Thermal and Spectroscopic Analyses of Next Generation Caustic Side Solvent Extraction Solvent Contacted with 3, 8, and 16 Molar Nitric Acid

F. F. Fondeur
S. D. Fink

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REVIEWS AND APPROVALS

AUTHORS:

_____
F.F. Fondeur, Separations and Actinide Science Programs   Date

TECHNICAL REVIEW:

_____
D. T. Hobbs, Separations and Actinide Science Programs   Date

APPROVAL:

_____
S.D. Fink, Manager and Co-author   Date
Separations and Actinide Science Programs

_____
S.L. Marra, Manager   Date
Environmental & Chemical Process Technology Research Programs

_____
B.A. Oard, Manager   Date
MCU Life Extension/NGS

_____
J. E. Occhipinti,   Date
SRR Engineering

EXECUTIVE SUMMARY

A new solvent system referred to as Next Generation Solvent or NGS, has been developed at Oak Ridge National Laboratory for the removal of cesium from alkaline solutions in the Caustic Side Solvent Extraction process. The NGS is proposed for deployment at MCU[a] and at the Salt Waste Processing Facility. This work investigated the chemical compatibility between NGS and 16 M, 8 M, and 3 M nitric acid from contact that may occur in handling of analytical samples from MCU or, for 3 M acid, which may occur during contactor cleaning operations at MCU.

This work shows that reactions occurred between NGS components and the high molarity nitric acid. Reaction rates are much faster in 8 M and 16 M nitric acid than in 3 M nitric acid. In the case of 16 M and 8 M nitric acid, the nitric acid reacts with the extractant to produce initially organo-nitrate species. The reaction also releases soluble fluorinated alcohols such as tetrafluoropropanol. With longer contact time, the modifier reacts to produce a tarry substance with evolved gases (NO_x and possibly CO). Calorimetric analysis of the reaction product mixtures revealed that the organo-nitrates reaction products are not explosive and will not deflagrate.

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[a] At the start of this work, the program plan included deployment in MCU. Current program plan is to deploy the NGS in SWPF without testing in MCU. However, the potential exists that NGS may still be deployed in MCU at a later date

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LIST OF ABBREVIATIONS

Cs-7SB (or modifier)	1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol
CSSX	Caustic-Side Solvent Extraction
DCiTDG	*N,N'*-dicyclohexyl-N"-isotridecylguanidine, marketed by Cognis as Lix®79
D_{Cs}	distribution ratio for cesium
DF	decontamination factor
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
HPLC	High Performance Liquid Chromatography
MaxCalix	1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy) calix[4]arene-benzocrown-6
MCU	Modular Caustic-Side Solvent Extraction Unit
NGS	Next Generation Solvent
ORNL	Oak Ridge National Laboratory
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
SVOA	Semi-volatile Organic Analysis

1.0 Introduction

A solvent extraction process for the removal of cesium from alkaline solutions utilizes a novel solvent composition developed at the Oak Ridge National Laboratory (ORNL).[1] This solvent composition consists of a calix[4]arene-crown-6 extractant dissolved in an inert hydrocarbon matrix. A modifier[a] is added to the solvent to enhance the extraction power of the calixarene and to prevent the formation of a third phase. An additional additive, tri-octyl amine, is used to improve stripping performance and to mitigate the effects of any surfactants present in the feed stream. The process that deploys this solvent system is known as Caustic Side Solvent Extraction (CSSX). The solvent system has been deployed at the Savannah River Site (SRS) in the Modular CSSX Unit (MCU) since 2008.

The MCU uses centrifugal contactors (10-in for extraction stages and 5-in for scrub and strip stages) to provide mechanical mixing and phase separation between the solvent and alkaline waste solutions by way of two separations. The first separation extracts cesium from the waste solutions into the solvent system; the second separation strips the cesium from the solvent system while providing a nominal cesium concentration factor of 15. From its radioactive start-up in April 2008 until the end of August 2011, MCU processed approximately 2 million gallons of HLW solution for disposition. The decontaminated salt solution is sent to the SRS Saltstone Production Facility and the concentrated cesium stream is transferred to the Defense Waste Processing Facility.

Subsequent development efforts by ORNL have identified an improved solvent system that can raise the expected decontamination factor (DF) in MCU from ~200 to more than 40,000.[2] The improved DF is attributed to an increased distribution ratio for cesium (D_{Cs}) in extraction from ~15 to ~60, an increased solubility of the calixarene in the solvent from 0.007 M to 0.050 M, and use of boric acid (H_3BO_3) for stripping that yields D_{Cs} values less than 0.01. The improved solvent system contains four components: 1) 0.050 M 1,3-*alt*-25,27-Bis(3,7-dimethyloctyloxy) calix[4]arene-benzocrown-6, also known as MaxCalix, as the extractant; 2) 0.50 M 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, or Cs-7SB, as the Modifier; 3) 0.003 M *N,N'*-dicyclohexyl-N''-isotridecylguanidine, a guanidine derivative designated DCiTDG (also known as LIX® 79), as the suppressor; and 4) C_{12}-isoparaffinic hydrocarbon, or Isopar® L, as the diluent. The modified solvent system is referred to as the Next Generation Solvent (NGS).

During MCU and Salt Waste Processing Facility operations, unexpected shut downs and planned shut downs for maintenance will occur. Periodically during operations, salts will deposit in the contactors requiring cleaning of the units. The flushing operation for cleaning the centrifugal contactors will use 3 M nitric acid. Also, processing samples from MCU in F/H Labs involves the potential risk of inadvertent disposal of residual solvent to the drain system or contact with concentrated (8M and 16M) nitric acid. For the baseline solvent, prior studies assessed the reaction rates of the solvent with various concentrations of nitric acid.[3,4,5] Savannah River National Laboratory (SRNL) conducted similar tests with the new solvent contacting 3, 8, and 16 M to provide analogous safety bases data.[6,7,8]

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[a] An alkylphenoxy alcohol modifier (1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, also known as Cs-7SB) added to the solvent enhances the extraction power of the calixarene and prevents the formation of a third phase.
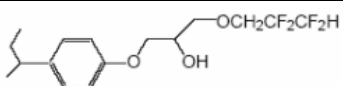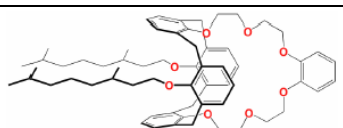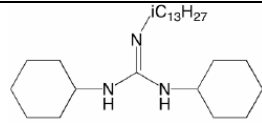
2.0 Experimental Procedure

Personnel took 20 mL of NGS (whose composition is shown in Table 1) and 40 mL of either 16 M, 8 M, or 3 M nitric acid and placed the two liquids in a 60 mL bottle (Teflon™ capped containing a 2 mm hole for gas release). The bilayer configuration (no mixing) represents likely scenarios during sampling disposal to waste drains or stagnant cleaning periods in the contactors. Two samples per each nitric acid concentration were prepared: one sample was used for visual tracking with time (photographs) and the other sample was used to provide samples of "physically" distinguishable layers for chemical analysis (by Fourier transform infrared spectroscopy, FTIR) and energetic screening by Differential Scanning Calorimetry (DSC). Additional aliquots (0.5 mL) of the NGS layer were analyzed to identify specific organic compounds by Semi-volatile Organic Analysis (SVOA) and High Performance Liquid Chromatography (HPLC). Each aliquot was placed in a 1 mL glass bottles (sized to avoid a large overhead that may change the composition of the removed liquid). Testing began at 08:10 on 14 September 2011, which is considered "time zero" for these studies.

