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UNCERTAINTIES OF ANION AND TOC MEASUREMENTS AT THE DWPF LABORATORY

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EXECUTIVE SUMMARY

The Savannah River Remediation (SRR) Defense Waste Processing Facility (DWPF) has identified a technical issue related to the amount of antifoam added to the Chemical Process Cell (CPC). Specifically, due to the long duration of the concentration and reflux cycles for the Sludge Receipt and Adjustment Tank (SRAT), additional antifoam has been required. The additional antifoam has been found to impact the melter flammability analysis as an additional source of carbon and hydrogen. To better understand and control the carbon and hydrogen contributors to the melter flammability analysis, SRR's Waste Solidification Engineering (WSE) requested that the Savannah River National Laboratory (SRNL) conduct an error evaluation of the measurements of key Slurry Mix Evaporator (SME) anions. Measurements for these anions, which included formate, nitrate, and oxalate, and for total organic carbon from recent SME batches were provided to SRNL by DWPF Laboratory Operations personnel.

The measurements generated by the DWPF Laboratory for recent SME batches are presented in this report, an evaluation of the uncertainties of these measurements is provided, and approaches for assessing the impact of these uncertainties on DWPF's strategies for controlling melter flammability and for monitoring antifoam additions are investigated.

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LIST OF ABBREVIATIONS

CPC	Chemical Process Cell
DWPF	Defense Waste Processing Facility
IC	Ion Chromatography
JMP	Statistical software package from SAS Institute, Inc. [4]
Lab OPS	Laboratory Operations
LFL	Lower Flammability Limit
ppm	parts per million
SB6	Sludge Batch 6
SB7a	Sludge Batch 7a
SME	Slurry Mix Evaporator
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
TOC	Total Organic Carbon
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WSE	Waste Solidification Engineering

1.0 INTRODUCTION

The Savannah River Remediation (SRR) Defense Waste Processing Facility (DWPF) has identified a technical issue related to the amount of antifoam added to the Chemical Process Cell (CPC). Specifically, due to the long duration of the concentration and reflux cycles for the Sludge Receipt and Adjustment Tank (SRAT), additional antifoam has been required. The additional antifoam has been found to impact the melter flammability analysis as an additional source of carbon and hydrogen. To better understand and control the carbon and hydrogen contributors to the melter flammability analysis, SRR's Waste Solidification Engineering (WSE) has requested, via a Technical Task Request (TTR) [1], that the Savannah River National Laboratory (SRNL) conduct an error evaluation of the measurements of key Slurry Mix Evaporator (SME) anions. SRNL issued a Task Technical and Quality Assurance Plan (TTQAP) [2] in response to that request, and the work reported here was conducted under the auspices of that TTQAP.

The TTR instructs SRNL to conduct an error evaluation of anion measurements generated by the DWPF Laboratory using Ion Chromatography (IC) performed on SME samples. The anions of interest include nitrate, oxalate, and formate. Recent measurements of SME samples for these anions as well as measurements of total organic carbon (TOC) were provided to SRNL by DWPF Laboratory Operations (Lab OPS) personnel for this evaluation. This work was closely coordinated with the efforts of others within SRNL that are investigating the Chemical Process Cell (CPC) contributions to the melter flammability [3]. The objective of that investigation was to develop a more comprehensive melter flammability control strategy that when implemented in DWPF will rely on process measurements. Accounting for the uncertainty of the measurements is necessary for successful implementation. The error evaluations conducted as part of this task will facilitate the integration of appropriate uncertainties for the measurements utilized in that control strategy.

The flammability control strategy presented in [3] relies on SME measurements of TOC and nitrate while one of the uses by WSE of the oxalate and formate measurement data will be the estimation of the amount of carbon coming from antifoam additions. The estimation is to be conducted by backing out contributions to the measured TOC concentration in the SME from the oxalate and the formate concentrations that are measured in the SME. The resulting adjusted TOC value will provide a basis for WSE to estimate the amount of antifoam that was added for that SME batch. The uncertainties of the oxalate, formate, and TOC measurements provided by the evaluations conducted as part of this task will allow for the propagation of their uncertainties into the estimated quantity of carbon coming from the added antifoam.

The purpose of this technical report is to present the measurements generated by the DWPF Laboratory for recent SME batches, to conduct an evaluation of their uncertainties, and to provide the approach for propagating the uncertainties associated with these measurements into DWPF's strategies for controlling melter flammability and for monitoring antifoam additions. JMP Version 7.0.2 was used to support the analyses presented in this report [4].

2.0 MEASUREMENTS PROVIDED BY DWPF LAB OPS

Measurements generated by the DWPF Laboratory for recent SME batches were provided to SRNL by Lab OPS personnel. These data are presented and their uncertainties investigated as part of this study. Section 2.1 discusses the IC measurement data and Section 2.2 discusses the TOC measurement data. Measurements of SME samples as well as standards were analyzed as part of these investigations.

2.1 IC Measurements by DWPF Laboratory

Table A1 in Appendix A provides the IC measurement data generated by the DWPF Laboratory for 21 recent SME batches. Included in these results for each of the SME batches are measurements for formate, nitrate, and oxalate for four SME samples along with standards at 2 parts per million (ppm) and 16 ppm for each of these anions.

2.1.1 *Formate, Nitrate, and Oxalate Standards*

Exhibit A1 in Appendix A provides plots of the DWPF Laboratory measurements from Table A1 for the 2 ppm and 16 ppm standards for formate, nitrate, and oxalate. Colors are used in these plots to represent the IC instrument that was used for the analyses and symbols (▪ for the before and + for the after) for the sequencing of the measurements of the standards relative to the processing of the SME samples. The measurements are grouped by SME batch number, and the IC instrument used to conduct the measurement is indicated. The set of measurements for each standard (e.g., the measurements for the 2 ppm formate standard) is investigated using a random effects analysis of variance to estimate the variation from one SME batch to the next SME batch in the measurements for that standard. For this analysis, the SME batch is a pseudo variable for time between the measurements of the standard. That is, the variance estimated by this approach, if statistically significant, is the variation that may be affecting the measurement of the SME samples that will not be reduced by the replication of the analyses (i.e., by more SME samples being analyzed or by the existing SME samples being analyzed more times). For the results of Exhibit A1, the estimate of this variance for each set of measurements is statistically significant at the 5% level. Statistical significance is indicated in the portion of the exhibit as shown in Exhibit 1 for the measurements of the 2 ppm formate standard.

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	0.10346	0.00517	20	4.3281	0.0008

Exhibit 1. Illustration of JMP Results Indicating a Statistically Significant Batch to Batch Variability

The "**Prob > F**" value in this exhibit being less than 0.05 indicates a statistically significant batch to batch variance for the measurements of the 2 ppm formate standard. If the "**Prob > F**" value is greater than 0.05, there is no indication of a statistically significant batch to batch variance. The estimate of the variance is provided in the portion of the exhibit as shown in Exhibit 2 for the measurements of the 2 ppm formate standard.

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.001989	62.463
Residual	0.001195	37.537
Total	0.003184	100.000

Exhibit 2. Illustration of JMP Results Indicating a Statistically Significant Batch to Batch Variability

The variance component of interest here is that labeled as "Batch#&Random," which is estimated as 0.001989 or over 62% of the total variance of the measurements for the 2 ppm formate standard. The estimate of the standard deviation of the batch to batch effect is computed as the square root of 0.001989, which is 0.0446. Expressing this variation as a percentage of the nominal value, 2, for this standard leads to a percent relative standard deviation of 2.23%.

The measurements of the other anion standards may be interpreted in a similar manner, and in each case the estimate of the batch to batch variance is statistically significant at the 5% level. This variance will need to be appropriately accounted for in determining the uncertainties of the SME measurements for formate, nitrate, and oxalate. To facilitate that process an analysis of variance was conducted using the measurements for both standards for each of the anions. In this analysis, the concentration of the standard (i.e., the 2 ppm and 16 ppm) was added as a fixed effect in the model with the batch to batch variation included once again as a random effect with the variance of this effect being of interest. The results from this analysis of variance for the formate, nitrate, and oxalate measurements are provided in Exhibit A3 in Appendix A. These results may be interpreted in a manner similar to that described for the results of Exhibit A2. This leads to the conclusion that there is a statistically significant batch to batch variance in the measurements of the standards for formate, for nitrate, and for oxalate. The estimate of the batch to batch component of variation from Exhibit A3 for each anion is provided in Table 1. Also in this table for each anion is the average of the measurements of the standards and the expression of the batch to batch variation as a percent relative (to the average) standard deviation for each anion.

Table 1. Summary Information from Exhibit A3

Anion	Batch to Batch Variance Component Estimate	Average of the Measurements of the Standards	% Relative Standard Deviation (%RSD)
Formate	0.0208	9.24	1.56%
Nitrate	0.0359	9.08	2.09%
Oxalate	0.0280	9.11	1.84%

For each anion, this estimated variance is considered as a contributor to the uncertainty in the measurements of the SME samples for this anion. Accounting for this variation as part of the uncertainty in the measurements of each of these anions is illustrated in the discussions that follow.

An additional investigation into the measurements of these standards is provided by Exhibit A4 in Appendix A. This exhibit provides a histogram and summary statistics for the mean of the measurements for each SME batch of each of the standards for each anion. A 95% confidence interval for the mean of each set of measurements is included as part of these results. If the nominal value of the standard is included in the confidence interval determined for the mean of that standard, then there is no indication of a statistically significant bias in the measurements at a 5% significance level. This leads to the following conclusions. For the formate results, there are statistically significant biases in the measurements for the 2 ppm and 16 ppm standards; the means of the measurements for both standards are high relative to the nominal values of the standards. For the nitrate results, there is no indication of a statistically significant bias for either the 2 or the 16 ppm standards. For the oxalate values, there is a bias in the 2 ppm results (the mean of the measurements of the 2 ppm oxalate standard are biased high), but there is no indication of a statistically significant bias for the measurements of the 16 ppm oxalate standard. How to conservatively account for the effects of a potential bias in the formate measurements on a value derived from these measurements will depend on the derivation itself. This issue is addressed below as part of subsequent discussions presented in this report.

2.1.2 *SME Sample Results for Formate, Nitrate, and Oxalate*

Exhibit A5 in Appendix A provides the plots of the formate, nitrate, and oxalate measurements of the SME samples. For each anion, a plot is provided of the measurements as milligram of anion per kilogram of slurry, which may also be interpreted as ppm. In addition, the measurements of the SME samples are shown as ppm per diluted sample. The latter plot for each anion provides an indication of how the measurements fall within the interval covered by the standards (i.e., 2 to 16 ppm). For both plots, the measurements are grouped by SME batch, and the IC instrument used for the measurements is indicated. Note that only a limited plot of the oxalate measurements is provided since the measurements for this anion have been below the detection limit of the IC process for most of the SME batches included in this study.

For each set of measurements in Exhibit A5, an analysis of variance was conducted with the objective of estimating two components of variation: the batch to batch component and the within batch (or residual) component. The results from these analyses are provided in Exhibit A6 of Appendix A. For the SME measurements of each anion, the batch to batch component is a statistically significant (at the 5% level) component of the variability in the measurements for the anion. Furthermore, the estimate of the residual variance may be interpreted as the square of a pooled estimate of the standard deviation of the measurements for the anion over the set of samples from a given SME batch. For example, consider the results for the formate mg/kg slurry measurements. The estimated residual variance is 1,488,412 (15.9% of the total variance of these measurements). The square root of that number is 1220 mg/kg slurry. Expressed as a percent of the mean response for the measurements (38233.42 mg/kg slurry), this becomes a percent relative standard deviation (%RSD) of 3.2%. Based upon this %RSD, the estimate of the 1-sigma standard uncertainty for the average of the formate measurements in mg/kg slurry for 4 SME samples would be (on a relative basis) 3.2%/2 = 1.6%. A similar interpretation of the results for the measurements for nitrate leads to the estimate of the 1-sigma standard uncertainty for the average of the nitrate measurements in mg/kg slurry for 4 SME samples as 100% (689.0958/22777.24)/2 = 1.5%. Note that there is insufficient oxalate data in Table A1 that is above the detection limit to allow for this type of analysis to be conducted for measurements of this anion.

Another, but similar, analysis of variance for these measurements is provided in Exhibit A7 of Appendix A. In these results, the differences among the averages of the measurements for an anion from one SME batch to another are interpreted as fixed effects with the estimated residual variance, once again, being representative of the repeatability of the sampling and analytical steps associated with these measurements for a given SME batch. The estimated residual variances from these analyses are identical to those of Exhibit A6. Once again, note that there is limited oxalate data to support this analysis for the SME measurements of this anion.

While the 1-sigma standard uncertainties for the average of the measurements for formate and the average of the measurements for nitrate for a given SME batch will be directly determined from the measurements of the SME samples for these anions, this pooled estimate may be used as an aid in understanding the impact of this variation on the uncertainty of values derived using measurements of these anions.

2.2 TOC Measurements by DWPF Laboratory

Table A2 in Appendix A provides the TOC measurement data generated by the DWPF Laboratory for ten recent SME batches. For each SME batch, this table provides four measurements: the results from two SME samples each being measured twice. Opening and closing measurements for TOC standards (one at 1 ppm and one at 20 ppm) are also part of the analytical protocol for measuring the TOC concentrations of SME samples, and the measurements for these standards are also provided in Table A2.

2.2.1 *TOC Standards*

The measurements in Table A2 of each of the TOC standards are plotted in Exhibit A8 in Appendix A. These measurements are grouped by SME batch and organized in line with the analytical protocol: the opening and closing measurements associated with the first SME sample and then the measurements associated with the second SME sample.

Some patterns are evident in these plots. For the 1 ppm standard, the measurement of the closing standard is almost always larger than the measurement of the corresponding opening standard for the SME batches represented in Exhibit A8. For the 20 ppm standard, the average of the measurements for the opening and closing standards for the first SME sample is almost always larger than the average of the opening and closing standards for the second SME sample. These patterns in the measurements are also revealed in the residual plots associated with the analyses of variance provided in Exhibit A9 of Appendix A. The batch to batch differences in the measurements of the standards are considered as the realizations of a random effect whose variance is estimated as part of the results of the exhibit. The residual plot in this exhibit for the 1 ppm standard shows a pattern of the residuals of the closing standard (red) being typically above the horizontal line at zero while the residuals of the opening standard (blue) are typically below the horizontal line at zero. For the 20 ppm standard, the pattern revealed in the residual plot is that of the small squares (first SME sample) being typically above the horizontal line at zero while the pluses (second SME sample) are typically below the horizontal line at zero. While these patterns are not anticipated to affect the results of this investigation, a more thorough study into the possible causes of these patterns may provide an opportunity for an improvement in the protocol used for the TOC measurements.

Another outcome from the analyses of Exhibit A9 is the indication of a statistically significant (at the 5% level) batch to batch variance in the measurements of each of these TOC standards. This random effect is considered as a contributor to the uncertainty of the TOC measurements of the SME samples. Exhibit A10 of Appendix A provides an analysis of variance to estimate the variance of this random effect. In this analysis, the concentration of the TOC standard (i.e., the 1 ppm and 20 ppm) was added to the model as a fixed effect along with a random term for the batch to batch effect, with the variance of this random effect being of interest. The results presented in Exhibit A9 may be interpreted in a manner similar to that described earlier for the interpretation of the analysis of the anion measurements. This leads to the conclusion that there is a statistically significant (at the 5% level) batch to batch variance for the measurements of the TOC standards. The estimate of this variance component relative to the average of the measurements for these standards may be expressed as 100% $(0.011827)^{0.5}/10.41663 = 1.04\%$. Thus, this estimated variance is a contributor to the uncertainty in the TOC measurements of the SME samples. Accounting for this variation as part of the uncertainty in the TOC measurements is illustrated in the discussions that follow.

An additional investigation into the measurements of the TOC standards is provided by Exhibit A11 in Appendix A. This exhibit provides a histogram and summary statistics for the measurements for the 1 ppm and 20 ppm TOC standards grouped by their position (opening or closing/first or second sample) in the analytical protocol. A 95% confidence interval for the mean of each set of measurements is included as part of these results. If the nominal value of the standard is included in the confidence interval determined for the mean of that standard, then there is no indication of a statistically significant bias in the measurements at a 5% significance level. This leads to the following conclusions. For the 1 ppm standard, the average for the opening set of measurements for the first SME sample, the average for the opening set of measurements for the second SME sample, and the closing set of measurements for the second SME sample all indicate a statistically significant (at the 5% level) low bias in these results. A statistically significant low bias is also indicated (at the 5% level) for the measurements of the opening 20 ppm standard for the second SME sample.

However, there is no indication of a statistically significant (at the 5% level) bias in the measurements of the closing 1 ppm standard for the first SME sample or in the measurements of the opening and closing 20 ppm standard for the first SME sample or in the measurements of the closing 20 ppm standard for the second SME sample. Thus, there does not appear to be a consistent bias in the measurements over the TOC standards, and as a consequence, for this uncertainty investigation, no adjustment for bias will be applied to the TOC measurements generated by the DWPF Laboratory for the SME samples.

2.2.2 *TOC Measurements of SME Samples*

A plot of the TOC measurements in Table A2 for the SME samples is provided in Exhibit A12 of Appendix A. The measurements are grouped by SME batch and arranged by sample number and analytical replicate. Table 2 provides summary statistics for these measurements.

Table 2. Summary Information for the TOC Measurements of the SME Samples

Batch #	N	Mean (TOC (ppm))	Standard Deviation (TOC (ppm))	Standard Error of the Mean (TOC (ppm))	%Relative Standard Error
559	4	14639.5	91.07	45.535	0.31
560	4	14136.8	84.49	42.244	0.30
561	4	12780.8	32.39	16.193	0.13
562	4	12428.0	63.77	31.885	0.26
563	4	12856.3	117.37	58.686	0.46
564	4	13207.0	59.43	29.713	0.22
565	4	12633.3	188.71	94.355	0.75
566	4	13489.0	363.38	181.688	1.35
567	4	10652.3	145.67	72.834	0.68
568	4	11628.8	54.91	27.457	0.24

The TOC concentration that is reported for each of the SME batches represented in Table 2 is given in the third column of Table 2. The value in this column, for a given SME batch, is the average of four measurements, and thus, the 1-sigma standard uncertainty (or the standard error) for this average is the sample standard deviation for the four values divided by 2 (i.e., the square root of the number of measurements in the sample, 4). The sample standard deviation values for the SME batches are provided in the fourth column of Table 2; the values of the standard error are provided in the fifth column; and these values as percentages of the means (i.e., as % relative standard errors) are given in the last column of Table 2. As seen in Table 2, the % relative standard errors fall in the interval from 0.13% to 1.35%. The determination of the 1-sigma standard relative uncertainty of the average TOC measurement for a given SME batch, the % relative standard error, is to be computed as shown here from the 4 measurements provided by DWPF Laboratory for the given SME batch. While this approach is applicable for the data that generated the results in Table 2, for the approach to better represent the uncertainty of the average of the 4 measurements in the future, it is recommended that the TOC analytical protocol be changed from 2 SME samples each being analyzed in duplicate to 4 SME samples each sample being analyzed only once.

3.0 THE MAXIMUM TOC/NITRATE RATIO AT 60% LFL

As stated in the Introduction, efforts are underway at SRNL to develop a comprehensive melter flammability control strategy. The strategy for Sludge Batch 6 (SB6) and Sludge Batch 7a (SB7a) has been developed by Choi [3], and it relies on the contents of the SME satisfying a constraint on the ratio of TOC to nitrate. Before a SME batch is to be transferred to the melter, WSE must establish that the ratio of the TOC concentration to the nitrate concentration satisfies the restrictions imposed by Choi's analysis. However, since the implementation of the strategy in DWPF will rely on process measurements, WSE must account for the uncertainties of the measurements to confidently achieve a successful implementation. The uncertainties of these measurements were investigated in the earlier discussion, and they will be revisited now in the context of the implementation of Choi's melter flammability control strategy.

