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IMPLICATIONS OF THE STATISTICAL REVIEW OF THE SIDE-BY-SIDE COMPARISON OF DWPF'S ICPS

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July 2004

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EXECUTIVE SUMMARY

The Statistical Consulting Section (SCS) of the Savannah River National Laboratory (SRNL) has conducted a statistical evaluation of side-by-side measurement data generated at the Defense Waste Processing Facility using two Inductively Coupled Plasma – Atomic Emission Spectrometers (ICPs): the production ICP, designated as M-14, and a new ICP, designated as M-13. The purpose of this report is to document the implications of the statistical evaluation relative to the qualification of the M-13 for use at DWPF. The statistical evaluation conducted by SCS provides the following conclusions:

- Applying the acceptance criteria outlined in the test plan for Sludge Receipt and Adjustment Tank (SRAT) product samples, which were prepared using a cold chemical (cold chem) dissolution method, yields: the category 1 oxides CaO, SiO_2, and U_3O_8 and the category 2 oxides B_2O_3 and K_2O did not meet the acceptance criteria. With the results from this study as a guide, measuring the SRAT samples prepared via cold chem using the M-13 would be expected to yield measurements that are less precise for approximately ½ of the oxides being tracked and slightly biased (low) for CaO, SiO_2, and U_3O_8 as compared to using the M-14. However, the SRAT measurements are used in support of the blending process and are not part of the Slurry Mix Evaporator (SME) acceptability decision of the Product Composition Control System (PCCS). Feedback provided from measurements of SME samples and from predictions made in PCCS (predictions for process and product quality as well as waste loading) is expected to lead to adjustments to and improvements in the blending strategy, if improvements are needed. Thus, using the M-13 as part of the analytical process for SRAT product samples will not be a problem for (and will therefore be acceptable to) DWPF Process Chemistry Engineering.

- Applying the acceptance criteria outlined in the test plan for the SME samples, which were prepared both by mixed acid and by fusion dissolution methods, yields: (a) for the fusion method, all category 1 and category 2 oxides met their respective criteria, (b) for the mixed acid method, the category 1 oxides Al_2O_3, CaO, Fe_2O_3, Li_2O, MnO, NiO, and U_3O_8 did not meet their respective acceptance criteria. These results led to the following recommended protocol for using the mixed acid and fusion measurements to represent a SME sample: for MgO, Na_2O, and ZrO_2 use the mixed acid measurements and for Al_2O_3, B_2O_3, CaO, Cr_2O_3, CuO, Fe_2O_3, K_2O, Li_2O, MnO, NiO, SiO_2, TiO_2, and U_3O_8 use the fusion measurements.

- Using the recommended protocol for representing the SME samples, 4 of 6 measurements for each and every one of the M-13 calibration blocks were selected and were found to satisfy all of the PCCS constraints. This included the sum of oxides constraints, even though the sum of oxides for an individual SME sample is expected to fail 65% more often for the M-13 than for the M-14 based upon the results of this study.

- It should also be noted that the estimated waste loadings for the M-13 samples had more variation than those estimated from the M-14 samples.

- For sludge/frit systems that are not durability limited (i.e., for systems in which the upper waste loading achievable via model predictions is not limited by the durability constraints), there is high confidence that adequate protection from a poor decision (due to ICP measurement uncertainty) regarding the glass quality of the SME samples is provided by the buffer between the durability value derived from the SME samples and the property acceptability region (PAR) limit for durability.

While additional work is needed to fully integrate the M-13 into DWPF's operational systems, use of this ICP (if the M-14 were to fail) will be adequate for sludge/frit blending and will lead to reliable SME acceptability decisions for product quality. For a sludge/frit system that is limited by a process property prediction such as viscosity or liquidus temperature as waste loading is increased, the SME blending strategy can be adjusted to lessen the impact of an incomplete definition of the M-13's measurement uncertainty on the acceptability decision until such time as the complete definition can be determined. However, the evaluations presented in this report result in no changes, nor recommendations for changes, to PCCS.

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LIST OF ACRONYMS

ARG-1	Analytical Reference Glass One
Cold chem	Cold chemical dissolution and sample preparation method
DWPF	Defense Waste Processing Facility
ICP	Inductively Coupled Plasma - Atomic Emission Spectrometer
JMP	A registered trademark of SAS Institute, Inc. (statistical software)
LOD	Limit of Detection
LOQ	Limit of Quantification
M-13	A new ICP being evaluated by DWPF
M-14	The production ICP in use at DWPF
MA	Mixed acid dissolution and sample preparation method
MAR	Measurement Acceptability Region in PCCS
MFT	Melter Feed Tank
NA	Not Applicable
NL	Normalized leachate releases
P	As the unit of measure for viscosity, this represents Poise.
PAR	Property Acceptability Region in PCCS
PCCS	Product Composition Control System (DWPF's SME acceptability system)
Prep	preparation
%RSD	Percent Relative Standard Deviation
SCS	Statistical Consulting Section
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
Std Dev	Standard Deviation
TTR	Technical Task Request
WL	Waste Loading
Wt%	Weight percent
T_L	Liquidus temperature in degrees Celsius
ΔG_p	Read as "del G p", this symbol represents the free energy of hydration term in units of kcal/100 g glass that is used in the modeling of glass durability.

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1.0 INTRODUCTION AND BACKGROUND

The Statistical Consulting Section (SCS) of the Savannah River National Laboratory (SRNL) received data from a series of side–by–side comparisons of two Inductively Coupled Plasma – Atomic Emission Spectrometers (ICPs) conducted by the Defense Waste Processing Facility (DWPF) Laboratory of Waste Laboratory Services. These two ICPs are designated as M-14 (the current production ICP) and M-13 (the new ICP being evaluated). The data received by SCS were outlined in the test plan [1] describing the series of tests, which involved three sample preparation methods, denoted as: "cold chem," fusion, and mixed acid. A cold chemical (cold chem) preparation is used for samples of the Sludge Receipt and Adjustment Tank (SRAT) product. Fusion and mixed acid dissolutions are used to prepare samples of the Slurry Mix Evaporator (SME).

