

Waste Tank Organic Safety Project

Analysis of Liquid Samples from Hanford Waste Tank 241-C-103

Technical Task Leader: K. H. Pool

Project Manager: R. M. Bean

Report contributors:

R. R. Adee	R. B. Lucke
D. L. Baldwin	G. M. Mong
R. M. Bean	K. H. Pool
S. A. Bryan	J. K. Rau
I. E. Burgeson	D. E. Rinehart
M. C. Burt	J. M. Robbins
J. A. Campbell	G. A. Ross
N. G. Colton	D. R. Sanders
L. C. Cronk	R. W. Sanders
S. A. Clauss	R. L. Sell
S. K. Fadeff	M. J. Steele
S. A. Homi	R. T. Steele
F. V. Hoopes	R. S. Strebin
E. W. Hoppe	S. W. Thompson
T. Y. Hosaka	J. M. Tingey
G. S. Klinger	J. J. Wagner
B. D. Lerner	

March 1994

Prepared for Westinghouse Hanford Company
and the U. S. Department of Energy
under contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Richland, Washington 99352

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Abstract

A suite of physical and chemical analyses has been performed in support of activities directed toward the resolution of an Unreviewed Safety Question concerning the potential for a floating organic layer in Hanford waste tank 241-C-103 to sustain a pool fire. The analysis program was the result of a Data Quality Objectives exercise conducted jointly with staff from Westinghouse Hanford Company and Pacific Northwest Laboratory (PNL). The organic layer has been analyzed for flash point, organic composition including volatile organics, inorganic anions and cations, radionuclides, and other physical and chemical parameters needed for a safety assessment leading to the resolution of the Unreviewed Safety Question. The aqueous layer underlying the floating organic material was also analyzed for inorganic, organic, and radionuclide composition, as well as other physical and chemical properties. This work was conducted to PNL Quality Assurance impact level III standards (Good Laboratory Practices).

Summary

On December 15, 1993, Pacific Northwest Laboratory (PNL) received five samples of organic liquid and one sample of underlying aqueous supernatant liquid taken from Hanford waste tank 241-C-103 (C-103). The analytical plan for the samples was formulated from a Data Quality Objectives (DQO) exercise conducted jointly by staff from Westinghouse Hanford Company and PNL. The analytical plan is contained in the DQO report. The purpose of the analytical work was to provide data for a Safety Analysis Report that addresses an Unreviewed Safety Question (USQ) concerning the potential for a pool fire in the organic layer of tank C-103, with subsequent loss of containment and possible radiation release to the surrounding environment.

Data obtained from execution of the analytical plan are summarized in Tables S.1, S.2 and S.3. Table S.1 gives results for the organic layer, Table S.2 gives results for the aqueous layer, and Table S.3 compares the inorganic analytes found in both phases. The data in Tables S.1, S.2, and S.3 are not qualified with respect to accuracy or precision; these qualifications are presented in the main body of this report.

Organic Layer Analyses (Table S.1)

Of major consequence to the safety analysis is the potential for combustion of the organic liquid. Thus, several data sets were generated that bear on the organic flammability: direct flash point determination, analysis of the bulk composition of the organic material, and determination of the vapor composition above the organic material at different temperatures.

Flash point measurements were made using an instrument designed to test small quantities of liquid, since sample was limited and contained radioactive elements. The instrument is presently undergoing certification by the American Society for Testing and Materials. Initial flash point measurements of C-103 organic indicated unexpected values exceeding 400°F, although compositional analysis showed that the volatile material present was about 25% by weight normal paraffin hydrocarbon (NPH). Results obtained for a check standard of dodecane were within 4°F of the expected flash point. Further tests with mixtures of pure NPH and tributylphosphate (TBP) resulted in establishing a modified test procedure that gave credible measurements with the samples, while still giving good agreement with a certified standard of n-dodecane. The modified procedure yielded an average value for the flash point of the C-103 organic layer of 246°F (119°C).

To support the experimental flash point measurement, composition information is required to enable calculations to be made that will estimate the lower flammability limit for the C-103 organic layer. Table S.1 indicates that both NPH and TBP were found to be the principal constituents of the organic layer. In addition to these components, branched alkanes and dibutyl butylphosphonate were also found in lesser quantities. The organic composition, determined by gas chromatography/mass spectrometry (GC/MS), only applies to material that is volatile enough to travel through a heated capillary separation column. Careful analysis has shown that 25% of the injected material cannot be accounted for by GC/MS analysis. Attempts to identify the missing material as partially hydrolyzed TBP or carboxylic acids through derivatization procedures were unsuccessful. Residues from heating to 320°C, in vacuo, account for approximately half of the missing material. Examination of the residues by scanning electron microscopy (SEM) and x-ray fluorescence (XRF) revealed the presence of inorganic salts primarily silicates and phosphates. Such nonvolatile materials will not contribute to ignition of the organic material.

This conclusion is further reinforced by a GC/MS analysis of the vapor over C-103 organic liquid heated to 40, 70, and 100°C. Although many volatile components were found in the vapor space, the major components at all temperatures were the constituent components of

NPH. It is gratifying to note that the total concentration of material found in the vapor space above the sample organic material at 40°C was well within the range of concentrations found from actual assays of volatile constituents in the vapor space in C-103, where tank temperatures approximate 40°C.

Table S.1. Summary Results of Analysis of Organic Supernatant Phase of C-103

Determination	Results
Flash point	~246°F, with tester in "Setaflash" mode
Organics by GC/MS	TBP:NPH = 67:33(w:w), 62:38 (v:v)
Organic volatiles	1.4 mg/L organic material equilibrated above surface at 40°C (mostly NPH and TBP)
Peroxides	Less than 2.5 µEquivalent/g
Nitroalkanes	No indication of nitroalkanes by RSST ^(a) experiment; less than 2 µmol/g by infrared analysis
Density	0.876 g/mL at 25°C, 0.868 g/mL at 44°C
Viscosity	4 cP at 25°C, 2.5 cP at 40°C
Gross alpha, beta	Alpha = 547 pCi/g Beta = 1.05 x 10 ⁶ pCi/g
⁹⁰ Sr	5.5 x 10 ⁵ pCi/g
Alpha emitters	²³⁸ Pu = 90.2, ²³⁹⁺²⁴⁰ Pu = 194, ²⁴¹ Am = 179 (pCi/g)
Gamma emitters	⁶⁰ Co = 7.45 x 10 ⁻⁴ , ¹³⁷ Cs = 4.13 x 10 ⁻² , ¹⁵⁴ Eu = 3.17 x 10 ⁻⁴ , ¹⁵⁵ Eu = 3.15 x 10 ⁻⁴ , ²⁴¹ Am = 2.11 x 10 ⁻⁴ (µCi/g)
Water content	1.31 wt%
Ammonia	24 µg NH ₃ /g
IC	F, Cl, NO ₂ , NO ₃ , SO ₄ , all <50 µg/g
ICP/AES (2% HNO ₃ leach)	Ag = 0.90, Al = 1.8, B = 11, Ca = 2.0, Cd = 2.1, Cu = 2.2, Fe = 0.33, Na = 70, Ni = 9.9, P = 605 (µg/g)

(a) RSST = Reactive system screening tool

Three different analysis methods for peroxides were used. Results varied widely between methods. The spectrophotometric iodometric method gave the highest value, 2.5 μ Equivalents peroxide/g. This value should be considered as an upper limit.

Analysis of the organic layer for nitroalkanes by infrared spectroscopy yielded an upper bound concentration value of 2 μ mol nitroalkane/g. This result confirms the results of energetics tests conducted by WHC staff that indicated no internal oxidant compounds are present in the organic liquid. (Bechtold, D. B., Adiabatic Calorimetry of C-103 Organic Liquid, Letter Report #9450575, to R. M. Bean, January 28, 1994.)

Analysis of the organic layer for density and viscosity provided a density of 0.868 g/mL and a viscosity of 2.5 cP at approximate tank temperature, 40°C. The low viscosity determined for the C-103 organic liquid indicates that the analytes measured in the laboratory are probably distributed uniformly throughout the organic layer in C-103. The reason we believe the organic contents are uniformly distributed is because of the low viscosity of the liquid together with the fact that the organic and aqueous waste layers are at a higher temperature than the dome space, encouraging convection.

Analysis of radioactivity in the organic layer was required in order to formulate an assessment of the potential source term in the event of an exothermic event causing the release of tank contents. The analytical plan for analysis of the organic layer for radiological chemistry required that threshold values of 11 pCi/g alpha activity and 2.7×10^4 pCi/g beta activity be exceeded before conducting detailed analysis for specific radionuclides. From the gross alpha and beta values given in Table S.1, these values were exceeded by more than an order of magnitude. The detailed radiochemical analyses given in Table S.1 are to be used in the dose assessments, as well as for an assessment of criticality potential.

Inorganic analyses of the organic layer are the last items entered in Table S.1. Water, 1.31% of the weight of the organic layer, was determined by Karl Fischer titration. The anions, analyzed by ion chromatography (IC), and the cations, analyzed by inductively coupled plasma/atomic emission spectroscopy (ICP/AES), were determined after extracting the organic material with water. In addition, dilute nitric acid was used to extract cations, and found to be slightly more effective for analyte extraction than non-acidified water.

Aqueous Layer Analyses (Table S.2)

While not as critical as the organic layer analysis, characterization of the aqueous layer was also deemed to be important in leading to removal of the USQ. An analysis of the vapor above the aqueous layer was requested in order to assess the contribution of that phase to the total organic vapor. The initial headspace analyses of the aqueous layer were not successful in meeting that goal because laboratory radiochemical restrictions would permit only 50 μ L of aqueous phase in the analytical laboratory where the GC/MS analysis was to be performed. The resulting headspace analysis, performed in 20-mL containers, was therefore performed under conditions where the organics analyzed were essentially all in the vapor phase. Another approach to the analysis of organic material in the aqueous layer was the determination of analytes in solvent extracts by GC/MS. Methylene chloride extracts of the aqueous layer were analyzed after a 30-fold concentration by evaporation. TBP, DBBP, and NPH were determined to be present at the μ g/mL level.

As expected, the radioanalytical analyses showed that the aqueous layer was moderately radioactive, with beta activity about 66 μ Ci/g. Alpha activity was about 0.040 μ Ci/mg. These values were 63 and 74 times the activity in the organic phase sample on a weight ratio basis for beta and alpha respectively.

The physical and chemical properties of the aqueous phase are not atypical for a waste tank with the history of C-103: basic pH of 10, organic carbon at 0.67%, inorganic carbon at

0.48%, and density slightly over 1 g/mL. The viscosity of the aqueous phase becomes dependent on shear rate at room temperature, but is quite low (2 cP) and newtonian at 40°C.

