PNNL-25254 Rev 1

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Compilation of PRF Canyon Floor Pan Sample Analysis Results

June 2016

KN Pool
MJ Minette
JH Wahl
LR Greenwood
DS Coffey
AM Melville
BK McNamara
SA Bryan
RD Scheele
C Delegard
C Rutherford
SI Sinkov
CZ Soderquist
SK Fiskum
GN Brown
J Carter
RA Clark

U.S. DEPARTMENT OF ENERGY
Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Pacific Northwest National Laboratory
Richland, Washington 99352

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ASO Surveillance Report for ASO-2016-006, QE Review of ASO ASR 9937 and ASR 9937.01 Data for ASO Project 68423; Eight Solid Samples: GEA, Anions, pH (Corrosivity), Am/Cm, Pu and U/AEA, ICP-OES and Organic Extraction /GC-MS Analysis

Summary

On September 28, 2015, debris collected from the PRF (236-Z) canyon floor, Pan J, was observed to exhibit chemical reaction. The material had been transferred from the floor pan to a collection tray inside the canyon the previous Friday. Work in the canyon was stopped to allow Industrial Hygiene to perform monitoring of the material reaction. Canyon floor debris that had been sealed out was sequestered at the facility, a recovery plan was developed, and drum inspections were initiated to verify no additional reactions had occurred. On October 13, in-process drums containing other Pan J material were inspected and showed some indication of chemical reaction, limited to discoloration and degradation of inner plastic bags. All Pan J material was sealed back into the canyon and returned to collection trays. Based on the high airborne levels in the canyon during physical debris removal, ETGS (Encapsulation Technology Glycerin Solution) was used as a fogging/lock-down agent. On October 15, subject matter experts confirmed a reaction had occurred between nitrates (both Plutonium Nitrate and Aluminum Nitrate Nonahydrate (ANN) are present) in the Pan J material and the ETGS fixative used to lower airborne radioactivity levels during debris removal. Management stopped the use of fogging/lock-down agents containing glycerin on bulk materials, declared a Management Concern, and initiated the Potential Inadequacy in the Safety Analysis determination process. Additional drum inspections and laboratory analysis of both reacted and unreacted material are planned.

This report compiles the results of many different sample analyses conducted by the Pacific Northwest National Laboratory on samples collected from the Plutonium Reclamation Facility (PRF) floor pans by the CH2MHill's Plateau Remediation Company (CHPRC).

Revision 1 added Appendix G that reports the results of the Gas Generation Rate and methodology.

The scope of analyses requested by CHPRC includes the determination of common anions, gamma spectrometry, metals, corrosivity, organics and alpha spectrometry (note: alpha spectrometry was cancelled during the performance of this work with concurrence from CHPRC). Results may help elucidate the components that led to the unexpected reaction in the canyon as well as inform the radiological and hazardous characteristics. The specific anions, gamma emitters, organics and metals requested by CHPRC are provided in the analytical reports sections.

The individual analyses were conducted under the Plutonium Finishing Plant (PFP) Floor Pan Evaluation Project Quality Assurance Project Plan (PFP Floor Pan Evaluation QAPP, Revision 0.) developed by PNNL specifically for this project. The final reports for each analysis set are included in this compilation of the results. Each package was reviewed under the PFP Floor Pan Evaluation Project Quality Assurance Project Plan so no additional reviews were conducted in this compilation task.

The Gas Generation Rates in Appendix G were also conducted under the Plutonium Finishing Plant (PFP) Floor Pan Evaluation Project Quality Assurance Project Plan (PFP Floor Pan Evaluation QAPP, Revision 0.) developed by PNNL specifically for this project.

Acronyms and Abbreviations

AEA	Alpha energy analyses
ALARA	As low as reasonably achievable
ANN	Aluminum Nitrate Nonahydrate
ASO	Analytical Support Operations (laboratory)
CHPRC	CH2MHill's Plateau Remediation Company
COC	Chain of custody
DOE	U.S. Department of Energy
DQO	Data quality objective
DR	Deficiency report
ETGS	Encapsulation Technology Glycerin Solution
FTIR	Fourier Transform Infrared
FY	Fiscal year
GC-MS	Gas chromatography mass spectrometry
GEA	Gamma energy analyses
HeNe	Helium-neon (laser)
HPGe	High purity germanium detector
IC	Ion Chromatography
ICP-MS	Inductively coupled plasma-mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectroscopy
ID	Identification
IP	Instrument performance
IPS	Instrument performance standard
IR	Infrared
ITR	Internal technical review
LEPS	Low-energy photon spectrometry
NCR	Nonconformance report
NDA	Non-destructive analysis
NIST	National Institute for Science and Technology
PFP	Plutonium Finishing Plant
PRF	Plutonium Reclamation Facility
PI	Principle investigator
PM	Project manager
PNNL	Pacific Northwest National Laboratory
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
QE	Quality engineer

RPL	Radiochemical Processing Laboratory
S/N	Signal-to-noise ratio
SOP	Standard operating procedure
SPME-GC-MS	Solid phase micro-extraction gas chromatography mass spectrometry
SRM	Standard reference material
TI	Test instruction
TRU	Transuranic

1.0 Introduction

On September 28, 2015, debris collected from the PRF (236-Z) canyon floor, Pan J, was observed to exhibit chemical reaction. The material had been transferred from the floor pan to a collection tray inside the canyon the previous Friday. Work in the canyon was stopped to allow Industrial Hygiene to perform monitoring of the material reaction. Canyon floor debris that had been sealed out was sequestered at the facility, a recovery plan was developed, and drum inspections were initiated to verify no additional reactions had occurred. On October 13, in-process drums containing other Pan J material were inspected and showed some indication of chemical reaction, limited to discoloration and degradation of inner plastic bags. All Pan J material was sealed back into the canyon and returned to collection trays. Based on the high airborne levels in the canyon during physical debris removal, ETGS (Encapsulation Technology Glycerin Solution) was used as a fogging/lock-down agent. On October 15, subject matter experts confirmed a reaction had occurred between nitrates (both Plutonium Nitrate and Aluminum Nitrate Nonahydrate (ANN) are present) in the Pan J material and the E T Glycerin Solution (ETGS) fixative used to lower airborne radioactivity levels during debris removal. Management stopped the use of fogging/lock-down agents containing glycerin on bulk materials, declared a Management Concern, and initiated the Potential Inadequacy in the Safety Analysis determination process. Additional drum inspections and laboratory analysis of both reacted and unreacted material are planned.

This report compiles the results of many different sample analyses conducted by the Pacific Northwest National Laboratory on samples collected from the Plutonium Reclamation Facility (PRF) floor pans by the CH2MHill's Plateau Remediation Company (CHPRC).

The individual analyses were conducted under the Plutonium Finishing Plant (PFP) Floor Pan Evaluation Project Quality Assurance Project Plan (68453-QAP-R0-001, Rev. 0, *Plutonium Finishing Plant (PFP) Floor Pan Evaluation Project Quality Assurance Project Plan*). The final reports for each analysis set are included in this compilation of the results. Each package was reviewed under the Project Quality Assurance Project Plan, and no additional reviews were conducted in this compilation task.

The samples provided by CHPRC from the PRF Canyon Floor Pans were assigned Analytical Support Operations (ASO) laboratory sample numbers. The sample numbers and descriptions are shown below and in Appendix A.

RPL Sample Number	Client Sample ID	Sample Description
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E Sample 1 (solid/sludge)
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)
16-0087	B33MK6 (F16-001-004)	PRF Canyon Pan J Sample 2 (solid/sludge)
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)

The samples discussed in many of the final reports compiled in this document will be referenced based upon the last two digits of the ASO Sample ID (e.g. sample 84 = ASO Sample ID 16-0084).

1.1 Report Structure

This report compiles the final analysis results for the PNNL Laboratory work. The samples results and supporting information is provided in the following sections:

- Section 2.0: Gamma Energy Analysis
- Section 3.0 Anion Results
- Section 4.0: Metals Results
- Section 5.0: Organic Analysis Results
- Section 6.0: Corrosivity Results
- Section 7.0: Isotopic Separations Analysis
- Section 8.0: Fourier Transform Infrared
- Section 9.0: Quality Assurance
- Appendix A: Sample Identification & Description
- Appendix B:

  ASO Occurrence Report Form OR-98620-12-9-15, "ASR 9937 – Sample Receipt Observations"

  ASO Deficiency Report Form DR-68453-12-16-15, "No Validation Plan for GC/MS moved from 331 to RPL"

  ASO Occurrence Report Form OR-98620-2-17-16, "Holding Time Limit Concern for Some GC-MS Samples for ASR 9937"
- Appendix C: Test Instructions List
- Appendix D: Procedure List
- Appendix E: Quality Assurance Plan
- Appendix F: Analytical Service Requests
- Appendix G: Gas Generation Rates

1.2 Sample Receipt

The sample shipment from CHPRC was received on Nov. 19, 2015. Chain of custody for each sample was signed by PNNL staff and the drums containing the samples moved into the RPL and staged in laboratory 506. The drums were opened and the individual one quart ice cream cartons containing the

bagged samples were removed and placed in a fume hood. On November 23, 2015, the ice cream cartons were then opened to inspect each of the bagged samples prior to gamma counting and eventual load in to the laboratory 506 glove box. The following observations of the samples were made by Cal Delegard prior to the samples being sent to the gamma counting laboratory.

Crystal Rutherford assisted by Truc Trang-Le opened the two sample drums containing the eight PRF samples. One drum contained six samples in individual tall 1-quart ice cream cartons, all within a single horse-tailed plastic bag. The second drum contained two samples in individual tall 1-quart ice cream cartons also within a horse-tailed plastic bag.

The drums were opened in Lab 506, the horse-tailed bags opened, and the tall 1-quart ice cream cartons containing the samples were taken to the northeast fume hood in 506 where they were opened. Note that radcon surveys/swipes were taken with each container/containment opening.

Inside each ice cream carton, each sample was contained in a taped thin yellow polyethylene bag, an approximately 4-inch diameter heavy wall-thickness yellow tube bag, horse-tailed and taped on both ends, and a ~22-mL amber glass vial with integral septum in the white cap which contained the sample itself. The thin yellow polyethylene bag was opened and horsetailed heavy walled bag was removed for the observations noted below.

The sample IDs and observations follow, in order of their opening. Note, however, that all observations were made through the thick-walled tube bags and sometimes were obscured further by overlap of the bag walls.

- *F16-001-003, Pan J, Sample 1 – this was the only sample that showed contamination (alpha) between the thin yellow polyethylene bag and the outside of the tube bag. Dark brown to black liquid was found within the tube bag and seemed to be the same material that was present within the glass vial. In fact, all items seemed to have present some amount of the dark brown material on the tube bag walls or on the inner vial's outer surface. The sample material itself for this item looked like dirty motor oil but did not flow readily.*
- *F16-001-006, Pan J, Sample 3 – similar to -003 but with less leakage to the innermost bag.*
- *F16-001-005, Pan O, Sample 1 – similar but seemingly more fluid (i.e., lower viscosity)*
- *F16-001-001, Pan E, Sample 1 – similar to Pan O, Sample 1, with dark liquid on solids*
- *F16-001-004, Pan J, Sample 2 – similar to above samples with dark liquid on solids*
- *F16-001-002, Pan J, Sample 4 – similar to others but with seemingly more grit than previous samples*
- *F16-001-007, Pan H, Sample 1 – inside of vial seemed to be covered everywhere within by dark liquid*
- *F16-001-008, Pan H, Sample 2 – still black or very dark brown but is the most gritty of the samples.*

In summary, the sample appearances were very similar to each other with dark liquid, like dirty motor oil, and gritty solids where solids could be observed.

All samples were returned to the original thin walled polyethylene bags taped withintheir respective ice cream cartons, taped into a polyethylene bag covering, and sent for gamma counting.

1.3 Ruptured Sample Vials

The following is from the ASO Occurrence Report Form, OR-98620-12-9-15 “ASR 9937 – Sample Receipt Observations” shown in full in Appendix B.

> *Following extended GEA counting, the samples within their individual ice cream cartons were returned to Lab 506 for complete opening down to the vial level. The vial packaging within the ice cream carton consisted of an exterior yellow bag containing the thicker, horsetailed PVC bag that contained the sample vial. The openings occurred on 9 December 2015. To do this unpackaging, the ice cream cartons were opened at the threshold of the fume hood, the thin yellow bag, with PVC sleeve and vial within, were removed from the ice cream carton into the fume hood and then to an adjacent glovebox by way of an interconnecting airlock. Individually, the exterior yellow plastic bags (which had already been torn open on 23 November 2015) were removed and the PVC bags cut open with scissors.*
>
> *Six intact vials were removed from the PVC bags, the outer surfaces of the vials wiped with moist paper towels (all vials had some level of dark-colored outside contamination, evident over white plastic caps and white labels), the PRF canyon floor sludge contents were examined through the clear glass (with best views through the bottom because the label covered the side walls), the vial caps opened to “burp” the contents and release any pent-up gas pressure, and the six intact vials set within a clean shallow plastic dish.*
>
> *The other two vials, for samples J/1 (16-0086) and J/2 (16-0087), were found to be broken cleanly and circumferentially at the bottom such that the vial bottom was separated from the remainder of the vial. These broken vials were left with the remaining contents within their PVC glovebox sleeves in a bottoms-up orientation to retain whatever materials still were left within the vials. However, significant amounts of sample were outside of the vials and smeared within the PVC sleeve.*

The bag from Pan J Sample 1 (16-0086) had been opened prior to identifying that the vail had been broken. The sample material remaining in the broken vial and spread on the inner wall of the PVC sleeve was collected and placed in a new vial and processed with the other 6 samples.

The inner bag that surrounded Pan J Sample 2 (16-0087) was not opened. PNNL contacted CHPRC to determine if the capturing of the reacted gas samples was of high importance. With CHPRC input, it was decides that Pan J Sample 2 would be analyzed for just the following information:

- The gasses in the inner bag would be collected and analyzed using gas chromatography/mass spectrometry (GC/MS, Section 5.3) and Fourier Transform Infrared (FTIR, Section 8), and
- The solids would be evaluated for gas generation rates.

The results of the gas generation analysis for Pan J Sample 2 are not part of this report as the gas generation testing is still on-going.

2.0 Gamma Energy Analysis

The final Gamma Energy Analysis (GEA) report is included in this section. The GEA results are reported in total grams of each isotope present in the samples as received. The precise mass of each sample received could not be determined. Two of the samples, Pan J sample 1 and Pan J sample 2 had ruptured the glass 22 mL vial and some of the vial contents had escaped into the horsetailed load out bags. For Pan J sample 1, the remaining sample in the broken vial along with some of the solids/sludge that had emptied from the sample vial into the bag were collected and transferred into a new 22 mL scintillation vial. Not all of the solids/sludge could be collected from the inner bag surface. For Pan J sample 2, this sample was left in the horsetailed load out bag until the gas sampling was completed and preparation for gas generation sample collection was completed. The bag was opened on Feb. 12, 2016. When the bag was opened, the sample had dried out and formed crusty solids. The loose, dry sample within the bag was emptied into a glass tray. The dry sample still within the broken vial was carefully removed by scrapping the dried solids from the surfaces within the vial and collected in the same glass tray. Not all the solids could be scrapped from the surfaces of the vial. The other six samples were received with intact sample vials. The weights of each of the "as received" vials were obtained. However, original tare weight information for the vials had not been obtained prior to sampling at the PRF. PNNL requested CHPRC provide 5 similar empty vials and caps such that an approximate tare weight could be obtained. PNNL added adhesive labels of similar size to the vials to replicate as closely as possible the "tare" weight of the sample vials used for sample collection. The average tare weight determined for the empty sample vial is 19.6 grams. The table below provides the net mass of sample for the six samples that were received intact using the 19.6 gram average tare weight of an empty sample vial. The mass numbers are approximations and do not reflect accurately the true mass of the samples that were measured by GEA.

RPL Sample Number	Sample Description	Net Sample Mass-grams
16-0084	PRF Canyon Pan E Sample 1 (solid/sludge)	6.4
16-0085	PRF Canyon Pan J Sample 4 (solid/sludge)	17.3
16-0088	PRF Canyon Pan O Sample 1 (solid/sludge)	20.2
16-0089	PRF Canyon Pan J Sample 3 (solid/sludge)	12.0
16-0090	PRF Canyon Pan H Sample 1 (solid/sludge)	12.4
16-0091	PRF Canyon Pan H Sample 2 (solid/sludge)	16.4

Battelle PNNL/RPL/ASO Radiochemistry Analysis Report
P.O. Box 999, 902 Battelle Blvd., Richland, Washington 99352

Gamma Energy Analysis (GEA)

Project / WP#: 68453/ N60251
ASR#: 9937.00
Client: M. Minette
Total Samples: 8

RPL ID	Client Sample ID
16-0084	B33MK3 (F16-001-001)
16-0085	B33MK4 (F16-001-002)
16-0086	B33MK5 (F16-001-003)
16-0087	B33MK6 (F16-001-004)
16-0088	B33MK7 (F16-001-005)
16-0089	B33MK8 (F16-001-006)
16-0090	B33MK9 (F16-001-007)
16-0091	B33ML0 (F16-001-008)

Analysis Type:	GEA- for all positively measured or non-detected target isotopes
Sample Processing Prior to Radiochemical Processing/Analysis	☒ None ☐ Digested as per RPG-CMC-129, Rev. 0, *HNO_3-HCl Acid Extraction of Solids Using a Dry Block Heater* ☐ Fusion as per RPG-CMC-115, Rev.0, *Solubilization of Metals from Solids Using a KOH-KNO_3 Fusion* ☐ Other: Preparation may have also involved attaining a GEA geometry that is compatible with the calibration geometry.
Analysis Procedure:	RPG-CMC-450, Rev. 2, *Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)*
Reference Date:	None
Analysis Date or Date Range:	November 23-December 2, 2015
Technician/Analyst:	T Trang-Le
Rad Chem Electronic Data File:	*RPG-RC\16-0084Minette _GamAbsPu239&240_Pu.xls*
ASO Project 98620 File:	*File Plan 5871, T4.4 Technical (Radiochemistry), Gamma Calibration, daily checks, and maintenance records; and T3 standard certificates and preparation. Also, balance calibration and Performance check records.*
M&TE Number(s):	*Detectors T (WD81868) (M & TE unique identifiers in attached supporting documents)*

L.R. Greenwood / 12-9-2015
Prepare **Date**

Reviewer / 12/9/15
Date

SAMPLE RESULTS

The samples were gamma counted and the activity results for the actinide isotopes are reported in the units of grams of each isotope per sample with estimates of total propagated uncertainty reported at the 1-sigma level. The measured weights and/or the minimum detectable activity converted to weights for the target gamma emitters are presented in the attached Excel spreadsheet for ASR 9937.00. Requested fission and activation products were not detected and the minimum detectable activities are reported in Bq units.

The samples contained actinides at levels high enough that gamma counting was able to quantify the isotopes of Pu, Am and Np. The gamma counting to quantify the actinides required the samples to be counted for extended periods of time in order to reduce the uncertainties in less abundant isotopes. These counting times varied from just over 5 hours to as long as 64 hours. The isotopes of Pu, Am and Np measured are; Pu-238, Pu-239, Pu-240, Pu-241, Am-241 and Np-237 (via the daughter Pa-233). The results for the measured actinides are presented in grams for Pu (summation of the individual Pu isotopes measured), Am and Np for each sample. The results are included in the attached Excel spreadsheet for ASR 9937.00.

Due to the large amount of plutonium in the samples, it was necessary to correct the data for gamma self-absorption in the samples. The corrections were determined empirically by adjusting the average "thickness" of plutonium to simultaneously fit gamma-rays emitted at various energies from Pu-239 so that all corrected gamma activities showed good agreement. The average gamma activities were then divided by the specific activities of each isotope to determine the weights of each isotope. The gamma absorption corrections assume that the corrections are due solely to the presence of plutonium in the sample and do not include any other materials since we do not have any information regarding the composition of the samples. This is believed to be a very good assumption since gamma absorption depends on the z of the material and is thus overwhelmingly dominated by the large fraction of plutonium in the samples. The total photon cross sections as a function of energy were taken from *E. Storm and H. Israel, Photon Cross Sections from 1 keV to 100 MeV for Elements Z=1 to Z=100, Nuclear Data Tables, Volume 7, Number 6, June 1970, Academic Press.* The effective thickness of plutonium in each sample was then varied empirically to obtain the lowest standard deviation of the average activity of Pu-239 in each sample. The standard deviations were typically around 1 to 2% but were as high as 8% in some samples. The weights of each plutonium isotope listed in the Excel spreadsheet have an unknown absolute uncertainty since the validity of our assumptions regarding the gamma self-absorption are unknown due to our lack of information regarding the composition and homogeneity of the samples. Self- absorption corrections varied from about 1%, for the highest energy gamma –rays from Pu-239 up to around 20% for the Pu isotopes with the lowest energy gammas in the samples that had the largest amount of plutonium (Pu-238, Pu-240, and Pu-241). Am-241 has the highest self-absorption corrections ranging from about 13% to 50% depending on the plutonium content in each sample.

ASO Project File, ASR 9937 has been created for this report including all appropriate supporting records which may include the Pipette Performance Check Worksheet form, Laboratory Bench Record and Gamma Energy Analysis printouts. Detector calibration records, control charts and balance calibration records can be found in the ASO Records.

Sample Preparation, Separation, Mounting and Counting Methods

The samples were gamma counted using the original 1-quart, paper ice cream cartons as the sample holder. The activity of the samples was high enough that the samples had to be counted at about 1 meter from the gamma detector using our track detector in order to reduce detector dead time. Prior to gamma counting, the paper ice cream cartons were opened, the outer plastic bag removed from the 22 mL sample

vial but the inner plastic sleeving was not opened. The plastic sleeved vial was then re-bagged, placed back in the ice cream carton and sent to the counting room for gamma counting. The ice cream cartons were positioned such that the center of the carton corresponded to a calibrated geometry assuming that the samples were positioned in the center of each carton.

QUALITY CONTROL RESULTS

Tracer:

Tracers are not used for ASO GEA methods.

Process Blank (PB):

There is no Process Blank for this sample.

Required Detection Limits

There are no required detection limits for this ASR.

Blank Spike (BS)/Laboratory Control Sample (LCS)/ Matrix Spike (MS):

There are no BS, LCS or MS samples analyzed for ASO GEA analyses. Instrument performance is assessed by the analyses of daily control counts and weekly background counts, as discussed below.

Duplicate Relative Percent Difference (RPD):

A client duplicate sample was not provided for analyses. GEA analyses is performed on samples "as received" without additional preparation or dilution in order to obtain lowest possible detection limits. A laboratory replicate sample is not routinely prepared for GEA analyses when no prior sample preparation was performed.

Instrument Calibration and Quality Control:

Gamma detectors are calibrated using multi-isotope standards that are NIST-traceable and prepared in the identical counting geometry to samples for all detectors. Counter control sources containing Am-241, Cs-137 and Co-60 are then analyzed daily before the use of each detector. Gamma counting was not performed unless the control counts were within the required limits. Background counts are performed on all gamma detectors at least weekly for either an overnight or weekend count. The most recent background is subtracted from all sample counts.

Assumptions and Limitations of the Data:

None

Interferences/Resolution:

None.

Uncertainty:

For gamma counting, the uncertainty in the counting data, photon abundance and the nuclear half-life are included in the calculation of the total uncertainty. The Canberra Genie software includes both random and systematic uncertainties in the calculation of the total uncertainties which are listed on the report. We conservatively estimate that 2% is the lowest uncertainty possible for our GEA measurements taking into account systematic uncertainties in gamma calibration standards. However, absolute uncertainties are higher than indicated on the report since the uncertainties in the empirical gamma self –absorption corrections in unknown at this time since we do not have any knowledge concerning the composition of the samples or the homogeneity.

Attachment: Data Report Sample Results for ASR 9937.

Pacific Northwest National Laboratory
PO Box 999, Richland, WA
Radiochemical Sciences and Engineering Group

filename: 16-0084Minette_GamAbsPu239&240_Pu.xls
12/3/2015

Client: Minette Project: 68453 Prepared by: LR Greenwood 12-3-15
ASR: 9937 WP: N60251
Concur: T Trang-Le 12-3-15

Procedures RPG-CMC-450, Rev. 2 Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)
Count date November 23-December 2, 2015
M & TE T

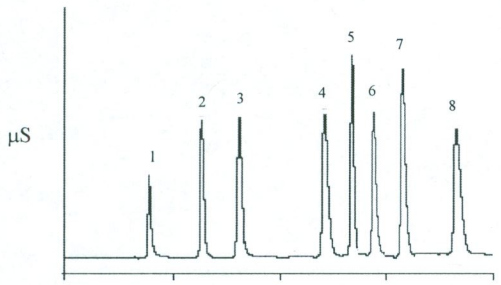
RPL ID		16-0084		16-0085		16-0086		16-0087		16-0088		16-0089		16-0090		16-0091	
Client ID		B33MK3 (F16-001-001)		B33MK4 (F16-001-002)		B33MK5 (F16-001-003)		B33MK6 (F16-001-004)		B33MK7 (F16-001-005)		B33MK8 (F16-001-006)		B33MK9 (F16-001-007)		B33ML0 (F16-001-008)	
	Nuclide	Wt, g	±%	Wt, g	±%	Wt, g	±%	Wt, g	±%	Wt, g	±%	Wt, g	±%	Wt, g	±%	Wt, g	±%
	Pu-238	1.22E-05	4.0	5.97E-05	2.0	3.59E-05	4.0	1.39E-05	5.0	5.97E-05	2.9	2.30E-05	6.0	1.76E-04	2.5	2.23E-04	3.3
	Pu-239	1.68E-01	2.0	2.60E-01	2.0	1.65E-01	2.0	7.12E-02	2.0	1.93E-01	2.0	1.14E-01	2.0	3.51E-01	5.4	4.09E-01	3.0
	Pu-240	1.39E-02	4.5	2.14E-02	2.0	1.44E-02	6.0	5.36E-03	9.0	2.24E-02	2.4	9.63E-03	5.0	4.50E-02	3.6	5.33E-02	5.5
	Pu-241	2.52E-04	2.2	3.89E-04	2.0	2.36E-04	3.0	9.12E-05	3.0	3.43E-04	2.0	1.66E-04	3.0	7.40E-04	2.1	8.95E-04	2.6
	Pu, g	**1.82E-01**	2.0	**2.82E-01**	2.0	**1.80E-01**	2.0	**7.66E-02**	2.0	**2.16E-01**	2.0	**1.24E-01**	2.0	**3.96E-01**	2.0	**4.64E-01**	2.0
	Am-241	6.83E-04	3.3	1.65E-03	2.0	1.15E-03	2.0	6.39E-04	2.0	1.31E-03	2.0	8.47E-04	2.0	2.55E-03	2.0	3.56E-03	3.3
	Np-237/Pa-233	4.07E-05	4.6	9.16E-05	2.0	6.40E-05	3.2	2.90E-05	4.0	8.17E-05	2.3	4.09E-05	3.0	4.51E-04	2.0	4.76E-04	2.2
	Pu-239,wt%	92.2%		92.3%		91.9%		92.9%		89.4%		92.1%		88.4%		88.3%	
	Pu240, wt%	7.6%		7.6%		8.0%		7.0%		10.4%		7.8%		11.3%		11.5%	
	Pu-238, wt%	0.007%		0.021%		0.020%		0.018%		0.028%		0.019%		0.044%		0.048%	
	Pu-241, wt%	0.1%		0.14%		0.13%		0.12%		0.16%		0.13%		0.19%		0.19%	
Ratio	Am241/Pu239	4.08E-03		6.35E-03		6.96E-03		8.98E-03		6.81E-03		7.43E-03		7.29E-03		8.69E-03	
		Activity, Bq															
	Co-60	<1.E+1		<5.E+0		<2.E+1		<2.E+1		<1.E+1		<1.E+1		<3.E+1		<5.E+1	
	Cs-137	<2.E+1		<2.E+1		<3.E+1		<4.E+1		<2.E+1		<2.E+1		<3.E+1		<6.E+1	
	Eu-152	<6.E+1		<2.E+1		<1.E+2		<8.E+1		<6.E+1		<6.E+1		<2.E+2		<3.E+2	
	Eu-154	<4.E+1		<2.E+1		<7.E+1		<5.E+1		<6.E+1		<4.E+1		<1.E+2		<2.E+2	
	Eu-155	<5.E+2		<4.E+2		<1.E+3		<7.E+2		<9.E+2		<6.E+2		<2.E+3		<2.E+3	

3.0 Anion Results

This section includes the final anion analysis results by Ion Chromatography (IC).

Battelle - Pacific Northwest National Laboratory
Analytical Support Operations – IC Report
PO Box 999, Richland, Washington 99352

Common Inorganic Anions
Dionex AS18 Column; Hydroxide Gradient



1 Fluoride
2 Chloride
3 Nitrite
4 Sulfate
5 Bromide
6 Oxalate
7 Nitrate
8 Phosphate

Client:	M. Minette	***ASR #:***	9937.01
Project #:	68453	***# Samples:***	7 liquids
Charge Code:	N60251		

Revision 1

***** RPL Numbers: 16-0084 thru 16-0086 and 16-0088 thru 16-0091*****

Procedure, Analysis, System, and Records Information

Analysis Procedure	RPG-CMC-212, Rev. 2, *"Determination of Common Anions by Ion Chromatography"*
Prep Procedure	For Solid: RPG-CMC-103, Rev. 0, *"Water Leach of Sludge, Soil, and Other Solids"* in RPL lab 516 (CR 12/16/15) Bench Dilution performed in RPL lab 400 (JCC 01/07/16)
Analyst	JC Carter
Analysis Date(s)	01/08/16 and 01/15/16
Calibration Date	01/08/16
Calibration Prep Date	01/07/16
Verification Prep Date	01/07/16
Excel Data File	IC-0229 9937 Minette results rev1.xls
M&TE Numbers	IC System (M&TE) 09080421
	Balances: 39080042
All Analysis Records	Chemical Measurement Center 98620: RIDS IC System File (IC-0229)

Prepared By — Date: 3-7-16

Reviewed By — Date: 3/7/16

IC Report

Revision 1 – Report revised to correct the result reporting units from ug/mL to ug/g. Note: The results do not change, just the units.

Sample Results

See Attachment: Sample Results ASR 9937

Sample Analysis/Results Discussion

Seven solid/sludge samples were prepared under test instruction, 98620-TI-001 and submitted to the Analytical Support Operations (ASO) for ion chromatography analysis under ASR 9937.01. The results are discussed in this report. The analytes of interest include fluoride, chloride, bromide, sulfate, nitrate, nitrite, oxalate and phosphate. The solid samples were prepared by water leaching per RPG-CMC-103, *Water Leach of Sludge, Soil, and Other Solids*.

This analysis was performed by adding equal mass of deionized (DI) water to the mass of sample. The sample and water were mixed by sonicating for 10 minutes. The mixed solutions were left to stand overnight giving the suspended solids time to settle. The solutions remained murky with visible suspended solids after settling overnight. The samples were transferred to conical centrifuge tubes and centrifuged. The centrifuged supernate was filtered through 0.2 micron syringe filters and collected for pH and anion analyses.

The filtered, centrifuged supernate was further diluted by adding one mL of the centrifuged supernate to 4 mL of DI water. The DI water used to make the sample dilutions was analyzed as the reagent blank (RB) sample. The sample results are reported in µg/g and have been adjusted for both analytical dilutions and water leach processing factors.

The reagent blank results have been calculated using the same dilution factor associated samples. The estimated method detection limits (MDL) are provided for each analyte of interest measured and the MDLs have been adjusted for all analytical dilutions and processing factors. The MDLs are set at one-tenth the lowest calibration standard, which is defined as the estimated quantitation limit (EQL).

Data Limitations

There are no failures which cause limitations to the data reported.

Quality Control Discussion

The method performance is evaluated against the acceptance criteria established by Analytical Support Operations QA Plan ASO-QAP-001.

IC Report

1. IC Workstation QC Results

Processing Blanks (Diluent): A reagent process blank (deionized water run through the sample preparation process) was analyzed with the sample set. Fluoride and sulfate were detected above the EQL but less than 5% of the concentration detected in the samples, thus meeting the acceptance criterion. There were no anions detected above the method detection limit (MDL) in the diluent blank (deionized water used to dilute the samples at the IC work station) meeting the acceptance criterion of < EQL.

Duplicate/Replicate (Precision): One replicate dilution was prepared for sample 16-0088 at the IC work station and analyzed. The NO_3 was the only anion with a concentration high enough to calculate and report and relative percent difference (RPD) value. The RPD is reported for all analytes which were measured at or above the EQL. The measured RPD of 1.0% was within the acceptance criterion of ≤ 20%.

Processing Laboratory Control/Blank Spike (LCS/BS): The LCS samples analyzed with the samples have recoveries ranging from 100% to 107%, meeting the acceptance criteria of 80% to 120% recovery.

Analytical Spike (AS) (Accuracy): One sample was processed as the analytical spike sample. The analytical spike is prepared by adding known concentrations of anions to one of the samples. The sample processed as the analytical was 16-0084. The analytical spike recoveries ranged from 84% to 111%. The analytical spike recoveries are all within the acceptance limits of 75% to 125%.

Continuing Calibration Verification (CCV) / Continuing Calibration Blank (CCB): Numerous CCVs and CCBs were analyzed throughout the analysis run (See attachment "QC Sample Results and Performance"). CCVs bracketing the reported results are all within the acceptance criteria of the QA Plan (i.e., 90% to 110% recovery for the CCV and results less than estimated quantitation limit or less than 5% of reported sample result for the CCB).

Deviations from Procedure

None

General Comments

- The reported "Final Results" have been corrected for all dilutions performed on the sample during processing or analysis.
- For each anion, the instrument EQL is defined as the concentration of the lowest calibration standard and the instrument MDL is set at one-tenth of the EQL. The MDLs and EQLs reported for each sample are adjusted for the sample dilution factors (processing and analysis) and assume non-complex aqueous matrices. Matrix-specific MDLs or EQLs may be determined, when requested.
- Routine precision and bias are typically ±15% or better for non-complex aqueous samples that are free of interference.

Ion Chromatography Data Report
ASR 9937.01

Sample Results ASR 9937.01

RPL Number	Client Sample ID	F		Cl		NO_2		SO_4		NO_3		PO_4	
		MDL µg/g	Result µg/g	MDL µg/g	Result µg/g	MDL µg/g	Result µg/g	MDL µg/g	Result µg/g	MDL µg/g	Result µg/g	MDL µg/g	Result µg/g
16-0084	B33MK3 (F16-001-001)	140	1660	170	[205]	225	---	340	[490]	4500	226,500	270	11,550
16-0085	B33MK4 (F16-001-002)	140	2915	170	[200]	225	---	340	[1100]	4500	197,000	270	19,850
16-0086	B33MK5 (F16-001-003)	140	2390	170	[375]	225	---	340	[1150]	4500	163,000	270	14,850
16-0088	B33MK7 (F16-001-005)	140	---	170	[1700]	225	[1200]	340	[950]	450	30,050	270	---
16-0088 Dup	B33MK7 (F16-001-005)	140	---	170	[1650]	225	[1250]	340	[950]	450	30,350	270	---
% RPD			NA		NA		NA		NA		0.99		NA
16-0089	B33MK8 (F16-001-006)	140	3640	170	---	225	---	340	[1450]	4500	211,500	270	24,400
16-0090	B33MK9 (F16-001-007)	140	---	170	[550]	225	---	340	[1050]	450	19,300	270	4,270
16-0091	B33ML0 (F16-001-008)	140	---	170	[550]	225	---	340	[1050]	450	19,600	270	4,090
9937-RB	Reagent Blank	0.315	[0.6]	0.375	---	0.5	---	0.75	[2.6]	1	---	0.6	---
Dilution Blank	Dilution Blank	0.063	---	0.075	---	0.1	---	0.15	---	0.2	---	0.12	---

RPL Number	Client Sample ID	C_2O_4	
		MDL µg/g	Result µg/g
16-0084	B33MK3 (F16-001-001)	225	6,650
16-0085	B33MK4 (F16-001-002)	225	10,350
16-0086	B33MK5 (F16-001-003)	2,250	31,800
16-0088	B33MK7 (F16-001-005)	225	---
16-0088 Dup	B33MK7 (F16-001-005)	225	---
% RPD			NA
16-0089	B33MK8 (F16-001-006)	225	5,400
16-0090	B33MK9 (F16-001-007)	225	225
16-0091	B33ML0 (F16-001-008)	225	225
9937-RB	Reagent Blank	0.50	---
Dilution Blank	Dilution Blank	0.10	---

Ion Chromatography Data Report
ASR 9937.01

Sample QC Results ASR 9937.01

Sample/Replicate Precision Results

RPL Number	Sample ID	F µg/g	Cl µg/g	NO_2 µg/g	SO_4 µg/g	NO_3 µg/g	PO_4 µg/g	C_2O_4 µg/g
16-0088	B33MK7 (F16-001-005)	--	[1700]	[1200]	[950]	30,050	---	---
16-0088 Dup	B33MK7 (F16-001-005)	--	[1650]	[1250]	[950]	30,350	---	---
RPD (%)		NA	NA	NA	NA	1.0	NA	NA

Sample Spike Results - At IC Workstation

RPL Number	Sample ID	F		Cl		NO_2		SO_4		NO_3		PO_4		C_2O_4	
		µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec
16-0084	B33MK3 (F16-001-001)	0.37	--	0.045	--	U	--	0.11	--	4.6	--	0.23	--	1.5	--
16-0084	B33MK3 (F16-001-001) AS	1.7	103	1.6	106	6.2	94	2.8	91	8.4	111	2.6	96	3.2	84
Spike True Value		1.3		1.5		6.6		3.0		3.5		2.5		2.0	

LCS/Blank Spike Results

Run ID	Sample ID	F		Cl		NO_2		SO_4		NO_3		PO_4		C_2O_4	
		µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec	µg/mL	%Rec
1/8/16 16:12	LCS	1.4	107	1.6	101	8.2	104	3.7	103	4.2	101	3.1	104	2.5	105
1/15/16 18:02	LCS	1.3	101	1.6	102	8.2	104	3.7	102	4.2	101	3.0	101	2.4	100
LCS True value		1.3		1.6		7.9		3.6		4.2		3		2.4	

AS = Analytical Spike: Spike performed at IC Workstation on Liquid Samples.
LCS = Laboratory Control Sample (or Blank Spike)
NA = Not Applicable
RPD = Relative Percent Difference
%Rec = Percent Recovery
[red] = Detected, Result are qualitative estimated values: Result >MDL but <EQL (Estimated Quantitation Limit
--- = Value Not Calculated or Place Holder for Blank Cell

4.0 Metals Results

This section includes the final metal results from the analysis by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES).

4.1 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

This analytical technique is capable of determining elemental concentration of most metals on the periodic chart. The detection limit achievable is element dependent and will range from part per million to sub part per billion. This technique provides information on the elements of interest to the CHPRC.

Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report
PO Box 999, Richland, Washington 99352

Project / WP#: 98453 / N60251
ASR#: 9937.01
Client: M. Minette
Total Samples: 7 (solid)

	First	Last
RPL#:	16-0084	16-0091
Client ID:	B33MK3 (F16-001-001)	B33ML0 (F16-001-008)
Sample Description	Pan E, Sample 1	Pan H, Sample 2
Sample Preparation: RPG-CMC-129, Rev. 0, "HNO_3-HCl Acid Extraction of Solids Using a Dry-Block Heater" 1/27/16 (RPL/506/cr).		

Procedure: RPG-CMC-211 Rev. 3, "Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)".

Analyst: G. Brown

Analysis Date (File): 02-08-2016 (C0663)

See Chemical Measurement Center 98620 file: ICP-325-405-3
(Calibration and Maintenance Records)

M&TE Number: N827583 (PerkinElmer 5300DV ICP-OES, S/N 077N5122002)
39080042 (Sartorius R200D, ID#: 360-06-01-028)
M19445 (Mettler AT201, ID#: 192720-62)

Daniel M. Brown 2/25/16
Preparer

2/25/16
Review and Concur

Battelle PNNL/RS&E/Inorganic Analysis ... ICP-OES Analysis Report

Seven solid samples submitted under Analytical Service Request (ASR) 9937.01 were analyzed by ICP-OES. The samples were prepared in laboratories 506 and 516 glove boxes following RPL procedure RPG-CMC-129. The samples (16-0084 through16-0086 and 16-0088 through 16-0091) were processed using 0.3291, 0.3418, 0.3275, 0.2818, 0.3780, 0.3815, and 0.3970 grams of sample, respectively. A duplicate of sample 16-0084 was processed using 0.2972 grams of sample. A matrix spike (MS) sample was processed using 0.2364 grams of sample. A reagent spike (RS) and reagent blank were also processed and prepared for analysis. The samples were diluted to final volumes ranging from 14.5 mL to 17.5 mL. After the acid digestion, the digestate solutions were subject to a Pu removal step using ion exchange (IX) chromatography. The Pu removal was performed following the instructions located in test instruction, 98620-TI-001.

5 mL of each sample digestate (including standards and blanks) were processed through the IX column. The rinses of the column brought the final processing volume to 25 mL, thus an additional 5x dilution factor was introduced in the step. The Pu removal step was needed to lower the Pu content of the samples to levels that meet the radiation work permit limits for the ICP-OES fume hood. In order to matrix match the nitric acid concentration, all samples were further diluted five-fold in deionized water prior to analysis by ICP-OES.

Eighteen Analytes of interest (AOIs) were specified in the ASR, and are listed in the upper section of the attached ICP-OES Data Report. The quality control (QC) results for the AOIs have been evaluated and are presented below. Other analytes are reported in the bottom section of the report, but have not been fully evaluated for QC performance. The results are reported on a mass to mass basis (µg/g) for each detected analyte. All data have been adjusted for instrument dilutions.

Calibration of the ICP-OES was done following the manufacturer's recommended calibration procedure using multi-analyte custom standard solutions traceable to the National Institute of Standards and Technology (NIST). Midrange calibration verification standards (MCVA and MCVB) were used to verify acceptance of the two-point calibration curves obtained for each analyte and for continuing calibration verification.

The controlling document was ASO-QAP-001, Rev. 10, *The Analytical Support Organization (ASO) Quality Assurance Plan.* Instrument calibrations, QC checks and blanks (e.g., ICV/ICB, CCV/CCB, LLS, ICS), post-spikes, and serial dilution were conducted during the analysis run.

Preparation Blank (PB):

A preparation blank (reagents only) was prepared for the extraction process. The concentration of all AOIs except Zn (783 µg/g) were within the acceptance criteria of ≤EQL (estimated quantitation level) or less than ≤5% of the concentration in the samples. The Zn level present in the blank is ~10x above the EQL. (See data limitations)

Blank Spike (BS)/Laboratory Control Sample (LCS):

A blank-spike (Components BPNL-QC-1A and 2B) was prepared and analyzed. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOIs meeting this requirement ranged from 95% to 119% and were within the acceptance criterion of 80% to 120%. The BS recovery for Zn is not reported because the level of Zn present in the blank is greater than 75% of the concentration in the spike standard.

Matrix-Spiked Sample:

A matrix-spike (Components BPNL-QC-1A and 2B) was conducted on Sample 16-0084. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOIs meeting this requirement ranged from 88% to 117% and were within the acceptance criterion of 75% to 125%.

Duplicate/Replicate Relative Percent Difference (RPD):

A duplicate was prepared using Sample 16-0084. RPDs are listed for all analytes that were measured at or above the EQL. The RPDs for the analytes ranged 1.6% to 18.6% and, with the exception of Ba (28.1%), and Zn (53.4%), were within the acceptance criterion of ≤20%.

Post-Spike/Analytical Spike Sample (A Component):

A post-spike (A Component) was conducted on Sample 16-0084. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. Recovery values for the AOIs meeting this requirement ranged from 86% to 101% and were within the acceptance criterion of 75% to 125%.

Post Spike/Analytical Spike Sample (B Component):

A post spike (B Component) was conducted on Sample 16-0084. Recovery values are listed for all analytes in the spike that were measured at or above the EQL, and that had a spike concentration ≥25% of that in the sample. No AOIs were included in the post spike (B Component).

Serial dilution:

Five-fold serial dilution was conducted on Sample 16-0084. Percent differences (%Ds) are listed for all analytes that had a concentration at or above the EQL in the diluted sample. The %D's for the AOIs ranged from 0.3% to 5.6% and were within the acceptance criterion of ≤10%.

Other QC:

Two instrument blanks exhibited negative Na concentrations (-0.239 to -0.311 µg/mL) that exceed the absolute value of the EQL (0.15 µg/mL). Several instrument continuing calibration verification (MCVA) solutions exhibited low negative recoveries for Be (-12% to -16%) and Tl (-11%) that exceeded the acceptance criterion of ±10%. All other instrument-related QC tests for the AOIs passed within their respective acceptance criteria.

Limitations:

Evaluation of the Zn results for the samples should take into account the high level of Zn measured in the blank. Zn values for the samples are likely biased high.

Comments:

1) The "Final Results" have been corrected for all laboratory dilutions performed on the samples during processing and analysis, unless specifically noted.
2) Instrument detection limits (IDL) and estimated quantitation limits (EQL) shown are for acidified water and/or fusion flux matrices as applicable. Method detection limits (MDL) can be estimated by multiplying the IDL by the "Multiplier". The estimated quantitation limit (EQL) for each concentration value can be obtained by multiplying the EQL by the "Multiplier".
3) Routine precision and bias is typically ±15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO_3 or less) at analyte concentrations > EQL up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000 µg/mL (0.5 per cent by weight). Note that bracketed values listed in the data report are within the MDL and the EQL, and have potential uncertainties greater than 15%. Concentration values < MDL are listed as "- -". Note, that calibration and QC standards are validated to a precision of ±10%.
4) Absolute precision, bias and detection limits may be determined on each sample if required by the client. The maximum number of significant figures for all ICP measurements is two.
5) Analytes included in the spike A component (for the AS/PS) are; Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Ta, Ti, Tl, V, W, Y, Zn, and Zr. Analytes included in the spike B component are; Ce, Dy, Eu, La, Nd, Pd, Rh, Ru, S, Te, Th, and U.

Battelle PNNL/RPG/Inorganic Analysis ... ICPOES Data Report

		Run Date >	2/8/2016	2/8/2016	2/8/2016	2/8/2016	2/8/2016	2/8/2016	2/8/2016	2/8/2016	2/8/2016	2/8/2016
		Multiplier >	1.0	1077.3	1139.5	1261.8	1097.1	1145.0	1330.7	992.1	950.2	913.1
		RPL/LAB >	405 diluent	RB-0084 @ 5x	16-0084 @ 5x	16-0084 Dup @ 5x	16-0085 @ 5x	16-0086 @ 5x	16-0088 @ 5x	16-0089 @ 5x	16-0090 @ 5x	16-0091 @ 5x
Instr. Det. Limit (IDL)	Est. Quant. Limit (EQL)	Client ID >	Lab Diluent	Reagent Blank	Pan E, Sample 1	Pan E, Sample 1 - Dup	Pan J, Sample 4	Pan J, Sample 1	Pan O, Sample 1	Pan J, Sample 3	Pan H, Sample 1	Pan H, Sample 2
(µg/mL)	(µg/mL)	(Analyte)	(µg/mL)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)	(µg/g)
0.0029	0.029	Ag	--	--	[27]	49.4	[28]	[33]	[34]	40.2	--	32.9
0.0170	0.170	Al	--	--	109,000	96,200	91,200	85,600	13,800	65,900	34,900	41,400
0.0013	0.013	Ba	--	--	162	215	291	230	2,840	265	265	374
0.0002	0.002	Be	--	--	[1.5]	[1.4]	2.85	[1.4]	[0.20]	1.92	2.74	3.93
0.0024	0.024	Cd	--	--	112	105	129	86.4	[13]	86.0	[15]	[15]
0.0043	0.043	Co	--	--	[17]	[19]	[36]	[23]	[18]	[16]	[7.1]	[13]
0.0040	0.040	Cr	--	[7.1]	1,720	1,870	2,100	1,650	1,670	1,590	733	901
0.0036	0.036	Cu	--	--	334	365	671	326	110	419	129	118
0.0700	0.700	K	--	--	1,630	1,950	2,640	1,740	1,040	1,670	2,270	2,000
0.0010	0.010	Mn	--	--	1,370	1,340	2,280	1,400	401	1,500	950	1,010
0.0150	0.150	Na	--	--	20,400	16,900	14,900	16,000	1,860	11,800	14,100	13,800
0.0054	0.054	Ni	--	[10]	1,290	1,270	1,970	1,420	2,000	1,280	483	473
0.0630	0.630	Pb	--	--	[260]	[330]	[300]	[410]	[230]	[180]	[530]	626
0.0440	0.440	Sb	--	--	--	--	--	[53]	--	--	--	--
0.0001	0.001	Sr	--	[0.11]	41.5	42.9	60.9	53.8	294	38.7	111	111
0.1200	1.200	Tl	--	--	--	--	--	--	--	--	--	--
0.0023	0.023	V	--	--	[6.0]	[3.3]	[8.9]	--	[24]	[7.0]	[12]	[13]
0.0074	0.074	Zn	--	783	3,880	2,240	2,890	2,090	1,040	2,210	1,300	1,170
Other Analytes												
0.1500	1.500	As	--	--	--	--	--	--	--	--	--	--
0.0099	0.099	B	[0.014]	[15]	[30]	[39]	[32]	[41]	[41]	[29]	[42]	[37]
0.0450	0.450	Bi	--	--	--	--	--	--	--	--	--	--
0.0140	0.140	Ca	--	[73]	8,840	9,230	12,500	11,000	47,500	7,980	21,700	21,300
0.0150	0.150	Ce	--	--	--	--	--	--	--	--	--	--
0.0044	0.044	Dy	--	--	--	--	--	--	--	[4.5]	--	--
0.0004	0.004	Eu	--	--	--	--	--	--	--	--	--	[0.72]
0.0019	0.019	Fe	--	59.9	34,200	35,100	61,000	29,400	27,200	34,300	24,600	28,600
0.0030	0.030	La	--	--	[3.5]	--	[4.9]	[6.6]	47.1	[3.5]	[21]	[17]
0.0011	0.011	Li	[0.0014]	--	--	[3.0]	[3.7]	--	[3.5]	--	--	[1.1]
0.0025	0.025	Mg	--	[16]	1,060	1,040	1,690	1,280	2,120	1,060	1,490	1,390
0.0076	0.076	Mo	--	--	[29]	[52]	[73]	[34]	[28]	[44]	[33]	[41]
0.0160	0.160	Nd	--	--	--	--	--	--	[41]	--	--	--
0.1100	1.100	P	--	--	18,200	25,100	22,800	14,600	15,500	17,100	75,400	82,300
0.0190	0.190	Pd	--	--	--	--	--	--	--	--	--	--
0.0140	0.140	Rh	--	--	--	[23]	--	--	--	--	--	--
0.1200	1.200	Ru	--	--	--	--	--	--	--	--	--	--
0.1300	1.300	S	--	[460]	1,670	1,700	2,130	2,270	3,520	1,590	1,260	1,450
0.2300	2.300	Se	[0.30]	--	[440]	[420]	--	[470]	--	[430]	[330]	--
0.0300	0.300	Si	--	--	--	--	[100]	[150]	[170]	[90]	[61]	[83]
0.0470	0.470	Sn	[0.057]	--	[54]	--	--	[93]	--	--	--	--
0.0270	0.270	Ta	--	--	--	--	--	--	--	--	--	--
0.0280	0.280	Te	--	--	--	--	--	--	--	--	--	--
0.0120	0.120	Th	--	--	--	--	--	--	--	--	--	--
0.0020	0.020	Ti	--	--	95.1	106	136	91.7	441	109	136	159
0.1100	1.100	U	--	--	--	--	--	--	--	--	--	--
0.0270	0.270	W	--	--	--	--	--	--	--	[40]	--	--
0.0007	0.007	Y	--	--	[1.1]	--	[1.1]	--	[3.4]	--	[2.1]	[1.5]
0.0044	0.044	Zr	--	--	--	[6.9]	[8.2]	--	[26]	[5.1]	[5.1]	[8.7]

1) "--" indicates the value is < MDL. The method detection limit (MDL) = IDL times the "multiplier" near the top of each column. The estimated sample quantitation limit = EQL (in Column 2) times the "multiplier". Overall error for values ≥ EQL is estimated to be within ±15%.

2) Values in brackets [ ] are ≥ MDL but < EQL, with errors likely to exceed 15%.

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QC Performance 02/08/2016

Criteria >	≤ 20%	80%-120%	75%-125%	75%-125%	75%-125%	≤ 10%
QC ID >	16-0084 Dup	LCS/BS	16-0084 MS	16-0084 + AS-A	16-0084 + AS-B	16-0084 5-fold Serial Dil
Analytes	RPD (%)	%Rec	%Rec	%Rec	%Rec	%Diff
Ag				90		
Al	12.4	112	nr	nr		3.6
Ba	28.1	112	111	101		2.8
Be		101	101	86		
Cd	6.4	110	112	95		
Co				95		
Cr	7.9	112	nr	92		3.1
Cu	8.8	119	110	97		5.0
K	17.7	108	111	98		
Mn	2.2	114	nr	96		3.8
Na	18.6	95	nr	98		0.3
Ni	1.6	113	88	93		4.4
Pb		111	117	95		
Sb				96		
Sr	3.4	111	109	99		5.6
Tl				88		
V		102	105	93		
Zn	53.4	nr	nr	87		3.6
Other Analytes						
As				95		
B		36	65	99		
Bi				91		
Ca	4.3	105	nr	96		3.2
Ce					98	
Dy					93	
Eu					90	
Fe	2.4	111	nr	96		4.2
La		27	24		87	
Li		116	119	103		
Mg	2.2	116	115	102		3.1
Mo		98	100	93		
Nd		87	85		94	
P	31.9		nr	86		0.4
Pd					86	
Rh					94	
Ru					89	
S	2.2	98	107		93	
Se				96		
Si			24	93		
Sn				89		
Ta				95		
Te					88	
Th					91	
Ti	10.5	104	103	98		
U					91	
W				100		
Y				95		
Zr		95	95	96		

Shaded results are outside the acceptance criteria.

nr = spike concentration less than 25% of sample concentration. Matrix effects can be assessed from the serial dilut

5.0 Organic Analysis Results

There were four sets of organic analysis that were conducted on the samples. All four sets used the Gas Chromatography-Mass Spectrometry (GC-MS) to analyze the sample aliquot. The difference in the four sets is in how the materials to be analyzed were extracted. The four methods of developing the material to be analyzed are:

1. For the seven samples (excluding Pan J Sample 2), a Methanol solvent extraction was analyzed through the GC-MS.

2. For the seven samples (excluding Pan J Sample 2), a Methylene Chloride solvent extraction was analyzed through the GC-MS.

3. Gas in the sealed inner bag surrounding Pan J Sample 2 a solid phase micro-extraction gas chromatography mass spectrometry process was used. The Solid phase micro-extraction fiber was inserted into the gasses inside the inner bag to collect the headspace gas above the sample. In that case, the sample was not modified beyond the reactions that had already occurred in the vial.

4. Gas in the sealed inner bag surrounding Pan J Sample 2 were collected by a syringe and injected into the GS-MS.

5.1 Organic Results

The results for the methanol solvent extraction, the methylene chloride extraction, headspace analysis collected with a solid phase micro-extraction gas chromatography mass spectrometry process, and the head gas sample collected via syringe, all of which were analyzed through the GC-MS analysis.

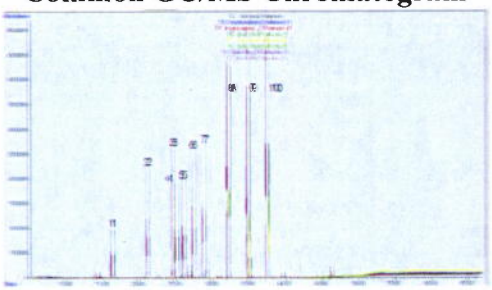
Note: the head space samples for the Pan J Sample 2 inner bag gasses were collected in one of two ways:

1. The gasses in the sealed inner bag surrounding Pan J Sample 2 were collected with a solid phase micro-extraction gas chromatography mass spectrometry process was used. The solid phase micro-extraction fiber was inserted into the gasses inside the inner bag to collect the headspace gas above the sample. In that case, the sample was not modified beyond the reactions that had already occurred in the vial.