For each of these three dissolution methods, several types of samples were prepared and measured (for chemical composition) by both ICPs. The samples included process samples (SRAT product for cold chem and SME product for fusion and mixed acid), blanks, check standards, and samples of the Analytical Reference Glass One (ARG-1). Groups of these samples were measured under 6 different calibrations of each of the two ICPs. The measurements of the process and ARG-1 samples were provided by element (16 elements in all) as weight percent concentrations. For these samples the elemental concentrations were converted to their corresponding oxide concentrations by using the appropriate gravimetric factors. In addition to these measurements, data associated with the determinations of the limit of detection (LOD) and limit of quantification (LOQ) for each element of interest for each ICP were provided to SCS.

SCS has conducted a statistical evaluation of the chemical composition measurement data in accordance with the test plan [1] and technical task request [2]. The purpose of this report is to document the implications of the statistical evaluation relative to the qualification of the M-13 for use at DWPF, with a more thorough treatment of the statistical tests and comparisons conducted as part of the evaluation available in a sister report[1]. The issues of interest in this report are:

- Evaluate the M-14 and M-13 measurements relative to the acceptance criteria for their differences that were outlined in the test plan [1].

  From [1], 4 categories of oxides for these measurements were defined; these are: 1) Element is greater than 0.5 Oxide Wt% and more than 10 times the Limit of Detection (LOD), 2) Element is less than 0.5 Oxide Wt% but greater than 10 times the LOD and 0.1 Oxide Wt%, 3) Element is less than 10 times the LOD or less than 0.1 Oxide Wt% and 4) Element is below LOD. The criteria are: for category 1, the biases between ICPs are expected to be less than 5%, for category 2, the biases between the ICPs are expected to be less than 25%, and no specified criteria for categories 3 and 4.

- Document the anticipated impact of the use of M-13 measurements on the SME Blending Process conducted by DWPF Process Chemistry Engineering.

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[1] All of the measurement data that were sent to SCS as well as the details of all of the statistical evaluations conducted by SCS are provided in the memorandum "A Statistical Review of the Side-by-Side Comparisons of DWPF's M-14 and M-13 ICPs," authored by T. B. Edwards as SRT-SCS-2004-00020 and dated July 19, 2004.

Based upon the review of these results with members of this engineering group and with their input, provide an assessment of the use of the M-13 for blending of sludge and frit with the SME heel.

- Investigate the sum of oxides for the ARG-1 measurements for the cold chem measurements and for the SME samples under the protocol for combining the mixed acid and fusion measurements that is suggested by the results of this study.

  The protocol currently being used at DWPF to represent the composition of a SME sample may be stated as follows: values for Al and B use only the fusion results, values for Si use the average of the mixed acid (MA) and fusion results, the values for all of the other elements use the MA results. The protocol for utilizing the M-13's MA and fusion measurements to represent a SME sample is developed in the discussion that follows and is recommended as a replacement for DWPF's current protocol for use with the M-13.

- Determine the acceptability of each of the 6 blocks of M-13 SME measurements relative to the current Product Composition Control System (PCCS) criteria as defined by [4].

  For these acceptability decisions, the protocol for selecting the 4 of 6 samples for each block of measurements as outlined in [5] is followed as well as the protocol for using the MA and fusion results to represent the SME sample measurements. One of the criteria for these decisions involves the sum of oxides, and for these evaluations the sum of oxides is determined by following both of these protocols. These acceptability decisions are made relative to estimates of measurement uncertainty that are currently utilized by PCCS (i.e., the measurement uncertainty associated with the M-14 ICP).

- Outline the impact to the PCCS algorithms if the M-13 were to be used to support SME acceptability decisions.

  Measurement uncertainties are accounted for in the PCCS algorithms that facilitate DWPF's SME acceptability decisions. These uncertainties estimate the random errors in the elemental concentration measurements of the SME samples that are associated with sampling the SME and analyzing the samples. The uncertainties are expressed as a covariance matrix; the diagonal values of this matrix are estimates of the variances of the random errors for the individual elements and the off-diagonal values are estimates of the covariances between the errors for pairs of these elements. The current PCCS covariance matrix was developed for the M-14 ICP. One objective of this report is to identify the PCCS coding issues associated with introducing a new ICP, and another objective is to assess the potential risk to the SME acceptability decisions of using the M-13 with the M-14 covariance matrix currently utilized by PCCS.

- Evaluate the anticipated impact of using the M-13 for estimating the waste loading (WL) of SME samples.

  Waste loading is an important metric for the DWPF operation. The issue here is: What is the likely effect of the M-13 on the uncertainty of the estimates of WL?

2.0 RESULTS

In this section the highlights of the statistical evaluation of the side-by-side measurements generated by the DWPF Laboratory are presented to address each of the items outlined in the Introduction. The statistical evaluations presented in this report were conducted using JMP Version 5 [3].

2.1 Cold Chem Comparisons

The cold chem method provides measurements for all 16 elements of interest. Tables 1 and 2 highlight the comparisons between the M-13 and M-14 measurements (as weight percent oxides) for the samples prepared by this method. In Table 1 are general comments summarizing some of the statistically significant observations from the measurements over all of the sample types. This table also presents the M-14 and M-13 average measurements for the SRAT samples that were involved in this testing. The percent relative difference between each pair of M-14 and M-13 averages is calculated and presented in this table. The percent relative difference entries that are shaded indicate that the two averages are statistically different (with approximately 95% confidence). Note that while most of the differences between the M-14 and M-13 averages are statistically significant, the only major SRAT components with M-13 averages that differ from the M-14 averages by more than 5% are CaO, SiO_2, and U_3O_8. This is reflected in the last column of Table 1. In this column, the 4 categories of oxides outlined in the test plan [1] are identified and an assessment of whether or not the corresponding acceptance criterion[2] for that category was met (i.e., a “yes”, “no”, or “NA” {not applicable} entry in this last column). Thus, the category 1 oxides CaO, SiO_2, and U_3O_8 and the category 2 oxides B_2O_3 and K_2O did not meet the acceptance criteria.

