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STATISTICAL STUDY OF WEIGHT % INSOLUBLE SOLIDS METHODS
FOR IN-TANK PRECIPITATION (ITP) COLD RUN SUPPORT (U)

SUMMARY

A statistical study was performed on two candidate methods for measuring the weight % insoluble solids in ITP slurry samples. This work was necessary because the preferred method of using a microwave power weight % solids analyzer was unsuccessful. The weight % solids measurements are needed to provide process control information during the ITP cold runs. The results support the following conclusions and recommendations:

- Standards containing insoluble TPB salts can be prepared and analyzed with excellent accuracy and precision. There is evidence of only a -0.04 weight % (wt%) bias in the preparation and analysis of the standards containing 1-10 wt% TPB. The method used for measuring insoluble TPB salts is the classical gravimetric method (this method will be called the "classical method"). The

only drawbacks to the classical method are the 2-3 days and relatively high skill level required to perform it.

- A method was tested that measures the wt% insoluble solids in a slurry by the difference in total and soluble solids (this method will be called the "difference method"). The difference method did not produce statistically significant bias in this study. However, the difference method is not nearly as precise as the classical method. A 95% prediction limit for the uncertainty for an individual analytical measurement is given by 0.93 wt%.
- We recommend that the difference method be used for ITP support during cold runs. Although this method is less precise than the classical method, it can be performed in about 20 hours, versus 2 or 3 days for the classical method. The difference method is also more convenient. This recommendation is made assuming that ITP Operations will accept the uncertainty of 0.93 wt% at the 95% confidence level that was determined in this study.
- We recommend that neither approach be considered for use during ITP hot operations. Both methods would be difficult to perform with manipulators in a shielded cell.

INTRODUCTION

ITP Operations needs to be able to reliably measure the wt% insoluble solids of process tank samples during cold runs. Weight % insoluble solids measurements are used to assess the homogeneity of TPB slurries and the performance of the tank sampling system. The measurements are also used for process control by indicating when the solids have been concentrated enough to feed the DWPF. To expedite sample turnaround, the wt% insoluble measurements will be performed in the ITP analytical laboratory.

The most obvious analytical method for insoluble solids in a material is to measure the total weight of the slurry, filter out the solids, and then dry and weigh the solids. This method is not applicable to ITP slurries because the solids are a mixture of KTPB, which is insoluble, and NaTPB, which is soluble in water but partially insoluble in the high sodium matrix of ITP salt solutions. This combination presents an experimental problem. The solids must be washed with water before drying to remove the soluble salts that are still in contact with the solids. The washing step would remove not only the unwanted soluble salts but also the NaTPB solids.

The preferred method for measuring wt% solids at SRTC is to use a commercial microwave power % solids analyzer. Insoluble solids may be rapidly measured from the difference in the total and soluble solids in a slurry. Experimentally, this determination is accomplished by first measuring the total solids in the slurry, then filtering the sample and measuring the soluble solids in the filtrate. The wt% soluble solids in the slurry is calculated from an equation using the two measured values (total solids and soluble solids in the filtrate). The difference in the measured total solids and the calculated soluble solids is the insoluble solids in the slurry.

Microwave drying of ITP samples was not successful. The high concentration of caustic and dissolved salts coupled with microwave power to dissolve the glass fiber pads used in the measurement. Moreover, the organic TPB solid was charred by the microwave-induced heat. Because TPB slurries containing low concentrations of salts have been successfully analyzed with the microwave analyzer, the charring may be from the heat generated by salts absorbing the microwaves.

After considering possible alternatives to microwave drying, two candidate methods for analyzing ITP nonradioactive samples were evaluated. The "classical method" converts soluble NaTPB in the slurry to highly insoluble KTPB. The KTPB is then collected by filtration, and dried to constant weight. Because the classical method requires 2 or 3 days to complete and considerable analytical technique, a more rapid and convenient method was sought.

The "difference method" is fundamentally the same as that described above for the microwave wt% solids except that a conventional drying oven is used to dry the sample. TPB slurry is dried between glass fiber pads at 105 °C for 20 hours. These drying conditions do not char the TPB residue, and the caustic solution does not dissolve the glass fiber pads. This method can be performed in half the time of the classical method and is considered somewhat easier to perform.

A statistical study was performed to assess the precision and accuracy of the two candidate methods. The results of this study are discussed in this report. Also included are the following appendices:

- Appendix 1. Preparation of TPB Standards Procedure
- Appendix 2. Classical Method Procedure
- Appendix 3. Difference Method Procedure
- Appendix 4. Basic Program for Calculating Insoluble Solids from Total Solids and Soluble Solids in the Filtrate Measurements
- Appendix 5. Variance Propagation for Inverse Prediction Problem

RESULTS AND DISCUSSION

Design of the Statistical Study

A total of 24 standards were prepared (Appendix 1) containing a mixture of insoluble KTPB and NaTPB. Three each of standards with nominal insoluble solids concentrations of 1, 5, and 10 wt% were analyzed with the classical method (the procedure for the classical method is in Appendix 2). Five each of standards with nominal insoluble solids concentrations of 1, 5 and 10 wt% were analyzed by the difference method (the procedure for the difference method is in Appendix 3). More analyses by the difference method were performed to gather additional data on the previously untested method. For both methods, triplicate determinations were performed on each standard. Care was taken to randomize the order of standard preparations and analyses.

Quantitative Comparison of the Two Methods

Results of determinations obtained by the classical method and difference method are compared with the theoretical wt% in Table 1. The classical method determinations were extremely close to the theoretical values. Table 2 presents the results of a linear regression analysis of the 9 standards analyzed using the classical method. The R^2 value of 0.99996, a Root Mean Square Error of only 0.025 wt%, and the plot of the residuals, all indicate a very good fit. The estimate of the intercept term, -0.04 wt%, is statistically different from zero at the 5% level. Thus, there is evidence of an absolute bias of -0.04 wt% in the classical method determinations. Errors in both the standard preparation and the classical method determination contribute to this bias from the theoretical value. There is no evidence of a relative bias in these determinations at the 5% level. The Root Mean Square Error of 0.025 wt% is a measure (at 1-sigma) of the precision of the standard preparations and classical determinations.

