-0248	uranium oxide 057-A010-0203
uranyl acetate 057-A008-0201	2.32					
uranyl nitrate dep. 057-A009-0202	0.57	3.23				
uranyl nitrate 057-A026-0218	**18.49**	**35.35**	**40.91**			
uranyl nitrate 057-A044-0248	1.77	0.60	1.98	**26.20**		
uranium oxide 057-A010-0203	**4.72**	**5.13**	**9.95**	**4.30**	**4.30**	
pitchblende 057-A010-0207	**35.30**	**46.97**	**44.23**	**75.53**	**43.80**	**53.26**

Table 1.2 u-tests for Isotopic Ratio $^{234}U/^{238}U$ Comparisons in Uranium Salts.

u-test comparison between uranium salts for $^{235}U/^{238}U$						
	uranyl acetate 057-A008-0200	uranyl acetate 057-A008-0201	uranyl nitrate dep. 057-A009-0202	uranyl nitrate 057-A026-0218	uranyl nitrate 057-A044-0248	uranium oxide 057-A010-0203
uranyl acetate 057-A008-0201	0.30					
uranyl nitrate dep. 057-A009-0202	1.06	0.34				
uranyl nitrate 057-A026-0218	**12.61**	**4.31**	**6.61**			
uranyl nitrate 057-A044-0248	0.32	0.11	0.69	**8.95**		
uranium oxide 057-A010-0203	0.40	0.41	0.77	**4.00**	0.40	
pitchblende 057-A010-0207	**11.51**	**7.70**	**11.36**	**26.21**	**10.96**	**5.62**

Table 1.3 u-tests for Isotopic Ratio $^{235}U/^{238}U$ Comparisons in Uranium Salts.

When the pitchblende sample was digested using the four different procedures it was found that all methods gave high yields for the amount of uranium extracted. The results for the uranium yield percentages were 94.3%, 97.4%, 100.3%, and 101.6% (see Appendix D) respectively for procedures 1 through 4. From these results it can be seen that microwave digestion results in complete recovery of all uranium contained within the ore. The u-test results tabulated in Table 1.4 show that even though the recoveries for procedure 1 are high, the recoveries achieved with microwave digestion in procedures 3 and 4 are significantly higher.

u test comparison between digestion procedures			
	digestion 1	digestion 2	digestion 3
digestion 2	1.00		
digestion 3	**3.54**	1.08	
digestion 4	**3.48**	1.41	0.83

Table 1.4 u-tests for digestion procedures.

Figure 1.4 shows the average results with uncertainty ranges included for each of the digestion methods used. The lowest uncertainty was achieved in digestion procedure 3, the highest uncertainty being in procedure 2.

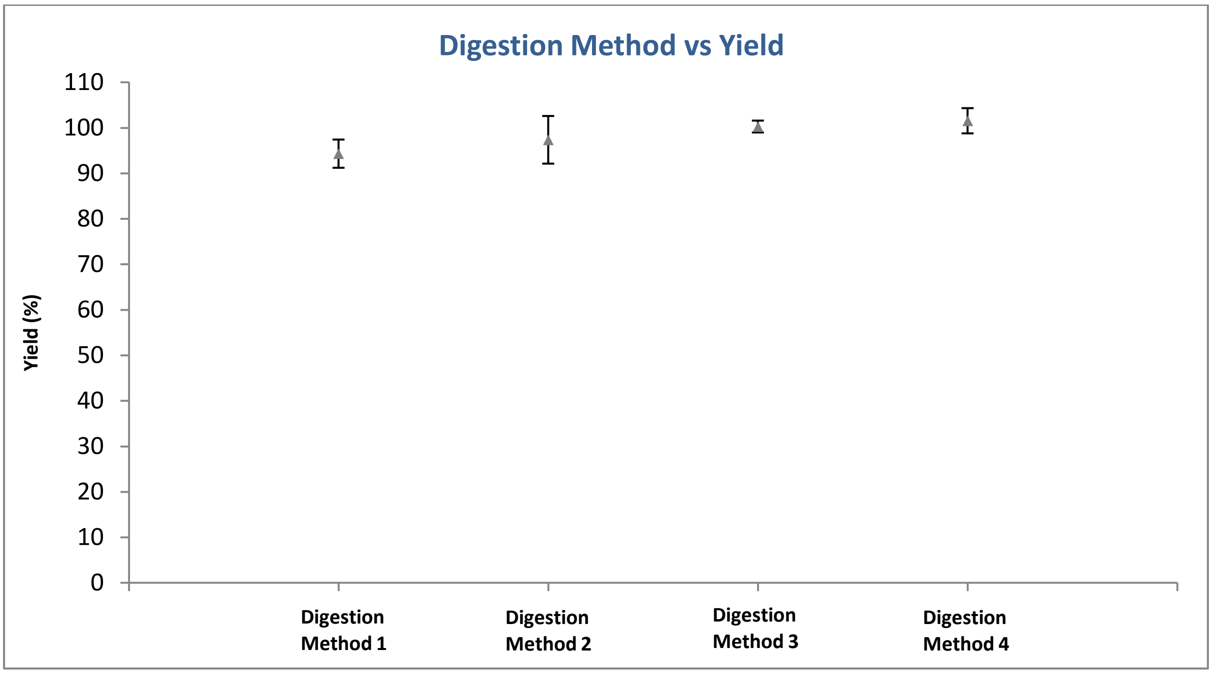

Figure 1.4 Plot of uranium recoveries for different digestion procedures of pitchblende.

