Tank 48H Waste Composition and Results of Investigation of Analytical Methods

by

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MASTER

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SUMMARY

This report serves two purposes. First, it documents the analytical results of Tank 48H samples taken between April and August 1996. Second, it describes investigations of the precision of the sampling and analytical methods used on the Tank 48H samples.

Analytical results for five Tank 48H sampling dates between April and August of 1996 are reported. This time period followed the removal of the majority of the benzene from Tank 48H and preceded the start of the Process Verification Test, Phase 1.(PVT-1). The major composition changes in Tank 48H were slow increases in the Cs-137 and potassium concentrations and a rapid decrease in the phenylboronic acid (1PB) concentration.

Investigations of the accuracy and precision of sampling and analytical methods used on the Tank 48H samples revealed the following.

- Routine analytical methods for Cs-137, free hydroxide, boron, potassium, nitrate, nitrite, and phenol have uncertainties of 11% or smaller.
- An unusual variability in the free hydroxide method was identified by this study which led to an instrument modification to correct the problem.
- Variability due to delays in analysis are small or nonexistent for most analytes. However, this depends on the rate of reactions of interest and this data was obtained when there were no rapid changes occurring in Tank 48H.
- The soluble copper concentration in Tank 48H samples taken between October 1995 and November 1996 varied between <.3 to 1.6 mg/L with no apparent consistent trend.

- The solids content in Tank 48H samples averaged 2.30 ± 0.36 wt % compared to an expected value of 2.7 wt %. The variability in this measurement is due to both tank sampling and the analytical method.
- The method for benzene measurements in radioactive slurries has a variability of $\pm 35\%$ and a bias of -70% . Several actions for improving this method are identified.

INTRODUCTION

The In-Tank Precipitation (ITP) process at the Savannah River Site (SRS) prepares high level radioactive waste for vitrification in the Defense Waste Processing Facility (DWPF). In Tank 48H of the ITP facility, cesium-137 and strontium-90 are removed from solution using two specialty chemicals, sodium tetraphenylborate (NaTPB) and monosodium titanate (MST). Sodium tetraphenylborate precipitates cesium and potassium. The MST removes strontium, uranium, and plutonium. The insoluble species are concentrated and washed using crossflow filters. Decontaminated filtrate is transferred to Tank 50H for ultimate disposal by the Saltstone facility. The concentrated cesium- and strontium-containing waste is transferred to Tank 49H for storage until processed for vitrification by the Late Wash Facility and DWPF.

During September 1995, ITP began radioactive operations by adding NaTPB solution to radioactive waste in Tank 48H. Between October and November 1995, benzene from the decomposition of NaTPB was detected in the Tank 48H vapor space. During November and December 1995, approximately 10,000 kg of sodium tetraphenylborate decomposed, leaving 20,000 kg of potassium and cesium tetraphenylborate in the tank. The rapid decomposition of NaTPB appears to have been caused by a combination of factors, including the high tank temperature and presence of copper and possibly other catalysts.¹ After it was established that the insoluble KTPB and CsTPB were decomposing at a slow rate, the benzene accumulated in the tank was removed by carefully mixing the tank contents.

Analytical results for samples taken from Tank 48H from September 1995 until April 1996 were reported previously.¹ Sampling continued at a reduced frequency from April 1996 until August 1996. The results from those samples are reported below.

In addition, investigations into the accuracy and precision of the analytical methods were undertaken. The analyses were provided by the Analytical Development Section (ADS) and Interim Waste Technology Section (IWTS, now called Waste

Processing Technology Section, WPTS) within the Savannah River Technology Center.

DISCUSSION

Tank 48H Sample Results

Analytical results on filtered portions of the Tank 48H samples taken between April and August 1996 are shown in Table I. Results prior to April 1996 and following August 1996 were reported previously.^{1,2} The analytical methods are described in Appendix A. Several components showed significant changes in concentration during the four-month period.

Cesium-137 increased slowly and the rate accelerated in August (Figure 1). The acceleration was verified in a sample taken prior to the start of the PVT-1 test on November 3, 1996. The reason for the increase in rate has not been determined but is under investigation by SRTC. The samples taken on April 13, 1996, showed Cs-137 concentrations significantly higher than the trend in previous and subsequent samples. Additional samples were analyzed to investigate the cause of the high values and the results are discussed in the section titled "Changes in Cs-137 with Time." Potassium increased proportionally to cesium (Figure 2) as the tetraphenylborate solids in the tank slowly decomposed.

Phenylboronic acid decreased by more than 90% between April and August 1996 (Figure 3). This is largely due to the decomposition, but some of the change is attributable to dilution of the tank contents by pump seal water leakage.

Free hydroxide, nitrate, and nitrite ion decreased in concentration. Although the decreases are due largely to dilution of the tank contents, adsorption of carbon dioxide and radiolytic decomposition reactions may also contribute to their decline.

The density of the solution decreased with time due to dilution of the waste with pump seal water. A correlation between density and the total salt concentration (expressed as the sodium ion concentration) is discussed in a later section of this report.

Variability Study on ADS Routine Methods

Table I listed the results from routine analytical methods provided by the Analytical Development Section of SRTC. The variability of the results was investigated using a set of three Tank 48H VDS samples. These samples were taken from the tank over six days (August 5 to August 11, 1996). Based on the slow trends in composition shown in Table 1, the tank

**Table I. Tank 48H Supernate Composition
April to August 1996**

Date taken	Date fixed	Sample ID	Cs-137 (nCi/g)	1PB* (mg/L)	Phenol (mg/L)	B (mg/L)	K (mg/L)	Na (molar)	Free OH (molar)	NHrate (molar)	Nitrite (molar)	Density (g/mL)	Other (molar)	Waste Vol (gallons)
28-Apr	29-Apr	ITP-287**	186	1161	1199	515	3.9	4.1	2.79	0.48	0.81	NR	Alt 0.13	182,000
2-Jun	4-Jun	ITP-296	249	499	1267	475	4.8	NR	1.96	0.46	0.59	NR		202,000
		ITP-297	262	460	1286	482	4.78	NR	2.01	0.47	0.59	NR		
28-Jun	2-Jul	ITP-311,312,313***	274±4	215±14	1358±5	470±3	4.90±0.3	3.6±1	1.71±0.6	40±0.6	48±0.6	1.140		208,000
11-Aug	14-Aug	ITP-356††	314±1	132±9	1335±11	479±20	5.34±0.8	NR	1.36±0.9	43±0.1	60±0.1	NR		227,000
		ITP-358††	328±3	140±2	1376±58	434±3	5.58±1.6	NR	1.30±1.4	42±0.1	60±0.2	NR		
		ITP-361††	326±2	122±24	1278±4	448±16	5.54±1.6	NR	1.34±1.1	41±0.1	57±0.1	NR		
30-Aug	5-Sep	ITP-370	422	57	1020	362	6.36	NR	1.46	0.35	0.45	1.124	Alt .11; CO3† .18	233,000
		ITP-371	423	86	1071	404	6.33	NR	1.42	0.35	0.46	1.126	Alt .12; CO3† .18	
		ITP-373 (blank)	0.15	<20	<20	<2	0.24	NR	<0.5	3 mg/L	<0.03	0.996	CO3† .006	

* 1PB = phenylboronic acid
 **ITP-284 and ITP-287 were received at SRTC on 4/28/96. ITP-284 was empty when received, so ITP-287 was prepared and analyzed alone.
 ***The three bottles were combined and duplicate aliquots were analyzed.
 † Al = aluminate; CO3 = carbonate
 ††Duplicate analyses. See additional data under "Variability Study on ADS Routine Methods."

Figure 1. Cs-137 Concentration in Tank 48H

Note: See Reference 1 for data from 0-190 days. See Reference 2 for datum on 11/3/96. For remaining data, see Table I of this report.

Figure 2. Potassium Concentration in Tank 48H

Figure 3. Phenylboronic Acid Concentration in Tank 48H

TABLE II. Test Matrix for Analytical Variability Study

Date	Sampling Order (Submission Order)**		
	ITP-356	ITP-359	ITP-361
8/14/96	2(2), 5(5)	1(3), 3(6)	4(1), 6(4)
8/20/96	4(1), 6(2)	1(3), 5(5)	2(4), 3(6)
8/26/96	3(1), 4(3)	2(2), 5(4)	1(5), 6(6)

Analyses Requested

Cesium-137	Nitrate	Phenol
Free hydroxide	Nitrite	Phenylboronic acid(1PB)
Boron	Potassium	

*Numbers without parentheses indicate the order in which the samples were taken. Numbers in parentheses indicate the order in which the samples were submitted for analysis.

composition did not change measurably over the six day period. Therefore, differences in results should reflect sampling and analytical variability. This investigation measured:

- (1) total variability,
- (2) differences between VDS bottles,
- (3) differences between samples removed from the same VDS bottle, and
- (4) differences caused by delays in analyzing samples.

A statistically designed test was performed in which three VDS bottles from Tank 48H (ITP-356, ITP-359, ITP-361) were sampled in duplicate on each of three dates over a period of twelve days. The sequence of taking samples and of submission to ADS was randomized within each sampling date. Typically, samples are analyzed by ADS in the order in which they are submitted. The test matrix is shown in Table II. This test was not designed to measure the accuracy of the methods, but rather the precision.

Table III lists the results from all analyses. Table IV provides a summary of the sources of variability. Appendix B gives the details of the statistical analysis of the data.

The data set was analyzed for the total percentage relative standard deviation (%RSD) and the components of variation contributing to the total. The results are shown in Table IV. The %RSD is the standard deviation of the measurements expressed as a percentage of the average of the measurements. It's magnitude indicates how close another measurement will be to the average values in Table III.