Table S.2. Summary Results of Analysis of Aqueous Supernatant Phase of C-103

<u>Determination</u>	<u>Result</u>
Extractable organics by GC/MS	TBP = 80 µg/g DBBP = 7 µg/g NPH = 1-3 µg/g
Volatiles by GC/MS	Only NPH and TBP identified in headspace
Gross alpha, beta	Alpha = 4.04×10^4 pCi/g Beta = 6.55×10^7 pCi/g
Gamma analysis	^{60}Co = 0.0474 µCi/g ^{137}Cs = 53.7 µCi/g
Ammonia	215 µg NH ₃ /g
pH	10.00, 9.99
Density	1.078 g/mL at 25°C, 1.076 g/mL at 44°C
Viscosity	1.5 - 4.5 cP at 25°C (depending on shear rate), 2 cP at 40°C
Carbon	TOC = 6700 µg/g, TIC = 4800 µg/g
IC	F ⁻ = 1100, Cl ⁻ = 400, NO ₂ ⁻ = 23,000, NO ₃ ⁻ = 2400, SO ₄ ²⁻ = 3000, PO ₄ ³⁻ = 2000 (µg/g)
ICP/AES	Ag = 11, Ca = 5, Cd = 0.8, Cr = 53, Fe = 3, K = 300, Na = 30400, Ni = 67, P = 2350, U = 1950, Zr = 280 (µg/g)
DSC/STG(a)/TOC of dried solids	Exotherm of 180 calories/g, between 240 and 430°C. TOC = 4.4 wt%

(a) STG = scanning thermogravimetry.

The anion analysis of the aqueous phase indicates that nitrite is the most abundant anion (2.3% by weight), about an order of magnitude more concentrated than either nitrate at 0.24% or sulfate at 0.30%. ICP results show that the overwhelmingly predominant cationic constituent of the aqueous phase is sodium (3.0 wt%). All other ICP element concentrations were found to be more than an order of magnitude lower.

The wide variability in ratios of analytes found common to both the aqueous phase and organic phase suggest that the water content of the organic layer is not simply entrained aqueous phase material.

The ratio of cation equivalent concentration to anion equivalent concentration of the aqueous phase (charge balance) was calculated to be 1.04 assuming that the total inorganic carbon is 1/2 bicarbonate and 1/2 carbonate. A measured charge balance ratio this close to the theoretical ratio of 1.00 strongly suggests that all significant ionic constituents were detected.

Total dissolved solids (TDS) in the aqueous phase was found to be 12.5 wt%. The dried solids contained 4.4% TOC and 3.5% TIC. An exotherm with an energy of approximately 180 calories/g of dried material was observed between 240 and 430°C. A weight loss of 16% (based on dried sample) is associated with this exotherm.

For ease of comparison, selected analytes determined in both organic and aqueous layers are presented in Table S.3.

Table S.3. Comparison of Inorganic Analytes Found in C-103 Organic and Aqueous Layer Samples

ICP Elements	Concentrations in $\mu\text{g/g}$		Ratio (Aqueous/Organic Acid Leach)	
	Organic Layer			Aqueous Layer
	Acid Leach	Water Leach		
P	605	450	2,350	3.9 ^(a)
Na	70	39	30,400	483
Ni	9.9	-	67	6.8
Cu	2.2	-	-	-
Cd	2.1	-	0.8	0.4
Ca	2.0	-	10	5
B	1.2	1.4	-	-
Al	1.8	-	-	-
Ag	0.9	0.33	11	12
Si	-	1.5	-	-
Ti	-	0.07	-	-
Cr	-	-	53	-
Fe	0.33	-	3	9
K	-	-	300	-
Mo	-	-	10	-
U	-	-	1,950	-
Zr	-	-	280	-
Ammonia	24	NA ^(b)	215	9
IC - Anions				
F ⁻	NA	<25	1,100	
Cl ⁻	NA	<25	400	
NO ₂ ⁻	NA	<50	23,000	
NO ₃ ⁻	NA	<50	2,450	
PO ₄ ³⁻	NA	NA	2,000	
SO ₄ ²⁻	NA	<50	3,000	

(a) Majority of phosphorus in aqueous phase and organic phase leachates is presumed to be other than phosphate.

(b) NA = not analyzed

Missing entries for ICP elements signify that values measured were below the detection limit.

Glossary of Acronyms

ACL	Analytical Chemistry Laboratory
AEA	alpha energy analysis
ASTM	American Society for Testing and Materials
ATR	Attenuated Total Reflectance
CCA	Closed Cup Analyzer
DBBP	dibutyl butylphosphonate
DQO	Data Quality Objectives
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared [spectroscopy]
GC/MS	gas chromatography/mass spectrometry
GEA	gamma energy analysis
HLRF	High-Level Radiation Facility
HP	Hewlett Packard
HRMS	high-resolution mass spectrometer
IC	ion chromatography
ICP/AES	inductively coupled plasma/atomic emission spectrometry
ISO	International Standards Organization
LCSW	laboratory control standard for water
NPH	normal paraffin hydrocarbon
PFTBA	perfluorotributylamine
PNL	Pacific Northwest Laboratory
QC	quality control
RPD	relative percent difference
RSD	relative standard deviation
RSST	reactive system screening tool
SEM	scanning electron microscopy
SST	single-shell tank
STG	scanning thermogravimetry
TBP	tributylphosphate
TC	total carbon
TDS	total dissolved solids
TIC	total inorganic carbon
TOC	total organic carbon
USQ	Unreviewed Safety Question
VOA	volatile organic analysis
WHC	Westinghouse Hanford Company
XRF	x-ray fluorescence

Acknowledgments

The Task Leader and Project Manager wish to thank all the participants on this task, who worked at a very high level of professional excellence in order to deliver high-quality data in very short turnaround times. Nancy J. Stajduhar, Project Secretary, worked diligently under pressure, and continued to be her normal pleasant self. Her dedication was critical to the prompt production of this document.

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1.0 Introduction

1.1 Unreviewed Safety Question

Tank 241-C-103 (C-103), a single-shell underground waste storage tank at the Hanford Site in the state of Washington, contains an organic layer floating on a highly radioactive aqueous solution. Uncertainty associated with the potential for the organic layer to sustain a pool fire that would cause the tank to lose containment has raised an Unreviewed Safety Question (USQ). The layer is believed to consist of tributylphosphate (TBP) and normal paraffin hydrocarbon (NPH), but its chemical composition and combustibility have not been accurately determined. Resolution of this USQ hinges on a more complete and detailed understanding of the flammability potential of this layer and vapors associated with it, as well as those vapors that could evolve in the event of a pool fire. Information about the propagation and energetics of such a pool fire, if initiated, and the source-term associated with a release event following a pool fire are needed for the safety analysis.

1.2 Data Quality Objectives

A team of scientists and managers representing both Westinghouse Hanford Company (WHC) and Pacific Northwest Laboratory (PNL)^(a) prepared a Data Quality Objectives (DQO) document (Wood et al. 1993) that addresses in detail the specific questions relevant to USQ closure. The DQO document defines the analytical measures that would be definitive for resolving the questions and outlines an optimized sampling and analytical plan for obtaining those measurements.

1.3. Analytical Plan

The analytical plan as presented in the DQO document calls for several sets of analyses including gas chromatography/mass spectrometry (GC/MS) for organic constituents of liquid and vapor evolving from it, flash point measurements, ion chromatography (IC) and inductively coupled plasma/atomic emission spectroscopy (ICP/AES) to characterize inorganic constituents, radiochemistry for selected radionuclides, differential scanning calorimetry (DSC) and scanning thermogravimetry (STG) for energetics, and viscosity measurements to help establish the degree of homogeneity of the layer.

This report gives the results obtained from analysis of four samples of the organic layer and one sample of the underlying aqueous phase. All DQO-specified analyses are reported here. In addition, this report describes the measurements of density, peroxide concentration, and Fourier transform infrared (FTIR) spectroscopy of the organic layer. The methods described in the analytical plan for analysis of volatile compounds evolved from organic layer samples were superseded/replaced due to the unanticipated availability of a headspace sampler. Data obtained from this instrumental technique are deemed to be more reproducible and representative than would be expected from the originally proposed methodology.

PNL Quality Assurance impact level III (WHC QA level IV) standards, were applied at a minimum to all work. Procedures cited by PNL-ALO number are found in PNL Manual MA-599. The manual gives procedural details used to carry out the applicable analysis. Where

(a) Operated for the U. S. Department of Energy by Battelle Memorial Institute.

procedures were developed or adapted for use in this study, they are described in the narrative of this report.

1.4 Sampling

Liquid samples were collected on December 15, 1993, in 100-mL glass collection bottles using dip sampling techniques. Six bottles of organic and one of aqueous phase were obtained. One of the organic phase sample bottles was sent to the WHC 222S Laboratory for adiabatic calorimetry testing. The other five organic sample bottles and the aqueous phase sample were delivered to PNL's 325 Building "B" hot-cell complex during the evening of December 15. One of the organic phase sample bottles was set aside as an "archive" sample. Aliquots of the four remaining organic phase samples and the aqueous phase sample were prepared and distributed to the various analysts.

1.5 Sample Receipt and Preparation for Analysis

Five organic and one aqueous sample were received from WHC in two shipments on December 15, 1993. The samples were subsequently logged into the PNL Analytical Chemistry Laboratory's (ACL's) Laboratory Information Management System. Laboratory tracking numbers were assigned as shown:

<u>Laboratory Identification Number</u>	<u>Client Identification</u>	<u>Originating Tank Layer</u>
94-02001	X-11	Organic
94-02002	X-12	Organic
94-02003	X-13	Organic
94-02004	X-14	Organic
94-02005	X-15	Organic
94-02006	X-17	Aqueous

All six samples were unloaded into the ACL Shielded Analytical Laboratory hot cells. All samples received appeared visually to be of a single phase and red in color. The degree of coloration is different between organic and aqueous phases; the organic phases are much darker. Each clear glass sample bottle was filled to capacity. The bottles were 100 mL total capacity with black phenolic caps. Sample 94-02003, X-13 was archived for future use. The five remaining samples were processed as follows:

Organic samples X-11, X-12, X-14, and X-15 were subsampled for flash point, GC/MS, total alpha/total beta/gamma energy analysis, and Karl Fischer water determinations. Aliquots of samples X-11 and X-12 were sent to the PNL High-Level Radiochemistry Facility (HLRF) for physical testing. Aliquots of samples X-14 and X-15 were 1) water leached and the resultant leachates sent for IC and ICP analysis, and 2) acid leached (2% HNO₃) for ICP analysis. Reagent blanks were provided with each preparation type.

The aqueous sample X-17 was subsampled and sent to the HLRF for physical testing. Water and nitric acid leaches were performed for IC and ICP, respectively. Duplicate pH determinations were done in the hot cell. The sample was analyzed remotely for total carbon (TC), total organic carbon (TOC), and total inorganic carbon (TIC). A matrix spike was performed during the carbon analysis. Aliquots of X-17 were taken for gross alpha/gross beta/gamma energy and volatile organic analysis (VOA)-headspace analyses.

1.6 Simulant Description

A simulant was used by several analysts for method development and verification before performing analyses on the real samples. The organic phase of this simulant consisted of 70 wt% TBP/30 wt% NPH equilibrated with an aqueous phase described in Table 1.1. The aqueous phase composition was derived from Tables 13 and 14 of 28110-PCL-048 (Internal Memo: WHC Process Chemistry Laboratories to Rhett K. Tranbarger, June 3, 1991), which summarize analyses performed on C-103 samples obtained from a previous sampling.