Table 3 summarizes the statistical analysis of the difference method performance. To evaluate this method, the nominal concentrations were used as the standards. The residual plot indicates a slight increase in the variability of the residuals as the wt% insoluble solids of the standards increase. The R^2 value is 0.993 and the Root Mean Square Error (RMSE) is 0.35 wt%. The RMSE is a measure of the scatter of the analytical measurements about the line fitted to the data. Since the estimate of the intercept term is not statistically significant at the 5% level (and thus is taken to be zero), there is no indication of an absolute bias for the difference method. The estimate of the slope is 1.04448 with a standard error of 0.0244. A 95% two-tailed confidence interval for the slope is given by

$$\begin{aligned} 1.04448 \pm t(0.025,13) \times 0.0244 &= 1.04448 \pm 2.160 \times 0.0244 \\ &= (0.992, 1.097) \end{aligned}$$

where $t(0.025, 13)$ is the upper 2.5 percentile for Student's t distribution with 13 degrees of freedom. Since 1 is included in this two-tailed confidence interval, the estimate of the slope is not statistically different from 1 at the 5% level. Note, however, a 95% lower limit for the slope (using $t(0.05, 13) = 1.771$) is given by

$$\begin{aligned} 1.04448 - t(0.05, 13) \times 0.0244 &= 1.04448 - 1.771 \times 0.0244 \\ &= 1.0013 \end{aligned}$$

Thus, if a positive relative bias is expected, so that a one-sided confidence interval is appropriate, the data provide evidence that such a relative bias exists in the difference method at the 5% level.

The result of this model fit should be used to bias-correct the analytical values. If y is the analytical value, a is the estimate of the y -intercept, and b is the estimate of the slope, then x , the estimate of the corresponding true wt% value, is given by

$$x = \frac{(y-a)}{b}$$

The uncertainty of this x value is computed using the method of variance propagation (see Appendix 5), and at the 95% confidence level, the estimated uncertainty associated with an individual measurement adjusted for bias is ± 0.79 wt%.

Procedures could be developed to determine a "calibration" for the difference method periodically, the results could be used to adjust the analytical measurements, and the uncertainty of the adjusted value could be computed via the approach of Appendix 5.

If no significant bias in the difference method is determined as new measurement data are acquired, no adjustment to the analytical measurement for the calibration curve will be needed in the difference method procedure. For this situation, the following simple statistical model is helpful in estimating the uncertainty of the difference method:

$$\text{Analytical Measurement} = \text{Standard Value} + \text{Error}$$

For this model, the deviations computed by subtracting the analytical values from the corresponding theoretical values are treated as deviations about the mean. Therefore, the average of these deviations is an estimate of the variance (the scatter of the analytical values about their corresponding theoretical values). The estimate of the variance is 0.1894 which gives a value of 0.435 wt% for the estimated standard deviation. A 95% prediction limit for the uncertainty (using $t(0.025, 15) = 2.131$) for an individual analytical measurement is given by ± 0.93 wt%.

The superior precision of the classical method is believed to result from the fact that the dried solids (KTPB) collected in the classical procedure are gravimetrically air

stable. In contrast, the solids (consisting of a mixture of TPB salts, NaOH, NaNO₃, Na₂CO₃ • H₂O, and other salts) after drying in the difference method are gravimetrically unstable in air. Solids in the classical method can be reliably dried to a constant weight, while the weight of dried solids from the difference method fluctuate up or down by a few milligrams. The solids in the difference method are so hygroscopic that they quickly absorb significant quantities of water. In one experiment, the solid weight increased at a rate of 18 mg per minute.

The difference method still yields good weight % insoluble analyses. Errors from unstable weights are minimized by the fact that only weight differences are important, rather than the absolute weights. Experimentally, weighing errors are further reduced by concurrently measuring the total solids and the soluble solids. Both total and soluble measurements are done under nearly identical drying and weighing conditions.

Analyses of 15 standards by the difference method did not indicate any statistically significant bias. However, the analyses of many standards and samples over the period of three months has shown that the difference method usually produces higher results than the classical method. Often the higher results are proportional to the wt% TPB solids in the sample. For example, the values obtained by the difference method for slurry standards containing 1, 5, or 10 wt% TPB are typically 1.04 %, 5.25 %, and 10.5 %. Among the results for the 15 standards analyzed as part of this study, only three of the analytical measurements using the difference method were found to have values below the nominal standard concentration.

It is not known if the differences are from analytical error, or if the method is measuring a real difference in the TPB content and the weight % insolubles. An analytical error that would cause a positive bias is insufficient drying of the TPB during the total solids measurement. The residual water would then be weighed as a solid. There has been no evidence that the samples are not dry. Experiments were performed to determine if 20 hours was adequate drying time. Pads containing the dried solid were weighed after 20 hours of heating, then heated for another 24 hours and weighed again. Although the sample weights were unstable because of the hygroscopic nature of the residue, there was no trend to lower weights as the drying time was increased from 20 to 44 hours. Drying conditions should be more than adequate to evaporate the 2-4 ml of water in the samples. The glass fiber pads also expedite drying by increasing the surface area.

It is possible that the difference method measures insolubles not measured by the classical method. The difference method would measure salts that are insoluble in the chemistry of salt slurry, but soluble in a water wash of the salts. The classical method would not measure these salts (NaTPB is, of course, the exception. It is dissolved while washing the insoluble TPB salts and then reprecipitated with K⁺.) Therefore, the difference method could legitimately measure higher weight % insoluble solids than the classical method.

Qualitative Discussion of the Two Methods

Two other factors besides the relative precision and accuracy of the methods were considered: (1) the time required to perform each method, and (2) the convenience of each method. The difference method is both more rapid and convenient. Very conservative drying times are used for both methods. The 20 hour drying time at 105 °C is used to ensure that the 5 ml of slurry is completely dry (in place of drying to a constant weight, which is very difficult to obtain because of the hygroscopic nature of the salts). The time required to perform the classical analysis is 2-3 days to allow for the drying, cooling, and weighing steps.

