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ESTABLISHING THE TRACEABILITY OF A URANYL NITRATE SOLUTION TO A STANDARD REFERENCE MATERIAL

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Establishing the Traceability of a Uranyl Nitrate Solution to a Standard Reference Material

by

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ABSTRACT

A uranyl nitrate solution for use as a Working Calibration and Test Material (WCTM) was characterized, using a statistically designed procedure to document traceability to National Bureau of Standards Reference Material (SRM-960). A Reference Calibration and Test Material (RCTM) was prepared from SRM-960 uranium metal to approximate the acid and uranium concentration of the WCTM. This solution was used in the characterization procedure. Details of preparing, handling, and packaging these solutions are covered.

Two outside laboratories, each having measurement expertise using a different analytical method, were selected to measure both solutions according to the procedure for characterizing the WCTM. Two different methods were also used for the in-house characterization work. All analytical results were tested for statistical agreement before the WCTM concentration and limit of error values were calculated. A concentration value was determined with a relative limit of error (RLE) of approximately 0.03% which was better than the target RLE of 0.08%.

The use of this working material eliminates the expense of using SRMs to fulfill traceability requirements for uranium measurements on this type material. Several years' supply of uranyl nitrate solution with NBS traceability was produced. The cost of this material was less than 10% of an equal quantity of SRM-960 uranium metal.

KEYWORDS: Calibration; characterization; reference materials; traceability standards; and uranyl nitrate solution

INTRODUCTION

Uranyl nitrate solutions are essential for use as standards in the surveillance of analytical methods, calibration of equipment and methods, and training and testing laboratory personnel. Because of these functions and the importance of uranium measurements for nuclear materials accounting purposes, the standards must be of unquestionable quality and clearly traceable to a primary standard reference material.

Ideally, for a standard to be used as a working calibration and test material it should:

1. be stable over extended storage periods,
2. closely match the material routinely analyzed,
3. have an uncertainty consistent with its intended use,
4. be convenient to use, and
5. be economical.
Uranium nitrate solutions, for use as working calibration and test materials, having uranium concentrations traceable to the National Bureau of Standards can be prepared in two ways. They can be synthesized from well characterized starting materials of known integrity such as Standard Reference Materials, using NBS certified mass and volume standards for the solution measurements. Using this procedure, the integrity of the starting material is transferred to the standard, which can be used as either a reference or working calibration test material. The second way uranium nitrate CRM's can be prepared is by characterizing a plant uranium nitrate solution by two different methods of analysis. The NBS traceability is established by calibrating the measurement systems used to characterize the CRM with a reference standard while concurrently analyzing both solutions.

The cost of NBS CRM's prohibits their use where large quantities of working standard are required for routine analytical measurement operations. Therefore, the second method was used in preparing a large supply of uranium nitrate CRM. The overall cost of procurement, preparation, and characterization was considerably less than the cost of preparing an equal quantity of the standard from CRM-960. By characterizing, the desired reliability was obtained and NBS traceability was established.

PREPARATION OF CALIBRATION AND TEST MATERIALS

Two uranium nitrate solutions were prepared as calibration and test materials as shown in Figure 1. A large quantity of uranium nitrate solution was prepared for characterizing and establishing traceability to the standard reference material. This quantity would meet the future needs for a working calibration and test material. After the specifications of the working standard had been determined, calculations were made to determine how much uranium and acid would be needed for the CRM. Then a small quantity of uranium nitrate solution was prepared for use as a reference standard to calibrate the measurement systems used in the characterization of the working standard.

Preparation of the Working Calibration and Test Material

Approximately 80 liters of uranium nitrate were obtained from a plant product tank and used in the preparation of the working standard.

The solution was filtered to remove insolubles and the filtrate was transferred to a large drum for mixing. The drum was covered and the solution thoroughly mixed by sparging overnight to ensure homogeneity. Samples were analyzed for concentration of acid, uranium, and impurities. The results of these analyses were satisfactory. The solution was mixed again and systematically transferred to four clean dry 27 liter poly bottles. The necks were sealed with a plastic film and closed with a screw cap to protect against evaporation until the solutions were packaged.