2. The gasses in the sealed inner bag surrounding Pan J Sample 2 were collected by a syringe and injected into the GS-MS.

Battelle - Pacific Northwest National Laboratory
Analytical Support Operations – GC/MS Report
PO Box 999, Richland, Washington 99352

Common GC/MS Chromatogram



Client:	M. Minette	***ASR #:***	9937.01
			14 liquids
Project #:	68453	***# Samples:***	3 headspace gas
Charge Code:	N60251		

***** RPL Numbers: 16-0084 thru 16-0086 and 16-0088 thru 16-0091*****
***** RPL Numbers for Head Space Samples 16-0087 *****
(see ASO OR-98620-12-9-15)

Procedure, Analysis, System, and Records Information

Analysis Procedure	RPL-GC-MS-01, Rev. 0, *Gas Chromatography/Mass Spectrometry*
Prep Procedure	Samples prepared for analyses following the preparation scheme outlined in Test Instruction, *98620-TI-001, Rev. 0, Section 4. PRF Canyon Sample Handling in Glove Box*
Analyst	AM Melville
Analysis Date(s)	01/07/16 - 02/12/16
Calibration Date	01/07/16, 02/03/16
Calibration Preparation Date	01/07/16
Verification Preparation Date	01/07/16
Excel Data File	NA
M&TE Numbers	GC/MS System (M&TE) Agilent AutoSampler 7693 Serial #: CN93801454; Agilent GC 7890A, Serial#: US10938023; Agilent MS 5975C Serial #: US93443429
	Balance: Sartorius R200D, SN:39080042, RPL/405 benchtop
All Analysis Records	ASR 9937.01 ASO Records, RPL/301

Prepared By — Date: 3-10-16

Reviewed By — Date: 3.10.16

Sample Collection

Samples were obtained per Test Instruction, 98620-TI-001, Rev. 0, Section 4. PRF Canyon Sample Handling in Glove Box. Sample weights and added methanol (MeOH) and methylene chloride ($MeCl_2$) are provided in Table 1. The MeOH used was obtained from Sigma Aldrich (Product # 34860, Lot# SHBD2740) and the $MeCl_2$ used from Burdick & Jackson (Catalog # 299, Lot # DH030). The liquid phases were analyzed from the extracted samples.

ASO Occurrence report (OR) documents a concern identified when samples were received: OR-98620-12-9-15; Sample Receipt Observations (ASR 9937) – Upon opening the sample outer and inner sample bags for Pan J Sample 1 and the outer bag for Pan J Samples 2, it was identified that the sample vials had broken cleanly and the glass bottoms of the vials had separated cleanly from the vial. Remaining materials were recovered from the vial in Pan J Sample 1. An alternative analysis approach was established for Pan J Sample 2 materials and in-bag gasses.

Table 1. Sample Collection Information

RPL #:	Customer Sample ID	Sample Description	Sample Weight (g)	Sample Weight + MeOH* (g)	Sample Weight + MeOH** + $MeCl_2$* (g)
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E Sample 1 (solid/sludge)	1.0705	2.8702	3.6218
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)	1.2518	2.8219	4.0574
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)	1.0290	2.7119	4.2103
16-0087	B33MK6 (F16-001-004)	PRF Canyon Pan J Sample 2 (solid/sludge)	NA	NA	NA
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)	1.2539	2.8788	3.5991
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)	1.0849	2.7642	3.8187
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)	1.1448	2.8712	3.6345
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)	1.0884	2.6467	3.7196

***These data are not intended to provide a basis for reporting quantitative results on a mass basis; results are qualitative.**
**** Total weight after a portion of MeOH was decanted after first solvent extraction**

MeOH samples were measured for dose rate and were too high for benchtop work. 2 mL of each sample was taken out of the glovebox and diluted 1:10 to reduce the dose rate to allow for further processing.

Sample Analysis Quality Control

Project Deficiency Report, DR-68453-12-16-16 was issued to address the fact that there was no time to follow the usual approach of writing and implementing a Validation Plan for the GC/MS moved from 331 to RPL/400. The GC/MS was moved and set-up by the users from 331 who

were the analyst and report preparer for the project's data collection activities using procedure, RPL-GCMS-01, Rev. 0, *Gas Chromatography/Mass Spectrometry*, which was issued on 12/16/15. The procedure contains steps to ensure the instrument is functioning properly when used. Sections 8.3 and 8.7 have steps for instrument use that needed to be completed successfully before proceeding with the analysis. Also, the Grob test mixture sample that has known compounds is required by the procedure to be analyzed before sample data could be collected.

GC/MS Quality Control Results

The mass spectrometer is tuned according to manufacturer's instructions specifications.

The instrument performance (IP) check was used to demonstrate the GC/MS instrument is operating and performing at a sufficient level and dynamic range. This check is not designed for quantitative assessments.

The instrument performance check used examined ten compounds of a Grob test mixture (Restek, Catalog #35000) at four different concentration levels. Instrumental performance standard one (IPS1) is the Grob test mixture used at the received concentrations, instrumental performance standard two (IPS2) represents a 10x dilution of ISP1, instrumental performance standard three (IPS3) represents a 100x dilution of IPS1 and instrumental performance standard three (IPS4) represents a 1000x dilution of IPS1. Table 2 list the compounds that were used for instrument performance check during this period. Table 2 results were generated with the Agilent Enhanced Data Analysis using a linear fit ($y = mx + b$) at concentrations values (x) of 1.00 (ISP1), 0.10 (ISP2), 0.01 (ISP3), and 0.001 (ISP4) per compound. Table 2 lists the experimental retention time (RT) shown in minutes, the slope (m) and intercept (b) and the correlation coefficient (R^2) as determined by the Agilent software for the linear fit. These results demonstrate that the instrument was performing adequately and Table 2 provides the basis to close the DR.

Table 2. Instrument Performance Check Results Summary

Peak #	Compound	RT	b	M	R^2
1	2,3 Butanediol	16.625	-100573	21757302	1.00
2	Decane	21.363	47064	11491126	1.00
3	Undecane	24.79	49761	12648012	1.00
4	Octanol	25.331	-33846	6897842	1.00
5	Nonanal	26.265	24045	5492163	1.00
6	Dimethylphenol	27.638	-61591	15627221	1.00
7	Dimethylaniline	29.036	-25421	18020918	1.00
8	Methyl decanote	32.375	74780	26682717	1.00
9	Methyl undecanote	35.102	79844	26540189	1.00
10	Methyl dodecanote	37.672	78690	27128737	1.00

Mid-Point IP Check Results

A 10x dilution of the Grob test mixture was used for an IP check during the experimental blocks. Over the period of this work, this 10x dilution of the Grob test mixture was examined numerous times. The stability of the instrument is reflected and is highlighted in the overlaid

chromatograms illustrated in Figure 1. Over the course of this study acceptable reproducibility for both chromatographic peak area and retention time were observed. The results shown in Figure 1 illustrate typical chromatographic signals that are commonly observed for 10's of ng per component and illustrate that the instrumental setup was performing at an acceptable level.

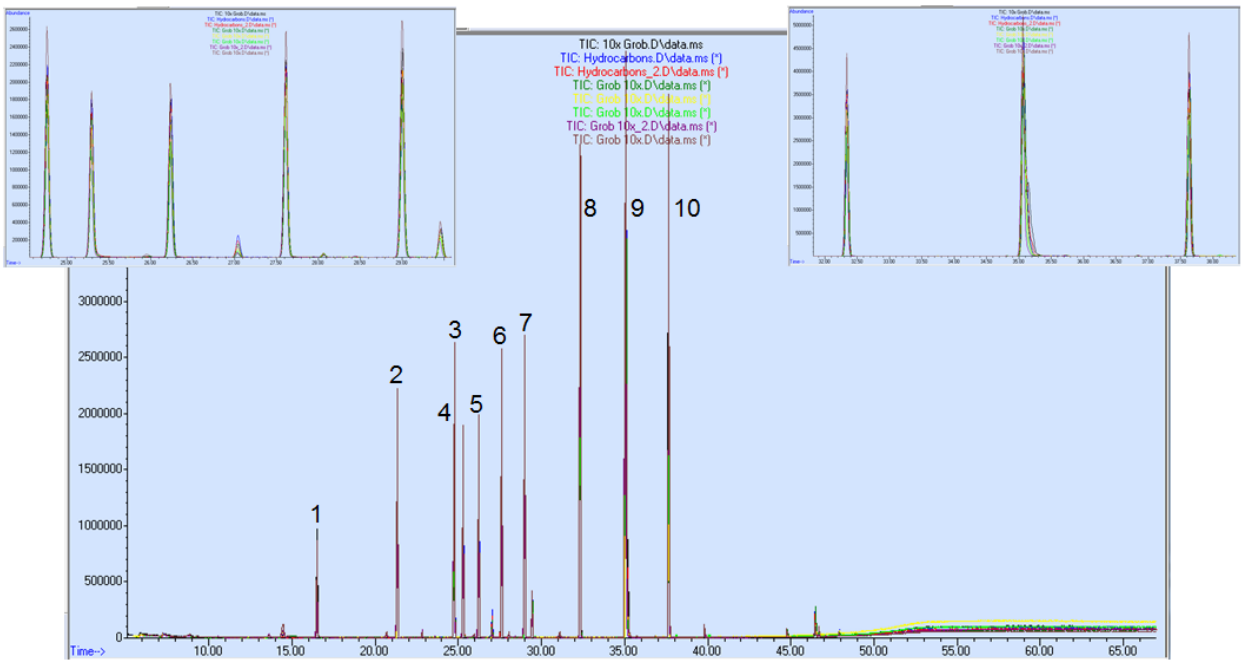


Figure 1. Overlaid 10x dilution of the Grob test mixture. The upper inserts are zoomed in portions from the main chromatogram. These results are the 10x from two IPS2's and all mid-point IP checks throughout the study. (Note: The sample vials between the mid-point IP and the hydrocarbon retention time check of the first block were mistakenly switched in the run sequence order, thus the file names are opposite.) See Table 2 for number nomenclature.

Sample Analysis/Results Discussion

GC/MS Methodology Summary

Seven methanol (MeOH) and seven methylene chloride ($MeCl_2$) organic solvent extracts from the seven solid/sludge samples noted above were submitted for gas chromatography / mass spectrometry (GC/MS) analysis under ASR 9937.01. The results are discussed in this report. The analytes of interest included glycerin and tributylphosphate (TBP) as these compounds were presumed to have been used or assumed to be present at the collection site; however, their presence within these solid/sludge samples was unknown for these random grab samples.

The GC/MS results are reported in both visual and tabular format listing tentative chemical identifications based upon a mass spectral library search and corresponding match factor. The chemical and data analysis performed is for ***qualitative*** sample assessment only as the original samples collected appear to be grab samples and any actual "target compounds" may be absent from the grab sample due to random collection variation or possible degradation with time and temperature. Again, the reader is directed to the results shown in Figure 1, which illustrates typical chromatographic signals commonly observed for 10's ng per component injected into the

GC/MS system. The samples discussed within this section will be referenced based upon the last two digits of the ASO Sample ID (e.g. sample 84 = ASO Sample ID 16-0084) unless noted.

Blank samples were prepared by adding an equal amount of extraction solvent to an identical empty glass container due to the lack of a control sample matrix.

A glycerin standard, ~470 μg/mL, was used to determine its corresponding retention time and verify the obtained mass spectra. It was prepared by adding 47.0 mg glycerin (Sigma Aldrich, Product #: G7893) to 10 mL of MeOH and diluting 1:10 with MeOH.

A tributyl phosphate (TBP) standard, ~47.6 μg/mL, was used to determine its corresponding retention time and verify the obtained mass spectra. It was prepared by adding 47.6 mg TBP (Sigma Aldrich, Product #:158615) to 10 mL of MeOH and diluting 1:100 with MeOH.

The alkane hydrocarbon mixture (C_8-C_{20}, Sigma-Aldrich, Product # 04070, ~40 mg/L each, in hexane) was used as received.

The Grob test mixture (Restek, Catalog#: 35000) was used at four different concentration levels. Grob test mixture IPS1 was used at the received concentration, IPS2 is a 10x dilution of ISP1, IPS3 is a 10x dilution of IPS2 and IPS4 is a 10x dilution of IPS4. All dilutions were with $MeCl_2$.

A portion of each solid/sludge sample was first extracted with MeOH (used because of glycerin's enhanced solubility), decanted, and then re-extracted with $MeCl_2$ (**Note:** the $MeCl_2$ extract will also contain any remaining MeOH not decanted). In addition, the headspace from sample 16-0087 was collected and analyzed via a 1 mL gas sample and two solid phase microextraction (SPME) devices. All the separations used the same column, oven temperature ramp rate program and mass spectrometric parameters unless noted. The chromatographic column used was a cyanopropy phenyl dimethyl polysiloxane, a mid-polarity type stationary phase (i.e. a "624"), which was chosen for improved chromatographic performance towards glycerin. The injection port liner was 4.0 mm ID cyclo inlet liner with wool (Restek #: 20706-200), which was chosen for improved chromatographic performance towards glycerin. This liner was also used for the gas and SPME collected samples to minimize the potential for radiological contamination and exposure from the previous liquid injections. All the liquid extracts used a 0.5 μL injection amount, chosen to minimize the potential for radiological contamination during the vapor expansion of MeOH during the GC injection. The $MeCl_2$ extracts were examined first and all the GC/MS analyses were performed without issue. The MeOH extracts were examined second, but the continuous GC/MS analyses of these samples was problematic due to autosampler issues. The samples were completed after three restart sequence attempts. The GC/MS sequence and analysis of the MeOH extracts failed due to the injection syringe plunger sticking and/or seizing when a MeOH extract sample was being examined. This effectively stopped the experimental run sequence at this point. This plunger seizing appeared random and not dependent on which extract sample was being analyzed and was likely due to the acidic nature of the extract. Ultimately the samples were completed by swapping out to a new syringe and restarting the sequence.

Each solvent extract will be discussed below with example chromatograms obtained and a listing of the tentatively identified components. At a high overview level, samples 88, 90 and 91 appeared to consistently contain both glycerin and TBP at varying amounts based upon the

chromatographic peaks. The $MeCl_2$ extracts appeared to contain a greater number and amount of alkane hydrocarbon (HC) type compounds, while the MeOH extracts had less as expected due to the highly polar nature of MeOH. General trends and chromatographic observations are highlighted in Figure 2.

As these samples appear to be “grab samples” and/or samples of opportunity, any actual target compound(s) may be absent due to random collection variation, sample inhomogeneity, or may have degraded with time and temperature pre-extraction for example. Again, accurate chemical identification is problematic based solely upon mass spectral library matching and obtaining corresponding standards for the possible chemical and number of chromatographic peaks is not realistic within the scope of the work. Moreover, quantitation and determination of solutes to an original sample is not possible as the chemical and data analysis performed is for qualitative survey only. Again, the reader is directed to the results shown in Figure 1, which illustrates typical chromatographic signals commonly observed for 10’s ng per component injected into the GC/MS system as guide for the signal variability per component from a GC/MS system as well as a visual guide to component signal strength at this concentration. For an accurate assessment a representative sample matrix would need to be obtained to understand the extraction efficiency from that matrix and validated for all components of interest, all possible side reactions, pH factors, and sample integrity for example. The extraction and chemical analysis methodology was guided towards the detection of glycerin, which was successful, as demonstrated by the large chromatographic peak observed in some of the samples. Even so, accurate quantitation is problematic without understanding the sample and extraction efficiency at a minimum.

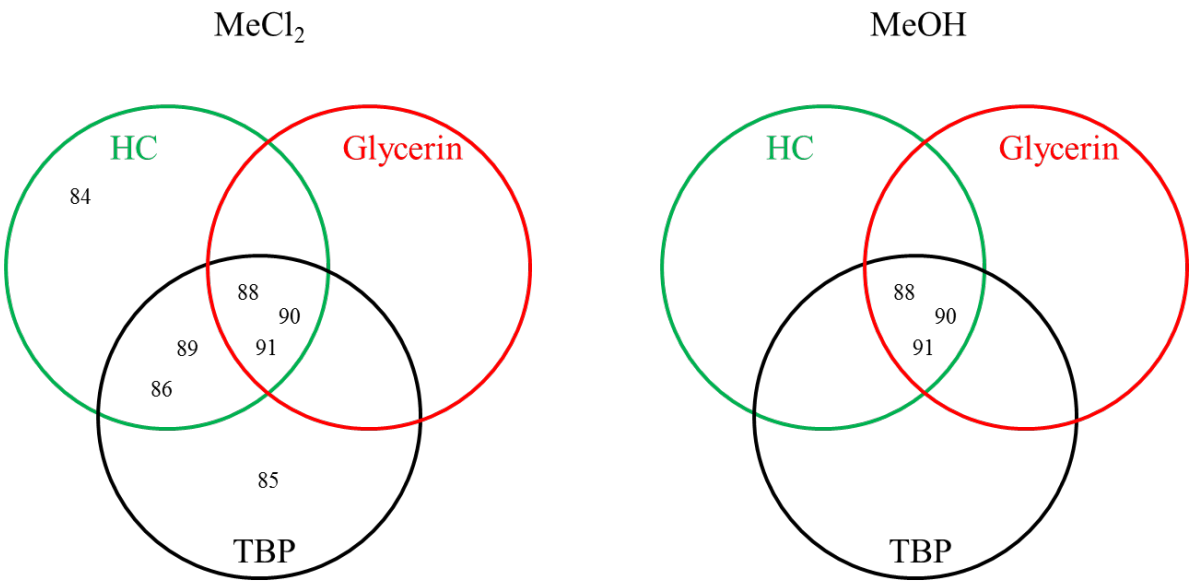


Figure 2. A simple Venn diagram highlighting some general trends/observations within and between the two solvent extracts. The Venn diagram is useful for presenting the common elements of the data results as shown by the areas of overlap among the circles. HC = alkane hydrocarbon type compounds, which are discussed later, ibid. Figure 6.

The data analysis was performed using the following software packages:

1. Automated Mass Spectral Deconvolution and Identification System (AMDIS Version 2.72, June 10, 2014, http://chemdata.nist.gov/mass-spc/amdis), see subsequent sections for parameters.
    a. Used for generating data files used in comparing among chromatograms.
    b. For a chromatographic peak/component detected by AMDIS to be considered for reporting, the following criteria were utilized:
        i. Only components with signal to noise ratio (S/N) greater than 20 as calculated via AMDIS were considered.
        ii. Only components with a weighted mass spectral match factor greater than or equal to 80 as determined by AMDIS (which consistent with a NIST match factor of 800 or greater) were considered.
            1. Note: Text taken from AMDIS "Weighted match factors are shown in the Information Lists area (3.3.3.2 Target Mode Details) and are identical to those computed in the NIST MS Search program".
        iii. Components consistent with a "siloxane" containing component were not considered.
        iv. Components also observed in blank samples were not considered: AMDIS can used to compared detected components between samples utilizing mass spectral and retention time information
2. Agilent Enhanced Chemstation (MSD ChemStation E.02.01.177, Agilent Technologies, Inc.)
3. NIST 14 mass spectral library and NIST MS search program v.2.2 (NIST/EPA/NIH. NIST Mass Spectral Library; National Institute of Standards and Technology, U.S. Secretary of Commerce, U.S. Government Printing Office: Washington, DC, June 2014)
    a. Used in conjunction with the Agilent and AMDIS software programs.

It is important to note that any compound names associated with the samples within these discussions and documentation are only **tentative** and are associated with the top mass spectral library hits and **should not** be regarded as a confirmed identification. For many chemical compounds, the mass spectral information alone is insufficient to distinguish between similar compounds. Chromatographic retention time information in the form of retention indices can also be used to aid in component identification. Retention indices are used to convert system specific retention times into system independent constants. Retention indices were also determined by AMDIS (using the hydrocarbon retention time check as a reference). The reader is directed to the AMDIS user manual for a complete discussion of this software (http://chemdata.nist.gov/mass-spc/amdis/docs/amdis.pdf).

Key definitions that will be used in the discussions below (unless otherwise noted with the text):

RT	retention time, minutes
RI	retention index,
MF	match factor as calculated via AMDIS
Model	the *m/z* valve used via AMDIS to determine S/N
S/N	Signal to Noise
SPME	Solid Phase MicroExtraction

$MeCl_2$ Extract

This section highlights the chemical and data analyses obtained from the $MeCl_2$ solvent extractions and subsequent GC/MS analyses. A larger list of the components tentatively identified from each extract/chromatogram and the detection and identification criteria used is given in subsequent sections below. In general, four of the chromatograms, obtained from samples 84, 86, 88, and 89, visually look very similar (Figure 3). The chromatogram obtained for sample 85 appears "unique", but likely was the most dilute extract examined, showing the fewest chromatographic peaks (Figure 4). The chromatograms obtained from samples 90 and 91 appeared identical and contain the greatest number of chromatographic peaks/components (Figure 5). Again, the reader is directed to"$MeCl_2$ Tentative Components" section below for greater listing of detected chromatographic peaks. All the chromatograms, except that from sample 85, appear to have a number of larger hydrocarbon components/peaks up to C27 (Figure 6). The exact MS library hits can be problematic, but hydrocarbon retention check sample provides insight to this hypothesis. There appears to be an unresolved complex mixture (UCM) of hydrocarbons (i.e. the chromatographic "hump" around 50 minutes) within all the samples except 85 (Figure 6). This UCM is a common feature observed in weathered petroleum hydrocarbons. All the samples, except sample 84, likely contain tributylphosphate (TBP), via *m/z* 99 at ~41.5 min. The 90 and 91 samples exhibit the greatest glycerin and tributylphosphate components. Table 3 lists some of the components found that appear common among all the $MeCl_2$ extracts.

Table 3. Likely Common Components among the $MeCl_2$ Extract Samples

CAS #	Name	RT	RI	MF
121437	Boric acid, trimethyl ester	6.04	604.4	94
98862	Acetophenone	25.6	1129.1	96
95169	Benzothiazole	30.6	1290.9	93
83330	1H-Inden-1-one, 2,3-dihydro-	32.7	1364.9	97

RT retention time, minutes; RI retention index; MF match factor as calculated via AMDIS

(**Note:** When the chemical is not listed in the tentative sample component list determined by AMDIS, the relevant mass spectral *m/z* values were visually confirmed within the chromatogram.)

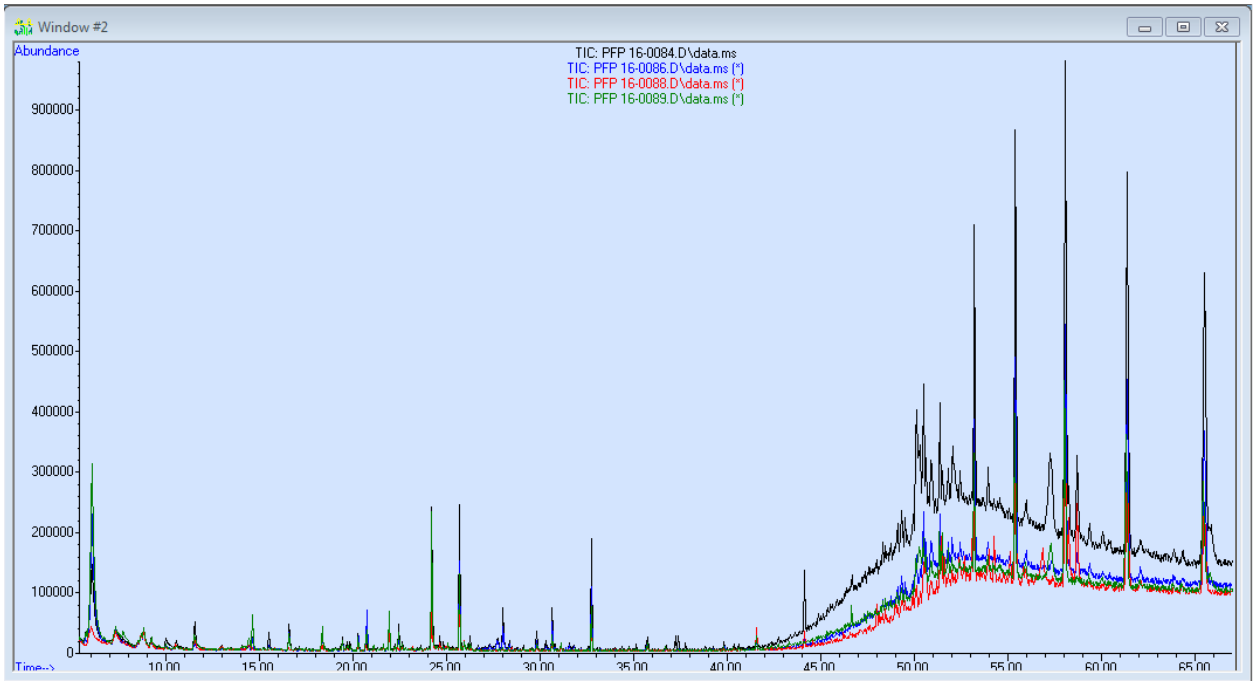


Figure 3. Overlaid chromatograms for samples 84, 86, 88 and 89. $MeCl_2$ Extract Samples

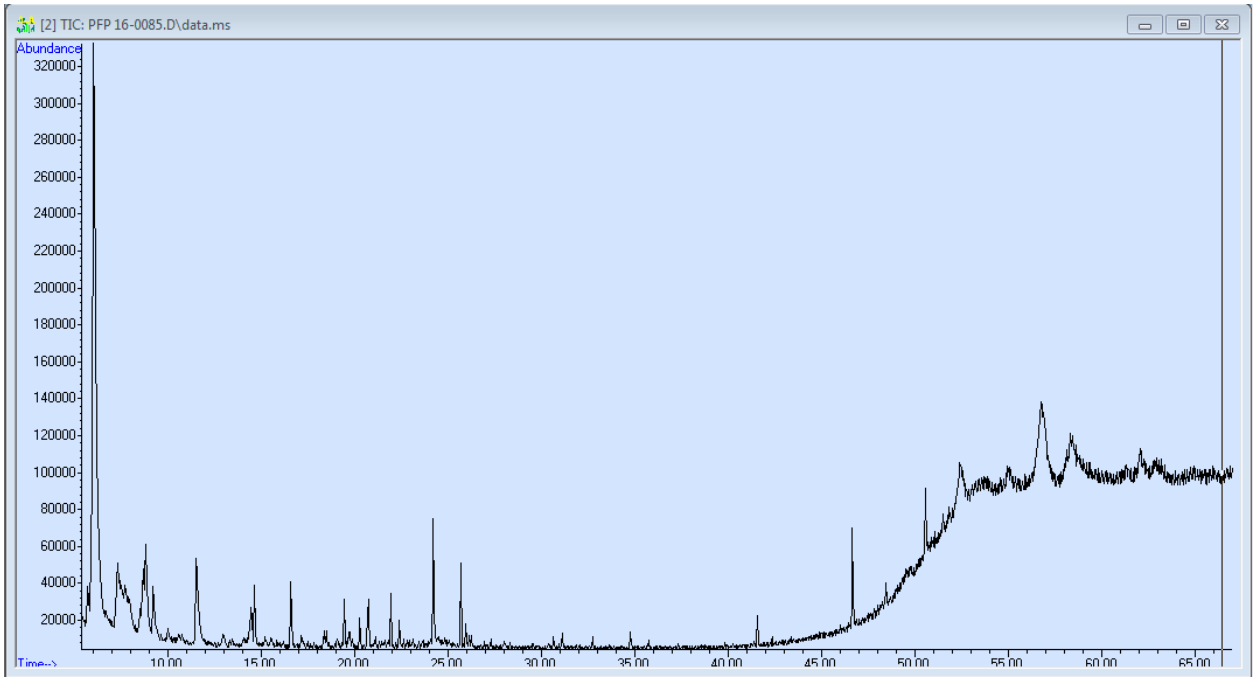


Figure 4. Chromatogram for sample 85. $MeCl_2$ Extract Samples

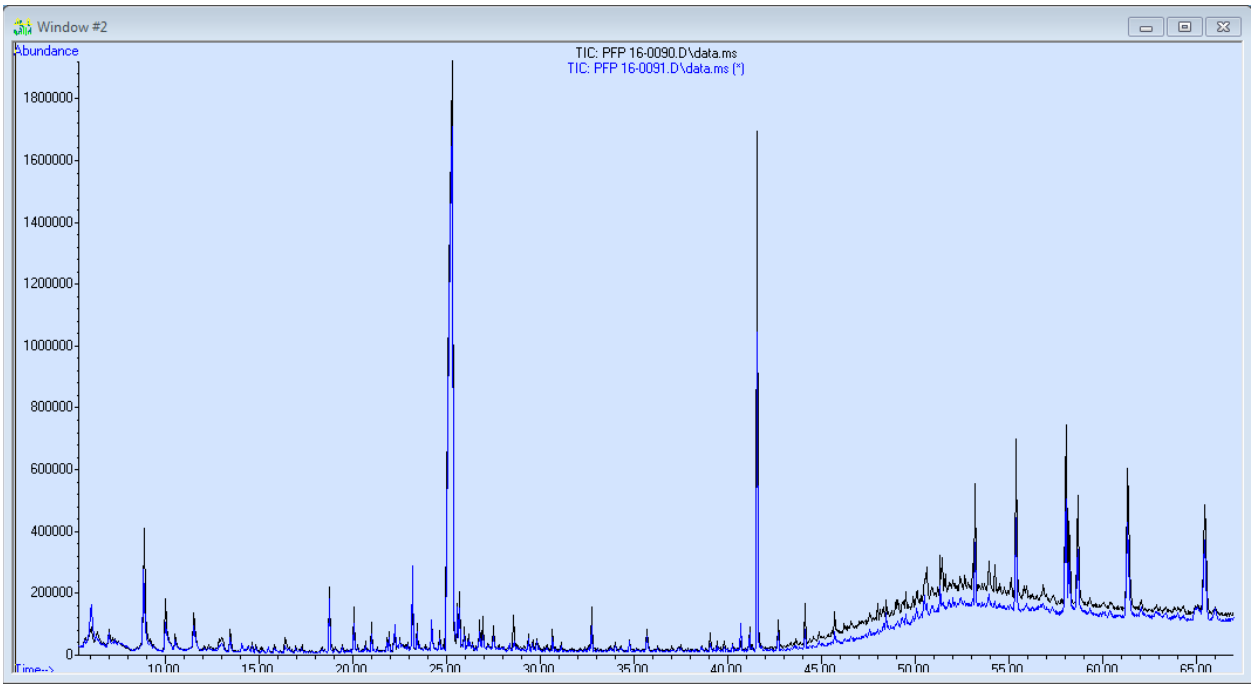


Figure 5. Overlaid chromatograms for 90 and 91. $MeCl_2$ Extract Samples

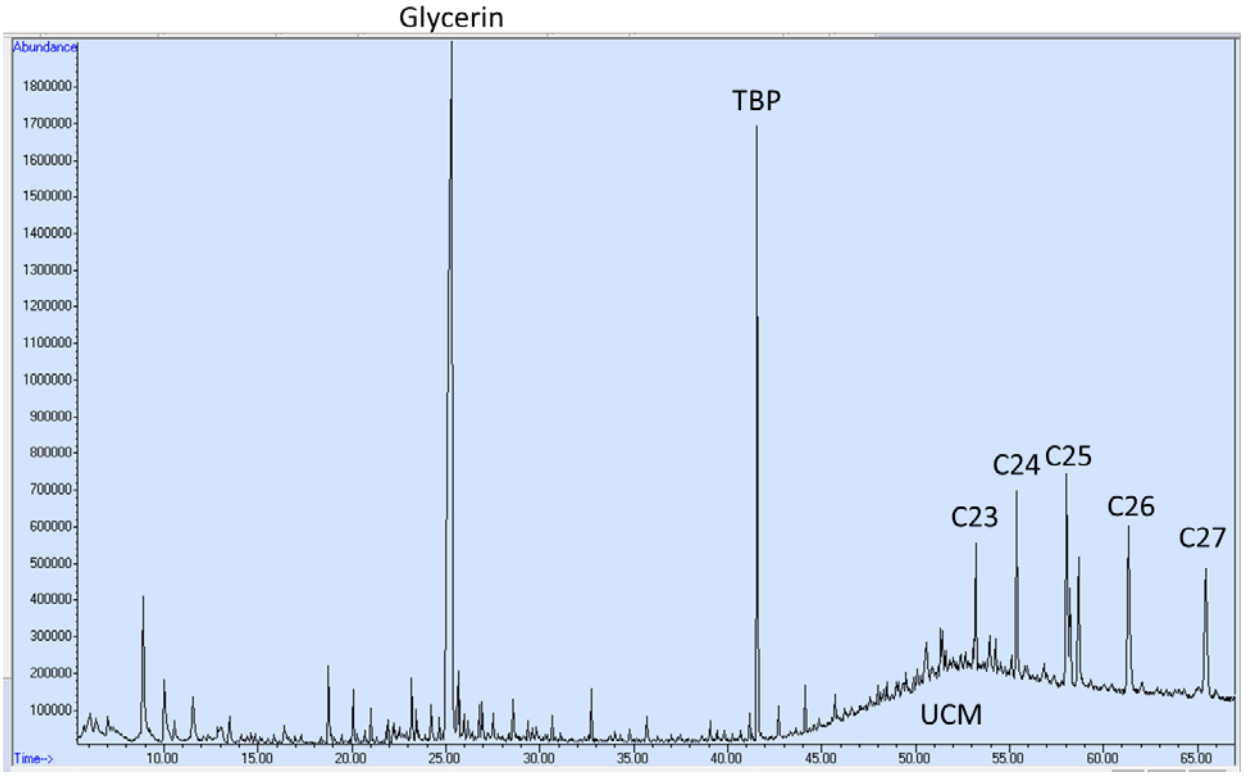


Figure 6. Chromatogram for sample 90 with components tentatively identifed. TBP = Tributylphosphate, UCM = Unresolved Complex Mixture region. $MeCl_2$ Extract Samples

MeOH Extract

This section highlights the chemical and data analyses obtained from the MeOH solvent extraction and subsequent GC/MS analyses. A larger list of the tentative identified components from each extract/chromatogram and the detection and identification criteria used is given in subsequent sections below. In general, four of the chromatograms, obtained from samples 84, 85, 86, and 89, visually looked very similar (Figure 8). Comparatively, the chromatograms obtained from samples 88, 90 and 91 appear similar, with each showing a large glycerin component, which is absent from the other four chromatograms (Figure 8). Again, the reader is directed to the "MeOH Tentative Components" section below for greater listing of detected chromatographic peaks. As expected, the glycerin peak is larger for the methanol extracts due to its increased solubility. As discussed, the chemical names listed to the corresponding chromatographic peaks are associated to the top mass spectral library hit. Interestingly, two of the largest chromatographic peaks for samples 84, 85, 86, and 89, at approximately 7 and 14 minutes, do not have a reliable library hit based upon the acceptance criteria utilized, but the mass spectra between these two peaks are very similar varying primarily in intensity (Figure 9). In general, all the samples and subsequent chromatograms showed fewer components compared with the methylene chloride extraction. Again, many compounds are present at low amounts within the extractants, but subsequent concentrating approaches are not possible at these radiological levels. Table 4 lists some of the components found that appear common among all the MeOH extracts.

Table 4. Likely Common Components among the MeOH Extracts Samples

CAS	Name	RT	RI	MF
64197	Acetic acid	9.05	716	95
96355	Acetic acid, hydroxy-, methyl ester	11.64	764	96
553902	Ethanedioic acid, dimethyl ester	17.14	888	93
98862	Acetophenone	25.69	1129	96
95169	Benzothiazole	30.64	1290	92
83330	>1H-Inden-1-one, 2,3-dihydro-	32.72	1364	95

RT retention time, minutes; RI retention index; MF match factor as calculated via AMDIS

(**Note:** When the chemical is not listed in the tentative sample component list determined by AMDIS, the relevant mass spectral *m/z* values were visually confirmed within the chromatogram.)

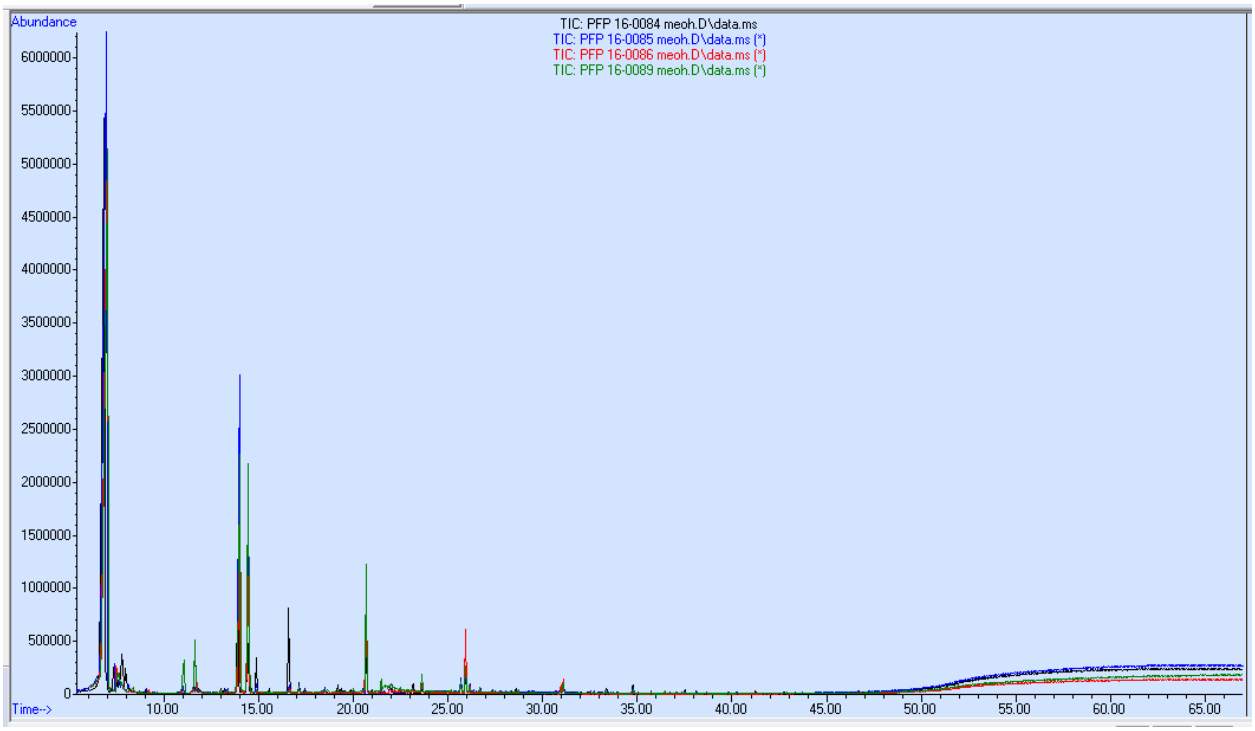


Figure 7. Overlaid chromatograms for samples 84, 85, 86 and 89. MeOH Extracts Samples

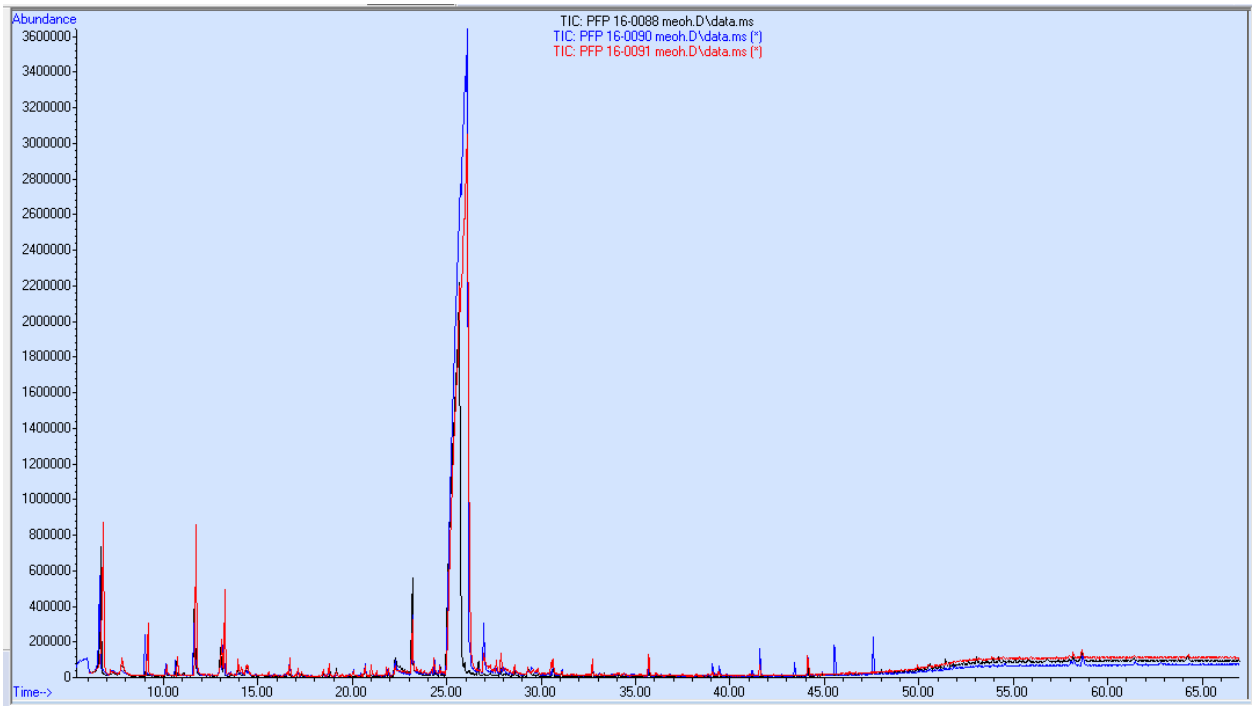


Figure 8. Overlaid chromatograms for samples 88, 90 and 91. MeOH Extracts Samples

~7 min ~14 min

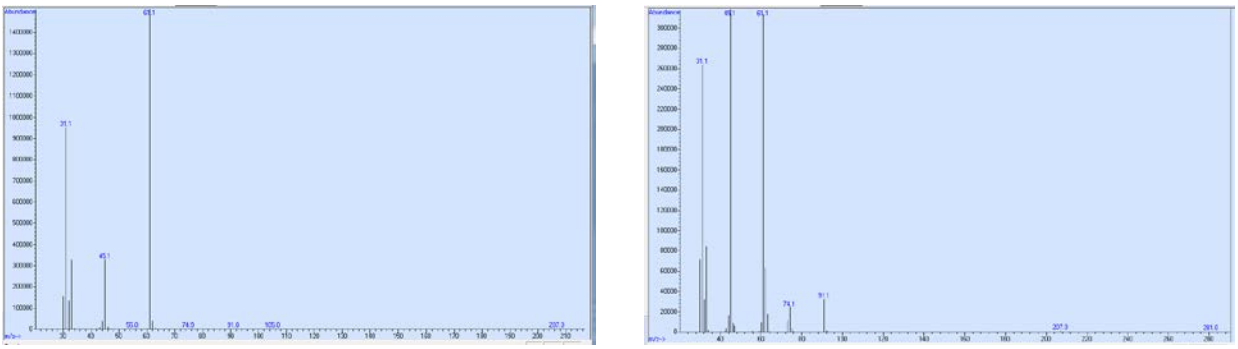


Figure 9. Mass spectra obtained from chromatographic peaks at approximately 7 and 14 minutes from sample 86. MeOH Extracts Samples

Gas and SPME Headspace

Analyses discussed within this section are obtained from the gaseous headspace collected within the bag containing the broken ASO Sample 16-0087 (refer to the Sample Collection section above). This section discusses the results obtained using solid phase microextraction (SPME) collection from two different SPME fiber types and a 1 mL gas sample analysis using a gas tight syringe for direct injection into the GC/MS instrument.

SPME is a sampling technique that involves the use of a fiber coated with an extracting phase that can extract different kinds of analytes/components (including both volatile and non-volatile) from the headspace/gas phase above a media. The quantity of analyte extracted by the fiber is proportional to its concentration in the sample and the equilibrium time. For the ASO 16-0087 grab sample, a polydimethylsiloxane (PDMS)/Carboxen fiber (for trace levels of volatiles) a PDMS/divinylbenzene (DVB) fiber (for semi-volatiles and larger volatiles) were used for separate collections. At a high level, the PDMS/Carboxen fiber (noted as “black”) will have a greater tendency to collect/release more volatile chemical components while the PDMS/DVB (noted as “pink”) will have a greater tendency to collect/release less volatile chemical components. There will also be a large fraction of chemical components that should be collected/released between these two SPME fibers that will be the same. A commercial portable SPME assembly with the above fiber type is utilized for possible radiologically contaminated samples (Figure 10). All decontamination precautions and measures were followed during and after sampling. All three headspace samples were collected and analyzed on the same day; the equilibrium time for SPME collection was approximately 60 minutes for each device.

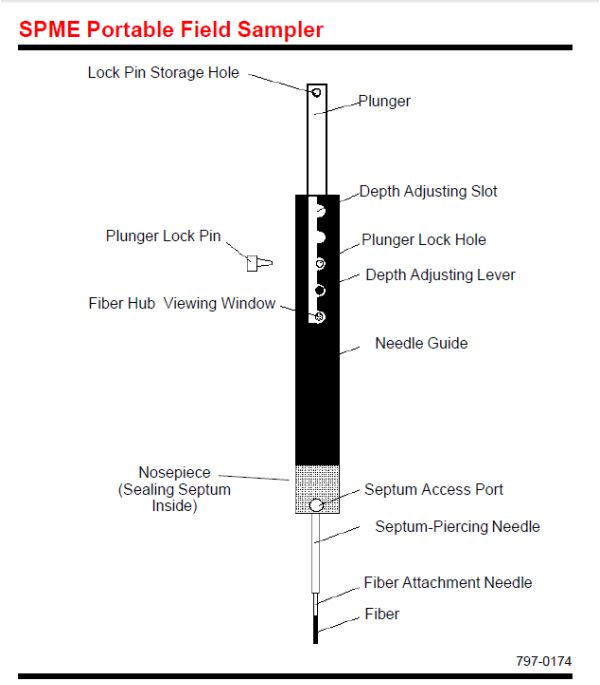


Figure 10. Example of SPME Portable Field Sampler.

Solid phase microextraction, using the Supelco™ SPME Portable Field Sampler, is a reliable way of concentrating, storing, and transporting samples of volatile and semivolatile compounds

in the field. After sampling, the SPME fiber is retracted into a protective outer needle. The needle is drawn within a replaceable sealing septum in the nosepiece and locked into place. The sampler – or samplers – then can be transported safely to the laboratory for analysis. The user has the option of immediately desorbing the analytes from the fiber and conducting the analysis, or storing the analytes on the fiber for analysis at a later time.

The 1 mL gas collection with direct injection into the GC/MS did not exhibit many chemical components as shown below in Figure 11 and Table 5.

The SPME sampling exhibited many more components, as SPME is a concentrating device. Each sample that was collected by a SPME fiber type was compared against the headspace collected from a portion of the transport bag material that was placed in a headspace vial. These results from the two SPME fiber types are highlighted and illustrated in the below figures and tables by showing: the AMDIS chromatogram for sample 16-0087 (Figure 12 and Figure 15), the overlaid chromatograms (inverted form) for sample 16-0087 vs. the “bag blank” per SPME fiber type (Figure 13 and Figure 16), the AMDIS post-process comparison, which shows the unique/significant components for sample 16-0087 (Figure 14 and Figure 17), and finally the tabulated results of the tentative chemical components (Table 6 and Table 7). Note: The AMDIS post-process comparison examines the similarity between retention time and mass spectral features, not the tentative chemical names. In general, most of the chromatographic peaks observed are likely from the bag and outgassed chemicals, as shown visually in the inverted overlaid chromatograms. However, the AMDIS post-process comparison does provide insight into possible unique component from the sample.

Tentative Components in 16-0087, 1 mL Gas Syringe

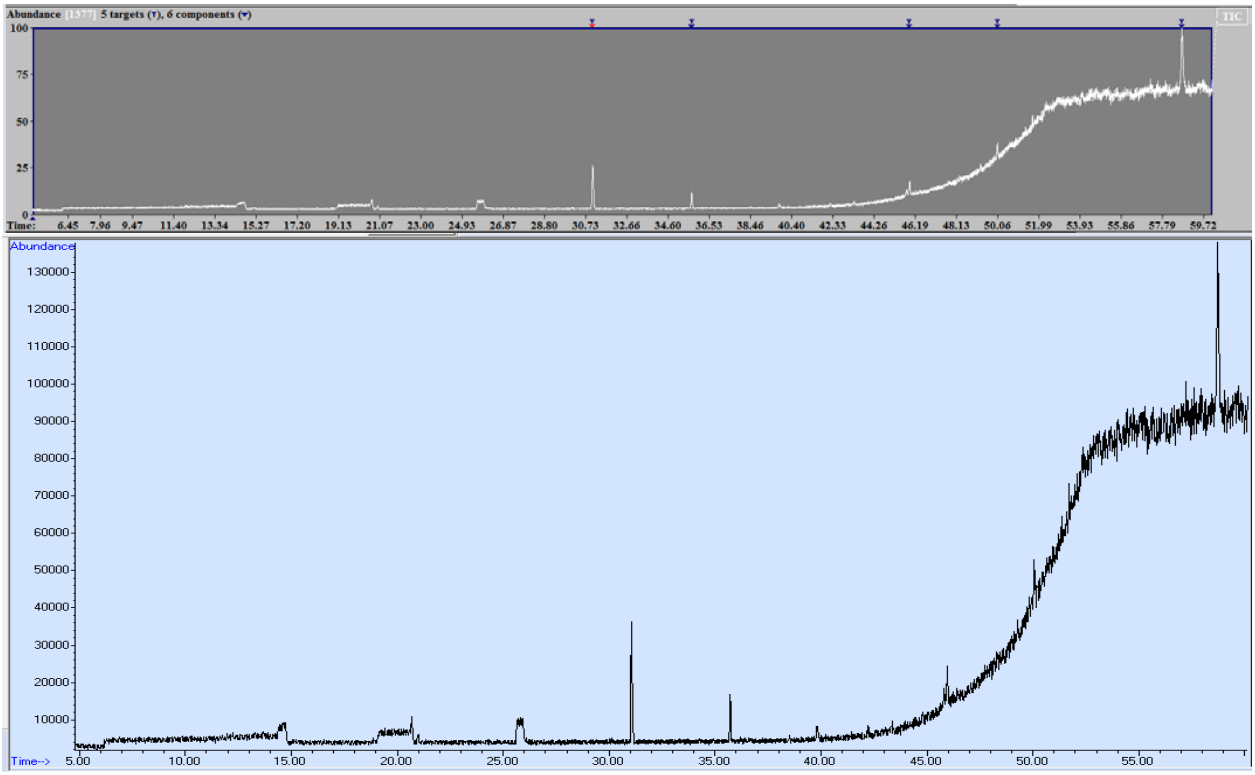


Figure 11. Chromatogram from 1 mL gas syringe sample (ASO 16-0087) Top chromatogram from AMDIS, Bottom chromatogram from Agilent software

Table 5. Top NIST library hits from AMDIS, 1 mL Gas Syringe.

CAS	Name	RT	RI	Model	S/N	MF
EPA-240362	>2-Morpholinomethyl-1,3-diphenyl-2-propanol	45.9386	1919.8	100 m/z	23	88
EPA-240362	>2-Morpholinomethyl-1,3-diphenyl-2-propanol	50.0585	2123.1	100 m/z	21	88
13674878	>Tris(1,3-dichloroisopropyl)phosphate	58.731	2551.2	TIC	44	81

NOTE: Any compound names are only tentative and **should not** be regarded as a confirmed identification.
RT retention time, minutes; RI retention index; MF match factor as calculated via AMDIS

Tentative Unique Components in 16-0087, SPME Pink

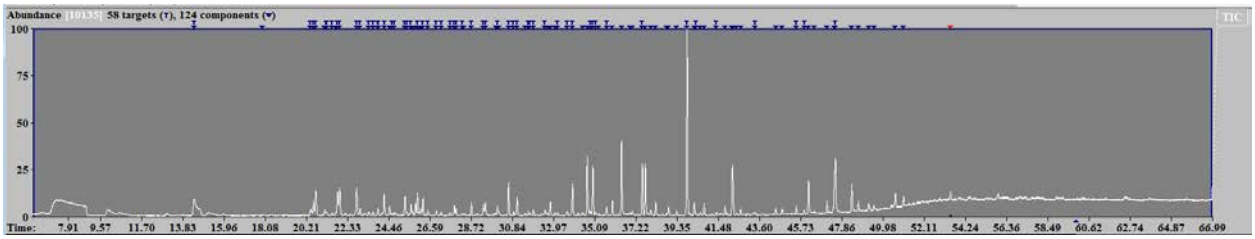


Figure 12. 16-0087 AMDIS Chromatogram, SPME Pink

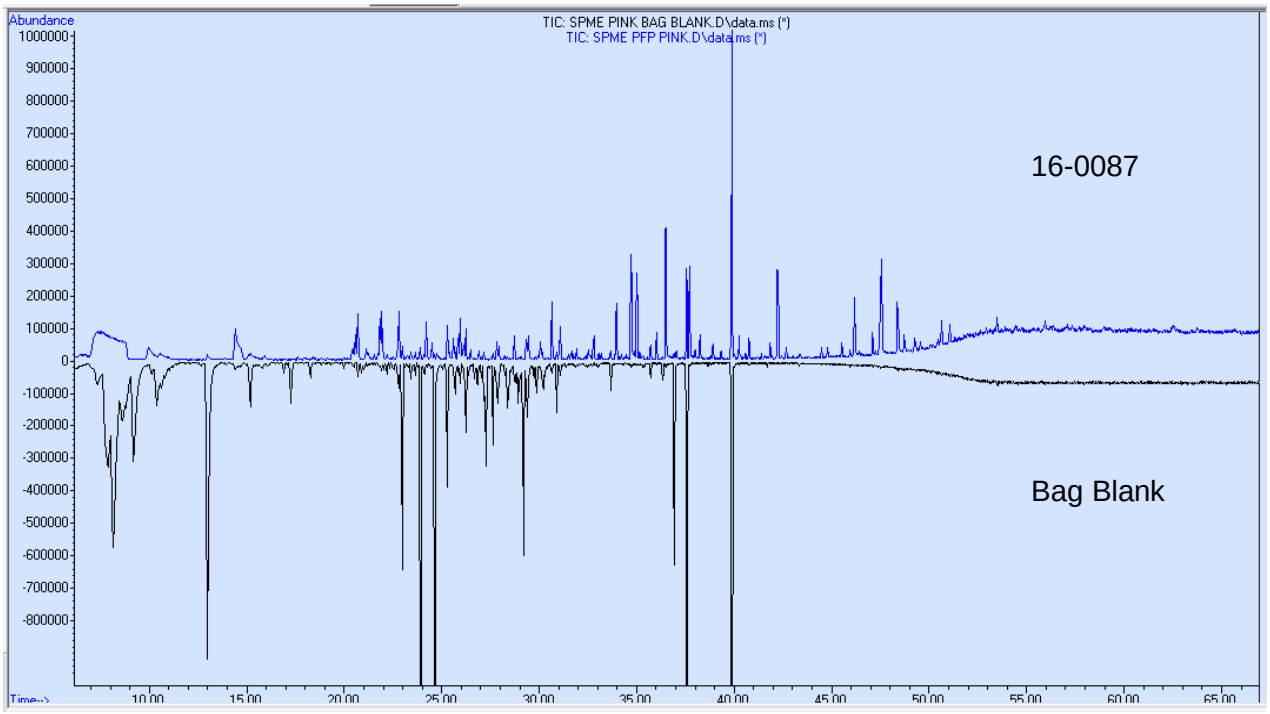


Figure 13. Agilent Overlaid Chromatograms (inverted format) for 16-0087 vs. bag blank, SPME Pink

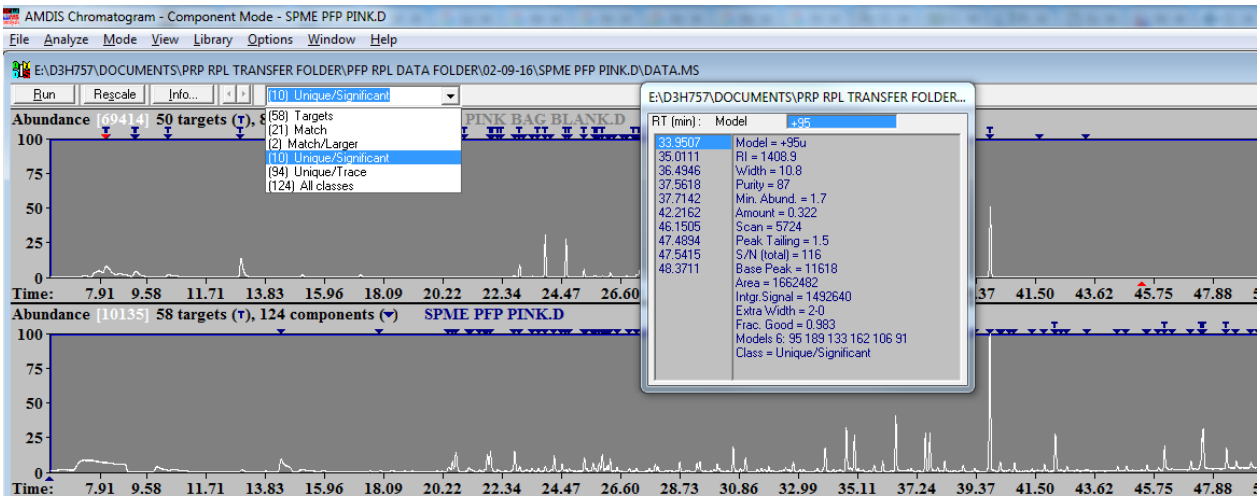


Figure 14. AMDIS post-process comparison for unique/significant components, SPME Pink.