FTIR analysis of the samples was conducted with a Nicolet Nexus 670 instrument using a single bounce attenuated reflectance diamond crystal. More than 100 scans were collected at a resolution of 4 cm^{-1} (total scan time was one minute) to obtain signal to noise ratios greater than 340.

DSC was conducted with Perkin Elmer PE7 instrument. Approximately 7.4 mg of sample was placed in a gold crucible that was covered loosely with a gold lid and then heated to 300 °C (and in some cases to 600 °C) at 20°C per min. The lid was placed on the gold cup to minimize liquid splashing out of the cup; however, the lid was not sealed, which allowed the release of any gas produced during the heating cycle.

Table 1. Component composition of Next Generation Solvent

Component	Next Generation Solvent concentration
1-(2,2,3,3-Tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-porpanol or Modifier	21 wt %
Isopar® L (diluent)	Linear/branched C-12 alkanes 74 wt %
MaxCalix (Extractant)	50 mM
DCiTDG (suppressor)	3 mM

3.0 Results and Discussion

Personnel analyzed the optical pictures using ImageJ[a] software to obtain both histogram and line profile to determine the width of the different layers in the bottles (as shown in Figure 3.1). The histogram was used to determine the color intensity in a given layer (peak height reflects number of pixels at that color). When two or more colors were present in a layer the histogram will show numerous distributions (some overlapping with each other). The mode of each peak was registered and used to determine the color of that layer. A typical image analysis is shown in Fig. 3.1 where a multimode histogram was de-convoluted into single peaks belonging to the different layers in a sample (in this case NGS in 16 M nitric acid). The peak mode for both the organic (top layer) and aqueous layer (bottom layer) and sometimes the interfacial layer was recorded as a function of time.

Count: 21252   Min: 19
Mean: 87.86029550   Max: 156
StdDev: 32.12677687 Mode: 82 (656)

Count: 13200   Min: 67
Mean: 102.44090909 Max: 156
StdDev: 23.72677632 Mode: 82 (620)

Count: 16368   Min: 85
Mean: 108.84707967 Max: 129
StdDev: 7.32491920 Mode: 111 (1024)

Sum of the above three

Count: 41316   Min: 19
Mean: 98.45377094 Max: 156
StdDev: 26.47989000 Mode: 114 (1114)

Final histogram
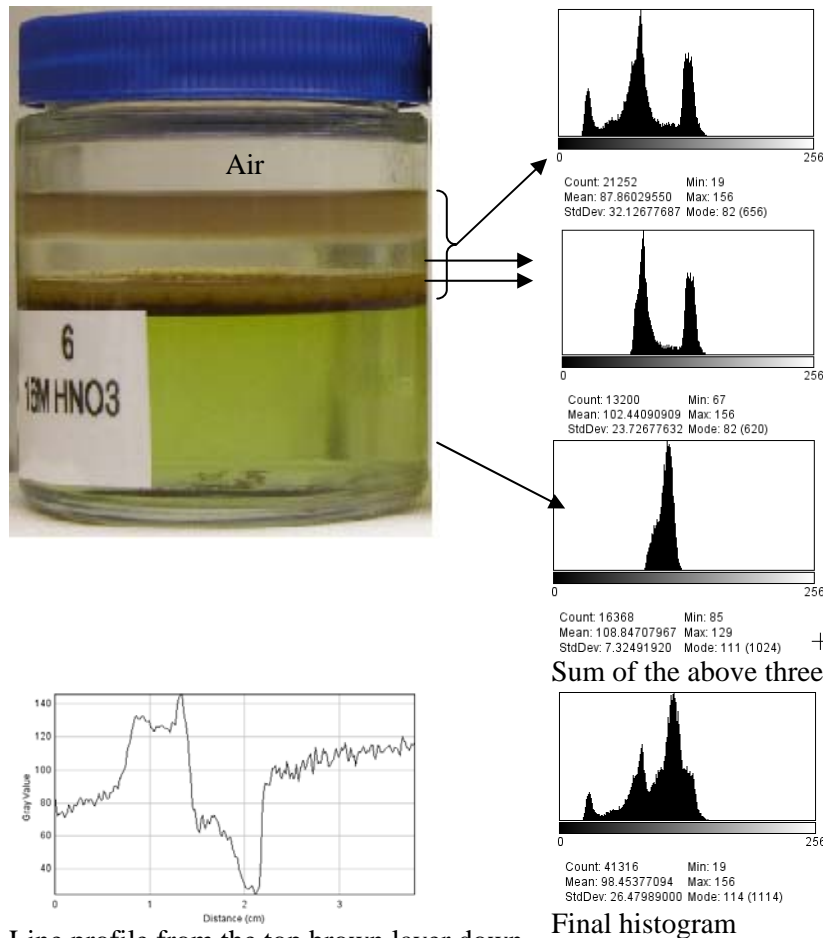
Line profile from the top brown layer down to aqueous layer (green)

Fig. 3.1. A typical breakdown of the histogram into the layers visible in a digital image. The mode of each peak was used to determine the color intensity with time. Also included is a line profile for estimating thickness of each layer.

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[a] ImageJ is the public domain software "Image Processing and Analysis in JAVA" available via the National Institute of Health.

Personnel also analyzed the different layers from the acid stability tests by FTIR and compared the spectra for the individual NGS components, which are shown in Figure 3.2. As can be seen from Fig. 3.2 each NGS component has a unique absorption peak that can be used for identification. Note that the modifier and extractant contain both aliphatic and aromatic carbon groups, whereas the diluent and suppressor contain only aliphatic carbon groups. In the case of nitration, nitro-alkanes have a unique peak in the 1601-1531 cm^{-1} region (1381-1310 cm-1 for the asymmetric stretching) while the nitro-aromatics have a unique peak at 1587-1555 cm-1 (1357-1318 for the asymmetric stretching).[9]
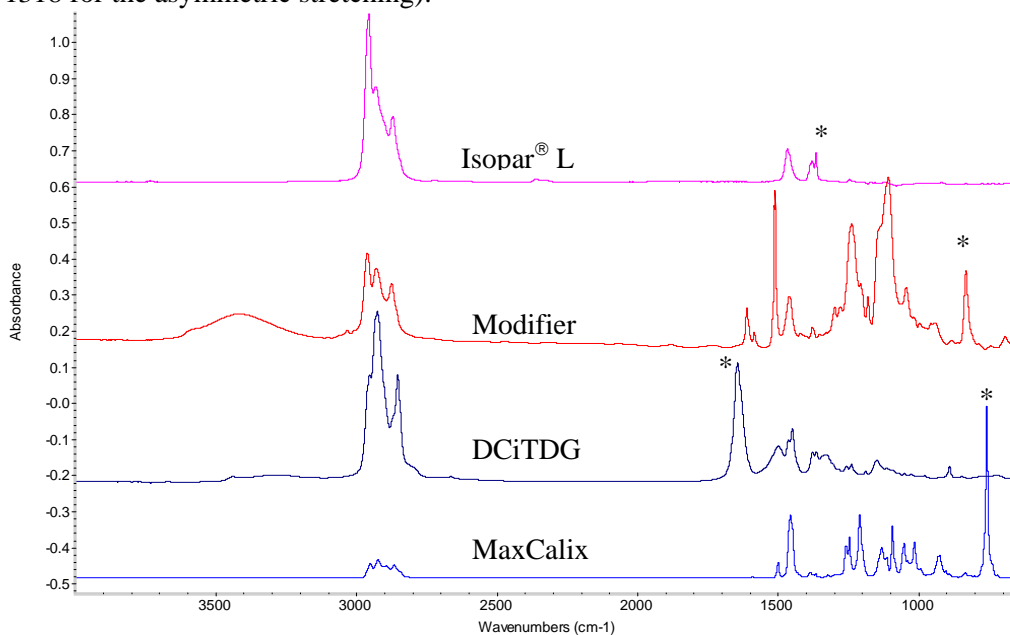

Fig. 3.2 The FTIR spectrum of the NGS components for identification in the subsequent figures. Asterisk indicate unique peak position.