Synthesizing the Reference Calibration and Test Material

The reference calibration and test material was prepared from NBS CRM-960 uranium metal to approximate the acid and uranium concentration of the CRM. The metal was pickled for approximately ten minutes in warm eight molar nitric acid to remove the surface oxides. The pickled metal was rinsed with water and acetone and air dried. The required quantity of metal was weighed several times alternately with NBS traceable Class S weights. The metal was transferred to a precleaned Erlenmeyer flask fitted with a standard taper air cooled condenser and reflux head. The metal was dissolved in eight molar nitric acid. The dissolution was completed in 24 hours using low heat. The solution was cooled and quantitatively transferred to a calibrated bubble neck flask having a screw cap enclosure. The acid concentration was adjusted before the solution was diluted to volume at the desired temperature. The solution was weighed several times on a double pan analytical balance, using the double transposition weighing technique. The mean weights were determined and corrected to the certified apparent masses of the Class S weights. The makeup value uncertainty error was propagated. Table 1 shows the actual data used and the calculations. The reference values were also calculated on a volume basis.

PACKAGING THE CALIBRATION AND TEST MATERIALS

The prepared solutions were packaged in various sizes of borosilicate glass ampules and
flame sealed the day after they were prepared. Specially fabricated 500 ml borosilicate glass ampuls were used for packaging large quantities of the VCTM for long term storage. The large ampuls will be opened as needed and repackaged in smaller ampuls. The ampuls were precleaned with hot four molar nitric acid, thoroughly rinsed and allowed to air dry prior to use. Several 2, 5, 10, 20, and 50 ml ampuls were filled for the characterization work and routine use.

A mechanical ampul filler was used to rapidly aliquot solution to the ampuls, which were immediately flame sealed with a commercial ampul sealer to prevent evaporation. Special precautions were taken when transferring the solution from the large poly bottles to the ampuls. Care was taken to prevent dripping solution in the ampul necks which could dry when the neck was sealed and affect the solution concentration.

The packaging provided 180 large ampuls containing about 130 grams of uranium which is equivalent to approximately five units of SRM-960 uranium metal. Many smaller ampuls were also filled.

PROCEDURE FOR CHARACTERIZING WORKING CALIBRATION TEST MATERIALS

Two analytical chemistry methods known to provide precise and accurate results were used to characterize the VCTM. They were a gravimetric uranium method based on the ignition of uranium to UO₃ and the New Brunswick Laboratory's modification of the Davies and Gray titrimetric method.

Two independent laboratories, selected for their measurement expertise, were contracted to analyze the solutions. In-house characterization of the two solutions was also performed using two different analytical methods.

ANALYTICAL MEASUREMENTS

NUREG-0253 lists criteria covering the selection of the number of replicate analyses for characterizing the working standard in section 5.3. The desired limit of error is related to the end use of the VCTM and is a function of the accuracy and precision of the plant material to which the VCTM applies. A relative limit of error (RLE) of less than 1/2 of the 0.25% RLE established for the plant material measurements was selected. The number of samples analyzed determines if satisfactory measurement precisions are attained. In characterizing the VCTM by two methods, the limit of error is a function of the precision of the two analytical methods used.

A minimum of five replicates is recommended in the NUREG. On the basis of the Safeguards Analytical Laboratory Evaluation Program Report of the "Average Within Lab Standard Deviation" for the two methods, nine replicate aliquots were selected for the titrimetric method and six were selected for the gravimetric method. These numbers should have given approximately equal estimates of the standard deviation of the means, but did not. The actual precision estimates are shown on page 1 of Appendix I. The in-house measurement precision estimates were well known, therefore, six replicate aliquots were chosen for the in-house characterization of the VCTM. An equal number of determinations were performed on both standards by each method.

Evaluation of the Analytical Measurements

The statistical tests given in NUREG-0253 were applied to the data to compare the confirmation analyses and establish an assigned value and limit of error for the working standard. The statistical comparison of the results of the two methods was accomplished following this scheme:

1. The means and associated standard deviations were calculated for each data set.
2. The precisions of the results obtained by both methods for the VCTM and RCTM were compared.
3. The two VCTM means were bias corrected for the difference observed between the RCTM analyses and its makeup value.
4. The VCTM population means, obtained using the two methods, were tested for equality of means. The approximate variances and degrees of freedom were derived by error
propagation.

