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# Occurrence and Chemistry of Organic Compounds in Hanford Site Waste Tanks

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U.S. Department of Energy Contract DE-AC27-99RL14047

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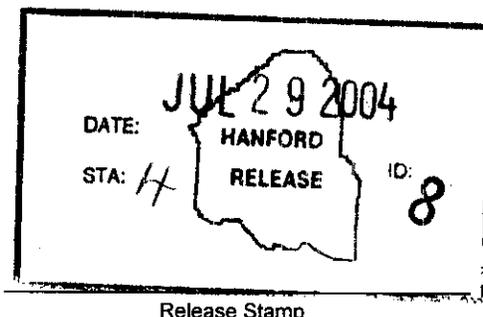
**Abstract:** Volatile and semivolatile organic compounds continuously evolve from the waste tanks at the Hanford Site. Some are identical to the compounds originally transferred to tanks and others are formed through interdependent chemical and radiolytic reactions. This document provides a technical basis for understanding the chemical consequences of long term storage, sluicing, the addition of chemicals, and the prediction of other organic compounds that may be present in the wastes.

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# OCCURRENCE AND CHEMISTRY OF ORGANIC COMPOUNDS IN HANFORD SITE WASTE TANKS

Prepared for the U.S. Department of Energy  
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy  
Office of River Protection under Contract DE-AC27-99RL14047

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## EXECUTIVE SUMMARY

Volatile and semivolatile organic compounds continuously evolve from the waste tanks at the Hanford Site. Some of these substances are identical to the compounds that were originally transferred to tanks as the waste from large-scale plant operations or from operations that supported the plant operations. The other organic compounds are formed in an ongoing cascade of interdependent chemical and radiolytic reactions of organic complexants, phosphate esters and hydrocarbons. Their occurrence, chemistry, the opportunity for the formation of as yet undetected organic compounds and the consequences of planned operations are discussed in this report.

Historical work established that eleven different complexants and two phosphate esters were used in large-scale plant operations together with organic hydrocarbon diluents. The commercial complexants and the phosphate esters were essentially single compounds. However, three of the four commercial hydrocarbon diluents were very complex mixtures; only the fourth diluent could accurately be called a mixture of normal paraffin hydrocarbons. It has been estimated that approximately 4000 metric tons of these organic chemicals were discharged to the waste tanks. Smaller amounts, perhaps 100 metric tons, of many other chemicals that were used in supporting operations were also discharged to the waste tanks.

The characterization program provides an important technical basis for the formulation of the chemistry and the propensity for volatile and semivolatile organic compound formation and release. The total organic carbon content measurements indicate the waste tanks contain 1280 metric tons of organic carbon. This organic waste is widely distributed among the tanks. Oxalate ion, an end product of oxidation, is the most abundance organic compound. The identification of the complexants and the remnants that remain in solid and liquid layers also show that oxidation is the principal reaction pathway for their degradation. Similar work on the phosphate esters and the diluents that remain in the solid and liquid layers is more limited. But, the results imply these compounds are widely distributed in the tanks. Analysis of the headspace vapors has identified 1230 different organic compounds in more than 100 single-shell waste tanks, and it is reasonable to assume that the headspaces of the double-shell tanks contain the same compounds. Small and large fragments of the original complexants, homologous series of organic compounds derived from the hydrocarbons and products of chemical reactions of the phosphate esters have been identified. The compounds are distributed among alkanes; alkenes, dienes and acetylenes; cyclic hydrocarbons; benzene derivatives; alcohols and ethers; aldehydes and ketones; acids and esters; amines and amides; other nitrogen compounds such as nitroso and

nitro compounds; heterocycles; halogen-containing compounds; and at least one mercury compound.

Targeted technical work has shown that oxidation is initiated by radioactive decay processes, by thermal chemical reactions and by other chemical reactions that do not involve free radicals. The decay processes produce hydrogen atoms, hydroxyl radicals, nitric oxide and nitrogen dioxide. Similar radical reagents are also obtained by thermal reactions. These reactive substances transform the organic constituents into organic radicals. The radicals react with oxygen and the reactive radicals to give other organic intermediates and products that also react with ionic reagents to give other products. These reactions occur in parallel, and many different products are obtained.

Radiolytic and Thermal Processes  $\rightarrow$  H, OH, NO, NO<sub>2</sub>

Organic Constituents + Reactive Free Radicals  $\rightarrow$  Organic Free Radicals

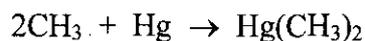
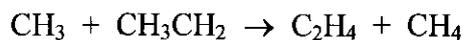
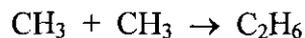
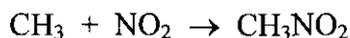
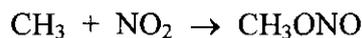
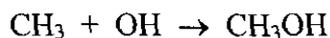
Organic Free Radicals + O<sub>2</sub>, OH, NO, NO<sub>2</sub> etc.  $\rightarrow$  Organic Intermediates and Products

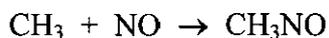
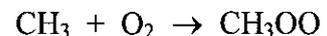
Organic Intermediates + Ionic Reagents  $\rightarrow$  Products

Generally, the organic intermediates formed in the initial reactions are more reactive than the compounds from which they were formed. Volatile organic compounds are obtained in both the beginning and later stages of the chemistry.

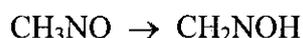
Reactive Organic Intermediates  $\rightarrow$   $\rightarrow$  Volatile Organic Products

A chemical model for the elementary radiolytic and chemical reactions provides a basis for the formulation of the initial reaction sequences of the complexants, phosphate esters, and hydrocarbon diluents. The chemistry and the propensity for volatile compounds formation become apparent when it is recognized that some complexants, the two phosphate esters, and all of the hydrocarbons degrade to produce methyl radicals which can react with many waste constituents.



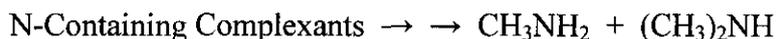


The products of the first five reactions have been analytically detected in the wastes. The formation of dimethyl mercury is possible and sampling for dimethyl mercury is planned, but results were not available at the time this report was completed. The hydroperoxyl radical shown in the seventh equation is reduced to form methyl hydroperoxide, which has not been analytically detected, but presumably exists in the waste. The nitroso compound shown in the eighth equation is spontaneously converted into formaldehyde through an intermediate oxime.



Other ionic reactions of methyl nitrite and methyl nitrate produce formaldehyde. Formaldehyde is converted to a hydrate and is oxidized to formate ion. Even though formaldehyde is almost completely converted to the non-volatile hydrate, it appears in the headspaces of some tanks. This phenomenon can be explained by recognizing that the constituents in the waste tanks are not in thermodynamic equilibrium. Many substances like formaldehyde are continuously formed and destroyed. Even when they are largely converted into nonvolatile forms, the remaining volatile forms can evaporate from the aqueous solution, micelles or organic films into the headspace.

Other methane derivatives including methylamine, dimethylamine and N-nitrosodimethylamine arise through oxidation and hydrolysis reactions of the nitrogen-containing complexants.



Methylamine is destroyed by nitrosation which converts it to methanol, but the nitrosation of dimethylamine yields the N-nitroso compound.

These reactions and many other related processes that are described more fully in the report blend with the initial thermal and radiolytic reactions to provide a comprehensive chemical reaction model that is consistent with the results of the characterization program and other technical investigations.

The consequences of long-term storage and operations such as waste transfer, acidification, and sluicing are also considered. Long-term storage alters the composition of the wastes. The complexants, which are predominantly in the liquid phases of the solid and liquid layers eventually degrade to formate, acetate, oxalate, and carbonate ion. These reactions occur so slowly that the complexants will persist in the waste tanks for many years. Tributyl phosphate is converting to mono- and dibutylphosphate, and its concentration in the wastes should decrease substantially during the next 25 years. In contrast, bis(2-ethylhexyl)phosphate is insoluble in water and does not hydrolyze. The radiolytic reactions of this insoluble substance are also quite slow. The insoluble hydrocarbons are volatile and evaporate from supernatant layers. When the complexants, phosphate esters, and hydrocarbons are retained in the solid layers, their decomposition reactions continue, but the volatile and non-volatile products are retained in the same way that hydrogen and the other gases are retained. Consequently, intrusive operations such as sluicing that disperse the solids can lead to their prompt evolution as demonstrated in the sluicing operations of tank 241-C-106. The chemical model provides insight concerning the formation of other organic compounds that have not been detected in analytical work. Compounds in this category include reactive intermediates with one and two carbon atoms and missing members of homologous series.

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Many persons generously provided information and suggestions for sources of information in the preparation of this report and contributed their special insights concerning different aspects of the problem. Any list would be incomplete, but it is appropriate to mention those who contributed to the earlier report on gas generation as well as those who contributed to this report: Steve Agnew, Blaine Barton, Roger Bauer, Dave Bechtold, Chris Brevick, Sam Bryan, Jim Campbell, Clark Carlson, Bob Cash, Don Camaioni, Bill Cowley, Bill Evans, Jim Field, Rich Hallen, Albert Hu, Jim Huckaby, Jerry Johnson, Nick Kirch, Louis Kovach, Dennis Lauhala, Lenna Mahoney, Joe Meacham, Dan Meisel, Larry Pederson, Dan Reynolds, David Sherwood, Edward Siciliano, Leslie Stauffer, Marcus Stauffer, Chuck Stewart, and Jim Zach.

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## TERMS

DBBP	dibutyl butylphosphate
DBP	dibutylphosphate ion
CAS	Chemical Abstracts Service
ED1A	ethylenediamineacetate ion
<i>s</i> -ED2A	<i>symmetrical</i> -ethylenediaminediacetate ion
<i>u</i> -ED2A	<i>unsymmetrical</i> -ethylenediaminediacetate ion
ED3A	ethylenediaminetriacetate ion
EDTA	ethylenediaminetetraacetate ion
DST	double-shell tank
g	gram
G value	molecules formed (or consumed) per 100 electron volts deposited
GC/MS	gas chromatography/mass spectrometry
IDA	iminodiacetate ion
H <sub>3</sub> HEDTA	(hydroxyethyl)ethylenediaminetriacetic acid
H <sub>4</sub> EDTA	ethylenediaminetetraacetic acid
IDA	iminodiacetate or iminodiacetic acid
kg	kilogram
kgal	kilogallon
kL	kiloliter
L	liter
m	meter
m <sup>3</sup>	cubic meters
mg	milligram
mL	milliliter
MBP	monobutylphosphate ion
MT	metric ton (1000 kg)
N/A	not available
ng	nanogram
NPH	<i>normal</i> paraffin hydrocarbon
NTA	nitrilotriacetate or nitrilotriacetic acid
ppb	parts per billion
ppm	parts per million
PUREX	plutonium uranium extraction
RGS	retained gas sample
SST	single-shell tank
TBP	tributyl phosphate
TCD	Tank Characterization Database
TNMHC	total non-methane hydrocarbon
TOC	total organic carbon
wt%	weight percent
μg	microgram

## 1.0 INTRODUCTION

Volatile and semivolatile organic compounds continuously evolve from the waste tanks at the Hanford Site. Some of these substances are identical to the compounds that were originally transferred to tanks as waste from large-scale plant operations or from operations that supported the plant operations. The other organic compounds that evolve from the waste are formed in an ongoing cascade of interdependent chemical and radiolytic reactions.

The organic chemicals that were used in the plant operations and in supporting operations are summarized in Section 2.0. Characterization work directed toward the determination the organic compounds that are presently in the waste tanks is presented in Section 3.0. The chemical reactions that are responsible for the ongoing transformations of the organic compounds in the wastes are described in Section 4.0. The information in Sections 2.0, 3.0, and 4.0 provides a technical basis for understanding the chemical consequences of long term storage, sluicing, the addition of chemicals, and the prediction of other organic compounds that may be present in the wastes. These matters are also examined in Section 5.0 together with the chemistry of compounds of special concern including formaldehyde and dimethylmercury.

## 2.0 THE SOURCES OF ORGANIC CHEMICALS

### 2.1 ORGANIC COMPOUNDS USED IN PRINCIPAL PLANT PROCESSES

Topical reports concerning the hazards associated with organic solvents (Cowley et al. 1998) and organic complexants (Meacham et al. 1998) describe the wide spread distribution of organic chemicals in the Hanford Site waste tanks. Considerable quantities of both classes of materials were used and eventually discharged as waste. Kupfer et al. (1999) provided an inventory of the organic chemicals in the waste tanks on the basis of process flowsheets (Scheider 1951, GE 1951), tank transaction records and information from the Hanford Defined Waste Model (Agnew 1995; Agnew et al. 1995a, 1995b, 1996, 1997), chemical usage summaries (McDonald 1968; McDonald and Hogan 1977; Hogan 1992) and other information (Sederburg and Reddick 1994a, 1994b). Major amounts of fifteen different substances were used in five different processes. The names and structures of the organic substances used in the processes are shown in Table 2-1.

**Table 2-1. The Names and Chemical Structures of Principal Process Chemicals**

Name of Chemical	Designation	Chemical Structure
Tributyl phosphate	TBP	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_3\text{P}=\text{O}$
bis(2-Ethylhexyl)phosphoric acid	HB2EHP	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{O})_2\text{P}(=\text{O})\text{OH}$
Hydrocarbon diluents		Mixtures of hydrocarbons
Acetic acid		$\text{CH}_3\text{CO}_2\text{H}$
Glycolic acid		$\text{HOCH}_2\text{CO}_2\text{H}$
Oxalic acid		$\text{HO}_2\text{CCO}_2\text{H}$
Tartaric acid		$\text{HO}_2\text{CCH}(\text{OH})\text{CH}(\text{OH})\text{CO}_2\text{H}$
Citric acid		$\text{HOC}(\text{CH}_2\text{CO}_2\text{H})_2\text{CO}_2\text{H}$
Gluconic acid		$\text{HOCH}_2(\text{CH}(\text{OH}))_4\text{CO}_2\text{H}$
Nitrilotriacetic acid	H3NTA	$\text{N}(\text{CH}_2\text{CO}_2\text{H})_3$
Ethylenediaminetetraacetic acid	H4EDTA	$(\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$
Diethylenetriaminepentaacetic acid	H5DTPA	$(\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$
Hydroxyethylethylenediaminetriacetic acid	H3HEDTA	$(\text{HO}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})\text{CH}_2\text{CH}_2\text{OH}$
Sucrose		beta-D-Fructofuranosyl-alpha-D-glucopyranoside
Methyl isobutyl ketone		$(\text{CH}_3)_2\text{CHC}(=\text{O})\text{CH}_3$

Source: Kupfer et al. (1999)

The acidic wastes from the plant operations were neutralized with sodium hydroxide before being discharged to the waste tanks. The acid form of a complexant such as ethylenediaminetetraacetic acid is conventionally abbreviated as H4EDTA and the basic form is abbreviated as EDTA. This convention has been adopted in this report.

Kupfer et al. (1999) estimated the amounts of each organic compound that was used in each process and the amount that was discharged to the waste tanks. Methyl isobutyl ketone is not included in Table 2-2 because Kupfer et al. concluded that it was not discharged to the waste tanks. They also estimated that 1,100 metric tons of sucrose was used for denitration, but that 95% of the sucrose was consumed in the process with the formation of 22 metric tons of organic carbon in the form of oxalic acid. The diluent is volatile and Kupfer et al. estimated that 80% of the 1,300 metric tons that was used in the plutonium uranium extraction (PUREX) process was lost by evaporation resulting in the transfer of about 220 metric tons of organic carbon to the waste tanks. The total organic carbon (TOC) information developed in their work is summarized in Table 2-2.

**Table 2-2. Amounts Total Organic Carbon Discharged to the Waste Tanks from Plant Operations**

Process	Oxalate (MT)	Acetate (MT)	Citrate (MT)	Tartrate (MT)	Glycolate (MT)	Gluconate (MT)	NTA (MT)
Bismuth Phosphate	95						
Uranium Recovery	25						
REDOX	30						
PUREX	163			42			
B Plant	1	1	318	42	446	21	6
Total	314	1	318	84	446	21	6
		HEDTA (MT)	EDTA (MT)	DTPA (MT)	Diluent (MT)	B2EHP (MT)	TBP (MT)
PUREX					221		404
B Plant		1386	758	4	5	44	23
Total		1386	758	4	226	44	427

Notes: REDOX = reduction-oxidation  
Source: Kupfer et al. (1999)

Kupfer et al. (1999) estimate that 4,000 metric tons of organic carbon was discharged to the waste tanks from process operations. In sharp contrast, Agnew et al. (1996, 1997) concluded that 1,880 metric tons of organic carbon was discharged to the waste tanks from this source. The discrepancy arises for the most part from differences in the estimated amounts of TOC employed in B Plant operations. Agnew et al. (1996, 1997) attribute 1,344 metric tons to B Plant operations and Kupfer et al. attribute 3,050 metric tons to this source. A portion of the discrepancy can be attributed to different assumptions about the volatility of the diluents.

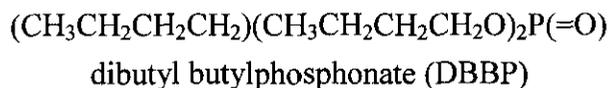
### 2.1.1 Composition of Complexants

Commercial organic products often contain other substances such as byproducts of the chemical reactions that were used to manufacture the material. However, the organic complexants were essentially single compounds.

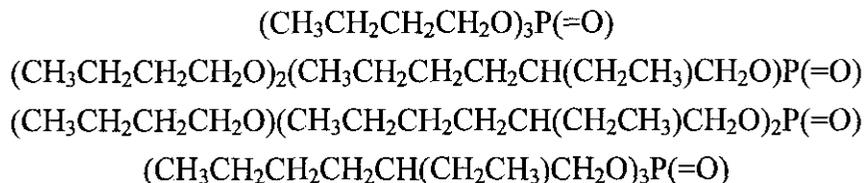
### 2.1.2 Composition of Diluents and Phosphate Esters

The impurities in the diluents and phosphate esters influenced the outcome of the separation process. Accordingly, their composition has been discussed in the technical literature.

**2.1.2.1. Phosphate Esters.** Some commercial grades of reduction-oxidation contained dibutylphosphate and tetrabutylpyrophosphate ions as well as dibutyl butylphosphonate (DBBP), butanol and butanal (Siddall and Brown 1984). Butanol and butanal, whether from this source or from subsequent degradation reactions of tributyl phosphate (TBP), are now common constituents in the waste tanks. Also, DBBP survived the plant operations and was discharged to the waste tanks.

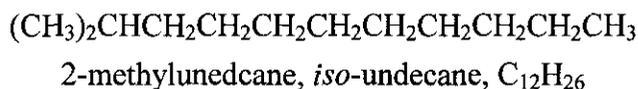


The butyl and 2-ethylhexyl groups in TBP and bis(2-ethylhexyl)phosphoric acid exchange in acid solution to produce a family of trialkyl esters. As discussed subsequently, these substances are found in the waste tanks.

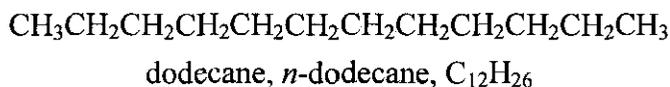


**2.1.2.2. Hydrocarbon Diluents.** Four different commercial diluents (Vandegrift 1984) were used in the Uranium Recovery and PUREX Processes. Shell<sup>1</sup> Spray Base, which was used for about five years in the original Uranium Recovery process, was a complex petroleum distillate that contained about 48% paraffinic hydrocarbons with branched and unbranched structures, 37% cyclic aliphatic hydrocarbons (naphthenes<sup>2\*</sup>) and 15% aromatic hydrocarbons.

The Spray Base was replaced by a second Shell product, Shell E2342, in 1955. It was used in the Uranium Recovery and PUREX processes for about six years. It contained 5 to 10% normal paraffinic hydrocarbons, 20 to 35% branched paraffinic hydrocarbons, and 60 to 70% cyclic aliphatic hydrocarbons (naphthenes) and only 0.1% aromatic hydrocarbons. A Phillips Petroleum Company product, Soltrol 170, was employed in the PUREX process for about six years. This diluent, which was produced by alkylation, was a mixture of branched hydrocarbons that was especially rich in alkanes with methyl groups in the 2 position (isoparaffinic hydrocarbons) as illustrated by 2-methylundecane.



The last diluent used in the last three years of Hanford Site operations was truly a mixture of normal paraffin hydrocarbons (NPH). It was obtained from the South Hampton Company and contained 10% decane, 30% undecane, 31% dodecane, 26% tridecane, and 3% tetradecane.



<sup>1</sup> Shell Chemical Company, Inc.

<sup>2</sup> Naphthenes are natural constituents of petroleum and typically contain a five or six membered ring. These materials should not be confused with naphtha (the petroleum fraction boiling between gasoline and kerosene), and naphthalene (an aromatic hydrocarbon).

Although, the phrase normal paraffin hydrocarbon (NPH) has been frequently used in Hanford Site reports to designate the diluent, it is evident that the first three commercial diluents were complex mixtures of hydrocarbons which contained more branched and cyclic paraffins and aromatic hydrocarbons than normal paraffins.

Finally, approximately 140 metric tons of sodium ferrocyanide was used for cesium removal, the cyanide ion in this compound is a potential source of organic carbon in the waste tanks (Lilga et al. 1996).

## 2.2 ORGANIC COMPOUNDS USED IN SUPPORTING WORK

Other organic compounds were used in laboratory work, decontamination efforts, and other tank farm operations. Kupfer et al. (1999) suggest that as much as 100 metric tons of TOC could have been discharged to the tank farms because of these activities. Several reports (Allen 1976; Jungfleisch 1984; Anderson 1990; Klem 1990; Gerber et al. 1992) provide information about these substances. This information has been reviewed and the organic chemicals and other commercial products used in supporting operations at the Hanford Site are listed in Tables 2-3 and 2-4.

**Table 2-3. Organic Chemicals Used in Support Work and Discharged to Waste Tanks  
(Page 1 of 2)**

Organic Compound	Structure
2-Butoxyethanol	$C_4H_9OCH_2CH_2OH$
Acetic acid	$CH_3CO_2H$
Acetone	$CH_3COCH_3$
Alizarin Yellow (Dihydroxyanthraquinone)	$C_{14}H_8O_4$
Benzene	$C_6H_6$
Bromocresol Purple	$CH_3C_6H_3(OH)Br$
Bromonaphthalene	$C_{10}H_7Br$
Butyl benzyl phthalate	$C_6H_4(CO_2C_4H_9)(CO_2CH_2C_6H_5)$
Carbon tetrachloride	$CCl_4$
Dibutyl butylphosphonate	$(CH_3CH_2CH_2CH_2)(CH_3CH_2CH_2CH_2O)_2P=O$
Dichloromethane	$CH_2Cl_2$
Diethyleneglycol monobutyl ether	$HOCH_2CH_2OC_2CH_2OC_4H_9$
N,N'-Diethylthiourea	$C_2H_5NHCONHC_2H_5$
Dioctyl phthalate	$C_6H_4(CO_2C_8H_{17})_2$
Ethanol	$CH_3CH_2OH$
Ethyl ether	$(CH_3CH_2)_2O$
Ethylene glycol	$HOCH_2CH_2OH$
Formaldehyde (solution)	$CH_2O$
Glycerol	$CH_2OHCHOHCH_2OH$
Hydroxyquinoline	$C_9H_6N(OH)$
Isoamyl acetate	$CH_3CO_2C_5H_{11}$
Isopropyl alcohol	$(CH_3)_2CHOH$
Mandelic acid	$C_6H_5CHOHCO_2H$

**Table 2-4. Organic Chemicals Used in Support Work and Discharged to Waste Tanks  
(Page 2 of 2)**

Organic Compound	Structure
Methanol	CH <sub>3</sub> OH
Methyl ethyl ketone	CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub>
Methyl lactate	CH <sub>3</sub> CH(OH)CO <sub>2</sub> CH <sub>3</sub>
Monohydroxyethyltrihydroxypropylethylenediamine	(HOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> )(HOCH <sub>2</sub> CH <sub>2</sub> )NCH <sub>2</sub> CH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>
Morpholine	C <sub>4</sub> H <sub>9</sub> NO
Naphthylamine	C <sub>10</sub> H <sub>7</sub> NH <sub>2</sub>
Nonylphenoxy poly(ethyleneoxy)ethanol	C <sub>9</sub> H <sub>19</sub> C <sub>6</sub> H <sub>4</sub> O(CH <sub>2</sub> CH <sub>2</sub> O)CH <sub>2</sub> CH <sub>2</sub> OH
Octylphenoxy poly(ethyleneoxy)ethanol	C <sub>8</sub> H <sub>17</sub> C <sub>6</sub> H <sub>4</sub> O(CH <sub>2</sub> CH <sub>2</sub> O)CH <sub>2</sub> CH <sub>2</sub> OH
o-Phenanthroline	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>
Polyester resin	Composition not established
Polyvinyl acetate	(CH <sub>2</sub> CH(OCOCH <sub>3</sub> )) <sub>n</sub>
s-Diphenyl carbazide	(C <sub>6</sub> H <sub>5</sub> NHHN) <sub>2</sub> CO
Sodium tetraphenylborate	NaB(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub>
Sodium xylenesulfonate	(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub> (SO <sub>3</sub> Na)
Tetrachloroethane	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>
Tetrahydroxyethylethylenediamine	(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>2</sub>
Thenoyltrifluoroacetone	(CH <sub>3</sub> ) <sub>3</sub> SCOCH <sub>2</sub> COCF <sub>3</sub>
Thymolphthalein	C <sub>28</sub> H <sub>30</sub> O <sub>4</sub>
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>
Trichloroethane	CH <sub>3</sub> CCl <sub>3</sub>
Trichloroethene	Cl <sub>2</sub> CCHCl
Triethanol amine	N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>
Tri-n-dodecylamine	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> ] <sub>3</sub> N
Tri-isooctylamine	[(CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>5</sub> ] <sub>3</sub> N
Tri-n-octylamine	[CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> ] <sub>3</sub> N
Tris(hydroxymethyl)aminomethane	(HOCH <sub>2</sub> ) <sub>3</sub> CNH <sub>2</sub>
Urea	CO(NH <sub>2</sub> ) <sub>2</sub>
Xylene	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>

Source: Klem (1990), Gerber et al. (1992)

**Table 2-4. Commercial Products Used in Support Work and Discharged to Waste Tanks  
(Page 1 of 2)**

Product Name	Composition
American Cyanamid S 4058 FLOC	Composition Not Established
Anti-Foam 60	Silicone fluid with other compounds
Arsenazo III	A mixture with an arsenic compound
Diversy Chemical 159	Composition Not Established
Dow N-20 FLOC	Composition Not Established
Dow XD 7889 FLOC	Composition Not Established
Dow Anti-Foam B	Silicone fluid with other compounds
Dowex 50 (IX Resin)	Styrene-divinylbenzene resin with sulfonate groups

**Table 2-5. Commercial Products Used in Support Work and Discharged to Waste Tanks  
(Page 2 of 2)**

Product Name	Composition
Dowex 21K/Amberlite XE-270 (IX Resin)	Styrene-divinylbenzene resin with trimethylammonium groups
Duolite ARC-359 (IX Resin)	Phenolic resin with sulfonate groups
Immunol 1468-2	Composition Not Established
Ionac A-580/Permutit SK (IX Resin)	Polyvinylpyridine with methyl groups
Jasco Paint Stripper	Methylene chloride, methanol
Keolite 25E	Composition Not Established
Keraff	Composition Not Established
Magniflox 581-C	Composition Not Established
Mineral Oil	Hydrocarbons
Oakite Clear Guard	Composition Not Established
Oakite Rust Stripper	Composition Not Established
Oakite Swift	Trichloroethane
Orvus K	Composition Not Established
Pace-S-Teen	Composition Not Established
Penvert 192	Composition Not Established
Perokleen	Composition Not Established
Resin IRN-150	Styrene-divinylbenzene resin
Saf-tee Solvent F.O. 128	Composition Not Established
Sani-Flush	Trialkylammonium chloride, oxalic acid, diethylthiourea
Spartan DC 13	Composition Not Established
Turco (Fabrifilm)	Toluene, butanol, isopropanol, acetone
Turco EPO Strip	Composition Not Established
Turco EPO Strip NP	Composition Not Established
Turco 2822	Methylene chloride, acetic acid
Turco 2844	Composition Not Established
Turco 4358-4A	Composition Not Established
Turco 4501 A	Potassium hydroxide, organic diamines
Turco 4518	Oxalic acid, sodium dodecylbenzene sulfonate
Turco 4521	Ammonium oxalate, oxalic acid, sodium dodecylbenzene sulfonate
Turco 4669	Composition Not Established
Turco 4715	Composition Not Established
Turco 4738 (Thin)	Composition Not Established
Turco T-5561	2-Butoxyethanol, dioctylphthalate, morpholine, mineral oil
Turco T-5589	Isopropanol, ammonium hydroxide
Turco Alkaline (Rust Remover)	Sodium hydroxide, kerosene
Turco Deseal Zit 2	Methylene chloride, acetic acid
Turco Plaudit	Composition Not Established
West Lode Degreaser	Aromatic hydrocarbons and other unidentified compounds
Wyandotte Kelvar	Composition Not Established
Wyandotte MF	Composition Not Established
Wyandotte P1075	Composition Not Established
Wyandotte 1112	Composition Not Established

Source: Klem (1990), Gerber et al. (1992)

Almost all of the compounds mentioned in these tables were identified by Klem (1990). However, valuable additional information has been supplied by Gerber (Gerber et al. 1992) and other investigators. Furthermore, anecdotal information suggests that plastic gloves, plastic tubing, cloth rags, elastomers, lubricating oils, pump oils, and related kinds of materials used during sampling operations and other activities were discarded in the waste tanks.

Only fragmentary information is available about the quantities of the organic materials that were used in support operations. However, it is evident that the quantities of these materials are much smaller than the quantities of materials that were used in plant operations. No attempt will be made to determine the quantities of these materials in this report.

