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Organic Evaporation and Oxidation Testing in Support of Hanford Sample-and-Send

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EXECUTIVE SUMMARY

The Hanford site has approximately 56 million gallons of radioactive mixed waste stored in 177 underground storage tanks. The Hanford Waste Treatment and Immobilization Plant (WTP) is being built to treat and immobilize the tank waste. The baseline method for immobilization of Low Activity Waste (LAW) through the WTP is vitrification, but additional immobilization capacity is needed to supplement the initial LAW melters. An alternative cementitious waste form is being investigated for that future immobilization method to supplement vitrification. However, one impediment to a cementitious waste form is the presence of Land Disposal Restricted (LDR) organic chemicals in tank waste. This work evaluates potential avenues to eliminate that impediment to permit possible use of a cementitious waste form and work towards a decision whether additional LDR organic pretreatment would be required. Savannah River National Laboratory (SRNL) performed testing using simulants to examine evaporation as a method to remove some prevalent organics from LAW. Spiking the caustic LAW simulant with selected regulated organic chemicals found one that clearly decomposes because of caustic instability. Oxidation testing of other organic chemicals found some LDR organics degrade as desired and others are stable in the presence of peroxide and permanganate. In addition to studies with simulants, a literature review was performed to evaluate radiological stability of LDR organics. Descriptions of the experimental details, equipment, and results are included in this report.

Evaporation testing consisted of preparing the LAW simulant, spiking that simulant with organic chemicals, and evaporating the mixture via differential distillation. The apparatus was a laboratory-scale vacuum evaporator operated at 60 ±5 torr absolute (vacuum evaporation) and also at atmospheric pressure. The LAW simulant represented the liquid expected to be retrieved from the Hanford tank farms at approximately 4.0 M [Na^+] total sodium ion concentration. The concentration of the organic chemicals added was significantly higher than typically found in the tank waste samples since the higher levels were necessary to assist in analytical measurement and tracking of the spiked species. Organic chemicals were chosen for the work with a consideration of how their volatility compares with that of methanol. This was done by comparing the ratio of the pure water Henry's law coefficient (K_h) of methanol to that of the compound in question (hereafter termed the K_h ratio), where ratios above unity indicated less volatility than methanol. Methanol was chosen because it is a common regulated chemical with relatively low volatility but which has been removed by evaporation in previous laboratory work.

While organic separation results depend on evaporator design, laboratory experiments verified that organic partitioning to the overhead condensate stream by evaporation is a practical process. The work reported here found difficulties in quantitative analysis of the organic chemicals in aqueous samples. Most of the time there was insufficient analysis to close a mass balance for evaporator runs, but qualitative evidence of carryover was obtained. The methods were also able to show whether organic chemicals were susceptible or resistant to solution oxidation in permanganate or hydrogen peroxide tests. Specific observations are:

- Atmospheric evaporation testing was found to strip n-nitrosodipropylamine (K_h ratio of 2.1) 4-choroaniline (K_h ratio of 4.8), 2-ethoxyethanol (K_h ratio of 9.7), and n-nitrosomorpholine (K_h ratio of 186) but not 4-Nitroaniline (K_h ratio of 2270) or phenol (deprotonates in LAW). Hence, compounds with a K_h ratio below at least 186 (and that are not present as charged species) are removed from LAW by atmospheric evaporation.
- Similar results were obtained using vacuum evaporation, however n-nitrosomorpholine (K_h ratio of 186) was not tested and the limiting K_h ratio demonstrated is 9.7 (corresponding to 2-ethoxyethanol).
- Vacuum evaporation resulted in more organic removed from LAW than atmospheric evaporation for all compounds tested under both conditions.

- Using the Henry's law coefficient data reported in RPP-RPT-63494 and the demonstrated lower volatility limits suggests that only 44 of the 207 LDR organics would not be removed by atmospheric evaporation and that 64 including the 44 would not be removed by vacuum evaporation. Additional testing with n-nitrosomorpholine (K_h ratio of 186) is needed to determine if similar results to those observed with atmospheric evaporation also apply to a vacuum system.
- Di-n-butyl phthalate appeared to decompose in the atmospheric evaporation tests resulting in the formation of n-butanol. In addition, 2,4-dinitrotoluene is not stable in caustic solution at room temperature and so is not be expected to exist in alkaline waste.
- Oxidation testing at 60 °C (1 hour exposure) and 25 °C (6 hour exposure) with permanganate demonstrated that phenol, phthalate, 4-chloroaniline, ortho-cresol, and 4,6-dinitrocresol appear to be treatable in the LAW simulant even in the presence of high concentration of nitrite and the organic acids acetate, formate, glycolate, and oxalate. In contrast, n-nitroso compounds (n-nitrosodipropylamine and n-nitrosomorpholine) appear to be more refractory.
- Hydrogen peroxide (60 °C with 6 hours of exposure) also showed some ability to oxidize 4-chloroaniline, phenol, ortho-cresol, and 4,6-dinitrocresol cresols, and 4-chloroaniline. It did not attack phthalate, n-nitrosodipropylamine, n-nitrosomorpholine, or the organic acids formate and oxalate.
- Air sparging at room temperature was not an effective process for treating organic chemicals that likely would be oxidation sensitive under caustic conditions – phenol, o-cresol, and diphenylamine.
- These results suggest that chemical oxidation of some LDR organics may be a viable treatment option, but that additional testing on a wider range of compounds and reaction conditions is needed.
- Analytical techniques were challenged when measuring the complex organic chemicals studied here. Semivolatile organic measurements rely on solvent extraction of aqueous samples, and low extraction efficiencies often resulted. Some regulated organic chemicals like phthalic acid deprotonate at high pH, preventing effective extraction. Adjustment of pH to the acid side would make the nitrite in the solution matrix reactive, possibly oxidizing organic analytes. The Nuclear Magnetic Resonance (NMR) analysis was also challenging because of the mixture of complexorganic compounds added to experimental simulants.

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LIST OF ABBREVIATIONS

AC&SM	Analytical Characterization and Sample Management (SRNL)
atm	atmospheres
C	Celsius
cm	centimeters
DFLAW	Direct Feed Low-Activity Waste
ETF	Effluent Treatment Facility
g	grams
H	Henry's Law coefficient, units atm-m3/mol
HLW	High Level Waste
^{1}HNMR	Nuclear Magnetic Resonance, hydrogen
hr	hour
IC-A	Ion Chromatography for Anions
ICP-ES	Inductively Coupled Plasma –Emission Spectroscopy
K_h	Henry's law coefficient
KOP	Knock Out Pot
L	Liter
LAW	Low Activity Waste
LDR	Land Disposal Restricted
m	meter
M	Molar
M&TE	Measurement and Test Equipment
mol	mole
mg	milligram
mL	milliliter
mm	millimeter
mM	millimolar
NMR	Nuclear Magnetic Resonance
ND	Not detected
NM	Not measured
ppm	Parts per million
pKa	Negative base 10 logarithm of acid dissociation constant
RCRA	Resource Conservation and Recovery Act
SLAW	Supplemental Low Activity Waste
SRNL	Savannah River National Laboratory
Std. Dev.	Standard Deviation

TIC	Tentatively identified compounds
TOC	Total Organic Carbon
TWINS	Tank Waste Information System
VOA	Volatile Organic Analysis
SVOA	Semi-volatile Organic Analysis
WRPS	Washington River Protection Solutions
wt %	Weight percent
WTP	Waste Treatment and Immobilization Plant

1.0 Introduction

The current plan at the Department of Energy's (DOE) Hanford Site for treatment of radioactive mixed tank waste is through immobilization by vitrification of high-level waste (HLW) and low activity waste (LAW) into glass waste forms. It is recognized that the current LAW vitrification facility will not have enough capacity to process LAW at a rate that will allow the HLW facility to continually operate at full capacity. A yet to be identified supplemental treatment system will be needed to handle an estimated 54 million gallons of LAW. Note that this volume includes the large volume of liquid added during waste retrieval.[1] The waste that will be processed by the supplemental treatment system is termed Supplemental Low Activity Waste, or SLAW.

One option under investigation for treating SLAW is to solidify and stabilize the material in a cementitious waste form that meets Resource Conservation and Recovery Act (RCRA) and DOE O 453.1 requirements. However, the presence of organic chemicals regulated under the Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDR) program adds complexity to treating and disposing of the LAW if a non-thermal treatment method like cementation is used. The complexity arises from the fact that the baseline vitrification method is considered by the Washington State Department of Ecology (Ecology) as providing adequate treatment for organics; a status not automatically extended to a low-temperature process, such as solidifying the waste in a cementitious waste form. In addition, the Environmental Protection Agency (EPA) LDR program is intended to ensure that wastes are properly treated prior to disposal. Proper treatment makes hazardous waste less harmful to groundwater by reducing the mobility and/or toxicity of the hazardous constituents in the waste. EPA guidance indicates that stabilization/solidification of waste for organics could be considered impermissible dilution under the LDR dilution prohibition. In addition, waste storage activities at Hanford have required transferring and blending waste within the tank system and these activities have potentially altered the concentrations of the hazardous constituents. The LDR dilution prohibition found in 40 Code of Federal Regulations (CFR) 268.3 states that "*… no generator, transporter, handler, or owner or operator of a treatment, storage, or disposal facility shall in any way dilute a restricted waste or the residual from treatment of a restricted waste as a substitute for adequate treatment …*" Hence, if LAW is to be treated using low temperature stabilization (such as cementation), then it is important to demonstrate how past storage activities have contributed to the removal (by vacuum evaporation) or destruction (by in situ decomposition) of the LDR organics and that cementation without additional treatment does not necessarily represent impermissible dilution.

It is also possible that additional removal or destruction of LDR organics may be needed for some Hanford LAW to meet regulatory standards in the final waste form. One treatment method that has been proposed is to remove the organics from the aqueous stream by evaporation with subsequent treatment of the aqueous condensate containing the removed organics in the RCRA-permitted Hanford Effluent Treatment Facility (ETF). [2] This approach would likely be similar to the current evaporative volume reduction of tank waste performed by the Hanford 242-A evaporator. A second possible method to treat LDR organics is to destroy them through oxidative reactions. Finally, if sufficient removal or destruction of LDR organics in Hanford tank waste has already occurred, a decision might be possible to meet LDR program requirements in treatment of SLAW without additional LDR organic pretreatment.

The work reported here supports both the need to quantify historic evaporation and in situ decomposition and the need to identify viable future removal or destruction processes for LDR organics by:

1. Providing an update of the water solubility compilation of the 207 land disposal restricted (LDR) organic chemicals potentially associated with Hanford tank waste (RPP-RPT-63493). This information is needed to evaluate which of the compounds could be present in retrieved LAW at significant concentrations compared to regulatory limits.

2. Providing an update of the alkaline reactivity of the 207 LDR organic chemicals to assess stability in LAW.
3. Providing an initial assessment of the decomposition of the LDR organics by radiolysis to assess the impact of in-tank radiation on chemical stability.
4. Reporting an assessment of Tank Waste Information System (TWINS) organic chemical data to identify both data gaps and compounds that might need further treatment.
5. Testing the volatility bounds for vacuum and atmospheric evaporation of organics in LAW both to determine the possible impacts of historic evaporation, and to evaluate if this is a plausible method to disposition the LDR organics if future treatment is needed.
6. Performing laboratory tests of regulated organic chemical oxidation by permanganate, hydrogen peroxide, and air under alkaline conditions to determine the efficacy of these oxidants as a means for destroying regulated organics from LAW, particularly those that cannot be removed by evaporation.

The first four tasks above are literature based and are provided in Appendices A through E of this report. Appendix A contains a table of literature information on the water solubilities of the 207 land disposal restricted (LDR) organic chemicals. Appendix B contains the latest alkaline reactivity assessment for the 207 restricted compounds. Appendix C contains an initial assessment of organic remediation by radiolysis provided by the radioactivity of the waste. Appendix D contains an examination of LDR regulated organic chemicals found in Hanford single and double shell tanks as compiled in the TWINS database. The content of Appendix D was provided by Rodney Skeen, PhD, P. E., of WRPS. Only 31 of the 156 unretrieved Hanford tanks have data in TWINS for LDR organic chemicals other than polychlorinated biphenyls (PCB). PCB have been measured in 93 of the 156 unretrieved tanks. Hence, 40% of the unretrieved tanks have no LDR organic measurements and another 40% have only PCB data in TWINS. Appendix E is an assessment of the negative base 10 logarithm of acid dissociation constants (pKa) of 207 regulated organic compounds.

2.0 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Savannah River Site manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Results are recorded in Electronic Laboratory Notebook #T7692-00094-11. This report documents completion tasks in the Task Technical and Quality Assurance Plan (TTQAP) SRNL-RP-2022-00065, Rev. 0.[3]

3.0 Experimental Procedure

3.1 Simulant Formulation Basis

A 4.0 molar (M) sodium base simulant developed for Direct Feed Low-Activity Waste (DFLAW) testing was prepared for evaporation and oxidation tests being reported here. The base simulant recipe development is reported in Russell et al.[4] That simulant was first developed to support Hanford LAW pretreatment process development. It is compositionally similar to simulants developed for Hanford Cast Stone work. Modifications were made for the current purposes. Chromate at 0.017 M for 4 M sodium was used (scaled from the 5 M sodium value reported in Russell et al).[5] This value represents the 95th percentile upper limit of chromate expected in Hanford LAW. Chromate was included because it might interact with the organic and oxidation chemistries in this current work. The trace amount of cesium in the Russell recipe was excluded because it was not a relevant tracer for this work and the simulant has sufficient alkali metal content. However, simple anionic organic species were added as described below.

One special note is the addition of 0.3 mg/L iodide. This is the Hanford Tank Waste Operations Simulator average value for iodine in a 4 M sodium Hanford waste given in Table 4.2 of Russell.[5] The reasoning for including such a trace component is that iodine may be important for the hydrogen peroxide tests. Iodide is a well-known catalyst for peroxide decomposition, such as in the "elephant toothpaste experiment". Iodide was included in all makeups of the simulant.

The base simulant recipe is shown in Table 3-1. The chemicals and concentrations along with the Russell oxalate concentration were implemented in previous SRNL work for Hanford.[6] The recipe is also shown in the TTQAP.[3] Oxalate was slightly adjusted, 8.25 vs. 9.1 millimolar, by customer review. Acetate, formate, and glycolate were added to the recipe because these were found to be prevalent in Hanford tank waste solutions. After discussions with the customer, concentrations of these simple organic species were included as shown in the TTQAP and in Table 3-2 below. The Table 3-2 values are averages of sodium-adjusted characterizations for 12 Hanford tanks. Further details on the averaging and input data are in the TTQAP.[3] The provision of background organic content was expected to impact oxidation strategies. This is because these non-regulated chemicals will consume added oxidants in competition with desired reactions that attack the regulated species. Batches of the simulant were subdivided for various evaporation, oxidation, and standard work, with spiking done as needed.

Table 3-1. Simulant Recipe for Evaporation and Oxidation Testing

Component	Concentration, mol/L
Sodium, Na^+	4.00
Potassium, K^+	0.0871
Aluminate, $Al(OH)_4^-$	0.119
Chloride, Cl^-	0.0871
Sulfate, SO_4^-	0.0472
Phosphate, PO_4^{-3}	0.0309
Nitrite, NO_2^-	0.729
Nitrate, NO_3^-	1.25
Carbonate, CO_3^{-2}	0.334
CrO_4^{-2}	0.017
Free OH^-	1.01

Table 3-2. Simple Organic Species for the 4M Sodium Simulant Recipe

Organic Anion	Concentration, mg/L (anion, not TOC)	Concentration, Millimole/L	Total Organic Carbon (TOC), mg/L *
Oxalate	726	8.25	198
Formate	1580	35.1	422
Acetate	1310	22.2	533
Glycolate (hydroxyacetate)	842	11.2	269
Total millimole/L as sodium salts:		85.0	Total TOC 1422

* Calculated from concentrations in this table.

3.2 Simulant Preparations

One-half or one-liter batches of the simulant were prepared as needed from reagent chemicals. The specific chemicals and target weights for a 1-liter batch are shown in Table 3-3. Simulant batches were prepared in either a 1-liter or 500 mL glass volumetric flask. A Teflon-coated magnetic stir bar in the flask was set in motion before chemicals are added. Table 3-3 gives the order of additions. About half of the deionized (DI) water was added before the sodium hydroxide solution was introduced. Adding the first two chemicals produces significant heat in each case, and additions are slow to avoid boiling. There was sufficient NaOH to keep the mixture basic versus the acidic aluminum nitrate salt so that nitrite and chromate did not react in any way later on. Subsamples were collected and analyzed by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-ES), and Ion Chromatography (IC). The simulant of Table 3-3 does not include the spikes of regulated chemicals that are the primary subject of this work. Various spiking levels of organic chemicals for the evaporation and oxidation runs are given in their respective sections below.

Table 3-3. Target Composition for Base Simulant with a 1 L Final Volume

Chemical	Formula	Target Mass, g
Sodium hydroxide 50 wt% solution	NaOH	118.87
Aluminum nitrate nonahydrate (60 wt% solution)	$Al(NO_3)_3 \cdot 9H_2O$	68.67
Potassium chloride	KCl	6.49
Sodium nitrate	$NaNO_3$	68.67
Sodium nitrite	$NaNO_2$	50.30
Sodium phosphate dodecahydrate	$Na_3PO_4 \cdot 12H_2O$	11.75
Sodium sulfate	Na_2SO_4	6.70
Sodium carbonate	Na_2CO_3	35.40
Sodium dichromate dihydrate	$Na_2Cr_2O_7 \cdot 2H_2O$	2.53
Potassium iodide*	KI	0.0004
Sodium oxalate	$Na_2C_2O_4$	1.11
Sodium formate	NaHCOO	2.39
Sodium acetate trihydrate	$C_2H_3NaO_2 \cdot 3H_2O$	3.02
Sodium Glycolate	$C_2H_3NaO_3$	0.85

* In lieu of adding solid KI, a serial dilution was performed by adding 0.0415g KI to DI water to obtain a combined mass of 50 g. A 0.0785 g aliquot of this dilute solution was then added to the base simulant.

3.3 Choice of Regulated Organic Chemicals and Surrogates

The TTQAP lists 32 chemicals (reproduced here as Table 3-4) that had been selected from the list of 207 LDR organics associated with Hanford tank waste.[3] These compounds are a subset of a list of 43 chemicals having no historic removal or destruction mechanism that was provided by the Washington River Protection Solutions (WRPS) customer.[7]

Further down-selection from the list in Table 3-4 was made in the current work based on ability to dissolve the chemical in water or simulant. The polyaromatic hydrocarbons (PAH) in particular are a group of chemicals known for having extremely low water solubility (Appendix A). Most PAHs tend to have solubilities that are lower than the 40 CFR 268.48 wastewater limit and so are unlikely to be present in retrieved waste at a regulatorily significant concentration. Both phthalate chemicals on the list, phthalic acid and di-n-butyl phthalate, were included in the current work, along with the two n-nitrosoamines, n-nitrosodi-n-propylamine and n-nitrosomorpholine, from the n-nitroso group. Both substituted anilines on the list were included in testing because their range of volatilities was of interest, and they might also be susceptible to oxidation attack.

Table 3-4. Organic Chemicals Considered for the Evaporator and Oxidation Work

Organic Chemical	**Ratio Kh of Methanol to Kh of Organic Chemical**	**Tentative Chemical Class**
Phthalic acid	**5.1E+06**	Phthalates
Di-n-butyl phthalate	9.5	
N-Nitrosomorpholine	**186**	N-nitrosoamines
N-Nitrosodimethylamine	2.9	
N-Nitrosodiethylamine	1.3	
N-Nitrosodi-n-propylamine	2.1	
Dibenzo(g,h,i)perylene	33.6	PAH's
Benz(a)anthracene	1.39	
Benzo(a)pyrene	10.5	
Benzo(b)fluoranthene	7.1	
Benzo(k)fluoranthene	8.1	
Dibenzo(a,h)anthracene	**316**	
Indeno(1,2,3-c,d)pyrene	2.9	
Dibenz(a,e)pyrene	101	
Silvex/2,4,5-TP	**519**	Substituted aromatic, deactivating side group
2-sec-butyl-4,6-dinotrophenol/Dinoseb	**High in alkali**	
1,4 Dioxane	1.1	
4,6-Dinitrocresol	**High in alkali**	
2,4,5-Trichlorophenol	**High in alkali**	
2,4,6-Trichlorophenol	**High in alkali**	
2,4-Dichlorophenol	**High in alkali**	
2-Nitrophenol	**High in alkali**	
2,4-Dinitrotoluene	30.	
Pentachlorophenol	**High in alkali**	
4-chloroaniline	4.8	Substituted Anilines
4-Nitroaniline	**2270**	
Cresols(ortho, meta, para)	**High in alkali**	Activated Phenolics
Phenol	**High in alkali**	
Diphenylamine	13.8	
Gamma-BHC	2.1	Hexachlorocyclohexanes
Beta-BHC	13.3	

Chemicals with aromatic hydroxide groups were chosen as representatives to cover nitrated, polychlorinated, and amine substitution. Tables 3-5 and 3-6 below show the organic compounds used in the evaporation and oxidation tests, respectively. Note that 2-ethoxyethanol is not regulated as an LDR organic in Hanford tank waste. However, it was tested in the evaporation work as a surrogate for compounds with a Henry's law coefficient approximately ten times lower than that of methanol. Use of a surrogate was necessary since there is no commercially available LDR organic compound that was stable in LAW, sufficiently water soluble, and had a Henry's law coefficient in this range.

3.4 Evaporation Testing

The major components of the vacuum evaporator consisted of a glass evaporator pot, a condenser, and a secondary knock-out pot (KOP) that was cooled by dry ice. These are shown in Figure 3-1, and a photograph is shown in Figure 3-2 (this image is composed of two merged pictures that were edited using Photoshop Elements). The lab-scale evaporator is not a continuous feed system but is operated in batch mode. In contrast, the Hanford 242-A evaporator is operated in a continuous fashion where the pot has higher sodium concentration than is found in the feed during processing.

Differences between a batch and continuous process, include the effects of temperature and sodium molarity over time, should result in higher organic removal in a continuous process. For example, batch processing starts at 4 M sodium for the current work and rises to ~8 M with time. In contrast, continuous evaporation starts and remains at the high value (8 M sodium). The higher salt content of the continuous process results in a higher boiling temperature and more salting-out. Both the steady higher temperature and steady higher salt content will tend to increase organic partitioning to the evaporator overhead.

An evaporation campaign started by adding feed to the pot and evacuating the system to 60 torr in the case of a vacuum run. For a run at atmospheric pressure, the system was open to the atmosphere at the point where the vacuum pump would otherwise be connected. Conditions of the experiment were monitored and recorded, including evaporator pot temperature, pressure, and time. Pot contents were then boiled down to provide target volumes of condensate. In an evaporator run, 400 mL of spiked feed simulant was initially weighed into the evaporator pot (about 475 grams, considering the 1.183 g/mL density). Masses were measured and volumes were calculated from densities of the liquids. An initial feed sample was then taken. The pressure was adjusted to approximately 60 torr (absolute) for vacuum work and the simulant was heated using a hot plate and stirred continuously with a Teflon-coated magnetic stir-bar. The pressure in the system was maintained at 60 ± 5 torr and the solution boiled at approximately 44 °C. The temperature of the simulant and the pressure in the system was measured in the evaporator pot. During the first concentration phase, the simulant was concentrated until ~100 mL of condensate was collected. At this point, boiling was paused and a ~30 mL sample was withdrawn from the evaporator pot and the accumulated condensate was collected. Pot, condensate, and KOP samples at this point are referred to as “middle” samples in this work. The system was sealed and boiling resumed until an additional 75 mL of condensate was collected. At this point, boiling was stopped and a final sample was withdrawn from the evaporator pot and the accumulated condensate was collected. Pot, condensate, and KOP samples at this point are referred to as “end” samples in this work.

During the design and construction of the evaporator, care was taken to have as few polymer parts as possible. This would prevent the simulant in the evaporator pot and the off-gas from coming into contact with polymeric materials. This was a precautionary measure to minimize loss of organic components that might absorb (partition) into such materials.

The apparatus was constructed almost entirely with glass and stainless-steel tubing. All testing was conducted inside a fume hood in a laboratory at SRNL. The evaporator pot was a 1-L modified glass beaker. The simulant was heated using a hot plate/stirrer and continuously stirred with a Teflon-coated magnetic stir bar. The absolute pot pressure, whether 60 torr or atmospheric, was displayed using an electronic pressure transducer. The pressure of vacuum runs at 60 torr was manually adjusted with continuous attendance. The vapors traveled unrestricted to the glass condenser. There was no engineered demisting element designed into the off-gas line to remove entrained particles, but the stainless-steel line was approximately 58 cm high, which should have precluded entrainment based on engineering judgement. As the gases cooled in the condenser, the condensate drained into the glass condensate vessel, which was a graduated cylinder with appropriate ground glass fittings. The exterior surface was coated with clear plastic for safety against implosion when evacuated.

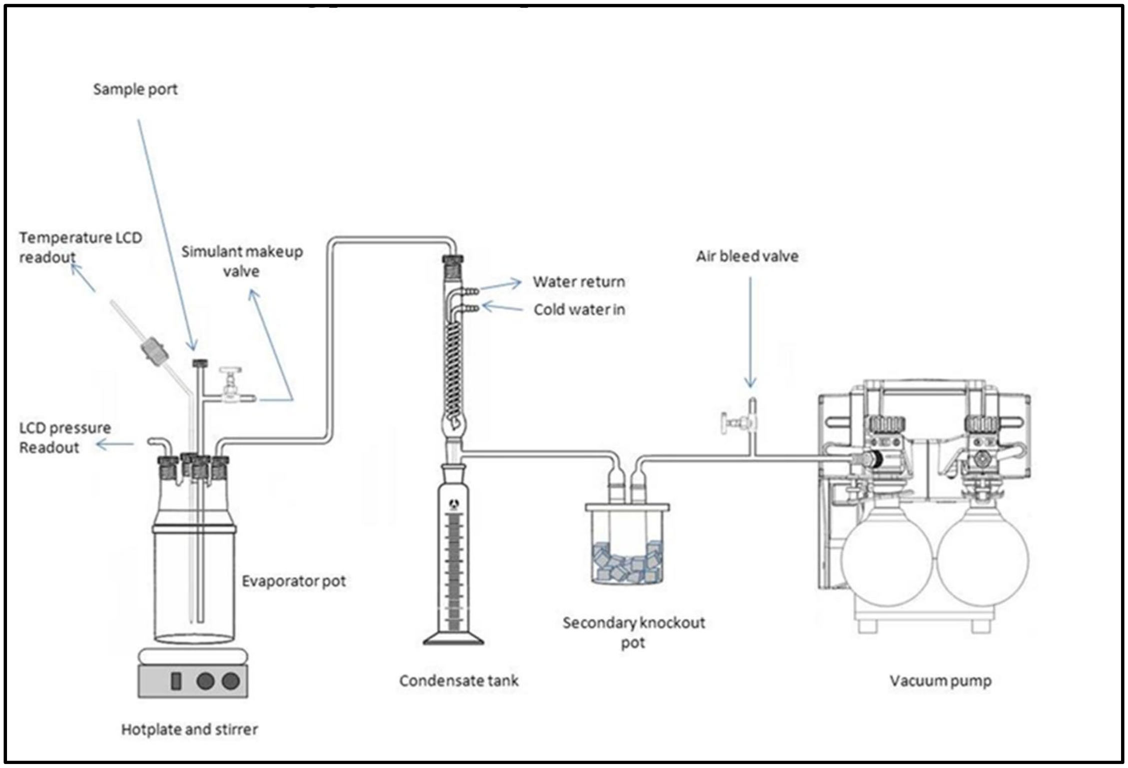

Figure 3-1. Evaporator Equipment Schematic

Figure 3-2. Image of Evaporator Equipment

The condenser was cooled using a VWR Scientific recirculating water bath. The chiller, supplemented with periodic additions of ice, maintained the cooling water at approximately 4-5 °C. Any vapors that passed through the condenser were condensed in the glass trap used as a secondary KOP. The KOP was submersed in a Dewar vessel with dry ice, where the temperature was maintained at approximately -78 °C. The vacuum in the system was created by a Vacuubrand® diaphragm vacuum pump, Type: MZ 2C.