5. An assigned value and associated standard deviation for the VCTM was calculated by weighting the bias corrected means for both methods.

6. The limit of error and relative limit of error were calculated for the VCTM and tested.

7. The 95\% confidence interval was calculated.

The results of the outside laboratories analyses are given in Appendix I with the statistical treatments listed above. When the VCTM mean results of the two laboratories were tested using the t-test of equality of means, the difference in population means was significant.

Investigation revealed that Laboratory II's analyses of the VCTM had better precision than the historical precision of the laboratory. Therefore, a pooled standard deviation was calculated from historical data and characterization data and used instead of the standard deviation of the VCTM and RCTM results. This was permissible since precision data previously obtained for a method used for similar sample analyses can be pooled with current data to compute a better estimate of the standard deviation with a larger number of degrees of freedom.

The results of the outside laboratories appeared to be positively biased from the make-up value and in-house analyses of the reference standard. However, no significant difference was observed between the laboratories' values for the working standard after correcting for the difference between the observed values and the reference value of the RCTM. These results confirmed the in-house assigned value of the VCTM.

SECOND CHARACTERIZATION PROGRAM

The unexplained bias of the reference standard caused in-house concern that our analytical results may have been negatively biased, so in 1978 a new reference standard was prepared for a second characterization of the working standard. Table II shows the actual data used in calculating the concentration and associated standard deviation values for the 1978 RCTM.

Several 500 ml ampuls of the VCTM were opened and six aliquots of each standard were analyzed by two methods as done previously. The analytical measurements and subsequent statistical treatment of this work are given in Appendix II.

These analyses confirmed the makeup value of the 1978 RCTM and the value previously assigned to the VCTM. The new assigned value of the VCTM was within the confidence interval established in the previous work.

Table III summarizes all of the analyses performed in the characterization effort. The mean value of all the analyses of the VCTM is 219.20 ±0.03 mg U/g.

SUMMARY

Detailed instructions are given in the regulatory guide for the preparation and characterization of a uranium nitrate VCTM. However, some potential problems that could be encountered are not specifically addressed. For example, the particular problems that we encountered with Laboratory II's very precise measurements and the apparent bias between the outside laboratories and in-house results, before they were corrected for, by using the techniques described in NUREG-0253.

Following the procedure, a uranium nitrate VCTM can be prepared from a plant uranium nitrate solution at a minimum cost, with NBS traceability, and within a predetermined limit of error.

FIGURES, TABLES AND APPENDICES

Table I. 1976 RCTM makeup value and associated standard deviation calculations.

Table II. 1978 RCTM makeup value and associated standard deviation calculations.
Table III. Characterization data summary generated by three different laboratories, using two different analytical chemistry methods, in two different years, while concurrently analyzing one of two different RCTM's. Each mean has been corrected for the apparent bias observed in the analysis of the RCTM.

Figure 1. Preparation schemes for calibration and test materials.

Appendix I. Statistical treatments of the RCTM characterization analyses from outside laboratories.

Appendix II. Statistical treatments of the RCTM characterization analyses by the in-house laboratory.
Table I. 1976 RCTM makeup value and associated standard deviation calculations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Component</th>
<th>Mean Value</th>
<th>Standard Deviation g/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>assigned makeup value</td>
<td>0.99975</td>
<td>0.000085</td>
</tr>
<tr>
<td>$S_A$</td>
<td>associated standard deviation</td>
<td>0.99992</td>
<td>0.0</td>
</tr>
<tr>
<td>$F$</td>
<td>purity of starting material</td>
<td>0.99975</td>
<td>0.000019</td>
</tr>
<tr>
<td>$b$</td>
<td>air buoyancy</td>
<td>0.99992</td>
<td>0.0</td>
</tr>
<tr>
<td>$W_1$</td>
<td>weight of starting material</td>
<td>166.45221</td>
<td>0.0034</td>
</tr>
<tr>
<td>$W_2$</td>
<td>tare weight of the flask</td>
<td>176.695</td>
<td>0.034</td>
</tr>
<tr>
<td>$W_3$</td>
<td>gross weight of solution &amp; flask</td>
<td>910.209</td>
<td>0.034</td>
</tr>
<tr>
<td>$W_4$</td>
<td>$W_2 - W_2$ = net weight of solution</td>
<td>733.513</td>
<td>0.048</td>
</tr>
<tr>
<td>$S$</td>
<td>standard deviation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$A = \frac{(F)(b)(W_1)}{W_4}$