### 3.0 ORGANIC COMPOUNDS DETECTED IN TANK WASTE

The compounds that were discharged to the Hanford Site waste tanks after their use in one of the principal plant operations or in a supporting operation were identified in Section 2.0. The organic chemicals that have been found in the waste tanks will be elaborated in this section.

#### 3.1 TOTAL ORGANIC CARBON INVENTORY

Analytical measurements of the TOC contents of cores withdrawn from the tanks during characterization programs have been supplemented, where necessary, by other work and engineering estimates to provide the Best-Basis Inventory (PNNL 2004). The total organic carbon inventories for the single-shell tanks (SSTs) and double-shell tanks (DSTs) are summarized in Tables 3-1 and 3-2.

**Table 3-1. Best-Basis Inventory of Total Organic Carbon in Single-Shell Tanks in 2004**  
(Page 1 of 2)

Tank	Inventory (kg)						
241-A-101	1.65E+04	241-BY-101	6.37E+03	241-SX-101	5.13E+03	241-TX-101	1.26E+03
241-A-102	2.56E+03	241-BY-102	6.45E+03	241-SX-102	9.91E+03	241-TX-102	5.43E+03
241-A-103	1.39E+04	241-BY-103	3.21E+04	241-SX-103	1.29E+04	241-TX-103	3.51E+03
241-A-104	0.00E+00	241-BY-104	1.56E+04	241-SX-104	8.15E+03	241-TX-104	5.66E+02
241-A-105	0.00E+00	241-BY-105	9.51E+03	241-SX-105	6.64E+03	241-TX-105	1.33E+04
241-A-106	4.31E+03	241-BY-106	1.10E+04	241-SX-106	8.24E+03	241-TX-106	8.50E+03
241-AW-101	2.04E+04	241-BY-107	6.37E+03	241-SX-107	9.52E+02	241-TX-107	7.03E+02
241-AW-102	1.46E+04	241-BY-108	5.58E+03	241-SX-108	3.08E+02	241-TX-108	2.96E+03
241-AW-103	1.06E+04	241-BY-109	9.67E+03	241-SX-109	1.66E+03	241-TX-109	1.20E+03
241-AW-104	2.27E+04	241-BY-110	1.32E+04	241-SX-110	4.74E+02	241-TX-110	9.95E+03
241-AW-105	4.75E+03	241-BY-111	1.12E+04	241-SX-111	1.02E+03	241-TX-111	7.46E+03
241-AW-106	2.36E+04	241-BY-112	1.49E+04	241-SX-112	7.10E+02	241-TX-112	1.42E+04
241-B-101	9.41E+02	241-C-101	1.19E+03	241-SX-113	1.03E+01	241-TX-113	1.58E+03
241-B-102	8.16E+02	241-C-102	1.57E+03	241-SX-114	9.52E+02	241-TX-114	1.07E+04
241-B-103	1.88E+02	241-C-103	5.70E+03	241-SX-115	2.74E+01	241-TX-115	1.28E+04

**Table 3-1. Best-Basis Inventory of Total Organic Carbon in Single-Shell Tanks in 2004**  
(Page 2 of 2)

Tank	Inventory (kg)	Tank	Inventory (kg)	Tank	Inventory (kg)	Tank	Inventory (kg)
241-B-104	2.62E+03	241-C-104	1.42E+04	241-T-101	1.98E+03	241-TX-116	7.63E+03
241-B-105	1.34E+03	241-C-105	4.74E+03	241-T-102	1.06E+02	241-TX-117	6.26E+03
241-B-106	2.67E+02	241-C-106	1.55E+01	241-T-103	1.17E+02	241-TX-118	1.45E+04
241-B-107	7.52E+02	241-C-107	7.36E+02	241-T-104	8.81E+02	241-TY-101	4.84E+02
241-B-108	4.10E+02	241-C-108	3.43E+02	241-T-105	1.33E+03	241-TY-102	5.00E+02
241-B-109	1.07E+03	241-C-109	7.60E+02	241-T-106	1.63E+02	241-TY-103	1.49E+03
241-B-110	4.79E+02	241-C-110	5.22E+02	241-T-107	8.82E+02	241-TY-104	2.49E+02
241-B-111	1.16E+03	241-C-111	2.44E+02	241-T-108	1.74E+01	241-TY-105	1.08E+03
241-B-112	6.50E+02	241-C-112	2.42E+03	241-T-109	1.75E-01	241-TY-106	2.48E+02
241-B-201	3.43E+02	241-C-201	1.92E+02	241-T-110	1.64E+03	241-U-101	2.47E+02
241-B-202	4.00E+02	241-C-202	1.41E+02	241-T-111	7.26E+03	241-U-102	1.42E+04
241-B-203	1.24E+02	241-C-203	3.41E+02	241-T-112	2.81E+02	241-U-103	1.91E+04
241-B-204	1.65E+02	241-C-204	3.07E+02	241-T-201	2.88E+01	241-U-104	3.84E+02
241-BX-101	1.96E+02	241-S-101	3.97E+03	241-T-202	3.48E+01	241-U-105	4.02E+04
241-BX-102	1.92E+02	241-S-102	7.32E+03	241-T-203	7.24E+01	241-U-106	2.33E+04
241-BX-103	3.56E+03	241-S-103	6.08E+03	241-T-204	6.28E+01	241-U-107	3.22E+03
241-BX-104	2.72E+03	241-S-104	1.81E+03			241-U-108	1.06E+04
241-BX-105	8.25E+02	241-S-105	3.55E+03			241-U-109	8.80E+03
241-BX-106	9.21E+02	241-S-106	6.33E+03			241-U-110	1.25E+03
241-BX-107	1.13E+03	241-S-107	3.45E+03			241-U-111	6.22E+03
241-BX-108	1.76E+02	241-S-108	1.42E+04			241-U-112	3.80E+02
241-BX-109	7.84E+02	241-S-109	2.24E+03			241-U-201	2.26E+00
241-BX-110	3.07E+03	241-S-110	5.49E+03			241-U-202	2.09E+00
241-BX-111	1.15E+03	241-S-111	3.94E+03			241-U-203	1.14E+00
241-BX-112	4.70E+02	241-S-112	4.34E+03			241-U-204	6.35E+00
						Total	7.25E+05

Source: PNNL (2004)

All information compiled from Tank Characterization Database (TCD)

**Table 3-2. Best-Basis Inventory of Total Organic Carbon in Double-Shell Tanks in 2004**

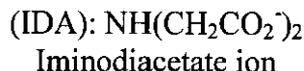
Tank	Inventory (kg)	Tank	Inventory (kg)
241-AN-101	1.97E+04	241-AX-101	1.19E+04
241-AN-102	1.14E+05	241-AX-102	7.00E+03
241-AN-103	1.05E+04	241-AX-103	4.00E+03
241-AN-104	1.93E+04	241-AX-104	0.00E+00
241-AN-105	2.23E+04	241-AY-101	7.60E+03
241-AN-106	1.67E+04	241-AY-102	7.50E+03
241-AN-107	1.47E+05	241-AZ-101	1.91E+03
241-AP-101	8.26E+03	241-AZ-102	7.59E+03
241-AP-102	1.20E+03	241-SY-101	2.76E+04
241-AP-103	2.46E+04	241-SY-102	1.86E+04
241-AP-104	1.73E+04	241-SY-103	2.67E+04
241-AP-105	7.52E+03		
241-AP-106	1.49E+04		
241-AP-107	1.04E+04		
241-AP-108	2.43E+03	Total	5.57E+05

Source: PNNL (2004). All information compiled from TCD.

The Best-Basis Inventory implies that the Hanford Site waste tanks contain about 1280 metric tons of organic carbon. This is about one third of the amount of organic carbon that Kupfer et al. (1999) estimated had been discharged to the waste tanks.

Three factors are apparently responsible for this large difference. First, the reduction of nitrate and nitrite ion with sucrose during plant operations simultaneously depleted the concentrations of the complexants. Specifically, glycolic acid and tartaric acid are structurally related to the organic intermediates formed during the oxidation of sucrose and would have been oxidized to oxalic acid or carbon dioxide in the same way as sucrose. Second, the hydrocarbon diluents are volatile and have evolved from the wastes during the evaporator campaigns and during interim storage. Third, ongoing conventional organic reactions and radiolytically induced reactions have oxidized the remaining diluents, phosphate esters and complexants to produce simple carboxylate ions including formate, acetate and oxalate ion together with inorganic carbonate ion and volatile alkanes, alkenes, alcohols, aldehydes and ketones, amines, and so forth. The rates of the chemical reactions which have significant activation energies would have proceeded more rapidly when the waste tanks were allowed to warm intentionally and when the wastes were concentrated in the evaporator. The reactions have slowed as the radioactive content has decreased and the tanks have cooled.

There is abundant evidence for the ongoing oxidation reactions. Early work (Delegard 1980, 1987) implied that new organic compounds derived from the original organic substances were being formed and were accumulating in the waste tanks. This suggestion was confirmed by subsequent work that demonstrated the presence of new substances such as iminodiacetate ion (IDA) and oxidized compounds such as formate ion, neither of which had been employed in



waste processing operations (Campbell et al. 1994). These results strongly suggested that the organic constituents had been oxidized during operations and were being oxidized during interim storage.

### 3.2 CONFIRMATION OF ORGANIC OXIDATION

The concentration of oxalate ion, which accumulates in the solid sludges and saltcake layers of the waste tanks, can be readily determined by ion chromatography, an analytical measurement routinely performed on waste to determine the concentrations of the major inorganic anions. The TOC and oxalate ion contents of more than 50 SSTs and 32 DSTs were assembled and considered by Meacham et al. (1998) and Stock (2001). The observations for 32 SSTs and 19 DSTs, which have more than 0.1% TOC, are summarized in Tables 3-3 and 3-4.

**Table 3-3. Organic Carbon and Oxalate Ion Contents for Single-Shell Tanks (Page 1 of 2)**

Tank	Mean TOC (wt%)	TOC Inventory (kg)	Oxalate Inventory (kg)	TOC as Oxalate (wt%)
241-A-101	0.31	19600	31300	44
241-A-102	1.11	3910	3140	22
241-AX-101	0.62	3050	4250	38
241-AX-102	1.87	3290	1450	12
241-AX-103	0.52	3260	5130	43
241-BX-110	0.15	2070	4710	62
241-BY-101	0.48	12300	33400	74
241-BY-102	0.38	6940	30400	99
241-BY-103	0.38	9960	36500	99
241-BY-104	0.67	6810	13100	52
241-BY-105	0.73	24200	84300	95
241-BY-106	0.51	21500	59000	75
241-BY-107	0.52	7630	22000	79
241-BY-108	0.39	5820	9750	46
241-BY-109	0.33	11900	37100	85
241-BY-110	0.64	16700	26300	43
241-BY-111	0.55	16700	52800	86
241-BY-112	0.71	13600	47700	96
241-C-104	1	16100	6390	11
241-S-101	0.22	5160	10200	52
241-S-102	0.33	11800	25400	57
241-S-106	0.23	6110	13000	58
241-S-107	0.2	4150	10200	67
241-S-111	0.17	6600	17300	71
241-SX-101	0.53	15800	32400	56
241-SX-106	0.39	13300	17600	36

**Table 3-3. Organic Carbon and Oxalate Ion Contents for Single-Shell Tanks (Page 2 of 2)**

Tank	Mean TOC (wt%)	TOC Inventory (kg)	Oxalate Inventory (kg)	TOC as Oxalate (wt%)
241-U-102	0.74	15900	10300	18
241-U-103	0.64	24000	7690	9
241-U-105	1.23	31200	24100	22
241-U-106	2.16	29600	12700	12
241-U-107	0.18	4950	6860	38
241-U-108	0.42	12900	12700	27

Source: Meacham et al. (1998)

**Table 3-4. Organic Carbon and Oxalate Ion Contents for Double-Shell Tanks**

Tank	Mean TOC ( $\mu\text{g/mL}$ )	TOC Inventory (kg)	Oxalate Inventory (kg)	TOC as Oxalate (wt%), (sd)
241-AN-103	3490	12600	28600	62
241-AN-104	4780	19100	25100	35
241-AN-105	6750	28800	19300	18
241-AP-102	3280	13700	3190	6
241-AP-105	2790	8130	4130	14
241-AP-108	1560	N/A	N/A	21
241-AW-101	3300	14000	2540	5
241-AW-104	4800	N/A	N/A	27
241-AW-105	5100	N/A	N/A	8
241-AY-101	6770	24000	13800	16
241-SY-101	25000	104000	92000	24
241-SY-102	1450	4070	10900	73
241-SY-103	12800	36200	44700	34

Notes:

N/A = not available.

Source: Meacham et al. (1998)

The observations show that six of the 32 SSTs have oxalate ion concentrations that account for more than 75% of the TOC, ten tanks have oxalate ion concentrations that account for 50 to 75% of the TOC and fifteen tanks have oxalate ion concentrations that account for 10% to 50% of the TOC. There is considerably more variation in the oxalate ion content of the DSTs with values ranging from 5% for tank 241-AW-101 to 73% for tank 241-SY-102. Only two of the 13 DSTs for which information is available have more than 50% of the TOC in the form of oxalate ion, and the fraction of the TOC in oxalate ion is generally smaller for the DSTs than for the SSTs. To illustrate, the tanks with large supernatant liquid layers such as tanks 241-AP-102, 241-AW-101, and 241-AW-105 have less than 10% of their organic carbon in oxalate ion. These observations are not unexpected since interim stabilization operations have transferred relatively TOC-rich, oxalate ion-poor supernatant liquids from the SSTs into the DSTs.

In summary, the analytical work concerning the oxalate ion content in more than 70 tanks establishes that oxalate ion, which is less reactive and less soluble than the other end products of the oxidation reactions, is now ubiquitous. The relatively high concentrations of this compound in the waste confirm the widespread oxidation of the organic complexants, diluents, and phosphate esters.

### 3.3 COMPLEXANTS AND CARBOXYLATE IONS IN SOLID AND LIQUID WASTE

The organic complexants in the solid and liquid wastes have been identified by gas and liquid chromatography and mass spectrometry and other advanced analytical methods (Campbell et al. 1994, 1995a, 1995b, 1996a, 1996b, 1997; Pool and Bean 1994; Wahl et al. 1995; Klinger et al. 2000; Evans et al. 2001). These investigations have shown that other new compounds derived from the original complexants are now present. The new anions include the fragmentation products of EDTA and HEDTA such as ethylenediaminetriacetate (ED3A), two isomers of ethylenediaminediacetate (*s*- and *u*-ED2A), ethylenediaminemonoacetate (ED1A), as well as nitrilotriacetate (NTA), IDA, glycinate, acetate, formate and oxalate ions.

Ethylenediaminetriacetate ion (ED3A):  $(^-\text{O}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{NH}(\text{CH}_2\text{CO}_2^-)$

*s*-Ethylenediaminediacetate ion (*s*-ED2A):  $(^-\text{O}_2\text{CCH}_2)\text{NHCH}_2\text{CH}_2\text{NH}(\text{CH}_2\text{CO}_2^-)$

*u*-Ethylenediaminediacetate ion (*u*-ED2A):  $(^-\text{O}_2\text{CCH}_2)_2\text{NCH}_2\text{CH}_2\text{NH}_2$

Ethylenediaminemonoacetate ion (ED1A):  $(^-\text{O}_2\text{CCH}_2)\text{NHCH}_2\text{CH}_2\text{NH}_2$

The concentrations of the original complexants and their principal oxidation products have been determined for samples from more than twenty SSTs and DSTs (Campbell et al. 1994, 1995a, 1995b, 1996a, 1996b, 1997; Pool and Bean 1994; Wahl et al. 1995; Klinger et al. 2000; Evans et al. 2001). The results for the SSTs (Meacham et al. 1998; Camaioni et al. 1998) are summarized in Table 3-5. The related observations for the DSTs are shown in Table 3-6.

**Table 3-5. Concentrations of Organic Complexant Derivatives in Single-Shell Tank Samples**

Tank and Sample	Acetate (wt%)	Citrate (wt%)	Glycolate (wt%)	Formate (wt%)	Oxalate (wt%)	EDTA (wt%)	HEDTA (wt%)	IDA (wt%)	NTA (wt%)	TOC (wt%)
241-A-101, C154, S10, UH	0.21			0.27	3.8	0.19		1.2		
241-A-102, 96-AUG-3	0.18	0.13		0.17	1.4					1
241-AX-102, 95-AUG-007		0.51	0.77	0.48	1.8	0.3	0.15	1.2		3.5
241-B-106, C93, S1, UH	0.003			0.012						0.2
241-BY-102, C157, S4	0.012			0.004	6.8					1.9
241-BY-104, C116, SLG		3			5.4					1.8
241-BY-105, C108, S1, DL	0.11	0.21		0.087						0.18
241-BY-107, C161, S1	0.14			0.06	2.6					0.88
241-BY-110, C101, S7	0.094			0.035	9.5					2.1
2451-BY-110, C103, S4, UH	0.045				3.7					0.75
241-BY-110, C113, S8	0.071			0.012	0.044					0.21
241-C-104, C162, S2, UH	0.25			0.19	0.23					0.91
241-C-105, C76, S1, SGL	0.23	0.39		0.046	0.051				0.1	0.35
241-C-201, TMK COMP	0.095			0.017	3.7				0.11	
241-U-105, C136, S7, UH	0.071	0.39	0.4	0.72	0.83	0.4	0.54			2.2
241-U-106, C148, S2, UH	0.036	0.59	0.45	0.27	0.48	0.63	0.67			2.4
241-U-107, C134, SLG	0.039	0.09		0.12	0.24					0.15
241-U-108, C141, S4, UH	0.06		0.16	0.18	0.5	0.1	0.026	0.16		0.63

## Notes:

AUG = auger

COMP = composite

DL = drainable liquid

LH = lower half

SLG = sludge

UH = upper half

Source: Meacham et al. (1998); Camaioni et al. (1998)

**Table 3-6. Concentrations of Organic Complexant Derivatives in Double-Shell Tank Samples**

Tank and Sample	Acetate (wt%)	Citrate (wt%)	Glycolate (wt%)	Formate (wt%)	Oxalate (wt%)	EDTA (wt%)	ED3A (wt%)	HEDTA (wt%)	IDA (wt%)	NTA (wt%)	TOC (wt%)
241-AW-101, C154, S10, UH	0.93	0.017	0.047	0.099	1.1					0.006	1.5
241-AN-107, Grab		0.49	0.94	0.45	1.4	0.2	0.29	0.044	0.33	0.035	1
241-SY-101, Convective	0.2	0.083	0.17	0.51	0.65	0.53	0.73		0.28	0.087	3.5
241-SY-101, Nonconvective		0.08		0.23	2.1	0.19	0.067		0.22	0.057	0.2
241-SY-103, Convective	0.15	0.11		0.45		0.13	0.06		0.055	0.037	1.9
241-SY-103, Nonconvective	0.17	0.15		0.34	2.2	0.16	0.039		0.044	0.042	1.8

Notes:

UH = upper half

Source: Meacham et al. (1998)

The SST wastes, Table 3-5, contain portions of the original four complexants together with a broad array of their derivatives. The most highly oxidized derivatives, formate and oxalate ion, are abundant in these samples. The SST results also show that glycolate ion, the most abundant original complexant according to the work described in Section 2.0, is absent from many waste samples and when present, its concentration is usually much less than the concentration of oxalate ion. Citrate ion is distributed in essentially the same way. The EDTA and HEDTA concentrations are below the detection limit in most samples. However, their remnants, IDA and NTA, are present in some wastes even though their precursors have been consumed.

The original organic complexants are absent from some wastes, for example, tanks 241-BY-102 and 241-BY-110, even though the total organic content is relatively high. Oxalate ion is the most abundant constituent organic constituent in these wastes. In contrast, the original complexants are still present in readily measured concentrations in wastes from tanks 241-U-105 and 241-U-106. Clearly, the oxidation reaction has not proceeded to the same extent in the wastes obtained from the BY and U tanks. The explanation for this difference can be found in the thermal history of the waste tanks. The wastes discharged to tanks 241-U-105 and 241-U-106 were processed and stored at much lower temperature than the wastes evaporated at high temperature and discharged to tanks 241-BY-102 and 241-BY-110. Results of this kind infer the thermal history of the waste and its storage temperature alter the rates at which the organic material is oxidized and, therefore, have a pronounced effect on the current organic content.

The organic constituents in the DST samples identified in Table 3-6 are similar to the organic constituents in the SSTs. The remnant molecules of the EDTA family are readily discernible in the samples from some tanks, and the concentrations of the low molecular weight organic carboxylate ions are high. In addition, the concentrations of oxalate ion in the convective and non-convective layers differ significantly. This ion accumulates in the solid phases of the waste because sodium ion further depresses its low solubility (Barney 1994, 1995, 1996, 1997).

The concentrations of acetate, formate, and oxalate ion have been determined in some other waste tanks (Meacham et al. 1998; Klinger et al. 2000; Evans et al. 2001). These limited results are in accord with the observations presented in the tables.

In summary, characterization work has established that the complexants have been oxidized and fragmented. The work provides conclusive evidence for the ongoing oxidation reactions of the organic constituents in the wastes.

### **3.4 HYDROCARBON DERIVATIVES IN LIQUID AND SOLID WASTE**

The complexants and their remnants and the simple one and two carbon atom carboxylate ions are ubiquitous constituents of the wastes, but many other organic substances have been detected during characterization work. Some of the compounds with only one or two carbon atoms (e.g., methane, methanol, ethanol, etc.) could have been obtained by the hydrolysis or oxidation of the phosphate esters or the complexants, but most of them (e.g., dodecane, cyclohexane, octane,

1-octanol, etc.) are recognized as components of the original hydrocarbon diluents or their oxidation products. The characterization work on these substances is described in this section.

### 3.4.1 Hydrocarbon Derivatives and Phosphate Esters in Waste Tank Cores

Gas Chromatography/Mass Spectrometry (GC/MS) was first employed to determine the organic chemicals in extracts of solid and liquid wastes in the early stages of the characterization program at the Hanford Site. It soon became apparent that the analyses of headspace samples could be performed more efficiently and more accurately than the analyses of the solid and liquid wastes, and only a few of these analyses were performed. Inspection of the database revealed that some entries were identified as "unknown" or "unknown C-12 alkanone" or were labeled "B" for blank contamination or "U" for a target analyte below the detection limit. These entries were excluded from consideration. The organic compounds that have been identified in the liquid and solid cores and recorded in the Tank Characterization Database (TCD) (PNNL 2004) on June 1, 2004 are shown in Table 3-7, and the concentrations of normal paraffin hydrocarbons and TBP in the cores samples are assembled in Table 3-8.

**Table 3-7. Organic Compounds in Solid and Liquid Waste (Page 1 of 2)**

Compound	CAS Number	Molecular Weight	DST Liquid Conc. (µg/mL)	DST Solid Conc. (µg/mL)	SST Liquid Conc. (µg/mL)	SST Solid Conc. (µg/mL)
1,1,1-Trichloroethane	71-55-6	133	0	0	0	16
1,1,2-Trichloro-1,2,2-trifluoroethane	79-34-5	187	0	0	0	8
1,2,4-Trichlorobenzene	120-82-1	181	0	0	0	3
1,4-Dioxane	123-91-1	88	0.4	0	0	0
1-Nitrocyclohexene	2562-37-0	127	0	0	0	22
2,2,6-Trimethyloctane	98060-52-7	156	0	0	0	185
2,2,8-Trimethyldecane	98060-54-9	184	0	0	0	25
2,2-Dimethyldecane		170	0	0	0	112
2,2-Dimethylheptane		128	0	0	0	152
2,3,7-Trimethyloctane		156	0	0	0	82
2,4,6-Trimethyloctane		156	0	0	0	308
2,5,6-Trimethyldecane		184	0	0	0	85
2,6,6-Trimethyloctane		156	0	0	0	48
2,6-bis(1,1-Dimethylethyl)-4-methylphenol	128-37-0	220	0	0	0	112
2,6-Dibromo-4-nitrophenol	99-28-5	297	0	0	0	52
2,6-Dibromophenol	608-33-3	252	0	0	0	13
2-Butanone	78-93-3	72	1	0	0	15
2-Butoxyethanol	111-76-2	118	6	0	0	0
2-Fluoro-4-nitrophenol	21571-34-6	157	0	0	77	90
2-Fluoronitrophenol		157	0	0	0	42
3,3-Dimethylhexane	563-16-6	114	0	0	0	12
3-Ethyl-5-methylheptane		142	0	0	0	15
4-Chloro-3-methylphenol	35421-08-0	143	0	0	0	4
6-Ethyl-2-methyloctane	13151-34-3	156	0	0	0	17

**Table 3-7. Organic Compounds in Solid and Liquid Waste (Page 2 of 2)**

Compound	CAS Number	Molecular Weight	DST Liquid Conc. (µg/mL)	DST Solid Conc. (µg/mL)	SST Liquid Conc. (µg/mL)	SST Solid Conc. (µg/mL)
Acenaphthene	83-32-9	154	0	0	0	3
Acetone	67-64-1	58	3	0	0	21
Aroclor 1254	27323-18-8	300	0	2	0	10
Benzene	71-43-2	78	0.01	0	0	0
bis(2-Ethylhexyl)phthalate	117-81-7	391	6	0	0	13
bis(3-tert-Butyl-4-hydroxy-6-methylphenyl) sulfide	96-69-5	359	0	0	0	15
Chlorocyclohexene	10297-06-0	117	0	0	0	19
Chloroform	67-66-3	119	0	0	0	9
Chloromethane	74-87-3	50	0	0	0	2
cis-2-Bromocyclohexanol	16536-57-5	179	0	0	25	0
Cyclohexene	110-83-8	82	16	0	0	0
Decahydronaphthalene	91-17-8	138	0	0	0	7
Decane	124-18-5	142	0	0	0	37
Dichlorocyclohexane	2108-92-1	153	0	0	0	102
Dichlorohexane		155	0	0	0	26
Di-N-Butylphthalate	84-74-2	278	0	0	8	0
Diocetyl adipate	103-23-1	371	0	0	0	14
Dodecane	112-40-3	170	0	0	96	1293
Dodecane,4,6-dimethyl-			0	0	0	13
Heptadecane	629-78-7	240	0	0	0	17
Hexadecane	544-76-3	226	0	0	0	20
Hexadecanoic Acid	57-10-3	256	0	0	0	26
Methoxytrimethylsilane	1825-61-2	104	0	0	0	884
Methylenechloride	75-09-2	85	0.2	0	0	1
Nitrobenzene	98-95-3	123	33	0	0	0
Nonane	111-84-2	128	0	0	0	105
Pentadecane	629-62-9	212	0	0	4	94
Phosphonic acid, dioctadecyl ester			0	0	0	71
Pyrene	129-00-0	202	0	0	0	4
Tetrachloroethene	127-18-4	166	0	0	0	0
Tetradecane	629-59-4	198	0	0	52	2318
Toluene	108-88-3	92	0.09	0	0	17
Tributyl phosphate	126-73-8	266	3320	0	40	372
Trichloroethene	79-01-6	131	0.05	0	0	0
Tridecane	629-50-5	184	0	0	82	3245
Trimethylsilanol	1066-40-6	90	0	0	0	439
Undecane	1120-21-4	156	0	0	3	80
Xylenes (total)	1330-20-7	319	0	0	0	1

Source: PNNL (2004) (Tank Characterization Database)

**Table 3-8. Concentrations of Normal Paraffin Hydrocarbons and Tributyl Phosphate in Core Composite Samples**

Waste Tank	Decane (µg/g)	Undecane (µg/g)	Dodecane (µg/g)	Tridecane (µg/g)	Tetradecane (µg/g)	Pentadecane (µg/g)	TBP (µg/g)	NPH/TBP
241-B111	17	36	80	1,700	1,100	55	22	140
241-B201			290	930	1,000	41		
241-BX-107								
Core 40			600	1,700	1,200	42	9	390
Core 41		14	620	1,400	1,100	50	6	530
241-BY-108	3	24	59	71	55	22	0.08	3,000
241-C-102								
Sample 1	110	550	2,100	3,500	1,800		2,100	4
Sample 2	230	1,300	4,500	2,500	3,700		2,700	5
241-C-110								
Core 38	2	19	860	2,000	1,500		9	490
Core 39	9	17	680	1,500	1,100	52	11	310
241-C-112		12	32	48	45	25	210	1
241-S-104			170	510	400	15		
241-T-104								
Core 45			180	670	570	26		
Core 46			95	420	390	15		
241-T-107								
Core 50			9	31	24		3	21
Core 52				32		28		
241-T-111								
Core 31	9	15	140	360	260	27		
Core 33			130	370	250	14		

## Notes:

The analytical data were abstracted from the Tank Characterization Reports.  
The Relative Standard Deviation ranges from 30 to 50% for replicate samples.

The hydrocarbon to TBP ratios shown in Table 3-8 vary substantially. The variability almost certainly arises because of differences in the alkalinity and temperature of the wastes. High alkalinity and low temperature lead to the selective loss of TBP because of its hydrolysis to dibutylphosphate ion (DBP). High temperature enhances the rate of hydrolysis of TBP to DBP and the rate of evaporation of the hydrocarbon diluents. Both substances disappear from supernatant layers. On the other hand, the rate of loss of the hydrocarbons from the solid layer is limited by mass transport.

Additional information is available from the work of the Waste Treatment Plant. Liquid and solid samples from tanks 241-C-104 (Evans et al. 2001) and tanks 241-AN-107 and 241-AW-101 (Klinger et al. 2000) were extracted into organic solvents and analyzed by GC/MS. As in the other instances, compounds that were flagged as suspect by the analysts or only partially identified were deleted from consideration. The restriction led to the elimination of four unidentified nitrate esters. There were two other serious complications. In particular, the use of

acetone as a cosolvent for the extraction of the desired organic constituents caused aldol condensation reactions in the samples from tanks 241-AN-107 and AW-101. These compounds were excluded from the tables. The acidification of the sample from tank 241-C-104 produced nitrous acid which converted the amines and phenols in the sample into N-nitroso compounds and nitrophenols. These compounds were not excluded from the results summarized in Table 3-9.