Table 1. Highlights of the M-13 versus M-14 Cold Chem Measurements

(Measurements are in wt% oxides and NA implies not applicable)

Oxide	Comments Regarding M-13 vs M-14	M-14 Avg.	M-13 Avg.	% Relative Difference	Category/ Criterion Met
Al_2O_3	M-13 is less precise and provides smaller concentration measurements.	10.656	10.307	-3.28%	1/yes
B_2O_3	There appear to be no issues for this oxide.	0.164	0.105	-35.97%	2/no
CaO	M-13 provides smaller concentration measurements.	2.376	2.111	-11.15%	1/no
Cr_2O_3	M-13 provides smaller concentration measurements.	0.185	0.145	-21.20%	2/yes
CuO	There appear to be no issues for this oxide.	0.052	0.051	-3.07%	3/NA
Fe_2O_3	There appear to be no issues for this oxide.	26.203	26.321	0.45%	1/yes
K_2O	M-13 is less precise.	0.118	0.385	226.57%	2/no
Li_2O	M-13 is less precise.	0.099	0.093	-6.50%	3/NA
MgO	There appear to be no issues for this oxide.	2.601	2.588	-0.49%	1/yes
MnO	There appear to be no issues for this oxide.	4.382	4.396	0.32%	1/yes
Na_2O	M-13 is somewhat less precise.	14.182	13.991	-1.34%	1/yes
NiO	There appear to be no issues for this oxide.	1.288	1.263	-1.91%	1/yes
SiO_2	There appear to be no issues for this oxide.	2.185	2.599	18.96%	1/no
TiO_2	M-13 is less precise and provides smaller concentration measurements.	0.029	0.020	-30.13%	3/NA
U_3O_8	M-13 provides smaller concentration measurements.	8.173	7.579	-7.27%	1/no
ZrO_2	M-13 is somewhat less precise.	0.113	0.117	3.90%	2/yes

---

[2] From [1], the 4 categories for the elements are: 1) Element is greater than 0.5 Oxide Wt% and more than 10 times the Limit of Detection (LOD), 2) Element is less than 0.5 Oxide Wt% but greater than 10 times the LOD and 0.1 Oxide Wt%, 3) Element is less than 10 times the LOD or less than 0.1 Oxide Wt% and 4) Element is below LOD. The criteria are: for category 1, the biases between ICPs are expected to be less than 5%, for category 2, the biases between the ICPs are expected to be less than 25%, and no specified criteria for categories 3 and 4.

Table 2 presents similar information for the M-14 and M-13 average measurements from the ARG-1 samples that were prepared using the Cold Chem method. As seen in this table, the category 1 oxides CaO and K_2O did not meet the acceptance criteria. The category 2 oxide in Table 2 met its criteria.

Table 2. Highlights of ARG-1 Cold Chem Measurements for the M-13 versus the M-14

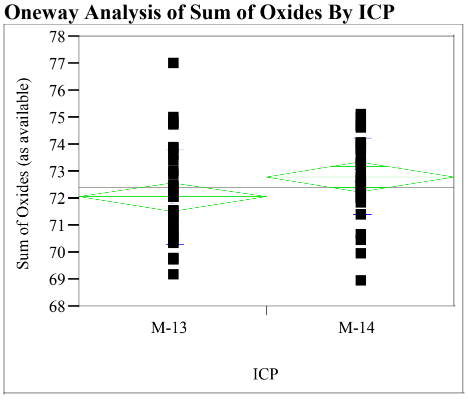
(Measurements are in wt% oxides and NA implies not applicable)

Oxide	M-14	M-13	% Relative Difference	Category/ Criterion Met
Al_2O_3	4.390	4.182	-4.75%	1/yes
B_2O_3	8.526	8.603	0.90%	1/yes
CaO	1.327	1.243	-6.33%	1/no
Cr_2O_3	0.097	0.092	-4.85%	3/NA
CuO	0.005	0.006	11.84%	3/NA
Fe_2O_3	13.856	14.011	1.11%	1/yes
K_2O	2.643	2.854	8.00%	1/no
Li_2O	3.186	3.121	-2.04%	1/yes
MgO	0.795	0.794	-0.12%	1/yes
MnO	1.796	1.821	1.43%	1/yes
Na_2O	11.180	11.244	0.57%	1/yes
NiO	1.018	1.017	-0.07%	1/yes
SiO_2	46.962	46.798	-0.35%	1/yes
TiO_2	1.135	1.121	-1.21%	1/yes
U_3O_8	0.071	0.174	145.92%	3/NA
ZrO_2	0.137	0.145	5.47%	2/yes

Figure 1 provides a look at the sum of oxides derived from the measurements of the SRAT samples by the two ICPs. Since these sums of oxides are not on a glass basis, they do not add to 100%. Note that, on average, the M-13 delivers approximately a 1-wt% smaller value than the M-14 for these sums of oxides and that the difference is not statistically significant at the 5% significance level.

Figure 1. Sum of Oxides for SRAT Samples by ICP

Type of Sample=SRAT
Oneway Analysis of Sum of Oxides By ICP



```
Oneway Anova
Summary of Fit
Rsquare                              0.051363
Root Mean Square Error               1.596558
Mean of Response                     72.43861
Observations (or Sum Wgts)                 72
t Test (Assuming equal variances)
                  Difference   t Test   DF    Prob > |t|
Estimate            -0.73261   -1.947   70       0.0556
Std Error            0.37631
Lower 95%           -1.48314
Upper 95%            0.01792
Analysis of Variance
Source       DF   Sum of Squares    Mean Square   F Ratio    Prob > F
ICP           1          9.66085        9.66085    3.7901      0.0556
Error        70        178.42990        2.54900
C. Total     71        188.09075
Means for Oneway Anova
Level       Number      Mean    Std Error    Lower 95%    Upper 95%
M-13            36   72.0723      0.26609       71.542       72.603
M-14            36   72.8049      0.26609       72.274       73.336
Std Error uses a pooled estimate of error variance
Means and Std Deviations
Level    Number     Mean  Std Dev  Std Err Mean   Lower 95%   Upper 95%
M-13         36  72.0723  1.76001       0.29334      71.477      72.668
M-14         36  72.8049  1.41434       0.23572      72.326      73.283
```

2.2 Impact to DWPF Process Chemistry Engineering's SME Blending[3]

An important input to the SME blending process conducted by DWPF Process Chemistry Engineering is the analysis of the SRAT product that is to be transferred into the SME heel along with an appropriate amount of frit. The composition of the SRAT product is assessed using samples that are measured via the cold chem analytical process. With the results from this study as a guide, measuring the SRAT samples prepared via cold chem using the M-13 ICP would be expected to yield measurements that are less precise for approximately ½ of the oxides being tracked and slightly biased (low) for CaO, SiO_2, and U_3O_8 as compared to using the M-14 ICP. However, the SRAT measurements are used in support of the blending process and are not part of the SME acceptability decision of PCCS. Feedback provided from measurements of SME samples and predictions made in PCCS (predictions for process and product quality as well as waste loading) is expected to lead to adjustments to and improvement in the blending strategy, if improvements are needed. Thus, using the M-13 as part of the analytical process for SRAT product samples will not be a problem for (and should therefore be acceptable to) DWPF Process Chemistry Engineering.