$S_A = \frac{1}{W_2} \left[ (W_2^2 (S_{W_1})^2 + (W_1)^2 S_F^2) + A^2 (S_{W_2}^2 + S_{W_3}^2) \right]^{\frac{1}{2}}$

$A = \frac{(0.99975)(0.99992)(166.45221 \text{ g U})}{733.512 \text{ g}}$

$A = 0.226851 \text{ g U/g}$

$S_A = \frac{1}{733.512} \left[ (0.99992)^2 \left( (0.99975)^2 (0.00019)^2 + (166.4522)^2 \right) 
+ (0.000085)^2 + (0.226851)^2 \left( (0.034)^2 + (0.034)^2 \right) \right]^{\frac{1}{2}}$

$S_A = 2.44 \times 10^{-5}$

Final concentration = $226.851 \pm 0.024 \text{ mg U/g}$
### Table II. 1978 HCTM makeup value and associated standard deviation calculations.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Component Description</th>
<th>Mean Value g/g</th>
<th>Standard Deviation g/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>assigned value</td>
<td>0.99975</td>
<td>0.000085</td>
</tr>
<tr>
<td>( S_A )</td>
<td>associated standard deviation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( F )</td>
<td>purity of NBS-960 metal</td>
<td>0.99992</td>
<td>0.0</td>
</tr>
<tr>
<td>( b )</td>
<td>air buoyancy correction</td>
<td>155.37830</td>
<td>0.00011</td>
</tr>
<tr>
<td>( W_1 )</td>
<td>weight of uranium metal</td>
<td>164.858</td>
<td>0.0083</td>
</tr>
<tr>
<td>( W_2 )</td>
<td>tare weight of flask</td>
<td>882.044</td>
<td>0.0132</td>
</tr>
<tr>
<td>( W_3 )</td>
<td>gross weight of solution &amp; flask</td>
<td>717.186</td>
<td>0.0156</td>
</tr>
<tr>
<td>( W_4 )</td>
<td>( W_3 - W_2 = ) net solution weight</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( S )</td>
<td>standard deviation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
A = \frac{(F)(b)(W_1)}{W_4}
\]

\[
1
S_A = \frac{1}{W_2} \left[ \left( \frac{F}{W_1} \right)^2 + \left( \frac{b}{W_1} \right)^2 \left( \frac{S_b}{W_1} \right)^2 \right]^{1/2}
\]

\[
A = \frac{(0.99975)(0.99992)(155.378304 \ g \ U)}{717.186 \ g} = 0.216578 \ g \ U/g
\]

\[
S_A = \frac{1}{717.186} \left[ (0.99992)^2 \left\{ (0.99975)^2 \left( 0.00011 \right)^2 + (155.3783)^2 \right\} + (0.000085)^2 + (0.216578)^2 \left\{ (0.013)^2 + (0.00826)^2 \right\} \right]^{1/2}
\]

\[
S_A = 1.9 \times 10^{-5}
\]

Final concentration = \( 216.578 \pm 0.019 \) mg U/g
Table III. Characterization data summary generated by three different laboratories, using two different analytical chemistry methods, in two different years, while concurrently analyzing one of two different RCTM's. Each mean has been corrected for the apparent bias observed in the analysis of the RCTM.