Exothermic reactions in the DSC were evaluated against reported enthalpy of explosives in Fig. 3.3.[10]

Thermal stability of nitrocompounds

Compounds	T_{onset} (°C)	$-\Delta H$ (J g^{-1})	$-\Delta H$ (kJ mol NO$_2^{-1}$)
Ammonium nitrate	250	1577	126
Nitrobenzene	380	2757	339
Nitromethane	320	5292	323
2-Nitrophenol	250	2481	345
3-Nitrophenol	310	2269	316
4-Nitrophenol	270	2155	300
2-Nitrotoluene	290	2404	329
3-Nitrotoluene	310	2070	284
4-Nitrotoluene	320	2322	318
2-Nitroaniline	280	2225	307
3-Nitroaniline	300	2269	314
4-Nitroaniline	310	2026	279
2-Nitrobenzoic acid	270	1894	297
3-Nitrobenzoic acid	300	1899	298
4-Nitrobenzoic acid	310	1934	304
1,2-Dinitrobenzene	280	3310	259
1,3-Dinitrobenzene	270	3488	293
1,4-Dinitrobenzene	350	3701	311
2,4-Dinitrotoluene	250	3574	298
3,4-Dinitrotoluene	280	3987	333
2,6-Dinitrotoluene	290	3451	288
1-Chloro-4-nitrobenzene	395	2283	360
2,4-Dinitrophenol	240	3598	331
2,4,6-Trinitrophenol	220	5130	391

T_{onset}: onset temperature; ΔH: enthalpy change.

Fig. 3.3 The enthalpy of decomposition of energetic (explosive) materials (see Ref. 10).

4

NGS and 16 M Nitric Acid

We observed that components of the NGS immediately react with 16M nitric acid as evidenced by the development of highly colored regions at the organic/aqueous interface and the aqueous phase. Fig. 3.4 shows a series of pictures taken after 2, 4.5 and 6 hours of contact. A plot of the mode for both the aqueous and organic layer as a function of time is shown in Fig. 3.5. As can be seen in Fig. 3.5, the pixel value for the aqueous layer decreased rapidly initially, remains constant for about 2 hours and the begins to decrease again. This behavior suggest at least two different diffusions into (or out of) the aqueous layer. Note that the data at 14:12 hours is difficult to analyze and interpret since NO_x gas was generated as evidenced by the reddish-brown fumes and the emulsified organic phase.

In contrast, the histogram mode for the organic layer exhibits a small increase during the first 90 minutes followed by a rapid decrease over the next five hours indicating a possible single phenomenon occurred (again the data at 14:12 cannot be analyzed as discussed above due to NO_x). For example, a steady diffusion and reaction of components in or out of the organic layer may give a steady color change. Due to the color intensity of the aqueous phase, the color of the organic phase may be due in part or largely to light scattering. However, isolation of an aliquot of the organic phase and visual inspection revealed that the color of the organic is due to colored species in the organic phase and not due to light scattering.

Results from spectroscopic and calorimetric analysis of samples taken from the upper organic phase, the highly colored interfacial region, and the lower aqueous phase are shown in Fig. 3.6 (after 4.5 hours of exposure). The upper organic layer is mostly Isopar® L with a small amount of nitrated modifier (1528 cm^{-1}). The modifier, the suppressor (a guanidine derivative), and the extractant, MaxCalix, reacted immediately with 16 M nitric acid leaving behind Isopar® L. This is the expected trend since the hydrocarbon diluent, Isopar® L, would be expected to be the least reactive organic component in the solvent system. On the other hand, solvent components with aromatic groups and hydroxyls (alcohols) are more susceptible to nitration and oxidation. Both the modifier and the extractant contain aromatic groups. Also, the guanidine suppressor contains an amine group with pKa value of 10 that readily ionizes and partitions to the aqueous phase.[11] The organic compounds formed upon reaction of the extractant, modifier and suppressor with nitric acid are much more polar and dense and would be expected to diffuse into the aqueous solution resulting in a separation from Isopar® L. The remaining organic layer gave an exothermic peak of -10.17 J/g indicating residual nitrated modifier (or extractant) in that layer.

The lower aqueous layer had a high concentration of organic (mostly reacted modifier). The organics in the aqueous layer did not decompose energetically as noted by the absence of an exothermic peak in the DSC plot and the absence of an organo-nitro peak (at 1530 cm^{-1}) in the FTIR spectra. However, the peak and 1620 and 1280 cm^{-1} could be due to a trinitroxy propane like molecule but since no energetic was detected in the DSC test, this molecule has no impact on this system. The large endothermic peak in the DSC figure is due to water boiling from the aqueous layer. Note that the boiling process did not steam-strip the organic from the sample since the baseline in the DSC curve was nearly restored to the values before the evaporation. For a large evaporation or mass loss, the baseline is always higher in value after the event.

The interface between the organic and aqueous layer was intensely colored and consisted mostly of nitrated organic as evidenced by the presence of strong bands around 1560, 1526 and 1341 cm^{-1} which are indicative of organo-nitro groups. The DSC analysis indicated a large and broad exothermic peak with an exothermic energy of -605 J/g. This energy is well below the lower bound energy of 1000 J/g for energetic compounds when they are screened by a DSC

instrument.[10] The exothermic decomposition is broad enough that the reaction does not meet the definition of a deflagration reaction.[12]

NGS and 8 M Nitric Acid

A series of pictures and sample removal was performed on the sample containing NGS and 8 M nitric acid. A characteristic set of pictures is shown in Fig. 3.7. A similar image analysis exercise was conducted on these images. The mode associated with the aqueous and organic layer was recorded (from the multimode histogram). As can be seen in Fig. 3.8, the organic layer proceeded steadily from its initial yellow color to the red color (an S-shaped curve resembling that of diffusion was observed) while the aqueous layer remained nearly transparent during this time. During this sequence a "yellow" colored front moving into the aqueous layer. This visual behavior indicates that the type of reactions and their kinetics are different from those observed in the 16 M nitric acid tests.

A spectroscopic and calorimetric analysis of the NGS sample (in 8 M nitric acid) is shown in Fig. 3.9. The organic layer is mostly the unreacted modifier containing a smaller concentration of Isopar® L (low Isopar may also be due to evaporation during sampling and testing of small sized samples) and an even smaller concentration of reacted modifier that contains little organo-nitro groups (as indicated by the small peak at 1560 cm^{-1} in the FTIR spectrum) after 126 hours of contact with 8M nitric acid. The corresponding calorimetric scan indicates a very weak and broad exotherm near 167 °C with an enthalpy value of -7.1 J/g. In this case it is possible that the nitric acid or it degradation product (NOx) migrated into the organic layer and reacted with the Modifier and the heat from that reaction may have evaporated Isopar® L.

The aqueous layer contains a small amount of organic that upon heating in the DSC generated a very small and broad exotherm near 160 °C after water boiled from the sample. Again, indicating the absence of energetic material in this layer.