**Table 3-9. Organic Compounds in Liquid and Solid Samples from Tanks 241-C-104, 241-AN-107, and 241-AW-101 (Page 1 of 5)**

Compound	C-104 Conc. Liquid (µg/L)	C-104 Conc. Solid (µg/kg)	AN-107 Conc. Liquid (µg/L)	AN-107 Conc. Solid (µg/kg)	AW-101 Conc. Liquid (µg/L)	AW-101 Conc. Solid (µg/kg)
<b>Alkanes</b>						
Butane		3000				920
Pentane		7400				150
Pentane, 3-ethyl-2,2-dimethyl-			2			
Hexane		9200				200
Hexane, 2-methyl-						9400
Methylcyclohexane				40		
Heptane	1900	6300				210
Octane	3800	4600				200
Nonane	6200	4500				250
Decane	42000	150000				278
Undecane	93000	480000				1772
Dodecane	49000	690000				73000
Tridecane	3800	980000		358		190000
Tetradecane	1200	200000		603		210000
Pentadecane	120					20000
<b>Alkenes</b>						
1-Propene,2-methyl-						70
1-Butene				45		45
1-Hexene						34
1-Heptene		5400				38
1-Octene		4600				62
1-Nonene		2900				49
1-Decene						59
4-Decene	5300	3100				
5-Undecene						70
5-Undecene, (Z)-		6200				
5-Undecene, (E)-		1600				
3-Dodecene, (Z)-						163
6-Dodecene, (E)-	8300					
6-Tridecene						102
<b>Aromatic Hydrocarbons</b>						
Benzene		60				10
Ethylbenzene		40				

**Table 3-9. Organic Compounds in Liquid and Solid Samples from Tanks 241-C-104, 241-AN-107, and 241-AW-101 (Page 2 of 5)**

Compound	C-104 Conc. Liquid (µg/L)	C-104 Conc. Solid (µg/kg)	AN-107 Conc. Liquid (µg/L)	AN-107 Conc. Solid (µg/kg)	AW-101 Conc. Liquid (µg/L)	AW-101 Conc. Solid (µg/kg)
<b>Alcohols and Ethers</b>						
1-Propanol					2	
1-Butanol			96	520	96	250
2-Butanol, 1-methoxy-					2100	
3-Buten-2-ol					1	
3-Pentanol, 2,2-dimethyl-	510			18000	3000	22000
1-Hexanol, 2-ethyl-					6	209
1-Heptanol					2	79
3-Heptanol, 6-methyl-						34000
1-Octanol						62
Butane, 2-methoxy-2-methyl-			1300			
Tetrahydrofuran			31	43	140	180
1,4-Dioxane					180	97
p-Dioxin, 2,3-dihydro-2,5,6-trimethyl-				13000		110000
<b>Aldehydes and Ketones</b>						
Propanal		1100				
Butanal			4			
Butanal, 3-hydroxy-			1			
Hexanal			4			
Decanal			2			
Benzaldehyde					1	
Acetone					360	13
2-Butanone	290	320	16	58	55	160
2-Butanone, 3-methyl-						34
2-Pentanone		99		75000		
2-Pentanone, 3-methyl-						36000
2-Pentanone, 4-methyl-						10
2-Hexanone	24	270				40
2,5-Hexanedione						17000
2-Heptanone	97	810		15		59
3-Heptanone	74	800				59
3-Heptanone, 2,6-dimethyl-		1900				
4-Heptanone		100				8
2-Octanone		1200				
2-Nonanone		3800				
2-Decanone	5100	5000				
3-Decanone	4800	4400				
4-Decanone		10000				
5-Decanone	12000					
2-Undecanone		37000				
3-Undecanone		25000				
5-Undecanone		44000				
5-Undecanone, 2-methyl-	9200					

**Table 3-9. Organic Compounds in Liquid and Solid Samples from Tanks 241-C-104, 241-AN-107, and 241-AW-101 (Page 3 of 5)**

Compound	C-104 Conc. Liquid (µg/L)	C-104 Conc. Solid (µg/kg)	AN-107 Conc. Liquid (µg/L)	AN-107 Conc. Solid (µg/kg)	AW-101 Conc. Liquid (µg/L)	AW-101 Conc. Solid (µg/kg)
2-Dodecanone	250	14000				
3-Dodecanone		23000				
4-Dodecanone		6700				
5-Dodecanone		67000				
2-Tridecanone	120	18000				
4-Tridecanone		47000				
5-Tridecanone				307		
4-Tetradecanone		10000				
2,6,6-Trimethylcyclohexen-1-yl-3-buten-2-one	270					
2,6-Dimethyl-8-nitro-2-hepten-4-one						32000
2(3H)-Furanone, dihydro-4,4-dimethyl-					580	
<b>Acids and Esters</b>						
Propanoic acid, 2,2-dimethyl					410	
Butanoic acid				5300	2000	
Pentanoic acid	680					
Hexanoic acid	6300					
Hexanoic acid, 2-ethyl-	160		740			
Heptanoic acid	7000		9500			
Octanoic acid	14000					
Nonanoic acid	5900					
Decanoic acid	3100					
Undecanoic acid	1100					
Dodecanoic acid	100					
Valproic acid	170					
Ethyl acetate				2500	1100	
1-Methylethyl acetate				23000		
2-Butanol, 3-methyl-, acetate				36000		
Methyl 2-hydroxy-2-isobutyrate		38000				
2-Propenoic acid, 2-methyl-, ethenyl-					440	
2-Butenoic acid, 3-methyl-, ethyl						99000
Ethyl 3-methylbutanoate				7300		
Butyl nonanoate	130					
2(3H)-Furanone, 5-ethylidihydro-	170					
Diethyl phthalate				150		
Bis(2,6-Ethylhexyl)phthalate	480	5900				
Tributyl phosphate			100			1800
Tri(2-ethylhexyl) phosphate					240	
<b>Nitrogen-containing Compounds</b>						
1-Propanamine, N,2-dimethyl-			2100			
1-Propanol, 3-amino-					390	
Cyclohexylamine, N-cyclohexyl-	95					
1-Naphthyl amine				5400		1400
Hydrazine, 1,1-diethyl-					96	

**Table 3-9. Organic Compounds in Liquid and Solid Samples from Tanks 241-C-104, 241-AN-107, and 241-AW-101 (Page 4 of 5)**

Compound	C-104 Conc. Liquid (µg/L)	C-104 Conc. Solid (µg/kg)	AN-107 Conc. Liquid (µg/L)	AN-107 Conc. Solid (µg/kg)	AW-101 Conc. Liquid (µg/L)	AW-101 Conc. Solid (µg/kg)
Acetonitrile			94	89		41
Hexanenitrile	140					
Octanenitrile		2200				
Nonanenitrile		2100				
Acrylonitrile		990				
Propanedinitrile, methylene	12000					
Pyridine				1400		
2-Methylpyridine	510					
Isoquinoline, 1-methyl-				4200		
Quinoline, 2-methyl-				12000		
Oxazole, 4,4-dihydro-2-methyl-			450			
Oxazole, 4,4-dihydro-2-methyl-	8800					
2-Pyrrolidinone	160					
1-Propanamine, N-methyl-N-nitroso-			3600			
N-Nitrosodimethyl amine	1900		260	2600	890	12000
N-nitrosomethyl ethyl amine					580	1300
4-Piperidinol, 1-nitroso-			16000	26000		
Morpholine, 4-nitroso-			3900	3800		
Ethanol, 2,2'-(nitrosoimino)bis-				5800		
N-nitroso-2-methyl-oxazolidine			740			
Piperazine, 1,4-dinitroso-			1500			
Ethane, 2,2'-(nitrosoimino)bis-			1000			
Piperidine, 2-methyl-1-nitroso-			160			
Piperidine, 4-methyl-1-nitroso-			230			
Pyrrolidine, 2,5-dimethyl-1-nitroso-			820			
Butane, 2,3-dimethyl-2-nitro-			1200			
1H-Indazole, 1-methyl-4-nitro-			840			
Nitric acid, ethyl ester			2200			
Nitric acid, propyl ester	370	40				
Acetamide, N-ethyl-				11000		
<b>Halogen-containing Compounds</b>						
Chloroform			380	3300	430	
Ethane, 1,1,2-trichloro-			380		160	
Ethane, 1,1,1,2-tetrachloro-			170			
Propane, 1-bromo-				1400		
Aldrin			3.7			
alpha-BHC	1.4	5.5		35.1		
beta-BHC	3.4					18.1
gamma-BHC		17.6				
Heptachlor				18.4	6.5	73.4
Heptachlor Epoxide	1.6	2.7				
delta-BHC		7.2				
alpha-Chlordane		2.2				

**Table 3-9. Organic Compounds in Liquid and Solid Samples from Tanks 241-C-104, 241-AN-107, and 241-AW-101 (Page 5 of 5)**

Compound	C-104 Conc. Liquid (µg/L)	C-104 Conc. Solid (µg/kg)	AN-107 Conc. Liquid (µg/L)	AN-107 Conc. Solid (µg/kg)	AW-101 Conc. Liquid (µg/L)	AW-101 Conc. Solid (µg/kg)
4,4'-DDE		5.6				
Endrin Aldehyde		4.3				
Arochlor-1016/1242	4.9	154				
Arochlor-1248	5.3	278				
Arochlor-1254	2.3	80		17		23
Arochlor-1260/1262		40				
<b>Other Compounds</b>						
2-Fluoro-6-nitrophenol	750			7500		
3-Fluoro-4-nitrophenol	300					
2-Chloro-4-nitrophenol				5400		
4-Methyl-2-nitrophenol	410					
5-Methyl-2-nitrophenol	180					
3-Methyl-4-nitro-phenol	89					
2-Methyl-3,5-dinitrophenol	230					
4,6-Dinitro-2-methylphenol	147					
Cyclotrisiloxane, hexamethyl-	9000					
Cyclotetrasiloxane, octamethyl-	3900					
p-Benzoquinone, 2-methyl-	400					
Silane, ethyldimethyl-						15000

Source: Evans et al. (2000); Klinger et al. (1999)

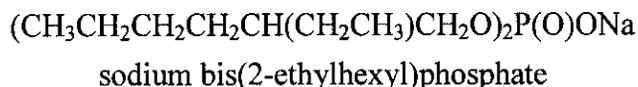
The concentrations of the organic compounds in the solid samples generally exceed their concentrations in the liquid samples. The composite sample from tank 241-C-104, which has the highest concentrations of organic compounds among the three tanks, contains 82% solids. Tanks 241-AN-107 and 241-AW-101 have 11 and 16% solids, respectively. Low molecular weight materials are underrepresented in this work because of the requirement for the concentration of the extraction solvents. The diverse array of compounds that were detected in these solid and liquid samples are comparable to the similarly broad range of compounds found in the samples from the headspaces of the SSTs as discussed in the next section. However, the finding of tris(2-ethylhexyl)phosphate confirms the expectation that the entire family of phosphate esters is present. The array of nitroso compounds is also notable. Although the analysts expressed concern that these substances may have been produced by nitrosation reactions that occurred during the separation of the organic compounds from the liquids and solids, compounds of this same class have been observed in the headspaces of the waste tanks where no such separations are used. The nitrophenols mentioned in Table 3-9 are also somewhat suspect because these substances are rapidly formed from phenols in the presence of nitrous acid. However, these compounds are retained in Table 3-9 because they signal the presence of the unnitrate original phenol. For example, the detection of 2-fluoro-6-nitrophenol implies that 2-fluorophenol was present and the detection of 2-chloro-4-nitrophenol implies that 2-chlorophenol was present. The observation for phenol reported for these samples accords with the early GC/MS work done at the Hanford Site shown in Table 3-7. Overall, the results shown in Table 3-9 for solids and liquids are comparable to the results for the headspace samples as discussed subsequently.

### 3.4.2 Hydrocarbon Derivatives and Phosphate Esters in a Separate Phase

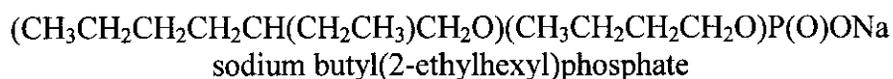
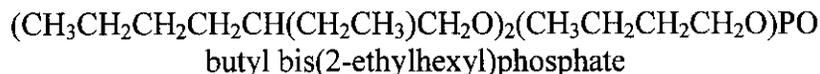
The complexants and the carboxylate ions derived from them are very soluble in alkaline solution. Most of the hydrocarbons and their intermediate oxidation products with five or more carbon atoms have very low solubility in such media. When the concentrations of these organic compounds are relatively high, separate liquid phases can form. Campbell and coworkers studied the organic phosphates and hydrocarbons in several C-Farm tanks (Campbell et al. 1994, 1995a, 1995b, 1996a, 1996b, 1997; Campbell and Mong 1999). In the course of this work, they examined the composition of the organic layer from tank 241-C-103 and an organic oil, which had separated from the waste from tank 241-C-106.

The chromatogram of the organic liquid from tank 241-C-103 showed there were several hydrocarbons and phosphate esters in relatively high abundance together with a large amount of other unresolved material. The main constituents were readily identified as 2.8% dodecane, 11.4% tridecane, 6.0% tetradecane, and 0.9% pentadecane together with 1.9% DDBP and 47.2% TBP. The unresolved and unidentified organic compounds accounted for approximately 30% of the material in the sample.

An oil was separated from the waste withdrawn from tank 241-C-106 before the sluicing operation in 1999. Infrared analyses showed that its principal component was sodium bis(2-ethylhexyl)phosphate.



Although this substance is a salt, it is hydrophobic and floats on aqueous solutions of sodium hydroxide (Camaioni and Linehan 1999). The analytical work (Campbell et al. 1996a, 1996b; and Campbell and Mong 1999) implies the oil contains about 45% sodium bis(2-ethylhexyl)phosphate, 17% butyl bis(2-ethylhexyl)phosphate, 13% sodium butyl(2-ethylhexyl)phosphate, 8% TBP, 4% tris(2-ethylhexyl)phosphate, and about 13% paraffinic hydrocarbons.



Some of these substances were used during B Plant operations as already discussed in Section 2.0; the others were formed during B Plant operations or interim storage as will be discussed in Section 4.0. The triester, tris(2-ethylhexyl)phosphate, has also been found in liquid samples from tank 241-AW-101.

### 3.5 ORGANIC GASES IN SOLID AND LIQUID LAYERS

#### 3.5.1 Retained Gas Program

The retained gas sample (RGS) program collected and analyzed samples of the retained gases in 14 tanks (Shekarriz et al. 1997; Mahoney et al. 1999; Mahoney 2000). The retained gas constitutes a small fraction of the convective layers ranging from about 0.2% by volume in tank 241-SX-106 to less than 3% by volume in the bubbly slurry that existed in tank 241-SY-101 before the waste was transferred in 2000. In contrast, the retained gas generally represents a larger fraction of the nonconvective layers ranging from about 4% by volume for the nonconvective layer in tank 241-AW-101 to approximately 26% in the nonconvective layer of tanks 241-SX-106 and S-102. The gas generation rates computed by the Hu model (Hu 1997; Hu 1999; Hu 2002; Hu et al. 1998; Hu and Barker 2003) are rather slow, and a few months are required for the generation of the modest amounts of gas retained in the convective layers. In contrast, years may be required for the generation of the rather large amounts of gas retained in the nonconvective layers (Stock 2001). The compositions of the retained gases are summarized in Table 3-10.

**Table 3-10. Retained Gas Composition (Mahoney et al. 1999; Mahoney 2000)**

Tank	Layer	Hydrogen (mol %)	Nitrogen (mol %)	Nitrous Oxide (mol %)	Ammonia (mol %)	NOx (mol %)	Methane (mol %)	Other Hydrocarbons (mol %)
241-A-101	C	15	69	9.2	3.5	0.7	1.7	1.5
241-A-101	NC	72	19	5.6	2.5	0.1	0.7	0.2
241-AX-101		62	18	11	6.3	0	2.5	0.7
241-BY-109	NC	51	29	17	0.2	0.0*	0.9	0.9
241-S-102	Tank	34	33	32	0.9	0	0.5	0.2
241-S-106	NC	64	26	9.8	0.3	0.1	0.3	0.4
241-S-111	C	6	91	1.2	0.2	0	0.3	1.1
241-S-111	NC	67	21	10.3	0.9	0	0.5	0.2
241-SX-106	C	18	70	7.2	0.7	0	2	2.7
241-SX-106	NC	51	21	24	4	0.0*	0.6	0.3
241-U-103	NC	24	36	38	0.7	0.1	0.4	0.6
241-U-109	NC	25	47	26	0.9	0	0.8	0.4
241-AN-103	Crust	63	29	6.5	1.4	0.0*	0.6	0.2
241-AN-103	C	19	73	4.8	0.9	0.5	1.4	1.1
241-AN-103	NC	62	32	3.8	0.6	0.1	0.6	0.8
241-AN-104	C	25	61	9	0.8	0.4	1.9	2.5
241-AN-104	NC	46	30	22	0.9	0.1	0.9	0.8
241-AN-105	C	25	62	7.2	0.6	1.8	1.4	2
241-AN-105	NC	61	25	12.5	0.5	0.3	0.7	0.3
241-AW-101	C	25	69	1.2	0.4	1.6	1	1.6
241-AW-101	NC	33	56	5.8	0.6	0.5	1.7	3.1
241-SY-101	Crust	38	30	21	10	0	0.6	0.6
241-SY-101	Liquid	33	41	19	4.5	0	1.5	1.4

Notes: The values for all the gases are given as ranges by Mahoney (2000). These values were averaged in this table. The detection limit for NOx is 0.01 mole %. When the value was above this limit but less than 0.1 it is reported as 0.0\*.

The retained gases contain several compounds of interest to the industrial hygiene programs. Ammonia and nitrous oxide are present in all the waste tanks. Many tanks also retain low concentrations (0.1%) of nitric oxide and nitrogen dioxide. They also contain between 0.3 and 2.5% methane and between 0.2 and 2.7% other hydrocarbons. Inasmuch as the hydrocarbons with 2 or 3 carbon atoms are often overlooked in conventional analyses of the headspaces, the RGS work provides evidence for the widespread occurrence of ethane, ethene, ethyne and propane, propene, cyclopropane, and propyne. As shown in Table 3-10, the sum of their concentrations is comparable to the concentration of methane.

Some of these gaseous substances such as methane and the other hydrocarbons have very low solubility, and are retained predominantly as gases. Ammonia is very soluble in the aqueous phases of the waste. The nitrogen oxides exhibit intermediate behavior. Nitrous oxide is the most soluble gas of this group and Mahoney et al. (1999) have shown that substantial portions of this gas are retained in the liquid phase.

### 3.5.2 Organic Compounds in the Retained Gas in Tank 241-SY-101

The composition of the volatile organic compounds retained within the waste in tank 241-SY-101 has been established by the analysis of a gas-rich slurry withdrawn from a location beneath the crust (Mahoney et al. 1999; Evans et al. 1999). The results are shown in Table 3-11.

**Table 3-11. Organic Compounds in Retained Gas from the Slurry in Tank 241-SY-101**  
(Page 1 of 4)

Compound	Conc (ppmv)	Conc (ppmv)
<b>ALKANES</b>		
Propane		152
2,2-Dimethylpropane		13
Butane	103	
2-Methylbutane		13
2,2-Dimethylbutane		2.0
Pentane	7.2	
2-Methylpentane		2.0
3-Methylpentane		1.7
Hexane	1.3	
3-Methylhexane		0.19
2,3,4-Trimethylhexane		0.12
Heptane	1.6	
3-Methylheptane		0.38
Octane	0.16	
Nonane	0.10	
Decane	0.75	
Undecane	1.4	
Dodecane	1.3	
Tridecane	2.9	
Tetradecane	7.3	

**Table 3-11. Organic Compounds in Retained Gas from the Slurry in Tank 241-SY-101  
(Page 2 of 4)**

Compound	Conc (ppmv)	Conc (ppmv)
<b>CYCLOALKANES</b>		
Cyclopropane		49
cis-1,2-Dimethylcyclopropane		1
Cyclobutane		3.5
Cyclopentane		
Methylcyclopentane		0.47
Cyclohexane	0.69	
Methylcyclohexane		0.84
<b>ALKENES</b>		
Propene		249
2-Methylpropene		36
1-Butene		48
2-Methylbutene		4.5
2-Butene (E)		151
2-Methyl-2-butene		3.4
1-Pentene		2.2
1-Hexene		1.0
2-Heptene		0.39
3-Heptene		0.16
Z-3-Heptene		0.07
3-Methyleneheptane		0.39
Z-2-Octene		0.23
<b>ALKADIENES AND ALKYNES</b>		
1,3-Butadiene		109
Propyne		7.8
<b>AROMATIC COMPOUNDS</b>		
Benzene	2.8	
Toluene	1.3	
o-Xylene	0.05	
m-and p-Xylene	0.24	
Ethylbenzene	0.06	
1-Ethyl-2-methylbenzene	0.03	
1,2,4-Trimethylbenzene	0.04	
1,3,5-Trimethylbenzene	0.03	
Styrene	0.04	
<b>ALCOHOLS AND ETHERS</b>		
Methanol	259	
Ethanol	265	
2-Butoxyethanol		3.4
1-Propanol	44	
2,2-Dimethyl-1-propanol		1.5
2-Propanol		10
2-Methyl-2-propanol		7.3
1-Butanol	103	

**Table 3-11. Organic Compounds in Retained Gas from the Slurry in Tank 241-SY-101  
(Page 3 of 4)**

Compound	Conc (ppmv)	Conc (ppmv)
2-Butanol		1.0
2-Methyl-2-butanol		0.36
1-Hexanol		
2-Ethyl-1-hexanol		0.07
3-Heptanol		1.2
3-Methyl-3-heptanol		0.15
Dimethyl ether		21
Tetrahydrofuran	44	
2,2,5,5-Tetramethyltetrahydrofuran		0.59
1,4-Dioxane		3.2
<b>ALDEHYDES AND KETONES</b>		
2-Butenal		0.51
Propanone	6.9	
2-Butanone	6.1	
2-Pentanone		
4-Methyl-2-pentanone	0.5	
2-Hexanone		0.12
2-Heptanone		0.03
Cyclohexanone	0.29	
<b>AMINES</b>		
Methyl amine		206
Dimethyl amine		2.8
Ethyl amine		31
1-Propanamine		0.37
2-Butanamine		0.42
1-Methylaziridine		8.0
7-Azabicyclo[4.1.0]heptane		0.09
Pyridine	73	
Pyrazine		1.4
Propanamide		0.36
<b>NITRO AND NITROSO COMPOUNDS</b>		
Nitromethane		1.9
2-Methyl-2-nitropropane		0.97
N-Nitrosodimethyl amine		1.9
<b>NITRILES</b>		
Acetonitrile	0.98	
Propanenitrile	0.14	
2-Propenenitrile		0.76
Butannitrile	0.10	
Pentanenitrile	0.10	
Hexanenitrile	0.11	
Octanenitrile		0.10

**Table 3-11. Organic Compounds in Retained Gas from the Slurry in Tank 241-SY-101  
(Page 4 of 4)**

Compound	Conc (ppmv)	Conc (ppmv)
<b>HALOCARBONS</b>		
Chloromethane	0.23	
Methylene chloride	0.70	
Chloroform	0.04	
Carbontetrachloride	0.04	
Chloroethane	0.26	
1,1-Dichloroethane	0.04	
1,2-Dichloroethane	0.04	
1,1,1-Trichloroethane	0.05	
1,1,2-Trichloroethane	0.04	
1,1,2,2-Tetrachloroethane	0.05	
1,2-Dichloropropane	0.05	
Vinyl chloride	0.21	
1,1-Dichloroethene	0.08	
cis-1,2-Dichloroethene	0.07	
Trichloroethene	0.04	
Tetrachloroethene	0.05	
cis-1,3-dichloropropene	0.04	
trans-1,3-dichloropropene	0.03	
Chlorobenzene	0.05	
1,2-Dichlorobenzene	0.02	
1,3-Dichlorobenzene	0.02	
1,4-Dichlorobenzene	0.02	
1,2,4-Trichlorobenzene	0.48	
Bromomethane	0.11	
Bromoform	0.13	
1,2-Dibromoethane	0.06	
Dichlorodifluoromethane	0.06	
Trichlorofluoromethane	0.07	
1,1,2-Trichloro-1,2,2-trifluoromethane	0.04	
1,2-Dichloro-1,1,2,2-tetrafluoroethane	0.15	
<b>OTHER COMPOUNDS</b>		
Trimethylsilanol		0.53
Methoxytrimethylsilane		2.3
Butoxytrimethylsilane		0.15
Octamethylcyclotetrasiloxane		0.99
Hexamethyldisiloxane		0.68
Carbon disulfide		0.75

## Notes

(1) The information that was obtained by Evans et al. (1999) for a sample from the bubbly slurry was used by Mahoney et al. (1999) to estimate the organic content of the gas in the mixed slurry.

Conc = concentration

The twenty most abundant compounds account for more than 90 mole% of the organic material. Eight of the 20 substances including propane, propene, cyclopropane, butane, the butenes, cyclobutane, and butadiene are essentially insoluble in the liquid waste and have boiling points that are less than the temperature of the waste. These substances have very low concentrations in the liquid and are retained in gaseous form. Eleven of the 20 substances including methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, acetone, 2-butanone, methylamine, dimethylamine, and ethylamine are soluble in the liquid waste. These substances like ammonia are stored principally in the liquid phase of the waste. The implication of the analytical work is that the convective layers of this tank contained rather high concentrations of these 11 soluble organic compounds.

In summary, the retained gas that was in tank 241-SY-101 before the waste was transferred in 2000 contained the hydrocarbon diluents together with fragmented alkanes, alkenes, cycloalkanes, ketones, and other compounds. The gas sample also contained relatively high concentrations of methylamine, ethylamine, dimethylamine, pyridine, and pyrazine.

### **3.6 ORGANIC COMPOUNDS IN THE DOME SPACES**

#### **3.6.1 Organic Compounds in the Dome Spaces of Single Shell Tanks**

The information about the organic compounds in the dome spaces of the SSTs was compiled several years ago to support a previous toxicological study (Stock and Huckaby 2000). Additional analyses have been carried out in the interval and the information in the Tank Characterization Database (TCD) on June 1, 2004 was reviewed and the report was revised to include the new information and reissued (Stock and Huckaby 2004).

In brief, the TCD contains headspace characterization data from 1992 to the present, and includes data for 109 SSTs. The extent to which different tank headspaces have been characterized varies greatly, but each farm and all major waste types are represented. Test plans specified that samples be analyzed for organic target compounds by GC/MS. The target compounds were to be positively identified by their retention times and mass spectra. Non-target organic compounds were tentatively identified by comparing their observed mass spectra with the spectra in the Wiley/National Institute of Standards and Technology library. This method of identification is widely used. Confidence that any given tentatively identified compound has been properly identified decreases as its concentration decreases, and as the number of chemical isomers increases.

The work identified about 1,230 compounds. As already mentioned, suspect results and results for ambiguously identified substances are not included. For convenience, the results are reproduced in Tables 3-12 to 3-29.