<table>
<thead>
<tr>
<th>LABORATORY</th>
<th>METHOD</th>
<th>CORRECTED MEAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN-HOUSE - 76</td>
<td>GRAVIMETRIC</td>
<td>219.20</td>
</tr>
<tr>
<td>OUTSIDE #1</td>
<td></td>
<td>219.18</td>
</tr>
<tr>
<td>IN-HOUSE - 78</td>
<td></td>
<td>219.24</td>
</tr>
<tr>
<td>IN-HOUSE - 76a</td>
<td>NBL-MODIFIED D.G.</td>
<td>219.17</td>
</tr>
<tr>
<td>IN-HOUSE - 76b</td>
<td></td>
<td>219.20</td>
</tr>
<tr>
<td>OUTSIDE #2</td>
<td></td>
<td>219.26</td>
</tr>
<tr>
<td>IN-HOUSE - 78</td>
<td></td>
<td>219.18</td>
</tr>
</tbody>
</table>

The average of these 7 means is 219.20 mc U/g solution.
Figure 1. Preparation schemes for calibration and test materials.
APPENDIX I

STATISTICAL TREATMENTS OF THE RCTM CHARACTERIZATION ANALYSES

1. Data Collected in Confirmation Work From Outside Laboratories

The Mean (M) and Standard Deviation (S) of each set of results were calculated using the following equations:

\[ M = \frac{\sum X_i}{n} \]

\[ S = \sqrt{\frac{\sum (X_i - M)^2}{n-1}} \]

\( n \) = number of samples in each set

<table>
<thead>
<tr>
<th>Outside Laboratory I</th>
<th>Outside Laboratory II</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCTM</td>
<td>WCTM</td>
</tr>
<tr>
<td>226.99</td>
<td>219.25</td>
</tr>
<tr>
<td>226.98</td>
<td>219.24</td>
</tr>
<tr>
<td>227.02</td>
<td>219.38</td>
</tr>
<tr>
<td>227.00</td>
<td>219.24</td>
</tr>
<tr>
<td>226.96</td>
<td>219.38</td>
</tr>
<tr>
<td>227.04</td>
<td>219.32</td>
</tr>
</tbody>
</table>

\( M_1 = 226.99 \quad M_2 = 219.31 \quad M_3 = 226.99 \quad M_4 = 219.39 \)

\( S_1 = 0.030 \quad S_2 = 0.063 \quad S_3 = 0.025 \quad S_4 = 0.011 \)

\( \text{RSD}_1 = 0.013 \quad \text{RSD}_2 = 0.029 \quad \text{RSD}_3 = 0.011 \quad \text{RSD}_4 = 0.005 \)

2. F-Test of Precision

Calculated F ratios for both methods are compared to tabulated F values at the 95% confidence level.

**Laboratory I**

\[ F = \frac{S_1^2}{S_2^2} = \frac{(0.030)^2}{(0.063)^2} = 0.226 \quad \frac{1}{F} = 4.42 \]

\( F(1-\alpha/2, n_1-1, n_2-1) \quad \text{or} \quad F(0.975,5,5) = 7.15 \quad \frac{1}{F} = 0.14 \)

Because 0.226 < 7.15 and > 0.140, the precisions are not different.

**Laboratory II**

\[ F = \frac{S_1^2}{S_2^2} = \frac{(0.025)^2}{(0.011)^2} = 5.6 \quad \frac{1}{F} = 0.178 \]

\( F(1-\alpha/2, n_1-1, n_2-1) \quad \text{or} \quad F(0.975,8,8) = 4.43 \quad \frac{1}{F} = 0.22 \)

Because 5.60 > 4.43, the precisions are different.

A pooled standard deviation of 0.87 was calculated from these and past data for Labora-
tory 2 and it was used in all subsequent calculations because the precision for the
FCIM was much better than past measurement performance.

3. Calculation of Methods Means Based on FCIM

The two FCIM means (\( \bar{X} \)) are bias corrected for the differences observed on the FCIM
analyses.

The 1976 FCIM reference value (R) = 226.851 mg U/g from Table I

\[ \bar{X}_2 = \bar{M}_2 (R/H_2) = 219.31 \frac{(226.851)}{(226.99)} = 219.176 \text{ mg U/g} \]

\[ \bar{X}_4 = \bar{M}_4 (R/H_4) = 219.39 \frac{(226.851)}{(226.99)} = 219.256 \text{ mg U/g} \]

\[ \bar{X}_{2+4} = 219.205 \]

4. Calculation of the Equality of the Means

The approximate variances (V) and degrees of freedom (f) for each mean are calculated.