Table 1.1. Composition of C-103 Aqueous Phase Simulant
(pH adjusted to 9.5 with NaOH)

<u>Component</u>	<u>Concentration (M)</u>
Na ₂ SO ₄	0.28
NaNO ₃	0.069
NaNO ₂	0.62
Na ₂ CO ₃	0.055
NaHCO ₃	0.345
Na ₂ HPO ₄	0.021

2.0 Results of Analysis

2.1 Organic Phase

2.1.1 Flash Point

Dewatered tank C-103 organic phase samples were tested for their flash point following draft flash point procedure PNL-ALO-234, "Flash Point by CCA-FLP Miniflash Closed Cup Tester." The procedure was revised to specify that the instrument be programmed for ignition following the American Society for Testing and Materials (ASTM) D3278-90 Setaflash Methodology. A 2 mL sample was placed in the test cup and heated to a temperature estimated to be close to, but below, the sample flash point. After 60 s at temperature with continuous magnetic stirring, the sample was tested for flash. If no flash occurred, the temperature was raised and the sample was tested again; if the sample flashed, then new samples were heated at successively lower test temperatures until no flash occurred. The flash point is expressed as the mean between the highest non-flash temperature and the lowest flash temperature, rounded up to the nearest whole number.

Flash point analyses were conducted using an International Standards Organization (ISO) 9001 Quality Certified Grabner Instruments (Latham, NY) CCA-FLP Miniflash Flash Point Tester instrument (WD16835), distributed by PETROLAB Corporation. The flash point chamber was initially thermally preconditioned by heating a water sample to 200°F.

The samples, NPH, and TBP test materials were all dried over calcium sulfate to remove entrained water prior to testing.

An n-dodecane standard (PETROLAB Corporation, Lot #83-28A) with a flash point of 184°F ± 2°F was analyzed as a check standard before and after analysis of all samples as a performance check on the instrument calibration. Flash point test results for the n-dodecane performance check standard were consistent with the ASTM-approved Setaflash closed cup test. Bias for this standard was within the ASTM guidelines of ±4°F.

To develop a predictive model for the flash point of NPH:TBP mixtures in other single-shell waste tanks, flash point tests were conducted on a NPH:TBP dilution series. Table 2.1 shows the results obtained from this strategy using different ratios of TBP and NPH.

Setaflash flash point data obtained from C-103 liquid organic samples are provided in Table 2.2. GC/MS analysis (Section 2.1.2) indicates that TBP and nonvolatile material account for approximately 72 wt% of the organic phase. The remaining 28% can be identified as NPH. Data presented in table 2.1 relating to the flash point of various TBP/NPH mixtures can be used to predict a flash point for 28 wt% NPH (volatile) + 72 wt% TBP and non-volatiles of 246°F. The agreement of flash points determined for TBP/NPH mixtures and actual C-103 organic layer samples is obviously excellent.

Table 2.1. Flash Point Measurements of TBP/NPH Mixtures: Flash Point Tester in "Setaflash" Mode

<u>% TBP^(a)</u> <u>(v:v)</u>	<u>% NPH^(b)</u> <u>(v:v)</u>	<u>% NPH^(c)</u> <u>(w:w)</u>	<u>No Flash</u> <u>Temp.^(d) (°F)</u>	<u>Flash</u> <u>Temp.^(e) (°F)</u>	<u>Estimated</u> <u>Flash Pt. °F^(f) (°C)</u>
0	100	100	185	190	188 (86)
10	90	88	200	202	201 (94)
20	80	76	205	207	206 (97)
30	70	65	210	212	213 (99)
40	60	55	217	220	219 (104)
50	50	45	222	224	223 (106)
60	40	35	230	235	233 (112)
70	30	26	245	247	246 (118)
80	20	17	257	259	258 (126)
100	0	0	355	360	358 (181)

- (a) TBP on a percent volume basis.
 (b) NPH on a percent volume basis.
 (c) Calculation of NPH concentration on a weight :weight (w:w) based on the following density values: TBP = 0.976 g/mL, NPH = 0.7845 g/mL.
 (d) Highest equilibrated sample temperature where a flash point was not detected.
 (e) Lowest sample equilibrated sample temperature where a flash point was detected.
 (f) Estimated flash point in °F and °C. Calculated to be midrange between the no-flash limit and temperature where flash point was detected.

Table 2.2. Flash Point Measurements of C-103 Organic Liquid: Flash Point Tester in "Setaflash" Mode^(a)

<u>Sample</u>	<u>No Flash</u> <u>Temp. (°F)</u>	<u>Flash</u> <u>Temp. (°F)</u>	<u>Approximate</u> <u>Flash Pt. °F (°C)</u>
X-11	240	245	243 (117)
X-12	245	248	247 (119)
X-14	245	247	246 (118)
X-15	245	250	247 (119)
Mean value			246 (118)

- (a) n-Dodecane standard, certified at 184 ±2°F, gave 185°F in duplicate trials using "Setaflash" mode.

2.1.2 GC/MS Analysis of Liquid Organic Samples

Each of four organic layer samples was diluted by 10,000X with methylene chloride and analyzed by GC/MS. A standard of NPH was obtained from WHC. Standards of TBP and dibutyl butylphosphonate (DBBP) were obtained from Aldrich and Pfalz and Bauer, respectively.

The GC/MS instrument was equipped with a Hewlett Packard (HP) 5980 gas chromatograph operated in the splitless mode. A fused-silica column (DB-5, 30 m x 0.25 mm i.d., 0.25 μ m film thickness, J & W Scientific, Folsom, CA) was used. The oven temperature was typically programmed in the following manner: 50°C for 1 min., 8°C/min. to 300°C, and hold at 300°C for 5min. The MS was tuned daily with perfluorotributylamine (PFTBA). In these studies, the MS was scanned from 50 to 500 amu and operated in the electron impact mode (70 eV). The source temperature was 200°C, the injector port temperature was 250°C, and the interfaces were also at 250°C.

Chemical ionization mass spectrometry was carried out with isobutane in the positive chemical ionization mode to obtain molecular weight information. The temperature of the source for positive ion chemical ionization mass spectrometry was 200°C. The MS was scanned from 70 to 500 amu in the positive ion mode.

Accurate mass measurements were performed on a JEOL SX 102/SX 102 high-resolution mass spectrometer (HRMS). The instrument was tuned to a resolution of 5000 (10% valley definition). Data were acquired by scanning the magnetic field exponentially down over the mass range of 10 to 600 according to the procedure in the instructions. Instrument tuning and real-time mass measurements were performed by leaking perfluorokerosene into the electron impact ion source from the septum inlet reservoir. Computer-assisted accurate mass assignments and subsequent elemental compositions were made on data obtained from averaging four consecutive scans over the gas chromatographic elution profile of the analyte. The instrument was equipped with an HP 5980 GC. The GC was fitted with a DB-5 fused-silica column. The GC oven temperature was held at 50°C for 2 min., then programmed at 5°C/min. to 250°C. Scanning was initiated after a 5-min delay.

2.1.2.1. Analysis of Organic Layer

Table 2.3 lists the tentative identifications of components in the organic layer, their retention times, and the absolute and relative weight percent of each component. Similar total ion chromatograms were obtained for all four organic layer samples.

The tentative identifications were based on the similarity of the mass spectrum of the component to the mass spectrum found in a data base or by manual interpretation. Confirmed identifications have been assigned based on comparison of mass spectra and GC retention times of the unknown component with authentic standard compounds. The identity of DBBP was confirmed by using the HRMS.

The semivolatiles found in the organic layer of tank C-103 are primarily TBP and related phosphate esters, a series of n-alkanes (undecane through pentadecane), and several branched-chain alkanes. It is very difficult to determine the exact structures of branched alkanes, primarily because of the lack of molecular weight information (nonexistent or weak parent ion). The electron impact mass spectra of most alkanes are practically identical.

The relative weight ratio of TBP:NPH is 67:33, if DBBP is included with the TBP, and the branched alkanes were included with NPH. Tributylphosphate constitutes 48.3% by volume of the organic layer. In addition, analyses of a weighed sample accounted for approximately 74% of the organic carbon.

A weighed sample of the organic layer was heated to 320°C for 15 min. under vacuum using a direct probe. The results indicate that 10-12% of the material by weight was not volatilized at 320°C. However, direct probe analysis of a mixture of TBP and NPH showed no remaining residue. In addition, direct probe analysis under chemical ionization conditions showed ions at m/z 267 and 534. These ions are attributed to TBP. A diluted sample of the organic layer was also analyzed by GC/MS using a thick film column. No lower molecular weight material was detected. The residue remaining in the capillary tubes from direct probe analyses was heated to approximately 600 and 1000°C in a carbon analyzer. The total organic

carbon value at 600°C was determined to be 2.9 mg C. A 5- μ L sample weighs 4.4 mg assuming a density of 0.88 mg/ μ L. The quantity of carbon is then 66%. From the results of analysis of the organic layer and assuming TBP is approximately 50% and NPH constitutes 25%, only 47% of the organic carbon is accounted for by NPH and TBP. Additional derivatization experiments for the analysis of chelators indicated no detectable chelator species. Therefore, there is a portion of the organic carbon that is not detected.

A 5- μ L sample of the original organic layer was also heated to 600°C and then subsequently heated to 1000°C in a carbon analyzer. No additional total organic carbon was detected. These results indicate that most of the total organic carbon has been volatilized at a temperature of approximately 320°C under vacuum. The remaining residue left after heating to 320°C was analyzed by scanning electron microscopy (SEM). Inorganic phases that were tentatively identified include $K_2Ca_2Mg(SO_4)_4$, $KAlSi_3O_8$, $Ca_3(PO_4)_2$, $FeOOH-CrOOH$, and $AlOOH$. These phases are probably not soluble in the organic phase, but may exist as colloidal particles. A 1-mL aliquot of the organic layer was heated overnight at 300°C in a muffle furnace. The remaining residue was examined using x-ray fluorescence (XRF). The elemental determinations on the radioactive sample must be considered as semiquantitative due to inadequate sample transfer. However, the major components detected were Si (8950 ppm) and P (75,100 ppm). Minor components detected included S, Ni, Ca, Cr, and Ti.

Table 2.3. Components Determined from GC/MS Analysis of Organic Layer

Component	Retention Time, min.	Wt%	Relative Wt%
Dodecane	10.51	2.8	3.8
Alkane	10.74	0.2	0.3
Alkane	11.85	1.1	1.5
Tridecane	12.38	11.4	15.5
Alkane	13.23	0.5	0.6
Alkane	13.72	1.0	1.3
Tetradecane	14.17	6.0	8.1
Alkane	15.17	0.7	1.0
Pentadecane	15.84	0.9	1.2
DBBP	17.60	1.9	2.6
TBP	18.09	47.2	64.0
Total		73.7	100.0

2.1.2.2. Analysis of Organic Layer Headspace

Aliquots (1 mL and 100 μ L) of one of the organic phase samples were placed in 20-mL headspace vials. Headspace analyses were performed with an HP 7694 headspace sampler interfaced to an HP 5890 GC equipped with a DB 624 column (30 m x 0.53 mm and 3- μ m film

thickness) and a flame ionization detector. A sample was heated to $40 \pm 3^\circ\text{C}$, equilibrated for 10 min., and analyzed. The sample was then heated and analyzed at $70 \pm 3^\circ\text{C}$ and $100 \pm 3^\circ\text{C}$. A 500- μL sample from the headspace of the sample heated to 40, 70, and 100°C was taken with a gas-tight syringe (10 mL) that had also been heated to the related temperatures, and analyzed using an HP mass selective detector equipped with a DB-5 MS column (30 M X 0.25mm and 0.25 μm film thickness).