The contents collected inside the KOP were always frozen when it was disconnected. KOP vessels had to be thawed before they could be transferred to the sample collection bottle. The inlet and outlet were covered with a cap to prevent entry of air and humidity during thawing to room temperature. Sample liquid was transferred to a glass container as soon as it had thawed to minimize vapor losses. During the test campaign, two separate KOPs were used, one to allow time to thaw the collected contents and the other placed back into the dry ice to allow testing to continue. All sample vials and bottles were glass and all caps used on these sample containers were lined with Teflon. Environmental I-Chem® containers were used for both vials and bottles.

Before simulant testing, water runs were performed to ensure that the equipment and instruments were operating correctly. The system operated at 60 +/- 5 torr and a temperature of 42 °C. This compares well with CRC Steam Tables that show a boiling point of water at 108.0 °F (42.2 °C) at 62.2 torr.[8]

Two sets of two evaporator tests were performed. They are listed in Table 3-5. The first set was an initial exploration that included phenol and di-n-butyl phthalate with the other chemicals shown in the table. While PubChem shows the Henry's Law coefficient for phenol at 3.33E-07 atm-m3/mole,[9] one order of magnitude less than methanol, it would be expected to be much lower under alkaline conditions that deprotonate phenol. Di-n-butyl phthalate cannot be sampled accurately because of its very low solubility in aqueous solutions, preventing a homogeneous solution. However, it might provide evidence of hydrolysis if phthalate or n-butanol is identified in evaporator samples. The second set of two evaporator runs used an adjusted list of spike chemicals. No phenol or di-n-butyl phthalate were used, but 4-chloroaniline was retained because of its volatility being approximately 20% that of methanol and its successful mass balance in Run 2. 2-ethoxyethanol, while only a surrogate for 40 CFR §268.48 regulated chemicals, was used because of its volatility being one order of magnitude less than that of methanol. N-nitrosodipropylamine and n-nitrosomorpholine were also included because of their low volatility relative to methanol and their water solubilities, allowing greater potential for accurate sample measurements.

The concentration factors in Table 3-5 are the amount of concentration that nonvolatile species in the evaporator pot saw relative to the start of the run. For example, a species like sodium would be concentrated by a factor of 1.36 at the middle of Run 1 and would be 1.87 times its initial concentration at the end of Run 1.

Table 3-5. Evaporator Campaigns, Spike Chemicals, and Concentration Factors.

Run #	Absolute System Pressure, torr	Temperature (°C)	Middle Concentration Factor	End Concentration Factor	Spike Chemicals
1	754 +/- 2	103 to 111	1.36	1.87	phenol, 4-chloroaniline, 4-nitroaniline, di-n-butyl phthalate
2	60 +/- 5	46 to 48	1.46	2.46	phenol, 4-chloroaniline, 4-nitroaniline, di-n-butyl phthalate
3	60 +/- 5	43 to 48	1.37	2.06	4-chloroaniline, 2-ethoxyethanol, n-nitrosodipropylamine
4	755 +/- 2	104 to 110	1.35	2.09	4-chloroaniline, 2-ethoxyethanol, n-nitrosodipropylamine, n-nitrosomorpholine

3.5 Oxidation Testing

All oxidation tests were performed using 40-mL I-Chem® glass vials with Teflon-lined caps. Since these tests needed to have temperature control and agitation, the equipment in Figure 3-3 was used. The figure shows a glass crystallizer dish with a Styrofoam block having a square pattern of nine vertical holes. The holes from the block as-received were bored through and were slightly enlarged so that 40-mL I-Chem® glass vials could fit through the block with just slight friction. The dish had a magnetic stir bar in the middle, so the middle hole position was not used. That stir bar was used to agitate the water bath. The white thermocouple on the right operated the stir plate temperature controller. The two thermocouples in the back left hole were calibrated and their readings were displayed on the Barnant® Model 15176100 electronic temperature reader on the left. The heating control was set so that the bath reached and held the desired temperature, either 60 or 25 °C. Vials were placed in holes at the front and sides of the block. They each had one small Teflon stir bar. Operation of the magnetic stir plate spun the bath stir bar and also the stir bars of each of five vials included in each oxidation test.

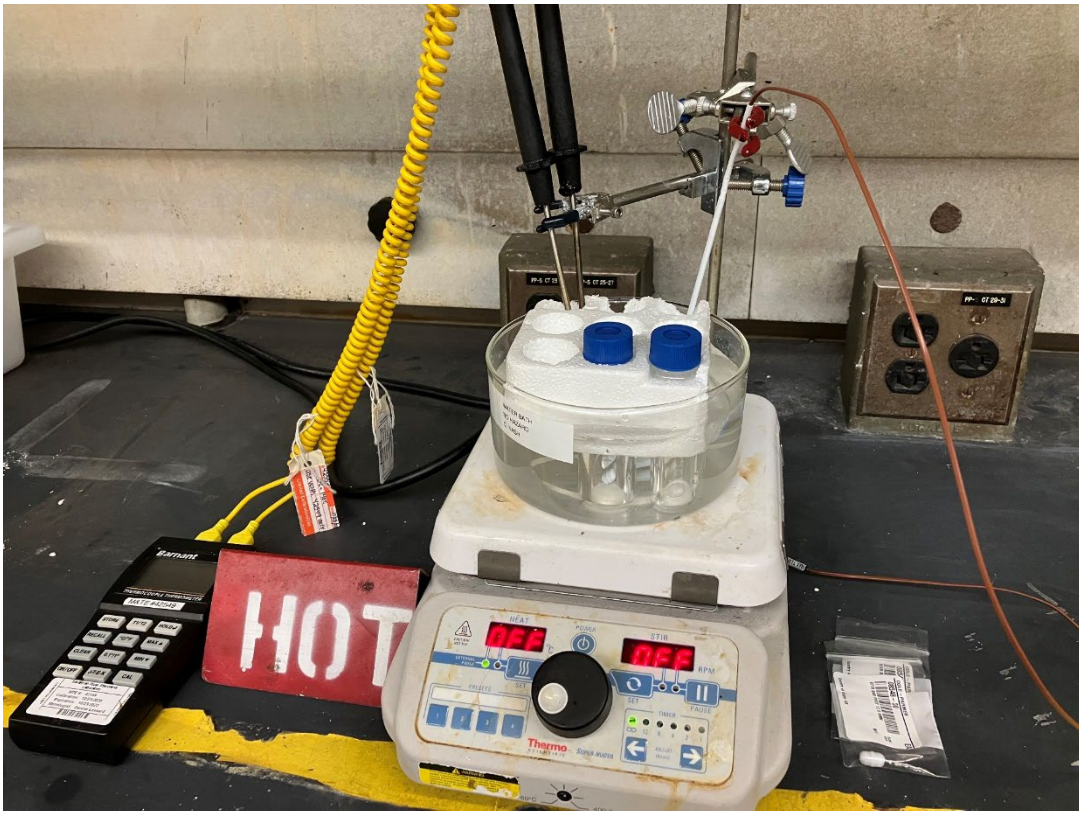

Figure 3-3. Picture of the Equipment for Vial Oxidation Tests

Preparation of the five stock solutions is shown in Table 3-6. 100 mL of 4 M simulant was used in each of the five cases.

Table 3-6. Simulant Solutions Spiked with Organic Compounds

Stock Bottle Number	Component	g/mole	g added	Volume, mL	Molarity	Concentration, mg/L
1	Phthalic acid	166.13	0.0133	101.13	7.92E-04	132
2	4-chloroaniline	127.57	0.0135	101.60	1.04E-03	133
	4,6-dinitro-o-cresol	198.13	0.015		7.45E-04	148
3	2-nitrophenol	139.11	0.0163	101.63	1.15E-03	160
	N-nitroso di-n-propylamine	130.19	0.0219		1.66E-03	216
4	2,4,6-trichlorophenol	197.45	0.0134	101.46	6.70E-04	132
	Ortho-cresol	108.14	0.015		1.37E-03	148
5	Phenol	94.11	0.0123	101.39	1.29E-03	121
	N-nitrosomorpholine	116.12	0.0136		1.16E-03	134

The general method for oxidation testing was to measure 30 mL of spiked simulants from the stock bottles into five vials, add the small Teflon coated magnetic stir bar into each vial, and bring the vials to the desired temperature by placing them in the water bath which was also stirred. The test commenced by adding oxidant while watching a timer. After the first vial was dosed with oxidant and time recorded, the next vial was dosed, often 1 or 2 minutes later, and time was again recorded. Vials were stirred for either 1 or 6 hours before being removed from the bath and the reaction quenched with 2M sodium thiosulfate. Quenching times were also recorded, with the first vial being quenched first, and the following vials quenched with the same timing used when the test started. In the case of gas sparging, the vials did not have a stir bar because sparging was considered sufficient to keep the solutions mixed. No quench was used for gas sparge tests. Vials were refrigerated after testing completed, and samples were also held in refrigeration by AC&SM.

This work used reagent grade 40 wt% sodium permanganate solution and also 23 wt% hydrogen peroxide. Measurements of reagent strength, or standardization, of these reagents are shown in Appendix F.

All oxidation testing using liquid oxidants drew spiked simulants from 5 stock bottles that had been prepared. Table 3-7 provides the amounts of oxidants used for the test sets. In this table, "Target stoichiometry" refers to the amount of oxidant added to each spiked solution when compared to the LDR organics. For every mole of regulated chemical spiked in, the multiplier (10X, 20X, 25X) is the number of moles of oxidant introduced. The target stoichiometry does not account for background organic chemicals – acetate, oxalate, formate, or glycolate.

In the first oxidation testing, 30 mL of each test solution was reacted with 10% w/w sodium permanganate by a ratio of 10 times the molar amount of each organic compound. The 40 wt% sodium permanganate solution had been pre-diluted from 40 wt% to 10 wt% in the 1 hour test to make measurement and pipetting easier. The 6 hour test, using twice the oxidant, used 40 wt% permanganate solution without dilution. The test solutions and control solutions (no sodium permanganate added) for the first permanganate test were heated at 60 °C for one hour. After an hour had passed, each test solution was quenched with one drop of 2M sodium thiosulfate. The solutions were allowed to cool to room temperature and stored in the refrigerator to allow all solids to settle. The test solutions were decanted to separate liquids from solids.

The spiked organic compound solutions were also tested by oxidation using hydrogen peroxide (last column in Table 3-7). In this case, 30 mL of each test solution was reacted with 23 wt% hydrogen peroxide by a ratio of 25 times the molar amount of each organic compound. The test solutions with hydrogen peroxide were temperature controlled to 60 °C for 6 hours.

Table 3-7. Spiked Simulant Solutions with Oxidizers Added

Target Stoichiometry:		**10X**	**20X**	**25X**
Temperature/time		60 °C / 1 hour	25 °C / 6 hour	60 °C / 6 hour
Stock Bottle #	**Component**	**Permanganate added, g, first set ***	**Permanganate added, g, second set**	**Peroxide added, g**
1	Phthalic acid	0.08426	0.1665	0.2381
2	4-chloroaniline 4,6-dinitro-o-cresol	0.1902	0.3714	0.5510
3	2-nitrophenol N-nitroso di-n-propylamine	0.299	0.5817	0.8587
4	2,4,6-trichlorophenol Ortho-cresol	0.2167	0.4216	0.6282
5	Phenol N-nitrosomorpholine	0.2602	0.5021	0.7527

*Weight of dilution water not included.

An air oxidation test was also performed at 25 °C for 6 hours. In that case the simulant in two vials had been spiked with phenol, ortho-cresol, and diphenylamine. The control vial was sparged with 200 mL/min argon while the test vial was sparged at a similar rate with air. The goal was to compare the effect of oxygen on the spike components.

3.6 Methods of Sample Analyses

Organic species spiked into the evaporator feed liquid, along with any identified breakdown products, were quantified by proton (^{1}HNMR) in addition to semi-volatile organic analysis (SVOA) and volatile organic analysis (VOA). The SVOA method required adjustment of samples to pH 5.5 to 7 using a phosphate buffer followed by methylene chloride extraction and use of gas chromatograph – mass spectroscopy. The pH adjustment was to enhance extractions of weak acids like phenol by protonating them to form neutral organic species. pH was not adjusted down to pH 2 per EPA methods because of other chemistry that can occur with nitrite bearing samples. Specifically, formation of nitrous acid could attack the organic constituents of interest.[10] VOA used a purge and trap method that did not involve a solvent or liquid-liquid extraction.

This work had attempted to contract with two offsite laboratories to obtain the organic analyses of liquid samples. One lab examined the chemistry description of the samples and declined the work based on safety related to their equipment. This service had previously been available.[11],[12] The other lab was offered to do the work at increased cost relative to environmental samples they normally process. SRNL and WRPS decided that samples would be analyzed in house at SRNL. Further discussion on difficulties of sample analyses is provided in Appendix G.

^{1}HNMR measurements used a Bruker 300 MHz Ultrashield AVANCE® Spectrometer. Liquid samples were held in glass Wilmad® Precision NMR sample tubes of outer diameter 5 millimeters and 7 inch length. The ^{1}HNMR experiment WATERGATE (Water Suppression by Gradient Tailored Excitation) was applied to suppress the large water signal at 5.1 ppm in the aqueous samples. This method relies on applying a gradient spin echo technique to separate the water magnetization (by diffusing it with two gradients) from other signals.[13] A hard 90-degree pulse is applied to magnetize the water followed by a 2 millisecond gradient pulse (a sine-shaped gradient of 50 millitesla/m was applied to diffuse it). Lastly, a train of pulses set at different angles acts as a 180-degree pulse for everything else in the sample except for water. The delay between the pulses was 355 microseconds, the spectral width was 72,000 hertz, and the time domain was 8000 data points (the acquisition time was 56 milliseconds). The method removes any signal that overlaps with the water signal which is the target of the attenuation. Usually, the water signal occupies an approximately 1 to 1.5 ppm wide region (depending on the level of hydrogen bonding) near 4.9 ppm, but hydrogens characteristic of each species does not need such signal for quantification. In addition, the hydrogen bonding interaction of the organic -OH group with water, such as with butanol, suppresses the hydrogen signal from that group.

Organic concentrations were calculated considering specific peak areas, number of hydrogens at specific locations in the target molecule, standard spike data, and molecular weights. Organic species at known concentrations, such as glycolate and acetate, were used as benchmarks to obtain concentrations. Standards of individual organic chemicals in water, such as with 4-chloroaniline and 2-ethoxyethanol, were also used.

4.0 Results and Discussion

4.1 Simulant Spiking

It was found that spiking the simulant with organic chemicals was not straightforward. It is notable that when the first simulant batch was spiked with 4-chloroaniline, 4-nitroaniline, diphenylamine, 2,4-

dinitrotoluene, and phenol, it unexpectantly turned brown. The color change was noticeable in 1-2 hours at room temperature and became much stronger overnight as seen in the center photograph of Figure 4-1. The degrading chemical was found to be 2,4-dinitrotoluene. The other spike chemicals were added to small portions of simulant individually and no visible evidence of instability were seen. No degradation of 4-chloroaniline or 4-nitroaniline was visible as shown in the right side photograph of Figure 4-1. While a lack of color change alone does not prove stability, these other chemicals were measured and observed to persist in testing. 2,4-dinitrotoluene was not included in further work.

Figure 4-1. 2,4-Dinitrotoluene Structure, Degradation in Simulant, Stable Chemicals

Other spiking issues were also observed. Di-n-butyl phthalate was used in the first two evaporation runs and was found to be an oil that did not dissolve in water or simulant. Its insolubility thus prevented accurate measurement of spikes because it would adhere to vessel walls and never form a uniform mixture with aqueous process fluids.

4-chloroaniline was slow to dissolve in simulant. However, it was discovered that heating the evaporator pot of simulant to about 70 °C caused the white particles of the 4-chloroaniline spike to disappear and presumably form a uniform mixture. The melting point of 4-chloroaniline is about 72 °C, so it is likely that the transition to melting assisted with mixing this chemical into the simulant. The material did not re-crystalize after the solution cooled to the experimental temperatures.

4.2 Evaporation

Four evaporator campaigns were performed. Run conditions and realized concentration factors are in Table 3-5 in the Experimental section. Absolute system pressures were determined by the prevailing barometric pressure, and these are shown with their measured ranges. Vacuum runs were all controlled to 60 torr as planned. The original plan for Run 1 spikes was to include 2,4-dinitrotoluene, but its decomposition as described in the previous section led to the decision to exclude that chemical.

For the analytical results below, a general statement on VOAs should be noted. All samples submitted for SVOA analysis were also submitted for VOA analysis to look for potential breakdown or degradation products of the spiked organics. Essentially all VOA results were reported as <0.25 mg/L except for n-butanol that was found in Evaporator Runs 1 and 2 samples. This also held true for oxidation work. If there were breakdown products, they might be anionic, such as the generation of oxalate or some other organic acid which would then not be volatile. The in-growth of oxalate when glycolate is oxidized would be an example. The SVOA analytical results were also subject to challenges due to the low aqueous solubility of the less volatile organics. These may have resulted in low recoveries during the sample extraction step for the SVOA method. This likely contributed to low overall recovery and incomplete mass balance for many of the spiked organics. Given the scoping nature of these tests the notable results amounted to the appearance of a particular organic compound in the condensate samples and the relative amounts compared to the levels reported in the evaporator pot samples.

For all the evaporation tables below, the feed is reported as about 400 mL. This was before the initial feed sample was pulled from the pot for analyses. “Middle Pot Sample” and “Middle Pot” rows in the tables are liquids of the same composition. “Middle Pot Sample” was drawn from the pot after 100 mL of condensate was collected, and “Middle Pot” has the calculated liquid volume remaining in the pot at that point. Milligrams of organic chemicals in these liquid portions are different because the volumes are different.

4.2.1 Runs 1 and 4 (Atmospheric Evaporation)

Run 1 samples were analyzed by SVOA but not NMR. SVOA mass totals are much less than spike amounts as shown in Table 4-1, likely indicating low extraction efficiencies. The amount of phenol measured in the pot probably has a wide uncertainty because of this – only about 10 to 16% of the spike content was measured. It is significant, though, that phenol (deprotonates in LAW) and 4-nitroaniline (K_h ratio of 2270) are not seen at all in the condensates while 4-chloroaniline (K_h ratio of 4.8) is. Dibutyl phthalate (K_h ratio of 9.5) was seen in condensates despite its insolubility. The condensates were cloudy at the time of the run but became less cloudy later. It is likely that the cloudy appearance was caused by a dispersed dibutyl phthalate phase that coalesced with time. Not shown in the table is n-butanol, which was reported at 0.78 mg/L in the middle condensate which is below the quantification limit of 1 mg/L. The presence of n-butanol suggests hydrolysis of the dibutyl phthalate during atmospheric evaporation.

Phthalate esters are expected to hydrolyze in caustic solution and some reaction products are also regulated. The regulated phthalate esters include di-n-butyl phthalate, bis(2-ethylhexyl)phthalate, butyl benzyl phthalate, diethyl phthalate, dimethyl phthalate, and di-n-octyl phthalate. Their hydrolysis results in regulated species n-butanol, methanol, and phthalate. Ethanol, hexanol, n-octanol, and benzyl alcohol are products that are not regulated. Phthalic acid or its sodium or disodium salts are regulated as phthalic anhydride.

The middle and end condensates of Run 1 appeared to be hazy as if a very low solubility species had carried over with condensate. The detection of dibutyl phthalate in the table below is definite evidence of its volatilization.

Table 4-1. Analytical Data for Atmospheric Evaporation (Run 1)

Run 1, 1 atmospheric, all organic chemical entries in mg					
Organic Chemical (Kh ratio)[a]:		Phenol (High[b])	4-Nitroaniline (2270)	4-Chloroaniline (4.8)	Dibutyl phthalate (9.5)
	Spike Mass, mg:	64.5	59.0	69.8	57.2
SAMPLE	Vol., mL	SVOA	SVOA	SVOA	SVOA
Feed	401.6[c]	10.5	10.4	1.6	<0.4
Middle Condensate	102.9	<0.1	<0.1	6.8	0.5
Middle Pot Sample	25.0	0.6	0.7	<0.025	<0.025
Middle Pot	261.2	6.3	7.3	<0.25	<0.25
End Condensate	75.9	<0.1	<0.1	1.6	0.6
End Pot	189.6	7.7	2.1	<0.2	<0.2

[a] Kh ratio is defined as $Kh_{,methanol}/Kh_{,i}$ where “i” is the compound in question.

[b] Phenol will be deprotonated in the simulant and so will not have a significant vapor pressure.

[c] Before removal of a 12.5 mL feed sample.

Evaporator Run 4, Table 4-2, is the only run where n-nitrosomorpholine was included as a spike. It also appears to be removed by atmospheric evaporation since the compound was found in the middle and end condensates and the amount in the end pot simultaneously diminishes. These results suggest that more than half of the spike was carried overhead, which would be remarkable given that n-nitrosomorpholine has a high affinity for water and its K_h ratio is 186. This result is a strong motivation to quantify and model salting out effects at high sodium content. In pure water no separation would occur with a chemical having a Henry's Law coefficient of 1.4E-06 atm-m^3/mol[6] and a K_h ratio of 186 puts n-nitrosomorpholine volatility about 60 times less than that. 2-ethoxyethanol (K_h ratio of 9.7) and n-nitrosodipropylamine (K_h ratio of 2.1) were also found to carry over into the overhead fractions, though it is not certain why more 2-ethoxyethanol carried over in the end condensate vs. the middle condensate.

Table 4-2. Analytical Data for Atmospheric Evaporation (Run 4)

Run 4, 1 atmosphere, all organic chemical entries in mg									
Organic Chemical (Kh ratio):		4-Chloroaniline (4.8)		2-Ethoxyethanol (9.7)		n-Nitrosodipropylamine (2.1)		n-Nitrosomorpholine (186)	
Spike Mass, mg:		61.6		60.7		57.3		58.2	
SAMPLE	Vol., mL	NMR	SVOA	NMR	SVOA	NMR	SVOA	NMR	SVOA
Feed	401.5[a]	51.0	<0.4	42.5	ND	11.6	12.0	8.1	8.3
Middle Condensate	99.2	15.8	3.7	0.6	ND	16.0	3.9	2.3	1.7
Middle Pot Sample	30.1	<0.12	<0.03	<0.12	ND	<0.12	<0.03	<0.12	0.7
Middle Pot	257.2	<1.0	<0.25	<1.0	ND	<1.0	0.7	<1.0	5.6
End Condensate	75.4	0.3	0.8	14.8	ND	0.3	<0.08	1.7	1.7
End Pot	165.4	<0.7	<0.17	<0.7	ND	<0.7	<0.17	3.3	3.1

ND = not detected, though this species is known to be in the sample.

[a] Before removal of a 15 mL feed sample.

In summary, in atmospheric evaporation it appears that di-n-butyl phthalate decomposes and forms n-butanol. In addition, compounds with a K_h ratio value below at least 186 (and that are not present as charged species) are removed from LAW and appear in the evaporator overhead condensate. The 4-nitroaniline shows that compounds with a K_h ratio of 2270 are not removed under these conditions.

4.2.2 Runs 2 and 3 (Vacuum Evaporation)

Run 2 (Table 4-3) tested the removal of three of the compounds tested in atmospheric evaporator Run 1 (phenol, 4-ntiroanaline and 4-chloroaniline) from LAW using vacuum evaporation conditions similar to those of the 242-A evaporator. Note that all Run 3 KOP samples were too small in volume for SVOA analysis, which needs more than 10 mL per sample. Hence, they were only analyzed by NMR.

Table 4-3 shows that a good mass balance for 4-chloroaniline was obtained by NMR. The amount found in feed (60 mg) is slightly higher than the spike mass (56.3 mg), but the middle condensate and middle KOP samples found a total of 61.3 mg of that chemical (105% of the amount measured by NMR in the feed). The end KOP and condensate showed little 4-chloroaniline, showing good stripping of that chemical from the pot for the run. 4-chloroaniline has a Henry's Law ratio of 4.8 relative to methanol (it is less volatile), so a salting out effect is likely help with stripping. As with the atmospheric evaporator tests neither 4-nitroaniline or phenol appeared to evaporate.

The fact that some phenol and 4-nitroaniline were found in the end pot shows some stability for these chemicals in the caustic solution (i.e. they neither decompose nor evaporate under the test conditions).

Table 4-3. Analytical Data for Vacuum Evaporation (Run 2)

Run 2, vacuum, all organic chemical entries in mg							
Organic Chemical (Kh ratio)[a]:		Phenol (High[b])		4-Nitroaniline (2270)		4-Chloroaniline (4.8)	
Spike Mass, mg:		59.5		57		56.3	
SAMPLE	Vol., mL	NMR	SVOA	NMR	SVOA	NMR	SVOA
Feed	380.9[c]	ND	7.0	ND	5.4	60.0	<0.4
Middle Condensate	100.0	ND	<0.1	ND	<0.1	34.0	<0.1
Middle KOP	21.5	ND	<0.05	ND	<0.05	27.3	<0.05
Middle Pot Sample	259.5	ND	0.5	ND	<0.25	<1.0	<0.25
Middle Pot	19.2	ND	6.5	ND	<0.1	<0.4	<0.1
End KOP	3.4	ND	Not Run	ND	Not Run	1.5	Not Run
End Condensate	75.4	ND	<0.1	ND	<0.1	<0.4	<0.1
End Pot	153.7	ND	5.6	ND	2.2	<0.6	<0.15

[a] Kh ratio is defined as $Kh_{,methanol}/Kh_{,i}$ where "i" is the compound in question.

[b] Phenol will be deprotonated in the simulant and so will not have a significant vapor pressure.

[c] Before removal of a 23.7 mL feed sample.

The three spike chemicals shown in Table 4-4 for vacuum evaporator Run 3 (4-chloraniline, 2-ethoxyethanol, and n-nitrosodipropylamine) show a trend of stripping for all, since the end condensates always show much less of the chemicals than the middle condensates. This is especially significant for 2-ethoxyethanol, since its K_h ratio in water is about 10. This observation suggests that a salting out effect is helping with stripping. Note that all Run 3 KOP samples were too small in volume for SVOA analysis, which needs more than 10 mL per sample. Hence, they were only analyzed by NMR.

Table 4-4. Analytical Data for Vacuum Evaporation (Run 3)

Run 3, vacuum, all organic chemical entries in mg							
Organic Chemical (Kh ratio):		4-Chloroaniline (4.8)		2-Ethoxyethanol (9.7)		n-Nitrosodipropylamine (2.1)	
	Spike Mass, mg:	57.2		58.0		58.2	
SAMPLE	Vol., mL	NMR	SVOA	NMR	SVOA	NMR	SVOA
Feed	402.0[a]	78	ND	98	ND	58	12.5
Middle Condensate	100.0	22	4.4	13	ND	22	3.8
Middle KOP	4.8	<0.02	Not Run	<0.02	Not Run	<0.02	Not Run
Middle Pot Sample	22.4	<0.1	<0.025	<0.2	ND	<0.2	<0.05
Middle Pot	264.1	<2.0	<0.25	<2.0	ND	<2.0	<0.25
End KOP	2.6	<0.02	Not Run	<0.02	Not Run	<0.02	Not Run
End Condensate	75.9	3	1.5	7	ND	3	1.3
End Pot	175.8	<0.7	<0.18	<0.7	ND	<0.7	<0.18

[a] Before removal of a 15.5 mL feed sample.

Detection of known analytes was often a problem for the analyses. “ND” or no detection is shown for the SVOA 2-ethoxyethanol because its affinity for water likely works against a methylene chloride extraction, even though pH is not an issue for this chemical. It is known that 2-ethoxyethanol was present based on the NMR data

Figure 4-2 presents the percent of the total chemicals spiked into the pot for Run 2 and 3 (vacuum evaporation) and Run 4 (atmospheric pressure evaporation) that were found in the condensates and KOP samples. The percentages are plotted as a function of the K_h ratio of the chemicals. The chemicals are n-nitrosodipropylamine (K_h ratio of 2.1), 4-chloroaniline (K_h ratio of 4.8), 2-ethoxyethanol (K_h ratio of 9.7), n-nitrosomorpholine (K_h ratio of 186), and 4-nitroaniline (K_h ratio of 2270). The figure suggests that evaporative removal is visible over a wide range of K_h ratios and that vacuum evaporation has a higher level of organic removal for all compounds that are removed under both conditions.