NGS in 3 M Nitric Acid

Figures 3.10 and 3.11 show the color evolution and histograms of NGS in contact with 3 M nitric acid. Fig. 3.12 shows the spectroscopic identification and calorimetric behavior of NGS and 3 M nitric acid. As can be seen in Fig. 3.10 and 3.11, both the color brightness and histogram of the NGS and 3 M nitric acid layers appear to reach a maximum value with time. This may indicate a possible change in lighting condition when the 14 September 2011 picture was taken. The spectroscopic and calorimetric analysis (Fig. 3.12) of this sample after 48 hours of exposure indicates that neither the organic layer nor the aqueous layer has changed significantly. This indicates a much slower reaction and that longer time is required to detect changes with these instruments. This conclusion is clearly seen upon longer contact as the NGS test in contact with 3 M nitric acid exhibits much less color development compared to the higher 8 M and 16 M tests (see Fig. 3.13).

Identification of Reaction Products between NGS and Nitric Acid

A picture taken on November 17, 2011, of NGS (top) in 16 M, 8 M, and 3 M nitric acid is shown in Figure 3.14. As can be seen in Fig. 3.14, the 16 M nitric acid sample shows foaming on the top layer and precipitates in the bottom layer. The 8 M nitric acid sample show a dense and dark third layer at the bottom of the glass vessel while the 3 M nitric acid sample show a darkening of the top layer (NGS) that is similar to that seen earlier in the 8 M nitric acid sample (Fig. 3.7).

Analysis of the aqueous layer from each test is shown in Table 2 using samples taken on 21 September 2011 representing 7824 hours of contact. Table 2 shows the presence of modifier dissolved in the aqueous layer of the 3 M nitric acid while no soluble starting organic was detected in the 8 M nitric acid sample. On the other hand, excess Isopar® L was detected in the 16 M nitric acid although this finding may have been due to a sampling error.

Analysis of the organic layer from test is shown in Table 3 using samples taken on 21 September 2011. Table 3 shows Isopar® L evaporation in the NGS sample that contacted the 3 M nitric acid solution. Exposure to higher nitric acid molarity decreased the concentration of the modifier and the extractant remaining in the organic layer. These results are consistent with the observations obtained earlier with the FTIR and DSC analysis. For example, in the case of the 16 M nitric acid sample, both extractant and modifier are completely missing in the organic layer due to reactions with nitric acid that produced volatile gases or polar compounds that diffuse into the aqueous phase. A small concentration of dinitrophenol was observed only in the test with 16 M nitric acid.

Further VOA results for the aqueous layer in the 16 M, 8 M, and 3 M tests are shown in Table 4. For the test with 3 M nitric acid, the only organic compound detected in the aqueous phase is 2-butanone, produced by the oxidative decomposition of the modifier. For the test with 8 M nitric acid, the only organic compounds detected in the aqueous phase are 2-butanone and tetrafluoropropanol, produced by the oxidative decomposition of the modifier. The list and quantities of organic compounds observed in the aqueous phase was highest in the test with 16 M nitric acid. The concentration of these compounds are very low (a few ppm) given the large ratio of organic to nitric acid used in this test. The small concentration of dinitrophenol and ethanedinitrate are consistent with the low energetics observed in the DSC test with aqueous phase sample from the test with 16 M nitric acid (Fig. 3.6). We observed no evidence of further degradation of tetrafluoropropanol to produce HF, a highly corrosive acid. Also, we observed no evidence that nitration of DCiTDG was detected (e.g. nitro or dinitro guanidine).

The presence of ethanedinitrate (or 1,2-dinitroethane) is attributed to the nitration reaction of the crown ether in the extractant with nitric acid leading to a breaking of the crown ether ring (as shown below). The tetrafluoropropanol results from the cleavage of the ether linkage at the fluoro-tail of the Cs-7SB molecule. The presence of butanetrinitrate (or butanetriol trinitrate) is due to cleavage and nitration of the butane tail of the Cs-7SB molecule. The presence of dinitrophenol is possibly due to direct nitration of the benzene rings in the calixarene cage of the extractant.
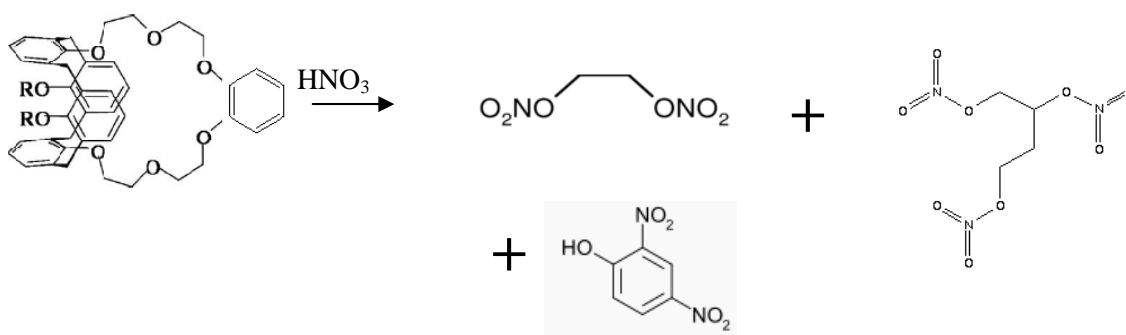
The explosive energy of 1,2-dinitroethane, 1,2,4-butanetriol trinitrate, and dinitrophenol are reported to be 1022 (Ref. 12), 1460 (Ref. 13), and 859 cal/g (Fig. 3.3 or Ref. 10), respectively.

Therefore, a bounding detonation energy for all the byproducts from the nitration of the extractant molecule is 1460 cal/g. One mole of extractant molecule can yield up to eight moles of energetic molecules (four ethanedinitrate and four dinitrophenol) due to nitration. One liter of solvent can potentially yield 400 millimoles of energetic material (if fully nitrated). Using a molecular weight of 152 g (a 50 mole % mixture of dinitrophenol and ethanedinitrate) gives a maximum of 60.8 grams of nitrated by product or 88,768 calories if all of it decomposes (that is 104 cal/g of solvent or 435 J/g of solvent). The calculated specific heat (of 104 cal/g or 435 J/g) is less than half the specific heat (enthalpy of explosion) listed for energetic materials in Fig. 3.3. As measured by the DSC the highest energy recorded was 605 J/g (or 144 cal/g of solvent see Fig. 3.6) at 280 °C. Proving again, whether by calculation or by measurements, the energy of decomposition of the byproduct formed from the reaction of NGS with 3 M, 8 M or 16 M nitric acid is not explosive, and it will not deflagrate.

4.0 Conclusions

A new solvent system referred to as Next Generation Solvent or NGS, has been developed at Oak Ridge National Laboratory for the removal of cesium from alkaline solutions in the Caustic Side Solvent Extraction process at MCU[a] and at the Salt Waste Processing Facility. This work investigated the chemical compatibility between NGS and 16 M, 8 M, and 3 M nitric acid from contact that may occur during handling of analytical and during contactor cleaning operations at MCU.

This work shows that rapid reactions occurred between NGS components and the high molarity nitric acid. The reactions are much faster in 8 M and 16 M nitric acid compared to 3 M nitric acid. In the case of 16 M and 8 M nitric acid, initially the extractant is nitrated and, with longer contact times, oxidation reactions convert the modifier into a tarry substance with gases (NO_x and possibly CO) evolving.

In addition to nitrated organics, the reaction of the modifier with nitric acid produces fluorinated alcohols such as tetrafluoropropanol. Calorimetric analysis of aliquots taken from the organic and aqueous phases revealed that the reaction products are not explosive and will not deflagrate.

