

Evaluation of Uranium Measurements in Water by Various Methods – 13571

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ABSTRACT

In December 2000, EPA amended its drinking water regulations for radionuclides by adding a Maximum Contaminant Level (MCL) for uranium (so called MCL Rule)[1] of 30 micrograms per liter ($\mu\text{g/L}$). The MCL Rule also included MCL goals of zero for uranium and other radionuclides. Many radioactively contaminated sites must test uranium in wastewater and groundwater to comply with the MCL rule as well as local publicly owned treatment works discharge limitations.

This paper addresses the relative sensitivity, accuracy, precision, cost and comparability of two EPA-approved methods for detection of total uranium: inductively plasma/mass spectrometry (ICP-MS) and alpha spectrometry. Both methods are capable of measuring the individual uranium isotopes U-234, U-235, and U-238 and both methods have been deemed acceptable by EPA. However, the U-238 is by far the primary contributor to the mass-based ICP-MS measurement, especially for naturally-occurring uranium, which contains 99.2745% U-238. An evaluation shall be performed relative to the regulatory requirement promulgated by EPA in December 2000. Data will be garnered from various client sample results measured by ALS Laboratory in Fort Collins, CO. Data shall include method detection limits (MDL), minimum detectable activities (MDA), means and trends in laboratory control sample results, performance evaluation data for all methods, and replicate results. In addition, a comparison will be made of sample analyses results obtained from both alpha spectrometry and the screening method Kinetic Phosphorescence Analysis (KPA) performed at the U.S. Army Corps of Engineers (USACE) FUSRAP Maywood Laboratory (UFML).

Many uranium measurements occur in laboratories that only perform radiological analysis. This work is important because it shows that uranium can be measured in radiological as well as stable chemistry laboratories and it provides several criteria as a basis for comparison of two uranium test methods. This data will indicate which test method is the most accurate and most cost effective.

This paper provides a benefit to Formerly Utilized Sites Remedial Action Program (FUSRAP) and other Department of Defense (DOD) programs that may be performing uranium measurements.

INTRODUCTION

EPA added a drinking water regulation for uranium of 30 $\mu\text{g/L}$ in December 2000. This is designated as the Maximum Contaminant Level (MCL) for uranium and the regulation is referred to as the MCL Rule. Some decision makers have been known to use the old alternative action level of 20 pCi/L as an approximate action level.

Testing for uranium in groundwater, wastewater and stormwater at FUSRAP sites and other

radiologically contaminated sites is typically performed by radiological laboratories and will usually involve alpha spectrometric determination of the uranium isotopes 234 (U-234), 235 (U-235) and 238 (U-238). In order to verify compliance with the MCL, each of the isotopic results, in units of pCi/L, must be converted to µg/L by dividing each result by its respective specific activity. As per EPA's National Primary Drinking Water Regulations: Analytical Method for Uranium [2], detection of uranium can also be achieved using ICP-MS. The cost of the ICP-MS measurement is typically cheaper than alpha spectrometry mainly because there is less labor for the sample preparation part of the ICP-MS determination. Samples from various sources shall be tested by both methods and evaluated for accuracy (including uncertainty and bias), precision, sensitivity, and cost.

In addition, a comparison will be made of sample analyses results obtained from both alpha spectrometry and KPA, the latter of which is a screening method, performed at the USACE FUSRAP Maywood Laboratory (UFML). KPA is a quick and inexpensive method for determination of total uranium (mass-based) so this comparison will provide readers with an understanding of the utility of this screening method to approximate total uranium in water samples. While it is a screening method, measurement of uranium by the KPA method is approved by EPA for monitoring purposes.