2.3 Fusion Comparisons

The fusion method provides measurements for 14 elements of interest. Table 3 and Table 4 highlight the comparisons between the M-13 and M-14 measurements (as weight percent oxides) for the samples prepared by this method. General comments summarizing some of the statistically significant observations from these measurements are provided in Table 3. In the two columns after the comments in this table, the M-14 and M-13 average measurements for the SME samples that were involved in this testing are provided. The percent relative difference (% Rel Diff) between each pair of M-14 and M-13 averages is calculated and presented in this table. The % Rel Diff entries are shaded for those M-14 and M-13 averages that are statistically different (with approximately 95% confidence). Thus, only B_2O_3 and SiO_2 yield M-14 and M-13 averages that are statistically different (with ~95% confidence). Also, note that all of the major oxides have % Rel Diffs less than 5%. This is reflected in the last column of Table 3. In this column, the 4 categories of oxides are identified and the assessment of whether or not the corresponding acceptance criterion for that category was met (i.e., a "yes", "no", or "NA" {not applicable} entry in this last column). From this table, all category 1 and category 2 oxides met their respective criteria.

---

[3] Much of the discussion presented in this section is based on an email received from Prabodh Patel, a member of the DWPF Process Chemistry Engineering Group, on June 16, 2004.

Table 3. Highlights of the M-13 versus M-14 Fusion Measurements

(SME Measurements are in wt% oxides and NA implies not applicable.)

Oxide	**Comments Regarding the Comparisons of M-13 vs M-14**	**M-14 Average**	**M-13 Average**	**% Relative Difference**	**Category/ Criterion Met**
Al_2O_3	M-13 is less precise.	4.701	4.740	0.83%	1/yes
B_2O_3	M-13 is less precise.	5.169	5.083	-1.66%	1/yes
CaO	M-13 is less precise.	1.138	1.119	-1.71%	1/yes
Cr_2O_3	M-13 is less precise.	0.090	0.091	0.13%	3/NA
CuO	M-13 is less precise.	0.025	0.016	-38.15%	3/NA
Fe_2O_3	M-13 is less precise.	12.517	12.429	-0.70%	1/yes
K_2O	M-13 is less precise.	0.537	0.546	1.74%	1/yes
Li_2O	M-13 is less precise.	5.147	5.332	3.61%	1/yes
MgO	M-13 is less precise.	0.990	0.994	0.41%	1/yes
MnO	M-13 is less precise.	1.443	1.449	0.40%	1/yes
Na_2O	Not Available	NA	NA	NA	
NiO	M-13 is somewhat less precise.	0.542	0.545	0.50%	1/yes
SiO_2	M-13 less precise but provides somewhat larger concentration measurements.	49.929	51.359	2.86%	1/yes
TiO_2	M-13 is less precise.	0.043	0.046	5.70%	3/NA
U_3O_8	No M-14 data were provided.	NA	3.191	NA	
ZrO_2	Not Available	NA	NA	NA	

Table 4 presents similar information for the M-14 and M-13 average measurements from the ARG-1 samples that were prepared using the fusion method. From Table 4, all of the category 1 and 2 oxides met their respective criteria for these measurements as well.

Table 4. Highlights of ARG-1 Fusion Measurements for the M-13 versus the M-14

(Measurements are in wt% oxides and NA implies not applicable.)

Oxide	**M-14 Avg.**	**M-13 Avg.**	**% Relative Difference**	**Category/ Criterion Met**
Al_2O_3	4.528	4.612	1.87%	1/yes
B_2O_3	8.296	8.170	-1.52%	1/yes
CaO	1.381	1.440	4.24%	1/yes
Cr_2O_3	0.100	0.093	-7.21%	2/yes
CuO	0.010	0.009	-16.33%	3/NA
Fe_2O_3	13.654	13.424	-1.68%	1/yes
K_2O	2.731	2.759	1.02%	1/yes
Li_2O	3.102	3.115	0.40%	1/yes
MgO	0.826	0.826	-0.05%	1/yes
MnO	1.789	1.756	-1.84%	1/yes
Na_2O	NA	NA	NA	NA
NiO	0.985	0.987	0.22%	1/yes
SiO_2	45.979	47.258	2.78%	1/yes
TiO_2	1.121	1.127	0.49%	1/yes
U_3O_8	NA	0.525	NA	NA
ZrO_2	NA	NA	NA	NA

2.4 Mixed Acid Comparisons

The mixed acid method provides measurements for 15 elements of interest. Table 5 and Table 6 highlight the comparisons between the M-13 and M-14 measurements (as weight percent oxides) for the samples prepared by this method. General comments summarizing some of the statistically significant observations from these measurements are provided in Table 5. In the two columns after the comments in this table, the M-14 and M-13 average measurements for the SME samples that were involved in this testing are provided. The percent relative difference (% Rel Diff) between each pair of M-14 and M-13 averages is calculated and presented in the last column of this table. The % Rel Diff entries are shaded for those M-14 and M-13 averages that are statistically different (with approximately 95% confidence). Thus, several of the oxides yield M-14 and M-13 averages that are statistically different (with ~95% confidence). Note that several of the major oxides (those oxides in the vitrified SME product at concentrations of at least 0.5 wt%) have % Rel Diffs greater than 5%. Also, note that for all of these oxides the M-13 averages are smaller than the M-14 averages. In the last column of Table 5, the 4 categories of oxides are identified and the assessment of whether or not the corresponding acceptance criterion for that category was met (i.e., a "yes", "no", or "NA" {not applicable} entry in this last column). Thus, the category 1 oxides Al_2O_3, CaO, Fe_2O_3, Li_2O, MnO, NiO, and U_3O_8 did not meet their respective acceptance criteria.