The constraint on the TOC to nitrate ratio developed by Choi maintains the contributors to the melter flammability issue to less than 60% of their lower flammability limit (LFL) [3]. The maximum allowable TOC to nitrate ratio was determined by Choi as a polynomial function of the nitrate concentration, and a different functional constraint was developed for each sludge batch: SB6 and SB7a. Since both constraints were developed over the interval of nitrate concentrations from 15,000 ppm to 30,000 ppm, that interval of nitrate concentrations is the range of applicability for these functions. If the contents of a SME batch yield an average nitrate measurement outside of the interval from 15,000 to 30,000 ppm, then satisfying the constraint on the TOC to nitrate ratio may not be a reliable control for addressing melter flammability concerns for that SME batch. In the sections that follow, the impacts of the TOC and nitrate measurement uncertainties that were determined in the earlier discussions of this report, on the assessment of the nitrate content of the SME and for controlling melter flammability are investigated.

3.1 Assessing the Nitrate Content of the SME

To implement the melter flammability control strategy described in [3], there is a need to assure with high confidence that the NO_3 content of the SME falls within the interval from 15,000 to 30,000 ppm. Demonstrating that this condition is met for a given SME batch will rely on the four nitrate measurements from that batch. The average of these measurements may be represented by $\overline{NO_3}$ and the standard error, or the 1-sigma standard uncertainty of this value, which is computed from the four nitrate values, may be represented by $se_{\overline{NO_3}}$. In addition from the discussion above, a batch to batch 1-sigma uncertainty of 2.09% was identified, by a review of measurements from the nitrate standards, as affecting the nitrate measurements. Following the guidelines and notational conventions presented in [5] (which may differ somewhat from the notation typically used in statistical models), an input term, δ_{NO_3}, representing this random effect in added to the measurement equation for the NO_3 content in the SME. If Y_{NO_3} is used to represent the estimated NO_3 content of the SME, then the measurement equation for the measurand, Y_{NO_3}, may be written as:

Equation 1.

$$Y_{NO_3} = \overline{NO_3} + \delta_{NO_3}$$

where $\overline{NO_3}$ represents the average of the NO_3 concentration measurements for the 4 samples of the given SME batch. It has a 1-sigma standard uncertainty of $se_{\overline{NO_3}}$, and

δ_{NO_3} represents the batch to batch source of variation affecting the nitrate measurements for a SME batch. For the evaluation of Y_{NO_3} by equation (1), the value of δ_{NO_3} is zero. Its 1-sigma standard uncertainty is represented by $s_{\delta_{NO_3}}$ and based upon the analyses presented above that value is given by 2.09% of the $\overline{NO_3}$ value.

The guidance provided in [5] relies on the use of a Taylor's series expansion of the measurement equation to approximate the variance of the measurand. The expression of this approximation is simplified if the errors associated with the inputs to the measurement equation are uncorrelated, which is the case for the errors associated with the two input terms of equation (1)[f]. For this simple measurement equation, the variance of Y_{NO_3} is equal to its Taylor's series expansion, and the estimation of the variance of Y_{NO_3} is facilitated by estimating the standard deviations of $\overline{NO_3}$ and δ_{NO_3} by $se_{\overline{NO_3}}$ and $s_{\delta_{NO_3}}$, respectively, as indicated in equation (2):

Equation 2.

$$\text{Est. Var}\left(Y_{NO_3}\right) = \left(se_{\overline{NO_3}}\right)^2 + \left(s_{\delta_{NO_3}}\right)^2$$

where $\text{Est.Var}\left(Y_{NO_3}\right)$ represents the estimated variance of Y_{NO_3}, the estimated nitrate content of the SME.

Thus, $\sqrt{\text{Est.Var}\left(Y_{NO_3}\right)}$ is the 1-sigma standard uncertainty of the estimated nitrate content of the SME. To determine the uncertainty at 95% confidence, $\sqrt{\text{Est.Var}\left(Y_{NO_3}\right)}$ must be multiplied by an appropriate Student's t statistic; in this case, a two-tailed t statistic is to be used. For this situation, 3 degrees of freedom will be assumed for the estimated variance of Y_{NO_3}. This is conservative since 3 degrees of freedom are associated with the 1-sigma standard uncertainty of $\overline{NO_3}$ and even more degrees of freedom are associated with the 1-sigma standard uncertainty for δ_{NO_3}. The upper 2.5%-tail of the Student's t distribution with 3 degrees of freedom is 3.182. Thus, the expanded uncertainty of the estimated nitrate concentration in the SME, Y_{NO_3}, is given by:

Equation 3.

$$\text{Uncertainty of } Y_{NO_3} \text{ at 95\% confidence} = 3.182 \times \sqrt{\text{Est. Var}\left(Y_{NO_3}\right)} = 3.182 \times \sqrt{\left(se_{\overline{NO_3}}\right)^2 + \left(s_{\delta_{NO_3}}\right)^2}$$

To illustrate these calculations, consider the four nitrate measurements for SME batch 566 from Table A1. The values in ppm are 23700, 23604, 23229, and 23433. The sample mean of these values, $\overline{NO_3}$, is given by 23491.5, and the 1-sigma standard uncertainty of the sample mean is given by sample standard deviation divided by the square root of the sample size, or 206.928/2=103.464. With $s_{\delta_{NO_3}}$ determined by 0.0209×23491.5=490.972, the expanded uncertainty at 95% confidence for the estimated nitrate content of the SME is given by $3.182 \times \sqrt{(103.464)^2 + (490.972)^2}$ = 1596.81. Thus, with 95% confidence the nitrate content of SME batch 566 is within 1596.81 of 23491.5 ppm or within the interval from 21894.7 ppm to 25088.3 ppm.

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[f] The errors associated with the terms in the other measurement equations investigated as part of this study are also assumed to be uncorrelated.

3.2 Controlling Melter Flammability

Of the two polynomials relating the TOC to nitrate ratio to nitrate concentration, the one for SB6 is the more restrictive [3]. It is a quadratic equation of the form:

Equation 4.

$$[TOC/NO_3] = 7.2791E\text{-}10 \times [NO_3]^2 - 5.0035E\text{-}05 \times [NO_3] + 1.5347$$

where the term $[TOC/NO_3]$ on the left hand side of the equation represents the maximum allowable TOC to nitrate ratio required to maintain the system below the 60% LFL, while the NO_3 term on the right hand side represents the nitrate content of the SME in ppm.

The direct utilization of equation (4) for melter flammability control yields this acceptability equation for a given SME batch:

Equation 5.

$$D = R_{[TOC/NO_3]} \times \overline{NO_3} - \overline{TOC} - other_C > 0$$

where D is the measurand, and it represents the difference in ppm between the carbon allowed by equation (4) and the carbon content of the SME,

$R_{[TOC/NO_3]}$ represents the quadratic equation (4) relating the TOC to nitrate ratio to nitrate concentration,

$\overline{NO_3}$ represents the average of the NO_3 concentration measurements for the samples of the given SME batch,

$\overline{TOC}$ represents the average of the TOC concentration measurements for the samples of the given SME batch, and

$other_C$ represents carbon that is present in the SME in a form that is not measured by the TOC analytical protocol. Note, however, that such carbon was included in the determination of the TOC to nitrate ratio of equation (4) [3].

The form of equation (5) is such that the value of D must be positive. That is, the amount of TOC allowed by the use of equation (4) must be greater than the TOC content of the given SME, and this must be true with high confidence after accounting for the uncertainties in the measurements used to make this determination.

Since the allowable amount of TOC for the SME batch is determined as a quadratic function of the nitrate content, the allowable amount of TOC is determined by multiplying equation (4) by the measured nitrate content of the given SME as indicated in equation (5). Substituting the quadratic function into equation (5) leads to:

Equation 6.

$$D = 7.2791E-10 \times \left(\overline{NO_3}\right)^3 - 5.0035E-05 \times \left(\overline{NO_3}\right)^2 + 1.5347 \times \left(\overline{NO_3}\right) - \overline{TOC} - other_C > 0$$

Following the approach and notational conventions of [5], equation (6) is modified to make it a more complete measurement equation for the determination of D. In the discussion above, a batch to batch 1-sigma relative uncertainty of 2.09% was identified as affecting the nitrate measurements and a batch to batch 1-sigma relative uncertainty of 1.04% was identified as affecting the TOC measurements. Representing the errors for these sources of variation as δ_{NO_3} and δ_{TOC}, respectively, they may be added to equation (6) to obtain a more complete measurement equation for D as follows:

Equation 7.

$$D = 7.2791E-10 \times \left(\overline{NO_3} + \delta_{NO_3}\right)^3 - 5.0035E-05 \times \left(\overline{NO_3} + \delta_{NO_3}\right)^2 + 1.5347 \times \left(\overline{NO_3} + \delta_{NO_3}\right) - \left(\overline{TOC} + \delta_{TOC}\right) - other_C > 0$$

The values of δ_{NO_3} and δ_{TOC} are zero in the determination of the value of D, but including these terms in the equation for D allows for their contributions to the variance of D to be included in the variance propagation for equation (7).

A Taylor's series expansion approach is used to estimate the variance of D [5]. Assuming that the errors in equation (7) are uncorrelated and that the value for $other_C$ is bounding and thus may be considered to be without error, the Taylor's series expansion approach yields:

Equation 8.

$$var(D) \approx \left(\frac{\partial D}{\partial \overline{NO_3}}\right)^2 \times \left(se_{\overline{NO_3}}\right)^2 + \left(\frac{\partial D}{\partial \delta_{NO_3}}\right)^2 \times \left(s_{\delta_{NO_3}}\right)^2 + \left(\frac{\partial D}{\partial \overline{TOC}}\right)^2 \times \left(se_{\overline{TOC}}\right)^2 + \left(\frac{\partial D}{\partial \delta_{TOC}}\right)^2 \times \left(s_{\delta_{TOC}}\right)^2$$

where $\frac{\partial D}{\partial \bullet}$ represents the partial derivative of D with respect to the variable (●), $se_{\overline{NO_3}}$ represents the 1-sigma standard uncertainty of the average nitrate measurement of the SME samples, $s_{\delta_{NO_3}}$ represents the 1-sigma standard uncertainty of the batch to batch variation in the nitrate measurements (based upon the analyses presented here that value is given by 2.09% of the $\overline{NO_3}$ value), $se_{\overline{TOC}}$ represents the 1-sigma standard uncertainty of the average TOC measurement of the SME samples, and $s_{\delta_{TOC}}$ represents the 1-sigma standard uncertainty of the batch to batch variation in the TOC measurements (based upon the analyses presented here that value is given by 1.04% of the $\overline{TOC}$ value). Once again, note that no error term is introduced in equation (8) for the $other_C$ input of equation (7).

Using this approach, the variance of D is estimated by:

Equation 9.

$$\begin{aligned}\mathrm{var(D)} \approx &\left(7.2791\mathrm{E}-10 \times 3 \times \left(\overline{NO_3}+\delta_{NO_3}\right)^2 - 5.0035\mathrm{E}-05 \times 2 \times \left(\overline{NO_3}+\delta_{NO_3}\right)^1 + 1.5347\right)^2 \times \left(se_{\overline{NO_3}}\right)^2 \\ &+ \left(7.2791\mathrm{E}-10 \times 3 \times \left(\overline{NO_3}+\delta_{NO_3}\right)^2 - 5.0035\mathrm{E}-05 \times 2 \times \left(\overline{NO_3}+\delta_{NO_3}\right)^1 + 1.5347\right)^2 \times \left(s_{\delta_{NO_3}}\right)^2 \\ &+ \left(se_{\overline{TOC}}\right)^2 + \left(s_{\delta_{TOC}}\right)^2\end{aligned}$$

In evaluating equation (9), all of the 1-sigma standard uncertainties are to be expressed in ppm. For example, $s_{\delta_{TOC}}$, which was described as being based on a 1.04% relative error, would be expressed as $0.0104 \times \overline{TOC}$.

3.3 Meeting the Constraint of the TOC to Nitrate Ratio

In meeting the constraint of the TOC to nitrate ratio, the value for the degrees of freedom for the estimate of the variance of D is taken to be 3. This is a conservative approach since it relies on only the degrees of freedom associated with the standard errors of the nitrate and TOC sample means. As indicated in equations (7), the value of D must be positive. To assure that the value of D is sufficiently positive it must be larger than its estimated uncertainty at 95% confidence. To determine the uncertainty at 95% confidence, the square root of the estimate of the variance of D must be multiplied by an appropriate Student's t statistic. Since only a one-sided expression of the uncertainty of D is needed, a one-tailed t statistic may be used. For 3 degrees of freedom, the upper 5%-tail of the Student's t distribution is 2.353. Thus, the SME batch is acceptable from a melter flammability perspective if:

Equation 10.

$$D - t_{(0.05,3)} \times (\text{Est. var(D)})^{0.5} > 0$$

Where D is determined using equation (7),

$t_{(0.05,3)}$ is the upper 5%-tail of the Student's t distribution (i.e., 2.353), and

Est. var(D) represents the estimate of the variance of D computed using equation (9).

To illustrate these calculations, they were performed for the nitrate and TOC values for SME batch 566 from Table A1 and Table A2, respectively. Exhibit 3 provides the results of these calculations. From this exhibit, the estimated difference as determined by equation (7) is 4148.0 ppm with a 1-sigma standard uncertainty (determined by the square root of the estimated variance of equation (9)) of 301.3 ppm. From equation (10), these results lead to an expanded uncertainty for the difference of 709.1 ppm. Since the estimated difference (4148.0) is greater than its expanded uncertainty (709.1), the TOC to nitrate ratio for the SME batch is acceptable. For completeness, the calculation of the confidence interval for the nitrate content of this batch is also shown as part of the results of the exhibit, and it demonstrates, once again, acceptable nitrate content for this SME batch.

TOC (ppm)		Average (ppm) TOC Content	1-sigma standard uncertainty (ppm)	batch to batch 1-sigma standard uncertainty (ppm)		
13771						
13153						
13834						
13198		13489	181.6879192	140.2856		

Nitrate (ppm)		Nitrate Content	1-sigma	batch to batch 1-sigma standard uncertainty (ppm)	1-sigma	exp unc 95%
23700						
23604						
23229						
23433		23491.5	103.4637618	490.97235	501.7555166	1596.811488

Interval of Possible Nitrate Content in SME
21894.6885 25088.31149 Acceptable

Other Carbon (ppm) 240

TOC (ppm)	Nitrate (NO3) (ppm)	TOC/NO3	Predicted Ratio for TOC to NO3 from Functional Relationship at 60% LFL	Partial wrt TOC	Std Error for TOC (ppm)	Partial wrt NO3	Std Error for NO3 (ppm)
13489	23491.5	0.5742	0.7610	-1	181.6879	0.3890	103.4637618

Partial wrt δNO3	1-sigma Batch to Batch Variation for δNO3 (ppm)	Partial wrt δTOC	1-sigma Batch to Batch Variation for δTOC (ppm)	Value of TOC Difference (must be positive)	1-sigma standard uncertainty for TOC Difference	Expanded Uncertainty for TOC Difference (95% confidence)	Acceptability
0.3890	490.9724	-1	140.2856	4148.0	301.3	709.1	Acceptable

Exhibit 3. Illustration of the Calculations for Equations (7), (9), and (10)

4.0 Estimation of Carbon Attributable to Antifoam Additions

Another use of the measurements investigated in this study is in the estimation of the amount carbon attributable to the antifoam added during DWPF's preparation of a given SME batch. One way of estimating the amount of carbon from the added antifoam is through the use of measurements of the SME contents. The estimation of the amount of carbon from the antifoam added during processing based upon the analysis of the SME samples is to be conducted by backing out contributions to the measured TOC concentration in the SME from the oxalate and the formate concentrations that are measured in the SME. The resulting adjusted TOC value will provide a basis for WSE to estimate the amount of antifoam that was added during the preparation of the given SME batch.

The uncertainties of the oxalate, formate, and TOC measurements provided by the evaluations performed above must be appropriately propagated into the estimated quantity of carbon from the added antifoam to determine the uncertainty of that estimated quantity. This process of adjusting the measured TOC may be framed as indicated by equation (11).

Equation 11.

$$\text{Antifoam}_C = \overline{\text{TOC}} - f_C \times \overline{\text{formate}} - o_C \times \overline{\text{oxalate}}$$

where $Antifoam_C$ is the measurand and it represents the adjusted concentration in ppm of the carbon attributable to antifoam,

$\overline{TOC}$ is (as above) the average of the TOC measurements in ppm for the samples from the given SME batch,

$\overline{formate}$ is the average of the formate measurements in ppm for the samples from the SME batch,

$\overline{oxalate}$ is the average of the oxalate measurements in ppm for the samples from the SME batch,

f_C is the conversion factor needed to determine the carbon contributed by the formate content of the SME in ppm, and

o_C is the conversion factor needed to determine the carbon contributed by the oxalate content of the SME in ppm.

The conversion factor for formate is 0.26681 ppm carbon per ppm of formate as determined by:

Equation 12.

$$\frac{1\text{ mg formate}}{\text{kg SMESlurry}} \times \frac{1\text{ gram}}{1000\text{ mg}} \times \frac{1\text{ gmole formate}}{45.0177\text{ g formate}} \times \frac{1\text{ gmole carbon}}{1\text{ gmole formate}} \times \frac{12.011\text{ g carbon}}{1\text{ gmole carbon}} \times \frac{1000\text{ mg}}{1\text{ gram}} = 0.266806 \frac{1\text{ mg carbon}}{\text{kg SMESlurry}}$$

and for oxalate, the factor is 0.27292 ppm carbon per ppm of oxalate as determined by

Equation 13.

$$\frac{1\text{ mg oxalate}}{\text{kg SMESlurry}} \times \frac{1\text{ gram}}{1000\text{ mg}} \times \frac{1\text{ gmole oxalate}}{88.019\text{ g oxalate}} \times \frac{2\text{ gmole carbon}}{1\text{ gmole oxalate}} \times \frac{12.011\text{ g carbon}}{1\text{ gmole carbon}} \times \frac{1000\text{ mg}}{1\text{ gram}} = 0.27292 \frac{1\text{ mg carbon}}{\text{kg SMESlurry}}$$

In using equation (11) to estimate the carbon content of the SME adjusted for contributions from sources other than antifoam, note the impact of oxalate values being below the detection limit of the analytical process. There are such values in Table A1 for oxalate, and they are represented in the table by values such as < 500 ppm. Representing the value for oxalate in equation (11) as a 0 leads to a conservative estimate of the amount of antifoam that was added since the TOC content would not be reduced at all for any carbon contribution by oxalate. However, if the measured oxalate concentrations are above detection, the adjusted TOC value is determined as indicated by (11). Thus, there are two equations to represent the carbon content of the SME due to antifoam: one equation without an oxalate term and one with an oxalate term.

In addition, equation (11) is to be modified in a conservative manner to handle the potential bias in the formate results (as suggested by the results from the formate standards, which were presented above). From the results of the formate standards, there was a consistently high bias for both the 2 and 16 ppm standards. While both biases are comparable on a relative basis, the relative bias of the 2 ppm results are greater and will be used to provide a conservative result. The mean of the measurements of the 2 ppm standard in Exhibit A4, was 2.069 so an estimate of the bias is given by

2.069 – 2 = 0.069 or 3.45%. An upper bound on this bias, using the 95% confidence interval for the mean provided in Exhibit A4, is given by 2.092 – 2 = 0.092 or 4.6% of the nominal 2 ppm value. In determining the estimated amount of carbon from antifoam additions, the formate measurement will be adjusted for the potential bias, and that adjustment will be made by reducing the amount of carbon contributed by the formate by 4.6% (i.e., by multiplying the average formate content by 0.954).