5.0 Recommendations, Path Forward or Future Work

We recommend conducting accelerating rate calorimetry of the material generated in the 8 M and 16 M nitric acid tests to evaluate scale-up effects on energetics.

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[a] At the start of this work, the program plan included deployment in MCU. Current program plan is to deploy the NGS in SWPF without testing in MCU. However, the potential exists that NGS may still be deployed in MCU at a later date.

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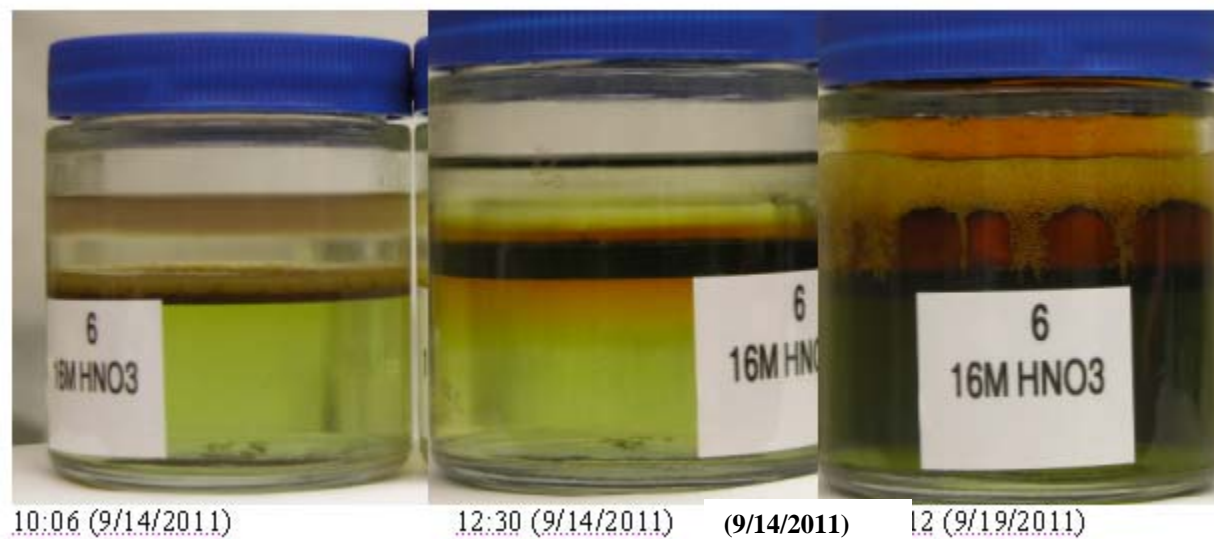
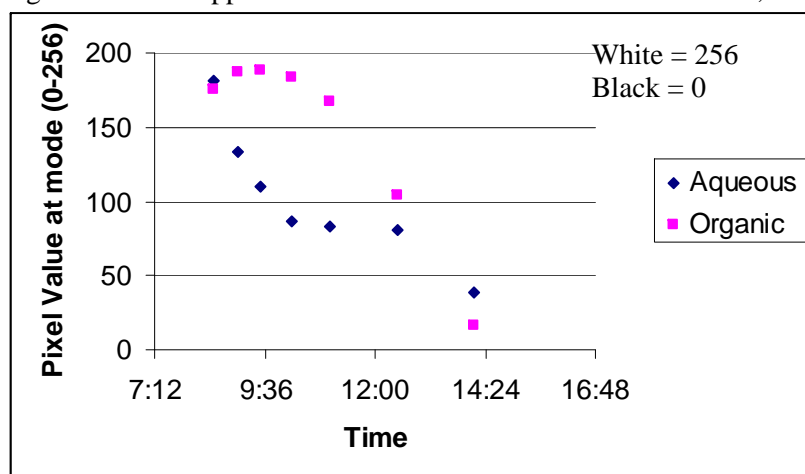Fig. 3.4. Visual appearance of NGS and 16 M nitric acid after 2, 4.5, and 6 hours of contact

Fig. 3.5 A plot of the histogram mode for both aqueous (16 M nitric acid) and organic layer (NGS) as a function of time.
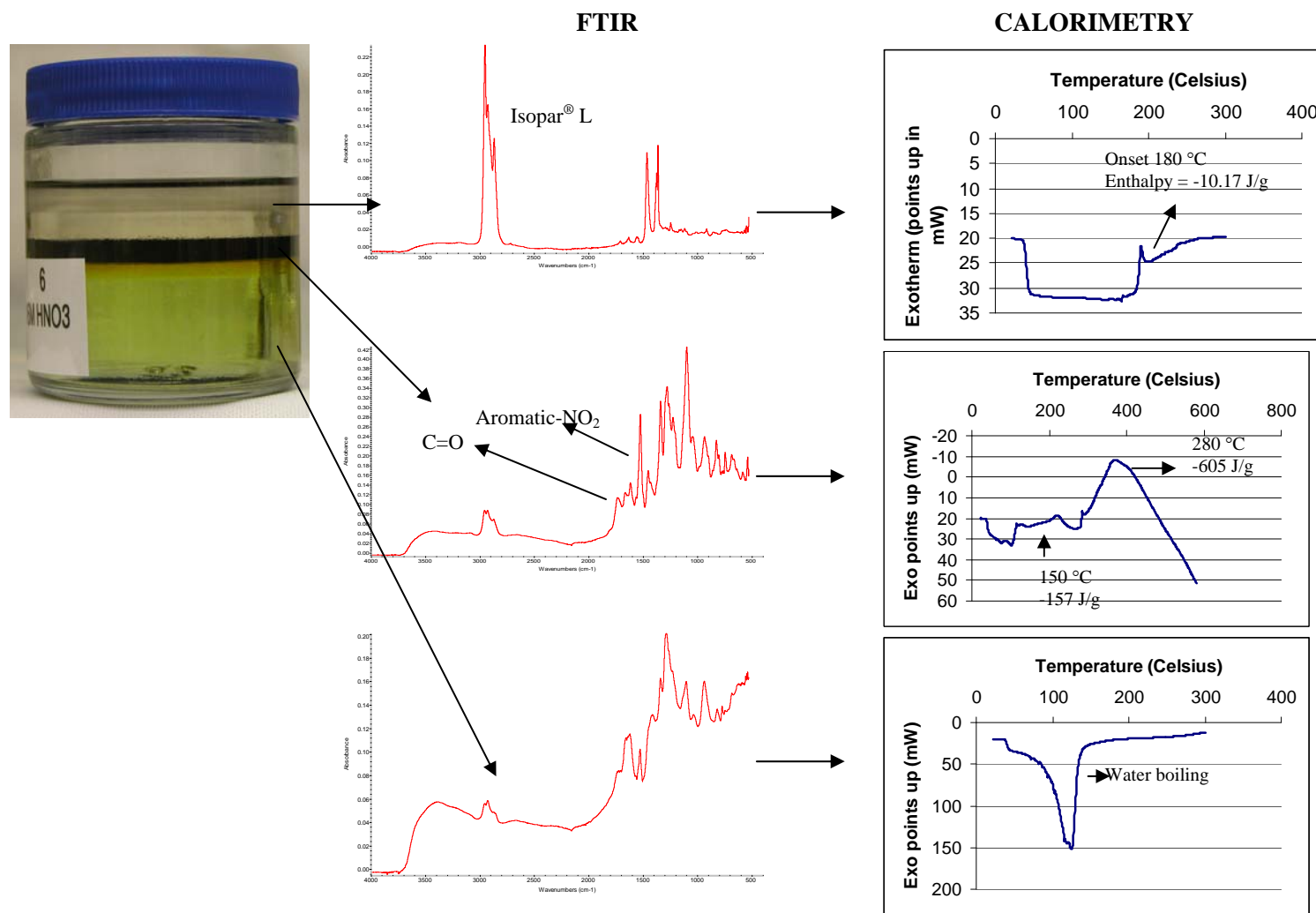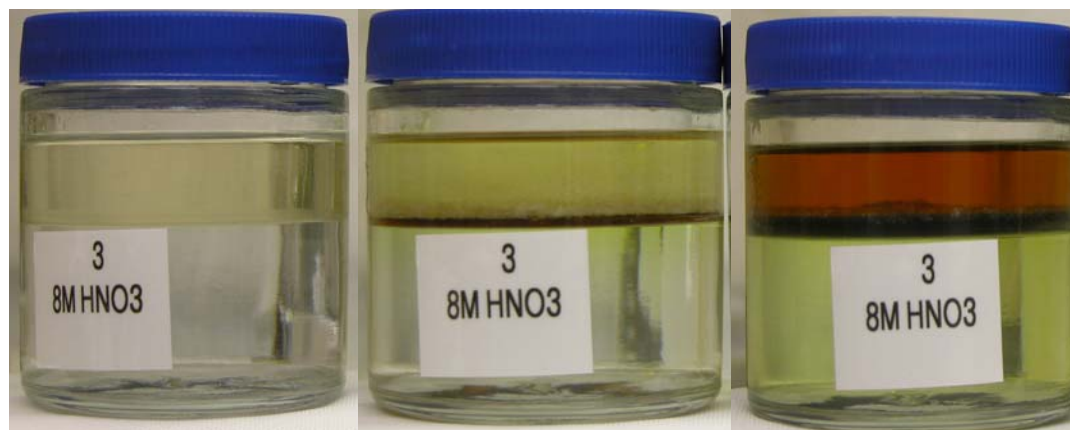
Figure 3.6. Appearance, FTIR and DSC of the organic and aqueous layers after 4.5 hours of contact between NGS and 16 M nitric acid

