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QUALIFICATION OF A CARBON ANALYZER TO SUPPORT THE DEFENSE WASTE PROCESSING FACILITY

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EXECUTIVE SUMMARY

The I-O Model 1030 carbon analyzer has been qualified for use at the Defense Waste Processing Facility (DWPF). The qualification was a side-by-side comparison of the Model 1030 system with the currently used Model 1010 Analyzer. This recommendation is based on side-by-side comparisons of the new unit to the currently used Model 1010 analyzer that are presented in this report. The side-by-side testing included standards and process samples. The standards, which were used for instrument calibration verifications in the measurement of total inorganic carbon (TIC) and of total organic carbon (TOC), were traceable back to the National Institute of Standards and Technology. The process samples included TIC analyses of Sludge Receipt and Adjustment Tank samples and TOC analyses for Slurry Mix Evaporator (SME) samples.

After the Model 1030 has been used for production reporting, DWPF should consider an investigation into the uncertainties associated with the TOC measurements to determine how far below the 18,916 ppm limit DWPF must control the average of the measurements for a set of SME samples to account for the uncertainties of the measurements from this new analyzer.

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LIST OF ABBREVIATIONS

DWPF	Defense Waste Processing Facility
HLW	High Level Waste
JMP	Statistical software package from SAS Institute, Inc. [3]
LIMS	Laboratory Information Management System
NIST	National Institute of Standards and Technology
ppm	Parts per million
SME	Slurry Mix Evaporator
SRAT	Slurry Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
TTR	Technical Task Request
TT&QA	Task Technical and Quality Assurance

1.0 INTRODUCTION

The Savannah River Remediation (SRR) Defense Waste Processing Facility (DWPF) Laboratory currently utilizes a carbon analyzer, Model 1010, manufactured by O-I Analytical to perform total inorganic carbon (TIC) and total organic carbon (TOC) measurements on process samples. The results from these analyses are used by Waste Solidification Engineering (WSE) primarily as inputs to the DWPF acid equation and to ensure that melter flammability limits are not exceeded. The current analyzer, which has been in service for more than six years, needs to be replaced. A replacement unit (Model 1030 manufactured by O-I Analytical) has been purchased and installed at the DWPF Laboratory by Waste Laboratory Services (WLS). Before the new instrument is to be utilized for production reporting, its performance is to be evaluated and qualified relative to the performance of the current production unit. The WLS ran side-by-side comparisons of the old and new analyzers using standards and process samples at the DWPF Laboratory to generate the data for this evaluation.

DWPF issued a Task Technical Request [1] for SRNL to conduct a statistical evaluation of the side-by-side data to facilitate the qualification of the new carbon analyzer. Based upon the scope of this request, SRNL was to

1. perform a statistical review of the data to assess the performance of the new carbon analyzer.
2. review these results with WSE and WSL personnel,
3. participate in the decision to qualify the new instrument, and
4. document the results from this qualification effort in a technical report that describes the results and the conclusions from this study.

This report provides the data generated by WLS and the subsequent analyses conducted by SRNL and reviewed with WSE and WSL that led to the recommendation for the qualification of the new O-I Model 1030.

2.0 EXPERIMENTAL PROCEDURE

Process samples from the Slurry Receipt and Adjustment Tank (SRAT) and the Slurry Mix Evaporator (SME) for several batches were analyzed by both the current and new instruments. The SRAT Receipt samples were analyzed for TIC and the SME samples for TOC. In addition to process samples, TIC standards at carbon concentrations of 1 and 20 ppm and TOC standards at carbon concentrations of 1 and 20 ppm were also prepared and analyzed for each of the two instruments. The standards are traceable back to the National Institute of Standards and Technology (NIST). The measurement data are provided in Table A1 of the Appendix, and they served as the basis for the comparisons between the two instruments that were conducted as part of this study. Exhibit A1 in the Appendix provides a plot of these measurements grouped by category (either check standard or process sample), type (for the check standards either 1 ppm or 20 ppm standards and for the process samples either SME or SRAT samples), measurement mode (either TIC or TOC), batch number, and Laboratory Information Management System (LIMS) number.

3.0 STATISTICAL ANALYSIS

In this section, the statistical comparisons of the measurements generated by the two carbon instruments are presented. JMP Version 7.0.2 [4] was used to perform these analyses. Of primary interest are investigations into any relative bias between the two measurement systems and into a comparison of their precisions. In addition, the measurements of the check standards from each instrument are investigated for a bias in their results.

3.1 Initial Evaluations of Relative Bias between the Two Instruments

Exhibit A2 in the Appendix provides an investigation into the relative bias between the two instruments using a paired-sample approach for the data of Table A1. The TIC and TOC measurements for check standards and process samples are considered in these analyses. None of these paired comparisons indicate a statistically significant bias, at the 5% level, between the two instruments. For the sake of consistency this paired approach was applied to all of the measurements in Table A1, but there is little correlation between the results for the two instruments for the check standards. Additional analyses of the measurements of the check standards are investigated in the discussion that follows.

3.2 Initial Evaluations of the Precision of the Instruments

Exhibit A3 in the Appendix provides an investigation into the precision of the two instruments using the measurement data of Table A1. In addition to a plot of the measurements for each instrument, there is a series of tests for equality of variance for the two sets of measurements. For this analysis, Levene's test will be used to make the comparisons of the precisions. If the "p-Value" for Levene's test comparing the variances of the measurements for the two instruments is less than or equal to 0.05, then the conclusion of the comparison is that there is a statistically significant difference, at the 5% level, in the variances. The conclusions from Exhibit A3 are that:

- For the 1 ppm check standards for TIC, the new model has a statistically significantly smaller measurement variance,
- For the 1 ppm check standards for TOC, the new model has a statistically significantly smaller measurement variance,
- For the 20 ppm check standards for TIC, there is no statistically significant difference between the precisions of the two instruments,
- For the 20 ppm check standards for TOC, there is no statistically significant difference between the precisions of the two instruments,
- For the SME samples for TOC, there is no statistically significant difference between the precisions of the two instruments, and
- For the SRAT samples for TIC, there is no statistically significant difference between the precisions of the two instruments.