The difference method is slightly more convenient to perform. The only technique used in the difference method is dispensing a well-mixed sample onto the glass fiber pads and weighing the pads before and after drying. The key to obtaining reliable values by the difference method is weigh the pads within seconds after they are removed from the oven to minimize weight gain. The classical method requires precipitations, filtrations, washing, and drying steps. Because of these additional steps, it is considered more technique dependent than the difference method.

Recommendations

- (1) The difference method is recommended for ITP cold runs because it yields reasonably high quality results in less than 24 hours.
- (2) TPB slurries must be prepared and analyzed concurrently with the ITP samples to ensure that the analytical method is in control. This recommendation applies to both methods.

References

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Tables

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- Table 2: Linear Regression of Classical Method Results versus Theoretical Standards
- Table 3: Linear Regression of Difference Method Results versus Nominal Standards
- Table 4: Estimation of Uncertainty (Error Variance) for Difference Method

Table 1
NaTPB Weight Percent Insoluble Solids Data

Sample ID	Nominal Wt%	Theoretical Wt%	Classical Method Wt%	Difference Method Wt%
S01	5	4.915		5.08
S02	1	1.000		1.13
S03	10	9.977	9.91	
S04	10	9.977		10.92
S05	1	1.000	0.98	
S06	10	9.969		9.49
S07	5	4.991		5.50
S08	10	9.980	9.93	
S09	10	9.972		10.74
S10	5	4.983		5.18
S11	5	4.990	4.94	
S12	1	1.000		1.02
S13	1	1.000		0.98
S14	1	1.000		0.70
S15	5	4.987	4.97	
S16	10	9.972		10.48
S17	10	9.972		10.26
S18	5	4.983		5.26
S19	10	9.973	9.94	
S20	5	4.990		5.52
S21	1	1.000	0.978	
S22	5	4.988	4.89	
S23	1	1.000		1.00
S24	1	1.000	0.954	

Table 2

Linear Regression of Classical Method Results versus Theoretical Standards

Response: Analytical

Summary of Fit	
Rsquare	0.999963
Root Mean Square Error	0.025245
Mean of Response	5.274444
Observations (or Sum Wgts)	9

Lack of Fit				
Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	5	0.00420245	0.000840	6.4986
Pure Error	2	0.00025867	0.000129	Prob>F
Total Error	7	0.00446112		0.1387

Parameter Estimates				
Term	Estimate	Std Error	t Ratio	Prob> t
Intercept	-0.039858	0.01482	-2.69	0.0311
Standard	0.9986161	0.00229	435.80	0.0000

Effect Test					
Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Standard	1	1	121.03515	189918	0.0000

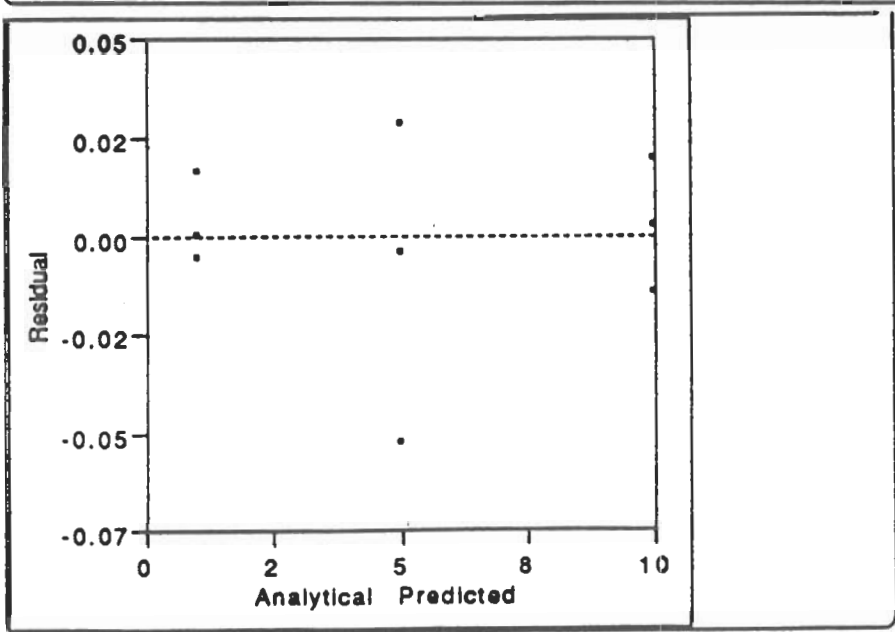


Table 3

Linear Regression of Difference Method Results versus Nominal Standards

Response: Analytical

Summary of Fit

Rsquare	0.992948
Root Mean Square Error	0.34817
Mean of Response	5.550667
Observations (or Sum Wgts)	15

Lack of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack of Fit	1	0.0838074	0.083807	0.6740
Pure Error	12	1.4920800	0.124340	Prob>F
Total Error	13	1.5758874		0.4277

Parameter Estimates

Term	Estimate	Std. Error	t Ratio	Prob> t
Intercept	-0.019869	0.15824	-0.13	0.9020
Standard	1.0444754	0.02442	42.78	0.0000

Effect Test

Source	Nparm	DF	Sum of Squares	F Ratio	Prob>F
Standard	1	1	221.82221	1829.882	0.0000