TABLE III. Results from Variability Study of ADS Routine Methods

Sample ITP-356									
Sampling Date	Sample order	Cs-137 (nCi/mL)	Free OH (molar)	B (molar)	Nitrate (molar)	Nitrite (molar)	K (mmolar)	Phenol (molar)	1PB* (mmolar)
8/14/96	2	356	1.42	0.0412	0.43	0.60	0.135	0.0141	1.03
	5	355	1.29	0.0425	0.43	0.60	0.138	0.0143	1.13
8/20/96	4	399	1.60	0.0431	0.39	0.48	0.145	0.0143	0.57
	6	391	1.44	0.0418	0.40	0.49	0.139	0.0142	0.57
8/26/96	3	401	1.56	0.0427	0.44	0.51	0.145	0.0137	0.71
	4	391	1.47	0.0428	0.43	0.51	0.139	0.0139	0.69
Sample ITP-359									
Sampling Date	Sample order	Cs-137 (nCi/mL)	Free OH (molar)	B (molar)	Nitrate (molar)	Nitrite (molar)	K (mmolar)	Phenol (molar)	1PB* (mmolar)
8/14/96	1	374	1.40	0.0456	0.42	0.59	0.148	0.0151	1.16
	3	369	1.20	0.0430	0.43	0.61	0.149	0.0142	1.15
8/20/96	1	400	1.52	0.0428	0.41	0.50	0.151	0.0142	0.68
	5	386	1.39	0.0425	0.41	0.50	0.149	0.0142	0.60
8/26/96	2	392	1.41	0.0453	0.43	0.54	0.145	0.0141	0.71
	5	385	1.31	0.0432	0.43	0.52	0.160	0.0139	0.75
Sample ITP-361									
Sampling Date	Sample order	Cs-137 (nCi/mL)	Free OH (molar)	B (molar)	Nitrate (molar)	Nitrite (molar)	K (mmolar)	Phenol (molar)	1PB* (mmolar)
8/14/96	4	367	1.42	0.0403	0.41	0.57	0.136	0.0136	0.88
	6	371	1.27	0.0400	0.40	0.57	0.135	0.0135	1.14
8/20/96	2	397	1.19	0.0401	0.38	0.46	0.139	0.0136	0.76
	3	467	1.12	0.0399	0.39	0.48	0.143	0.0133	0.83
8/26/96	1	391	1.31	0.0410	0.42	0.59	0.140	0.0131	0.65
	6	392	1.17	0.0423	0.40	0.50	0.142	0.0131	0.67

TABLE IV. Sources of Variability in Tank 48H Results

Source of Variability	Cs-137 (nCi/mL)	Free OH (molar)	B (molar)	Nitrate (molar)	Nitrite (molar)	K (mmolar)	Phenol (molar)	1PB* (mmolar)
Total* (%RSD)	6.9	11.1	4.8	4.9	10.7	5.2	4.1	30.0
Component*								
Sample bottle*	1.0	7.2	4.1	2.8	2.8	1.5	3.4	0.0
Day (random)*	5.1	0.0	1.3	3.5	10.2	4.2	1.7	27.6
Residual*	4.6	8.4	2.1	1.8	1.6	2.6	1.5	11.9

*The total variation is not a simple sum of the component variations, but is the square root of the sum of the squares of the component RSDs.

The total %RSDs for all of the analytes except 1PB were 11% or smaller (1-sigma or 67% confidence interval). This range of values is very similar to previously reported results for Extended Sludge Process (ESP) test samples.³ The high variability for free OH⁻ (11.1%) results from an instrument problem discovered by this study and described below. The relatively high variability for nitrite (10.7%) remains unexplained and is particularly puzzling given the lower variability of nitrate (4.9%). The two compounds are measured simultaneously on the same instrument. The high variability for 1PB results from a time-dependent decrease in the concentration (see below) and to the low concentration. The average concentration (0.81 mmolar) was only four times the detection limit (0.2 mmolar). The 1PB peak in the HPLC trace tails more than phenol, causing greater uncertainty in the peak integration at levels close to the detection limit. Subsequent to this study, a modification of the method has improved the sharpness of the 1PB peak and may have decreased the variability at low concentrations.

In five of the eight routine methods studied, the majority of the total RSD results from day-to-day variations. This source includes day-to-day variations in instrument performance (calibration, operator, standards) and sample preparation (other than removing the subsample from the VDS bottle). The three exceptions are free OH⁻, boron, and phenol. The variability in free OH⁻ was traced to an instrument problem discussed below. For boron and phenol, the total variabilities were so low (4.8 and 4.1 %) that identifying the individual sources is of little importance.

Differences between VDS bottles were statistically significant for five of the eight analytes. However, the differences were small (<4%) except for free OH⁻ (which was only 7.2%). Low variability for soluble components between samples taken from a well-mixed waste tank is expected. However, this result may not be true for insoluble components (see below under "Weight Percentage Solids"). Since the samples were taken on separate days with mixing in between, this result supports the assumption that samples are being removed from a well-mixed region of the tank (although it does not prove that the entire tank is well mixed).

The residual RSD includes differences between duplicate subsamples taken from a VDS bottle on the same day. It also includes aspects of sample preparation and analysis that vary from minute-to-minute but not day-to-day. Although this source was a significant fraction of the total variability for several analytes, they were small (<5%) except for free OH⁻ (8.4%) and 1PB (11.9%). These results confirm that reproducible samples of soluble components can be removed from a VDS bottle. The behavior for free OH⁻ and 1PB could be due to subsampling from the VDS bottle, although this is unlikely since components that were analyzed are soluble and

the bottle is easily mixed by shaking. It is more likely that the residual RSD indicates significant variability (subsample-to-subsample) in the sample preparation or instrument. For 1PB, this includes the extraction performed in the sample preparation. For free OH, the source was traced to a instrument problem discussed below.

The day-to-day variability discussed above was further investigated to determine if there were consistent trends with time. Trends were observed for five analytes, although in most cases these were <4% change in twelve days. Two analytes, 1PB and nitrite, showed larger trends. Qualitatively, these results suggest that samples should be analyzed as soon as possible after removing them from the tank. Quantitatively, however, the magnitudes of the trends for most analytes indicate delays of up to two weeks are not important. There is no single recommendation for analytical turnaround times that applies in all situations. The rates of reactions of interest must be considered and these can vary considerably in the tank. Furthermore, the data below does not provide an answer to the question of whether the analytical results should apply to the tank on the day the sample was taken or on the day the analysis was performed. Again, for most analytes the difference is insignificant, but for others (such as 1PB and nitrite), it may be important.

The free hydroxide concentration in two of the sample bottles trended upward and one trended down. When the data from all three bottles are considered together, no significant trend was found. It is expected that hydroxide will trend downward over long time periods due to adsorption of carbon dioxide from the air and depletion from radiolytic decomposition of tetraphenylborate compounds. The results from this experiment indicate that the downward trend is not significant over a twelve day interval.

The phenol concentration in each bottle trended down. When all three were considered together, the downward trend was statistically significant (-.04 mmolar per day). However, over a two week period, this change is only -0.3 mmolar, or only a 2% change in the phenol concentration. The only likely chemical explanation for a downward trend in phenol is decomposition from radiolysis. Over a two week period, this trend is not important for most uses of the data.

The boron concentration in two sample bottles trended upward and one was virtually flat. Taken together, the trend was not significant. It is expected that a long-term increase will occur in the boron concentration due to slow decomposition of the tetraphenylborate solids. The rate of increase in boron should mimic increases in Cs-137 and potassium. The change in potassium (Figure 3) indicates that the boron should increase by 0.005 mmolar per day. Over a

two week period, this corresponds to a change of less than 0.2% of the average boron concentration.

For nitrite, none of the individual bottles showed a significant trend, but when taken together, a downward trend was statistically significant (-0.006 molar/day, or -14% over twelve days). The long-term trend in Tank 48H has been downward due largely to dilution of the waste by pump seal water. In addition to dilution, radiolysis of the waste solution converts nitrate into nitrite. In the presence of organics, nitrite is converted to nitrous oxide and ammonia. Thus, nitrate will decrease, but nitrite can increase or decrease depending on the relative rates of production and destruction. At the current radiolysis rates in the tank, the reactions are expected to be slow and not detectable. A detailed analysis of the data may reveal a trend in the tank when corrections for dilution are included. However, the ratio of nitrate to nitrite does not appear to have changed since October 1995. The data from this test suggests that nitrite undergoes a more rapid decrease in the sample bottle than occurs in the tank. However, due to the small size of the data set, it is suggested that this result be confirmed before significant changes are made to sampling and analysis plans.

The concentration of 1PB trended down in all three bottles. When considered together, the downward trend was statistically significant (-0.03 mmolar/day). This trend is expected since the 1PB concentration in Tank 48H dropped by over 90% during the three month period that included the variability test (Figure 3). This downward trend explains much of the large day-to-day variation (27.6%) for 1PB shown in Table IV. From the fitted line regressing 1PB over time, the root mean square error (the sigma for the scatter about the line) is 0.142 mmolar. At day = 0, 1PB was approximately 1 mmolar, so the random error is only 14.2% after accounting for a linear decrease in concentration with time compared to 27.6% if the decrease with time is neglected.

The results were examined for a dependence on the order of submission (i.e., ADS LIMS number). Typically, samples submitted as groups are analyzed in the order submitted. Free hydroxide was the only method that showed a statistically significant trend, decreasing in the order in which they were analyzed. This trend was traced to an autosampler located in a radiohood. It appears that the high air flow rate over the samples awaiting analysis resulted in significant adsorption of carbon dioxide during the time required to run a set of six samples (approximately 45 minutes). Surprisingly, standard solutions placed at the beginning and end of sample sets did not show the effect. The problem was corrected by erecting a wind shield around the samples. Table V shows results for the same set of samples with and without the shield in place. With the shield in place, the average value

Table V. Effect of Autosampler Shield on Free OH⁻

<u>Order of Analysis</u>	<u>Sample</u>	<u>Free Hydroxide (molar)</u>	
		<u>Without shield</u>	<u>With shield</u>
1	ITP-356	1.596	1.725
2	ITP-359	1.520	1.703
3	ITP-356	1.445	1.733
4	ITP-359	1.388	1.691
5	ITP-361	1.191	1.664
6	ITP-361	1.122	1.696
	Average	1.377	1.702
	Standard Dev.	.186 (14%)	.025 (1.5%)

of the results increased by 0.32 molar and the variability decreased by an order of magnitude.