Table 3-12. Alkanes (Page 1 of 6)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Methane	74-82-8	15	11	16.043	17,000	241-C-103
Ethane	74-84-0	2	0.11	30.070	89	241-TX-111
Propane	74-98-6	42	8.5	44.097	4,700	241-C-105
2-Methylpropane	75-28-5	13	1.6	58.124	656	241-BY-106
2,2-Dimethylpropane	463-82-1	7	0.16	72.151	54	241-A-101
Butane	106-97-8	53	18	58.124	7,712	241-C-103
2-Methylbutane	78-78-4	12	7.2	72.151	2,454	241-BY-108
2,2-Dimethylbutane	75-83-2	8	0.56	86.178	160	241-BY-105
2,3-Dimethylbutane	79-29-8	1	0.029	86.178	8.3	241-U-107
2,2,3-Trimethylbutane	464-06-2	1	0.092	100.206	22	241-TY-104
2,2,3,3-Tetramethylbutane	594-82-1	3	0.22	114.233	47	241-BX-111
Pentane	109-66-0	47	17	72.151	5,700	241-BY-105
2-Methylpentane	107-83-5	21	14	86.178	3,901	241-BY-108
3-Methylpentane	96-14-0	12	2.3	86.178	650	241-BY-108
3-Ethylpentane	617-78-7	2	0.89	100.206	217	241-TY-104
2,2-Dimethylpentane	590-35-2	1	0.047	100.206	11	241-TY-104
2,3-Dimethylpentane	565-59-3	18	2.9	100.206	716	241-TY-101
2,4-Dimethylpentane	108-08-7	6	0.55	100.206	134	241-U-102
3,3-Dimethylpentane	562-49-2	8	1.3	100.206	313	241-TY-101
3-Ethyl-2-methylpentane	609-26-7	1	0.022	114.233	4.7	241-BY-106
2,3,3-Trimethylpentane	560-21-4	4	1.3	114.233	278	241-TX-116
2,3,4-Trimethylpentane	565-75-3	1	0.29	114.233	62	241-TX-116
Hexane	110-54-3	72	7.9	86.178	2,237	241-BY-108
2-Methylhexane	591-76-4	18	3.4	100.206	828	241-TY-101
3-Methylhexane	589-34-4	23	5.1	100.206	1,253	241-TY-101
2,3-Dimethylhexane	584-94-1	3	1.0	114.233	216	241-BY-107
2,4-Dimethylhexane	589-43-5	8	1.6	114.233	334	241-BY-108
2,5-Dimethylhexane	592-13-2	4	0.21	114.233	45	241-AX-102
2,2,3-Trimethylhexane	16747-25-4	2	0.017	128.260	3.3	241-U-107
2,2,4-Trimethylhexane	16747-26-5	1	0.011	128.260	2.1	241-TY-104
2,2,5-Trimethylhexane	3522-94-9	3	0.060	128.260	11	241-SX-107
2,3,3-Trimethylhexane	16747-28-7	1	0.0018	128.260	0.35	241-T-107
2,3,5-Trimethylhexane	1069-53-0	6	0.27	128.260	52	241-BX-103
2,2,5,5-Tetramethylhexane	1071-81-4	1	0.024	142.287	4.1	241-U-106
3,3,4,4-Tetraethylhexane	5171-86-8	1	0.075	198.395	9.3	241-BY-107

Table 3-12. Alkanes (Page 2 of 6)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Heptane	142-82-5	70	4.0	100.206	984	241-BY-108
2-Methylheptane	592-27-8	8	1.8	114.233	392	241-BY-108
3-Methylheptane	589-81-1	12	0.51	114.233	110	241-BY-108
3-Ethylheptane	15869-80-4	2	0.035	128.260	6.6	241-T-111
4-Methylheptane	589-53-7	2	1.8	114.233	392	241-C-103
2,3-Dimethylheptane	3074-71-3	6	0.26	128.260	49	241-BY-108
2,4-Dimethylheptane	2213-23-2	9	0.61	128.260	117	241-BY-101
2,5-Dimethylheptane	2216-30-0	3	0.11	128.260	21	241-TX-116
2,6-Dimethylheptane	1072-05-5	6	0.50	128.260	96	241-BY-108
3,3-Dimethylheptane	4032-86-4	1	0.017	128.260	3.3	241-C-110
3,5-Dimethylheptane	926-82-9	1	0.20	128.260	38	241-BY-108
2,2,4-Trimethylheptane	14720-74-2	4	0.66	142.287	113	241-TX-116
2,3,5-Trimethylheptane	20278-85-7	1	1.7	142.287	299	241-BY-108
2,3,6-Trimethylheptane	4032-93-3	2	1.7	142.287	299	241-BY-108
3,3,5-Trimethylheptane	7154-80-5	4	0.21	142.287	36	241-AX-104
2-Methyl-3-ethylheptane	14676-29-0	7	0.067	142.287	11	241-BY-104
2-Methyl-5-ethylheptane	13475-78-0	1	0.041	142.287	7.1	241-BY-102
5-Methyl-3-ethylheptane	52896-90-9	2	1.0	142.287	173	241-C-102
4-(1-methylethyl)heptane	52896-87-4	2	0.40	142.287	69	241-BY-108
4-Ethyl-2,2,6,6-tetramethylheptane	62108-31-0	2	0.34	184.368	45	241-AX-104
4-Propylheptane	3178-29-8	1	0.0087	142.287	1.5	241-A-102
2,2,4,6,6-Pentamethylheptane	13475-82-6	4	0.22	170.341	32	241-B-103
2,2,3,4,6,6-Hexamethylheptane	62108-32-1	1	0.013	184.368	1.7	241-TY-104
Octane	111-65-9	60	1.6	114.233	353	241-C-103
2-Methyloctane	3221-61-2	3	0.018	128.260	3.5	241-BY-106
3-Methyloctane	2216-33-3	5	0.57	128.260	108	241-BY-108
4-Methyloctane	2216-34-4	5	1.1	128.260	210	241-BX-103
3-Ethyl-2,7-dimethyloctane	62183-55-5	2	0.013	170.341	1.8	241-U-107
4-Ethylloctane	15869-86-0	2	0.064	142.287	11	241-BY-109
2,5-Dimethyloctane	15869-89-3	2	0.30	142.287	52	241-C-101
2,6-Dimethyloctane	2051-30-1	6	0.30	142.287	52	241-BY-107
3,4-Dimethyloctane	15869-92-8	1	0.0080	142.287	1.4	241-BY-105
3,5-Dimethyloctane	15869-93-9	2	0.15	142.287	25	241-BY-104
2,3,3-Trimethyloctane	62016-30-2	1	0.64	156.314	100	241-BY-107
2,3,7-Trimethyloctane	62016-34-6	4	2.8	156.314	445	241-BX-104
2,5,6-Trimethyloctane	62016-14-2	2	0.028	156.314	4.4	241-U-107

Table 3-12. Alkanes (Page 3 of 6)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
2-Methyl-5-ethyloctane	62016-18-6	1	0.16	156.314	26	241-C-101
2-Methyl-6-ethyloctane	62016-19-7	5	0.27	156.314	42	241-BY-108
Nonane	111-84-2	62	1.6	128.260	297	241-C-103
2-Methylnonane	871-83-0	2	0.12	142.287	20	241-BY-107
3-Methylnonane	5911-04-6	3	0.22	142.287	38	241-BY-108
4-Methylnonane	17301-94-9	10	0.65	142.287	112	241-C-102
2,6-Dimethylnonane	17302-28-2	12	3.8	156.314	602	241-C-103
4,5-Dimethylnonane	17302-23-7	2	0.0078	156.314	1.2	241-BY-105
3,7-Dimethylnonane	17302-32-8	6	2.2	156.314	344	241-BY-108
2-Methyl-5-propylnonane	31081-17-1	1	0.0018	184.368	0.24	241-T-107
3-Methyl-5-propylnonane	31081-18-2	5	0.60	184.368	80	241-U-106
5-(2-Methylpropyl)nonane	62185-53-9	2	0.052	184.368	6.9	241-BY-110
5-Propylnonane	998-35-6	1	0.0037	170.341	0.53	241-C-104
5-Butylnonane	17312-63-9	4	0.31	184.368	41	241-BY-107
2,2,4,4,6,6,8,8-Heptamethylnonane	4390-04-9	1	0.012	226.449	1.3	241-S-105
Decane	124-18-5	58	16	142.287	2,835	241-C-103
2-Methyldecane	6975-98-0	16	1.9	156.314	301	241-C-102
3-Methyldecane	13151-34-3	9	1.0	156.314	158	241-C-102
4-Methyldecane	2847-72-5	14	0.92	156.314	143	241-C-204
5-Methyldecane	13151-35-4	5	0.82	156.314	128	241-C-102
5-Propyldecane	17312-62-8	3	0.026	184.368	3.4	241-T-107
2,4-Dimethyldecane	2801-84-5	1	0.0030	170.341	0.43	241-BY-106
2,5-Dimethyldecane	17312-50-4	3	2.9	170.341	421	241-C-101
2,9-Dimethyldecane	1002-17-1	2	0.0078	170.341	1.1	241-A-102
3,8-Dimethyldecane	17312-55-9	5	0.27	170.341	39	241-BX-104
2,2,3-Trimethyldecane	62338-09-4	1	0.013	184.368	1.7	241-AX-102
2,2,8-Trimethyldecane	62238-01-1	2	0.26	184.368	34	241-U-106
2,3,5-Trimethyldecane	62238-11-3	3	0.04	184.368	5.7	241-BY-109
2,3,6-Trimethyldecane	62238-12-4	6	0.65	184.368	86	241-BY-108
2,3,7-Trimethyldecane	62238-13-5	3	0.92	184.368	122	241-BX-104
2,3,8-Trimethyldecane	62238-14-6	4	0.24	184.368	32	241-BY-107
2,4,6-Trimethyldecane	62108-27-4	3	22	184.368	2,918	241-C-103
2,5,9-Trimethyldecane	62108-22-9	1	0.027	184.368	3.5	241-BY-109
2,6,6-Trimethyldecane	62237-97-2	2	0.015	184.368	1.9	241-TY-104
2,6,7-Trimethyldecane	62108-25-2	4	1.3	184.368	170	241-BY-107
2,6,8-Trimethyldecane	62108-26-3	2	0.013	184.368	1.7	241-TY-104

Table 3-12. Alkanes (Page 4 of 6)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
2-Methyl-6-ethyldecane	62108-21-8	1	2.0	184.368	267	241-C-102
5-Methyl-5-ethyldecane	17312-74-2	1	0.0091	184.368	1.2	241-TX-118
2,3,5,8-Tetramethyldecane	UAK014-02	1	0.15	198.395	18	241-BY-108
Undecane	1120-21-4	61	84	156.314	13,192	241-C-103
2-Methylundecane	7045-71-8	15	26	170.341	3,684	241-C-103
3-Methylundecane	1002-43-3	14	16	170.341	2,368	241-C-103
4-Methylundecane	2980-69-0	16	12	170.341	1,711	241-C-103
5-Methylundecane	1632-70-8	14	6.3	170.341	908	241-C-103
6-Methylundecane	17302-33-9	10	3.2	170.341	461	241-C-102
3-Ethylundecane	17312-58-2	1	0.0022	184.368	0.29	241-TY-104
5-Ethylundecane	17453-94-0	5	1.2	184.368	158	241-C-102
6-Ethylundecane	17312-60-6	1	0.0027	184.368	0.36	241-BY-106
2,2-Dimethylundecane	17312-64-0	1	0.015	184.368	1.9	241-U-107
2,3-Dimethylundecane	17312-77-5	3	0.89	184.368	118	241-BY-108
2,4-Dimethylundecane	17312-80-0	9	14	184.368	1,824	241-C-103
2,5-Dimethylundecane	17301-22-3	1	0.091	184.368	12	241-C-110
2,6-Dimethylundecane	17301-23-4	23	38	184.368	4,984	241-C-103
2,7-Dimethylundecane	17301-24-5	2	0.55	184.368	73	241-BY-108
2,8-Dimethylundecane	17301-25-6	4	0.78	184.368	103	241-BY-107
2,9-Dimethylundecane	17301-26-7	2	0.22	184.368	29	241-BY-107
2,10-Dimethylundecane	17301-27-8	14	36	184.368	4,741	241-C-103
3,4-Dimethylundecane	17312-78-6	2	0.65	184.368	86	241-TY-103
3,5-Dimethylundecane	17312-81-1	1	0.0009	184.368	0.12	241-C-112
3,6-Dimethylundecane	17301-28-9	2	0.092	184.368	12	241-BY-107
3,7-Dimethylundecane	17301-29-0	8	20	184.368	2,675	241-C-103
3,8-Dimethylundecane	17301-30-3	5	3.8	184.368	511	241-C-102
3,9-Dimethylundecane	17301-31-4	2	0.17	184.368	23	241-A-106
4,4-Dimethylundecane	17312-68-4	4	0.52	184.368	69	241-TY-103
4,6-Dimethylundecane	17312-82-2	3	4.8	184.368	632	241-C-101
4,7-Dimethylundecane	17301-32-5	4	2.1	184.368	280	241-BY-108
4,8-Dimethylundecane	17301-33-6	5	0.46	184.368	61	241-C-102
5,5-Dimethylundecane	17312-73-1	1	1.3	184.368	170	241-BX-104
5,7-Dimethylundecane	17312-83-3	3	0.74	184.368	98	241-TY-103
6,6-Dimethylundecane	17312-76-4	1	0.82	184.368	108	241-BY-108
Dodecane	112-40-3	62	355	170.341	51,054	241-C-103
2-Methyldodecane	1560-97-0	3	2.7	184.368	365	241-C-102

Table 3-12. Alkanes (Page 5 of 6)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
3-Methyldodecane	17312-57-1	5	1.6	184.368	219	241-C-102
4-Methyldodecane	6117-97-1	15	17	184.368	2,310	241-C-103
5-Methyldodecane	17453-93-9	3	0.52	184.368	69	241-BY-108
6-Methyldodecane	6044-71-9	4	0.72	184.368	96	241-BY-108
2,5-Dimethyldodecane	56292-65-0	9	2.3	198.395	282	241-BY-108
4,6-Dimethyldodecane	61141-72-8	9	57	198.395	7,005	241-C-103
4,9-Dimethyldodecane	3054-63-5	2	0.023	254.504	2.2	241-BY-103
2,6,10-Trimethyldodecane	3891-98-3	15	54	212.422	6,225	241-C-103
2,7,10-Trimethyldodecane	74645-98-0	6	4.9	212.422	559	241-C-102
2,6,11-Trimethyldodecane	31295-56-4	11	44	212.422	5,065	241-C-103
2-Methyl-6-propyldodecane	55045-08-4	4	0.037	226.449	4.0	241-BY-104
2-Methyl-8-propyldodecane	55045-07-3	8	2.7	226.449	287	241-BY-108
5,8-Diethyldodecane	24251-86-3	2	0.070	226.449	7.5	241-BY-107
2,2,4,9,11,11-Hexamethyldodecane	6304-50-3	1	0.015	254.504	1.4	241-S-105
Tridecane	629-50-5	68	465	184.368	61,759	241-C-103
2-Methyltridecane	1560-96-9	19	19	198.395	2,373	241-C-103
3-Methyltridecane	6418-41-3	9	11	198.395	1,356	241-C-103
4-Methyltridecane	26730-12-1	13	1.4	198.395	169	241-BY-108
5-Methyltridecane	25117-31-1	4	11	198.395	1,356	241-C-103
6-Methyltridecane	13287-21-3	14	27	198.395	3,276	241-C-103
7-Methyltridecane	26730-14-3	14	11	198.395	1,356	241-BY-108
2,5-Dimethyltridecane	56292-66-1	1	0.0078	212.422	0.90	241-BY-103
4,8-Dimethyltridecane	55030-62-1	9	2.0	212.422	232	241-BY-108
3-Ethyltridecane	13286-73-2	3	1.0	212.422	116	241-BY-107
5-Propyltridecane	55045-11-9	4	1.7	226.449	188	241-BY-107
Tetradecane	629-59-4	58	111	198.395	13,670	241-C-103
3-Methyltetradecane	18435-22-8	5	0.35	212.422	40	241-BY-108
4-Methyltetradecane	25117-24-2	4	2.8	212.422	327	241-BX-104
5-Methyltetradecane	25117-32-2	1	0.0018	212.422	0.21	241-T-107
4-Ethyltetradecane	55045-14-2	1	0.037	226.449	4.0	241-BY-104
2,5-Dimethyltetradecane	56292-69-4	1	0.0092	226.449	1.0	241-BY-103
4,11-Dimethyltetradecane	55045-12-0	3	0.0092	226.449	1.0	241-BY-105
6,9-Dimethyltetradecane	55045-13-1	1	0.0009	226.449	0.10	241-T-107
2,6,10-Trimethyltetradecane	14905-56-7	4	0.17	240.476	18	241-BY-107
Pentadecane	629-62-9	33	34	212.422	3,904	241-C-103
2-Methylpentadecane	1560-93-6	6	0.30	226.449	33	241-C-102

Table 3-12. Alkanes (Page 6 of 6)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
3-Methylpentadecane	2882-96-4	1	0.059	226.449	6.3	241-C-110
2,6,10-Trimethylpentadecane	3892-00-0	5	0.086	254.504	8.3	241-BY-107
2,6,10,14-Tetramethylpentadecane	1921-70-6	5	0.052	268.531	4.8	241-BY-107
8-Hexylpentadecane	13475-75-7	2	0.066	296.585	5.4	241-BY-107
Hexadecane	544-76-3	28	31	226.449	3,365	241-C-103
2-Methylhexadecane	1560-92-5	2	0.061	240.476	6.2	241-BY-107
3-Methylhexadecane	6418-43-5	2	0.40	240.476	41	241-BY-107
7,9-Dimethylhexadecane	21164-95-4	3	0.011	254.504	1.1	241-B-103
2,6,10,14-Tetramethylhexadecane	638-36-8	9	0.28	282.558	25	241-BY-110
Heptadecane	629-78-7	20	40	240.476	4,101	241-C-103
3-Methylheptadecane	6418-44-6	1	0.047	254.504	4.5	241-C-110
7-Methylheptadecane	20959-33-5	1	0.46	254.504	44	241-BY-108
8-Methylheptadecane	13287-23-5	1	0.0018	254.504	0.18	241-C-107
2,6,10,14-Tetramethylheptadecane	18344-37-1	1	0.042	296.585	3.5	241-BY-107
2,6,10,15-Tetramethylheptadecane	54833-48-6	1	0.0073	296.585	0.60	241-C-107
9-Octylheptadecane	7225-64-1	1	0.25	352.693	17	241-TY-103
Octadecane	593-45-3	8	0.068	254.504	6.5	241-BY-108
2-Methyloctadecane	1560-88-9	2	0.83	268.531	76	241-TY-103
2,6-Dimethyloctadecane	75163-97-2	1	0.0018	282.558	0.16	241-T-107
Nonadecane	629-92-5	3	0.0027	268.531	0.25	241-C-107
9-Methylnonadecane	13287-24-6	2	0.011	282.558	1.0	241-B-103
Eicosane	112-95-8	6	0.19	282.558	17	241-BY-107
Heneicosane	629-94-7	1	0.012	296.585	1.0	241-C-107
Docosane						
7-Hexyldocosane	55373-86-9	1	0.056	394.774	3.5	241-C-110
Hexacosane	630-01-3	1	0.27	366.720	18	241-BY-108
<b>Summation</b>			<b>1,785</b>		<b>274,443</b>	

Source: Stock and Huckaby (2004)

Table 3-13. Cycloalkanes (Page 1 of 5)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>CYCLOALKANES</b>						
Cyclopropane	75-19-4	31	0.55	42.081	320	241-BY-105
Methylcyclopropane	594-11-6	1	0.16	56.108	68	241-C-104
Ethylcyclopropane	1191-96-4	5	6.7	70.135	2,333	241-BY-108
1,1-Dimethylcyclopropane	1630-94-0	4	0.47	70.135	163	241-BY-107
cis-1,2-Dimethylcyclopropane	930-18-7	3	1.1	70.135	370	241-BY-105
trans-1,2-Dimethylcyclopropane	2402-06-4	1	0.045	70.135	16	241-BY-110
Propylcyclopropane	2415-72-7	7	0.60	84.163	173	241-C-102
(1-Methylethyl)cyclopropane	3638-35-5	3	0.27	84.163	77	241-BY-104
Butylcyclopropane	930-57-4	5	2.3	98.190	571	241-BY-108
trans-1-Butyl-2-methylcyclopropane	38851-70-6	1	0.010	112.217	2.2	241-B-103
(1-Methylbutyl)cyclopropane	5458-16-2	1	0.027	112.217	5.8	241-BY-110
Pentylcyclopropane	2511-91-3	3	0.055	112.217	12	241-BY-109
Octylcyclopropane	1472-09-9	2	1.1	154.298	174	241-C-102
1,2-Dibutylcyclopropane	41977-32-6	(a) 1	0.038	154.298	6.1	241-BY-110
1-Pentyl-2-propylcyclopropane	41977-33-7	(a) 1	1.5	154.298	232	241-C-101
1-Ethyl-2-heptylcyclopropane	74663-86-8	(a) 1	0.055	168.325	8.0	241-BY-104
1-Ethyl-2-pentylcyclopropane	62238-08-8	(a) 1	0.0012	140.271	0.21	241-T-107
1,1,2-Trimethyl-3-(2-methylpropyl)cyclopropane	41977-43-9	(a) 1	0.0092	140.271	1.6	241-BY-105
1-Heptyl-2-methylcyclopropane	74663-91-5	(a) 1	0.014	154.298	2.2	241-BY-106
1-Butyl-1-methyl-2-propylcyclopropane	41977-34-8	1	0.0050	154.298	0.80	241-BY-105
1-(2-Butyl)-1-(2-methylbutyl)cyclopropane	UCY012-08	1	0.0060	168.325	0.87	241-TY-104
Cyclobutane	287-23-0	3	0.41	56.108	180	241-BY-107
Methylcyclobutane	598-61-8	1	1.3	70.135	447	241-BY-108
Ethylcyclobutane	4806-61-5	1	0.52	84.163	152	241-BY-107
(1-Methylethyl)cyclobutane	872-56-0	4	0.16	98.190	39	241-BY-106
cis-1,2-Diethylcyclobutane	MCYCY00-01	1	0.42	112.217	92	241-C-102
trans-1,2-Diethylcyclobutane	19341-98-1	2	0.29	112.217	64	241-C-101
1,1,2,3,3-Pentamethylcyclobutane	57905-86-9	1	0.0073	126.244	1.4	241-C-108
Cyclopentane	287-92-3	5	0.60	70.135	208	241-BY-107
Methylcyclopentane	96-37-7	8	1.9	84.163	559	241-BY-108
Ethylcyclopentane	1640-89-7	3	0.037	98.190	9.1	241-BY-104
Dimethylcyclopentane	2452-99-5	(a) 5	0.31	98.190	78	241-S-103
cis-1,2-Dimethylcyclopentane	1192-18-3	3	0.081	98.190	20	241-SX-110
trans-1,2-Dimethylcyclopentane	822-50-4	5	0.45	98.190	112	241-BY-108
cis-1,2-Dimethyl-trans-3-methylcyclopentane	15890-40-1	2	0.032	112.217	7.0	241-SX-114

Table 3-13. Cycloalkanes (Page 2 of 5)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
cis-1-Ethyl-3-methylcyclopentane	2613-66-3	1	0.0005	112.217	0.12	241-TY-104
cis-1,3-Dimethylcyclopentane	2532-58-3	1	0.0055	98.190	1.4	241-BY-106
trans-1,3-Dimethylcyclopentane	1759-58-6	2	0.016	98.190	4.0	241-SX-111
1,1,3-Trimethylcyclopentane	4516-69-2	2	0.33	112.217	72	241-BY-108
1,2,3-Trimethylcyclopentane	2815-57-8	(a) 1	0.0044	112.217	0.96	241-AX-102
1,2,4-Trimethylcyclopentane	2815-58-9	(a) 1	0.16	112.217	36	241-S-103
a,a,b-1,2,4-Trimethylcyclopentane	4850-28-6	3	0.027	112.217	6.0	241-BY-104
(2-Methylpropyl)cyclopentane	3788-32-7	1	0.023	126.244	4.4	241-TX-118
(1-Methylbutyl)cyclopentane	4737-43-3	2	0.22	140.271	38	241-BY-107
(2-Methylbutyl)cyclopentane	53366-38-4	2	0.32	140.271	56	241-BY-108
1,2-Dimethyl-3-(1-methylethyl)cyclopentane	489-20-3	(a) 2	0.29	140.271	51	241-BY-107
1,3-Dimethyl-2-(1-methylethyl)cyclopentane	32281-85-9	(a) 5	0.70	140.271	121	241-BY-108
1-Methyl-3-(2-methylpropyl)cyclopentane	29053-04-1	(a) 5	0.52	140.271	91	241-BY-108
1-Butyl-2-ethylcyclopentane	72993-32-9	(a) 2	0.10	154.298	16	241-BY-107
1-Butyl-2-propylcyclopentane	62199-50-2	(a) 1	0.15	168.325	21	241-BY-107
1-Hexyl-3-methylcyclopentane	61142-68-5	(a) 6	0.25	168.325	36	241-C-110
1-Hexyl-3,3-dimethylcyclopentane	61142-66-3	1	0.025	180.336	3.4	241-BY-110
1-Pentyl-2-propylcyclopentane	62199-51-3	(a) 4	0.43	182.352	58	241-C-102
Decylcyclopentane	1795-21-7	1	4.9	210.406	565	241-C-103
2-Ethyl-1,1-dimethylcyclopentane	54549-80-3	1	0.0020	126.244	0.39	241-SX-106
cis-1,1,3,4-Tetraethylcyclopentane	53907-60-1	1	0.018	126.244	3.6	241-BY-104
trans-1-Methyl-2-(4-methylpentyl)cyclopentane	66553-50-2	1	0.0005	168.325	0.080	241-TY-104
3-Hexyl-1,1-dimethylcyclopentane	61142-65-2	1	0.0032	182.352	0.43	241-TY-104
Cyclohexane	110-82-7	27	3.9	84.163	1,145	241-C-103
Methylcyclohexane	108-87-2	27	1.5	98.190	365	241-TY-101
Ethylcyclohexane	1678-91-7	5	0.42	112.217	92	241-BY-108
(1-Methylethyl)cyclohexane	696-29-7	1	0.0064	126.244	1.2	241-BY-106
1,1-Dimethylcyclohexane	590-66-9	1	0.0043	112.217	0.94	241-TX-118
1,2-Dimethylcyclohexane	583-57-3	(a) 1	0.23	112.217	50	241-BY-108
cis-1,3-Dimethylcyclohexane	638-04-0	4	0.31	112.217	68	241-BY-108
1,4-Dimethylcyclohexane	589-90-2	(a) 2	0.26	112.217	56	241-C-204
cis-1-Ethyl-2-methylcyclohexane	4923-77-7	1	0.015	126.244	2.8	241-BY-106
Diethylcyclohexane	1331-43-7	(a) 1	0.017	140.271	3.0	241-C-110
Cyclopropylcyclohexane	32669-86-6	3	0.26	124.228	51	241-BY-108
Propylcyclohexane	1678-92-8	3	0.10	126.244	20	241-C-102
1,1,2-Trimethylcyclohexane	7094-26-0	2	1.4	126.244	266	241-C-204

Table 3-13. Cycloalkanes (Page 3 of 5)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
1,1,3-Trimethylcyclohexane	3073-66-3		9	0.74	126.244	144	241-BY-108
1,2,3-Trimethylcyclohexane	1678-97-3	(a)	2	0.0030	126.244	0.59	241-T-107
a,b,b-1,2,4-Trimethylcyclohexane	7667-60-9		1	0.013	126.244	2.5	241-T-111
a,a,a-1,3,5-Trimethylcyclohexane	1795-27-3		1	0.018	126.244	3.6	241-BY-104
1,3,5-Trimethylcyclohexane	1839-63-0	(a)	2	0.0078	126.244	1.5	241-BY-105
Butylcyclohexane	1678-93-9		4	1.4	140.271	240	241-BY-108
(1-Methylpropyl)cyclohexane	7058-01-7		5	1.9	140.271	336	241-C-103
(2-Methylpropyl)cyclohexane	1678-98-4		1	0.0084	140.271	1.5	241-A-102
cis-1-Ethyl-4-methylcyclohexane	4926-78-7		6	0.52	126.244	101	241-BX-104
trans-1-Ethyl-4-methylcyclohexane	6236-88-0		5	0.16	126.244	30	241-BY-108
1-Methyl-2-propylcyclohexane	4291-79-6	(a)	2	0.071	140.271	12	241-T-111
1-Methyl-3-propylcyclohexane	4291-80-9	(a)	4	0.54	140.271	94	241-C-102
1-Methyl-3-(1-methylethyl)cyclohexane	16580-24-8	(a)	1	0.31	140.271	54	241-C-101
1-Methyl-4-(1-methylethyl)cyclohexane	99-82-1	(a)	2	0.02	140.271	3.7	241-T-111
cis-1-Methyl-4-(1-methylethyl)cyclohexane	6069-98-3		3	0.32	140.271	56	241-BY-108
1,1,2,3-Tetramethylcyclohexane	6783-92-2	(a)	9	0.37	140.271	64	241-C-204
cis-1,1,3,5-Tetramethylcyclohexane	50876-32-9		3	0.42	140.271	74	241-BX-104
trans-1,1,3,5-Tetramethylcyclohexane	50876-31-8	(a)	2	0.019	140.271	3.4	241-C-110
1,1,4,4-Tetramethylcyclohexane	2223-52-1	(a)	1	0.38	140.271	66	241-BY-108
a,a,a,a-1,2,4,5-Tetramethylcyclohexane	61142-24-3		1	0.047	196.379	5.8	241-C-110
1,2,4,5-Tetramethylcyclohexane	2090-38-2	(a)	1	0.0092	140.271	1.6	241-BY-105
(1,2-Dimethylpropyl)cyclohexane	51284-29-8	(a)	1	0.16	154.298	25	241-BY-107
Pentylcyclohexane	4292-92-6		19	2.2	154.298	349	241-C-204
1-Ethyl-2-propylcyclohexane	62238-33-9	(a)	3	0.39	154.298	62	241-BY-108
1,1-Dimethyl-2-propylcyclohexane	81983-71-3		5	0.27	154.298	44	241-C-102
1-Ethyl-2,2,6-trimethylcyclohexane	UCY011-04	(a)	2	0.50	154.298	80	241-BY-108
(3-Methylpentyl)cyclohexane	61142-38-9		1	0.60	168.325	87	241-C-102
(4-Methylpentyl)cyclohexane	61142-20-9		5	2.5	168.325	360	241-BY-108
Hexylcyclohexane	4292-75-5		14	0.61	168.325	89	241-BY-107
1-(1,5-Dimethylhexyl)-4-methylcyclohexane	29799-19-7	(a)	2	0.0025	210.406	0.29	241-C-106
1-Methyl-2-pentylcyclohexane	54411-01-7	(a)	3	0.49	168.325	71	241-BY-108
1-Methyl-3-pentylcyclohexane	54411-02-8	(a)	3	0.071	168.325	10	241-C-110
1-Methyl-4-(1-methylbutyl)cyclohexane	54411-00-6	(a)	4	0.12	168.325	17	241-BY-107
1,2-Diethyl-1-methylcyclohexane	61141-79-5		4	0.33	154.298	52	241-BY-108
1,2-Diethyl-3-methylcyclohexane	61141-80-8	(a)	4	0.43	154.298	68	241-BY-108
2,4-Diethyl-1-methylcyclohexane	61142-70-9		4	0.26	154.298	41	241-BY-107