Table 5. Highlights of the M-13 versus M-14 Mixed Acid Measurements

(SME Measurements are in wt% oxides and NA implies not applicable.)

Oxide	Comments Regarding the Comparisons of M-13 vs M-14	M-14 Average	M-13 Average	% Relative Difference	Category/ Criterion Met
Al_2O_3	M-13 provides smaller concentration measurements.	5.017	4.699	-6.34%	1/no
B_2O_3	Not Available (NA)	NA	NA	NA	NA
CaO	M-13 provides smaller concentration measurements.	1.210	1.113	-8.05%	1/no
Cr_2O_3	M-13 is less precise and provides smaller concentration measurements.	0.101	0.079	-22.08%	2/yes
CuO	M-13 less precise	0.026	0.016	-38.74%	3/NA
Fe_2O_3	M-13 provides smaller concentration measurements.	13.176	12.493	-5.19%	1/no
K_2O	M-13 less precise	0.493	0.415	-15.89%	2/yes
Li_2O	M-13 is less precise and provides smaller concentration measurements.	5.415	4.723	-12.77%	1/no
MgO	There appear to be no issues for this oxide.	1.039	1.010	-2.83%	1/yes
MnO	M-13 provides smaller concentration measurements.	1.555	1.450	-6.76%	1/no
Na_2O	M-13 provides smaller concentration measurements.	9.902	9.536	-3.69%	1/yes
NiO	M-13 provides smaller concentration measurements.	0.600	0.558	-7.09%	1/no
SiO_2	There appear to be no issues for this oxide.	49.953	49.092	-1.72%	1/yes
TiO_2	M-13 is less precise and provides smaller concentration measurements.	0.051	0.044	-14.12%	3/NA
U_3O_8	M-13 provides smaller concentration measurements.	3.617	3.071	-15.10%	1/no
ZrO_2	M-13 is less precise and provides smaller concentration measurements.	0.064	0.054	-15.58%	3/NA

Table 6 presents similar information for the M-14 and M-13 average measurements from the ARG-1 samples that were prepared using the mixed acid method. For these measurements, the category 1 oxides Al_2O_3, Fe_2O_3, Li_2O, MnO, Na_2O, NiO, and TiO_2 did not meet their respective acceptance criteria.

Table 6. Highlights of ARG-1 Mixed Acid Measurements for the M-13 versus the M-14

(Measurements are in wt% oxides and NA implies not applicable.)

Oxide	M-14 Avg.	M-13 Avg.	% Relative Difference	Category/ Criterion Met
Al_2O_3	4.600	4.359	-5.24%	1/no
B_2O_3	NA	NA	NA	NA
CaO	1.443	1.374	-4.78%	1/yes
Cr_2O_3	0.104	0.092	-11.29%	2/yes
CuO	0.008	-0.004	-151.85%	3/NA
Fe_2O_3	14.124	13.364	-5.38%	1/no
K_2O	2.712	2.588	-4.58%	1/yes
Li_2O	3.194	2.739	-14.25%	1/no
MgO	0.848	0.825	-2.72%	1/yes
MnO	1.895	1.765	-6.88%	1/no
Na_2O	11.526	10.925	-5.22%	1/no
NiO	1.049	0.960	-8.54%	1/no
SiO_2	45.959	45.287	-1.46%	1/yes
TiO_2	1.190	1.102	-7.42%	1/no
U_3O_8	0.189	0.046	-75.54%	3/NA
ZrO_2	0.139	0.119	-14.64%	2/yes

2.5 Reporting SME Chemical Compositions

For the M-14 measurements, the reported SME compositions rely on the fusion values for Al_2O_3 and B_2O_3, the average of the fusion and mixed acid values for SiO_2, and the mixed acid values for all other oxides. Table 7 provides the combinations of the fusion and mixed acid values from the M-13 ICP that were used to represent the SME compositions for this evaluation. Based upon the results from this study, the use of the mixed acid results to represent the SME compositions was limited with only MgO, Na_2O, and ZrO_2 measurements being provided by this preparation method. Thus, Table 7 is the recommended way of using the mixed acid and fusion measurements generated by the M-13.

Table 7. Representing the SME Measurements from the M-13

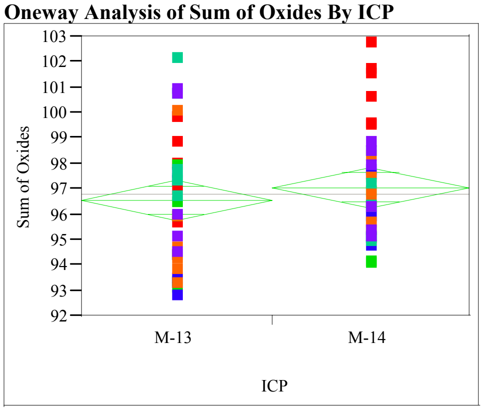
Oxide	Represented by
Al_2O_3	Fusion
B_2O_3	Fusion
CaO	Fusion
Cr_2O_3	Fusion
CuO	Fusion
Fe_2O_3	Fusion
K_2O	Fusion
Li_2O	Fusion
MgO	Mixed Acid
MnO	Fusion
Na_2O	Mixed Acid
NiO	Fusion
SiO_2	Fusion
TiO_2	Fusion
U_3O_8	Fusion
ZrO_2	Mixed Acid

2.6 Sum of Oxides Comparisons between ICPs

Using the M-13 data as indicated in Table 7 and the M-14 data as currently done for PCCS, a sum of oxides was computed for each SME sample. Figure 2 provides a comparison of the resulting values from the two ICPs. The comparisons suggest that, even though the M-13 sums are on average ~ 0.5 wt % smaller than those of the M-14, there is no statistically significant difference between the means or variances of these values for sum of oxides from the two ICPs.