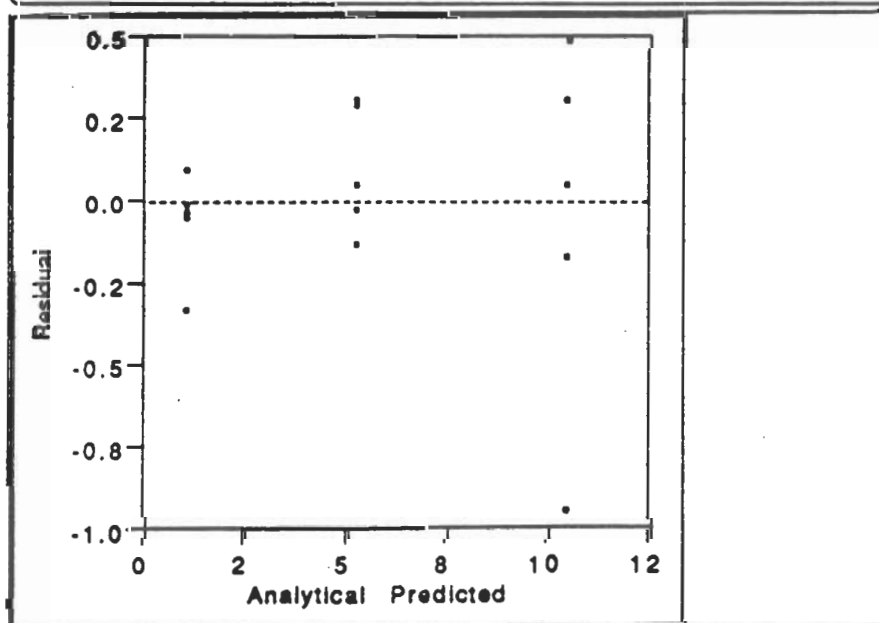


Table 4

Estimation of Uncertainty (Error Variance) for Difference Method

Sample ID	Nominal Standard Wt%	Theoretical Standard Wt%	Difference Method Wt%	Deviations (Theoretical - Analytical) Wt%
S02	1	1.000	1.13	-0.130
S23	1	1.000	1.00	+0.000
S18	5	4.983	5.26	-0.277
S12	1	1.000	1.02	-0.020
S13	1	1.000	0.98	+0.020
S10	5	4.983	5.18	-0.197
S06	10	9.969	9.49	+0.479
S17	10	9.972	10.26	-0.288
S01	5	4.915	5.08	-0.165
S20	5	4.990	5.52	-0.530
S07	5	4.991	5.50	-0.509
S14	1	1.000	0.70	+0.300
S16	10	9.972	10.48	-0.508
S04	10	9.977	10.92	-0.943
S09	10	9.972	10.74	-0.768

Estimate of Error Variance 0.189

Estimate of Error Standard Deviation 0.435

APPENDIX 1

Procedure for Preparing Wt % Insoluble Solids Standards

The following procedure may be used to prepare standard slurries for insoluble solids measurements. Each standard contains 100 grams of slurry but larger or smaller standards can be prepared by proportionally increasing or decreasing each of the components.

Three solutions are required to prepare the standards: 0.750 molar sodium tetraphenylborate (NaTPB), 2.500 molar potassium nitrate, and a salt solution. The volumes given below will provide enough solutions to make about twenty 100 gram standards. The density of the NaTPB and potassium nitrate solutions must be measured but this can be done as the solutions are prepared. The standards are prepared by accurately weighing the components into a polyethylene bottle. A 4-place analytical balance should be used in all weighing.

The highest purity chemicals should be used in preparing the standards. ACS reagent grade is acceptable. The most critical component is the sodium tetraphenylborate and it should be 99.5+% pure. Pre-drying is not required.

Preparation of Potassium Nitrate Solution (100 mL)

1. Prepare a 2.5 molar potassium nitrate solution by dissolving a 25.275 grams of KNO_3 in water in a 100 mL volumetric flask. Weigh the dry, empty flask before use, then reweigh afterwards to get the density of the solution.

Source of KNO_3 : _____
(Manufacturer and Lot #)

Date & Initials: _____

Balance#: _____

Empty wt: _____(A)

Wt of KNO_3 : _____(B)

Wt when full: _____(C)

Density= $(C-A)/100$ _____(D)

- $$K = [B/100.00] / D =$$

TPB = [B/500.00] /D = _____

1. This salt solution is added to the standards to give a final liquid phase composition similar to that in the slurry prepared for the ITP Cold Runs. The salt solution composition and the final liquid phase composition in the standards are given below. All components (except sodium, hydroxide, and nitrate) are diluted during preparation of the standards so that they end at the target concentration. To obtain the target concentrations of these components requires adding solid sodium nitrate and sodium hydroxide to each standard.

<u>Component</u>	Concentration (molar)	
	<u>Salt Solution</u>	<u>Standard</u> (target)
Na ⁺	6.40	4.94
OH ⁻	5.00	2.77
NO ₃ ⁻	2.66	1.50
NO ₂ ⁻	1.09	0.37
AlO ₂ ⁻	0.89	0.30
SO ₄ ²⁻	0.089	0.030
CO ₃ ²⁻	0.065	0.022

2. Prepare this salt solution in a 1.00 L volumetric flask. Record the amount used and the manufacturer and lot number for each chemical.

Dissolve the components in the following order:

- dissolve all of the NaOH in about 1/3 the volume of water.
- add the aluminum nitrate and dissolve all of it. If necessary, add more water but leave enough empty volume for the remaining chemicals (about 100 mL).
- add the remaining components and dissolve them.
- cool the solution to room temperature before filling to the line with water.

[Note: it is important to dissolve the sodium hydroxide and aluminum nitrate before adding the sodium nitrite. The aluminum nitrate produces an acidic solution which will decompose the nitrite to NO gas which converts to brown NO₂ gas on contact with air.]

Date & Initials: _____

Balance: _____

<u>Compound</u>	Amount <u>Required</u>	Amount <u>Used</u>	<u>Manufacturer and Lot #</u>
NaOH	200.00 g	_____	_____
Al(NO ₃) ₃ ·9H ₂ O	332.75 g	_____	_____
Na ₂ CO ₃ ·H ₂ O	8.06 g	_____	_____
Na ₂ SO ₄	12.60 g	_____	_____
NaNO ₂	75.49 g	_____	_____

Procedure for Preparing Wt% Solids Standards

1. The following steps may be followed in preparing wt % standards with nominal values of 1, 5, and 10 wt %. The exact wt % solids are calculated from the amounts of each component used.
2. Locate and label the required number of 100-mL p.e. bottles. Place a stir bar into each bottle.
3. Carefully measure the indicated amount of 0.750 M NaTPB into each bottle. Note: 1 drop of liquid is about 0.03 g. It is not necessary to obtain the exact amount listed, but any discrepancies will affect the wt % solids.
4. Next, weigh in the indicated amount of water.
5. Next weigh in the indicated amount of 2.50 M KNO₃ solution. A white precipitate of KTPB will form. Mix thoroughly the bottle thoroughly at this time to assure that all of the potassium has been precipitated.
6. Weigh in the indicated amount of the salt solution into each bottle and mix some more. Addition of the salt solution will cause some of the excess NaTPB to precipitate, although this will not cause a noticeable change in the appearance of the standard.
7. Next, weigh in the indicated amount of NaNO₃. Record the manufacturer and lot# for NaNO₃.