Note that while this analysis was applied to all of the measurements from Table A1, the use of the measurements from the process samples was less than ideal since the sample to sample variation appears to be a dominant source of variation in these measurements. However, for the measurements available for this study, the precision of the new instrument, Model 1030, is at least as good as if not better than that of the current instrument, Model 1010. That is, there is no indication of a precision issue for the new instrument relative to the precision of the current instrument.

3.3 Additional Evaluations of Relative Bias between the Two Instruments

Exhibit A4 in the Appendix provides an investigation into the relative bias between the two instruments for the measurement data of Table A1 for the check standards. The TIC and TOC measurements for both the 1 and 20 ppm check standards are considered in these analyses. In this exhibit, the results from Levene's test are repeated, and they are used to indicate which t-test should be used to assess the statistically significance of the bias between the two instruments. The results from two t-tests are included in the exhibit. One t-test is appropriate if the variances of the two sets of measurements are equal and the other t-test is appropriate if the variances are unequal. The conclusions from Exhibit A4 are that:

- ❖ For the 1 ppm check standards for TIC, the t-test for unequal variances is appropriate and from it, there is no indication of a statistically significant bias, at the 5% level, between the two instruments. In addition, the bound at 95% confidence on any potential bias is 0.047 ppm (i.e., 4.7%).
- ❖ For the 1 ppm check standards for TOC, the t-test for unequal variances is appropriate and from it, there is no indication of a statistically significant bias, at the 5% level, between the two instruments. In addition, the bound at 95% confidence on any potential bias is 0.124 ppm (i.e., 12.4%).
- ❖ For the 20 ppm check standards for TIC, the t-test for variances is appropriate and from it, there is no indication of a statistically significant bias, at the 5% level, between the two instruments. In addition, the bound at 95% confidence on any potential bias is 0.605 ppm (i.e., 3.0%),
- ❖ For the 20 ppm check standards for TOC, the t-test for variances is appropriate and from it, there is a statistically significant bias, at the 5% level, between the two instruments. In addition, the bound at 95% confidence on this bias is 0.760 ppm (i.e., 3.8%).

Thus for these comparisons of relative bias between the two instruments, there does not appear to be any issues of practical concern.

3.4 Additional Evaluations of Bias for Each of the Two Instruments

Exhibit A5 in the Appendix provides an investigation into the bias of each of the two instruments using the measurement data of Table A1 for the check standards. The TIC and TOC measurements for both the 1 and 20 ppm check standards are considered in these analyses. In this exhibit, the results from JMP's descriptive statistics platform are provided for each set of data for each instrument. These results include a histogram of the data, quantiles, the mean, and the standard deviation as well as a 95% confidence interval for the mean. In addition, a t-test is provided for each set of measurements for each instrument with the null hypothesis of the mean being the reference value for the standard. The conclusions from Exhibit A4 are that:

- ❖ For the 1 ppm check standards for TIC for Model 1010, the t-test for a mean of 1 ppm is rejected at the 5% significance level and the 95% confidence interval for the mean is given as (1.016, 1.102) ppm.
- ❖ For the 1 ppm check standards for TIC for Model 1030, the t-test for a mean of 1 ppm is rejected at the 5% significance level and the 95% confidence interval for the mean is given as (1.040, 1.074) ppm.
- ❖ For the 20 ppm check standards for TIC for the Model 1010, the t-test for a mean of 20 ppm is rejected at the 5% significance level and the 95% confidence interval for the mean is given as (20.145, 20.764) ppm.
- ❖ For the 20 ppm check standards for TIC for the Model 1030, the t-test for a mean of 20 ppm is not rejected at the 5% significance level and the 95% confidence interval for the mean is given as (19.935, 20.627) ppm.
- ❖ For the 1 ppm check standards for TOC for Model 1010, the t-test for a mean of 1 ppm is not rejected at the 5% significance level and the 95% confidence interval for the mean is given as (0.946, 1.119) ppm.
- ❖ For the 1 ppm check standards for TOC for Model 1030, the t-test for a mean of 1 ppm is not rejected at the 5% significance level and the 95% confidence interval for the mean is given as (0.952, 1.044) ppm.

- For the 20 ppm check standards for TOC for the Model 1010, the t-test for a mean of 20 ppm is not rejected at the 5% significance level and the 95% confidence interval for the mean is given as (19.462, 20.161) ppm.
- For the 20 ppm check standards for TOC for the Model 1030, the t-test for a mean of 20 ppm is rejected at the 5% significance level and the 95% confidence interval for the mean is given as (20.015, 20.388) ppm.

Thus for these comparisons of bias for each of the two instruments, there does not appear to be any issues of practical concern.

3.5 Additional Evaluations of Bias for Each of the Two Instruments

One other conclusion from these comparisons between the two instruments is warranted. In 2003, Edwards [4] used available TOC measurement data, which had been generated by the DWPF Laboratory using the Model 1010 carbon analyzer, to estimate the uncertainties associated with TOC measurements. The purpose of that study was an investigation to determine how far below the 18,916 ppm limit DWPF must control the average of the measurements for a set of SME samples to account for the uncertainties of the measurements. That study concluded that using a control limit set at 5% below the 18,916 ppm value provides a greater margin for error than required for the measurement uncertainties of the Model 1010 analyzer based upon the data and investigations presented in that study [4].

The limited TOC data available for the Model 1030 for this comparative study to Model 1010 precludes a revision of the uncertainty analysis of [4] as part of the effort presented here. However, the TOC results presented in this study indicate that the precision of the Model 1030 is as good as or better than the precision of the Model 1010 (see the results for comparisons of the TOC measurements in Exhibits A3 through A5). In each of these cases, the standard deviation of the Model 1030 TOC measurements is smaller than the standard deviation of the Model 1010 TOC measurements. However, it is recommended that DWPF consider evaluating results from the production use of the Model 1030 at some point in the future to revisit the uncertainty analysis presented in [4].