Table 3-13. Cycloalkanes (Page 4 of 5)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
1,5-Diethyl-2,3-dimethylcyclohexane	74663-66-4	(a)	2	0.52	168.325	76	241-C-102
(1,2-Dimethylbutyl)cyclohexane	61142-37-8		1	0.0076	168.325	1.1	241-B-103
(2,2-Dimethylcyclopentyl)cyclohexane	61142-23-2		4	0.28	180.336	39	241-BX-104
2-Butyl-1,1,3-trimethylcyclohexane	54676-39-0	(a)	17	3.1	182.352	418	241-C-102
Octylcyclohexane	1795-15-9		6	0.12	196.379	15	241-B-103
1,1,3-Trimethyl-2-(3-methylpentyl)cyclohexane	54965-05-8	(a)	5	0.68	210.406	79	241-BX-104
cis-(1-Cyclohexylmethyl)-2-methylcyclohexane-	54824-04-3		1	0.10	194.363	13	241-BY-107
trans-(1-Cyclohexylmethyl)-2-methylcyclohexane	54823-94-8		1	0.23	194.363	29	241-BY-108
cis-(1-Cyclohexylmethyl)-4-methylcyclohexane	66826-95-7		1	0.73	194.363	92	241-BY-108
(2-Ethylcetyl)cyclohexane	13151-74-1		3	0.044	224.433	4.8	241-BY-104
cis-(1-Cyclohexylmethyl)-2-ethylcyclohexane	54934-93-9		3	0.92	208.390	108	241-BY-108
1,3,5-Trimethyl-2-octadecylcyclohexane	55282-34-3	(a)	2	0.13	378.731	8.3	241-BX-104
2-Propyl-1,1,3-trimethylcyclohexane	UCY012-04	(a)	1	0.0055	168.325	0.80	241-BY-106
1,2-Dimethyl-3-pentylcyclohexane	UCY013-03	(a)	1	0.0085	182.352	1.1	241-BY-112
trans-1-(Cyclohexylmethyl)-4-methylcyclohexane	54823-98-2		1	0.0092	194.363	1.2	241-BY-105
cis-1-(Cyclohexylmethyl)-4-ethylcyclohexane	54934-95-1		1	0.0043	208.390	0.51	241-C-109
(1-Propylheptyl)cyclohexane	13151-75-2		1	0.0018	224.433	0.20	241-C-111
Decylcyclohexane	1795-16-0		1	0.0018	224.433	0.20	241-BY-105
2-Cyclohexyloctane	2883-05-8		1	2.4	196.379	297	241-BY-108
Cyclooctane	292-64-8		1	0.0055	112.217	1.2	241-TY-104
Butylcyclooctane	16538-93-5		1	0.30	168.325	44	241-C-102
cis-1,4-Dimethylcyclooctane	13151-99-0		1	0.037	140.271	6.4	241-BY-104
1,5-Dimethylcyclooctane	21328-57-4	(a)	1	0.0092	140.271	1.6	241-BY-105
Cycloundecane							
1,1,2-Trimethylcycloundecane	62376-15-2	(a)	1	0.038	196.379	4.8	241-BY-109
Cyclododecane	294-62-2		7	2.5	168.325	360	241-C-102
Ethylcyclododecane	28981-49-9		1	0.025	196.379	3.1	241-TY-103
Cyclohexadecane	295-65-8		4	0.092	224.433	10	241-S-110
Cyclotetradecane	295-17-0		4	15	196.379	1,826	241-C-103
<b>DECALINS</b>							
Decahydronaphthalene	91-17-8	(a)	2	0.39	138.255	70	241-BY-108
trans-Decahydronaphthalene	493-02-7		13	4.3	138.255	762	241-C-103
trans-2-Methyldecahydronaphthalene	2958-76-1		15	19	152.282	3,091	241-C-103
trans-1,2-Dimethylmethyldecahydronaphthalene	3604-14-6	(a)	1	1.3	166.309	189	241-C-102
trans-1,5-Dimethylethyldecahydronaphthalene	66552-62-3	(a)	3	0.027	166.309	3.9	241-BY-110
trans-1,6-Dimethylethyldecahydronaphthalene	1750-51-2	(a)	5	0.33	166.309	49	241-BY-108

Table 3-13. Cycloalkanes (Page 5 of 5)

Compound	TCID Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
trans-2,3-Dimethylmethyldecahydronaphthalene	1008-80-6	(a)	7	2.8	166.309	418	241-C-204
trans-2,6-Dimethylmethyldecahydronaphthalene	1618-22-0	(a)	6	2.3	166.309	337	241-C-204
trans-2-Butyl-1-methyldecahydronaphthalene	6305-52-8	(a)	1	0.29	194.363	37	241-BY-108
<b>INDANES</b>							
cis-Octahydro-1H-indene	4551-51-3		1	0.034	124.228	6.7	241-BY-110
trans-2,2,4,4,7,7-Hexamethyloctahydro-1H-indene	54832-83-6		1	0.18	208.390	22	241-BY-107
<b>OTHER BICYCLIC AND TRICYCLIC MOLECULES</b>							
1,1'-Bicyclohexyl	92-51-3		1	0.042	166.309	6.2	241-BY-107
cis-2-Methyl-1,1'-bicyclohexyl	50991-08-7		1	0.11	180.336	15	241-BX-104
trans-2-Methyl-1,1'-bicyclohexyl	50991-09-8		1	0.020	180.336	2.7	241-C-110
Bicyclo[2.2.1]heptane	279-23-2		2	0.17	96.174	44	241-BY-107
Bicyclo[4.1.0]heptane	286-08-8		1	0.021	96.174	5.4	241-C-110
2-Methyl-7-pentylbicyclo[4.1.0]heptane	55937-92-3	(a)	1	1.2	180.336	162	241-C-204
3-Methyl-7-pentylbicyclo[4.1.0]heptane	41977-48-4	(a)	1	0.38	180.336	51	241-BY-108
Bicyclo[2.2.2]octane							
1,2,3,6-Tetramethylbicyclo[2.2.2]octane	62338-45-8	(a)	1	0.055	166.309	8.1	241-C-110
Bicyclo[3.3.1]nonane	280-65-9		1	0.043	124.228	8.5	241-T-111
<b>Summation</b>				<b>115</b>		<b>21,185</b>	
Note: (a) The positional or geometrical isomer has not been defined.							
Source: Stock and Huckaby (2004)							

Table 3-14. Alkenes (Page 1 of 6)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
ALKENES							
Ethene							
Cyclooctylethene	61142-41-4		1	0.088	138.255	16	241-BY-107
Propene	115-07-1		30	7.6	42.081	4,421	241-BY-108
2-Methylpropene	115-11-7		49	15	56.108	6,392	241-C-103
1-Cyclohexyl-1-propene	5364-83-0		1	0.92	124.228	180	241-BY-105
Cyclohexane,1,1'-(1-methylethylidene)bis-	54934-90-6		1	0.021	208.390	2.5	241-B-103
Cyclopentane,1,1,3-trimethyl-3-(2-methyl-2-propenyl)-	74421-09-3	(*)	1	0.0092	166.309	1.3	241-BY-105
Cyclopentane,1-methyl-2-(2-propenyl)-,trans-	50746-53-7	(*)	1	0.027	124.228	5.4	241-BY-104
1-Butene	106-98-9		26	21	56.108	9,188	241-C-103
2-Methyl-1-butene	563-46-2		3	1.2	70.135	410	241-BY-105
3-Methyl-1-butene	563-45-1		4	1.4	70.135	479	241-BY-108
3,3-Dimethyl-1-butene	558-37-2		1	0.029	84.163	8.5	241-U-106
2,3-Dimethyl-1-butene	563-78-0		1	0.023	84.163	6.7	241-BY-105
2-(Ethyl-1-methylcyclohexyl)-1-butene	74810-42-7		1	0.0018	180.336	0.25	241-BY-106
Cyclohexane,(2-ethyl-1-methylbutylidene)-	74810-41-6	(*)	1	0.012	180.336	1.6	241-B-103
2-Butene	107-01-7		3	0.85	56.108	372	241-BY-104
2-Methyl-2-butene	513-35-9		3	0.15	70.135	51	241-BY-104
2,3-Dimethyl-2-butene	563-79-1		1	0.12	84.163	35	241-BY-104
E-2-Butene	624-64-6		2	0.12	56.108	52	241-C-104
Z-2-Butene	590-18-1		2	1.5	56.108	639	241-C-103
1-Pentene	109-67-1		15	9.2	70.135	3,196	241-C-103
2-Methyl-1-pentene	763-29-1		5	2.4	84.163	692	241-BY-108
4-Methyl-1-pentene	691-37-2		8	2.3	84.163	666	241-BY-108
3,4-Dimethyl-1-pentene	7385-78-6		2	1.6	98.190	411	241-BY-108
4,4-Dimethyl-1-pentene	762-62-9		2	0.046	98.190	11	241-TX-111
2,2,4-Trimethyl-1-pentene	107-39-1		1	0.017	112.217	3.8	241-T-111
2-Pentene	109-68-2		5	0.87	70.135	304	241-BY-108
2,4-Dimethyl-2-pentene	625-65-0		2	0.034	98.190	8.4	241-B-103
3-Ethyl-2-pentene	816-79-5		1	0.0092	98.190	2.3	241-TY-104
2-Methoxy-2-pentene	61142-47-0	(*)	1	0.0023	100.162	0.56	241-T-107
E-2-Pentene	646-04-8		1	0.65	70.135	227	241-BY-107
E-4-Methyl-2-pentene	674-76-0		1	0.026	84.163	7.5	241-BY-106
Z-2-Pentene	627-20-3		4	1.2	70.135	415	241-BY-108

Table 3-14. Alkenes (Page 2 of 6)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
1-Hexene	592-41-6		14	12	84.163	3,462	241-C-103
2-Methyl-1-hexene	6094-02-6		1	0.0037	98.190	0.91	241-BY-106
4-Methyl-1-hexene	3769-23-1		1	0.40	98.190	100	241-S-103
5-Methyl-1-hexene	3524-73-0		3	1.5	98.190	365	241-BY-108
4-Ethyl-1-hexene	16746-85-3		1	0.19	112.217	42	241-S-103
3,4-Dimethyl-1-hexene	16745-94-1		4	0.31	112.217	68	241-BY-107
4,5-Dimethyl-1-hexene	16106-59-5		3	0.31	112.217	68	241-BY-108
5,5-Dimethyl-1-hexene	7116-86-1		2	0.016	112.217	3.6	241-C-110
3,4,5-Trimethyl-1-hexene	56728-10-0		1	0.036	126.244	6.9	241-TX-111
3,5,5-Trimethyl-1-hexene	4316-65-8		1	0.0092	126.244	1.8	241-BY-105
2-Hexene	592-43-8		1	0.046	84.163	13	241-BY-104
2,4-Dimethyl-2-hexene	14255-23-3	(*)	1	0.0082	112.217	1.8	241-C-105
E-2-Hexene	4050-45-7		1	0.081	84.163	23	241-BY-104
Z-2-Hexene	7688-21-3		2	0.037	84.163	11	241-BY-105
Z-4,4,5-Trimethyl-2-hexene	55702-61-9		1	0.031	126.244	6.0	241-U-106
Z-3-Hexene	7642-09-3		1	0.021	84.163	6.1	241-BY-105
Z-2,3,4,5-Tetramethyl-3-hexene	60643-93-8		2	0.072	140.271	13	241-C-110
Z-3-Ethyl-2,5-dimethyl-3-hexene	62338-08-3		2	0.26	140.271	45	241-BY-107
1-Heptene	592-76-7		15	1.6	98.190	388	241-BY-108
3-Methyl-1-heptene	4810-09-7		2	0.71	112.217	156	241-BY-108
5-Methyl-1-heptene	13151-04-7		2	0.10	112.217	22	241-BY-109
6-Methyl-1-heptene	5026-76-6		2	0.68	112.217	148	241-BY-108
2,4-Dimethyl-1-heptene	19549-87-2		1	0.11	126.244	21	241-BX-102
2-Heptene	592-77-8		5	0.59	98.190	146	241-BY-105
E-2-Heptene	14686-13-6		4	0.029	98.190	7.3	241-B-103
Z-2-Heptene							
Z-3-Methyl-2-heptene	3404-75-9		1	0.70	112.217	153	241-TX-116
3-Heptene	592-78-9	(*)	1	0.024	98.190	5.9	241-B-103
4-Propyl-3-heptene	4485-13-6		1	0.012	140.271	2.1	241-B-103
Z-3-Heptene	14686-14-7		2	0.021	98.190	5.3	241-BY-104
Z-2,2,3,5,5,6,6-Heptamethyl-3-heptene	54845-26-0		2	0.20	196.379	25	241-C-101
1-Octene	111-66-0		6	0.84	112.217	184	241-BY-108
3-Ethyl-1-octene	74630-08-3		1	0.17	140.271	30	241-S-103
7-Methyl-1-octene	13151-06-9		1	0.020	126.244	3.9	241-C-104

Table 3-14. Alkenes (Page 3 of 6)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
2-Octene	111-67-1	(*)	1	0.68	112.217	148	241-TX-116
E-3-Octene	14919-01-8		1	0.12	112.217	26	241-BY-104
Z-3-Octene	592-98-3		2	0.36	112.217	78	241-BY-108
E-4-Octene	14850-23-8		1	0.0092	112.217	2.0	241-BY-105
1-Nonene	124-11-8		2	0.42	126.244	82	241-BY-108
4-Nonene							
5-Methyl-4-nonene	15918-07-7	(*)	1	0.0027	140.271	0.48	241-BY-106
5-Butyl-4-nonene	7367-38-6	(*)	5	0.13	182.352	17	241-TY-103
E-2-Nonene	6434-78-2		1	0.00060	126.244	0.12	241-TY-104
Z-4-Nonene							
Z-2,3,3-Trimethyl-4-nonene	63830-68-2		3	0.52	168.325	76	241-BY-108
1-Decene	872-05-9		5	0.040	140.271	7.0	241-U-103
4-Methyl-1-decene	13151-29-6	(*)	1	0.0073	154.298	1.2	241-TY-104
5-Methyl-1-decene	54244-79-0		1	0.0017	154.298	0.28	241-TY-104
3,4-Dimethyl-1-decene	50871-03-9		1	0.012	168.325	1.7	241-TY-104
E-2-Decene	20063-97-2		1	0.39	140.271	69	241-C-102
Z-2-Decene							
Z-4-Methyl-2-decene	74630-30-1		2	0.60	154.298	96	241-C-102
3-Decene	19398-37-9	(*)	2	0.14	140.271	24	241-C-101
4-Decene							
7-Methyl-4-decene	UAE011-05	(*)	1	0.0064	182.352	0.86	241-TY-104
E-4-Decene							
E-3-Methyl-4-decene	62338-47-0		1	0.17	154.298	28	241-BY-107
5-Decene	19689-19-1	(*)	1	0.68	140.271	118	241-BY-108
E-5-Decene	7433-56-9		2	0.021	140.271	3.7	241-B-103
1-Undecene	821-95-4		4	0.29	154.298	46	241-BY-108
4-Methyl-1-undecene	74630-39-0		3	1.4	168.325	200	241-BY-108
7-Methyl-1-undecene	74630-42-5		2	0.073	168.325	11	241-C-110
8-Methyl-1-undecene	74630-40-3		1	0.046	168.325	6.7	241-C-110
2-Undecene							
4-Methyl-2-undecene	91695-32-8	(*)	1	0.0032	168.325	0.47	241-TY-104
2,5-Dimethyl-2-undecene	49622-16-4	(*)	1	0.083	182.352	11	241-BY-107
E-2-Undecene							
E-6-Methyl-2-undecene	74630-61-8		1	0.16	168.325	24	241-BY-107

Table 3-14. Alkenes (Page 4 of 6)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
E-7-Methyl-2-undecene	UAE012-03		1	0.075	168.325	11	241-BY-107
E-4,5-Dimethyl-2-undecene	55170-92-8		1	0.010	182.352	1.4	241-U-106
Z-2-Undecene	821-96-5		1	0.00055	154.298	0.087	241-TY-104
Z-8-Methyl-2-undecene	74630-44-7		2	0.35	168.325	51	241-BY-108
3-Undecene							
5-Methyl-3-undecene	UAE012-06	(*)	1	0.0073	168.325	1.1	241-TY-104
8-Methyl-3-undecene	UAE012-04	(*)	1	0.0092	168.325	1.3	241-BY-105
E-3-Undecene	1002-68-2		2	0.021	154.298	3.3	241-T-111
Z-3-Undecene							
Z-2-Methyl-3-undecene	74630-48-1		2	3.0	168.325	439	241-C-102
4-Undecene							
4-Methyl-4-undecene	61142-40-3	(*)	2	1.8	168.325	266	241-C-102
6-Methyl-4-undecene	UAE012-05	(*)	2	0.22	168.325	32	241-BX-104
E-4-Undecene	693-62-9		1	0.0037	154.298	0.58	241-C-107
Z-4-Undecene							
Z-5-Methyl-4-undecene	74630-69-6		1	0.25	168.325	36	241-C-102
5-Undecene	4941-53-1	(*)	10	1.4	154.298	218	241-BY-108
E-5-Undecene	764-97-6		2	1.0	154.298	160	241-C-102
E-7-Methyl-5-undecene	74630-66-3		1	0.68	168.325	99	241-C-102
Z-5-Undecene	764-96-5		1	0.0091	154.298	1.4	241-B-103
Z-7-Methyl-5-undecene	74630-62-9		1	0.10	168.325	15	241-BY-107
1-Dodecene	112-41-4		6	0.39	168.325	57	241-C-102
2-Dodecene							
4-Methyl-2-dodecene	56851-45-7	(*)	1	0.020	182.352	2.7	241-C-110
E-3-Dodecene	7206-14-6		4	0.16	168.325	23	241-TY-103
Z-3-Dodecene	7239-23-8		1	0.27	168.325	40	241-BY-108
4-Dodecene	2030-84-4	(*)	1	0.028	168.325	4.1	241-TY-103
E-4-Dodecene	7206-15-7		2	0.56	168.325	81	241-C-102
Z-5-Dodecene	7206-28-2		1	0.0067	168.325	0.97	241-BY-106
E-6-Dodecene	7206-17-9		1	0.0092	168.325	1.3	241-BY-105
1-Tridecene	2437-56-1		7	0.092	182.352	12	241-C-110
6-Tridecene	24949-38-0	(*)	3	0.10	182.352	14	241-TY-103
7-Methyl-6-tridecene	24949-42-6	(*)	5	2.1	196.379	263	241-BY-108
1-Tetradecene	1120-36-1		4	5.2	196.379	651	241-C-103

Table 3-14. Alkenes (Page 5 of 6)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
E-3-Tetradecene	41446-68-8	3	0.65	196.379	81	241-BY-107
Z-3-Tetradecene	41446-67-7	1	0.23	196.379	29	241-C-110
E-5-Tetradecene	41446-66-6	2	0.58	196.379	72	241-BY-108
Z-6-Tetradecene	41446-61-1	2	0.037	196.379	4.6	241-BY-105
7-Tetradecene	10374-74-0 (*)	3	0.017	196.379	2.2	241-T-111
Z-7-Tetradecene	41446-60-0	1	0.0023	196.379	0.29	241-TY-104
1-Pentadecene	13360-61-7	4	0.30	210.406	35	241-BY-107
1-Hexadecene	629-73-2	6	2.4	224.433	260	241-C-103
Z-3-Hexadecene	34303-81-6	2	0.037	224.433	4.0	241-BY-104
Z-7-Hexadecene	35507-09-6	3	0.20	224.433	22	241-BY-108
1-Heptadecene	6765-39-5	1	0.0071	238.461	0.73	241-SX-103
1-Octadecene	112-88-9	1	0.0018	252.488	0.18	241-C-111
1-Nonadecene	18435-45-5	1	0.00092	266.515	0.084	241-C-109
E-5-Eicosene	74685-30-6	1	0.62	280.542	54	241-BY-108
<b>CYCLOALKENES</b>						
Cyclohexene	110-83-8	1	0.0092	82.147	2.7	241-BY-105
1-Ethylcyclohexene	1453-24-3	1	0.62	110.201	138	241-C-101
1-Ethyl-6-ethylidenecyclohexane	61141-57-9 (*)	2	0.014	136.239	2.5	241-SX-106
1-Methyl-3-(1-methylethyl)cyclohexene	13828-31-4 (*)	1	0.0049	138.255	0.88	241-TY-104
1-Methyl-4-(1-methylethenyl)cyclohexene	5989-27-5 (*)	1	0.17	136.239	31	241-U-112
1-Methyl-4-(1-methylethenyl)cyclohexene	138-86-3 (*)	2	0.13	136.239	23	241-BX-103
1-Pentylcyclohexene	15232-85-6	2	0.049	152.282	7.9	241-C-110
4-Ethenylcyclohexene	100-40-3 (*)	1	0.0073	108.185	1.7	241-TY-104
<b>OTHER CYCLIC COMPOUNDS</b>						
cis-1,2-Dimethyl-3-methylenecyclopropane	4866-55-1	1	0.018	82.147	5.5	241-BY-105
1-Butyl-2-ethylcyclopropene	50915-91-8	1	0.015	124.228	2.9	241-BY-106
<b>ALKADIENES</b>						
1,3-Butadiene	106-99-0	14	0.49	54.092	223	241-C-204
2-Methyl-1,3-butadiene	78-79-5	3	0.15	68.120	53	241-BY-104
2,3-Dimethyl-1,3-butadiene	513-81-5	1	0.044	82.147	13	241-BY-106
1,2-Pentadiene	591-95-7	1	0.030	68.120	11	241-BY-105
E-1,3-Pentadiene	2004-70-8					
Z-1,3-Pentadiene	1574-41-0	1	0.077	68.120	28	241-BY-110
2-Methyl-1,3-pentadiene	1118-58-7	4	1.4	82.147	409	241-BY-108

Table 3-14. Alkenes (Page 6 of 6)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
1,3-Pentadiene	504-60-9	(*)	1	0.025	68.120	8.9	241-BY-106
2,3-Dimethyl-1,3-pentadiene	1113-56-0		1	0.010	96.174	2.6	241-TY-104
1,4-Pentadiene	591-93-5						
2,3-Dimethyl-1,4-pentadiene	758-86-1	(*)	1	0.0069	96.174	1.7	241-SX-106
Z-1,3-Hexadiene	592-48-3	(*)	1	0.40	82.145	120	241-BY-105
Z-3-Ethyl-2-methyl-1,3-hexadiene	74752-97-9		1	0.0048	124.228	0.94	241-AX-101
1,4-Hexadiene	592-45-0		3	0.15	82.147	44	241-BY-104
2,3-Dimethyl-1,4-hexadiene	18669-52-8	(*)	1	0.0046	110.201	1.0	241-AX-101
4-Methyl-1,4-hexadiene	1116-90-1	(*)	2	0.027	96.174	7.0	241-BY-104
1,5-Hexadiene	592-42-7	(*)	1	0.11	82.147	33	241-BY-104
2,6-Octadiene	4974-27-0	(*)					
4,5-Dimethyl-2,6-octadiene	18476-57-8	(*)	1	0.026	138.255	4.5	241-BY-109
3,4-Nonadiene	37050-03-6		1	0.44	124.228	87	241-BY-108
4,5-Nonadiene	821-74-9		1	0.55	124.228	108	241-C-102
E,E-4,6-Decadiene							
E,E-3,8-Dimethyl-4,6-decadiene	67730-63-6		2	0.43	166.309	63	241-BY-108
1,11-Dodecadiene	5876-87-9	(*)	1	0.0037	166.309	0.54	241-TY-104
1,12-Tridecadiene	21964-48-7	(*)	1	0.0046	180.336	0.62	241-C-105
Bicyclo[4.2.0]octa-1,3,5-triene	694-87-1		1	0.13	104.153	30	241-C-101
POLYENES							
2,6,10,14,18,22-Tetracosahexaene							
2,6,10,19,23-Pentamethyl-2,6,10,14,18,22-tetracosahexaene	59681-06-0		2	1.0	396.706	62	241-BY-109
2,6,10,15,19,23-Hexamethyl-2,6,10,14,18,22-tetracosahexaene	7683-64-9		1	1.1	410.733	65	241-BY-109
Summation				126		39,460	

Note: (a) The positional or geometrical has not been defined.  
Source: Stock and Huckaby (2004)

Table 3-15. Alkynes

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Propyne	74-99-7	5	0.56	40.065	341	241-C-102
4-Nonyne	20184-91-2	1	0.37	124.228	72	241-BY-108
3-Decyne	2384-85-2	2	0.47	138.255	83	241-BY-108
3-Hexadecyne	61886-62-2	1	0.46	222.418	50	241-C-102
1-Nonyne	3452-09-3	1	0.0092	124.228	1.8	241-BY-105
1-Octadecyne	629-89-0	1	0.0018	250.472	0.18	241-T-107
<b>Summation</b>			<b>1.9</b>		<b>548</b>	

Source: Stock and Huckaby (2004)

Table 3-16. Benzene, Biphenyl, Napthalene, Fluorene, and Their Derivatives (Page 1 of 2)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>BENZENE AND ALKYL BENZENES</b>						
Benzene	71-43-2	69	6.9	78.115	2,152	241-BY-104
Monosubstituted Benzenes						
Methylbenzene	108-88-3	84	4.4	92.142	1,158	241-BX-103
Ethylbenzene	100-41-4	41	0.60	106.169	139	241-BX-103
(1-Methylethyl)benzene	98-82-8	2	0.43	120.196	88	241-C-102
(1-Methylpropyl)benzene	135-98-8	1	0.018	134.223	3.3	241-T-111
Propylbenzene	103-65-1	4	0.026	120.196	5.2	241-C-110
(1,1-Dimethylethyl)benzene	98-06-6	2	0.049	134.223	8.9	241-C-110
(1,1-Dimethylpropyl)benzene	2049-95-8	1	0.017	148.250	2.9	241-T-111
Pentylbenzene	538-68-1	2	1.3	148.250	212	241-C-102
(1-Methylpentyl)benzene	6031-02-3	1	0.82	162.277	123	241-C-102
(1-Methylhexyl)benzene	2132-84-5	1	0.66	176.304	92	241-C-102
(1-Methylheptyl)benzene	777-22-0	1	0.16	190.331	21	241-C-102
(1-Methyldecyl)benzene	4536-88-3	2	0.0055	232.413	0.58	241-C-104
(1-Propylonyl)benzene	2719-64-4	2	0.0046	246.440	0.45	241-C-104
(1-Butylheptyl)benzene	4537-15-9	2	0.0046	232.413	0.48	241-C-104
(1-Pentylheptyl)benzene	2719-62-2	2	0.0064	246.440	0.64	241-C-104
(1-Ethylonyl)benzene	4536-87-2	1	0.0073	232.413	0.77	241-C-105
(1-Butyloctyl)benzene	2719-63-3	1	0.0055	246.440	0.55	241-C-105
(1-Methylundecyl)benzene	2719-61-1	1	0.0046	246.440	0.45	241-C-104
Disubstituted Benzenes						
1,2-Dimethylbenzene	95-47-6	35	0.71	106.169	165	241-BY-108
1,3-Dimethylbenzene	108-38-3	8	0.072	106.169	17	241-U-106
1,4-Dimethylbenzene	106-42-3	17	1.0	106.169	232	241-BY-108
Dimethylbenzene	1330-20-7	(*) 44	1.7	106.169	382	241-BX-103
1-Ethyl-2-methylbenzene	611-14-3	18	0.040	120.196	8.2	241-C-110
1-Ethyl-3-methylbenzene	620-14-4	1	0.036	120.196	7.3	241-SX-107
1-Ethyl-4-methylbenzene	622-96-8	3	0.00049	120.196	0.10	241-TX-118
1-Methyl-2-propylbenzene	1074-17-5	1	0.80	134.223	145	241-C-102
1-Methyl-3-(1-methylethyl)benzene	535-77-3	1	0.013	134.223	2.3	241-T-111
1-Isopropyl-2-methylbenzene	527-84-4	1	0.020	134.223	3.6	241-SX-107
Trisubstituted Benzenes						
1,2,3-Trimethylbenzene	526-73-8	1	0.024	120.196	4.9	241-SX-107
1,2,4-Trimethylbenzene	95-63-6	25	0.074	120.196	15	241-C-107
1,3,5-Trimethylbenzene	108-67-8	22	0.048	120.196	10	241-U-112

Table 3-16. Benzene, Biphenyl, Napthalene, Fluorene and Their Derivatives (Page 2 of 2)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
bis-1,1'-(1,4-Butanediyl)benzene	1083-56-3		1	0.012	210.322	1.4	241-TX-105
<b>BIPHENYL</b>							
1,1'-Biphenyl	92-52-4		6	14	154.214	2,180	241-C-103
2-Methyl-1,1'-biphenyl	643-58-3		3	1.6	168.241	240	241-C-102
2,2'-Diethyl-1,1'-biphenyl	13049-35-9		4	0.0025	210.322	0.29	241-TX-105
<b>OTHER ARENES</b>							
Naphthalene	91-20-3		8	0.045	128.175	8.6	241-SX-112
1-Methylnaphthalene	90-12-0		1	0.024	142.202	4.1	241-SX-107
2-Methylnaphthalene	91-57-6		1	0.025	142.202	4.3	241-T-111
1,7-Dimethylnaphthalene	575-37-1		1	0.010	156.229	1.6	241-T-111
2,3-Dimethylnaphthalene	581-40-8		1	0.011	156.229	1.7	241-T-111
(9H)Fluorene	86-73-7		1	0.42	166.225	62	241-C-102
<b>ALKENYLBENZENES</b>							
Benzene							
1-Ethenylbenzene	100-42-5		23	1.2	104.153	280	241-C-103
(1-Methylethenyl)benzene	98-83-9	(*)	3	0.013	118.180	2.7	241-B-103
(1-Propenyl)benzene	637-50-3	(*)	3	0.58	118.180	119	241-C-102
(2-Propenyl)benzene	300-57-2	(*)	2	0.27	118.180	55	241-C-101
(2-Methyl-2-propenyl)benzene	3290-53-7	(*)	1	0.54	132.207	100	241-C-102
<b>Summation</b>				<b>38.4</b>		<b>8,061</b>	

Note: (a) The positional or geometrical has not been defined.  
Source: Stock and Huckaby (2004)