Copper

Copper concentrations in filtered samples from Tank 48H have been measured on three occasions by inductively coupled plasma emission spectroscopy (ICP-ES). The results are shown in Table VI. In December 1995, several samples were prepared, analyzed, and results reported.¹ Although the combination of very low copper concentration (~1 mg/L) and high salt concentration made the analysis very difficult, quality assurance measures taken at that time indicated the results were dependable. In July of 1996, additional samples and some of the previous samples were submitted for analysis and problems were encountered with low recoveries when the samples were spiked with 1 mg/L copper. The results of the July analyses are included in Table VI for comparison. When the problem was encountered, a program was initiated to identify and correct the problem with the low spike recoveries. The problem was corrected by a modification to the sample preparation to ensure the highly alkaline samples were made sufficiently acidic to keep copper in solution (at the sacrifice of sensitivity due to additional dilution). The original and additional samples were analyzed by the new procedure in February 1997. The results for the three analysis dates are quite consistent, indicating that the differences are real and are not due to analytical variability. They may result from time-dependent changes in the tank composition (chemistry effect) or from inhomogeneities in the tank (sampling problem). Examples of chemistry effects are solubility, adsorption, and complexation. Copper is believed to shift between two oxidation state during the tetraphenylborate decomposition reaction. If there are significant differences in the solubility, adsorption properties, or complexation between Cu(I) and Cu(II), the changes in the tank may reflect changes in the Cu(I)/Cu(II) ratio. Understanding the changes is not important if soluble copper at 0 to 1.5 mg/L is not the

Table VI. Copper Concentration in Tank 48H Filtrate

<u>Sample</u>	<u>Date analyzed:</u>	<u>Cu Concentration (mg/L)</u>		
		12/95*	7/96	2/97
10/12/95 (ITP-164)		1.2		1.6
11/7/95**		1.2	1.3	1.3
12/1/95 (ITP-208)		<.2		<.3
12/18/95 (ITP-216/217) [†]		1.4		1.1
2/10/96 (ITP-245)			<.14	
2/10/96 (ITP-246)				<.3
4/13/96 (ITP-278/79/80/81) [†]			.30	
4/13/96 (ITP-278)				<.3
7/96 (ITP-320-25, 328-331) [†]			.73	1.1
11/3/96 (ITP-382) ^{††}				<.3
Tank 49H (ITP-276)			<.14	<.3

*Data reported previously in Reference 1.

**Sample from the second filtration run, Filtrate Hold Tank #5, obtained from the ITP laboratory (Sample#51013 dated 11/7/95).

[†]Obtained from combining the indicated samples. For the 7/96 combined sample, the original samples were taken on three different days (7/13, 7/14, and 7/17).

^{††}Datum reported previously in Reference 2

dominant decomposition catalyst. Nevertheless, Tank 48H should continue to be monitored periodically for soluble copper. In addition, monitoring copper during simulant tests should be considered since it could reveal chemical effects.

In addition to the Tank 48H samples shown in Table VI, Tank 49H solution was analyzed twice and no copper was detected either time.

Weight Percentage Solids

The insoluble solids concentration in Tank 48H was 2.30 wt % (± 0.34) in August 1996. This result is the average of seven measurements of five VDS samples (Table VII). It is consistent with estimates of the tank solids content from previous measurements. The weight percentage solids in Tank 48H slurry samples is measured in the Shielded Cells facility by a gravimetric method (see Appendix A).

The variability in the measured solids concentration helps determine the consistency of the Tank 48H sampling procedure and the analytical method. Because the solids tend to settle or float in Tank 48H (depending on the density of the salt solution), it is very difficult to obtain a representative

Table VII. Weight Percentage Solids in Tank 48H.

<u>Sample</u>	<u>Date</u>	<u>Solids(wt %)</u>
ITP-356	8/5/96	2.87
ITP-359	8/10/96	2.28
ITP-360	8/11/96	2.59, 2.15, 2.32
ITP-361	8/11/96	2.02
ITP-371	8/30/96	1.87
Average of 7 measurements:		2.30
Variability: σ (sample-to-sample)		0.28 (12%)
σ (analytical)		0.22 (10%)
total		0.36 (16%)
ITP-373*	8/30/96	0.012
SL-96-10**		1.60, 1.35
Average of two measurements:		1.48
Variability		± 0.18 (12%)

*ITP-373 was a blank sample (distilled water).

**Nominal 2 wt % slurry prepared from reagent grade chemicals. Analysis of the control in a non-radioactive laboratory yielded 1.77 ± 0.09 wt %.

sample. It proves necessary to mix the tank contents with slurry pumps, stop the pumps, then quickly obtain the sample before the solids settle significantly. During mid-1996, numerous samples were taken from Tank 48H and sent to SRTC for analysis and experiments. The sampling method yielded obviously low or no solids in almost half of the samples. A modification to the sampling procedure (mix, then sample within two hours) greatly improved the consistency of the samples so that all appeared to have significant amounts of solids present. Following the modification, several samples were analyzed to determine the precision of the analysis method and of the tank sampling method. The results are shown in Table VII. Over the period in which the samples were taken (8/5 to 8/30), the tank volume increased slightly (4%). The total random variability (ignoring the dilution) is 16%, with approximately equal contributions from the analytical method and Tank 48H sampling variability. Thus, improvement of the reliability of the results can be obtained by improvements in both sampling and analysis. The analytical method also appears biased low by 15% (compared to the control slurry SL-96-10). This should also be investigated in any attempt to improve the analytical method.

The expected solids concentration in Tank 48H can be calculated from previous measurements. Prior to addition of NaTPB in September 1995, an extensive tank sampling program

estimated that the solids content of the tank was 0.55 wt %.⁵ The tank contained 460,000 gallons of waste with an average density of 1.24 g/mL, corresponding to 11,900 kg of solids. Addition of NaTPB in September 1995 created 14,000 kg of additional KTPB solids,¹ for a total of 25,900 kg of solids. The majority of the solids are KTPB with a density of 1.18 g/mL. These solids account for approximately 5600 gallons of the tank waste volume. In August 1996, the time period for the sample results in Table VII, the slurry volume was 227,000 gallons with a solution density of 1.13 g/mL (Table 1). The estimated solids content is 2.7 wt %, which agrees within 15% of the measured value.

These results indicate that the current sampling and measuring method is accurate to about $\pm 15\%$. There is currently no required need for this analysis. As currently performed, the procedure measures the combined tetraphenylborate, titanate, and sludge insolubles. It does not satisfy the process requirement to measure the weight percentage of K/Cs tetraphenylborate solids in transfers from Tank 49H to S Area.⁶ A potential application is to use it in conjunction with the benzene analysis to improve the estimates of the tank benzene inventory. It is probably sufficiently accurate for this purpose. No further development of this analysis is recommended until a requirement and accuracy are defined.

Benzene

Several VDS bottles have been analyzed for benzene by a method designed to measure easily evaporable benzene. The method was intended to estimate the amount of benzene in Tank 48H that could evaporate rapidly when the pumps were running. The method is described in Appendix A. The results (Table VIII) indicate that the tank contained 2,000 to 6,000 kg of benzene. However, because of the poor reproducibility of the method, the information was thought not to be reliable. In retrospect, the results did indicate the correct order of magnitude and the method did reflect the loss of the benzene from tank mixing during April and May 1996. However, the large variability severely limits the usefulness of the data.

Identifying the source of the variability can direct attempts to improve the method. The variability may be due to the analytical method, differences in tank samples, or both. Samples taken between January and June 1996 did not contain representative portions of solids because the tank could not be stirred immediately prior to sampling. Benzene associated with the insoluble solids in the tank and differences in the solids content could account for the variability in benzene concentrations. Solids measurements were not made on the bottles used for the benzene analysis so the results could not be corrected for differences in solids content.

Table VIII. Benzene Analyses on Tank 48H Samples*

<u>Date</u>	<u>Sample</u>	<u>Benzene (g/L)</u>
1/21/96	ITP-235	6.3
1/26/96	ITP-239	3.1
2/10/96	ITP-245	4.1
	ITP-246	9.7
3/22/96	ITP-267	4.4
	ITP-268	2.8
4/13/96	ITP-280	0.41
5/4/96	ITP-286	0.021

*Results through 4/13/96 were reported in Ref.1.

TABLE IX. Variability of Benzene Measurements

<u>Elapsed Time (days)</u>	<u>Location</u>	<u>Measured Benzene Concentration (g/kg)</u>	
		<u>Slurry A</u> (2.2 g/kg)*	<u>Slurry B</u> (10.8 g/kg)*
0	Laboratory	1.8, 2.3	6.1, 4.4
1	Laboratory	1.7, 2.2	10.9, 10.2
1	Shielded Cells	0.4	3.1
7	Shielded Cells	1.0	2.0
14	Shielded Cells	0.7, 0.8	4.0, 2.5

*The slurries were spiked with 2.2 and 10.8 grams of benzene per kg of slurry. The slurry density was 1.13 g/mL.

Subsequently, an experiment using simulated slurry was undertaken to estimate the variability associated with the method of analysis. The results of this test are shown in Table IX. A non-radioactive slurry simulating the Tank 48H composition (5 wt % KTPB and 3 M Na⁺ salt solution) was placed into two VDS bottles and spiked with 2.2 and 10.8 grams of benzene per kilogram of slurry. The spike was added via syringe through the rubber septum in the cap of each VDS bottle. After shaking briefly, the samples were analyzed. The samples were allowed to sit overnight at room temperature and were analyzed a second time on the following day. They were placed into the Shielded Cells and the procedure used on the Tank 48H samples initiated. The VDS bottles were kept in

the Shielded Cells and the analysis repeated one and two weeks later.

As can be seen from Table IX, the laboratory analysis for Slurry A (2.2 g/kg) was reasonably accurate both days. The average (2.0 g/kg) was within one standard deviation (0.3 g/kg, or 15%) of the expected value (2.2 g/kg). For Slurry B (10.8 g/kg), the first day's results were biased low by 50%, averaging 5.2 g/kg with a standard deviation of 1.2 g/kg (23%). The next day the results were excellent, with the average (10.6 g/kg) well within one standard deviation (0.5 g/kg, or 5%) of the expected value (10.8 g/kg). The reason for the poor result on the first day is not known, but suggests that the sample preparation method needs improvement.

The results of the analyses from the Shielded Cells samples are biased low. This is expected because the extra handling and sample preparation steps required for Shielded Cells samples provides more opportunities to lose benzene. Slurry A results were biased low by 67% (average 0.73 g/kg, standard deviation 38%) and the Slurry B results were biased low by 73% (average 2.9 g/kg, standard deviation 31%). The bias in the Shielded Cells method (compared to the laboratory method) indicates that about 64-65% of the benzene is lost through the extra steps.

The data suggests that the rate of loss of benzene from the VDS bottle is not very large (at these benzene concentrations). This result should be verified if improvements to the method significantly reduce the random error and bias.