4.0 CONCLUSIONS AND RECOMMENDATIONS

Based upon the results presented in this report, it is recommended that the Model 1030 carbon analyzer is qualified for use. This recommendation is based on side-by-side comparisons of the new unit to the currently used Model 1010 analyzer that are presented in this report. The side-by-side testing included standards for instrument calibration verifications for TIC and TOC, and process samples. The standards were traceable back to NIST. The process samples included TIC analyses of SRAT Receipt samples and TOC analyses for SME samples.

At some point in the future, after the Model 1030 has been used for production reporting, DWPF should consider an investigation into the uncertainties associated with the TOC measurements to determine how far below the 18,916 ppm limit DWPF must control the average of the measurements for a set of SME samples to account for the uncertainties of the measurements from this new analyzer.

REFERENCES

[1] Bricker, J.M., "Technical Task Request: Analyze Results for DWPF Laboratory Carbon Analyzer Qualification," HLW-DWPF-TTR-2010-00034, August 8, 2010.

[2] Edwards, T.B., "Task Technical & QA Plan: Analyze Results for DWPF Laboratory Carbon Analyzer Qualification," SRNL-RP-2010-01273, Revision 0, August, 2010.

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

[4] Edwards, T.B., "Accounting for Uncertainties in DWPF's Measurement of Total Organic Carbon (U)," WSRC-TR-2003-00310, Revision 0, July 2003.

APPENDIX

Table A1. Carbon Measurements (ppm) by Instrument

Category	TYPE	MODE	BATCH	LIMS ID	Bottle ID	Model 1030 (ppm C)	Model 1010 (ppm C)
sample results	SRAT-1	TIC	531	200000055	9473	2.628	2.519
sample results	SRAT-1	TIC	531	200000055	9474	2.576	2.586
sample results	SRAT-1	TIC	532	200001281	1306	1.898	1.737
sample results	SRAT-1	TIC	532	200001281	1307	2.353	2.244
sample results	SRAT-1	TIC	533	200001503	1116	2.258	2.041
sample results	SRAT-1	TIC	533	200001503	1119	2.244	2.169
sample results	SRAT-1	TIC	536	200002107	3214	2.369	2.266
sample results	SRAT-1	TIC	536	200002107	3217	2.373	2.419
sample results	SRAT-1	TIC	537	200002297	4183	2.274	2.252
sample results	SRAT-1	TIC	537	200002297	4182	2.631	2.724
sample results	SME-1	TOC	530	20074	1177	15.375	14.639
sample results	SME-1	TOC	530	20074	1178	15.537	15.385
sample results	SME-1	TOC	531	200001376	1414	15.337	14.848
sample results	SME-1	TOC	531	200001376	1415	16.447	16.561
sample results	SME-1	TOC	532	200001546	1734	14.932	15.008
sample results	SME-1	TOC	532	200001546	1737	14.175	14.433
sample results	SME-1	TOC	535	200002271	3990	17.587	17.581
sample results	SME-1	TOC	535	200002271	3991	16.371	17.232
check standard	1ppm	TIC	531	0	0	1.055	1.093
check standard	20 ppm	TIC	531	0	0	20.75	19.817
check standard	1ppm	TIC	531	0	0	1.004	1.051
check standard	20 ppm	TIC	531	0	0	20.938	20.33
check standard	1ppm	TIC	532	0	0	1.069	1.119
check standard	20 ppm	TIC	532	0	0	19.904	19.854
check standard	1ppm	TIC	532	0	0	1.088	1.024
check standard	20 ppm	TIC	532	0	0	20.956	20.195
check standard	1ppm	TIC	533	0	0	1.071	0.934
check standard	20 ppm	TIC	533	0	0	20.16	20.92
check standard	1ppm	TIC	533	0	0	1.041	1.01
check standard	20 ppm	TIC	533	0	0	19.953	20.938
check standard	1ppm	TIC	536	0	0	1.083	1.038
check standard	20 ppm	TIC	536	0	0	20.098	20.303
check standard	1ppm	TIC	536	0	0	1.053	1.134
check standard	20 ppm	TIC	536	0	0	20.566	20.594
check standard	1ppm	TIC	537	0	0	1.045	1.089
check standard	20 ppm	TIC	537	0	0	19.6	20.571
check standard	1ppm	TIC	537	0	0	1.063	1.1
check standard	20 ppm	TIC	537	0	0	19.885	21.027
check standard	1ppm	TOC	530	0	0	0.968	1.126
check standard	20 ppm	TOC	530	0	0	20.34	19.367
check standard	1ppm	TOC	530	0	0	0.962	1.142
check standard	20 ppm	TOC	530	0	0	20.37	19.394
check standard	20 ppm	TOC	531	0	0	20.266	20.451
check standard	1ppm	TOC	531	0	0	1.09	1.061
check standard	20 ppm	TOC	531	0	0	20.176	20.192
check standard	1ppm	TOC	532	0	0	0.958	1.075
check standard	20 ppm	TOC	532	0	0	20.25	19.737
check standard	1ppm	TOC	532	0	0	0.962	0.979
check standard	20 ppm	TOC	532	0	0	20.453	19.377
check standard	1ppm	TOC	535	0	0	1.033	0.946
check standard	20 ppm	TOC	535	0	0	19.776	20.132
check standard	1ppm	TOC	535	0	0	1.013	0.896
check standard	20 ppm	TOC	535	0	0	19.982	19.84