09:56 (9/14/2011)   11:53 (9/16/2011)   14:14 (9/19/2011)

Fig.3.7 Visual appearance of NGS and 8 M nitric acid after 2, 4, and 6 hours of contact
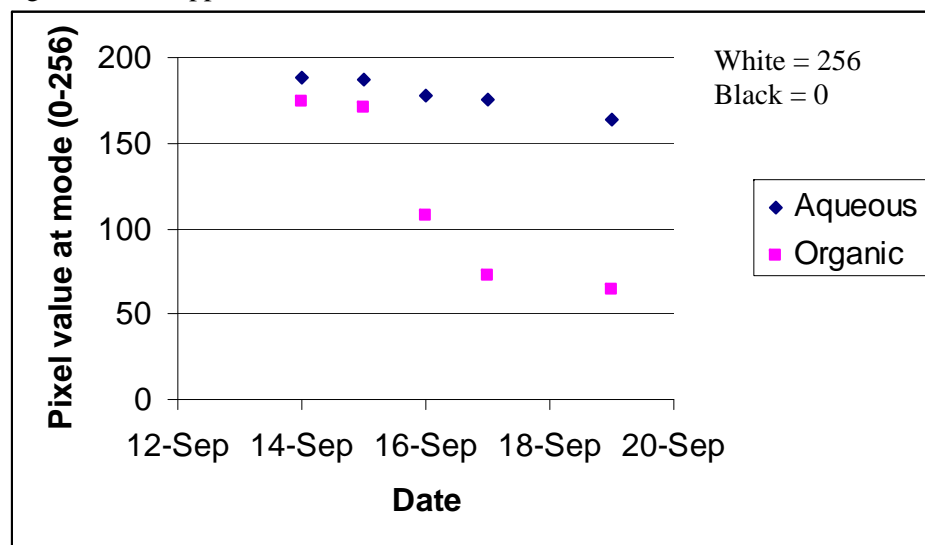

Fig. 3.8 The temporal evolution of the histogram mode for both aqueous (8 M nitric acid) and NGS
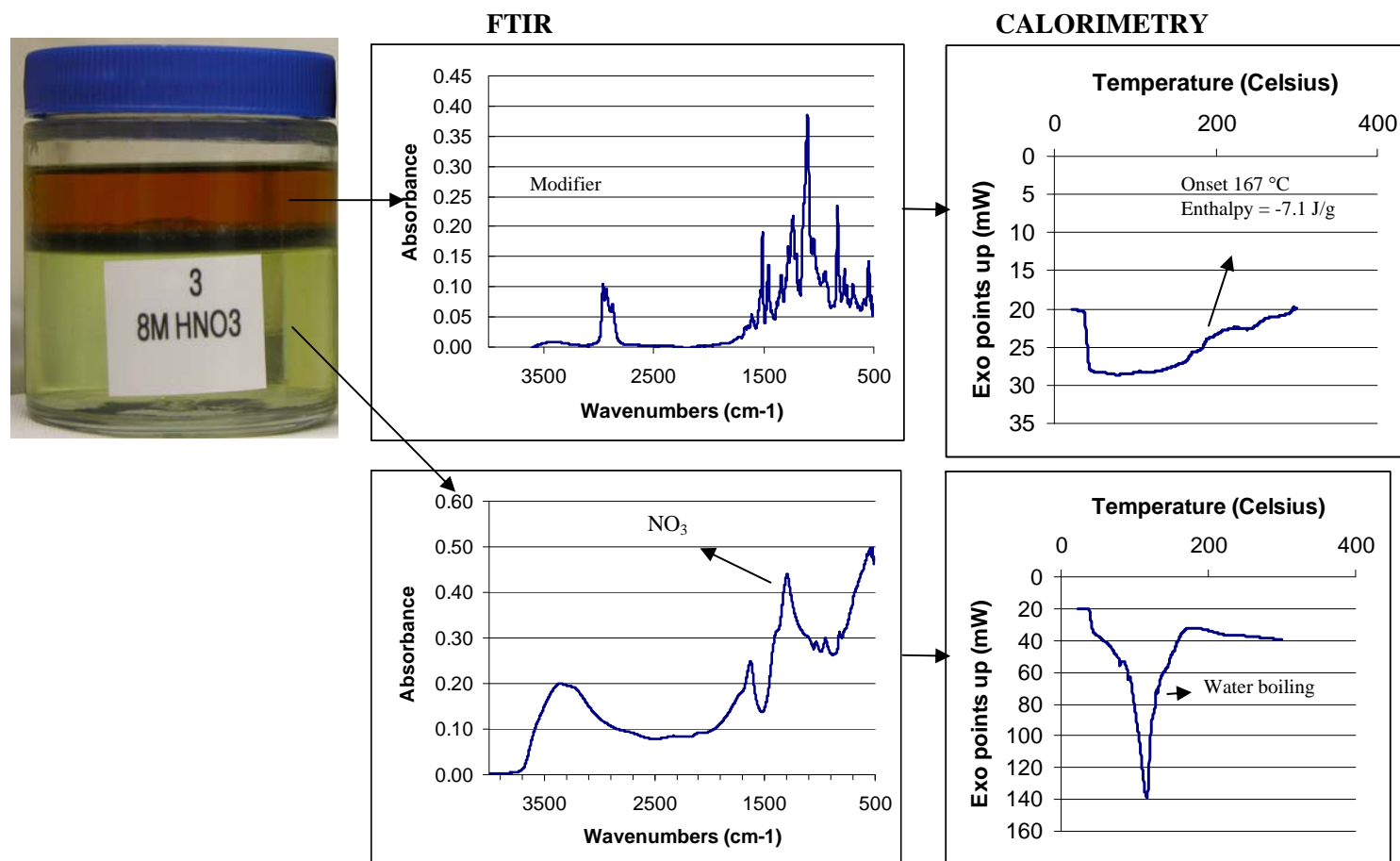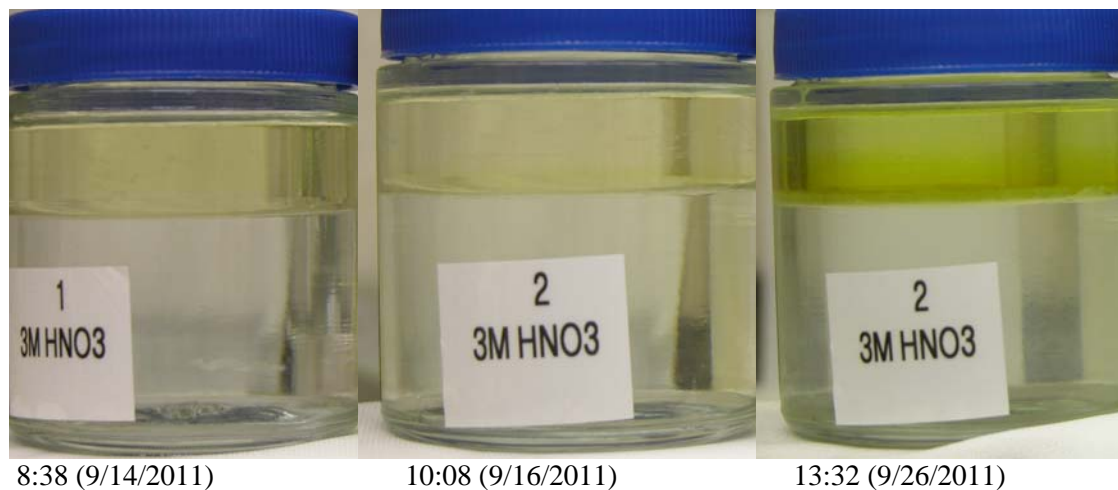
Figure 3.9. Appearance, FTIR and DSC of the organic and aqueous layers after 126 hours of contact between NGS and 8 M nitric acid (taken on 14:14 9/19/11)