Figure 2. Comparisons of Sums of Oxides for SME Samples

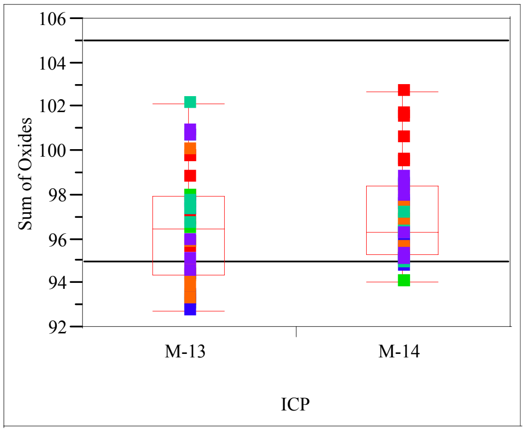
Type of Sample=SME
Oneway Analysis of Sum of Oxides By ICP



```
Oneway Anova
Summary of Fit
Rsquare                              0.011129
Adj Rsquare                           -0.0032
Root Mean Square Error               2.414064
Mean of Response                     96.81208
Observations (or Sum Wgts)                 71
t Test
Assuming equal variances
              Difference   t Test   DF    Prob > |t|
Estimate        -0.50499   -0.881   69        0.3813
Std Error        0.57305
Lower 95%       -1.64819
Upper 95%        0.63821
Means for Oneway Anova
Level    Number      Mean   Std Error   Lower 95%   Upper 95%
M-13         35   96.5560     0.40805      95.742      97.370
M-14         36   97.0610     0.40234      96.258      97.864
Std Error uses a pooled estimate of error variance
```

Figure 3 provides an additional comparison, a comparison of box plots, of the sum of oxides for the SME samples. The top and bottom of each box provides the 75th and 25th percentiles for the set of measurements, and the line across the box indicates the 50th percentile, or median, for the data. This box plot comparison includes all of the replicates for all of the calibration blocks. Horizontal lines are displayed on the graph to indicate the 95 and 105 wt% limits imposed on the sum of oxides by PCCS. The graph suggests that the M-13 values are more likely to fail the lower 95% wt% limit than the M-14 values (~28% of the M-13 measurements are below this limit versus ~17% of the M-14 measurements). Thus, the M-13 may fail the sum of oxides constraint approximately 65% more often than the M-14 for a single SME sample based upon the results of this study. Note however, that DWPF's process control strategy does not rely on the sums of oxides for individual samples, as discussed in the next section.

Figure 3. Box Plot Comparisons of Sums of Oxides for SME Samples with 95 and 105% Limits



2.7 Acceptability of M-13 Measurements for Each Calibration Block

The chemical composition measurements of SME samples are critical for process control and product quality assurance as each SME batch is processed. A decision on the acceptability of each SME batch is facilitated by PCCS. In this section, the measurements for each of the 6 M-13 calibration blocks are judged for acceptability against the PCCS constraints. For each of the calibration blocks, there were 6 measurements from which 4 were selected. The set of 4 measurements for each calibration block served as input to the PCCS evaluation process. For DWPF, the selection protocol involves two steps: 1) selecting which elements were used from which dissolution method (Table 7 was used for this step) and 2) selecting the best 4 out of 6 digestions (the protocol described in [5] was used for this second step).

The selection of the 4 of 6 replicates in each block for input into the PCCS evaluation was conducted as follows. For each calibration block, the 6 mixed acid replicates were ranked 1 through 6 using the absolute difference of each of their sums of oxides relative to a reference value of 91 wt% for this sum, with the smallest difference being given the ranking of 1. A similar ranking was conducted for the fusion replicates for each calibration block relative to a reference sum of oxides of 84.8 wt%. For each calibration block, the 4 highest ranked mixed acid replicates were combined in ranked order with the 4 highest ranked fusion replicates to define the 4 of 6 measured compositions for evaluation against the PCCS constraints. The evaluation was conducted using the assessment method established in [6] and utilized the Measurement Acceptability Region (MAR) criteria (the more restrictive criteria used by PCCS). Each of the 6 calibration sets yielded composition measurements that met all of the PCCS constraints at the current MAR level[4]. Table 8 provides a listing of predictions for some of the more important process and product quality properties for each of the calibration sets. The first column of this table identifies the calibration set; the second column provides the MAR limit for lithium (Li) durability (expressed as a limit on ΔG_p, the free energy of hydration variable used to model durability [7]); the third column provides the value of the free energy of hydration variable, ΔG_p, determined for the sample measurements; the fourth column is the predicted normalized leachate releases (NL) for lithium based upon the ΔG_p value (whose unit of measure is in kcal/100 g of glass); the fifth column is the predicted

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[4] One of the inputs to the MAR is a covariance matrix that estimates the random errors due to sampling and analytical uncertainties. For the assessments discussed in this section, the current covariance matrix of PCCS was used. The next section provides additional discussion of the PCCS covariance matrix.

liquidus temperature (T_L) in degrees Celsius (°C), the sixth column is the predicted viscosity in Poise (P), and the last column is the sum of oxides in wt%. Two of the columns associated with durability will be revisited in the next section to support the discussion there. Once again, the average of the 4 of 6 measurements for each and every one of the M-13 calibration blocks met all of the constraints when evaluated at the PCCS MAR. Thus, the M-13's measurements consistently led to the appropriate PCCS conclusion of acceptability for these samples.

Table 8. Evaluation Against the PCCS Constraints Using 4 of 6 Replicate Samples to Represent Each M-13 Calibration Block

Calibration Set	Li ΔG_p MAR Limit	Li ΔG_p Value	Predicted NL[Li (g/L)]	Predicted T_L (°C)	Predicted Viscosity (P)	Sum of Oxides (wt%)
1	-12.395	-8.224	0.46	971.0	70.0	97.4
2	-12.395	-8.062	0.43	960.6	67.2	96.0
3	-12.395	-7.761	0.39	958.4	73.3	95.7
4	-12.395	-8.834	0.56	982.8	57.6	96.1
5	-12.395	-8.593	0.52	929.7	63.8	97.3
6	-12.395	-8.445	0.49	959.1	66.3	95.4

2.8 Impact to PCCS Algorithms

In the previous section, an acceptability decision was offered for each of the M-13 calibration sets based upon the measurements of the set and the current PCCS algorithms. One of the inputs to the MAR algorithms of PCCS is the covariance matrix that estimates the random errors in the elemental concentration measurements; these errors are due to sampling and analytical uncertainties. For the assessments discussed in the previous section, the covariance matrix that is currently programmed into PCCS for the M-14 was used. As more information on the performance of the M-13 is generated, a covariance matrix can be estimated to capture the sampling and analytical random errors that would be representative of the M-13's use to provide measurements for PCCS. Note that the contribution to the uncertainty from the sampling errors (historically, the dominant source of uncertainty in the measurement of the SME samples) is associated with the use of "peanut" vials with the Hydragard® sampling system and will remain the same regardless of the ICP being used.