This approach leads to the following pair of equations:

Equation 14.

$$\text{Antifoam}_{1C} = \overline{\text{TOC}} - f_C \times \overline{\text{formate}} \times 0.954 - o_C \times \overline{\text{oxalate}}$$

where Antifoam_{1C} is the measurand, and it represents the estimated amount of carbon attributable to antifoam when the oxalate measurements are above their detection limit,

$\overline{\text{TOC}}$ represents the average TOC measurement in ppm for the SME batch,

$\overline{\text{formate}}$ is the average of the formate measurements in ppm for the samples from the SME batch,

$\overline{\text{oxalate}}$ is the average of the oxalate measurements in ppm for the samples from the SME batch, where all of the oxalate values are above detection,

f_C is the conversion factor needed to determine the carbon contributed by the formate content of the SME in ppm, and

o_C is the conversion factor needed to determine the carbon contributed by the oxalate content of the SME in ppm.

Equation 15.

$$\text{Antifoam}_{2C} = \overline{\text{TOC}} - f_C \times \overline{\text{formate}} \times 0.954$$

where Antifoam_{2C} is the measurand, and it represents the estimated amount of carbon in ppm attributable to antifoam when all of the oxalate values are below detection,

$\overline{\text{TOC}}$ represents the average TOC measurement in ppm for the SME batch,

$\overline{\text{formate}}$ is the average of the formate measurements in ppm for the samples from the SME batch, and

f_C is the conversion factor needed to determine the carbon contributed by the formate content of the SME in ppm.

Note that in Equation (15), there is no contribution to the carbon content of the SME from oxalate and the formate content is reduced by 4.6% to account for (in a bounding way) the potential bias in the formate measurements.

Two equations have been developed to estimate the carbon content attributable to antifoam for a given SME batch. The uncertainties of the two estimates resulting from the use of these equations are now determined. To facilitate this process, the equations are modified using notational conventions suggested by [5] to develop more complete measurement equations. This involves introducing terms for the batch to batch effects for formate, $\delta_{formate}$, and oxalate, $\delta_{oxalate}$, (the necessity for these terms is indicated in Table 1) and for TOC, δ_{TOC}, (as utilized in the previous section). The measurement equations resulting from these additions are given by:

Equation 16.

$$\text{Antifoam}_{1C} = \overline{\text{TOC}} + \delta_{\text{TOC}} - f_C \times \left(\overline{\text{formate}} + \delta_{\text{formate}}\right) \times 0.954 - o_C \times \left(\overline{\text{oxalate}} + \delta_{\text{oxalate}}\right)$$

Equation 17.

$$\text{Antifoam}_{2C} = \overline{\text{TOC}} + \delta_{\text{TOC}} - f_C \times \left(\overline{\text{formate}} + \delta_{\text{formate}}\right) \times 0.954$$

where Antifoam_{1C} is the measurand of equation (16), and it represents the estimated amount of carbon in ppm attributable to antifoam when the oxalate values for the SME batch are all above detection,

Antifoam_{2C} is the measurand of equation (17), and it represents the estimated amount of carbon in ppm attributable to antifoam when the oxalate values for the SME batch are all below detection,

$\overline{\text{TOC}}$ represents the average TOC measurement in ppm for the SME batch,

δ_{TOC} represents the random batch to batch variation in the TOC measurements,

$\overline{\text{formate}}$ is the average of the formate measurements in ppm for the samples from the SME batch,

$\delta_{oxalate}$ represents the random the batch to batch variation in the oxalate measurements,

$\overline{\text{oxalate}}$ is the average of the oxalate measurements in ppm for the samples from the SME batch with all of the measurements being above detection,

$\delta_{formate}$ represents the random the batch to batch variation in the formate measurements,

f_C is the conversion factor needed to determine the carbon contributed by the formate content of the SME in ppm, and

o_C is the conversion factor needed to determine the carbon contributed by the oxalate content of the SME in ppm.

For the evaluation of equations (16) and (17), the values of δ_{TOC}, $\delta_{formate}$, and $\delta_{oxalate}$ are taken to be zero. The variances of the estimates of the carbon contribution from the antifoam for both of these equations will be estimated using a Taylor's series expansion approach as utilized above. The resulting estimates of the variances are provided in the following pair of equations:

Equation 18.

$$\mathrm{var}(\mathrm{Antifoam}_{1C}) \approx \left(se_{\overline{TOC}}\right)^2 + \left(s_{\delta_{TOC}}\right)^2 + (f_C \times 0.954)^2 \times \left(\left(se_{\overline{formate}}\right)^2 + \left(s_{\delta_{formate}}\right)^2\right) + (o_C)^2 \times \left(\left(se_{\overline{oxalate}}\right)^2 + \left(s_{\delta_{oxalate}}\right)^2\right)$$

Equation 19.

$$\mathrm{var}(\mathrm{Antifoam}_{2C}) \approx \left(se_{\overline{TOC}}\right)^2 + \left(s_{\delta_{TOC}}\right)^2 + (f_C \times 0.954)^2 \times \left(\left(se_{\overline{formate}}\right)^2 + \left(s_{\delta_{formate}}\right)^2\right)$$

where $\mathrm{var}(\mathrm{Antifoam}_{1C})$ represents the estimate of the variance of the estimate of the carbon content due to the antifoam with all available oxalate values being above detection,

$\mathrm{var}(\mathrm{Antifoam}_{2C})$ represents the estimate of the variance of the estimate of the carbon content due to the antifoam with all available oxalate values being below detection,

f_C is the conversion factor needed to determine the carbon contributed by the formate content of the SME in ppm,

$se_{\overline{TOC}}$ represents the 1-sigma standard uncertainty of the average TOC measurement of the SME samples,

$s_{\delta_{TOC}}$ represents the 1-sigma standard uncertainty of the batch to batch variation in the TOC measurements (based upon the analyses presented here that value is given by 1.04% of the $\overline{TOC}$ value),

$se_{\overline{formate}}$ represents the 1-sigma standard uncertainty of the average formate measurement of the SME samples,

$s_{\delta_{formate}}$ represents the 1-sigma standard uncertainty of the batch to batch variation in the formate measurements (based upon the results in Table 1 that value is given by 1.56% of the $\overline{formate}$ value),

$se_{\overline{oxalate}}$ represents the 1-sigma standard uncertainty of the average oxalate measurement of the SME samples, where all oxalate values are above detection, and

$s_{\delta_{oxalate}}$ represents the 1-sigma standard uncertainty of the batch to batch variation in the oxalate measurements (based upon the results in Table 1 that value is given by 1.84% of the $\overline{oxalate}$ value), The uncertainty of each of the estimated quantities $Antifoam_{1C}$ and $Antifoam_{2C}$ at 95% confidence is determined by multiplying the square root of the estimate of their variance by an appropriate Student's t statistic. In this case a one-sided confidence statement is needed; so, an upper 5%-tail of the Student's t distribution will be used. Again, utilizing a conservative 3 degrees of freedom for each of the estimated variances, the t value is 2.353. Thus, the upper limit at 95% confidence for each estimate of the carbon content of the SME attributable to antifoam is given by:

Equation 20.
(when all available oxalate values for the SME batch are above detection)

$$Antifoam_{1C} + 2.353 \times (\text{Est. var}(Antifoam_{1C}))^{0.5}$$

Equation 21.
(when all available oxalate values for the SME batch are below detection)

$$Antifoam_{2C} + 2.353 \times (\text{Est. var}(Antifoam_{2C}))^{0.5}$$

A sample calculation is provided in Exhibit 4 utilizing the data from SME batch 366. Note that for this SME batch all of the oxalate data are below detection. Therefore, the calculation represented in the exhibit corresponds to equations (17), (19), and (21). That is, the determination of the quantity of carbon attributable to antifoam uses equation (17). In the exhibit that value is labeled as "Adjusted TOC Quantity – Carbon Attributable to Antifoam (ppm)," and its value is 2734.823 ppm. The estimated variance for this quantity is given by equation (19). In the exhibit, the square root of the variance is labeled as "1-sigma standard uncertainty of the Adjusted TOC Quantity," and its value is 299.4 ppm. The upper limit, at 95% confidence, on the quantity of carbon attributable to antifoam is given by equation (21). In the exhibit, this limit is labeled as "Upper Limit at 95% confidence for the Carbon from Antifoam Additions," and its value is 3439.536 ppm.

TOC (ppm)	Average (ppm) TOC Content	1-sigma standard uncertainty (ppm)	batch to batch 1-sigma standard uncertainty (ppm)
13771			
13153			
13834			
13198	13489	181.68792	140.2856

Formate (ppm)	Formate Content	1-sigma standard uncertainty (ppm)	batch to batch 1-sigma standard uncertainty (ppm)
42144			
42827			
41246			
42783	42250	369.2639074	659.1

Oxalate	(Enter values only if above detection.) Oxalate Content	1-sigma standard uncertainty (ppm)	batch to batch 1-sigma standard uncertainty (ppm)

TOC (ppm)	Std Error for TOC (ppm)	Partial wrt TOC	Partial wrt δTOC	1-sigma Batch to Batch Uncertainty for δTOC (ppm)	Carbon Contribution from Formate	Partial wrt Formate	Std Error for Formate (ppm)	Carbon Contribution from Oxalate
13489	181.68792	1	1	140.2856	10754.17727	-0.25454	369.26391	

Partial wrt Oxalate	Std Error for Oxalate (ppm)	Partial wrt δformate	1-sigma Batch to Batch Variation for δformate (ppm)	Partial wrt δoxalate	1-sigma Batch to Batch Variation for δoxalate (ppm)	Adjusted TOC Quanity - Carbon Attributed to Antifoam (ppm)	1-sigma standard uncertainty the for the Adjusted TOC Quantity	One-sided Uncertainty at 95% confidence	Upper Limit at 95% confidence for the Carbon from Anifoam Additions
		-0.25454	659.1			2734.823	299.4	704.7	3439.536

Exhibit 4. Illustration of Calculations of Equations (17), (19), and (21)

A sample calculation is provided in Exhibit 5 utilizing the data from SME batch 366 modified to include simulated, above-detection measurements for oxalate. The oxalate values were determined by multiplying the detection limits for these measurements given in Table A1 by 10. Therefore, the calculation represented in the exhibit corresponds to the determination of the quantity of carbon attributable to antifoam using equation (16). In the exhibit that value is labeled as “Adjusted TOC Quantity – Carbon Attributable to Antifoam (ppm),” and its value is 1332.69624 ppm. The estimated variance for this quantity is given by equation (18). In the exhibit, the square root of the variance is labeled as “1-sigma standard uncertainty of the Adjusted TOC Quantity,” and its value is 300.7 ppm. The upper limit, at 95% confidence, on the quantity of carbon attributable to antifoam is given by equation (20). In the exhibit, this limit is labeled as “Upper Limit at 95% confidence for the Carbon from Antifoam Additions,” and its value is 2040.270 ppm.

TOC (ppm)				batch to batch
13771			1-sigma	1-sigma
13153		Average (ppm)	standard	standard
13834		TOC Content	uncertainty (ppm)	uncertainty (ppm)
13198		13489	181.68792	140.28560

Formate (ppm)				batch to batch
42144			1-sigma	1-sigma
42827			standard	standard
41246		Formate Content	uncertainty (ppm)	uncertainty (ppm)
42783		42250	369.26391	659.10000

Oxalate	(Enter values only if above detection.)			batch to batch
5200			1-sigma	1-sigma
5110			standard	standard
5170		Oxalate Content	uncertainty (ppm)	uncertainty (ppm)
5070		5137.5	29.26175	94.53000

TOC (ppm)	Std Error for TOC (ppm)	Partial wrt TOC	Partial wrt δTOC	1-sigma Batch to Batch Uncertainty for δTOC (ppm)	Carbon Contribution from Formate	Partial wrt Formate	Std Error for Formate (ppm)	Carbon Contribution from Oxalate
13489	181.68792	1	1	140.28560	10754.17727	-0.25454	369.26391	1402.12650

Partial wrt Oxalate	Std Error for Oxalate (ppm)	Partial wrt δformate	1-sigma Batch to Batch Variation for δformate (ppm)	Partial wrt δoxalate	1-sigma Batch to Batch Variation for δoxalate (ppm)	Adjusted TOC Quanity - Carbon Attributed to Antifoam (ppm)	1-sigma standard uncertainty for the Adjusted TOC Quantity	One-sided Uncertainty at 95% confidence	Upper Limit at 95% confidence for the Carbon from Anifoam Additions
-0.27292	29.26175	-0.25454	659.1	-0.27292	94.53000	1332.69624	300.7	707.6	2040.270

Exhibit 5. Illustration of Calculations of Equations (16), (18), and (20)

5.0 SUMMARY

In this report, the formate, nitrate, oxalate, and TOC measurements generated by the DWPF Laboratory for recent SME batches are presented. These measurements were provided to SRNL by DWPF Laboratory OPS personnel. An evaluation of the uncertainties of these measurements is provided as well as approaches for assessing the impact of these uncertainties on DWPF's strategies for controlling melter flammability and for monitoring antifoam additions.

REFERENCES

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[3] Choi, A.S., "DWPF Melter Off-Gas Flammability Assessment (Sludge Batch 6 and for Sludge Batch 7a)," Revision 5, X-CLC-S-00164, April, 2011.

[4] JMP Version 7.0.2, SAS Institute, Inc., Cary NC, 1989-2007.

[5] International Organization for Standardization (ISO), **Guide to the Expression of Uncertainty in Measurement**, ISO, Geneva, 1993, Corrected and reprinted, 1995.

APPENDIX A.

Supplemental Tables and Exhibits

Table A1. DWPF Laboratory Measurements of Anions by IC

(LIMS Numbers in Red: M-14 instrument was used; LIMS Numbers in Blue: M-13 Instrument was used)

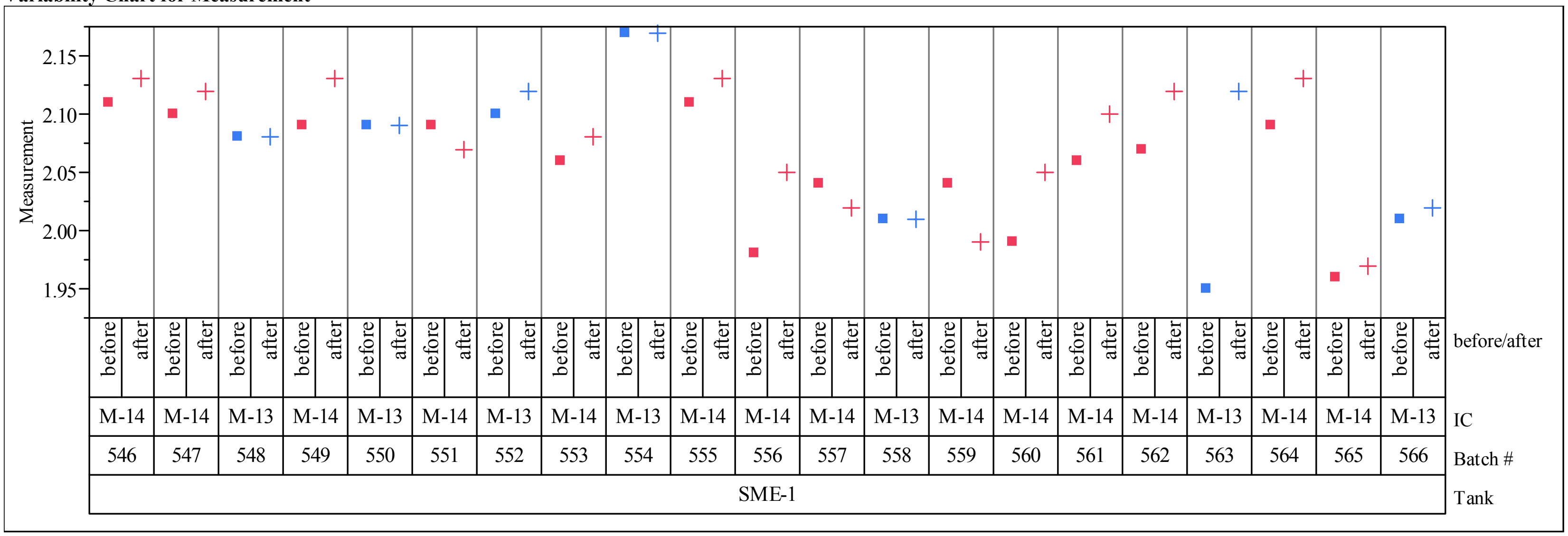
	IC Instrument	M-13	M-14	M-14	M-13	M-14	M-14	M-14	M-14	M-13	M-14	M-14	M-14	M-13	M-14	M-13	M-14	M-13	M-14	M-13	M-14	M-14
LIMS number		5839	5699	5623	5489	5413/33	5312	5254	5167	5067/133	4877/133	4707	4567/97/07	4422	4317	4253	4127	4017/42	3822	3758	3602	3532
Tank		SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1	SME-1
Batch #		566	565	564	563	562	561	560	559	558	557	556	555	554	553	552	551	550	549	548	547	546
Date		3/13/11	3/8/11	3/3/11	2/23/11	2/18/11	2/12/11	2/8/11	2/3/11	1/29/11	1/20/11	1/11/11	1/6/11	12/30/11	12/23/10	12/20/10	12/14/10	12/10/10	11/28/10	11/23/10	11/14/10	11/11/10
mg/kg slurry	TOC	13489	12633	13207	12856	12428	12781	14137	14595	12185	16394	14464	14043	14097	13669	13140	14934	15207	14070	13390	12389	12780
mg/kg slurry	Formate	42144	38476	41700	42526	37874	39285	40655	38610	34289	40136	39474	37562	41167	35639	35908	38648	45575	36696	34411	33028	36418
	Formate	42827	39478	41251	39648	36930	37927	39569	37894	32272	35218	39443	37822	39761	36340	36059	38966	49557	36429	34982	34111	36032
	Formate	41246	39581	41058	40330	37495	39067	41389	37828	32379	38621	38515	39598	40162	36638	36081	38343	40008	36580	34602	33766	36078
	Formate	42783	38684	42795	40941	37970	37860	40555	39327	31138	37987	38400	37686	39535	36739	36577	38079	41955	36797	34320	33993	35384
	Nitrate	23700	23250	22058	22742	23652	23163	26075	20305	21758	24414	21801	23335	27315	22162	20143	21877	25500	19740	24397	24475	19897
	Nitrate	23604	23254	22004	22305	24501	23108	26329	20782	21807	21339	21120	22814	26366	22706	20179	22027	27837	19089	24392	25501	19644
	Nitrate	23229	23273	21801	22771	23180	22759	26481	19817	22042	23405	20735	22946	26498	22581	20189	21622	22351	20660	24123	25226	19513
	Nitrate	23433	23000	22361	22313	24453	23148	26010	19792	21003	22948	20725	22347	26057	23033	20596	21781	23811	19736	24181	25600	19291
	Oxalate	< 520	< 542	< 513	605	< 496	< 517	563	< 484	< 487	< 542	< 515	<542	< 515	< 500	< 490	< 507	764	< 501	<483	< 533	< 491
	Oxalate	< 511	< 534	< 514	585	< 505	< 510	565	< 513	< 503	< 551	< 498	<488	< 481	< 506	< 485	< 538	891	< 495	<485	< 550	< 506
	Oxalate	< 517	< 512	< 506	501	< 497	< 515	570	< 503	< 498	< 500	< 517	<536	< 505	< 503	< 492	< 521	750	< 492	<493	< 527	< 485
	Oxalate	< 507	< 516	< 497	599	< 492	< 518	553	< 498	< 490	< 548	<500	<530	< 500	< 509	< 491	< 493	779	< 495	<477	< 549	< 473
Actual ppm	Formate	8.02	7.00	7.94	8.34	7.51	7.70	7.78	7.72	6.95	7.48	7.84	6.97	8.47	7.14	7.22	7.19	8.40	7.25	7.01	6.14	7.12
from IC	Formate	8.31	7.30	7.93	7.91	7.22	7.55	7.80	7.33	6.26	6.75	8.18	7.51	8.46	7.17	7.38	6.97	8.83	7.29	7.07	6.18	6.97
instrument	Formate	8.15	7.50	7.91	7.97	7.36	7.69	7.94	7.54	6.39	7.64	7.56	7.11	7.76	7.35	7.22	7.04	7.16	7.33	7.00	5.97	7.34
	Formate	8.07	7.35	8.44	8.11	7.50	7.36	8.02	7.65	6.36	6.82	7.93	6.83	7.48	7.13	7.37	7.43	7.70	7.29	7.21	6.48	7.41
	Nitrate	4.51	4.23	4.20	4.46	4.69	4.54	4.99	4.06	4.41	4.55	4.33	4.32	5.62	4.44	4.05	4.07	4.70	3.90	4.88	4.55	3.89
	Nitrate	4.58	4.30	4.23	4.45	4.79	4.60	5.19	4.02	4.23	4.09	4.38	4.53	5.61	4.48	4.13	3.94	4.96	3.82	4.97	4.62	3.80
	Nitrate	4.59	4.41	4.20	4.50	4.55	4.48	5.08	3.95	4.34	4.63	4.07	4.12	5.12	4.53	4.04	3.97	4.00	4.14	4.93	4.46	3.97
	Nitrate	4.42	4.37	4.41	4.42	4.83	4.50	5.15	3.85	4.29	4.12	4.28	4.05	4.93	4.47	4.15	4.25	4.37	3.90	5.07	4.88	4.04
	Oxalate				1.21													1.47				
	Oxalate				1.15													1.64				
	Oxalate				1.01													1.37				
	Oxalate				1.21													1.42				
2 ppm Before	Formate	2.01	1.96	2.09	1.95	2.07	2.06	1.99	2.04	2.01	2.04	1.98	2.11	2.17	2.06	2.10	2.09	2.09	2.09	2.08	2.10	2.11
2 ppm Before	Nitrate	1.89	2.14	2.10	1.87	2.06	2.09	2.05	2.03	1.97	2.05	1.93	1.95	2.02	1.90	1.98	2.00	1.99	1.91	2.12	2.09	2.15
2 ppm Before	Oxalate	2.10	2.07	2.08	2.05	2.08	2.07	2.03	2.05	2.13	2.09	2.11	2.02	2.17	2.10	2.12	2.07	2.20	2.10	2.18	2.23	2.23
16 ppm Before	Formate	16.36	16.36	16.57	15.83	16.13	16.40	15.88	16.31	16.49	16.44	16.71	16.82	17.11	16.31	16.88	16.15	16.60	16.17	16.06	16.47	16.46
16 ppm Before	Nitrate	16.05	16.13	16.31	15.83	15.75	16.06	15.54	16.02	15.89	15.98	16.14	16.16	16.45	15.65	16.06	15.67	16.70	15.76	16.88	16.20	17.18
16 ppm Before	Oxalate	16.08	16.10	16.29	15.70	15.78	16.08	15.56	16.05	15.93	16.08	16.23	16.38	16.52	15.87	16.12	15.67	16.90	15.74	16.33	16.56	16.53
2 ppm After	Formate	2.02	1.97	2.13	2.12	2.12	2.10	2.05	1.99	2.01	2.02	2.05	2.13	2.17	2.08	2.12	2.07	2.09	2.13	2.08	2.12	2.13
2 ppm After	Nitrate	1.89	2.06	2.15	2.10	2.05	2.15	2.11	2.18	1.97	1.92	1.96	2.00	2.00	1.95	2.00	1.95	2.05	1.98	2.10	1.99	2.12
2 ppm After	Oxalate	2.09	2.07	2.08	2.05	2.07	2.06	2.01	2.05	2.13	2.03	2.06	2.14	2.15	2.09	2.12	2.08	2.19	2.08	2.17	2.22	2.20
16 ppm After	Formate	16.37	16.38	16.63	15.87	16.11	16.40	15.94	16.43	16.49	16.42	16.71	16.86	17.11	16.33	16.71	16.12	16.61	16.19	16.07	16.46	16.51
16 ppm After	Nitrate	16.05	16.34	16.26	15.67	15.82	16.06	15.55	16.06	15.89	15.94	16.16	16.20	16.44	16.03	16.07	15.71	16.69	15.79	16.82	16.20	17.18
16 ppm After	Oxalate	16.08	16.13	16.30	15.60	15.84	16.08	15.58	16.06	15.93	16.06	16.25	16.40	16.52	15.88	16.13	15.68	16.68	15.74	16.30	16.50	16.51