The estimated concentrations of the components at 40, 70, and 100°C are listed in Table 2.4. The tentative identifications of the components are based on mass spectral interpretation and best match with the mass spectral library. The concentrations are based on the response factor for a 50-ppm liquid sample of tridecane. Dashes indicate component was not detected. Detection limits were estimated to be 0.006 mg/L.

At 40°C , the major components are NPH-related. The component at a retention time of 22.724 min. is DBBP. At 40°C , there is a small contribution from TBP. At 70°C , there are nitrile compounds tentatively identified. These include hexanenitrile, heptanenitrile, and octanenitrile. The estimated concentrations for NPH are higher than for TBP. In addition, several ketones were also identified. The estimated concentrations of NPH are much higher than TBP at 100°C . Other alkane-related components were also tentatively identified, as were other ketones.

At 40°C , the sum of the NPH-related components amounts to 1.32 mg/L. This is comparable to the analysis (range 0.55 to 1.31 mg/L) performed on the headspace in the tank (Ligotke et al. 1994).

Table 2.4. Determined Concentrations of Tentatively Identified Components (mg/L) in Headspace Analysis of Organic Fraction

Component	Retention Time, min.	40°C	70°C	100°C
Hexanenitrile	7.494	-	0.01	0.06
Ketone	7.983	-	0.02	0.17
Alkane	8.461	-	0.01	0.10
Ketone	10.206	-	0.01	0.12
Heptanenitrile	10.923	-	0.02	0.10
Branched alkane	11.235	-	0.01	0.14
Decane	11.525	-	0.02	0.12
Alkane	11.609	-	0.01	0.06
Branched alkane	12.087	-	0.01	0.03
Octanenitrile	13.459	-	0.01	0.04
Undecane	13.887	0.06	0.22	1.46
Branched alkane	15.031	-	0.06	0.18
Branched alkane	15.250	-	0.03	0.32
Branched alkane	15.375	-	0.02	0.17
Alkane	15.75	-	0.07	0.18
Ketone	15.769	-	-	0.76
Dodecane	15.95	0.32	2.4	13.8
Alkane	16.185	0.05	0.32	2.2
Alkane	16.77	-	0.13	0.72
Alkane	17.28	0.08	0.62	3.6
Alkane	17.662	-	-	0.12
Tridecane	17.87	0.46	4.2	18.2
Alkane	18.101	-	0.10	0.64
Alkane	19.09	0.07	0.36	0.64
Tetradecane	19.51	0.22	1.2	6.4
Alkane	20.47	0.03	0.11	0.68
Pentadecane	21.10	0.02	0.12	0.70
DBBP	22.72	0.01	0.04	0.58
TBP	23.20	0.14	0.78	8.4

2.1.3 Peroxides

The analysis of peroxides is an indirect analysis based on the oxidation of a reagent. These tests are subject to false positives, because any species in the matrix that has an oxidation potential greater than the reagent will oxidize that reagent. Examples include NO_3^- , NO_2^- , Fe^{3+} , and dissolved O_2 . Since the specific species of peroxide that might be in the matrix is unknown, results are reported in micro-equivalents (μEq) of oxidant per gram.

2.1.3.1 Merck Peroxide Test Strips

Application of a E. Merck test strip analysis (Merckoquant[®] 10011 Peroxide Test Strip, EM Science, Gibbstown, NJ) usually used for laboratory ethers gave a value of $\leq 0.5 \mu\text{g/mL}$ as hydrogen peroxide. Assuming there is a one to one mole ratio of peroxide to colored product in this test, this translates to $0.2 \mu\text{Eq/g}$ of oxidant in the matrix by this test. Because this test is not reliable for non-volatile matrixes, two other analytical techniques were applied.

2.1.3.2 Iodometric Spectrophotometry

A procedure for the analysis of peroxides in organic liquids by iodometric spectrophotometry written by S. D. Harvey and R. B. Lucke (1990). This procedure indirectly determines peroxide by measuring the oxidation of iodide to iodine. Hydrogen peroxide, 30% (Fisher Scientific, Fair Lawn, New Jersey), was used as a standard. An HP 8451A Ultraviolet Spectrophotometer (Palo Alto, CA) was used.

Because of the highly colored nature of the matrix, a 50-fold dilution of the sample was necessary. The average of three measurements was $74 \mu\text{g/mL}$ of oxidant as hydrogen peroxide with a relative standard deviation of 2.1%. There is a one-to-one mole ratio of hydrogen peroxide to iodine produced. Therefore, there were $2.5 \mu\text{Eq/g}$ of oxidant by this technique.

2.1.3.3 Chromatographic Method

This procedure was also written by S. D. Harvey. It is titled, "Analytical Determination of Peroxide by the Oxidation of N,N'-di(2-naphthyl)phenylene-1,4-diamine to Form a Highly Colored Diimine Product," and is given in Appendix A. Benzoyl peroxide, 55% (Pfaltz & Bauer, Waterbury, CT), was used as a standard. The high-performance liquid chromatography was performed on a Waters Associates System (Milford, MA). An Alltech, (Deerfield, IL) Cyano, 25 cm x 4.6 mm column was used.

The average of three measurements was $67 \mu\text{g/mL}$ of oxidant as benzoyl peroxide with a relative standard deviation (RSD) of 7.4%. There is a one-to-one mole ratio of benzoyl peroxide to diimine produced. Therefore, $0.32 \mu\text{Eq/g}$ of oxidant were found by this technique.

2.1.3.4 Discussion

Based on these test results, an upper limit of $2.5 \mu\text{Equivalent peroxide/g}$ sample is indicated. There is a possibility that any peroxides that form in the tank would be summarily reduced when contacted by the nitrite in the aqueous layer. This may not happen at the pH of the aqueous layer, but this should be investigated.

2.1.4 Infrared Analysis for Nitroalkanes

The organic layer of tank C-103 was analyzed by FTIR methods to determine the presence of nitroalkane materials within the tank waste. Two tank C-103 samples (X-11 and X-12) were analyzed and compared to organic phase simulant materials containing both primary nitroalkanes and secondary nitroalkanes to measure the presence of nitroalkanes within the actual tank waste.

Infrared absorption bands characteristic of primary and secondary nitroalkanes were not observed in either of the tank C-103 samples analyzed. There were, however, absorption bands not identified that could possibly be assigned to nitro-organic complexes. The intensity of these bands indicate that the upper-bound threshold concentration of nitroalkanes in the organic phase of tank C-103 to be 0.01 wt% (as NO₂), or 2 μmol nitroalkane/g.

2.1.4.1 Experimental Analysis

Standard solutions containing various concentrations of 1-nitrohexane or 2-nitrooctane were prepared using a tributylphosphate-normal paraffin hydrocarbon mixture (70% TBP, 30% NPH) as the solvent. These solutions were analyzed by IR techniques using a Nicolet FTIR spectrometer equipped with an attenuated total reflectance (ATR) tunnel cell with a zinc-selenide optical element. The asymmetric stretching band of the NO₂ group at 1552 cm⁻¹ was used as a monitor of the concentration of the nitroalkane in solution.

Linear-regression treatment of the absorbance vs standard concentration data yields Equations (1) and (2) for the 1-nitrohexane and 2-nitrooctane solutions respectively,

$$y = 0.170 x + 0.0030; \quad r^2 = 0.9998 \quad (1)$$

$$y = 0.186 x + 0.0020; \quad r^2 = 0.99994 \quad (2)$$

where y represents absorbance and x is the concentration of the nitroalkane (as wt% NO₂).

It is significant that the absorbance maximum for the NO₂ group asymmetric stretch is identical in both the 1-nitrohexane and 2-nitrooctane spectra. This indicates that this functional group is not perturbed differently in the primary- vs secondary-alkane environment and thus would probably be in the same location in any primary or secondary alkane of equal or larger size. Secondly, the slope and intercept of the fitted equations to this data (Equations 1 and 2) indicate that the wt% nitro content (wt% as NO₂) can be evaluated accurately whether a primary or secondary nitroalkane (or a mix of both) was present within the solution.

FTIR analysis of tank C-103 samples shows no absorption bands at 1552 cm⁻¹. There are, however, absorption bands within the actual tank waste spectra which are not identified. One unidentified band (absorbance < 0.003; located at 1539 cm⁻¹) in all the tank waste spectra is near the absorption maximum for the nitroalkane compound. This is most likely not a nitroalkane, but further testing is required to absolutely identify this source compound for this specific absorption. Even if this band was a result of a nitroalkane, we estimate an upper bound threshold of < 0.01 wt% (as NO₂) as its concentration based on the standard equations described above.

2.1.5 Physical Properties

2.1.5.1 Viscosity

The viscosity analyses were performed according to PNL technical procedure PNL-ALO-502, "Laboratory Procedure for Measurement of Physical and Rheological Properties with a Cone and Plate Viscometer." The viscosity measurements were performed on a Bohlin CS viscometer modified for glovebox operation. Concentric cylinders with a 25-mm-diameter inner cylinder and a 2.5-mm gap between the cylinders was the measuring geometry used. This geometry on the Bohlin system is maintained with a C25 measuring sensor. Shear stress as a function of shear rate was obtained by measuring the shear stress produced at a specific shear rate. Viscosity as a function of shear rate is then calculated from these data. Calibration checks were made with certified 25-cP and 10-cP viscosity standards.

At 25°C the viscosity of the organic layer sample is approximately 4 cP over a shear rate range from 25 to 300 s⁻¹. The viscosity drops slightly when the temperature is increased to 40°C (2.5 cP over the same shear rate range). The organic layer sample viscosity is essentially newtonian over this shear rate range.

2.1.5.2 Density

The density analyses were performed according to PNL technical procedure PNL-ALO-502, "Laboratory Procedure for Measurement of Physical and Rheological Properties with a Cone and Plate Viscometer." Densities were calculated from measured masses of specific volumes of the sample. The samples were placed in tared 10-mL volumetric flasks. The mass of the sample was then determined using a 4 decimal place Mettler balance (Greifensee, Switzerland). The samples were held at 40°C in a drying oven for a minimum of 1 hr before measuring the 44°C densities.

The determined density of the organic sample was 0.876 g/mL at 25°C, and 0.868 g/mL at 44°C. The difference is statistically significant.

2.1.6 Radiological Properties of Organic Phase

2.1.6.1 Background

The analytical plan for radiochemical analysis of the tank C-103 organic layer called for a phased approach. An initial determination of gross alpha, gross beta and identifiable gamma-emitting radioisotopes by gamma energy analysis (GEA) was to be performed. If predetermined threshold concentrations of gross alpha and gross beta were exceeded, more detailed radiological characterization would be performed.

2.1.6.2 Results

Initial gross alpha and gross beta concentrations were found to exceed threshold values by factors of 50 and 40, respectively. Therefore, more detailed characterization was done. Reports of both the initial (screening) phase and more extensive radiochemical analyses follow.

Gross Alpha and Gross Beta Results

Four organic samples were analyzed for gross alpha activity according to procedures PNL-ALO-460, "Source Preparation for Gross Alpha Analysis," and PNL-ALO-461, "Alpha Counting Procedure," and for gross beta activity according to procedures PNL-ALO-462, "Source Preparation for Gross Beta Analysis," and PNL-ALO-463, "Beta Counting Procedure." The analyses were run in one batch for each analyte. Included with each batch were a sample duplicate, method blank, and blank spike. The latter two quality control (QC) samples were prepared with a simulated organic matrix (see Section 1.6).