\[ V_2 \approx \frac{(\bar{X}_2)^2}{n_1 \bar{M}_1^2} + \frac{(\bar{X}_2)^2}{n_2 \bar{M}_2^2} \]

\[ V_2 \approx \frac{(219.157)^2}{(6)(226.99)^2} + \frac{(0.030)^2}{(6)(219.30)^2} \approx 0.00088 \]

\[ V_4 \approx \frac{(\bar{X}_4)^2}{n_3 \bar{M}_3^2} + \frac{(\bar{X}_4)^2}{n_4 \bar{M}_4^2} \]

\[ V_4 \approx \frac{(219.256)^2}{(9)(226.99)^2} + \frac{(0.087)^2}{(9)(219.39)^2} \approx 0.0016 \]

\[ f_2 = \frac{(\bar{X}_2)^2}{\frac{S_2^2}{n_1 \bar{M}_1^2} + \frac{S_2^2}{n_2 \bar{M}_2^2}} \]

\[ f_2 = \frac{(219.18)^2}{(6)(226.99)^2} + \frac{(219.18)^2}{(6)(219.39)^2} \approx 5^{*} \]

\[ f_4 = \frac{(\bar{X}_4)^2}{\frac{S_4^2}{n_3 \bar{M}_3^2} + \frac{S_4^2}{n_4 \bar{M}_4^2}} \]

\[ f_4 = \frac{(219.26)^2}{(9)(226.99)^2} + \frac{(219.26)^2}{(9)(219.39)^2} \approx 8^{*} \]

* Rounded to the nearest integer.
5. Compute the T Statistic with f Degrees of Freedom Using the Following Equation:

\[ T = \frac{\bar{X}_2 - \bar{X}_a}{\sqrt{\frac{V_2}{f_2} + \frac{V_a}{f_a}}} \]

in which \( T = \frac{219.176 - 219.256}{\sqrt{0.00088 + 0.0016}} = 1.60 \)

\[ f \simeq \frac{(V_2 + V_a)^2}{V_2 + \frac{V_a}{f_a}} \]

in which \( \frac{(0.00088 + 0.0016)^2}{5} + \frac{(0.0016)^2}{8} \simeq 13 \)

T from T-Table @ T(1-\(\alpha/2, f\)) = T(0.975, 13) = 2.16

Because 1.60 < 2.16, the means are not different.

6. Assignment of WCTM Concentration Value (\( \lambda \)) by Weighting the Bias Corrected Means from each Method

\[ A = W_2 X_2 + W_a X_a \]

\[ W_2 = \frac{1}{V_2} = \frac{1}{0.00088 + 0.0016} = 0.6452 \]

\[ W_a = 1 - W_2 = 0.3548 \]

\[ A = (219.176)(0.6452) + (219.256)(0.3548) = 219.204 \text{ mg/l} \text{ U/f solution} \]

7. Calculation of the Standard Deviation (\( S_\lambda \)) Associated with \( \lambda \), with \( f_\lambda \) Degrees of Freedom

\[ S_\lambda \simeq \left[ \frac{1}{N_a} \left\{ 1 + 4W_2 W_a \left( \frac{1}{f_2} + \frac{1}{f_a} \right) \right\} \right]^{1/2} \]

\[ W = \left( \frac{1}{V_2} + \frac{1}{V_a} \right) = 1761 \]

\[ S_\lambda \simeq \left[ \frac{1}{1761} \left\{ 1 + 4 (0.6452)(0.3548) \left( \frac{1}{5} + \frac{1}{8} \right) \right\} \right]^{1/2} \]

\[ S_\lambda \simeq 0.027 \text{ mg/l U/f} \]

\( N_a \) is the number of degrees of freedom used in calculating the limit of error for \( \lambda \).

\[ N_a \simeq \frac{1}{\frac{V_2}{f_2} + \frac{V_a}{f_a}} \simeq \frac{(0.6452)^2}{5} + \frac{(0.3548)^2}{8} \simeq 10 \]

8. Calculation of the Limit of Error (LE) and Relative Limit of Error (RLE)

\[ LE = 2S_\lambda = 2(0.027) = 0.054 \text{ mg/l U/f} \]

\[ RLE = \frac{100\% \ LE}{\lambda} = \frac{(0.0540)(100\%)}{219.204} = 0.025\% \]

9. Test to Determine if the RLE Meets the Requirement of \( < 1/3 \) of the Plant RLE of 0.25% which is 0.08%.

The target RLE of 0.08% is \( > 0.025\% \) of the WCTM, therefore the WCTM characterization is satisfactory.