DESCRIPTION

Alpha Spectrometry and ICP-MS Analyses

Forty-seven water samples were collected from three different clients. The samples were collected from sites with a range of uranium contamination ranging from very depleted uranium to very enriched uranium. The samples were shipped in several batches using standard chain-of-custody (COC) protocols to ALS Laboratory in Fort Collins, CO. Samples were received in plastic bottles. The COCs requested testing of the samples for isotopic uranium (U-238, U-235 and U-234) by alpha spectrometry. In order to conduct the comparison described in this paper, the samples were also analyzed by ICP-MS. ALS Standard Operating Procedures (SOPs) 776 rev14 (purification using anion exchange) and 714 rev12 (alpha spectrometry) were employed for the alpha spectrometry method. For the ICP-MS measurement, SOP 827 rev9 (EPA Method 6020A) was used [3, 4]. The samples were not filtered by the lab because they appeared clear with no visible turbidity.

Sample representativeness was ensured by shaking the contents of each sample bottle for approximately 10 seconds, then immediately drawing the desired sample aliquot. The sample aliquot size is 150 mls for isotopic uranium by alpha spectrometry, and 50 mls for the ICP-MS sample.

Nine sample batches were analyzed by both alpha spectrometry and ICP-MS. Each sample batch for both methods included a method blank, laboratory control sample (LCS) or blank spike, a laboratory replicate pair and a matrix spike. For the alpha spectrometry method, in lieu of a matrix spike, each field sample and batch QC sample was spiked with a tracer. The tracer is an isotope of the same element as the isotope(s) of interest so that it behaves similarly to the isotopes of interest. Thus any method anomalies such as losses by absorption onto material surfaces or unexpected reactions will occur to the same extent between the tracer and the isotopes of interest. The sample results are normalized to the recovery of the tracer, so that any method anomalies are accounted for.

Results for U-238 and U-235 obtained by the two methods are shown in Table I. The rationale for only presenting U-238 and U-235 results, and excluding U-234, is provided in the Discussion section.

Table I. U-238 and U-235 Results for Water Samples Analyzed by ALS using both Alpha Spectrometry and ICP-MS

Sample ID	Alpha Spec U-238 (pCi/L)	Alpha Spec U-238 (µg/L) ⁱ	Alpha Spec U-235 (pCi/L)	Alpha Spec U-235 (µg/L) ⁱ	Alpha Spec U-235 + U-238 (µg/L)	ICP-MS U-238 (µg/L)	ICP-MS U-238 + U-235 (µg/L) ⁱⁱ
1208100-1	26.20	77.9	1.61	0.745	78.6	83.4	84.1
1208100-3	39.20	116.5	1.18	0.546	117.0	141.0	142.2
1208100-4	13.90	41.3	0.61	0.282	41.6	42.6	42.9
1208100-6	0.79	2.3	0.06	0.028	2.3	1.5	1.5
1208100-7	113.00	335.9	3.00	1.39	337.3	351.0	352.4
1208100-8	10.10	30.0	0.85	0.393	30.4	32.7	33.1
1208100-9	53.90	160.2	3.77	1.744	161.9	143.8	145.5
1208100-10	17.50	52.0	0.94	0.435	52.4	55.9	56.3
1208306-4	20.20	60.0	0.88	0.407	60.4	50.9	51.3
1208306-8	19.00	56.5	0.67	0.310	56.8	50.6	50.9
1208303-17	0.86	2.6	0.84	0.389	3.0	2.0	2.4
1208303-27	3.26	9.7	1.00	0.463	10.2	9.5	10.0
1208206-1	28.36	84.3	1.27	0.587	84.9	73.1	73.7
1208206-3	69.50	206.6	3.33	1.540	208.1	197.0	198.5
1208206-4	23.70	70.5	0.57	0.264	70.8	59.9	60.2
1208206-6	0.31	0.9	0.01	0.005	0.9	1.2	1.2
1208206-7	103.00	306.2	1.45	0.671	306.9	289.1	289.8
1208206-8	12.60	37.5	0.46	0.213	37.7	30.6	30.8
1208206-9	14.50	43.1	0.76	0.352	43.5	37.6	38.0
1208206-10	18.40	54.7	0.84	0.389	55.1	49.2	49.6
1208460-2	1.64	4.9	0.35	0.162	5.1	6.3	6.5
1208460-3	0.94	2.8	0.27	0.125	2.9	3.6	3.7
1208460-4	2.88	8.6	0.51	0.236	8.8	7.8	8.0
1208460-5	1.22	3.6	0.21	0.097	3.7	3.5	3.6
1208460-6	0.74	2.2	0.23	0.106	2.3	3.5	3.6