Table A2. Total Organic Carbon (TOC) Measurements by SME Batch

LIMS number		6158		6083		5839		5699		5623		5489		5413/33		5312		5254		5167	
Tank		SME-1		SME-1		SME-1		SME-1		SME-1		SME-1		SME-1		SME-1		SME-1		SME-1	
Batch #		**568**		**567**		**566**		**565**		**564**		**563**		**562**		**561**		**560**		**559**	
Date						3/13/11		3/8/11		3/3/11		2/23/11		2/18/11		2/12/11		2/8/11		2/3/11	
mg/kg slurry	TOC					13489		12633		13207		12856		12428		12781		14137		14595	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
1ppm opening		0.89	0.9	0.98	0.97	0.93	0.89	0.91	0.91	0.92	0.92	0.95	0.95	0.94	0.94	0.94	0.94	0.98	0.98	1.03	1.03
20 ppm opening		19.52	19.25	19.91	19.56	19.9	19.6	19.96	19.77	20.38	20.16	20.05	19.74	20.01	19.74	20.13	19.82	19.37	19.06	20.16	19.86
ppm at instrument		13.702	13.702	11.856	11.898	15.338	14.65	14.396	14.002	15.01	14.233	13.285	15.819	14.751	14.689	13.226	13.421	15.057	14.087	14.769	14.956
TOC		11708	11596	10758	10796	13771	13153	12828	12470	13293	13184	12754	12976	12402	12350	12762	12822	14236	14050	14578	14750
ppm at instrument		13.602	13.693	13.616	13.568	15.309	14.605	14.332	14.006	14.856	14.244	13.288	15.793	14.262	14.253	13.213	13.387	14993	14.123	14.87	14.939
TOC		11623	11588	10546	10509	13834	13198	12762	12473	13157	13194	12757	12938	12484	12476	12749	12790	14175	14086	14677	14553
1ppm closing		0.94	0.92	0.98	0.98	0.93	0.92	0.98	0.96	0.92	0.91	0.97	0.96	0.96	0.97	0.96	0.96	1.04	1.00	1.07	1.05
20 ppm closing		20.05	19.69	19.81	19.51	20.78	20.31	20.44	20.09	20.44	20.1	20.01	19.66	20.34	20.01	19.9	19.61	19.34	19.3	20.01	19.8

Exhibit A1. Variability Plots of the Measurements of the IC Standards for Formate, Nitrate, and Oxalate

Standard=Formate, Standard Value (ppm)=2
Variability Chart for Measurement



Standard=Formate, Standard Value (ppm)=16
Variability Chart for Measurement

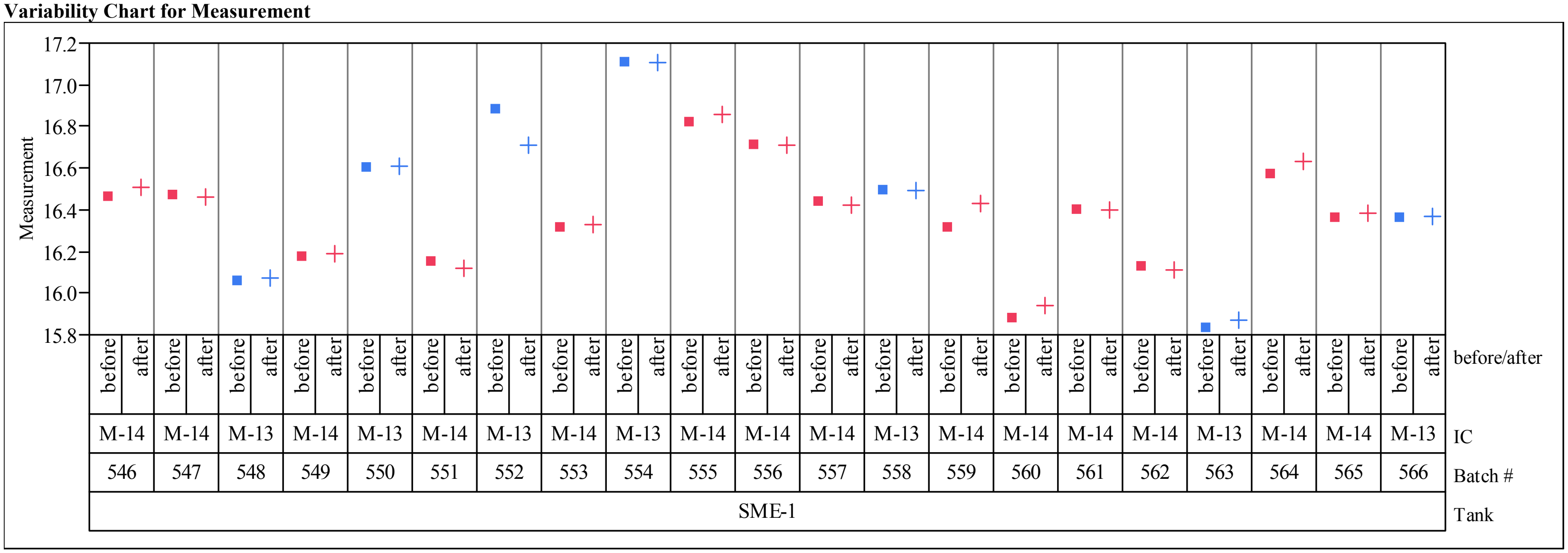
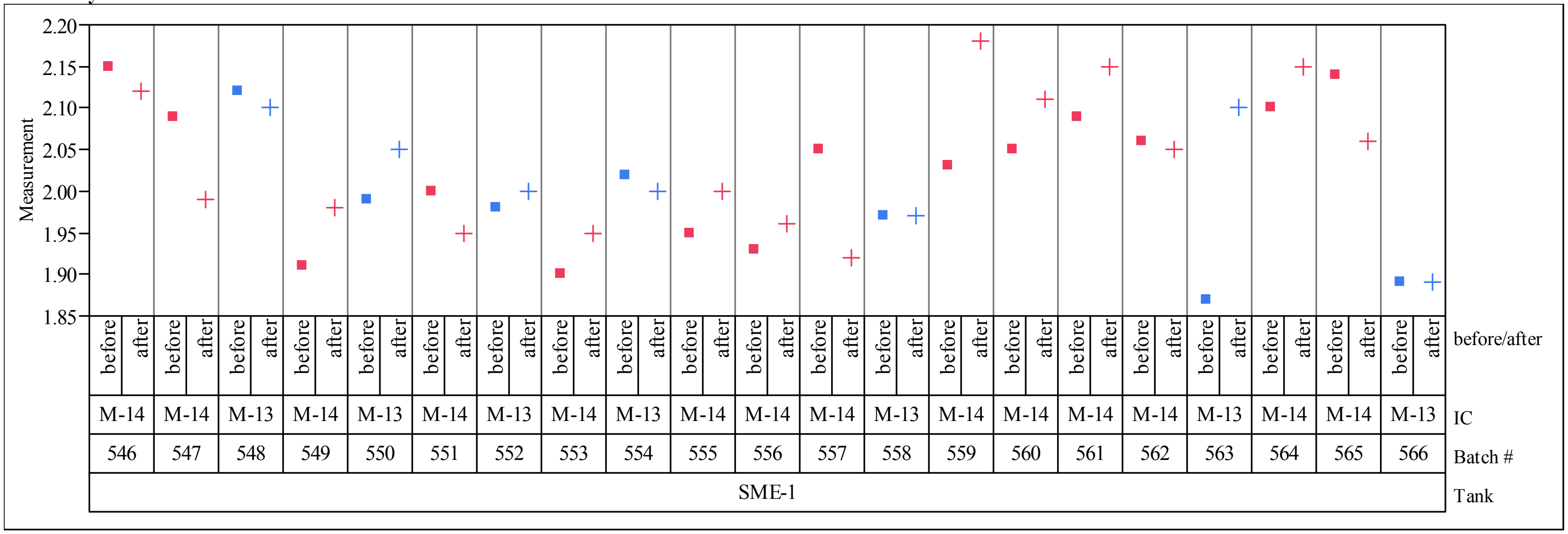


Exhibit A1. Variability Plots of the Measurements of the IC Standards for Formate, Nitrate, and Oxalate

Standard=Nitrate, Standard Value (ppm)=2
Variability Chart for Measurement



Variability Gauge Standard=Nitrate, Standard Value (ppm)=16
Variability Chart for Measurement

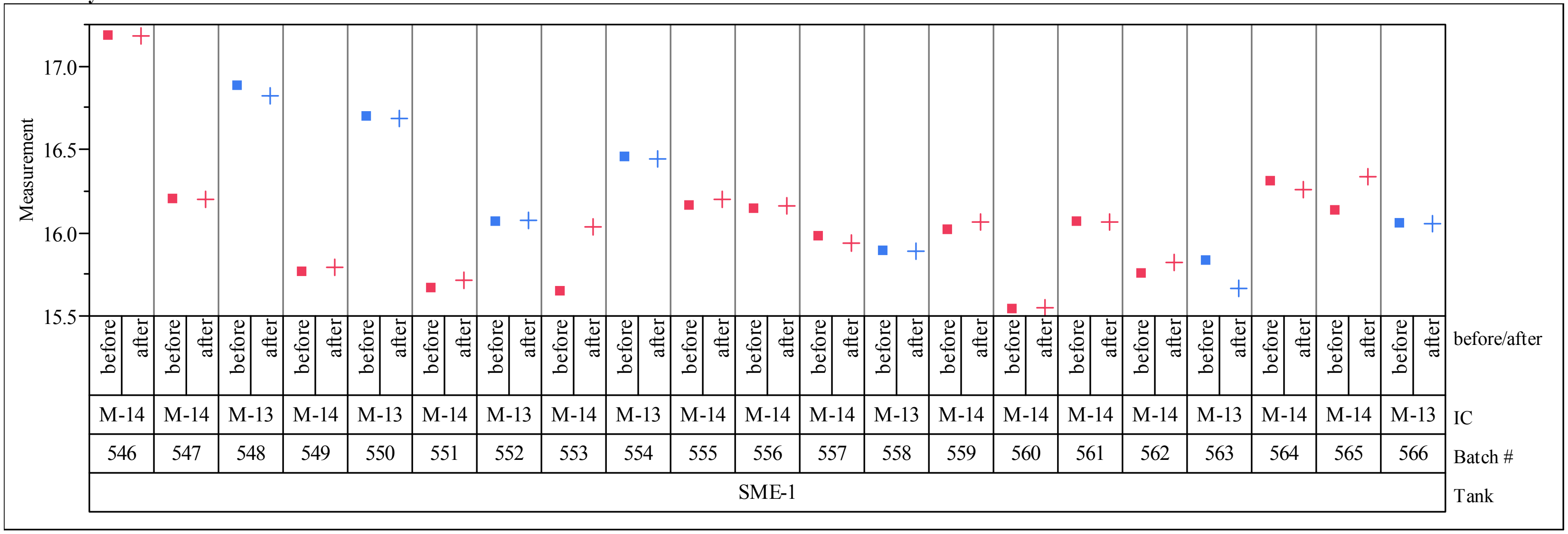
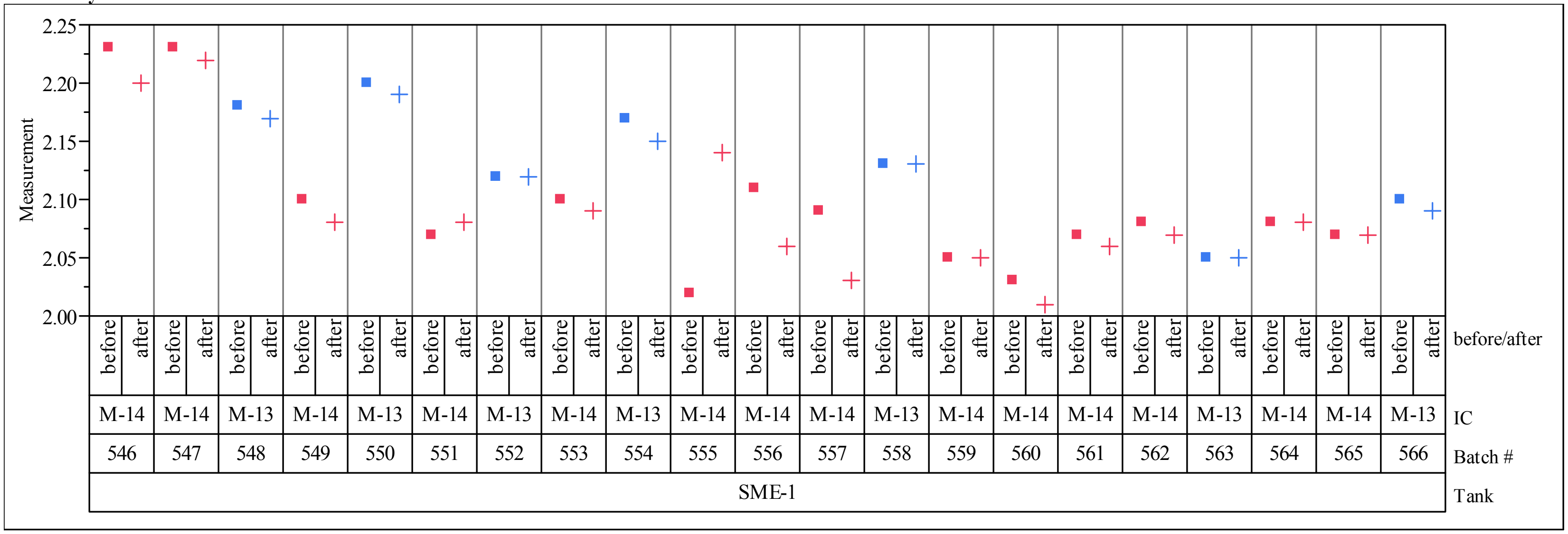


Exhibit A1. Variability Plots of the Measurements of the IC Standards for Formate, Nitrate, and Oxalate

Standard=Oxalate, Standard Value (ppm)=2
Variability Chart for Measurement



Standard=Oxalate, Standard Value (ppm)=16
Variability Chart for Measurement

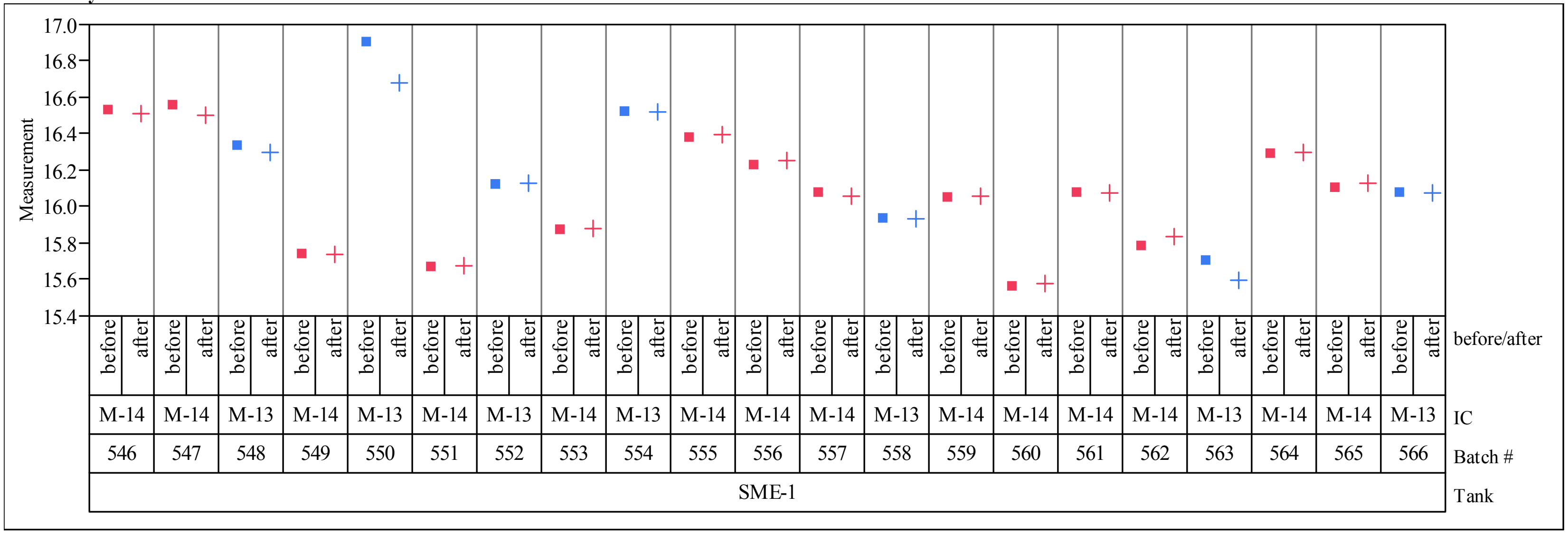
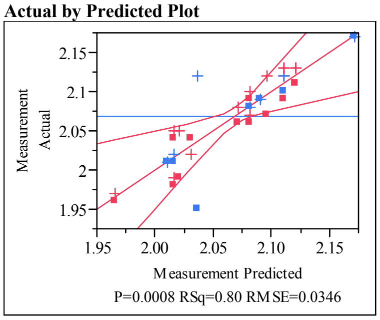


Exhibit A2. Random Effects Model for Batch to Batch Variation in the Measurement of Each Standard

Response Measurement Standard=Formate, Standard Value (ppm)=2
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.804763
RSquare Adj	0.618824
Root Mean Square Error	0.034572
Mean of Response	2.069048
Observations (or Sum Wgts)	42

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	0.10346190	0.005173	4.3281
Error	21	0.02510000	0.001195	**Prob > F**
C. Total	41	0.12856190		0.0008

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	2

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.001989	62.463
Residual	0.001195	37.537
Total	0.003184	100.000

These estimates based on equating Mean Squares to Expected Value.