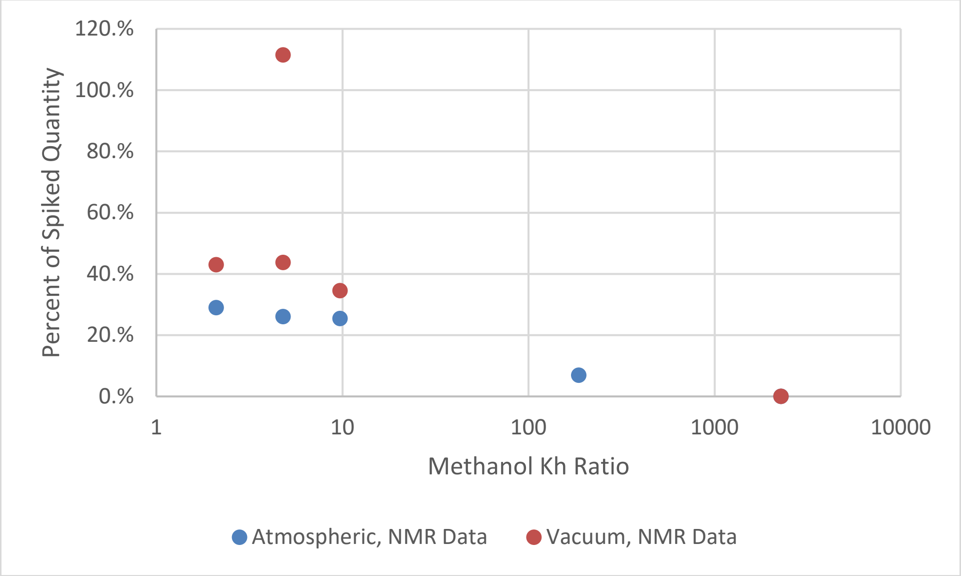

Figure 4-2. Percent of Organic in (Condensate + KOP), Run 4

Unfortunately, vacuum evaporator testing in FY22 did not include n-nitrosomorpholine (K_h ratio of 186) since the compound was removed by atmospheric evaporation. Work in FY23 should assess this compound to determine if the lower volatility limit for possible removal in the Hanford 242-A evaporator can further lowered for the current demonstrated limit set by 2-ethoxyethanol.

In summary, for vacuum evaporation conditions like that of the 242-A unit, it appears that compounds with a K_h ratio value below at least 9.7 (and that are not present as charged species) are removed from LAW and appear in the evaporator overhead condensate. Compounds with a K_h ratio of 2270 are not removed under these conditions. Comparison of atmospheric and vacuum evaporation results indicates that vacuum evaporation has a higher level of organic removal for all compounds that are removed under both conditions.

4.3 Chemical Oxidation

4.3.1 Oxidation using Permanganate

Sodium permanganate reagent solution was used to treat organic spiked simulants at 60 ℃ for one hour (Figure 4-3) and at 25 ℃ for six hours. Spikes of the sodium permanganate solution were added by mass using an electronic pipette. In both sets of permanganate tests, it appeared that time and temperature conditions were well matched to essentially complete the reactions that were going to occur. This assertion is based on the observation that vial contents at the end appeared to be yellow simulant and brown solids. In only one case, the second permanganate set vial number 3, was the liquid dark in color from soluble manganese still in high oxidation states, likely (VI) and VII). This would have been unreacted manganate and permanganate. Note that this vial had the highest amount of permanganate added of all the vials tested.

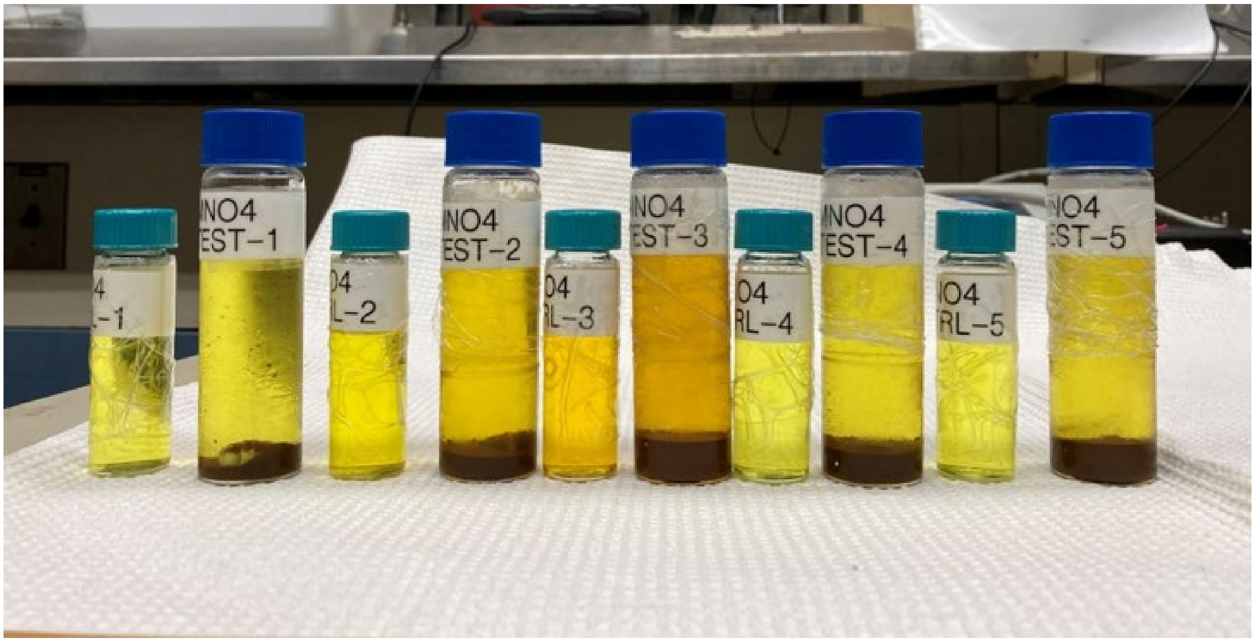

Figure 4-3. Photograph of the Oxidation by Permanganate Test (60 °C) and Control Solutions

A photograph of the test solutions after reacting at 60 °C at one hour with sodium permanganate, and the control solutions, is provided in Figure 4-3. Vial numbers 1 to 5 indicate the specific organic chemicals and amounts added per Table 3-6. The control samples are the smaller vials to the left of the larger test vials. The control vial and test vial each have the same visible number on the sample labels. Upon addition of the sodium permanganate to the test solutions, a greenish color appeared followed by a suspension of brown solids (most likely manganese dioxide).

The second set of tests were incubated for six hours at 25 °C with twice the oxidant molarity as the 1 hour tests at 60 °C (see Table 3-6 for test conditions). The purpose for running longer time, lower temperature tests was to evaluate conditions that would be more easily implemented as a chemical strike for a large volume of retrieved LAW. Both the NMR and SVOA results in Table 4-5 show that n-nitrosodipropylamine and n-nitrosomorpholine resist oxidation. Only NMR detected 2,4,6-trichlorophenol, 2-nitrophenol, and 4,6-dinitrocresol. Results for these chemicals indicate resistance to degradation by permanganate under this set of process conditions.

4-chloroaniline shows substantial degradation across both permanganate tests by NMR. Phenol shows degradation with agreement between SVOA and NMR for both permanganate tests. Ortho-cresol data from the 60 °C 1-hour test shows substantial degradation by both SVOA and NMR. It can be concluded that these three chemicals can be oxidized in practice using permanganate. The two test sets show general consistency that these chemicals are treatable at these process conditions and that the others in Table 4-5 are resistant.

Table 4-5. Permanganate Runs – Percent of Organic Chemical Remaining

CHEMICAL (Vial number)	60 °C, 1 hr, 10X molar oxidant		25 °C, 6 hr, 20X molar oxidant	
	SVOA	NMR	SVOA	NMR
Phthalate (1)	ND (pH effect)*	97%	ND (pH effect)*	93%
4-chloroaniline (2)	ND	17%	ND	14%
4,6-dinitrocresol (2)	ND	83%	ND	93%
2-nitrophenol (3)	ND	92%	ND	72%
n-nitrosodipropylamine (3)	94%	75%	100%	83%
2,4,6-trichlorophenol (4)	ND	104%	ND	85%
ortho-cresol (4)	28%	16%	0%	ND
Phenol (5)	35%	54%	46%	40%
n-nitrosomorpholine (5)	57%	ND	94%	92%

* "pH effect" is noted because it is likely that phthalate does not extract at pH's above the first pKa of 2.9 for phthalic acid.

4.3.2 Oxidation using Peroxide

Peroxide showed little reaction with all regulated chemicals as shown in Table 4-6. The over-100% result for phenol is likely due to an extraction problem with SVOA. The degradation of phenol is unclear because while NMR showed good reaction, the chemically related ortho-cresol was not degraded very much. Both SVOA and NMR show little degradation of ortho-cresol. Overall, hydrogen peroxide did not appear to be a practical oxidant under these conditions when added to the caustic simulant with organic spikes and significant amounts of organic acids present.

Table 4-6. Organic Degradation by Peroxide - Percent of Organic Chemical Remaining

CHEMICAL (Vial number)	60 °C, 6 hr, 25X molar oxidant (peroxide)	
	SVOA	NMR
Phthalate (1)	ND (pH effect)	96%
4-chloroaniline (2)	ND	99%
4,6-dinitrocresol (2)	ND	97%
n-nitrosodipropylamine (3)	92%	87%
2-nitrophenol (3)	ND	ND
2,4,6-trichlorophenol (4)	ND	56%
ortho-cresol (4)	86%	102%
n-nitrosomorpholine (5)	98%	ND
Phenol (5)	142%*	11%

* Likely due to an extraction efficiency problem with the sample.

4.3.3 Oxidation by Air under Alkaline Conditions

Air sparging a solution containing phenol, o-cresol, and diphenylamine showed no significant effect in reducing the concentration of these dissolved chemicals. Table 4-7 shows slightly increased amounts of these in some cases, and this is believed to be analytical uncertainty or possibly differences caused by solubility of the chemicals. Phenol appeared to be the easiest of the chemicals to dissolve in the lab, and diphenylamine the most difficult of these to dissolve. The water solubility of diphenylamine in PubChem is 53 mg/L, which is approximately what was measured in this test.[14]

Table 4-7. Air Sparge Results

CHEMICAL	Phenol, mg/L	Ortho-Cresol, mg/L	Diphenylamine, mg/L
Inert Vial	39.4	42.3	48.1
Air Sparged Vial	39	45.1	52.1
Percent REMAINING	99%	107%	108%

4.3.4 Oxidative Reactions with Anions

All samples from oxidation testing were analyzed by IC Anions (IC-A) and NMR to evaluate reaction of compounds other than the regulated organics. Nitrate and nitrite did not show concentration changes greater than a %RSD of 5%. This is within the 10% uncertainty of IC-A analysis. Nitrite was thus not found to react with permanganate or peroxide in this testing and so did not consume the oxidant.

Table 4-8 shows IC-A data for the fifteen samples. Peroxide was found to not attack either formate or oxalate. Permanganate was found to attack formate and glycolate and often drove formate concentration below detection limits. The indicated rise of oxalate concentration had been found in past work to originate from permanganate oxidation of glycolate.[15] Glycolate was reported only as a percentage of the control sample content in NMR analysis. IC-A did not report acetate, and there was difficulty in quantifying acetate by NMR, so no results are shown.

Table 4-8. Oxidative Attack of Simple Anions

Control Average Value (mg/L):		1564 +/-104	720 +/- 22	percent
Test Set	**Stock Bottle Number**[a]	Formate, mg/L	Oxalate, mg/L	Glycolate by NMR
Permanganate, 60 °C / 1 hour	1	1080	892	81%
	2	<100	1110	50%
	3	<100	1320	2%
	4	626	1130	52%
	5	247	1230	48%
Permanganate, 25 °C / 6 hour	1	1627	1121	28%
	2	<200	1439	2%
	3	<200	1514	<1%
	4	<200	1511	3%
	5	890	1460	<1%
Peroxide 60 °C / 6 hour	1	1650	709	NM[b]
	2	1660	709	NM
	3	1690	724	NM
	4	1670	709	NM
	5	1740	730	NM

[a] See Tables 3-6 and 3-7 for LDR organic chemicals associated with each stock bottle condition.
[b]NM = not measured.

Stock bottle 1 tests likely showed less reaction of measured organic compounds because that stock solution only had one regulated spike chemical, phthalate, while stock solutions 2 to 5 had two chemicals. Since the amount of permanganate added depends on the moles of target regulated chemical in the test, vial numbered "1" in each set had less oxidant added.

5.0 Conclusions

Atmospheric evaporation testing was found to strip from LAW n-nitrosodipropylamine (K_h ratio of 2.1) 4-choroaniline (K_h ratio of 4.8), 2-ethoxyethanol (K_h ratio of 9.7), and n-nitrosomorpholine (K_h ratio of 186) but not 4-Nitroaniline (K_h ratio of 2270) or phenol (deprotonates in LAW). These results suggest that a salting-out effect is likely helping the evaporative stripping. In addition, compounds with a K_h ratio below at least 186 (and that are not present as charged species) are removed from LAW by atmospheric evaporation. Using the Henry's law coefficient data reported in RPP-RPT-63494 and assuming n-nitrosomorpholine as the lower limit for atmospheric evaporation suggests that only 44 of the 207 LDR organics would not be removed, at least to some degree, if LAW were treated in this manner. Twenty-six (26) of these 44 compounds exist as a charged species in LAW and the remainder have a Henry's law coefficient lower than that of n-nitrosomorpholine. Hence, atmospheric evaporation could be a useful treatment method if additional organic removal from retrieved LAW was needed to meet yet-to-be determined concentration-based standards before solidifying in a cementitious waste form. However, additional work is needed to assess which organics in tank waste are most likely to exceed the limits, the amount of waste that could have an exceedance, and the extent that the compounds in question can be removed by evaporation. The analysis in Appendix D provides a starting point for the evaluation.

Similar results were obtained using vacuum evaporation, however n-nitrosomorpholine (K_h ratio of 186) was not tested. Hence, the compounds observed to be removed from LAW were n-nitrosodipropylamine (K_h ratio of 2.1) 4-choroaniline (K_h ratio of 4.8), 2-ethoxyethanol (K_h ratio of 9.7), but not 4-Nitroaniline (K_h ratio of 2270) or phenol (deprotonates in LAW). These results suggest that compounds with a K_h ratio below at least 9.7 (and that are not present as charged species) are removed from LAW by vacuum evaporation. Also note that vacuum evaporation achieved greater removal fractions than atmospheric evaporation for n-nitrosodipropylamine (K_h ratio of 2.1) 4-choroaniline (K_h ratio of 4.8), 2-ethoxyethanol (K_h ratio of 9.7) which suggests that this method will likely remove n-nitrosomorpholine (K_h ratio of 186). Additional testing with n-nitrosomorpholine (K_h ratio of 186) should be conducted in FY23 with the vacuum system.

This work also identified n-butanol in atmospheric evaporator condensate for runs using di-n-butyl phthalate, giving evidence of caustic hydrolysis. In addition, 2,4-dinitrotoluene is not stable in caustic solution at room temperature and so is not be expected to exist in alkaline waste.

Oxidation testing at 60 °C (1 hour exposure) and with permanganate demonstrated that phenol, 4-chloroaniline, ortho-cresol, 4,6-dinitrocresol, and n-nitrosomorpholine appear to be treatable in the LAW simulant even in the presence of high concentrations of nitrite and the organic acids acetate, formate, glycolate, and oxalate. In contrast, n-nitrosodipropylamine, 2,4,6-trichlorophenol, and phthalate appear to be more refractory. Oxidation testing at 25 °C (6 hour exposure) with permanganate showed generally increased destruction of spiked organics including phthalate but apparent reduced effectiveness against n-nitrosomorpholine. All results were subject to competing oxidation load due to the organic acids present at 30X to 100X the molar concentration of the spiked organics. Permanganate oxidized glycolate to oxalate, consistent with what SRS has found for their work on caustic glycolate remediation with permanganate.[15] Formate presents an oxidative load for permanganate processing, but nitrite did not. These results suggest that chemical oxidation of some LDR organics may be a viable treatment option, but that additional testing on a wider range of compounds and reaction conditions is needed.

Peroxide (60 °C with 6 hours of exposure) only showed ability to oxidize phenol and perhaps ortho-cresol. It did not attack the other spiked organic chemicals significantly nor did it attack formate and oxalate. Air sparging at room temperature was not an effective process for treating organic chemicals that likely would be oxidation sensitive under caustic conditions – phenol, ortho-cresol, and diphenylamine.

As a final note, sample analyses are not trivial for these higher molecular weight organic chemicals that may ionize in solution, may have high affinity for the aqueous phase, or may have similar signals to other chemicals being used. While methylene chloride is polar it may not always have a favorable partition coefficient for all analytes of interest, such as 2-ethoxyethanol. NMR was a complimentary method of sample analysis, sometimes providing measurements of organic chemicals that were not visible to the SVOA method. NMR with the WATERGATE solvent suppression method has an advantage that aqueous liquid samples can be measured without sample preparation steps like pH buffering or solvent extraction.

6.0 Recommendations for Further Work

- The carryover of n-nitrosomorpholine under vacuum evaporation from high sodium feed needs further investigation. There may be a higher salting out effect than previously expected, especially for chemicals that have high solubility in pure water.
- The impacts of salting out on LDR organic aqueous solubility and volatility should be explored to determine if predictive correlations can be established between vapor and liquid concentrations to allow the use of tank headspace measurements to screen tanks for potential regulatory exceedances.
- Analytical extraction efficiencies were generally very low for the regulated chemicals by SVOA. Some of these were expected, such as for the stronger acids like phthalic acid, but in general sample preparation methods need improvement for this difficult salt matrix with nitrite, chromate, and perhaps other acid-reactive species. Improvements in this area would also support the search for oxidation and caustic degradation byproducts.
- Other analytical methods like liquid chromatography – mass spectroscopy may be found to be helpful in analyzing samples in the high sodium matrix.
- Additional oxidation testing is needed to better define the compounds that can be oxidized by permanganate or other chemical oxidants such as hydrogen peroxide or sodium peroxydisulfate. Testing efforts should focus on the LDR organic compounds most prevalent in tank waste samples at elevated concentrations, particularly those that cannot be removed by evaporation.

7.0 References

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Appendix A

Water Solubilities of 207 Regulated Organic Chemicals

This section gives an initial assessment of regulated organic chemical solubilities in pure water at 25 °C. The compilation was done by John Dekarske.

Note that all 207 compounds have been assessed in this appendix but only a subset of these compounds have been used at Hanford or have been detected in tank waste samples and thus would be expected to potentially be present in Hanford liquid or dissolved saltcake waste. Solubilities will be different in salt solutions, so this compilation only shows the order of magnitude of solubility when there is no alkaline chemistry or decomposition. References for the solubility compilation follow the main table in this appendix.

Line Number	Compound	CAS Number	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Average (mg/L)	%RSD		
1	Dibenz(a,e)pyrene	192-65-4	0.00016	EPA Estimate	0.0000802	ChemIDplus															0.0001201	46.983%		
2	Benzo(g,h,i)perylene	191-24-2	0.00026	Alegbeleye	0.00026	Mackay	0.00026	CRC1	0.00026	Ran	0.00025	Marshall	0.0003	Ghosh	0.00026	Gomez-Gutierrez	0.00026	CRC			0.00026375	5.710%		
3	Benz(a)anthracene	56-55-3	0.01	Alegbeleye	0.0094	ChemIDplus	0.014	Mackay	0.011	Shiu	0.0147	Ran	0.011	Marshall	0.011	Ghosh	0.011	Gomez-Gutierrez	0.0093	CRC	0.011266667	16.753%		
4	Benzo(a)pyrene	50-32-8	0.0038	Alegbeleye	0.00162	ChemIDplus	0.0038	Mackay	0.003	Shiu	0.00142	Ran	0.0039	Marshall	0.0016	Gomez-Gutierrez	0.0043	CRC			0.00293	40.999%		
5	Benzo(b)fluoranthene	205-99-2	0.0015	Alegbeleye	0.0012	ChemIDplus Note: Tempera	0.0041	Ran	0.00454	Marshall	0.0015	Ghosh	0.0015	Gomez-Gutierrez	0.002	CRC					0.002334286	59.230%	Average excluding outlier	%RSD
6	Benzo(k)fluoranthene	207-08-9	ND	Alegbeleye	0.0008	ChemIDplus	0.00082	Ran	0.00081	Marshall	0.0008	Ghosh	0.008	Gomez-Gutierrez	0.00008	CRC (20C)					0.001885	159.673%	0.0008075	1.185668
7	Dibenzo(a,h)anthracene	53-70-3	0.0005	Alegbeleye	0.00249	ChemIDplus	0.0006	Shiu	0.00061	Marshall	0.0005	Ghosh	0.0025	Gomez-Gutierrez	0.0005	CRC					0.0011	86.739%	Average excluding outlier	%RSD
8	Indeno(1,2,3-c,d) pyrene	193-39-5	Insoluble	Alegbeleye	0.00019	ChemIDplus	0.00019	Pearlman	0.00019	Marshall	0.062	Ghosh	0.062	Balasurbramanian	0.00019	Gomez-Gutierrez	0.0002	CRC (20C)			0.017851429	168.946%	0.00019	0
9	Naphthalene	91-20-3	31	Pearlman	31.7	Mackay	31.5	Shiu	33.7	Ran	30.8	Marshall	31	Ghosh	31.6	CRC	31.6227766	Kim			31.61534708	2.876%		
10	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9	7.45627E-08	Ran	2.29E-07	Oleszek-Kudlak °C	7.45627E-08	Ruelle °C	0.00000023	CRC	0.000000074	Shiu1	7.45627E-08	Li							1.26115E-07	63.500%		
11	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD)	35822-46-9	2.39164E-06	Ran	2.56456E-06	Friesen, Note T is 26 °C	0.0000024	Friesen, Note T is 20 °C	2.39164E-06	Ruelle	2.39164E-06	Li									2.42789E-06	3.150%		
12	HxCDDs (All Hexachlorodibenzo-p-dioxins)	NA	4.38597E-05	Ran	7.89618E-06	Friesen, Note T is 26 °C	0.00000442	Friesen, Note T is 20 °C	4.38597E-05	Ruelle	4.38597E-06	Li									2.08843E-05	100.659%		
13	PeCDDs (All Pentachlorodibenzo-p-dioxins)	NA	0.00011802	Ran	0.000165021	Friesen, Note T is 26 °C	0.000118	Friesen, Note T is 20 °C	0.00011802	Ruelle	0.00011802	Li									0.000127416	16.498%		
14	TCDDs (All Tetrachlorodibenzo-p-dioxins) (1,2,3,7-Tetrachlorodibenzo-p-dioxin)	NA	0.000720868	Ran	0.00072772	Friesen, Note T is 26	0.00042	Friesen, Note T is 20	0.000414816	Ruelle	0.00041962	Li									0.000540605	31.023%		
15	1,2,3,4,6,7,8,9-Octachlorodibenzofuran (OCDF)	39001-02-0	1.14048E-06	Ran	4.09E-07	Oleszek-Kudlak	1.16705E-06	Ruelle	1.16705E-06	Li											9.70896E-07	38.604%		
16	1,2,3,4,6,7,8-Heptachlorodibenzofuran (1,2,3,4,6,7,8-HpCDF)	67562-39-4	1.35532E-06	Ran	1.35532E-06	Ruelle	1.35532E-06	Li	1.35478E-06	Friesen1	1.34896E-06	Kim									1.35394E-06	0.206%		
17	1,2,3,4,7,8,9-Heptachlorodibenzofuran (1,2,3,4,7,8,9-HpCDF)	55673-89-7	7.29413E-07	Kim (note: calculated using equation 8																	7.29413E-07			
18	HxCDFs (All Hexachlorodibenzofurans)	NA	8.20109E-06	Ran	2.98E-06	Oleszek-Kudlak	8.20109E-06	Ruelle	8.20109E-06	Li	8.24696E-06	Friesen1									7.16604E-06	32.656%		
19	PeCDFs (All Pentachlorodibenzofurans)	NA	0.000235511	Ran	0.000235511	Ruelle	0.000236054	Li	0.000235569	Friesen1											0.000235661	0.112%		
20	TCDFs (All Tetrachlorodibenzofurans) (2,3,7,8-Tetrachlorodibenzofuran)	NA	0.000422359	Ran	0.000422359	Ruelle	0.000419451	Li	0.000419182	Friesen1											0.000420838	0.418%		
21	p,p'-DDD	72-54-8	0.090196709	Ran	0.09	Lewis, Note T is 20	0.05	Gomez-Gutierrez	0.02	Khan	0.05	Finizio	0.049566778	Ruelle	0.09	Cappiello					0.062823355	43.905%		
22	o,p'-DDT	789-02-6	0.056181294	Ran	0.01696648	Ruelle	0.05	Finizio	0.09	Cappiello											0.053286943	56.155%		
23	o,p'-DDD	53-19-0	0.098898725	Ran	0.10	Finizio	0.098898725	Ruelle	0.1	Luxenhofer	0.1	Cappiello									0.09955949	0.606%		
24	o,p'-DDE	3424-82-6	0.138820765	Ran	0.07	Finizio	0.100566754	Ruelle	0.04	Cappiello											0.08734688	48.424%		
25	p,p'-DDT	50-29-3	0.028157347	Ran	0.025	Lewis	0.0055	Gomez-Gutierrez	0.0017	Khan	0.01	Finizio	0.003017114	Ruelle	0.0055	Chiou	0.00402	Yakata	0.01	Cappiello	0.010321607	93.662%		
26	p,p'-DDE	72-55-9	0.040036346	Ran	0.12	Lewis	0.04	Gomez-Gutierrez	0.04	Khan	0.03	Finizio	0.040036346	Ruelle	0.12	Tagert	0.008	Prosen			0.054759086	76.180%		
27	Endosulfan sulfate	1031-07-8	0.48	Lewis Note at 20C	0.117	EPA	0.22	EPA	0.22	Bakouri Note at 22C											0.25925	59.776%		
28	Endosulfan I	959-98-8	0.32	Lewis Note at 20C	0.164	EPA	0.53	EPA	0.32	Bakouri Note at 22C	0.53	Khan	0.51	Cappiello							0.395666667	38.210%		
29	Endosulfan II	33213-65-9	0.45	Lewis Note at 20C	0.07	EPA	0.28	EPA	0.33	Bakouri Note at 22C	0.28	Khan	0.4	Cappiello							0.301666667	43.748%		
30	Anthracene	120-12-7	0.079612417	Ran	0.044	CRC	0.073	Mackay	0.045	Shiu	0.0659451	Marshall	0.05	Ghosh	0.045	Gomez-Gutierrez					0.057508217	26.098%		
31	Acenaphthene	83-32-9	3.615035256	Ruelle	3.8	CRC	3.93	Mackay	3.8	Shiu	4.47209	Marshall	3.8	Ghosh	3.9	Gomez-Gutierrez					3.902446465	6.934%		
32	Chrysene	218-01-9	0.006004902	Ran	0.0019	CRC	0.00198841	Ruelle	0.002	Mackay	0.002	Shiu	0.0059358	Marshall	0.002	Ghosh	0.0018	Gomez-Gutierrez			0.002953639	63.087%		
33	Fluoranthene	206-44-0	0.260548472	Ran	0.21	CRC	0.20225	Ruelle	0.26	Mackay	0.26	Shiu	0.262925	Marshall	0.26	Ghosh	0.21	Gomez-Gutierrez			0.240715434	11.505%		
34	Fluorene	86-73-7	2.044952751	Ran	1.9	CRC	1.6622	Ruelle	1.98	Mackay	1.9	Shiu	1.99464	Marshall	1.9	Ghosh	1.8	Gomez-Gutierrez			1.897724094	6.388%		
35	Pyrene	129-00-0	0.13362525	Ran	0.139	CRC	0.130583568	Ruelle	0.135	Mackay	0.132	Shiu	0.14562	Marshall	0.13	Ghosh	0.15	Gomez-Gutierrez			0.136978602	5.364%		
36	Phenanthrene	85-01-8	1.098957272	Ran	1.2	CRC	0.979446699	Ruelle	1.29	Mackay	1.1	Shiu	1.283256	Marshall	1.1	Ghosh	1.3	Gomez-Gutierrez			1.168957496	10.027%		
37	Acenaphthylene	208-96-8	16.68730167	Ran	16	CRC	16.68730167	Ruelle	15.219	Marshall	3.9	Ghosh	16.1	Gomez-Gutierrez							14.09893389	35.646%		
38	2-Acetylaminofluorene	53-96-3	4.454822171	Sahyun																	4.454822171			
39	2-Chloronaphthalene	91-58-7	11.78005315	Ran	11.7	CRC	11.78005315	Ruelle	11.7	Mackay1											11.74002657	0.394%		
40	3-Methylcholanthrene	56-49-5	0.0029	Mackay	0.001633333	Davis	0.003226277	Ran													0.002586537	32.532%		
41	Aldrin	309-00-2	0.2	Mackay1	0.178720291	Ran	0.18	Khan	0.0087	Hermanson	0.02	Cappiello	0.2	CRC	0.18	Biggar					0.138202899	61.622%		
42	Dieldrin	60-57-1	0.25	Mackay1	0.195348901	Ran	0.14	Khan	0.2	CRC	0.195	Biggar	0.179023	Robeck	0.468	Chiou					0.2324817	46.800%		
43	Parathion	56-38-2	11.9	Mackay1 (Note: 20C)	12.9	CRC	11	Tomlin	24	Chiou	11	Leistra									14.16	39.240%		
44	Phthalic acid	100-21-0	65	CRC																	65			
45	Methapyrilene	91-80-5	4443.63	Lordi																	4443.63			
46	4,4-Methylene bis(2-chloroaniline)	101-14-4	4245.693	Wu																	4245.693			
47	Phenacetin	62-44-2	940.5599303	Yalkowsky																	940.5599303			
48	1,3-Phenylenediamine	108-45-2	261700	Sidgwick																	261700			
49	Acrylamide	79-06-1	370000	CRC Note: 20C																	370000			
50	Silvex/2,4,5-TP	93-72-1	140	CRC																	140			
51	5-Nitro-o-toluidine	99-55-8	370	Ishihara																	370			
52	Famphur	52-85-7	100	Lewis Note at 20C																	100			
53	Phthalic anhydride	85-44-9	6200	CRC Note: 27C																	6200			
54	2,4,5-Trichlorophenoxyacetic acid/2,4,5-T	93-76-5	280	CRC																	280			

Regulated organic chemical solubility data in water, continued.