Table 3-17. Halogen Containing Compounds (Page 1 of 3)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>HALO ALKANES</b>						
Methane						
Chloromethane	74-87-3	37	0.21	50.488	100	241-TX-110
Dichloromethane	75-09-2	60	6.3	84.933	1,815	241-BY-108
Chlorodifluoromethane	75-45-6	8	6.0	86.469	1,685	241-BX-111
Bromomethane	74-83-9	10	0.054	94.939	14	241-U-112
Dichlorofluoromethane	75-43-4	13	0.23	102.924	54	241-AX-102
Trichloromethane	67-66-3	26	0.073	119.378	15	241-TX-105
Dichlorodifluoromethane	75-71-8	41	0.099	120.914	20	241-SX-101
Trichlorofluoromethane	75-69-4	91	166	137.369	29,533	241-BY-104
Tetrachloromethane	56-23-5	38	2.0	153.823	317	241-TX-105
Ethane						
Chloroethane	75-00-3	15	0.10	64.515	39	241-C-107
1,1-Dichloroethane	75-34-3	8	0.044	98.960	11	241-U-112
1,2-Dichloroethane	107-06-2	6	0.049	98.960	12	241-TX-106
1-Chloro-1,1-difluoroethane	75-68-3	17	3.0	100.496	736	241-U-109
1,1-Dichloro-1-fluoroethane	1717-00-6	6	0.86	116.951	180	241-S-101
1,1,1-Trichloroethane	71-55-6	27	0.060	133.405	11	241-BY-108
1,1,2-Trichloroethane	79-00-5	12	0.45	133.405	83	241-BY-108
1,1,2,2-Tetrachloroethane	79-34-5	12	0.17	167.850	25	241-BY-108
1,2-Dichloro-1,1,2,2-tetrafluoroethane	76-14-2	10	0.15	170.922	22	241-BY-108
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1	37	0.42	187.376	55	241-TY-104
1,2-Dibromoethane	106-93-4	13	0.077	187.862	10	241-U-112
Propane						
1-Fluoropropane	460-13-9	1	0.15	62.088	58	241-BY-110
1,2-Dichloropropane	78-87-5	5	0.060	112.987	13	241-BY-108
1-Chloro-2,2-dimethylpropane	753-89-9	1	0.016	106.596	3.8	241-U-105
Butane						
1-Chlorobutane	109-69-3	6	0.57	92.569	150	241-C-106
2-Bromobutane	78-76-2	2	0.13	137.020	23	241-C-101
Octane						
2-Chlorooctane	628-61-5	1	0.0043	148.678	0.7	241-TX-118
<b>HALO ALKENES</b>						
Ethene						
Fluoroethene	75-02-5	2	0.38	46.045	200	241-C-109

Table 3-17. Halogen Containing Compounds (Page 2 of 3)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Chloroethene	75-01-4	8	0.028	62.499		
1,1-Dichloroethene	75-35-4	32	0.083	96.944	21	241-S-101
Z-1,2-Dichloroethene	156-59-2	10	0.039	96.944	9.8	241-BY-108
Trichloroethene	79-01-6	18	0.38	131.389	70	241-BY-108
Tetrachloroethene	127-18-4	50	0.71	165.834	104	241-BY-107
Propene						
2-Fluoropropene	1184-60-7	6	1.3	60.072	522	241-BY-108
3-Chloropropene	107-05-1	2	0.020	76.526	6.4	241-U-112
E-1,3-Dichloropropene	10061-02-6	7	0.045	110.971	10	241-BY-108
Z-1,3-Dichloropropene	10061-01-5	8	0.042	110.971	9.2	241-U-112
1,3-Butadiene						
Hexachlorobutadiene	87-68-3	(a)				
<b>AROMATIC HALOGEN COMPOUNDS</b>						
Benzene						
Chlorobenzene	108-90-7	13	0.069	112.560	15	241-BY-108
1,2-Dichlorobenzene	95-50-1	10	0.050	147.005	8.4	241-BY-108
1,3-Dichlorobenzene	541-73-1	15	0.060	147.005	10	241-BY-108
1,4-Dichlorobenzene	106-46-7	17	0.047	147.005	7.8	241-U-112
1,2,4-Trichlorobenzene	120-82-1	10	0.12	181.450	16	241-BY-110
1-Bromo-2-fluorobenzene	1072-85-1	1	0.31	175.000	43	241-U-108
1,1'-Biphenyl						
2-Chloro-1,1'-biphenyl	2051-60-7	5	0.035	188.659	4.5	241-TY-103
3-Chloro-1,1'-biphenyl	2051-61-8	2	0.033	188.659	4.3	241-B-103
4-Chloro-1,1'-biphenyl	2051-62-9	1	0.0026	188.659	0.33	241-TY-104
2,2'-Dichloro-1,1'-biphenyl	13029-08-8	2	0.0057	223.104	0.6	241-BY-112
2,3-Dichloro-1,1'-biphenyl	16605-91-7	1	0.0010	223.104	0.11	241-TY-104
2,5-Dichloro-1,1'-biphenyl	34883-39-1	1	0.00092	223.104	0.10	241-TY-104
2,6-Dichloro-1,1'-biphenyl	33146-45-1	1	0.0032	223.104	0.35	241-TY-104
3,3'-Dichloro-1,1'-biphenyl	2050-67-1	1	0.0069	223.104	0.8	241-TX-118
4,4'-Dichloro-1,1'-biphenyl	2050-68-2	1	0.0038	223.104	0.41	241-TY-104
2,2,4'-Trichloro-1,1'-biphenyl	7012-37-5	1	0.0024	257.549	0.23	241-TY-104
2,4,5'-Trichloro-1,1'-biphenyl	16606-02-3	1	0.0035	257.549	0.33	241-TY-104
2,3,4'-Trichloro-1,1'-biphenyl	55702-46-0	1	0.0017	257.549	0.17	241-TY-104
2,3,3',5'-Tetrachloro-1,1'-biphenyl	41464-49-7	2	0.0045	291.994	0.38	241-TY-101
2,3,4',6'-Tetrachloro-1,1'-biphenyl	52663-58-8	2	0.0023	291.994	0.19	241-TX-105

Table 3-17. Halogen Containing Compounds (Page 3 of 3)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>OTHER</b>							
1,1,1-Trifluoropropanone	421-50-1		1	0.048	112.052	10	241-U-103
1-Butanamine							
1,1,2,2,3,3,4,4,4-Nonafluoro-N-1-butanamine	311-89-7		1	0.076	671.097	2.8	241-C-109
Benzeneethanamine							
N-[Perfluorophenyl]-beta,4-bis[TMSoxy]benzeneethanamine	55429-85-1	(b)	1	0.075	475.611	3.9	241-U-112
Butanamide							
Perfluoro-N-[2-TMSoxy-2-[4-TMSoxy]phenyl]ethylbutanamide	55471-01-7	(b)	1	0.16	493.574	8.2	241-U-106
Silane							
Fluorotrimethylsilane	420-56-4		1	0.0018	92.190	0.49	241-T-107
<b>Summation</b>				<b>191</b>		<b>36,077</b>	
Notes:							
(a) The trimethylsilyl fragment is designated as TMS in this table.							
Source: Stock and Huckaby (2004)							

Table 3-18. Alcohols, Phenols, and Ethers (Page 1 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>ALKANOLS</b>						
Methanol	67-56-1	66	37	32.042	28,000	241-C-105
Dimethyl-(cyclooctyl)methanol	16624-06-9	1	0.016	170.297	2.4	241-T-111
Phenylmethanol	100-51-6	9	0.045	108.141	10	241-U-106
Phenyl-1,1-dimethylmethanol	617-94-7	5	12	136.195	2,139	241-C-103
Ethanol	64-17-5	77	40	46.070	20,986	241-S-102
2-Butoxyethanol	111-76-2	8	0.29	118.177	61	241-BY-104
2-Tetradecyloxyethanol	2136-70-1	1	1.9	258.448	182	241-BY-108
1-Propanol	71-23-8	71	12	60.097	5,000	241-C-105
2-Methyl-1-propanol	78-83-1	5	0.055	74.124	18	241-TY-104
2,2-Dimethyl-1-propanol	75-84-3	8	7.1	88.151	1,983	241-C-103
1-Cyclopentyl-2,2-dimethyl-1-propanol	UOH010-01	1	0.011	154.240	1.7	241-U-112
2-Propanol	67-63-0	61	4.9	60.097	1,977	241-BY-108
1-(1-Methylethoxy)-2-propanol	3944-36-3	1	0.030	118.177	6.3	241-U-107
2-Methyl-2-propanol	75-65-0	27	0.39	74.124	130	241-BY-105
1-Butanol	71-36-3	89	177	74.124	58,361	241-BY-108
2-Methyl-1-butanol	137-32-6	4	0.15	88.151	41	241-C-101
3-Methyl-1-butanol	123-51-3	2	0.10	88.151	28	241-BX-104
2-Ethyl-1-butanol	97-95-0	1	0.059	102.178	14	241-TY-103
3,3-Dimethyl-1-butanol	624-95-3	3	0.076	102.178	18	241-TX-111
2-Butanol	78-92-2	20	0.62	74.124	206	241-BY-107
2-Methyl-2-butanol	75-85-4	2	0.064	88.151	18	241-BY-104
1-Pentanol	71-41-0	16	0.17	88.151	48	241-BX-104
4-Methyl-2-propyl-1-pentanol	54004-41-0	1	0.032	144.259	5.4	241-TY-103
5-Methoxy-1-pentanol	4799-62-6	1	0.010	118.177	2.1	241-BY-106
2-Pentanol	6032-29-7	2	0.50	88.151	140	241-BY-107
2-Methyl-2-pentanol	590-36-3	5	0.21	102.178	50	241-BY-107
2,3-Dimethyl-2-pentanol	4911-70-0	2	0.0058	116.205	1.2	241-BY-106
3-Ethyl-2-methyl-2-pentanol	19780-63-3	1	0.00092	130.232	0.17	241-T-107
3-Pentanol						
2-Methyl-3-pentanol	565-67-3	3	0.14	102.178	33	241-BY-107
2,3,4-Trimethyl-3-pentanol	3054-92-0	1	0.0092	130.232		
1-Hexanol	111-27-3	14	0.19	102.178	46	241-BX-103
2-Ethyl-1-hexanol	104-76-7	38	1.5	130.232	275	241-C-103
2-Hexanol						
5-Methyl-2-hexanol	627-59-8	1	0.0025	116.205	0.52	241-T-107

Table 3-18. Alcohols, Phenols, and Ethers (Page 2 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
2,3-Dimethyl-2-hexanol	19550-03-9	1	0.00064	130.232	0.12	241-TY-104
3-Hexanol	623-37-0	1	0.034	102.178	8.1	241-U-106
2-Methyl-3-hexanol	617-29-8	1	0.085	116.205	18	241-BY-102
1-Heptanol	111-70-6	14	1.9	116.205	405	241-C-103
2-Heptanol	543-49-7	2	0.25	116.205	52	241-BY-107
2-Methyl-2-heptanol	625-25-2	2	0.0030	130.232	0.57	241-BY-106
3-Ethyl-2-methyl-2-heptanol	19780-59-7	1	0.0063	158.286	0.98	241-BY-112
3-Heptanol	589-82-2	16	0.28	116.205	60	241-BY-107
1-Octanol	111-87-5	15	0.33	130.232	62	241-BY-108
2-Butyl-1-octanol	3913-02-8	5	0.32	186.340	42	241-BY-108
2-Octanol	123-96-6	4	0.38	130.232	71	241-BY-107
2-Methyl-2-octanol	628-44-4	1	0.033	144.259	5.6	241-BY-102
3-Octanol						
6-Ethyl-3-octanol	19781-27-2	1	0.0082	158.286	1.3	241-B-103
3,7-Dimethyl-3-octanol	57706-88-4	1	0.0081	158.286	1.2	241-T-111
1-Nonanol	143-08-8	8	0.022	144.259	3.7	241-BY-102
1-Decanol	112-30-1	2	0.0018	158.286	0.28	241-C-109
2-Ethyl-1-decanol	21078-65-9	1	0.00089	186.340	0.12	241-TY-104
2-Decanol	1120-06-5	1	0.0044	158.286	0.68	241-TY-104
3-Decanol	1565-81-7	1	0.016	158.286	2.5	241-BY-103
5-Decanol	5205-34-5	1	0.023	158.286	3.5	241-B-103
1-Undecanol	112-42-5	1	0.0049	172.313	0.69	241-TX-118
2-Undecanol	1653-30-1	1	0.0032	172.313	0.46	241-TY-104
4-Undecanol	4272-06-4	1	0.0021	172.313	0.30	241-T-107
1-Dodecanol	112-53-8	3	0.0073	186.340	0.96	241-C-104
3-Dodecanol	10203-30-2	1	0.0078	186.340	1.0	241-TY-104
6-Dodecanol	6836-38-0	2	0.013	186.340	1.7	241-B-103
Tridecanol	26248-42-0	(*) 1	0.0089	200.368	1.1	241-T-111
2-Tridecanol	1653-31-2	1	0.0046	200.368	0.56	241-C-105
1-Tetradecanol	112-72-1	2	0.0092	214.395	1.0	241-BY-105
1-Pentadecanol	629-76-5	1	0.019	228.422	2.1	241-TY-101
1-Hexadecanol	36653-82-4	15	10	242.449	1,017	241-C-204
2-Methyl-1-hexadecanol	2490-48-4	1	0.0041	256.476	0.39	241-C-108
1-Heptadecanol	1454-85-9	1	0.021	256.476	2.0	241-BY-110
16-Methyl-1-heptadecanol	41744-75-6	1	0.0037	270.503	0.33	241-C-111
1-Octadecanol	112-92-5	4	11	270.503	994	241-C-204

Table 3-18. Alcohols, Phenols, and Ethers (Page 3 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
1-Nonadecanol	1454-84-8	1	0.0082	284.530	0.71	241-S-105
<b>CYCLOALKANOLS</b>						
Cyclopentanol	96-41-3	5	6.7	86.135	1,900	241-C-103
Cyclohexanol	108-93-0	1	0.0020	100.162	0.49	241-S-111
4-(1,1,3,3-Tetramethylbutyl)cyclohexanol	4631-98-5	1	0.0039	212.379	0.45	241-BY-106
4-Methyl-1-(1-methylethyl)cyclohexanol	470-65-5 (*)	1	0.0012	156.270	0.19	241-TY-104
Cycloheptanol						
1-Methylcycloheptanol	3761-94-2	1	0.00092	128.216	0.17	241-TY-104
4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-ol	13040-03-4	1	0.0055	152.238	0.88	241-C-104
<b>ALKANDIOLS</b>						
1,2-Propanediol	57-55-6	12	0.47	76.096	150	241-A-101
2,3-Butanediol						
2,3-Dimethyl-2,3-butanediol	76-09-5	1	0.0082	118.177	1.7	241-BY-103
3-Hexyne-2,5-diol						
2,5-Dimethyl-2,5-hexyne-2,5-diol	142-30-3	1	0.0021	142.200	0.36	241-TY-104
2,7-Octanediol						
2,7-Dimethyl-2,7-octanediol	19781-07-8	1	0.019	174.286	2.7	241-T-111
1,12-Dodecanediol	5675-51-4	1	0.00092	202.340	0.11	241-C-109
<b>ALKENOLS, ALKENDIOLS, AND ALKYNOLS</b>						
2-Propen-1-ol	107-18-6	2	0.0087	58.081	3.7	241-SX-106
Z-2-Buten-1-ol	4088-60-2	2	0.11	72.108	37	241-C-101
3-Buten-1-ol	627-27-0	2	16	72.108	5,595	241-BY-108
3-Buten-2-ol	598-32-3	7	4.4	72.108	1,492	241-BY-108
1,4-Pentadien-3-ol	922-65-6	1	0.025	84.119	7.2	241-BY-110
5-Hexen-1-ol	821-41-0	1	0.065	100.162	16	241-AX-102
Z-3-Octen-2-ol						
Z-2-Methyl-3-octen-2-ol	18521-07-8	2	0.34	142.243	58	241-C-101
1-Pentyn-3-ol						
3,4-Dimethyl-1-pentyn-3-ol	1482-15-1	1	0.0025	112.173	0.54	241-SX-106
1-Dodecyn-4-ol	74646-36-9	1	0.038	182.309	5.2	241-BY-103
6,10-Dodecadien-1-ol						
3,7,11-Trimethyl-6,10-dodecadien-1-ol	51411-24-6 (*)	1	2.4	224.390	260	241-C-103
1-Tridecyn-4-ol	74646-37-0	1	0.0052	196.336	0.65	241-C-110
Z-9-Octadecen-1-ol	143-28-2	1	0.0046	268.487	0.42	241-C-111
<b>ETHERS</b>						
Dimethyl ether	115-10-6	9	3.8	46.070	2,043	241-C-103

Table 3-18. Alcohols, Phenols, and Ethers (Page 4 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Trimethylene oxide	503-30-0	1	1.3	58.080	560	241-C-105
Ethane						
1,2-Dimethoxyethane	110-71-4	1	0.0092	90.123	2.5	241-BY-105
Propane						
2-Ethoxy-2-methylpropane	637-92-3	1	0.0010	102.178	0.24	241-TY-104
Butane						
1-Methoxybutane	628-28-4	3	1.5	88.151	430	241-BY-105
Dipropylether	108-20-3	1	0.40	102.178	97	241-BY-107
Dibutylether	142-96-1	7	2.1	130.232	396	241-C-103
Pentane						
1-Methoxypentane	628-80-8	1	0.032	102.178	7.7	241-BY-104
E-5-Pentyloxy-2-pentene	56052-85-8	2	0.022	156.270	3.4	241-C-104
Hexane						
3-Methoxyhexane	54658-01-4	2	0.22	116.205	46	241-BY-107
1-Ethoxyhexane	5756-43-4	1	0.10	130.232	19	241-TY-103
Cycloheptane						
Methoxycycloheptane	42604-04-6	2	0.10	128.216	19	241-C-101
trans-1,3-Dimethoxycycloheptane	29887-79-4	1	0.0018	158.243	0.28	241-T-107
Didecylether	2456-28-2	3	0.89	298.557	73	241-BY-108
Divinylether	109-93-3	1	0.089	70.092	31	241-C-107
Diphenylether	101-84-8	2	0.16	170.213	24	241-T-111
Methylphenylether						
1-Butoxy-4-methoxybenzene	20743-95-7	1	0.0037	180.249	0.50	241-C-105
<b>PHENOLS</b>						
Phenol	108-95-2	12	0.080	94.114	21	241-BY-107
2-Methylphenol	95-48-7	2	0.037	108.141	8.3	241-BY-104
3-Methylphenol	108-39-4	2	0.0092	108.141	2.1	241-BY-105
4-Propylphenol	645-56-7	1	0.0028	136.195	0.51	241-SX-103
4-(1,1-Dimethylethyl)phenol	98-54-4	3	0.0012	150.222	0.19	241-C-109
(1,1-Dimethylethyl)-4-methoxyphenol	121-00-6	1	0.0037	180.249	0.50	241-TY-104
2-(1,1-Dimethylethyl)-4-methoxyphenol	25013-16-5	1	0.0027	180.249	0.37	241-BY-106
2,6-bis(1,1-Dimethylethyl)-4-methylphenol	128-37-0	3	4.6	220.358	509	241-C-103
1,3-Benzenediol						
2-Methyl-1,3-benzenediol	608-25-3	1	0.0050	124.141	0.99	241-C-107
4-Hexyl-1,3-benzenediol	136-77-6	1	0.0050	194.276	0.63	241-C-105
<b>Summation</b>			<b>367</b>		<b>136,375</b>	

Source: Stock and Huckaby (2004)

Table 3-19. Aldehydes (Page 1 of 2)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>ALIPHATIC ALDEHYDES</b>						
Ethanal	75-07-0	42	22	44.054	12,000	241-C-105
Propanal	123-38-6	7	0.62	58.081	260	241-C-105
2-Methylpropanal	78-84-2	2	0.010	72.108	3.4	241-S-110
2,2-Dimethylpropanal	630-19-3	1	0.027	86.135	7.8	241-B-103
Butanal	123-72-8	66	19	72.108	6,600	241-C-105
2-Methylbutanal	96-17-3	3	0.073	86.135	21	241-BX-104
3-Methylbutanal	590-86-3	3	0.10	86.135	29	241-B-103
Pentanal	110-62-3	12	0.84	86.135	239	241-C-101
2-Methylpentanal	123-15-9	2	0.21	100.162	51	241-BY-104
3-Methylpentanal	15877-57-3	2	0.17	100.162	43	241-U-111
Hexanal	66-25-1	28	5.2	100.162	1,276	241-C-103
3-Methylhexanal	19269-28-4	3	0.67	114.189	143	241-BY-108
2-Ethylhexanal	123-05-7	2	0.17	128.216	33	241-B-103
Heptanal	111-71-7	25	0.55	114.189	118	241-C-102
Octanal	124-13-0	21	2.4	128.216	455	241-C-103
7-Hydroxy-3,7-dimethyloctanal	107-75-5	1	0.00092	172.270	0.13	241-T-107
Nonanal	124-19-6	25	6.0	142.243	1,040	241-C-103
Decanal	112-31-2	16	0.028	156.270	4.4	241-BY-109
Undecanal	112-44-7	3	0.0037	170.297	0.53	241-C-111
Dodecanal	112-54-9	3	0.0050	184.324	0.67	241-C-111
Tridecanal	10486-19-8	1	0.0018	198.352	0.23	241-C-107
Hexadecanal	629-80-1	1	0.0043	240.433	0.44	241-BY-111
<b>ALKENALS</b>						
Prop-2-enal	107-02-8	1	0.014	56.065	6.0	241-B-103
2-Methylprop-2-enal	78-85-3	3	0.073	70.092	26	241-TY-104
But-2-enal	4170-30-3	(*) 8	0.066	70.092	23	241-C-105
2-Methylbut-2-enal	1115-11-3	1	0.048	84.119	14	241-B-103
Pent-4-enal						
2-Ethylpent-4-enal	5204-80-8	1	0.064	112.173	14	241-BY-104
2-Hexenal	505-57-7	2	0.27	98.146	66	241-C-101
2-Ethyl-2-hexenal	645-62-5	(*) 2	0.11	126.200	21	241-C-105
E-Hex-2-enal	6728-26-3	2	0.28	98.146	71	241-C-101
Z-3-Hexenal	6789-80-6	1	0.019	98.146	4.8	241-U-103
E-2-Heptenal	18829-55-5	2	0.0073	112.173	1.6	241-AX-101
Z-Hept-4-enal	6728-31-0	2	0.0092	112.173	2.0	241-BY-105

Table 3-19. Aldehydes (Page 2 of 2)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Hept-5-enal						
2,6-Dimethylhept-5-enal	106-72-9	1	0.38	140.227	67	241-BY-108
E-2-Octeneal	2548-87-0	1	0.0082	126.200	1.6	241-AX-101
E-Non-2-enal	18829-56-6	3	0.016	140.227	2.9	241-BY-110
E,E-2,4-Nonadienal	5910-87-2	1	0.0049	138.211	0.88	241-AX-101
E-2-Deceneal	3913-81-3	1	0.0039	154.254	0.62	241-AX-101
E,E-DodecaN-7,9-dienal	UAD012-01	1	0.49	180.280	67	241-C-204
Octadec-2-enal	56554-96-2	(*) 2	0.022	266.471	2.0	241-BY-103
2-Dodeceneal	4826-62-4	(*) 1	0.0037	182.309	0.49	241-C-109
<b>CYCLIC COMPOUNDS</b>						
Cyclohexanal						
4-(1-Methylethyl)cyclohexanal	UAD010-02	1	0.019	140.235	3.4	241-C-110
Cyclohex-3-en-1-al						
1,3,4-Trimethylcyclohex-3-en-1-al	40702-26-9	(*) 1	0.0046	152.238	0.74	241-TY-104
<b>AROMATIC ALDEHYDES</b>						
Benzaldehyde	100-52-7	5	0.029	106.125	6.8	241-U-106
Phenoxybenzaldehyde	UAD000-02	(*) 1	0.0027	198.223	0.34	241-C-112
3-Phenoxybenzaldehyde	39515-51-0	1	0.0018	198.223	0.23	241-C-107
<b>Summation</b>			<b>60</b>		<b>22,728</b>	
Note: (a) The positional or geometrical has not been defined.						
Source: Stock and Huckaby (2004)						

Table 3-20. Ketones (Page 1 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>ALIPHATIC KETONES</b>						
2-Propanone	67-64-1	99	46	58.081	19,200	241-C-103
2-Butanone	78-93-3	74	38	72.108	13,055	241-C-103
3-Methyl-2-butanone	563-80-4	17	6.5	86.135	1,848	241-C-103
3,3-Dimethyl-2-butanone	75-97-8	16	0.11	100.162	27	241-TX-110
2-Pentanone	107-87-9	60	4.1	86.135	1,171	241-C-103
3-Methyl-2-pentanone	565-61-7	6	0.15	100.162	36	241-BY-107
4-Methyl-2-pentanone	108-10-1	37	3.8	100.162	940	241-C-103
4,4-Dimethyl-2-pentanone	590-50-1	13	0.13	114.189	27	241-BY-112
3-Pentanone	96-22-0	4	0.038	86.135	11	241-BY-110
2-Methyl-3-pentanone	565-69-5	4	0.055	100.162	13	241-BY-104
2,4-Dimethyl-3-pentanone	565-80-0	1	0.092	114.189	20	241-BY-107
2,2,4-Trimethyl-3-pentanone	5857-36-3	2	0.010	128.216	1.9	241-BY-112
2-Hexanone	591-78-6	59	2.5	100.162	600	241-C-103
4-Methyl-2-hexanone	105-42-0	3	5.0	114.189	1,080	241-C-103
5-Methyl-2-hexanone	110-12-3	7	0.17	114.189	37	241-C-102
6-Methoxy-3-hexanone	29006-00-6	1	0.00060	130.188	0.11	241-TY-104
3-Cyclohexyliden-4-ethyl-2-hexanone	UKE014-03	1	0.25	208.330	29	241-C-102
3-Hexanone	589-38-8	15	26	100.162	6,266	241-C-103
2,5-Dimethyl-3-hexanone	1888-57-9	1	0.030	128.216	5.8	241-AX-102
5-Methyl-3-hexanone	623-56-3	1	0.0081	114.189	1.7	241-AX-102
4-Ethyl-3-hexanone	6137-12-8	1	0.0031	128.216	0.59	241-AX-102
2-Heptanone	110-43-0	58	2.8	114.189	608	241-C-103
3-Methyl-2-heptanone	2371-19-9	3	0.045	128.216	8.6	241-BY-102
4-Methyl-2-heptanone	6137-06-0	5	0.092	128.216	17	241-BY-107
6-Methyl-2-heptanone	928-68-7	30	11	128.216	2,098	241-C-103
4,6-Dimethyl-2-heptanone	19549-80-5	1	0.0056	142.243	1.0	241-BY-112
3-Heptanone	106-35-4	46	8.4	114.189	1,800	241-C-105
6-Methyl-3-heptanone	624-42-0	3	0.027	128.216	5.2	241-BY-104
4-Heptanone	123-19-3	17	2.0	114.189	432	241-C-103
3-Methyl-4-heptanone	15726-15-5	1	0.018	128.216	3.5	241-B-103
2-Octanone	111-13-7	51	1.4	128.216	262	241-C-103
3-Octanone	106-68-3	4	2.3	128.216	437	241-C-103
4-Octanone	589-63-9	7	2.5	128.216	472	241-C-103
3-Methyl-4-octanone	20754-04-5	1	0.016	142.243	2.8	241-AX-102
2-Nonanone	821-55-6	20	9.2	142.243	1,576	241-C-103

Table 3-20. Ketones (Page 2 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
3-Nonanone	925-78-0	1	0.82	142.243	142	241-C-103
4-Nonanone	4485-09-0	3	0.72	142.243	124	241-C-102
5-Nonanone	502-56-7	3	0.014	142.243	2.4	241-BY-104
2-Decanone	693-54-9	8	0.18	156.270	29	241-TY-103
5,9-Dimethyl-2-decanone	33933-82-3	1	0.022	184.324	2.9	241-C-104
4-Decanone	624-16-8	2	0.016	156.270	2.6	241-C-105
5-Decanone	820-29-1	2	0.039	156.270	6.2	241-T-111
2-Undecanone	112-12-9	7	2.6	170.297	369	241-C-103
6,10-Dimethyl-2-undecanone	1604-34-8	1	0.33	198.352	41	241-C-102
3-Undecanone	2216-87-7	6	0.73	170.297	105	241-C-102
4-Undecanone	14476-37-0	1	0.075	170.297	11	241-C-110
5-Undecanone	33083-83-9	4	0.12	170.297	17	241-BX-103
2-Methyl-5-undecanone	50639-02-6	12	1.6	184.324	207	241-C-102
2-Dodecanone	6175-49-1	3	0.13	184.324	17	241-TY-103
3-Dodecanone	1534-27-6	13	8.3	184.324	1,107	241-C-103
4-Dodecanone	6137-26-4	1	0.19	184.324	26	241-BX-103
11-Methyl-4-decanone	29366-35-6	1	0.023	198.352	2.8	241-TY-104
5-Dodecanone	19780-10-0	2	0.20	184.324	27	241-TY-103
6-Dodecanone	6064-27-3	8	0.68	184.324	90	241-TY-103
2-Tridecanone	593-08-8	4	2.0	198.352	249	241-C-101
3-Tridecanone	1534-26-5	18	4.9	198.352	610	241-C-103
4-Tridecanone	26215-90-7	1	0.16	198.352	19	241-BX-103
5-Tridecanone	30692-16-1	4	0.027	198.352	3.4	241-AX-102
6-Tridecanone	22026-12-6	8	0.81	198.352	99	241-TY-103
2-Tetradecanone	2345-27-9	6	0.10	212.379	12	241-TY-103
3-Tetradecanone	629-23-2	3	1.3	212.379	148	241-C-103
4-Tetradecanone	26496-20-8	1	0.012	212.379	1.4	241-TY-104
2-Pentadecanone						
6,10,14-Trimethyl-2-pentadecanone	502-69-2	1	0.0052	268.487	0.48	241-BY-105
2-Heptadecanone	2922-51-2	2	0.00092	254.460	0.088	241-BY-105
<b>ALIPHATIC DIKETONES</b>						
2,3-Pentadione	600-14-6	1	0.064	100.118	16	241-BY-104
2,5-Hexandione	110-13-4	1	0.0071	114.145	1.5	241-AX-102
<b>CYCLOALKANONES</b>						
Cyclobutanone	1191-95-3	1	0.14	70.092	48	241-BY-104
2-Ethylcyclobutanone	10374-14-8	1	0.020	98.146	5.0	241-C-110