The large bias in the test results suggest that the actual benzene concentration in the tank samples was three times higher than the values shown in Table VIII. This is not unreasonable. The samples were taken from an unstirred tank. Without stirring, the solids will either settle or rise to the surface and become more concentrated than if they were distributed evenly in tank. Since the benzene tends to associate with the solids, it will also become concentrated. Therefore, if a tank sample is taken from the zone containing the solids, the benzene concentration would be expected to be high relative to the tank average. Based on observations of small samples, concentrating by a factor of 3 through gravity settling is not unreasonable. This bias could be corrected if the average solids content of the tank is known and the solids content of the sample is measured. However, if the benzene is not evenly distributed in the solids then this correction may not be accurate either.

If the ability to accurately measure benzene concentrations in slurries is required, then the following actions are recommended. The first recommendation is applicable to

laboratory simulant measurements; the second to both laboratory and tank measurements, and the remainder are applicable to waste tank measurements.

- Improve the reliability of the benzene measurements in the laboratory.
 - Optimize sample size, container size, and method of stirring to promote benzene evaporation from the viscous slurry.
- Determine the benzene distribution in unstirred slurries in and the relationship to the solids content.
 - Results of a benzene distribution study may place a limit on the potential accuracy of the method.
- Determine the loss of benzene during VDS sampling operations.
 - Operation of the VDS sampler requires pouring slurry from the sampler into the VDS bottle. This allows evaporation of benzene. The magnitude of this loss needs to be measured.
- Decrease benzene losses from samples generated in the Shielded Cells.
 - The probable reasons for the low bias for Shielded Cells samples are the extra handling steps and time required to remove sample from the cell and then analyze in a radiohood.

Salt Solution Density

Salt solution density correlates well with the total salt concentration. Measuring the density is an easy and rapid method to estimate the sodium concentration in the tank. The relationship between salt concentration and solution density was reported previously for simulated waste solutions.⁷ Equations relating density to total sodium ion concentration were obtained for three anion distributions (average, high-nitrate, and high-hydroxide anion distributions). These equations are not accurate for the very high hydroxide composition in Tank 48H. Therefore, a new correlation was obtained based on the approximate Tank 48H composition shown in Table X. The simulant solution was prepared from reagent grade chemicals, weighed to accuracies better than 1%, and diluted in volumetric glassware accurate to $\pm 1\%$ err. Portions of the initial 5.2 M Na^+ solution were measured by weight and diluted in volumetric glassware to obtain the two dilutions at 2.7 and 1.52 molar Na^+ . The density of the dilutions and the correlation are shown in Table XI. With the correlation, the sodium concentration can be estimated from a density measurement quickly, and possibly more accurately, than by routine analytical methods. This method of estimating sodium concentration should be used

TABLE X. Tank 48H Simulant Composition

<u>Component</u>	<u>Concentration</u>
Na ⁺	5.25
OH ⁻	3.13
NO ₃ ⁻	0.60
NO ₂ ⁻	0.80
CO ₃ ²⁻	0.22
AlO ₂ ⁻	0.19
SO ₄ ²⁻	0.012
PO ₄ ³⁻	0.013
Cl ⁻	0.015
F ⁻	0.010
K ⁺	0.033

TABLE XI. Density of Tank 48H Simulant at 23°C

<u>Na⁺ (molar)</u>	<u>Density (g/mL)</u>
5.25	1.2093
3.71	1.1489
1.54	1.0646

Correlation: $\rho = 1.0045 + 0.03899[\text{Na}^+]$
 where ρ = density (g/mL)
 $[\text{Na}^+]$ = concentration of sodium ion (molar)

TABLE XII. Comparison of Predicted and Measured Sodium Concentrations in Tank 48H Solutions

<u>Date</u>	<u>Sample</u>	<u>Density (g/mL)</u>	<u>Na⁺ (molar)</u>	
			<u>Predicted</u>	<u>Measured*</u>
6/95	**	1.207	5.19	5.04±.59
10/7/95	ITP-161	1.203		
	ITP-162	1.204		
10/12/95	ITP-163	1.202		
	ITP-164	1.197		
	Average:	1.201±.003	5.04±.008	4.01±.07
12/1/95	ITP-208	1.160	3.99	4.01
6/28/96	ITP-311†	1.140	3.48	3.6±.1
	ITP-312			
	ITP-313			

*Measured by atomic absorption or emission spectroscopy.

**Based on samples taken prior to addition of NaTPB. See Reference 5.

†The three bottles were combined and a portion analyzed.

cautiously since changes in the anion distribution will change the density relationship. Table XII lists Tank 48H densities and measured sodium concentrations and compares them to predicted sodium concentrations. Inspection of the results shows that the equation agrees well with most of the measured values. The measured Na^+ value for the October 1995 sample (4.01 M) is probably low, since most evidence indicates that the initial batch concentration was 4.7 molar sodium. The previously reported high hydroxide correlation equation predicts 10% lower Na^+ concentrations.

The correlation of density to salt concentration suggests a potential application of this measurement to test for inadvertent dilution of samples. During the PVT-1 tests, three VDS bottles were found to contain diluted samples, presumably caused by VDS sampler operation.² Dilution was concluded from the results of several analyses, including phenol, nitrate, and nitrite. A measurement of density would also have corroborated the other results, or could have been used as a quality assurance test of the sample prior to submission for the other analyses. A 20% dilution is easily detected by the density measurement.

Changes in Cs-137 with Time

During April and May 1996, two Tank 48H sample sets had Cs-137 concentrations significantly higher than expected from recent trends in the tank. A graph of the data is shown in Figure 4. The results for ITP-278, ITP-279, ITP-285, and ITP-286 are significantly above the line defined by the previous and subsequent samples. The samples were tested in several ways to determine the origin of the high values. The tests and Cs-137 results are listed in Table XIII and they indicate the following.

- The initial high values were real and reproducible.
- The Cs-137 values decreased with time. Expected values were achieved after 1-2 weeks storage.
- The high values were not due to sample preparation or analytical variability.

The high Cs-137 concentrations were probably not due to contamination in the Shielded Cells. Contamination in the Shielded Cells is typically less than 1 nCi/g as shown by the blank sample from August 30 (Table I) and subsequent blanks taken during the PVT-1 tests.¹

The high Cs-137 concentrations were not due to adulteration of the sample. Dilution with water could cause high Cs-137 by dissolving some of the precipitate. Additional characterization of the first samples showing high Cs-137 (ITP-278 and ITP-279) indicated no dilution had occurred.¹

TABLE XIII. Cs-137 Concentrations

Action	ITP-278	ITP-279	Sample ITP-280	ITP-287	ITP-285	ITP-286
Date removed from Tk 48H	13-Apr	13-Apr	13-Apr	28-Apr	4-May	4-May
Date portion of slurry filtered (0.45 μ filter)	15-Apr	15-Apr		30-Apr	8-May	8-May
Cs-137 (nCi/g) initial gamma scan	308	380		186	289	432
repeat scan on same sample	308	379				
Date portion of slurry filtered (duplicates or triplicates, 0.45 μ)	3-May	3-May	3-May	3-May	10-May	10-May
Cs-137(nCi/g) (after one pass through filter)	181, 181	241, 239	192, 191, 190	184, 182	230	286
(after second pass through same filter)					241	299
Date portion of slurry filtered					14-May	14-May
Cs-137 (nCi/g) 0.45 μ filter					203	259
0.20 μ filter					202	258

Figure 4. Cs-137 Concentrations in Tank 48H Samples

The high values were initially postulated to be linked to extended pump operation. Excessive pump operation may produce submicron-sized particles that cannot be removed by the 0.45 micron filters used for sample preparation. However, after examining four sampling events, no clear correlation was found between high Cs-137 concentrations and pump operations. Subsequently the Tank 48H sampling procedure was changed so that pumps were always run immediately prior to sampling but the high Cs-137 values did not occur again. Attempts to improve filtration during sample preparation included passing the filtrate through the same filter a second time (the solids accumulated in the first pass could help filter finer particles during the second pass) and using a finer filter (0.2 micron instead of 0.45 micron pore size). Neither method decreased the Cs-137 concentration, but they were attempted on samples that were not far above the expected value.

This observation has not been adequately explained and cannot be further investigated with current tank samples since the phenomenon has not occurred again. If it occurs again, the following actions are recommended.

- Test finer filters (0.2 micron or smaller) on samples that are far above expected values.
- Test filtration with a cross-flow filter in the Shielded Cells to determine if the phenomenon will occur during plant operations.

If it is determined that this phenomenon could occur in the ITP facility and impact plant operations, then additional actions can be planned.

Cs-137/Total Cesium Ratio in Tank 48H

The ratio of Cs-137 to total cesium in Tank 48H is important in the evaluation of CsTPB solubility. Knowing the ratio, one can calculate the total cesium concentration in the supernate from a measurement of the Cs-137 gamma activity. The ratio of total cesium to Cs-137 was obtained by a combination of gamma spectroscopy and ICP-MS measurements on a dissolved slurry sample. Aliquots (1 mL) of the Tank 48H sample taken August 30, 1997 (ITP-370) were digested in nitric or in nitric/hydrofluoric acid and diluted with water. The results of the analyses are shown in Table XIV. The atom percentage of Cs-137 corresponds to waste with an average age of 35 years (assuming no Cs-133 has been introduced), which is not unreasonable for the mix of waste in Tank 48H.

Table XIV. Cesium Content of Tank 48H Slurry*

Digestion method	<u>Concentration in original slurry</u>	
	HNO ₃	HNO ₃ /HF
Cs-137 (Ci/L)	0.51	0.50
(mg/L) **	5.9	5.8
Cs-133 (mg/L) ***	13.7±.2	13.8±.5
Cs-137 (wt %)	30.1±.4	29.6±1.1
(atom %)	29.5±.4	29.0±1.1

*Based on analysis of Sample ITP-370, taken from Tank 48H on August 30, 1996.

**Calculated based on 0.01153 grams of Cs-137 per curie.

***Measured by ICP-MS.

CONCLUSIONS AND RECOMMENDATIONS

The major composition changes in Tank 48H between April and August 1996 were a slow increase in the Cs-137 and potassium concentrations, and a slow decrease in the phenylboronic acid (1PB) concentration.

An investigation of the precision of sampling and analytical methods show that most routine methods are reproducible to ±11%. A significant exception is 1PB which has a total variability of ±30%, but half of this variability is due to a downward trend in concentration over the duration of the experiment. Several trends due to delays in analysis were detected, but they were small and did not significantly effect the results except for 1PB and nitrite. Changes in sample composition during the time required for the free hydroxide analysis were identified and the problem was corrected.