NaNO₃: _____
8. Finally, weigh in the indicated amount of NaOH.
9. Cap the bottle and mix thoroughly to dissolve the sodium nitrate and sodium hydroxide. The 1% and 5% standards can be stirred, but the 10% standard will probably be too thick. It can be mixed by vigorous shaking. Note: the slurry will get warm due to dissolution of the NaOH.
10. Calculate the theoretical wt % solids for each standard using the exact amounts of each component added.
 - a. Sum the weights of all components added to the bottle (1).
 - b. Calculate the grams of NaTPB added by multiplying the weight of NaTPB solution added by the value of g NaTPB/g sol'n (TPB) obtained when preparing the NaTPB solution.

- c. Subtract the amount of NaTPB expected to be soluble in the salt solution. (Note: the amount subtracted will change if the salt solution composition changes significantly or if a different size standard is used).
- d. Calculate the moles of NaTPB by dividing (3) by 342.23.
- e. Calculate the grams of KNO₃ added by multiplying the weight of the KNO₃ solution added by the value of g KNO₃/g sol'n (K) obtained when preparing the KNO₃ solution.
- f. Convert grams of KNO₃ (5) into moles of KNO₃ by dividing by 101.10.
- g. Calculate the weight of KTPB produced by multiplying (6) by 358.34.
- h. Calculate the moles of excess NaTPB by subtracting [(4)-(6)]=(8).
- i. Convert moles of excess NaTPB to grams by multiplying (8) by 342.23.
- j. Find the total weight of solids by adding (7)+(9)=(10).
- k. Calculate the wt % solids by dividing (10)/(1).

Date & Initials: _____ Balance: _____

1 wt % Standards:

Bottle # _____

NaTPB sol'n: 4.21 g
used: _____

Water: 49.95 g
used: _____

KNO₃ sol'n: 0.90 g
used: _____

Salt Solution: 35.63 g
used: _____

NaNO₃ req'd: 1.91 g
used: _____

NaOH req'd: 7.41 g
used: _____

Calculations:

Total added: _____ (1)

NaTPB added: _____ (2)

(less soluble: -.0640 g NaTPB _____ (3)

moles NaTPB _____ (4)

KNO₃ added: _____ (5)

moles KNO₃ _____ (6)

wt of KTPB _____ (7)

moles excess NaTPB _____ (8)

g excess NaTPB _____ (9)

Total solids: _____ (10)

Wt % solids: _____

Date & Initials: _____ Balance: _____

5 wt % Standards:

Bottle # _____

NaTPB sol'n: 20.00 g
used: _____

Water: 33.07 g
used: _____

KNO₃ sol'n: 4.48 g
used: _____

Salt Solution: 34.19 g
used: _____

NaNO₃ req'd: 1.16 g
used: _____

NaOH req'd: 7.11 g
used: _____

Total added: _____

Calculations:

Total added: _____ (1)

NaTPB added: _____ (2)

(less soluble: -.0610 g

g NaTPB _____ (3)

moles NaTPB _____ (4)

KNO₃ added: _____ (5)

moles KNO₃ _____ (6)

wt of KTPB _____ (7)

moles excess _____

NaTPB _____ (8)

g excess NaTPB _____ (9)

Total solids: _____ (10)

Wt % solids: _____

Date & Initials: _____ Balance: _____

10 wt % Standards:

Bottle # _____

NaTPB sol'n: 39.73 g
used: _____

Water: 11.96 g
used: _____

KNO₃ sol'n: 8.96 g
used: _____

Salt Solution: 32.39 g
used: _____

NaNO₃ req'd: 0.224 g
used: _____

NaOH req'd: 6.74 g
used: _____

Total added: _____

Calculations:

Total added: _____ (1)

NaTPB added: _____ (2)

(less soluble: -.0579 g

g NaTPB _____ (3)

moles NaTPB _____ (4)

KNO₃ added: _____ (5)

moles KNO₃ _____ (6)

wt of KTPB _____ (7)

moles excess

NaTPB _____ (8)

g excess NaTPB _____ (9)

Total solids: _____ (10)

Wt % solids: _____

APPENDIX 2

CLASSICAL METHOD PROCEDURE

1. Clean Gooch crucible filters ("F" frit) with concentrated nitric acid. Then rinse the crucibles with water. Clean the filters a second time with a 1 M solution of sodium hydroxide. Rinse the filters thoroughly with de ionized water and dry at 105°C before use.
2. Tare a 4-place analytical balance. Place a Gooch crucible filter on the balance and weigh it to the nearest 0.1 mg. Record the weight in the Data Sheet. This crucible will be referred to as the "first" crucible in this procedure.
3. Mix the TPB slurry by either shaking or stirring continuously with a magnetic stir bar.
4. Cut the tip off a disposable pipet tip to enlarge the hole to avoid plugging. Use the pipet to transfer some of the slurry to the crucible. Transfer enough slurry to yield 0.1- 0.5 grams of solid after drying. For example, if the slurry contains 5 weight % insoluble TPB salts, then 5 ml of this slurry will yield 0.25 g of solid after drying. Check with the Task Supervisor if in doubt about the amount of transfer.
5. Reweigh the crucible filter with the sample in it. Record the weight of the first filter + sample on line the data sheet.
6. Attach a vacuum hose to the crucible filter. Turn on the vacuum and filter the sample. Discard the filtrate (salt solution).
7. Wash the solids in the filter 3 times with 15 ml of deionized water. During the washing steps, stir the solids with a metal spatula. Be sure to rinse all the solid off the spatula and into the filter during the final rinsing step. **Collect the washwater that passes through the filter.**
8. Transfer the washwater quantitatively to a beaker. Add a stir bar. Place the beaker on a magnetic stirrer and turn it on.
9. Add 15 ml of a 1.0 M potassium nitrate (KNO_3) solution. The potassium ions will precipitate any soluble TPB ions in the solution, turning it cloudy.