Table 3-20. Ketones (Page 3 of 4)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
3,3-Dimethylcyclobutanone	1192-33-2		1	0.0043	98.146	1.1	241-TX-118
2,3,3-Trimethylcyclobutanone	28290-01-9		1	0.010	112.173	2.2	241-BY-106
<b>Cyclopentanone</b>							
3-Methylcyclopentanone	1757-42-2		2	0.089	98.146	22	241-C-101
2,4-Dimethylcyclopentanone	1121-33-1	(*)	1	0.024	112.173	5.2	241-C-110
trans-3,4-Dimethylcyclopentanone	19550-73-3		1	0.00055	112.173	0.12	241-TY-104
2,2,5-Trimethylcyclopentanone	4573-09-5		1	0.014	126.200	2.7	241-B-103
2-Methyl-4-(2-methylpropyl)cyclopentanone	69770-96-3	(*)	1	0.43	154.254	68	241-BY-108
<b>Cyclohexanone</b>							
3-Methylcyclohexanone	108-94-1		22	0.34	98.146	85	241-BY-108
2,6-Dimethylcyclohexanone	591-24-2		1	0.019	112.173	4.2	241-T-111
2,6-Dimethylcyclohexanone	16519-68-9	(*)	1	0.0037	154.254	0.58	241-BY-106
4-Hydroxy-4-methylcyclohexanone	17429-02-6		1	0.0018	128.172	0.35	241-C-107
2,2,6-Trimethylcyclohexanone	2408-37-9		2	0.17	140.227	30	241-C-101
3,3,5-Trimethylcyclohexanone	873-94-9		2	0.19	140.227	34	241-C-101
5-Methyl-2-(1-methylethylidene)cyclohexanone	15932-80-6	(*)	1	0.27	152.238	43	241-BY-104
5-Methyl-2-(1-methylethenyl)cyclohexanone	89-82-7	(*)	1	2.3	152.238	368	241-C-204
1,4-Cyclohexanedione	637-88-7		1	0.016	112.129	3.4	241-U-106
<b>Bicyclo[4.1.0]heptan-3-one</b>							
4,7,7-Trimethylbicyclo[4.1.0]heptan-3-one	4176-04-9		1	0.53	152.238	85	241-C-204
<b>ALKENONES</b>							
<b>3-Buten-2-one</b>							
3-Buten-2-one	78-94-4		19	3.3	70.092	1,151	241-C-103
3-Methyl-3-buten-2-one	814-78-8		2	0.073	84.119	21	241-BY-104
<b>3-Penten-2-one</b>							
3-Penten-2-one	625-33-2						
4-Methyl-3-penten-2-one	141-79-7		3	0.079	98.146	20	241-AX-102
<b>3-Hexen-2-one</b>							
3-Hexen-2-one	763-93-9		2	0.045	98.146	11	241-AX-102
5-Methyl-3-hexen-2-one	5166-53-0		1	0.016	112.173	3.4	241-AX-102
<b>3-Hepten-2-one</b>							
3-Hepten-2-one	1119-44-4						
3-Methyl-3-hepten-2-one	39899-08-6	(*)	1	0.13	126.200	25	241-AX-102
4-Methyl-3-hepten-2-one	22319-25-1	(*)	1	0.037	126.200	7.1	241-TX-118
<b>4-Hepten-3-one</b>							
4-Hepten-3-one							
5-Ethyl-2,4-dimethyl-4-hepten-3-one	22319-29-5		1	0.21	168.281	31	241-BY-107
<b>5-Hepten-2-one</b>							
5-Hepten-2-one	6714-00-7						
6-Methyl-5-hepten-2-one	110-93-0		1	0.0064	126.200	1.2	241-C-107
<b>1-Octen-3-one</b>							
1-Octen-3-one	4312-99-6		1	0.031	126.200	6.0	241-BY-106
<b>4-Octen-3-one</b>							
4-Octen-3-one	14129-48-7	(*)	3	0.018	126.200	3.6	241-BY-104
<b>7-Octen-2-one</b>							
7-Octen-2-one	3664-60-6	(*)	1	0.0064	126.200	1.2	241-BY-106

Table 3-20. Ketones (Page 4 of 4)

Compound	TCD Identification Number		Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
1-Nonen-3-one							
2-Methyl-1-nonen-3-one	51756-19-5		1	0.0055	154.254	0.87	241-TY-104
2-Nonen-4-one	32064-72-5	(*)	1	0.058	140.227	10	241-U-106
5,9-Undecadien-2-one							
E-6,10-Dimethyl-5,9-undecadien-2-one	3796-70-1		1	0.00064	194.320	0.081	241-AX-103
Z-6,10-Dimethyl-5,9-undecadien-2-one	3879-26-3		3	0.0061	194.320	0.77	241-C-107
2-Pentanone							
4-Cyclohexylidene-3,3-diethyl-2-pentanone	UKE015-01		1	0.16	222.358	17	241-BY-108
10-Undecen-4-one							
2,2,6,6-Tetramethyl-10-undecen-4-one	42565-49-1		1	0.013	224.390	1.4	241-A-102
2-Cyclopenten-1-one							
2,3-Dimethyl-2-cyclopenten-1-one	1121-05-7		1	0.0060	110.157	1.3	241-A-102
3-Cyclopenten-1-one							
2,3,4-Trimethyl-3-cyclopenten-1-one	83321-16-8	(*)	1	0.0041	124.184	0.81	241-TX-118
Cyclohexanone							
2,5-Dimethyl-2-(1-methylethenyl)cyclohexanone	6711-26-8	(*)	1	0.0027	166.266	0.40	241-C-107
2-Cyclohexen-1-one							
4,5-Dimethyl-2-cyclohexen-1-one	5715-25-3	(*)	1	0.023	124.184	4.5	241-BY-102
4-Ethyl-3,4-dimethyl-2-cyclohexen-1-one	17622-46-7	(*)	1	0.0030	152.238	0.49	241-BY-106
3,4-Undecadiene-2,10-dione							
6,6-Dimethyl-3,4-undecadiene-2,10-dione	52588-78-0	(*)	1	0.0018	208.303	0.22	241-BY-106
<b>AROMATIC KETONES AND QUINONES</b>							
1H-Inden-1-one							
2,3-Dihydro-3,3-dimethyl-1H-inden-1-one	26465-81-6		1	0.0027	160.218	0.42	241-C-107
Ethanone							
1-Phenylethanone	98-86-2		19	2.2	120.152	448	241-C-103
1-(2,4,5-Trimethylphenyl)ethanone	2040-07-5		1	0.016	162.234	2.3	241-T-111
1-(3-Methylphenyl)ethanone	585-74-0		1	0.0018	134.179	0.33	241-T-107
1-(5,6,7,8-Tetrahydro-3,5,5,6,8,8-ethanone	1506-02-1	(*)	1	0.00092	258.407	0.087	241-C-109
bis-1,1'-(1,4-phenylene)ethanone	1009-61-6		1	0.0027	162.190	0.41	241-TY-104
1-Propanone							
1-Phenyl-1-propanone	93-55-0		1	0.26	134.179	47	241-C-101
9H-Fluoen-9-one	486-25-9		2	0.016	180.208	2.1	241-C-110
2,5-Cyclohexdiene-1,4-dione							
2,6-bis(1,1-dimethylethyl)-2,5-cyclohexdiene-1,4-dione	719-22-2		8	0.026	220.314	2.9	241-SX-107
<b>Summation</b>				<b>210</b>		<b>58,211</b>	
Note: (a) The positional or geometrical has not been defined.							
Source: Stock and Huckaby (2004)							

Table 3-21. Acids

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>ALKANOIC ACIDS</b>						
Ethanoic acid	64-19-7	19	0.64	60.053	261	241-C-104
Propanoic acid	79-09-4	4	0.016	74.080	5.1	241-C-108
Butanoic acid	107-92-6	2	3.0	88.107	840	241-C-103
Decanoic acid	334-48-5	2	0.0027	172.270	0.39	241-C-111
Dodecanoic acid	143-07-7	6	0.28	200.324	35	241-BY-108
Tetradecanoic acid	544-63-8	22	3.7	228.378	393	241-C-103
12-Methyltetradecanoic acid	5746-58-7	2	0.0087	242.405	0.88	241-C-107
Pentadecanoic acid	1002-84-2	13	2.2	242.405	222	241-C-103
Hexadecanoic acid	57-10-3	29	3.8	256.432	367	241-C-103
Octadecanoic acid	57-11-4	1	0.0037	284.486	0.32	241-C-108
Cyclohexanecarboxylic acid						
trans-2-(1,1-Dimethylethyl)cyclohexanecarboxylic acid	27392-16-1	1	0.0018	184.281	0.24	241-C-112
<b>ALKENOIC ACIDS</b>						
Propenoic acid	79-10-7	1	4.0	72.064	1,369	241-C-103
Hexenoic acid	142-62-1	1	0.0037	116.161	0.77	241-C-109
2-Ethylhexanoic acid	149-57-5	1	0.0018	144.216	0.31	241-C-109
Pentadec-14-enoic acid	17351-34-7	3	0.038	240.389	3.9	241-BY-107
Hexadec-9-enoic acid	2091-29-4	(*) 14	3.4	254.416	326	241-C-103
Z-Octadec-9-enoic acid	112-80-1	5	0.064	282.470	5.6	241-BY-107
<b>Summation</b>			<b>21</b>		<b>3,829</b>	
Note: (a) The positional or geometrical has not been defined.						
Source: Stock and Huckaby (2004)						

Table 3-22. Esters (Page 1 of 3)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>ALKANE ESTERS</b>						
Methanoic Acid Ester						
Methyl formate	107-31-3	1	0.0018	60.053	0.75	241-T-107
2-Methylpropyl formate	542-55-2	1	0.27	102.134	66	241-B-103
Vinyl acetate	108-05-4	1	0.0027	86.091	0.78	241-U-112
2-Propenyl formate	1838-59-1	1	3.8	86.091	1,067	241-C-103
Butyl formate	592-84-7	4	3.0	102.134	724	241-C-103
2,6-Dimethylhept-5-en-2-yl formate	UES010-02	3	0.34	170.244	49	241-BY-108
Ethanoic Acid Ester						
Methyl acetate	79-20-9	2	0.13	74.080	42	241-U-103
Ethyl acetate	141-78-6	3	43	88.107	11,957	241-C-103
2-Propenyl acetate	591-87-7	1	4.2	100.118	1,030	241-C-103
Butyl acetate	123-86-4	9	16	116.161	3,280	241-C-103
1-Hepten-1-yl acetate	35468-97-4	1	0.021	156.227	3.3	241-A-103
1-Hexadecyl acetate	629-70-9	3	0.049	284.486	4.3	241-BY-107
Oxoacetic Acid Ester						
Ethyl oxoacetate	6295-06-3	1	0.0013	130.145	0.24	241-AX-103
Propanoic Acid Ester						
2-Propyn-1-yl propionate	1932-92-9	1	0.0055	112.129	1.2	241-U-112
Butyl propionate	590-01-2	1	1.0	130.188	189	241-C-103
Octyl propionate	142-60-9	1	0.027	186.297	3.6	241-U-106
2-Methylpropanoic Acid Ester						
Butyl 2-methylpropionate	97-87-0	1	0.024	144.216	4.0	241-AX-102
1-(1,1-Dimethylethyl)-2-methyl-1,3-propanediyl 2-methylpropionate	74381-40-1	8	0.060	286.415	5.1	241-TY-104
3-Hydroxy-2,4,4-trimethylpentyl 2-methylpropionate	74367-34-3	3	0.0046	216.323	0.52	241-C-109
Butanoic Acid Ester						
1-Methylpropyl butanoate	819-97-6	1	0.00092	144.216	0.16	241-T-107
Butyl butanoate	109-21-7	6	2.4	144.216	404	241-C-103
E-2-Hexenyl butanoate	53398-83-7	1	0.037	170.254	5.3	241-BY-105
Hexyl butanoate	2639-63-6	1	0.00092	172.270	0.13	241-C-109
4-Cyanophenyl butanoate	29052-10-6	1	0.0027	189.216	0.36	241-C-107
Butanedioic Acid Ester						
Diethyl butanedioate	123-25-1	1	4.8	174.198	669	241-C-103
2-Oxo-3-methylpentanoic Acid Ester						

Table 3-22. Esters (Page 2 of 3)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Methyl 2-oxo-3-methylpentanoate	3682-42-6	1	0.021	144.172	3.6	241-U-106
Hexanoic Acid Ester						
Butyl 2-ethylhexanoate	68443-63-0	1	0.010	200.324	1.2	241-AX-102
Pentanoic Acid Ester						
Hexyl pentanoate	1117-59-5	1	0.016	186.297	2.0	241-B-103
Hexandioic Acid Ester						
bis(1-Methylpropyl) hexanedioate	38447-22-2	1	0.0018	258.361	0.17	241-C-107
Diethyl hexandioate	123-79-5	4	1.5	370.578	97	241-C-103
2-Ethylhexyl hexandioate	4337-65-9	1	0.027	258.361	2.6	241-B-103
bis(2-Ethylhexyl) hexandioate	103-23-1	1	0.059	370.578	3.9	241-S-105
E-Hexa-2-enoic Acid Ester						
(E,E)-2-Hexenyl 2-hexenoate	54845-28-2	1	0.28	196.292	35	241-C-102
4-Methylphenyl 2-hexenoate	69687-91-8	(*) 1	0.012	204.271	1.4	241-U-103
Heptanoic Acid Ester						
Butyl heptanoate	5454-28-4	2	0.0082	186.297	1.1	241-C-105
Tetradecanoic Acid Ester						
1-Methylethyl tetradecanoate	110-27-0	7	1.8	270.459	166	241-C-103
Butyl tetradecanoate	110-36-1	4	2.3	284.486	197	241-C-103
Pentadecanoic Acid Ester						
Butyl pentadecanoate	35996-97-5	1	0.0075	298.514	0.62	241-C-106
Hexadecanoic Acid Ester						
1-Methylethyl hexadecanoate	142-91-6	32	0.40	298.514	33	241-BY-108
2,3-Dihydroxypropyl hexadecanoate	542-44-9	1	0.0037	330.512	0.27	241-C-107
Butyl hexadecanoate	111-06-8	1	0.0024	312.541	0.19	241-C-106
Octadecanoic Acid Ester						
Butyl octadecanoate	123-95-5	1	0.027	340.595	1.9	241-C-105
E-9-Octadecenoic Acid Ester						
Methyl E-9-octadecenoate	1937-62-8	1	0.0078	296.498	0.64	241-C-107
a-Hydroxybenzeneacetic Acid Ester						
Methyl a-hydroxybenzeneacetate	20698-91-3	1	0.0072	166.178	1.1	241-SX-103
Ethyl a-hydroxybenzeneacetate	774-40-3	1	0.013	180.205	1.7	241-SX-106
<b>BENZENE ESTERS</b>						
1,2-Benzenedicarboxylic Acid Ester						
Diethyl phthalate	84-66-2	11	1.2	222.243	131	241-U-106
Dibutyl phthalate	84-74-2	2	0.0055	278.351	0.48	241-C-104

Table 3-22. Esters (Page 3 of 3)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Butyl cyclohexyl phthalate	84-64-0	1	0.073	304.390	5.9	241-S-110
Butyl 2-methylpropyl phthalate	17851-53-5	1	0.010	278.351	0.89	241-C-108
Butyl 2-ethylhexyl phthalate	85-69-8	1	0.0082	334.460	0.60	241-C-104
bis(2-Ethylhexyl) phthalate	117-81-7	1	0.0046	390.568	0.29	241-C-108
4-(1,1-Dimethylethyl)benzoic Acid Ester						
Methyl 4-(1,1-dimethylethyl)benzoate	26537-19-9	1	0.0041	192.260	0.52	241-C-108
<b>PHOSPHATE ESTERS</b>						
Butylphosphoric Acid Ester						
Dibutyl butylphosphate	78-46-6	13	0.71	250.321	70	241-C-103
Phosphoric Acid Ester						
Tributyl phosphate	126-73-8	26	5.9	266.320	539	241-C-103
<b>Summation</b>			<b>93</b>		<b>20,806</b>	

Note: (a) The positional or geometrical isomer has not been defined.  
Source: Stock and Huckaby (2004)

Table 3-23. Nitriles

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration	
<b>ALKANE NITRILES</b>							
Acetonitrile	75-05-8	84	22	41.053	13,000	241-C-103	
Hydroxyacetoneitrile	107-16-4	1	0.0027	57.052	1.1	241-TY-104	
Propanenitrile	107-12-0	66	12	55.080	5,300	241-C-103	
2-Methylpropanenitrile	78-82-0	2	0.055	69.107	19	241-BY-104	
2,2-Dimethylpropanenitrile	630-18-2	3	0.071	83.134	21	241-TX-111	
Butanenitrile	109-74-0	60	7.2	69.107	2,562	241-C-103	
Pentanenitrile	110-59-8	57	3.7	83.134	1,078	241-C-103	
Hexanenitrile	628-73-9	57	3.4	97.161	854	241-C-103	
Heptanenitrile	629-08-3	45	2.9	111.188	645	241-C-103	
Octanenitrile	124-12-9	22	1.7	125.215	340	241-C-103	
Nonanenitrile	2243-27-8	19	0.84	139.243	148	241-C-103	
Decanenitrile	1975-78-6	2	0.010	153.270	1.6	241-U-106	
Undecanenitrile	2244-07-7	1	0.0020	167.297	0.29	241-TY-104	
Tridecanenitrile	629-60-7	1	0.082	195.351	10	241-BY-107	
2,4-Pentadienenitrile	1615-70-9	(*)	1	0.0027	79.102	0.85	241-U-112
<b>ALKENE NITRILES</b>							
2-Propenenitrile	107-13-1	3	0.006	53.064	2.6	241-TX-118	
2-Methyl-2-propenenitrile	126-98-7	1	0.10	67.091	37	241-C-101	
2-Butenenitrile	4786-20-3	(*)	2	0.016	67.091	5.7	241-C-110
3-Butenenitrile	109-75-1	2	0.057	67.091	21	241-BY-106	
<b>CYCLOALKANE NITRILES</b>							
Cyclopropanenitrile	5500-21-0	2	0.020	67.091	7.3	241-C-107	
<b>AROMATIC NITRILES</b>							
Benzonitrile	100-47-0	4	0.069	103.125	16	241-C-110	
<b>Summation</b>			<b>54</b>		<b>24,071</b>		

Note: (a) The positional or geometrical isomer has not been defined.  
Source: Stock and Huckaby (2004)

Table 3-24. Amines and Amides (Page 1 of 2)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>ALIPHATIC AMINES</b>						
Methanamine						
N, N-Dimethylmethanamine	75-50-3	1	1.6	59.112	645	241-C-103
N-(1-Methylbutylidene)methanamine	22431-09-0	5	0.53	99.177	131	241-BY-107
N-(1-Methylhexylidene)methanamine	22058-71-5	1	0.012	127.231	2.3	241-C-104
N-(4-Hydroxy-2-methoxyphenyl)methanamine	1196-92-5	1	0.019	153.182	3.1	241-SX-106
Propanamine						
3-Cyanopropanamine	151-18-8	1	0.0021	70.095	0.74	241-T-107
2-Hydroxypropanamine	2799-17-9	1	0.58	75.110	190	241-C-105
Butanamine						
N-Ethylidene-1-butanamine	6898-74-4	2	0.032	99.177	7.9	241-U-106
1-Butanone						
4-(Dimethylamino)-1-phenyl-1-butanone	3760-63-2	1	0.015	191.275	1.9	241-C-110
1-Pentanamine						
5-Hydroxy-1-pentanamine	2508-29-4	2	0.0027	103.165	0.65	241-TY-104
1-Octadecanamine						
N,N-Dimethyl-1-octadecanamine	124-28-7	1	0.0037	297.572	0.30	241-TY-104
Ethylenediamine	107-15-3	1	0.56	60.099	230	241-C-105
1,4-Butanediamine	110-60-1	1	0.0011	88.154	0.31	241-TY-104
<b>CYCLIC ALIPHATIC AMINES</b>						
Aziridine						
2-Methylaziridine	75-55-8	3	0.13	57.096	55	241-S-102
2-Ethylaziridine	2549-67-9	5	0.16	71.123	57	241-A-101
Pyrrolidine	123-75-1	2	1.9	71.123	662	241-C-103
4-Piperidinemethanol						
1-Methyl-4-piperidinemethanol	20691-89-8	1	0.039	129.204	7.5	241-U-106
1,3,5,7-Tetraazatri(3.3.1.1(3,7))decane	100-97-0	9	0.029	140.189	5.1	241-TY-101
<b>AROMATIC AMINES</b>						
Benzeneamine						
N-Phenylbenzeneamine	122-39-4	11	0.21	169.228	30	241-BY-108
2-Ethylbenzeneamine	578-54-1	1	0.0076	121.184	1.5	241-A-102
Benzamide						
N-Methylbenzamide	613-93-4	1	0.0018	135.167	0.33	241-C-107
<b>ALIPHATIC AMIDES</b>						
Cyanamide						

Table 3-24. Amines and Amides (Page 2 of 2)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Dimethylcyanamide	1467-79-4	1	0.12	70.095	42	241-U-106
Formamide	75-12-7	3	0.008	45.041	4.2	241-BY-112
N-(2-Methylpropyl)formamide	6281-96-5	1	0.024	101.150	5.8	241-BY-106
N-Butylformamide	871-71-6	2	0.055	101.150	13	241-A-101
Acetamide	60-35-5	2	0.0077	59.068	3.2	241-AX-102
N,N-Dimethylacetamide	127-19-5	2	0.046	87.122	13	241-C-105
N-Methylacetamide	79-16-3	1	0.0011	73.095	0.37	241-TY-104
Butanamide	541-35-5	2	0.071	87.122	20	241-AX-102
N-Hexylbutanamide	10264-17-2	1	0.00037	171.285	0.05	241-AX-103
Octanamide						
N-(2-Hydroxyethyl)octanamide	7112-02-9	2	0.026	187.284	3.4	241-A-103
Nonanamide	1120-07-6	1	0.0073	157.258	1.1	241-TY-104
Decanamide						
N-(2-hydroxyethyl)decanamide	7726-08-1	1	0.0050			
Dodecanamide						
N-(2-Hydroxyethyl)dodecanamide	142-78-9	1	0.0071	243.393	0.72	241-TY-104
Hexadecanamide	629-54-9	1	0.0027	255.448	0.26	241-C-108
<b>CYCLIC ALIPHATIC AMIDES</b>						
2-Pyrrolidinone	616-45-5	5	0.88	85.106	253	241-C-103
1-Methyl-2-pyrrolidinone	872-50-4	1	0.10	99.134	25	241-BY-109
2,5-Pyrrolidenedione						
1-Methyl-2,5-pyrrolidione	1121-07-9	2	0.026	113.117	5.5	241-B-103
3-Piperidinecarboxamide						
N-Methyl-3-piperidinecarboxamide	5115-98-0	1	0.0086	142.202	1.5	241-SX-106
<b>Summation</b>			<b>7.2</b>		<b>2,423</b>	

Source: Stock and Huckaby (2004)

Table 3-25. Nitrous and Nitric Acid Esters, Nitroso and Nitro Compounds (Page 1 of 2)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>NITROUS ACID ESTERS</b>						
Methyl nitrite	624-91-9	13	0.80	61.041	319	241-A-101
Butyl nitrite	544-16-1	5	0.70	103.122	165	241-B-103
<b>NITRATE ESTERS</b>						
Methyl nitrate	598-58-3	13	0.47	77.040	150	241-C-104
Ethyl nitrate	625-58-1	14	1.5	91.067	390	241-C-105
1-Methylethyl nitrate	1712-64-7	4	0.14	105.094	32	241-C-102
Propyl nitrate	627-13-4	21	5.2	105.094	1,200	241-C-105
2-Methylpropyl nitrate	543-29-3	1	0.0020	119.121	0.41	241-TX-105
2,2-Dimethyl-1-propyl nitrate	926-42-1	6	0.16	133.148	29	241-AX-102
Butyl nitrate	928-45-0	19	1.8	119.121	360	241-C-105
3-Methyl-1-butanyl nitrate	543-87-3	5	0.23	133.148	42	241-BX-103
Pentyl nitrate	1002-16-0	11	0.87	133.148	160	241-C-105
Hexyl nitrate	20633-11-8	13	0.57	147.175	94	241-BX-103
Heptyl nitrate	20633-12-9	3	0.036	161.202	5.4	241-TX-111
Nonyl nitrate	20633-13-0	1	0.0013	189.257	0.17	241-TY-104
Decyl nitrate	2050-78-4	1	0.0079	203.284	0.9	241-TX-118
Dinitrate-1,3-propanediol	3457-90-7	1	0.12	166.091	18	241-C-204
Dinitrate-1,4-butanediol	3457-91-8	4	1.9	180.118	261	241-C-103
Dinitrate-1,5-pentanediol	3457-92-9	4	0.026	194.145	3.2	241-B-103
1-Nitrate-1,2,3-propanetriol	624-43-1	1	0.15	137.093	26	241-C-204
1,3-Dinitrate-1,2,3-propanetriol	623-87-0	2	0.077	182.091	10	241-TX-106
<b>NITRO COMPOUNDS</b>						
Methane						
Nitromethane	75-52-5	3	0.13	61.041	51	241-U-112
Trinitrofluoromethane	1840-42-2	2	0.10	12.011	205	241-BX-103
Propane						
1-Nitropropane	108-03-2	2	0.13	89.095	36	241-TY-105
2-Nitro-2-methylpropane	594-70-7	26	0.16	103.122		
2-Methyl-1-nitropropane	625-74-1	1	0.0082	103.122	2.0	241-U-112
Butane						
1-Nitrobutane	627-05-4	5	1.6	103.122	391	241-C-204
2-Nitrobutane	600-24-8	1	0.0050	103.122	1.2	241-U-112

Table 3-25. Nitrous and Nitric Acid Esters, Nitroso and Nitro Compounds (Page 2 of 2)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Z-1-Nitropropene	27675-36-1	1	0.0073	87.079	2.1	241-TY-104
Benzene						
Nitrobenzene	98-95-3	2	0.014	123.112	2.7	241-TX-118
1-Nitro-2-methylbenzene	88-72-2	1	0.0078	137.139	1.4	241-TY-104
1-Nitro-3-methylbenzene	99-08-1	1	0.0011	137.139	0.20	241-TY-104
1-Nitro-4-methylbenzene	99-99-0	1	0.0018	137.139	0.33	241-T-107
1-Nitro-4-chlorobenzene	100-00-5	1	0.0049	157.557	0.75	241-C-107
<b>NITROSO COMPOUNDS</b>						
Nitrosomethane	865-40-7	1	0.17	45.041	95	241-TX-118
4-Nitrosomorpholine	59-89-2	1	0.046	116.121	9.7	241-U-108
Methanamine						
N-Methyl-N-nitrosomethanamine	62-75-9	19	0.25	74.083	82	241-U-108
N-Methoxy-N-nitrosomethanamine	16339-12-1	1	0.021	90.082	5.7	241-TX-111
<b>Summation</b>			<b>17</b>		<b>4,153</b>	
Source: Stock and Huckaby (2004)						

Table 3-26. Heterocyclic Compounds (Page 1 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Oxirane	75-21-8	1	0.048	44.054	26	241-TY-104
Ethylloxirane	106-88-7	1	0.25	72.108	84	241-B-103
Ethenylloxirane	930-22-3	4	2.3	70.092	799	241-BY-108
cis-2-Ethyl-3-propylloxirane	56052-94-9	1	0.15	114.189	31	241-BX-104
(1-Methylbutyl)oxirane	53229-39-3	1	0.0022	114.189	0.47	241-S-111
2-Methyl-2-pentylloxirane	53907-75-8	1	0.015	128.216	2.8	241-C-104
1,3,6-Trioxocane	1779-19-7	1	0.0076	118.134	1.6	241-U-112
Furan	110-00-9	9	8.9	68.076	3,194	241-C-103
2-Methylfuran	534-22-5	2	3.4	82.103	1,010	241-C-103
2-Propylfuran	4229-91-8	2	2.7	110.157	590	241-BY-109
2-Pentylfuran	3777-69-3	2	0.015	138.211	2.6	241-AX-101
2-Heptylfuran	3777-71-7	1	0.30	166.266	44	241-BY-108
2,5-Dimethylfuran	625-86-5	1	0.037	96.130	9.3	241-BY-104
2-Ethyl-5-methylfuran	1703-52-2	2	0.046	110.157	10	241-BY-104
2-Octylfuran	4179-38-8	1	0.0060	180.293	0.81	241-BY-106
2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	1	0.0041	194.276	0.52	241-C-105
2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	1	0.0047	198.223	0.58	241-SX-106
2,3-Dihydrofuran	1191-99-7	5	0.046	70.092	16	241-C-110
3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	1	0.0027	126.200	0.53	241-BY-105
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1	0.0050	126.200	0.98	241-AX-102
2,5-Dihydrofuran	1708-29-8	5	5.2	70.092	1,823	241-C-103
Tetrahydrofuran	109-99-9	62	15	72.108	4,973	241-C-103
2,5-Diethyltetrahydrofuran	41239-48-9 (*)	1	0.10	128.216	19	241-A-101
2,5-Dipropyltetrahydrofuran	4457-62-9 (*)	1	0.0062	156.270	0.98	241-TY-104
trans-2,4-Dimethyltetrahydrofuran	39168-02-0	1	0.013	100.162	3.1	241-B-103
Dihydro-2(3H)-Furanone	96-48-0	9	3.2	86.091	911	241-C-103
5-Methyldihydro-2(3H)-furanone	108-29-2	4	0.040	100.118	10	241-AX-102
5-Ethyldihydro-2(3H)-furanone	695-06-7	9	0.082	114.145	17	241-U-106
5-Propyldihydro-2(3H)-furanone	105-21-5	7	0.010	128.172	1.9	241-C-104
5-Butyldihydro-2(3H)-furanone	104-50-7	3	0.0050	142.200	0.87	241-TY-104
5-Hexyldihydro-2(3H)-furanone	706-14-9	2	0.0055	170.254	0.79	241-C-104
3,5-Dimethyldihydro-2(3H)-furanone	5145-01-7	2	0.65	114.145	139	241-C-102
4,4-Dimethyldihydro-2(3H)-furanone	13861-97-7	1	0.0055	114.145	1.2	241-BY-112
5-Ethenyl-5-methyl-2(3H)-furanone	1073-11-6 (*)	1	0.0023	126.157	0.44	241-SX-106
5-Ethyl-5-methyl-2(3H)-furanone	2865-82-9	1	0.0072	128.172	1.4	241-TX-105