8:38 (9/14/2011)   10:08 (9/16/2011)   13:32 (9/26/2011)

Fig. 3.10 Visual appearance of NGS and 3 M nitric acid after 0.5, 50 and 293 hours of contact.
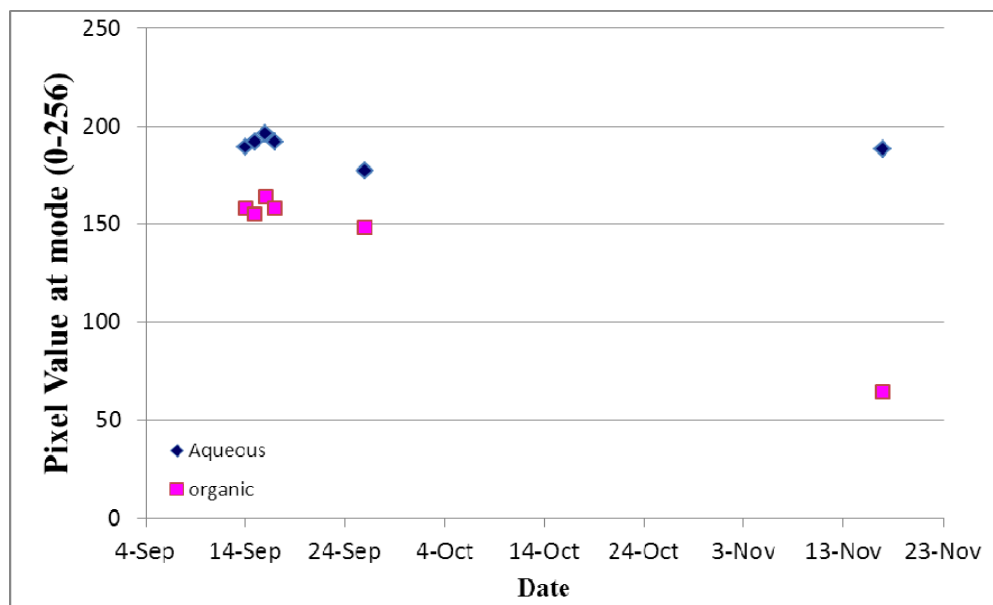

Fig. 3.11 Temporal evolution of the histogram for both 3M nitric acid and NGS
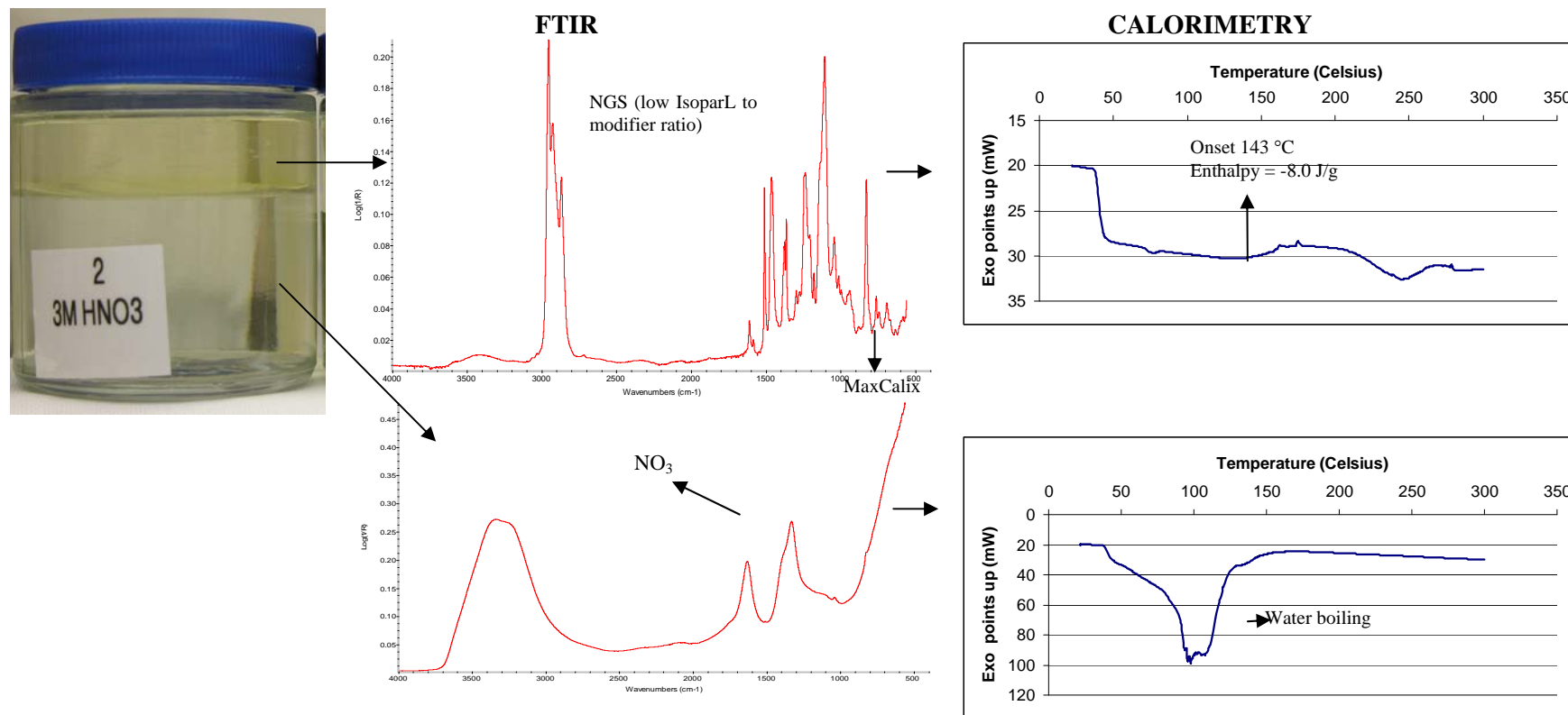
14