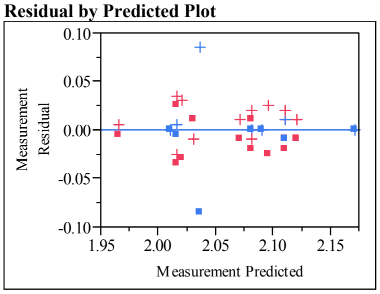
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.0012	21	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	0.10346	0.00517	20	4.3281	0.0008

Residual by Predicted Plot

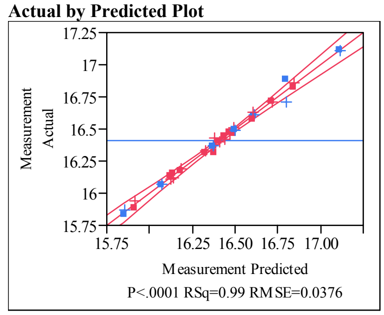


Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
0.10346190	4.3281	20	0.0008

Denominator MS Synthesis:
Residual

Response Measurement Standard=Formate, Standard Value (ppm)=16
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.992278
RSquare Adj	0.984923
Root Mean Square Error	0.037639
Mean of Response	16.41024
Observations (or Sum Wgts)	42

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	3.8227476	0.191137	134.9205
Error	21	0.0297500	0.001417	**Prob > F**
C. Total	41	3.8524976		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	2

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.09486	98.529
Residual	0.001417	1.471
Total	0.096277	100.000

These estimates based on equating Mean Squares to Expected Value.

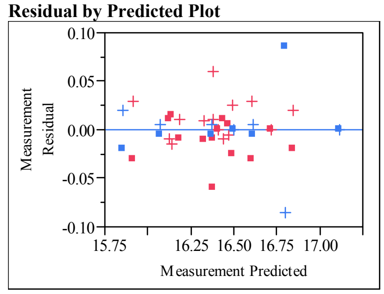
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.00142	21	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	3.82275	0.19114	20	134.9205	<.0001

Residual by Predicted Plot



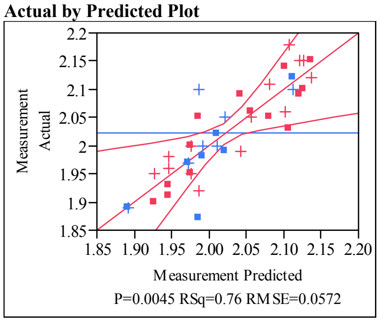
Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
3.8227476	134.9205	20	<.0001

Denominator MS Synthesis:
Residual

Exhibit A2. Random Effects Model for Batch to Batch Variation in the Measurement of Each Standard

Response Measurement Standard=Nitrate, Standard Value (ppm)=2
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.758855
RSquare Adj	0.529192
Root Mean Square Error	0.057217
Mean of Response	2.023095
Observations (or Sum Wgts)	42

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	0.21634762	0.010817	3.3042
Error	21	0.06875000	0.003274	**Prob > F**
C. Total	41	0.28509762		0.0045

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	2

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.003772	53.534
Residual	0.003274	46.466
Total	0.007046	100.000

These estimates based on equating Mean Squares to Expected Value.

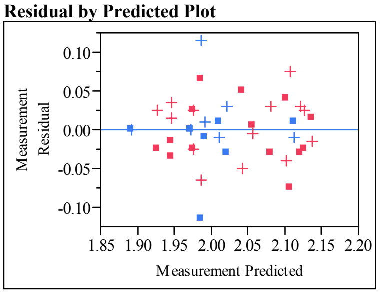
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.00327	21	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	0.21635	0.01082	20	3.3042	0.0045

Residual by Predicted Plot

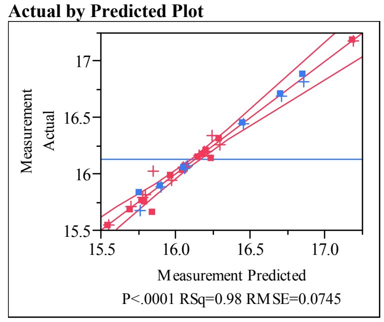


Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
0.21634762	3.3042	20	0.0045

Denominator MS Synthesis:
Residual

Response Measurement Standard=Nitrate, Standard Value (ppm)=16
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.982116
RSquare Adj	0.965083
Root Mean Square Error	0.074514
Mean of Response	16.12714
Observations (or Sum Wgts)	42

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	6.4030571	0.320153	57.6605
Error	21	0.1166000	0.005552	**Prob > F**
C. Total	41	6.5196571		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	2

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.1573	96.591
Residual	0.005552	3.409
Total	0.162853	100.000

These estimates based on equating Mean Squares to Expected Value.

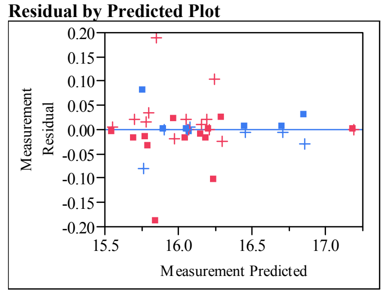
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.00555	21	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	6.40306	0.32015	20	57.6605	<.0001

Residual by Predicted Plot



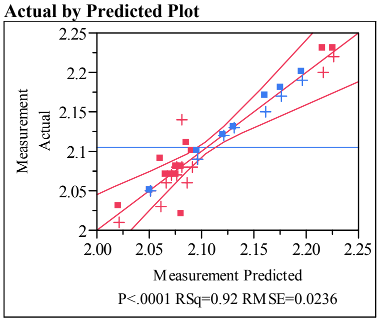
Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
6.4030571	57.6605	20	<.0001

Denominator MS Synthesis:
Residual

Exhibit A2. Random Effects Model for Batch to Batch Variation in the Measurement of Each Standard

Response Measurement Standard=Oxalate, Standard Value (ppm)=2
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.917865
RSquare Adj	0.83964
Root Mean Square Error	0.023604
Mean of Response	2.105238
Observations (or Sum Wgts)	42

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	0.13074762	0.006537	11.7338
Error	21	0.01170000	0.000557	**Prob > F**
C. Total	41	0.14244762		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	2

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.00299	84.294
Residual	0.000557	15.706
Total	0.003547	100.000

These estimates based on equating Mean Squares to Expected Value.

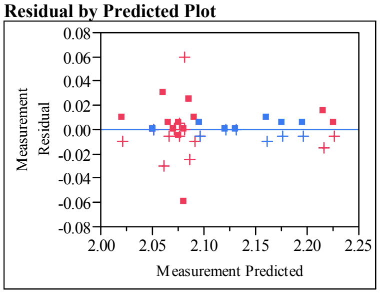
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.00056	21	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	0.13075	0.00654	20	11.7338	<.0001

Residual by Predicted Plot

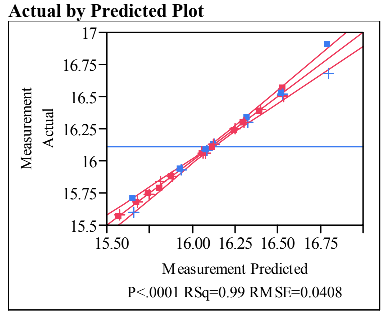


Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
0.13074762	11.7338	20	<.0001

Denominator MS Synthesis:
Residual

Response Measurement Standard=Oxalate, Standard Value (ppm)=16
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.991975
RSquare Adj	0.984331
Root Mean Square Error	0.040796
Mean of Response	16.1131
Observations (or Sum Wgts)	42

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	4.3199476	0.215997	129.7838
Error	21	0.0349500	0.001664	**Prob > F**
C. Total	41	4.3548976		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	2

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.107167	98.471
Residual	0.001664	1.529
Total	0.108831	100.000

These estimates based on equating Mean Squares to Expected Value.

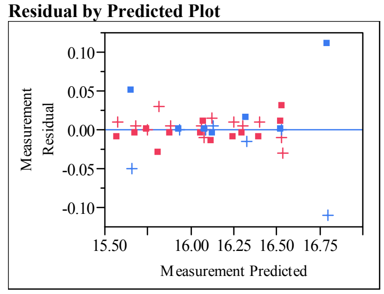
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.00166	21	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	4.31995	0.216	20	129.7838	<.0001

Residual by Predicted Plot



Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
4.3199476	129.7838	20	<.0001

Denominator MS Synthesis:
Residual

Exhibit A3. Random Effects Model for Batch to Batch Variation in the Measurement of the Formate, Nitrate and Oxalate Standards

Response Measurement Standard=Formate
Whole Model
Summary of Fit

RSquare	0.999595
RSquare Adj	0.999457
Root Mean Square Error	0.168101
Mean of Response	9.239643
Observations (or Sum Wgts)	84

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	21	4321.2937	205.776	7282.043
Error	62	1.7520	0.028	**Prob > F**
C. Total	83	4323.0457		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	20	1.6971452	0.084857	64.9773
Pure Error	42	0.0548500	0.001306	**Prob > F**
Total Error	62	1.7519952		<.0001
				Max RSq
				1.0000

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Standard Value (ppm)	Batch #&Random
Intercept	0	0	0
Standard Value (ppm)	0	42	0
Batch #&Random	0	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.020799	42.397
Residual	0.028258	57.603
Total	0.049057	100.000

These estimates based on equating Mean Squares to Expected Value.

Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Standard Value (ppm)	0.02826	62	Residual
Batch #&Random	0.02826	62	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Standard Value (ppm)	4319.06	4319.06	1	152844.0	<.0001
Batch #&Random	2.22906	0.11145	20	3.9441	<.0001

Standard Value (ppm)
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
4319.0646	152844.0	1	<.0001

Denominator MS Synthesis:
Residual

Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
2	2.069048	0.02593857	2.0690
16	16.410238	0.02593857	16.4102

Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
2.2290643	3.9441	20	<.0001

Denominator MS Synthesis:
Residual

Response Measurement Standard=Nitrate
Whole Model
Summary of Fit

RSquare	0.999289
RSquare Adj	0.999049
Root Mean Square Error	0.219005
Mean of Response	9.075119
Observations (or Sum Wgts)	84

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	21	4181.2384	199.107	4151.219
Error	62	2.9737	0.048	**Prob > F**
C. Total	83	4184.2121		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	20	2.7883810	0.139419	31.5921
Pure Error	42	0.1853500	0.004413	**Prob > F**
Total Error	62	2.9737310		<.0001
				Max RSq
				1.0000

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Standard Value (ppm)	Batch #&Random
Intercept	0	0	0
Standard Value (ppm)	0	42	0
Batch #&Random	0	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.035897	42.806
Residual	0.047963	57.194
Total	0.08386	100.000

These estimates based on equating Mean Squares to Expected Value.

Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Standard Value (ppm)	0.04796	62	Residual
Batch #&Random	0.04796	62	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Standard Value (ppm)	4177.41	4177.41	1	87095.73	<.0001
Batch #&Random	3.83102	0.19155	20	3.9937	<.0001

Standard Value (ppm)
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
4177.4073	87095.73	1	<.0001

Denominator MS Synthesis:
Residual

Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
2	2.023095	0.03379328	2.0231
16	16.127143	0.03379328	16.1271

Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
3.8310238	3.9937	20	<.0001

Denominator MS Synthesis:
Residual

Exhibit A3. Random Effects Model for Batch to Batch Variation in the Measurement of the Formate, Nitrate and Oxalate Standards

Response Measurement Standard=Oxalate
Whole Model
Summary of Fit

RSquare	0.999586
RSquare Adj	0.999446
Root Mean Square Error	0.16594
Mean of Response	9.109167
Observations (or Sum Wgts)	84

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	21	4123.4114	196.353	7130.786
Error	62	1.7072	0.028	**Prob > F**
C. Total	83	4125.1186		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	20	1.6605786	0.083029	74.7527
Pure Error	42	0.0466500	0.001111	**Prob > F**
Total Error	62	1.7072286		<.0001
				Max RSq
				1.0000

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Standard Value (ppm)	Batch #&Random
Intercept	0	0	0
Standard Value (ppm)	0	42	0
Batch #&Random	0	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.027992	50.411
Residual	0.027536	49.589
Total	0.055528	100.000

These estimates based on equating Mean Squares to Expected Value.

Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Standard Value (ppm)	0.02754	62	Residual
Batch #&Random	0.02754	62	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Standard Value (ppm)	4120.62	4120.62	1	149645.2	<.0001
Batch #&Random	2.79012	0.13951	20	5.0663	<.0001

Standard Value (ppm)
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
4120.6213	149645.2	1	<.0001

Denominator MS Synthesis:
Residual

Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
2	2.105238	0.02560503	2.1052
16	16.113095	0.02560503	16.1131

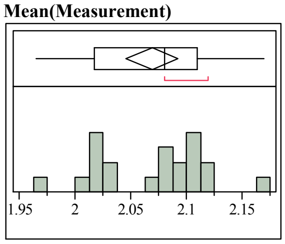
Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
2.7901167	5.0663	20	<.0001

Denominator MS Synthesis:
Residual

Exhibit A4. Histograms and Summary Statistics of the Measurements of the Anion Standards

Distributions Standard=Formate, Standard Value (ppm)=2
Mean(Measurement)



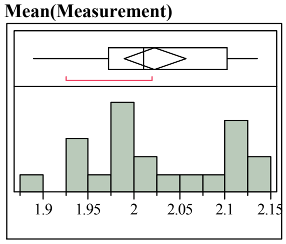
Quantiles

100.0%	maximum	2.1700
99.5%		2.1700
97.5%		2.1700
90.0%		2.1200
75.0%	quartile	2.1100
50.0%	median	2.0800
25.0%	quartile	2.0175
10.0%		2.0110
2.5%		1.9650
0.5%		1.9650
0.0%	minimum	1.9650

Moments

Mean	2.0690476
Std Dev	0.0508581
Std Err Mean	0.0110982
upper 95% Mean	2.092198
lower 95% Mean	2.0458973
N	21

Distributions Standard=Nitrate, Standard Value (ppm)=2
Mean(Measurement)



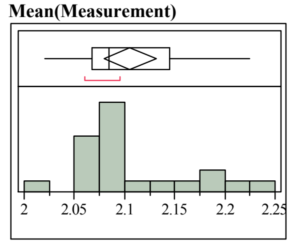
Quantiles

100.0%	maximum	2.1350
99.5%		2.1350
97.5%		2.1350
90.0%		2.1240
75.0%	quartile	2.1025
50.0%	median	2.0100
25.0%	quartile	1.9725
10.0%		1.9290
2.5%		1.8900
0.5%		1.8900
0.0%	minimum	1.8900

Moments

Mean	2.0230952
Std Dev	0.0735438
Std Err Mean	0.0160486
upper 95% Mean	2.056572
lower 95% Mean	1.9896185
N	21

Distributions Standard=Oxalate, Standard Value (ppm)=2
Mean(Measurement)



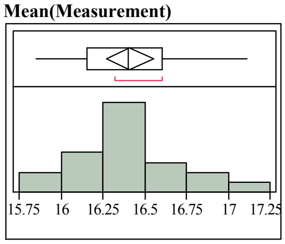
Quantiles

100.0%	maximum	2.2250
99.5%		2.2250
97.5%		2.2250
90.0%		2.2110
75.0%	quartile	2.1450
50.0%	median	2.0850
25.0%	quartile	2.0675
10.0%		2.0500
2.5%		2.0200
0.5%		2.0200
0.0%	minimum	2.0200

Moments

Mean	2.1052381
Std Dev	0.0571725
Std Err Mean	0.0124761
upper 95% Mean	2.1312627
lower 95% Mean	2.0792135
N	21

Distributions Standard=Formate, Standard Value (ppm)=16
Mean(Measurement)



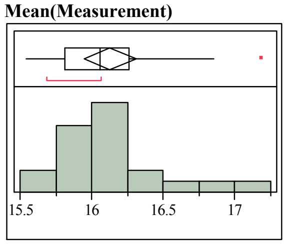
Quantiles

100.0%	maximum	17.110
99.5%		17.110
97.5%		17.110
90.0%		16.831
75.0%	quartile	16.603
50.0%	median	16.400
25.0%	quartile	16.158
10.0%		15.941
2.5%		15.850
0.5%		15.850
0.0%	minimum	15.850

Moments

Mean	16.410238
Std Dev	0.3091419
Std Err Mean	0.0674603
upper 95% Mean	16.550958
lower 95% Mean	16.269518
N	21

Distributions Standard=Nitrate, Standard Value (ppm)=16
Mean(Measurement)



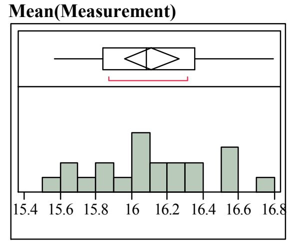
Quantiles

100.0%	maximum	17.180
99.5%		17.180
97.5%		17.180
90.0%		16.819
75.0%	quartile	16.260
50.0%	median	16.060
25.0%	quartile	15.813
10.0%		15.702
2.5%		15.545
0.5%		15.545
0.0%	minimum	15.545

Moments

Mean	16.127143
Std Dev	0.4000955
Std Err Mean	0.087308
upper 95% Mean	16.309264
lower 95% Mean	15.945022
N	21

Distributions Standard=Oxalate, Standard Value (ppm)=16
Mean(Measurement)



Quantiles

100.0%	maximum	16.790
99.5%		16.790
97.5%		16.790
90.0%		16.528
75.0%	quartile	16.353
50.0%	median	16.080
25.0%	quartile	15.843
10.0%		15.655
2.5%		15.570
0.5%		15.570
0.0%	minimum	15.570