Table 6. Top NIST library hits from AMDIS post-process comparison for unique/significant components, SPME Pink.

CAS	Name	RT	RI	Model	S/N	MF
95-16-9	Benzothiazole This component appears significant	30.6576	1290.9		119	
1137128	>1,2,4-Methenoazulene, decahydro-1,5,5,8a-tetramethyl-, [1S-(1à,2à,3aá,4à,8aá,9R*)]-(Longicyclene)	33.9507	1408.9	95 m/z	116	94
475207	>Longifolene	35.0111	1449.2	161 m/z	145	96
31600-69-8	1-Butanol, 4-(1-methylethoxy)-	36.4946	1505.9		180	76
EPA-401120	>2,5-cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-hydroxy-4-methyl-	37.5618	1549	165 m/z	151	85
4541-13-3	1-Butanol, 4-(hexyloxy)-	37.7142	1555.1		152	72
97443-86-2	Butanamide, N-methyl-4-(methylthio)-2-(2,2-dimethylpropylidene)amino-	42.2162	1746.3		145	61
74793-66-1	2-Butanol, 3-(2,2-dimethylpropoxy)-	46.1505	1930.2		118	67
31600-69-8	1-Butanol, 4-(1-methylethoxy)-	47.4894	1996.3		116	68
112958	>Eicosane	47.5415	1998.9	57 m/z	136	93
4541-13-3	1-Butanol, 4-(hexyloxy)-	48.3711	2039.8		109	67

RT retention time, minutes; RI retention index; MF match factor as calculated via AMDIS; S/N signal/noise ratio
Green represents components meeting a match factor of >80.
Blue represents components determined as “unique”, but that do not meet the NIST search criteria.
Gray see comment below chemical name in table above.
Note: Any compound names that are identified as only tentative **should not** be regarded as a confirmed identification.

Tentative Unique Components in 16-0087, SPME Black

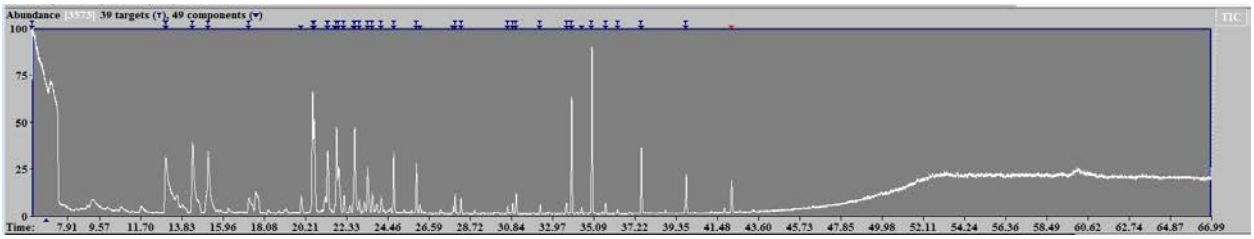


Figure 15. 16-0087 AMDIS Chromatogram, SPME Black

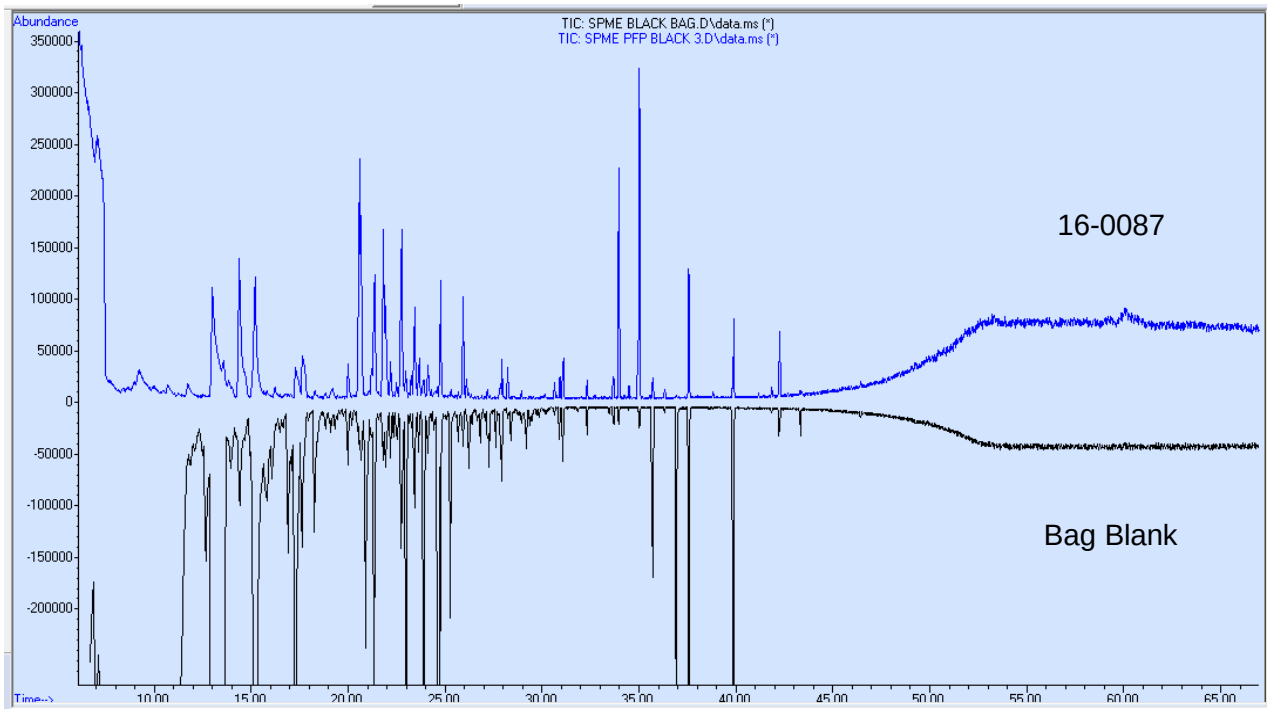


Figure 16. Agilent Overlaid Chromatograms (inverted format) for 16-0087 vs. bag blank, SPME Black

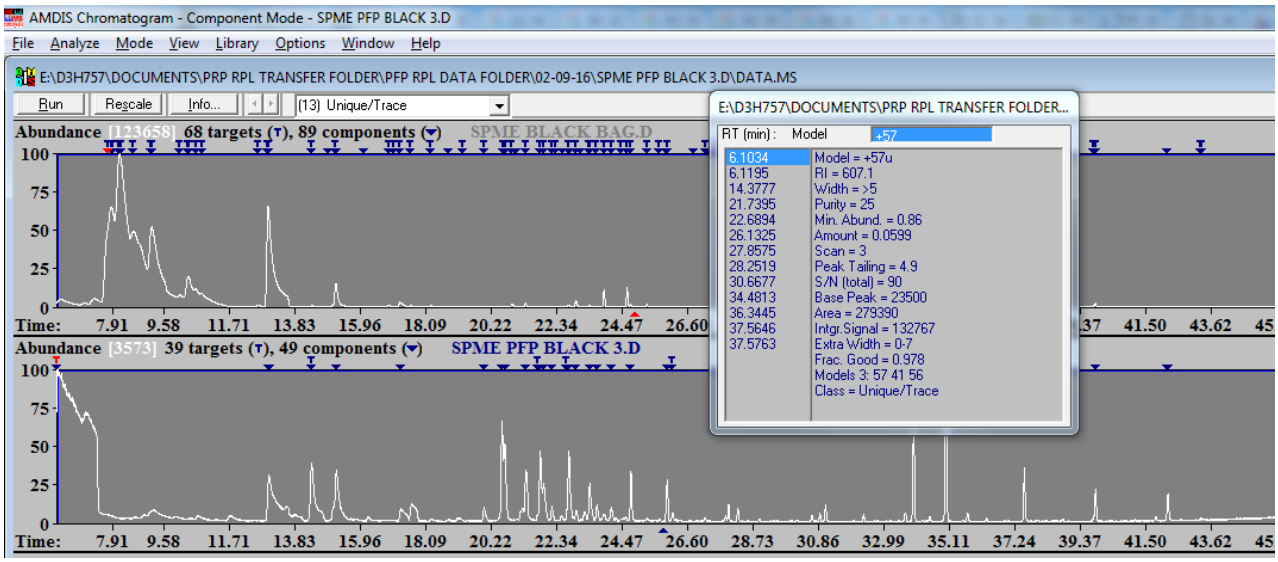


Figure 17. AMDIS post-process comparison for unique/trace components, SPME Black.
Note: 6.1034 and 6.1195 are the same component, 37.5646 and 37.5763 are the same component, 14.3777 is a siloxane component and not counted.

Table 7. Top NIST library hits from AMDIS post-process comparison for unique/significant components, SPME Black.

CAS	Name	RT	RI	Model	S/N	MF
EPA-386402	>2-Ethyl-oxetane	6.1195	607.8	57 m/z	88	93
50739-80-5	1,4-Benzenedicarboxamide, 2-nitro-	21.7395	1015.3		32	71
61310-53-0	3-Ethoxyacrylonitrile	22.6894	1041.8		31	88
56114-69-3	2,5-Dihydroxybenzaldehyde, 2TMS derivative	26.1325	1142.8		36	78
498-81-7	Cyclohexanemethanol, α,α,4-trimethyl-	27.8575	1197.0		28	77
464493	>(+)-2-Bornanone ((+)-Camphor)	28.2519	1210	TIC	48	90
272162	>1,2-Benzisothiazole	30.6677	1291.2	135 m/z	34	90
1137128	>1,2,4-Methenoazulene, decahydro-1,5,5,8a-tetramethyl-, [1S-(1à,2à,3aá,4à,8aá,9R*)]-(Longicyclene) This component appears significant	33.9618	1409.3	94 m/z	136	95
	2H-2,4a-Methanonaphthalene, 1,3,4,5,6,7-hexahydro-1,1,5,5-tetramethyl-, (2S)-(Isolongipholene)	34.4813	1429.1		28	77
475207	>Longifolene This component appears significant	35.0149	1449.3	161 m/z	162	96
62108218	>Decane, 6-ethyl-2-methyl-	36.3445	1499.9	TIC	24	83
EPA-401120	>2,5-cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-hydroxy-4-methyl-	37.5646	1549.1	165 m/z	101	83

RT retention time, minutes; RI retention index; MF match factor as calculated via AMDIS; S/N signal/noise ratio
Green represents components meeting a match factor of >80.
Blue represents components determined as "unique", but that do not meet the NIST search criteria.
Gray see comment below chemical name in table above.
Note: Any compound names that are identified as only tentative **should not** be regarded as a confirmed identification.

Data Limitations

There were no failures on the head gas analysis that caused limitations to the data reported. For the liquid samples, an occurrence report, OR-98620-2-17-16; Holding Time Limit Concern for Some GC-MS Samples for ASR 9937 was issued. ASO test instruction, 98620-TI-001, *Rev. 0, PRF Canyon Sample Handling in Glove Box* in Section 4, Part 2, Organics Testing: Preparation for Gas Chromatography- Mass Spectrometry (GC-MS) lists holding time limits imposed by the project Statement of Work, Statement of Work for Contract 495170-40, Rev. 0, 236-Z PRF Canyon Floor Debris Sample Analysis (CHPRC to PNNL Supplier) FY16, 11/5/2015. The holding time limits imposed were:

Semi-VOA in Soil – 14 days from date of extraction
VOA in Soil – 14 days from date of extraction

Seven samples were received for analysis under this ASR; there were four samples that were MeOH extracted on 1/5/16 and analyzed by GC-MS on 1/23/16 (16-0086, 16-0088, 16-0089, and 16-0091) were outside the 14-day holding time limit window by 4 days.

Retention Time Check and Results

A hydrocarbon standard containing octane (C_8), nonane (C_9), decane (C_{10}), undecane (C_{11}), dodecane (C_{12}), tridecane (C_{13}), tetradecane (C_{14}), pentadecane (C_{15}), hexadecane (C_{16}), heptadecane (C_{17}), octadecane (C_{18}), nonadecane (C_{19}), and eicosane (C_{20}) (Sigma Aldrich, 04070, C_8-C_{20}, ~40 mg/L each, in hexane) was used for the retention time check standard. The results obtained were used to generate the retention indices marker values. Over the period of the study both liquid extracts and headspace GC/MS analyses were performed using the retention time check standard. Excellent retention time stability was observed through the course of this work. This is demonstrated in Figure 18, which shows the overlaid chromatograms (and zoomed in portions) from the retention time checks from the very first block of liquid samples examined ($MeCl_2$) and the very last set of headspace samples (Note: the headspace results were obtained by collecting the headspace create from a 5 µL aliquot of the retention time standard in a manner similar to which the sample 16-0087 was collected via solid phase microextraction, SPME). In general, the hydrocarbon retention time checks exhibited excellent retention time stability throughout the study across very different sample injection modes.

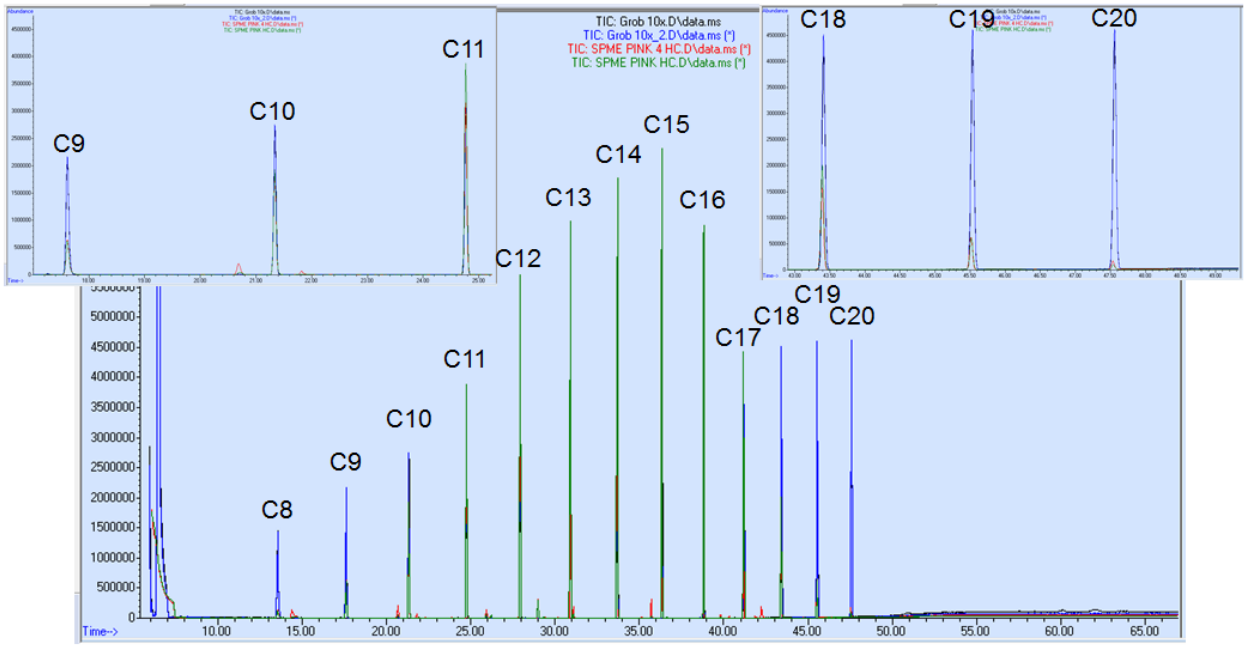


Figure 18. Overlaid chromatograms from the alkane retention time check

Glycerin and Tributyl Phosphate Standard Check

Individual glycerin and tributyl phosphate standards (Sigma-Aldrich Glycerin, G7893, Sigma-Aldrich TBP, 158615) were prepared in methanol and analyzed by GC/MS. These standards were used to determine their retention times and confirm their mass spectrum for their possible presence within the extracted samples. Shown in Figure 19 is the NIST MS library hit comparisons for the chromatographic peaks from these two components when injected separately onto the GC/MS. The red MS is that obtained from the experimental run and the blue MS is that obtained from the NIST library. The retention time (RT) reflects the nominal retention time of the chromatographic peak for that solute. In both cases the match factor is greater than 90 and both are the top NIST MS library hits for the components.

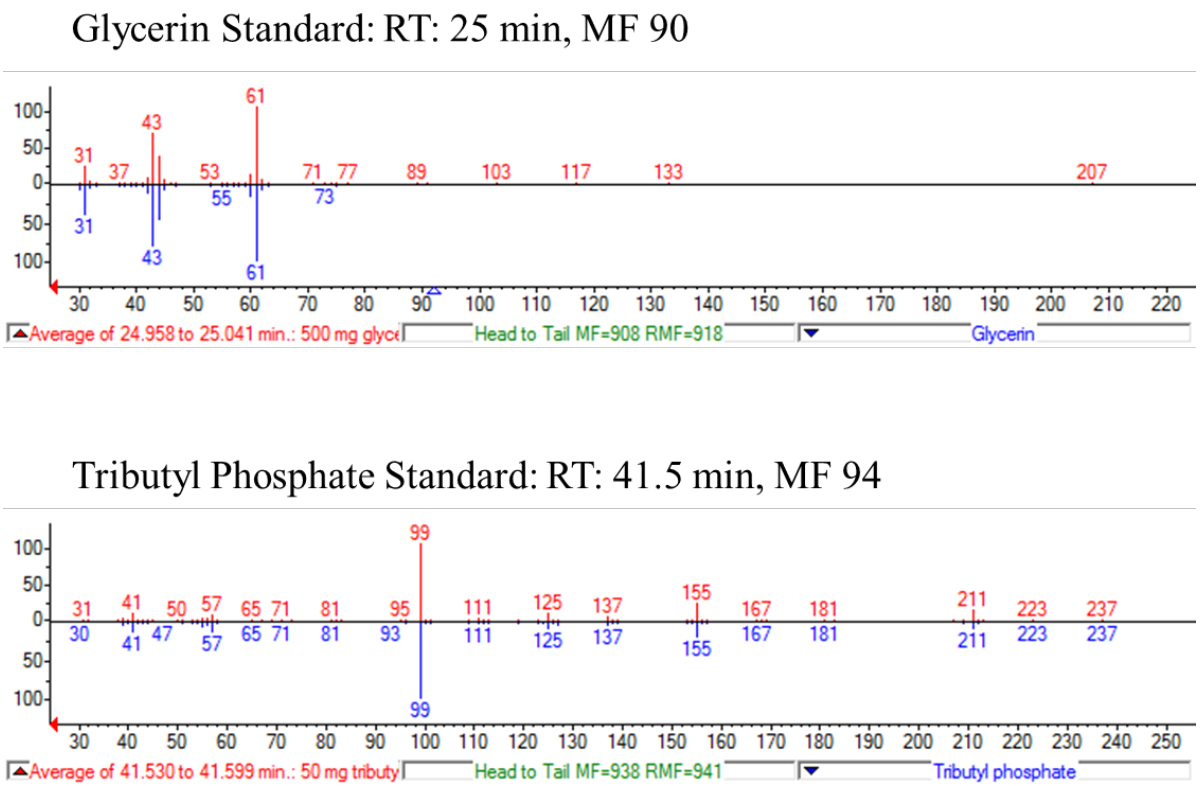
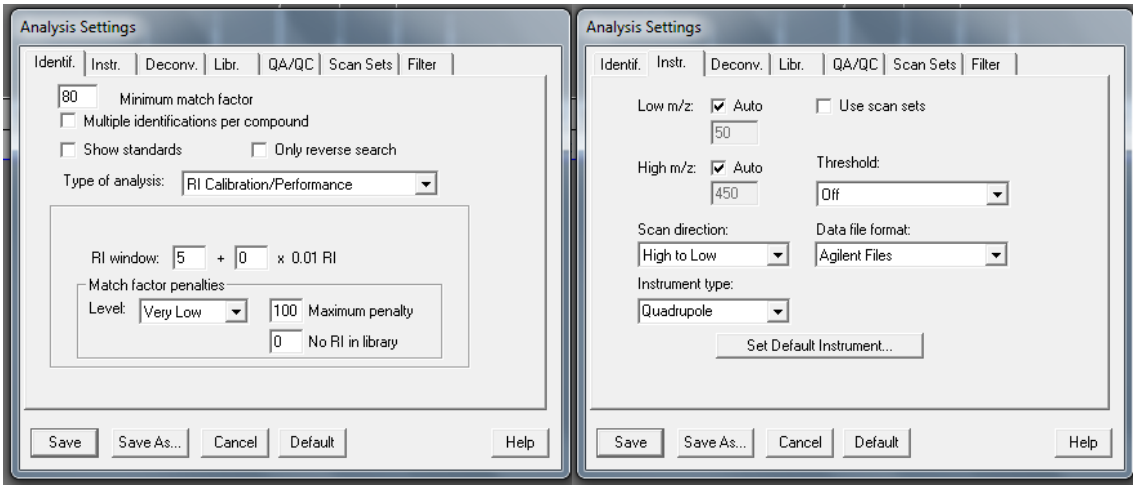
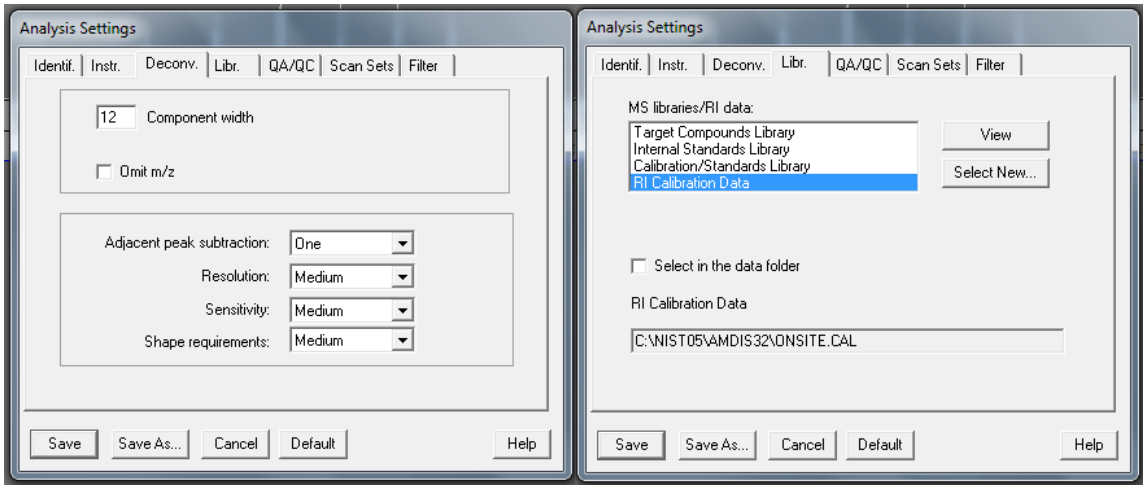


Figure 19. NIST MS library hit comparison for Glycerin and Tributyl Phosphate Standards

AMDIS Parameter Screen Captures

The first hydrocarbon retention time standard check chromatogram was used in conjunction with AMIDS to create a retention index (RI) calibration file to generate subsequent retention index values for the analytical samples. Figure 20 illustrates the parameters used in AMDIS. The utilization of this retention time calibration file can be used to standardize retention results in any future characterization when using the same chromatographic column type. Because of the column type used comparison of the determined RI's with the NIST values should be used with caution.





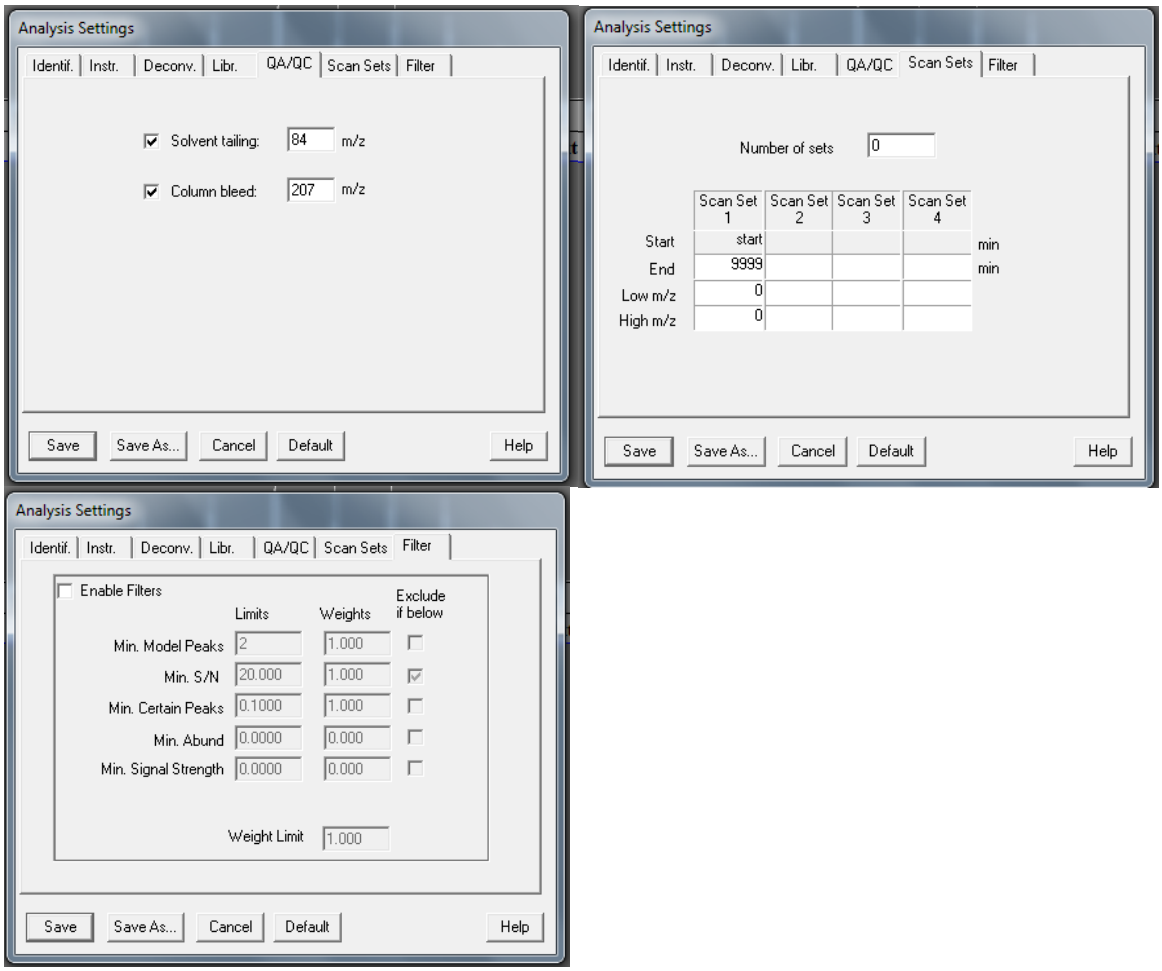
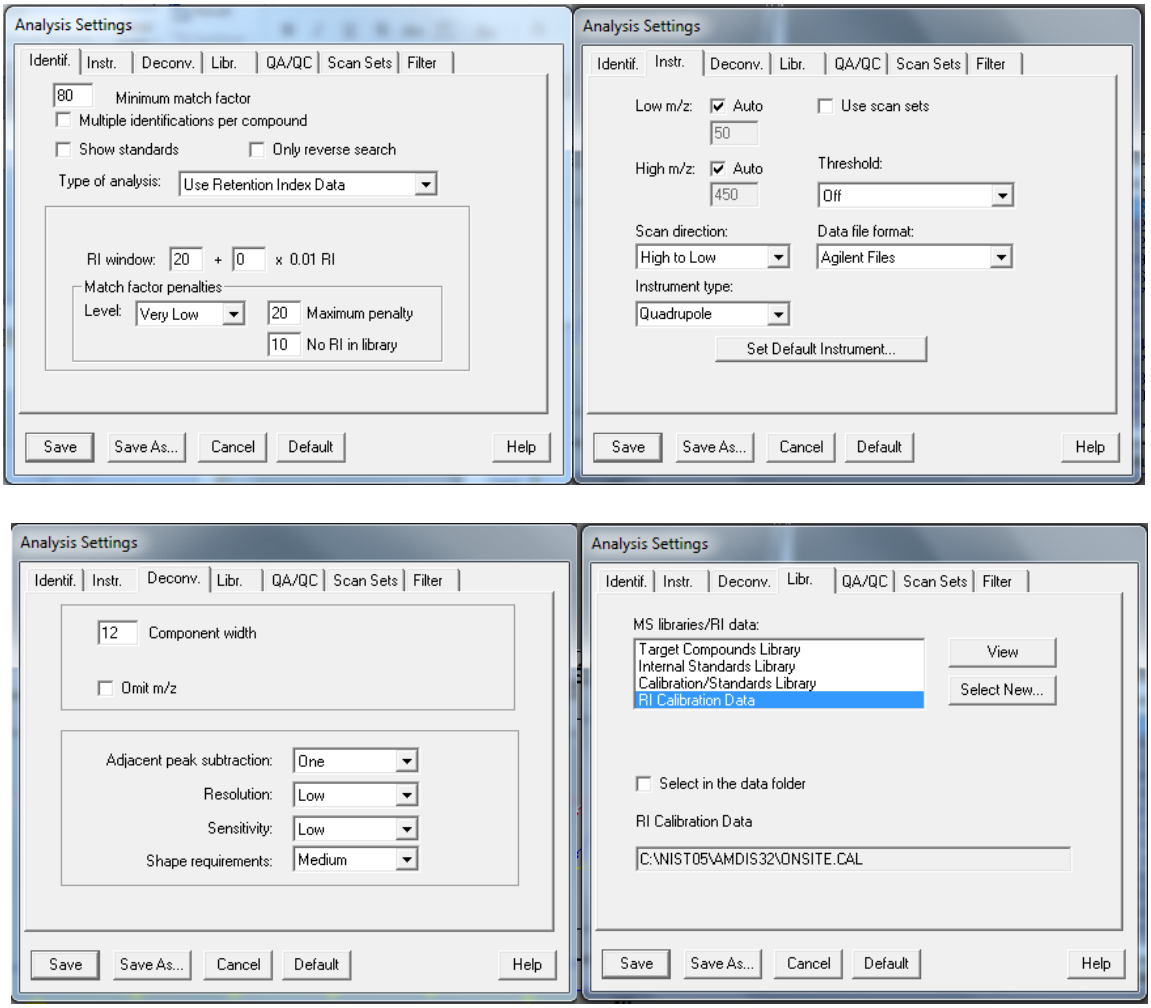


Figure 20. Computer screen captures of the AMDIS Setting for Hydrocarbon Retention Time Standards Calibration File

Figure 21 illustrates the eight data analyses setting used with AMDIS for sample data analysis. Only components with a mass spectral match factor greater than 80 are reported with a chemical name. Retention indices were not incorporated in identification because of the type of the chromatographic column type used. The column type was chosen for improved chromatographic performance for glycerin.



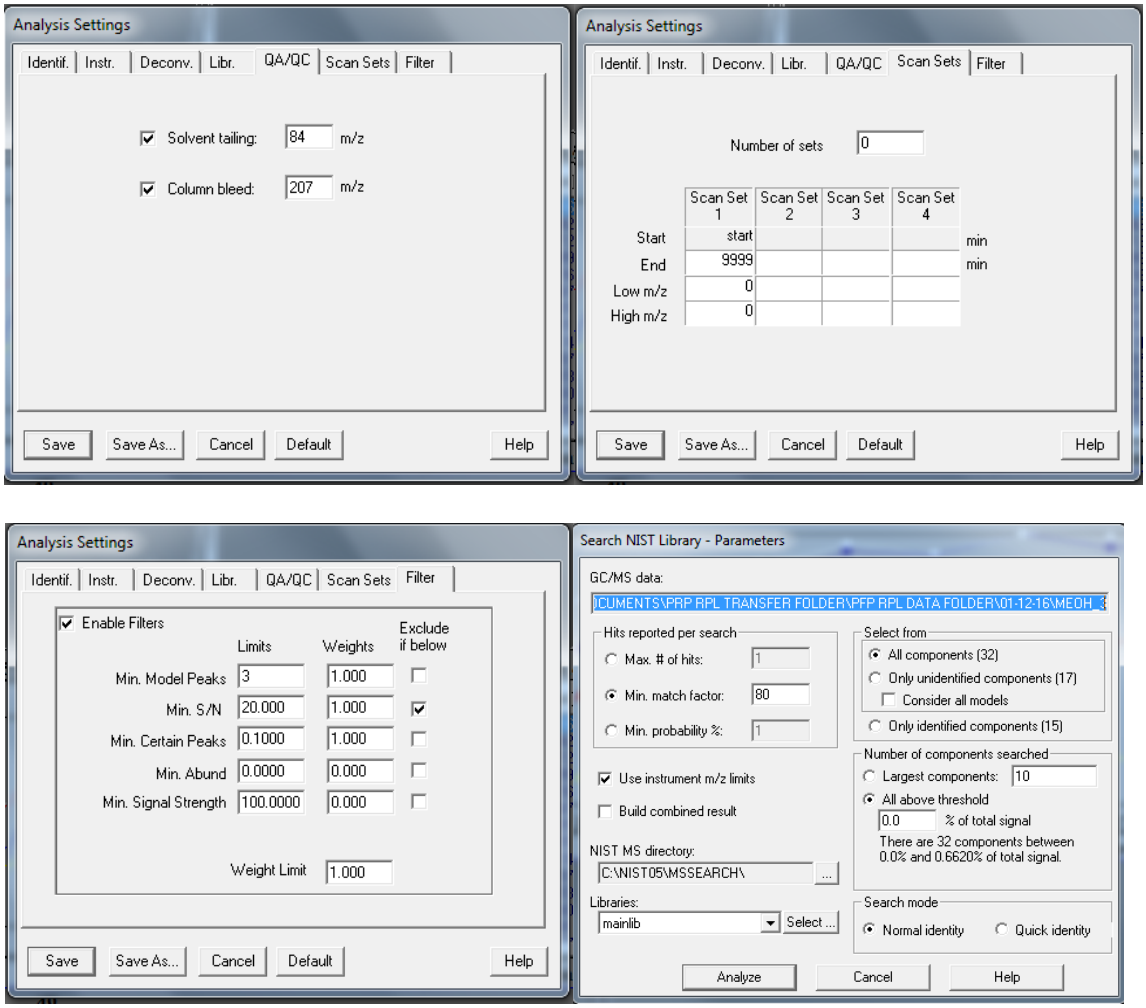


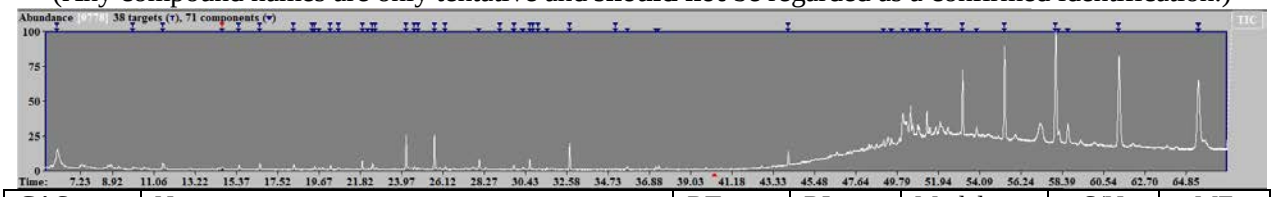
Figure 21. Analysis settings from AMDIS used throughout the data analyses.

General Comments

- The chromatographic column used was a cyanopropy phenyl dimethyl polysiloxane mid polarity type stationary phase (i.e. a “624”)
    - Chosen for improved chromatographic performance towards glycerin.
- The injection port liner was 4.0 mm ID cyclo inlet liner with wool (Restek # 20706-200)
    - Chosen for improved chromatographic performance towards glycerin.
    - Though not optimal, this liner was also used for the gas and SPME collected samples to minimize the potential for radiological contamination and exposure from the previous liquid injections.
- All the liquid extracts used a 0.5 µL injection amount.
    - Chosen to minimize the potential for radiological contamination during the vapor expansion of MeOH during the GC injection process
- Over the cross of the study the performance of the system was very good considering the type of samples (e.g. acidic) examined as represented by the stability of the mid-point IP and retention time stability.
- The MeOH extracts did not run in a continuous GC/MS sequence due to the injection syringe plunger sticking and/or seizing when a MeOH extract sample was being examined. This effectively stopped the experimental run sequence at that point. This plunger seizing appeared random towards which MeOH extract sample and was likely due to the acidic nature of the extract. Ultimately the samples were completed by swapping out to a new syringe and restarting the sequence.

$MeCl_2$ Tentative Components in 16-0084

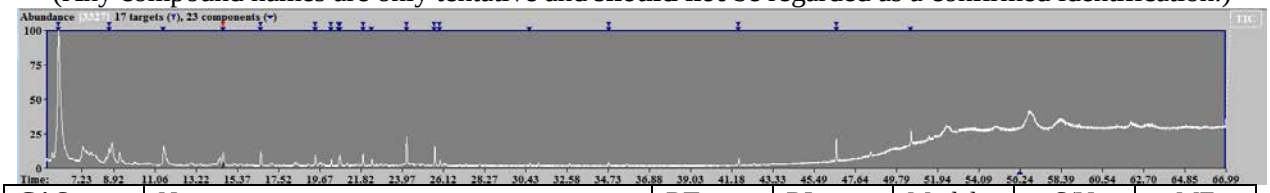
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
121437	>Boric acid, trimethyl ester	6.0359	604.1	73 m/z	69	95
71363	>1-Butanol	9.9877	733.7	TIC	31	85
96355	>Acetic acid, hydroxy-, methyl ester	11.5486	762.8	TIC	53	85
7119893	>Methane, dichloronitro-	14.6368	826.8	85 m/z	38	93
30934975	>Glycolaldehyde dimethyl acetal	15.52	848.5	75 m/z	46	93
EPA-186023	>Acetic acid, 3-[1,3]dioxolan-2-ylpropyl ester	16.6042	875.1	73 m/z	53	81
100425	>Styrene	18.3657	920.9	104 m/z	49	94
149735	>Methane, trimethoxy-	19.3292	947.9	75 m/z	21	89
108941	>Cyclohexanone	19.4533	951.3	TIC	39	90
79345	>Ethane, 1,1,2,2-tetrachloro-	20.2868	974.6	85 m/z	45	92
100527	>Benzaldehyde	21.9485	1021.1	106 m/z	67	96
4013347	>Benzene, (1-methoxyethyl)-	22.4699	1035.7	121 m/z	52	92
271896	>Benzofuran	22.6403	1040.5	118 m/z	29	90
766825	>3-Methylphenylacetylene	24.228	1084.8	115 m/z	133	94
108952	>Phenol	24.6564	1096.8	94 m/z	35	89
90028	>Benzaldehyde, 2-hydroxy-	24.8381	1102.1	122 m/z	24	85
98862	>Acetophenone	25.6954	1129.1	105 m/z	135	96
56143216	>Benzeneacetic acid, à-methoxy-, methyl ester, (ñ)-	26.2592	1146.8	121 m/z	39	90
122009	>Ethanone, 1-(4-methylphenyl)-	29.1166	1239.1	TIC	21	80
524425	>1,2-Naphthalenedione	29.8445	1263.6	102 m/z (103)	27	81
95169	>Benzothiazole	30.6614	1291	135 m/z	72	94
615134	>2H-Inden-2-one, 1,3-dihydro-	30.8158	1296.2	TIC	23	86
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7462	1365.2	132 m/z	120	96
606235	>1H-Indene-1,3(2H)-dione	35.1566	1454.7	TIC	26	89
4237449	>Phenol, 2-(1-phenylethyl)-	44.1359	1834	183 m/z	81	86
646311	>Tetracosane	51.3595	2187.3	57 m/z	106	87
629947	>Heneicosane	53.2086	2278.6	TIC	182	92
630013	>Hexacosane	55.4004	2386.8	57 m/z	207	92
630013	>Hexacosane	58.0733	2518.7	57 m/z	217	91
630013	>Hexacosane	61.3567	2680.8	85 m/z	175	89
629947	>Heneicosane	65.4907	2884.8	TIC	127	88
593497	>Heptacosane	65.5145	2886	TIC	120	87

$MeCl_2$ Tentative Components in 16-0085

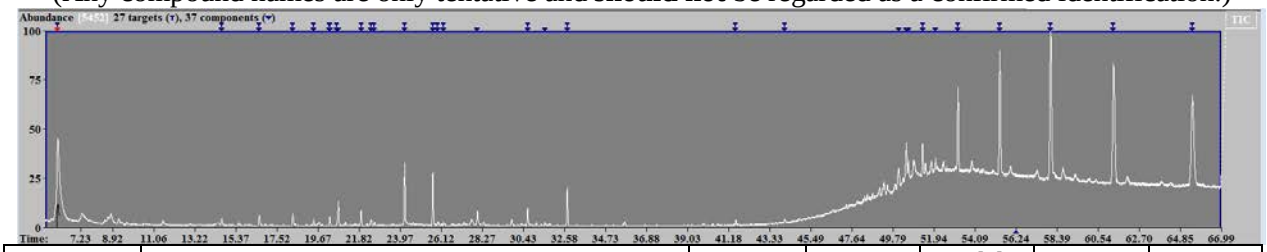
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
121437	>Boric acid, trimethyl ester	6.0442	604.4	73 m/z	118	94
75854	>Amylene hydrate	8.6835	709.3	59 m/z	42	85
7119893	>Methane, dichloronitro-	14.6403	826.9	TIC	48	93
EPA-186023	>Acetic acid, 3-[1,3]dioxolan-2-ylpropyl ester	16.5999	875	73 m/z	50	84
108941	>Cyclohexanone	19.4568	951.4	TIC	43	91
79345	>Ethane, 1,1,2,2-tetrachloro-	20.2855	974.6	TIC	35	87
96048	>Acetyl valeryl	20.7441	987.4	TIC	44	80
100527	>Benzaldehyde	21.9393	1020.9	106 m/z	48	96
673325	>Benzene, 1-propynyl-	24.2188	1084.6	115 m/z	73	95
98862	>Acetophenone	25.6906	1128.9	105 m/z	61	95
88993	>1,2-Benzenedicarboxylic acid	34.7789	1440.4	104 m/z	28	93
126738	>Tributyl phosphate	41.5692	1717.3	99 m/z	34	85
112390	>Hexadecanoic acid, methyl ester	46.6628	1955.5	74 m/z	65	91

$MeCl_2$ Tentative Components in 16-0086

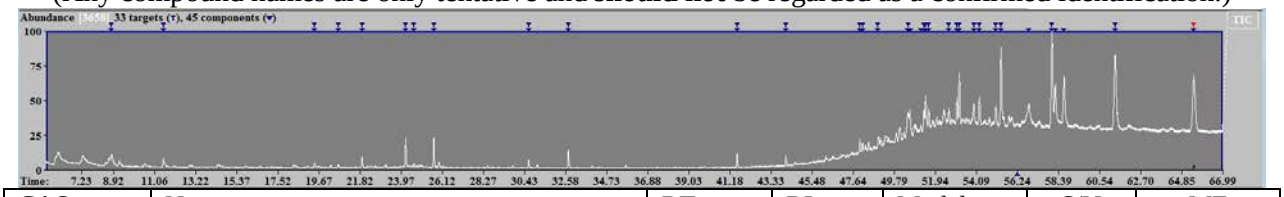
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
121437	>Boric acid, trimethyl ester	6.0442	604.4	73 m/z	102	94
7119893	>Methane, dichloronitro-	14.6281	826.6	83 m/z	37	91
EPA-186023	>Acetic acid, 3-[1,3]dioxolan-2-ylpropyl ester	16.5989	875	73 m/z	48	84
100425	>Styrene	18.3648	920.9	104 m/z	49	96
108941	>Cyclohexanone	19.4558	951.4	TIC	35	92
79345	>Ethane, 1,1,2,2-tetrachloro-	20.2816	974.5	83 m/z	43	91
79345	>Ethane, 1,1,2,2-tetrachloro-	20.2972	974.9	83 m/z	43	92
100527	>Benzaldehyde	21.9398	1020.9	106 m/z	57	96
4013347	>Benzene, (1-methoxyethyl)-	22.4632	1035.5	121 m/z	35	91
271896	>Benzofuran	22.6355	1040.3	TIC	26	91
766825	>3-Methylphenylacetylene	24.2198	1084.6	115 m/z	117	95
98862	>Acetophenone	25.695	1129.1	105 m/z	108	96
56143216	>Benzeneacetic acid, à-methoxy-, methyl ester, (ñ)-	26.2588	1146.8	121 m/z	25	90
95169	>Benzothiazole	30.6615	1291	135 m/z	60	94
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7428	1365.1	132 m/z	91	96
126738	>Tributyl phosphate	41.5677	1717.3	99 m/z	31	84
4237449	>Phenol, 2-(1-phenylethyl)-	44.135	1833.9	TIC	24	90
3891983	>Dodecane, 2,6,10-trimethyl-	51.3552	2187.1	TIC	77	85
646311	>Tetracosane	53.2038	2278.4	57 m/z	131	91
646311	>Tetracosane	55.3874	2386.1	69 m/z	160	91
629947	>Heneicosane	58.0661	2518.4	57 m/z	150	91
629947	>Heneicosane	61.3568	2680.8	TIC	131	90
646311	>Tetracosane	65.4844	2884.5	TIC	88	84
593497	>Heptacosane	65.4932	2885	TIC	78	80

$MeCl_2$ Tentative Components in 16-0088

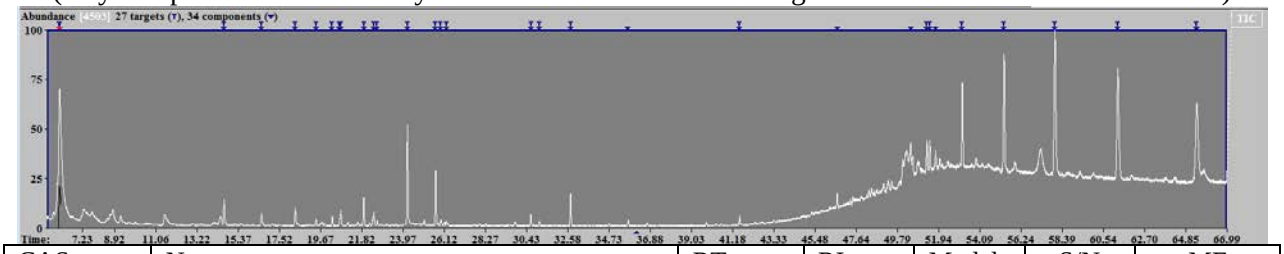
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
994058	>Butane, 2-methoxy-2-methyl-	8.8144	711.8	73 m/z	37	90
96355	>Acetic acid, hydroxy-, methyl ester	11.5486	762.8	TIC	32	88
108941	>Cyclohexanone	19.4587	951.5	TIC	32	92
100527	>Benzaldehyde	21.9373	1020.8	106 m/z	47	96
766825	>3-Methylphenylacetylene	24.2236	1084.7	115 m/z	78	96
108952	>Phenol	24.6521	1096.7	94 m/z	28	87
98862	>Acetophenone	25.693	1129	105 m/z	81	95
272162	>1,2-Benzisothiazole	30.6634	1291.1	135 m/z	38	89
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7408	1365	132 m/z	62	96
126738	>Tributyl phosphate	41.5837	1718	99 m/z	50	85
4237449	>Phenol, 2-(1-phenylethyl)-	44.1315	1833.8	TIC	41	87
41464395	>1,1'-Biphenyl, 2,2',3,5'-tetrachloro-	47.9986	2021.5	TIC	47	88
41464420	>1,1'-Biphenyl, 2,3',5,5'-tetrachloro-	48.153	2029.1	292 m/z	33	85
41464419	>1,1'-Biphenyl, 2,2',5,6'-Tetrachloro-	48.9612	2069	TIC	38	85
32690930	>Biphenyl, 2,4,4',5-tetrachloro-	50.5576	2147.8	292 m/z (117)	57	88
629970	>Docosane	51.3512	2186.9	TIC	66	81
70424703	>1,1'-Biphenyl, 2',3,4,5,5'-Pentachloro-	51.4452	2191.6	TIC	65	89
77589301	>1-Methyl-1-iodotetrachlorocyclotriphosphazene	51.4636	2192.5	292 m/z (328)	30	81
70424703	>1,1'-Biphenyl, 2',3,4,5,5'-Pentachloro-	51.6	2199.2	254 m/z	52	88
73575561	>1,1'-Biphenyl, 2,2',3,5,6-Pentachloro-	52.6701	2252	326 m/z	40	83
70424703	>1,1'-Biphenyl, 2',3,4,5,5'-Pentachloro-	53.0903	2272.8	324 m/z	60	90
629947	>Heneicosane	53.2207	2279.2	71 m/z	99	90
74472438	>2,3,3',4,5',6-Hexachloro-1,1'-biphenyl	53.972	2316.3	360 m/z	42	82
70424703	>1,1'-Biphenyl, 2',3,4,5,5'-Pentachloro-	54.2573	2330.4	328 m/z	64	91
39635331	>3,3',4,5,5'-Pentachloro-1,1'-biphenyl	54.2704	2331	328 m/z (258)	64	84
41411636	>2,3,4,4',5,6-Hexachloro-1,1'-biphenyl	55.1239	2373.1	288 m/z	47	85
646311	>Tetracosane	55.3922	2386.4	57 m/z	121	93
646311	>Tetracosane	58.0519	2517.7	TIC	124	88
629925	>Nonadecane	61.3645	2681.2	TIC	81	85
31295564	>Dodecane, 2,6,11-trimethyl-	65.4824	2884.4	TIC	63	81

$MeCl_2$ Tentative Components in 16-0089

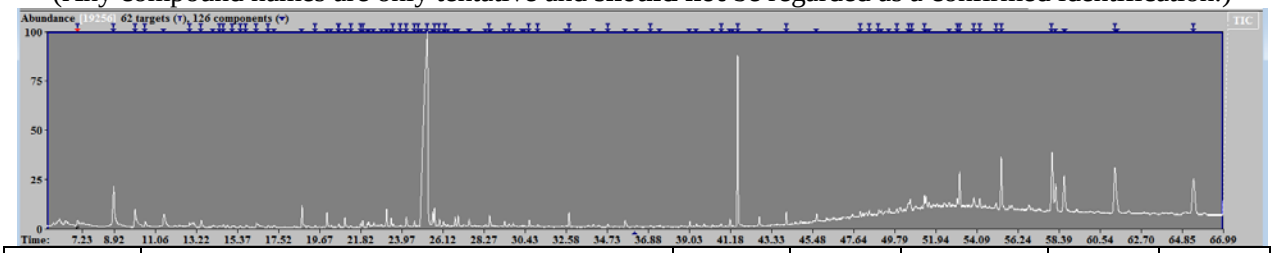
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
121437	>Boric acid, trimethyl ester	6.0723	605.7	73 m/z	91	93
7119893	>Methane, dichloronitro-	14.6416	826.9	83 m/z	64	94
EPA-186023	>Acetic acid, 3-[1,3]dioxolan-2-ylpropyl ester	16.6032	875.1	73 m/z	44	84
100425	>Styrene	18.3647	920.9	104 m/z	52	95
108941	>Cyclohexanone	19.4557	951.4	TIC	34	90
79345	>Ethane, 1,1,2,2-tetrachloro-	20.2897	974.7	TIC	41	92
96048	>Acetyl valeryl	20.743	987.4	43 m/z	50	82
100527	>Benzaldehyde	21.9402	1020.9	106 m/z	72	98
4013347	>Benzene, (1-methoxyethyl)-	22.4631	1035.5	121 m/z	46	91
271896	>Benzofuran	22.6398	1040.4	TIC	28	90
766825	>3-Methylphenylacetylene	24.2202	1084.6	116 m/z	134	95
98862	>Acetophenone	25.6895	1128.9	105 m/z	100	97
56143216	>Benzeneacetic acid, à-methoxy-, methyl ester, (ñ)-	26.2572	1146.7	121 m/z	25	87
95169	>Benzothiazole	30.6633	1291.1	135 m/z	44	91
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7349	1364.8	132 m/z	76	95
126738	>Tributyl phosphate	41.5603	1716.9	99 m/z	39	90
544763	>Hexadecane	51.3399	2186.4	TIC	68	84
24536683	>trans-1,1'-Bibenzoindanylidene	51.4889	2193.7	117 m/z	61	82
629947	>Heneicosane	53.1876	2277.6	57 m/z	120	91
646311	>Tetracosane	55.3624	2384.9	57 m/z	135	91
629947	>Heneicosane	58.027	2516.4	127 m/z	143	90
646311	>Tetracosane	61.3124	2678.6	TIC	105	89
646311	>Tetracosane	65.4108	2880.9	TIC	82	85

$MeCl_2$ Tentative Components in 16-0090

(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)