* Rounded to the nearest integer.
10. **Calculation of the 95\% Confidence Interval (CI) for the Assigned Value**

\[ CI = \bar{x} \pm t \left( \frac{1-\alpha/2}{N_0} \right) S_A \]

\[ t (0.975,10) = 2.228 \]

\[ CI = 219.20 \pm 2.228 (0.027) = 219.14 \text{ to } 219.26 \text{ mg/mL Solution} \]
APPENDIX II

STATISTICAL TREATMENT OF THE WCTM CHARACTERIZATION ANALYSES

1. Data Collected in Confirmation Work from 1978 In-house Analyses

The Mean (M) and Standard Deviation (S) of each set of results were calculated using the following equations:

\[ M = \frac{\sum X_i}{n} \]

\[ S = \sqrt{\frac{\sum (X_i - M)^2}{n-1}} \]

n = number of samples in each set

<table>
<thead>
<tr>
<th>Gravimetric Results</th>
<th>Titrmetric Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCTM</td>
<td>WCTM</td>
</tr>
<tr>
<td>216.555</td>
<td>219.209</td>
</tr>
<tr>
<td>216.584</td>
<td>219.153</td>
</tr>
<tr>
<td>216.509</td>
<td>219.192</td>
</tr>
<tr>
<td>216.519</td>
<td>219.247</td>
</tr>
<tr>
<td>216.521</td>
<td>219.324</td>
</tr>
<tr>
<td>216.658</td>
<td>219.182</td>
</tr>
</tbody>
</table>

\[ M_1 = 216.558 \quad M_2 = 219.217 \quad M_3 = 216.582 \quad M_4 = 219.183 \]

\[ S_1 = 0.057 \quad S_2 = 0.061 \quad S_3 = 0.077 \quad S_4 = 0.116 \]

RSD_3 = 0.026 \quad RSD_2 = 0.028 \quad RSD_3 = 0.036% \quad RSD_4 = 0.053%

2. F-Test of Precision

Calculated F ratios for both methods are compared to tabulated F values at the 95% confidence level.

Method (1)

\[ F = \frac{S_1^2}{S_4^2} = \frac{(0.057)^2}{(0.061)^2} = 0.873 \quad \frac{1}{F} = 1.15 \]

\[ F(1-\alpha/2, n_1-1, n_2-1) \quad \text{or} \quad F(0.975, 5, 5) = 7.15 \quad \frac{1}{F} = 0.14 \]

Because 0.873 < 7.15 and > 0.140, the precisions are not different.

Method (2)

\[ F = \frac{S_2^2}{S_4^2} = \frac{(0.077)^2}{(0.116)^2} = 0.44 \quad \frac{1}{F} = 2.27 \]

Because 2.27 < 7.15 and > 0.140, the precisions are not different.

3. Calculation of Method Means Based on the RCTM

The two WCTM means (\( \bar{X} \)) are bias corrected for the differences observed on the RCTM analyses.
The KCTM reference value \( R \) = 216.578 mg U/g from Table II.

\[
\bar{X}_2 = R (M/H) = 219.217 (216.578/216.558) = 219.237
\]

\[
\bar{X}_4 = R (M/H) = 219.183 (216.578/216.562) = 219.179
\]

\[
\bar{X}_2 + \bar{X}_4 = 219.208
\]