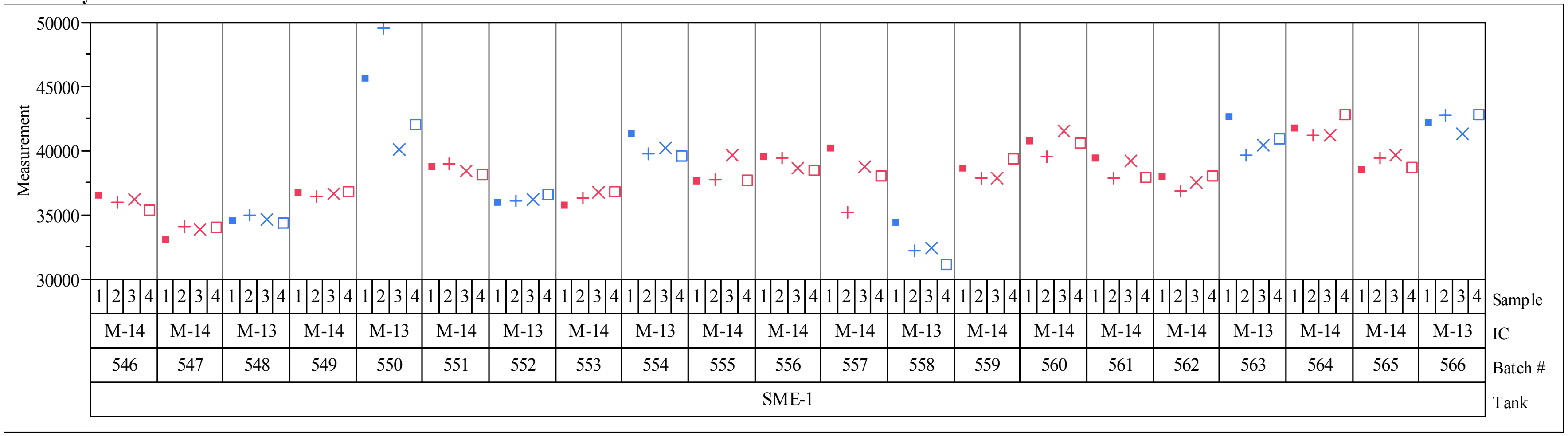
Moments

Mean	16.113095
Std Dev	0.3286315
Std Err Mean	0.0717133
upper 95% Mean	16.262687
lower 95% Mean	15.963504
N	21

Exhibit A5. Anion Measurements by SME Batch

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Analyte=Formate (mg/kg slurry)
Variability Chart for Measurement



Analyte=Formate (ppm/diluted sample)
Variability Chart for Measurement

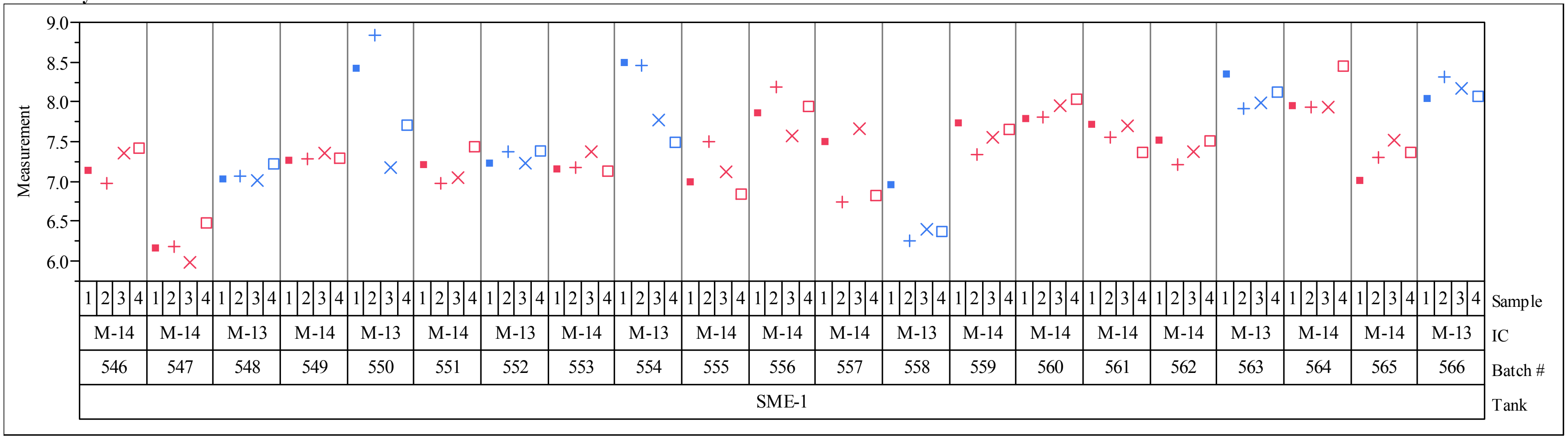
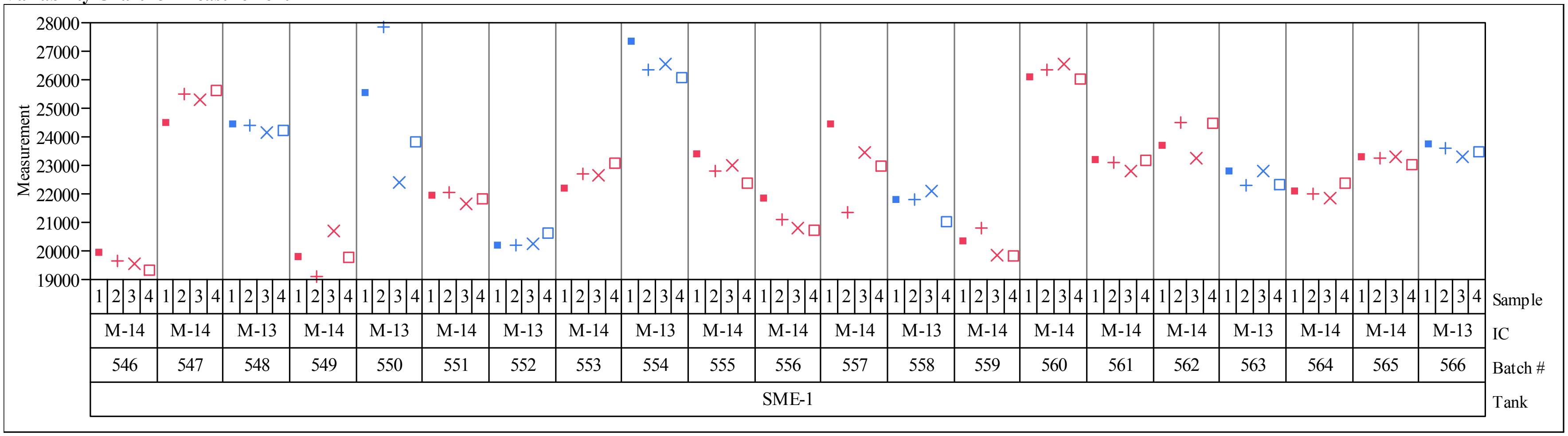


Exhibit A5. Anion Measurements by SME Batch

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Analyte=Nitrate (mg/kg slurry)
Variability Chart for Measurement



Analyte=Nitrate (ppm/diluted sample)
Variability Chart for Measurement

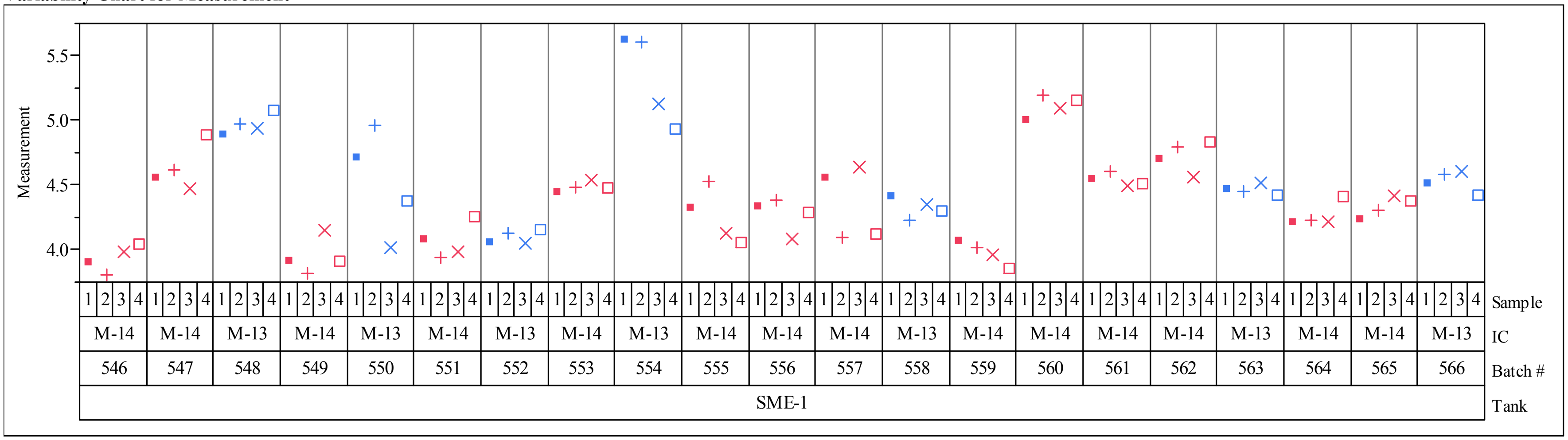


Exhibit A5. Anion Measurements by SME Batch
(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Analyte=Oxalate (ppm/diluted sample)
Variability Chart for Measurement

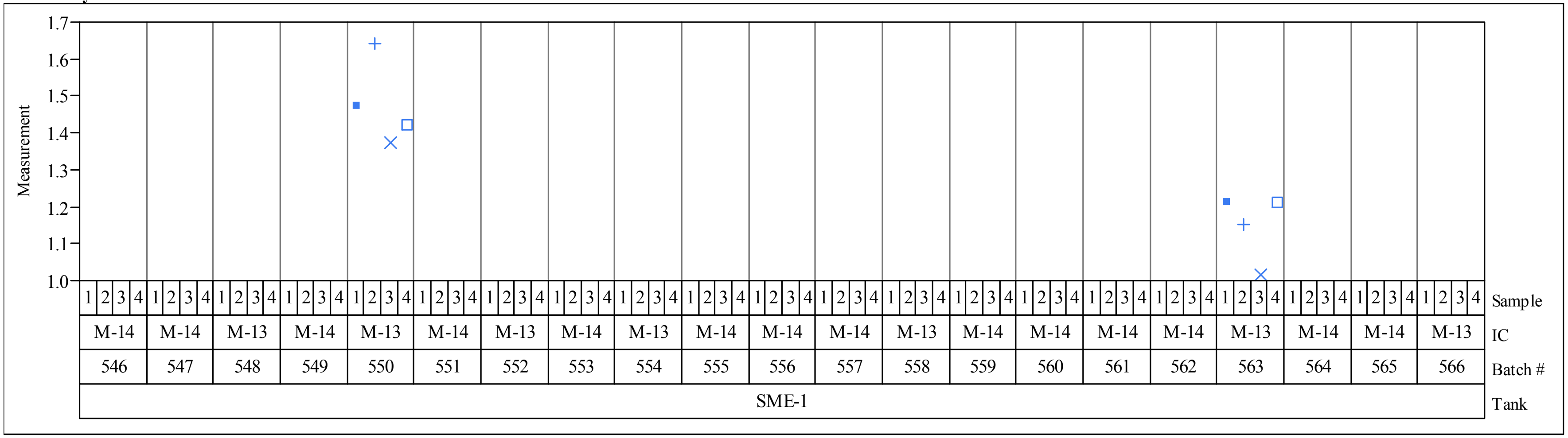
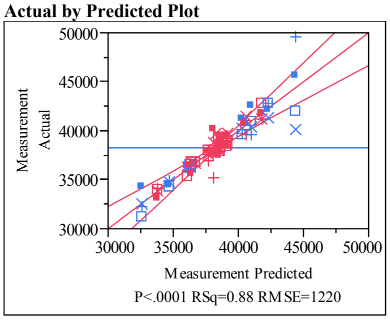


Exhibit A6. Components of Variation for Anion Measurements of the SME Samples

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Response Measurement analyte=Formate (mg/kg slurry)
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.875197
RSquare Adj	0.835577
Root Mean Square Error	1220.005
Mean of Response	38233.42
Observations (or Sum Wgts)	84

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	657571962	32878598	22.0897
Error	63	93769985	1488412.5	**Prob > F**
C. Total	83	751341946		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	7847546	84.057
Residual	1488412	15.943
Total	9335959	100.000

These estimates based on equating Mean Squares to Expected Value.

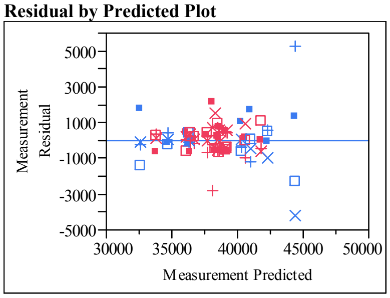
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	1488412	63	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	6.58e+8	3.29e+7	20	22.0897	<.0001

Residual by Predicted Plot

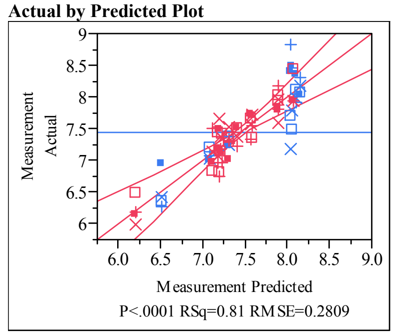


Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
657571962	22.0897	20	<.0001

Denominator MS Synthesis:
Residual

Response Measurement analyte=Formate (ppm/diluted sample)
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.813934
RSquare Adj	0.754865
Root Mean Square Error	0.280944
Mean of Response	7.43369
Observations (or Sum Wgts)	84

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	21.752181	1.08761	13.7795
Error	63	4.972575	0.07893	**Prob > F**
C. Total	83	26.724756		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.25217	76.161
Residual	0.07893	23.839
Total	0.3311	100.000

These estimates based on equating Mean Squares to Expected Value.

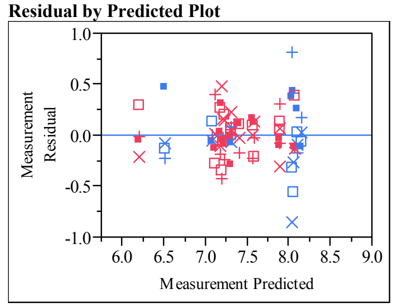
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.07893	63	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	21.7522	1.08761	20	13.7795	<.0001

Residual by Predicted Plot



Batch #&Random
Effect Test

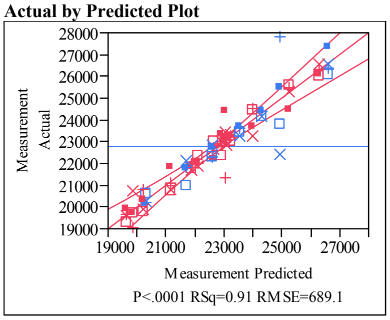
Sum of Squares	F Ratio	DF	Prob > F
21.752181	13.7795	20	<.0001

Denominator MS Synthesis:
Residual

Exhibit A6. Components of Variation for Anion Measurements of the SME Samples

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Response Measurement analyte=Nitrate (mg/kg slurry)
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.913037
RSquare Adj	0.885429
Root Mean Square Error	689.0958
Mean of Response	22777.24
Observations (or Sum Wgts)	84

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	314088986	15704449	33.0722
Error	63	29915738	474852.98	**Prob > F**
C. Total	83	344004723		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	**Intercept**	**Batch #&Random**
Intercept	0	0
Batch #&Random	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	3807399	88.911
Residual	474853	11.089
Total	4282252	100.000

These estimates based on equating Mean Squares to Expected Value.

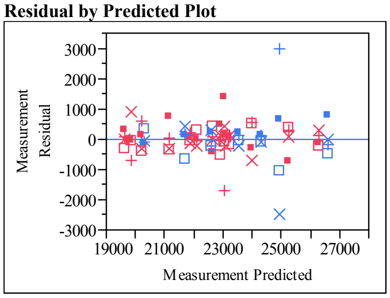
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	474853	63	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	3.14e+8	1.57e+7	20	33.0722	<.0001

Residual by Predicted Plot

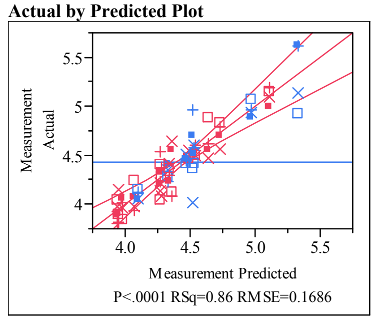


Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
314088986	33.0722	20	<.0001

Denominator MS Synthesis:
Residual

Response Measurement analyte=Nitrate (ppm/diluted sample)
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.86011
RSquare Adj	0.8157
Root Mean Square Error	0.168591
Mean of Response	4.427857
Observations (or Sum Wgts)	84

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	20	11.009764	0.550488	19.3677
Error	63	1.790650	0.028423	**Prob > F**
C. Total	83	12.800414		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	**Intercept**	**Batch #&Random**
Intercept	0	0
Batch #&Random	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.130516	82.117
Residual	0.028423	17.883
Total	0.158939	100.000

These estimates based on equating Mean Squares to Expected Value.

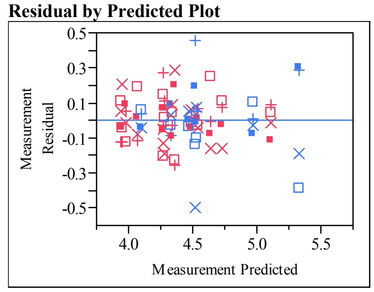
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.02842	63	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	11.0098	0.55049	20	19.3677	<.0001

Residual by Predicted Plot



Batch #&Random
Effect Test

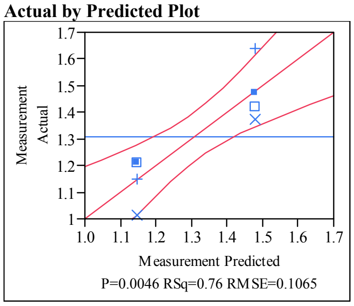
Sum of Squares	F Ratio	DF	Prob > F
11.009764	19.3677	20	<.0001

Denominator MS Synthesis:
Residual

Exhibit A6. Components of Variation for Anion Measurements of the SME Samples

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Response Measurement analyte=Oxalate (ppm/diluted sample)
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.762071
RSquare Adj	0.722417
Root Mean Square Error	0.106458
Mean of Response	1.31
Observations (or Sum Wgts)	8

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	1	0.21780000	0.217800	19.2176
Error	6	0.06800000	0.011333	**Prob > F**
C. Total	7	0.28580000		0.0046

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	1.31	0.037639	34.80	<.0001
Batch #[550]	0.165	0.037639	4.38	0.0046

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.051617	81.996
Residual	0.011333	18.004
Total	0.06295	100.000

These estimates based on equating Mean Squares to Expected Value.