Exhibit A1. Variability Chart for Carbon (ppm) Measurements

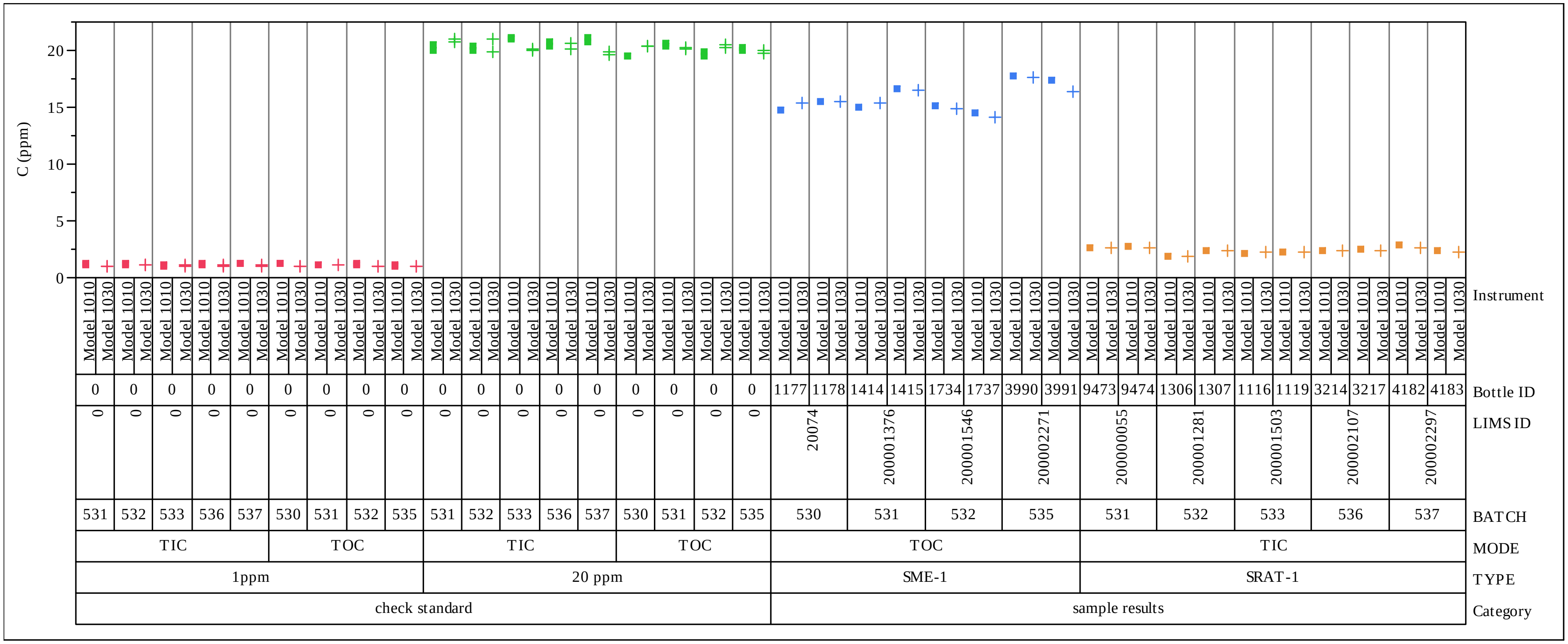


Exhibit A2. Paired Comparisons of Measurement Data

Matched Pairs Category=check standard, TYPE=1ppm, MODE=TIC
Difference: Model 1010 (ppm C)-Model 1030 (ppm C)

Model 1010 (ppm C)	1.0592	t-Ratio	0.09277
Model 1030 (ppm C)	1.0572	DF	9
Mean Difference	0.002	Prob > |t|	0.9281
Std Error	0.02156	Prob > t	0.4641
Upper95%	0.05077	Prob < t	0.5359
Lower95%	-0.0468		
N	10		
Correlation	-0.1478		

Matched Pairs Category=check standard, TYPE=1ppm, MODE=TOC
Difference: Model 1010 (ppm C)-Model 1030 (ppm C)

Model 1010 (ppm C)	1.03214	t-Ratio	0.757703
Model 1030 (ppm C)	0.998	DF	6
Mean Difference	0.03414	Prob > |t|	0.4773
Std Error	0.04506	Prob > t	0.2387
Upper95%	0.1444	Prob < t	0.7613
Lower95%	-0.0761		
N	7		
Correlation	-0.3203		

Matched Pairs Category=check standard, TYPE=20 ppm, MODE=TIC
Difference: Model 1010 (ppm C)-Model 1030 (ppm C)

Model 1010 (ppm C)	20.4549	t-Ratio	0.712787
Model 1030 (ppm C)	20.281	DF	9
Mean Difference	0.1739	Prob > |t|	0.4940
Std Error	0.24397	Prob > t	0.2470
Upper95%	0.7258	Prob < t	0.7530
Lower95%	-0.378		
N	10		
Correlation	-0.4157		

Matched Pairs Category=check standard, TYPE=20 ppm, MODE=TOC
Difference: Model 1010 (ppm C)-Model 1030 (ppm C)

Model 1010 (ppm C)	19.8113	t-Ratio	-1.93362
Model 1030 (ppm C)	20.2016	DF	7
Mean Difference	-0.3904	Prob > |t|	0.0944
Std Error	0.20189	Prob > t	0.9528
Upper95%	0.08701	Prob < t	0.0472
Lower95%	-0.8678		
N	8		
Correlation	-0.546		

Matched Pairs Category=sample results, TYPE=SRAT-1, MODE=TIC
Difference: Model 1010 (ppm C)-Model 1030 (ppm C)

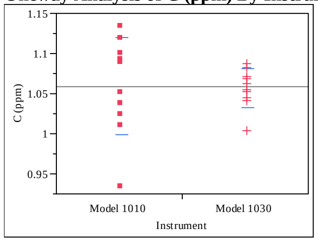
Model 1010 (ppm C)	2.2957	t-Ratio	-2.13705
Model 1030 (ppm C)	2.3604	DF	9
Mean Difference	-0.0647	Prob > |t|	0.0613
Std Error	0.03028	Prob > t	0.9693
Upper95%	0.00379	Prob < t	0.0307
Lower95%	-0.1332		
N	10		
Correlation	0.96038		