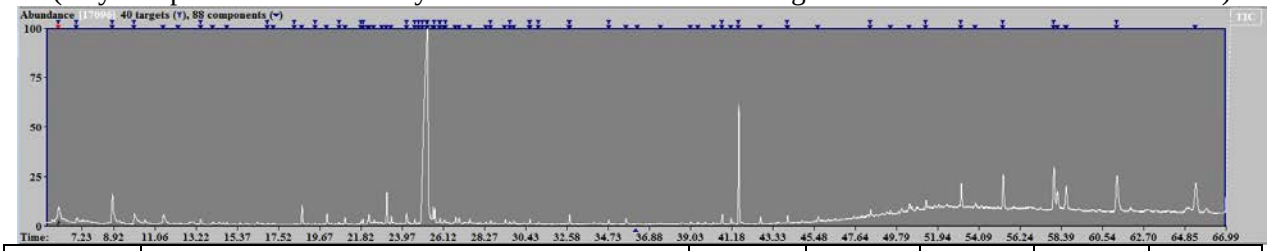


CAS	Name	RT	RI	Model	S/N	MF
141468	>Acetaldehyde, hydroxy-	7.009	647.6	TIC	58	90
64197	>Acetic acid	8.8995	713.4	TIC	151	96
71363	>1-Butanol	10.0086	734	56 m/z	109	94
116096	>2-Propanone, 1-hydroxy-	10.5475	744.1	TIC	61	91
79094	>Propanoic acid	12.866	787.3	74 m/z	44	92
41632897	>Propane, 1,1-dimethoxy-2-methyl-	13.4716	798.6	75 m/z	59	86
75127	>Formamide	14.4268	821.6	TIC	29	92
7119893	>Methane, dichloronitro-	14.6377	826.8	TIC	42	93
57556	>Propylene Glycol	15.1089	838.4	TIC	33	82
30934975	>Glycolaldehyde dimethyl acetal	15.5233	848.6	75 m/z	30	93
109080	>Pyrazine, methyl-	15.83	856.1	94 m/z	41	87
107926	>Butanoic acid	16.3655	869.3	60 m/z	57	89
60355	>Acetamide	16.977	884.3	TIC	37	94
108941	>Cyclohexanone	19.4518	951.3	98 m/z	43	90
110134	>2,5-Hexanedione	21.3174	1003.5	TIC	25	85
591811	>Butanoic acid, 4-hydroxy-	21.8374	1018	TIC	58	92
100527	>Benzaldehyde	21.944	1021	105 m/z	68	88
53951443	>1,3-Dioxolane-4-methanol, 2-ethyl-	23.5375	1065.5	101 m/z	41	82
EPA-411448	>2-Ethyl-1-hexanol	23.929	1076.5	TIC	28	83
673325	>Benzene, 1-propynyl-	24.2211	1084.7	116 m/z	84	95
108952	>Phenol	24.652	1096.7	94 m/z	70	95
90028	>Benzaldehyde, 2-hydroxy-	24.8379	1102.1	TIC	29	92
56815	>Glycerin	25.3195	1117.3	61 m/z	385	90
98862	>Acetophenone	25.6948	1129.1	105 m/z	117	96
56143216	>Benzeneacetic acid, à-methoxy-, methyl ester, (ñ)-	26.2615	1146.9	121 m/z	23	82
106616	>1,2,3-Propanetriol, 1-acetate	28.5737	1220.9	43 m/z	92	91
123568	>Succinimide	29.6039	1255.5	99 m/z	41	90
95169	>Benzothiazole	30.6569	1290.9	135 m/z	68	93
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7373	1364.9	132 m/z	105	97
88993	>1,2-Benzenedicarboxylic acid	34.7729	1440.1	104 m/z	50	95
85449	>Phthalic anhydride	34.7846	1440.6	104 m/z	48	90
120503	>Benzoic acid, 2-methylpropyl ester	37.0256	1527.3	TIC	36	90
EPA-322994	>Butylphosphonic acid, butyl isobutyl ester	40.7112	1680	139 m/z	42	86

126738	>Tributyl phosphate	41.5714	1717.4	99 m/z	364	94
4237449	>Phenol, 2-(1-phenylethyl)-	44.1226	1833.4	183 m/z	94	85
41464395	>1,1'-Biphenyl, 2,2',3,5'-tetrachloro-	48	2021.5	TIC	55	88
EPA-315174	>Phthalic acid, 6-ethyl-3-octyl butyl ester	48.4596	2044.2	TIC	55	88
41464419	>1,1'-Biphenyl, 2,2',5,6'-Tetrachloro-	48.9562	2068.7	TIC	45	86
32690930	>Biphenyl, 2,4,4',5-tetrachloro-	49.9051	2115.6	TIC	29	82
41464420	>1,1'-Biphenyl, 2,3',5,5'-tetrachloro-	50.5448	2147.1	292 m/z (184)	62	89
77589301	>1-Methyl-1-iodotetrachlorocyclotriphosphazene	50.6885	2154.2	292 m/z	32	86
544763	>Hexadecane	51.3506	2186.9	57 m/z	91	85
31508006	>1,1'-Biphenyl, 2,3',4,4',5-pentachloro-	53.0785	2272.2	TIC	68	90
70424703	>1,1'-Biphenyl, 2',3,4,5,5'-Pentachloro-	53.0882	2272.7	328 m/z	63	91
629947	>Heneicosane	53.1992	2278.1	57 m/z	157	92
35065271	>1,1'-Biphenyl, 2,2',4,4',5,5'-hexachloro-	53.9504	2315.2	290 m/z	45	84
70424703	>1,1'-Biphenyl, 2',3,4,5,5'-Pentachloro-	54.2484	2329.9	256 m/z	63	89
39635353	>2,3,3',4,5,5'-Hexachloro-1,1'-biphenyl	55.1097	2372.4	362 m/z	52	87
646311	>Tetracosane	55.3789	2385.7	57 m/z (155)	188	82
630013	>Hexacosane	58.0333	2516.7	TIC	190	91
630013	>Hexacosane	58.0372	2516.9	57 m/z	183	91
630013	>Hexacosane	61.3245	2679.2	TIC	150	90
629947	>Heneicosane	61.3381	2679.9	TIC	127	89
593497	>Heptacosane	65.4404	2882.4	TIC	96	83

$MeCl_2$ Tentative Components in 16-0091

(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)

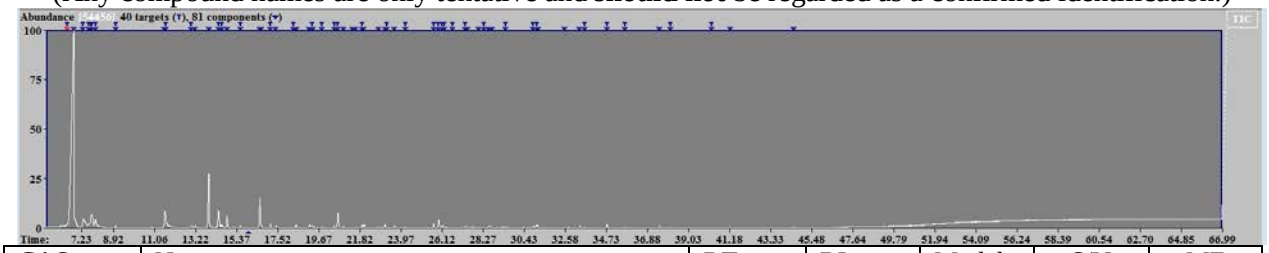


CAS	Name	RT	RI	Model	S/N	MF
121437	>Boric acid, trimethyl ester	6.0396	604.2	103 m/z	75	94
141468	>Acetaldehyde, hydroxy-	6.988	646.6	TIC	51	90
64197	>Acetic acid	8.8576	712.6	43 m/z	116	95
71363	>1-Butanol	10.0032	733.9	TIC	84	93
41632897	>Propane, 1,1-dimethoxy-2-methyl-	13.4667	798.5	75 m/z	54	86
60355	>Acetamide	16.959	883.8	TIC	33	94
100425	>Styrene	18.3558	920.7	TIC	27	93
108941	>Cyclohexanone	19.4381	950.9	98 m/z	35	89
591811	>Butanoic acid, 4-hydroxy-	21.832	1017.9	TIC	47	93
100527	>Benzaldehyde	21.9425	1020.9	106 m/z	56	88
673325	>Benzene, 1-propynyl-	24.2152	1084.5	116 m/z	87	94
108952	>Phenol	24.6505	1096.7	94 m/z	54	93
90028	>Benzaldehyde, 2-hydroxy-	24.8511	1102.5	122 m/z	24	86
1003298	>1H-Pyrrole-2-carboxaldehyde	25.0322	1108.2	95 m/z	30	89
56815	>Glycerin	25.3073	1116.9	61 m/z	358	92
98862	>Acetophenone	25.6895	1128.9	105 m/z	96	95
56143216	>Benzeneacetic acid, à-methoxy-, methyl ester, (ñ)-	26.2455	1146.4	121 m/z	23	85
106616	>1,2,3-Propanetriol, 1-acetate	28.596	1221.6	TIC	42	86
123568	>Succinimide	29.6063	1255.6	99 m/z	34	93
95169	>Benzothiazole	30.6511	1290.7	108 m/z	54	92
272162	>1,2-Benzisothiazole	30.6623	1291.1	135 m/z	59	84
83330	>1H-Inden-1-one, 2,3-dihydro-	32.731	1364.6	TIC	79	96
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7378	1364.9	132 m/z	79	95
88993	>1,2-Benzenedicarboxylic acid	34.7748	1440.2	104 m/z	52	94
78466	>Dibutyl butanephosphonate	40.7029	1679.7	139 m/z	81	92
126738	>Tributyl phosphate	41.568	1717.3	99 m/z	289	94
4237449	>Phenol, 2-(1-phenylethyl)-	44.1075	1832.7	184 m/z	65	84
84742	>Dibutyl phthalate	48.4513	2043.8	149 m/z	56	89

EPA-309202	>Sulfurous acid, 2-ethylhexyl hexyl ester	51.3442	2186.6	TIC	71	83
629947	>Heneicosane	53.1856	2277.5	57 m/z	125	91
646311	>Tetracosane	55.3687	2385.2	TIC	142	92
629992	>Pentacosane	58.0245	2516.3	57 m/z	142	90
646311	>Tetracosane	61.3172	2678.8	71 m/z	111	85

MeOHTentative Components in 16-0084

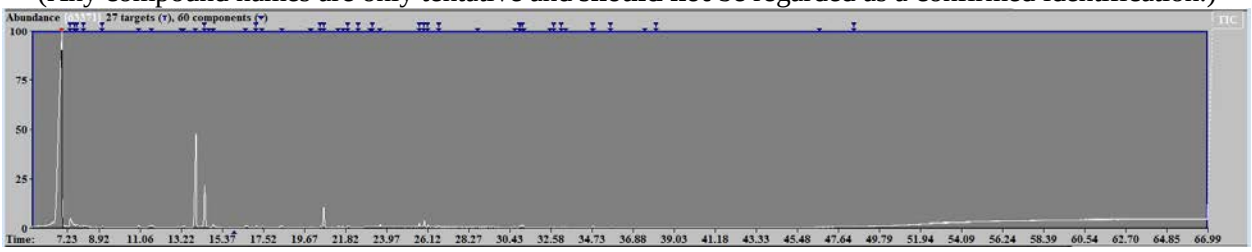
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
74840	>Ethane	6.5187	625.6	30 m/z	24	99
64186	>Formic acid	7.3274	661.8	45 m/z	134	94
64197	>Acetic acid	9.03	715.8	60 m/z	57	96
96355	>Acetic acid, hydroxy-, methyl ester	11.6522	764.7	31 m/z	99	82
2155308	>Propanoic acid, 2-hydroxy-, methyl ester, (ñ)-	13.0067	789.9	45 m/z	46	86
598550	>Carbamic acid, methyl ester	14.5904	825.6	44 m/z	80	91
30934975	>Glycolaldehyde dimethyl acetal	15.5656	849.6	75 m/z	57	94
553902	>Ethanedioic acid, dimethyl ester	17.1426	888.3	59 m/z	91	94
635518	>Butanedioic acid, phenyl-	18.3666	921	104 m/z	27	86
89918	>Acetic acid, dimethoxy-, methyl ester	19.3437	948.3	TIC	53	94
2517444	>Ethane, 1,1,2,2-tetramethoxy-	19.8408	962.2	75 m/z	47	96
108598	>Propanedioic acid, dimethyl ester	20.499	980.6	101 m/z	56	93
100527	>Benzaldehyde	21.9455	1021	106 m/z	71	98
100470	>Benzonitrile	23.2415	1057.3	103 m/z	27	85
766972	>Benzene, 1-ethynyl-4-methyl-	24.2196	1084.6	116 m/z	31	92
98862	>Acetophenone	25.6948	1129.1	105 m/z	87	96
93583	>Benzoic acid, methyl ester	26.1515	1143.4	105 m/z	62	95
56143216	>Benzeneacetic acid, à-methoxy-, methyl ester, (ñ)-	26.262	1146.9	121 m/z	30	84
98953	>Benzene, nitro-	26.7017	1160.7	TIC	37	87
119368	>Methyl salicylate	29.4476	1250.2	TIC	26	80
100970	>Methenamine	30.9247	1299.9	TIC	56	85
34303816	>3-Hexadecene, (Z)-	33.6112	1396.2	TIC	29	87
88993	>1,2-Benzenedicarboxylic acid	34.7812	1440.4	104 m/z	80	97
120616	>1,4-Benzenedicarboxylic acid, dimethyl ester	38.1143	1571.2	163 m/z	40	92
2765119	>Pentadecanal-	40.2574	1660.7	TIC	25	84

MeOHTentative Components in 16-0085

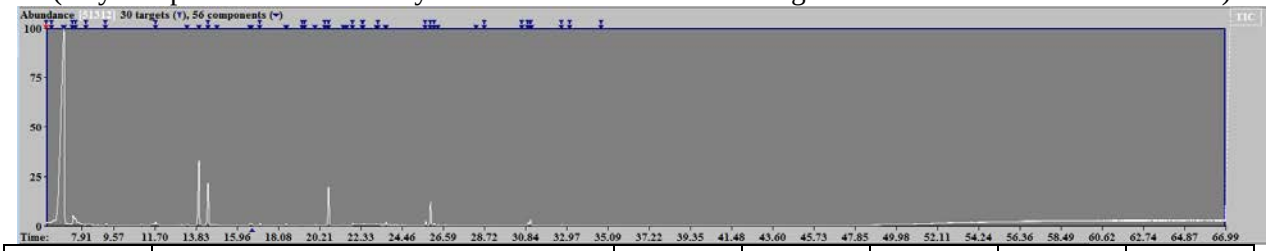
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
64186	>Formic acid	7.3937	664.8	46 m/z	148	94
64197	>Acetic acid	9.0992	717.1	60 m/z	56	91
553902	>Ethanedioic acid, dimethyl ester	17.146	888.4	TIC	70	95
108598	>Propanedioic acid, dimethyl ester	20.519	981.1	101 m/z	55	93
100527	>Benzaldehyde	21.9533	1021.2	106 m/z	66	96
4013347	>Benzene, (1-methoxyethyl)-	22.4865	1036.2	TIC	36	88
100470	>Benzonitrile	23.2435	1057.3	TIC	33	91
98862	>Acetophenone	25.6978	1129.1	105 m/z	101	96
93583	>Benzoic acid, methyl ester	26.1486	1143.3	TIC	81	97
98953	>Benzene, nitro-	26.7153	1161.1	TIC	46	93
100970	>Methenamine	30.9827	1302	140 m/z	61	92
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7432	1365.1	104 m/z	34	89
769788	>Vinyl benzoate	33.1322	1379	TIC	29	91
88993	>1,2-Benzenedicarboxylic acid	34.7695	1440	76 m/z	57	97
120616	>1,4-Benzenedicarboxylic acid, dimethyl ester	38.105	1570.9	163 m/z	30	92
84742	>Dibutyl phthalate	48.4601	2044.2	149 m/z	30	85

MeOHTentative Components in 16-0086

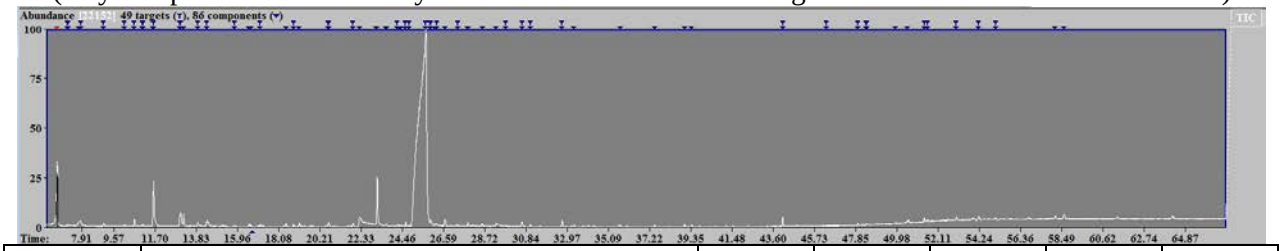
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
74840	>Ethane	6.3769	619.3	30 m/z	24	87
64186	>Formic acid	7.4689	668.1	46 m/z	142	95
64197	>Acetic acid	9.17	718.4	60 m/z	54	91
96355	>Acetic acid, hydroxy-, methyl ester	11.749	766.5	31 m/z	79	92
553902	>Ethanedioic acid, dimethyl ester	17.1463	888.4	59 m/z	64	92
89918	>Acetic acid, dimethoxy-, methyl ester	19.3372	948.1	75 m/z	37	92
108941	>Cyclohexanone	19.4468	951.2	TIC	23	88
108598	>Propanedioic acid, dimethyl ester	20.493	980.4	TIC	29	83
100527	>Benzaldehyde	21.9434	1021	106 m/z	62	96
74840	>Ethane	22.4244	1034.4	30 m/z	20	82
4013347	>Benzene, (1-methoxyethyl)-	22.4809	1036	121 m/z	37	88
100470	>Benzonitrile	23.2399	1057.2	103 m/z	22	87
98862	>Acetophenone	25.6849	1128.7	105 m/z	94	93
93583	>Benzoic acid, methyl ester	26.1445	1143.2	105 m/z	68	96
272162	>1,2-Benzisothiazole	30.6524	1290.7	135 m/z	25	83
100970	>Methenamine	30.9757	1301.7	140 m/z	80	95
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7226	1364.3	103 m/z	36	92
5062306	>Phenacylidene diacetate	33.131	1379	105 m/z	23	94
88993	>1,2-Benzenedicarboxylic acid	34.7679	1439.9	104 m/z	27	84

MeOHTentative Components in 16-0088

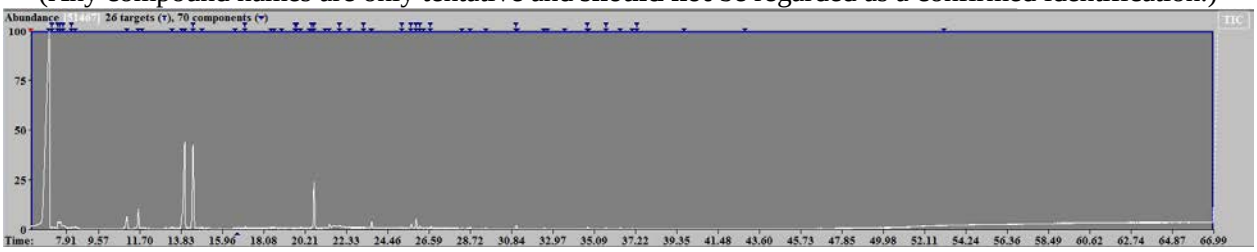
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
67663	>Trichloromethane	7.2187	656.9	85 m/z	31	89
64197	>Acetic acid	9.0518	716.2	60 m/z	57	95
71363	>1-Butanol	10.138	736.5	TIC	37	92
116096	>2-Propanone, 1-hydroxy-	10.654	746.1	43 m/z	81	93
96355	>Acetic acid, hydroxy-, methyl ester	11.6399	764.5	31 m/z	185	96
2155308	>Propanoic acid, 2-hydroxy-, methyl ester, (ñ)-	12.9939	789.7	45 m/z	87	86
556525	>Glycidol	13.0431	790.6	44 m/z	90	93
68122	>Formamide, N,N-dimethyl-	15.8299	856.1	73 m/z	20	80
553902	>Ethanedioic acid, dimethyl ester	17.1415	888.3	59 m/z	41	93
504632	>1,3-Propanediol	18.8528	934.6	57 m/z	44	87
100527	>Benzaldehyde	21.9381	1020.8	106 m/z	55	96
673325	>Benzene, 1-propynyl-	24.2127	1084.4	116 m/z	38	91
108952	>Phenol	24.6509	1096.7	94 m/z	61	95
90028	>Benzaldehyde, 2-hydroxy-	24.8446	1102.3	122 m/z	23	85
56815	>Glycerin	25.6864	1128.8	TIC	345	93
56143216	>Benzeneacetic acid, à-methoxy-, methyl ester, (ñ)-	26.2512	1146.5	121 m/z	32	88
524425	>1,2-Naphthalenedione	29.8175	1262.7	130 m/z	25	86
95169	>Benzothiazole	30.6481	1290.6	108 m/z	67	92
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7274	1364.5	132 m/z	77	95
4237449	>Phenol, 2-(1-phenylethyl)-	46.345	1939.8	183 m/z	22	86
41464419	>1,1'-Biphenyl, 2,2',5,6'-Tetrachloro-	47.978	2020.4	TIC	34	87
84742	>Dibutyl phthalate	48.4395	2043.2	TIC	29	88
37680732	>1,1'-Biphenyl, 2,2',4,5,5'-pentachloro-	51.4147	2190.1	326 m/z	48	86
31508006	>1,1'-Biphenyl, 2,3',4,4',5-pentachloro-	51.5783	2198.1	328 m/z	31	84
31508006	>1,1'-Biphenyl, 2,3',4,4',5-pentachloro-	53.0608	2271.3	TIC	44	87
70424703	>1,1'-Biphenyl, 2',3,4,5,5'-Pentachloro-	53.0642	2271.5	256 m/z	42	83
31508006	>1,1'-Biphenyl, 2,3',4,4',5-pentachloro-	54.2235	2328.7	TIC	42	87
41411636	>2,3,4,4',5,6-Hexachloro-1,1'-biphenyl	55.0886	2371.4	362 m/z	29	82

MeOHTentative Components in 16-0089

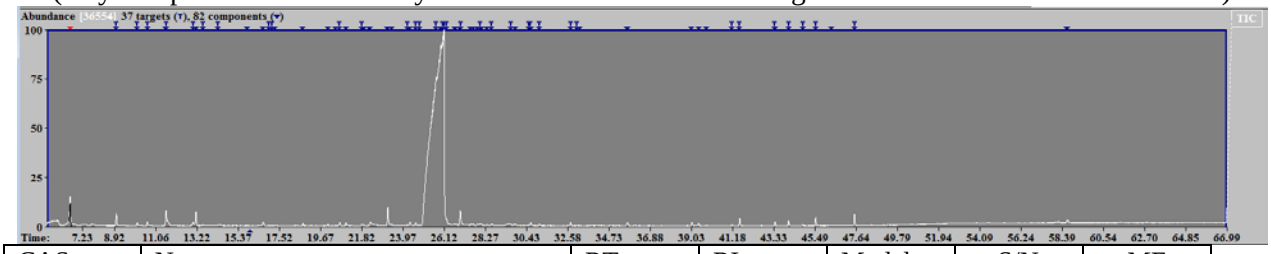
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
67663	>Trichloromethane	7.1979	656	83 m/z	33	93
64186	>Formic acid	7.4983	669.4	TIC	119	93
553902	>Ethanedioic acid, dimethyl ester	17.1494	888.5	59 m/z	61	94
74840	>Ethane	19.8091	961.3	30 m/z	20	85
108598	>Propanedioic acid, dimethyl ester	20.5613	982.3	TIC	50	87
100527	>Benzaldehyde	22.0024	1022.6	106 m/z	51	95
100470	>Benzonitrile	23.2303	1056.9	103 m/z	24	88
98862	>Acetophenone	25.6929	1129	TIC	90	85
93583	>Benzoic acid, methyl ester	26.1437	1143.2	105 m/z	69	94
98953	>Benzene, nitro-	26.6997	1160.6	77 m/z	59	87
88993	>1,2-Benzenedicarboxylic acid	34.7641	1439.8	104 m/z	54	94
EPA-315634	>Phthalic acid, 4-fluoro-2-nitrophenyl methyl ester	37.3148	1539	163 m/z	20	81

MeOHTentative Components in 16-0090

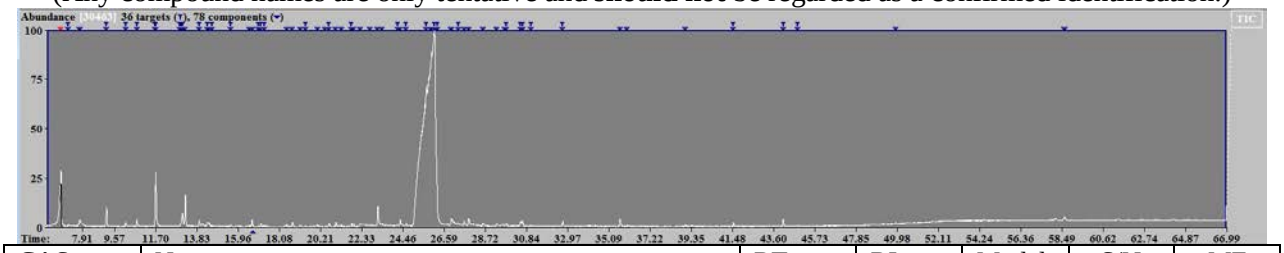
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
64197	>Acetic acid	9.0243	715.7	43 m/z	135	96
71363	>1-Butanol	10.1017	735.8	56 m/z	75	94
116096	>2-Propanone, 1-hydroxy-	10.6353	745.7	43 m/z	85	92
96355	>Acetic acid, hydroxy-, methyl ester	11.6178	764	31 m/z	146	94
556525	>Glycidol	13.0341	790.4	44 m/z	66	91
107211	>1,2-Ethanediol	13.5365	799.8	TIC	36	92
60355	>Acetamide	16.9699	884.1	TIC	30	93
553902	>Ethanedioic acid, dimethyl ester	17.1398	888.3	TIC	35	92
591811	>Butanoic acid, 4-hydroxy-	21.8307	1017.8	TIC	52	95
766972	>Benzene, 1-ethynyl-4-methyl-	24.2144	1084.5	TIC	33	89
108952	>Phenol	24.6453	1096.5	94 m/z	66	94
90028	>Benzaldehyde, 2-hydroxy-	24.8497	1102.5	TIC	29	89
98862	>Acetophenone	25.712	1129.6	TIC	104	83
56815	>Glycerin	26.1258	1142.6	61 m/z	550	91
1125888	>Benzaldehyde dimethyl acetal	26.2539	1146.6	121 m/z	63	91
822366	>1H-Imidazole, 4-methyl-	26.9988	1170	81 m/z	40	90
10447935	>1H-Imidazole, 1,5-dimethyl-	28.0007	1201.6	TIC	45	89
106616	>1,2,3-Propanetriol, 1-acetate	28.6191	1222.4	TIC	47	85
123568	>Succinimide	29.6132	1255.8	99 m/z	22	87
100970	>Methenamine	30.5446	1287.1	140 m/z	38	87
95169	>Benzothiazole	30.6571	1290.9	135 m/z	69	94
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7379	1364.9	132 m/z	76	96
17417571	>1,4-Dihydro-4-oxopyridazine	33.0802	1377.2	TIC	30	86
629787	>Heptadecane	41.1675	1699.4	TIC	47	82
126738	>Tributyl phosphate	41.5662	1717.2	99 m/z	113	94
593453	>Octadecane	43.4075	1799.7	TIC	80	93
4237449	>Phenol, 2-(1-phenylethyl)-	44.1213	1833.3	TIC	89	83
934349	>2(3H)-Benzothiazolone	44.8642	1868.3	TIC	33	87
629925	>Nonadecane	45.5376	1900	57 m/z	120	94
112958	>Eicosane	47.5624	1999.9	71 m/z	134	96

MeOHTentative Components in 16-0091

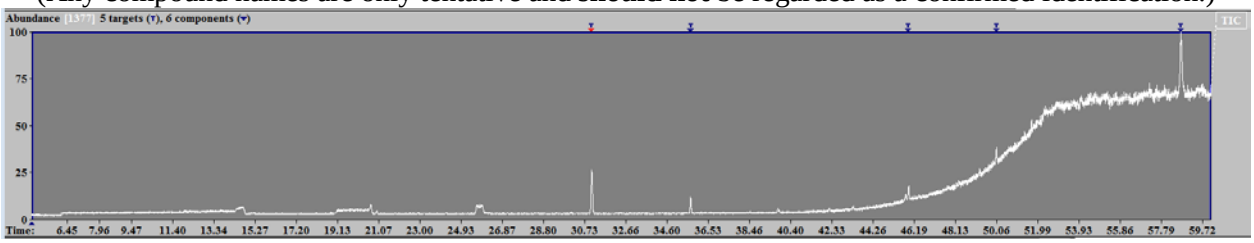
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
67663	>Trichloromethane	7.2024	656.2	85 m/z	39	88
64197	>Acetic acid	9.1766	718.5	43 m/z	152	96
71363	>1-Butanol	10.1586	736.8	56 m/z	70	94
116096	>2-Propanone, 1-hydroxy-	10.7428	747.7	43 m/z	94	92
74810836	>Benzene, 2-methoxy-1-(2-nitroethenyl)-3-(phenylmethoxy)-	11.6723	765.1	91 m/z	55	82
96355	>Acetic acid, hydroxy-, methyl ester	11.7175	765.9	31 m/z	256	97
79094	>Propanoic acid	12.9571	789	74 m/z	26	82
2155308	>Propanoic acid, 2-hydroxy-, methyl ester, (ñ)-	13.0462	790.7	45 m/z	77	85
556525	>Glycidol	13.0949	791.6	44 m/z	110	93
598550	>Carbamic acid, methyl ester	14.6032	826	TIC	30	85
30934975	>Glycolaldehyde dimethyl acetal	15.5798	849.9	75 m/z	43	94
60355	>Acetamide	17.0024	884.9	TIC	30	94
553902	>Ethanedioic acid, dimethyl ester	17.147	888.5	59 m/z	59	94
98011	>Furfural	17.3281	892.9	95 m/z	38	85
108941	>Cyclohexanone	19.4523	951.3	TIC	26	86
591811	>Butanoic acid, 4-hydroxy-	21.8234	1017.6	42 m/z	63	94
766972	>Benzene, 1-ethynyl-4-methyl-	24.1954	1083.9	TIC	33	88
108952	>Phenol	24.6472	1096.6	94 m/z	54	93
98862	>Acetophenone	25.6837	1128.7	105 m/z	110	93
56815	>Glycerin	26.1029	1141.9	61 m/z	339	92
56143216	>Benzeneacetic acid, à-methoxy-, methyl ester, (ñ)-	26.2456	1146.4	121 m/z	52	91
253667	>Cinnoline	29.8177	1262.7	130 m/z	22	81
100970	>Methenamine	30.5465	1287.2	140 m/z	78	95
95169	>Benzothiazole	30.6492	1290.6	135 m/z	72	94
83330	>1H-Inden-1-one, 2,3-dihydro-	32.7228	1364.4	132 m/z	85	96
126738	>Tributyl phosphate	41.5428	1716.2	99 m/z	67	95
4237449	>Phenol, 2-(1-phenylethyl)-	44.1052	1832.5	183 m/z	92	83
934349	>2(3H)-Benzothiazolone	44.8618	1868.2	TIC	26	81

1 mL Gas, Syringe Tentative Components in 16-0087

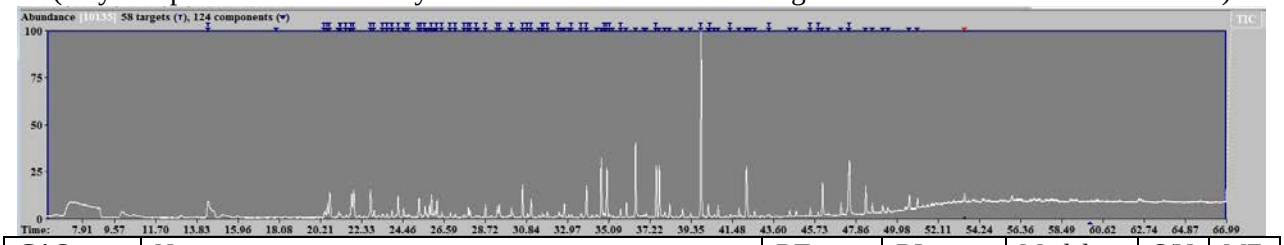
(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
EPA-240362	>2-Morpholinomethyl-1,3-diphenyl-2-propanol	45.9386	1919.8	100 m/z	23	88
EPA-240362	>2-Morpholinomethyl-1,3-diphenyl-2-propanol	50.0585	2123.1	100 m/z	21	88
13674878	>Tris(1,3-dichloroisopropyl)phosphate	58.731	2551.2	TIC	44	81

SPME Pink Tentative Components in 16-0087

(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)

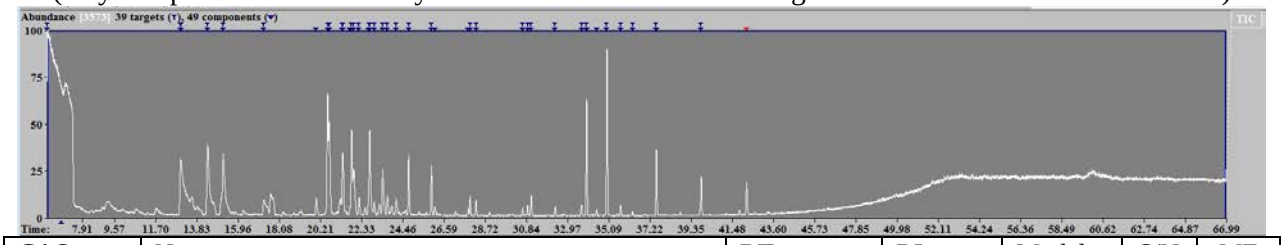


CAS	Name	RT	RI	Model	S/N	MF
141593	>tert-Octyl mercaptan	20.4208	978.4	TIC	49	88
106514	>p-Benzoquinone	20.579	982.8	108 m/z	76	96
1879078	>Cyclohexane, 1-methyl-4-(1-methylethenyl)-, cis-	21.2587	1001.8	95 m/z	30	85
EPA-222866	>Oxime-, methoxy-phenyl-_	21.5474	1009.9	133 m/z	33	81
591811	>Butanoic acid, 4-hydroxy-	21.8259	1017.7	42 m/z	99	96
100527	>Benzaldehyde	21.9354	1020.7	106 m/z	100	96
110634	>1,4-Butanediol	22.8064	1045.1	42 m/z	98	94
527844	>o-Cymene	22.9826	1050	119 m/z	52	81
62199068	>Heptane, 5-ethyl-2,2,3-trimethyl-	23.4291	1062.5	TIC	41	83
17301289	>Undecane, 3,6-dimethyl-	23.6604	1069	TIC	42	84
104767	>1-Hexanol, 2-ethyl-	23.9009	1075.7	57 m/z (146)	46	92
541731	>Benzene, 1,3-dichloro-	23.9208	1076.3	146 m/z	31	88
29619565	>2-Butene-1,4-diol, diformate	24.2271	1084.8	42 m/z	94	81
108952	>Phenol	24.6521	1096.7	94 m/z	30	87
1120214	>Undecane	24.7646	1099.8	TIC	36	83
7525624	>Benzene, 1-ethenyl-3-ethyl-	25.3074	1116.9	117 m/z	86	91
29619565	>2-Butene-1,4-diol, diformate	25.3951	1119.6	TIC	41	87
3454077	>Benzene, 1-ethenyl-4-ethyl-	25.6166	1126.6	117 m/z	69	94
124196	>Nonanal	26.2378	1146.1	98 m/z	86	96
108576	>Benzene, 1,3-diethenyl-	26.4998	1154.3	128 m/z	48	93
105066	>Benzene, 1,4-diethenyl-	26.9287	1167.8	TIC	42	85
103093	>Acetic acid, 2-ethylhexyl ester	27.1794	1175.7	TIC	39	86
4161244	>1-Butanol, 4-butoxy-	27.641	1190.2	TIC	35	84
498817	>Cyclohexanemethanol, à,à,4-trimethyl-	27.8576	1197	59 m/z	63	90
112403	>Dodecane	27.9448	1199.7	TIC	54	92
464493	>(+)-2-Bornanone	28.2549	1210.1	TIC	25	85
4748781	>Benzaldehyde, 4-ethyl-	28.7335	1226.2	133 m/z	74	92
4748781	>Benzaldehyde, 4-ethyl-	29.3503	1247	134 m/z	67	90
14371109	>Cinnamaldehyde, (E)-	29.4618	1250.7	132 m/z	74	90
14371109	>Cinnamaldehyde, (E)-	30.0811	1271.5	131 m/z	64	91
95169	>Benzothiazole	30.6576	1290.9	135 m/z	119	95
629505	>Tridecane	30.9137	1299.5	TIC	42	90
626197	>Isophthalaldehyde	31.6659	1326.5	105 m/z	45	93
22699703	>m-Ethylacetophenone	31.7593	1329.8	TIC	30	89

626197	>Isophthalaldehyde	31.9307	1336	134 m/z	50	95
122576	>3-Buten-2-one, 4-phenyl-	32.5335	1357.6	103 m/z	47	85
17719709	>Vinyl trans-cinnamate	33.182	1380.8	131 m/z	37	82
22469529	>1,2,4-Metheno-1H-indene, octahydro-1,7a-dimethyl-5-(1-methylethyl)-, [1S-(1à,2à,3aá,4à,5à,7aá,8S*)]-	33.6747	1398.5	TIC	38	83
1137128	>1,2,4-Methenoazulene, decahydro-1,5,5,8a-tetramethyl-, [1S-(1à,2à,3aá,4à,8aá,9R*)]-	33.9507	1408.9	95 m/z	116	94
22699703	>m-Ethylacetophenone	34.865	1443.6	TIC	35	80
475207	>Longifolene	35.0111	1449.2	161 m/z	145	96
112549	>Dodecanal	35.1474	1454.4	TIC	34	86
EPA-401120	>2,5-cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-hydroxy-4-methyl-	37.5618	1549	165 m/z	151	85
777957	>1,6-Dioxacyclododecane-7,12-dione	39.8719	1644.4	55 m/z	285	89
14035348	>2,6-Bis(1,1-dimethylethyl)-4-(1-oxopropyl)phenol	40.3165	1663.2	233 m/z	21	83
EPA-240362	>2-Morpholinomethyl-1,3-diphenyl-2-propanol	41.3851	1709.1	100 m/z	34	84
17312811	>Undecane, 3,5-dimethyl-	43.391	1799	TIC	28	83
629925	>Nonadecane	45.5176	1899	TIC	56	91
629925	>Nonadecane	45.5215	1899.2	85 m/z	58	91
EPA-240362	>2-Morpholinomethyl-1,3-diphenyl-2-propanol	45.9242	1919.1	100 m/z	39	86
112958	>Eicosane	47.5415	1998.9	57 m/z	136	93

SPME Black Tentative Components in 16-0087

(Any compound names are only tentative and **should not** be regarded as a confirmed identification.)



CAS	Name	RT	RI	Model	S/N	MF
EPA-386402	>2-Ethyl-oxetane	6.1195	607.8	57 m/z	88	93
108883	>Toluene	13.0335	790.4	92 m/z	46	85
120923	>Cyclopentanone	15.2005	840.6	TIC	80	91
106423	>p-Xylene	17.2989	892.2	TIC	38	82
106514	>p-Benzoquinone	20.593	983.2	108 m/z	134	94
124185	>Decane	21.3739	1005	142 m/z	89	93
591811	>Butanoic acid, 4-hydroxy-	21.8277	1017.7	42 m/z	112	95
100527	>Benzaldehyde	21.9397	1020.9	106 m/z	78	97
13475826	>Heptane, 2,2,4,6,6-pentamethyl-	22.2069	1028.3	TIC	51	89
62016197	>Octane, 6-ethyl-2-methyl-	22.7625	1043.9	71 m/z	108	86
527844	>o-Cymene	22.9913	1050.3	119 m/z	41	81
2051301	>Octane, 2,6-dimethyl-	23.6675	1069.2	TIC	53	85
62238157	>Decane, 2,3,4-trimethyl-	24.1383	1082.3	TIC	43	86
1120214	>Undecane	24.7742	1100.1	57 m/z	96	93
112403	>Dodecane	27.9568	1200.1	57 m/z	55	92
464493	>(+)-2-Bornanone	28.2519	1210	TIC	48	90
272162	>1,2-Benzisothiazole	30.6677	1291.2	135 m/z	34	90
629505	>Tridecane	30.9262	1299.9	57 m/z	42	91
110429	>Decanoic acid, methyl ester	32.341	1350.7	74 m/z	34	85
62238124	>Decane, 2,3,6-trimethyl-	33.711	1399.8	71 m/z	30	84
1137128	>1,2,4-Methenoazulene, decahydro-1,5,5,8a-tetramethyl-, [1S-(1à,2à,3aá,4à,8aá,9R*)]-	33.9618	1409.3	94 m/z	136	95
475207	>Longifolene	35.0149	1449.3	161 m/z	162	96
62108218	>Decane, 6-ethyl-2-methyl-	36.3445	1499.9	TIC	24	83
EPA-401120	>2,5-cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-hydroxy-4-methyl-	37.5646	1549.1	165 m/z	101	83
777957	>1,6-Dioxacyclododecane-7,12-dione	39.8767	1644.6	54 m/z	79	88

6.0 Corrosivity Results

This section provides the final results of corrosivity testing. The corrosivity measurements were performed by adding an equal mass of water to the mass of solids/sludge sample used.

Pacific Northwest National Laboratory
Radiochemical Science and Engineering Group
pH Report – pH for Soil Samples

PO Box 999, Richland, Washington 99352

Project Number: 68453
Charge Code: N60251
ASR Numbers: 9937
Client: M Minette
Total Samples: 7

RPL Sample Number	Client Sample ID	Sample Description
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E Sample 1 (solid/sludge)
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)

Analysis Procedure	PNL-ALO-290, Rev. 0, *Determination of pH in Soil Samples*
Sample Preparation Procedure	None
Analyst	C. Rutherford/S. Sinkov
Analysis Date	12/22/15
Cal/Verify Standards	Orion Lot# SS2; exp. 8/31/2016 (pH 4.01) Orion Lot# SX2; exp. 3/31/2016 (pH 7.00) Ricca #1406C21; exp. 6/30/16 (pH 7; ICV/CCV)
Excel Data File	NA
M&TE Numbers	Beckman Coulter 560 meter, 110650046 Cole-Parmer S1494 FF03 microprobe
All Analysis Records	ASR 9937

2/12/16
Prepared By: **Date**

2/12/16
Reviewed By: **Date**

Sample Analysis/Results Discussion

The samples analyzed for this ASR are associated with solid samples related to the sample collection from the PRF Canyon Floor Pans. The controlling document for this work is the ASO-QAP-001, Rev. 9. The measurement of pH in soils utilizes ASO method RPG-CMC-290. This analysis was performed by adding equal mass of DI water to the mass of sample. The sample and water were mixed by sonicating for 10 minutes. The mixed solutions were left to stand overnight giving the suspended solids time to settle. The solutions remained murky with visible suspended solids after settling overnight. The samples were transferred to conical centrifuge tubes and centrifuged. The centrifuging was successful; however the resulting centrifuged supernate for most of the samples was still murky brown, ruling out the application of pH paper for the pH measurements. The centrifuged supernate was filtered through 0.2 micron syringe filters and collected for pH and anion analyses. Approximately 0.5 mL of the filtered supernate was transferred out of the glove box for pH measurement using pH meter and thin shaft pH electrode.

The pH meter was calibrated using pH buffers of 4 and 7. Calibration verification was performed using a second source pH 7 buffer; the results of the verification checks for the second run were 7.04 and 6.91. The closing CCV for the first run failed and the instrument was re-calibrated and the ICV/CCV samples re-analyzed. The pH probe was cleaned between samples with dilute HCl and DI water after each sample. Sample results ranged from pH 2.66 to pH 7.76.

Sample number 16-0087 (B33MK6, F16-001-004, Pan J Sample 2) was not analyzed in this batch. This sample has been retained, with CHPRC concurrence, in the original inner packaging for gas sampling of the inner package. The disposition and planned course of action for gas sampling of the inner sample packaging is documented in ASO occurrence report, OR-98620-12-19-15.

Background

Project 68453 required a corrosivity measurement (50/50 weight % with water).

Sample Preparation

The samples were prepared by mixing equal mass of DI water with the mass of sample.

Quality Control Discussion

Calibration Check Standards: The calibration of the pH measurement system is checked by analyzing an initial calibration verification check standard (ICV) and continuing calibration verification check samples (CCV). For this analyses batch, the result for the ICV was 7.04 and the CCVs was 6.91 meeting the procedure acceptance criterion of agreement within $\pm$ 0.1 pH unit of the certified value for the pH buffer solution.

Duplicates: Precision of the pH measurements is demonstrated by analyzing at least one sample/ sample duplicate sample pair in every 10 samples; the procedure DQO criterion is agreement between duplicates within 0.1 pH unit of the sample result. In this case one duplicate sample pair was analyzed (16-0086 and 16-0086 rep) in this batch and the duplicate pair results of 2.63 and 2.66 were within the 0.1 pH unit criterion. (See data table below for tabulated results).

Deviation from Procedure

The pH measurement was performed on an equal mass of DI water to mass of sample. This differs from the procedure where the volume of water added to the sample is normally a 10:1 ratio.

General Comments

None

RPL Sample Number	Client Sample ID	Sample Description	Result (pH Units)
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E Sample 1 (solid/sludge)	**2.39**
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)	**2.56**
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)	**2.63**
16-0086 Rep	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)	**2.66**
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)	**7.76**
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)	**2.44**
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)	**3.74**
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)	**3.46**

7.0 Isotopic Separations Analysis

The nitric acid/ hydrochloric acid digestion process used to extract the radiochemistry samples for isotopic analysis was not able to provide all of the radioactive materials in the acid digestion solution. The activity in the digests were anywhere from 2 to 10 times less than the expected activity. Additionally, there were residuals of undissolved solids after the digestion process.

In discussions with staff from the CH2MHill's Plateau Remediation Company (CHPRC), it was discussed that gamma data (see Section 2) provided very good isotopic information on the Pu and the Am-241. The remaining radiochemistry separations and alpha spectrometry would only be providing new information on the Uranium isotopes and Curium (if present). Since the Uranium and Curium would not change the waste designation for the canyon floor drums, it was decided not to proceed with the isotopic separations process.

8.0 Fourier Transform Infrared

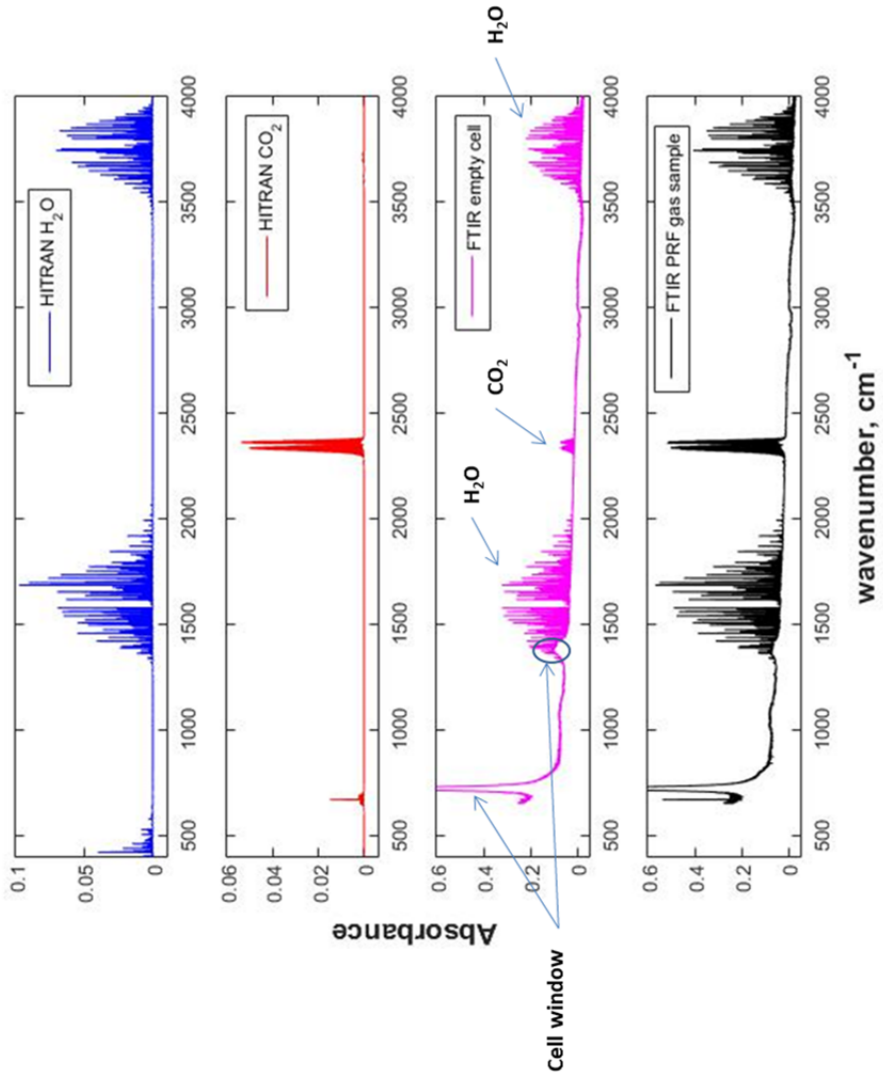
Gasses were collected from inner bag of Pan J Sample 2 with a syringe. The gasses were then run through the Fourier Transform Infrared (FTIR). The FTIR analysis did not identify anything worth noting in the IR analyses of the gas from the sample bag. The FTIR analysis did resolve water and CO_2, but these are attributed to normal atmosphere and not from the sample.

No additional FTIR analyses were reported from the Pan J Sample 2 bag gasses.

Below are the researcher's notes:

> *I have just plotted out the FTIR spectra, with very cursory analysis. The gases observed in the gas cell contain water vapor (H_2O) and carbon dioxide (CO_2), the same you would expect from normal atmospheric gases. There is not any evidence of other products of combustion (NO, NO_2, CH-containing hydrocarbons).*
>
> *The plot on the next page is of the FTIR spectra of the gas cell loaded with 20 mL of reaction gas. Also on this plot, there are three other spectra, one containing the FTIR measurement of the evacuated (empty) cell, and two HITRAN data base spectra for H_2O and CO_2 respectively. The HITRAN data base spectra for CO_2 and H_2O match the gas phase spectra for the PRF gas sample.*

These data were not submitted for review since results were not above background.


HITRAN H_2O
HITRAN CO_2
FTIR empty cell
FTIR PRF gas sample
H_2O
CO_2
H_2O
Cell window
Absorbance
wavenumber, cm^{-1}

9.0 QA Program Activities

The sample preparation and analysis activities reported in previous sections of this report were performed under the quality assurance (QA) program defined in the document 68453-QAP-R0-001, Rev. 0, *Plutonium Finishing Plant (PFP) Floor Pan Evaluation Project Quality Assurance Project Plan* with an effective date of December, 2015 (Appendix E). The Analytical Support Operations (ASO) laboratory participation was performed under their QA Plan, ASO QAP-001, Rev. 9, *ASO Quality Assurance Plan* with an effective date of 5 March 2014, and a revision of their QA plan SO QAP-001, Rev. 10, *ASO Quality Assurance Plan* with an effective date of 4 February 2016, and their existing procedures.

Processes for sample preparation were documented as test instructions (TIs), which are listed in Appendix C of this report. These TIs were reviewed and approved by a technical reviewer, a Quality Engineer (QE), the project manager (PM) and Principal Investigator (PI) prior to use. Completed TIs were reviewed by a technical reviewer and a QE, and were then saved as a portable document format (.pdf) document ready to be submitted as a project record.

Procedures for performing analyses were mostly existing procedures or new procedures developed specifically to support this project. The ASO analyses were performed using their pre-existing procedures. Refer to Appendix D of this report for a list of the procedures used. Wherever possible, procedures addressed calibration, calibration verification and quality control (QC) activities to assess procedure performance in terms of precision and accuracy.

Data verification activities were performed to confirm and document that the reported results presented herein are accurate and reflect the characterization analyses that were actually performed, and that any QC sample results and data met the applicable requirements.

A number of approaches were employed to verify the data from origination through final reporting and these approaches are discussed in this section of the report.

Project records will be stored using the Pacific Northwest National Laboratory (PNNL) electronic records management and storage system (HP Records Manager (HPRM) software) at the completion of the project under project number 68453.

Revision 1 to this report added Appendix G to document the Gas Generation Rate analysis and methodology conducted on the residual sample materials. The Gas Generation Rates in Appendix G were also conducted under the Plutonium Finishing Plant (PFP) Floor Pan Evaluation Project Quality Assurance Project Plan (PFP Floor Pan Evaluation QAPP, Revision 0.) developed by PNNL specifically for this project.

9.1 Sample Receipt, Preparation and Analysis

Table 9.1 summarizes the verification review requirements corresponding to the documentation of sample receipt.

Table 9.1. Summary of Verification Records for Sample Receipt and Creation

Requirement	Verification Record
Completed COC form	Signed and dated the shipping COC form
Observations of samples	Included in Section 1

ASO sample numbers were assigned to the samples upon sample opening. Sample IDs assigned at PNNL were in the format YY- XXXX, where YY was 16 to indicate the fiscal year when the sample was received or created and XXXX was the assigned sequential sample identification number.

Table 9.2 summarizes the approach for verification reviews to evaluate work against requirements corresponding to sample receipt, subsampling, and other characterization testing controlled via test instructions.

Table 9.2. Summary of Verification Activities for Test Instructions

Requirement	Verification Record
Planning	
Work document (TI) included steps to create and track samples and data meeting technical compliance	Technical reviewer signature and date
Work document collected data and samples consistent with the QA Plan	Project manager signature and date
Work document appropriately captures measurement and test equipment requirements and documentation.	QE signature and date
Execution/Completion	
Steps in work document (TI) were completed, changes have been documented, records are logical and understood, and collected data are in technical compliance with project objectives	Technical reviewer signature and date
Steps in work document (TI) were conducted in accordance with QA requirements	QE signature on completed TI
Transcriptions into data-calculation spreadsheets and data-reduction calculations and measurement uncertainties from completed TI are properly conducted	Technical and QE reviewers' signatures and dates on spreadsheets
Overall check for completeness of each TI, data traceability, associated attachments, and spreadsheets including identification and disposition of all issues	QE reviewer's signature and dates on completed TI

The activities were documented in detailed TIs. Upon the completion of the Gas Generation Analysis that is currently on going, the TIs are reviewed by at least one technical reviewer, and the QE before being issued to verify that all objectives and data needs were addressed during planning for sample processing and analysis activities. After the TIs are completed, the primary user performs a completeness review and the technical reviewer performs a technical review. Calculation spreadsheets developed for each TI are reviewed. Spreadsheet reviews include a technical review of data entries from TIs into the

calculation spreadsheet, calculation algorithms, and overall reasonableness and consistency of the data. The calculation spreadsheets, with signatures and dates of the reviews will be included as part of the completed TIs. The Tis will be stored with the project records.

9.2 Sample Analysis and Characterization

Table 9.3 provides a summary of the records created to verify the procedures used for various stages of work planning and execution.

Table 9.3. Summary of Verification Records for Analytical Sample Preparation and Analysis

Requirement	Verification Record
Planning	
Work documents (TIs) identified all subsamples and specific analyses to be performed. All applicable method and QC requirements were identified and properly communicated to the analysts in the phase of analysis procedure development, review and approval.	Signed TIs and procedures indicating review and approval prior to use.
Execution/Completion	
For each analysis, a technical review has been performed, consisting of the following elements: • transcription accuracy • correctness of calculations • evaluation of overall consistency and reasonableness of data	Technical reviewer signature on the data report.
For each analysis, a QE review has been performed, consisting of the following elements: • evaluation of project, TI, and method objectives against any QC sample results • transcription accuracy • correctness of calculations • evaluation of overall consistency and reasonableness of data • implementation of appropriate corrective action, when necessary • data traceability • documentation of QC sample results not meeting objectives or other data quality issues	QE reviewer prepares a surveillance report for the ASR data for Tasks 1 and 2
Documentation of issues as occurrences (OR), deficiencies (DR), or nonconformance (NCR) reports	OR, DR or NCR forms are signed by the Project Manager and the QE

9.3 Data Reporting

All preliminary data reports received internal technical reviews. Each ASO data report received a technical and QE review prior to final reporting. ASO data reports include sections that address each of the analytical QC samples and data quality objective compliance to the procedure requirements. Each ASO analysis report was reviewed and signed by the preparer and the technical reviewer. The report and supporting data were then forwarded to the ASO QE for review. The QE reviews were documented as ASO surveillance reports and were performed to verify that data were what they purported to be (i.e., the reported results reflected what was actually done and the results meet applicable requirements,

particularly procedure and project data quality objectives). Identified issues and concerns were discussed and resolved before the QE signed and issued the surveillance report. All QE review comments were resolved before the analytical report was finalized. The QE review and comment resolution are documented in surveillance reports that are available in the ASO records. The ASO Lead also performed a final review of each ASO report for completeness and provided authorization to release the data.