The aliquot size for each determination was 0.044 g or 0.050 mL (corresponding to a density of 0.88 g/mL). The samples were weighed into a counting planchet, evaporated to dryness, and counted on a gas proportional counter (beta) and a zinc sulfide scintillation counter (alpha). Residual solids were less than 1 mg.

Alpha and beta activity was detected in all the samples. A summary of analytical results is presented in the table below. The sample activities are virtually identical among the four samples. The standard deviations of the samples are within the precisions of the methods. The threshold level of alpha activity for this study was determined to be 1×10^{-8} Ci/L (10 pCi/mL or 11 pCi/g since the density equals approximately 0.88 g/mL) and the ⁹⁰Sr/⁹⁰Y (beta) activity threshold was determined to be 2.4×10^{-5} Ci/L (2.4×10^4 pCi/mL or 2.7×10^4 pCi/g) (Wood et al. 1993). The

results obtained clearly indicate the alpha and beta activity are significantly above these threshold levels.

<u>Analyte</u>	<u>Average Result</u>	<u>Threshold Level</u>	<u>Factor Above Threshold Level</u>
Alpha activity	547 ± 22 pCi/g	11 pCi/g	50
Beta activity	1.05 x 10 ⁶ pCi/g ± 3.7 x 10 ⁴ pCi/g	2.7 x 10 ⁴ pCi/g	40

Activities in the method blanks were insignificant compared to the samples (less than 0.01% for beta, and not detected for alpha). The blank spike recoveries for gross alpha (²³⁹Pu) and gross beta (⁹⁰Sr/⁹⁰Y) were 108% and 107%, respectively. This indicates a slightly positive bias (+8%) may be associated with the sample results. The relative percent differences (RPDs) of the duplicate sample results are ± 8% alpha and ± 3% beta. The propagated error associated with each measurement is indicated with each measurement.

The gross alpha activities are determined relative to detectors calibrated with ²³⁹Pu, which is a typical alpha emitter of concern. Other alpha emitters may have significantly different counting efficiencies. The gross beta activities are determined relative to detectors calibrated with ⁹⁰Sr/Y. Other beta emitters may have significantly different counting efficiencies. Therefore, these determinations should be considered qualitative.

Gamma Energy Analysis

GEA was performed on four C-103 organic phase samples. The average values found for the four samples and duplicate of X-11 are given in Table 2.5. Ten-mL aliquots were analyzed as received from the shielded analytical lab, using procedure PNL-ALO-450, "Gamma Energy analysis - Track Detector." The nuclides observed, in descending activity levels, were ¹³⁷Cs, ⁶⁰Co, ¹⁵⁴Eu, ¹⁵⁵Eu, and ²⁴¹Am. The data suggest that samples X-11, X-12, X-14, and X-15 are from a homogeneous source.

No significant trends, deviations, or analytical problems were noted.

Table 2.5. GEA of C-103 Organic Phase Samples^(a)

<u>Constituent</u>	<u>Activity (μCi/g)^(b)</u>
⁶⁰ Co	7.45 x 10 ⁻⁴ (1.6)
¹³⁷ Cs	4.13 x 10 ⁻² (2.4)
¹⁵⁴ Eu	3.17 x 10 ⁻⁴ (2.3)
¹⁵⁵ Eu	3.15 x 10 ⁻⁴ (4.4)
²⁴¹ Am	2.11 x 10 ⁻⁴ (6.9)

(a) Decay values corrected to 1/1/93.

(b) Values in parentheses are percent RSD of five determinations.

Note: One of four liquid samples showed a weak presence of ⁴⁰K above background at 3.8 x 10⁻⁵ μCi/g.

Radioisotope Analyses on Tank C-103

The screening results on the four organic samples exceeded the thresholds defined in the Analytical Plan (Wood et al. 1993). The samples were analyzed for the following specific radionuclides: ^{90}Sr , ^{238}Pu , $^{239+240}\text{Pu}$, and ^{241}Am . Included with each analytical batch was a sample duplicate, method blank, and method blank spike. The latter two QC samples were prepared with a simulated organic matrix (see Section 1.6).

A preliminary actinide screen was performed to determine appropriate sample size and tracer spike activity. The aliquot size for each determination was nominally 0.044 g or 0.05 mL. Tracers, spikes, and calcium carrier were added to the samples. Before analysis could commence according to standard operating procedures, the organic matrix was destroyed. Volatiles were evaporated. The mixture was then heated to 500°C overnight to oxidize remaining organics. The residue was then wet ashed with HNO_3 and H_2O_2 .

^{90}Sr

The ^{90}Sr analysis was conducted according to PNL-ALO-476, "Strontium Determination Using Sr-Spec[®]," Section 5.2, "Soil Leachates, Aqueous Samples or Equivalent, Which Need Pretreatment." The sample aliquot was dried onto a beta planchet. The yield was determined by gamma counting the ^{85}Sr tracer (PNL-ALO-494, "Counting Procedure for Low Energy Photon and Gamma Spectroscopy"), and the ^{90}Sr activity was determined on a gas proportional counter (PNL-ALO-463, "Beta Counting Procedure"). The gamma spectrum obtained for the ^{85}Sr yield determination showed virtually no other gamma peaks, thus indicating that excellent purity of the Sr fraction was obtained. Precision, as measured by the RPD of the duplicate samples, is $\pm 9\%$. The bias, as measured by the blank spike yield corrected analyte recovery, is +6%. The sample activities are virtually identical, averaging $5.46 \times 10^5 \pm 5\%$ pCi/g (the standard deviation is well within the precision of the method). This activity is virtually half of the total beta activity found in the samples (1.05×10^6 pCi/g); it is highly probable the remaining activity is due to ^{90}Y , which quickly establishes secular equilibrium with ^{90}Sr .

^{238}Pu , $^{239+240}\text{Pu}$, and ^{241}Am

The Pu separation was conducted according to PNL-ALO-417, "Separation of Americium and Plutonium and Actinide Screen by Extraction Chromatography," precipitation plating according to PNL-ALO-496, "Precipitation Plating of Actinides for High Resolution Alpha Spectrometry," and alpha energy analysis according to PNL-ALO-469, "Counting Procedure for Alpha Spectrometry." This separation scheme includes the sequential separation of Am; ^{241}Am was also determined to verify the results obtained by GEA. Chemical yields were traced with ^{242}Pu and ^{243}Am . Again, results from all four samples and the sample duplicate are virtually identical. The averages and RSDs are indicated below.

Constituent	Average (pCi/g)	RSD
^{238}Pu	90.2	6%
$^{239+240}\text{Pu}$	194	3%
^{241}Am	179	2%
Total	463	

The standard deviation of each average value is within the precision of the method. The batch bias, determined with a blank spike sample, was +5% for Pu and -2% for ²⁴¹Am. The ²⁴¹Am results by GEA analysis agree to within 10% (after correcting for sample density) with the alpha energy analysis (AEA) determination. The latter determination provides higher precision and less uncertainty.

The gross alpha results indicate 547 pCi/g alpha is present in the samples. As indicated in the above table, the alpha activity attributable to the isotopes analyzed is 463 pCi/g. Approximately 84 pCi/g alpha activity remains unaccounted for. This discrepancy is thought to be attributable to alpha-emitting daughter products of Pu and Am and to the uncertainty of the gross alpha screen. The preliminary actinide screen (by AEA, procedure PNL-ALO-417, "Separation of Americium and Plutonium and Actinide Screen by Extraction Chromatography," group actinide separation) indicated no other actinide alpha emitters were present in significant quantity.

2.1.7 Water Content

The water content of C-103 organic layer samples was determined by coulometric Karl Fischer titration using a Fisher Model 447 Coulomatic™ K-F titrimer (Pittsburgh, PA). Samples and standards were introduced into the titrimer reaction chamber using a gas-tight syringe. Water in the sample was titrated with coulometrically generated iodine in the presence of excess SO₂ and imidazole, all in an alcoholic solvent, using an amperometric end point. The instrument digitally displayed the mass of water titrated that was used to calculate the weight percent water in a sample. The procedure recommended in the instrument manufacturer's instruction manual was used. The analytical session consisted of 1) certified standard in duplicate, 2) a blank, 3) each of the four samples in triplicate, 4) certified standard in duplicate, and 5) a blank.

Blanks before and after analysis of samples were zero.

Recoveries of standards ranged between 97.6 and 99.1%.

The average weight percent water found, along with the standard deviation, for each sample is given in Table 2.6.

Table 2.6. Water Content of C-103 Organic Phase Samples

<u>Sample ID</u>	<u>Wt% Water Found and Standard Deviation</u>
X-11	1.32 ±0.01
X-12	1.31 ±0.02
X-14	1.24 ±0.003
X-15	1.38 ±0.02

The overall, grand average, water content is calculated to be 1.31 ±0.06 wt%.

2.1.8 Inorganics

The analytical plan, as outlined by Wood et al. (1993), calls for determining inorganic analytes in the organic phase if the water content of the organic phase is greater than 1%. The water content was found to be 1.31%.

2.1.8.1 Anions by IC

Determination of anions by IC was conducted using procedure PNL-ALO-212, "Determination of Inorganic Anions by Ion Chromatography." The analysis was conducted using a Dionex Series 4500i IC (Sunnyvale, CA) equipped with an autosampler/autodiluter. The IC system was calibrated on the date of analysis. Verification standards and blank spike recoveries were satisfactory.

The organic samples were extracted with ten volumes of water in a vortex mixer for 5 min. The leach samples from the organic layer were analyzed at approximately 100X dilutions because of the presence of an organic layer (film) on the solutions and the possibility of resultant contamination of the IC column by the organic material.

The analysis met the required detection limits of 0.1% for the anions of interest. Results are reported in Table 2.7.

Table 2.7. Analysis of C-103 Organic Layer for Anions by IC (data expressed as $\mu\text{g/mL}$ organic phase)^(a)

Anion	Sample X-14	Sample X-15
F ⁻	<26, <24	<23, <24
Cl ⁻	<26, <24	<23, <24
NO ₂ ⁻	<51, <47	<47, <49
NO ₃ ⁻	<51, <47	<47, <49
SO ₄ ²⁻	<51, <47	<47, <49

(a) All analyses were performed on aqueous extracts, 100 water: 1 organic. All results were below detection limits.

2.1.8.2 Cations by ICP/AES

The analyses were conducted according to PNL-ALO-211, "Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry." The water extraction procedure for sample preparation was performed by adding approximately 3.5 g of organic phase C-103 material to about 33 g of water (10:1 water:organic partition ratio), then mixing for 5 min. using a vortex mixer. A 20-mL aliquot of the settled, clear extract (aqueous phase) was removed using a glass transfer pipet, placed into a polyethylene scintillation vial, and capped with polypropylene cap. No acid was added to the water extract. ICP/AES analysis of the water extract was performed approximately 8 days later. An aliquot of the water used to extract the organic phase material was included and labeled as a process blank.

The acid extraction procedure was performed in a manner identical to that used for the water extract except 2% v:v acid (70% HNO₃) was used instead of water. ICP/AES analysis of the acid extract was performed approximately 6 days later. A process blank was also included. The blank consisted of an aliquot (about 20 mL) of the 2% HNO₃ acid used to extract the organic phase material (the blank was not "extracted").

