

## Appendix B



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**TO:** Raymond H. Johnson, Ph.D.  
USGS, MS 964D [rhjohnso@usgs.gov](mailto:rhjohnso@usgs.gov)

**FROM:** Michael E. Ketterer, Ph.D., Professor, Chemistry and Biochemistry  
[Michael.Ketterer@nau.edu](mailto:Michael.Ketterer@nau.edu) Phone 001 928 853 7188

**SUBJECT:** Results for the determination of  $^{234}\text{U}/^{238}\text{U}$  Activity ratios and U concentrations in TC-series and WP-series samples by ICPMS

I am pleased to provide results for the determination of  $^{234}\text{U}/^{238}\text{U}$  activity ratios and U concentrations in 59 water and soil leachate samples.

**Analytical Procedures:** U concentrations were determined by quadrupole ICPMS. Samples were diluted 5-fold (or in some cases, 50-fold) with an aqueous 0.16 M solutions containing 2.136  $\mu\text{g/L}$  Ir as an internal standard. A uranium concentration standard was prepared using a commercially available U concentration standard (10,000  $\mu\text{g/L}$ , CPI Scientific). The ICPMS was a Thermo X Series II equipped with a concentric glass nebulizer and a Peltier-cooled glass spray chamber. Seawater (North Atlantic) was used as a check sample; although this is not a sample with “certified” concentration, it is known that seawater contains approximately 3.3  $\mu\text{g/L}$  U. Two aliquots of seawater resulted in U concentrations found of 3.02 and 3.11  $\mu\text{g/L}$ , lending credence to the determination of U concentrations in unknown samples. A detection limit of 0.01  $\mu\text{g/L}$  U was obtained for the water samples analyzed in this manner.

The U AR data were acquired with a quadrupole ICPMS (Thermo X Series II) equipped with an APEX HF sample introduction system and concentric FEP Teflon nebulizer. Three integrations were acquired for each sample. The seawater samples and aliquots of U were used to evaluate the “mass discrimination” occurring during the measurements. “Mass discrimination” refers to a systematic difference in ion transmission efficiency of equal intensities of different ions. In this case, with the X-II, the mass discrimination leads to an artificially high measured  $^{234}\text{U}/^{235}\text{U}$  ratio, which can also be verified by similar observations in  $^{235}\text{U}/^{238}\text{U}$  measured in a natural U standard. For the coral and seawater samples, activity ratios of 1.165 – 1.174 were observed, which generated a mass discrimination factor of 1.0176:  $(^{234}\text{U}/^{235}\text{U})_{\text{corrected}} = (^{234}\text{U}/^{235}\text{U})_{\text{measured}} / 1.0176$ , using the seawater activity ratio of  $1.148 \pm 0.002$ .

In order to perform the activity ratio measurements, U was first separated from the sample matrix; 20 mL aliquots of sample solution were taken, mixed with 2 mL of 16 M  $\text{HNO}_3$ , and loaded onto a lab-fabricated 30 mg UTEVA resin column (resin from [www.eichrom.com](http://www.eichrom.com)). The columns were rinsed with three successive 1 mL portions of 2 M  $\text{HNO}_3$  to remove un-retained constituents, and U was eluted with the following sequence: 1 mL water, 1 mL 0.05 M

ammonium oxalate, and 1 mL water. U fractions were diluted as required before ICPMS analysis in cases where the  $^{235}\text{U}^+$  ion signal exceeded  $\sim 500,000$  counts/second.

In cases where the U concentration in the original sample was very low, typically  $< 0.1 \mu\text{g/L}$ , it was not possible to obtain adequate ion counts for  $^{234}\text{U}^+$  in the separated U fraction. However, it was still possible to obtain suitable data for most of the low-concentration samples in the batch. Nevertheless, the uncertainties obtained ( $\pm$  one standard deviation of the 3 sequential measurements) reflect the counting statistics limitations in measuring the activity ratio with many samples of lower U concentration.

Results are as shown on the following pages. I believe that you will find the AR<sub>234238</sub> results to be of use for your studies, and I would welcome the opportunity to discuss interpretations with you.

Respectfully submitted, 

Michael E. Ketterer, Ph.D., May 16, 2011

Lab ID	USGS ID	U, ug/L	234/238 AR	234/238 sd
1	TC08RK-02A	0.06	1.045	0.040
2	TC08RK-02C	0.14	1.491	0.052
3	TC08RK-05	0.07	1.733	0.013
4	TC08SS03-1	0.02		
5	TC08SS03-2	0.43	1.388	0.018
6	TC08B12-1	0.04	1.565	0.051
7	TC08B12-2	0.05	1.534	0.047
8	TC08B12-3	0.10	1.772	0.069
9	TC08B12-6	0.12	1.924	0.018
10	TC08B12-7	0.06	2.011	0.040
11	TC08B12-8	0.04	1.613	0.068
12	TC08B12-9	0.03	1.620	0.164
13	TC08B12-10	0.05	1.860	0.019
14	TC08B12-11	0.05	1.935	0.049
15	TC08B15-4	0.18	2.008	0.045
16	TC08B15-5	0.10	1.959	0.078
17	TC08B15-6	0.08	1.929	0.080
18	TC08B15-7	0.07	1.678	0.078
19	TC08B15-8	0.09	1.917	0.041
20	TC08B29-1	0.08	0.836	0.002
21	TC08B29-2	0.23	1.485	0.056
22	TC08B29-7	0.32	1.912	0.031
23	TC08B29-9	0.23	1.946	0.050
24	TC08B29-10	0.24	2.050	0.021
25	TC08B29-12	0.16	2.046	0.033
26	TC08B29-13	0.13	2.073	0.048
27	TC08B29-14	0.08	2.006	0.024
28	TC08B29-15	0.10	1.994	0.021
29	TC08B29-16	0.16	1.956	0.053
30	TC08B29-17	0.14	1.709	0.031
31	TC08B29-18	0.11	2.042	0.023
32	TC09B29-19	0.12	1.891	0.047
33	TC08B29-20	0.09	2.017	0.031
34	TC08B33-3	0.24	2.037	0.004
35	TC08B33-4	0.26	2.102	0.009
36	TC08B33-5	0.18	2.082	0.028
37	TC08B33-6	0.28	1.732	0.138
38	TC08B33-7	0.12	1.664	0.324
39	TC08B33-8	0.05		
40	TC08B33-9	0.05		
41	TC08B33-10	0.06		
42	TC08B33-11	0.02		
43	TC08B33-12	0.07	1.570	0.356
44	TC08B33-13	0.12	2.001	0.079
45	TC08B33-14	0.17	2.081	0.025
46	WP-01S-7.5	0.16	1.278	0.038
47	WP-01S-10	0.08	1.284	0.011
48	WP-01S-12.5	0.10	1.233	0.044
49	WP-01S-15	0.10	1.186	0.083

50	WP-01S-17.5	0.08	1.415	0.024
51	WP-01S-27.5	0.19	1.798	0.033
52	WP-01S-30	0.05		
53	WP-01S-32.5	0.02		
54	WP-01S-35	0.02		
55	WP-01S-37.5	0.04		
56	WP-07-3	0.02		
57	WP-07-4-5	0.01		
58	WP-07-6	0.01		
59	WP-07-8-9	0.02		

**Note: samples shown with yellow fill contained U concentrations too low to adequately measure the <sup>234</sup>U/<sup>238</sup>U activity ratio.**