10. Let the mixture from Step 9 stir for about 5 minutes. While it is stirring, weight a "second" crucible filter on the analytical balance. Record the weight of the second crucible in the data sheet.
11. Transfer quantitatively the mixture from Step 9 to the crucible filter. Vacuum filter the contents through the crucible filter.
12. Wash the solid residue with 3 15 ml-portions of deionized water.
13. Place both the first and second filters into the drying oven set at 105°C.
14. After heating for 24 hours, remove the filters from the oven. Let them cool for 30 minutes.
15. Weigh the first filter + the dried solids. Record the weight in the data sheet. This is the first of a t least two weighings required to ensure that the sample reaches constant weight.

Note: The crucibles are cooled in the air, not in a dessicator

16. Weigh the second crucible + dried solids and record the weight in the data sheet.
17. Place both filters back in the oven for another 24 hours or heating.
18. Repeat Steps 14-16.
19. After heating and weighing the filter + solid for the second time, compare the weights. If they agree to within ± 0.5 mg, the weights are stable. Proceed on to the Calculation Section if the weights agree in this range.

If the weights do not agree, place the crucible back in the oven and heat for another 24 hours or until the weights agree.

CALCULATIONS

Note: Refer to the data sheet for weight % solids by the classical method.

1. Calculate the weight of the sample transferred to the first filter.

$$\begin{array}{r} \text{Weight of filter + sample} \\ - \text{Weight of filter} \\ \hline = \text{Weight of sample} \end{array}$$

2. Calculate the weight of solid in the first filter.

$$\begin{array}{r} \text{Weight of 1st filter + solid} \\ - \text{Weight of 1st filter} \\ \hline = \text{Weight of solid in 1st filter} \end{array}$$

3. Calculate the weight of solid in the second filter.

$$\begin{array}{r} \text{Weight of 2nd filter + solid} \\ - \text{Weight of 2nd filter} \\ \hline = \text{Weight of solid in 2nd filter} \end{array}$$

4. Calculate the total weight of solid in the sample. The weight of the solid in the first filter is used without adjustment. The weight of the solid in the second filter must be corrected to an equivalent weight of sodium tetraphenylborate. This correction is necessary because some of the sodium tetraphenylbotrate is converted to potassium tetraphenylborate in the washing and precipitation steps. The correction is accomplished by multiplying the weight of solid in the 2nd filter by

$$\begin{array}{r} 342.24 \\ \times \quad \hline 358.34 \end{array}$$

To obtain the total solids in the sample, sum the solids in the 1st filter and the solids in the second filter multiplied by the correction factor.

$$\begin{array}{r} \text{Weight of solid in 1st filter} \\ + \quad \text{Weight of solid in 2nd filter} \times 342.24/358.34 \\ \hline = \quad \text{Total weight of solid in the sample} \end{array}$$

5. Calculate the weight % insoluble solids by dividing the total weight of solid (4) by the total weight of the sample (1).

$$\text{Weight \% insoluble solids} = \frac{\text{total weight of solid}}{\text{total weight of sample}}$$

DATA SHEET FOR THE CLASSICAL PROCEDURE METHOD

Note: Prepare a separate data sheet for each replicate analysis performed by the Classical Procedure.

- | | | | |
|-----|--|-------|---|
| (1) | Wt. of 1st Crucible Filter | _____ | g |
| (2) | Wt. of Sample + 1st Filter | _____ | g |
| (3) | Wt. of 2nd Filter | _____ | g |
| (4) | Wt. of 1st Filter + Dried Sample
(1st weighing) | _____ | g |
| (5) | Wt. of 2nd Filter + Dried Sample
(1st weighing) | _____ | g |
| (6) | Wt. of 1st Filter + Dried Sample
(2nd weighing) | _____ | g |
| (7) | Wt. of 2nd Filter + Dried Sample | _____ | g |

APPENDIX 3

DIFFERENCE METHOD PROCEDURE

PROCEDURE 1

Weight % Total Solids

1. Preheat a drying oven to 105 ± 5 °C.
2. Place a magnetic stirring bar in the sample bottle.
3. Place the sample bottle on a magnetic stirrer. Turn on the stirrer at a high enough rate to smoothly mix the sample. If the KTPB sample is not too viscous, the slurry should be visibly swirling in the bottle. If the slurry cannot be mixed well with the magnetic stirrer, mix the sample by vigorously shaking the bottle as described in Step 8.
4. Tare the analytical balance.
5. Place a stack of 4 glass fiber pads on the balance pan. Make sure that the pads do not touch the balance floor. Record the weight of the pads on line 1 in the Data Sheet.
6. Trim with scissors about 1/2 inch off the disposable tip used with 5 ml pipets. This increases the opening diameter so that the slurry can pass through without selectively removing any particles.
7. Remove the glass fiber pads from the balance pan.
8. Uncap the sample bottle. If the sample is being mixed efficiently with the magnetic stirring bar, use the 5 ml pipet to remove the sample as it is being mixed. If the sample is too viscous to be mixed efficiently with a magnetic stirrer, then shake the bottle vigorously for at least 2 minutes before removing an aliquot. Have the pipet ready to transfer the sample from the bottle to the pads immediately to minimize settling of the solids.
9. Hold a stack of 4 pads on the outside edges with the finger tips of one hand. With the other hand, draw up 5 ml of the well-mixed sample into the pipet. Dispense the sample evenly onto the pads. Immediately put the pipet aside. Transfer the bottom pad to the top

to make "sandwich" consisting of 3 pads on the bottom, the sample in the middle, and the top pad. This operation should be done as quickly as possible to absorb the sample on the pads and to prevent the sample from leaking through the pads.