Line Number	Compound	CAS Number	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Average (mg/L)	%RSD
55	N-Nitrosomorpholine	59-89-2	861527.5	Ruiz																	861527.5	
56	2,4-Dichlorophenoxyacetic acid/2,4-D	94-75-7	7000	CRC																	7000	
57	N-Nitrosopyrrolidine	930-55-2	1000000	Ruiz																	1000000	
58	Kepone	143-50-0	4000	CRC Note: 100C																	4000	
59	Chlorobenzilate	510-15-6	10	CRC Note: 20C																	10	
60	2-Naphthylamine	91-59-8	189	CRC Note: 20C																	189	
61	4-Aminobiphenyl	92-67-1	130	Belcher Note: In form of sulfate salt																	130	
62	Methyl parathion	298-00-0	38	CRC Note: 20C																	38	
63	Aramite	140-57-8	0.59	Lewis Note at 20C																	0.59	
64	Methoxychlor	72-43-5	0.05	CRC																	0.05	
65	1,4-Dinitrobenzene	100-25-4	13200	CRC Note: 20C																	13200	
66	p-Dimethylaminoazobenzene	60-11-7	1.4	CRC Note: 20C																	1.4	
67	bis(2-Chloroethoxy)methane	111-91-1	7800	Beilstein Organischen Chemie																	7800	
68	2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	50	Martins. Note: at pH 4.																	50	
69	1,2-Diphenylhydrazine	122-66-7	68	New Jersey Department of Environmental Protection																	68	
70	p-Cresidine	120-71-8	2810	Report on Carcinogens, Fifteenth Edition																	2810	
71	N-Nitrosopiperidine	100-75-4	76480	Ruiz																	76480	
72	o-Anisidine (2-methoxyaniline)	90-04-0	12600	CRC																	12600	
73	N-Nitrosodimethylamine	62-75-9	1000000	New Jersey Department of Environmental Protection																	1000000	
74	4,6-Dinitro-o-cresol	534-52-1	130	CRC																	130	
75	Cresols (m,p,o)	1319-77-3	See individual cresols																		See Individual Cresols	
76	N-Nitrosomethylethylamine	10595-95-6	300000	Ruiz																	300000	
77	Disulfoton	298-04-4	25	Chiou	15	Huang. Note: 20C															20	
78	2,4-Dimethylaniline (2,4-xylidine)	95-68-1	5900	Stephenson. Note: 20C	6400	Amoore Note: Common name is chloroprene															6150	
79	Diphenylamine	122-39-4	55	CRC Note: 20C																	55	
80	gamma-BHC	58-89-9	7.8	CRC																	7.8	
81	N-Nitrosodiethylamine	55-18-5	106000	CRC Note: 24C																	106000	
82	Methyl methanesulfonate	66-27-3	531000	Gregoire																	531000	
83	2,6-Dichlorophenol	87-65-0	2620	CRC																	2620	
84	Endrin aldehyde	7421-93-4	0.024	Shiu																	0.024	
85	Phorate	298-02-2	22	Chiou																	22	
86	Methanol	67-56-1	Fully Miscible	Riddick																	Miscible	
87	1,4-Dioxane	123-91-1	Fully Miscible	EPA Fact Sheet for 1,4-Dioxane																	Miscible	
88	beta-BHC	319-85-7	0.2	CRC																	0.2	
89	delta-BHC	319-86-8	10.7	Khan																	10.7	
90	Toxaphene	8001-35-2	0.74	New Jersey Department of Environmental Protection																	0.74	
91	n-Butyl alcohol	71-36-3	79000	CRC																	79000	
92	alpha-BHC	319-84-6	1.8	CRC																	1.8	
93	Pyridine	110-86-1	455172.9904	Huuskonen																	455172.9904	
94	Cyclohexanone	108-94-1	105000	CRC																	105000	
95	Safrole	94-59-7	588.876297	Huuskonen1 : Note: Reacts	92	Samuelly															340.4381485	
96	Endrin	72-20-8	0.25	CRC																	0.25	
97	Isobutyl alcohol	78-83-1	88000	CRC																	88000	
98	Acetonitrile	75-05-8	Fully Miscible	Riddick																	Miscible	
99	Heptachlor epoxide	1024-57-3	0.200	New Jersey Department of Environmental Protection																	0.2	
100	tris-(2,3-Dibromopropyl) phosphate	126-72-7	8	Lopez																	8	
101	Ethyl cyanide/Propanenitrile	107-12-0	115000	CRC																	115000	
102	Isodrin	465-73-6	0.014	Lewis Note at 20C																	0.014	

Regulated organic chemical solubility data in water, continued.

Line Number	Compound	CAS Number	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Solubility in Water (mg/L) at 25 °C	Reference	Average (mg/L)	%RSD
103	Chlordane (alpha and gamma isomers)	57-74-9	0.6	CRC																	0.6	
104	Acrolein	107-02-8	263000	CRC Note: 20C																	263000	
105	1,2-Dibromo-3-chloropropane	96-12-8	1230	CRC Note: 20C																	1230	
106	Ethylene oxide	75-21-8	1000000	EPA Toxicological Profile for Ethylene Oxide																	1000000	
107	Ethyl acetate	141-78-6	87900	CRC																	87900	
108	Methacrylonitrile	126-98-7	26400	CRC Note: 20C. Called 2-Methylacrylonitrile																	26400	
109	Heptachlor	76-44-8	0.18	CRC																	0.18	
110	Methyl methacrylate	80-62-6	15800	CRC Note: 20C																	15800	
111	bis(2-Chloroisopropyl)ether	39638-32-9	1964.031585	Huuskonen1																	1964.031585	
112	Benzal chloride	98-87-3	250	CRC Note: 30C. Called (Dichloromethyl)benzene																	250	
113	Isosafrole	120-58-1	33.4	Samuelly	144	EPA Estimate															88.7	
114	Ethyl methacrylate	97-63-2	5400	Ullmann's Encyclopedia of Industrial Chemistry																	5400	
115	Bromoform	75-25-2	3000	CRC Note: Called tribromomethane																	3000	
116	1,2-Dibromoethane/Ethylene dibromide	106-93-4	4140	CRC Note: 20C																	4140	
117	Dibromomethane	74-95-3	13000	CRC Note: 20C																	13000	
118	Ethyl Ether	60-29-7	63000	CRC																	63000	
119	Pentachloroethane	76-01-7	490	CRC																	490	
120	1,1,1,2-Tetrachloroethane	630-20-6	1070	CRC																	1070	
121	trans-1,3-Dichloropropylene (note, hydrolysis)	10061-02-6	2800	CRC Note: 20C.																	2800	
122	Hexachloropropylene	1888-71-7	11.8	CRC Note: 20C.																	11.8	
123	Xylene(m,p,o)	1330-20-7	175	New Jersey Department of Environmental Protection																	175	
124	Iodomethane	74-88-4	14000	CRC Note: 20C.																	14000	
125	2-Chloroethyl vinyl ether	110-75-8	429	Enfield																	429	
126	3-Chloropropylene	107-05-1	4000	CRC																	4000	
127	2-Chloro-1,3-butadiene	126-99-8	480	Amoore Note: Common name is chloroprene																	480	
128	1,1,2-Trichloro-1,2,2-trifluroethane	76-13-1	170	CRC																	170	
129	1,1,1-Trichloroethane	71-55-6	1290	CRC																	1290	
130	1,1-Dichloroethylene	75-35-4	2420	CRC																	2420	
131	1,2-Dichloroethane	107-06-2	8600	CRC																	8600	
132	2,4,5-Trichlorophenol	95-95-4	1000	CRC																	1000	
133	2,4-Dinitrotoluene	121-14-2	270	CRC Note: 32C.																	270	
134	2-Butanone	78-93-3	344000	CRC																	344000	
135	4-Methyl-2-pentanone	108-10-1	18800	CRC																	18800	
136	Acetone	67-64-1	Miscible	Merck Index																	Miscible	
137	All Aroclors	1336-36-3	0.70	New Jersey Department of Environmental Protection																	0.7	
138	Benzene	71-43-2	1770	CRC Note: 20C.																	1770	
139	Butyl benzyl phhalate	85-68-7	2.69	New Jersey Department of Environmental Protection																	2.69	
140	Carbon tetrachloride	56-23-5	650	CRC																	650	
141	Chloroform	67-66-3	8000	CRC																	8000	
142	di-n-Butyl phthalate	84-74-2	11.2	CRC																	11.2	
143	Hexachlorobutadiene	87-68-3	4100	CRC																	4100	
144	Hexachloroethane	67-72-1	50	CRC																	50	
145	Methylene chloride	75-09-2	17600	CRC																	17600	
146	Nitrobenzene	98-95-3	2100	CRC	4690	Gregoire															3395	
147	Tetrachloroethylene	127-18-4	286	CRC Note: 20C.																	286	
148	Trichloroethylene	79-01-6	1280	CRC																	1280	
149	Vinyl chloride	75-01-4	2700	CRC																	2700	
150	1,1,2,2-Tetrachloroethane	79-34-5	2830	CRC																	2830	
151	1,1,2-Trichloroethane	79-00-5	4590	CRC																	4590	
152	1,1-Dichloroethane	75-34-3	5000	CRC																	5000	
153	1,2,4-Trichlorobenzene	120-82-1	37	CRC																	37	
154	1,2-Dichlorobenzene	95-50-1	150	CRC																	150	
155	1,2-Dichloropropane	78-87-5	2740	CRC																	2740	
156	1,3-Dichlorobenzene	541-73-1	103	CRC																	103	
157	1,4-Dichlorobenzene	106-46-7	80	CRC																	80	
158	2,4,6-Trichlorophenol	88-06-2	690	CRC																	690	
159	2,4-Dichlorophenol	120-83-2	5500	CRC																	5500	
160	2,4-Dimethyl phenol	105-67-9	7870	CRC Note: Commonly called 2,4-Xylenol																	7870	
161	2,4-Dinitrophenol	51-28-5	69	CRC																	69	
162	2-Chlorophenol	95-57-8	23200	CRC																	23200	
163	2-Nitroaniline	88-74-4	14900	CRC Note: 30C.																	14900	
164	2-Nitrophenol	88-75-5	1700	CRC																	1700	
165	4-Bromophenyl phenyl ether	101-55-3	0.13	Tittlemier Note: Compound	18	Hardy Note: Compound is d	9.795164839	Ballschmiter Note: Compound is 4-chlorodiphenyl ether											See notes in refs in this row re: related compounds.			
166	4-Chloroaniline	106-47-8	2750	CRC Note: 20C.	3230	Gregoire															2990	

Regulated organic chemical solubility data in water, continued.

Line Number	Compound	CAS Number	Solubility in Water (mg/L) at 25 ℃	Reference	Solubility in Water (mg/L) at 25 ℃	Reference	Solubility in Water (mg/L) at 25 ℃	Reference	Solubility in Water (mg/L) at 25 ℃	Reference	Solubility in Water (mg/L) at 25 ℃	Reference	Solubility in Water (mg/L) at 25 ℃	Reference	Solubility in Water (mg/L) at 25 ℃	Reference	Solubility in Water (mg/L) at 25 ℃	Reference	Solubility in Water (mg/L) at 25 ℃	Reference	Average (mg/L)	%RSD
167	4-Nitroaniline	100-01-6	730	CRC Note: 30C.																	730	
168	bis(2-Chloroethyl)ether	111-44-4	10500	CRC Note: 20C.																	10500	
169	bis(2-ethylhexyl)phthalate	117-81-7	0.27	CRC																	0.27	
170	Bromodichloromethane	75-27-4	3000	CRC Note: 30C.																	3000	
171	Bromomethane	74-83-9	18300	CRC Note: 20C.																	18300	
172	Carbon disulfide	75-15-0	2100	CRC Note: 20C.																	2100	
173	Chlorobenzene	108-90-7	500	CRC																	500	
174	Chloroethane	75-00-3	6700	CRC																	6700	
175	Chloromethane	74-87-3	5350	CRC																	5350	
176	cis-1,3-Dichloropropylene	10061-01-5	2700	CRC Note: 20C.																	2700	
177	Dibromochloromethane	124-48-1	2510	CRC Note: 30C.																	2510	
178	Dichlorodifluoromethane	75-71-8	280	CRC Note: 20C.																	280	
179	Diethyl phthalate	84-66-2	1200	CRC																	1200	
180	Dimethyl phthalate	131-11-3	4000	CRC	3180	Gregoire															3590	
181	Di-n-octyl phthalate	117-84-0	0.0200	New Jersey Department of Environmental Protection																	0.02	
182	Ethyl benzene	100-41-4	161	CRC																	161	
183	Hexachlorobenzene	118-74-1	0.0096	CRC																	0.0096	
184	Hexachlorocyclopentadiene	77-47-4	1.80	New Jersey Department of Environmental Protection																	1.8	
185	N-Nitroso-di-n-propylamine	621-64-7	9890	New Jersey Department of Environmental Protection																	9890	
186	Pentachlorophenol	87-86-5	21	CRC																	21	
187	Phenol	108-95-2	91700	CRC																	91700	
188	p-Nitrophenol	100-02-7	15800	CRC Note: 20C.																	15800	
189	Toluene	108-88-3	519	CRC																	519	
190	Trichlorofluoromethane	75-69-4	1100	CRC Note: 20C.																	1100	
191	Diphenylnitrosamine	86-30-6	35	CRC																	35	
192	N-Nitroso-di-n-butylamine	924-16-3	1270	Ruiz																	1270	
193	Pentachlorobenzene	608-93-5	0.5	CRC																	0.5	
194	Pentachloronitrobenzene	82-68-8	0.44	CRC Note: 20C.																	0.44	
195	Pronamide	23950-58-5	15	CRC Note: Also called propyzamide																	15	
196	1,2,4,5-Tetrachlorobenzene	95-94-3	0.6	CRC																	0.6	
197	2,3,4,6-Tetrachlorophenol	58-90-2	170	CRC																	170	
198	1,2,3-Trichloropropane	96-18-4	2000	CRC																	2000	
199	Acetophenone	98-86-2	6700	CRC Note: 20C. Note: on g	8860	Gregoire															7780	
200	Acrylonitrile	107-13-1	79300	CRC Note: 20C.																	79300	
201	Aniline	62-53-3	35000	CRC																	35000	
202	p-Chloro-m-cresol	59-50-7	4000	CRC																	4000	
203	o-Cresol	95-48-7	31800	CRC Note: 40C.																	31800	
204	m-Cresol	108-39-4	25700	CRC Note: 40C.																	25700	
205	p-Cresol	106-44-5	23100	CRC Note: 40C.																	23100	
206	trans-1,2-Dichloroethylene	156-60-5	4500	CRC																	4500	
207	2,6-Dinitrotoluene	606-20-2	182	New Jersey Department of Environmental Protection																	182	

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Appendix B

Alkaline Reactivity Assessment for 207 Regulated Organic Chemicals

This section gives an initial assessment alkaline reactivity of regulated organic chemicals. Note that all 207 compounds have been assessed in this appendix but only a subset of these compounds have been used at Hanford or have been detected in tank waste samples and thus would be expected to potentially be present in Hanford liquid or dissolved saltcake waste. The compilation was by Charles Nash with some assistance by Tom White. Tom continued compiling some entries and also assessed Nash entries in his comments. Some generalities can be made concerning reactivities. Esters, nitriles, and amides hydrolyze in caustic. Esters would form the parent acid salt and an alcohol. The ester dibutyl phthalate, for example, would form butanol and sodium phthalate, both of which are regulated. Nitriles form ammonia and an organic acid salt with alkaline hydrolysis. As an example, acetonitrile forms ammonia and sodium acetate. Amides also hydrolyze to form ammonia and an organic acid salt. The two dinitrotoluenes are shown as reactive because the 2,4-isomer was found to readily be degraded at room temperature in current lab work. PAH’s are very stable and insoluble and would be expected to persist in a waste tank.

								T. White	C. Nash
								Comments	Reactive or Stable in Caustic?
	The list includes the constituents associated with waste codes on the Part A For SST/DST excluding F039.				From Appendix B in SRNL-STI-2021-00453	Rule 0	Rule 1		
Line Number	**Name**	**CAS Number**	**Waste code/UHC**	**WAC 173-303-090 Designation limit (mg/L TCLP)**	**pKa**	**pKa Reference**	**Notes**		
1	Phthalic acid	100-21-0	NA/UHC	---	2.89, 5.51	ChemBook	diprotic	Two carboxylic acid protons pKa1 and pKa2. Other protons >30	Stable
2	Methapyrilene	91-80-5	NA/UHC	---	8.85 H^{+}CB	PubChem	Conj Acid	Basic amine is a conjugate base (CB) that under acidic conditions can protonate. This protonated CB of the first amine has a pKa of 8.85	Stable
3	4,4-Methylene bis(2-chloroaniline)	101-14-4	NA/UHC	---	3.33 +/- 0.25 H^{+}CB	ChemBook	Conj Acid	Amine protanated CB where the first protonated amine has a pKa of 3.33	Stable
4	2-Acetylaminofluorene	53-96-3	NA/UHC	---	alkaline hydrolysis	hydrolysis	amides hydrolyze	Agreed	Reacts - alkaline hydrolysis
5	Phenacetin	62-44-2	NA/UHC	---	alkaline hydrolysis	hydrolysis	amides hydrolyze	Agreed	Reacts - alkaline hydrolysis
6	1,3-Phenylenediamine	108-45-2	NA/UHC	---	2.65, 4.88 PubChem H^{+}CB	PubChem	Conj Acid	Amine protanated CB with both pKas	Reacts - air oxidation, PubChem
7	Acrylamide	79-06-1	NA/UHC	---	alkaline hydrolysis	hydrolysis	hydrolysis	Agreed	Reacts - alkaline hydrolysis
8	Silvex/2,4,5-TP	93-72-1	NA/UHC	1	2.84 PubChem	PubChem	--	Carboxilic acid	Stable
9	5-Nitro-o-toluidine	99-55-8	NA/UHC	---	2.35 PubChem H^{+}CB	PubChem	--	Amine protonated CB where the protonated amine has a pKa of 2.35	Stable
10	Famphur	52-85-7	NA/UHC	---	(-5) Pred H^{+}CB	ChemBook		Amine protonated CB where the protonated amine has a pKa of 2.35	Reacts - alkaline hydrolysis
11	Phthalic anhydride	85-44-9	NA/UHC	---	alkaline hydrolysis	anhydride	sodium phthalate	Agreed	Reacts - alkaline hydrolysis
12	2,4,5-Trichlorophenoxyacetic acid/2,4,5-T	93-76-5	NA/UHC	---	2.88 PubChem	PubChem	--	Carboxilic acid	Stable
13	N-Nitrosomorpholine	59-89-2	NA/UHC	---	stable	T White	pKa out of range	pKa of protanate CB morpholine not given (~ 8)	Stable - n-nitroso
14	2,4-Dichlorophenoxyacetic acid/2,4-D	94-75-7	NA/UHC	10	2.73	PubChem	--	Carboxilic acid	Stable
15	Dibenz(a,e)pyrene	192-65-4	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
16	N-Nitrosopyrrolidine	930-55-2	NA/UHC	---	(- 3.14) Pred H^{+}CB	ChemBook	pKa out of range	Protonated CB	Stable - n-nitroso
17	Kepone	143-50-0	NA/UHC	---	no hydrogen		--	Agreed	Stable - PubChem
18	Chlorobenzilate	510-15-6	NA/UHC	---	alkaline hydrolysis	PubChem	Ester group	Agreed	Reacts - alkaline hydrolysis
19	2-Naphthylamine	91-59-8	NA/UHC	---	--	T White	pKa out of range	Amine protonated CB not given (~4.16)	Stable - SRNL-STI-2021-00453r1
20	4-Aminobiphenyl	92-67-1	NA/UHC	---	4.35 H^{+}CB	PubChem	Conj Acid	Amine protonated CB	Stable
21	Methyl parathion	298-00-0	NA/UHC	---	alkaline hydrolysis	NIH	i.nlm.nih.gov/pmc/article	Agreed	Reacts - alkaline hydrolysis
22	Aramite	140-57-8	NA/UHC	---	alkaline hydrolysis	ChemicalBook	.com/ChemicalProductPr	Agreed	Reacts - alkaline hydrolysis
23	Methoxychlor	72-43-5	NA/UHC	10	alkaline hydrolysis	und/Methoxychlor#section=Other-Experim		pKa is likely near 30	Reacts - alkaline hydrolysis
24	1,4-Dinitrobenzene	100-25-4	NA/UHC	---	>14	Bordwell estimat	pKa out of range	This pKa is likely above 30	Stable
25	p-Dimethylaminoazobenzene	60-11-7	NA/UHC	---	3.23 H^{+}CB	PubChem	Conj Acid	Amine protonated CB	Stable to hydrolysis, Pubchem
26	Parathion	56-38-2	NA/UHC	---	alkaline hydrolysis	s.org/doi/pdf/10.1021/jp503382j		Agreed	Reacts - alkaline hydrolysis
27	Endosulfan sulfate	1031-07-8	NA/UHC	---	alkaline hydrolysis	PubChem	--	Agreed	Reacts - alkaline hydrolysis
28	Benzo(g,h,i)perylene	191-24-2	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
29	bis(2-Chloroethoxy)methane	111-91-1	NA/UHC	---	>16.9	Bordwell estimate	pKa out of range	This pKa is likely above 30	Reacts - alkaline hydrolysis of Cl
30	2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	NA/UHC	---	4.62	PubChem	--	Phenol type compound	Stable - Herbicide

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Line Number	Name	CAS Number	Waste code/UHC	WAC 173-303-090 Designation limit (mg/L TCLP)	pKa	pKa Reference	Notes		
31	1,2-Diphenylhydrazine	122-66-7	NA/UHC	---	unstable/reacts	PubChem		Agreed	Reacts - PubChem
32	p-Cresidine	120-71-8	NA/UHC	---	4.66 Pred H^+CB	ChemicalBook	Conj Acid	Amine protonated CB	Stable
33	N-Nitrosopiperidine	100-75-4	NA/UHC	---	(-3.2 Pred) H^+CB	ChemicalBook	pKa out of range	protonated CB	Stable - n-nitroso
34	o-Anisidine (2-methoxyaniline)	90-04-0	NA/UHC	---	4.53 H^+CB	PubChem	Conj Acid	Amine protonated CB	Stable - n-nitroso
35	N-Nitrosodimethylamine	62-75-9	NA/UHC	---	>30	T White	pKa out of range	pKa for protonated CB not given (~-3)	Stable - n-nitroso
36	4,6-Dinitro-o-cresol	534-52-1	NA/UHC	---	5	T White	--	Phenol type compound	Stable
37	Cresols (m,p,o)	1319-77-3	F004/NA	200	10	T White	--	Phenol type compound	Reacts with air - Bretherick, L. Handbook
38	N-Nitrosomethylethylamine	10595-95-6	NA/UHC	---	<1 H^+CB, >30	nitroso	pKa out of range	Agreed	Stable - n-nitroso
39	Disulfoton	298-04-4	NA/UHC	---	alkaline hydrolysis	23&identifier=Disu	--	Agreed	Reacts - alkaline hydrolysis
40	2,4-Dimethylaniline (2,4-xylidine)	95-68-1	NA/UHC	---	4.89 H^+CB	ChemicalBook	Conj acid	Amine protonated CB	Stable
41	Diphenylamine	122-39-4	NA/UHC	---	0.78 H^+CB	PubChem	Conj acid	Amine protonated CB	Stable - see writeup on 14 chems
42	gamma-BHC	58-89-9	NA/UHC	0.4	>30	BHC	pKa out of range	Agreed	Reacts - Ngabe, Base Hydrolysis
43	N-Nitrosodiethylamine	55-18-5	NA/UHC	---	<1 H^+CB, >30	T White	pKa out of range	Amine protonated CB	Stable - n-nitroso
44	Methyl methanesulfonate	66-27-3	NA/UHC	---	alkaline hydrolysis	PubChem		Agreed	Reacts - alkaline hydrolysis
45	2,6-Dichlorophenol	87-65-0	NA/UHC	---	6.79	PubChem	--	Phenol type compound	Stable
46	Endrin aldehyde	7421-93-4	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Likely closer to 25	Stable
47	Phorate	298-02-2	NA/UHC	---	alkaline decomposition	PubChem	ES%5CINDEX%20DATA%5	Agreed	Reacts - alkaline hydrolysis
48	Methanol	67-56-1	NA/UHC	---	16	T White	pKa out of range	Agreed	Stable - SRNL-STI-2020-00582
49	1,4-Dioxane	123-91-1	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - see writeup on 14 chems
50	beta-BHC	319-85-7	NA/UHC	---	>30	T White	pKa out of range	Agreed	Reacts - Checa-Fernandez, BetaBHC
51	delta-BHC	319-86-8	NA/UHC	---	>30	T white	pKa out of range	Agreed	Reacts
52	3-Methylcholanthrene	56-49-5	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable- PAH
53	Toxaphene	8001-35-2	NA/UHC	0.5	>14	Bordwell estimate	pKa out of range	Agreed	Stable
54	p,p′-DDD	72-54-8	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Kucher and Schwarzbauer
55	o,p′-DDT	789-02-6	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable
56	n-Butyl alcohol	71-36-3	NA/UHC	---	16	T White	pKa out of range	Agreed	Stable - SRNL-STI-2020-00582
57	alpha-BHC	319-84-6	NA/UHC	---	>30	T White	pKa out of range	Agreed	Reacts - Ngabe, Base Hydrolysis
58	o,p′-DDD	53-19-0	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Kucher and Schwarzbauer
59	Pyridine	110-86-1	D038/UHC	5	5.25 H^+CB	T White	pKa out of range	Amine protonated CB	Stable - SRNL-STI-2020-00582
60	Cyclohexanone	108-94-1	NA/UHC	---	16.7	db.ca/compounds/	pKa out of range	Agreed	Reacts - alkaline aldol condensation
61	Safrole	94-59-7	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Reacts - alk rxn to isosafrole PubChem
62	Endrin	72-20-8	NA/UHC	0.02	>14	Bordwell estimate	pKa out of range	Agreed	Stable
63	Dieldrin	60-57-1	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable
64	Isobutyl alcohol	78-83-1	NA/UHC	---	16	T White	pKa out of range	Agreed	Stable - simple alcohol
65	Aldrin	309-00-2	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable - SRNL-STI-2021-00453r1
66	Acetonitrile	75-05-8	NA/UHC	---	alkaline hydrolysis	T White	nitriles hydrolyze	Agreed	Reacts - nitriles SRNL-STI-2019-00471
67	o,p′-DDE	3424-82-6	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Kucher and Schwarzbauer
68	Heptachlor epoxide	1024-57-3	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable
69	tris-(2,3-Dibromopropyl) phosphate	126-72-7	NA/UHC	---	alkaline hydrolysis	10665/37119/924157173X-eng.pdf?sequen		Agreed	Reacts - alkaline hydrolysis
70	p,p′-DDT	50-29-3	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Reacts - dehydrochlorination
71	Ethyl cyanide/Propanenitrile	107-12-0	NA/UHC	---	alkaline hydrolysis	T White	nitriles hydrolyze	Agreed	Reacts - alkaline hydrolysis
72	p,p′-DDE	72-55-9	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable
73	Isodrin	465-73-6	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - PubChem
74	Chlordane (alpha and gamma isomers)	57-74-9	NA/UHC	0.03	alkaline hydrolysis	PubChem	also ChemBook	Agreed	Reacts - alkaline hydrolysis
75	Endosulfan I	959-98-8	NA/UHC	---	alkaline hydrolysis	effect_of_water_	--	Agreed	Reacts - alkaline hydrolysis
76	Endosulfan II	33213-65-9	NA/UHC	---	alkaline hydrolysis	effect_of_water_	--	Agreed	Reacts - alkaline hydrolysis
77	Acenaphthylene	208-96-8	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
78	Acrolein	107-02-8	NA/UHC	---	>30	T White	pKa out of range	Agreed	Reacts - alkali, PubChem, reactive
79	1,2-Dibromo-3-chloropropane	96-12-8	NA/UHC	---	alkaline hydrolysis	PubChem	--	Agreed	Reacts - alkaline hydrolysis
80	Ethylene oxide	75-21-8	NA/UHC	---	alkaline hydrolysis		--	Agreed	Reacts - alkaline hydrolysis