The analysis reports for each section of this report were subject to a minimum of technical and QE reviews. Technical reviews are documented by the reviewer signing and dating the data package. QE reviews are documented as surveillances and were performed to verify that data were what they purported to be, as defined in the previous paragraph. Identified issues and concerns were discussed and resolved before the final report was prepared. When necessary, Occurrence Reports (OR) were initiated to track discussions on issues of concern and to determine whether the occurrence needed to be elevated to a Deficiency Report (DR) or Nonconformance Report (NCR).

9.3.1 Occurrences, Deficiencies, and Nonconformances

The processes for documenting issues of concern and determining whether significant conditions adverse to quality were initiated during sample receipt, or during reviews of completed TIs, reviews of completed work by the technical and QE reviewers, and by the PM or PI as needed. Identified issues requiring corrective actions greater than resolution via modification of TIs and reports or impacting the use or quality of the data can be addressed in several ways:

- Addressing in the report in an Assumptions and Limitations section describing the issue and impact on data use and interpretation

- Completing an Occurrence Report form allowed review by the ASO Lead or Project Manager and include a determination as to whether or not a DR or NCR was needed to 1) elevate the concern to a higher level and 2) require additional documented corrective actions.
    - Occurrences are defined as any issue affecting sample integrity or data quality. Occurrences were tracked to document any issue of concern to bring the issue to the attention of project management and to define appropriate corrective actions or paths forward.
    - Deficiencies are defined as failures to follow work-controlling documents such as test plans, TIs, or procedures. DRs may result from ORs that are determined by the responsible manager to be a significant condition adverse to quality requiring corrective action and tracking to closure, or may be issued without an OR when it is clear that a failure to follow work-controlling documents occurred.
    - Nonconformances are defined as failures of items to meet specifications or to operate as expected; this includes using out-of-service equipment and measuring and test equipment used outside of a valid calibration interval and other types of calibration-related issues. NCRs result from occurrences that are determined by the responsible manager to be a significant condition adverse to quality requiring disposition of the item (e.g., use as-is, reject, repair, re-work), corrective action, and tracking to closure.

Occurrence and deficiency reports were uniquely identified and included a description of the issue, affected samples, investigative findings, recommended actions, and an assessment of significant impact to

data quality. Table 9.4 provides summaries of the issued reports. No NCRs were generated for this scope of work.

Table 9.4. Occurrence and Deficiency Report Summary

Date Initiated& Closed	Summary
	Deficiency Reports
12/16/15 & 3/9/16	DR-68453-12-16-16; No Validation Plan for GC/MS moved from 331 to RPL/400 - Generally when new M&TE are purchased or acquired and installed and readied for use to collect data for project reporting, a formal validation plan is developed allowing check-out of the instrument and software and providing documentation that the instrument is ready to report data. When applicable, a performance testing sample is also obtained and analyzed demonstrating that analysts have demonstrated their proficiency and that the capability of the instrument to produce valid data has been evaluated and passed. This is a HASQARD requirement. The moving of the GC/MS from 331 to RPL was a unique situation required by needing an instrument that could analyze a rad sample within the very short project period of performance. The GC/MS was moved and set-up by the users from 331 who will also operate it to collect project data using procedure, RPL-GCMS-01, Rev. 0, *Gas Chromatography/Mass Spectrometry*, which was issued on 12/16/15. The procedure contains step to ensure the instrument is functioning properly when used. Sections 8.3 and 8.7 have steps for instrument use that need to be completed successfully before proceeding with the analysis. Also a Grob Test Mix sample which has known compounds must be analyzed before sample data can be collected. Moving, installing and using an instrument in a very short time period is a high risk undertaking; however, the instrument analysts were confident this could be a successful undertaking. If the capability cannot be successfully defended, the data will not be reported to the project client and an alternative approach will be developed. The GC/MS system was moved to the RPL facility and installed in lab 400. Performance testing was completed and the system was accepted to use. The system was then used to analysis the CHPRC PFP Canyon Floor samples and the acceptable data for the Grob Test Mix formed the basis for closure of the DR.
ASO Issues	**Occurrence Reports**
12/9/15 & 12/21/15	OR-98620-12-9-15; **Sample Receipt Observations (ASR 9937) –** Upon opening the sample outer and inner sample Bags for Pan J Sample 1 and the outer bag for Pan J Samples 2, it was identified that the sample vials had broken cleanly and the glass bottoms of the vials had separated cleanly from the vial. Remaining materials were recovered from the Vial in Pan J Sample 1. An Alternative analysis approach was established for Pan J Sample 2 materials and in bag gasses.
2/17/16 & 2/18/16	OR-98620-2-17-16; **Holding Time Limit Concern for Some GC-MS Samples** for ASR 9937 - ASO test instruction, 98620-TI-001, *Rev. 0, PRF Canyon Sample Handling in Glove Box* in Section 4, Part 2, Organics Testing: Preparation for Gas Chromatography- Mass Spectrometry (GC-MS) lists holding time limits imposed by the project Statement of Work, Statement of Work for Contract 495170-40, Rev. 0, 236-Z PRF Canyon Floor Debris Sample Analysis (CHPRC to PNNL Supplier) FY16, 11/5/2015. Semi-VOA in Soil – 14 days from date of extraction VOA in Soil – 14 days from date of extraction Seven samples were received for analysis under this ASR; there were four samples that were MeOH extracted on 1/5/16 and analyzed by GC-MS on 1/23/16 (16-0086, 16-0088, 16-0089, and 16-0091) were outside the 14-day holding time limit window by 4 days.

9.4 Surveillances

A QE surveillance of Test Instruction 98620-TI-001 Revision 0, *PRF Canyon Sample Handling in Glove Box*, has been performed. The observations monitored the volume measurements of the Gas Generation measurement system. Surveillances for work performed by ASO were performed for Analytical Service Requests as noted in Table 9.5 below:

Table 9.5. Surveillance Report Summary

Number	Subject	Report Issued/ Summary of Concerns
ASO-2016-006	QE Review of ASO ASR 9937 and ASR 9937.01 for ASO Project 68423; Eight Solid Samples: GEA, Anions, pH (Corrosivity), , ICP-OES and Organic Extraction /GC-MS Analysis	3/10/16 There were no outstanding issues that were identified to be findings or observations.

10.0 References

Date, AR, and AL Gray. 1989. Applications of Inductively Coupled Plasma Source Mass Spectrometry. Blackie, Glasgow, UK.

Hall, GEM. 1992. "Inductively Coupled Plasma Mass Spectrometry in Geoanalysis." Journal of Geochemical Exploration 44(1-3):201-49.

Appendix A

Sample Identifications and Descriptions

Appendix A

Sample Identifications and Descriptions

RPL Sample Number	Client Sample ID	Sample Description
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E Sample 1 (solid/sludge)
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)
16-0087	B33MK6 (F16-001-004)	PRF Canyon Pan J Sample 2 (solid/sludge)
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)

Appendix B

Completed ASO Occurrence Report Form OR-98620-12-9-15 "ASR 9937 – Sample Receipt Observations"

Appendix B

Completed ASO Occurrence Report Form OR-98620-12-9-15 “ASR 9937 – Sample Receipt Observations”

ASO Occurrence Report Form

Title: ASR 9937 – Sample Receipt Observations | **Date:** 12-9-15

Unique Identifier: OR-98620-12-9-15

Primary Person Identifying Issue: K Pool/ C. Delegard

Distribution: (Email and posting on ASO Share-Point)
DS Coffey, ASO QE
KN Pool, ASO Lead
T Trang Le, ASO Administrator –
ASR# 9937 file
Others: MJ Minette, Project 68453
KN Pool, Project 68453
J

Date Submitted to ASO Records:

Occurrence Description: Eight samples were provided to ASO under ASR 9937:

RPL Sample Number	Client Sample ID	Sample Description
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E Sample 1 (solid/sludge)
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)
16-0087	B33MK6 (F16-001-004)	PRF Canyon Pan J Sample 2 (solid/sludge)
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)

Following extended GEA counting, the samples within their individual ice cream cartons were returned to Lab 506 for complete opening down to the vial level. The openings occurred on 9 December 2015. To do this unpackaging, the ice cream cartons were opened at the threshold of the fume hood, the thin yellow bag, with PVC sleeve and vial within, were removed from the ice cream carton into the fume hood and then to an adjacent glovebox by way of an interconnecting airlock. Individually, the thin plastic bags (which had already been torn open on 23 November 2015) were removed and the PVC bags cut open with scissors.

Six intact vials were removed from the PVC bags, the outer surfaces of the vials wiped with moist paper towels (all vials had some level of dark-colored outside contamination, evident over white plastic caps and white labels), the PRF canyon floor sludge contents were examined through the clear glass (with best views through the bottom because the label covered the side walls), the vial caps opened to "burp" the contents and release any pent-up gas pressure, and the six intact vials set within a clean shallow plastic dish.

The other two vials, for samples J/1 (16-0086) and J/2 (16-0087), were found to be broken cleanly and circumferentially at the bottom such that the vial bottom was separated from the remainder of the vial. These broken vials were left with the remaining contents within their PVC glovebox sleeves in a bottoms-up orientation to retain whatever materials still were left within the vials. However, significant amounts of sample were outside of the vials and smeared within the PVC sleeve. Further observations on packaging and PRF canyon floor sludge samples are summarized in Table 1.

Table 1. Observations of Unpackaging PRF Canyon Floor Samples on 9 December 2015

Location, Pan/Sample	Order Opened	Observations
E/1 16-0084	7	Bag not (further) yellowed. Contents similar to J/3 but more solids present (like J/4).
J/4 16-0085	6	Bag not (further) yellowed. Contents similar to J/3 but more solids present.
J/1 16-0086	2	Vial bottom broken. Tan mud observed within broken vial. PVC sleeve more yellowed compared with most other bags.
J/2 16-0087	3	Vial bottom broken. Contents darker than J/1. PVC sleeve yellowed.
O/1 16-0088	1	Contaminated on outside (like all vials). Contents like heavy dark oil, flow slowly.
J/3 16-0089	5	Contents appear as sticky lumps up to ~5-mm diameter of coarse sand.
H/1 16-0090	4	PVC sleeve yellowed but vial intact. Contents look like coarse sand stuck together.
H/2 16-0091	8	Bag not (further) yellowed. Yellowish-tan mud but not flowing, wetter than J/3 & J/4.

Impact of Occurrence:

Reportable per 10 CFR Part 21: No [X] Yes [ ]

Significant Condition Adverse to Quality? Yes _____ No X

The ASO Lead makes the determination of significant condition adverse to quality.

Evaluated by: Karl N. Pool **Date:** 12/21/15
KN Pool, ASO Lead

Further Disposition: *The ASO Lead makes the determination of further disposition*

☒ **No** ☐ **Yes** **If yes,** ☐ **Nonconformance?** ☐ **Deficiency?**

Date Occurrence Closed: 12/21/15

Signature/Date of Responsible QE: Deborah Coffey 12/21/15

Signature/Date of ASO Lead: Karl N. Pool 12/21/15

Comments:

Unpackaging PRF Canyon Floor Samples

Unpackaging of the eight samples taken from the Plutonium Reclamation Facility (PRF) canyon floor was done at PNNL in Lab 506 of the 325 (Radiochemical Processing Laboratory, or RPL) in two stages, on 23 November 2015 and on 9 December 2015.

The samples were packaged within the following sequence of containment, from the outside-in: 1) two steel drums, each ~15-inch diameter and ~30-inches tall, one holding six samples and the other holding two samples; 2) a thick plastic bag, horsetailed and taped at the top, covering six and two, respectively, 1-quart ice cream cartons; 3) ice cream carton, taped shut; 4) a thin ~8×10-inch yellow plastic bag, twisted and taped; 5) a heavy-wall yellow PVC glovebox sleeve, horsetailed and taped at each end, of nominal ~4- to 5-inch diameter; and 6) a ~20-mL clear glass vial holding each sample. Each vial had a white cap with a ~1-cm diameter septum in the middle and had a white label completely covering the curved vial wall.

The initial unpackaging took place on Monday, 23 November 2015, and consisted of opening the drums, cutting the outer bags and removing the ice cream cartons, opening the ice cream carton, and placing the thin plastic bag containing the PVC glovebox sleeve and vial into a fume hood for examination. Once in the fume hood, each thin plastic bag was torn open to expose the heavy-wall PVC sleeve and view the sample vial within. The vials, within the PVC sleeve, were maneuvered so that a photo could be taken and the vial and contents examined as well as possible within the heavy-walled PVC bag but without further breeching of the sample containment.

The unpackaging took place one-at-a-time with the individual samples returned to their ice cream cartons before the next sample was opened. Once visual observations were taken and photographs gathered, the samples in vials with PVC sleeve and outer breeched thin plastic bag were returned to their individual ice cream cartons, and the cartons taped. Once all packages were examined they were taken for gamma energy analysis (GEA). Radcon exams took place throughout these operations to determine dose rates and especially radioactive contamination.

Visual observations recorded during the 23 November 2015 unpackaging are presented in Table 1.

Table 1. Observations of Unpackaging PRF Canyon Floor Samples on 23 November 2015

Sample ID, F16-001-	Location, Pan/Sample	Order Opened	Observations
001	E/1	4	Similar to O/1, with dark liquid on solids.
002	J/4	6	Seems to have more grit than previously opened 5 samples.
003	J/1	1	Only sample that showed contamination (α) between the thin yellow polyethylene bag and the outside of the PVC sleeve. Dark brown to black liquid was found within the tube bag and seemed to be the same material that was present within the glass vial. In fact, all items seemed to have present some amount of the dark brown material on the tube bag walls or on the inner vial's outer surface. The sample material itself for this item looked like dirty motor oil (or crankcase sludge) but did not flow readily.
004	J/2	5	Similar to J/1, J/3, O/1, & E/1 with dark liquid on solids.
005	O/1	3	Similar to J/3 but seemingly more fluid (i.e., lower viscosity).
006	J/3	2	Similar to J/1 but with less leakage to the innermost bag.
007	H/1	7	Inside of vial seemed to be "painted" everywhere within by dark liquid.
008	H/2	8	Still black or very dark brown but is the most gritty of the samples.

In summary, the sample appearances were very similar to each other with dark liquid, like dirty motor oil, and gritty solids where solids could be observed. The observations made of the samples within the vials (Table 1) were made difficult by the heavy yellow PVC bag covering and the white label that covered, almost completely, the curved walls of each vial.

Following extended GEA counting, the samples within their individual ice cream cartons were returned to Lab 506 for complete opening down to the vial level. The openings occurred on 9 December 2015. To do this unpackaging, the ice cream cartons were opened at the threshold of the fume hood, the thin yellow bag, with PVC sleeve and vial within, were removed from the ice cream carton into the fume hood and then to an adjacent glovebox by way of an interconnecting airlock. Individually, the thin plastic bags (which had already been torn open on 23 November 2015) were removed and the PVC bags cut open with scissors.

The six intact vials were removed from the PVC bags, the outer surfaces of the vials wiped with moist paper towels (all vials had some level of dark-colored outside contamination, evident over white plastic caps and white labels), the PRF canyon floor sludge contents examined through the clear glass (with best views through the bottom because the label covered the side walls), the vial caps opened to "burp" the contents and release any pent-up gas pressure, and the six intact vials set within a clean shallow plastic dish.

The other two vials, for samples J/1 and J/2, were found to be broken cleanly and circumferentially at the bottom such that the vial bottom was separated from the remainder of the vial. These broken vials were left with the remaining contents within their PVC glovebox sleeves in a bottoms-up orientation to retain whatever materials still were left within the vials. However, significant amounts of sample were outside of the vials and smeared within the PVC sleeve. Further observations on packaging and PRF canyon floor sludge samples are summarized in Table 2.

Table 2. Observations of Unpackaging PRF Canyon Floor Samples on 9 December 2015

Location, Pan/Sample	Order Opened	Observations
E/1	7	Bag not (further) yellowed. Contents similar to J/3 but more solids present (like J/4).
J/4	6	Bag not (further) yellowed. Contents similar to J/3 but more solids present.
J/1	2	Vial bottom broken. Tan mud observed within broken vial. PVC sleeve more yellowed compared with most other bags.
J/2	3	Vial bottom broken. Contents darker than J/1. PVC sleeve yellowed.
O/1	1	Contaminated on outside (like all vials). Contents like heavy dark oil, flow slowly.
J/3	5	Contents appear as sticky lumps up to ~5-mm diameter of coarse sand.
H/1	4	PVC sleeve yellowed but vial intact. Contents look like coarse sand stuck together.
H/2	8	Bag not (further) yellowed. Yellowish-tan mud but not flowing, wetter than J/3 & J/4.

Appendix B

Completed Deficiency Report Form DR-68453-12-16-16; No Validation Plan for GC/MS

Project 98453 Deficiency Report Form

Assessment/Audit #: NA

Deficiency/Finding #: DR-68453-12-16-15

Associated Occurrence Form? No

Title: No Validation Plan for GC/MS moved from 331 to RPL | **Date:** 1216/15

Responsible Person: MJ Minette and KN Pool, 68453 PMs

Finding Submitted to: MJ Minette and/or KN Pool, 68453 PMs

Response Due Date:

Finding:

Generally when new M&TE are purchased or acquired and installed and readied for use to collect data for project reporting, a formal validation plan is developed allowing check-out of the instrument and software and providing documentation that the instrument is ready to report data. When applicable, a performance testing sample is also obtained and analyzed demonstrating that analysts have demonstrated their proficiency and that the capability of the instrument to produce valid data has been evaluated and passed.

Requirement:

For the 68453 project, GC/MS data acquisition activities have been determined to meet HASQARD requirements.

Background/Condition Observed: Initial 12/21/15

The moving of the GC/MS from 331to RPL is a unique situation required by needing an instrument that could analyze a rad sample within the very short project period of performance. The GC/MS was moved and set-up by the users from 331 who will also operate it to collect project data using procedure, RPL-GCMS-01 which was issued on 12/16/15.

Instructions for Response:

Significant Condition Adverse to Quality? Yes ____ No X

Evaluated by: Karl N. Pool **Date:** 12/21/15
MJ Minette and/or KN Pool, 68453 PMs

Signature of Finding Owner: Karl N. Pool **Date:** 12/21/15
MJ Minette and/or KN Pool, 68453 PMs

Part A

Assessment/Audit #: NA

Deficiency/Finding #: DR-68453–12-16-15

Identify the cause of the deficiency/deficiencies. *Use the 5 Whys Process.*

This was discussed previously. Moving a GCMS to RPL was a unique situation required by needing an instrument that could analyze a rad sample within the very short project period of performance.

1) Determine the impact of the deficiency/deficiencies.

The procedure contains step to ensure the instrument is functioning properly when used. Sections 8.3 and 8.7 have steps for instrument use that need to be completed successfully before proceeding with the analysis. Also a Grob Test Mix sample which has known compounds must be analyzed before sample data can be collected.

Moving, installing and using an instrument in a very short time period is a high risk undertaking; however, the instrument analysts are confident this can be a successful undertaking. If the capability cannot be successfully defended, the data will not be reported to the project client and an alternative approach will be developed.

Reportable per 10 CFR Part 21: No [X] Yes [ ]

2) Identify what corrective actions have been or will be taken to correct the immediate problem(s). Include the person responsible and the proposed due date or date completed

CA1: See above. **Responsible Person(s):** J Wahl/A Melville **Proposed Due Date:** Within 14 days of sample receipt.

3) Identify what preventive actions have been or will be taken to prevent recurrence. Include the person responsible and the proposed due date or date completed

There are no preventive actions proposed.

Verification Actions/Comments: (See following pages)

Date Response Submitted: 12-21-15

Response Accepted: Yes ✓ No ____ **Date of Evaluation:** 12-21-15

Corrective Action Verification:

CA 1 Yes ✓ No ____ **Date of Evaluation:** 3/4/16

See attached pages 1-6 from the GC/MS Report that pertains to this issue.

Date Finding Closed:

Deborah Coffey 3/4/16

Signature of Responsible QA Staff or Audit Team Member **Date**

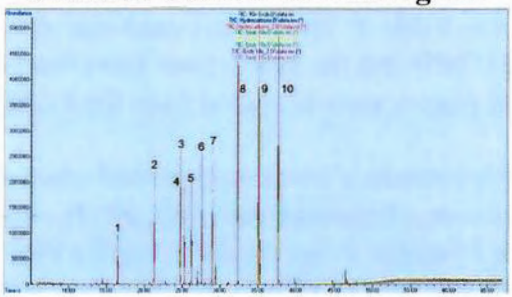
Signature of 68453 PM	**Date** 3/9/16

Distribution: (Email and posting on 68453 SharePoint Share-Point)

DS Coffey, Project 68453QE
MJ Minette l, 68453 PM
KN Pool, 68453 PM
Others: A Melville, J Wahl

Battelle - Pacific Northwest National Laboratory
Analytical Support Operations – GC/MS Report
PO Box 999, Richland, Washington 99352

Common GC/MS Chromatogram



Client:	M. Minette	***ASR #:***	9937.01
			14 liquids
Project #:	68453	***# Samples:***	3 headspace gas
Charge Code:	N60251		

***** RPL Numbers: 16-0084 thru 16-0086 and 16-0088 thru 16-0091*****
***** RPL Numbers for Head Space Samples 16-0087 *****
(see ASO OR-98620-12-9-15)

Procedure, Analysis, System, and Records Information

Analysis Procedure	RPL-GC-MS-01, Rev. 0, *Gas Chromatography/Mass Spectrometry*
Prep Procedure	Samples prepared for analyses following the preparation scheme outlined in Test Instruction, *98620-TI-001, Rev. 0, Section 4. PRF Canyon Sample Handling in Glove Box*
Analyst	AM Melville
Analysis Date(s)	01/07/16 - 02/12/16
Calibration Date	01/07/16, 02/03/16
Calibration Preparation Date	01/07/16
Verification Preparation Date	01/07/16
Excel Data File	NA
M&TE Numbers	GC/MS System (M&TE) Agilent AutoSampler 7693 Serial #: CN93801454; Agilent GC 7890A, Serial#: US10938023; Agilent MS 5975C Serial #: US93443429
	Balance: Sartorius R200D, SN:39080042, RPL/405 benchtop
All Analysis Records	ASR 9937.01 ASO Records, RPL/301

_____ _____
Prepared By Date

_____ _____
Reviewed By Date

Sample Collection

Samples were obtained per Test Instruction, 98620-TI-001, Rev. 0, Section 4. PRF Canyon Sample Handling in Glove Box. Sample weights and added methanol (MeOH) and methylene chloride ($MeCl_2$) are provided in Table 1. The MeOH used was obtained from Sigma Aldrich (Product # 34860, Lot# SHBD2740) and the $MeCl_2$ used from Burdick & Jackson (Catalog # 299, Lot # DH030). The liquid phases were analyzed from the extracted samples.

ASO occurrence report (OR) documents a concern identified when samples were received: OR-98620-12-9-15; Sample Receipt Observations (ASR 9937) – Upon opening the sample outer and inner sample bags for Pan J Sample 1 and the outer bag for Pan J Samples 2, it was identified that the sample vials had broken cleanly and the glass bottoms of the vials had separated cleanly from the vial. Remaining materials were recovered from the vial in Pan J Sample 1. An alternative analysis approach was established for Pan J Sample 2 materials and in-bag gasses.

Table 1. Sample Collection Information

RPL #:	Customer Sample ID	Sample Description	Sample Weight (g)	Sample Weight + MeOH* (g)	Sample Weight + MeOH** + $MeCl_2$* (g)
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E Sample 1 (solid/sludge)	1.0705	2.8702	3.6218
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)	1.2518	2.8219	4.0574
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)	1.0290	2.7119	4.2103
16-0087	B33MK6 (F16-001-004)	PRF Canyon Pan J Sample 2 (solid/sludge)	NA	NA	NA
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)	1.2539	2.8788	3.5991
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)	1.0849	2.7642	3.8187
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)	1.1448	2.8712	3.6345
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)	1.0884	2.6467	3.7196

***These data are not intended to provide a basis for reporting quantitative resnlts on a mass basis; results are qualitative.**

**** Total weight after a portion of MeOH was decanted after first solvent extraction**

MeOH samples were measured for dose rate and were too high for benchtop work. 2 mL of each sample was taken out of the glovebox and diluted 1:10 to reduce the dose rate to allow for further processing.

Sample Analysis Quality Control

Project Deficiency Report, DR-68453-12-16-16 was issued to address the fact that there was no time to follow the usual approach of writing and implementing a Validation Plan for the GC/MS moved from 331 to RPL/400. The GC/MS was moved and set-up by the users from 331 who

were the analyst and report preparer for the project's data collection activities using procedure, RPL-GCMS-01, Rev. 0, *Gas Chromatography/Mass Spectrometry*, which was issued on 12/16/15. The procedure contains steps to ensure the instrument is functioning properly when used. Sections 8.3 and 8.7 have steps for instrument use that needed to be completed successfully before proceeding with the analysis. Also, the Grob test mixture sample that has known compounds is required by the procedure to be analyzed before sample data could be collected.

GC/MS Quality Control Results

The mass spectrometer is tuned according to manufacturer's instructions specifications.

The instrument performance (IP) check was used to demonstrate the GC/MS instrument is operating and performing at a sufficient level and dynamic range. This check is not designed for quantitative assessments.

The instrument performance check used examined ten compounds of a Grob test mixture (Restek, Catalog #35000) at four different concentration levels. Instrumental performance standard one (IPS1) is the Grob test mixture used at the received concentrations, instrumental performance standard two (IPS2) represents a 10x dilution of ISP1, instrumental performance standard three (IPS3) represents a 100x dilution of IPS1 and instrumental performance standard three (IPS4) represents a 1000x dilution of IPS1. Table 2 list the compounds that were used for instrument performance check during this period. Table 2 results were generated with the Agilent Enhanced Data Analysis using a linear fit ($y = mx + b$) at concentrations values (x) of 1.00 (ISP1), 0.10 (ISP2), 0.01 (ISP3), and 0.001 (ISP4) per compound. Table 2 lists the experimental retention time (RT) shown in minutes, the slope (m) and intercept (b) and the correlation coefficient (R^2) as determined by the Agilent software for the linear fit. These results demonstrate that the instrument was performing adequately and Table 2 provides the basis to close the DR.

Table 2. Instrument Performance Check Results Summary

Peak #	Compound	RT	b	M	R^2
1	2,3 Butanediol	16.625	-100573	21757302	1.00
2	Decane	21.363	47064	11491126	1.00
3	Undecane	24.79	49761	12648012	1.00
4	Octanol	25.331	-33846	6897842	1.00
5	Nonanal	26.265	24045	5492163	1.00
6	Dimethylphenol	27.638	-61591	15627221	1.00
7	Dimethylaniline	29.036	-25421	18020918	1.00
8	Methyl decanote	32.375	74780	26682717	1.00
9	Methyl undecanote	35.102	79844	26540189	1.00
10	Methyl dodecanote	37.672	78690	27128737	1.00

Mid-Point IP Check Results

A 10x dilution of the Grob test mixture was used for an IP check during the experimental blocks. Over the period of this work, this 10x dilution of the Grob test mixture was examined numerous times. The stability of the instrument is reflected and is highlighted in the overlaid

chromatograms illustrated in Figure 1. Over the course of this study acceptable reproducibility for both chromatographic peak area and retention time were observed. The results shown in Figure 1 illustrate typical chromatographic signals that are commonly observed for 10's of ng per component and illustrate that the instrumental setup was performing at an acceptable level.

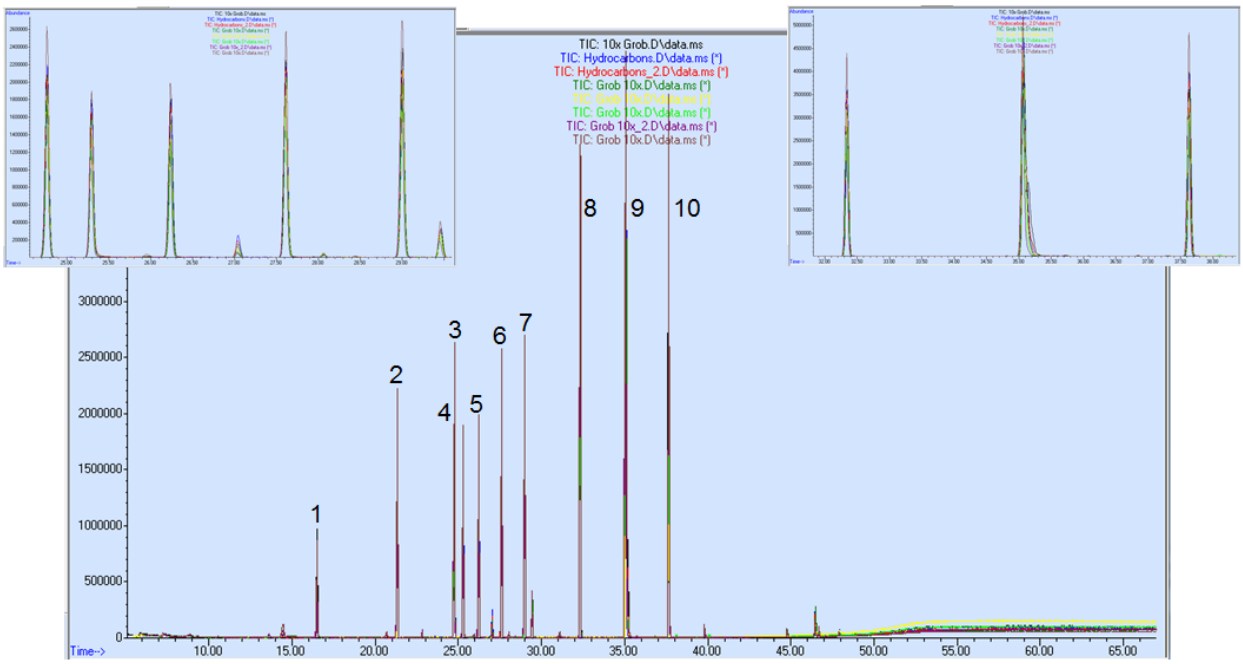


Figure 1. Overlaid 10x dilution of the Grob test mixture. The upper inserts are zoomed in portions from the main chromatogram. These results are the 10x from two IPS2's and all mid-point IP checks throughout the study. (Note: The sample vials between the mid-point IP and the hydrocarbon retention time check of the first block were mistakenly switched in the run sequence order, thus the file names are opposite.) See Table 2 for number nomenclature.

Sample Analysis/Results Discussion

GC/MS Methodology Summary

Seven methanol (MeOH) and seven methylene chloride ($MeCl_2$) organic solvent extracts from the seven solid/sludge samples noted above were submitted for gas chromatography / mass spectrometry (GC/MS) analysis under ASR 9937.01. The results are discussed in this report. The analytes of interest included glycerin and tributylphosphate (TBP) as these compounds were presumed to have been used or assumed to be present at the collection site; however, their presence within these solid/sludge samples was unknown for these random grab samples.

The GC/MS results are reported in both visual and tabular format listing tentative chemical identifications based upon a mass spectral library search and corresponding match factor. The chemical and data analysis performed is for ***qualitative*** sample assessment only as the original samples collected appear to be grab samples and any actual "target compounds" may be absent from the grab sample due to random collection variation or possible degradation with time and temperature. Again, the reader is directed to the results shown in Figure 1, which illustrates typical chromatographic signals commonly observed for 10's ng per component injected into the

GC/MS system. The samples discussed within this section will be referenced based upon the last two digits of the ASO Sample ID (e.g. sample 84 = ASO Sample ID 16-0084) unless noted.

Blank samples were prepared by adding an equal amount of extraction solvent to an identical empty glass container due to the lack of a control sample matrix.

A glycerin standard, ~470 µg/mL, was used to determine its corresponding retention time and verify the obtained mass spectra. It was prepared by adding 47.0 mg glycerin (Sigma Aldrich, Product #: G7893) to 10 mL of MeOH and diluting 1:10 with MeOH.

A tributyl phosphate (TBP) standard, ~47.6 µg/mL, was used to determine its corresponding retention time and verify the obtained mass spectra. It was prepared by adding 47.6 mg TBP (Sigma Aldrich, Product #:158615) to 10 mL of MeOH and diluting 1:100 with MeOH.

The alkane hydrocarbon mixture (C_8-C_{20}, Sigma-Aldrich, Product # 04070, ~40 mg/L each, in hexane) was used as received.

The Grob test mixture (Restek, Catalog#: 35000) was used at four different concentration levels. Grob test mixture IPS1 was used at the received concentration, IPS2 is a 10x dilution of ISP1, IPS3 is a 10x dilution of IPS2 and IPS4 is a 10x dilution of IPS4. All dilutions were with $MeCl_2$.

A portion of each solid/sludge sample was first extracted with MeOH (used because of glycerin's enhanced solubility), decanted, and then re-extracted with $MeCl_2$ (**Note:** the $MeCl_2$ extract will also contain any remaining MeOH not decanted). In addition, the headspace from sample 16-0087 was collected and analyzed via a 1 mL gas sample and two solid phase microextraction (SPME) devices. All the separations used the same column, oven temperature ramp rate program and mass spectrometric parameters unless noted. The chromatographic column used was a cyanopropy phenyl dimethyl polysiloxane, a mid-polarity type stationary phase (i.e. a "624"), which was chosen for improved chromatographic performance towards glycerin. The injection port liner was 4.0 mm ID cyclo inlet liner with wool (Restek #: 20706-200), which was chosen for improved chromatographic performance towards glycerin. This liner was also used for the gas and SPME collected samples to minimize the potential for radiological contamination and exposure from the previous liquid injections. All the liquid extracts used a 0.5 µL injection amount, chosen to minimize the potential for radiological contamination during the vapor expansion of MeOH during the GC injection. The $MeCl_2$ extracts were examined first and all the GC/MS analyses were performed without issue. The MeOH extracts were examined second, but the continuous GC/MS analyses of these samples was problematic due to autosampler issues. The samples were completed after three restart sequence attempts. The GC/MS sequence and analysis of the MeOH extracts failed due to the injection syringe plunger sticking and/or seizing when a MeOH extract sample was being examined. This effectively stopped the experimental run sequence at this point. This plunger seizing appeared random and not dependent on which extract sample was being analyzed and was likely due to the acidic nature of the extract. Ultimately the samples were completed by swapping out to a new syringe and restarting the sequence.

Each solvent extract will be discussed below with example chromatograms obtained and a listing of the tentatively identified components. At a high overview level, samples 88, 90 and 91 appeared to consistently contain both glycerin and TBP at varying amounts based upon the

chromatographic peaks. The $MeCl_2$ extracts appeared to contain a greater number and amount of alkane hydrocarbon (HC) type compounds, while the MeOH extracts had less as expected due to the highly polar nature of MeOH. General trends and chromatographic observations are highlighted in Figure 2.

As these samples appear to be "grab samples" and/or samples of opportunity, any actual target compound(s) may be absent due to random collection variation, sample inhomogeneity, or may have degraded with time and temperature pre-extraction for example. Again, accurate chemical identification is problematic based solely upon mass spectral library matching and obtaining corresponding standards for the possible chemical and number of chromatographic peaks is not realistic within the scope of the work. Moreover, quantitation and determination of solutes to an original sample is not possible as the chemical and data analysis performed is for qualitative survey only. Again, the reader is directed to the results shown in Figure 1, which illustrates typical chromatographic signals commonly observed for 10's ng per component injected into the GC/MS system as guide for the signal variability per component from a GC/MS system as well as a visual guide to component signal strength at this concentration. For an accurate assessment a representative sample matrix would need to be obtained to understand the extraction efficiency from that matrix and validated for all components of interest, all possible side reactions, pH factors, and sample integrity for example. The extraction and chemical analysis methodology was guided towards the detection of glycerin, which was successful, as demonstrated by the large chromatographic peak observed in some of the samples. Even so, accurate quantitation is problematic without understanding the sample and extraction efficiency at a minimum.

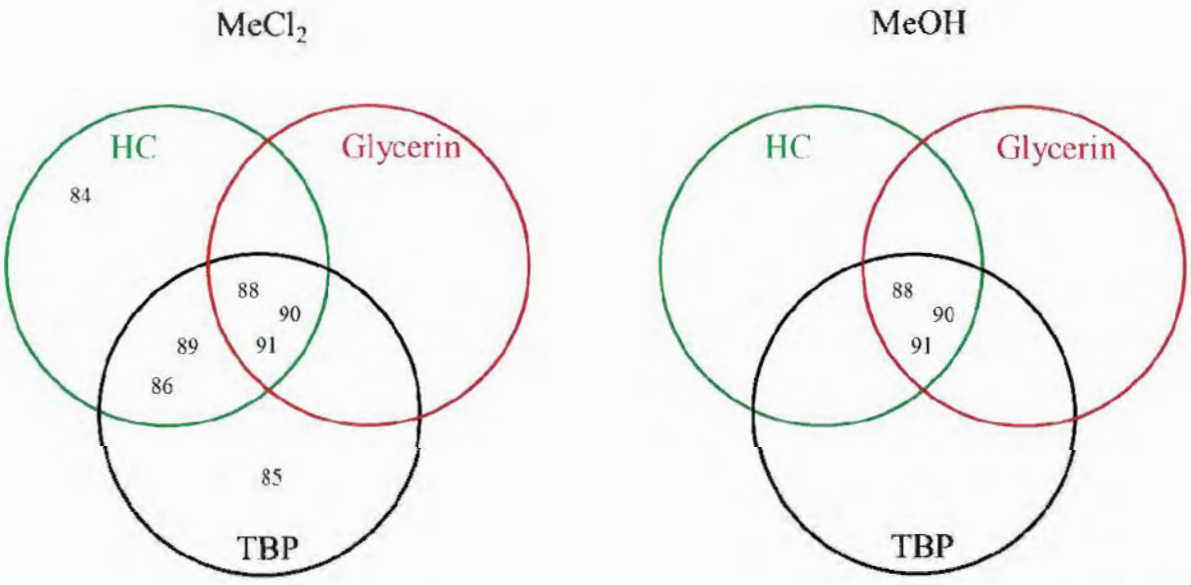


Figure 2. A simple Venn diagram highlighting some general trends/observations within and between the two solvent extracts. The Venn diagram is useful for presenting the common elements of the data results as shown by the areas of overlap among the circles. HC = alkane hydrocarbon type compounds, which are discussed later, ibid. Figure 6.

Appendix B

Completed ASO Occurrence Report Form OR-98620-2-17-16, “Holding Time Limit Concern for Some GC-MS Samples for ASR 9937”

ASO Occurrence Report Form

Title: Holding Time limit Concern for Some GC-MS Samples for ASR 9937	**Date: 2/17/16**

Unique Identifier: OR-98620-2-17-16

Primary Person Identifying Issue: Jon Wahl

Distribution: (Email and posting on ASO Share-Point)
LA Carr, ASO QE
DS Coffey, ASO QE
KN Pool, ASO Lead
T Trang Le, ASO Administrator –
ASR# 9937 file (when applicable)
Others: A Melville, J Wahl

Date Submitted to ASO Records:

Occurrence Description:
ASO test instruction, 98620-TI-001, *Rev. 0, PRF Canyon Sample Handling in Glove Box* in Section 4, Part 2, Organics Testing: Preparation for Gas Chromatography- Mass Spectrometry (GC-MS) lists holding time limits imposed by the project Statement of Work, Statement of Work for Contract 495170-40, Rev. 0, 236-Z PRF Canyon Floor Debris Sample Analysis (CHPRC to PNNL Supplier) FY16, 11/5/2015.

Semi-VOA in Soil – 14 days from date of extraction
VOA in Soil – 14 days from date of extraction

Seven samples were received for analysis under this ASR and were the following:

RPL Sample Number	Client Sample ID	Sample Description
16-0084	B33MK3 (F16-001-001)	**PRF Canyon Pan** E Sample 1 (solid/sludge)
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)

There were four samples that were MeOH extracted on 1/5/16 and analyzed by GC-MS on 1/23/16 (16-0086, 16-0088, 16-0089, and 16-0091) were outside the 14-day holding time limit window by 4 days.

Impact of Occurrence:

The impact of the holding time exceedance is unknown. The samples were extracted with both methanol and methylene chloride. All the methylene chloride extractions were analyzed within the 14 day holding time. Three of the methanol extracted samples were analyzed within the 14 day holding time. Evaluation of the data from the

methylene chloride extractions to the methanol extracted samples showed reasonable comparison for the 3 samples extracted within holding time and the 4 samples extracted 4 days after the holding time limit. The two extractions are expected to show different results based on the extraction efficiency of the different solvents.

Reportable per 10 CFR Part 21: No [X] Yes [ ]

Significant Condition Adverse to Quality? Yes ____ No X

Evaluated by: Karl N. Pool **Date:** 2/18/16
KN Pool, ASO Lead

Further Disposition:
☒ **No** ☐ **Yes** **If yes,** ☐ **Nonconformance?** ☐ **Deficiency?**

Date Occurrence Closed: 2/18/16

Signature/Date of Responsible QE: Deborah Coffey 2/18/16

Signature/Date of ASO Lead: Karl N. Pool 2/18/16

Comments:

Appendix C

Test Instructions List

Appendix C

Test Instructions List

Number	Rev.	Title	Signed/Effective Date
98620-TI-001	0	PRF Canyon Sample Handling in Glove Box	12/15/15
68453-TI-001	0	PRF Canyon Sample Gas Evolution Testing	1/22/16

Appendix D

Procedure List

Appendix D

Procedure List

Number	Rev.	Title	Signed/ Effective Date
PFP Floor Pan Evaluation QAPP	0	Plutonium Finishing Plant (PFP) Floor Pan Evaluation Project Quality Assurance Project Plan	12/16/15
RPL-GCMS-01	0	Gas Chromatography/Mass Spectrometry	12/16/15
RPL-NSD-01	0	Dissolution of PuO2 and Separation of Impurities Using Anion Exchange	10/30/15
RPL-NDS-01	1	Dissolution of PuO2 and Separation of Impurities Using Anion Exchange	1/7/16
Vac-General-001	1	Use of a Vacuum Line for Radioactive and Non-Radiological Materials and Operational Requirements with Reactive Gases	10/27/14
ADM-RSEG-BALANCES	1	Balance Performance Checks	9/13/12
RPL-OP-001	13	Routine Research Operations	6/25/15
ASO-QAP-001	9	ASO QA Plan	3/5/14
ASO-QAP-001	10	ASO QA Plan	2/4/16
PNL-AS0-052	2	Balance Performance Checks	9/11/12
PNL-AS0-058	1	ASO Data Reporting	9/29/15
PNL-AS0-062	2	Standards	5/12/14
PNL-AS0-065	1	Control Charting	4/12/13
PNL-AS0-066	0	Pipette Performance Check - Determination of Delivery Volume	10/27/03
PNL-AS0-070	1	Sample Management: Overview	9/30/15
PNL-AS0-071	1	Sample Management: Receipt and Inspection	9/30/15
PNL-AS0-072	2	Sample Management: Labeling, Login, and Work Authorization	9/30/15
PNL-AS0-073	1	Sample Management: Storage and Security	9/30/15
PNL-AS0-074	1	Sample Management: Distribution and Transfer of Unprocessed and Processed Samples	9/30/15
PNL-AS0-075	1	Sample Management: Disposition and Waste Disposal	9/30/15
PNL-AS0-076	0	ASO Records Management	8/23/12
PNL-AS0-077	0	ASO Document Control	2/3/14
PNL-AS0-079	0	ASO Occurrences, Deficiencies and Nonconformances	9/21/15
RPG-CMC-103	0	Water Leach of Sludge, Soil, and Other Solids	4/25/07

Number	Rev.	Title	Signed/ Effective Date
RPG-CMC-129	0	HN03-HC1 Acid Extraction of Solids Using a Dry-Block Heater	9/26/12
RPG-CMC-211	3	Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)	6/7/10
RPG-CMC-212	2	Determination of Common Anions by Ion Chromatography	2/1/16
RPG-CMC-290	0	Determination of pH in Soil Samples	4/29/14
RPG-CMC-450	2	Gamma Energy Analysis (GEA) and Low-Energy Photon Spectroscopy (LEPS)	12/11/12

Appendix E

Quality Assurance Plan

Appendix E

Quality Assurance Plan

Plutonium Finishing Plant (PFP) Floor Pan Evaluation Project: Quality Assurance Project Plan

(PFP Floor Pan Evaluation QAPP), Revision 0:

ISSUED BY PACIFIC NORTHWEST NATIONAL LABORATORY

Approvals:

Deborah Coffey, Project Quality Representative	12/16/2015 Date
Michael Minette, Project Manager	12/16/2015 Date
Karl Pool, Project Manager	12/16/15 Date
Steve Schlahta, Project Management Office Director	12/16/15 Date

Table of Contents

1.0 ACRONYMS

AP	Administrative Procedure
AQP	Acquisition Quality Procedure
B2B	Business to Business
CHPRC	CH2MHill's Plateau Remediation Company
DOE	Department of Energy
DR	Deficiency Report
FTIR	Fourier Transform Infrared Spectrophotometry
HASQARD	Hanford Analytical Services Quality Assurance Requirements Documents
HDI	How Do I - Standards Based Management System
IOPS	Integrated Operations System
M&TE	Measuring and Test Equipment
NCR	Nonconformance Report
OR	Occurrence Report
P-Card	Procurement Card
PFP	Plutonium Finishing Plant
PISA	Potential Inadequacy of the Safety Analysis
PNNL	Pacific Northwest National Laboratory
PR	Purchase Requisition
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QAS	Quality Assurance Services
SPME	Solid Phase Micro-extraction

2.0 DEFINITION OF TERMS

Approval	An act of endorsing or adding positive authorization or both.
Assessment	The act of monitoring or observing to verify whether an item or activity conforms to specified requirements. The term, "surveillance", is interchangeable with the term "assessment"
Calibration	Periodic and documented comparison to known standards or reference libraries to determine the accuracy of measuring and test equipment (M&TE), to determine the as-found condition and to adjust the equipment or to provide a calibration curve).
Condition Adverse to Quality	An all-inclusive term used in reference to any of the following: failures, malfunctions, deficiencies, defective items, and non-conformances. A significant condition adverse to quality is one, which if uncorrected, could have a major adverse impact on the environment, health or safety, mission, cost, or reputation of Pacific Northwest National Laboratory (PNNL) or CH2MHill's Plateau Remediation Company's (CHPRC) Plutonium Finishing Plant (PFP) 236-Z Canyon Stabilization Team.
Configuration Control	Knowing the present configuration and maintaining the knowledge by ensuring that document changes are accomplished only in accordance with accepted document control methods.
Corrective Action	Measures taken to rectify conditions adverse to quality and, where necessary, to preclude repetition.
Document	Any written or pictorial information describing, defining, specifying, reporting, or certifying activities, requirements, procedures, test instructions or results. A document is not considered to be a record until it satisfies the definition of a record as defined in this Quality Assurance Project Plan (QAPP).
Evaluated Supplier	A supplier who has been evaluated by Acquisition Quality Support Services and determined capable to provide items or services (e.g., special processes, calibration, analyses, and material control) and to implement specified QA measures, as defined in the procurement document.
File Plan	A systematic method of identifying the specific types of information maintained (record and non-record); file classification descriptions, disposition authorities, retention periods and disposition instructions.
Internal Assessment	An assessment to evaluate the degree of implementation and effectiveness of those portions of the project's QA Program retained under the organization's direct control and within its organizational structure.
Measuring and Test Equipment (M&TE)	Devices or systems used to calibrate, measure, gauge, test, inspect, or control in order to acquire research, development, test, or operational data or to determine compliance with design specifications or other technical requirements. M&TE includes installed process measuring or monitoring gauges and instrumentation used for non-data purposes.
Nonconformance (NCR)	A nonconformance is defined as a failure of items to meet requirements or specifications or to operate as expected; this includes using out-of-service equipment and M&TE used outside of a valid calibration interval and other types of calibration-related issues. NCR reports may result

	from occurrences that are determined by the Analytical Support Operations (ASO) laboratory Lead to be a significant condition adverse to quality requiring disposition of the item (e.g., reject and follow up with the supplier,), corrective action (e.g., repair, re-work), or justify use with no corrective action (e.g., use as-is) and tracking to closure. NCRs are issued when it is clear that an item has failed to meet requirements or specifications.
Occurrence	Occurrences are defined to be any issue affecting sample integrity or data quality. Occurrence Reports (OR) are tracked to document any issue of concern to bring the issue to the attention of project management and the customer and when applicable, to define appropriate corrective actions and/or paths forward.
Procurement	The processes used for obtaining of specified items or services from a supplier.
Procurement Documents	Purchase requisitions, purchase orders, PCard log purchases, memoranda purchase orders, store orders, inter-laboratory authorizations, drawings, contracts, specifications, or instructions are all used to define requirements for purchase.
Project Files	In the past working area file cabinets and drawers were used to contain project records; ASO requires hard copy records. For this project, the working area is a SharePoint site which will include documents in various states of completion. Scanned materials will be submitted as project records.
Procedures/ Documents	Procedures are used to define requirements, methods/processes, hazards/mitigation, and responsibilities for various activities. The procedures that have been identified for this project are listed in Appendices A and B.
QA Project Plan	A document that identifies the requirements and the QA implementing procedures that are expected to apply to project work. This QAPP also identifies any additional QA program and quality control (QC) activities, samples and requirements or acceptance criteria provided to PFP 236-Z Canyon Stabilization Team.
Quality	The degree to which an item or process meets or exceeds the user's requirements and expectations.
Quality Assurance (QA)	All planned and systematic actions necessary to provide adequate confidence that the program and the deliverables resulting from that program meet the PFP 236-Z Canyon Stabilization Team requirements.
Quality Assurance Clauses	Quality-related requirements that are added to a purchase request and/or purchase order associated with the procurement of an item or service is defined by PNNL QA Clauses.
Quality Control (QC)	The activities that are performed to ensure that data are of known and documented quality and meet the requirements or acceptance criteria for their intended use.
Receiving Inspection	An inspection performed in accordance with established procedures and inspection instructions, to verify by objective evidence such features as proper configuration; identification; dimensional, physical, and other characteristics; freedom from shipping

	damage; and cleanness.
Records	Information, regardless of its media (e.g., hard copy, electronic, microfilm), created or received in connection with PNNL business or research activities that documents research and administrative functions, policies, decisions, procedures, operations, or other activities, and which is preserved for its value.
Routine	A prescribed activity that is performed regularly (i.e., more than once).
Shall, Will, Must, Should, May	"Shall", “will”, and “must” denotes a requirement that is required to be met, "should" denotes a recommendation or guideline, and "may" denotes permission, but not a requirement.
Stop Work Request	A Stop Work request is a management tool to request stoppage of any activity that is not in substantial compliance with safety or QA requirements or procedures, or of any activity for which corrective action is not implemented in a timely manner.
Supplier	Any individual or organization that furnishes items or services in accordance with a procurement document. An all-inclusive term used in place of any of the following: vendor, seller, contractor, subcontractor, fabricator, consultant, and their sub tier levels.
Technical Oversight Representative	An individual technically knowledgeable in the requirements for the items or services requested or purchased.
Verify	To review, inspect, test, check, compare, audit, or otherwise determine, confirm, substantiate, or ensure that items, activities (including field and laboratory), data, data analysis and interpretation, processes, services, and documents conform to, or have been implemented in accordance with, specified requirements, procedures, plans, etc.

3.0 MANAGMENT REQUIREMENTS

3.1 SCOPE OF WORK

On September 28, 2015, debris collected from the Plutonium Recovery Facility (PRF) Building 236-Z canyon floor, Pan J, was observed to exhibit chemical reaction. The material had been transferred from the floor pan to a collection tray inside the canyon the previous Friday. Work in the canyon was stopped to allow Industrial Hygiene to perform monitoring of the material reaction. Canyon floor debris that had been sealed out was sequestered at the facility, a recovery plan was developed, and drum inspections were initiated to verify no additional reactions had occurred. On October 13, in-process drums containing other Pan J material were inspected and showed some indication of chemical reaction, limited to discoloration and degradation of inner plastic bags. All Pan J material was sealed back into the canyon and returned to collection trays. Based on the high airborne levels in the canyon during physical debris removal, Encapsulation Technology Glycerin Solution a.k.a. ETGS) was used as a fogging/lock-down agent. On October 15, subject matter experts confirmed a reaction had occurred between nitrates (both plutonium nitrate and aluminum nitrate nonahydrate (a.k.a. ANN) are present) in the Pan J material and the ETGS fixative used to lower airborne radioactivity levels during debris removal. Management stopped the use of fogging/lock-down agents containing glycerin on bulk materials, declared a Management Concern, and initiated the Potential Inadequacy in the Safety Analysis (PISA) determination process. Additional drum inspections and laboratory analysis of both reacted and unreacted material are planned.

This document has been prepared to address the basic quality aspects and protocols needed to support PNNL's participation in the analysis of these materials. The general objectives for the PNNL work are for the evaluation of residual materials that have accumulated in the PRF floor pans so CHPRC can determine if the addition of glycerin fog may have caused the residuals to become reactive. Additionally, PNNL is to provide technical expertise to CHPRC on the reactivity of the residuals with the glycerin fog. There is a potential for chemical analysis of radioactive materials and thermal reaction studies.

3.2 ORGANIZATION

Purpose

This section identifies the organizational structure, functional responsibilities, levels of authority, lines of communication, and organizational interfaces (internal and external) of the CHPRC Floor Pan Evaluation Project to assure that quality-related activities are performed by the responsible organization/staff. Referenced PNNL documents in this plan are listed in Appendices A and B.

Requirements

Persons or organizations responsible for assuring that the *Plutonium Finishing Plant (PFP) Floor Pan Evaluation Quality Assurance Project*

Plan (QAPP) have been established, and for verifying that activities affecting quality have been correctly performed will have sufficient authority, access to work areas, direct access to management, independence from cost and schedule considerations, and organizational freedom to:

- identify quality-related problems
- initiate, recommend, or provide solutions to quality-related problems through designated channels
- verify implementation of solutions
- control further processing, delivery, installation, or use of an item or service until final disposition of a nonconforming item or condition adverse to quality.

Differences of opinion involving QAPP requirements will be brought to the attention of the Project Managers and, if not resolved, will be elevated to successively higher levels of management.

If necessary, a pause in work or a stop work request will be issued for activities not in compliance to the QAPP or for activities for which corrective action is not implemented in a timely manner, as determined on a case-by-case basis. Completion of appropriate corrective action(s) will be verified before work continues or a stop work request is lifted.

PNNL's Worker Safety and Health Management & Operations (M&O) Divisions have been established to provide a safe and healthful workplace for all staff, visitors, vendors and subcontractors. Division resources aid researchers in the identification, evaluation, and control of hazards in the workplace by providing direct technical assistance to those conducting work. Elements of the project safety requirements are implemented through workflows, and work controls delivered in How Do I (HDI), electronic tools, and organization-specific manuals and procedures. Worker safety and health at PNNL is a primary responsibility of every staff member.

All PNNL staff have authority to stop unsafe work within their areas of responsibility, and will not perform work that is considered unsafe.

The project's organizational structure and responsibility assignments will be such that:

- quality is achieved and maintained by those who have been assigned responsibility for performing work, and
- quality achievement (technical and Quality Engineer [QE] review) is verified by those not directly responsible for performing the work.

Project staff performing work are responsible for the quality of their work and will be knowledgeable of the requirements for the work they perform and the capability of the tools and processes they use.

3.2.1 PNNL Organization

PNNL is managed by the Director of PNNL. Associate Laboratory Directors, including the Operations Director, report directly to the Director of PNNL. The Operations Director has direct access to the Director of PNNL and reports at a management level such that required authority and organizational freedom are provided, including sufficient independence from cost and schedule considerations, to achieve PNNL quality performance objectives.

The project Quality Representative reports to the Manager within the Planning and Performance Management Directorate. The manager of the Planning and Performance Management Directorate reports to the Operational Systems Director, who reports directly to the PNNL Laboratory Director. Therefore, the project Quality Representative can be considered to be independent from the work being performed. The Quality group maintains QE staff and quality administrative procedures to support supplier evaluations, inspections, lead auditor qualification, and internal and external assessments. The project Quality Representative will have appropriate knowledge and experience in QA program requirements and program implementation and in the technical areas to assure that adequate quality for the intended use of the data is defined and attained.