The soluble copper concentration in Tank 48H between August and November 1996 varied between <.3 to 1.6 mg/L. Highly consistent results were obtained for samples analyzed on three occasions over a period of 15 months. The reason why the concentration varied in the tank samples is unresolved.

Weight percentage solids in Tank 48H averaged 2.30±.36 wt % in good agreement with an expected concentration of 2.7 wt %. There appears to be a -15% low bias in the method which could be corrected by additional work.

Benzene measurements on tank samples prepared in the Shielded Cells facility are biased low by 70% so the current method

predicts only the order of magnitude to the benzene concentration. Several means to improve the method are suggested.

The following are recommendations regarding the analytical methods.

- Routine analytical methods
 - No changes are recommended for the routine analytical methods for Cs-137, free hydroxide, nitrate, nitrite, boron, potassium, and phenol
- Phenylboronic acid
 - No changes in the analytical method are recommended, but delays between sampling and analysis should be considered since detectable changes in the concentration can occur over time. This recommendation also applies to measurements of tetraphenylborate, triphenylborane, and diphenylborinic acid.
- Copper
 - Further improvements to the copper method are not recommended at this time. However, it is recommended that copper concentrations in Tank 48H and simulant tests be monitored.
- Insoluble solids
 - The variability in this method can be reduced by improvements to both the sampling and analytical methods. The potential use and required accuracy of the method need to be defined before attempting improvements.
- Benzene
 - This method can be improved by optimizing the sample preparation method to promote benzene evaporation from the viscous slurry samples and by determining the benzene distribution on solids in unstirred slurries. These results are applicable to both laboratory simulant and Tank 48H samples.
 - Tank 48H sample results can be improved by eliminating (or quantifying) benzene losses during VDS sampling operations and sample preparation steps used in the Shielded Cells. These steps are recommended after establishing an accuracy requirement for tank benzene measurements

QUALITY ASSURANCE

The data in this report is recorded in the following technical notebooks WSRC-NB-95-023 (D. D. Walker) and WSRC-NB-96-613 (D. D. Walker).

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APPENDIX A

Description of Analytical Methods

Cesium-137

Cs-137 was measured by gamma spectroscopy counting methods using 3 mL samples. A high-purity germanium gamma spectroscopy system operated through a Canberrra Genie PC software interface was used for the analysis. The method is described in Manual L16.1, Procedure #ADS-2420.

Organic Compounds in Salt Solution

Phenylboronic acid (1PB) and phenol were measured by high performance liquid chromatography (HPLC) on a Hewlett Packard LC with a 2.1x250 mm Dychrom Chemosorb 5-ODS-UH column using acetonitrile-water eluent. The HPLC instrument methods are described in Manual L16.1, Procedure #ADS-2655. The methodology of sample preparation, standards, and standard preparation for HPLC analyses is described in SRT-ADS-96-0438.

Potassium and Sodium

Potassium and sodium ion concentrations were measured by flame atomic absorption using a Varian SpectrAA-400 spectrometer. Each sample is diluted 1:4 (sample:suppressant) in a suppressant solution of 2000 µg/mL cesium. For more concentrated samples, additional dilutions are made with 1600 µg/mL cesium. The method is described in Manual L16.1, Procedure #ADS-1549.

Boron and Aluminum

Boron and aluminum concentrations were measured by Inductively Coupled Plasma Emission Spectroscopy (ICPES) using an ARL 3580 instrument.

Copper

Copper concentrations were measured by Inductively Coupled Plasma Emission Spectroscopy (ICPES) using an ARL 3580 instrument. Samples were diluted 10X and acidified to a pH less than or equal to 2 using 5 wt % nitric acid. Spiked samples were analyzed with each sample to verify that there is no loss of copper. A 1000 mg/L copper standard purchased from High Purity, Inc. was used to prepare the spikes. The method is described in Manual L16.1, Procedure #ADS-1509 and in Reference 8.

Results from the ICPES method were verified by Inductively Coupled Plasma Mass Spectrometry (ICPMS) using a Fisons PQ1 instrument. Samples were diluted 100X and acidified to pH ≤ 2 using 0.6 wt % nitric acid. Spiked samples were analyzed with each sample as verification that there is no

loss of copper. A 1000 mg/L copper purchased from High Purity, Inc. was used to prepare the spikes. The method is described in Manual L16.1, Procedure #ADS-1551 and in Reference 8.

Nitrate and Nitrite Ion

Nitrate and nitrite concentrations were determined using ion chromatography. Samples were diluted to within linear calibration range (1-40 ppm) and eluted from a low capacity ion exchange resin column (AG4A/AS4A, Dionex) using carbonate/bicarbonate eluent. The instrument used was a Dionex Series 2000 Advanced Chromatography System with isocratic elution and conductivity detection. The method is described in Manual L16.1, Procedure #ADS-2306.

Free Hydroxide and Carbonate

Free hydroxide was measured by titration with 0.1 N HCl using a Radiometer VIT90 Autotitration System. The sample was first saturated with strontium chloride to precipitate the carbonate. The hydroxide was then measured by titration to an endpoint of pH 4. The method is described in Manual L16.1, Procedure #ADS-2256.

Weight Percentage Solids

Weight percentage solids were measured by gravimetric methods in the Shielded Cells. A slurry sample (5-10 g) was filtered through a preweighed filter paper (Whatman, fiberglass, 0.45 micron, 5.5 cm diameter), the solids washed with three 5 mL portions of water, and the filter paper dried to constant weight at 100 °C.

Benzene

In the Shielded Cells, a 1-mL aliquot of slurry from a VDS bottle was placed into a capped flask (~50 mL internal volume) and stirred to allow the benzene to evaporate. A 0.200 mL sample of the vapor space was removed through a septum using a locking syringe. The syringe was locked (closed), removed from the Shielded Cells, and taken to a radiohood. The syringe contents were emptied into a septum vial (~60 mL internal volume). Samples from the septum vial were injected into a gas chromatograph to measure the benzene concentration. The instrument was an HNU Model 301 gas chromatograph with 10.2 eV photoionization detector and 1/8 inch x 3 ft long column packed with 3 wt % SP-2100 on Chromosorb 120/140 (Whatman, Co.). The gas chromatograph was calibrated daily with standards obtained from Scott Specialty Gases. The methods used are described in Manual L12.1, Procedure ITP-006, Rev.3 12/20/94 (calibration) and Procedure ITP-OP-005, Rev.3, 12/20/94 (operation).

APPENDIX B

Statistical Analysis of Tank 48H Variability Study

OVERVIEW OF TANK 48H DATA

Samples of Tank 48H slurry have been taken and analyzed. Three dip bottles were taken on the following dates as indicated:

Sample ID	Date	Coded ID
ITP-356	8/05/96	A
ITP-359	8/10/96	B
ITP-361	8/11/96	C

Over time, each of these three samples was subsampled on three occasions, denote these as Day 0, Day 6 and Day 12. Two subsamples were taken on each of these three occasions for each of the three samples. Measurements were made for several analytes on each of these subsamples. The resulting data for the analytes of interest are presented in Table 1.

Table 1: Analytical Results from Tank 48H Samples

Sample	Day	Sampling Order	Analytical Order	Cs-137 (nCi/mL)	Free OH (molar)	B (molar)	Nitrate (molar)	Nitrite (molar)	K (mmolar)	Phenol (molar)	IPB (mmolar)
B	0	1	3	374	1.40	0.04561	0.42	0.59	0.1450	0.01506	1.157
A	0	2	2	356	1.42	0.04117	0.43	0.60	0.1350	0.01411	1.034
B	0	3	6	369	1.20	0.04302	0.43	0.61	0.1394	0.01419	1.148
C	0	4	1	367	1.42	0.04033	0.41	0.57	0.1445	0.01360	0.861
A	0	5	5	355	1.29	0.04246	0.43	0.60	0.1381	0.01428	1.132
C	0	6	4	371	1.27	0.03996	0.40	0.57	0.1389	0.01355	1.140
B	6	1	3	400	1.52	0.04283	0.41	0.50	0.1509	0.01424	0.681
C	6	2	4	397	1.19	0.04006	0.38	0.46	0.1448	0.01361	0.763
C	6	3	6	467	1.12	0.03987	0.39	0.48	0.1601	0.01332	0.829
A	6	4	1	399	1.60	0.04311	0.39	0.48	0.1483	0.01431	0.574
B	6	5	5	386	1.39	0.04246	0.41	0.50	0.1494	0.01422	0.599
A	6	6	2	391	1.44	0.04181	0.40	0.49	0.1494	0.01424	0.574
C	12	1	5	391	1.31	0.04098	0.42	0.50	0.1402	0.01306	0.648
B	12	2	2	392	1.41	0.04533	0.43	0.54	0.1394	0.01408	0.714
A	12	3	1	401	1.56	0.04274	0.44	0.51	0.1361	0.01372	0.714
A	12	4	3	391	1.47	0.04283	0.43	0.51	0.1350	0.01388	0.689
B	12	5	4	385	1.31	0.04385	0.43	0.52	0.1427	0.01394	0.755
C	12	6	6	392	1.17	0.04228	0.40	0.50	0.1422	0.01313	0.673

OBJECTIVE OF THE STATISTICAL ANALYSES

The objective of these statistical analyses is to investigate the variation (and its sources) for the data of Table 1. The repeated measurements (over time) and replicate samples provide an opportunity for investigating a number of interesting questions. These questions and their answers are addressed in this appendix of the report.

What are the sources of significant variation in these results? To answer this question, the data for each analyte of Table 1 were analyzed against a random effects model. Experiments conducted to diagnose sources of variability in a laboratory method or in a manufacturing process often use a random effects model. A factor such as time could influence an analyte's measurements in a fixed or random manner. Time would be considered a fixed factor for an analyte if there were a consistent (for each of the three samples) trend in the analyte's measurements over time. If the analyte's measurements

varied over time, but in more of a random fashion, then time would be considered to have a random effect. For each analyte, the type of effect anticipated for a factor influences the assumptions and interpretation of the term for this factor in the statistical model for this analyte's measurements.