								T. White	C. Nash
								Comments	Reactive or Stable in Caustic?
	The list includes the constituents associated with waste codes on the Part A For SST/DST excluding F039.				**From Appendix B in SRNL-STI-2021-00453**	**Rule 0**	**Rule 1**		
Line Number	**Name**	**CAS Number**	**Waste code/UHC**	**WAC 173-303-090 Designation limit (mg/L TCLP)**	**pKa**	**pKa Reference**	**Notes**		
81	Ethyl acetate	141-78-6	NA/UHC	---	alkaline hydrolysis	T White	saponification	Agreed	Reacts - alkaline hydrolysis
82	Methacrylonitrile	126-98-7	NA/UHC	---	alkaline hydrolysis	Bordwell estimate	nitriles hydrolyze	Agreed	Reacts - alkaline hydrolysis
83	Heptachlor	76-44-8	NA/UHC	0.008	>30	T White	pKa out of range	Agreed	Reacts - alkaline hydrolysis, PubChem
84	Methyl methacrylate	80-62-6	NA/UHC	---	alkaline hydrolysis	m.nih.gov/pmc/ar	--	Agreed	Reacts - alkaline hydrolysis
85	bis(2-Chloroisopropyl)ether	39638-32-9	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Reacts - hydrolysis, PubChem
86	Benzal chloride	98-87-3	NA/UHC	---	alkaline hydrolysis	ce/bitstream/211	--	Agreed	Reacts - alkaline hydrolysis
87	Isosafrole	120-58-1	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable
88	Ethyl methacrylate	97-63-2	NA/UHC	---	alkaline hydrolysis	ce/bitstream/211	--	Agreed	Reacts - alkaline hydrolysis
89	Bromoform	75-25-2	NA/UHC	---	alkaline hydrolysis	PubChem	--	Agreed	Reacts - alkaline hydrolysis
90	1,2-Dibromoethane/Ethylene dibromide	106-93-4	NA/UHC	---	alkaline hydrolysis	PubChem	--	Agreed	Reacts - alkaline hydrolysis
91	Dibromomethane	74-95-3	NA/UHC	---	alkaline hydrolysis	PubChem	--	Agreed	Reacts - alkaline hydrolysis
92	Ethyl Ether	60-29-7	NA/UHC	---	>30	T White	pKa out of range	Agreed	Reacts - strong peroxide former
93	Pentachloroethane	76-01-7	NA/UHC	---	alkaline hydrolysis	PubChem	--	Agreed	Reacts - alkaline hydrolysis
94	1,1,1,2-Tetrachloroethane	630-20-6	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Reacts- alkaline hydrolysis
95	trans-1,3-Dichloropropylene (note, hydrolysis)	10061-02-6	NA/UHC	---	alkaline hydrolysis	see paper	SUserFiles/50600000/Pro	Agreed	Reacts - alkaline hydrolysis
96	Hexachloropropylene	1888-71-7	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable
97	Xylene(m,p,o)	1330-20-7	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable - simple aromatic
98	Iodomethane	74-88-4	NA/UHC	---	alkaline hydrolysis	MRID 45593705		Agreed	Reacts - alkaline hydrolysis
99	2-Chloroethyl vinyl ether	110-75-8	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable
100	3-Chloropropylene	107-05-1	NA/UHC	---	alkaline hydrolysis	PubChem		Agreed	Reacts - see writeup on 14 chems
101	2-Chloro-1,3-butadiene	126-99-8	NA/UHC	---	reactive-polymerizes	PubChem	see chloroprene	Agreed	Reacts - polymerizes
102	1,1,2-Trichloro-1,2,2-trifluroethane	76-13-1	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - see writeup on 14 chems
103	1,1,1-Trichloroethane	71-55-6	F001/NA	---	>30	T White	pKa out of range	Agreed	Reacts - SRNL-STI-2021-00453r1
104	1,1-Dichloroethylene	75-35-4	D029/UHC	0.7	>30	T White	pKa out of range	Agreed	Stable
105	1,2-Dichloroethane	107-06-2	D028/UHC	0.5	>30	T White	pKa out of range	Agreed	Stable to hydrolysis, PubChem
106	2,4,5-Trichlorophenol	95-95-4	D041/UHC	400	7	T White	--	Phenol type compound	Reacts - SRNL-STI-2021-00453r1
107	2,4-Dinitrotoluene	121-14-2	D030/UHC	0.13	alkaline decomposition	Lab work 2022	decomposes	Acidic methyl group	Reacts - hydrolysis current lab work
108	2-Butanone	78-93-3	F005/D035	200	20	T White	pKa out of range	Agreed	Stable - simple ketone, PubChem
109	4-Methyl-2-pentanone	108-10-1	F003/NA	---	20	T White	pKa out of range	Agreed	Stable - simple ketone
110	Acetone	67-64-1	F003/NA	---	20	T White	pKa out of range	Agreed	Stable - SRNL-STI-2020-00582
111	All Aroclors	1336-36-3	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable - SRNL-STI-2021-00453r1
112	Benzene	71-43-2	D018/UHC	0.5	>30	T White	pKa out of range	Agreed	Stable - simple aromatic
113	Butyl benzyl phhalate	85-68-7	NA/UHC	---	alkaline hydrolysis	ester		Agreed	Reacts - alkaline hydrolysis
114	Carbon tetrachloride	56-23-5	D019/UHC	0.5	>30	T White	pKa out of range	Agreed	Reacts - Weckhuysen
115	Chloroform	67-66-3	D022/UHC	6	16	T White	pKa out of range	Agreed	Reacts https://pubmed.ncbi.nlm.nih.gov/
116	di-n-Butyl phthalate	84-74-2	NA/UHC	---	alkaline hydrolysis	ester		Agreed	Reacts - alkaline hydrolysis
117	Hexachlorobutadiene	87-68-3	D033/UHC	0.5	>30	T White	pKa out of range	Agreed	Reacts in water - PubChem
118	Hexachloroethane	67-72-1	D034/UHC	3	>30	T White	pKa out of range	Agreed	Stable - SRNL-STI-2021-00453r1
119	Methylene chloride	75-09-2	F002/NA	---	>30	T White	pKa out of range	Agreed	Reacts - SRNL-STI-2021-00453r1
120	Nitrobenzene	98-95-3	D036/UHC	2	>30	T White	pKa out of range	Agreed	Reacts - Dermer and Druker
121	Tetrachloroethylene	127-18-4	D039/UHC	0.7	20 - 30	T White	pKa out of range	Agreed	Reacts - SRNL-STI-2021-00453r1
122	Trichloroethylene	79-01-6	D040/UHC	0.5	20 - 30	T White	pKa out of range	Agreed	Reacts - SRNL-STI-2021-00453r1
123	Vinyl chloride	75-01-4	D043/UHC	0.2	>30	T White	pKa out of range	Agreed	Reacts - SRNL-STI-2021-00453r1
124	1,1,2,2-Tetrachloroethane	79-34-5	NA/UHC	---	20 - 30	T White	pKa out of range	Agreed	Reacts - alkaline hydrolysis
125	1,1,2-Trichloroethane	79-00-5	NA/UHC	---	20 - 30	T White	pKa out of range	Agreed	Reacts - SRNL-STI-2021-00453r1
126	1,1-Dichloroethane	75-34-3	NA/UHC	---	>30	T White	pKa out of range	Agreed	Reacts - alkaline hydrolysis
127	1,2,4-Trichlorobenzene	120-82-1	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable - SRNL-STI-2021-00453r1
128	1,2-Dichlorobenzene	95-50-1	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - see writeup on 14 chems
129	1,2-Dichloropropane	78-87-5	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable
130	1,3-Dichlorobenzene	541-73-1	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable

								T. White	C. Nash
								Comments	Reactive or Stable in Caustic?
	The list includes the constituents associated with waste codes on the Part A For SST/DST excluding F039.				**From Appendix B in SRNL-STI-2021-00453**	**Rule 0**	**Rule 1**		
Line Number	**Name**	**CAS Number**	**Waste code/UHC**	**WAC 173-303-090 Designation limit (mg/L TCLP)**	**pKa**	**pKa Reference**	**Notes**		
131	1,4-Dichlorobenzene	106-46-7	NA/UHC	7.5	>30	T White	pKa out of range	Agreed	Stable - SRNL-STI-2021-00453r1
132	2,4,6-Trichlorophenol	88-06-2	NA/UHC	2	7.00	T White	--	Phenol type compound	Stable
133	2,4-Dichlorophenol	120-83-2	NA/UHC	---	7.89	Pubchem	--	Phenol type compound	Stable
134	2,4-Dimethyl phenol	105-67-9	NA/UHC	---	10.60	Pubchem	--	Phenol type compound	Stable
135	2,4-Dinitrophenol	51-28-5	NA/UHC	---	5.00	T White	--	Phenol type compound	Stable
136	2-Chloronaphthalene	91-58-7	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable
137	2-Chlorophenol	95-57-8	NA/UHC	---	8.56	Pubchem	--	Phenol type compound	Stable - see writeup on 14 chems
138	2-Nitroaniline	88-74-4	NA/UHC	---	(-0.28) H^+CB	Pubchem	pKa out of range	Amine protonated CB	Stable - see writeup on 14 chems
139	2-Nitrophenol	88-75-5	NA/UHC	---	7.00	T White	--	Phenol type compound	Stable - KB Shaw
140	4-Bromophenyl phenyl ether	101-55-3	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Reacts - FR Xiu, NaOH hydrolysis
141	4-Chloroaniline	106-47-8	NA/UHC	---	3.98 H^+CB	Pubchem	conj acid	Amine protonated CB	Stable - PubChem
142	4-Nitroaniline	100-01-6	NA/UHC	---	~~12.99~~ 1.0 H^+CB	ChemicalBook	conj acid	Amine protonated CB. This value should be 1	Stable - see writeup on 14 chems
143	Acenaphthene	83-32-9	NA/UHC	---	>30, PAH	T White	pKa out of range	Agreed	Stable - PAH
144	Anthracene	120-12-7	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
145	Benz(a)anthracene	56-55-3	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
146	Benzo(a)pyrene	50-32-8	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
147	Benzo(b)fluoranthene	205-99-2	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
148	Benzo(k)fluoranthene	207-08-9	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
149	bis(2-Chloroethyl)ether	111-44-4	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Reacts - alkaline hydrolysis
150	bis(2-ethylhexyl)phthalate	117-81-7	NA/UHC	---	alkaline hydrolysis	ester		Agreed	Reacts - alkaline hydrolysis
151	Bromodichloromethane	75-27-4	NA/UHC	---	12.90	nutz.eu/chem/pka	--	Agreed	Reacts - alkaline hydrolysis
152	Bromomethane	74-83-9	NA/UHC	---	alkaline hydrolysis	PubChem	--	Agreed	Reacts - see writeup on 14 chems
153	Carbon disulfide	75-15-0	NA/UHC	---	no hydrogens	T White	pKa out of range	Agreed	Reacts - slow alk hydrolysis PubChem
154	Chlorobenzene	108-90-7	NA/UHC	100	>30	T White	pKa out of range	Agreed	Stable - SRNL-STI-2021-00453r1
155	Chloroethane	75-00-3	NA/UHC	---	stable	PubChem	--	Agreed	Stable - PubChem
156	Chloromethane	74-87-3	NA/UHC	---	>30	T White	pKa out of range	Agreed	Reacts - alkaline hydrolysis
157	Chrysene	218-01-9	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
158	cis-1,3-Dichloropropylene	10061-01-5	NA/UHC	---	alkaline hydrolysis	erFiles/50600000/Products-Reprints/2004/		Agreed	Reacts - alkaline hydrolysis
159	Dibenzo(a,h)anthracene	53-70-3	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
160	Dibromochloromethane	124-48-1	NA/UHC	---	no hydrogens		--	Agreed	Reacts- alkaline hydrolysis
161	Dichlorodifluoromethane	75-71-8	NA/UHC	---	no hydrogens		--	Agreed	Stable - see writeup on 14 chems
162	Diethyl phthalate	84-66-2	NA/UHC	---	alk hydrolysis	ester		Agreed	Reacts - alkaline hydrolysis
163	Dimethyl phthalate	131-11-3	NA/UHC	---	alk hydrolysis	ester	--	Agreed	Reacts - alkaline hydrolysis
164	Di-n-octyl phthalate	117-84-0	NA/UHC	---	alk hydrolysis	ester		Agreed	Reacts - alkaline hydrolysis
165	Ethyl benzene	100-41-4	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable - Aromatic
166	Fluoranthene	206-44-0	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
167	Fluorene	86-73-7	NA/UHC	---	>30, PAH	T White	pKa out of range	Agreed	Stable - PAH
168	Hexachlorobenzene	118-74-1	NA/UHC	0.13	no hydrogens			Agreed	Stable to hydrolysis -PubChem
169	Hexachlorocyclopentadiene	77-47-4	NA/UHC	---	no hydrogens			Agreed	Reacts- hydrolysis, PubChem
170	Indeno(1,2,3-c,d) pyrene	193-39-5	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH

								T. White	C. Nash
								Comments	Reactive or Stable in Caustic?
	The list includes the constituents associated with waste codes on the Part A For SST/DST excluding F039.				**From Appendix B in SRNL-STI-2021-00453**	**Rule 0**	**Rule 1**		
Line Number	**Name**	**CAS Number**	**Waste code/UHC**	**WAC 173-303-090 Designation limit (mg/L TCLP)**	**pKa**	**pKa Reference**	**Notes**		
171	Naphthalene	91-20-3	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable - PAH
172	N-Nitroso-di-n-propylamine	621-64-7	NA/UHC	---	stable	T White	pKa out of range	Agreed	Stable - n-nitroso
173	Pentachlorophenol	87-86-5	NA/UHC	100	5.00	T White	--	Phenol type compound	Stable
174	Phenanthrene	85-01-8	NA/UHC	---	>30	PAH	pKa out of range	Agreed	Stable - PAH
175	Phenol	108-95-2	NA/UHC	---	10	T White	--	Phenol type compound	Reacts - alkaline oxidation
176	p-Nitrophenol	100-02-7	NA/UHC	---	7.15	PubChem	--	Phenol type compound	Stable
177	Pyrene	129-00-0	NA/UHC	---	>30, PAH	T White	pKa out of range	Agreed	Stable - PAH
178	Toluene	108-88-3	NA/UHC	---	>30	T White	pKa out of range	Agreed	Stable - nonsubstituted aromatic
179	Trichlorofluoromethane	75-69-4	NA/UHC	---	>30	T White	pKa out of range	Agreed	Reacts - alkaline hydrolysis
180	Diphenylnitrosamine	86-30-6	NA/UHC	---	(-5.8 predicted H^+CB)	ChemicalBook	pKa out of range	Amine protonated CB	Stable - n-nitroso
181	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD)	35822-46-9	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable to hydrolysis -PubChem
182	1,2,3,4,6,7,8-Heptachlorodibenzofluran (1,2,3,4,6,7,8-HpCDF)	67562-39-4	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Aronson
183	1,2,3,4,7,8,9-Heptachlorodibenzofluran (1,2,3,4,7,8,9-HpCDF)	55673-89-7	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Aronson
184	HxCDDs (All Hexachlorodibenzo-p-dioxins)	NA	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Aronson
185	HxCDFs (All Hexachlorodibenzofurans)	NA	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Aronson
186	N-Nitroso-di-n-butylamine	924-16-3	NA/UHC	---	(-3.14) H^+CB	ChemicalBook	pKa out of range	Amine protonated CB	Stable - n-nitroso
187	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Aronson
188	1,2,3,4,6,7,8,9-Octachlorodibenzofluran (OCDF)	39001-02-0	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable - Aronson
189	Pentachlorobenzene	608-93-5	NA/UHC	---	>14, stable	PubChem	pKa out of range	Agreed	Stable to hydrolysis, PubChem
190	PeCDDs (All Pentachlorodibenzo-p-dioxins)	NA	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable, https://www.cdc.gov/niosh/docs/
191	PeCDFs (All Pentachlorodibenzofurans)	NA	NA/UHC	---	>14	Bordwell estimate	pKa out of range	Agreed	Stable to hydrolysis, PubChem
192	Pentachloronitrobenzene	82-68-8	NA/UHC	---	no hydrogens			Agreed	Stable - EPA 600/6-84-011
193	Pronamide	23950-58-5	NA/UHC	---	alkaline hydrolysis	PubChem	Amides hydrolyze	Agreed	Reacts - alkaline hydrolysis
194	1,2,4,5-Tetrachlorobenzene	95-94-3	NA/UHC	---	>14, stable	PubChem	pKa out of range	Agreed	Stable - see writeup on 14 chems
195	TCDDs (All Tetrachlorodibenzo-p-dioxins)	NA	NA/UHC	---	>14, stable	Bordwell estimate	pKa out of range	Agreed	Stable https://www.cdc.gov/niosh/docs/
196	TCDFs (All Tetrachlorodibenzofurans)	NA	NA/UHC	---	>14, stable	Bordwell estimate	pKa out of range	Agreed	Stable to hydrolysis, PubChem
197	2,3,4,6-Tetrachlorophenol	58-90-2	NA/UHC	---	5.22	Pubchem	--	Phenol type compound	Stable to hydrolysis
198	1,2,3-Trichloropropane	96-18-4	NA/UHC	---	>14	Bordwell estimate	Chem: alk hydr needs hig	Agreed	Stable at normal temps, PubChem
199	Acetophenone	98-86-2	NA/UHC	---	16	T White	pKa out of range	Agreed	Stable - SRNL-STI-2020-00582
200	Acrylonitrile	107-13-1	NA/UHC	---	>14	Bordwell estimate	alkaline hydrolysis	Agreed	Reacts - nitriles SRNL-STI-2019-00471
201	Aniline	62-53-3	NA/UHC	---	4.6 H^+CB	Pubchem	Conj Acid	Amine protonated CB	Reacts with air
202	p-Chloro-m-cresol	59-50-7	NA/UHC	---	9.55	Pubchem	--	Phenol type compound	Reacts with air
203	o-Cresol	95-48-7	F004/NA	200	10	T White	--	Phenol type compound	Reacts with air - Bretherick, L. Handbook
204	m-Cresol	108-39-4	F004/NA	200	10	T White	--	Phenol type compound	Reacts with air - Bretherick, L. Handbook
205	p-Cresol	106-44-5	F004/NA	200	10	T White	--	Phenol type compound	Reacts with air - Bretherick, L. Handbook
206	trans-1,2-Dichloroethylene	156-60-5	NA/UHC	---	>14	Bordwell estimate	--	Agreed	Stable
207	2,6-Dinitrotoluene	606-20-2	NA/UHC	---	alkaline decomposition	2022 Lab work	alkaline decomposition	We did not look at H^+CB of nitro groups which would be > -10. The Methyl group would be acid at about 14	Stable

References for Reactivity Table. All Internet references were accessed on August 19, 2022.

1. Chemicalbook: https://www.chemicalbook.com

2. Pubchem: https://pubchem.ncbi.nlm.nih.gov

3. T. White, SRNL-STI-2021-00453, Rev. 1: Nash, C.A., Skeen, R.S., Miskho, A.G., White, T.L., McCabe, D.J., “Potential for Evaporation and In Situ Reaction of Organic Compounds in Hanford Supplemental LAW “, SRNL-STI-2021-00453, Rev. 1, January 2022.

4. NIH: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6140667/

5. Chemicalbook for Aramite: https://www.chemicalbook.com/ChemicalProductProperty_EN_CB3304743.htm

6. Methoxychlor reference: https://pubchem.ncbi.nlm.nih.gov/compound/Methoxychlor#section=Other-Experimental-Properties

7. Bordwell: https://organicchemistrydata.org/hansreich/resources/pka/

8. Disulfoton reference: https://webwiser.nlm.nih.gov/substancesubstanceId=223&identifier=Disulfoton&identifierType=name&menuItemId=44&catId=51

9. Cyclohexanone reference: https://foodb.ca/compounds/FDB003418

10. tris-(2,3-Dibromopropyl) phosphate reference: https://apps.who.int/iris/bitstream/handle/10665/37119/924157173X-eng.pdf?sequence=1&isAllowed=y

11. Endosulfan references: https://www.canr.msu.edu/news/effect_of_water_ph_on_the_stability_of_pesticides

12. Methylmethacrylate reference: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3382811/

13. Benzal chloride reference: https://eprints.lib.hokudai.ac.jp/dspace/bitstream/2115/24785/1/12%283%29_P223-229.pdf

14. Ethyl methacrylate reference: https://eprints.lib.hokudai.ac.jp/dspace/bitstream/2115/24785/1/12%283%29_P223-229.pdf

15. trans-1,3-Dichloropropylene reference: https://www.ars.usda.gov/ARSUserFiles/50600000/Products-Reprints/2004/1102.pdf

16. Lab work 2022: SRNL-STI-2022-00391, in revision

17. ester: Esters undergo alkaline hydrolysis.

18. Bromodichloromethane reference: http://www.stenutz.eu/chem/pka.php?s=3&p=42

19. cis-1,3-Dichloropropylene reference: https://www.ars.usda.gov/ARSUserFiles/50600000/Products-Reprints/2004/1102.pdf

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The WRPS customer had requested a reactivity assessment for 14 of the LDR chemicals. Charles Nash had provided the response below on June 7, 2022.

1. Diphenylamine: Not reactive, no deprotonation (Bordwell pKa Table, https://organicchemistrydata.org/hansreich/resources/pka/#kaamine, viewed 02/14/2022).
    - Reactive to air oxidation along with a list of other oxidants under alkaline conditions, Willard, H.H., and Manalo, G.D., "Derivatives of Diphenylamine as Oxidation-Reduction Indicators on Alkaline Solution", Analytical Chemistry, 19, 3, March 1947.
2. 1,4 Dioxane: Not reactive, but has a slight tendency to form organic peroxides as other ethers do with air.
    P. Howard, "Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Volume I - Large Production and Priority Solvents", Lewis Publishers, Chelsea, Michigan, 1989.
    Surprenant, K. S., "1,4 Dioxane", in Ullmann's Encyclopedia of Industrial Chemistry (6th ed.), Vol. 10, pp.543-548, Weinheim, Germany: Wiley-VCH Verlag, (2003).
3. Methacrylonitrile: Reactive - Nitriles readily hydrolyze to NH3 and carboxylic acid in alkali.*
4. 3-chloropropylene: Reactive - hydrolyses with alkali in solution.

Antony, R., Nandagopal, G., Manikrishna, C., and Narayanasamy, S., "Experimental Comparison on Efficiency of Alkaline Hydrolysis Reaction in Circular Microreactors over Conventional Batch Reactor", Journal of Scientific and Industrial Research 74(7), 390-394, July 2015.

PubChem (https://pubchem.ncbi.nlm.nih.gov/compound/Allyl-chloride#section=Toxic-Combustion-Products) viewed 02/14/2022.

5. 1,1,2-trichloro-1,2,2-trifluoroethane: Not reactive at ambient temperature.
   European patent EP0355907A1 (Inventors Lerot, L., Wilmet, V., and Pirotton, J., 1992) finds this chemical reacts with alkali metal hydroxides in a vapor flow system at temperatures recommended to exceed 200 °C.
6. 1,2-dichlorobenzene: Not reactive by alkaline hydroysis,
   Ellenton, J.J., Stancil, F.E., Payne, W.D., and Trusty, C.D., "Measurements of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal: Volume 3, Data on 70 Chemicals", EPA/600/S3-88/028, 1988.
7. 2-chlorophenol: Not reactive,
   Serpone, N., Maruthamuthua, N., Pichat, P., Pelizzettic, E., Hidakad, H., "Exploiting the interparticle electron transfer process in the photocatalysed oxidation of phenol, 2-chlorophenol and pentachlorophenol: chemical evidence for electron and hole transfer between coupled semiconductors", Journal of Photochemistry and Photobiology A: Chemistry, 85, 3, pp. 247-255, January 1995.
8. 4-chloroaniline: Not reactive,
   https://pubchem.ncbi.nlm.nih.gov/compound/4-Chloroaniline, citing Lyman WJ et al; Handbook of Chemical Property Estimation Methods. Washington, DC: American Chemical Society, pp. 7-4, 7-5 (1990) Viewed 02/12/2022.
9. 4-nitroaniline: Not reactive in alkali.
   Gabbay J., Davidson M., Donagi A.E., Analyst, 101, 128 (1976).
10. Bromomethane: Reactive. Base-catalyzed hydrolysis is rapid. The rate constant for the aqueous hydrolysis of bromoethane at 25 °C and pH 7 has been reported to be 2.64 × 10–7/s, which corresponds to a half-life of 30 days (Mabey & Mill, 1978). Jeffers & Wolfe (1997) report half-lives of 21 and 5 days for bromoethane at 25 °C and 35 °C, respectively.
    Mabey W., Mill T. (1978) Critical reviews of hydrolysis of organic compounds in water under environmental conditions. Journal of Physical and Chemical Reference Data, 7:383–415.
    Jeffers P.M., Wolfe N.L. (1997) Hydrolysis of methyl bromide, ethyl bromide, chloropicrin, 1,4-dichloro-2-butene, and other halogenated hydrocarbons. Fumigants, 652:32–41.
11. Dibenzo(a,h)anthracene: Not reactive, water solubility very low, - PAH.
12. Dichlorodifluoromethane: Not reactive, - would be less reactive than trichlorofluoromethane due to more fluorination, see:
    SRNL-STI-2021-00453, rev. 1, Appendix B, "Trichlorofluoromethane".
    Jeffers, P.M., Wolfe, N.L.. “Homogeneous hydrolysis rate constants - Part II: Additions, corrections and halogen effects,” Environmental Toxicology and Chemistry, 15(7), pp. 1066-1070, (1996)
13. 1,2,4,5-tetrachlorobenzene: Not reactive. Very low water solubility. Alkaline hydrolysis needs >260 °C.
    US Patent 2,799,713, "Method of Making Trichlorophenols from Tetrachlorobenzenes", (inventors Widiger, A.H., Aaron, M.L., and Dugan, G.F., 1957).
    Sodium Methoxide/methanol can promote base hydrolysis. Qiu, Y., Eriksson, J., Granelli, L., and Bergman, A., "Improved method for assessing relative nucleophilic substitution reactivities of polychlorinated benzenes", Chemosphere 75, pp. 78–82, (2009).
14. Acrylonitrile: Reactive - Nitriles readily hydrolyze to NH3 and carboxylic acid in alkali.*

*Nitriles (acetonitrile and acetonitrile) vanished quickly in alkaline hydrolysis in Taylor-Pashow, K., Choi, A.S., McClane, D.L., McCabe, D.J., “Iodine Distribution During Evaporation of Hanford Waste Treatment Plant Direct Feed Low Activity Waste Effluent Management Facility Simulant”, SRNL-STI-2019-00471, October 2019.
Also SRNL-STI-2021-00453, rev. 1, Appendix B, nitriles.

Appendix C

Radiolysis

Charles L. Crawford, Ph. D.