Responsibilities

The responsibilities and authorities associated with PNNL organizations and management positions responsible for achieving and maintaining quality are defined within HDI. These specific responsibilities and authorities are described as *Roles, Responsibilities, Accountabilities, and Authorities* within HDI.

3.2.2 PFP Floor Pan Evaluation Project Organization

PFP Floor Pan Evaluation Project organization is depicted in Figure 1. The project is sub-divided into phases based on the priorities and type of analytical methods, and technical task leaders are assigned based on their technical expertise.

The relationship between the project staff and other organizations is depicted in Figure 2. PNNL uses a matrixed organizational system. This chart shows the managerial relationship from the PNNL Laboratory Director through the Energy & Environment Directorate down to the Project Managers. It also shows the managerial relationship from the Laboratory Director through the Quality organization to the Quality Representative(s). The Project Management Office Director is responsible for oversight of the risks associated with this and other projects that involve chemical, biological and nuclear work. The Project Managers are the primary points of contact for the customer on all matters concerning management issues, technical aspects of the project,

and data reporting. The Quality Representative is the point of contact for questions concerning implementation of the QAPP, conditions adverse to quality and corrective actions. Responsibilities related to the QAPP are defined in the various sections of this document and the referenced procedures. The individuals responsible for establishing and executing the QAPP may delegate any or all of the work to others, but will retain responsibility thereof. Project staff performing work need to be trained to the QA Program and have completed a read and sign training assignment.

Responsibilities related to specific project activities are defined identified for key personnel. At a minimum, key personnel will include the Project Managers, Task Leads, and the Project Quality Representative.

Reports will be provided for individual analyses and no summary report is necessary. Preliminary results are expected by January 8, 2016. ASO final reports and any additional information are due at the end of February, 2016. PNNL is to dispose of the wastes.

Task 1- ASO Analysis Reports – K Pool (Task Lead)

For 8-10 radioactive solid PRF Floor Pan Samples (containing Special Nuclear Materials), conduct the following analyses to the HASQARD Quality Standards:

- ICP metals (at a minimum arsenic, barium, cadmium, chromium, lead, iron, selenium, and silver)
- Mercury by ICP/MS
- Anions (nitrate and phosphate at a minimum, chloride, fluoride, nitrite, and sulfate if it is part of the standard analyte list)
- Isotopic uranium
- Isotopic plutonium
- Isotopic americium
- GEA (Cs-137, Co-60, Eu-152/154/155 at a minimum, plus anything else that shows up)
- Corrosivity (50/50 weight % with water)

Task 2- Gas Chromatography–Mass Spectrometry (GC-MS) – K Pool and J Wahl (Task Leads)

PNNL will analyze PRF Floor Pan samples to evaluate if glycerol by solid phase micro-extraction (SPME) and GC/MS is possible for this application. Methods of using solvent extraction of the solid and pulling the organics into the solvent will also be considered. This will leave the radionuclides behind in the aqueous phase and is expected to reduce the radioactive to levels where a non-rad GC/MS can be used.

The task deliverable is to identify glycerol and its related oxidized forms in the 8-10 samples above. The deliverables will be individual reports. This work will be conducted under the ASO QA Program. PNNL is to dispose of the wastes.

Task 3- Technical Expert Support- M Minette (Task Lead)

PNNL will provide technical experts to consult and conduct technical support activities. The staff work will be coordinated by PFP leadership to help quickly resolve the technical issues related to chemistry and reactivates of the PRF waste materials. Experts to be provided will include but not be limited to R Scheele, C Delegard and B McNamara.

Task 4 – Organic and Potential Other Analyses of Captured Gases KN Pool and J Wahl (Task Leads)

Using the captured reaction gasses still contained in the inner Pan J Sample 2 bag, PNNL will:

- Collect 2 each SPME fiber samples (a needle system that inserts a fiber into the gas space) and analyze those fibers in the GC/MS for organics
- Collect 1 each vapor sample for GC/MS for organics
- Collect 1 each vapor sample for potential runs by Fourier Transform Infrared Spectrophotometry (FTIR)
- Provide a preliminary report, and if necessary, a final report for the SPME work and for the FTIR work

Task 5 – Gas Pressure Rates and Gases Determinations – Task Lead- M Minette

PNNL will use small portions of the sample materials from either or both of Pan J Samples 1 and/or 2 to place in a container that is attached to a tube that would monitor pressure over time. This would give the gas generation rate. The container may be water heated to move the material into the reaction state. Connected to the tube will be a valved tube that will allow us to collect reaction gasses into a vacuum cell. The vacuum cell will then be analyzed on the radiologically-controlled FTIR system.

Responsibilities

Significant responsibilities include:

Quality Representative

Interpreting PNNL QA Project requirements and determining appropriate application.

Interpreting the PFP requirements and determining appropriate application.

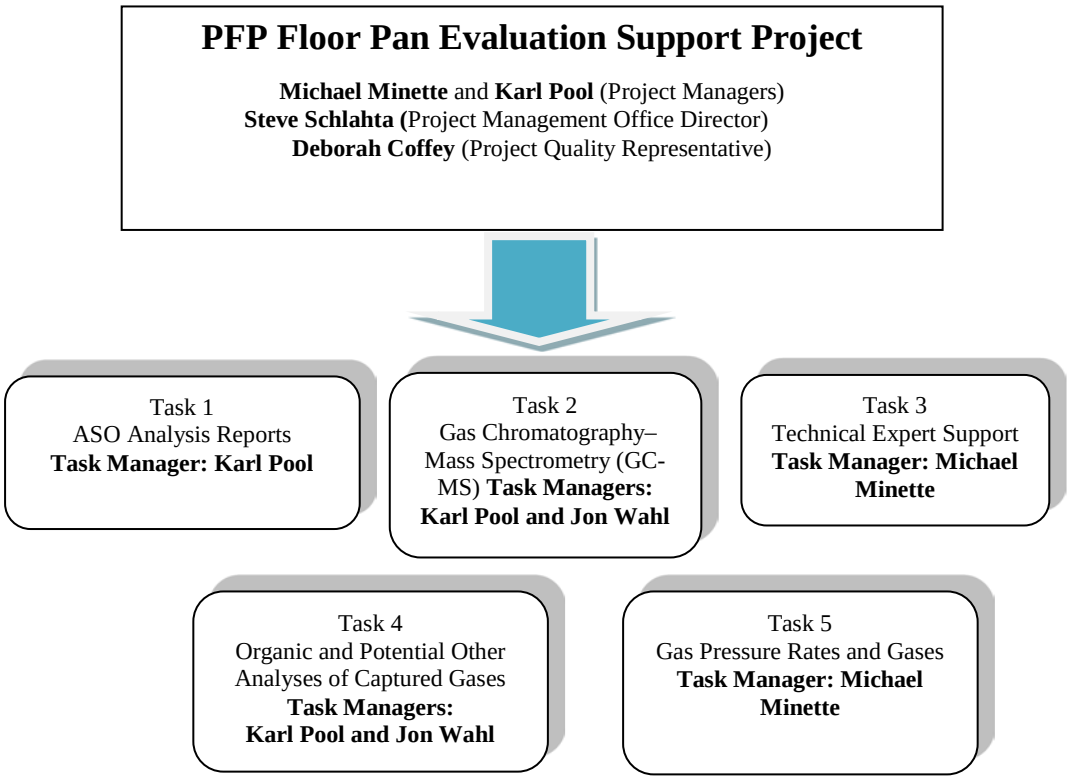
Providing quality-related training support to project management and staff, as needed, to meet performance, qualification, and compliance objectives.

Utilizing appropriate procedures and staff to support supplier evaluations, nondestructive inspections, and lead auditor qualification, when necessary, when required by the project.

	Coordinating the activities of other Quality and Assurance Services staff that may provide assistance to the project. Verifying compliance with QA requirements and assisting the Project Managers and staff in application of the QAPP. Reviewing and maintaining the QAPP. Participating in quality planning, assessment, and continuous improvement efforts as needed. Identifying conditions adverse to quality requiring timely corrective action. Performing activities defined in implementing procedures/documents. Interfacing with customers on QA matters, as appropriate. Reviewing the project QA requirements and advising the Project Managers concerning those requirements. Providing independent reviews of work in progress via witnessing or surveillance activities, reviewing data and performing data quality reviews, and performing technical system audits as directed by the Project Managers. Coordinating and participating in internal or external assessments/audits of the quality program as directed by the Project Manager.
Project Managers	Overall project management operations in accordance with the QAPP and customer agreements/contracts. Back-up for each other when one is unavailable. Assures that staff comply with the requirements of the QAPP. Providing resources needed to ensure the quality of laboratory operations. Appointing personnel to key positions and identify delegates to key positions. Reviewing, providing input to, and approving the QAPP. Requesting project surveillances, assessments, audits, and data reviews as deemed necessary or warranted.
Project Staff	Responsible for the quality of work, knowing the requirements for the work performed, and the capability of the tools and processes used.

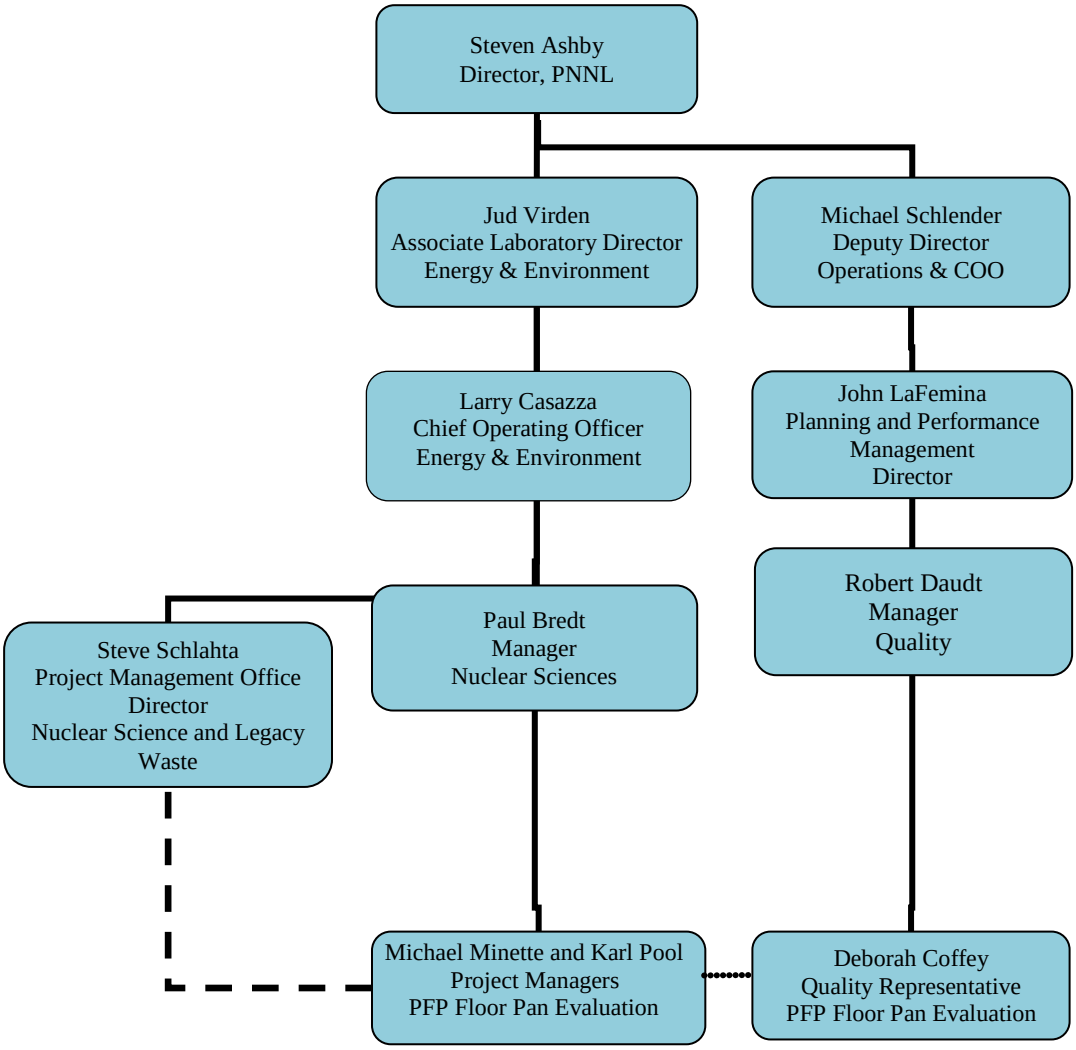
Informing the Project Manager or the Quality Representative when encountering situations or conditions that could adversely impact the quality of work.

Figure 1
PFP Floor Pan Evaluation Project Organization Chart



Staff listed above and others currently participating in the project are listed in Appendix C. Additional staff may be recruited in the future as needed.

Figure 2. PNNL Organization Chart



Dashed line denotes Project Management Office oversight
Dotted line denotes QA support

3.3 QUALITY SYSTEM

3.3.1 Quality Assurance Project Plan

Purpose

This section describes the quality assurance project requirements and structure. Using a graded approach, activities affecting quality will be planned and accomplished under suitably controlled conditions. This QAPP and ASO-QAP-001, Rev. 9, *Analytical Support Operations (ASO) Quality Assurance Plan*, ASO procedures and project 68453 procedures referenced herein, apply to all Task 1, 2, and 5 project activities. The ASO QA Program has been demonstrated to be compliant with DOE/RL-96-68, *Hanford Analytical Services Quality Assurance Requirements Document* (HASQARD). There are no customer-specific quality requirements for Task 3 activities. The project has adopted compliance to the PNNL HDI requirements and guidelines.

Requirements

PNNL's quality program as implemented through HDI conforms to the requirements of 10 CFR 830, *Energy/Nuclear Safety Management*, Subpart A, *Quality Assurance Requirements*, and Department of Energy (DOE) Order 414.1D, *Quality Assurance*. PNNL has adopted and implemented a Quality Assurance Program based on ASME/ANSI NQA-1-2000, Part I and Subparts 2.7 & 4.2 as implemented through a graded approach throughout PNNL's Core Business Processes and Management & Operations programs. Specific QA requirements for PNNL projects are defined in lower-tier project-specific QA plans, such as the QAPP described by this document.

This QAPP has been designed to comply with PNNL requirements and the PFP 236-Z Canyon Stabilization Team's expectations for activities and services performed by the project, and implemented commensurate with PNNL's responsibility for:

- health and safety of workers and the public
- reliability and continuity of operations
- acquisition of valid data.

This QAPP will be prepared, reviewed, approved, issued, implemented, and maintained. The QAPP will identify the requirements specific to the project, including project QA and technical implementing procedures, and references to applicable requirements of HDI.

Revisions to HDI and the QAPP will be reviewed to determine if changes are necessary to the referenced procedures.

The project QA and technical implementing procedures are identified in Appendix B. Due to the nature of the project scope and accelerated timeline, some technical procedures may be generated after the approval of the QAPP and therefore will not be included in the listing. Technical procedures used may be located within the project record files. Other quality affecting activities are governed by HDI, acquisition procedures,

Quality Assurance Services (QAS) procedures, and Quality Management – Management & Operations Program procedures applicable to QAS staff performing audits, surveillances, and evaluations related to acquired items and services, and project activities.

Analytical activities that are currently associated with the Analytical Services Operation (ASO) will follow the established ASO QA program and implementing procedures. The QA program and implementing procedures are based on and are intended to meet the requirements of the Department of Energy's *Hanford Analytical Services Quality Assurance Requirements Documents, DOE/RL-96-68* (HASQARD).

Responsibilities

Significant responsibilities include:

Project Manager

Provide input to, review, and approve the QAPP.

Monitoring the adequacy and effectiveness of the QAPP.

Interfacing with the PFP Floor Pan Evaluation Project team to assure QA requirements are clearly defined and documented for project activities.

Planning activities adequately to assure accomplishment of project objectives and milestones, and informing staff of project requirements.

Provide input to, review, and approve the QAPP.

Receives direction from the PFP 236-Z Canyon Stabilization Team and coordinates with the staff to execute requested and authorized work.

Assigns technically competent technical staff and resources to tasks, including technical reviewers.

Reviews project deliverables.

Quality Representative

Reviewing and approving documentation as required by the QA implementing procedures, HDI, and appropriate acquisition procedures. This review includes determining whether changes in HDI or the QA implementing procedures impact this QAPP.

Planning and implementing QA activities.

Making sure activities comply with the requirements of this QAPP and the expectations of the PFP 236-Z Canyon Stabilization Team.

Assisting the Project Manager in the QA planning process, including identifying applicable quality requirements, and assist in the development of the QAPP and implementing procedures.

3.3.2 Quality System Goals and Objectives

The Project quality system goals and objectives are as follows:

- To assure that laboratory results provided to the PFP Floor Pan Evaluation Project are reliable and scientifically sound.
- To establish a formal quality assurance project plan that is based on industry standards and the expectations of the PFP 236-Z Canyon Stabilization Team.
- To use procedures that is valid, dependable, reproducible, and adequate for the intended purpose.
- To monitor operational performance.
- To maintain quality, excellence and integrity.
- To provide the necessary training for personnel to carry out the provisions of the quality system.

3.4 DOCUMENTS

3.4.1 Procedures and Plans

Purpose

This section identifies the requirements for the preparation, review, approval, and use of implementing documents. Implementing documents are used to make sure that activities affecting quality will be performed consistently and correctly. Activities performed to comply with the QA requirements are prescribed in PNNL lab-level work flows and work controls referenced in Appendix A of this plan and the administrative and technical Procedures listed in Appendix B. Technical activities affecting quality make use of procedures or instructions when, without these documents, there would be a reasonable chance of performing the work incorrectly and obtaining unacceptable or undesirable results. The type and use of these documents and the level of detail required should be appropriate to the nature and circumstances of the work being performed and consequences of errors.

This section is closely related to section 3.4.2, *Document Control*, which describes how these documents are controlled (i.e., distributed).

Requirements

Activities affecting quality will be prescribed by quality (administrative) and technical procedures. Analytical activities that fall under the Analytical Services Organization (ASO) Quality Program will utilize that program's administrative and technical procedures. Due to the short timeframe for this project, it is not expected that any newly created procedures will be needed. For procedures that currently exist, the existing format is acceptable. Work will be performed in accordance with these approved documents.

Staff using a procedure have the authority to immediately deviate from or curtail the use of the procedure only when personnel hazard or equipment damage is imminent. Staff will secure processes, equipment, or systems as necessary to mitigate the situation and will notify other impacted workers. Staff will inform Project management of the situation as soon as reasonably possible. Project management should evaluate the situation to determine any impacts on the project results, similar procedures, processes, equipment, or systems.

Responsibilities

Significant responsibilities include:

Project Staff

Generating test instructions and procedures for the activities performed in accordance with HDI requirements or the ASO Quality Program requirements.

Performing reviews of procedures and/or test instructions to ensure completeness and adequacy for the work activity to be performed.

Using only approved test instructions and procedures for the activities performed.

Immediately deviate from or curtail the use of a procedure if personnel hazard or equipment damage is imminent. Secure processes, equipment, or systems as necessary to mitigate the situation and notify other impacted workers and Project management.

Quality Representative

Reviewing and approving procedures and instructions, to assure that QA requirements and objectives are adequately addressed.

3.4.2 Document Control

Purpose

This section identifies the requirements for the control of documents that prescribe activities affecting quality (e.g., instructions, procedures) and changes to those documents, to assure that the versions used are complete, correct, current, and available at the location of the work.

Distribution is controlled to make sure that document holders have the latest approved version. Workplace copies of technical documents are controlled to make sure that they are at the workplace and that they are current.

Requirements

Changes to implementing documents and documents that specify technical or quality requirements will be reviewed and implemented in accordance with HDI workflow, *Create or Update Procedures or Other Work Instructions.*

There will be limited release and distribution of the implementing documents. The distribution may be accomplished either in electronic or hardcopy form and must follow the “business-sensitive” conduct described below in section 3.8. The preferred method is electronic. The project staff will have access to a PFP Floor Pan Evaluation Project SharePoint site. All of the data, data reduction, reporting of spreadsheets, and final reports will be accomplished by maintaining this SharePoint site to which only current versions of documents are maintained. The implementing documents will be controlled in accordance with HDI work flow, *Manage Controlled Documents*.

ASO Occurrence Reports (OR), Deficiency Reports (DR), and Nonconformance Reports (NCR) will be used in accordance with PNL-ASO-079, Rev. 0, *ASO Occurrences, Deficiencies and Noncomformances*, to document any planned or unplanned purposeful deviation from a

prescribed process. Project-level conditions will be documented using a project-level form for ORs, DRs, or NCRs and these forms can be found on the project SharePoint site. Planned deviations will be approved by the Quality Manager, and will not adversely affect the quality of products released to the PFP 236-Z Canyon Stabilization Team. If an unplanned deviation results in a situation where the quality or usability of data or item(s) are indeterminate or unacceptable, or where the project- or activity-specific products or processes do not meet established requirements, section 3.10, *Corrective Action*, will be followed.

Responsibilities

Significant responsibilities include:

Quality Manager/Representative

Approving QA implementing procedures at the project level. Reviewing and approving implementing procedures/documents as required and as requested.

Project Manager

Controlling the review, comment resolution, approval, and distribution for test instructions and procedures. Assuring that project staff works to current controlled copies of instructions and procedures.

Project Coordinator

Distributing QA implementing procedures, technical procedures, and other project-specific documents.

Project Staff

Performing work only to the most recent revision of a document located at the workplace.

Notifying project management when a procedure or document cannot or should not be followed as written, or has inaccurate information (e.g., incorrect description of equipment or software).

Documenting planned and unplanned purposeful deviations from procedures and obtaining approval.

3.5 REVIEW OF REQUESTS AND CONTRACTS

Purpose

This section identifies the requirements associated with meeting established PFP 236-Z Canyon Stabilization Team goals in terms of performance, schedule, and budget by managing risks, uncertainties, expectations, constraints, and resources. The Project Manager integrates all aspects of the work, makes available the proper knowledge and resources when and where needed, and above all, produces the expected work in a timely, cost-effective manner.

Requirements

The Project Manager will plan the scope of work in accordance with the HDI *Plan Project* workflow, and *Limitations on Staff and Project Activities* exhibit within the *Basic Staff Practices* work control. It is the project's policy that staff will not engage in activities that would diminish confidence in its competence, impartiality, judgment or operational integrity.

Implementing the Worker, Safety and Health (WS&H) program and controlling special risks in the facility will be in accordance with the HDI *Integrated Operations System (IOPS),* and *Conduct Initial Risk Assessment* and *Develop Special Controls for Research and Development Activities* workflows, as appropriate.

Responsibilities Significant responsibilities include:

Project Manager Planning and executing work in accordance with the above requirements.

Project Staff Executing work in accordance with the above requirements and established work procedures.

3.6 SUBCONTRACTING OF WORK

Purpose This section identifies the requirements associated with subcontracting customer authorized work. It is not applicable to purchases of items or services associated with performing the work authorized by the customer, e.g., calibration of supporting equipment.

Requirements It may be required at some point to subcontract customer authorized work to an outside supplier due to unforeseen workload or incapacity. In this case, the work will be subcontracted to an organization capable of performing the work in accordance with the customer requirements. The applicable customer requirements will be passed to the subcontracted supplier. However, there are no plans at this time to subcontract any work; this is especially unlikely due to the short period of performance for the assigned tasks.

For quality affecting items and services, acceptable suppliers are those that have been evaluated by the Quality Assurance Services Department as described in section 3.7, *Purchasing Services and Supplies*.

The project will advise the customer in writing of the intent to subcontract any part of the project scope of work, and will obtain the approval of the customer, preferably in writing (the approval will be documented in some manner).

The project is responsible for the subcontractor's work, except when it is the customer that specified which subcontractor to be used.

Note: Samples may be transferred to a laboratory of the customer's choosing without a subcontract or supplier evaluation based on specific direction from the customer.

Responsibilities Significant responsibilities include:

Project Manager Communicating and obtaining approval for proposed subcontracted work.

Subcontracting work to an approved supplier.

Communicating with subcontractor regarding work performed.

3.7 PURCHASING SERVICES AND SUPPLIES

3.7.1 Procurement Document Control

Purpose

This section identifies the necessary controls exercised over procurement documents to assure that the documents adequately specify the quality and technical requirements needed to obtain an item or service that is satisfactory for its intended use. The correct specification of requirements will also help prevent schedule delays and cost increases resulting from receiving an incorrect item or service. The controls are intended to make sure that the item or service is clearly and correctly specified, that the supplier will be capable of providing a quality product, that exceptions or changes are satisfactory to PNNL, and that adequate evidence of item or service quality will be provided and verified.

The planning for these activities is done during the preparation of the purchase requisition (PR).

Requirements

The PR should be prepared by staff who have the appropriate background and information related to the items or services to be procured. The PR will contain all technical and quality information necessary to specify clearly the required items or services. For off the shelf items the manufacturer's model number and/or catalog number and a brief description are sufficient.

As appropriate to the procurement, QA clauses will be invoked to require such actions as pre-award evaluation of the supplier, independent receiving inspection, source inspection or source surveillance per the following HDI workflows: *Acquire Product or Service via Purchase Order-Subcontract*, *Perform At-Site Inspection*, and *Receive and Inspect Product or Service*.

The Technical Oversight Representative and a Contracts Representative will approve the PR. Other reviews and approvals may be necessary and may include Laboratory Safety, the Pressure Systems Engineer, and other disciplines, as appropriate, per the HDI workflow, *Acquire Product or Service via Purchase Order-Subcontract*. If the procurement is to subcontract customer work, the customer will also approve (see section 3.6).

Items or services that do not require any quality requirements may be purchased using the Procurement Card (P-Card) or Business-to-Business (B2B) process. Requirements for P-Card and B2B purchases, including prohibited purchases are specified in the HDI workflows, *Acquire Product or Service via P-Cards* and *Acquire Product via Business-to-Business (B2B).*

Responsibilities

Significant responsibilities include:

Technical Oversight Rep.

Making sure that the procurement document contains required technical specifications and quality assurance provisions appropriate to the nature, and complexity of the item or service.

Obtaining review and approval of the procurement document by required staff and/or organizations.

Supporting the Contracts Specialist with resolution of procurement and subcontract issues.

Quality Representative

Reviewing and approving requirements for all items or services on each PR presented for review.

Supporting Project staff in determining correct and adequate quality requirements during the procurement planning process.

Assisting with the determination if items or services may be purchased with a P-Card or B2B Program.

3.7.2 Control of Purchased Items and Services

Purpose

This section identifies the controls exercised over procured items and services to make sure that they conform to specified requirements. These controls help to make sure that purchased items and services conform to the procurement document requirements.

Pre-award evaluations are performed before the contract is awarded to determine the supplier's capability to provide items or services in accordance with the procurement document requirements. Source verification activities are used primarily to help preclude delivery of items or services that have hidden defects or other characteristics difficult to verify after delivery, or which could cause project delays/costs or failure to meet project requirements.

Receiving inspection activities are performed to verify conformance of the item or service and supplier documentation to procurement document requirements.

The extent to which these controls are applied is dependent on the importance, complexity, and quantity of the item or service, the need to confirm the quality of the item or service, and the supplier's quality performance.

Requirements

Determinations will be made of the need for evaluated supplier evaluation, source verification, supplier furnished documents, supplier nonconformance reporting, and receiving inspection. Appropriate QA clauses will be included in procurement documents to meet the determined needs as required by the HDI workflow, *Acquire Product or Service via Purchase Order-Subcontract*.

Verifications (i.e., supplier evaluations, source verifications, and receiving inspections), when required, will be performed as early as practical by qualified personnel in accordance with the Acquisition Quality Support Services procedures: AQP-03, *Desk Surveys and At-Site Evaluations*, AQP-18, *Quality Inspection of a Deliverable* and AQP-19, *Quality At-Site Source Inspection/Test or Surveillance*. Verifications will not relieve the supplier of the responsibility for the verification of quality achievement.

Supplier documentation will be reviewed and approved or accepted in accordance with the Acquisition Quality Support Services procedure AQP-06, *Review of Supplier/Subcontractor Submitted Documents*.

Determinations will be made of the acceptability for use of the purchased items and services in accordance with HDI workflow, *Receive and Inspect Product or Service*.

Continuing supplier performance is evaluated and tracked by the Acquisition Quality Support Services Point of Contact in accordance with procedures AQP-03, *Desk Surveys and At-Site Evaluations*, and AQP-16, *Pacific Northwest National Laboratory's Evaluated Suppliers Listing and Integrated Supplier Information Services (ISIS)*.

Responsibilities

Significant responsibilities include:

Project Staff

Implementing requirements for the receipt and control of purchased items and services.

Coordinating independent receiving inspection activities for determining item acceptability for use, as necessary, including the use and monitoring of process blanks.

Quality Representative

Coordinating the performance of pre-award surveys, source verifications, and periodic audits of suppliers.

3.8 SERVICE TO THE PFP 236-Z Canyon Stabilization Team

Purpose

This section identifies the requirements associated with protecting the confidentiality of information. It is the project's policy to protect the confidentiality of the PFP 236-Z Canyon Stabilization Team information. The information will be protected and communicated in a "business-sensitive" manner.

Requirements

In regard to confidentiality, the project staff will **not**:

- Share or release specific data to parties other than the PFP 236-Z Canyon Stabilization Team members and support members, unless specifically requested in writing. Final reports may not be publically released unless otherwise specified by the PFP 236-Z Canyon Stabilization Team. Currently, Task reports will have a limited release and are not expected to need to be cleared through ERICA.

- Divulge project confidential information to persons within DOE or other PNNL staff without the need to know for business purposes.

Responsibilities

Significant responsibilities include:

Project Manager

Communicating to staff any PFP-specific requirements for information security. Only the Project Manager of Task 1, Task 2 and Task 4 (Karl Pool) will release analytical data to CHPRC. Only the Manager of Task 3 and Task 5 (Mike Minette) will release technical expert support information to CHPRC.

Project Staff

Discussing or releasing confidential or proprietary information to only those persons authorized as discussed above.

3.9 CONTROL OF NONCONFORMING ITEMS AND TESTING

Purpose

This section identifies the controls established for the documentation, and disposition of nonconforming items to prevent their inadvertent use.

Requirements

Nonconforming items will be identified, documented, controlled, evaluated, and dispositioned. The HDI workflow, *Calibrate Equipment for Use*, will be followed for nonconforming M&TE. The HDI workflow, *Receive and Inspect Product or Service* and work control *Basic Laboratory and Operations Practices* (subsection *Properly Handle Equipment and Materials*) will be followed for purchased items that are determined to be nonconforming.

Test procedures will identify appropriate actions for testing activities that do not conform to specified criteria (i.e., calibration, QC measures). Procedures for data review and reporting will be followed for the disposition of test results found to be nonconforming, see section 4.10, *Reporting of Results*. Testing activities that are found to be nonconforming after release to the PFP 236-Z Canyon Stabilization Team will be addressed in accordance with section 3.10, *Corrective Action.*

Responsibilities

Significant responsibilities include:

Project Manager

Approving the disposition of nonconforming items.

Project Staff

Identifying, segregating, or otherwise controlling and documenting nonconforming items.

Withholding nonconforming items from use until approval of the disposition has been obtained and any necessary repair or rework completed.

Identifying any results potentially affected by the nonconforming item, and determining the impact.

Implementing actions to resolve the nonconformance.

3.10 CORRECTIVE ACTION

Purpose

This section identifies requirements when conditions adverse to quality are recognized. Conditions adverse to quality are reported and corrective action is taken to minimize the likelihood of recurrence.

Requirements

Conditions adverse to quality will be documented and corrected in a timely manner. Conditions adverse to quality may also be found through various assessment and/or review activities. These conditions will be documented in accordance with the HDI workflows: *Conduct Internal Assessment or Audit; Conduct Critique and Cause Analysis; Develop Corrective or preventive Actions;* and *Complete Corrective Actions and Evaluate Performance.*

Conditions adverse to quality will be documented and corrective action taken to prevent recurrence. Conditions adverse to quality will be evaluated to determine if it is a significant condition adverse to quality. The determination of when a condition adverse to quality is significant is partly a function of the significance of the items; including data that the condition impacts or could impact in the future if not corrected. A graded approach is used for the correction and prevention of conditions adverse to quality. This graded approach is addressed within the HDI workflows identified above.

When results have been determined to be negatively impacted due to an adverse condition, the Project Manager will notify the PFP 236-Z Canyon Stabilization Team in writing and address the impact on the data. Additionally, the PFP 236-Z Canyon Stabilization Team will be notified if corrective actions are significant in terms of cost or schedule.

Responsibilities

Significant responsibilities include:

Project Staff

Notifying the Project Manager or Quality Representative when a condition adverse to quality is identified.

Participating in the corrective action process and assuring that corrective action is implemented within the scope of their responsibility.

Project Manager

Determining in consultation with the Quality Representative as necessary, when documentation should be initiated for conditions potentially adversely affecting quality.

Notifying the PFP 236-Z Canyon Stabilization Team of any negatively impacted results.

Notifying the PFP 236-Z Canyon Stabilization Team if corrective actions will result in significant cost or schedule changes.

Scheduling follow-up assessments, as deemed necessary, when adverse conditions are noted.

Assuring that corrective actions are completed in a timely manner.

Quality Representative

Verifying adequate, appropriate, and satisfactory implementation of corrective actions as required or requested.

Concurring with planned actions in response to corrective action requests.

Escalating corrective action issues to management attention when corrective or preventive action has not been effective.

3.11 RECORDS MANAGEMENT

Purpose

This section identifies the requirements for maintaining a records system to assure availability of documented evidence of activities performed. Records systems need to provide for protection against loss, damage, or deterioration of records. The records system also needs to provide for the identification, storage, retrieval, and final disposition of these records.

Requirements

The project records system will be implemented in accordance with the HDI workflow, *Manage Project Records*. Included are in-process requirements for record generators and custodians to follow while generating and maintaining records. Also included are transfer and storage requirements once activities documented by the records are complete.

When not in use, records will be stored in a manner to protect from damage, loss, or access by those without the business need. Stored records must also be readily retrievable.

Records that are stored in an electronic form during data processing will be backed-up to prevent inadvertent loss.

Records that are stored in electronic form will be retained in PNNL's records system and may be accessed for the lifetime of the record. This project will use a SharePoint to collect records that will be submitted as final project records.

Technical records will contain sufficient information to facilitate, if possible, identification of factors affecting the results uncertainty, to investigate the cause of poor analysis performance, and to enable the analysis to be repeated under conditions as close as possible to the original conditions. Staff will record observations, data, and calculations at the time they are made and will make sure that the information is traceable from the original sample to the final results, including: identification of the staff performing the activity, the date, traceability to the instrumentation, calibration, standards, and software (as applicable). For hardcopy records, additions and corrections will be initialed and dated by the person making

the change. Handwritten records will be in ink which can be scanned for electronic storage or transmission.

Responsibilities Significant responsibilities include:

Project Manager Identifying the appropriate schedule and retention period for records with the assistance of the PNNL Records Specialist.

Preparing a File Plan to delineate the records for inventory and the schedule for disposition.

Annually reviewing and approving the project File Plan.

Project Staff Generating, correcting, and maintaining records in accordance with the HDI and above record requirements.

Project Records Custodian(s) Filing records and protecting them from damage or loss.

Transferring and/or disposing of records according to the governing File Plan in accordance with the HDI records management requirements.

Quality Representative Annually reviewing and approving the project File Plan.

3.12 ASSESSMENTS

Purpose This section identifies the requirements for assessments performed to verify compliance and determine effectiveness of the quality system and determine where corrective action is needed. Timely corrective action is taken to correct the specific deficiencies identified and to prevent future occurrences of the same or similar deficiencies. Corrective actions are tracked to make sure that timely and effective corrective action is taken in response to identified deficiencies (see section 3.10, *Corrective Action*).

Assessments and audits provide information on scientific, business, and operational performance to management and staff and provide mechanisms to detect and prevent quality problems and facilitate continuous improvement.

Requirements Generally, program assessments are scheduled, planned, performed, and documented, and the results communicated to affected staff, and an assessment would be conducted by the Quality Representative at a minimum of annually, or as directed by the Project Manager. Due to the planned short period of performance for these tasks, no annual assessment is planned or required. When performed, assessment results are documented including any deficiencies and agreed upon improvement opportunities in order to track the actions and assessment to closure.

If needed, performance of audits or assessments on organizations external to PNNL will be coordinated through the contract representative or procurement quality point of contact (see section 3.7, *Purchasing Services and Supplies*).

Responsibilities Significant responsibilities include:

Program Staff	Participating and fully cooperating in internal assessments.
Program Manager	Scheduling assessments.
	Investigating deficiencies from assessments and determining appropriate corrective action(s).
	Scheduling and implementing corrective actions, including measures to prevent recurrence, as appropriate.
	Identifying items and processes needing improvement.
	Communicating assessment results with staff including, lessons learned, best practices, and improvement opportunities.
Quality Manager	Assist with scheduling assessments.
	Making sure assessment results are reported to management and affected staff.
	Reviewing assessment responses for adequacy and reporting assessment completion.
	Performing follow-up, as requested, to verify completion of corrective action.
	Reviewing assessment reports and other quality-related information to identify items and processes needing improvement.

4.0 TECHNICAL REQUIREMENTS

4.1 GENERAL

Many factors contribute to the correctness and reliability of the analyses performed. These factors include:

- human factors (section 4.2);
- accommodations and environmental conditions (section 4.3);
- test and calibration methods/validation (section 4.4);
- equipment (section 4.5);
- measurement traceability (section 4.6);
- sampling (section 4.7);
- handling of analysis items (section 4.8);
- and reporting the results (sections 4.9 and 4.10).

The project will take into consideration these factors during the development of project procedures, including procedures related to sample handling, analysis, calibration, and training.

Reagents used in the preparation of samples, standards, and sample analysis will be purchased, prepared, controlled and labeled in accordance

with the *Chemical Storage and Labeling of Containers* exhibit within the HDI work control, *Chemical - General*.

4.2 PERSONNEL

Purpose

To perform acceptable work; project staff must be qualified in both the technical and quality assurance aspects of their job function.

Requirements

Staff training will be in accordance with the requirements of the HDI work control, *Prepare Staff for Work*, and at a minimum include documented training to the QAPP and implementing procedures. Project training will be identified and tracked to completion.

The Employee Job Task Analysis and the IOPS Training Matrix are used to identify PNNL-level required training and PNNL's Enterprise Learning Management System (database) is used to assign and track the PNNL-level training.

Significant requirements of the training project include, as appropriate:

- QA project orientation.
- Assignment of work based on qualifications (education and experience).
- Training to specific QA and technical aspects of the assigned job function prior to allowing personnel to perform activities.
- Maintenance of qualification and re-training, as necessary.
- Maintenance of records of personnel selection, qualification, and training.

Qualifications and training will be reassessed on a regular basis (at least annually) and whenever significant changes are made to the job function (e.g., when applicable procedures are revised, when the scope of work changes).

Staff have access to the Hanford Technical Library which provides scientific and technical literature to aid in maintaining technical competency and education.

Responsibilities

Significant responsibilities include:

Project Manager

Implementing the project-specific training and for staff that performs quality-affecting activities.

Assuring that records of training and qualifications are maintained.

Assigning project staff based on applicable training, experience, and qualifications.

Reassessing training, qualifications, and certifications on at least an annual basis.

Assuring project staff have necessary training to perform assigned work.

Quality Representative

Assuring that inspection/examination personnel are trained, qualified, and certified, as appropriate.

Conducting QA-related training, as requested.

Project Staff

Participating in required training and indoctrination, and performing work activities for which they are qualified.

4.3 FACILITIES AND ENVIRONMENTAL CONDITIONS

Purpose

This section describes the analysis facilities and environmental conditions that are necessary in order to prevent conditions that may adversely affect the quality and protection of the measurement results. Work activities for the project occur in several facilities in PNNL's complex in Richland, Washington.

Requirements

Samples received for analysis will be protected from laboratory contamination that may adversely affect the measurement and data quality, which include: cross contamination between samples, contamination from the laboratory environment to the samples, and contamination from the samples to the laboratory. This requirement may be met in a variety of ways depending on the sample type and analysis method. Contamination control practices will be defined in technical procedures as appropriate, and may include prevention, monitoring, and mitigation measures. At a minimum, staff will adhere to good housekeeping practices.

Facility-level contamination control measures are defined and staff are trained through IOPS. In addition, at the facility-level routine surveys are conducted of hallways, laboratories and fume hoods by the Radiological Protection organization. The location of sample receipt and subsequent sample preparations and separations work is determined based on the radiological activity level and type of incoming samples. Procedures for sample handling and analysis will be followed to prevent contamination. Contamination that may impact the quality of the measurement results will be monitored as appropriate through mechanisms such as preparation blanks, and analysis blanks.

Laboratory environmental conditions (e.g., temperature, humidity) known to impact laboratory analyses and hence, results, are required to be monitored and if needed, controlled.

Access to facilities and laboratory spaces will be in accordance with HDI work flow, *Host a Visitor or Non-Staff Worker*, and work control, *Basic Staff Practices (*section 2 - *Staff Responsibilities and Limitations, Security Requirements, and Use of PNNL Facilities).* PNNL facilities are

monitored during off-shift hours by security personnel and controls are in place that does not allow public access. The IOPS controls the access to facility laboratory spaces via training requirements and in some cases via electronic locks on doors. Sample custody will be in accordance with procedure PNL-ASO-071, Rev. 1, *Sample Management: Receipt and Inspection*. PNNL's safety program is described in section 3.2, *Organization*.

Responsibilities Significant responsibilities include:

Project Manager The Project Manager will assure that appropriate laboratory workspace is provided in which to perform project activities and that there is sufficient separation of incompatible activities to minimize contamination and cross-contamination.

Project Staff Defining appropriate contamination control practices in technical procedures.

Adhering to good housekeeping practices.

Following approved procedures for sample handling and analysis.

4.4 TECHNICAL METHODS AND CONTROL OF DATA

4.4.1 Method Validation and Measurement Uncertainty

Purpose This section identifies the requirements for analysis method selection, developing and validation of technical methods and determining measurement uncertainties.

Requirements Method performance is monitored during analyses when applicable by analysis of standard reference materials, initial and continuing calibration verification samples, laboratory control samples, and analysis of blank and blank spike samples; all of which are used to evaluate method accuracy. Repeated analysis of samples of known activity or concentration provides an indication of method precision and contributes to determining method uncertainty. Repeated analysis of blanks, spiked blanks, and replicate samples also aids in determining uncertainty. Instrument response is a way of determining and reporting measurement uncertainty and many instrument operating systems collect and report this information.
Staff will select appropriate methods for the required analyses and determine and report method detection limits and uncertainty of results.

Responsibilities Significant responsibilities include:

Project Staff Participating in the selection of methods, validation of methods, determination of uncertainty, and documentation of the method in technical procedures or instructions per the requirements above.

4.4.2 Computer Software

Purpose

This section identifies requirements for the development, modification, and use of software to make sure that data produced by the software are valid representations of the design model. Software design inputs are developed and reviewed to provide a sound basis for the design process. Newly developed or modified software is reviewed to eliminate as many deficiencies as possible before testing and initial configuration management. Software that has been developed or modified is tested to verify and validate its outputs. Configuration management, access control, and physical protection are applied, as necessary, to protect the software against unauthorized changes, loss, or deterioration. The application of software is reviewed, approved, and documented to increase confidence that the application is correct and problems encountered are properly documented and resolved.

This section does not apply to M&TE which contains firmware that will be tested as part of the calibration of the equipment. Software commercially available such as Word®, Excel®, etc., need not be controlled, however these must be used in accordance with the requirements below.

Requirements

Software developed or acquired for use by the project will be developed, used, and controlled in accordance with the HDI work flow, *Use or Develop Software for Analysis*.

Single-use and multiple-use spreadsheets used for the purpose of data reduction and reporting, or in the support of data reported to the PFP 236-Z Canyon Stabilization Team, will be used and controlled in accordance with procedure PNL-ASO-080, Rev. 0, *ASO Instrument Software, Multiple- and Single-use Spreadsheets*.

Responsibilities

Significant responsibilities include:

Project Staff

Determining the requirements for software control and following appropriate HDI and project procedures related to software.

Preparing software documentation and performing testing activities, as appropriate.

Controlling software configuration, as appropriate.

Protecting software and databases from unauthorized changes or loss.

4.5 MEASURING AND TEST EQUIPMENT

Purpose

This section identifies the requirements for M&TE used for activities affecting quality to assure that M&TE is controlled and at specified periods, calibrated and adjusted to within specified limits. M&TE selected for use will be the proper type, range, accuracy, tolerance, and precision for the intended function.

Requirements

M&TE controls will include calibrating at prescribed intervals to established standards, documenting evaluation of impact on data when M&TE are found out-of-tolerance, maintaining records, and suitably marking M&TE to indicate calibration status, as appropriate to the equipment.

The method and interval of calibration for each item will be defined, based on the type of equipment, stability characteristics, required accuracy, intended use, and other conditions affecting measurement control.

The requirements of the HDI work control, *Basic Laboratory and Operations Practices*; subsection *Properly Handle Equipment and Materials* will be followed for handling M&TE. When M&TE is found out of calibration, an evaluation will be performed and documented of the validity of previous results. M&TE that is out of calibration will be tagged or segregated and not used until it has been recalibrated or a Calibration Extension generated. If any M&TE is consistently found to be out of calibration, it will be repaired or replaced. When the accuracy of the M&TE is suspect, a calibration will be performed.

The requirements of the HDI workflow, *Calibrate Measuring & Test Equipment for Use*, will be followed for the calibration and use of user-calibrated M&TE and the acquisition of calibration services. Procedures that define the calibration of user-calibrated M&TE will be generated and controlled in accordance with section 3.4, *Documents*.

When M&TE require intermediate checks, staff will check the M&TE prior to use for proper performance. Examples of these required performance checks are for balances and pipettes and are found in procedures PNL-ASO-052, Rev. 2, *Balance Performance Checks* and PNL-ASO-066, Rev. 0, *Pipette Performance Check-Determination of Delivery Volume*. Intermediate checks for other M&TE will be defined and documented in technical procedures as per section 3.4, *Documents*.

Responsibilities

Significant responsibilities include:

Project Manager

Assigning responsibility for maintenance of M&TE records.

Taking necessary actions when M&TE has been found to be in a discrepant condition.

Project Staff

Making sure that M&TE are properly selected, identified, calibrated, and controlled.

Making sure that evaluation of discrepant M&TE is performed, and any necessary corrective action is implemented.

Verifying that documentation of discrepant M&TE is reviewed and an evaluation of impact on data is performed.

4.6 MEASUREMENT TRACEABILITY

Purpose

This section identifies the requirements for calibration, traceability of results to a valid calibration, and standard material control and traceability.

Requirements

Staff will comply with the requirements of section 4.5, *Measuring and Test Equipment* for requirements related to M&TE use, handling, and calibration.

Traceability of the calibration to the International System of Units (SI Units) must be established through an unbroken chain of calibrations or comparisons linking the calibration standards to the relevant primary standards of the SI units of measurement. When traceability to SI units is not possible and/or not relevant, traceability will be established to other appropriate standards. In this case the technical justification for the use of the standard must be documented and placed in the record file.

When used, reference standard databases will be purchased or acquired from reputable agencies that are nationally or internationally recognized if possible. The source and version of the reference standard database will be referenced in the procedure or traceable to the resultant data. Examples of acceptable instrument library sources for gamma spectrometry libraries are: www.nndc.bnl.gov/ and http://ie.lbl.gov/education/isotopes.htm. Many reference standard databases are included within the instrument operating system and are not acquired separately.

All primary and secondary stock standards must be assigned an expiration date, and expired standards must not be used as standards past their expiration date. In rare cases, the standard may be used past its original expiration date, but only if it is re-verified and there is justifiable data or a reason to believe the standard material has maintained its integrity and has not degraded over time. Contact the Quality Representative regarding re-verification of standards.

Responsibilities

Significant responsibilities include:

Project Manager

Complying with the requirements of the above.

Quality Representative

Assisting with the re-verification of standards, as requested.

Project Staff

Complying with the requirements of the above and assuring traceability of the calibration to SI units and standards.

4.7 SAMPLING

Purpose

This section identifies the requirements for sample splitting or portioning.

Requirements

Processing and analysis procedures/instructions will include the necessary sample splitting or sub-sampling process, and where reasonable, be based on appropriate statistical methods to assure that a subsample collected is representative of the whole. Sampling procedures/instructions will

describe the necessary factors to be controlled to assure the validity of the analysis result.

Sample splitting and portioning activities will be documented including the identification of the staff member performing the activity, the procedure used (as applicable), and if relevant the following: environmental conditions, diagram/photo or description of the sampling, and statistical basis for the sample splitting or portioning activity (as appropriate).

Responsibilities

Significant responsibilities include:

Project Staff

Complying with the processing instructions from the Project Managers and Quality Manager. Complying with the sampling requirements of procedures or instructions and documenting the approach used.

4.8 SAMPLE HANDLING

Purpose

This section identifies requirements for the transportation, receipt, handling, protection, storage, retention and/or disposal of samples. Handling, storage and shipping activities are controlled in order to protect sample integrity, the interests of the laboratory, the interests of the PFP 236-Z Canyon Stabilization Team, and safety of the staff and the public.

Requirements

Project staff will transport, receive, handle, protect, store, retain and dispose of samples in accordance with procedure PNL-ASO-075, Rev. 1, *Sample Management: Disposition and Waste Disposal*. All samples will be received and managed in accordance with ASO Procedures and forms by ASO staff:

PNL-ASO-070	*Sample Management: Overview*
PNL-ASO-071	*Sample Management: Receipt and Inspection*
	*E*xhibit 1 – Example: ASO SICL Form
	Exhibit 2 – Example: ASO Field Chain of Custody Form
	Exhibit 3 – Example: ASO Analytical Service Request Form
	Exhibit 4 – Example: ASO Sample Receipt and Inspection Form.
	Exhibit 5 – Example: ASO Laboratory Chain of Custody Form
	Exhibit 6 – Example: ASO External Chain of Custody Form
PNL-ASO-072	*Sample Management: Labeling, Login, and Work Authorization*
	Exhibit 1 – ASO Guidelines for Labelling Sub-samples and Processed
PNL-ASO-073	*Sample Management: Storage and Security*
PNL-ASO-074	*Sample Management: Distribution and Transfer of Unprocessed and Processed Samples*
PNL-ASO-075	*Sample Management: Disposition and Waste Disposal*

Responsibilities

Significant responsibilities include:

Project Staff

Complying with Project Managers' direction and sample handling and chain of custody procedures.

4.9 ASSURING THE QUALITY OF ANALYSIS RESULTS

4.9.1 Quality Control

Purpose

The project utilizes QC measures for monitoring the reliability and validity of the analysis.

Requirements

Analysis procedures will include appropriate QC activities, measures and samples, acceptance criteria and failure actions for each analysis and/or preparation as appropriate in accordance with section 3.4, *Documents*. QC sample failures may require re-analysis, and should be reported promptly to project management in the case that re-analysis may be costly. The technical review of analysis results will include a review of the QC sample data to determine that the result meets acceptance criteria and that the data are appropriate for reporting to the PFP 236-Z Canyon Stabilization Team, and/or the PFP 236-Z Canyon Stabilization Team is apprised of any limitations on the results per the data review and reporting requirements.

Quality control measures/samples that may be applicable to the preparation and analysis method include:

- Method/Instrument Blanks (used to assess instrument/system contamination)
- Bench/Check Standards (used to assess method performance)
- Laboratory Control Standards (used to assess method performance)
- Internal Standards/Spikes (used to assess method performance)
- Carriers/Tracers (used to assess method performance)
- Duplicate/Replicate/Split Samples (used to assess precision)
- Control Charts (used to assess method performance)

Responsibilities

Significant responsibilities include:

Project Manager

Conducting the review of results including quality control measures in accordance with the review and reporting requirements.

Staff

Preparing, utilizing, and analyzing the results of appropriate QC samples during preparation and/or analysis of PFP Floor Pan Evaluation Project samples in accordance with approved technical procedures/instructions.

4.10 REPORTING OF RESULTS

Purpose

This section identifies the requirements for reviewing and communicating technical and scientific information, opinions, and interpretations reported to the PFP 236-Z Canyon Stabilization Team.

Requirements

All technical and scientific information will be technically reviewed prior to transmittal to any individual outside of PNNL (including the PFP 236-Z Canyon Stabilization Team). Technical reviewers will be qualified in the scientific discipline being reviewed and independent from the work being reviewed. Technical review comments will be resolved and will be

documented in the project records.

The technical review will include an evaluation of completeness, correctness, and conformance/compliance of each data set against the method or procedure specifications. A data package will be generated which may consist of (but not limited to) chain-of-custody documentation, sample preparation sheets; spreadsheets, instrument print outs for blanks, control standards, samples, duplicates and spikes analyzed; traceability to all instruments utilized for the analysis, and any relevant calculations. The package will also serve as a traceability tool if it is necessary to recover the underlying raw analytical data. The sources for this information may be in the form of a combination of laboratory record books, instructions, worksheets, instrument raw data, spreadsheets, etc. The independent reviewer may elect to employ a data verification checklist in the review, but at a minimum must verify the accuracy and completeness of the following:

- Sample preparation information/directions, weights, aliquot sizes, dilution volumes and standard information
- Instrumentation calibration information including the traceability and expiration dates of calibration standards used
- Required quality control samples (e.g., blanks, spikes, standards, laboratory control samples, etc.) have been analyzed at the required frequency along with process samples at the frequencies specified by the procedure
- Data acceptance objectives and criteria have been satisfied as specified by the procedure, and when not satisfied, an adequate discussion is provided in the case narrative of the report
- When additional measurement controls and/or acceptance criteria were implemented for a special application or testing of the measurement method, then the reviewer will document that these controls and/or acceptance criteria have been satisfied, or when not satisfied that an adequate discussion of the impact to and the limitations of the data are provided in the case narrative of the report
- Accuracy of transcription and verification that any analytical data hand-calculated or entered into a spreadsheet for data reduction has been validated.

A sample analysis report will be generated that includes, at a minimum, a brief description of the requested work and the following:

- References to the associated procedures and instructions
- Description of the sample receipt condition and sample preparation and portioning activities
- Includes a case narrative that describes sample preparation procedures and any associated problems, the analyses and any associated analysis or instrument problems, interferences affecting results, quality check failures and resolution, assumptions and limitations of the data
- Results of the analyses with measurement uncertainty as appropriate,
- Results associated with quality control sample analyses, as appropriate

- Analysis reference date in the case of radionuclides
- Opinions and interpretations; clearly identified as opinions or interpretations and the basis for the opinion or interpretation
- Reference to the data package which will serve as a traceability tool if it is necessary to recover the underlying raw analytical data.

The sample analysis report will be technical reviewed prior to issue to assure consistency between the data package and the report, including reviews by the Quality Representative, Technical Reviewer, and Project Manager.

Appropriate methods to document a technical review are:

- Technical reviewer's signature on hard-copy document or review record,
- Documented verification and validation of the software process that generates the information.

Technical information and data reports will be transferred to the customer by the Task Leads and the information must have at least a documented technical-review and when required, a QE review, before it is provided.

Historical information may be released to the PFP 236-Z Canyon Stabilization Team as appropriate, by the Project Managers provided the transmittal includes a description of the information's source and/or history (i.e., its provenance) and the extent to which it was or was not technically reviewed is clearly documented in the transmittal.

Preliminary technical information may not be released because the project has a very short period or performance and data reports as work is performed are the report deliverables. A final summary data report is not needed for this work.

Responsibilities

Significant responsibilities include:

Task Lead/Project Manager

Assuring that final results sent to the customer has received a documented technical review and when required, a QE review.

Project Staff

Obtaining technical review of any technical or scientific information that will be transmitted outside of PNNL and to the PFP 236-Z Canyon Stabilization Team.

Allowing the technical reviewer adequate time and access to necessary information so that an appropriate level of review can be conducted.

Opinion or interpretations of data are not necessary except when requested by the Project Manager and customer, clearly stating the basis for the opinion or interpretation, and clearly stating that the information provided is an opinion or interpretation.