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1208460-7	2.80	8.3	0.50	0.231	8.5	7.3	7.5
1208380-3	4.34	12.9	0.26	0.120	13.0	11.9	12.0
1208380-6	1.91	5.7	0.25	0.116	5.8	4.3	4.4
1208380-9	3.68	10.9	0.12	0.056	11.0	9.3	9.4
1208380-12	1.73	5.1	0.06	0.028	5.1	4.9	4.9
1208380-15	1.80	5.4	0.24	0.111	5.5	4.0	4.1
1208381-4	3.73	11.1	0.39	0.180	11.3	11.9	12.1
1208346-1	49.90	148.3	2.22	1.027	149.3	119.0	120.0
1208346-3	81.00	240.8	3.21	1.485	242.3	216.0	217.5
1208346-4	15.80	47.0	0.96	0.444	47.4	39.1	39.5
1208346-6	0.82	2.4	0.11	0.051	2.5	1.3	1.4
1208346-7	125.00	371.6	2.60	1.203	372.8	341.0	342.2
1208346-8	11.20	33.3	0.63	0.291	33.6	30.7	31.0
1208346-9	28.40	84.4	2.05	0.948	85.3	81.4	82.3
1208346-10	22.10	65.7	0.80	0.370	66.1	57.8	58.2
1208346-16	0.28	0.8	0.06	0.028	0.8	1.3	1.3
1208346-18	0.45	1.3	-0.05	-0.023	1.3	1.4	1.4
1208346-21	0.54	1.6	0.23	0.106	1.7	1.4	1.5
1208334-5	1.21	3.6	0.00	-0.001	3.6	4.0	4.0
1208334-11	3.03	9.0	0.19	0.088	9.1	8.3	8.4
1208334-17	2.80	8.3	0.03	0.014	8.3	6.8	6.8
1208334-23	0.19	0.6	0.08	0.037	0.6	0.03	0.07

- i. See Discussion section below for explanation of how alpha spectrometry results were converted from pCi/L to µg /L
- ii. See Discussion section below for explanation of how the total uranium value for ICP-MS was calculated

Alpha Spectrometry and KPA Analyses

Twenty-two wastewater samples were analyzed by UFML using Standard Methods for the Examination of Water and Wastewater method 7500-U [5] which employs alpha spectroscopy as the detection method, as well as the screening method KPA using ASTM method D5174, Trace Uranium in Water using Pulsed Laser Phosphorimetry [6]. All samples were filtered using a 0.45 micron filter and were verified to have a pH of less than two. The results are shown below in Table II. A comparison of results obtained by these two methods, which is described in the Discussion section, provides an indication of the utility of the KPA as a screening method for total uranium. Similar to the alpha spectroscopy – ICP-MS comparison, the rationale for only presenting U-238 results, and excluding U-234 and U-235 results, is provided in the Discussion section.

Table II. Results for Water Samples Analyzed by UFML using both Alpha Spectrometry (AS - U-238) and KPA (Total Uranium)

Sample ID	U-238 by AS (pCi/L)	U-238 by AS (µg/L) ⁱ	KPA (µg/L)	Sample ID	U-238 by AS (pCi/L)	U-238 by AS (µg/L) ⁱ	KPA (µg/L)
07a-081034	2.08	6.18	5.6	10a-080991	0.89	2.65	1.35
07a-081035	2.83	8.41	5.92	10a-081011	0.18	0.535	0.664
10a-080842	0.603	1.79	1.49	10a-081012	ND	NA	5.61
10a-080875	0.326	0.969	1.13	10a-081018	0.555	1.65	1.95
10a-080876	0.153	0.455	0.765	10a-081048	0.913	2.71	2.92
10a-080922	0.113	0.336	0.281	10a-081049	0.126	0.375	0.274
10a-080927	0.251	0.746	0.359	12b-080845	1.18	3.51	6.64
10a-080949	ND	NA	2.07	12b-080846	1.4	4.16	6.54
10a-080950	ND	NA	1.99	12b-081010	6.85	20.4	20
10a-080958	3.52	10.46	ND	12b-081162	1.31	3.89	3.03
10a-080965	0.53	1.58	1.4	12b-081163	1.26	3.75	2.26

i. See Discussion section below for explanation of how alpha spectrometry results were converted from pCi/L to µg/L