There was a question that decades of radioactivity in Hanford nuclear waste tanks might beneficially degrade regulated organic chemicals in the waste in a way that might be claimed as treatment. At SRNL Charles Crawford looked into the radiolysis issue and generally found that (1) high salt and alkali, and (2) low organic chemical concentration work against chemical degradation by radiolysis in alkaline tank waste.

Charles Crawford used the PNNL-11909 report that shows thermolysis is of more significance. He pointed out that chemicals with aromatic rings are extra stable against radiolysis compared to alkanes, chains, etc. PNNL report PNNL-11312 shows very high gamma doses needed to remove specific chemicals that were spiked into simulants of Hanford tank supernates. This is a complicated topic, but it is likely that the Hanford 222-S analytical laboratory would stop detecting regulated organics in tank samples if the years of waste aging was effective in removing the unwanted organic chemicals.

The work in this appendix reports “G-values”. These are in units of the number of molecules of degradation product per 100 electron volts of ionizing radiation energy absorbed by a material. G values appear in the y-axes of the figures below.

The ‘Organic G Values’ Canadian Journal of Chemistry article pertains to dilute acidic aqueous solutions of organics with no competing, highly concentrated solutes such as those found in caustic nuclear waste salt solutions, i.e., nitrate, nitrite, hydroxide and others.[i] Thus the G-values shown in this paper from Tables I through IV are likely not representative of expected G-values for the radiolytic destruction of ~ 0.1 Molar soluble organics in aqueous nuclear waste solutions. The chemical reactions cited in this paper for reactions 1-7 pertain to water decomposition products ($H^{\cdot}$ and $OH^{\cdot}$) reacting with the dissolved organic solutes which leads to their destruction. It is likely in the presence of relatively higher concentrations of salt solution solutes (Nitrate, Nitrite and Hydroxide) that these reactions shown in 1-7 would be significantly reduced due the ‘competition kinetics’ of the other inorganic solutes reacting with these same water decomposition products ($H^{\cdot}$ and $OH^{\cdot}$).

The PNNL ‘Waste Aging Studies Final Report’ details experimental and modeling for concentrated organic complexants and their radiolytic degradation in the presence of inorganic solutes shown in Table 4.1 of the PNNL report.[ii] References to tables and equations below are referring to tables and equations in the PNNL report. The most applicable section of this report is Section 3.0 presenting relative rate constants and experimental data for both formate and glycine destruction in presence of typically 1.25 M nitrite, 3.75 M nitrate and 2 M hydroxide. Tables 3-2 and 3-4 offer kinetic modeling equations for the radiolysis of the caustic simulant in presence of formate (Equations 1-28) and glycine (Equations 29-36), respectively. For instance, equations 8, 10, 12 and 13 of Table 3-2 show reactions of formate with water radiolysis primary products. Similar reactions are shown in Table 3-4 as Equations 29 – 32 for glycine. Experimental data for radiolysis of these simulants is shown in Table 3.3 for carbonate product yields vs. increasing formate concentration (with nitrite, nitrate and hydroxide held constant), and in Table 3.5 for change in glycine destruction vs. increase in nitrite (with nitrate and hydroxide held constant).

Figure 1 and Figure 2 below show the formate (Molar) data (from Table 3.3) plotted with all data and only the lower concentrations of formate, respectively. Figure 3 and Figure 4 show similar plots with formate expressed as mg/L concentrations. These data show a significant drop in carbonate product formation as the formate concentration goes below ~ 0.4 Molar or ~ 18,000 mg/L. The plots show a finite production of product carbonate with a G-value of ~ 0.2 even as formate goes to zero concentration. This data is interpreted as a decreasing role of formate plus water decomposition products (Equations 8, 10, 12 and 13 of Table 3-2) as the initial formate concentration decreases, allowing all the other reactions of Table 3-2 to preferentially take place, i.e., a demonstration of 'competition kinetics'.

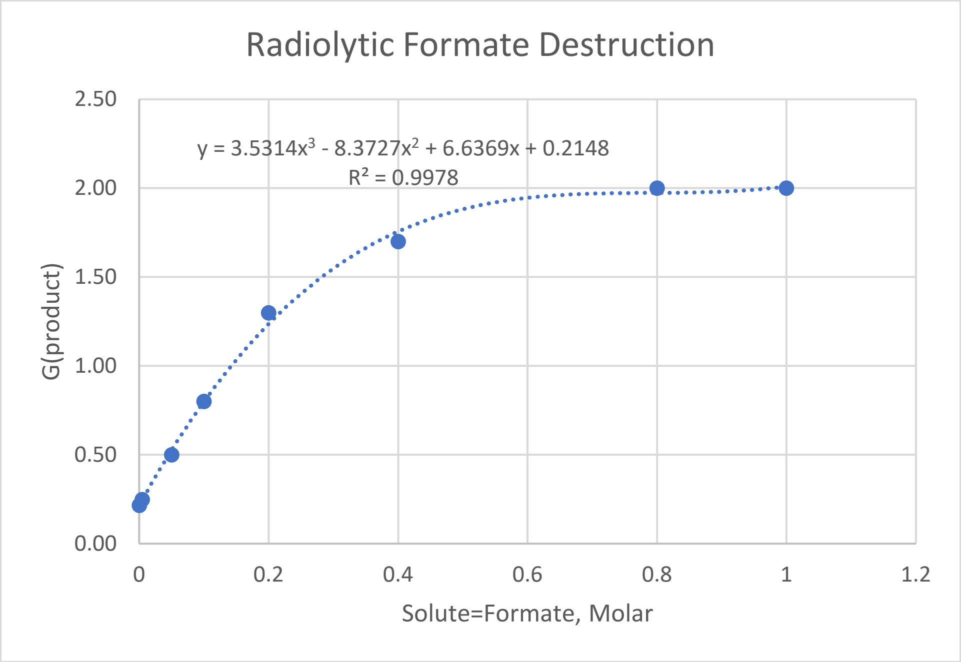

Figure 1. Radiolytic Formate Destruction – Full Data, Molar Formate

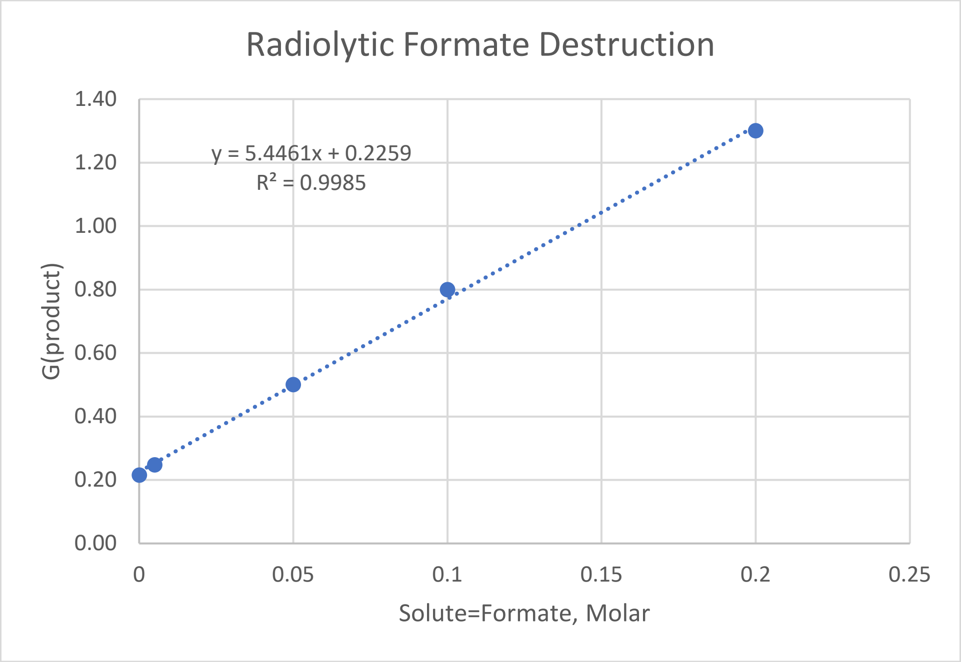

Figure 2. Radiolytic Formate Destruction – Lower Concentrations of Molar Formate

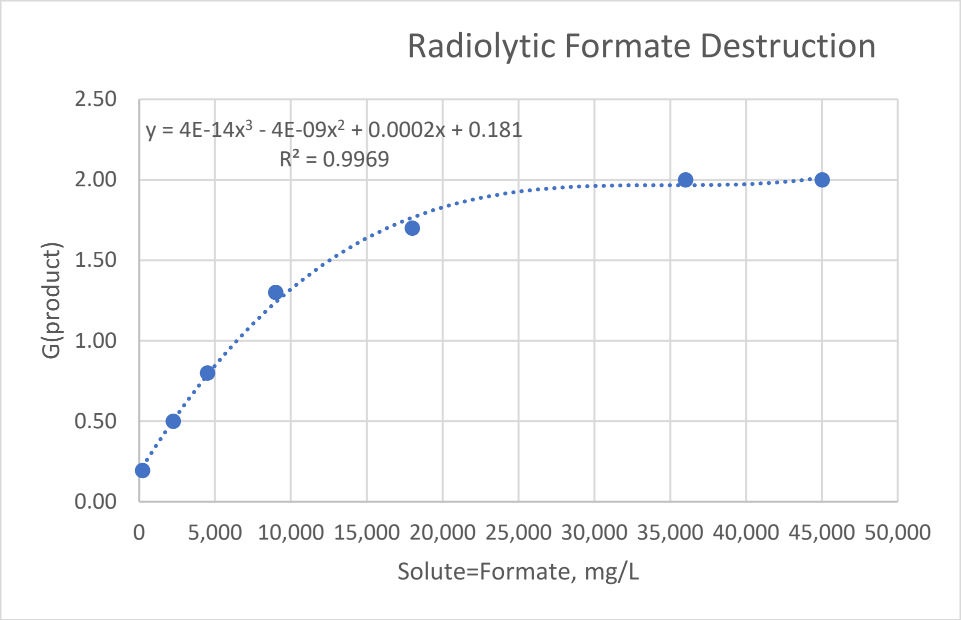

Figure 3. Radiolytic Formate Destruction – Full Data, mg/L Formate

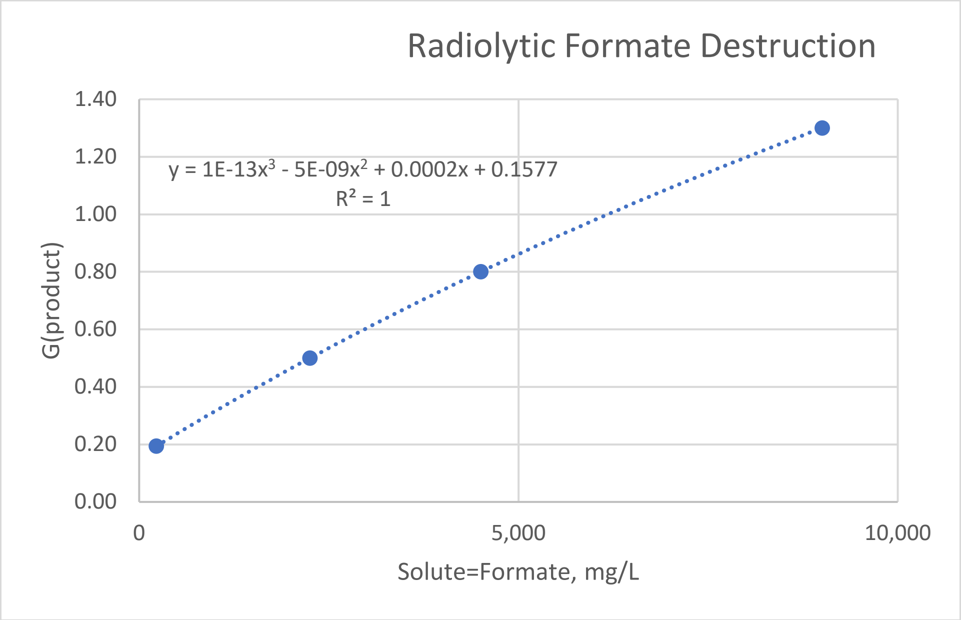

Figure 4. Radiolytic Formate Destruction – Lower Concentrations of mg/L Formate

Figure 5 uses Table 3-5 data and shows the change (decrease) in the destruction of initial glycine (constant 0.08 Molar concentration) as the nitrite concentration is increased with nitrate and hydroxide held constant

(3.75 M nitrate and 2 M hydroxide). With no nitrite present, the initial glycine shows a G-(glycine) of ~ 3.7 molecules/100 eV. As the nitrite is increased, the 'reactivity' of the initial glycine decreases due to the competition of increasing nitrite with the initial water decomposition products, i.e., Equations 29-32 of Table 3-4 become less dominant as competing nitrite is increased.

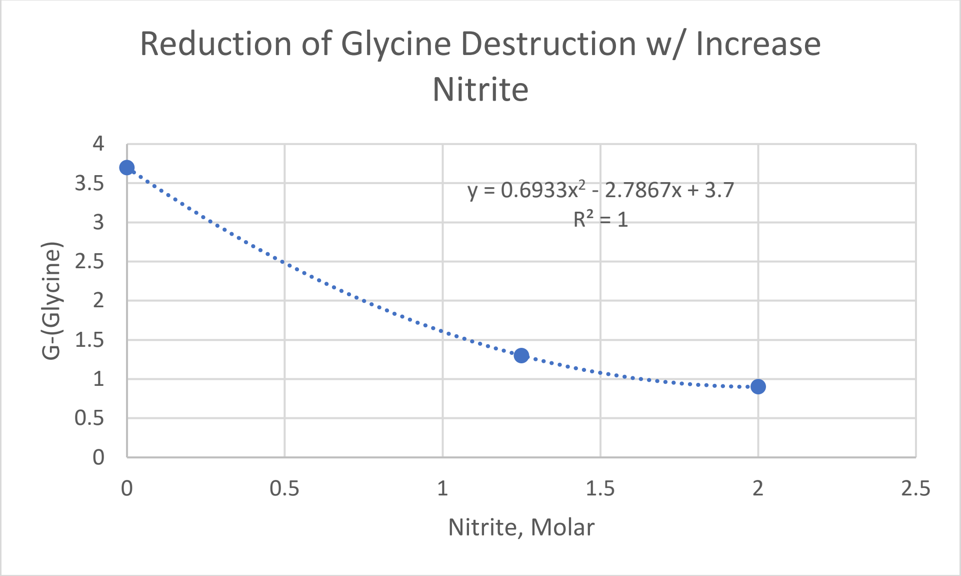

Figure 5. Decrease in Radiolytic Destruction of Glycine as Nitrite is Increased

Both of these experimental data sets (formate and glycine) emphasize the role of organic concentration in the resulting radiolytic destruction in presence of relatively high levels of the inorganic solutes nitrate, nitrite and hydroxide. These data and the model equations indicate that as the organic concentration in a relatively high concentrated salt solution decreases, it is expected that lower radiolytic decomposition of the organic occurs.

References:

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[i] R. J. Woods and J. W. T. Spinks, "The Radiolysis of Some Organic Halogen Compounds in Aqueous Solution", Can. J. Chem., Vol. 38, 1960.

[ii] D. M. Camaioni, W.D. Samuels, J.C. Linehan, A.K. Sharma, S.T. Autrey, M.A. Lilga, M.O. Hogan, S.A. Clauss, K.L. Wahl, and J.A. Campbell, "Organic Tanks Safety Program Waste Aging Studies Final Report", PNNL-11909, Rev. 1, UC-2030, September 1998.

Appendix D

Rodney Skeen, PhD, P.E.

This section gives an initial assessment of Hanford tank exceedances of regulated organic chemicals.

Methods

Source Data

LDR compound concentration data from liquid and solid samples were extracted on August 18, 2022 from TWINS source data using the Tableau-based LDR Compound visualization tool developed by the Pacific Northwest National Laboratory (PNNL). The data for all LDR compounds were downloaded from Tableau and imported into Excel. The subset of LDR organic compounds that could be expected to be present in Hanford tank waste was extracted from the Excel workbook that accompanies RPP-RPT-63493, Rev. 0 (*Tank Waste LDR Organics Data Summary for Sample-and-Send*). Data on the current status of each single shell tank (SST) and double shell tank (DST) were derived from Tables 4.1 and 3.1 in HNF-EP-0182, Rev. 413 (*Tank Waste Summary Report for Month Ending May 31,2022*). Data for the sodium concentrations, phase volumes, and phase densities of waste in each tank were downloaded from the Best Basis Inventory (BBI) section of the TWINS web-based interface on August 8, 2022. Estimates of the amount of liquid waste that would be generated during the retrieval of SST saltcake and sludges were derived from TopSim model run MR-50717 (*2022 Baseline Planning Basis Modeling Scenario*).

Data Reduction

Tanks with at least one solid or liquid sample result for an LDR organic other than PCBs, and those with at least one solid or liquid sample result for PCBs, were identified. Entries for both detections and non-detections were considered since both indicate information on the concentration of these compounds within a tank. Note that the Tableau LDR compound interface identifies a non-detected value based on the presence of an associated “U” analytical qualifier flag in TWINS. Also, Tableau selects only TWINS results labeled as a “Primary_Result” since those labeled “Duplicate_Result” or “Triplicate_Result” have been determined to be laboratory splits used in quality assurance calculations and do not always carry the correct analytical qualifier flags (Michael Lindberg, personal communication).

Starting with the full data download the Excel filter feature was used to create subsets of the data for:

1. detection and non-detection results for LDR organics, including PCBs,
2. detection and non-detection results for LDR organics excluding PCBs,
3. detection and non-detection results for only PCBs,
4. detections for LDR organics, including PCBs,
5. detections for LDR organics excluding PCBs, and
6. detections for only PCBs.

These six data subsets were then accessed by various Excel VLOOKUP functions to identify the unique tanks in each in each of the six subsets. Tanks with only PCB data were identified as those tanks that are part of Subset 3 but not Subset 2 (or if non-detects are excluded then part of Subset 6 but not Subset 5).

Liquid sample data were converted to a final concentration in a cementitious waste form to compare with the 40 CFR 268.40 and §48 non-wastewater (NWW) standards by assuming that tank supernate would be directly retrieved and then the solution would be adjusted to 5.5 M sodium since the material would be processed through a tank side cesium removal system (TSCR) prior to solidification. For all cases, this resulted a decrease from of the in-tank concentration of between 3% and 84%. Next it was assumed that the 5.5 M sodium solution would be mixed with solidifying reagents to make a waste form similar to Cast Stone (PNNL-25194). Adding the solidification materials was assumed to increase the volume of the waste by 80% and create a final waste form having a density of 1.77 g/mL (SRNL-RP-2018-0087, *Report of Analysis of Approaches to Supplemental Treatment of Low-Activity Waste at the Hanford Nuclear Reservation*). Equation 1 describes the relationship between the in-tank measured liquid concentration and the concentration in the final waste form:

$$C_{i,grout} = C_{i,liquid} \cdot \frac{5.5}{C_{Na}} \cdot \frac{r_{l/g}}{\rho_{grout}} \qquad (1)$$

Where:

$C_{i,grout}$ = Concentration of the ith organic in the solidified waste form (mg/Kg)
$C_{i,liquid}$ = Concentration of the ith organic measured in tank waste liquid (mg/L)
C_{Na} = Concentration of Na in the waste stream (M)
$r_{l/g}$ = Liquid to solid volume ratio (0.556 L_{liquid}/L_{solid})
ρ_{grout} = Density of the final solid waste form (1.77 g/mL).

For solid samples, the concentration of the organic in the final waste form was estimated by first assuming the material would be completely extracted and dissolved in the volume of retrieval liquid estimated by TopSim (for SSTs), or by a volume that is 3x the volume of the tank solids (for DSTs, see Section A.4.9 of RPP-RPT-62957, Rev. 1, *Direct Feed High-Level Waste Washing Evaluation*). For tanks that contained both saltcake and sludge, the retrieval liquid volume (and consequently the organic compound concentration) was adjusted to produce a sodium concentration of 5.5 M. No adjustment based on sodium was made for tanks that were all sludge since the sodium content of the retrieved solutions were so low (0.53 M or less) that concentrating the material to 5.5 M sodium would not result in a liquid solution. The final waste form was assumed to be similar to Cast Stone and adding the solidification materials would increase the volume of the waste by 80% and create a final waste form having a density of 1.77 g/mL. Equations 2 and 3 describe the relationship between the in-tank LDR organic compound solids concentration and the final waste form for tanks that contain saltcake or sludge and saltcake (Equation 2), or tanks that only contain sludge (Equation 3).

$$C_{i,grout} = C_{i,solids} \cdot \frac{M_{solids}}{V_{retrieve}} \cdot \frac{5.5}{C_{Na}} \cdot \frac{r_{l/g}}{\rho_{grout}} \qquad (2)$$

(3)

$$C_{i,grout} = C_{i,solids} \cdot \frac{M_{solids}}{V_{retrieve}} \cdot \frac{r_{l/g}}{\rho_{grout}}$$

Where:

$C_{i,solids}$ =	Concentration of the i^{th} organic measured in tank waste solids (mg/Kg)
M_{solids} =	Mass of solids (saltcake and sludge) in the tank (Kg)
$V_{retrieve}$=	Retrieval volume calculated by TopSim (L)

Results

Extent of Tank Sampling Data

Figures 1 and 2 represent the number of unretrieved tanks that have LDR organic data for either a liquid or solid sample recorded in TWINS as of August 18, 2022. Retrieved tanks (Table 1) were excluded from this portion of the assessment since while information on the historic concentration of LDR organics is these tanks is relevant to what organics may be found in Hanford tanks, it is not relevant to future waste treatment decisions that must be made for unretrieved tanks. The retrieved tanks excluded from this assessment are indicated in Table 1. This list includes the DST AY-102 and the SSTs labeled in Table 4.1 of HNF-EP-0182, Rev 413 as having a status of in retrieval, retrieval complete, or retrieval complete but in review.

Table 1: Retrieved Tanks

Count	Tank	Count	Tank
1	AX-102	12	C-107
2	AX-103	13	C-108
3	AX-104	14	C-109
4	AY-102	15	C-110
5	S-112	16	C-111
6	C-101	17	C-112
7	C-102	18	c-201
8	C-103	19	C-202
9	C-104	20	C-203
10	C-105	21	C-204
11	C-106	--	--

Entries for both detections and non-detections were included in this assessment since both indicate information on the concentration of these compounds within a tank. Note that information on polychlorinated biphenyls (PCBs) is treated independent of the other LDR organics since it is measured using a unique analytical method and PCB analysis has been emphasized at Hanford to support Toxic Substance Control (TSCA) decisions. Hence, the presence of a PCB measurement does not indicate that other LDR organics were also measured for that sample. In contrast, the analytical methods used to measure most of the other LDR organics simultaneously measure multiple compounds.

As indicated in Figures 1 and 2 there are 31 unretrieved tanks with LDR organics (excluding PCBs) information in TWINS and 93 unretrieved tanks with PCB information. Appendix D-1 provides a list of the 156 unretrieved tanks along with an indication if TWINS data is available for PCBs or the other LDR organics.

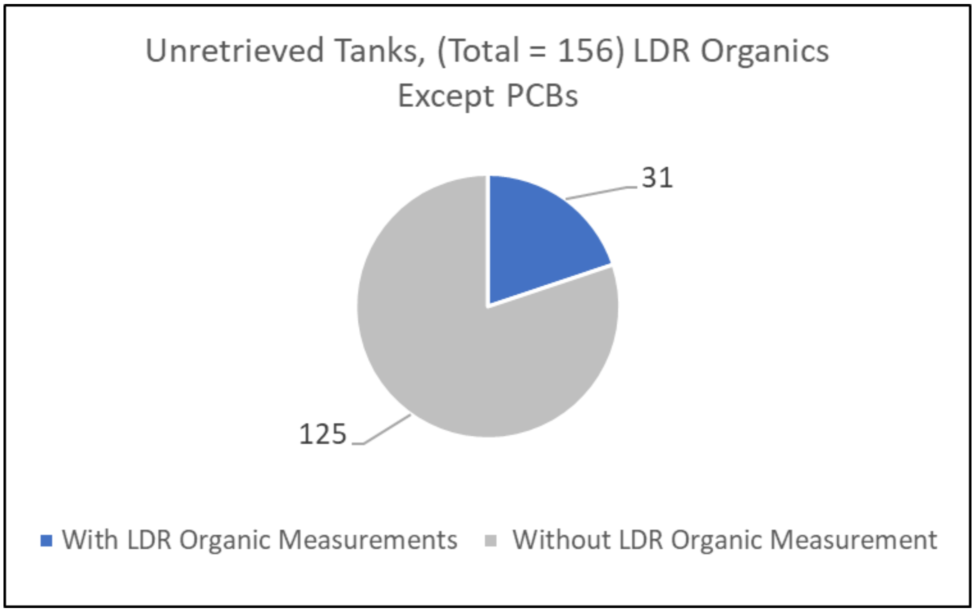

Figure 1: Number of unretrieved tanks with LDR organic compound data (excluding PCBs) in the TWINS data base. Reported detected and undetected values were included in the data set evaluated.

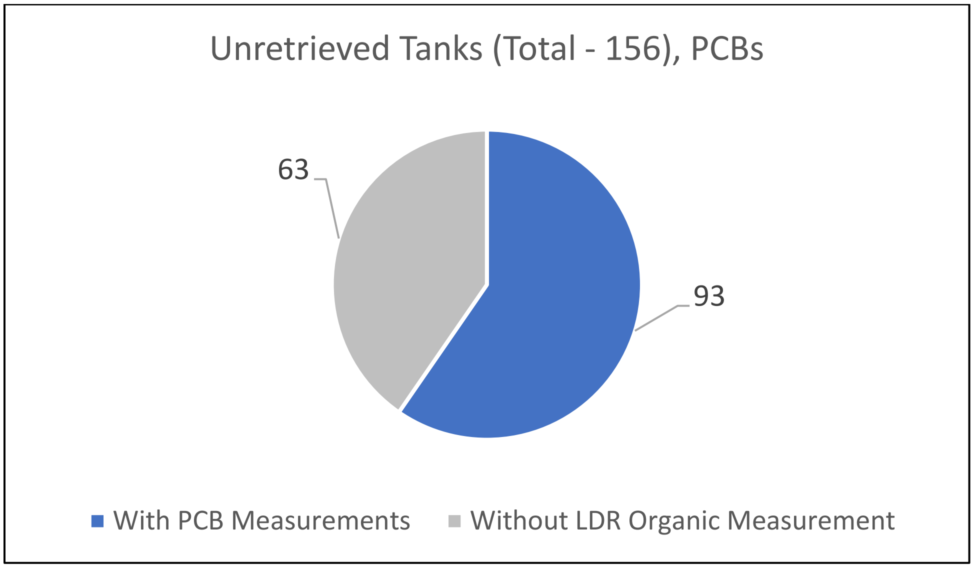

Figure 2: Number of unretrieved tanks with PB data in the TWINS data base. Reported detected and undetected values were included in the data set evaluated.

A review of which of the 207 LDR organic compounds associated with Hanford Tank Waste have data in TWINS that 124 have at least one detection or a non-detection entry. Table 2 provides a list of the 207 LDR organic compounds and an indication of the number of entries in TWINS that correspond to each. Compounds with no data in TWINS are identified in Table 2 with a “No Values” entry in the last column.

It is important to note that a data quality objective (DQO) process specific to sampling tank waste for solidification and stabilization in a cementitious waste form is needed to identify if additional analytical methods are necessary.