Note: The reason that the pads are held rather than placed on the bench top is to prevent the bench top from drawing the liquid through the pads. If liquid leaks through the pads to the bench top, the pads act as a filter by letting the liquid pass through while retaining the solids. The effect is to increase the insoluble solids relative to the liquid, which can cause a high bias. The bias is most noticeable for measurements of low weight percent insoluble solids samples. The bottom of the pads may be damp when the pads are suspended, but no error is introduced if the pads are immediately placed on the balance pan to obtain the total weight of the pads and slurry. Even if the damp pads transfer a small amount of liquid to the balance pan, this liquid would be evaporated during the drying step. Of course, another way to avoid any filtering effect is to use additional pads to absorb all the liquid.

10. Place the pads on the balance pan. Record the weight of the pads + sample on line 2 of the Data Sheet.
11. Transfer the pads from the balance pan to the top rack in the oven and close the oven door. Note in the Data Sheet which oven and the location in the oven where the pads are placed.
12. Repeat steps 4-10 for the next 2 replicates. Put replicate 2 on the middle rack in the oven and replicate 3 on the bottom rack. Note the location in the Data Sheet.

PROCEDURE 2

Weight % Soluble Solids in Filtrate

1. Mix the slurry sample well before filtering. (The mixing is done to ensure that a representative sample is removed from the bottle so as to not corrupt the sample in case additional analyses are performed. The actual weight % soluble solids in the filtrate does

not require that a representative sample be removed from the bottle.)

2. Filter the sample through a Nalgene disposable cup filter with 115 ml capacity and 0.45 micron diameter pore size. Enough of the slurry must be filtered to yield at least 15 ml of liquid. Pour the sample into a labeled 30 plastic bottle and cap the bottle.
3. Tare the analytical balance.
4. Place a stack of 4 glass fiber pads on the balance pan. Make sure that the pads do not touch the balance floor. Record the weight of the pads in line 1 of the Data Sheet.
5. Remove the glass fiber pads from the balance pan.
6. Pipet 5 ml of the filtrate evenly on the stack of 4 glass fiber pads. Transfer the bottom pad in the stack to the top to make a "sandwich" consisting of 1 pad on top and 3 pads on the bottom.

Note: Because the filtrate contains no **solids**, it is unnecessary to take precautions against the fiber pads filtering the **solids** as described in Step 9 of the procedure for total weight % **solids**.

7. Place the pads on the balance pan. Record the weight of the pads + sample in the Data Sheet.
8. Transfer the pads to the top rack of the oven. This set of filtrate pads will then be next to a set of pads containing the solids.
9. Repeat Steps 2-8 for other 2 replicates.

Leave the **pads** in the 105°C oven for at least 20 hours. It is common practice to have the pads in the oven by noon and take them out of the oven at 8 A.M. the next morning to be weighed.

While the pads are being heated, subtract the weight of the **pads** (line 1 in the Data Sheet) from the weight of the pads + **sample** (line 2 in the Data Sheet). Record the **remainder** as the **weight** of the sample in line 3 of the Data Sheet.

III. WEIGHING PROCEDURE AFTER DRYING

1. Tare the analytical balance.
2. Remove the set of pads in the top rack of the oven that contains the total solids.
3. Quickly place the pads on the balance pan. After about 5 seconds, the balance readout will become relatively stable, then the weight will increase quite rapidly as the salts on the pads absorb water. **Record the weight when the readout is relatively stable about 5 seconds after the pads are first placed on the balance pad.** This weight is the weight of the pads + solid. Record this weight in line 4 of the Data Sheet.
4. Repeat Steps 1-3 for the remaining pads in the oven.
5. Subtract the weight of the pads (line 1 in the Data Sheet) from the weight of the pads + solid (line 4 in the Data Sheet). This is the weight of the solids. Record this value on line 5 of the Data Sheet.
6. Divide the weight of solid (line 5 in Data Sheet) by the weight of sample (line 3 in the Data Sheet). Then multiply by 100 to yield the weight % total solids for the slurry sample and weight % soluble solids in the filtrate. Record these values on line 6 of the Data Sheet for both the slurry and the filtrate.

CALCULATIONS

The weight % insoluble solids in the slurry sample is the difference between total solids and soluble solids in the slurry. The total solids measurement is determined directly in Procedure 1. The soluble solids in the slurry are obtained by measuring the soluble solids in the filtrate. An equation is then used to convert this value to the soluble solids in the slurry.

Insoluble Solids (IS) = Total solids (TS) - Filtrate Solids (FS)

$$IS = TS - (100-TS) \times \frac{(FS/100)}{(1-FS/100)}$$

Example Calculation: For a slurry containing 29.88 wt % total solids and 26.15 wt % solids in the filtrate.

$$IS = 29.88 \text{ wt\%} - (100-29.88) \text{ wt \%} \frac{(26.15/100)}{(1-26.15/100)} \text{ wt\%}$$

$$IS = 29.88 \text{ wt\%} - (70.12) \text{ wt\%} \times \frac{(0.2615)}{(0.7385)} \text{ wt\%}$$

$$IS = 29.88 \text{ wt\%} - (70.12) \text{ wt\%} \times (0.3541) \text{ wt\%}$$

$$IS = 29.88 \text{ wt\%} - 24.83 \text{ wt\%}$$

$$IS = 5.05 \text{ wt\%}$$

DATA SHEET FOR DIFFERENCE METHOD

PROCEDURE 1.