DISCUSSION

Basis for Comparison

Alpha Spectrometry and ICP-MS

The MCL drinking water regulation described earlier sets a limit of 30 µg/L for total uranium. If a laboratory is analyzing water samples by ICP-MS, they only need to compare the sum of the concentrations of U-234, U-235 and U-238 to 30 µg/L. For a laboratory analyzing water samples for U-238, U-235 and U-234 by alpha spectrometry, the activity-based values must be converted to mass-based values to allow comparison to the action level. One approach is to convert the U-238 activity concentration in pCi/L to concentration in µg/L by dividing by its specific activity of 0.3364 pCi/µg [7]. Since the U-238 isotope contributes 99.2745% [8] to the total uranium mass in naturally occurring uranium, one would only have to convert the U-238 activity concentration to mass-based concentration and in so doing would only incur a small low bias of approximately 0.7%. In fact, the bias could be eliminated entirely by converting the U-238 concentration to total uranium concentration by multiplying the U-238 concentration by (100/99.2745), or 1.0073. This assumes a natural distribution. The natural percentages and specific activities of the uranium isotopes are shown in Table III.

Table III. Uranium Natural Abundances and Specific Activities

Isotope	Natural Abundance (percent by mass)	Specific Activity (pCi/µg)
U-234	0.0054	6252
U-235	0.72	2.162
U-238	99.2745	0.3364

The only potential drawback to this approach is when the uranium is enriched, in which case the U-235 concentration will be higher. Thus, if one were to only convert the U-238 activity to mass-based concentration, the low bias error would increase. The U-234 activity may also be higher when one encounters enriched uranium. However, the mass-based contribution from U-234 is so small, that most enrichment scenarios do not increase the mass-based contribution from U-234. For example, in this data set, even for the most enriched uranium data point, the mass-based contribution from U-234 is only 0.1% and so U-234 data is not included in the comparison.

For the data presented here, the uranium isotopic distribution spans the spectrum from somewhat enriched (highest enrichment is about 13% U-235 by mass) to somewhat depleted (lowest depletion is about 0.22% U-235 by mass). The U-235 percentage in naturally occurring uranium is 0.72%.

To perform the comparison, the U-238 and U-235 activity results obtained by alpha spectrometry were divided by their specific activities (0.3364 pCi/µg and 2.163 pCi/µg, respectively) [7] to convert the activities in pCi/L to concentrations in µg/L, then the concentrations were summed to obtain total uranium by alpha spectrometry converted to mass. For the ICP-MS measurement, due to the high U-238 percentage by mass, the laboratory only analyzed the samples for U-238. Therefore, to obtain total uranium by ICP-MS, the converted mass-based U-235 result from the alpha spectroscopy determination was added to the U-238 ICP-MS result.

Alpha Spectrometry and KPA Analyses

The U-234 and U-235 results were excluded from the total uranium result obtained by converting the alpha spectroscopy results to a mass-based value. The U-234 was excluded for the same reason as stated above for the alpha spectroscopy – ICP-MS comparison as its contribution to uranium mass is

insignificant. The U-235 results were non-detect in 17 of the 22 samples. For four out of the five samples for which it was detected, it contributed (as one would expect for U-235 in naturally occurring uranium) one percent or less to the total uranium mass. For the fifth positive result, it contributed approximately 2.5% of the total mass (0.04 µg/L out of 1.62 µg/L). For these reasons, the U-235 values were not included in the total uranium calculation. So, the comparison in this case was simply the U-238 alpha spectroscopy value converted to mass versus the total uranium KPA value.