Table 2: List of 207 LDR Compounds Along with an Indication of the Number of Entries for Each in TWINS

Name	CAS Number	Number of Entries in TWINS
All Aroclors	1336-36-3	6452
Acetone	67-64-1	347
2-Butanone	78-93-3	336
1,2,4-Trichlorobenzene	120-82-1	321
n-Butyl alcohol	71-36-3	318
1,4-Dichlorobenzene	106-46-7	306
Hexachloroethane	67-72-1	299
Trichloroethylene	79-01-6	288
Toluene	108-88-3	286
Benzene	71-43-2	273
1,2-Dichlorobenzene	95-50-1	273
4-Methyl-2-pentanone	108-10-1	268
Chlorobenzene	108-90-7	265
1,1-Dichloroethylene	75-35-4	264
Pentachlorophenol	87-86-5	263
Butyl benzyl phhalate	85-68-7	250
Phenol	108-95-2	247
Methylene chloride	75-09-2	245
N-Nitroso-di-n-propylamine	621-64-7	240
Acenaphthene	83-32-9	240
p-Chloro-m-cresol	59-50-7	240
2,4-Dinitrotoluene	121-14-2	240
Pyrene	129-00-0	239
Nitrobenzene	98-95-3	239
2,4,5-Trichlorophenol	95-95-4	239
p-Nitrophenol	100-02-7	238
2-Chlorophenol	95-57-8	238
Hexachlorobutadiene	87-68-3	238
di-n-Butyl phthalate	84-74-2	234
bis(2-ethylhexyl)phthalate	117-81-7	233
Di-n-octyl phthalate	117-84-0	233

Name	CAS Number	Number of Entries in TWINS
2-Nitrophenol	88-75-5	230
Fluoranthene	206-44-0	230
Naphthalene	91-20-3	230
2,4,6-Trichlorophenol	88-06-2	230
1,2-Dichloroethane	107-06-2	228
o-Cresol	95-48-7	228
Xylene(m,p,o)	1330-20-7	227
Chloroform	67-66-3	225
Carbon tetrachloride	56-23-5	225
Tetrachloroethylene	127-18-4	224
Vinyl chloride	75-01-4	224
Ethyl benzene	100-41-4	222
1,1,1-Trichloroethane	71-55-6	217
trans-1,3-Dichloropropylene	10061-02-6	217
1,1,2-Trichloroethane	79-00-5	217
Carbon disulfide	75-15-0	217
Diethyl phthalate	84-66-2	216
1,1,2,2-Tetrachloroethane	79-34-5	213
Hexachlorobenzene	118-74-1	211
Benzo(a)pyrene	50-32-8	207
Dibenzo(a,h)anthracene	53-70-3	207
2,4-Dinitrophenol	51-28-5	201
4-Nitroaniline	100-01-6	201
4,6-Dinitro-o-cresol	534-52-1	201
2-Nitroaniline	88-74-4	201
Anthracene	120-12-7	201
Benzo(k)fluoranthene	207-08-9	201
Chrysene	218-01-9	201
Dimethyl phthalate	131-11-3	201
Phenanthrene	85-01-8	201
bis(2-Chloroethoxy)methane	111-91-1	201
Acenaphthylene	208-96-8	201
2,4-Dichlorophenol	120-83-2	201
2,4-Dimethyl phenol	105-67-9	201
2-Chloronaphthalene	91-58-7	201
4-Bromophenyl phenyl ether	101-55-3	201
4-Chloroaniline	106-47-8	201

Name	CAS Number	Number of Entries in TWINS
Benz(a)anthracene	56-55-3	201
Benzo(b)fluoranthene	205-99-2	201
Fluorene	86-73-7	201
Indeno(1,2,3-c,d) pyrene	193-39-5	201
2,6-Dinitrotoluene	606-20-2	201
Benzo(g,h,i)perylene	191-24-2	199
bis(2-Chloroethyl)ether	111-44-4	199
1,1-Dichloroethane	75-34-3	194
Chloromethane	74-87-3	193
Bromomethane	74-83-9	193
Chloroethane	75-00-3	193
cis-1,3-Dichloropropylene	10061-01-5	191
Hexachlorocyclopentadiene	77-47-4	191
Bromoform	75-25-2	189
1,2-Dichloropropane	78-87-5	189
Bromodichloromethane	75-27-4	188
Dibromochloromethane	124-48-1	188
1,3-Dichlorobenzene	541-73-1	164
Pyridine	110-86-1	148
p-Cresol	106-44-5	117
Isobutyl alcohol	78-83-1	113
N-Nitrosomorpholine	59-89-2	112
Diphenylnitrosamine	86-30-6	112
Cyclohexanone	108-94-1	110
N-Nitrosodimethylamine	62-75-9	94
Diphenylamine	122-39-4	85
Trichlorofluoromethane	75-69-4	85
1,1,2-Trichloro-1,2,2-trifluroethane	76-13-1	82
Ethyl acetate	141-78-6	81
Ethyl Ether	60-29-7	80
1,2-Dibromoethane/Ethylene dibromide	106-93-4	62
Cresols (m,p,o)	1319-77-3	55
trans-1,2-Dichloroethylene	156-60-5	52
Dichlorodifluoromethane	75-71-8	50
1,2-Dibromo-3-chloropropane	96-12-8	49
m-Cresol	108-39-4	20
Acetonitrile	75-05-8	12
1,4-Dioxane	123-91-1	8

Name	**CAS Number**	**Number of Entries in TWINS**
Methoxychlor	72-43-5	3
Endosulfan sulfate	1031-07-8	3
gamma-BHC	58-89-9	3
beta-BHC	319-85-7	3
delta-BHC	319-86-8	3
p,p′-DDD	72-54-8	3
alpha-BHC	319-84-6	3
Endrin	72-20-8	3
Dieldrin	60-57-1	3
Aldrin	309-00-2	3
Heptachlor epoxide	1024-57-3	3
p,p′-DDT	50-29-3	3
p,p′-DDE	72-55-9	3
Endosulfan I	959-98-8	3
Endosulfan II	33213-65-9	3
Heptachlor	76-44-8	3
1,1,1,2-Tetrachloroethane	630-20-6	3
Phthalic anhydride	85-44-9	1
Phthalic acid	100-21-0	No Values
Methapyrilene	91-80-5	No Values
4,4-Methylene bis(2-chloroaniline)	101-14-4	No Values
2-Acetylaminofluorene	53-96-3	No Values
Phenacetin	62-44-2	No Values
1,3-Phenylenediamine	108-45-2	No Values
Acrylamide	79-06-1	No Values
Silvex/2,4,5-TP	93-72-1	No Values
5-Nitro-o-toluidine	99-55-8	No Values
Famphur	52-85-7	No Values
2,4,5-Trichlorophenoxyacetic acid/2,4,5-T	93-76-5	No Values
2,4-Dichlorophenoxyacetic acid/2,4-D	94-75-7	No Values
Dibenz(a,e)pyrene	192-65-4	No Values
N-Nitrosopyrrolidine	930-55-2	No Values
Kepone	143-50-0	No Values
Chlorobenzilate	510-15-6	No Values
2-Naphthylamine	91-59-8	No Values
4-Aminobiphenyl	92-67-1	No Values
Methyl parathion	298-00-0	No Values
Aramite	140-57-8	No Values
1,4-Dinitrobenzene	100-25-4	No Values

Name	CAS Number	Number of Entries in TWINS
p-Dimethylaminoazobenzene	60-11-7	No Values
Parathion	56-38-2	No Values
2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	No Values
1,2-Diphenylhydrazine	122-66-7	No Values
p-Cresidine	120-71-8	No Values
N-Nitrosopiperidine	100-75-4	No Values
o-Anisidine (2-methoxyaniline)	90-04-0	No Values
N-Nitrosomethylethylamine	10595-95-6	No Values
Disulfoton	298-04-4	No Values
2,4-Dimethylaniline (2,4-xylidine)	95-68-1	No Values
N-Nitrosodiethylamine	55-18-5	No Values
Methyl methanesulfonate	66-27-3	No Values
2,6-Dichlorophenol	87-65-0	No Values
Endrin aldehyde	7421-93-4	No Values
Phorate	298-02-2	No Values
Methanol	67-56-1	No Values
3-Methylcholanthrene	56-49-5	No Values
Toxaphene	8001-35-2	No Values
o,p′-DDT	789-02-6	No Values
o,p′-DDD	53-19-0	No Values
Safrole	94-59-7	No Values
o,p′-DDE	3424-82-6	No Values
tris-(2,3-Dibromopropyl) phosphate	126-72-7	No Values
Ethyl cyanide/Propanenitrile	107-12-0	No Values
Isodrin	465-73-6	No Values
Chlordane (alpha and gamma isomers)	57-74-9	No Values
Acrolein	107-02-8	No Values
Ethylene oxide	75-21-8	No Values
Methacrylonitrile	126-98-7	No Values
Methyl methacrylate	80-62-6	No Values
bis(2-Chloroisopropyl)ether	39638-32-9	No Values
Benzal chloride	98-87-3	No Values
Isosafrole	120-58-1	No Values
Ethyl methacrylate	97-63-2	No Values
Dibromomethane	74-95-3	No Values
Pentachloroethane	76-01-7	No Values
Hexachloropropylene	1888-71-7	No Values
Iodomethane	74-88-4	No Values
2-Chloroethyl vinyl ether	110-75-8	No Values

Name	CAS Number	Number of Entries in TWINS
3-Chloropropylene	107-05-1	No Values
2-Chloro-1,3-butadiene	126-99-8	No Values
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD)	35822-46-9	No Values
1,2,3,4,6,7,8-Heptachlorodibenzofluran (1,2,3,4,6,7,8-HpCDF)	67562-39-4	No Values
1,2,3,4,7,8,9-Heptachlorodibenzofluran (1,2,3,4,7,8,9-HpCDF)	55673-89-7	No Values
HxCDDs (All Hexachlorodibenzo-p-dioxins)	NA	No Values
HxCDFs (All Hexachlorodibenzofurans)	NA	No Values
N-Nitroso-di-n-butylamine	924-16-3	No Values
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9	No Values
1,2,3,4,6,7,8,9-Octachlorodibenzofluran (OCDF)	39001-02-0	No Values
Pentachlorobenzene	608-93-5	No Values
PeCDDs (All Pentachlorodibenzo-p-dioxins)	NA	No Values
PeCDFs (All Pentachlorodibenzofurans)	NA	No Values
Pentachloronitrobenzene	82-68-8	No Values
Pronamide	23950-58-5	No Values
1,2,4,5-Tetrachlorobenzene	95-94-3	No Values
TCDDs (All Tetrachlorodibenzo-p-dioxins)	NA	No Values
TCDFs (All Tetrachlorodibenzofurans)	NA	No Values
2,3,4,6-Tetrachlorophenol	58-90-2	No Values
1,2,3-Trichloropropane	96-18-4	No Values
Acetophenone	98-86-2	No Values
Acrylonitrile	107-13-1	No Values
Aniline	62-53-3	No Values

Extent of Potential NWW Standard Exceedances in Grouted Tank Waste

Table 3 summarizes the estimated potential exceedances of the NWW standard for cementitious waste forms made from retrieved tank waste. Measured supernate levels of n-butyl alcohol in four DSTs (AP-104, AP-107, AW-102, and AW-104) are sufficient to result in a waste form that exceeds the NWW standard. The range of final waste form concentrations is from 1.6 to 6.3 times the NWW standard of 2.6 mg/Kg. N-Nitrosomorpholine supernate levels measured in 2019 in the DST AN-107 are sufficient to result in a predicted cementitious waste form that is 1.1 times the NWW standard of 2.3 mg/Kg. It is important to note that the current contents of all theses DSTs except AN-107 are not the same as that represented in Table 3 since there have been significant transfers in and out of each tank since the date the exceeding concentration was measured (see Column 5 of Table 3). A review of the tank transfer data from TWINS that occurred after the indicated sample date in Table 3 for AP-104, AP-107, and AW-102 indicate more than 4 million gallons of supernate has been both added and removed from each tank since the date of the sample indicated in Table 3. For AW-104, the removal volume (904,000 gallons) and addition volume (802,000 gallons) are also significant when compared to the volume in the tank when the sample was taken (approximately 900,000 gallons). Some of the transfers out of each of these tanks were to support 242-A evaporator campaigns and work at SRNL in FY20 indicates that n-butyl alcohol would be removed by 242-A style evaporation (SRNL-STI-2020-00582, Rev. 0, *Hanford Supplemental Low Activity Waste Simulant Evaporation Testing for Removal of Organics*). In addition, for AP-104, AP-107, AW-102, and AW-104 there is data in TWINS for n-butyl alcohol from later samples that show supernate concentrations that would not result in an exceedance of the NWW standard in a cementitious final waste form made from the retrieved material. Hence, while the data in Table 3 indicates there have been measured concentrations in DST supernate that could result in a cementitious waste that exceeds the NWW standard, the results does not reflect the result that would be obtained if the current material in the tank was retrieved and solidified.

In contrast to the other DSTs in Table 3, waste in AN-107 has been segregated from other tank waste until complexed TRU materials can be removed (HNF-SD-WM-OCD-015, Rev. 56, *Tank Farms Waste Transfer Compatibility Program*). Hence, there has been little change in volume since the 2019 sample and the concentration listed likely represents the current tank contents.

Retrieved solids[1] from one SST, T-105, contain enough PCBs to potentially result in a final waste form made from the retrieval liquid to exceed the NWW standard of 10 mg/Kg by a factor of 8.9. Since there is no record of significant transfers in or out of T-105 after the sample data, and since there is no later sample showing a lower PCB concentration, it is assumed that the sample value is likely represents the current tank contents. It should be noted however, that the estimated concentration of PCBs in the hypothetical retrieval liquid is approximately 400 times the water solubility, indicating that most of PCBs would likely be sorbed to undissolved solids or present as a separate organic phase rather than associated with the retrieval liquid. In addition, if the retrieved waste from T-105 were processed through a TSCR type system then filtration would likely remove both the suspended solids and any separate organic liquid phase and the likelihood of having sufficient quantities of PCBs in the resulting liquid to result in a solidified waste form that exceeds the NWW standard is not credible.

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[1] In-tank solids are reported in Table 4.1 of HNF-EP-0182, Rev 413 as 100% sludge.

Table 3: Samples With an Estimated Exceedances of the NWW Standard in a Final Cementitious Waste Form

Tank	Sampled Phase	Compound	Cas Number	Sample Date	Concentration in Retrieved Waste (mg/L)	Concentration in Final Waste Form (mg/Kg)	Ratio to NWW Standard
241-AN-107	Liquid	N-Nitrosomorpholine	59-89-2	5/6/2019	8.30	2.60	1.13
241-AP-104	Liquid	n-Butyl alcohol	71-36-3	1/31/1996	22.11	6.94	2.67
241-AP-107	Liquid	n-Butyl alcohol	71-36-3	8/1/1993	13.53	4.25	1.63
	Liquid	n-Butyl alcohol	71-36-3	8/1/1993	14.49	4.55	1.75
	Liquid	n-Butyl alcohol	71-36-3	1/30/1995	21.26	6.67	2.57
	Liquid	n-Butyl alcohol	71-36-3	1/31/1995	20.29	6.37	2.45
	Liquid	n-Butyl alcohol	71-36-3	2/1/1995	21.26	6.67	2.57
241-AW-102	Liquid	n-Butyl alcohol	71-36-3	1/8/2007	26.04	8.17	3.14
	Liquid	n-Butyl alcohol	71-36-3	1/8/2007	31.48	9.88	3.80
	Liquid	n-Butyl alcohol	71-36-3	1/9/2007	33.58	10.54	4.05
	Liquid	n-Butyl alcohol	71-36-3	1/9/2007	26.23	8.23	3.17
241-AW-104	Liquid	n-Butyl alcohol	71-36-3	8/23/2000	27.19	8.54	3.28
	Liquid	n-Butyl alcohol	71-36-3	8/24/2000	52.10	16.35	6.29
	Liquid	n-Butyl alcohol	71-36-3	8/24/2000	34.32	10.77	4.14
241-T-105	Solid	All Aroclors	1336-36-3	06/24/97	282.21	88.58	8.86

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Appendix D-1.

Table A-1: Tanks LDR Organics Data in TWINS for at Least One Sample

Number	**Tank Name**	**Type**	**LDR Organic Data in TWINS**	**PCB Data in TWINS**	**Data of Latest LDR Organic Sample**	**Date of the Latest PCB Sample**
1	241-A-101	SST	--	X	--	7/11/96
2	241-A-102	SST	--	--	--	--
3	241-A-103	SST	--	--	--	--
4	241-A-104	SST	X	X	10/29/19	10/29/19
5	241-A-105	SST	X	X	2/1/19	2/1/19
6	241-A-106	SST	--	--	--	--
7	241-AN-101	DST	--	X	--	9/8/21
8	241-AN-102	DST	--	X	--	7/24/19
9	241-AN-103	DST	--	X	--	9/13/96
10	241-AN-104	DST	--	X	--	8/8/96
11	241-AN-105	DST	--	X	--	6/10/96
12	241-AN-106	DST	X	X	7/14/08	2/25/21
13	241-AN-107	DST	X	X	10/9/19	10/9/19
14	241-AP-101	DST	X	X	8/1/07	3/25/21
15	241-AP-102	DST	X	X	4/28/93	2/12/20
16	241-AP-103	DST	X	X	6/23/15	6/23/15
17	241-AP-104	DST	X	X	12/28/15	12/28/15
18	241-AP-105	DST	X	X	6/27/07	9/1/15
19	241-AP-106	DST	X	X	11/17/94	1/16/20
20	241-AP-107	DST	X	X	11/8/17	2/8/21
21	241-AP-108	DST	X	X	1/23/03	1/23/03
22	241-AW-101	DST	X	X	2/4/91	7/24/02
23	241-AW-102	DST	X	X	7/19/18	7/19/18
24	241-AW-103	DST	X	X	4/4/19	4/4/19
25	241-AW-104	DST	X	X	6/2/17	6/2/17
26	241-AW-105	DST	X	X	3/21/06	9/5/18
27	241-AW-106	DST	X	X	3/7/18	3/7/18
28	241-AX-101	SST	--	X	--	1/5/98
29	241-AY-101	DST	X	X	3/30/16	5/2/18
30	241-AZ-101	DST	X	X	5/22/00	5/29/19
31	241-AZ-102	DST	X	X	9/4/14	6/6/18
32	241-B-101	SST	--	X	--	6/23/95
33	241-B-102	SST	--	--	--	--
34	241-B-103	SST	--	--	--	--

Number	Tank Name	Type	LDR Organic Data in TWINS	PCB Data in TWINS	Data of Latest LDR Organic Sample	Date of the Latest PCB Sample
35	241-B-104	SST	--	X	--	6/9/95
36	241-B-105	SST	--	--	--	--
37	241-B-106	SST	--	X	--	7/18/95
38	241-B-107	SST	--	X	--	9/5/97
39	241-B-108	SST	--	X	--	9/4/96
40	241-B-109	SST	--	X	--	8/23/96
41	241-B-110	SST	--	--	--	--
42	241-B-111	SST	X	--	10/2/91	--
43	241-B-112	SST	--	--	--	--
44	241-B-201	SST	X	--	7/23/91	--
45	241-B-202	SST	X	--	7/12/91	--
46	241-B-203	SST	--	--	--	--
47	241-B-204	SST	--	--	--	--
48	241-BX-101	SST	--	--	--	--
49	241-BX-102	SST	--	--	--	--
50	241-BX-103	SST	--	X	--	5/30/95
51	241-BX-104	SST	--	--	--	--
52	241-BX-105	SST	--	X	--	10/5/94
53	241-BX-106	SST	--	--	--	--
54	241-BX-107	SST	X	--	5/19/92	--
55	241-BX-108	SST	--	--	--	--
56	241-BX-109	SST	--	X	--	4/11/95
57	241-BX-110	SST	--	X	--	5/19/97
58	241-BX-111	SST	--	X	--	5/30/97
59	241-BX-112	SST	--	X	--	11/30/95
60	241-BY-101	SST	--	--	--	--
61	241-BY-102	SST	--	X	--	7/8/96
62	241-BY-103	SST	--	X	--	3/10/95
63	241-BY-104	SST	--	X	--	11/15/95
64	241-BY-105	SST	--	X	--	7/23/98
65	241-BY-106	SST	--	X	--	1/2/96
66	241-BY-107	SST	--	X	--	7/25/96
67	241-BY-108	SST	--	X	--	8/16/95
68	241-BY-109	SST	--	X	--	6/6/97
69	241-BY-110	SST	--	X	--	10/28/95
70	241-BY-111	SST	--	X	--	8/29/96
71	241-BY-112	SST	--	X	--	10/3/96
72	241-S-101	SST	--	X	--	3/26/96

Number	Tank Name	Type	LDR Organic Data in TWINS	PCB Data in TWINS	Data of Latest LDR Organic Sample	Date of the Latest PCB Sample
73	241-S-102	SST	--	--	--	--
74	241-S-103	SST	--	--	--	--
75	241-S-104	SST	X	X	8/2/92	7/31/92
76	241-S-105	SST	--	X	--	8/28/01
77	241-S-106	SST	--	--	--	--
78	241-S-107	SST	--	X	--	9/25/95
79	241-S-108	SST	--	--	--	--
80	241-S-109	SST	--	X	--	7/8/96
81	241-S-110	SST	--	X	--	6/3/98
82	241-S-111	SST	--	X	--	4/8/98
83	241-SX-101	SST	--	X	--	12/10/97
84	241-SX-102	SST	--	X	--	6/30/98
85	241-SX-103	SST	--	X	--	5/5/98
86	241-SX-104	SST	--	--	--	--
87	241-SX-105	SST	--	X	--	2/25/98
88	241-SX-106	SST	--	X	--	10/13/97
89	241-SX-107	SST	--	--	--	--
90	241-SX-108	SST	--	X	--	9/19/95
91	241-SX-109	SST	--	--	--	--
92	241-SX-110	SST	--	--	--	--
93	241-SX-111	SST	--	--	--	--
94	241-SX-112	SST	--	--	--	--
95	241-SX-113	SST	--	X	--	5/10/95
96	241-SX-114	SST	--	--	--	--
97	241-SX-115	SST	--	X	--	--
98	241-SY-101	DST	X	X	11/15/18	11/15/18
99	241-SY-102	DST	--	X	--	3/14/19
100	241-SY-103	DST	--	X	--	7/8/15
101	241-T-101	SST	--	--	--	--
102	241-T-102	SST	--	--	--	--
103	241-T-103	SST	--	X	--	5/1/96
104	241-T-104	SST	X	--	8/27/92	--
105	241-T-105	SST	--	X	--	6/24/97
106	241-T-106	SST	--	X	--	8/11/95
107	241-T-107	SST	X	--	3/10/93	--
108	241-T-108	SST	--	X	--	7/21/95
109	241-T-109	SST	--	--	--	--
110	241-T-110	SST	--	--	--	--

Number	Tank Name	Type	LDR Organic Data in TWINS	PCB Data in TWINS	Data of Latest LDR Organic Sample	Date of the Latest PCB Sample
111	241-T-111	SST	X	--	11/5/91	--
112	241-T-112	SST	--	--	--	--
113	241-T-201	SST	--	--	--	--
114	241-T-202	SST	--	--	--	--
115	241-T-203	SST	--	--	--	--
116	241-T-204	SST	--	--	--	--
117	241-TX-101	SST	--	--	--	--
118	241-TX-102	SST	--	--	--	--
119	241-TX-103	SST	--	--	--	--
120	241-TX-104	SST	--	X	--	2/18/98
121	241-TX-105	SST	--	--	--	--
122	241-TX-106	SST	--	--	--	--
123	241-TX-107	SST	--	--	--	--
124	241-TX-108	SST	--	--	--	--
125	241-TX-109	SST	--	--	--	--
126	241-TX-110	SST	--	--	--	--
127	241-TX-111	SST	--	--	--	--
128	241-TX-112	SST	--	--	--	--
129	241-TX-113	SST	--	X	--	4/15/99
130	241-TX-114	SST	--	--	--	--
131	241-TX-115	SST	--	--	--	--
132	241-TX-116	SST	X	X	4/15/03	8/5/02
133	241-TX-117	SST	--	--	--	--
134	241-TX-118	SST	--	X	--	3/26/98
135	241-TY-101	SST	--	--	--	--
136	241-TY-102	SST	--	--	--	--
137	241-TY-103	SST	--	--	--	--
138	241-TY-104	SST	--	X	--	2/28/95
139	241-TY-105	SST	--	--	--	--
140	241-TY-106	SST	--	X	--	3/3/95
141	241-U-101	SST	--	--	--	--
142	241-U-102	SST	--	X	--	4/29/96
143	241-U-103	SST	--	X	--	9/30/96
144	241-U-104	SST	--	--	--	--
145	241-U-105	SST	--	X	--	3/18/96
146	241-U-106	SST	--	X	--	5/10/96
147	241-U-107	SST	--	X	--	6/9/03
148	241-U-108	SST	--	X	--	4/26/96

Number	Tank Name	Type	LDR Organic Data in TWINS	PCB Data in TWINS	Data of Latest LDR Organic Sample	Date of the Latest PCB Sample
149	241-U-109	SST	--	X	--	4/22/98
150	241-U-110	SST	--	--	--	--
151	241-U-111	SST	--	X	--	--
152	241-U-112	SST	--	X	--	9/12/97
153	241-U-201	SST	--	X	--	3/17/95
154	241-U-202	SST	--	X	--	3/22/95
155	241-U-203	SST	--	X	--	4/3/95
156	241-U-204	SST	--	X	--	4/5/95

Appendix E
Assessment of the Negative Base 10 logarithm of the Acid Dissociation Constants (pKa) for 207 Regulated Organic Chemicals

This section gives an assessment of the negative base 10 logarithm of the acid dissociation constants (pKa) for 207 regulated organic chemicals. Note that all 207 compounds have been assessed in this appendix but only a subset of these compounds have been used at Hanford or have been detected in tank waste samples and thus would be expected to potentially be present in Hanford liquid or dissolved saltcake waste.