4. Conclusion

The results for the alpha spectroscopy analysis of the pitchblende samples were consistent with published results for the isotopic abundances in natural uranium. Further, the experimental uncertainties were consistently low, especially for ^{234}U and ^{238}U. Although the higher uncertainty for ^{235}U translated to higher uncertainty in the ratios ^{235}U/^{238}U, the results for the ^{234}U/^{238}U ratios were accurate and reproducible.

The ratios of the isotopes were determined in all samples and it was found that the analysis performed has the ability to distinguish between the uranium salt samples if there is sufficient difference in their uranium isotopic abundance. This technique was successful in distinguishing these salt samples from a sample of natural uranium in ore using both ratios. The lower uncertainty in the ^{234}U/^{238}U ratio meant that more of the salt samples could be distinguished using this characteristic.

When the pitchblende sample was digested using four different methods, it was found that the microwave digestion procedures resulted in complete recovery of all the uranium contained within the ore. In all procedures investigated, over 90 percent of the uranium in the sample was recovered. Based on such high recoveries it could be concluded that any of these digestion procedures is adequate for qualitative analysis of uranium in the pitchblende matrix. For quantitative analysis, microwave digestion would be more appropriate in the absence of a tracer radionuclide.

5. References

Firestone RB, Shirley VS, Baglin CM, Frank Chu SY & Jipkin J 1999. *Table of Isotopes, Eighth Edition Volume II*, Lawrence Berkeley National Laboratory, University of California.

IAEA (International Atomic Energy Agency) 2011. *Features: Depleted Uranium*, Vienna International Centre, Vienna, Austria. <http://www.iaea.org/newscenter/features/du/du_qaa.shtml>

McLeish J 2009. *RAS Quality Manual, ERH-RAS-SOP-2203, Electrodeposition*, Australian Radiation Protection and Nuclear Safety.

Milestone Microwave Laboratory Systems 2005a. *Application notes for Digestion, DG-EN-12, Rev. 03_04*, Milestone Inc., Shelton, Connecticut, USA.

Milestone Microwave Laboratory Systems 2005b. *Application notes for Digestion, DG-EN-13, Rev. 03_04*, Milestone Inc., Shelton, Connecticut, USA.

Milestone Microwave Laboratory Systems 2005c. *Application notes for Digestion, DG-EN-14 Rev. 03_04*, Milestone Inc., Shelton, Connecticut, USA.

Sdraulig S 2007. *RAS Quality Manual, ERH-RAS-SOP-2207, Preparation of Water Samples for the Measurement of Uranium*, Australian Radiation Protection and Nuclear Safety Agency.

Shakhashiro A, Trinkl A, Benesch T & Sansone U 2005. *Proficiency test on the Determination of α, β and γ –emitting Radionuclides*, Department of Nuclear Sciences and Applications Physics, Chemistry and Instrumental Laboratory Chemistry Unit, International Atomic Energy Agency.

6. Glossary

Activity

the measure of quantity of radioactive materials, except when used in the term ‘human activity’.

Alpha particle

two protons and two neutrons bound together identically to a helium nucleus emitted as a result of alpha decay.

Alpha spectrometry

analytical technique used to quantify the alpha activity of alpha emitting radionuclides

Becquerel (Bq)

the unit of activity in System Internationale (SI), equivalent to one disintegration per second.

Elecrodeposition

application of a current to facilitate the deposition of ion species onto a resultant charged surface.

Isotope

nuclides having the same atomic number but different mass number.

Nuclide

an individual species of atom characterised by its mass number and atomic number.

Matrix

components of a sample not including the analyte of interest.

Pitchblende

also known as uranite, a radioactive mineral and ore containing oxidised uranium.

Radioactive

the property of certain nuclides of emitting energy (radiation) by the spontaneous transformation of their nuclei.

Radioactive decay

the spontaneous transformation of the nucleus of an atom into another state, accompanied by the emission of radiation.

Radioactive tracer

a known quantity of radionuclide added to a solution of a chemically equivalent radionuclide of unknown concentration so that the yield of chemical separation can be monitored.

Radionuclide

a species of atomic nucleus which undergoes radioactive decay.

Appendix A: Mass Percentages of Uranium Isotopes in Uranium Salts.