Of the 22 samples, 18 returned positive detects for both U-238 by alpha spectroscopy and total uranium by KPA. Of the remaining four result pairs, three were non-detect for U-238 and positive for KPA, while one was non-detect for KPA and positive for U-238.

Results Comparison

Alpha Spectrometry and ICP-MS

As shown in Table I, the U-238 and U-235 alpha spectrometry data in pCi/L were converted to µg/L values by dividing each pCi/L value by its specific activity, 0.3364 pCi/µg and 2.163 pCi/µg, respectively for U-238 and U-235 [5]. The average concentrations of U-238 analyzed by alpha spectrometry and ICP-MS are 60.7 ug/L and 57.2 ug/L, respectively. The comparison of total uranium by alpha spectrometry converted to mass with total uranium by ICP-MS is expressed as the Relative Percent difference (RPD) between the values. As noted in the Basis for Comparison (see the last Paragraph under Alpha Spectrometry and ICP-MS), the alpha spectrometry total uranium value is the sum of the U-235 and U-238 values after conversion of mass-based units, and the total uranium ICP-MS result is the sum of the U-238 ICP-MS result and the converted mass-based U-235 result from the alpha spectroscopy determination. The RPD is calculated as follows.

$$[(\text{Result (alpha spec)} - \text{Result (ICP-MS)}) / ((\text{Result (alpha spec)} + \text{Result (ICP-MS)}) / 2)] \times 100 \quad (\text{Eq. 1})$$

The RPD between the two average values is $(3.5/58.95) \times 100$, or 6.0%. If one calculates the RPD for each data pair using the absolute difference between the alpha spectrometry and ICP-MS total uranium values, the average RPD and standard deviation are $15.5\% \pm 12.3\%$ (one non-detect value was not included) based upon 46 data points. Since the relative variability tends to be greater for low activity or low concentration results, we recalculated the average RPD after eliminating all data points with low activity or low mass-based concentrations of less than 10%; i.e., 3 µg/L, of the regulatory action level. The revised average RPD and standard deviation are $11.8\% \pm 6.9\%$ based upon 37 points. The range of RPD values for these 37 points is 3.0% to 28.2%. All alpha spectrometry results have an associated counting uncertainty. The relative uncertainty for U-238 equals: $(\text{the uncertainty (or one standard deviation)}/\text{activity}) \times 100$. The average relative uncertainty for U-238 for the 37 points is 11.6% so much of the difference between alpha spectrometry and ICP-MS results may be attributed to the alpha spectrometry counting uncertainty.

Alpha Spectrometry and KPA Analyses

The average and standard deviation of the RPD was calculated for 18 of the 22 result pairs which yielded positive results for both total uranium by alpha spectroscopy (U-235 + U-238) converted to mass and total uranium by KPA. The average and standard deviation are $30.9\% \pm 21.1\%$ based upon 18 points. Nine of the RPD values show alpha spec total uranium values that are greater than the KPA total uranium by more

than 10% relative, while six of the points show KPA total uranium values that are greater than the alpha spec total uranium values by more than 10% relative. Three of the RPD values were less than 10% relative. Thus, there was no discernible trend of one method having consistently higher values than the other method. The RPD values ranged from 2.5% to 70%. The lowest RPD value was observed for the highest concentration of approximately 20 µg/L. The remaining concentrations ranged from 0.3 µg/L to 6.6 µg/L. While an average RPD of 31% between a screening is encouraging, four of the result pairs showed one positive result and one non-detect result, which indicates poorer precision but also the potential for false positive results. Three of the four pairs show a non-detect for the alpha spectroscopy results and a positive KPA result. The positive KPA results ranged from 2.0 µg/L to 5.6 µg/L. The positive results may be an indication of the greater susceptibility of KPA to interferences. The fourth pair showed a non-detect for the KPA and a positive result of 3.5 pCi/L for U-238 (10.5 µg/L). Based upon this fairly limited data set, a conservative rule of thumb for KPA measurements is that the result is within a factor of two of the true value.