The data that were generated by this side-by-side study were not sufficient for the estimation of a new covariance matrix for the M-13. However, efforts are underway to generate the necessary measurements. Once this information is available, an appropriate covariance matrix for the M-13 can be estimated, the impact of its use in PCCS can be evaluated, and a decision can then be made on the need to update PCCS to fully integrate a new covariance matrix for the M-13 or to leave the current covariance matrix as is. The latter decision would be an option if the current covariance matrix were seen to adequately bound the likely M-13 errors. However, the evaluations presented in this report result in no changes, nor recommendations for changes, to PCCS.

If the M-13 were called into service before this covariance matrix assessment was completed, what is the likely impact to the reliability of the PCCS acceptability decision? The impact due to the covariance matrix on the acceptability region for durability (the critical product quality metric) may be seen by the difference between the Li MAR limit of –12.395 for ΔG_p and the Li PAR limit, which has the value –12.781 for ΔG_p [4]. For the MAR limit the critical value is shifted 0.386 ΔG_p units in the positive direction. As seen in this example, the impact of going from the MAR to the PAR limit for durability is a shift in the value of ΔG_p by an amount that is typically 0.3 to 0.6 units. The shift in ΔG_p limits needed to account for the M-13 MAR is expected to be close to these values. The values in the third column of Table 8 reveal that for sludge/frit systems that are not durability limited (such as the SB2/Frit 320 system, whose samples were used in this study), there is a large buffer between the ΔG_p value derived from the SME samples and the PAR limit (> 3.9 units). The difference is many times larger than the shift of .ΔG_p values in going from the PAR to the MAR as measurement uncertainty is accommodated. For sludge/frit systems that are not durability limited, there is high confidence that adequate protection from a poor decision (due to measurement uncertainty) regarding the glass quality of the SME samples is provided by this buffer between the ΔG_p value derived from the SME samples and the PAR limit for durability.

If DWPF's sludge/frit system becomes limited by a process property prediction such as viscosity or liquidus temperature as waste loading is increased, then the confidence of satisfying the MAR constraint for this limiting property may be less than the nominal 95% and will depend upon how close the SME property prediction is to the MAR limit for the property (i.e., the bigger the difference between the property prediction and the MAR limit, the less of an issue this becomes). If it were to become a necessity to use the M-13 for production control, this issue could be mitigated by a judicious use of the SME blending strategy as part of the risk-based management of the DWPF operation.

2.9 Impact Using M-13 Measurements for Estimating Waste Loading at the SME

As seen in Table 3, the data from this study suggest that Li measurements by the M-13 for samples prepared using the fusion method are less precise than these same measurements by the M-14. One issue of concern regarding this observation is the impact on estimates of waste loading (WL) that are made from the SME samples. WL is an important metric of DWPF performance; it is estimated for each of the four samples of a SME batch; and an overall estimate of the SME batch itself is determined by averaging the four sample results. The equation for estimating the WL for a SME sample is given by

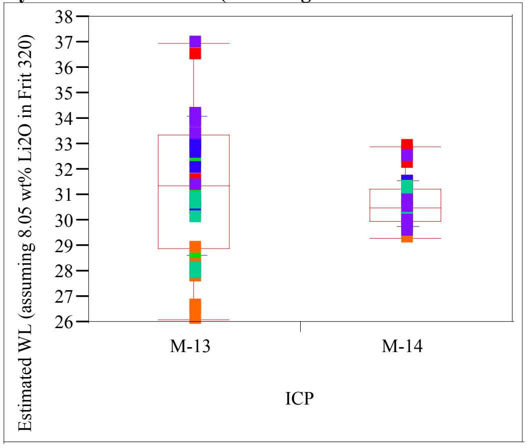
$$\mathrm{WL} = 100 \cdot \left(1 - \frac{\mathrm{Li_2O} \big/ (\text{Sum of Oxides})}{\mathrm{Frit}_{\mathrm{Li_2O}} \big/ 100} \right)$$

where $\mathrm{Li_2O}$ is the measured wt% value for this oxide in the SME sample, Sum of Oxides is the sum of oxides in wt% for the sample, and $\mathrm{Frit}_{\mathrm{Li_2O}}$ is the wt% of lithium oxide in the frit used to process the sludge (e.g., Frit 320 for Sludge Batch 2).

Figure 4 is presented to provide some initial insight into this issue. This figure provides a plot of the WLs determined from all the sample replicates for all of the calibration blocks for both the M-13 and M-14. In these determinations a constant value of 8.05 wt% was used for $\mathrm{Frit}_{\mathrm{Li_2O}}$. The means of the two sets of WLs are not statistically different, but, as seen in this plot, there is more variation in the M-13 values than in the M-14's. In fact (under the assumption of normality for the underlying populations), the two variances are statistically different. Thus, even though, the average estimate of WLs for the 2 ICPs is comparable, the M-13's values have more scatter in them than the estimates generated from the M-14's measurements for the results of this study.

Figure 4. Box Plot Comparisons of SME Waste Loadings by ICP

Type of Sample=SME with all data used
Oneway Analysis of Estimated WL (assuming 8.05 wt% Li2O in Frit 320) By ICP



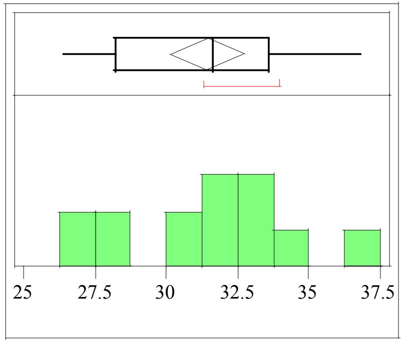
Means and Std Deviations

Level	Number	Mean	Std Dev	Std Err Mean	Lower 95%	Upper 95%
M-13	35	31.3290	2.72503	0.46061	30.393	32.265
M-14	36	30.6815	0.91581	0.15263	30.372	30.991

Figure 5 provides an additional look at WLs generated by the M-13 results. In this plot, WLs are computed for the 4 of 6 samples used to represent each calibration set of the previous sections. The WL values range from a low of 26.44 to a high of 36.735%.