Figure 3.12. Appearance, FTIR and DSC of the organic and aqueous layers after 126 hours of contact between NGS and 3 M nitric acid (taken 10:08 9/16/11)
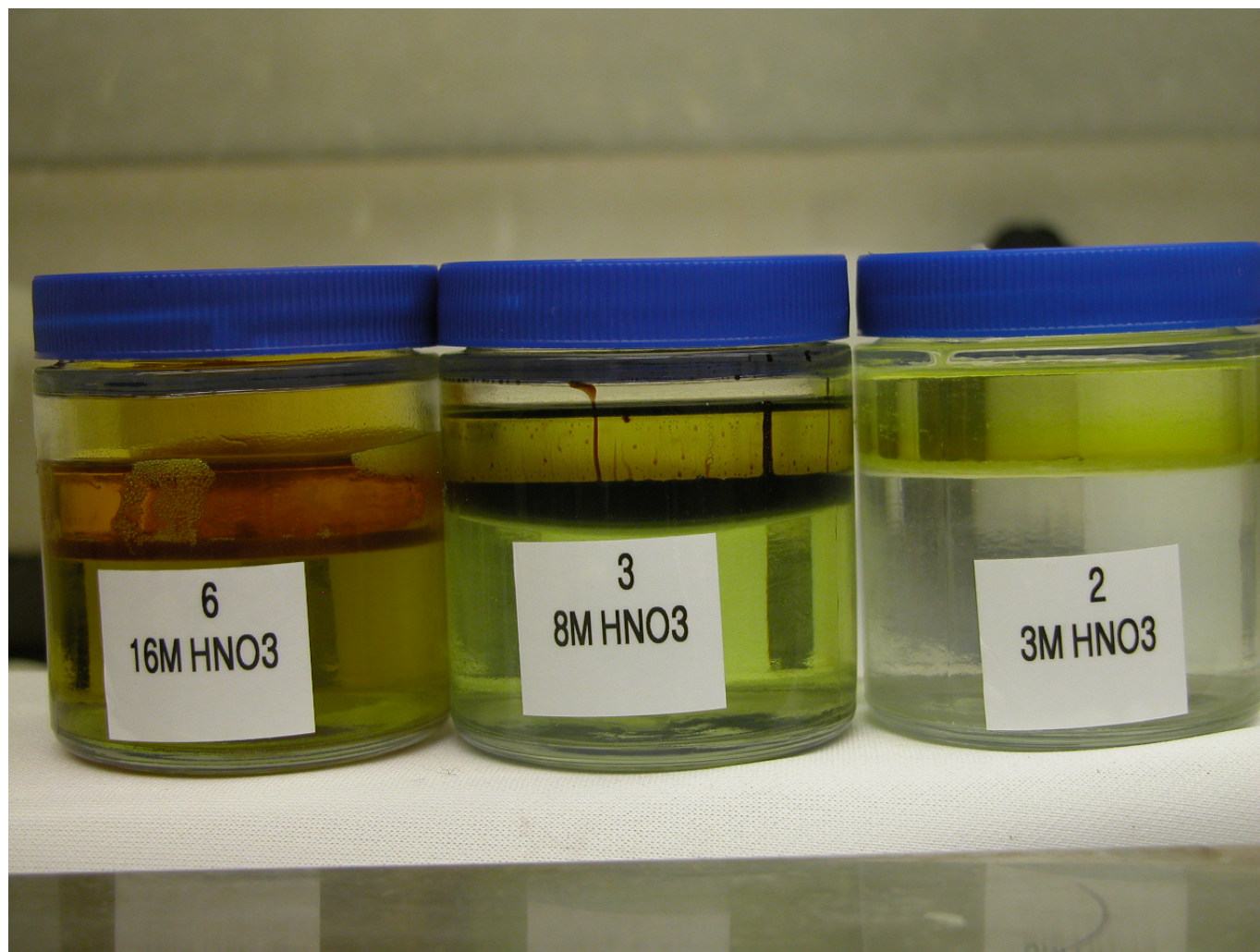
Fig. 3.13. Appearance of NGS and aqueous phases after 288 hours of contact with 16 M, 8 M and 3 M nitric acid (note the lower total liquid level at higher nitric acid concentration)

Table 2. SVOA analysis of the aqueous layer (3M, 8M and 16 M nitric) taken on 21 September 2011 (~ 7 days of contact between nitric acid and NGS). All units reported in mg/L.

	Isopar®L	Modifier	2,4-Dinitrophenol
3 M Aqueous Layer	320	550	ND
8 M Aqueous Layer	< 33	< 20	ND
16 M Aqueous Layer	902	<20	33

Dectetion limit 10 mg/L (different from quantitation limit)
One σ is 20 mg/L

Table 3. HPLC and VOA analysis of the organic layer (3M, 8M and 16 M nitric) taken on 21 September 2011 (~ 7 days of contact between nitric acid and NGS).

Component (Organic Phase)	NGS (mg/L)	3 M (mg/L)	8 M (mg/L)	16 M (mg/L)
Isopar® L [#]	6.08E+05	4.40E+05	5.80E+05	6.2 E+05
Modifier [#]	1.69E+05	3.25E+05	1.05E+05	< 500
Extractant [$]	4.78E+04	7.77E+04	2.00E+03	< 100

[#] One sigma is 10 %
[$] One sigma is 20 %

Table 4. A more detailed description of the molecular fragments detected in the aqueous layer (nitric acid) from the data in Table 2. All units are reported in mg/L.

Component	3 M	8 M	16 M	Likely Source
2-Butanone	2.7	-	2.1	Modifier
Tetrafluoropropanol	-	3.9	27	Modifier
Butane trinitrate	-	2.2	-	Extractant
Ethane dinitrate	-	-	11	Extractant
Dinitrophenol	-	-	33	Extractant
Acetyloxyacetic acid	-	-	9.0	Modifier and Extractant
2-methylbutanenitrile	-	-	3.8	Modifier
Dipropanoyl-1,2-propanediol	-	-	1.1	Modifier and Extractant

Figure 3.14. Appearance of NGS and aqueous phases upon after 2 months of contact between NGS with 16M, 8M, and 3M nitric acid (picture taken 11/17/2011).

Distribution:

A. B. Barnes, 999-W
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
J. C. Griffin, 773-A
T. B. Peters, 773-42A
R. A. Pierce, 773-A
F. F. Fondeur, 773-A

R. T. McNew, 704-27S
J. E. Occhipinti, 704-S
J. W. Ray, 704-S
H. B. Shah, 766-H
D. C. Sherburne, 704-S
R. E. Edwards, 773-67A
M. W. Geeting, 241-152H
B. A. Gifford, 704-56H
B. A. Oard, 241-197H
A. Samadi, 241-197H
S. McLeskey, 241-152H
D. J. Martin, 241-152H
E. J. Freed, 704-56H

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C. Conner, Parsons
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P. G. Suggs, 704-S
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