Matched Pairs Category=sample results, TYPE=SME-1, MODE=TOC
Difference: Model 1010 (ppm C)-Model 1030 (ppm C)

Model 1010 (ppm C)	15.7109	t-Ratio	-0.05422
Model 1030 (ppm C)	15.7201	DF	7
Mean Difference	-0.0093	Prob > |t|	0.9583
Std Error	0.1706	Prob > t	0.5209
Upper95%	0.39417	Prob < t	0.4791
Lower95%	-0.4127		
N	8		
Correlation	0.9231		

Exhibit A3. Evaluation of Precision Using Measurement Data from the Check Standards

Oneway Analysis of C (ppm) By Instrument Category=check standard, TYPE=1ppm, MODE=TIC

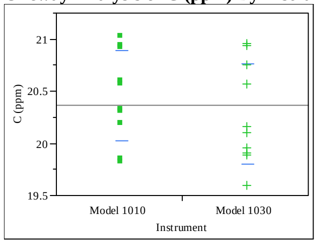


Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	10	0.0602934	0.0478000	0.0478000
Model 1030	10	0.0241330	0.0176000	0.0176000

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	2.9798	1	18	0.1014
Brown-Forsythe	6.2128	1	18	0.0227
Levene	6.8328	1	18	0.0176
Bartlett	6.3281	1	.	0.0119
F Test 2-sided	6.2419	9	9	0.0118

Oneway Analysis of C (ppm) By Instrument Category=check standard, TYPE=20 ppm, MODE=TIC

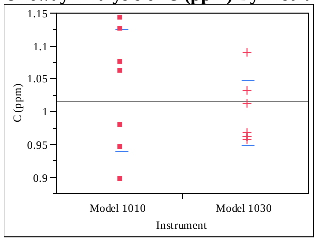


Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	10	0.4325697	0.3551000	0.3551000
Model 1030	10	0.4838365	0.4172000	0.3930000

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.2826	1	18	0.6015
Brown-Forsythe	0.1063	1	18	0.7482
Levene	0.4397	1	18	0.5157
Bartlett	0.1067	1	.	0.7439
F Test 2-sided	1.2511	9	9	0.7441

Oneway Analysis of C (ppm) By Instrument Category=check standard, TYPE=1ppm, MODE=TOC

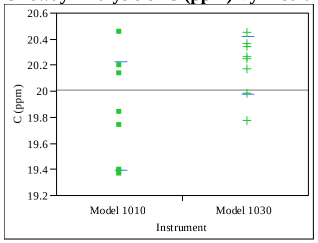


Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	7	0.0933871	0.0786939	0.0765714
Model 1030	7	0.0500100	0.0405714	0.0371429

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	3.3965	1	12	0.0902
Brown-Forsythe	2.2519	1	12	0.1593
Levene	4.8983	1	12	0.0470
Bartlett	2.0329	1	.	0.1539
F Test 2-sided	3.4871	6	6	0.1540

Oneway Analysis of C (ppm) By Instrument Category=check standard, TYPE=20 ppm, MODE=TOC



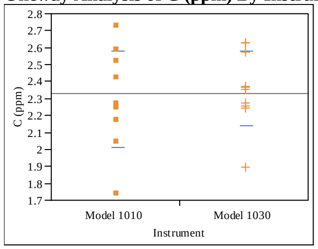
Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	8	0.4180737	0.3425000	0.3425000
Model 1030	8	0.2227169	0.1677188	0.1556250

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	4.0287	1	14	0.0644
Brown-Forsythe	4.1780	1	14	0.0602
Levene	4.2008	1	14	0.0596
Bartlett	2.4360	1	.	0.1186
F Test 2-sided	3.5237	7	7	0.1186

Exhibit A3. Evaluation of Precision Using Measurement Data from the Check Standards

Oneway Analysis of C (ppm) By Instrument Category=sample results, TYPE=SRAT-1, MODE=TIC

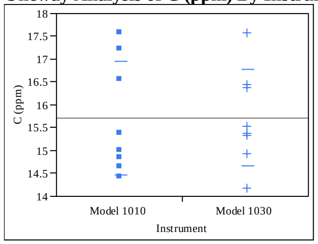


Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	10	0.2850567	0.2130400	0.2071000
Model 1030	10	0.2203327	0.1550000	0.1550000

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.5253	1	18	0.4779
Brown-Forsythe	0.4766	1	18	0.4988
Levene	0.6394	1	18	0.4343
Bartlett	0.5594	1	.	0.4545
F Test 2-sided	1.6738	9	9	0.4547

Oneway Analysis of C (ppm) By Instrument Category=sample results, TYPE=SME-1, MODE=TOC



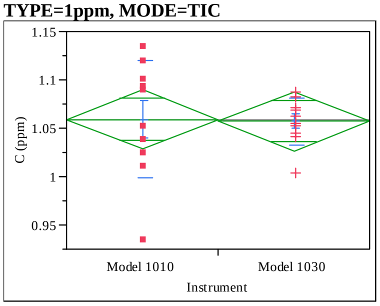
Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	8	1.234074	1.060344	0.9788750
Model 1030	8	1.051882	0.811156	0.7653750

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.3180	1	14	0.5817
Brown-Forsythe	0.2924	1	14	0.5972
Levene	0.8384	1	14	0.3753
Bartlett	0.1660	1	.	0.6837
F Test 2-sided	1.3764	7	7	0.6840

Exhibit A4. Evaluation of Relative Bias Using Measurement Data from the Check Standards

Oneway Analysis of C (ppm) By Instrument Category=check standard, TYPE=1ppm, MODE=TIC