The random effects model for each analyte of interest is given by

$$y_{ijk} = \mu + \alpha_i + \beta_{j|i} + \epsilon_{k(ij)} \quad (1)$$

where

$i=1, 2, \text{ and } 3$ (the sample index, corresponding to coded sample ID's A, B, and C),

$j=1, 2, \text{ and } 3$ (the time index, corresponding to Day 0, Day 6, and Day 12),

$k=1 \text{ and } 2$ (the measurement index, corresponding to the two replicates),

y_{ijk} is the k^{th} measurement for the given analyte at time j on sample i ,

μ is the true underlying analyte value for the tank,

α_i is the random effect attributable to the i^{th} sample,

$\beta_{j|i}$ is the random effect attributable to the j^{th} time for the i^{th} sample, and

$\epsilon_{k(ij)}$ is the residual random effect (due to analytical/measurement errors) attributable with the k^{th} measurement at time j on sample i .

For this model, each term present (except for μ) is considered as a random variable (i.e., all of the factors are considered as random effects) with a zero mean and a constant variance. These random variables are assumed to be independent, and each is usually assumed to follow a normal probability distribution. Let the variances due to sample, time, and residual variation be denoted by σ_s^2 , σ_t^2 , and σ^2 , respectively. The objective of this analysis is to estimate each of these sigmas which will lead to an understanding of the errors associated with estimating μ .

The statistical model given in (1) was estimated for each of the thirteen analytes using JMP® [1]. Portions of the JMP output are provided in Exhibits 1-7 at the end of this appendix.

This information has been summarized and expanded in Table 2 below.

Table 2. Summary Information Derived from Random Effects Models for Analytes

Analyte	Mean		Number of Obs.	95% Confidence Interval for the Mean	
	Mean	Sum of Squares		Lower Limit	Upper Limit
Cs-137 (nCi/mL)	388	413.167	18	367.4	408.6
Free OH (molar)	1.361	0.07097	18	1.091	1.631
B (molar)	0.04226	0.00002	18	0.038	0.047
Nitrate (molar)	0.4139	0.00087	18	0.384	0.444
Nitrite (molar)	0.5294	0.00317	18	0.472	0.586
K (mmolar)	0.143294	0.00004	18	0.137	0.150
Phenol (molar)	0.013919	0.00000137	18	0.013	0.015
IPB (mmolar)	0.815787	0.00476	18	0.746	0.886

Analyte	Components of Variation Variance			
	Sample	Day	Residual	Total
Cs-137 (nCi/mL)	15.88248	386.1325	317.8718	719.88678
Free OH (molar)	0.009631	0	0.013185	0.022816
B (molar)	0.000003	3.17E-07	8.03E-07	0.00000412
Nitrate (molar)	0.000136	0.000219	0.000057	0.000412
Nitrite (molar)	0.000217	0.002939	0.000072	0.003228
K (mmolar)	0.000004	0.000037	0.000014	0.000055
Phenol (molar)	2.201E-07	5.795E-08	4.45E-08	3.2255E-07
IPB (mmolar)	0	0.050511	0.00935	0.059861

Analyte	Components of Variation % of Total Variance				Components of Variation % Relative Standard Deviation			
	Sample	Day	Residual	Total	Sample	Day	Residual	Total
Cs-137 (nCi/mL)	2.2%	53.6%	44.2%	100%	1.0%	5.1%	4.6%	6.9%
Free OH (molar)	42.2%	0.0%	57.8%	100%	7.2%	0.0%	8.4%	11.1%
B (molar)	72.8%	7.7%	19.5%	100%	4.1%	1.3%	2.1%	4.8%
Nitrate (molar)	33.0%	53.2%	13.8%	100%	2.8%	3.6%	1.8%	4.9%
Nitrite (molar)	6.7%	91.0%	2.2%	100%	2.8%	10.2%	1.6%	10.7%
K (mmolar)	7.3%	67.3%	25.5%	100%	1.4%	4.2%	2.6%	5.2%
Phenol (molar)	68.2%	18.0%	13.8%	100%	3.4%	1.7%	1.5%	4.1%
IPB (mmolar)	0.0%	84.4%	15.6%	100%	0.0%	27.5%	11.9%	30.0%

- indicates that variation from this source is not significant at the 5% level

Specifically, a 95% confidence interval for the mean Tank 48H value of each analyte is computed as well as the components of variation of the data in Table 1. These components of variation are presented as (estimated) variances (the estimates of σ_s^2 , σ_d^2 , and σ_r^2) and as percent relative (to the mean) standard deviations. The variance from each source (sample, day and residual) is also expressed as a percentage of the total variance. Table 2 provides an opportunity for a number of insights into the analytical measurements from Tank 48H. First of all, sample to sample variation is statistically

significant for five of the eight analytes. The largest % relative standard (%RSD) for the sample variation is that for Free OH which is 7.2% --- all others have a %RSD less than 4.1%. Secondly, variation due to time (when it is considered as a random effect, denoted by the factor "Day") is statistically significant for all analytes except Free OH and B. The three largest %RSD's due to "Day" variation are 27.5% (IPB), 10.2% (Nitrite), and 5.1% (Cs-137). The %RSD's due to time for the other analytes are all less than 4.2%. Finally, the two largest %RSD's for the residual variation (due to subsampling, preparation, and measurement) are 11.9% (IPB) and 8.4% (Free OH). The % RSD's due to residual variation for the other analytes are all less than 4.6%. Note that this residual variation is a measure of the reproducibility of the analytical derivations from a sample bottle.

Table 2 also shows the total variation and provides a breakdown of the total variance as a percentage contribution from each of the factors: sample, day, and residual. These variances are used to determine 95% confidence intervals for the mean value of each analyte for Tank 48H. In decreasing sequence, the uncertainties of the analytes mean values, expressed as a $\pm$ %, are:

Relative Uncertainties in the Average Measurement at a 95% Confidence Level

19.8%	11.9%	10.8%	8.6%	7.2%	7.1%	5.3%	4.9%
Free OH	B	Nitrite	IPB	Nitrate	Phenol	Cs-137	K

In the discussion above, the time factor (denoted by the variable "Day") was considered as a random factor; let's now turn our attention to the question of possible systematic effects (specifically, trends) between time and these analytical measurements. Exhibits 5-19 provide analyses for time trends considering each of the three samples individually. There are no analytes for which a significant (at the 5% level) time trend is seen in these analyses.

In the analysis just discussed, each sample was investigated individually. At each point in time (i. e., Day 0, 6, and 12), variations are introduced into the analytical and measurement procedures from a number of sources that may influence all (three samples and replicate) determinations on that day for a particular analyte. One such source is the calibration of the instrumentation. Variation from this source may cause the results for a given day to track higher or lower than the results from a previous or later day; thus, the data across the three samples may not be independent for any given day.

If this possibility is ignored and the data across the samples are assumed independent, a different model may be fitted. This model relates each analyte to two fixed-effect variables: sample and day. The results of fitting this model to the analyte measurements are presented in Exhibit 13- 16 at the end of this appendix.

One or both of these effects are statistically significant at the 5% level for the following analytes:

Analyte	Sample Effect			Day Effect
	A	B	C	
Free OH (molar)	0.065	-.027	-.038	0.0032
B (molar)	-0.000468	0.001028	-0.0005602	ns
Nitrite (molar)	ns	ns	ns	-0.006
Phenol (molar)	-8.5e-6	1.9e-4	-1.8e-4	-4.1e-5
1PB (mmolar)	ns	ns	ns	-0.032
ns - indicates not significant at the 5% level				

The significant "Day" effect for 1PB indicates that the concentration of this analyte may be decreasing over time. This may help explain the large variance from the "Day" component in Table 2 for 1PB. The root mean square error (RMSE) of 0.1495 mmolar for the 1PB analysis presented in Figure 16 provides an estimate of the random variation affecting the 1PB measurements after accounting for this trend over time.

As a final point of interest, the analytical order in which the measurements were generated was investigated. Figure 17 at the end of this appendix provides a chart of the measurements for each analyte in analytical sequence. One point regarding these charts is worth mentioning. The Free OH (molar concentration) chart reveals a statistically significant decreasing sequence when plotted in analytical order.

References

- [1] SAS Institute, JMP®: Statistics and Graphics Guide, Version 3.0, SAS Institute, Inc., Cary, NC, 1994.

Exhibit 1. Random Effects Model Evaluation for Cs-137 and Free OH**Cs-137 (nCi/mL)****Summary of Fit**

RSquare	0.595978
Root Mean Square Error	17.82896
Mean of Response	388
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	4	1456.3333	364.083	1.2245
Pure Error	9	2676.0000	297.333	Prob>F
Total Error	13	4132.3333		0.3659

Variance Component Estimates

Component	Var Comp Est
Sample	15.88248
Day	386.1325
Residual	317.8718

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob>F
Sample	826.333	413.167	2	1.2998	0.3058
Day	5269.33	2634.67	2	8.2885	0.0048

Free OH (molar)**Summary of Fit**

RSquare	0.464516
Root Mean Square Error	0.114826
Mean of Response	1.360556
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	4	0.08915556	0.022289	2.4389
Pure Error	9	0.08225000	0.009139	Prob>F
Total Error	13	0.17140556		0.1227

Variance Component Estimates

Component	Var Comp Est
Sample	0.009631
Day	-0.00164
Residual	0.013185

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob>F
Sample	0.14194	0.07097	2	5.3828	0.0198
Day	0.00674	0.00337	2	0.2558	0.7781

Exhibit 2. Random Effects Model Evaluation for B and Nitrate

B (molar)

Summary of Fit

RSquare	0.782425
RSquare Adj	0.715479
Root Mean Square Error	0.000896
Mean of Response	0.04226
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	4	0.00000331	8.287e-7	1.0468
Pure Error	9	0.00000712	7.916e-7	Prob>F
Total Error	13	0.00001044		0.4353

Variance Component Estimates

Component	Var Comp Est
Sample	0.000003
Day	3.171e-7
Residual	8.03e-7

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob>F
Sample	0.00003	0.00002	2	20.0053	0.0001
Day	5.41e-6	2.71e-6	2	3.3694	0.0662

Nitrate (molar)

Summary of Fit

RSquare	0.858667
Root Mean Square Error	19.85245
Mean of Response	1309.889
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	4	1008.5556	252.139	0.5515
Pure Error	9	4115.0000	457.222	Prob>F
Total Error	13	5123.5556		0.7032

Variance Component Estimates

Component	Var Comp Est
Sample	1949.434
Day	513.2115
Residual	394.1197

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob>F
Sample	24181.4	12090.7	2	30.6778	0.0000
Day	6946.78	3473.39	2	8.8130	0.0038