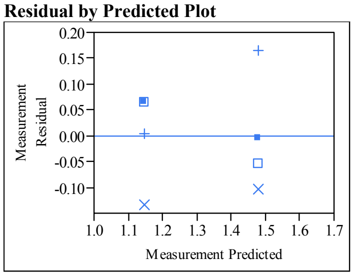
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.01133	6	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	0.2178	0.2178	1	19.2176	0.0046

Residual by Predicted Plot



Batch #&Random
Effect Test

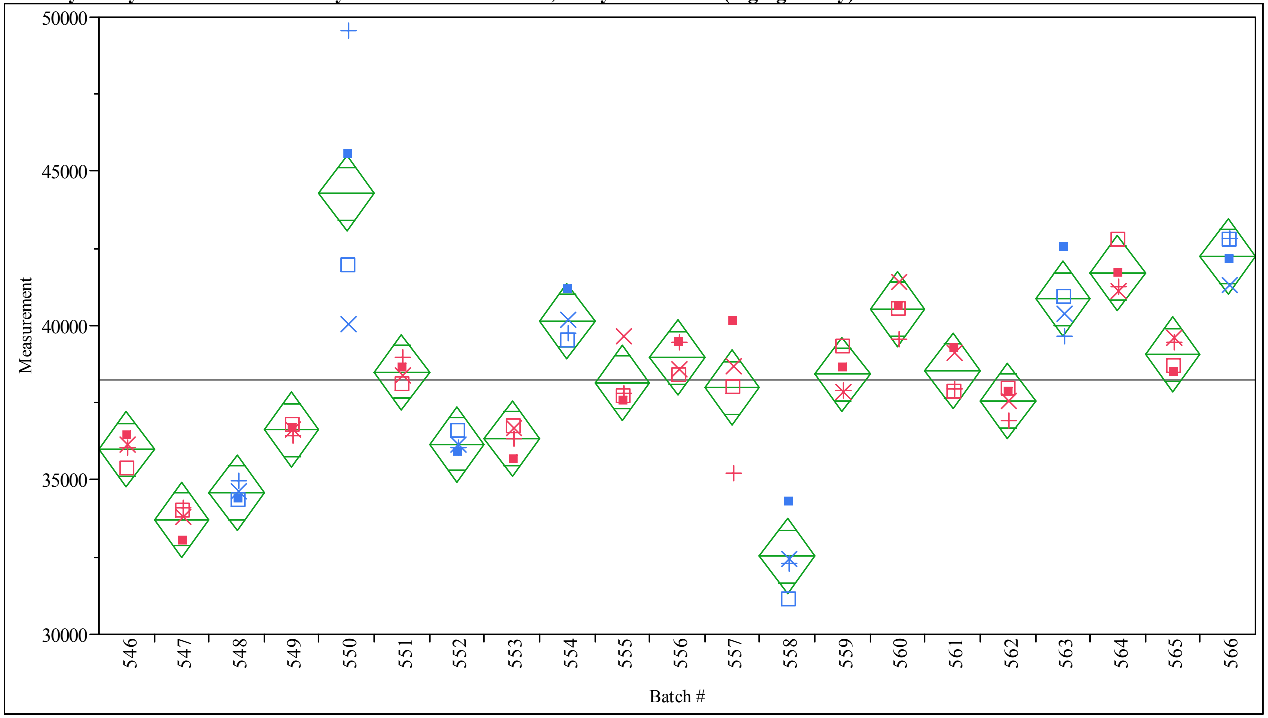
Sum of Squares	F Ratio	DF	Prob > F
0.21780000	19.2176	1	0.0046

Denominator MS Synthesis: Residual

Exhibit A7. Simple Analysis of Variance of Anion Measurements by SME Batch

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Oneway Analysis of Measurement By Batch # Tank=SME-1, analyte=Formate (mg/kg slurry)



Oneway Anova
Summary of Fit

Rsquare	0.875197
Adj Rsquare	0.835577
Root Mean Square Error	1220.005
Mean of Response	38233.42
Observations (or Sum Wgts)	84

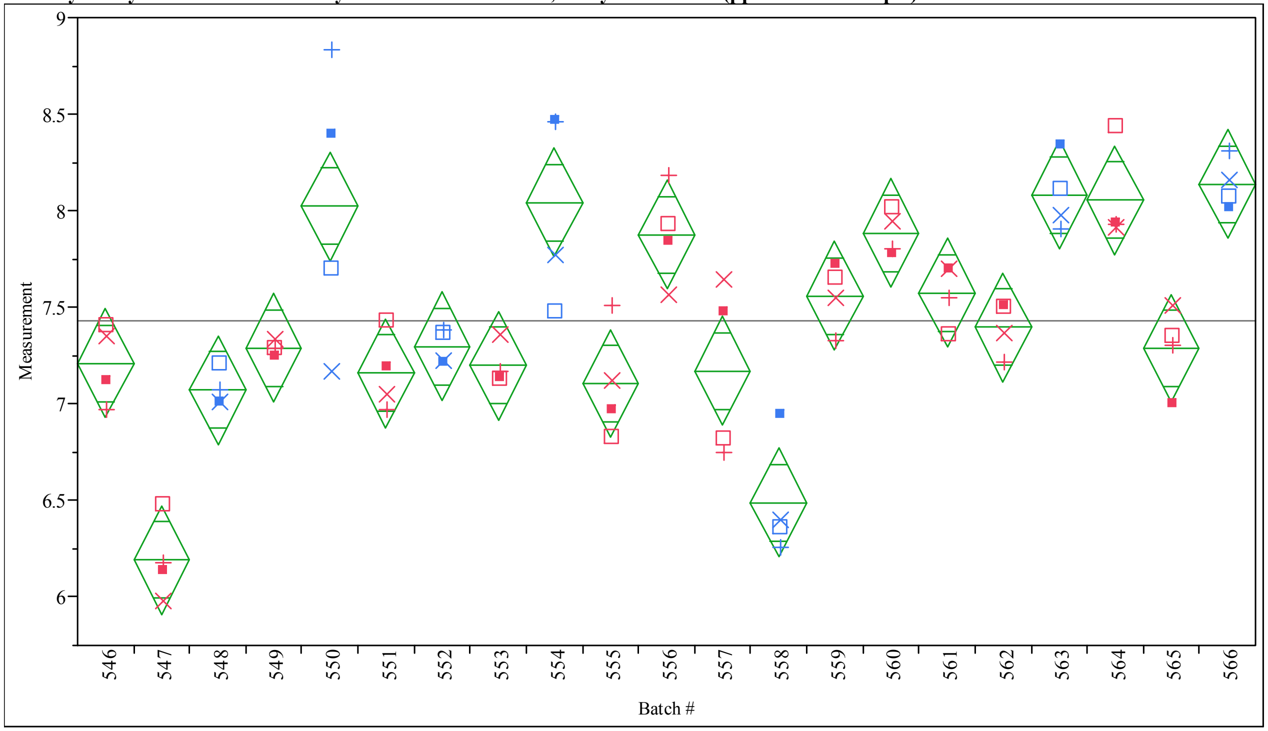
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Batch #	20	657571962	32878598	22.0897	<.0001
Error	63	93769985	1488412.5		
C. Total	83	751341946			

Exhibit A7. Simple Analysis of Variance of Anion Measurements by SME Batch

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Oneway Analysis of Measurement By Batch # Tank=SME-1, analyte=Formate (ppm/diluted sample)



Oneway Anova
Summary of Fit

Rsquare	0.813934
Adj Rsquare	0.754865
Root Mean Square Error	0.280944
Mean of Response	7.43369
Observations (or Sum Wgts)	84

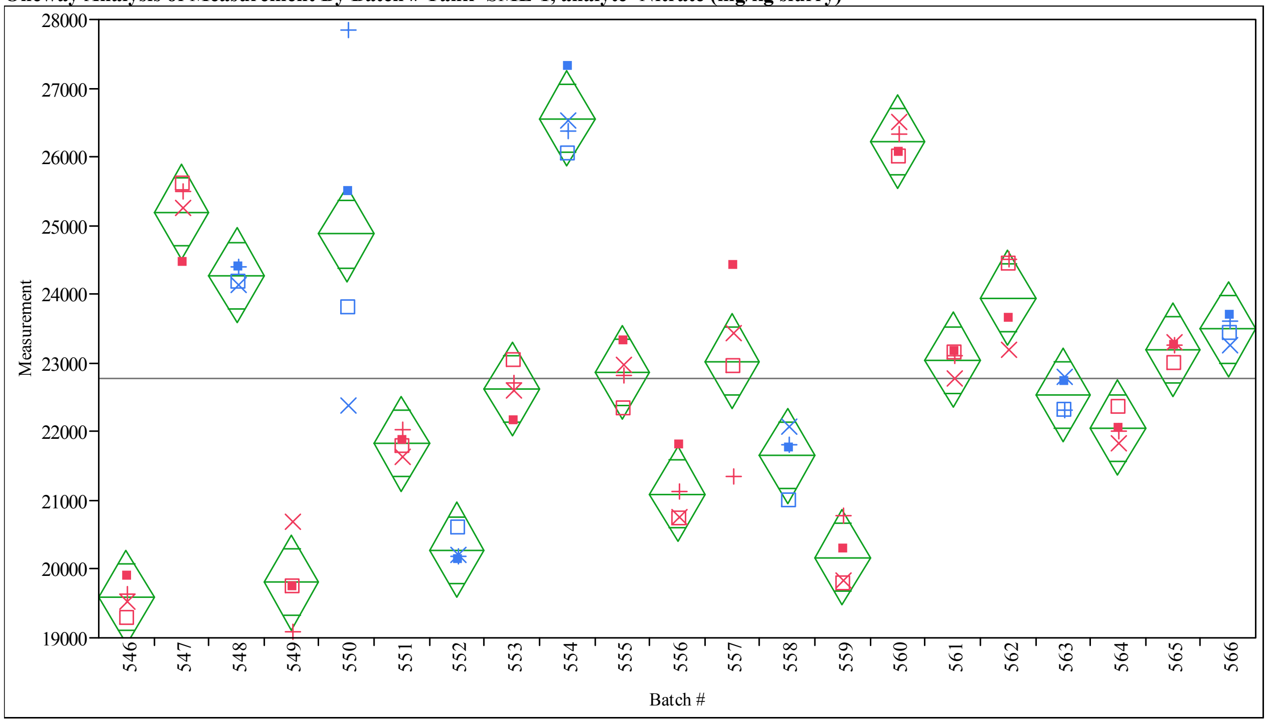
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Batch #	20	21.752181	1.08761	13.7795	<.0001
Error	63	4.972575	0.07893		
C. Total	83	26.724756			

Exhibit A7. Simple Analysis of Variance of Anion Measurements by SME Batch

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Oneway Analysis of Measurement By Batch # Tank=SME-1, analyte=Nitrate (mg/kg slurry)



Oneway Anova
Summary of Fit

Rsquare	0.913037
Adj Rsquare	0.885429
Root Mean Square Error	689.0958
Mean of Response	22777.24
Observations (or Sum Wgts)	84

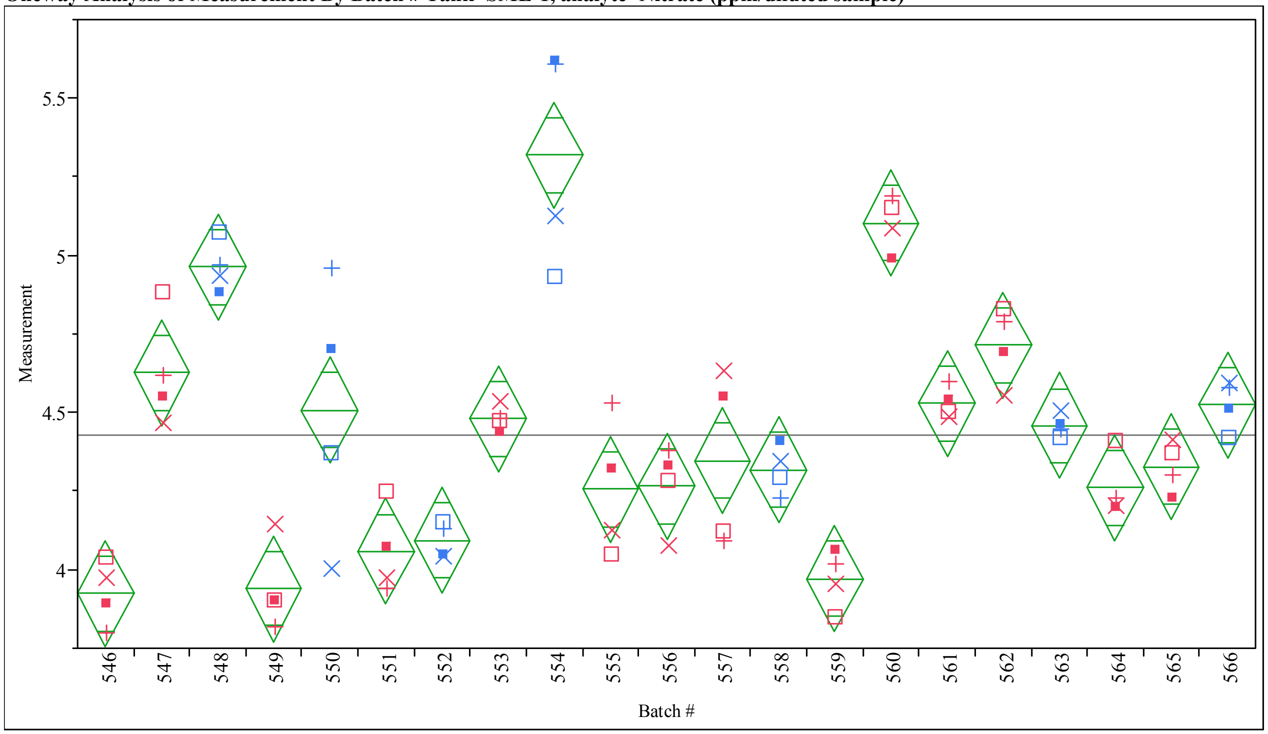
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Batch #	20	314088986	15704449	33.0722	<.0001
Error	63	29915737	474852.98		
C. Total	83	344004723			

Exhibit A7. Simple Analysis of Variance of Anion Measurements by SME Batch

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Oneway Analysis of Measurement By Batch # Tank=SME-1, analyte=Nitrate (ppm/diluted sample)



Oneway Anova
Summary of Fit

Rsquare	0.86011
Adj Rsquare	0.8157
Root Mean Square Error	0.168591
Mean of Response	4.427857
Observations (or Sum Wgts)	84

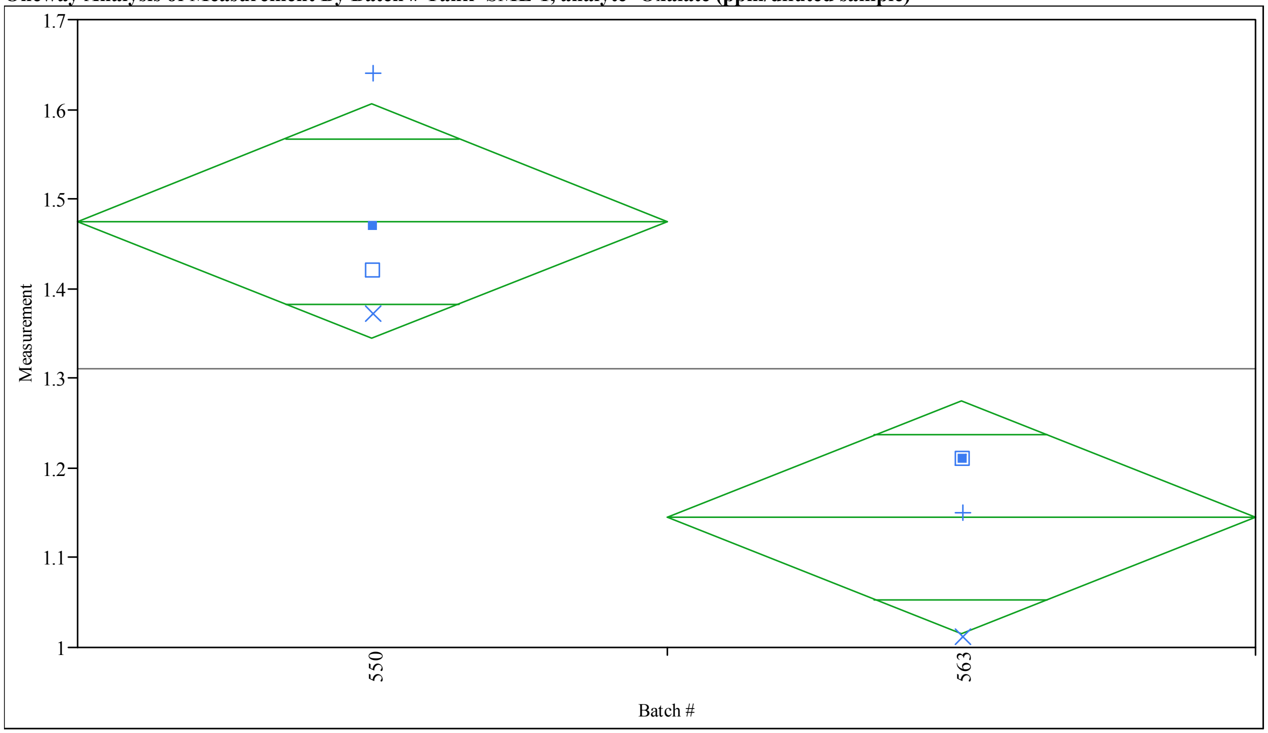
Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Batch #	20	11.009764	0.550488	19.3677	<.0001
Error	63	1.790650	0.028423		
C. Total	83	12.800414			

Exhibit A7. Simple Analysis of Variance of Anion Measurements by SME Batch

(as reported for the SME sample in mg/kg of slurry and as indicated by the IC instrument in ppm for the diluted sample)

Oneway Analysis of Measurement By Batch # Tank=SME-1, analyte=Oxalate (ppm/diluted sample)



Oneway Anova
Summary of Fit

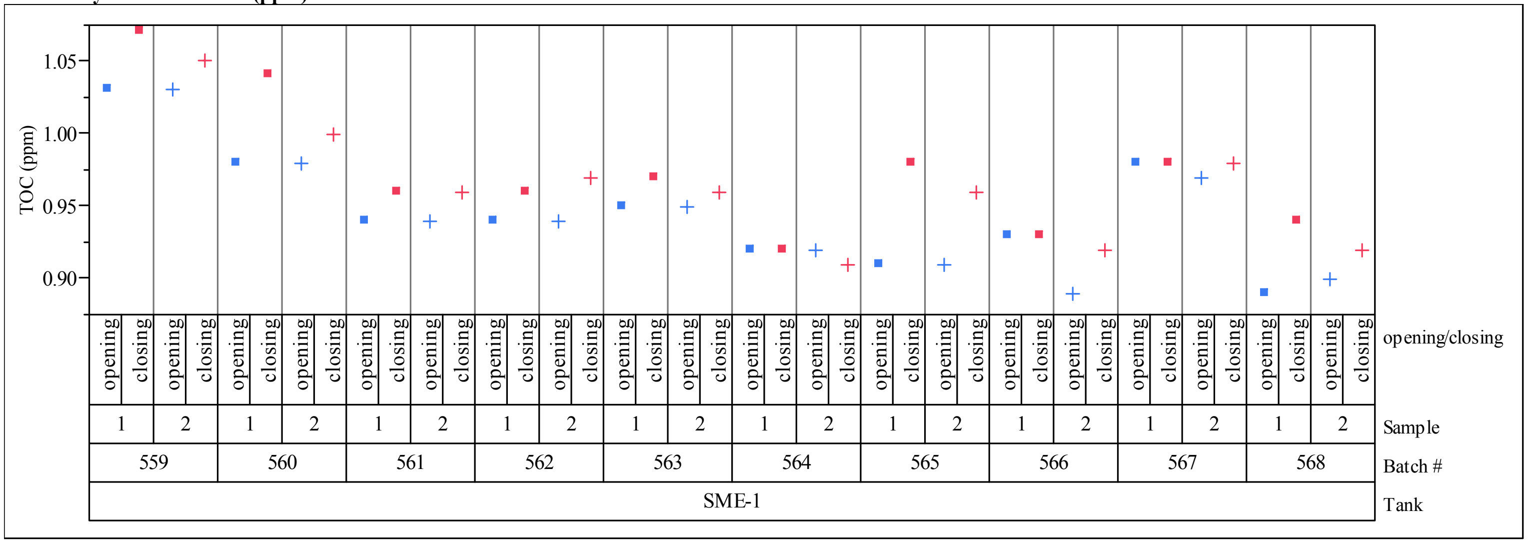
Rsquare	0.762071
Adj Rsquare	0.722417
Root Mean Square Error	0.106458
Mean of Response	1.31
Observations (or Sum Wgts)	8

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Batch #	1	0.21780000	0.217800	19.2176	0.0046
Error	6	0.06800000	0.011333		
C. Total	7	0.28580000			

Exhibit A8. Plots of the DWPF Laboratory Measurements of the TOC Standards

Type of Sample=std, ref ppm=1
Variability Chart for TOC (ppm)