Sample ID/RSIN	mass/mass isotopic percentage			isotopic ratio	
	^{234}U	^{235}U	^{238}U	^{234}U/^{238}U	^{235}U/^{238}U
uranyl acetate	0.002425	0.508	99.490	2.43E-05	5.11E-03
057-A008-0200	0.002483	0.525	99.473	2.49E-05	5.28E-03
	0.002593	0.493	99.504	2.60E-05	4.95E-03
mean	**0.002501**	**0.509**	**99.489**	**2.51E-05**	**5.11E-03**
Uncertainty *(k=2)*	0.000099	0.018	0.018	1.0E-06	1.9E-04
uranyl acetate	0.002251	0.474	99.524	2.261E-05	4.76E-03
057-A008-0201	0.002219	0.457	99.541	2.230E-05	4.59E-03
	0.002289	0.545	99.453	2.303E-05	5.48E-03
mean	**0.002253**	**0.492**	**99.506**	**2.265E-05**	**4.94E-03**
Uncertainty *(k=2)*	0.000041	0.054	0.054	4.2E-07	5.4E-04
uranyl nitrate depleted	0.002462	0.491	99.506	2.472E-05	4.93E-03
057-A009-0202	0.002459	0.440	99.558	2.471E-05	4.42E-03
	0.002400	0.480	99.518	2.412E-05	4.82E-03
mean	**0.002441**	**0.470**	**99.527**	**2.452E-05**	**4.73E-03**
Uncertainty *(k=2)*	0.000040	0.031	0.031	4.0E-07	3.1E-04
uranyl nitrate	0.000669	0.2568	99.7426	6.71E-06	2.58E-03
057-A026-0218	0.000652	0.2513	99.7481	6.54E-06	2.52E-03
	0.000639	0.2647	99.7346	6.41E-06	2.66E-03
mean	**0.000653**	**0.2576**	**99.7418**	**6.55E-06**	**2.58E-03**
Uncertainty *(k=2)*	0.000017	0.0078	0.0078	1.7E-07	8.2E-05
uranyl nitrate	0.002326	0.524	99.4735	2.339E-05	4.888E-03
057-A044-0248	0.002237	0.485	99.5130	2.251E-05	4.874E-03
	0.002277	0.494	99.5042	2.291E-05	4.965E-03
mean	**0.002280**	**0.501**	**99.4969**	**2.294E-05**	**4.909E-03**
Uncertainty *(k=2)*	0.000060	0.026	0.0257	5.1E-07	5.6E-05
uranium oxide	0.0020315	0.538	99.460	2.042E-05	5.83E-03
057-A010-0203	0.0020425	0.465	99.533	2.050E-05	4.67E-03
	0.0020844	0.513	99.485	2.091E-05	5.16E-03
mean	**0.0020528**	**0.505**	**99.493**	**2.061E-05**	**5.22E-03**
Uncertainty *(k=2)*	0.0000077	0.067	0.067	3.0E-07	6.7E-04
0.527% U_3O_8 Pitchblende	0.00534	0.719	99.275	5.34E-05	7.25E-03
057-A010-0207	0.00522	0.776	99.219	5.24E-05	7.82E-03
	0.00514	0.725	99.269	5.14E-05	7.31E-03
mean	**0.00523**	**0.740**	**99.255**	**5.24E-05**	**7.46E-03**
Uncertainty *(k=2)*	0.00012	0.036	0.036	1.2E-06	3.6E-04

Appendix B: Uranium Recoveries from Digestion Methods of Pitchblende.

0.527% U3O8 Pitchblende RSIN 057-A010-0207 Digestion Yields (% mass/mass)		
Digestion Method 1	**Replicate 1**	95.5
	Replicate 2	91.3
	Replicate 3	96.2
	Mean	**94.3**
	Uncertainty *(k=2)*	**3.1**
Digestion Method 2	**Replicate 1**	100.5
	Replicate 2	92.2
	Replicate 3	99.4
	Mean	**97.4**
	Uncertainty *(k=2)*	**5.2**
Digestion Method 3	**Replicate 1**	101.5
	Replicate 2	100.2
	Replicate 3	99.2
	Mean	**100.3**
	Uncertainty *(k=2)*	**1.3**
Digestion Method 4	**Replicate 1**	101.8
	Replicate 2	103.8
	Replicate 3	99.1
	Mean	**101.6**
	Uncertainty *(k=2)*	**2.8**

Appendix C: Definition of U-test Conditions

Condition	Probability	Status
u < 1.64	Greater than 0.1	The reported result does not differ significantly from the expected value
1.95 > u < 1.64	Between 0.1 and 0.05	The reported result probably does not differ significantly from the expected value
2.58 > u < 1.95	Between 0.05 and 0.01	It is not clear whether the reported result does not differ significantly from the expected value
3.29 > u < 2.58	Between 0.01 and 0.001	The reported result is probably significantly different from the expected value
u > 3.29	Less than 0.001	The reported result is significantly different from the expected value

Definition of U-test Conditions (Shakhashiro et al. 2005)