Exhibit 3. Random Effects Model Evaluation for Nitrite and K

Nitrite (molar)

Summary of Fit

RSquare	0.975984
Root Mean Square Error	0.008498
Mean of Response	0.529444
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	4	0.00028889	0.000072	1.0000
Pure Error	9	0.00065000	0.000072	Prob>F
Total Error	13	0.00093889		0.4558

Variance Component Estimates

Component	Var Comp Est
Sample	0.000217
Day	0.002939
Residual	0.000072

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob>F
Sample	0.00274	0.00137	2	19.0000	0.0001
Day	0.03541	0.01771	2	245.1538	0.0000

K (mmolar)

Summary of Fit

RSquare	0.755807
RSquare Adj	0.680671
Root Mean Square Error	0.003685
Mean of Response	0.143294
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	4	0.00001257	0.000003	0.1726
Pure Error	9	0.00016395	0.000018	Prob>F
Total Error	13	0.00017652		0.9470

Variance Component Estimates

Component	Var Comp Est
Sample	0.000004
Day	0.000037
Residual	0.000014

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob>F
Sample	0.00008	0.00004	2	2.9676	0.0868
Day	0.00047	0.00023	2	17.1507	0.0002

Exhibit 4. Random Effects Model Evaluation for Phenol and 1PB**Phenol (molar)****Summary of Fit**

RSquare	0.858667
RSquare Adj	0.815181
Root Mean Square Error	0.000211
Mean of Response	0.013919
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	4	0.00000011	2.847e-8	0.5515
Pure Error	9	0.00000046	5.162e-8	Prob>F
Total Error	13	0.00000058		0.7032

Variance Component Estimates

Component	Var Comp Est
Sample	2.201e-7
Day	5.795e-8
Residual	4.45e-8

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob>F
Sample	2.73e-6	1.37e-6	2	30.6778	<.0001
Day	7.84e-7	3.92e-7	2	8.8130	0.0038

1PB (mmolar)**Summary of Fit**

RSquare	0.839196
RSquare Adj	0.789718
Root Mean Square Error	0.096696
Mean of Response	0.815787
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	4	0.07081089	0.017703	3.1399
Pure Error	9	0.05074157	0.005638	Prob>F
Total Error	13	0.12155246		0.0711

Variance Component Estimates

Component	Var Comp Est
Sample	-0.00077
Day	0.050511
Residual	0.00935

Tests wrt Random Effects

Source	SS	MS Num	DF Num	F Ratio	Prob>F
Sample	0.00952	0.00476	2	0.5090	0.6126
Day	0.62483	0.31242	2	33.4129	<.0001

Exhibit 5. Time Effects for Cs-137 Across the Three Samples

Linear Fit Sample=A: Summary of Fit

$$\text{Mean}(\text{Cs-137 (nCi/mL)}) = 361.917 + 3.375 \text{ Day}$$

RSquare 0.768507
Root Mean Square Error 15.71756
Mean of Response 382.1667
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	361.91667	14.3481	25.22	0.0252
Day	3.375	1.852332	1.82	0.3196

Linear Fit Sample=B: Summary of Fit

$$\text{Mean}(\text{Cs-137 (nCi/mL)}) = 375.833 + 1.41667 \text{ Day}$$

RSquare 0.561892
Root Mean Square Error 10.61446
Mean of Response 384.3333
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	375.83333	9.689628	38.79	0.0164
Day	1.4166667	1.250926	1.13	0.4605

Linear Fit Sample=C: Summary of Fit

$$\text{Mean}(\text{Cs-137 (nCi/mL)}) = 386.25 + 1.875 \text{ Day}$$

RSquare 0.124172
Root Mean Square Error 42.2537
Mean of Response 397.5
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	386.25	38.57217	10.01	0.0634
Day	1.875	4.979646	0.38	0.7707

Exhibit 6. Time Effects for Free OH Across the Three Samples

Linear Fit Sample=A: Summary of Fit

$$\text{Mean(Free OH (molar))} = 1.38333 + 0.01333 \text{ Day}$$

RSquare	0.726585
Root Mean Square Error	0.069402
Mean of Response	1.463333
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	1.383333	0.063355	21.83	0.0291
Day	0.013333	0.008179	1.63	0.3503

Linear Fit Sample=B: Summary of Fit

$$\text{Mean(Free OH (molar))} = 1.34167 + 0.005 \text{ Day}$$

RSquare	0.14734
Root Mean Square Error	0.102062
Mean of Response	1.371667
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	1.3416667	0.093169	14.40	0.0441
Day	0.005	0.012028	0.42	0.7492

Linear Fit Sample=C: Summary of Fit

$$\text{Mean(Free OH (molar))} = 1.29917 - 0.00875 \text{ Day}$$

RSquare	0.304278
Root Mean Square Error	0.112268
Mean of Response	1.246667
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	1.2991667	0.102486	12.68	0.0501
Day	-0.00875	0.013231	-0.66	0.6280

Exhibit 7. Time Effects for B Across the Three Samples

Linear Fit Sample=A: Summary of Fit

$$\text{Mean(B (molar))} = 0.04187 + 0.00008 \text{ Day}$$

RSquare 0.964286
Root Mean Square Error 0.000132
Mean of Response 0.042353
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0418671	0.000121	346.97	0.0018
Day	0.0000809	0.000016	5.20	0.1210

Linear Fit Sample=B: Summary of Fit

$$\text{Mean(B (molar))} = 0.04371 + 0.00002 \text{ Day}$$

RSquare 0.017442
Root Mean Square Error 0.001473
Mean of Response 0.043848
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0437095	0.001345	32.51	0.0196
Day	0.0000231	0.000174	0.13	0.9157

Linear Fit Sample=C: Summary of Fit

$$\text{Mean(B (molar))} = 0.03984 + 0.00012 \text{ Day}$$

RSquare 0.657534
Root Mean Square Error 0.000755
Mean of Response 0.04058
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0398397	0.00069	57.78	0.0110
Day	0.0001233	0.000089	1.39	0.3980

Exhibit 8. Time Effects for Nitrate Across the Three Samples **Linear Fit Sample=A:
Summary of Fit**

$$\text{Mean(Nitrate (molar))} = 0.4175 + 0.00042 \text{ Day}$$

RSquare	0.013158
Root Mean Square Error	0.030619
Mean of Response	0.42
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.4175	0.027951	14.94	0.0426
Day	0.0004167	0.003608	0.12	0.9268

**Linear Fit Sample=B:
Summary of Fit**

$$\text{Mean(Nitrate (molar))} = 0.41917 + 0.00042 \text{ Day}$$

RSquare	0.057692
Root Mean Square Error	0.014289
Mean of Response	0.421667
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.4191667	0.013044	32.14	0.0198
Day	0.0004167	0.001684	0.25	0.8456

**Linear Fit Sample=C:
Summary of Fit**

$$\text{Mean(Nitrate (molar))} = 0.3975 + 0.00042 \text{ Day}$$

RSquare	0.035714
Root Mean Square Error	0.018371
Mean of Response	0.4
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.3975	0.016771	23.70	0.0268
Day	0.0004167	0.002165	0.19	0.8790

Exhibit 9. Time Effects for Nitrite Across the Three Samples

Linear Fit Sample=A: Summary of Fit

$$\text{Mean(Nitrite (molar))} = 0.57667 - 0.0075 \text{ Day}$$

.RSquare	0.553531
Root Mean Square Error	0.057155
Mean of Response	0.531667
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.5766667	0.052175	11.05	0.0574
Day	-0.0075	0.006736	-1.11	0.4659

Linear Fit Sample=B: Summary of Fit

$$\text{Mean(Nitrite (molar))} = 0.57833 - 0.00583 \text{ Day}$$

RSquare	0.46519
Root Mean Square Error	0.053072
Mean of Response	0.543333
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.5783333	0.048448	11.94	0.0532
Day	-0.005833	0.006255	-0.93	0.5222

Linear Fit Sample=C: Summary of Fit

$$\text{Mean(Nitrite (molar))} = 0.54833 - 0.00583 \text{ Day}$$

RSquare	0.46519
Root Mean Square Error	0.053072
Mean of Response	0.513333
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.5483333	0.048448	11.32	0.0561
Day	-0.005833	0.006255	-0.93	0.5222

Exhibit 10. Time Effects for K Across the Three Samples **Linear Fit Sample=A:
Summary of Fit**

$$\text{Mean(K (mmolar))} = 0.14084 - 0.00009 \text{ Day}$$

RSquare	0.004777
Root Mean Square Error	0.010441
Mean of Response	0.140324
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.1408355	0.009531	14.78	0.0430
Day	-0.000085	0.00123	-0.07	0.9560

**Linear Fit Sample=B:
Summary of Fit**

$$\text{Mean(K (mmolar))} = 0.14503 - 0.0001 \text{ Day}$$

RSquare	0.013551
Root Mean Square Error	0.006943
Mean of Response	0.144459
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.1450341	0.006338	22.88	0.0278
Day	-0.000096	0.000818	-0.12	0.9257

**Linear Fit Sample=C:
Summary of Fit**

$$\text{Mean(K (mmolar))} = 0.14535 - 0.00004 \text{ Day}$$

RSquare	0.00162
Root Mean Square Error	0.008979
Mean of Response	0.145098
Observations (or Sum Wgts)	3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.1453538	0.008197	17.73	0.0359
Day	-0.000043	0.001058	-0.04	0.9744

Exhibit 11. Time Effects for Phenol Across the Three Samples

Linear Fit Sample=A: Summary of Fit

$$\text{Mean(Phenol (molar))} = 0.01429 - 0.00003 \text{ Day}$$

RSquare 0.604839
Root Mean Square Error 0.000228
Mean of Response 0.01409
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0142891	0.000208	68.73	0.0093
Day	-0.000033	0.000027	-1.24	0.4328

Linear Fit Sample=B: Summary of Fit

$$\text{Mean(Phenol (molar))} = 0.01459 - 0.00005 \text{ Day}$$

RSquare 0.973285
Root Mean Square Error 0.000072
Mean of Response 0.014286
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.014592	0.000065	223.32	0.0029
Day	-0.000051	0.000008	-6.04	0.1045