Total Solids Measurements

	Trial 1	Trial 2	Trial 3
(1) Pads wt.-----			
(2) Pads + Slurry-----			
(3) Slurry wt. (2) - (1)---			
(4) Pads + Solid-----			
(5) Solid wt. (4) - (1)----			
(6) wt% total solids-----			
(5)			
----- x 100			
(3)			

Soluble Solids in the Filtrate

	Trail 1	Trial 2	Trial 3
(1) Pads wt.-----			
(2) Pads + Filtrate -----			
(3) Filtrate wt. (2) - (1)----			
(4) Pads + Solid -----			
(5) Solid wt. (4) - (1)-----			
(6) wt% solubles in Filtrate--			
(5)			

(3)			

Use program to calculate
wt% insoluble solids -----

APPENDIX 4

Basic Program for Calculations Insoluble Solids from Total Solids and Soluble Solids in the Filtrate Measurements

```
CLS
PRINT "    Calculation of insoluble solids in a slurry sample after"
PRINT "    measuring the total solids in the slurry and the soluble"
PRINT "    solids in the filtered sample."
PRINT
'    "    J. E. Young, C. J. Coleman and D. D. Walker"
PRINT "    Savannah River Technology Center 1992"
'    "    October 13, 1992"
'    "    final program issue date"
PRINT
'
'    The mathematical solution was derived concurrently
'    and independently by J. C. Marek.
'    TNX Oportions, in August 1992.
nexter:
'a=sol solids, %
'b=aqueous, %
'c=insoluble solids, %
'd=total solids, % measured
'f=total solids measured in filtered sample, %
'iss=insoluble solids calculated
INPUT "What is the total solids, in wt%"; e
IF e = 0 THEN GOTO cheks
INPUT "What is the solids content, in wt%,
      of the filtered sample"; f
IF f <=e THEN GOTO totchekok
PRINT "Verify sample has no visible particulates to confirm insoluble
      solids = 0"
GOTO cheks
totchekok:
PRINT " total      tot filt      soluble      insol"
a = (100 - e) * ((f / 100) / ((1 - (f / 100))))
iss = e - a
PRINT USING " ###.###  ###.###      ###.###  ###.### ";
          e; f; a; iss

cheks:
PRINT
IF e = 0 THEN
    INPUT "Quit now ? y/n"; a$: IF UCASE$(a$) <> "N" THEN END
GOTO nexter
END
```

Appendix 5

Variance Propagation for Inverse Prediction Problem

Let x be the true TPB level and y the difference method's analytical value for a given sample. The linear calibration equation is given by

$$y = A + Bx + \varepsilon \quad (1)$$

where A and B represent the unknown model parameters and ε represents the error term. The equation of the inverse calibration is given by

$$x = \frac{(y - A)}{B} - \frac{\varepsilon}{B} \quad (2)$$

Estimates a and b of the parameters A and B , respectively, of equation (1) are determined from the data. Estimates of the variance of ε and the variances and covariance of the estimates a and b are also determined by fitting the data to equation (1). Let σ_{aa} , σ_{bb} , and σ_{ab} be the estimates of the variance of a , the variance of b , and the covariance of a and b , respectively. Fitting (1) to the difference method data from this study gives the following values:

$$\sigma_{aa} = 0.0250 \quad \sigma_{bb} = 0.000596 \quad \sigma_{ab} = -0.00318$$

There is a systematic error for estimating x using a and b in equation (2). The variance of this error may be estimated by a propagation of variance (reference 1) as follows:

$$s_{xx} \approx \left(\frac{\partial x}{\partial a}\right)^2 \sigma_{aa} + \left(\frac{\partial x}{\partial b}\right)^2 \sigma_{bb} + 2 \left(\frac{\partial x}{\partial a}\right) \left(\frac{\partial x}{\partial b}\right) \sigma_{ab} \quad (3)$$

where $\frac{\partial x}{\partial \cdot}$ represents the partial derivative of equation (2) evaluated at the mean level of the random variable.

Appendix 5 (con't)

These partials derivatives are:

$$\frac{\partial x}{\partial a} = -\frac{1}{b} \qquad \frac{\partial x}{\partial b} = -\frac{(y-a)}{b^2}$$

Substituting these partial derivatives into equation (3) gives

$$s_{xx} \approx \left(-\frac{1}{b}\right)^2 \sigma_{aa} + \left(-\frac{(y-a)}{b^2}\right)^2 \sigma_{bb} + 2 \left(-\frac{1}{b}\right) \left(-\frac{(y-a)}{b^2}\right) \sigma_{ab} \quad (4)$$

The variance of the random error for x is given by

$$r_{xx} \approx \frac{\sigma_{\varepsilon\varepsilon}}{b^2} \quad (5)$$

where $\sigma_{\varepsilon\varepsilon}$ is the variance of the error term ε estimated from fitting the data to equation (1).

The variance of the total error of x is given by the sum of the systematic error variance in equation (4) and the random error variance in equation (5):

$$\sigma_{xx} \approx s_{xx} + r_{xx} \quad (6)$$

The uncertainty, U, for an individual x at the 95% level is given by

$$t_{.025, n-2} \sqrt{\sigma_{xx}} \quad (7)$$

where $t_{.025, n-2}$ is the critical value of Student's t with n-2 degrees of freedom and n equals the number of standards analyzed during the fit of the calibration curve for the difference method.

For n=15,

$$t_{.025, n-2} = t_{.025, 13} = 2.160.$$

Appendix 5 (con't)

For the data from the difference method tests, using equations (4) through (7) gives

y	x	s_{xx}	r_{xx}	$\sqrt{\sigma_{xx}}$	95% U
1	0.98	0.02	0.11	0.36	0.78
2	1.93	0.01	0.11	0.35	0.76
3	2.89	0.01	0.11	0.35	0.75
4	3.85	0.01	0.11	0.35	0.75
5	4.81	0.01	0.11	0.34	0.74
6	5.76	0.01	0.11	0.34	0.74
7	6.72	0.01	0.11	0.35	0.75
8	7.68	0.01	0.11	0.35	0.75
9	8.64	0.01	0.11	0.35	0.76
10	9.59	0.02	0.11	0.36	0.77
11	10.55	0.02	0.11	0.37	0.79

Therefore, an estimate of the uncertainty of an adjusted analytical measurement at the 95% confidence level is given by 0.79 wt%.

Reference:

- [1] Coleman, H. W. and Steele, W. G., Experimentation and Uncertainty Analysis for Engineers, Wiley, New York, 1989, page 193.