4. Calculation of the Equality of the Means

The approximate variances (\( V \)) and degrees of freedom (\( f \)) for each mean are calculated:

\[
V_2 = \frac{1}{n_1} \left( \frac{S_1^2}{n_1 H_1^2} + \frac{S_2^2}{n_2 H_2^2} \right)
\]

\[
V_2 = (219.237)^2 \left( \frac{(0.057)^2}{(6)(216.558)^2} + \frac{(0.061)^2}{(6)(219.217)^2} \right) = 0.00118
\]

\[
V_4 = \frac{1}{n_3} \left( \frac{S_3^2}{n_3 H_3^2} + \frac{S_4^2}{n_4 H_4^2} \right)
\]

\[
V_4 = (219.179)^2 \left( \frac{(0.077)^2}{(6)(216.582)^2} + \frac{(0.116)^2}{(6)(219.183)^2} \right) = 0.00325
\]

\[
f_2 = \frac{\left( \frac{V_2}{n_1} \frac{S_1^2}{H_1^2} \right)^2 + \left( \frac{V_2}{n_2} \frac{S_2^2}{H_2^2} \right)^2}{n_1 - 1}
\]

\[
f_2 = \frac{(0.00118)^2}{5} = 10
\]

\[
f_4 = \frac{\left( \frac{V_4}{n_3} \frac{S_3^2}{H_3^2} \right)^2 + \left( \frac{V_4}{n_4} \frac{S_4^2}{H_4^2} \right)^2}{n_3 - 1}
\]

\[
f_4 = \frac{(0.00325)^2}{5} = 9
\]

5. Compute the T Statistic with \( f \) Degrees of Freedom Using the Following Equation:

\[
T = \frac{\bar{X}_2 - \bar{X}_4}{\frac{1}{f_2} + \frac{1}{f_4}}\text{ in which } T = \frac{219.237 - 219.179}{\sqrt{0.00118 + 0.00325}} = 0.071
\]

\[
f_a = \frac{(V_2 + V_4)^2}{f_2 + f_4}\text{ in which } f_a = \frac{(0.00118 + 0.00325)^2}{10 + 9} = 14
\]

* Rounded to the nearest integer.
T from T-Table 0 t(1-α/2, f) = T(0.975,14) = 2.145

Conclude the two means are not different since 0.871 < 2.145

6. Assignment of WCTM Concentration Value (A) by Weighting the Bias Corrected Means from each Method

\[ A = W_2 \bar{X}_2 + W_4 \bar{X}_4 \]

\[ W_2 = \frac{1}{V_2} + \frac{1}{V_4} = \frac{1}{0.00118} + \frac{1}{0.00325} = 0.73363 \]

\[ W_4 = 1 - 0.73363 = 0.26637 \]

\[ A = (219.237)(0.73363) + (219.179)(0.26637) = 219.22 \text{ mg U/g solution} \]

7. Calculation of the Standard Deviation (S_A) Associated with A, with f_A Degrees of Freedom

\[ S_A \approx \frac{1}{W} \left[ 1 + \left\{ 4 \frac{W_2 W_4}{f_2} \left( \frac{1}{f_2} + \frac{1}{f_4} \right) \right\} \right]^{1/2} \]

\[ W = \frac{1}{V_2} + \frac{1}{V_4} = 1155.15 \]

\[ S_A \approx \frac{1}{1155.15} \left[ 1 + \left\{ 4 \left( 0.73363 \right) \left( 0.26637 \right) \left( \frac{1}{f_2} + \frac{1}{f_4} \right) \right\} \right]^{1/2} = 0.0318 \text{ mg U/g} \]

\[ Na \text{ is the number of degrees of freedom used in calculating the limit of error for A.} \]

\[ Na = \frac{1}{W_2^2 + W_4^2} = \frac{1}{0.73363^2} + \frac{1}{0.26637^2} = 16 \]

8. Calculation of the Limit of Error (LE) and Relative Limit of Error (RLE)

\[ LE = 2S_A = 2(0.0318) = 0.0636 \text{ mg U/g} \]

\[ RLE = \frac{100\% \ LE}{A} = \frac{(0.0636)100\%}{219.22} = 0.029\% \]

9. Test to Determine if the RLE Meets the Requirement of <1/3 of the Plant RLE of 0.25% which is 0.083%

The target RLE of 0.08% is >0.03% of the WCTM, therefore the WCTM characterization is satisfactory.

10. Calculation of the 95% Confidence Interval (CI) for the Assigned Value

\[ CI = A \pm t (1-\alpha/2, n_A) (S_A) \]

\[ t (0.975,16) = 2.120 \]

\[ CI = 219.22 \pm 2.12 (0.0318) = 219.15 \text{ to } 219.29 \text{ mg U/g solution} \]

* Rounded to the nearest integer.