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Results of Analyses of the Next Generation Solvent for Parsons

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EXECUTIVE SUMMARY

Savannah River National Laboratory (SRNL) prepared a nominal 150 gallon batch of Next Generation Solvent (NGS) for Parsons. This material was then analyzed and tested for cesium mass transfer efficiency. The bulk of the results indicate that the solvent is qualified as acceptable for use in the upcoming pilot-scale testing at Parsons Technology Center.

LIST OF ABBREVIATIONS

AD – Analytical Development
EDL – Engineering Development Laboratory
ESS – Extraction, Scrub, Strip
FTIR – Fourier Transform Infrared Spectroscopy
HPLC – High Performance Liquid Chromatography
NGS – Next Generation Solvent
RSD – relative standard deviation
SRNL - Savannah River National Laboratory
SVOA – Semi Volatile Organic Analysis

1.0 Introduction

This report describes the analysis and testing of a batch of Next Generation Solvent (NGS) prepared in support of pilot-scale testing in the Parsons Technology Center.¹ A total of ~150 gallons of NGS solvent was prepared in late November of 2011. Details for the work are contained in a controlled laboratory notebook.²

2.0 Experimental Procedure

In late November 2011, the Engineering Development Laboratory (EDL) prepared ~150 gallons of NGS solvent and contained the material in three stainless steel drums. Two samples from each drum were removed and archived, generating six samples in total. 10 mL from each archived sample were combined into a single bottle and mixed to generate a solvent composite. The three drums were shipped to Parsons Technology Center on 5 December 2011 along with ~270 lb of Isopar[®] L, ~70 lb of Modifier, ~1 kg of a guanidine derivative, and the unused portion of the MaxCalix extractant.

This composite sample from the three drums was then analyzed via Semi-Volatile Organic Analysis (SVOA), High Performance Liquid Chromatography (HPLC), Fourier Transform Infra-Red (FTIR) spectroscopy and tested for cesium mass transfer efficiency in an Extraction-Scrub-Strip (ESS) test.

3.0 Results and Discussion

Three, 50 gallon batches of the NGS solvent was prepared in three different clean, stainless steel drums (#1, #3 and #5). The same procedure was used used to mix the components in each drum.³ First, half the required weight of Isopar[®] L was added, followed by the entire weight of the Modifier.[√] Then, the entire weight of the guanidine^γ was added, followed by the entire weight of the MAXCalix.[♥] Finally, the remainder of the Isopar[®] L was added. The contents of the drum were then mixed for ~ 1hour. There was no active temperature control, and the activity took place at room temperature (~20-22 °C).The masses of each material were recorded in each addition. Mixing was provided by an overhead mixer inserted into the drum. Table 1 lists the weights of each component used in each drum in kilograms.

Table 1. Weights of Components in Each Drum (kg)

Component	Drum #1	Drum #3	Drum #5
Isopar [®] L	119	119	119
Modifier	32.2	32.1	32.2
MAXCalix	9.08	9.08	9.08
Guanidine	0.230	0.230	0.230

[√] Modifier stands for 1-(2,2,3,3,-Tetrafluoropropoxy)-3-(4-sec-butylphenoxy)-2-propanol

^γ “guanidine”, the suppressor, is short for N, N'-cyclohexyl, N''-isotridecyl guanidine

[♥] The extractant, MaxCalix, stands for 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy)calix[4]arenebenzocrown-6

Two, 30 mL samples from the contents of each prepared drum were removed. From each of these six samples, SRNL removed 10 mL of sample and composited these into a single Teflon™ bottle. The density of the solvent composite was measured once using a 2 mL density tube, and three times using a 10 mL electronic pipette. The average of these measurements gave a density of 0.845 g/mL with a residual standard deviation (RSD) of 0.25% (T=25 °C). This result is higher than what is predicted to be the correct density (0.827 – 0.839 g/mL at 25 °C).^{4,5} SRNL re-measured the solvent in triplicate, using only 2mL density tubes, and taking care to minimize reading errors. In this re-measurement, the density was measured to be 0.828 g/mL with a RSD of 0.16% (T=21.5 °C). SRNL feels that this second set of measurements is more accurate. We have found that with lighter density organic materials, using 10 mL pipettes to measure the density is problematic. We recommend preferentially using the 2mL glass tubes in the future.

Given the very small difference between the target and measured density, SRNL does not recommend trying to trim the solvent.

After the density measurement, samples of the composite were analyzed by SVOA, HPLC, and FTIR. The results are reported in Table 2.

The analytical results are consistent with each other. The Isopar® L concentration appears slightly low, with the Modifier slightly high and the Extractant concentration on target. The HPLC and FTIR data suggests very little variance from the nominal results while SVOA data shows a greater variance. Historically, SVOA tends to not agree as well as the other two methods. However, these results are all within the analytical method uncertainties of being on target (100%).