Keeping documentation of technical and scientific information sent to the PFP 236-Z Canyon Stabilization Team in the project record files via use of the Project SharePoint.

Assuring documentation that supports the transmitted information, the data package described above, is placed in the project records.

Appendix A – Referenced PNNL Documents

HDI Work Flows:

- *Plan for Project, Organizational, and Individual Information Management*
- *Request and Receive Classified Information from External Sources*
- *Create or Update Procedures or Other Work Instructions*
- *Create, Acquire, Use, and Store Information*
- *Transmit or Publish Classified Information*
- *Dispose of Information*
- *Manage Project Records*
- *File and Maintain Project Records*
- *Manage Laboratory Record Book*
- *File and Maintain Project Records*
- *Participate in External Audit or Assessment.*
- *Calibrate Equipment for Use*
- *Manage Sample*
- *Plan Project*
- *Receive and Inspect Product or Service*
- *Acquire Product or Service via Purchase Order-Subcontract*
- *Acquire Product or Service via P-Cards*
- *Acquire Product via Business-to-Business (B2B)*
- *Perform At-Site Inspection*
- *Receive and Inspect Product or Service*
- *Conduct Initial Risk Assessment*
- *Develop Special Controls for Research and Development Activities*
- *Prepare Staff for Work*
- *Host a Visitor or Non-Staff Worker*
- *Use or Develop Software for Analysis*
- *Integrated Operations System (IOPS)*

HDI Work Controls:

- *Chemical – General,* exhibit *Chemical Storage and Labeling of Containers*
- *Basic Laboratory and Operations Practices,* exhibit *Stopping and Restarting Work*
- *Basic Laboratory and Operations Practices*; subsection *Properly Handle Equipment and Materials*
- *Basic Lab Practices,* section 1 – *Staff Rights and Concerns*
- *Basic Staff Practices,* exhibit *Limitations on Staff and Project Activities*
- *Basic Staff Practices,* section 2 - *Staff Responsibilities and Limitations, Security Requirements, and Use of PNNL Facilities*

Other Referenced Documents:

- *Roles, Responsibilities, Accountabilities, and Authorities* within HDI
- *Lessons Learned/Operating Experience* website
- Acquisition Management & Operations Program procedures: AQP-03, Desk Surveys and At-Site Evaluations; AQP-06, Review of Supplier/Subcontractor Submitted Documents; AQP-16, Pacific Northwest National Laboratory's Evaluated Suppliers Listing and Integrated Supplier Information Services (ISIS); AQP-18, Quality Inspection of a Deliverable; and AQP-19, Quality At-Site Source Inspection/Test or Surveillance.
- ASO-QAP-001, Rev. 9, *Analytical Support Operations (ASO) Quality Assurance Plan*
- ASME NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*
- 10 CFR 830, *Energy/Nuclear Safety Management,* Subpart A, *Quality Assurance Requirements*
- DOE Order 414.1D, *Quality Assurance*
- HASQARD, *Hanford Analytical Quality Assurance Requirements*

Appendix B –Project Procedures

Implementing Procedures:

ASO-QAP-001	ASO QA Plan
PNL-ASO-052	*Balance Performance Checks*
PNL-ASO-062	*Standards*
PNL-ASO-066	*Pipette Performance Check – Determination of Delivery Volume*
PNL-ASO-065	*Control Charting*
PNL-ASO-058	*ASO Data Reporting*
PNL-ASO-070	*Sample Management: Overview*
PNL-ASO-071	*Sample Management: Receipt and Inspection*
PNL-ASO-072	*Sample Management: Labeling, Login, and Work Authorization*
PNL-ASO-073	*Sample Management: Storage and Security*
PNL-ASO-074	*Sample Management: Distribution and Transfer of Unprocessed and Processed Samples*
PNL-ASO-075	*Sample Management: Disposition and Waste Disposal*
PNL-ASO-076	*ASO Records Management*
PNL-ASO-077	*ASO Document Control*
RPG-CMC-129	*HNO_3-HC1 Acid Extraction of Solids Using a Dry-Block Heater*
RPG-CMC-211	*Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)*
RPG-CMC-212	*Determination of Common Anions by Ion Chromatography*
RPG-CMC-290	*Determination of pH in Soil Samples*
RPG-CMC-292	*Determination of Elemental Composition by Inductively Coupled Argon Plasma Mass Spectrometry (ICP-MS)*
RPG-CMC-450	*Gamma Energy Analysis (GEA) and Low-Energy Photon Spectroscopy (LEPS)*
RPG-CMC-474	*Measurement of Alpha and Beta Activity by Liquids Scintillation Spectrometry*
RPL-GC-MS-01	*Gas Chromatography/Mass Spectrometry*
RPL-OP-001	*Routine Research Operations*
RPL-NSD-01	*Dissolution of PuO_2 and Separation of Impurities Using Anion Exchange*

Need to add FTIR procedure

Appendix C – Participating Project Staff

Project Manager
Michael Minette
Project Manager, Experimental Fluid Mechanics
B.S. Mining Engineering, MBA Finance, Professional Engineer
+30 years experience

Project Manager/Analytical Services Operations Manager
Karl N. Pool
Project Manager, Nuclear Chemistry & Engineering
B.S. Chemistry
+25 years experience

Director
Steve Schlahta
Project Management Office Director, Nuclear Science and Legacy Waste

Project Quality Representative
Deborah Coffey
Sr. Quality Engineer, Quality
B.S. Biology (Minor in Chemistry)
MS Resource Ecology
+30 years experience

Staff participating in sample characterization/analysis, reporting, and technical review:

Garrett N. Brown
Staff Scientist, EED
Ph.D. Chemistry
20+ years

Sam Bryan
Scientist, Radiochemical Science
Ph.D. Inorganic Chemistry
35 years experience

Michael G. Cantaloub
Scientist
M.S., Radiation Health Physics
+20 years

Katharine J. Carson
Research Scientist, Energy and Environment Division
B.S., Biology
+30 years experience

Jenn Carter
Scientist, Actinide Science
B.S. Chemistry
15 years experience

Cal Delegard
Scientist, Actinide Science
B.S. Chemistry
42 years of experience

Sandra Fiskum
Senior Research Scientist
B.S. Chemistry
30+ years experience

Larry R. Greenwood
Laboratory Fellow, National Security Division
Ph.D. Nuclear Physics
+35 years experience

Bruce McNamara
Senior Research Scientist, Actinide Science Team
Radiochemical Science and Engineering Group
Ph.D. Physical Chemistry
+25 years experience

Angie Melville
Research Scientist
B.S. General Science (Chemistry, Math, Geology)
+15 years experience

Crystal Rutherford
Technician, Radiochemical Science
B.S. Biology
+6 years experience

Randy Scheele
Scientist, Radiochemical Science
B.S. Chemistry
41 years Experience

Chuck Z. Soderquist
Scientist, Nuclear Sciences Division
M. S., Chemistry
+30 years experience

Chris Thompson
Sr. Scientist, Environmental Systems
Ph.D. Analytical Chemistry
+21 years experience

Truc Trang Le
Senior Technician
B.S. Mathematics/Actuary
+20 years

Jon H. Wahl
Senior Research Scientist
Ph.D., Analytical Chemistry
B.S., Chemistry
+20 years experience

Appendix F

Analytical Service Requests

Appendix F

Analytical Service Requests

Analytical Service Request (ASR)

(Information on this COVER PAGE is applicable to all samples submitted under this ASR)

Requestor --- Complete all fields on this COVER PAGE, unless specified as optional or ASR is a revision

Requestor:
Signature [signature]
Print Name Mike Minette
Phone 375-5367 MSIN K7-15

Project Number: 68453
Work Package: N60251

Matrix Type Information

- ♦ **Liquids:** ☐ Aqueous ☐ Organic ☐ Multi-phase
- ♦ **Solids:** X Soil X Sludge ☐ X Sediment
  ☐ Glass ☐ Filter ☐ Metal
  ☐ Smear ☐ Organic ☐ Other
- ♦ **Other:** ☐ Solid/Liquid Mixture, Slurry
  ☐ Gas ☐ Biological Specimen

(If sample matrices vary, specify on Request Page)

Disposal Information

♦ **Disposition of Virgin Samples:**
Virgin samples are returned to requestor unless archiving provisions are made with receiving group!

If archiving, provide:
Archiving Reference Doc: _____

♦ **Disposition of Treated Samples:**
X Dispose ☐ Return

QA/Special Requirements

♦ **QA Plan:**
X ASO-QAP-001 (Equivalent to HASQARD)
☐ Additional QA Requirements, List Document Below:
Reference Doc Number: _____

♦ **Field COC Submitted?** ☐ No X Yes

♦ **Lab COC Required?** X No ☐ Yes

♦ **Sample/Container Inspection Documentation Required?**
X No ☐ Yes

♦ **Hold Time:** ☐ No X *Yes*

***If Yes,* Contact ASO Lead before submitting Samples**

☐ Use SW 846 (PNL-ASO-071, identify analytes/methods where holding times apply)

X Other? Specify: Client SOW

♦ **Special Storage Requirements:**
X None ☐ Refrigerate ☐ Other, Specify: _____

♦ **Data Requires ASO Quality Engineer Review?** ☐ No X Yes

Data Reporting Information

♦ **Is Work Associated with a Fee-Based Milestone?** ☐ No **X** Yes
If yes, milestone due date: _____

♦ **Preliminary Results Requested, As Available?** ☐ No **X** Yes

♦ **Data Reporting Level**
X ASO-QAP-001 (Equivalent to HASQARD).
☐ Minimum data report.
☐ Project Specific Requirements:
Contact ASO Lead or List Reference Document: _____

♦ **Requested Analytical Work Completion Date:** _____
(Note: Priority rate charge for < 10 business day turn-around time)

♦ **Negotiated Commitment Date:**
All Final Reports by 2/15/16-7 However, analyses need be completed as quickly as possible and reported as the work is completed.
(To be completed by ASO Lead)

Waste Designation Information

♦ **ASO Sample Information Check List Attached?** X No (☒ Yes) 12/4/15
If no, Reference Doc Attached: _____
or, Previous ASR Number: _____
or, Previous RPL Number: _____

Does the Waste Designation Documentation Indicate Presence of PCBs?
X No ☐ Yes

Send Report To: Mike Minette **MSIN** K7-15
MSIN _____

Additional or Special Instructions _____

Receiving and Login Information *(to be completed by ASO staff)*

Date Delivered: 11/19/15
Delivered By (optional) J. Maddox
Time Delivered (optional) 10:50
Group ID (optional) _____
CMC Waste Sample? X No ☐ Yes

Received By: K. Pool/T. Trang-Le

ASR Number: 9937 Rev.: 00

RPL Numbers: 16-0084 thru 16-0091
(first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** [signature] 12/2/15

Analytical Services Request (ASR)

(REQUEST PAGE ---- Information Specific to Individual Samples)

Provide Analytes of Interest and Required Detection limits - ☐ **Below** ☐ **Attached**

ASO Staff Use Only RPL Number	Client Sample ID	Sample Description (& Matrix if varies)	Analyses Requested	ASO Staff Use Only Test	ASO Staff Use Only Library
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E, Sample 1 (solid/sludge)	1) GEA - Cs-137, Co-60, Eu-152,154 and 155 2) Water Leach - 103 a) Anions - NO_3, PO_4, Cl, F, NO_2, SO_4 3) pH - (Corrosivity Test) - SEE Test Instructions 4) Acid Digestion - 129 (Acid Leach) a) Pu - AEA b) U - AEA c) Am/Cm - AEA d) Pu removal by IX - See Test instructions i) ICP/MS - Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Pb, Ag, Mn, Hg, Ni, K, Na, Sr, Tl, V and Zn. 5) Organic Extraction - GC/MS		
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J, Sample 4 (solid/sludge)			
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J, Sample 1 (solid/sludge)			
16-0087	B33MK6 (F16-001-004)	PRF Canyon Pan J, Sample 2 (solid/sludge)			
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O, Sample 1 (solid/sludge)			
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J, Sample 3 (solid/sludge)			
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H, Sample 1 (solid/sludge)			
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H, Sample 2 (solid/sludge)			

ASR #____9937_____ Rev:_00____

ASO Sample Information Checklist (SICL) Form

Sample Location, Owner and Hazard Description Information
To be completed by the sample custodian relinquishing the sample(s) and based on best available information.

ASO Customer Information:

Company: PNNL
Project #: 68453
Point of Contact (name. telephone#): M. Minette 375-5367

Comments:

Sample Description (medium, collection location, known contaminants, purpose of sample collection):

Sample Collection Date: 11/19/2015 Sample Collection Time: 10:50 am

Is the sample known to be radioactive? ☒ Yes ☐ No

Comments *(list known isotopes)*:
Pu+Am

Is the sample known to contain or have come in contact with PCBs? ☐ Yes ☒ No
List any hazardous sample constituents known to be present:

Constituent/Chemical	Concentration	Comment

Are any other comments applicable to sample receipt, storage, handling, or disposition?

Checklist Prepared By:
Trc Trang-le T Trang-le 12/4/15
Printed Name Signature Date

Analytical Service Request (ASR)

(Information on this COVER PAGE is applicable to all samples submitted under this ASR)

Requestor --- Complete all fields on this COVER PAGE, unless specified as optional or ASR is a revision

Requestor:
Signature: K.N. Pool for M. Minette
Print Name: Mike Minette
Phone: 375-5367 MSIN: K7-15

Project Number: 68453
Work Package: N60251

Matrix Type Information

- ♦ **Liquids:** ☐ Aqueous ☐ Organic ☐ Multi-phase
- ♦ **Solids:** X Soil X Sludge ☐ X Sediment ☐ Glass ☐ Filter ☐ Metal ☐ Smear ☐ Organic ☐ Other
- ♦ **Other:** ☐ Solid/Liquid Mixture, Slurry ☐ Gas ☐ Biological Specimen

(If sample matrices vary, specify on Request Page)

Disposal Information

♦ **Disposition of Virgin Samples:**
Virgin samples are returned to requestor unless archiving provisions are made with receiving group!
If archiving, provide:
Archiving Reference Doc: _____

♦ **Disposition of Treated Samples:**
X Dispose ☐ Return

QA/Special Requirements

♦ **QA Plan:**
X ASO-QAP-001 (Equivalent to HASQARD)
☐ Additional QA Requirements, List Document Below:
Reference Doc Number: _____

♦ **Field COC Submitted?** ☐ No X Yes

♦ **Lab COC Required?** X No ☐ Yes

♦ **Sample/Container Inspection Documentation Required?**
X No ☐ Yes

♦ **Hold Time:** ☐ No X *Yes*
If *Yes*, Contact ASO Lead before submitting Samples
☐ Use SW 846 (PNL-ASO-071, identify analytes/methods where holding times apply)
X Other? Specify: Client SOW

♦ **Special Storage Requirements:**
X None ☐ Refrigerate ☐ Other, Specify: _____

♦ **Data Requires ASO Quality Engineer Review?** ☐ No X Yes

Data Reporting Information

♦ **Is Work Associated with a Fee-Based Milestone?** ☐ No X Yes
If yes, milestone due date: _____

♦ **Preliminary Results Requested, As Available?** ☐ No X Yes

♦ **Data Reporting Level**
X ASO-QAP-001 (Equivalent to HASQARD).
☐ Minimum data report.
☐ Project Specific Requirements:
Contact ASO Lead or List Reference Document: _____

♦ **Requested Analytical Work Completion Date:** _____
(Note: Priority rate charge for < 10 business day turn-around time)

♦ **Negotiated Commitment Date:** 2/19/16
(To be completed by ASO Lead)

Waste Designation Information

♦ **ASO Sample Information Check List Attached?** X No ☐ Yes
If no, Reference Doc Attached: _____
or, Previous ASR Number: _____
or, Previous RPL Number: _____

Does the Waste Designation Documentation Indicate Presence of PCBs?
X No ☐ Yes

Send Report To: Mike Minette **MSIN** K7-15
MSIN _____

Additional or Special Instructions _____

Receiving and Login Information *(to be completed by ASO staff)*

Date Delivered: 11/19/15
Delivered By (optional): J. Maddox
Time Delivered (optional): 10:50
Group ID (optional): _____
CMC Waste Sample? X No ☐ Yes

Received By: K. Pool/T. Trang-Le
ASR Number: 9937 Rev.: 01
RPL Numbers: 16-0084 thru 16-0091 (first and last)

ASO Work Accepted By: KN Pool **Signature/Date:** K.N. Pool 2/15/16

Analytical Services Request (ASR)

(REQUEST PAGE ---- Information Specific to Individual Samples)

Provide Analytes of Interest and Required Detection limits - ☐ **Below** ☐ **Attached**

ASO Staff Use Only **RPL Number**	Client Sample ID	Sample Description (& Matrix if varies)	Analyses Requested	ASO Staff Use Only **Test**	ASO Staff Use Only **Library**
	Revision 1: ASR revised to 1) Remove Pu-AEA, U-AEA and Am/Cm-AEA, 2) Add oxalate to the Anions and 3) Remove Hg from the ICP/MS-OES analyses.				
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E, Sample 1 (solid/sludge)	1) GEA - Cs-137, Co-60, Eu-152,154 and 155 2) Water Leach - 103 a) Anions - **NO_3**, **PO_4**, Cl, F, NO_2, SO_4, C_2O_4 3) pH - (Corrosivity Test) - SEE Test Instructions 4) Acid Digestion - 129 (Acid Leach) a) Pu removal by IX - See Test instructions i) ICP/MS-OES - Al, Sb, Ba, Be, Cd, Cr, Co,Cu, Pb, Ag, Mn, Ni, K, Na, Sr, Tl, V and Zn. 5) Organic Extraction - GC/MS		
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J, Sample 4 (solid/sludge)			
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J, Sample 1 (solid/sludge)			
16-0087	B33MK6 (F16-001-004)	PRF Canyon Pan J, Sample 2 (solid/sludge)			
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O, Sample 1 (solid/sludge)			
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J, Sample 3 (solid/sludge)			
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H, Sample 1 (solid/sludge)			
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H, Sample 2 (solid/sludge)			

ASR #____9937_____ Rev:_01____

PLANNING

Topic/Issue to be Evaluated: QE Review of ASO **ASR 9937 and ASR 9937.01** for ASO Project 68423; Eight Solid Samples: GEA, Anions, pH (Corrositivity), Am/Cm, Pu and U/AEA, ICP-OES and Organic Extraction /GC-MS Analysis

PERFORMANCE

Date Initiated: 12/2/15	**Location:** RPL
Date Submitted: GEA: 12/7/15 Anions: 2/12/16; oxalate added 2/16/16 by ASR 9937.01 pH (corrositivity): 12/22/15 Am/Cm, Pu and U/AEA: cancelled 2/16/01by ASR 9937.01 ICP-MS/ ICP-OES allowed by ASR 9937.01: 2/18/16 Organic Extraction /GC-MS Analysis: 3/9/16 **Date Completed**: GEA: 12/8/15 Anions: 2/19/16 pH (corrosivity): 12/22/15 Am/Cm, Pu and U/AEA: cancelled ICP-OES: 2/19/16 Organic Extraction /GC-MS Analysis:3/9/16	**DRAFT Report Issued:** GEA: 12/7/15; closed 12/9/15 Anions: 2/18/16 pH (corrosivity): 12/22/15 Am/Cm, Pu and U/AEA: cancelled ICP-OES: 2/19/16 Organic Extraction /GC-MS Analysis: 3/9/16 **FINAL Report Issue**d: 3/10/16
Contacts: G Brown, J Carter**,** L Greenwood, A Melville, C Parker, K Pool, C Rutherford, S Sinkov, C Soderquist, T Trang Le, Jon Wahl	**Org Code:** PE 137, D9H63
Surveillance Team: Deborah Coffey	

PRELIMINARY INFORMATION

ASO Analytical Services Request (ASR) 9937 requires that a QE review of the data package be performed prior to delivery of final data to Project 68453.

Source of Requirement(s):

- ASO QA Plan, ASO QAP-001, Rev. 9
- ASO QA Plan, ASO QAP-001, Rev. 10 after training assignment on 2/12/16.
- Test Instruction 98620-TI-001, Rev. 0, *PRF Canyon Sample Handling in Glove Box*

- Test Instruction 68453-TI-001, Rev. 0, *PRF Canyon Sample Gas Evolution Testing*; Effective Date: 1/22/16. pp. 29

Other Applicable Documents:

- RPL-OP-001, Rev. 13, *Routine Research Operations*
- ASR 9937
- PNL-ASO-058, *ASO Data Reporting*
- PNL-ASO-052, *Balance Performance Checks*
- PNL-ASO-062, *Standards*
- PNL-ASO-066, *Pipette Performance Check – Determination of Delivery Volume*
- RPG-CMC-103, Rev. 0, *Water Leach of Sludge, Soil, and Other Solids*
- RPG-CMC-129, Rev. 0, *HNO_3-HCl Acid Extraction of Solids Using a Dry-Block Heater*
- RPG-CMC-211, Rev. 3, *Determination of Elemental Composition by Inductively Coupled Argon Plasma Optical Emission Spectrometry (ICP-OES)*
- RPG-CMC-212, Rev. 2, *Determination of Common Anions by Ion Chromatography*
- RPG-CMC-290, Rev. 0, *Determination of pH in Soil Samples*
- RPG-CMC-450, Rev. 2, *Gamma Energy Analysis (GEA) and Low-Energy Photon Spectrometry (LEPS)*
- RPL-GCMS-01, Rev. 0, *Gas Chromatography/Mass Spectrometry*

PURPOSE

This surveillance was undertaken to verify that the data and supporting records for the client's reported data met the ASR, procedure and QA Plan requirements and project objectives specified in the previously cited requirements documents.

The objective evidence reviewed is available in the Project Manager's file. There may be supporting information available in the audit file which is available in the Lead Auditor's office, Building 325, 5-G.

METHOD USED

ASR 9937 and later, ASR 9937.01, requested analysis of the eight (8) two samples submitted for GEA, anions [F, Cl, NO_2, NO_3, SO_4, PO_4 and oxalate, C_2O_4 (a late addition by ASR 9937.01)], pH (Corrosivity), Am/Cm, Pu and U/AEA (later cancelled via 9937.01) , ICP-MS (Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Pb, Ag, Mn, Ni, K, NA, Sr, Ti, V and Zn; Hg deleted by 9937.01 and use of ICP-OES allowed) and Organic Extraction /GC-MS Analysis.

Table 1. RPL/ASO ID, Client Sample ID, Sample Description and Sample Preparation and Analysis Dates

RPL Sample Number	Client Sample ID	Sample Description	Analysis Dates:
16-0084	B33MK3 (F16-001-001)	PRF Canyon Pan E Sample 1 (solid/sludge)	GEA: 11/23/15 to 12/2/15 Anions: 1/8/16 pH (corrosivity): 12/22/15 Am/Cm, Pu and U/AEA: cancelled ICP-OES: 2/8/16 Organic Extraction /GC-MS Analysis:1/7/16 to 2/12/16
16-0085	B33MK4 (F16-001-002)	PRF Canyon Pan J Sample 4 (solid/sludge)	
16-0086	B33MK5 (F16-001-003)	PRF Canyon Pan J Sample 1 (solid/sludge)	
16-0087	B33MK6 (F16-001-004)	PRF Canyon Pan J Sample 2 (solid/sludge)	
16-0088	B33MK7 (F16-001-005)	PRF Canyon Pan O Sample 1 (solid/sludge)	
16-0089	B33MK8 (F16-001-006)	PRF Canyon Pan J Sample 3 (solid/sludge)	
16-0090	B33MK9 (F16-001-007)	PRF Canyon Pan H Sample 1 (solid/sludge)	
16-0091	B33ML0 (F16-001-008)	PRF Canyon Pan H Sample 2 (solid/sludge)	

ASO Occurrence Report, OR-98620-12-9-15; Sample Receipt Observations (ASR 9937) documented a condition that was noted upon opening the sample outer and inner sample Bags for Pan J Sample 1 and the outer bag for Pan J Samples 2, it was identified that the sample vials had broken cleanly and the glass bottoms of the vials had separated cleanly from the vial. Remaining materials were recovered from the Vial in Pan J Sample 1. An Alternative analysis approach was established for Pan J Sample 2 materials and in bag gasses.

ASR 9931.01 requested analysis of two aqueous samples as-received (16-0073and 16-0074) which were delivered to the ASO laboratory on 11/13/15 at 0730 (7:30 am) for the analysis noted above. The ASR noted preliminary data were to be provided. Final data were due by 11/19/15. The ASR stated that a comprehensive data report and QE review were needed.

The QE review of the submitted laboratory data was conducted between 12/3/15 and 3/9/16. The ASO ASR requirements and the applicable analytical procedures were used in lieu of a checklist.

GEA Analysis (as- received samples); reviewed 12/8/15; closed 12/9/15

1. Data traceability for submitted data was not evident in the instrument data provided for review. 1a) initially electronic data files were submitted, but these lacked evidence of analyst signature, technical review and selection of reported. 1b) Hard copy data (still required as per ASO QA Plan) did not identify which data were selected for reporting; this was added by the QE during the review.

All data reported for sample results were verified and spreadsheets were inspected. However, the presence of self-absorption data and thicknesses are not routine ASO GEA data and it is not clear why extra data are being reported seemingly without adequate V/V of the spreadsheets.

The information submitted for review for GEA analysis of as-received samples is listed below:

- ASR 9937

- Several GEA instrument data reports for varying count times (usually 3 per sample)
- Several Excel worksheets – one for each of the eight samples.
  1. These worksheets do not have a unique Excel file name clearly noted. Fixed. Closed.

  2. These worksheets appear to have been prepared explicitly for this project and seem to meet ASO requirements for single-use spreadsheets. The ASO procedure, PNL-ASO-080, Rev. 0, ASO Instrument Software, Multiple- and Single-use Spreadsheets but there is no indication that the spreadsheet/worksheet was reviewed as per procedure requirements (See Section 7.2.3, V/V of ASO Single-Use Spreadsheets). The review would result in the presence of the review form (see Attachment 1, ASO Single-Use Spreadsheet Review Form of PNL-ASO-080). ASO Single-Use Spreadsheet Review Form present and extensive explanation added in narrative. Fixed. Closed.

3. Calculations for total cross-section and self-abs and thickness are of concern as these likely came from an unidentified software source that may or may not have been verified/validated (prior to this use). Extensive explanation added in narrative. Fixed. Closed.

- Final data report including, cover sheet, narrative and data summary were provided; report was prepared by K Pool and technically reviewed by L Greenwood. There are several concerns with the report:

Cover sheet

4. Check the sample for the correct ID for 16-0091, it seems more likely that the client sample ID is B33M10 (F16-001-008) than B33ML0 (F16-001-008). ID verified as being correct as written. Closed.

5. Only one detector, T, was used. The Radiochemistry M&TE list was not included giving the unique identified for the detector; in this case the info for the single detector can be added to the cover page. Fixed. Closed.

6. Consider editorial comments on the cover page. Considered and fixed. Closed.

Narrative

7. Consider editorial comments on the narrative. Considered and fixed. Closed.

Data Report

8. Data report appears to also be an Excel spreadsheet and it was unclear who performed technical review of this spreadsheet, particularly for calculations of Pu isotopes and % contributions to the total. Addressed and closed.

Quality Control Samples:

ASO performed a first analysis and a second analysis and concluded that the results of the 2nd analysis verified the results for the first analysis. Therefore, all data were reported.

ASO-prepared duplicate samples were analyzed and reported; the results were RPD= <1% for the pairs reported; DQO is ± 20% RPD.

Although client provided duplicates were submitted ASO does not calculate or report the RPD for these samples; this is a client responsibility.

The lab blank was below the detection limit. The RS results were reported as 99% and 102% recovery; DQO is ± 20%.

Corrrosivity Analysis – reviewed 12/22/15; final report received 2/12/16 verbal release by QE 12/22/16

The information received for the corrosivity analysis was the following:

- ASR 9937
- Two benchsheets for RPG-CMC-290, Determination of pH in Soil and Waste Samples Benchsheet – Work was performed in RPL/506 and in the fumehood of room 516. The first run on 12/22/15 failed the closing CCV, so as per the procedure a second run was performed that passed the ICV and CCV check. The 7 samples were analyzed and one sample (16-0086) was analyzed in duplicate. Orion pH standards were used for calibration (pH 4.01 and 7.00) and a pH 7.00 buffer was used for the ICV/CCCV.

  The calibration of the pH measurement system is checked by analyzing an initial calibration verification check standard (ICV) and continuing calibration verification check samples (CCV). For this analyses batch, the result for the ICV was 7.04 and the CCVs was 6.91 meeting the procedure acceptance criterion of agreement within ± 0.1 pH unit of the certified value for the pH buffer solution.

  Precision of the pH measurements was evaluated by analyzing a one sample/ sample duplicate pair in the sample set. The DQO criterion is agreement between duplicates within 0.1 pH unit of the sample result. In this case, one duplicate sample pair was analyzed (16-0086 and 16-0086 rep) and the duplicate pair results of 2.63 and 2.66 were within the 0.1 pH unit criterion.

Cover Page

Eight samples were submitted for analysis; one sample (16-0087) was not analyzed. This is addressed by OR-98620-12-9-15 which documents a broken sample container.

Narrative

No concerns identified.

Data Report

No concerns identified.

Anion Analysis – submitted for QE review 2/12/16; reviewed 2/15-18/16; draft QE review provided 2/19/16; comment resolution 2/24/16 and report released for client

The information received for the anion analysis was the following:

- ASO Multiple-Use Workbook/Worksheet Review form -0229, Signed by J Carter 1/18/16
- Calibration Review Worksheet page 1 of 1- Copy not in color so review criterion exceedances are not visible

Tab- ASR

- ASR 9937 and revised ASR 9937.01 issued on 2/16/16
- Data Package Checklist for IC-0229 (run), KN Poll -1/18/16 (no signature)

Tab- Sample Prep Pipette Check

- Bench sheet for RPG-CMC-290, Determination of pH in Soil and Waste Samples Benchsheet – This bench sheet documents a 1:1 ratio of sample to added DI water on 12/22/15. Page 16 from test instruction, Test Instruction 98620-TI-001, Rev. 0, *PRF Canyon Sample Handling in Glove Box*, Steps 3.1 through 3.5.6 on the TI, documents addition of 4 mL DI water to 1: 1 sample (Step 3.5.1) and then 1 mL was removed and added to 4 mL of DI water (Step 3.5.3); this resulted in a 5X sample dilution. The sample was then filtered and screened for Pu (50 mircoliter aliquot into LSC vail; results requested and provided).
- Sample, LCS/BS, MS Preparation Worksheet 1/7/16; signed by J Carter 1/7/16; form has no place for a technical reviewer signature. Technical reviewer signature/date added. Reminder sent to KN Pool to update macro to fix this on 2/24/16. Closed
- Three Pipette Performance Check Worksheets all dated 1/7/16 and all signed 1/7/16; technical reviewer K Pool signed all on 2/4/16. Question: These are all typed; is there a hand-written counterpart? No, as these are entered at the instrument.

Tab- Verification & Calibration

- Calibration Stock Standards – J Carter 1/7/16, expire 11/17
- Calibration Working Standards – Cal 1 through Cal 9, C Parker, 1/7/`6; J Carter reviewed 1/8/16
- Verification Standard Prep – 1/7/16 C Parker; J Carter reviewed 1/15/16
- Verification Stock Standards 12/7/16 - Who prepared? C Parker SIGNTURE IS UNREADABLE- KN Pool brought up at group meeting; J Carter reviewed 1/15/16. Closed.
- Calibration and Verification Standard Concentrations – worksheet – How do we know if these passed or not? Need to go to QC Sample Results and Perf Review Worksheet; see yes column. Closed.
- Two pages Final Sample Results Ext. Dil factors NOT applied

Tab – Chromatograms

- For run on 1/8/16 verified standards against expected concentrations

Tab – System Sample Run Log, System Method and QNT, Sample Tray Location Log

- Preliminary data were delivered to the customer, but the date of this delivery is unknown. Preliminary results are annotated on 2/12/16 and say that oxalate was reported in final data report but not in preliminary data report.

Tab – Macro Worksheets

2 pages – Final Sample Results
3 pages – QC Sample Results and Performance Review Worksheet
2 pages – MS and RPD/%RSD Selection Worksheet
Page 7 of 8 (Where are 1-6 and 8? Found – see below) – All Tabulated Results Review WorkSheet – the missing pages were there, sheet 7 out-of-order
4 pages – Retention Time Worksheet
2 pages – CCV Frequency Check Review Worksheet
4 pages – Raw Data Summary

7+1 pages - All Tabulated Results Review Worksheet – 8 pp.
4 pages - Sample Results Review Worksheet -

Cover Page

Eight samples were submitted to ASO for analysis; one sample (16-0087) was not analyzed. This is addressed by OR-98620-12-9-15 which documents a broken sample container. The seven remaining samples are reported.

1. Procedures need to include Rev. # -212 is Rev. 2 and -103 is Rev. 0. Put procedure titles in italics. -103 title – Change "Sledge" to "Sludge". All fixed. Closed.
2. We are trying to define rooms in RPL as RPL/516, not lab 516. Fixed. Closed.
3. There was a discrepancy between the IC System unique ID in two ways 1) use serial numbers – It's 09090421 on the validation plan. 2) The property # on the validation plan is WD 81499, so why does it say WD81129 on the cover sheet? This was discussed by KN Pool and resolved by providing a photograph of the sticker. The property # part of the 3-ring binder for the validation plan. The property # on the Validation Plan is correct. Just fix the cover page. Fixed. Requested that serial number be added. to the report as primary unique ID. Closed.

Narrative

4. I had a concern about oxalate being reported as it was not an AOI; I received ASR 9937.01 on 2/16/16 which corrects this concern. No response required.
5. I originally did not see a work sheet for anion QC samples, but then found "Sample, LCS/BS, MS Preparation Worksheet 1/7/16; signed by J Carter 1/7/16; this sheet has no place to document a technical reviewer signature, why not? Technical reviewer signature/date added; macro needs to be revised to fix this permanently. Closed.
6. The narrative does not discuss preparation of the sample duplicate (16-0088 and 16-0088 dup), the LCS, the AS? Fixed in each section below. Closed.
7. I have a question about the MDL – Is it set at the lowest calibration standard run (Cal 1) or the lowest calibration standard used (Cal 3)? Discussed with Jenn Carter; it is set at the lowest Cal std used for data reporting; here Cal 3. Closed.
8. RPD discussion – Do changes to data reporting (see below) affect RPD discussion? I think the discussion should include the sentence, "Only one duplicate sample pair was able to be calculated and this was for NO_3, the RPD was 0.99%." Fixed adequately. Closed.
9. LCS sample results – The LSC sample results ranged from 101 to 107% recovery. I think the discussion should include this information. Fixed. Closed.
10. AS sample results – I this an MS or an AS? The AS (or MS) sample results ranged from 84-111% - I think the discussion should include this information. Fixed. Closed.
11. CCV/CCB issue-NO_2 failures are not addressed in this section and need to be – so can the data be reported? Actual data are all either below MDL for between MDL and EQL, so really no sample to report but can't just gloss over the issue. Discussed. Closed.

Data Report

12. The data report generated by the macros is not an appropriate ASO data report. ASO data reports do not report data below the MDL; instead "---" is in that field. Result values

between the MDL and EQL are report in brackets and are red and are noted as being estimated, qualitative values. Also, there were some significant figure issues. A draft revision to the data report is provided (L Carr graciously helped prepare this). This was accepted and provides a template for further reports. KN Pool will go over with Jenn Carter. Closed.

13. The RPDs turned out to be unable to be calculated based on the results obtained, except for NO_3. We usually report the duplicate and sample together and the RPD right under it. Fixed. Closed.
14. Some macro results have the wrong procedure Revision on the pages; can this be easily changed from Rev. 0 to Rev. 2 of -212? Reminder sent to KN Pool to update macro to fix this on 2/24/16. Closed

ICP-OES Results – reviewed 2/19/15; comment resolution 2/25/16; data cleared for release

The information received for the ICP-OES analysis of 18 metals (Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Pb, Ag, Mn, Ni, K, Na, Sr, Tl, V and Zn) was the following:

- ASR 9937
- ASR 9937.01 Added by QE – No Hg and allows use of ICP-OES, not ICP-MS
- Benchsheets for RPG-CMC-129, Rev. 0, *HNO_3-HCl Acid Extraction of Solids Using a Dry-Block Heater*. Work was performed in RPL/506 and in the fumehood of room 516 beginning on 1/14/16. The benchsheet was signed by the Analyst, C Rutherford on 1/27/16 and technical review was performed by KN Pool on 1/27/16.
- ICP Package for C0663
  - Independent Technical Review: ICP Solids Data Worksheet - C Thompson 2/9/15
  - ICP-OES ASO Single-Use Spreadsheet Review Form for C0663 (ASR 9937) – 1 p. C Thompson 2/10/16 ASR # missing on sheet. Added/Fixed. Closed.
  - ICP-OES Data Review Checklist (ASR 9937) C Thompson 2/10/16, 2pp.
  - Archive File checklist – G Brown 2/9/16
  - Client Checklist (ASR 9937– G Brown 2/9/16
  - QC Failure Notes – G Brown 2/9/16, pp.14, included
  - QC statistical summaries including % recoveries (yes, thanks!) 5 pp.
  - ICPOES Data Report – 6 pp.
  - ICPOES Data Report – 4 pp.
  - ICP-OES Daily Log – Dated 2/08/16 for C0663 for ASR 9937). G Brown 2/8/16 with technical review by C Thompson 2/10/16, 1 p. Why are System Performance Test Results so atypical? Reviewed with KN Pool. Discussed defensibility of run which is acceptable based on QC and calibration standards. May be an indication of mirror degradation over time. Closed.
  - Pipette Performance Check Worksheet – – for at instrument dilutions – prepared 2/8/16; signed by G Brown 2/8/16 with Technical review by C Thompson - 2/10/16.
  - Summary: ICP-OES Run Log – C0663 for ASR 9937 dated 2/8/16
  - ICPOES Data Summary Report – 2/8/16 for C0663 – G Brown 2/8/16
    For two records above – ICB/CCB not obvious; are paired with MCVA and MCVB samples, but listed as ICP03.0 – why can't these samples be called what they are instead of custom standard name? Discussed. Closed.
  - Instrument Data - for 2/8/16 12:38 p.m. to 3:59 p.m. – 30 pp.

Cover Page

Eight samples were submitted for analysis; one sample (16-0087) was not analyzed. This is addressed by OR-98620-12-9-15 which documents a broken sample container.

1. ASR # is ASR 9937 and 9937.01 which allows ICP-OES instead of ICP-MS and dropping Hg from the AOI list. Noted. Closed.
2. Sample Descriptions do not match ASR. – A line was added to clarify descriptions. Closed.

Narrative

3. Does the Pu removal step track to a procedure or TI-98620-001? To the TI; added a reference. Closed.
4. Also need to cite the ASO QA Plan Rev. 10 which was issued on 2/4/16 (samples were analyzed on 2/8/16). This was added. Closed.
4. Is there any explanation for the high [Zn} in the blank? Suggest customer might consider blank correction of the data? Issue addressed in Limitations section and pointer added to that section. Closed.
5. I don't see adequate ICB/CCB paired with MCVA and MCVB samples? We need to discuss. Additional MCVA was added for investigative purposes as Be was not meeting specifications. Closed.
6. See duplicate RPD section. Range is 1.6 to 18.6 % with Ba (28.6%) and Zn (53.4%) exceptions. Fixed. Closed.
7. PS section – Either address QC results for all non-AOIs or don't in this section. Remove non-AOI discussion as our policy is not to go there. This was deleted. Closed.

Data Report

No concerns identified.

GC/MS Report; Final report submitted for QE review 3/9/16; QE review completed 3/9/16 -comment resolution 3/10/16 and cleared for release on 3/10/16

The information received for the GC/-MS analysis of 14 liquids and 3 headspace gas samples was the following:

- ASR 9937 and ASR 9937.01
- Test Instruction 68453-TI-001, Rev. 0, *PRF Canyon Sample Gas Evolution Testing*; Effective Date: 1/22/16. pp. 29 Mostly completed at the time of the review
- Draft report with chromatograms and tentatively identified components tables for MeOH and MeCl sample extracts for samples 16-0084 thru 16-0086 and 16-0088 thru 16-0091 and for head space samples for sample 16-0087.

Note: The ASO Lead and QE reviewed draft versions of the report and a comment resolution was held on 3/8/16 culminating in the version of the report reviewed in this reported activity. Most QE review comments were addressed in this process.

Note: Project Deficiency Report, DR-68453-12-16-16 was issued to address the fact that there was no time to follow the usual approach of writing and implementing a Validation Plan for the GC/MS moved from 331 to RPL/400; the data needed to close this DR are contained in this report and are presented in Table 2 and Figure 1 for the analysis of the Grob test mixture: used at the received concentrations, instrumental performance standard two (IPS2) represents a 10x dilution of ISP1, instrumental performance standard three (IPS3) represents a 100x dilution of IPS1 and instrumental performance standard three (IPS4) represents a 1000x dilution of IPS1. The DR was closed on 3/9/16 as the results were satisfactory.

There was another issue identified and documented as Occurrence Report, OR-98620-2-17-16, Holding Time Limit Concern for Some GC-MS Samples for ASR 9937. ASO test instruction, 98620-TI-001, *Rev. 0, PRF Canyon Sample Handling in Glove Box* in Section 4, Part 2, Organics Testing: Preparation for Gas Chromatography- Mass Spectrometry (GC-MS) lists holding time limits imposed by the project Statement of Work, Statement of Work for Contract 495170-40, Rev. 0, 236-Z PRF Canyon Floor Debris Sample Analysis (CHPRC to PNNL Supplier) FY16, 11/5/2015. These limits were:

Semi-VOA in Soil – 14 days from date of extraction
VOA in Soil – 14 days from date of extraction

Seven samples were received for analysis under this ASR; there were four samples that were MeOH extracted on 1/5/16 and analyzed by GC-MS on 1/23/16 (16-0086, 16-0088, 16-0089, and 16-0091) were outside the 14-day holding time limit window by 4 days. The impact of this condition was determined to be unknown. Because MeCl extractions were analyzed within the limit, these data were compared to the MeOH extraction data and showed a reasonable similarity, but of course, the extractions methods had differing efficiencies.

Cover Page

No concerns were identified. Everything previously identified was corrected.

Narrative

The narrative was reviewed and sections regarding sample collection, sample analysis quality control, sample analysis/results discussion (i.e., Venn diagrams to group results for common components [hydrocarbons, glycerin, and tributylphosphate (TBP)]) as well as for each extraction method (MeOH and MeCl) and the SPME samples presenting chromatograms and tentatively identified components in tables was the agreed upon approach.. Data from the TI were previously reviewed to assure transcription from the TI to the data report were correct.

Data Report

No concerns identified; the data report and narrative are presented together in this report.

M&TE Used: Most M&TE used is documented on the cover sheets of the individual analysis reports for the major analysis areas

Model and Manufacturer	Serial Number	Location	Calibration Status	Performance? Used On?
Balance	39080042	RPL/4055	Expires 8/2016	1/7/16 (anions)
Balance Mettler AT400	1113292667 a.k.a. 360-06-01-037	RPL/420 fumehood #13	Expires: 8/16	BPCL 11/6/15 Used 11/13/15 and 11/23/15; Performance verified
Balance Sartorius ME414S	22006647	RPL/420 benchtop	Expires: 2/16	BPCL 11/6/15 Used 11/23/15; Performance verified
Beckman Coulter pH 560 Meter		RPL/516	With use; documented on benchsheet	ICV/CCV 12/22/15
Cole-Parmer S1494 FF03 Microprobe		RPL/516	"	"

SUMMARY

Summary of Results:

There were no outstanding issues that resulted in findings or observations that have not been addressed and closed. All minor concerns identified were adequately addressed.

CORRECTIVE ACTION

[X] None Required [ ] Complete [ ] Follow-up Corrective Action

Surveillance Performed By:

Deborah Coffey

Deborah Coffey, QE

Date: 10 March 2016

REPORTING

Distribution: ASO Lead: K.N. Pool (also Project 68453 Manager)
ASO Administrator, Truc Trang Le
Project 68453 Manager, Mike Minette

Appendix G

Gas Generation Rates

Appendix G
Gas Generation Rates

Prepared by:

BK McNamara
RA Clark
C Delegard
KN Pool
RD Scheele
DS Coffey
MJ Minette

Summary

Eight samples, taken from the Plutonium Reclamation Facility (PRF) canyon floor were unpackaged at PNNL in the Radiochemistry Processing Laboratory (RPL)/ 506 on 23 November 2015 and on 9 December 2015. The samples were as received in 20 mL scintillation vials with the packaging appropriate for radiological containment. Two of eight sample vials were found to have their bottoms cleanly sheared off. This indicated to us that a pressure build up had occurred in these two vials that breached the vials; as opposed to a shipping/receiving incident that would have resulted in a cracked vial. Two of the samples were subsequently tested for indications of reactivity. These two samples are referred to as Pan J/2 Sample (16-0087) and Pan J/4 sample (16-0085)

The two samples had a very different visual appearance and displayed different reactivity upon further examination. For the reactivity testing, the samples were confined in a pressure vessel and gas generation rates were evaluated for each. Subsequent examination of gases produced during the sample confinements confirmed that the reactivity in Pan J/2 Sample (16-0087) was low or non-existent compared to that of Pan J/4 sample (16-0085), which demonstrated residual room temperature and elevated temperature reactivity that appeared to be diminished over the month of the reactivity testing experiments. Gas generation rates at room temperature and at 70°C were calculated and discussed. Infrared and mass spectroscopic data were acquired to provide the identity of the degradation products that resulted from the reactivity experiments.

Unpackaging PRF Canyon Floor Samples

Eight samples collected from the Plutonium Reclamation Facility (PRF) canyon floor were unpackaged at PNNL in RPL/ 506 on 23 November 2015 and on 9 December 2015. This effort was performed under a test instruction (TI) 98620-TI-001, *PRF Canyon Sample Handling in Glove Box.*

The initial unpackaging consisted of opening the transport drums, cutting the outer bags and removing the ice cream cartons, and the PVC glovebox sleeve containing the sample vials into a fume hood for examination. Once in the fume hood, the vials, within the PVC sleeve, were maneuvered so that a photo could be taken, and the vial and contents were examined as well as possible through the heavy-walled PVC bag, without further breach of the sample containment.

Once each sample was photographed, all were taken for gamma energy analysis (GEA). Radcon exams took place throughout these operations to determine dose rates and radioactive contamination.

Visual observations, as recorded during the 23 November 2015 unpackaging are presented in Table 1.

Table 1. Observations of Unpackaging PRF Canyon Floor Samples on 23 November 2015

RPL Sample Number	Client Sample ID	Location, Pan/ Sample	Order Opened	Sample Description
16-0084	B33MK3 (F16-001-001)	E/1	4	PRF Canyon Pan E Sample 1 (solid/sludge) Similar to O/1, with dark liquid on solids.
16-0085	B33MK4 (F16-001-002)	J/4	6	PRF Canyon Pan J Sample 4 (solid/sludge) Seems to have more grit than previously opened 5 samples.
16-0086	B33MK5 (F16-001-003)	J/1	1	PRF Canyon Pan J Sample 1 (solid/sludge) Only sample that showed contamination (α) between the thin yellow polyethylene bag and the outside of the PVC sleeve. Dark brown to black liquid was found within the tube bag and seemed to be the same material that was present within the glass vial. In fact, all items seemed to have some amount of the dark brown material on the tube bag walls or on the inner vial's outer surface. This item's sample material looked like dirty motor oil (or crankcase sludge) but did not flow readily.
16-0087	B33MK6 (F16-001-004)	J/2	5	PRF Canyon Pan J Sample 2 (solid/sludge) Similar to J/1, J/3, O/1, & E/1 with dark liquid on solids.
16-0088	B33MK7 (F16-001-005)	O/1	3	PRF Canyon Pan O Sample 1 (solid/sludge) Similar to J/3 but seemingly more fluid (i.e., lower viscosity).
16-0089	B33MK8 (F16-001-006)	J/3	2	PRF Canyon Pan J Sample 3 (solid/sludge) Similar to J/1 but with less leakage to the innermost bag.
16-0090	B33MK9 (F16-001-007)	H/1	7	PRF Canyon Pan H Sample 1 (solid/sludge) Inside of vial seemed to be "painted" everywhere within by dark liquid.
16-0091	B33ML0 (F16-001-008)	H/2	8	PRF Canyon Pan H Sample 2 (solid/sludge) Still black or very dark brown but is the most gritty of the samples.

In summary, the J/2 and J/4 sample appearances were very similar to each other with dark liquid, like dirty motor oil, and gritty solids where solids could be observed. The observations made of the samples within the vials (Table 1) were difficult because of the heavy yellow PVC bag covering and the white label that almost completely covered the curved walls of each vial.

Following extended GEA counting by the Analytical Support Operations (ASO) laboratory under Analytical Service Request (ASR) 9937, the eight samples were returned to RPL/ 506 for complete

opening down to the vial level. Six intact vials were removed from the PVC bags on 9 December 2015 inside a fume hood and then brought into an adjacent glovebox by way of an interconnecting airlock. The outer surfaces of the vials were wiped with moist paper towels (all vials had some level of dark-colored outside contamination, evident over white plastic caps and white labels), the PRF canyon floor sludge contents were examined through the clear glass (with best views through the bottom because the label covered the side walls), the vial caps opened to "burp" the contents and release any pent-up gas pressure, and the six intact vials set within a clean shallow plastic dish.

Pan J/1 (16-0086) and J/2 (16-0087) sample containers were found to be broken cleanly and circumferentially at the bottom such that the vial bottom was separated from the remainder of the vial. This suggests over-pressurization in the glass vials due to gas generation from the two samples. These broken vials were left with the remaining contents within their PVC glovebox sleeves in a bottoms-up orientation to retain whatever materials still were left within the vials. However, significant amounts of sample were outside of the vials and smeared within the PVC sleeve. Further observations on packaging and PRF canyon floor sludge samples are summarized in Table 2.

Table 2. Observations of Unpackaging PRF Canyon Floor Samples on 9 December 2015

Location, Pan/Sample	Order Opened	Observations
E/1	7	Bag not (further) yellowed. Contents similar to J/3 but more solids present (like J/4).
J/4	6	Bag not (further) yellowed. Contents similar to J/3 but more solids present.
J/1	2	Vial bottom broken. Tan mud observed within broken vial. PVC sleeve more yellowed compared with most other bags.
J/2	3	Vial bottom broken. Contents darker than J/1. PVC sleeve yellowed.
O/1	1	Contaminated on outside (like all vials). Contents like heavy dark oil, flow slowly.
J/3	5	Contents appear as sticky lumps up to ~5-mm diameter of coarse sand.
H/1	4	PVC sleeve yellowed but vial intact. Contents look like coarse sand stuck together.
H/2	8	Bag not (further) yellowed. Yellowish-tan mud but not flowing, wetter than J/3 & J/4.

Experimental Setup for Reactivity Testing

A 2-inch diameter, ½ inch height high vacuum pressure, cell made of 316 stainless steel, was equipped with an isolation (ball) valve. The sample cell was to be attached to a vacuum line with ¼ inch Swageloc fittings. Low temperature heating of the sample cell was accomplished by wrapping the sample cell with heat tape and insulation. Two thermocouples were attached to the sample cell under the heat tape. One thermocouple was used to control the temperature and a second was used as a passive temperature monitor. For room temperature measurements, a calibrated thermocouple that recorded room temperature over the course of the day was fixed to, but outside of the fumehood, where the vacuum system was housed. The vacuum line was pumped down with a roughing pump and a diffusion pump set up. A picture of the vacuum line is shown in Exhibit I of this report. The positions of the pressure sampling cell, the sampling space and the pressure readout are shown. The sample chamber or sample cell is labeled SC in Exhibit I. The yellow (2) orange (1b) and red highlighted (1a) areas are referred to in the text as the sampling space. When the sample cell valve is opened, the sampling space then becomes these highlighted areas plus the sample cell volume.

In a typical experiment, both the empty sample cell and the sampling space above the sample cell on the vacuum line was evacuated overnight and leak tested by a helium leak detector valved into the vacuum line near position 1b. The evacuated space (sampling space + cell) was then isolated and allowed to sit for several hours to record a "leak" rate. The sample cell was removed and brought into a glove box where the canyon sludge sample was added to it. The cell was brought out of the glove box and attached to the same position on the vacuum line. The glove box atmosphere was not removed from the sample cell by evacuation. Rather, the isolation valve was opened and the glove box atmosphere was expanded into the sampling space.

Any increase in pressure relative to this initial pressure would thus be an indication of sample reactivity. Testing was done at room temperature and at 60°C for the first sample tested, and at room temperature and at 70°C for the 2nd sample tested. For sufficient reactivity from a given sludge sample, the identities of gases produced could be ascertained by infrared spectroscopy (IR) and/or mass spectrometry (MS). The infrared spectrometer was a Nicolet Infrared (Model Magna 750) Spectrometer. The position of the infrared (IR) sampling cell is shown on the vacuum line setup in Exhibit I. Any gases produced in the sampling space could thus be partitioned to the IR cell directly. The IR cell was used as a feed to the inlet of the mass spectrometer (Extrel, TMAX).

The volumes of the vacuum line the sample cell and the IR cell were each calibrated. The calibration data was repeated for reactivity tests 1 and 2 as a new sample cell was built for the 2nd reactivity test. The volume calibration data are provided as Exhibits II, III, and IV.

Pressure Testing of a Pan J/2 Sample (16-0087)

Guided by test instruction (TI)-68453-TI-001, *PRF Canyon Sample Gas Evolution Testing*, the sample cell was filled on 02/12/2016 in a glovebox with Pan J/2 Sample (16-0087). The mass of the sample was 1.8470 g, as was recorded by the difference of the container mass before and after the removal of sample from the container. The sample cell contained about 1 atm (~760 torr) of the glove box atmosphere.

Prior to opening the sample cell, Table 3 suggests the baseline leak rate was very low (below 0.05 torr*h^{-1}). This baseline "leak" was likely an artifact caused by slight off gassing of moisture from the walls of the vacuum line.

The sample cell was opened and the gas present in the cell (~760 torr from the glovebox) was expanded into the sampling space volume. The total recorded pressure was 243.2 torr. The data in Table 3 also show that the zero reading on the pressure readout was 73.6 torr. The zero-adjusted total recorded pressure expanded from the sample cell to the sampling space is about 169 torr. Expansion of ~760 torr of the glove box atmosphere from the sample cell into the sampling space should have resulted in a total pressure of 166 torr. The observed pressure from Tables 1 and 2 was 243.2-73.6~ 169 torr. Again, this pressure originated from the glovebox atmosphere rather that the sample itself.

The data in Table 4 and plotted in Figure 1 indicate that a continuous drop in pressure of about 26 torr was observed over a 6-day period. In the middle of the 5th day there was a 2 degree ambient temperature increase relative to the previous day's recordings. This caused a slight pressure increase, but by 6:00 PM on 02/16/2016, the temperature had dropped back to about 21.5°C and the pressure decrease continued.

The pressure decrease could be due to a variety of factors such as hydration of the crystals (from the glovebox atmosphere) or by reaction of the oxidizing product gases, such as NO_2, with residual organics or by absorption of product gases by the walls of the vacuum manifold. At the time of the gas-generation pressure test, almost 2 months had passed since the initial observation of the Pan J/2 Sample (16-0087). In contrast to the sludge-like material, as observed at the time of receipt of the samples, the Pan J/2 Sample (16-0087) appeared as a dry crystalline salt at the time of filling (02/12/2016) of the sample cell. Crystallization and formation of a hydrated salt is an exothermic process (e.g. stabilizes the salt) and thus could draw moisture out of the sampling space, thereby lowering the pressure. A well-known laboratory example of this desiccating behavior is calcium sulfate, but sodium nitrate and hydroxide are also desiccating salts. An alternative pressure loss mechanism is that the sample may have emitted gases into the sample space and these may have been gradually adsorbed onto the (walls) larger surface area of the sampling space. Product gases may have back-reacted with the residual solids and depending on the stoichiometric requirements of such a reaction resulted in a drop in pressure. Understanding the cause of the pressure decrease would require knowledge of the chemical mechanisms in this closed system.