A laboratory control standard for water (LCSW) was analyzed during each ICP analysis session. The LCSW was prepared using ICV1(0692) multi-analyte standard according to U.S. Environmental Protection Agency instructions. The LCSW was analyzed multiple times and passed. Tolerance limits for all (18) of the analytes present was 90% to 110% of certified value. This provided a means of confirming accuracy of calibration using an independent source.

Table 2.8 summarizes the ICP results for the organic phase. All results have been adjusted for processing and are reported as microgram of analyte present per gram of organic phase tank material (water and acid extracts of the organic phase).

Major analytes found in the water extract of the organic phase were P(450), Na(39), K(23). All other ICP elements were 2 ppm or less. Values in parentheses are the approximate average in μg of analyte per gram organic phase tank material. Only Cd(0.2) was present in the organic phase "water extract" blank. Boron may also be associated with contamination from glass pipets, vessels, etc. used during the extraction procedure. No explanation for the Ti can be found, although it is within a factor of three of the instrument detection limit.

Major analytes found in the "acid extract" of the organic phase included P(605), Na(70), Ni(9.9). All other ICP elements were 2.2 ppm or less. Values in parentheses are the approximate average in μg of analyte per gram organic phase tank material. Ca(2), Fe(0.4), Na(7), and Si(10) were also present in the organic phase "acid extract" blank." Al may have resulted from contamination or other causes; the value is within three times the instrument detection limit and therefore suspect.

Table 2.8. Analysis of C-103 Organic Layer for Cations by ICP/AES
(data expressed as $\mu\text{g/g}$ organic phase)

Analyte	2% HNO ₃ Extract (10 acid: 1 Organic) ^(a)		Water Extract (10 water: 1 Organic) ^(a)	
Ag	0.9	(0)	0.33	(17)
Al	1.8	(29)	-	
B	1.2	(11)	1.4	(69)
Ca	2.0	(0)	-	
Cd	2.1	(0)	-	
Cu	2.2	(3)	-	
Fe	0.33	(15)	-	
K	<DL		23	(25)
Na	70	(3)	39	(6)
Ni	9.9	(8)	-	
P	605	(6)	450	(4)
Si	-		1.5	(38)
Ti	-		0.07	(16)

(a) Values in parentheses indicate % RSD, n = 4.

2.1.8.3 Ammonia

Ammonia analyses were performed on the same acid extracts as used for ICP analyses using well established ion selective electrode methodology according to procedure PNL-ALO-

226, "Ammonia (N) in Aqueous Samples." Results are shown in Table 2.9. Precipitates formed when ionic strength-adjusting buffer (NaOH) was added to the samples.

Table 2.9 Analysis of C-103 Organic Layer for Ammonia

Sample ID	ALO#	$\mu\text{g/mL}$ NH_3	processing (dilution) factor	$\mu\text{g NH}_3/\text{g}$ in sample
X-14	94-02004	2.85	9.25	26.4
X-14	94-02004 dup.	2.43	9.66	23.5
Blank	94-02004	<0.06	-	-
X-15	94-02005	2.19	9.75	21.3
X-15	94-02005 dup.	2.55	9.63	24.6

The average value found was calculated to be $24 \mu\text{g NH}_3/\text{g}$ with a standard deviation of $2 \mu\text{g NH}_3/\text{g}$.

2.2 Aqueous Phase

2.2.1 Analysis of Solvent Extract by GC/MS

A 5-mL aliquot of the aqueous layer was combined with 5 mL of doubly distilled water and extracted 3 times with 10 mL of methylene chloride. This was done in duplicate. The methylene chloride fraction was passed through a column of sodium sulfate and the volume was reduced to 1 mL. The samples were then acidified and extracted 3 times with 10 mL of methylene chloride. The acid fraction was also reduced to 1 mL. Both the base-neutral and acid fractions were then analyzed by GC/MS.

The results of GC/MS analysis of the base-neutral fraction show that DBBP and TBP are the major organic constituents. The average concentration of DBBP was found to be $7 \mu\text{g/mL}$, and the average concentration of TBP was $80 \mu\text{g/mL}$. The percent difference was approximately 10%. NPH was found at just above detection levels. Concentration of NPH was estimated to be $1\text{-}3 \mu\text{g/mL}$. No additional material was detected in the acid fraction.

2.2.2 Headspace Analysis by GC/MS

Due to radioactivity limits of the laboratory, only $40 \mu\text{L}$ of aqueous sample could be placed in a 2-mL vial. Table 2.1.0 lists the concentrations of the components in the headspace of the aqueous layer at 40, 70, and 100°C .

The total ion chromatograms obtained at 70°C and 100°C are very similar to that obtained at 40°C . The spectra are predominantly NPH, NPH-related components, and TBP.

Table 2.10. Determined Concentrations (mg/L) of Components in Headspace of Aqueous Phase

<u>Component</u>	<u>40°C</u>	<u>70°C</u>	<u>100°C</u>
Tridecane	0.001	0.002	0.02
Tetradecane	0.001	0.01	0.01
DBBP		0.002	0.01
TBP	0.004	0.07	0.24

2.2.3 Radiological Properties of Aqueous Phase

Gross alpha, gross beta, and GEA measurements were performed in duplicate for the single aqueous phase sample available.

Gross Alpha and Gross Beta Results

The aqueous sample was analyzed for gross alpha activity according to procedures PNL-ALO-460, "Source Preparation for Gross Alpha Analysis," and PNL-ALO-461, "Alpha Counting Procedure," and for gross beta activity according to procedures PNL-ALO-462, "Source Preparation for Gross Beta Analysis," and PNL-ALO-463, "Beta Counting Procedure." The analyses were run in one batch for each analyte. Included with each batch run were a sample duplicate, method blank, and blank spike.

The sample aliquot size for each determination was equivalent to 1.3×10^{-4} mL, prepared by serial dilution. The sample and a duplicate were sampled from the same dilution into a counting planchet, evaporated to dryness, and counted on a gas proportional counter (beta) and a zinc sulfide scintillation counter (alpha). Residual solids were less than 0.5 mg.

Activities in the method blanks were not detected. The blank spike recoveries for gross alpha (^{239}Pu) and gross beta ($^{90}\text{Sr}/^{90}\text{Y}$) were 108% and 106%, respectively. This indicates that a slightly positive bias may be associated with the sample results. The RPDs of the duplicate sample results are $\pm 9.6\%$ alpha and $\pm 2.1\%$ beta. The propagated error associated with each measurement is indicated with each measurement.

A comparison of the alpha and beta activity in the aqueous sample relative to the organic sample is presented in the table below.

<u>Analyte</u>	<u>Average Activity Organic Layer^(a)(pCi/mL)</u>	<u>Average Activity Aqueous Layer (pCi/mL)</u>	<u>Aqueous to Organic Layer Activity Ratio (volume basis)</u>
Alpha	4.81×10^2	$4.35 \times 10^4 \pm 4 \times 10^3$	90
Beta	9.24×10^5	$7.06 \times 10^7 \pm 1 \times 10^6$	76

(a) Density corrected, 0.88 g/mL.

The gross alpha activities are determined relative to detectors calibrated with ^{239}Pu , which is a typical alpha emitter of concern. Other alpha emitters may have significantly different counting efficiencies. The gross beta activities are determined relative to detectors calibrated with $^{90}\text{Sr}/\text{Y}$. Other beta emitters may have significantly different counting efficiencies. Therefore, one should consider these determinations to be qualitative.

GEA procedure (PNL-ALO-450, "Gamma Energy Analysis - Track Detector") was used to analyze splits of one aqueous phase sample (Table 2.11). Cesium-137 and ^{60}Co were observed, with Cs at activity levels approximately three orders of magnitude greater than Co. The standard deviation values suggest excellent precision.

Table 2.11. Measured Activities ($\mu\text{Ci/mL}$)

Sample	Activity (Error)	
	^{60}Co	^{137}Cs
Aqueous phase	5.04×10^{-2} (4%)	5.76×10^1 (2%)
Aqueous phase duplicate	5.18×10^{-2} (4%)	5.81×10^1 (2%)
Mean value	5.11×10^{-2}	5.79×10^1
% Standard deviation	1.37%	0.43%

Note: Error estimates are one-sigma total analytical errors, not including contributions from sampling or experimental handling.

2.2.4 Inorganics

2.2.4.1 Anions by IC

General procedures for the IC analysis of the aqueous phase are as described in Section 2.1.8.1. The aqueous layer was analyzed by IC following a nominal 1000X preparation dilution. Results are summarized in Table 2.12. A matrix interference peak was present beside the fluoride peak which affected the quantitation of fluoride. It is estimated that the "true" value may be 10% higher than the reported value for fluoride.

Table 2.12. Analysis of C-103 Aqueous Layer for Anions by IC
(data expressed as $\mu\text{g/g}$ sample)

Anion	Concentration
F ⁻	1,100 (a) (b)
Cl ⁻	400
NO ₂ ⁻	23,000
NO ₃ ⁻	2,450
PO ₄ ³⁻	2,000
SO ₄ ²⁻	3,000

- (a) Matrix interference: actual value may be 10% higher.
(b) RPDs between duplicate analyses were $\leq 4\%$.

2.2.4.2 Cations by ICP/AES

The procedures followed were identical to those mentioned in Section 2.1.8.2. The aqueous phase sample from C-103 was prepared for ICP analysis by adding approximately 0.5 g of C-103 "aqueous phase" to approximately 50 g of 2% HNO₃ acid, then mixing using a vortex mixer.

The aqueous phase values are reported in Table 2.13 as microgram of analyte present per gram of aqueous phase tank material.

Analytes found in the aqueous phase included Ag(11), Ca(25), Cd(1), Cr(53), Fe(7), K(300), Mo(10), Na(30,000), Ni(66), P(2300), Si(88), U(1900), and Zr(280). Values in parentheses are the approximate average in μg of analyte per gram aqueous phase tank material. Ca(20), Fe(4), Na(70), and Si(110) were also present in the "aqueous phase blank."

Cr, Mo, U, and Zr were found in the aqueous phase material, but not in the organic phase material.

Na (~3.0 wt%) was the highest measured concentration followed by P (~0.23 wt%), U (~0.19 wt%), and Zr (280 $\mu\text{g/g}$). All were associated with the aqueous phase material from tank C-103.

**Table 2.13. Analysis of C-103 Aqueous Phase for Cations by ICP
(data expressed as $\mu\text{g/g}$ sample)**

Cations	Concentration
Ag	11 (0) ^(a)
Al	nd ^(b)
B	nd
Ca	5 (100)
Cd	0.8 (50)
Cu	nd
Cr	53 (11)
Fe	3 (0)
K	300 (0)
Mo	10 (0)
Na	30,400 (10)
Ni	67 (10)
P	2350 (21)
Si	\pm ^(c)
Ti	nd
U	1950 (15)
Zn	nd
Zr	280 (14)

(a) Computed RPD in percent.

(b) Not detected.

(c) Less than blank.

2.2.4.3 pH

pH was measured using a Corning (Corning, NY) pH meter equipped with a Beckman (Fullerton, CA) gel-filled electrode. The meter was calibrated using buffers at pH 7 and pH 10, and the calibration checked after the determination using a second pH 10 buffer. Duplicate determinations of the aqueous layer from tank C-103 gave pH values of 10.00 and 9.99.