The guanidine analysis concentration appears low. However, while the SVOA analysis is derived from ORNL protocols,⁶ the equivalent SRNL method has not been rigorously developed for this compound and preference is given to the gravimetric data from preparations. Analytical Development (AD) is still qualifying the analytical method for this analyte. The calibration curves for this analysis are not within acceptable parameters at this point. Therefore, this low result compared to nominal values should not be taken to mean the guanidine is low, but that the method is still being developed. (The ORNL equipment is a dedicated instrument for the research program; the SRNL instrument is used for multiple programs and routine analyses. Hence, less optimal performance for the SRNL equipment is not unexpected.).

Table 2. Sample Results for the NGS Composite

Analysis	Method	LIMS #	Result (mg/L) [#]	Nominal Result (mg/L)	% of (Result ÷ Nominal Result)
Isopar [®] L	SVOA	300295789	570,000	629,000	90.6%
Isopar [®] L	FTIR	NA	610,000	629,000	97.0%
average	all	NA			93.8%
Modifier	SVOA	300295789	185,000	170,000	109%
Modifier	HPLC	300295789	179,000	170,000	105%
Modifier	FTIR	NA	165,000	170,000	97.1%
average	all	NA			104%
guanidine	SVOA	300295789	650	1,220	53.3%
Extractant	HPLC	300295789	46,000	47,900	96.0%
Extractant	FTIR	NA	49,300	47,900	103%
average	All	NA			99.5%

[#] Analytical uncertainty is 20% for SVOA and 10% for HPLC. FTIR analytical uncertainty is 15% for Isopar[®] L, 10% for Modifier and 25% for Extractant. Density results from the average of replicate volumetric trials typically have a percentage standard deviation of <1% between each value and the average.

NA = not applicable

3.1 ESS Testing

For the ESS tests, we followed the same protocol established for recent work.^{7,8} The ESS test is a series of organic (solvent) to aqueous (Tank 49H simulant) contacts. There are extraction step, two scrub steps, and three strip steps. Between each step we separate the phases, remove a portion of each phase for analysis, and place one of the phases back in the funnel and contact it with a new organic or aqueous phase (Table 3). The two phases are allowed to contact for ~24 hours before proceeding to the next step.

Table 3. ESS Test Steps

Step #	Type	Nominal Volume ORGANIC	Nominal Volume AQUEOUS	O/A Ratio
1	Extraction	30 mL	120 mL	0.25
2	Scrub #1	30 mL	7.5 mL	3.75
3	Scrub #2	30 mL	7.5 mL	3.75
4	Strip #1	30 mL	7.5 mL	3.75
5	Strip #2	30 mL	7.5 mL	3.75
6	Strip #3	30 mL	7.5 mL	3.75

The original Cs-containing aqueous phase was a waste simulant spiked with ^{137}Cs . The scrub aqueous phase is 0.025 M sodium hydroxide, and the strip aqueous phase is 0.001 M boric acid.

The Cs content for each phase in each step is measured by gammascan with a typical 5% analytical uncertainty. Once corrected for operating temperature ⁹ -- each step has its own temperature correction factor -- the distribution values are calculated. The distribution factor, D_{Cs} , for any particular step is equal to the Cs concentration in the organic phase divided by the Cs concentration in the aqueous phase. For comparative purposes, we present the data from this test and from a previous baseline test performed under similar conditions, with the exception that the aqueous phase was actual Tank 49H material. See Table 4 for the results of both tests. The tabulated results are all temperature corrected (to 23 °C for extraction and scrub steps, and to 33 °C for strip steps).

Table 4. Cesium Distribution Values for the ESS Test

Material	Extraction	Scrub #1	Scrub #2	Strip #1	Strip #2	Strip #3
Acceptable Range ⁹	>60	2-4	1-2.5	<0.33	<0.007	<0.003
NGS solvent, this batch	104	5.79	2.70	0.00283	<0.00350	<0.0284
NGS solvent, previous test ¹⁰	80.6	3.63	1.13	0.00947	0.00235	0.337

Both tests show excellent extraction results compared to what is currently used as the acceptable range of results, and both show the same trends. Scrub #1 D_{Cs} results are high, as is typical with the NGS results. ^{11,12,13} Strip #1 and #2 values are also quite good and within the acceptable range. In numerous experiments -- both at SRNL and ORNL -- Strip #3 distribution values have shown modest increases over Strip #2 values. In this data set, the trend is indeterminate due to the relatively high detection limits.

High distribution values in the extraction steps are important as they indicate transference of Cs from the aqueous phase into the organic phase. Low values are important in the strip steps as they indicate successful removal of the cesium. The scrub values should show moderate values indicating not much transfer in either direction.

SRNL measured the pH of the aqueous phase of each scrub and strip step. The results are listed in Table 5.

Table 5. Aqueous Phase pH Results From the ESS Test

Material	Scrub #1	Scrub #2	Strip #1	Strip #2	Strip #3
NGS solvent, this batch	13	13	8	6	5.5

The pH results have a 0.5 pH unit uncertainty and are typical of the NGS ESS tests.

4.0 Conclusions

Analysis of the Parsons NGS solvent indicates that the material is acceptable for use. SRNL is continuing to improve the analytical method for the guanidine.

5.0 References

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