Figure 5. Histograms of Waste Loadings for 4 of 6 SME Samples for Each Calibration Set

Estimated WL (assuming 8.05 wt% Li2O in Frit 320)



Quantiles

100.0%	maximum	36.736
99.5%		36.736
97.5%		36.736
90.0%		35.464
75.0%	quartile	33.610
50.0%	median	31.618
25.0%	quartile	28.221
10.0%		26.776
2.5%		26.440
0.5%		26.440
0.0%	minimum	26.440

Moments

Mean	31.416622
Std Dev	2.9329266
Std Err Mean	0.6115575
upper 95% Mean	32.684915
lower 95% Mean	30.14833
N	23

Table 9 provides summary statistics of these values by calibration set. The mean, standard deviation, and standard error of the mean (i.e., the standard deviation divided by the square root of the sample size). To put these values in perspective, consider the WLs for SME batches 234 through 265 (information for these SME batches is available on the WG09 server), which yield an average standard error of 0.46% with values for the standard error ranging from a low of 0.06% to a high of 1.17%. Thus, while the standard errors of the M-13's mean WLs for the 6 calibration sets of this study are somewhat at the upper end of this interval and some additional variation in the M-13's estimated WLs would be expected, they are not out of line with the standard errors seen over recent SME batches.

Table 9. Estimated WL by Calibration Block Using 4 of 6 Replicate Samples to Represent Each M-13 Calibration Block

Calibration Block	Mean WL (%)	Standard Deviation (%)	Standard Error (%) of the Mean
1	33.98	1.99	0.99
2	32.67	0.98	0.49
3	31.51	1.27	0.63
4	27.05	0.77	0.39
5	29.50	1.59	0.80
6	34.56	1.89	0.94

2.10 Viable Replacement

In the discussions above, an array of issues associated with the viability of the M-13 as a replacement for the current production ICP (the M-14) has been addressed. No roadblocks were encountered at any point in this discussion for such a replacement if the M-14 were to fail. While additional work is needed to fully integrate the M-13 into DWPF's operational systems, use of this ICP will be adequate for sludge/frit blending and will lead to reliable SME acceptability decisions for product quality. For a sludge/frit system that is limited by a process property prediction such as viscosity or liquidus temperature as waste loading is increased, the SME blending strategy can be adjusted to lessen the impact of an incomplete definition of the M-13's MAR on the acceptability decision until such time as the complete definition can be determined.

3.0 CONCLUSIONS

Even though most of the differences between the M-14 and M-13 averages for the cold chem SRAT measurements are statistically significant, the only major SRAT components with M-13 averages that differ from their M-14 counterparts by more than 5% are CaO, SiO_2, and U_3O_8. Applying the acceptance criteria outlined in the test plan [1] for SRAT samples prepared using the cold chem method yields: the category 1 oxides CaO, SiO_2, and U_3O_8 and the category 2 oxides B_2O_3 and K_2O did not meet the acceptance criteria. With the results from this study as a guide, measuring the SRAT samples prepared via cold chem using the M-13 would be expected to yield measurements that are less precise for approximately ½ of the oxides being tracked and slightly biased (low) for CaO, SiO_2, and U_3O_8 as compared to using the M-14. However, the SRAT measurements are used in support of the blending process and are not part of the SME acceptability decision of PCCS. Feedback provided from measurements of SME samples and predictions made in PCCS (predictions for process and product quality as well as waste loading) is expected to lead to adjustments to and improvement in the blending strategy, if improvements are needed. Thus, using the M-13 as part of the analytical process for SRAT product samples will not be a problem for (and should therefore be acceptable to) DWPF Process Chemistry Engineering.

For the fusion SME measurements, only B_2O_3 and SiO_2 yield M-14 and M-13 averages that are statistically different (with ~95% confidence). Also, note that all of the major oxides have % relative differences between the two ICPs of less than 5%. Several of the oxides yield M-14 and M-13 averages for the mixed acid SME data that are statistically different (with ~95% confidence). Several of the major oxides have % relative differences between the two ICPs that are greater than 5%. For all of these oxides, the M-13 averages are smaller than the corresponding M-14 averages for the mixed acid SME data.

Applying the acceptance criteria outlined in the test plan [1] yields: (a) for the SME samples prepared using the fusion method, all category 1 and category 2 oxides met their respective criteria, (b) for the SME samples prepared using the mixed acid method, the category 1 oxides Al_2O_3, CaO, Fe_2O_3, Li_2O, MnO, NiO, and U_3O_8 did not meet their respective acceptance criteria. These results led to the following recommended protocol for using the M-13's mixed acid and fusion measurements for a SME sample: for MgO, Na_2O, and ZrO_2 use the mixed acid measurements and for Al_2O_3, B_2O_3, CaO, Cr_2O_3, CuO, Fe_2O_3, K_2O, Li_2O, MnO, NiO, SiO_2, TiO_2, and U_3O_8 use the fusion measurements. . Using this protocol, 4 of 6 measurements for each and every one of the M-13 calibration blocks were selected, and when the each set of 4 samples were evaluated against the PCCS MAR constraints, they met all of the constraints. This included the sum of oxides constraint, even though the sum of oxides for an individual SME sample is expected to fail 65% more often for the M-13 than for the M-14. For sludge/frit systems that are not durability limited, there is high confidence that adequate protection from a poor decision (due to measurement uncertainty) regarding the glass quality of the SME samples is provided by this buffer between the ΔG_p value derived from the SME samples and the PAR limit for durability.

In the discussions above, an array of issues associated with the viability of the M-13 as a replacement for the current production ICP (the M-14) has been addressed. No roadblocks were encountered at any point in this discussion for such a replacement if the M-14 were to fail. While additional work is needed to fully integrate the M-13 into DWPF's operational systems, use of this ICP will be adequate for sludge/frit blending and will lead to reliable SME acceptability decisions for product quality. For a sludge/frit system that is limited by a process property prediction such as viscosity for liquidus temperature as waste loading is increased, the SME blending strategy can be adjusted to lessen the impact of an incomplete definition of the M-13's MAR on the acceptability decision until such time as the complete definition can be determined. However, the evaluations presented in this report result in no changes, nor recommendations for changes, to PCCS.

4.0 REFERENCES

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