Method Comparison

Since it is understood that the KPA is a screening method which is considered semi-quantitative and more susceptible to interferences, this comparison is only performed for the alpha spectrometry and ICP-MS methods.

Accuracy

The accuracy of each method is estimated from examination of method blank results, laboratory control sample (LCS) results, and the uncertainty associated with each sample result. The accuracy for a given sample can best be determined by testing matrix spike samples. A LCS is a blank matrix, in this case, deionized water, that is spiked with a known amount of the analyte of interest. A method blank is a sample of deionized water. Both the method blank and the LCS are processed in the same manner as the field samples. Any contamination, non-matrix interferences, analyte losses, or other method anomalies and inaccuracies should be reflected in the LCS and method blank results.

The accuracy for the LCS is determined by calculating the percent recovery as follows:

$$\text{Percent Recovery, \%R} = C_{\text{measured}}/C_{\text{added}} \times 100 \quad (\text{Eq. 2})$$

Recoveries lower than 100% indicate a low bias while recoveries higher than 100% indicate a high bias for the method using the LCS. For alpha spectrometry and ICP-MS, 240 and 199 LCS %R values, respectively, were calculated for LCS analyzed between November 2011 and October 2012. For method blanks, 240 and 111 blanks were analyzed between November 2011 and October 2012 for alpha spectrometry and ICP-MS, respectively. The mean LCS %R, mean method blank, and plus or minus two and three standard deviation limits around the mean LCS %R and mean method blank value are shown in Table IV below.

Table IV. Laboratory Control Sample Mean and Two and Three Sigma Control Limits

-3 std. deviations	-2 std. deviations	Mean	+2 std. deviations	+3 std. deviations
<i>Alpha Spectrometry LCS (%R for pCi/L values)</i>				
82.42	88.13	99.54	111.0	116.7
<i>Alpha Spectrometry Method Blank (pCi/L)</i>				
-0.0242	-0.0132	0.0088	0.0308	0.0418

<i>ICP-MS LCS (%R for µg/L values)</i>				
87.86	91.67	99.30	106.93	110.74
<i>ICP-MS Method Blank (µg/L)</i>				
-0.0256	-0.016	0.0032	0.0224	0.0320

The accuracy of the LCS results is excellent for both alpha spectrometry and ICP-MS. No inherent method bias is indicated since the mean %R values are so close to 100%. The alpha spectrometry LCS variability is slightly higher than that for ICP-MS as seen in the standard deviation values (5.71% vs. 3.81%). The method blank values are also excellent; i.e., low. The mean alpha spectrometry blank value of 0.0088 pCi/L is only 0.044% of the approximate action level of 20 pCi/L, while the ICP-MS mean blank value of 0.0032 µg/L is only 0.011% of the action level of 30 µg/L.

The accuracy of results for the actual sample matrix is typically determined through the use of matrix spike samples. For alpha spectrometry, a tracer is used in lieu of a matrix spike. The tracer for isotopic uranium is uranium-232 (U-232) and it is added to every field sample and batch QC sample. The isotopic result is normalized to the recovery of the tracer. For example, if the U-238 result is 5 pCi/L, and the tracer recovery is 80%, then the value is normalized by dividing 5 by 0.8 to yield a final value of 6.25 pCi/L. Most of the tracer recovery values varied between 43% and 99%. One tracer recovery was 35%.

For the ICP-MS, the average matrix spike recovery was calculated for the most recent 11 batches. The recoveries ranged from 98% to 104% and the average %R is 100%. The matrix spike concentration was 10 µg/L of U-238.

Of the 37 RPD values discussed for the alpha spectrometry – ICP-MS results comparison, 28 showed a higher alpha spec total uranium value. The overall average alpha spectroscopy U-238 value is 20.4 pCi/L while the overall average ICP-MS result converted to activity is 19.2 pCi/L. Relative to the ICP-MS average, the alpha spectroscopy average value is 6.2% higher. This may be an indication of a small high bias associated with the alpha spectroscopy measurement, a small low bias associated with the ICP-MS measurement, or a combination of both. The excellent matrix spike recovery for the ICP-MS would suggest that most of the bias associated with this comparison is associated with the alpha spectroscopy measurement.