Line Number	Name	CAS Number	pKa	pKa Reference	Notes	Does pH=14 reduce Volatility ?	Reference Number
1	Phthalic acid	100-21-0	2.89, 5.51	ChemicalBook	diprotic	Y	1
2	Methapyrilene	91-80-5	8.85	PubChem	Conj Acid	N	2
3	4,4-Methylene bis(2-chloroaniline)	101-14-4	.33 +/- 0.25 Pred C	ChemicalBook	Conj Acid	N	1
4	2-Acetylaminofluorene	53-96-3	alkaline hydrolysis	3	amides hydrolyze	N/A	4
5	Phenacetin	62-44-2	alkaline hydrolysis	3	amides hydrolyze	N/A	4
6	1,3-Phenylenediamine	108-45-2	2.65, 4.88 PubChem	PubChem	Conj Acid	N	2
7	Acrylamide	79-06-1	alkaline hydroly	3	hydrolysis	N/A	4
8	Silvex/2,4,5-TP	93-72-1	2.84 PubChem	PubChem	--	Y	2
9	5-Nitro-o-toluidine	99-55-8	2.35 PubChem	PubChem	--	Y	2
10	Famphur	52-85-7	-5 Pred CB	ChemicalBook	pKa out of range	N	1
11	Phthalic anhydride	85-44-9	alkaline hydrolysis	See Phthalic acid	sodium phthalate	N/A	1
12	2,4,5-Trichlorophenoxyacetic acid/2,4,5-T	93-76-5	2.88 PubChem	PubChem	--	Y	2
13	N-Nitrosomorpholine	59-89-2	stable	SRNL rpt, -00453r1	pKa out of range	N	5
14	2,4-Dichlorophenoxyacetic acid/2,4-D	94-75-7	2.73	PubChem	--	Y	2
15	Dibenz(a,e)pyrene	192-65-4	>30	PAH	pKa out of range	N	3
16	N-Nitrosopyrrolidine	930-55-2	-3.14 Pred	ChemicalBook	pKa out of range	N	1
17	Kepone	143-50-0	no hydrogen		--	N	3
18	Chlorobenzilate	510-15-6	alkaline hydrolysis	PubChem	Ester group	N/A	2, 3
19	2-Naphthylamine	91-59-8	--	SRNL rpt, -00453r1	pKa out of range	N	5
20	4-Aminobiphenyl	92-67-1	4.35	PubChem	Conj Acid	N	2, 3
21	Methyl parathion	298-00-0	alkaline hydrolysis	NIH	lm.nih.gov/pmc/arti	N/A	6
22	Aramite	140-57-8	alkaline hydrolysis	PubChem	PubChem	N/A	2
23	Methoxychlor	72-43-5	alkaline hydrolysis	PubChem		N/A	2, 7
24	1,4-Dinitrobenzene	100-25-4	>14	Bordwell estimate	pKa out of range	N	8
25	p-Dimethylaminoazobenzene	60-11-7	3.23	PubChem	Conj Acid	N	2
26	Parathion	56-38-2	alkaline hydrolysis	cs.org/doi/pdf/10.1021/jp503382j		N/A	9
27	Endosulfan sulfate	1031-07-8	alkaline hydrolysis	PubChem	--	N/A	2
28	Benzo(g,h,i)perylene	191-24-2	>30	PAH	pKa out of range	N	3
29	bis(2-Chloroethoxy)methane	111-91-1	>16.9	Bordwell estimate	pKa out of range	N	8
30	2-sec-Butyl-4,6-dinitrophenol/Dinoseb	88-85-7	4.62	PubChem	--	Y	2
31	1,2-Diphenylhydrazine	122-66-7	unstable/reacts	PubChem		N/A	2
32	p-Cresidine	120-71-8	4.66 Pred	ChemicalBook	Conj Acid	N	1
33	N-Nitrosopiperidine	100-75-4	(-3.2 Pred)	ChemicalBook	pKa out of range	N	1
34	o-Anisidine (2-methoxyaniline)	90-04-0	4.53	PubChem	Conj Acid	N	2
35	N-Nitrosodimethylamine	62-75-9	>30	SRNL rpt, -00453r1	pKa out of range	N	5
36	4,6-Dinitro-o-cresol	534-52-1	5	SRNL rpt, -00453r1	--	Y	5
37	Cresols (m,p,o)	1319-77-3	10	SRNL rpt, -00453r1	--	Y	5
38	N-Nitrosomethylethylamine	10595-95-6	<1, >30	nitroso	pKa out of range	N	3
39	Disulfoton	298-04-4	alkaline hydrolysis	223&identifier=Disulf	--	N/A	10
40	2,4-Dimethylaniline (2,4-xylidine)	95-68-1	4.89	ChemicalBook	Conj acid	N	1
41	Diphenylamine	122-39-4	0.78	PubChem	Conj acid	N	2
42	gamma-BHC	58-89-9	>30	BHC	pKa out of range	N	3
43	N-Nitrosodiethylamine	55-18-5	<1, >30	SRNL rpt, -00453r1	pKa out of range	N	5
44	Methyl methanesulfonate	66-27-3	alkaline hydroly	PubChem		N/A	2
45	2,6-Dichlorophenol	87-65-0	6.79	PubChem	--	Y	2
46	Endrin aldehyde	7421-93-4	>14	Bordwell estimate	pKa out of range	N	8
47	Phorate	298-02-2	kaline decompositi	PubChem	%5CINDEX%20DATA	N/A	2, 11
48	Methanol	67-56-1	16	SRNL rpt, -00453r1	pKa out of range	N	5
49	1,4-Dioxane	123-91-1	>14	Bordwell estimate	pKa out of range	N	8

Line Number	Name	CAS Number	pKa	pKa Reference	Notes	Does pH=14 reduce Volatility ?	Reference Number
50	beta-BHC	319-85-7	>30	SRNL rpt, -00453r1	pKa out of range	N	5
51	delta-BHC	319-86-8	>30	SRNL rpt, -00453r1	pKa out of range	N	5
52	3-Methylcholanthrene	56-49-5	>30	PAH	pKa out of range	N	3
53	Toxaphene	8001-35-2	>14	Bordwell estimate	pKa out of range	N	8
54	p,p′-Dichlorodiphenyldichloroethane (DDD)	72-54-8	>14	Bordwell estimate	pKa out of range	N	8
55	o,p′-DDT	789-02-6	>14	Bordwell estimate	pKa out of range	N	8
56	n-Butyl alcohol	71-36-3	16	SRNL rpt, -00453r1	pKa out of range	N	5
57	alpha-BHC	319-84-6	>30	SRNL rpt, -00453r1	pKa out of range	N	5
58	o,p′-DDD	53-19-0	>14	Bordwell estimate	pKa out of range	N	8
59	Pyridine	110-86-1	>30	SRNL rpt, -00453r1	pKa out of range	N	5
60	Cyclohexanone	108-94-1	16.7	odb.ca/compounds/F	pKa out of range	N	12
61	Safrole	94-59-7	>14	Bordwell estimate	pKa out of range	N	8
62	Endrin	72-20-8	>14	Bordwell estimate	pKa out of range	N	8
63	Dieldrin	60-57-1	>14	Bordwell estimate	pKa out of range	N	8
64	Isobutyl alcohol	78-83-1	16	SRNL rpt, -00453r1	pKa out of range	N	5
65	Aldrin	309-00-2	>30	SRNL rpt, -00453r1	pKa out of range	N	5
66	Acetonitrile	75-05-8	alkaline hydrolysis	SRNL rpt, -00453r1	nitriles hydrolyze	N/A	5
67	o,p′-Dichloro-2,2-bis(p-chlorophenyl) ethylene (DDE)	3424-82-6	>14	Bordwell estimate	pKa out of range	N	8
68	Heptachlor epoxide	1024-57-3	>30	SRNL rpt, -00453r1	pKa out of range	N	5
69	tris-(2,3-Dibromopropyl) phosphate	126-72-7	alkaline hydrolysis	e/10665/37119/924157173X-eng.pdf?sequ		N/A	13
70	p,p′-Dichlorodiphenyltrichloroethane (DDT)	50-29-3	>14	Bordwell estimate	pKa out of range	N	8
71	Ethyl cyanide/Propanenitrile	107-12-0	alkaline hydrolysis	SRNL rpt, -00453r1	nitriles hydrolyze	N/A	5
72	p,p′-DDE	72-55-9	>14	Bordwell estimate	pKa out of range	N	8
73	Isodrin	465-73-6	>14	Bordwell estimate	pKa out of range	N	8
74	Chlordane (alpha and gamma isomers)	57-74-9	alkaline hydrolysis	PubChem	also ChemicalBook	N	1,2
75	Endosulfan I	959-98-8	alkaline hydrolysis	s/effect_of_water_p	--	N/A	14
76	Endosulfan II	33213-65-9	alkaline hydrolysis	s/effect_of_water_p	--	N/A	14
77	Acenaphthylene	208-96-8	>30	PAH	pKa out of range	N	3
78	Acrolein	107-02-8	>30	SRNL rpt, -00453r1	pKa out of range	N	5
79	1,2-Dibromo-3-chloropropane	96-12-8	alkaline hydrolysis	PubChem	--	N/A	2
80	Ethylene oxide	75-21-8	alkaline hydrolysis	PubChem	--	N/A	2
81	Ethyl acetate	141-78-6	alkaline hydrolysis	SRNL rpt, -00453r1	saponification	N/A	5
82	Methacrylonitrile	126-98-7	alkaline hydrolysis	Bordwell estimate	nitriles hydrolyze	N/A	3, 8
83	Heptachlor	76-44-8	>30	SRNL rpt, -00453r1	pKa out of range	N	5
84	Methyl methacrylate	80-62-6	alkaline hydrolysis	nlm.nih.gov/pmc/arti	--	N/A	15
85	bis(2-Chloroisopropyl)ether	39638-32-9	>14	Bordwell estimate	pKa out of range	N	8
86	Benzal chloride	98-87-3	alkaline hydrolysis	ace/bitstream/2115/	--	N/A	16
87	Isosafrole	120-58-1	>14	Bordwell estimate	pKa out of range	N	8
88	Ethyl methacrylate	97-63-2	alkaline hydrolysis	ace/bitstream/2115/	--	N/A	16
89	Bromoform	75-25-2	alkaline hydrolysis	PubChem	--	N/A	2
90	1,2-Dibromoethane/Ethylene dibromide	106-93-4	alkaline hydrolysis	PubChem	--	N/A	2
91	Dibromomethane	74-95-3	alkaline hydrolysis	PubChem	--	N/A	2
92	Ethyl Ether	60-29-7	>30	SRNL rpt, -00453r1	pKa out of range	N	5
93	Pentachloroethane	76-01-7	alkaline hydrolysis	PubChem	--	N/A	2
94	1,1,1,2-Tetrachloroethane	630-20-6	>14	Bordwell estimate	pKa out of range	N	8
95	trans-1,3-Dichloropropylene (note, hydrolysis)	10061-02-6	alkaline hydrolysis	see paper	serFiles/50600000/P	N/A	17
96	Hexachloropropylene	1888-71-7	>14	Bordwell estimate	pKa out of range	N	8
97	Xylene(m,p,o)	1330-20-7	>30	SRNL rpt, -00453r1	pKa out of range	N	5
98	Iodomethane	74-88-4	alkaline hydrolysis	MRID 45593705		N/A	18
99	2-Chloroethyl vinyl ether	110-75-8	>14	Bordwell estimate	pKa out of range	N	8
100	3-Chloropropylene	107-05-1	alkaline hydrolysis	PubChem		N/A	2
101	2-Chloro-1,3-butadiene	126-99-8	eactive-polymerize	PubChem	see chloroprene	N	2
102	1,1,2-Trichloro-1,2,2-trifluroethane	76-13-1	>14	Bordwell estimate	pKa out of range	N	8
103	1,1,1-Trichloroethane	71-55-6	>30	SRNL rpt, -00453r1	pKa out of range	N	5
104	1,1-Dichloroethylene	75-35-4	>30	SRNL rpt, -00453r1	pKa out of range	N	5
105	1,2-Dichloroethane	107-06-2	>30	SRNL rpt, -00453r1	pKa out of range	N	5
106	2,4,5-Trichlorophenol	95-95-4	7	SRNL rpt, -00453r1	--	Y	5
107	2,4-Dinitrotoluene	121-14-2	13.5	ChemicalBook		Y	1
108	2-Butanone	78-93-3	20	SRNL rpt, -00453r1	pKa out of range	N	5
109	4-Methyl-2-pentanone	108-10-1	20	SRNL rpt, -00453r1	pKa out of range	N	5
110	Acetone	67-64-1	20	SRNL rpt, -00453r1	pKa out of range	N	5

Line Number	Name	CAS Number	pKa	pKa Reference	Notes	Does pH=14 reduce Volatility ?	Reference Number
111	All Aroclors	1336-36-3	>30	SRNL rpt, -00453r1	pKa out of range	N	5
112	Benzene	71-43-2	>30	SRNL rpt, -00453r1	pKa out of range	N	5
113	Butyl benzyl phhalate	85-68-7	alkaline hydrolysis	ester		N/A	3
114	Carbon tetrachloride	56-23-5	>30	SRNL rpt, -00453r1	pKa out of range	N	5
115	Chloroform	67-66-3	16	SRNL rpt, -00453r1	pKa out of range	N	5
116	di-n-Butyl phthalate	84-74-2	alkaline hydrolysis	ester		N/A	3
117	Hexachlorobutadiene	87-68-3	>30	SRNL rpt, -00453r1	pKa out of range	N	5
118	Hexachloroethane	67-72-1	>30	SRNL rpt, -00453r1	pKa out of range	N	5
119	Methylene chloride	75-09-2	>30	SRNL rpt, -00453r1	pKa out of range	N	5
120	Nitrobenzene	98-95-3	>30	SRNL rpt, -00453r1	pKa out of range	N	5
121	Tetrachloroethylene	127-18-4	20 - 30	SRNL rpt, -00453r1	pKa out of range	N	5
122	Trichloroethylene	79-01-6	20 - 30	SRNL rpt, -00453r1	pKa out of range	N	5
123	Vinyl chloride	75-01-4	>30	SRNL rpt, -00453r1	pKa out of range	N	5
124	1,1,2,2-Tetrachloroethane	79-34-5	20 - 30	SRNL rpt, -00453r1	pKa out of range	N	5
125	1,1,2-Trichloroethane	79-00-5	20 - 30	SRNL rpt, -00453r1	pKa out of range	N	5
126	1,1-Dichloroethane	75-34-3	>30	SRNL rpt, -00453r1	pKa out of range	N	5
127	1,2,4-Trichlorobenzene	120-82-1	>30	SRNL rpt, -00453r1	pKa out of range	N	5
128	1,2-Dichlorobenzene	95-50-1	>14	Bordwell estimate	pKa out of range	N	8
129	1,2-Dichloropropane	78-87-5	>14	Bordwell estimate	pKa out of range	N	8
130	1,3-Dichlorobenzene	541-73-1	>30	SRNL rpt, -00453r1	pKa out of range	N	5
131	1,4-Dichlorobenzene	106-46-7	>30	SRNL rpt, -00453r1	pKa out of range	N	5
132	2,4,6-Trichlorophenol	88-06-2	7.00	SRNL rpt, -00453r1	--	Y	5
133	2,4-Dichlorophenol	120-83-2	7.89	Pubchem	--	Y	2
134	2,4-Dimethyl phenol	105-67-9	10.60	Pubchem	--	Y	2
135	2,4-Dinitrophenol	51-28-5	5.00	SRNL rpt, -00453r1	--	Y	5
136	2-Chloronaphthalene	91-58-7	>14	Bordwell estimate	pKa out of range	N	8
137	2-Chlorophenol	95-57-8	8.56	Pubchem	--	Y	2
138	2-Nitroaniline	88-74-4	(-0.28)	Pubchem	pKa out of range	N	2
139	2-Nitrophenol	88-75-5	7.00	SRNL rpt, -00453r1	--	Y	5
140	4-Bromophenyl phenyl ether	101-55-3	>14	Bordwell estimate	pKa out of range	N	8
141	4-Chloroaniline	106-47-8	3.98 conj acid	Pubchem	conj acid	N	2
142	4-Nitroaniline	100-01-6	12.99	ChemicalBook	conj acid	N	1
143	Acenaphthene	83-32-9	>30, PAH	SRNL rpt, -00453r1	pKa out of range	N	5
144	Anthracene	120-12-7	>30	PAH	pKa out of range	N	3
145	Benz(a)anthracene	56-55-3	>30	PAH	pKa out of range	N	3
146	Benzo(a)pyrene	50-32-8	>30	PAH	pKa out of range	N	3
147	Benzo(b)fluoranthene	205-99-2	>30	PAH	pKa out of range	N	3
148	Benzo(k)fluoranthene	207-08-9	>30	PAH	pKa out of range	N	3
149	bis(2-Chloroethyl)ether	111-44-4	>30	PAH	pKa out of range	N	3
150	bis(2-ethylhexyl)phthalate	117-81-7	alkaline hydrolysis	ester		N/A	3
151	Bromodichloromethane	75-27-4	12.90	enutz.eu/chem/pka.	--	Y	19
152	Bromomethane	74-83-9	alkaline hydrolysis	PubChem	--	N/A	2
153	Carbon disulfide	75-15-0	no hydrogens	SRNL rpt, -00453r1	pKa out of range	N	5
154	Chlorobenzene	108-90-7	>30	SRNL rpt, -00453r1	pKa out of range	N	5
155	Chloroethane	75-00-3	stable	PubChem	--	N	2
156	Chloromethane	74-87-3	>30	SRNL rpt, -00453r1	pKa out of range	N	5
157	Chrysene	218-01-9	>30	PAH	pKa out of range	N	3
158	cis-1,3-Dichloropropylene	10061-01-5	alkaline hydrolysis	serFiles/50600000/Products-Reprints/200		N/A	20
159	Dibenzo(a,h)anthracene	53-70-3	>30	PAH	pKa out of range	N	3
160	Dibromochloromethane	124-48-1	no hydrogens		--	N	3
161	Dichlorodifluoromethane	75-71-8	no hydrogens		--	N	3
162	Diethyl phthalate	84-66-2	alk hydrolysis	ester		N/A	3
163	Dimethyl phthalate	131-11-3	alk hydrolysis	ester	--	N/A	3
164	Di-n-octyl phthalate	117-84-0	alk hydrolysis	ester		N/A	3
165	Ethyl benzene	100-41-4	>30	SRNL rpt, -00453r1	pKa out of range	N	5
166	Fluoranthene	206-44-0	>30	PAH	pKa out of range	N	3
167	Fluorene	86-73-7	>30, PAH	SRNL rpt, -00453r1	pKa out of range	N	5
168	Hexachlorobenzene	118-74-1	no hydrogens			N	3
169	Hexachlorocyclopentadiene	77-47-4	no hydrogens			N	3
170	Indeno(1,2,3-c,d) pyrene	193-39-5	>30	PAH	pKa out of range	N	3

Line Number	Name	CAS Number	pKa	pKa Reference	Notes	Does pH=14 reduce Volatility ?	Reference Number
171	Naphthalene	91-20-3	>30	SRNL rpt, -00453r1	pKa out of range	N	5
172	N-Nitroso-di-n-propylamine	621-64-7	stable	SRNL rpt, -00453r1	pKa out of range	N	5
173	Pentachlorophenol	87-86-5	5.00	SRNL rpt, -00453r1	--	Y	5
174	Phenanthrene	85-01-8	>30	PAH	pKa out of range	N	3
175	Phenol	108-95-2	10	SRNL rpt, -00453r1	--	Y	5
176	p-Nitrophenol	100-02-7	7.15	PubChem	--	Y	2
177	Pyrene	129-00-0	>30, PAH	SRNL rpt, -00453r1	pKa out of range	N	5
178	Toluene	108-88-3	>30	SRNL rpt, -00453r1	pKa out of range	N	5
179	Trichlorofluoromethane	75-69-4	>30	SRNL rpt, -00453r1	pKa out of range	N	5
180	Diphenylnitrosamine	86-30-6	(-5.8 predicted)	ChemicalBook	pKa out of range	N	1
181	1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (1,2,3,4,6,7,8-HpCDD)	35822-46-9	>14	Bordwell estimate	pKa out of range	N	8
182	1,2,3,4,6,7,8-Heptachlorodibenzofluran (1,2,3,4,6,7,8-HpCDF)	67562-39-4	>14	Bordwell estimate	pKa out of range	N	8
183	1,2,3,4,7,8,9-Heptachlorodibenzofluran (1,2,3,4,7,8,9-HpCDF)	55673-89-7	>14	Bordwell estimate	pKa out of range	N	8
184	HxCDDs (All Hexachlorodibenzo-p-dioxins)	NA	>14	Bordwell estimate	pKa out of range	N	8
185	HxCDFs (All Hexachlorodibenzofurans)	NA	>14	Bordwell estimate	pKa out of range	N	8
186	N-Nitroso-di-n-butylamine	924-16-3	(-3.14)	ChemicalBook	pKa out of range	N	1
187	1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9	>14	Bordwell estimate	pKa out of range	N	8
188	1,2,3,4,6,7,8,9-Octachlorodibenzofluran (OCDF)	39001-02-0	>14	Bordwell estimate	pKa out of range	N	8
189	Pentachlorobenzene	608-93-5	>14, stable	PubChem	pKa out of range	N	2
190	PeCDDs (All Pentachlorodibenzo-p-dioxins)	NA	>14	Bordwell estimate	pKa out of range	N	8
191	PeCDFs (All Pentachlorodibenzofurans)	NA	>14	Bordwell estimate	pKa out of range	N	8
192	Pentachloronitrobenzene	82-68-8	no hydrogens			N	3
193	Pronamide	23950-58-5	alkaline hydrolysis	PubChem	Amides hydrolyze	N/A	2,3
194	1,2,4,5-Tetrachlorobenzene	95-94-3	>14, stable	PubChem	pKa out of range	N	2
195	TCDDs (All Tetrachlorodibenzo-p-dioxins)	NA	>14, stable	Bordwell estimate	pKa out of range	N	8
196	TCDFs (All Tetrachlorodibenzofurans)	NA	>14, stable	Bordwell estimate	pKa out of range	N	8
197	2,3,4,6-Tetrachlorophenol	58-90-2	5.22	Pubchem	--	Y	2
198	1,2,3-Trichloropropane	96-18-4	>14	Bordwell estimate	hem: alk hydr needs	N	2, 8
199	Acetophenone	98-86-2	16	SRNL rpt, -00453r1	pKa out of range	N	5
200	Acrylonitrile	107-13-1	>14	Bordwell estimate	alkaline hydrolysis	N/A	8
201	Aniline	62-53-3	4.6 conj acid	Pubchem	Conj Acid	N	2
202	p-Chloro-m-cresol	59-50-7	9.55	Pubchem	--	Y	2
203	o-Cresol	95-48-7	10	SRNL rpt, -00453r1	--	Y	5
204	m-Cresol	108-39-4	10	SRNL rpt, -00453r1	--	Y	5
205	p-Cresol	106-44-5	10	SRNL rpt, -00453r1	--	Y	5
206	trans-1,2-Dichloroethylene	156-60-5	>14	Bordwell estimate	--	N	8
207	2,6-Dinitrotoluene	606-20-2	1.8 conj acid	Pubchem	Conj Acid	N	2

References for pKa Table. All Internet references were accessed on September 13, 2022.

1. ChemicalBook : https://www.chemicalbook.com

2. PubChem: https://pubchem.ncbi.nlm.nih.gov

3. Note: references to chemicals like “PAH” or “ester” give pKa information or why pKa is not available. Polyaromatic hydrocarbons (PAH) are stable and do not ionize and their pKa is out of the range of water 0 to 14. Esters hydrolyze and do not have a pKa because they are reactive in alkali. Amides hydrolyze in strong alkali. Benzene Hexachlorides (BHC) are stable and do not have hydrogens. Their pKa for protonation would be out of the 0-14 pH range for water. Conjugate acids are initially neutral species that are then protonated (giving a positive charge) below the pKa shown.

4. Roberts and Caserio: https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Book%3A_Basic_Principles_of_Organic_Chemistry_(Roberts_and_Caserio)/24%3A_Organonitrogen_Compounds_II_-_Amides_Nitriles_and_Nitro_Compounds/24.04%3A_Hydrolysis_of_Amides

5. SRNL-STI-2021-00453, Rev. 1: Nash, C.A., Skeen, R.S., Miskho, A.G., White, T.L., McCabe, D.J., "Potential for Evaporation and In Situ Reaction of Organic Compounds in Hanford Supplemental LAW ", SRNL-STI-2021-00453, Rev. 1, January 2022.

6. NIH: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6140667/

7. https://pubchem.ncbi.nlm.nih.gov/compound/Methoxychlor#section=Other-Experimental-Properties

8. Bordwell estimate, uses chemical group data from this site: https://organicchemistrydata.org/hansreich/resources/pka/

9. https://pubs.acs.org/doi/pdf/10.1021/jp503382j

10. https://webwiser.nlm.nih.gov/substance?substanceId=223&identifier=Disulfoton&identifier Type=name &menuItemId=44&catId=51

11. https://nepis.epa.gov/Exe/ZyNET.exe/9101EM0F.txt?ZyActionD=ZyDocument&Client=EPA&Index=1976%20Thru%201980&Docs=&File=D%3A%5CZYFILES%5CINDEX%20DATA%5C76THRU80%5CTXT%5C00000029%5C9101EM0F.txt&User=ANONYMOUS&Password=anonymous

12. https://foodb.ca/compounds/FDB003418

13. https://apps.who.int/iris/bitstream/handle/10665/37119/924157173X-eng.pdf?sequence=1&isAllowed=y

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15. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3382811/

16. https://eprints.lib.hokudai.ac.jp/dspace/bitstream/2115/24785/1/12%283%29_P223-229.pdf

17. https://www.ars.usda.gov/ARSUserFiles/50600000/Products-Reprints/2004/1102.pdf

18. https://www.epa.gov/pesticide-analytical-methods/ecm-iodomethane-water-mrid-45593715

19. http://www.stenutz.eu/chem/pka.php?s=3&p=42

20. https://www.ars.usda.gov/ARSUserFiles/50600000/Products-Reprints/2004/1102.pdf

Appendix F

Standardization of Reagent Sodium Permanganate Solution and Hydrogen Peroxide

Oxidation tests used reagent sodium permanganate solution and hydrogen peroxide which were standardized per the following measurements.

1. Sodium Permanganate. The reagent was Aldrich Lot MKBV5633V, SRNL bar code 2054577, catalog number 519073. It was standardized using both density and soluble manganese assay.

1.1 Density. 10-mL portions were measured into 10-mL volumetric flasks and weighed. The same volumetric flasks were also checked with deionized water. The table below shows all masses for 10 mL of liquid.

Liquid to Weigh	Mass of 10 mL, g
Sodium Permanganate Solution	13.6302
	13.6215
	13.6828
Average Density, Std. Dev.	1.3645 +/- 0.0033
DI Water	9.9619
	9.9758
	9.9558
Average Density, Std. Dev.	0.9965 +/- 0.001

This density gives an assay of 41 wt% per Novotny, P., and Sohnel, O., "Densities of Binary Aqueous Solutions of 306 Inorganic Substances", J. of Chemical Engineering Data, vol. 33, pp. 49-55, 1988.

1.2 Soluble Manganese Assay.

This method weighed a known amount of the sodium permanganate solution into 0.842 +/- 1% M sodium sulfite solution to reduce the permanganate. This was followed by addition of 2 M nitric acid to dissolve the manganese-bearing solids, producing solutions for ICP-ES analysis of manganese.

ITEM	Flask 1	Difference	Flask 2	Difference
Empty Flask, g	18.7382		18.8158	
0.8M Na2SO3, g	26.9787	8.2405	30.6141	11.7983
40 wt% NaMnO4, g	27.2375	0.2588	30.8085	0.1944
2 M Nitric Acid, g	35.6968	8.4593	37.486	6.6775
DI Water, g	44.8252	9.1284	44.9751	7.4891
Contents weight, g:	26.0870		26.1593	
Density, g/mL:	1.0435		1.0464	
Manganese, mg/L by ICP-ES	1630		1240	

Resulting weight percent values from this method are 40.7 and 41.2 wt%, respectively, for Flask 1 and Flask 2.

2. Hydrogen Peroxide. The reagent was Fisher Lot 120554, SRNL bar code 2063277, catalog number H325-500 mL. Ten-mL portions were measured into 10-mL volumetric flasks and weighed. The same volumetric flasks were also checked with deionized water. The table below shows all masses for 10 mL of liquid.

Liquid to Weigh	Mass of 10 mL, g
Hydrogen Peroxide Solution	10.8520
	10.8597
	10.8483
Average Density, Std. Dev.	1.0853 +/- 0.0006
DI Water	9.9826
	9.9721
	9.9782
Average Density, Std. Dev.	0.9978 +/- 0.0005

Interpolation of values from the International Critical Tables gives 23.3 wt%, +/- 0.06% hydrogen peroxide.

The literature reference here is Washburn, E.W., editor, “International Critical Tables of Numerical Data, Physics, Chemistry and Technology”, vol. 3, pp. 49-55, McGraw-Hill, 1928.

Appendix G

Teams Meeting Summary, SRNL and Hanford 222-S Laboratory, June 9, 2022

Attendees: Charles Nash (SRNL), Rod Skeen (WRPS), Heather Anastos (222-S), Michael Lindberg (222-S), Michael Cain (222-S), Therese Clauss (222-S), Andrew Boggess (SRNL), Ridha Mabrouki (WRPS).

The purpose of the meeting was to review the technologies available to prepare Hanford tank waste / supplemental LAW aqueous samples for analyses. These samples have difficult chemistry and can show chemical interferences when steps are taken to improve extraction efficiency for Semi-Volatile Organic Analyses (SVOA). Dissolved aluminum, nitrite, nitrate, and chromate are challenges when pH needs to be adjusted. pH adjustments are desired to greatly enhance extraction of organic analytes. Aluminum has a solubility minimum around neutral pH, leading to solids formation. Low pH will make components like nitrite and chromate reactive to attack organic analytes.

Samples are generally solvent extracted after pH adjustments, then the solvent is partly evaporated for concentration of analytes, then analyzed by SVOA by Gas Chromatograph/Mass Spectroscopy (GC/MS). Detection and identification of trace organic species is the first goal of sample analysis. Different organic analytes can exhibit varied extraction efficiencies and their results are not always quantitative.

222-S reported extraction improvements, first of all, in reversing the order of sample pH adjustment before extraction. They specifically saw improved phenol extraction by pH adjustment to 2 followed by methylene chloride extraction. Their previous technique performed alkaline side (>11 pH) extraction first. They found they can avoid aluminum hydroxide precipitation by lowering the pH rapidly.

222-S also reported an innovation by producing and using glass micro-extractors of a size smaller than those that are commercially available. Processing smaller radioactive samples reduces dose as well as consuming less sample for an analysis.

SRNL has historically taken a different approach. Report SRNL-STI-2014-00088 describes use of a dihydrogen phosphate buffer to drop pH only to just below neutral. This would allow phenol extraction without creating nitrous acid. Aluminum does precipitate, but SRNL found that overnight decantation allows sufficient separation of the solvent phase for GC/MS use. Phenol is still of interest in analyzing SRS waste, and this method appears to be quantitative. Stronger organic acids would need lower pH for good solvent extraction.

SRNL has more recently used NMR as a separate analytical technique for aqueous samples, with SRNL-STI-2020-00582 r0 providing a demonstration with simulants. The hydrogen NMR experiment WATERGATE (Water Suppression by Gradient Tailored Excitation) was applied to suppress the large water signal at 5.1 ppm in the aqueous samples. This method does not require pH adjustment of the liquid samples.

The paths forward mentioned in the meeting are that 222-S is proceeding to apply the Twister® stir bar solvent extraction (SBSE) method for sample preparations. SRNL will continue to apply SVOA/VOA to their current simulant work in support of Sample-and-Send, but will step up the application of NMR in hopes of improved quantitation.

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