2.2.4.4 TOC/TIC/TC

This work was done by the hot persulfate oxidation/coulometry detector method PNL-ALO-381, rev. 0, "Determination of TC, TOC, and TIC in Radioactive Liquids, Soils and Sludges by Hot Persulfate Method." The TOC standard used was alpha-d-glucose, Kodak (Rochester, NY) lot# B1F, and the TIC standard was Na_2CO_3 . Both materials were used in liquid form, dissolved in water, for system standards as well as matrix spikes. The estimated precision was $\pm 10\%$ and the estimated accuracy was $\pm 15\%$.

The TOC/TIC/TC was measured directly on the as-received aqueous layer sample (Table 2.14). All QC results were within acceptable limits. The TIC and TOC system standards recovery ranged from 91.9% to 101.5%. The system blanks were consistent. Matrix spike recovery results were 94% and 101%, respectively, for TIC and TOC.

Table 2.14. TIC/TOC Measurements on C-103 Aqueous Phase

Sample	Sample Vol. (mL)	TIC (ug/mL)	RPD (%)	TOC (ug/mL)	RPD (%)	TC ^(a) (ug/mL)	RPD (%)
C-103 Aq.-1	0.1984	5160		7020		12200	
C-103 Aq.-2	0.1984	5170	0.3	7360	5	12500	3
C-103 Aq. Spike	0.1984		94% recovery (TIC) ^(b)		101% recovery (TOC) ^(b)		

- (a) Only TIC and TOC are actually measured. The TC is the sum of TIC and TOC.
 (b) Percent recovery is determined for TIC and TOC using the respective standards, Na₂CO₃ or glucose, and all sample results are corrected for percent recovery. All results are blank-corrected.

Using a density of 1.078 g/mL (see Section 2.2.5.2) and the results given in Table 2.14, the TOC, TIC, and TC content of the aqueous phase can be summarized as follows. The average TOC was found to be 0.67 wt%, average TIC was found to be 0.48 wt%, and TC calculated to be 1.15 wt%. All samples were analyzed in duplicate and all showed 5% RPD or less.

2.2.4.5 Ammonia

A calibration check standard was analyzed prior to and following sample analyses. Recoveries were 98 and 90%, respectively.

Ammonia analyses were performed on acidified aliquots of the C-103 aqueous sample (X-17). These measurements were made during the same analytical session as the organic phase extract samples. Procedures were identical to those described in Section 2.1.8.3. Results for the same QC samples (check standards) as given in Section 2.1.8.3 apply. Sample spike recoveries were 83% and 89%. The average value found for duplicate sample aliquots was 215 µg NH₃/g sample. RPD for the duplicates was 26%.

2.2.5 Physical Properties

2.2.5.1 Viscosity

The procedure for determining of the aqueous sample viscosity is the same as described in Section 2.1.5.1. The viscosity of the aqueous sample increased as the shear rate increased. At 25°C the viscosity of the aqueous layer increased from 1.5 to 4.5 cP over the shear rate range from 25 to 500 s⁻¹. At 40°C the viscosity of the sample exhibited essentially newtonian behavior with a viscosity of between 1.5 and 2 cP over a shear rate range from 25 to 200 s⁻¹. Higher shear rate ranges could not be achieved at this temperature, because of the low viscosity of the sample.

2.2.5.2 Density

The procedure for determination of the aqueous sample density is the same as described in Section 2.1.5.2. The determined density of the aqueous sample was 1.078 g/mL at 25°C and 1.076 g/mL at 44°C. The difference is not statistically significant.

2.2.6 Thermal Analysis/TOC of Dried Solids

2.2.6.1 DSC/STG

DSC and STG were performed in duplicate on sample X-17 from the dip sample taken from tank C-103 in December of 1993. These two thermal analysis techniques are useful in determining the thermal stability or reactivity of the sample. DSC measures heat released or absorbed while the temperature of the sample is increased at a constant rate. These data are often used to measure thermal decomposition temperatures, heats of reaction, reaction temperatures, melting points, and solid-solid transition temperatures. STG measures the changes in the mass of a sample while the temperature of the sample is increased at a constant rate; therefore, gaseous reaction products result in weight losses and oxidation reactions may result in weight gains. The data obtained from STG are often used to measure thermal decomposition temperatures, water contents, reaction products, and reaction temperatures. These two methods provide complementary information that can be used to determine the energies and products of thermally induced reactions.

The Perkin-Elmer Model 2 DSC and STG were used in the analysis of the C-103 sample. The calibration of the DSC and STG were checked before running these samples. An indium and a zinc standard were run on the DSC to check the temperature and enthalpy calibration. The measured onset temperature and enthalpy for the indium and zinc standards were 157°C and 6.72 cal/g, and 417°C and 23.9 cal/g, respectively. The literature values for these two standards are 157°C and 6.78 cal/g for indium and 419°C and 25.9 cal/g for zinc. An alumel and perkalloy curie point standard were run on the STG to check the temperature calibration. The measured curie point for the alumel and perkalloy were 163 and 598°C, respectively. The literature values for these curie points are 163°C for alumel and 596°C for perkalloy.

The thermal analysis samples from tank C-103 were performed according to procedure PNL-ALO-508, rev. 0, "Laboratory Procedure for Operation of the Differential Scanning Calorimeter (DSC), Thermogravimetric Analyzer (TG), and High Temperature Differential Thermal Analyzer (DTA) and DSC." Preparation of these samples prior to the analyses was different from the normal procedure as described below.

One hundred microliters of sample were placed in each of two gold DSC pans and dried at 60°C prior to analysis. The data provided on the thermograms are calories per gram of dried weight. The density of sample X-17 as reported earlier is 1.078; therefore, 108 mg of sample was placed in each pan. The dried weight for the two samples was 14 mg for the sample (94-02006-DSC1) and 13 mg for the duplicate (94-02006-DSC2). Therefore, the total dissolved solids for the aqueous phase material is calculated to be 12.5%. Energetics data from DSC measurements are summarized in Table 2.15.

STG was performed in duplicate on the as-received X-17 sample. The samples were weighed at the beginning of each run, and then the samples were allowed to sit at ambient temperature in the thermogravimeter with air flowing over the sample for 1 hour prior to increasing the temperature. The mass loss of the samples was monitored during this time, and between 75% and 80% of the mass of the sample was lost. This loss is due to the evaporation of water. Results of STG analyses are given in Table 2.16.

An exotherm with an energy of approximately 180 calories/gram of dried sample was observed between 240 and 430°C. (See Table 2.15.) A weight loss of 16% (based on dried sample) is associated with this exotherm. Water evaporation from the sample is observed as an endotherm between ambient temperature and 230°C. A weight loss is also associated with this water loss. At least three types of water (e.g., (see Table 2.16) free water, waters of hydration, and loosely bound water) are observed in this sample.

Table 2.15. Energetic Data for the Aqueous Layer from C-103

<u>Sample</u>	<u>Temperature (°C)</u>		<u>Enthalpy (cal/g)</u>
	<u>Onset</u>	<u>Range</u>	
94-02006-DSC1	158	113 - 227	9.1
	315	237 - 439	-185
94-02006-DSC2	121	37 - 227	73
	255	250 - 441	-171

Table 2.16 . Mass Loss of the Aqueous Layer from C-103 as a Function of Temperature

<u>Sample</u>	<u>Temperature Range (°C)</u>	<u>Mass Loss (%)</u>
94-02006-TGA1	Ambient Isotherm	78.8
	30 - 58	5.1
	58 - 165	3.7
	165 - 440	2.0
94-02006-TGA2	Ambient Isotherm	75.0
	30 - 67	9.5
	67 - 165	3.2
	165 - 440	2.0

2.2.6.2 Direct Determination of TOC/TIC in C-103 Dried Aqueous Layer Sample

This work was done according to Test Procedure PNL-ALO-381, rev. 0, "Determination of TC, TOC, and TIC in Radioactive Liquids, Soils and Sludges by Hot Persulfate Method." TOC standard used was alpha-d-glucose, Kodak lot# B1F. The standard was used in liquid form, dissolved in water, for system standards as well as matrix spikes. The estimated precision is $\pm 10\%$ and the estimated accuracy is $\pm 15\%$.

The TOC/TIC/TC was measured directly on the as-received dried aqueous sample. All QC results were within acceptable limits. The TOC system standards recovery ranged from 90.1% to 93.6%. The TOC system blanks were consistent. The RPDs for the sample, analyzed in duplicate, were 4.7% for TIC, 1.2% for TOC, and 1.4% for TC. The TOC matrix spike recovery was 90%. The results are reported in Table 2.17 in $\mu\text{g/g}$, based on the as-received dried material.

Table 2.17 TOC/TIC in C-103 Dried Aqueous Sample

<u>ALO No.</u>	<u>sample wt (g)</u>	<u>TIC (µg/g)</u>	<u>RPD (%)</u>	<u>TOC (µg/g)</u>	<u>RPD (%)</u>	<u>TC (µg/g)</u>	<u>RPD (%)</u>
C-103 Dried Aq.-1 94-2006	0.0787	33800		44000		77800	
C-103 Dried Aq.-2 94-2006	0.0653	35400	4.7	43500	1.2	78900	1.4
TOC Matrix Spike 94-2006	0.0489			90% Recovery			

Notes:

- (1) Only TIC and TOC are actually measured. The TC is the sum of TIC and TOC.
- (2) Percent recovery is determined for TOC using glucose, and all sample results are corrected for percent recovery. All results are blank-corrected.
- (3) The reported results have been rounded to two or three significant places, so some may slightly disagree with the spreadsheet review report. The RPDs were rounded to the nearest integer, but were calculated based upon the full displayed digits in the spreadsheet review report.

3.0 References

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Appendix A

**Analytical Determination of Peroxide by the Oxidation of
N,N'-di(2-naphthyl)phenylene-1,4-diamine to Form a Highly
Colored Diimine Product**

Appendix A

Analytical Determination of Peroxide by the Oxidation of N,N'-di(2-naphthyl)phenylene-1,4-diamine to Form a Highly Colored Diimine Product

Scott. D. Harvey

Background

The following procedure represents a modification and extension of the work of Ferracini and Lima (1). These authors describe the colorimetric determination of peroxide based on the reaction of N,N'-di(2-naphthyl)phenylene-1,4-diamine with peroxide to form a highly colored product that was hypothesized to be the corresponding diimine. The work described here arose out of a need to determine total peroxide content in highly complex waste matrices. Our approach was to utilize the same reaction as Ferracini and Lima followed by the chromatographic determination of the resulting diimine product. Although colorimetric determination of the diimine product is inherently specific due to the diimine absorption maximum at 482 nm, it was felt that the additional selectivity offered by the chromatographic separation and quantification of the reaction product would allow for the analysis of peroxides in unusually complex samples.

Our initial work essentially repeated the colorimetric studies described by Ferracini and Lima. This work proved important for identifying variables that were essential for a successful assay. For example, it was determined that commercially available N,N'-di(2-naphthyl)phenylene-1,4-diamine (Pfaltz & Bauer, Flushing, NY) was not sufficiently pure for use in the peroxide reaction. Purification of this reagent required recrystallization from toluene prior to preparation of stock solutions. It was additionally noted that use of freshly distilled toluene was essential to avoid high blank values. Distillation probably served to remove dissolved oxygen from the toluene solutions. It was also found that the N,N'-di(2-naphthyl)phenylene-1,4-diamine and catalyst stock solutions should be maintained in the dark. This was achieved by wrapping flasks containing these solutions with aluminum foil.