Oneway Anova
Summary of Fit

Rsquare	0.000527
Adj Rsquare	-0.055
Root Mean Square Error	0.045922
Mean of Response	1.0582
Observations (or Sum Wgts)	20

t Test
Model 1030-Model 1010
Assuming equal variances

Difference	-0.00200	t Ratio	-0.09739
Std Err Dif	0.02054	DF	18
Upper CL Dif	0.04115	Prob > |t|	0.9235
Lower CL Dif	-0.04515	Prob > t	0.5383
Confidence	0.95	Prob < t	0.4617

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Instrument	1	0.00002000	0.000020	0.0095	0.9235
Error	18	0.03795920	0.002109		
C. Total	19	0.03797920			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Model 1010	10	1.05920	0.01452	1.0287	1.0897
Model 1030	10	1.05720	0.01452	1.0267	1.0877

Std Error uses a pooled estimate of error variance

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
Model 1010	10	1.05920	0.060293	0.01907	1.0161	1.1023
Model 1030	10	1.05720	0.024133	0.00763	1.0399	1.0745

t Test
Model 1030-Model 1010
Assuming unequal variances

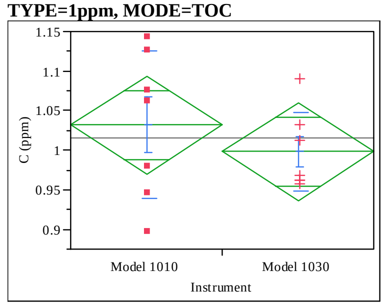
Difference	-0.00200	t Ratio	-0.09739
Std Err Dif	0.02054	DF	11.81157
Upper CL Dif	0.04283	Prob > |t|	0.9241
Lower CL Dif	-0.04683	Prob > t	0.5380
Confidence	0.95	Prob < t	0.4620

Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	10	0.0602934	0.0478000	0.0478000
Model 1030	10	0.0241330	0.0176000	0.0176000

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	2.9798	1	18	0.1014
Brown-Forsythe	6.2128	1	18	0.0227
Levene	6.8328	1	18	0.0176
Bartlett	6.3281	1	.	0.0119
F Test 2-sided	6.2419	9	9	0.0118

Oneway Analysis of C (ppm) By Instrument Category=check standard, TYPE=1ppm, MODE=TOC



Oneway Anova
Summary of Fit

Rsquare	0.057134
Adj Rsquare	-0.02144
Root Mean Square Error	0.074907
Mean of Response	1.015071
Observations (or Sum Wgts)	14

t Test
Model 1030-Model 1010
Assuming equal variances

Difference	-0.03414	t Ratio	-0.85273
Std Err Dif	0.04004	DF	12
Upper CL Dif	0.05310	Prob > |t|	0.4105
Lower CL Dif	-0.12138	Prob > t	0.7947
Confidence	0.95	Prob < t	0.2053

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Instrument	1	0.00408007	0.004080	0.7271	0.4105
Error	12	0.06733286	0.005611		
C. Total	13	0.07141293			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Model 1010	7	1.03214	0.02831	0.97046	1.0938
Model 1030	7	0.99800	0.02831	0.93631	1.0597

Std Error uses a pooled estimate of error variance

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
Model 1010	7	1.03214	0.093387	0.03530	0.94577	1.1185
Model 1030	7	0.99800	0.050010	0.01890	0.95175	1.0443

t Test
Model 1030-Model 1010
Assuming unequal variances

Difference	-0.03414	t Ratio	-0.85273
Std Err Dif	0.04004	DF	9.179788
Upper CL Dif	0.05616	Prob > |t|	0.4155
Lower CL Dif	-0.12445	Prob > t	0.7922
Confidence	0.95	Prob < t	0.2078

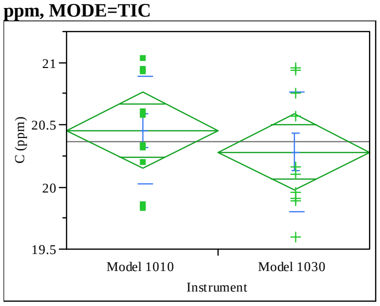
Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	7	0.0933871	0.0786939	0.0765714
Model 1030	7	0.0500100	0.0405714	0.0371429

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	3.3965	1	12	0.0902
Brown-Forsythe	2.2519	1	12	0.1593
Levene	4.8983	1	12	0.0470
Bartlett	2.0329	1	.	0.1539
F Test 2-sided	3.4871	6	6	0.1540

Exhibit A4. Evaluation of Relative Bias Using Measurement Data from the Check Standards

Oneway Analysis of C (ppm) By Instrument Category=check standard, TYPE=20 ppm, MODE=TIC



Oneway Anova
Summary of Fit

Rsquare	0.038356
Adj Rsquare	-0.01507
Root Mean Square Error	0.45892
Mean of Response	20.36795
Observations (or Sum Wgts)	20

t Test
Model 1030-Model 1010
Assuming equal variances

Difference	-0.17390	t Ratio	-0.84732
Std Err Dif	0.20524	DF	18
Upper CL Dif	0.25728	Prob > |t|	0.4079
Lower CL Dif	-0.60508	Prob > t	0.7960
Confidence	0.95	Prob < t	0.2040

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Instrument	1	0.1512060	0.151206	0.7180	0.4079
Error	18	3.7909289	0.210607		
C. Total	19	3.9421349			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Model 1010	10	20.4549	0.14512	20.150	20.760
Model 1030	10	20.2810	0.14512	19.976	20.586