Type of Sample=std, ref ppm=20
Variability Chart for TOC (ppm)

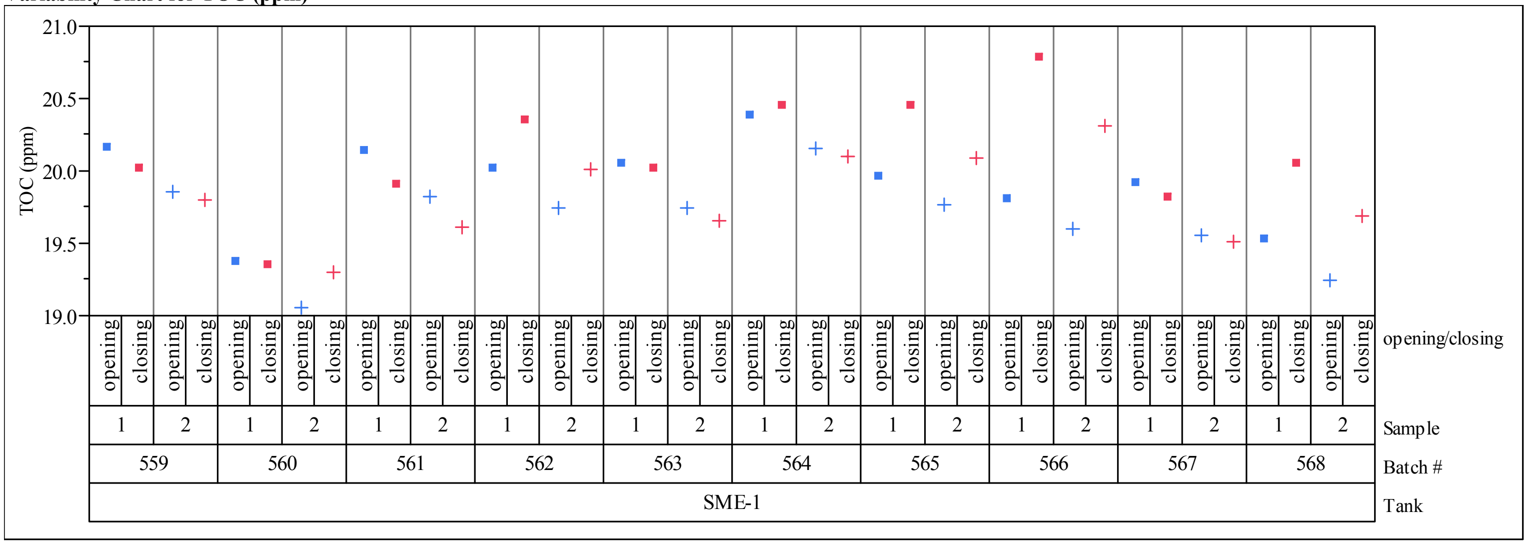
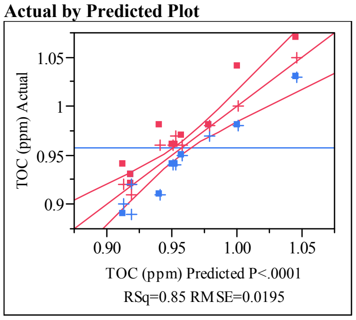


Exhibit A9. Analysis of Variance for Batch to Batch Random Effects for Each TOC Standard

Response TOC (ppm) Tank=SME-1, Type of Sample=std, ref ppm=1
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.84503
RSquare Adj	0.798539
Root Mean Square Error	0.019451
Mean of Response	0.957
Observations (or Sum Wgts)	40

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	0.06189000	0.006877	18.1762
Error	30	0.01135000	0.000378	**Prob > F**
C. Total	39	0.07324000		<.0001

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.001625	81.111
Residual	0.000378	18.889
Total	0.002003	100.000

These estimates based on equating Mean Squares to Expected Value.

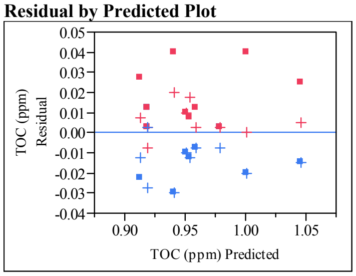
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.00038	30	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	0.06189	0.00688	9	18.1762	<.0001

Residual by Predicted Plot

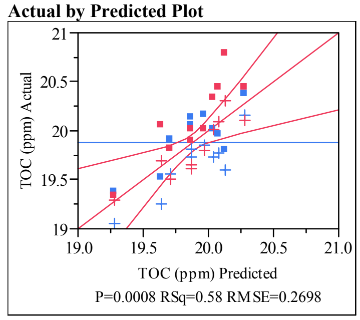


Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
0.06189000	18.1762	9	<.0001

Denominator MS Synthesis:
Residual

Response TOC (ppm) Tank=SME-1, Type of Sample=std, ref ppm=20
Whole Model
Actual by Predicted Plot



Summary of Fit

RSquare	0.576929
RSquare Adj	0.450007
Root Mean Square Error	0.269838
Mean of Response	19.87625
Observations (or Sum Wgts)	40

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	9	2.9787625	0.330974	4.5456
Error	30	2.1843750	0.072813	**Prob > F**
C. Total	39	5.1631375		0.0008

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	Intercept	Batch #&Random
Intercept	0	0
Batch #&Random	0	4

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.06454	46.989
Residual	0.072813	53.011
Total	0.137353	100.000

These estimates based on equating Mean Squares to Expected Value.

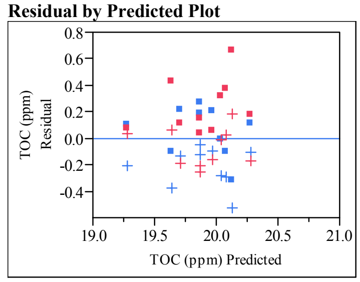
Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.07281	30	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	2.97876	0.33097	9	4.5456	0.0008

Residual by Predicted Plot



Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
2.9787625	4.5456	9	0.0008

Denominator MS Synthesis:
Residual

Exhibit A10. Analysis of Variance for Batch to Batch Random Effects Over Both TOC Standards

Response TOC (ppm)
Whole Model
Summary of Fit

RSquare	0.999459
RSquare Adj	0.99938
Root Mean Square Error	0.237098
Mean of Response	10.41663
Observations (or Sum Wgts)	80

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	10	7160.1179	716.012	12736.89
Error	69	3.8789	0.056	**Prob > F**
C. Total	79	7163.9968		<.0001

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	9	1.6831513	0.187017	5.1104
Pure Error	60	2.1957250	0.036595	**Prob > F**
Total Error	69	3.8788762		<.0001
				Max RSq
				0.9997

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	10.416625	0.026508	392.96	<.0001
ref ppm[1]	-9.459625	0.026508	-356.9	<.0001
Batch #[559]	0.084625	0.079525	1.06	0.2910
Batch #[560]	-0.282875	0.079525	-3.56	0.0007
Batch #[561]	-0.009125	0.079525	-0.11	0.9090
Batch #[562]	0.072125	0.079525	0.91	0.3676
Batch #[563]	-0.005375	0.079525	-0.07	0.9463
Batch #[564]	0.177125	0.079525	2.23	0.0292
Batch #[565]	0.085875	0.079525	1.08	0.2840
Batch #[566]	0.103375	0.079525	1.30	0.1980
Batch #[567]	-0.079125	0.079525	-0.99	0.3232

Expected Mean Squares
The Mean Square per row by the Variance Component per column

EMS	**Intercept**	**Batch #&Random**	**ref ppm**
Intercept	0	0	0
Batch #&Random	0	8	0
ref ppm	0	0	40

plus 1.0 times Residual Error Variance

Variance Component Estimates

Component	Var Comp Est	Percent of Total
Batch #&Random	0.011827	17.382
Residual	0.056216	82.618
Total	0.068043	100.000

These estimates based on equating Mean Squares to Expected Value.

Test Denominator Synthesis

Source	MS Den	DF Den	Denom MS Synthesis
Batch #&Random	0.05622	69	Residual
ref ppm	0.05622	69	Residual

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob > F
Batch #&Random	1.3575	0.15083	9	2.6831	0.0098
ref ppm	7158.76	7158.76	1	127344.7	<.0001

Batch #&Random
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
1.3575012	2.6831	9	0.0098

Denominator MS Synthesis:
Residual

Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
559	10.501250	0.08382690	10.5013
560	10.133750	0.08382690	10.1338
561	10.407500	0.08382690	10.4075
562	10.488750	0.08382690	10.4888
563	10.411250	0.08382690	10.4113
564	10.593750	0.08382690	10.5938
565	10.502500	0.08382690	10.5025
566	10.520000	0.08382690	10.5200
567	10.337500	0.08382690	10.3375
568	10.270000	0.08382690	10.2700

ref ppm
Effect Test

Sum of Squares	F Ratio	DF	Prob > F
7158.7604	127344.7	1	<.0001

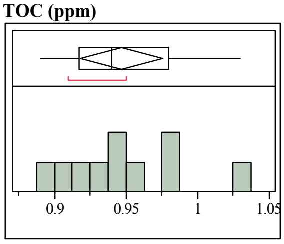
Denominator MS Synthesis:
Residual

Least Squares Means Table

Level	Least Sq Mean	Std Error	Mean
1	0.957000	0.03748853	0.9570
20	19.876250	0.03748853	19.8763

Exhibit A11. Histograms and Summary Statistics for the Measurements of the TOC Standards

Distributions Tank=SME-1, Type of Sample=std, ref ppm=1, Sample=1, opening/closing=opening
TOC (ppm)



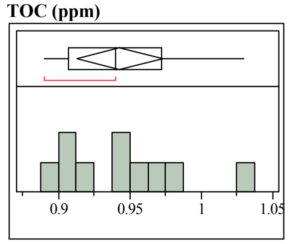
Quantiles

100.0%	maximum	1.0300
99.5%		1.0300
97.5%		1.0300
90.0%		1.0250
75.0%	quartile	0.9800
50.0%	median	0.9400
25.0%	quartile	0.9175
10.0%		0.8920
2.5%		0.8900
0.5%		0.8900
0.0%	minimum	0.8900

Moments

Mean	0.947
Std Dev	0.0405654
Std Err Mean	0.0128279
upper 95% Mean	0.9760188
lower 95% Mean	0.9179812
N	10

Distributions Tank=SME-1, Type of Sample=std, ref ppm=1, Sample=2, opening/closing=opening
TOC (ppm)



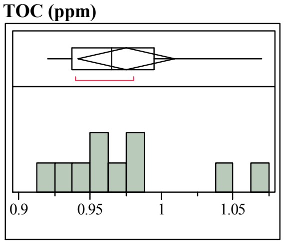
Quantiles

100.0%	maximum	1.0300
99.5%		1.0300
97.5%		1.0300
90.0%		1.0250
75.0%	quartile	0.9725
50.0%	median	0.9400
25.0%	quartile	0.9075
10.0%		0.8910
2.5%		0.8900
0.5%		0.8900
0.0%	minimum	0.8900

Moments

Mean	0.943
Std Dev	0.0421769
Std Err Mean	0.0133375
upper 95% Mean	0.9731715
lower 95% Mean	0.9128285
N	10

Distributions Tank=SME-1, Type of Sample=std, ref ppm=1, Sample=1, opening/closing=closing
TOC (ppm)



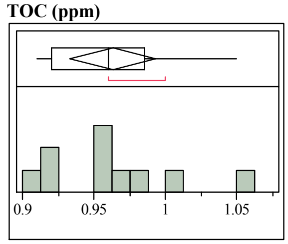
Quantiles

100.0%	maximum	1.0700
99.5%		1.0700
97.5%		1.0700
90.0%		1.0670
75.0%	quartile	0.9950
50.0%	median	0.9650
25.0%	quartile	0.9375
10.0%		0.9210
2.5%		0.9200
0.5%		0.9200
0.0%	minimum	0.9200

Moments

Mean	0.975
Std Dev	0.0471993
Std Err Mean	0.0149257
upper 95% Mean	1.0087644
lower 95% Mean	0.9412356
N	10

Distributions Tank=SME-1, Type of Sample=std, ref ppm=1, Sample=2, opening/closing=closing
TOC (ppm)



Quantiles

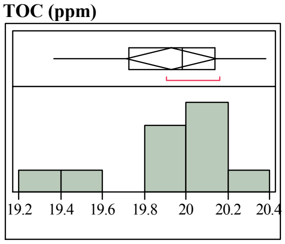
100.0%	maximum	1.0500
99.5%		1.0500
97.5%		1.0500
90.0%		1.0450
75.0%	quartile	0.9850
50.0%	median	0.9600
25.0%	quartile	0.9200
10.0%		0.9110
2.5%		0.9100
0.5%		0.9100
0.0%	minimum	0.9100

Moments

Mean	0.963
Std Dev	0.0419126
Std Err Mean	0.0132539
upper 95% Mean	0.9929825
lower 95% Mean	0.9330175
N	10

Exhibit A11. Histograms and Summary Statistics for the Measurements of the TOC Standards

Distributions Tank=SME-1, Type of Sample=std, ref ppm=20, Sample=1, opening/closing=opening
TOC (ppm)



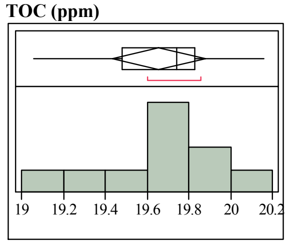
Quantiles

100.0%	maximum	20.380
99.5%		20.380
97.5%		20.380
90.0%		20.358
75.0%	quartile	20.138
50.0%	median	19.985
25.0%	quartile	19.730
10.0%		19.385
2.5%		19.370
0.5%		19.370
0.0%	minimum	19.370

Moments

Mean	19.929
Std Dev	0.3011257
Std Err Mean	0.0952243
upper 95% Mean	20.144412
lower 95% Mean	19.713588
N	10

Distributions Tank=SME-1, Type of Sample=std, ref ppm=20, Sample=2, opening/closing=opening
TOC (ppm)



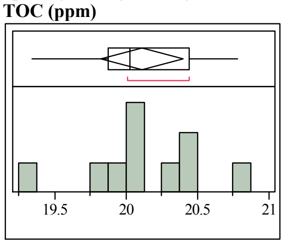
Quantiles

100.0%	maximum	20.160
99.5%		20.160
97.5%		20.160
90.0%		20.130
75.0%	quartile	19.830
50.0%	median	19.740
25.0%	quartile	19.483
10.0%		19.079
2.5%		19.060
0.5%		19.060
0.0%	minimum	19.060

Moments

Mean	19.656
Std Dev	0.3130566
Std Err Mean	0.0989972
upper 95% Mean	19.879947
lower 95% Mean	19.432053
N	10

Distributions Tank=SME-1, Type of Sample=std, ref ppm=20, Sample=1, opening/closing=closing
TOC (ppm)



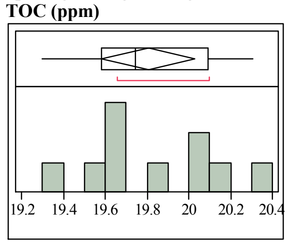
Quantiles

100.0%	maximum	20.780
99.5%		20.780
97.5%		20.780
90.0%		20.746
75.0%	quartile	20.440
50.0%	median	20.030
25.0%	quartile	19.878
10.0%		19.387
2.5%		19.340
0.5%		19.340
0.0%	minimum	19.340

Moments

Mean	20.112
Std Dev	0.4041672
Std Err Mean	0.1278089
upper 95% Mean	20.401124
lower 95% Mean	19.822876
N	10

Distributions Tank=SME-1, Type of Sample=std, ref ppm=20, Sample=2, opening/closing=closing
TOC (ppm)



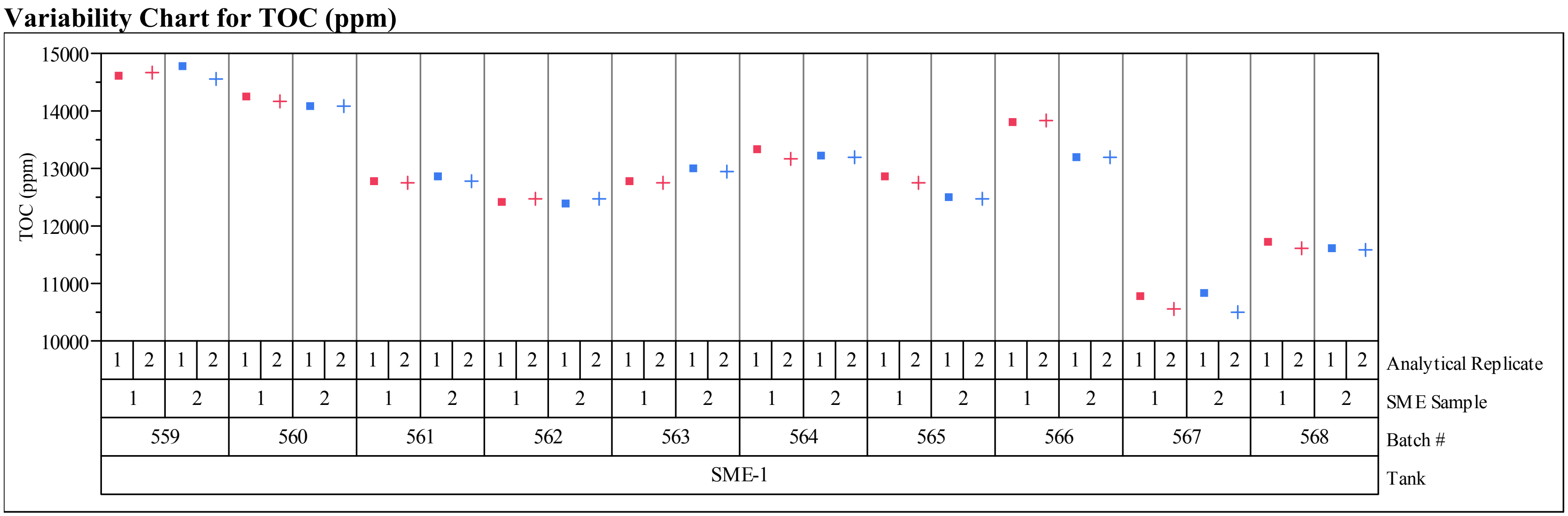
Quantiles

100.0%	maximum	20.310
99.5%		20.310
97.5%		20.310
90.0%		20.289
75.0%	quartile	20.093
50.0%	median	19.745
25.0%	quartile	19.585
10.0%		19.321
2.5%		19.300
0.5%		19.300
0.0%	minimum	19.300

Moments

Mean	19.808
Std Dev	0.3126162
Std Err Mean	0.0988579
upper 95% Mean	20.031632
lower 95% Mean	19.584368
N	10

Exhibit A12. DWPF Laboratory's TOC Measurements for the SME Samples



Distribution:

Name:	Location:
Sharon Marra	773-A
Connie Herman	999-W
Charles J. Coleman	773-A
Clint Gregory	773-A
Mark Barnes	773-A
Patricia Lee	703-41A
Gene Shine	703-41A
Damon R. Click	773-A
L. Curtis Johnson	773-A
Michael Stone	999-W
Alex Choi	773-42A
John Pareizs	773-A
David Peeler	999-W
Tommy Edwards	999-W
Kevin Fox	999-W
Fabienne Johnson	999-W
Charles Crawford	773-42A
David Best	999-W
John Occhipinti	704-S
Jonathan Bricker	704-27S
John Iaukea	704-30S
Aaron Staub	704-27S
Jeff Ray	704-S
Robert Hinds	704-S
Terri Fellinger	704-26S
Ryan McNew	704-S
Michael T. Hart	210-S
Roger N. Mahannah	704-28S
Michael T. Feller	704-28S
Omar Cardona-Quiles	704-24S
Amanda Shafer	704-27S
Mason Clark	704-27S
Helen Pittman	704-27S
Hank Elder	704-24S
Bill Holtzscheiter	704-15S
Pat Vaughan	773-41A