Linear Fit Sample=C: Summary of Fit

$$\text{Mean(Phenol (molar))} = 0.01362 - 0.00004 \text{ Day}$$

RSquare 0.906716
Root Mean Square Error 0.000108
Mean of Response 0.01338
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0136188	0.000099	137.56	0.0046
Day	-0.00004	0.000013	-3.12	0.1976

Exhibit 12. Time Effects for 1PB Across the Three Samples

Linear Fit Sample=A:
Summary of Fit

$$\text{Mean(IPB (mmolar))} = 0.97689 - 0.03179 \text{ Day}$$

RSquare 0.519231
Root Mean Square Error 0.259551
Mean of Response 0.786164
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.9768936	0.236936	4.12	0.1515
Day	-0.031788	0.030588	-1.04	0.4878

Linear Fit Sample=B:
Summary of Fit

$$\text{Mean(IPB (mmolar))} = 1.05141 - 0.03486 \text{ Day}$$

RSquare 0.58762
Root Mean Square Error 0.247829
Mean of Response 0.84222
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	1.0514083	0.226236	4.65	0.1349
Day	-0.034865	0.029207	-1.19	0.4439

Linear Fit Sample=C:
Summary of Fit

$$\text{Mean(IPB (mmolar))} = 0.9892 - 0.02837 \text{ Day}$$

RSquare 0.986209
Root Mean Square Error 0.028467
Mean of Response 0.818977
Observations (or Sum Wgts) 3

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.9891988	0.025987	38.07	0.0167
Day	-0.02837	0.003355	-8.46	0.0749

Exhibit 13. Sample and Time Effects for Cs-137 and Free OH

Tank 48 Samples(Analyte=Cs-137 (nCi/mL)) Summary of Fit

RSquare	0.289369
Root Mean Square Error	22.78523
Mean of Response	388
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	4592.3333	918.467	3.0890
Pure Error	9	2676.0000	297.333	Prob>F
Total Error	14	7268.3333		0.0675

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	374.66667	8.491554	44.12	<.0001
Sample[A-C]	-5.833333	7.595076	-0.77	0.4552
Sample[B-C]	-3.666667	7.595076	-0.48	0.6367
Day	2.2222222	1.096255	2.03	0.0621

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Sample	2	2	826.3333	0.7958	0.4706
Day	1	1	2133.3333	4.1091	0.0621

Tank 48 Samples(Analyte=Free OH (molar))

Summary of Fit

RSquare	0.457217
Root Mean Square Error	0.111401
Mean of Response	1.360556
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	0.09149167	0.018298	2.0022
Pure Error	9	0.08225000	0.009139	Prob>F
Total Error	14	0.17374167		0.1723

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	1.3413889	0.041517	32.31	<.0001
Sample[A-C]	0.1027778	0.037134	2.77	0.0151
Sample[B-C]	0.0111111	0.037134	0.30	0.7692
Day	0.0031944	0.00536	0.60	0.5607

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Sample	2	2	0.14194444	5.7189	0.0153
Day	1	1	0.00440833	0.3552	0.5607

Exhibit 14. Sample and Time Effects for B and Nitrate**Tank 48 Samples(Analyte=B (molar)) Summary of Fit**

RSquare	0.72138
Root Mean Square Error	0.000977
Mean of Response	0.04226
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	0.00000624	0.000001	1.5775
Pure Error	9	0.00000712	7.916e-7	Prob>F
Total Error	14	0.00001337		0.2600

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0418054	0.000364	114.80	<.0001
Sample[A-C]	0.0000925	0.000326	0.28	0.7806
Sample[B-C]	0.001588	0.000326	4.88	0.0002
Day	0.0000758	0.000047	1.61	0.1292

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Sample	2	2	0.00003213	16.8239	0.0002
Day	1	1	0.00000248	2.5998	0.1292

Tank 48 Samples(Analyte=Nitrate (molar)) Summary of Fit

RSquare	0.348034
Root Mean Square Error	0.015603
Mean of Response	0.413889
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	0.00295833	0.000592	11.8333
Pure Error	9	0.00045000	0.000050	Prob>F
Total Error	14	0.00340833		0.0010

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.4113889	0.005815	70.75	<.0001
Sample[A-C]	0.0061111	0.005201	1.17	0.2596
Sample[B-C]	0.0077778	0.005201	1.50	0.1570
Day	0.0004167	0.000751	0.56	0.5876

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Sample	2	2	0.00174444	3.5827	0.0554
Day	1	1	0.00007500	0.3081	0.5876

Exhibit 15. Sample and Time Effects for Nitrite and K

Tank 48 Samples(Analyte=Nitrite (molar)) Summary of Fit

RSquare	0.521245
Root Mean Square Error	0.036564
Mean of Response	0.529444
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	0.01806667	0.003613	50.0308
Pure Error	9	0.00065000	0.000072	Prob>F
Total Error	14	0.01871667		<.0001

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.5677778	0.013626	41.67	<.0001
Sample[A-C]	0.0022222	0.012188	0.18	0.8579
Sample[B-C]	0.0138889	0.012188	1.14	0.2736
Day	-0.006389	0.001759	-3.63	0.0027

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Sample	2	2	0.00274444	1.0264	0.3837
Day	1	1	0.01763333	13.1897	0.0027

Tank 48 Samples(Analyte=K (mmolar)) Summary of Fit

RSquare	0.114812
Root Mean Square Error	0.006761
Mean of Response	0.143294
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	0.00047594	0.000095	5.2253
Pure Error	9	0.00016395	0.000018	Prob>F
Total Error	14	0.00063989		0.0159

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.1437411	0.00252	57.05	<.0001
Sample[A-C]	-0.00297	0.002254	-1.32	0.2087
Sample[B-C]	0.0011651	0.002254	0.52	0.6132
Day	-0.000075	0.000325	-0.23	0.8219

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Sample	2	2	0.00008059	0.8816	0.4359
Day	1	1	0.00000240	0.0526	0.8219

Exhibit 16. Sample and Time Effects for Phenol and 1PB**Tank 48 Samples(Analyte=Phenol (molar)) Summary of Fit**

RSquare	0.847263
Root Mean Square Error	0.000211
Mean of Response	0.013919
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	0.00000016	3.211e-8	0.6220
Pure Error	9	0.00000046	5.162e-8	Prob>F
Total Error	14	0.00000063		0.6875

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	0.0141666	0.000079	179.89	<.0001
Sample[A-C]	0.0001712	0.00007	2.43	0.0291
Sample[B-C]	0.0003678	0.00007	5.22	0.0001
Day	-0.000041	0.00001	-4.06	0.0012

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Sample	2	2	0.00000273	30.5707	<.0001
Day	1	1	0.00000074	16.5192	0.0012

Tank 48 Samples(Analyte=1PB (mmolar)) Summary of Fit

RSquare	0.585961
Root Mean Square Error	0.149517
Mean of Response	0.815787
Observations (or Sum Wgts)	18

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	0.26223210	0.052446	9.3024
Pure Error	9	0.05074157	0.005638	Prob>F
Total Error	14	0.31297367		0.0023

Parameter Estimates

Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	1.0058336	0.055722	18.05	<.0001
Sample[A-C]	-0.029624	0.049839	-0.59	0.5617
Sample[B-C]	0.0264333	0.049839	0.53	0.6042
Day	-0.031674	0.007194	-4.40	0.0006

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Sample	2	2	0.00951872	0.2129	0.8108
Day	1	1	0.43341200	19.3875	0.0006

Exhibit 17. Analyte Measurements in Analytical Sequence

Cs-137 (nCi/mL) By Analytical Order

Free OH (molar) By Analytical Order

B (molar) By Analytical Order

Nitrate (molar) By Analytical Order

Nitrite (molar) By Analytical Order

K (mmolar) By Analytical Order

**Exhibit 17. Analyte Measurements in Analytical Sequence
(Continued)**

Phenol (molar) By Analytical Order

IPB (mmolar) By Analytical Order

Keywords: In-Tank Process, Benzene

Retention: Permanent

CC: D. B. Amerine, 704-56H
K. Andringa, 773-41A
J. L. Barnes, 704-S
M. J. Barnes, 773-A
A. L. Blancett, 773-A
W. T. Boyce, 773-A
T. E. Britt, 732-B
B. T. Butcher, 773-43A
J. T. Carter, 704-25S
G. L. Cauthen, 241-119H
W. C. Clark, 704-56H
P. F. Cloessner, 773-A
C. J. Coleman, 773-43A
C. L. Crawford, 773-41A
D. P. Diprete, 773-41A
D. E. Doughty, 704-56H
L. O. Dworjany, 779-2A
S. J. Eberlein, 704-56H
T. B. Edwards, 773-42A
A. A. Ekechukwu, 773-A
H. H. Elder, 704-S
T. J. Fiske, 241-120H
J. R. Fowler, 704-Z
F. R. Graham, 773-A
J. C. Griffin, 773-A
M. S. Hay, 773-A
M. J. Hitchler, 730-2B
D. T. Hobbs, 773-A
E. W. Holtzscheiter, 773-A
C. W. Hsu, 773-A
M. L. Hyder, 773-A
R. A. Jacobs, 704-T
M. D. Johnson, 704-56H
M. T. Keefer, 704-56H
E. A. Kyser, 773-A
L. F. Landon, 704-T
T. J. Lex, 719-4A
L. S. Livingston, 703-H
P. E. Lowe, 773-41A
J. C. Marek, 704-T
D. J. McCabe, 773-43A
J. D. Menna, 730-2B
M. S. Miller, 704-56H
M. J. Montini, 704-56H
J. P. Morin, 719-4A
C. A. Nash, 676-1T
L. M. Nelson, 773-43A
L. M. Papouchado, 773-A
R. A. Peterson, 773-A
S. F. Peterson, 773-41A
C. T. Randall, 704-T
P. L. Rutland, 242-152H
R. M. Satterfield, 719-4A
W. E. Stevens, 773-A
P. C. Suggs, 703-H
R. F. Swingle, 773-A
W. L. Tamosaitis, 773-A
M. C. Thompson, 773-A
L. L. Tovo, 773-A
R. C. Tuckfield, 773-42A
W. B. VanPelt, 676-1T
D. D. Walker, 773-A
M. J. Whitaker, 773-A
A. W. Wiggins, 241-152H
W. R. Wilmarth, 773-42A
A. L. Wooten, 732-B
G. T. Wright, 773-A
TIM, 703-43A
LWP Files c/o A. Patterson, 773-A
ITP Files c/o A.G. Wiest, 241-119H