Std Error uses a pooled estimate of error variance

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
Model 1010	10	20.4549	0.432570	0.13679	20.145	20.764
Model 1030	10	20.2810	0.483837	0.15300	19.935	20.627

t Test
Model 1030-Model 1010
Assuming unequal variances

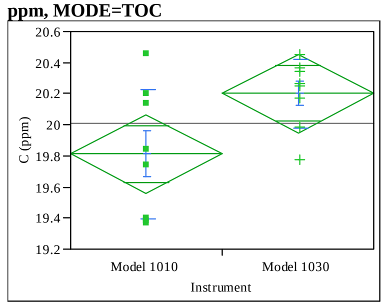
Difference	-0.17390	t Ratio	-0.84732
Std Err Dif	0.20524	DF	17.77882
Upper CL Dif	0.25767	Prob > |t|	0.4081
Lower CL Dif	-0.60547	Prob > t	0.7960
Confidence	0.95	Prob < t	0.2040

Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	10	0.4325697	0.3551000	0.3551000
Model 1030	10	0.4838365	0.4172000	0.3930000

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	0.2826	1	18	0.6015
Brown-Forsythe	0.1063	1	18	0.7482
Levene	0.4397	1	18	0.5157
Bartlett	0.1067	1	.	0.7439
F Test 2-sided	1.2511	9	9	0.7441

Oneway Analysis of C (ppm) By Instrument Category=check standard, TYPE=20 ppm, MODE=TOC



Oneway Anova
Summary of Fit

Rsquare	0.279582
Adj Rsquare	0.228124
Root Mean Square Error	0.334954
Mean of Response	20.00644
Observations (or Sum Wgts)	16

t Test
Model 1030-Model 1010
Assuming equal variances

Difference	0.390375	t Ratio	2.330916
Std Err Dif	0.167477	DF	14
Upper CL Dif	0.749578	Prob > |t|	0.0352
Lower CL Dif	0.031172	Prob > t	0.0176
Confidence	0.95	Prob < t	0.9824

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Instrument	1	0.6095706	0.609571	5.4332	0.0352
Error	14	1.5707194	0.112194		
C. Total	15	2.1802899			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
Model 1010	8	19.8113	0.11842	19.557	20.065
Model 1030	8	20.2016	0.11842	19.948	20.456

Std Error uses a pooled estimate of error variance

Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
Model 1010	8	19.8113	0.418074	0.14781	19.462	20.161
Model 1030	8	20.2016	0.222717	0.07874	20.015	20.388

t Test
Model 1030-Model 1010
Assuming unequal variances

Difference	0.390375	t Ratio	2.330916
Std Err Dif	0.167477	DF	10.67696
Upper CL Dif	0.760355	Prob > |t|	0.0405
Lower CL Dif	0.020395	Prob > t	0.0202
Confidence	0.95	Prob < t	0.9798

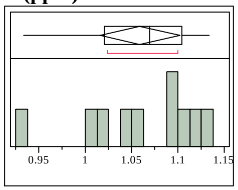
Tests that the Variances are Equal

Level	Count	Std Dev	MeanAbsDif to Mean	MeanAbsDif to Median
Model 1010	8	0.4180737	0.3425000	0.3425000
Model 1030	8	0.2227169	0.1677188	0.1556250

Test	F Ratio	DFNum	DFDen	p-Value
O'Brien[.5]	4.0287	1	14	0.0644
Brown-Forsythe	4.1780	1	14	0.0602
Levene	4.2008	1	14	0.0596
Bartlett	2.4360	1	.	0.1186
F Test 2-sided	3.5237	7	7	0.1186

Exhibit A5. Evaluation of Bias Using Measurement Data from the Check Standards

Distributions Category=check standard, MODE=TIC, TYPE=1ppm, Instrument=Model 1010
C (ppm)



Quantiles

100.0%	maximum	1.1340
99.5%		1.1340
97.5%		1.1340
90.0%		1.1325
75.0%	quartile	1.1048
50.0%	median	1.0700
25.0%	quartile	1.0205
10.0%		0.9416
2.5%		0.9340
0.5%		0.9340
0.0%	minimum	0.9340

Moments

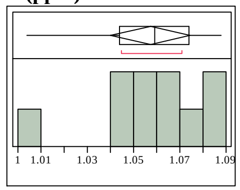
Mean	1.0592
Std Dev	0.0602934
Std Err Mean	0.0190664
upper 95% Mean	1.1023313
lower 95% Mean	1.0160687
N	10

Test Mean=value

Hypothesized Value	1
Actual Estimate	1.0592
df	9
Std Dev	0.06029

	t Test
Test Statistic	3.1049
Prob > |t|	0.0126
Prob > t	0.0063
Prob < t	0.9937

Distributions Category=check standard, MODE=TIC, TYPE=1ppm, Instrument=Model 1030
C (ppm)



Quantiles

100.0%	maximum	1.0880
99.5%		1.0880
97.5%		1.0880
90.0%		1.0875
75.0%	quartile	1.0740
50.0%	median	1.0590
25.0%	quartile	1.0440
10.0%		1.0077
2.5%		1.0040
0.5%		1.0040
0.0%	minimum	1.0040

Moments

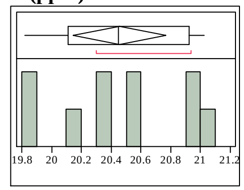
Mean	1.0572
Std Dev	0.024133
Std Err Mean	0.0076315
upper 95% Mean	1.0744637
lower 95% Mean	1.0399363
N	10

Test Mean=value

Hypothesized Value	1
Actual Estimate	1.0572
df	9
Std Dev	0.02413

	t Test
Test Statistic	7.4952
Prob > |t|	<.0001
Prob > t	<.0001
Prob < t	1.0000

Distributions Category=check standard, MODE=TIC, TYPE=20 ppm, Instrument=Model 1010
C (ppm)



Quantiles

100.0%	maximum	21.027
99.5%		21.027
97.5%		21.027
90.0%		21.018
75.0%	quartile	20.925
50.0%	median	20.451
25.0%	quartile	20.110
10.0%		19.821
2.5%		19.817
0.5%		19.817
0.0%	minimum	19.817