Novel aspects of study

Our preliminary work also represents a significant extension of the studies described by Ferracini and Lima. These authors were able to obtain a mass spectrum of the diimine produced by oxidation of N,N'-di(2-naphthyl)phenylene-1,4-diamine by the very strong inorganic oxidizer, chromium trioxide. In the work presented here, mass-spectral data were obtained that verify that N,N'-di(2-naphthyl)phenylene-1,4-diimine is also the product produced by the reaction of benzoyl peroxide with N,N'-di(2-naphthyl)phenylene-1,4-diamine. Additionally, preliminary chromatographic data were collected which define the normal-phase chromatographic conditions leading to reasonable retention times of the diimine product.

Procedure

For development of this procedure, the following stock solutions were prepared as described below:

1. Recrystallized N,N'-di(2-naphthyl)phenylene-1,4-diamine (0.050 g) was brought to a total volume of 100.0 ml of freshly distilled toluene to give a 0.05 % solution (w/v). This solution was stored in the dark and used immediately.

2. A 0.2 % cobalt(II)napthenate catalyst solution was prepared from a commercially available mineral oil solution (Pfaltz & Bauer), containing 6 % cobalt(II)napthenate, by diluting 333 μ l to a total volume of 100 ml with freshly distilled toluene. This solution was likewise stored in the dark.

3. A 1003 ppm benzoyl peroxide concentrated stock solution was prepared by diluting 0.18244 g of 55 % benzoyl peroxide (Pfaltz & Bauer) to 100.0 ml with freshly distilled toluene. Standards were prepared from the standard stock solution as described below:

Volume of 100 ppm Benzoyl Peroxide Stock Solution	Total Volume of Standard After Dilution	Concentration of Standard
50 μ l	10.0 ml	5.0 ppm
100 μ l	10.0 ml	10.0 ppm
250 μ l	10.0 ml	25.0 ppm
500 μ l	10.0 ml	50.0 ppm
1000 μ l	10.0 ml	100 ppm

Colorimetric Reaction Conditions

The following amounts of reagents were combined in a 5.0 ml Reacti-Vial and heated at 70 °C for 25 min at which time the absorbance at 482 nm was determined against the blank.

Determination	Volume Peroxide Solution	Volume Co(II)-napthenate	Volume DNPD Solution	Absorbance
5.0 ppm	1.0 ml	1.0 ml	2.0 ml	0.059
10.0 ppm	1.0 ml	1.0 ml	2.0 ml	0.119
25.0 ppm	1.0 ml	1.0 ml	2.0 ml	0.289
50.0 ppm	1.0 ml	1.0 ml	2.0 ml	0.511
Blank	†	1.0 ml	2.0 ml	0.000

† For the blank, 1.0 ml of toluene was added rather than a peroxide solution.

The regression equation for the resulting standard curve is:

$$\text{Abs} = 0.0117 + 0.0102 C(\text{ppm}) \quad r^2 = 0.995$$

The limit of detection for this spectrophotometric assay is approximately 1 ppm peroxide.

For application to waste samples, 1.0 ml of waste would be substituted for the benzoyl peroxide solution. Comparison to a standard curve, run concurrently with the waste sample, would form the basis for quantification.

Chromatographic Analysis of N,N'-di(2-naphthyl)phenylene-1,4-diamine

The solubility of the diimine in acetonitrile was found to be low. Conversely, the diimine was found to exhibit high solubility in nonpolar solvents such as hexane and toluene. These solubilities were a good indication that separations based on normal-phase principals would be

the most effective approach. Chromatography on a cyanopropyl silica column with an isopropanol/hexane mobile phase was chosen. Hexane solutions of the diimine were injected (5 μ l) on the 15 cm x 2 mm i.d., 5 μ m cyanopropyl silica column by a WISP (Waters, Milford, MA) automatic injector. Detection was accomplished with a Waters Model 484 detector at 482 nm. The column was developed with various isocratic compositions of mobile phases delivered by a pair of Waters Model 510 pumps at a flow rate of 200 μ l/min. An hexane/isopropanol composition of 75:25 gave a reasonable retention of the diimine (16 min). The approximate dead volume of the column was determined by noting the negative peak that resulted at 4 min from an injection of hexane when detected at 210 nm. This indicates that the diimine product is retained with a k' of approximately 3.

Reference

1. V. L. Ferracini and C. G. Lima, Evaluation of N,N'-Di(2-naphthyl)phenylene-1,4-diamine as a Reagent for the Spectrophotometric Determination of Organic Peroxides, *Analyst*, **106**:574-583 (1981).

Appendix B

A Comparison of Flash Point Measurement Methods

Appendix B

A Comparison of Flash Point Measurement Methods

Scott A. Clauss, James M. Robbins and Roger M. Bean

Chemical Sciences Department
Pacific Northwest Laboratory

There is an extensive literature on flash point definitions, methods, and result application in the Hanford Technical Library. This report summarizes items of interest found during a brief search of that literature, and includes a discussion with Jim Robbins, who has conducted flash point measurements at Pacific Northwest Laboratory (PNL).

Flash point is defined as the minimum temperature at which a liquid gives off sufficient vapor to form an ignitable mixture with the air near the surface of the liquid, or within the vessel used.¹ Thus, the lower the flash point the more of a fire hazard the material is expected to pose. There is a closely related measurement known as the fire point. This is also called the ignition or autoignition temperature. At this temperature, there is sufficient vapor above the liquid to create a self-sustaining flame. Another related item is the lower explosion limit (LEL). The LEL is the minimum concentration of a vapor in air below which a flame will not occur. All of these measurements are related to the vapor pressure of the material. The flash point in an actual situation will also vary with the availability of oxygen and atmospheric pressure.²

By definition a "combustible" liquid has a flash point at or above 100°F (37.8°C). A "flammable" liquid has a flash point below 100°F and a vapor pressure below 40 psia at 100°F.¹ Tributyl phosphate (TBP) is thus a combustible liquid, specifically, a Class IIIB combustible liquid, since its flash point is over 200°F.^{1,3} This is the lowest combustion class listed in National Fire Protection Association (NFPA) Code 321.¹

Many different methods are listed in the American Society for Testing and Materials (ASTM) manuals for measuring flash point. Eight methods are currently used. There are criteria for choosing a flash point determination method; for example, the method should take into account the use and type of material involved. Open cup methods are more applicable to open containers or spills, while closed cup is appropriate for closed containers.⁴

List of ASTM Flash Point Methods

ASTM D56	Tag Closed Cup
ASTM D92	Cleveland Open Cup
ASTM D93	Pensky-Martens Closed Cup
ASTM D1310	Tag Open Cup
ASTM D3278	Setaflash Closed Cup
ASTM D3828	Setaflash Closed Cup
ASTM D3934	A Closed-Cup Method
ASTM D3941	A Closed-Cup Method

References for the flash point of TBP appear in three publications:

- NIOSH Pocket Guide to Chemical Hazards: 295°F, open cup³
- Aldrich Catalog, 1990-1991: 380°F, closed cup⁵
- Merck Index, 11 ed.: 295°F, not described.⁶

Aldrich used ASTM method D3278. The ASTM methods used in the NIOSH Guide and the Merck Index were not cited.

The flash points being determined by PNL are done on a Grabner Instrument (Latham, NY) Miniflash CCA-FLP Flash Point Tester. This instrument emulates the Pensky-Martens (ASTM D93-90) and Setaflash (ASTM D3278-89) closed cup Testers.^{7,8} The Grabner instrument emulates a flash point by measuring the equivalent over-pressure associated with a flame, with a thickness of approximately 3 mm, that covers 50% to 90% of the surface of the organic substance⁹. The equivalent over-pressure associated with this flash is between 4, and 6 kPa. For a more complete discussion of the Grabner instrument, contact Jim Robbins or Danny Sanders of the PNL Analytical Chemistry Laboratory (ACL).

The National Fire Protection Association¹ recommends the Pensky-Martens⁸ test for liquids with, among other criteria, flash points over 200°F. However, the Department of Transportation¹⁰ recommends a Setaflash Closed Tester for mixtures that have flash points above 100°F. Thus, this test is appropriate for TBP. The U.S. Navy¹¹ has generated quality assurance data for the Grabner instrument, and the ASTM is evaluating a draft method for this instrument. Flash point measurements on an n-dodecane standard by PNL compared well with those reported by the Navy, with both studies meeting the ASTM established value for n-dodecane of 184°F ±4°F.

The Setaflash result on the Grabner instrument for TBP was 358°F. Previous test results by H. A. Lee of Atlantic Richfield Hanford listed the flash point of TBP to be 275°F¹². The result cited in the Lee document was obtained using a manual Pensky-Martens closed cup tester. The results by Robbins and Sanders are closer to the Setaflash closed cup tester results listed in Aldrich⁵. Measurement of flash point using the standard manual Pensky-Martens device is highly dependent on a skilled operator. Operator errors, such as those listed below, are avoided by substituting the Grabner automated flash point instrument used by PNL.

- The instrument must be in a draft-free area (e.g., not in a hood).
- The testing flame must be maintained at 5/32 inch in diameter.
- The heating rate must be between 9 and 11°F per minute, which may be difficult to establish with a bunsen burner as used in the original procedure. More recently, a rheostat has been substituted for the burner to obtain better control of the temperature ramping.
- The cup must be stirred at 90 rpm and the stirrer turned off before each test.
- There can be condensation of vapors on the cooler portions of the cup.
- The cup must be properly cooled between each test.

The flash points of mixtures of normal paraffin hydrocarbons (NPH) and TBP have been examined as well. A closed cup apparatus is probably more suitable for this test, since preferential evaporation of the more volatile liquid in an open cup may bias the results.

ASTM's E 502-84, *Standard Test Methods for Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods*,¹³ describes the differences between the tests and also gives a selection guide. It is probably the most general and informative of the ASTM documents we found. It recommends the Setaflash or Pensky-Martens test for materials with a flash point above 93°C (200°F). The difference between these two methods is that the Setaflash is equilibrated and tested at a specified temperature near the flash point, and the Pensky-Martens is tested every 2°F while heating at a controlled rate of 10°F/min. The Pensky-Martens test produces a higher flash point for organic mixtures, because lower-end volatiles are burned off in small amounts throughout the test, whereas the Setaflash method allows the volatile components to concentrate in the tester for 60 seconds while equilibrium is being established. ASTM E 502-84 also includes a commentary on flash point tests in its appendix. Comments of note include the following:

- "X1.1 While the flash point can be used to indicate the flammability of liquid and solid chemicals for certain uses, flash point does not represent the minimum temperature at which a material can evolve flammable vapors."

- "Note X1.2--...a single test such as a flash point should not be relied upon to characterize completely the flammability of a material. Process and handling conditions should be carefully considered and additional tests may be warranted."

Thus, the flash point isn't the only element to be examined in a fire hazard assessment.

In conclusion, the Setaflash flash point test conducted by PNL, according to draft test procedure PNL-ALO-234, "Flash Point by CCA-FLP Miniflash Closed Cup Tester," was the best test for the intended purpose. At this time, the reason for the difference between the TBP flash point measurements by PNL and those of Lee¹² cannot be fully explained. It would be necessary to obtain precision and accuracy validation documentation for the Lee data to fully investigate this discrepancy. Regardless of the finding, the investigator is cautioned that flash point is just one element in the assessment of fire hazard.

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