Precision

Precision for a given sample analyzed by a given method is determined from examination of laboratory replicates results. Eleven and eleven replicate pairs, respectively, were analyzed by alpha spectrometry and ICP-MS. The average relative percent differences (RPD) for the alpha spectrometry and ICP-MS result pairs are 8.0% and 3.2%, respectively. One alpha spectrometer value was not used as it was non-detect. The precision values are very good.

The two sigma uncertainty is reported with every alpha spectrometer result. The average percent relative standard deviation (%RSD) ((one sigma uncertainty/result) X 100) of the alpha spectrometer U-238 results is 12.8%.

Sensitivity

Sensitivity is measured by the minimum detectable activity (MDA) for alpha spectrometry measurements, and by the method detection limit (MDL) for ICP-MS. Both methods have more than adequate sensitivity. Typical MDA values for U-238 and U-235 by alpha spectrometry are 0.3 pCi/L each for a 150 ml sample aliquot and count time of 300 minutes. The MDL and reporting limit (RL) for U-238 by

ICP-MS are 1.0 part-per-trillion (ppt) and 10 ppt, respectively.

Cost

Typical costs for U-238 measurement by alpha spectrometry and ICP-MS are \$100-\$110/sample and \$20-\$30/sample, respectively.

CONCLUSION

This study has shown that ICP-MS is a very good method for determining MCL Rule compliance for total uranium in drinking water. ICP-MS shows sensitivity and accuracy that is comparable to alpha spectrometry, while the precision of the ICP-MS method is slightly better than that of alpha spectroscopy. The ICP-MS method is significantly cheaper than the alpha spectrometry method.

Most of the mass-based contribution to total uranium comes from U-238, approximately 99.3% in naturally occurring uranium. The U-235 contribution is about 0.7% while the U-234 contribution is insignificant. The U-235 percentage increases as uranium enrichment increases.

Very good agreement was observed for total uranium results generated by ICP-MS and alpha spectroscopy. The average RPD for total uranium between the two methods, for concentrations greater than 3.0 µg/L is 11.8%. Observation of a large number of LCS and method blank results for both methods indicate excellent accuracy with virtually no bias when the method is performed with a clean water matrix.

Alpha spectroscopy was also compared to the KPA screening method for total uranium. For a limited data set of 22 points, 18 of the 22 points showed an average RPD of about 31% between the two methods, a reasonably good difference for comparison of results from a screening method to an established radioanalytical method. However, four of the 22 points showed one non-detect and one detect for each pair indicating the potential for false positives in the KPA method due to its greater susceptibility to interferences.

REFERENCES

1. USEPA, Radionuclides Rule: A Quick Reference Guide, EPA 816-F-01-003, June 2001.
2. USEPA, National Primary Drinking Water Regulations: Analytical Method for Uranium; Code of Federal Regulations, 40 CFR 141, August 25, 2004.
3. ALS Standard Operating Procedures (SOP); SOP 776 rev14 Purification using Anion Exchange and SOP 714 rev12, Alpha Spectrometry were employed for the alpha spectrometry method. SOP 827 rev9 was employed for the ICP-MS measurement
4. USEPA, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846), 1997 plus updates through 2008.
5. American Public Health Association (APHA), the American Water Works Association (AWWA), and the Water Environment Federation (WEF), Standard Methods for the Examination of Water and Wastewater, 22nd edition, 2012.
6. American Society for the Testing of Materials (ASTM) International, Standard Test Method for Trace Uranium in Water by Pulsed-Laser Phosphorimetry, D5174-02, May 2002

WM2013 Conference, February 24 – 28, 2013, Phoenix, Arizona USA

7. Integrated Environmental Management, Inc., Table of Specific Activities, 2010
8. Web Elements: the Periodic Table on the www, Naturally occurring isotopes of uranium and their natural abundances by mass, 2012