Moments

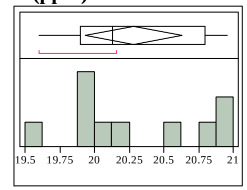
Mean	20.4549
Std Dev	0.4325697
Std Err Mean	0.1367905
upper 95% Mean	20.764342
lower 95% Mean	20.145458
N	10

Test Mean=value

Hypothesized Value	20
Actual Estimate	20.4549
df	9
Std Dev	0.43257

	t Test
Test Statistic	3.3255
Prob > |t|	0.0089
Prob > t	0.0044
Prob < t	0.9956

Distributions Category=check standard, MODE=TIC, TYPE=20 ppm, Instrument=Model 1030
C (ppm)



Quantiles

100.0%	maximum	20.956
99.5%		20.956
97.5%		20.956
90.0%		20.954
75.0%	quartile	20.797
50.0%	median	20.129
25.0%	quartile	19.899
10.0%		19.629
2.5%		19.600
0.5%		19.600
0.0%	minimum	19.600

Moments

Mean	20.281
Std Dev	0.4838365
Std Err Mean	0.1530025
upper 95% Mean	20.627116
lower 95% Mean	19.934884
N	10

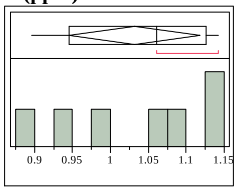
Test Mean=value

Hypothesized Value	20
Actual Estimate	20.281
df	9
Std Dev	0.48384

	t Test
Test Statistic	1.8366
Prob > |t|	0.0995
Prob > t	0.0497
Prob < t	0.9503

Exhibit A5. Evaluation of Bias Using Measurement Data from the Check Standards

Distributions Category=check standard, MODE=TOC, TYPE=1ppm, Instrument=Model 1010
C (ppm)



Quantiles

100.0%	maximum	1.1420
99.5%		1.1420
97.5%		1.1420
90.0%		1.1420
75.0%	quartile	1.1260
50.0%	median	1.0610
25.0%	quartile	0.9460
10.0%		0.8960
2.5%		0.8960
0.5%		0.8960
0.0%	minimum	0.8960

Moments

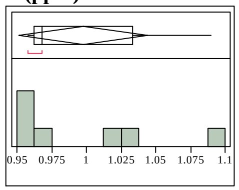
Mean	1.0321429
Std Dev	0.0933871
Std Err Mean	0.035297
upper 95% Mean	1.1185115
lower 95% Mean	0.9457742
N	7

Test Mean=value

Hypothesized Value	1
Actual Estimate	1.03214
df	6
Std Dev	0.09339

	t Test
Test Statistic	0.9106
Prob > |t|	0.3976
Prob > t	0.1988
Prob < t	0.8012

Distributions Category=check standard, MODE=TOC, TYPE=1ppm, Instrument=Model 1030
C (ppm)



Quantiles

100.0%	maximum	1.0900
99.5%		1.0900
97.5%		1.0900
90.0%		1.0900
75.0%	quartile	1.0330
50.0%	median	0.9680
25.0%	quartile	0.9620
10.0%		0.9580
2.5%		0.9580
0.5%		0.9580
0.0%	minimum	0.9580

Moments

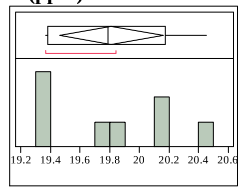
Mean	0.998
Std Dev	0.05001
Std Err Mean	0.018902
upper 95% Mean	1.0442515
lower 95% Mean	0.9517485
N	7

Test Mean=value

Hypothesized Value	1
Actual Estimate	0.998
df	6
Std Dev	0.05001

	t Test
Test Statistic	-0.1058
Prob > |t|	0.9192
Prob > t	0.5404
Prob < t	0.4596

Distributions Category=check standard, MODE=TOC, TYPE=20 ppm, Instrument=Model 1010
C (ppm)



Quantiles

100.0%	maximum	20.451
99.5%		20.451
97.5%		20.451
90.0%		20.451
75.0%	quartile	20.177
50.0%	median	19.789
25.0%	quartile	19.381
10.0%		19.367
2.5%		19.367
0.5%		19.367
0.0%	minimum	19.367

Moments

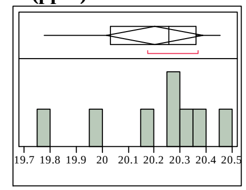
Mean	19.81125
Std Dev	0.4180737
Std Err Mean	0.1478114
upper 95% Mean	20.160768
lower 95% Mean	19.461732
N	8

Test Mean=value

Hypothesized Value	20
Actual Estimate	19.8113
df	7
Std Dev	0.41807

	t Test
Test Statistic	-1.2770
Prob > |t|	0.2423
Prob > t	0.8788
Prob < t	0.1212

Distributions Category=check standard, MODE=TOC, TYPE=20 ppm, Instrument=Model 1030
C (ppm)



Quantiles

100.0%	maximum	20.453
99.5%		20.453
97.5%		20.453
90.0%		20.453
75.0%	quartile	20.363
50.0%	median	20.258
25.0%	quartile	20.031
10.0%		19.776
2.5%		19.776
0.5%		19.776
0.0%	minimum	19.776

Moments

Mean	20.201625
Std Dev	0.2227169
Std Err Mean	0.0787423
upper 95% Mean	20.387821
lower 95% Mean	20.015429
N	8

Test Mean=value

Hypothesized Value	20
Actual Estimate	20.2016
df	7
Std Dev	0.22272

	t Test
Test Statistic	2.5606
Prob > |t|	0.0375
Prob > t	0.0188
Prob < t	0.9812

Distribution:

Name:	Location:
Sharon Marra	773-A
Connie Herman	999-W
Charles J. Coleman	773-A
Clint Gregory	773-A
Lori Chandler	773-A
Patricia Lee	703-41A
Gene Shine	703-41A
Damon R. Click	773-A
L. Curtis Johnson	773-A
Michael Stone	999-W
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