Table 3. Initial Vacuum Line Data to Establish a Baseline Prior to Opening the Sample Cell

date	time	cumm time, min	pressure, torr
2/12/2016	11:50	0	73.6
	12:00	10	73.6
	12:30	40	73.6
	13:30	100	73.8

Table 4. Pressure Data from 2/12 to 2/17/2016 after Expansion of Glovebox Gases in Sample Cell into the Sampling Volume, at Room Temperature. (A slow, continuous drop in pressure was observed.)

date	time	cumulative time, min	cumulative time, hr	pressure, torr	temperature, C
2/12/2016	13:30	0	0	243.2	21.1
	13:50	20	0.3	243.0	21.1
	14:20	50	0.8	242.9	21.3
	15:40	130	2.2	242.6	21.3
	16:00	150	2.5	242.4	21.2
2/15/2016	15:00	4410	73.5	220.2	21.8
2/15/2016	18:30	4620	77.0	219.9	22.6
2/16/2016	9:00	5490	91.5	218.5	21.5
	12:30	5700	95.0	218.8	23.1
	13:00	5730	95.5	219.1	23.3
	13:30	5760	96.0	219.1	22.3
	17:30	6000	100.0	218.7	21.8
2/17/2016	11:45	7095	118.3	217.7	21.9

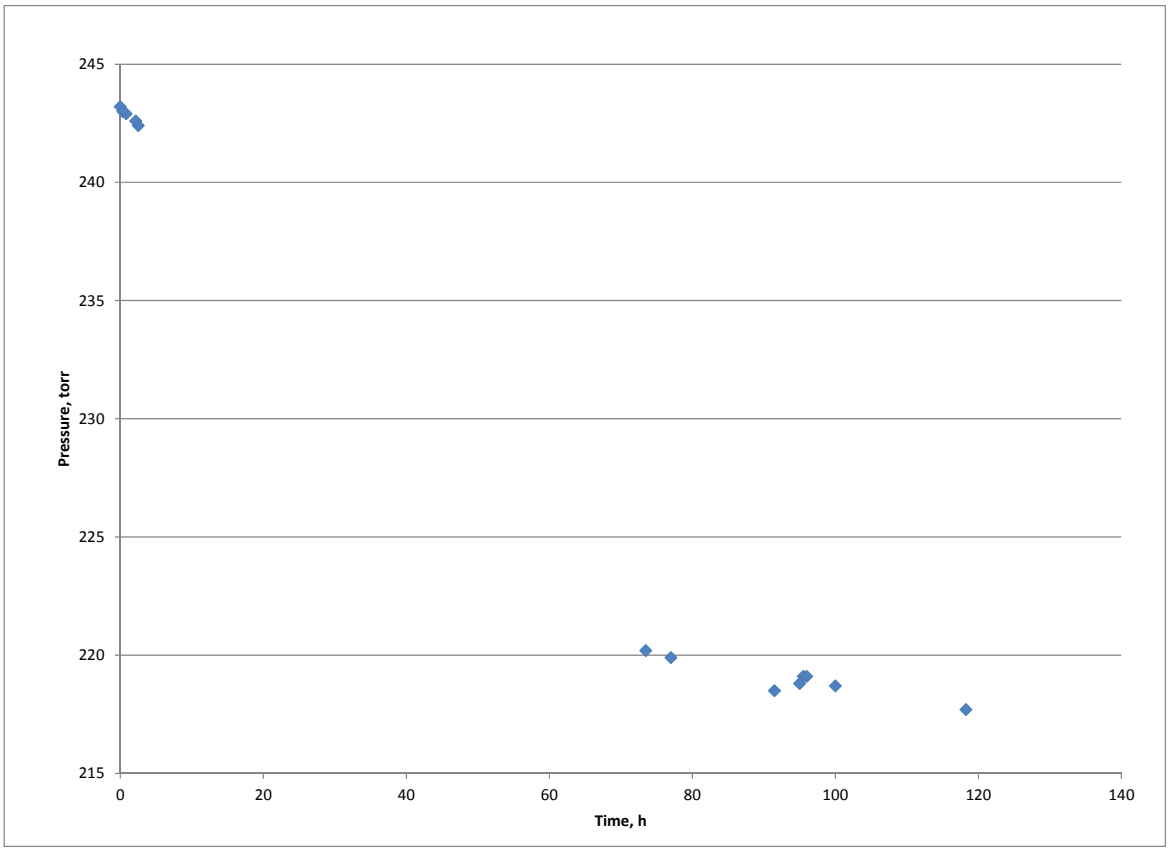


Figure 1. Pan J/2 sample (16-0087): Sample Pressure @ Room Temperature over Time. (Sample appeared to display some desiccating behavior.)

Constant Temperature 60°C: Pressure Testing of a Pan J/2 Sample (16-0087)

To determine the effects of temperature that would accelerate gas-producing reactions, we determined gas production at 60°C. The valve to the sample cell had been closed on 02/17/2015. The valve to the sample cell was opened. The first pressure in Table 5 was taken at 21.2°C. The assembly was then heated to 60°C and pressure readings were recorded as indicated in Table 5.

By the end of the first day, a pressure that exceeded the expected pressure with temperature increase (based on ideal gas law) was recorded (calculated as approximately 126 torr). During the second day, the observed pressure continued to increase but at a slower rate than the first day.

After the second day, the sample cell was isolated from the vacuum manifold and the sampling space above the sample cell was evacuated. The pressure in the sampling space was monitored at 60°C for 1-h to provide a system baseline leak rate. Based on the second section of Table 5, the "leak" or desorption rate of material from the vacuum line walls at 60°C was
about 10 torr*h^{-1}.

Figure 2 shows the initial pressure increase which may have resulted from some water volatility from the solid, or may have been the result of a reaction of the solid sample with heating. The pressure increase was modest and the rate of increase slowed as indicated. The "leak" data are also plotted and demonstrate a similar slope over 1-hr duration of the "leak" testing.

No further testing of this sample was carried out because it did not appear to us that this sample was exhibiting behavior consistent with rapid gas-producing reactivity. We already knew that the constituents in Pan J/2 sample (16-0087) had reacted producing sufficient gases to rupture one of two sample vials during shipping and/or receipt. In retrospect the decision to not continue testing may have been premature given the reactivity observed for the Pan J/4 sample (16-0085) as provided later**.**

Sample J/2 was less than ½ the mass of Sample J/4 yet it developed a similar pressure over a significantly shorted period of time. This would indicate that heating the Sample J/2 did initiate production of gaseous products. This indicates that elevated temperatures initiate latent reaction in sample J/2.

Table 5. Pan J/2 Sample (16-0087): Pressure Readings at Constant Temperature 60°C.

date	time	cumm time, min	cumm time, hr	pressure, torr	TC_1, Temperature, C	TC_2, Temperature, C
2/23/2016	11:00	0	0	105.3	21.1	NA
	11:30	30.00	0.5	110.1	60	60
	0:00	30.50	1.0	129.1	60	61
	12:30	90.00	1.5	157	60	62
	13:30	140.00	2.3	197	60	61
	15:00	240.00	4.0	242.7	60	61
	16:30	330.00	5.5	272.7	60	62
	19:00	480.00	8	308.9	60	61
2/24/2016	0:00		18	427.4	60	63
	11:00		24.0	462	60	63
	19:00		32.0	527	60	63

Close valve to pressure vessel. Evacuate space above cell.

Leak Test space above pressure cell

date	time	cumm time, min	cumm time, hr	pressure, torr	TC_1, Temperature, C	TC_2, Temperature, C
2/24/2016	19:30	0	18	82.4	60	62
	20:00	30	18.5	86	60	62
	20:30	60	19	92.9	60	62

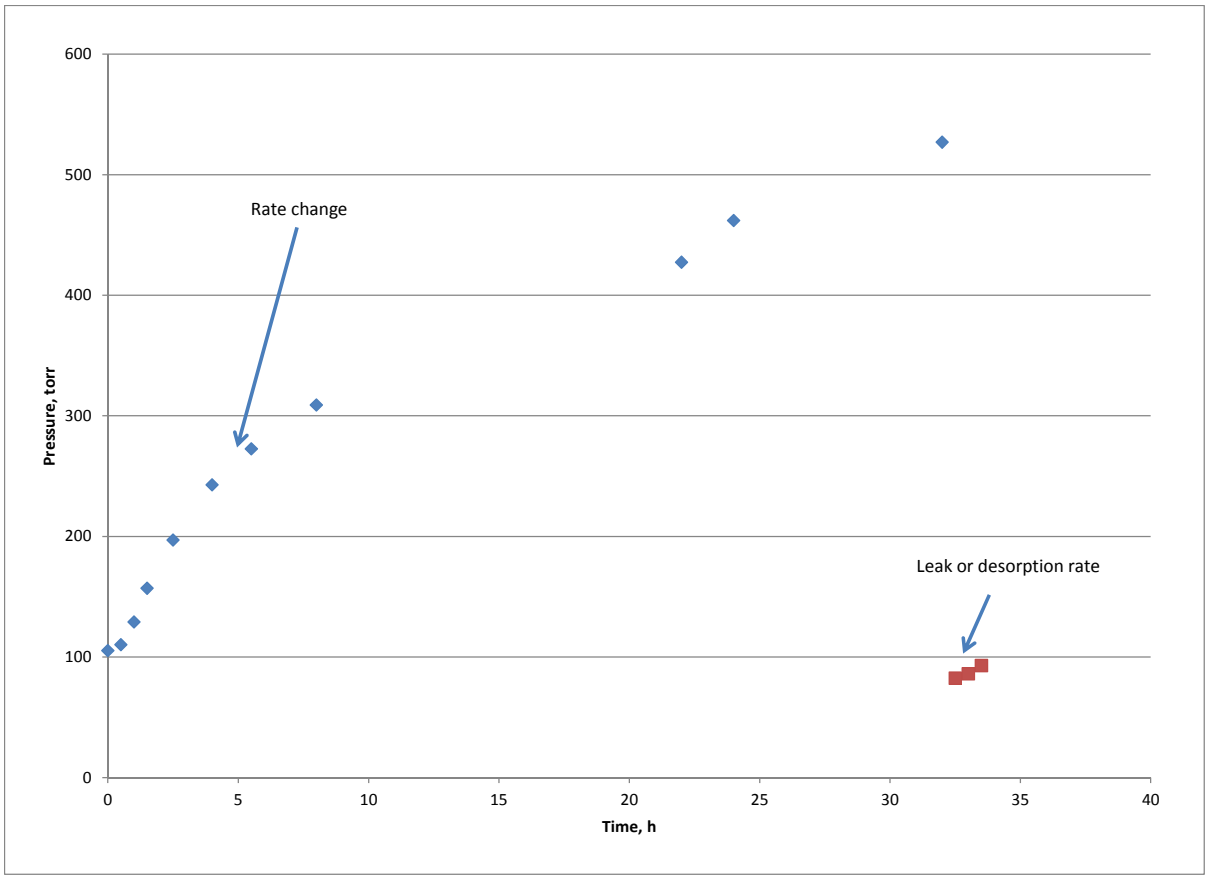


Figure 2. Reactivity Test Pan J/2 Sample (16-0087): Pressure @ 60°C over Time

Reactivity Testing of a Pan J/4 Sample (16-0085) at Room Temperature and 70°C

A second TI, 68453-TI-002, *PRF Canyon Sample Gas Evolution Testing on Pan J Sample* was issued for additional testing. The new sample cell was filled on 03/30/2016 in a glovebox with Sample Pan J/4 material (16-0085). The material had maintained its appearance as described in Table 2. The mass of the sample was 4.0507 g, based on the difference of the container mass before and after the transfer of sample from the container. The sample cell contained about 1 atm (~760 torr) of the glove box atmosphere. The sample cell was removed from the glovebox and attached to the vacuum line.

The space above the cell on the vacuum line was evacuated. As provided in Table 6, the pressures measured when the vacuum line was isolated from the sample cell and allowed to sit for 0.3 h there was either a very small 15.3 torr/h leak (Table 6) or that the interior walls of the vacuum line were off gassing water or other adsorbed gases.

As provided in Table 6, after opening the sample cell the pressure increased to 24.7 torr. The pressure rose with an increase in temperature over a 5.5 h period to 47.2 torr. This slow increase continued over a total of 6 days. On 04/01/2016 the cell was isolated from the vacuum line for an hour to establish if there was obvious independent behavior (leaking). This was not observed (highlighted in Table 6) the cell was opened to reach to a total cell plus line pressure of 163.3 torr. The increase in pressure recorded in Table 6 was different than the pressure decreases observed in the first room temperature reactivity test on the Pan J/2 sample (16-0087).

Table 6. Initial Vacuum Leak Testing and Set Up Data for Sample J/4 (16-0085)

date	time	cumulative time, min	pressure, torr	Temp, C	
3/30/2016	12:00	0	18.7	22.4	closed cell
	12:20	20	23.3	21.5	close cell
test run					
	12:40	40	24.7	21.5	open cell
	12:49	49	26.5	21.9	open cell
	13:20	80	30.1	22.5	open cell
	14:15	135	34.9	22.9	open cell
	14:35	155	36.5	23.2	open cell
	14:50	170	37.6	23.5	open cell
	15:00	180	39.4	23.6	open cell
3/30/2016	17:00	300	45.8	24.8	open cell
3/30/2016	17:30	330	47.2	24.8	open cell
3/31/2016	9:00	1260	85.9	24.7	open cell
3/31/2016	12:00	1440	91.9	22.3	open cell
4/1/2016	15:10	1630	108.2	22.7	open cell
4/1/2016	15:50	1670	107.8	22.7	close cell
4/1/2016	17:00	1740	110.2	22.7	open cell
4/4/2016	13:30	5850	163.3	22.8	open cell

At this point, it was difficult to gauge at room temperature (which varied during testing from 21.4 to 24.8°C) if this pressure increase was a very slow leak, was general off gassing, or was a result of gases generated from the sample. In retrospect and with the following experiments, we can conclude that the sample was likely slowly producing gaseous degradation products at room temperature as the same behavior was observed and more clearly defined at slightly elevated temperature.

The sample was heated to 70°C. Over about 25 hours the pressure increased to 580 torr (Table 7). The cell was cooled down to room temperature to establish if the observed pressure increase was due to PVT (Pressure, Volume, Temperature) behavior, but the pressure only decreased from 580 to 561 torr (highlighted line in Table 7 and plotted in Figure 3). At this point, we decided to allow the increase to exceed 1 atmosphere to unambiguously prove that reaction gases were being produced.

Table 7. Pressure Test at 70°C. Increase in Pressure Exceeded Expected Pressure from PVT**.**

date	time	cumulative time, min	cumulative time, hr	pressure, torr	TC_1/TC_2,°C
4/4/2016	13:30	0	0	164	22.8/70
	14:00	30.00	0.5	181.5	22.7/70
	14:30	60.00	1.0	196.1	22.7/70
	15:30	120.00	2.0	246.1	22.8/70
	16:00	150.00	2.5	276.3	22.8/70
	17:00	210.00	3.5	319.9	22.8/70
	18:30	300.00	5.0	365	22.8/70
4/5/2016	10:30	1260.00	21.0	584	23.2/70
	11:00	1290.00	21.5	574.8	23.2/45
	12:00	1350.00	22.5	565.4	23.2/29.2
	13:15	1425.00	23.75	562.2	22.6/21.9
	14:45	1515.00	25.25	560.8	21.6/18.1

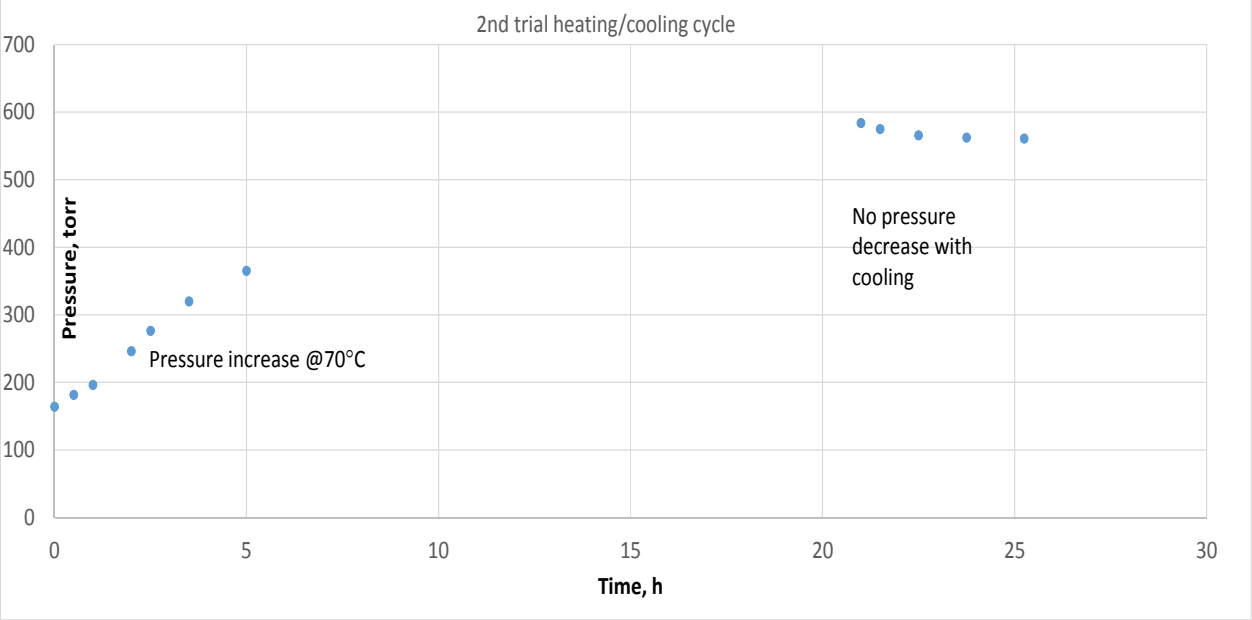


Figure 3. Gas Pressure Arising from Pan J/4 sample at 70°C. The sample pressure was clearly not a PVT behavior. For PVT behavior, the pressure should decrease to the initial pressure reading at room temperature on cooling.

The cell was cooled to room temperature with the isolation valve closed. The gases above the sample cell were evacuated. The sample was heated to 70°C again. The valve to the cell was opened and a new pressure increase was observed to exceed atmosphere (919 torr) over a 431 h period (Table 8). That the pressure exceeds atmospheric confirms that the sample was producing gases at elevated temperature and was very likely producing gases at room temperature.

Table 8. Cell Cooled to Room Temperature and Then Heated Again to 70°C. The pressure above atmospheric pressure is highlighted

date	time	time, min	time, h	pressure, torr	Temp, C
4/8/2016	15:30	0	195.5	18.3	22.8
	15:35	5	195.6	24.2	23.1
	15:50	20	195.8	26.8	24.0
	16:00	30	196.0	27.9	24.2
	16:12	42	196.2	28.7	24.2
	16:35	65	196.6	29.6	24.3
	16:35	0	196.6	145.2	24.3
	16:50	15	196.8	142.5	24.3
	17:00	25	197.0	142.5	24.8/70
	17:30	55	197.5	148.1	24.8/70
	17:45	70	197.8	153.8	24.8/70
4/11/2016	10:50	3975	262.8	595	21.3/70
	13:50	4155	265.8	607	23.1/70
	16:15	4300	268.3	608.5	23.1/70
	17:20	4365	269.3	614.5	22.9/70
	17:20	4365	269.3	622	22.9/70
4/12/2016	11:30	5455	287.5	669	24.3/70
	13:30	5575	289.5	679	21.6/70
	16:30	5755	292.5	687	21.5/70
4/13/2016	11:20	6885	311.3	733	21.8/70
	14:10	7055	314.2	742	22.1/70
	18:30	7315	318.5	753.9	22.4/70
4/14/2016	10:00	8245	334.0	783.9	22.4/70
	17:00	8665	341.0	796.2	21.3/70
4/15/2016	11:30	9775	359.5	830	21.2/70
	17:30	10135	365.5	843.7	23.3/70
4/18/2016	10:00	14005	430.0	916.5	23.1/70
	11:30	14095	431.5	919.8	23.1/70
Cell opened here for sample transfer to IR cell					
/18/2016	11:30	0	431.5	352.7	23.3/70
	13:15	105	433.3	362.1	23.3/70
	15:30	240	435.5	368	23.3/70

Figure 4 summarizes the gas production behavior of sample J/4 at various temperatures as a function of time. The pressure change rates or slopes are also illustrated in Figure 4. Table 9 provides the gas generation rates in mols total gas*h^{-1}*g^{-1} calculated from the recorded pressures in Tables 6-8 assuming ideal gas behavior. Rates are plotted in Figure 4 for activities: 1) the pressure increase observed at 70°C to 560 torr. 2a) initial pressure increase at 70°C after the cell was cooled to room temperature and gas was removed 2b), the pressure increase at 70°C to over atmospheric (+99.8 torr) and, 3) the continued` but slowing pressure increase after the IR cell was filled. The calculations for the gas generation rates are provided in Exhibit V.

The rates clearly show that the initial testing (marked 1) at 70°C caused the sample to produce gases faster than at room temperature. Comparison of initial 70°C data marked 1 with later testing at 70°C 2b and 3 shows a faster generation rate suggesting that the available reactants are diminishing. Comparison of data marked 1, 2a finds that after removing product gases the gas generation rate is faster. This occurred in the data marked 3 as well, albeit at a slower initial rate. The fast chemical in 2a rate is likely due to gases effusing out of the solid sample into the evacuated space. Once the effusion from the sample is complete, the actual chemical rate for gas generation is observed (2b). Consequently 2b would indicate the best pressure generation rate for that period of the samples life. In a similar fashion, the initial rate in 3 is followed by a slower gas generation rate than seen in 2b. Again this indicates a diminishment in rate but not the necessarily the ultimate total pressure. These reactions appear to slowly release gases and will continue to do so at lower and lower generation rates as reactants are consumed.

The reactivity testing of J/4 indicates that even though the materials were >5 months old and had produced sufficient amounts of gas to rupture a glass vial in the as received samples, there remains sufficient amounts of reactants to continue to produce gases and that increasing temperature can significantly increase the reaction rates or induce a different reaction mechanism. The higher temperature reaction could be the low temperature reaction or it could be a second reaction mechanism between the same reactants or another completely different reaction. Additional temperature testing would be required to fully assess the temperature dependency and sample aging on the reactions that occur in this complex chemical system.

These remarks are made here so as to not overstate or understate the importance of a fast generation (initial rate) or its slower partner. These effects were observed at the time of unpacking of the as-received samples, wherein the bottoms of 2 sample vials had been sheared off either by an initial rate or the slower chemical generation rate, ostensibly at ambient conditions. The ultimate total pressure build up is mass dependent and the total pressure generated can be estimated from data as shown in 1, 2, and 3. The kinetics of these reactions is unknown and the mass dependence of the reactions is also unknown.

The pressure data clearly point to residual self-sustaining reaction(s) occurring in the Pan J/4 Sample material and in the 60°C data for the Pan J/2 sample as well. This testing also showed that the self-sustaining reactions in this aged material are capable of still producing significant amounts of gases that can exceed atmospheric pressure in a closed sealed system at 70°C in less than100 h. The pressures were measured in the total sampling volume as indicated in Exhibit I. The pressure build up in the sampling space at 70°C was > 560 torr. This can be back-calculated to give a pressure in the sample cell actually experienced in the sampling cell of >5 atmospheres.

To further substantiate these results, a Fourier Transform Infrared (FTIR) spectrum of the gases in the sampling cell was acquired. For additional clarification of the cell contents, the mass spectrum of the gases was obtained using the same IR cell contents as feed to the mass spectrometer.

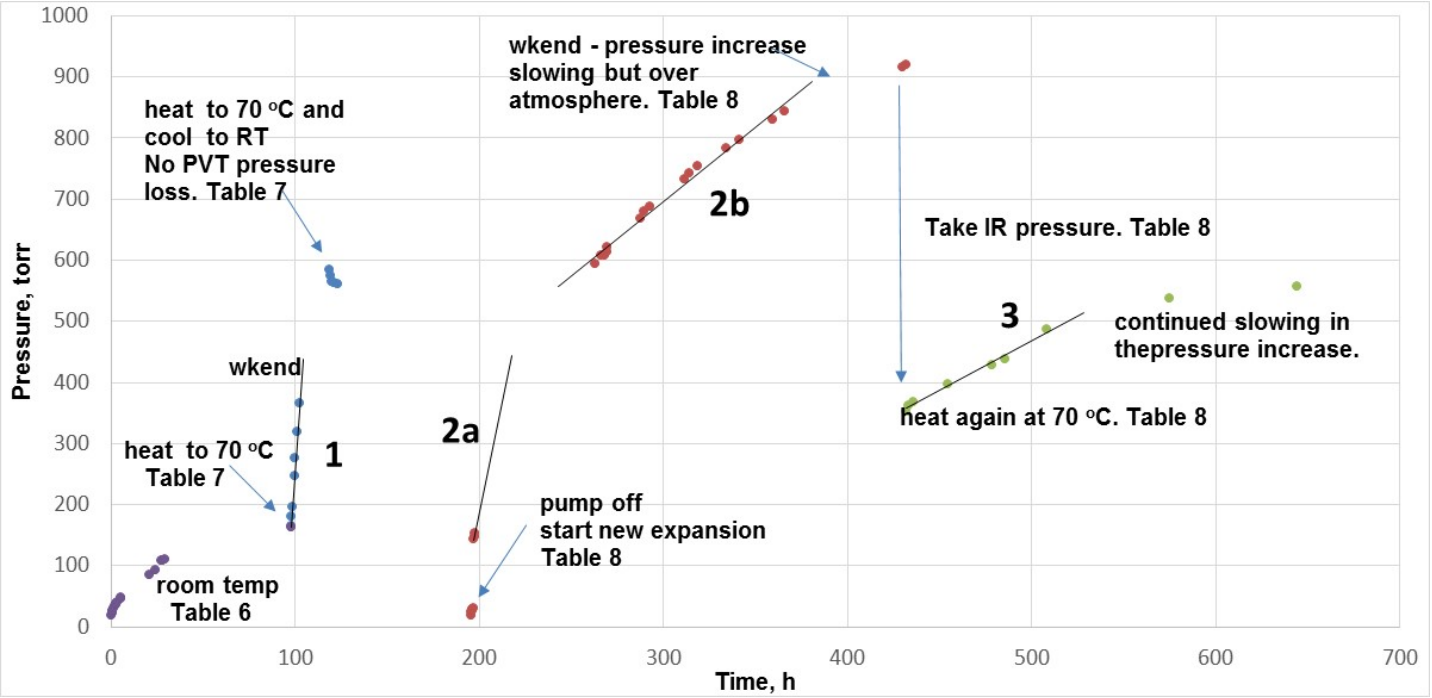


Figure 4. Reactivity Testing of J/4 Sample at Room Temperature and 70°C. Gas generation rates were calculated from the recorded pressures in Tables 6-8.

Table 9 provides the gas generation rates in mols total gas*hr^{-1}*g^{-1} calculated from the recorded pressures in Tables 6-8 assuming ideal gas behavior. The gaseous production rates provided in Table 9 range from 32 µmol h^{-1} g^{-1} to 1 µmol h^{-1}*g^{-1} with the rates declining with aging at 70°C. These rates are likely representative of the unique J/4 sample.

Table 9. Gas Generation Rates for Pan J/4 Sample at 70°C

Gas Generation	
Section	**Rate mol*hr^{-1}*g^{-1}**
1	3.23E-05
2a	1.11E-05
2b	1.87E-06
3	1.23E-06

Gas FTIR Analysis of Gases Produced from the Pan J/4 Sample

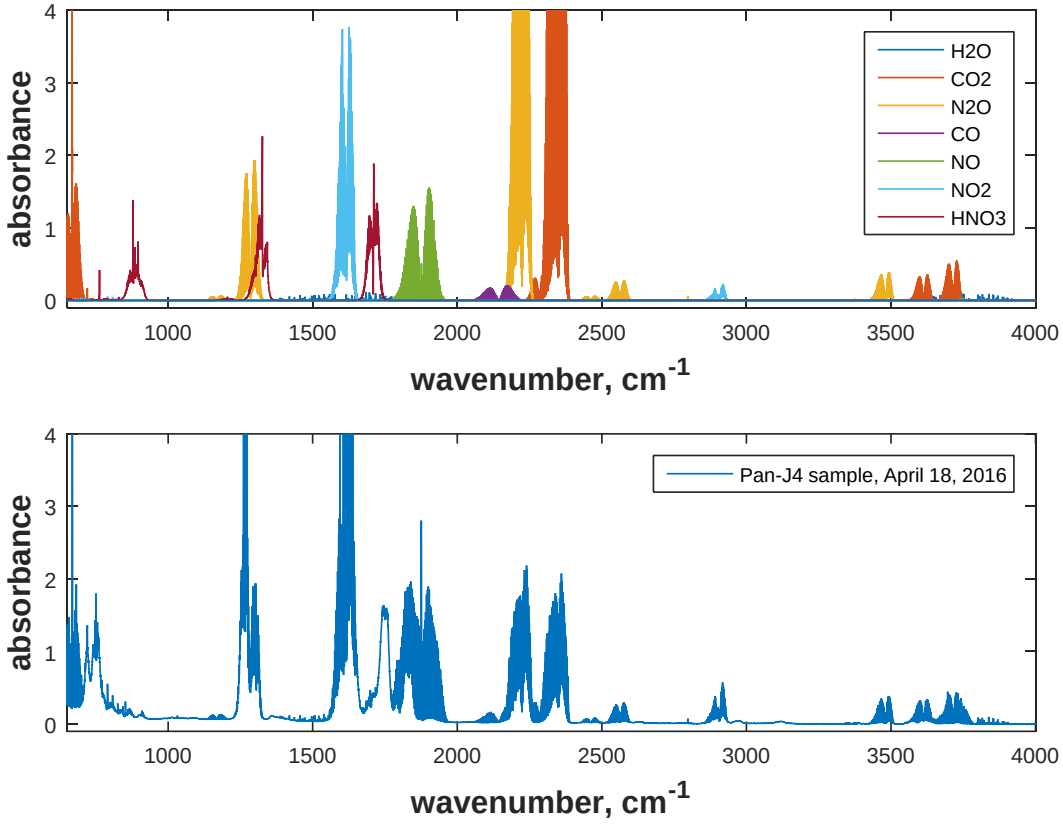
The gas sample was loaded into a 10 cm path length FTIR cell with CaF_2 optics. The pressure of gas loaded into the cell was ~500 torr. The gases evolved in the pressure experiments clearly contained at least NO_x where x = 3, 2, 1 as is indicated by the orange brown gas in Figure 5. FTIR data were acquired from this cell, at room temperature, using a spectral resolution of 0.125 cm^{-1}.

Figure 5. Photograph of Gas Sample Cell, Showing Visual Evidence of Presence of NOx Gases (orange color)

The infrared spectra in Figure 6 indicate that a complex mixture of several products arising from reaction of nitrates/nitrites with organics was present as a result of the sample reactivity. The resolved structure of each absorption band is a signature that the individual components of the mixture were small molecular fragments. This implies that alkanes, alcohols, aldehydes were not present at detectable levels in the IR spectrum. This negative result is significant as these products are flammable and would have implied higher energy density emanating from the sample.

The (HITRAN) HIgh resolution Transmission spectral database was used to assist identification and initial quantification of the gases in the FTIR cell. Multiple gas phase species (See Figure 6) were identified by comparison with known standard spectra, including: H_2O, CO_2, N_2O, CO, NO, NO_2, and possibly HNO_3. Water and carbon monoxide (CO) were present in the lowest

concentrations as is shown by the relative gas concentrations as output of the HITRAN calculation Figure 6 and Table 10. NO, CO_2, N_2O and NO_2 were present in relatively larger concentrations. The NO_x gases are consistent with decomposition of nitrate or nitric acid or more specifically with their oxidation of glycerin, while the CO_2 and CO were likely present from degradation of glycerin.



- **Figure 6.** Comparison between HITRAN Database Spectra and Pan-J/4 Sample Spectrum

Table 10. HITRAN Spectra Calculations: Output from HITRAN Database

molecule	pressure, atm
H_2O	**1.00E-03**
CO_2	**2.00E-02**
N_2O	**2.50E-02**
CO	**8.33E-04**
NO	**2.00E-02**
NO_2	**1.25E-02**
HNO_3	**1.00E-02**

For a more sensitive clarification of the cell contents, the mass spectrum of the gases (Figure 7) was obtained using the same IR cell contents as feed to the MS. The sensitivity of the mass experiment is orders of magnitude higher than the IR spectrum can provide.

The mass experiment confirmed the presence of CO_2, CO, NO_X products, water but also O_2, and N_2 that are not infrared active. Again there was no indication of low mass volatile alkanes, alcohols, and aldehydes. These products, as well as hydrogen might be formed radiolytically and would add to the reactivity potential of the product gas mixture because of the combination of oxidants and fuels. Consequently, the degradation of the sample J materials appears to be a purely thermal oxidation reduction reaction, initiated by the introduction of an organic (glycerin) to a nitrate containing solid.

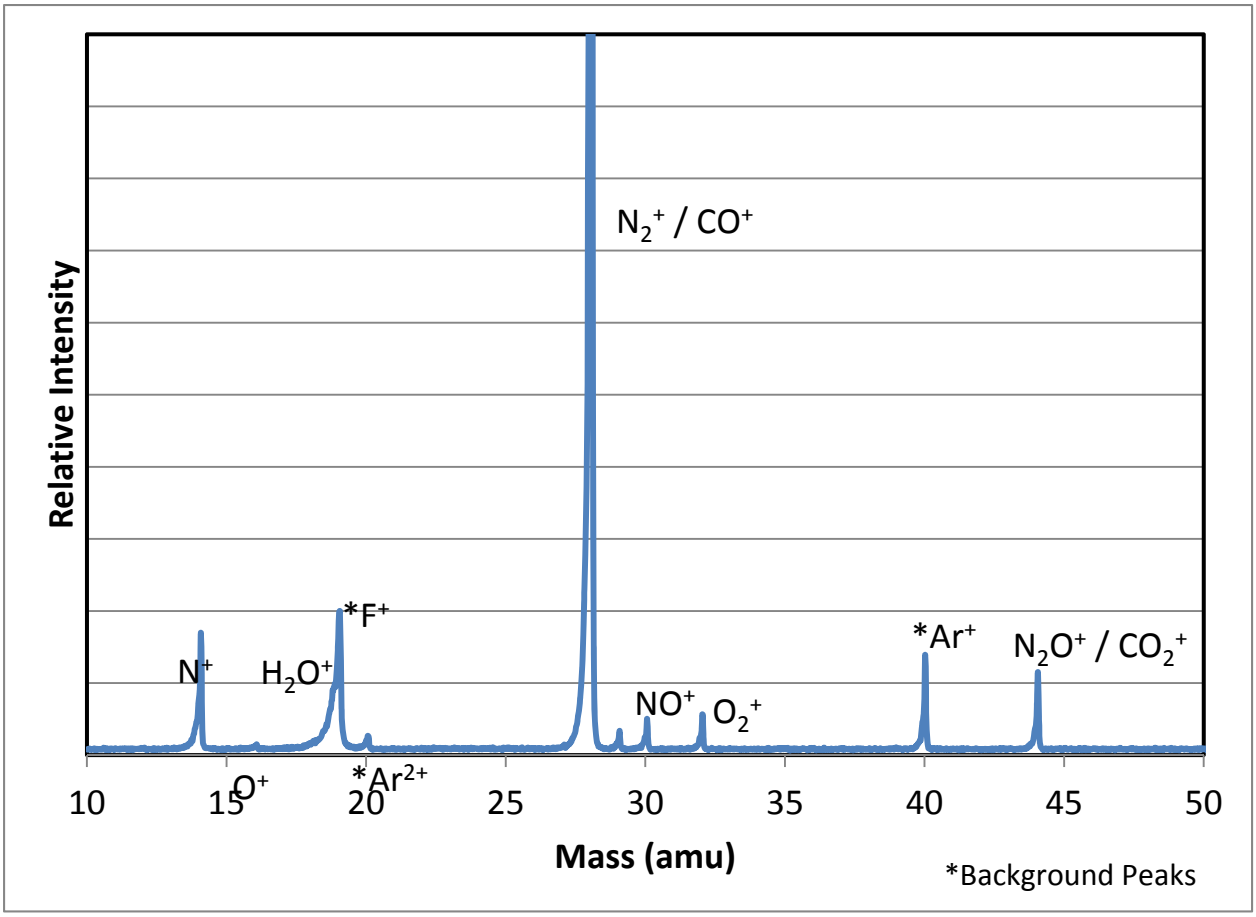


Figure 7. Mass Spectrum of the Gaseous Contents of the Pan-J/4 Sample as Loaded from the IR Cell

Summary and Conclusions

Of eight samples collected from the Plutonium Reclamation Facility (PRF) canyon floor and unpackaged at PNNL, two sample vials were found to have been breached as a result of over pressurization. To test for residual activity, we measured gas production at room temperature and 60°C or 70°C from a solid from one of the breached containers and from an intact sample that had been vented upon receipt. Gas production is a measure of whether sample constituents were thermally reacting or radiolytically decomposing. The use of two temperatures provided some limited insights into the thermal sensitivities of any reactions. Product gases from the intact sample were also characterized to determine the nature of any gas-producing reactions and to distinguish between thermal and radiolytic mechanisms. These two samples are referred to as Pan J/2 Sample (16-0087) and Pan J/4 sample (16-0085).

These studies found:

- No gas production from the Pan J/2 sample at room temperature during the limited test duration indicates that there was no observable latent reaction at room temperature.

- Significant gas production from the Pan J/2 sample at 60°C during a limited test duration, indicates that elevated temperature initiates latent reaction(s) in the sample.
- The Pan J/4 sample produced gases at room temperature indicating that constituents in the greater than 5 months old sample were reacting with one another.
- When heated to 70°C, the rate of gas production from Pan J/4 sample increased indicating that the room temperature reaction accelerates upon exposure to higher temperatures or that a second more thermally sensitive (higher activation energy) reaction mechanism occurs.
- With time at 70°C, the rate of gas production from the Pan J/4 sample declines indicating that the reactants for this reaction are being consumed.
- Gas generation rates of up to 32 $\mu mol*g^{-1}*h^{-1}$ and declining to 1.6 $\mu mol*g^{-1}*h^{-1}$ were observed.
- The FTIR and MS analyses of the product gases found oxides of nitrogen, carbon dioxide and carbon monoxide, and water indicating that nitrates/nitrites are reacting with organics in the sample.
- The FTIR and MS analyses confirmed the absence of alkanes, alcohols, or aldehydes indicating that radiolytic degradation of the organics was not occurring.

The overall conclusions from this limited scope of reactivity testing are 1) that low temperature (room temperature) reactions between the nitrate/nitrite and organic constituents in at least one material continue to occur even in samples that are several months old, 2) that the reaction(s) that can occur are thermally sensitive and accelerate or initiate upon heating, and 3) that the reaction(s) that occur at higher temperature consume the reacting constituents for this particular reaction.

Should additional information be required to understand and further define the risks, nature, and thermal sensitivities of these materials, studies using techniques such as accelerating calorimetry and differential thermal analysis coupled with thermogravimetry could be used to determine and further understand the thermal sensitivities of observed reaction(s) and when coupled with off-gas analysis the nature and number of reactions contributing to the production of gases at various temperatures.

Exhibit I: Valve and Sampling Setup for Pan J Reactivity Testing

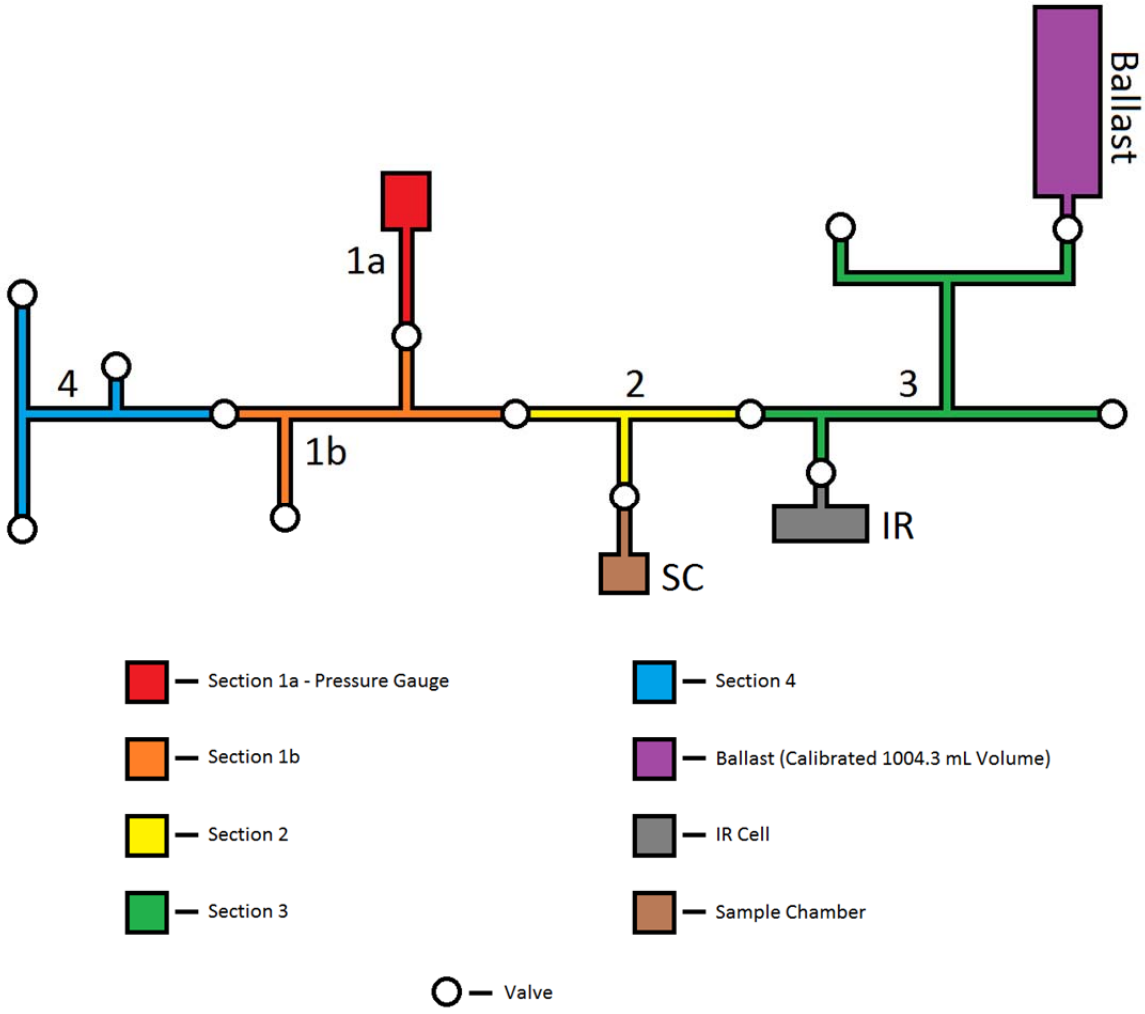


Exhibit II: Calibration data for the 1st sample cell and the sample space used for pressure testing Pan J/2 Sample (16-0087)

		18 Jan 2016				4 Jan 2016			
	Units	Run 1	Run 2	Run 3	Run 4	Run 5	Run 6	Average	St. Dev.
Volume Ballast	mL	1004.3	1004.3	1004.3	1004.3	1004.3	1004.3		
Pressure Ballast	torr	847.2	765.5	691.7	827.4	746.6	620.4		
Pressure Initial Line & Samples	torr	21.7	22.0	22.1	21.4	21.3	21.1		
Final Pressure (Ballast + Line)	torr	771.9	697.6	630.5	752.9	680.3	565.7		
Volume Line	mL	**100.80**	**100.94**	**101.02**	**102.28**	**101.04**	**100.87**	**101.16**	**0.56**
						1st	2nd		
Volume (Previous)		1105.10	1105.24	1105.32	1106.58	1105.34	1209.80		
Final Pressure (Previous + Sample)	torr	765.5	691.7	625.2	746.6	674.6	514.6		
Volume Sample Chamber	mL	**9.51**	**9.74**	**9.71**	**9.61**	**9.64**	**9.81**	**9.67**	**0.10**
						2nd	1st		
Volume (Previous)						1114.98	1105.17		
Final Pressure (Previous + IR)	torr					620.4	518.6		
Volume IR Cell	mL					**100.87**	**104.63**	**102.75**	**2.66**

Exhibit III: Calibration data for the 2nd sample cell and the sampling space used for pressure testing of Pan J/4 Sample (16-0085)

Project: 68453

Test Instruction: 68453-TI-002

		28 Mar 2016				
	Units	**Run 1**	**Run 2**	**Run 3**	**Average**	**St. Dev.**
Volume Ballast	**mL**	1004.3	1004.3	1004.3		
Pressure Ballast	**torr**	268.1	243.4	221.3		
Pressure Initial Line & Samples	**torr**	39.0	38.7	38.7		
Final Pressure (Ballast + Line)	**torr**	245.7	223.4	203.4		
Volume Line	**mL**	**108.84**	**108.75**	**109.15**	**108.91**	**0.21**
Volume (Previous)		1113.14	1113.05	1113.45		
Final Pressure (Previous + Sample)	**torr**	243.4	221.3	201.6		
Volume Sample Chamber	**mL**	**12.53**	**12.80**	**12.30**	**12.54**	**0.25**

This volume is V8 to V4 with V2 open

The last time we did the calibration we got 101.2 mL
The gear for the reactor vessel explains the difference

Exhibit IV: Calibration data for the sampling space used for pressure testing of Pan J/4 Sample (16-0085); volumes of specific vacuum line sections for calculation of mols of gas.

After reactions were over, these volume calibrations were performed on the line to establish mols of gas for the pressure generation data
The vacuum line set up is shown in Attachment 1.

		Sections 1-3					Section 3		
	Units	Run 1	Run 2	Run 3		Units	Run 1	Run 2	Run 3
Volume Ballast	mL	1004.3	1004.3	1004.3	Volume Ballast	mL	1004.3	1004.3	1004.3
Pressure Ballast	torr	896.2	816.9	744.6	Pressure Ballast + Section 3	torr	679.6	653.7	628.9
					Volume Line (Sections 1, 2, & 3)	mL	102.4	102.4	102.4
Pressure Initial Line	torr	39.0	39.0	38.8	Pressure Initial Line & Samples	torr	38.8	38.9	38.9
Final Pressure (Ballast + Line)	torr	816.9	744.6	679.6	Final Pressure (Ballast + Line)	torr	653.7	628.9	605.0
Volume Line (Sections 1, 2, & 3)	mL	102.38	102.91	101.87	Volume Section 3	mL	57.66	57.74	57.56
		Average	St. Dev.				Average	St. Dev.	
		102.39	0.52				57.65	0.09	

		Sections 1 & 2					Sections 1a & 1b		
	Units	Run 1	Run 2	Run 3		Units	Run 1	Run 2	Run 3
Volume Ballast	mL	1004.3	1004.3	1004.3	Volume Section 1	mL	32.3	32.3	32.3
Pressure Ballast + Section 2 & 3	torr	605.0	588.5	572.5	Pressure Section 1a	torr	556.9	239.1	116.2
Volume Line (Sections 1, 2, & 3)	mL	102.4	102.4	102.4					
Pressure Initial Line & Samples	torr	38.9	39.0	38.9	Pressure Initial Section 1b	torr	39.0	39.0	39.0
Final Pressure (Ballast + Line)	torr	588.5	572.5	556.9	Final Pressure (Section 1)	torr	239.1	116.2	68.7
Volume Section 2 + 3	mL	70.13	70.16	70.03	Volume Section 1b	mL	19.81	19.83	19.86
		Average	St. Dev.				Average	St. Dev.	
		70.11	0.07				19.83	0.03	
Volume Section 2	mL	12.48	12.51	12.38	Volume Section 1a	mL	12.47	12.45	12.42
		Average	St. Dev.				Average	St. Dev.	
		12.46	0.07				12.45	0.03	
Volume Section 1	mL	32.26	32.22	32.35					
		Average	St. Dev.						
		32.28	0.07						

		Section 4					
	Units	Run 1	Run 2	Run 3			Volume (mL)
Volume Ballast + Section 2 & 3	mL	1074.4	1074.4	1074.4		Section 1	32.3
Pressure Ballast + Section 2 & 3	torr	542.7	513.3	485.6		Section 1a	12.4
						Section 1b	19.8
						Section 2	12.5
Pressure Initial Line & Samples	torr	38.9	39.0	38.9		Section 3	57.7
Final Pressure (Ballast + Line)	torr	513.3	485.6	459.4		Section 4	34.4
Volume Section 4	mL	34.31	34.36	34.66			
		Average	St. Dev.				
		34.44	0.19				

Exhibit V: Calculations for the gas generation rates for activities: 1) the pressure increase observed at 70°C to 560 torr. 2a) initial pressure increase at 70°C after the cell was cooled to room temperature and gas was pumped off, 2b) the pressure increase at 70°C to over atmosphere (99.8 torr) and, 3) the continued but slowing pressure increase after the IR cell was filled.

Closed Cell Vol. 0.0447 L
Open Cell Vol. 0.0573 L

Mass of Sample 4.0507 g

T 25 °C leak testing and 22 °C isothermal

Pan-J 4 material

	total cumm Time, min	total cumm time, hr	pressure, torr	gas, mol	gas generation, mol/g	Rate Measurement Section	slope, mol/(hr*g)	Temp, °C	Notes
Room Temperature - Offgas	0	0.0	18.7	4.52E-05	1.11E-05		8.23E-06	22.4	Closed cell
	20	0.3	23.3	5.63E-05	1.39E-05			21.5	Close cell
	40	0.7	24.7	7.64E-05	1.89E-05			21.5	Open cell
	49	0.8	26.5	8.19E-05	2.02E-05			21.9	Open cell
	80	1.3	30.1	9.31E-05	2.30E-05			22.5	Open cell
	135	2.3	34.9	1.08E-04	2.66E-05			22.9	Open cell
	155	2.6	36.5	1.13E-04	2.79E-05			23.2	Open cell
	170	2.8	37.6	1.16E-04	2.87E-05			23.5	Open cell
	180	3.0	39.4	1.22E-04	3.01E-05		2.17E-06	23.6	Open cell
	300	5.0	45.8	1.42E-04	3.50E-05			24.8	Open cell
	330	5.5	47.2	1.46E-04	3.60E-05			24.8	Open cell
	1260	21.0	85.9	2.66E-04	6.56E-05			24.7	Open cell
	1440	24.0	91.9	2.84E-04	7.02E-05			22.3	Open cell
	1630	27.2	108.2	3.35E-04	8.26E-05			22.7	Open cell
	1670	27.8	107.8	*3.33E-04	*8.23E-05			22.7	Close cell
	1740	29.0	110.2	3.41E-04	8.41E-05			22.7	Open cell
	5850	97.5	163.3	5.05E-04	1.25E-04			22.8	Open cell

Heat to 70 °C isothermal to about 600 torr **Pan-J 4 material**

	total cumm Time, min	total cumm time, hr	Pressure, torr	gas, mol	gas generation, mol/g	Rate Measurement Section	slope (mol/hr)	TC_1, TC2, °C	
1 - 70C Gas Generation	5850	97.5	164	5.07E-04	1.25E-04			22.8/70	
	5880	98.0	181.5	5.61E-04	1.39E-04			22.7/70	
	5910	98.5	196.1	6.06E-04	1.50E-04			22.7/70	
	5970	99.5	246.1	7.61E-04	1.88E-04	1	3.23E-05	22.8/70	
	6000	100.0	276.3	8.54E-04	2.11E-04			22.8/70	
	6060	101.0	319.9	9.89E-04	2.44E-04			22.8/70	
	6150	102.5	365	1.13E-03	2.79E-04			22.8/70	
	7110	118.5	584	1.81E-03	4.46E-04			23.2/70	
Chill	7140	119.0	574.8	1.78E-03	4.39E-04			23.2/45	
	7200	120.0	565.4	1.75E-03	4.32E-04		-3.84E-06	23.2/29.2	
	7275	121.3	562.2	1.74E-03	4.29E-04			22.6/21.9	
	7365	122.8	560.8	1.73E-03	4.28E-04			21.6/18.1	

Continued heating at 70 °C of Pan J material 4 **Pump off expansion volume to pressure cell valve.**

Offgas	11730	195.5	18.3	4.42E-05	1.09E-05			22.8	Leak check of volume above cell. This increase is the off gas rate.
	11735	195.6	24.2	5.84E-05	1.44E-05			23.1	Off gasing from volume walls
	11750	195.8	26.8	6.47E-05	1.60E-05		5.17E-06	24.0	Cell closed
	11760	196.0	27.9	6.74E-05	1.66E-05			24.2	Cell closed
	11772	196.2	28.7	6.93E-05	1.71E-05			24.2	Cell closed
	11795	196.6	29.6	7.15E-05	1.76E-05			24.3	Cell closed

	11795	196.6	145.2	4.49E-04	1.11E-04		-8.24E-06	24.3	Cell opened , Room Temperature
	11810	196.8	142.5	4.41E-04	1.09E-04			24.3	Cell opened , Room Temperature
2 - 70C Gas Generation	11820	197.0	142.5	4.41E-04	1.09E-04	2a	1.11E-05	24.8/70	Cell opened , heated
	11850	197.5	148.1	4.58E-04	1.13E-04			24.8/70	Cell opened , heated
	11865	197.8	153.8	4.76E-04	1.17E-04			24.8/70	Cell opened , heated
	15770	262.8	595	1.84E-03	4.54E-04	2b	1.87E-06	21.3/70	Cell opened , heated
	15950	265.8	607	1.88E-03	4.63E-04			23.1/70	Cell opened , heated
	16095	268.3	608.5	*1.88E-03	*4.65E-04			23.1/70	Cell closed, heated
	16160	269.3	614.5	*1.90E-03	*4.69E-04			22.9/70	Cell closed, heated
	16160	269.3	622	1.92E-03	4.75E-04			22.9/70	Cell opened , heated; jump here suggests cell is producing pressure
	17250	287.5	669	2.07E-03	5.11E-04			24.3/70	Cell opened , heated
	17370	289.5	679	2.10E-03	5.18E-04			21.6/70	Cell opened , heated
	17550	292.5	687	2.12E-03	5.24E-04			21.5/70	Cell opened , heated
	18680	311.3	733	2.27E-03	5.60E-04			21.8/70	Cell opened , heated
	18850	314.2	742	2.29E-03	5.66E-04			22.1/70	Cell opened , heated
	19110	318.5	753.9	2.33E-03	5.76E-04			22.4/70	Cell opened , heated
	20040	334.0	783.9	2.42E-03	5.98E-04			22.4/70	Cell opened , heated
	20460	341.0	796.2	2.46E-03	6.08E-04			21.3/70	Cell opened , heated
	21570	359.5	830	2.57E-03	6.34E-04			21.2/70	Cell opened , heated
	21930	365.5	843.7	2.61E-03	6.44E-04			23.3/70	Cell opened , heated
	25800	430.0	916.5	2.83E-03	7.00E-04		1.68E-06	23.1/70	Cell opened , heated
	25890	431.5	919.8	2.84E-03	7.02E-04			23.1/70	Cell opened , heated

Cell opened here for transfer to IR cell

3 - 70C Gas Generation	25890	431.5	352.7	1.09E-03	2.69E-04	3	1.23E-06	23.3/70
	25995	433.3	362.1	1.12E-03	2.76E-04			23.3/70
	26130	435.5	368	1.14E-03	2.81E-04			23.3/70
	27270	454.5	398	1.23E-03	3.04E-04			23.1/70
	28710	478.5	429	1.33E-03	3.28E-04			23.1/70
	29130	485.5	439	1.36E-03	3.35E-04			24.1/70
	30510	508.5	486	1.50E-03	3.71E-04			24.2/70
	34500	575	538.2	1.66E-03	4.11E-04		2.08E-07	23.5/70
	38640	644	557	1.72E-03	4.25E-04			22.2/70

*Open cell volume used to prevent artificial drop in mols generated due to volume drop (both sections at same pressure)

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