Table 3-26. Heterocyclic Compounds (Page 2 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
5-Pentyl-2(3H)-furanone	104-61-0	1	0.016	156.227	2.4	241-AX-102
Dihydro-2,5-furandione	108-30-5	1	0.0082	100.075	2.0	241-SX-103
2,4(3H,5H)-Furandione						
3-Methyl-2,4(3H,5H)-furandione	1192-51-4	1	0.016	114.102	3.5	241-AX-102
Tetrahydrofuranmethanol						
trans-5-Methyltetrahydrofuranmethanol	54774-28-6	1	0.0031	116.161	0.66	241-TX-118
Tetrahydrofuranmethanyl acetate	637-64-9	1	0.0027	144.172	0.47	241-T-107
Benzofuranone						
3a,4,5,6-Tetrahydro-3a,6,6-trimethylbenzofuranone	16778-26-0	6	0.67	180.249	91	241-BY-108
Tetrahydrofuranmethanol	97-99-4	1	0.069	102.134	16	241-C-102
Furanacetaldehyde						
alpha-Propylfuranacetaldehyde	31681-26-2	1	0.18	152.195	29	241-BY-107
1,3-Dioxane						
4,4-Dimethyl-1,3-dioxane	766-15-4	1	0.0082	116.161	1.7	241-C-105
1,3-Benzodiox-2-one	20192-66-9	1	0.0021	142.156	0.36	241-C-107
1,4-Dioxane	123-91-1	9	0.29	88.107	81	241-U-111
7-Oxabicyclo[4.1.0]heptane						
1-Methyl-7-oxabicyclo[4.1.0]heptane	1713-33-3	1	0.010	112.173	2.2	241-AX-102
2,3-Dioxabicyclo[2.2.2]oct-5-ene						
1-Methyl-4-(1-methylethyl)-2,3-dioxabicyclo[2.2.2]oct-5-ene	512-85-6	1	13	168.238	1,865	241-C-103
2,2-Bioxepane	74793-02-5	6	0.049	198.308	6.1	241-AX-102
2H-Pyran						
3,4-Dihydro-2-carboxaldehyde-2H-pyran	100-73-2	1	0.0072	112.129	1.6	241-A-102
Tetrahydro-2-(1,1-dimethylethoxy)-2H-pyran	1927-69-1	1	0.0046	158.243	0.71	241-TY-104
2H-Pyran-2-one						
Tetrahydro-5,6-dimethyl-2H-pyran-2-one	24405-16-1	5	1.1	128.172	210	241-BY-108
Tetrahydro-6-hexyl-2H-pyran-2-one	710-04-3	1	0.0025	184.281	0.33	241-S-111
Tetrahydro-6,6-dimethyl-2H-pyran-2-one	2610-95-9	1	0.0027	128.172	0.52	241-C-112
Dihydro-2H-pyran-3(4H)-one	23462-75-1	1	0.0041	100.118	1.0	241-C-107
1H-Imidazole						
2-Methyl-1H-imidazole	693-98-1	1	0.0015	82.106	0.44	241-TY-104
1H-Indole						
2-Phenyl-1H-indole	948-65-2	1	0.0051	193.250	0.65	241-SX-106
1H-Pyrrole	109-97-7	2	0.011	67.091	4.0	241-C-107
2,5-Dimethyl-1H-pyrrole	625-84-3	1	0.010	95.145	2.6	241-SX-106

Table 3-26. Heterocyclic Compounds (Page 3 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
1-Pyrrolidinamine						
2-(Methoxymethyl)-1-pyrrolidinamine	59983-39-0	1	0.0016	130.191	0.31	241-TY-104
1-Pyrrolidinecarboxylaldehyde	3760-54-1	1	0.00055	99.134	0.14	241-TY-104
4(3H)-Pyrimidinone	51953-17-4	1	0.020	96.089	5.1	241-BY-102
1H-Pyrrolo(2,3-b)pyridine						
6-Amino-2,3-diphenyl-1H-pyrrolo(2,3-b)pyridine	UHC000-11	1	0.015	285.340	1.3	241-SX-106
Hexahydro-1H-azepin-1-amino						
N-Ethylidenehexahydro-1H-azepin-1-amino	75268-01-8	1	0.0076	140.230	1.3	241-C-112
Pyridine	110-86-1	35	0.39	79.102	122	241-BY-108
2-Methylpyridine	109-06-8	1	0.12	93.129	31	241-C-104
3-Methylpyridine	108-99-6	5	0.14	93.129	36	241-C-101
4-Methylpyridine	108-89-4	5	0.034	93.129	8.9	241-C-105
2-Ethylpyridine	100-71-0	2	0.010	107.156	2.3	241-AX-102
2,4-Dimethylpyridine	108-47-4	4	0.46	107.156	105	241-C-103
2,5-Dimethylpyridine	589-93-5	1	0.082	107.156	19	241-C-104
3,4-Dimethylpyridine	583-58-4	1	0.0065	107.156	1.5	241-S-111
2,6-Dimethylpyridine	108-48-5	1	0.011	107.156	2.5	241-C-104
5-Ethyl-2-methylpyridine	104-90-5	2	0.013	121.184	2.6	241-C-104
2,3,6-Trimethylpyridine	1462-84-6	1	0.00060	121.184	0.12	241-TY-104
1,2,3,6-Tetrahydropyridine	694-05-3	2	0.10	83.134	30	241-U-106
Pyrimidine	289-95-2	3	0.092	80.090	28	241-S-101
4-Methylpyrimidine	3438-46-8	1	0.035	94.117	9.0	241-TX-111
Pyrazine	290-37-9	31	0.39	80.090	119	241-U-102
Methylpyrazine	109-08-0	9	0.021	94.117	5.5	241-TX-111
Ethylpyrazine	13925-00-3	4	0.029	108.144	6.6	241-TX-111
2,3-Dimethylpyrazine	5910-89-4	3	0.014	108.144	3.1	241-A-103
2,5-Dimethylpyrazine	123-32-0	1	0.0017	108.144	0.39	241-S-111
2,5-Dimethyl-3-(3-methylbutyl)pyrazine	18433-98-2	1	0.0092	178.280	1.3	241-C-104
1H-1,2,4-Triazole	288-88-0	2	0.025	69.066	8.8	241-U-103
1-Ethyl-1H-1,2,4-triazole	16778-70-4	1	0.12	97.120	30	241-BY-107
4H-1,2,4-Triazole						
3-Amino-4-ethyl-4H-1,2,4-triazole	42786-06-1	1	0.0087	112.135	1.9	241-C-108
1H-Pyrazole						
1-Methyl-1H-pyrazole	930-36-9	1	0.0060	82.106	1.8	241-TX-118
3-Methyl-1H-pyrazole	1453-58-3	3	0.21	82.106	63	241-BX-104

Table 3-26. Heterocyclic Compounds (Page 4 of 4)

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
4,5-Dihydro-1H-pyrazole						
5-Methyl-4,5-dihydro-1H-pyrazole	1568-20-3	1	0.061	84.122	18	241-U-106
4,5-Dimethyl-4,5-dihydro-1H-pyrazole	28019-94-5	1	0.022	98.149	5.5	241-U-106
5-Propyl-4,5-dihydro-1H-pyrazole	75011-90-4	1	0.021	112.176	4.6	241-U-103
4,5-Dihydrooxazole						
2-Methyl-4,5-dihydrooxazole	1120-64-5	6	0.057	85.106	16	241-U-106
2-Propyl-4,5-dihydrooxazole	53833-32-2	3	0.043	139.199	7.6	241-S-102
2-Oxazolidinone						
5-Methyl-3-(2-propenyl)-2-oxazolidinone	55956-20-2	4	0.061	141.171	11	241-U-106
Isothiazole	288-16-4	2	0.0027	85.128	0.79	241-C-112
Benothiazole	95-16-9	4	0.055	135.189	10	241-BY-106
2-Phenylbenothiazole	883-93-2	4	0.057	211.287	6.6	241-SX-106
<b>Summation</b>			<b>60</b>		<b>16,780</b>	
Note: (a) The positional or geometrical has not been defined.						
Source: Stock and Huckaby (2004)						

Table 3-27. Sulfur Compounds

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>THIOPHENES</b>						
2-Methoxy-5-methylthiophene	31053-55-1	1	0.021	128.194	4.0	241-C-104
<b>THIOLS</b>						
1-Propanethiol						
2,2-Dimethyl-1-propanethiol	1679-08-9	1	0.28	104.215	67	241-C-105
<b>SULFONES</b>						
Propane						
2-[(1,1-Dimethylethyl)sulfonyl]-2-methylpropane	1886-75-5	3	0.0043	178.295	0.59	241-S-111
Benzene						
Ethylsulfonylbenzene	599-70-2	1	0.081	170.232	12	241-C-109
<b>THIOCARBOXYLIC ACIDS, ESTERS AND AMIDES</b>						
Butanethioic Acid Ester						
S-Decyl ester of Butanethiolate	2432-55-5	3	0.22	244.443	22	241-U-106
Benzenesulfonamide						
N-Butylbenzenesulfonamide	3622-84-2	39	1.4	213.301	158	241-BY-108
N-Ethyl-N-methylbenzenesulfonamide	80-39-7	1	0.012	199.273	1.5	241-BY-112
N-Hexylbenzenesulfonamide	7250-80-8	1	0.0043	241.355	0.44	241-C-108
<b>Summation</b>			<b>2.0</b>		<b>264</b>	
Source: Stock and Huckaby (2004)						

Table 3-28. Silicon Compounds

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>SILANES AND SILOXANES</b>						
Silane						
Trimethylsilane	993-07-7	1	0.040	74.199	13	241-TX-111
Chlorotrimethylsilane	75-77-4	7	0.044	108.644	9.9	241-AX-102
Dimethoxydimethylsilane	1112-39-6	3	0.051	120.225	10	241-S-102
bis(trimethyl)silane						
4,5-Dimethyl-1,4-cyclohexadiene-1,2-diyl bis(trimethyl)silane	101300-62-3	1	0.0057	252.551	0.55	241-S-111
Heptasiloxane						
Hexdecamethylheptasiloxane	541-01-5	1	0.020	533.159	0.92	241-AX-102
Silanol						
Trimethylsilanol	1066-40-6	7	0.098	90.199	26	241-S-107
Cyclotrisiloxane						
Hexamethylcyclotrisiloxane	541-05-9	50	5.8	222.467	635	241-C-103
Cyclotetrasiloxane						
Octamethylcyclotetrasiloxane	556-67-2	44	4.9	296.622	408	241-C-103
Decamethylcyclotetrasiloxane	141-62-8	1	0.034	310.693	2.7	241-A-103
<b>SILANE ESTERS</b>						
Ethanedioic acid						
bis(TMS) ester of ethanedioic acid	18294-04-7	(*) 4	0.13	234.402	13	241-A-102
Propanedioic acid						
2-(TMSoxy)-bis(TMS) ester of propanedioic acid	38165-93-4	(*) 1	0.010	336.612	0.73	241-AX-102
E-2-Hexenedioic acid						
bis(TMS) ester of E-2-hexenedioic acid	55494-10-5	(*) 1	0.0084	288.495	0.71	241-SX-106
2-[(TMS)oxy]benzoic acid						
TMS ester of 2-[(TMS)oxy]benzoic acid	3789-85-3	(*) 18	0.20	282.491	17	241-A-103
alpha,4-bis(TMSoxy)benzeneacetic acid						
Methyl ester of alpha,4-bis(TMSoxy)benzeneacetic acid	55334-40-2	(*) 2	0.031	326.544	2.3	241-BY-103
TMS ester of alpha,4-bis(TMSoxy)benzeneacetic acid	37148-64-4	(*) 2	0.0064	384.700	0.41	241-C-107
alpha-[(TMS)oxy]benzenepropanoic acid						
TMS Ester of alpha-[(TMS)oxy]benzenepropanoic acid	27750-45-4	(*) 1	0.026	310.545	2.0	241-A-102
<b>OTHER SILICON COMPOUNDS</b>						
2,2,4,4,5,5,7,7-Octamethyl-3,6-dioxo-2,4,5,7-tetrasilaoctane	4342-25-0	1	0.019	294.693	1.6	241-AX-102
1-[4-[(Trimethylsilyl)oxy]phenyl]-1-propanone	33342-89-1	1	0.036	222.362	3.9	241-S-102
<b>Summation</b>			<b>11</b>		<b>1,150</b>	

Note: (a) The trimethylsilyl fragment has been designated as TMS in this table.  
Source: Stock and Huckaby (2004)

Table 3-29. Other Organic Compounds

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
<b>ISOCYANATES</b>						
Methane						
Isocyanatomethane	624-83-9	1	0.042	57.052	18	241-U-106
Propane						
2-Isocyanatopropane	1795-48-8	1	0.040	85.106	12	241-C-110
<b>HYDRAZINES</b>						
Hydrazine						
Methylhydrazine	60-34-4	1	0.0026	46.072	1.4	241-TY-101
1,1-Dimethylhydrazine	57-14-7	4	0.0075	60.099	3.1	241-TX-105
<b>Summation</b>			<b>0.093</b>		<b>34</b>	

Source: Stock and Huckaby (2004)

Table 3-30. Inorganic Compounds

Compound	TCD Identification Number	Number of Tanks	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Molecular Weight (g/mol)	Maximum Concentration (ppbv)	Tank with Maximum Concentration
Hydrogen	1333-74-0	53	107	2.016	1,293,000	241-C-107
Carbon monoxide	630-08-0	17	114	28.011	100,000	241-A-106
Carbon dioxide	124-38-9	76	3,125	44.010	1,737,000	241-B-102
Nitrous oxide	10024-97-2	69	1,979	44.013	1,100,000	241-U-102
Nitric oxide	10102-43-9	37	2.0	30.006	1,600	241-C-103
Nitrogen dioxide	10102-44-0	15	1.1	46.006	600	241-BY-102
Ammonia	7664-41-7	96	726	17.031	1,043,000	241-BY-108
Sulfur oxides	UIN000-01 (*)	1	n.a.	n.a.	370	241-C-104
Carbonyl sulfide	463-58-1	2	0.064	60.075	26	241-TY-101
Carbon disulfide	75-15-0	4	2.5	76.139	795	241-C-103

Note: (a) Because this entry includes various oxides, the molecular weight is ambiguous and the maximum concentration in mg/m<sup>3</sup> cannot be calculated.  
n.a. = not available

Source: Stock and Huckaby (2004)

**Table 3-31. Total Nonmethane Hydrocarbon Measurements and Summations of GC/MS Analyses**

Based on TNMHC		Based on Canister Collection		Based on Absorbant Collection	
Tank	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Tank	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)	Tank	Maximum Concentration (mg/m <sup>3</sup> at 25 °C)
241-C-103	520	241-C-204	220	241-C-103	2100
241-BY-108	310	241-BY-104	210	241-BY-108	580
241-C-204	160	241-BY-108	170	241-C-102	290
241-BX-104	130	241-C-102	130	241-BY-107	170
241-BY-101	57	241-BX-104	110	241-C-101	98
241-BX-103	52	241-TY-103	95	241-BX-104	85
241-TY-103	51	241-C-101	87	241-S-102	68
241-S-102	28	241-BY-107	84	241-TY-103	65
241-BY-102	20	241-BX-103	55	241-BY-101	48
241-TX-111	16	241-BY-110	50	241-BY-104	45

Source: Stock and Huckaby (2004)

The compounds with the least number of carbon atoms are listed first in each table. The next columns show the Chemical Abstracts Service number (CAS), the total number of analytical observations for the compound, the maximum observed concentration in mg/m<sup>3</sup>, the molecular weight, the maximum observed concentration in ppbv, and the tank from which the sample having the maximum concentration was obtained. The results are given for the alkanes; cycloalkanes; alkenes and alkadienes; alkynes; arenes; halogen compounds; alcohols, phenols, and ethers; aldehydes; ketones; acids; esters; nitriles; amines and amides; nitroso and nitro compounds; heterocycles; sulfur-containing compounds; silicon compounds; and miscellaneous organic compounds. In those few cases where a compound could be included in more than one table, the compounds were included only in the table of perceived greater toxicological interest. For example, chloroethene is in the halogen-containing compound list and not in the alkene list. Table 3-30 lists results for some inorganic gases including the nitrogen oxides.

Supplementary information about the concentrations of the organic compounds in the tank headspaces is provided in Table 3-31. This table, which is also derived from information in the TCD, lists the 10 tanks with the highest total concentrations of organic carbon based on three different analytical measurements.

Table 3-32 provides a summary of the results. This table provides perspective on the relationship between the total number of different compounds listed in the category with the number of compounds in the same category that have been observed in one tank or only at low concentration. The table lists the sum of the maximum concentration of the compounds in the category in ppbv. Table 3-32 also lists the number of compounds reported to have concentrations in excess of 100, 500, and 1,000 ppbv for each structural group.

Table 3-32. Summary of Observations

Category	Total Number of Different Compounds	Total Number of Compounds Observed in Only One Tank	Sum of Maximum Concentration of Compounds (ppmv)	Total Number of Compounds at less than 0.025 mg/m <sup>3</sup>	Total Number of Compounds at more than 1000 ppbv	Total Number of Compounds at more than 500 ppbv	Total Number of Compounds at more than 100 ppb
Alkanes	204	51	274	39	33	43	90
Cycloalkanes	155	71	21	43	4	8	36
Alkenes and Alkadienes	169	92	39	55	5	9	39
Alkynes	6	4	0.55	2	0	0	1
Arenes	47	20	8.1	21	3	3	14
Halogen Compounds	61	18	36	17	3	5	10
Alcohols, Phenols and Ethers	119	62	136	59	12	15	25
Aldehydes	46	18	23	21	4	4	9
Ketones	118	59	58	46	11	15	28
Acids	17	5	3.8	8	1	2	7
Esters	54	36	21	28	4	7	12
Nitriles	21	5	24	8	4	6	8
Amines and Amides	38	22	2.4	20	0	2	6
Nitro and Nitroso Compounds	37	15	4.2	13	1	1	10
Heterocycles	98	57	17	54	5	8	13
Sulfur Compounds	8	5	0.26	5	0	0	1
Silicon Compounds	18	9	1.1	7	0	1	2
Miscellaneous Organic Compounds	4	3	0.034	3	0	0	0
Inorganic Compounds	10	1	5,276	0	6	8	9
<b>Total</b>	<b>1,230</b>	<b>553</b>	<b>5,947</b>	<b>449</b>	<b>96</b>	<b>137</b>	<b>320</b>

Generally, gaseous samples can be analyzed more accurately than liquids or solids. The procedures for the analysis of liquids or solids are necessarily more complex and require that the desired organic analytes be extracted into an inert solvent. The concentration of the sample prior to chromatographic separation almost inevitably leads to the loss of volatile analytes. Moreover, many more headspace samples have been analyzed and the analysts have regularly improved their methodology. Consequently, it is not surprising that many more organic compounds have been observed in the headspaces of the waste tanks than in the liquid or solid samples. Inasmuch as the condensed phases of the wastes are the only sources of these compounds, the compounds that have been observed in the headspaces must, with the possible exception of the Freons, also exist in the liquids and solids.

The alkanes (about 200 compounds), cycloalkanes (about 150 compounds), and alkenes (about 150 compounds) are only modestly more numerous than the other compounds with organic functional groups. There are about 120 ketones, about 110 alcohols, phenols and ethers and about 100 heterocycles. Many semivolatile alkanes and cycloalkanes are recognized as constituents of the hydrocarbon diluents used in various Hanford Site extraction processes as discussed in Section 2.0. Virtually all of the other alkanes, alkenes, alkynes, arenes, alcohols and ethers, aldehydes, ketones, acids, esters, amides and amines, nitroso and nitro compounds and nitriles can be accounted for as products of the thermally and radiolytically induced free radical and ionic fragmentation and oxidation reactions of the hydrocarbons, phosphate esters, and complexants as discussed in Section 4.0.

Few of the molecules containing halogen, silicon, or sulfur atoms can arise from the compounds that were used in plant operations. Some observations may be spurious, even though some of these compounds were target analytes. Many of the compounds that cannot be directly related to the principal source term arise from substances that were used in supporting operations listed in Tables 2-3 and 2-4. The bromine- and chlorine-containing compounds may arise from the halocarbons that are also listed in these tables. The unusual trifluoro ketone, trifluoropropanone, which is listed in Table 3-17, can be traced thenoyltrifluoroacetone, a compound used in supporting operations (Table 2-3). However, the origins of the Freons have not been definitely established. These substances may arise from sources other than the liquid and solid wastes. The principal silicon-containing compounds, the bis(trimethylsilyl) derivative of 2-hydroxybenzoic acid and cyclic hexa- and octamethylcyclsiloxane, may originate from silicone fluids that were also used in supporting operations. The origin of N-butylbenzenesulfonamide, the most frequently observed sulfur-containing compound, is uncertain. The benzenesulfonic acid portion of this compound logically originates from sulfonated benzene resins used during operations as noted in Table 2-4. The formation of the amide in alkaline solution is more puzzling.

In summary, many different samples from the SSTs have been analyzed during the past 10 years and a broad array of inorganic and organic compounds have been observed in their headspaces. Although few DSTs have been analyzed, it is reasonable to assume that the same compounds are as prevalent in the DSTs.

### **3.6.2 Blind Spots in Analytical Procedures**

Although the GC/MS method has unquestioned capabilities, there are several blind spots. Compounds that have high volatility and low volatility appear to be underrepresented in the analyses of the headspaces. Although ubiquitous, ethane, ethene, and acetylene are usually neglected. Other potential compounds of interest such as methanol and ethanol and the simple amines appear to be underreported. Semivolatile compounds including TBP and other phosphate esters are among this group. Many of these problems can be overcome by the adoption of special analytical procedures as has been done for formaldehyde and dimethylmercury.

The work on solid and liquid samples is compromised by the requirement that solvents be used for the extraction of the organic compounds from the waste mixtures. Compounds that are more volatile than the extraction solvent are removed from the mixture during these operations. As already discussed, the use of reactive solvents or the acidification of the reaction mixtures can cause serious difficulties.

The general strategy for GC/MS analysis requires the selection of target analytes. The analysis of these target analytes is typically accomplished quantitatively by using known concentrations of pure compounds for the calibration of the analytical procedures. The retention times and the mass spectra are defined in this approach. There are two concerns. First, the selection of the target analytes is often biased by the immediate goal of the organizational unit that is paying for the analyses. This bias can lead to the addition of "impossible" compounds such as agricultural pesticides to the target analyte list. Second, the analysts focus on the target analytes can divert attention from other compounds of possibly even greater interest, for example dimethylmercury.

The laboratory procedures that are now used for the tentatively identified analytes are inefficient and inaccurate. They deserve immediate improvement. At a minimum, the analytical laboratories should be required to test tentative assignments by comparing the observed relative retention times for these analytes with a seriatim list of relative retention times observed in the technical literature or in their own laboratories. This procedure can be readily implemented because conventional columns with well defined properties are being used in the analytical laboratories. The technical information that has already been compiled and the vast literature in this area provide a secure basis for the construction of a list of this kind. Once that list is compiled, the identification of a tentatively identified compound in a new sample can be made not only on the basis of the mass spectral library search, but also on the basis of the relative retention time.

#### **4.0 THE CHEMICAL AND RADIOLYTIC REACTIONS OF ORGANIC COMPLEXANTS, DILUENTS AND PHOSPHATE ESTERS.**

##### **4.1 INTRODUCTION**

The chemical and radiolytic reactions that oxidize the organic compounds in the wastes have been reviewed previously (Stock and Pederson 1997; Stock 2001). Those discussions were focused on the pathways that yield hydrogen and other inorganic gases. This discussion is focused on the formation of volatile and semivolatile organic compounds. For completeness, the discussion integrates much of the material that was discussed in the previous report with the material of special interest to the industrial hygiene community.

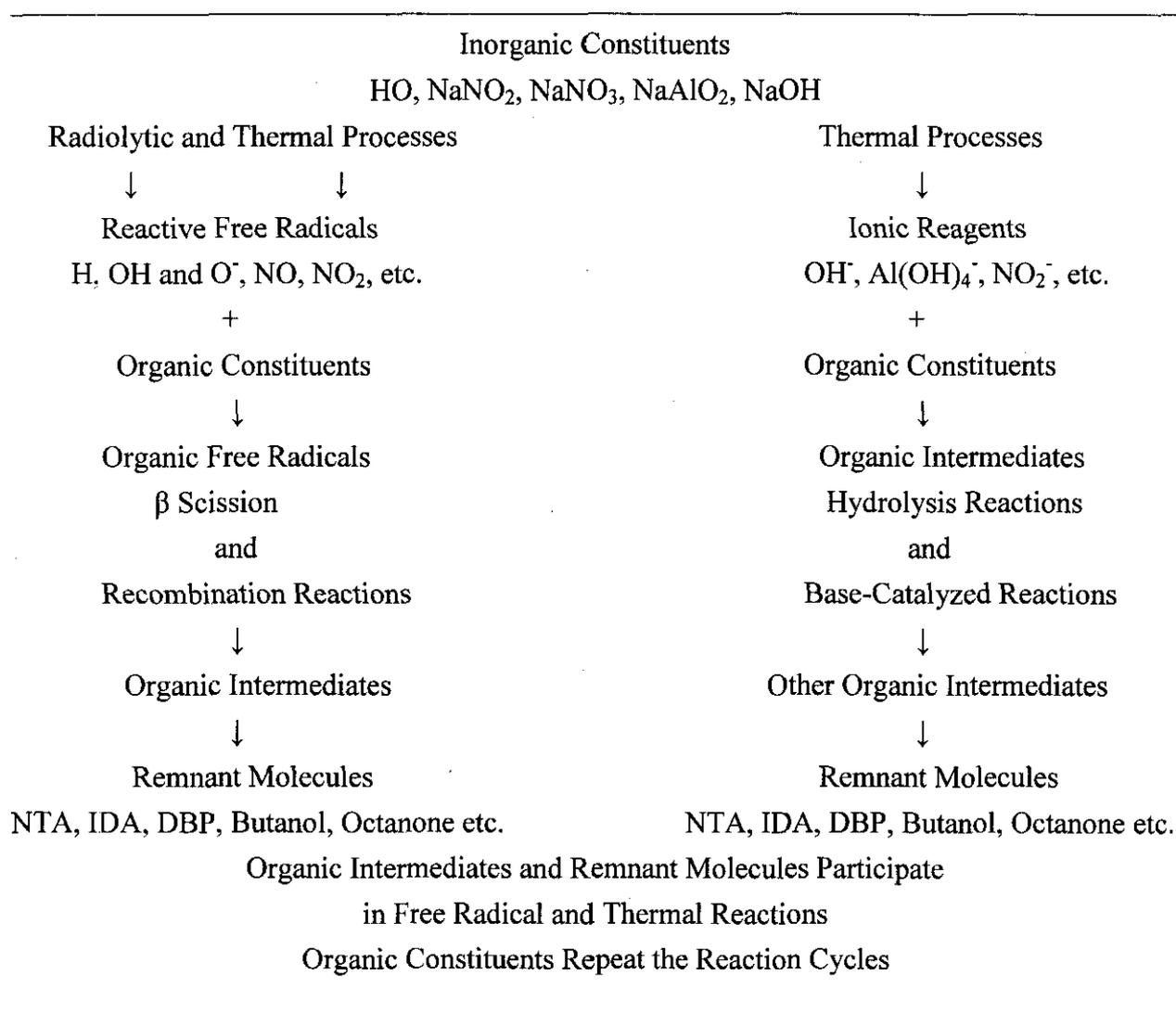
Fundamental and targeted investigations of the rates and products of the organic oxidation reactions, which occur in waste, have been carried out at the Hanford Site, Argonne National Laboratory, Georgia Institute of Technology, and Pacific Northwest National Laboratory. The results of these investigations when combined with the results of other investigations of the key pathways in radiation chemistry and information from the chemical literature about conventional free radical and ionic organic reactions provide a technical basis to describe the behavior of tank waste and to construct chemical models having predictive capabilities. The chemical model is based upon the results of the extensive laboratory studies of the factors governing the reaction rates and product distributions and analytical investigations of the compounds detected in the solid, liquid and gas phases of the tank waste.

Overall, the organic complexants, the hydrocarbon diluents and the phosphate esters are oxidized through long sequences of chemical reactions to form volatile compounds, which emerge from the waste, or sodium carboxylates and sodium carbonate, which are retained. As the organic compounds are oxidized, inorganic oxidants are reduced to form nitrogen-containing gases and hydrogen.

The radiolysis of water and the inorganic nitrogen compounds and the subsequent reactions of the radicals produced from these substances provide the reagents necessary for the initiation of the oxidation of the organic compounds in the waste. The radicals produced in these reactions abstract a hydrogen atom or an electron from the organic constituents to initiate chemical transformations. The initial radiolytic processes have negligible activation energies, but the rates of the ensuing chemical reactions are temperature dependent. Other reactions are initiated by the slow decomposition of inorganic constituents, particularly nitrite ion. These reactions, of course, have higher activation energies. Conventional ionic reactions, some of which are oxidation reactions, occur simultaneously. This chemistry is described in this section of the report.

Meisel et al. (1991a, 1991b, 1993) demonstrated that the radiolytic processes are synergistically coupled with other chemical reactions to fragment and oxidize the organic substances in the waste. Both ionic and free radical reactions contribute to their oxidation. Ionic processes, which occur in the absence of radiation, include the base-catalyzed fragmentation reaction of citrate ion (Ashby et al. 1993, 1994; Barefield et al. 1995, 1996; Camaioni et al. 1998), the aluminate ion-catalyzed oxidation of complexants with hydroxyl groups (Delegard, 1980, 1987; Ashby et al. 1993, 1994; Barefield et al. 1995, 1996; Camaioni et al. 1998; Camaioni and Autrey 2000), and the base-catalyzed oxidation of aldehydes that are responsible for most of the hydrogen generated in the waste (Ashby et al. 1993, 1994; Barefield et al. 1995, 1996; Karpoor et al. 1995). Reactions between the original complexants and hydrocarbons and water are not significant, but tributyl phosphate slowly reacts with water in alkaline solution to form butanol and sodium dibutylphosphate (Burger 1955; Davis 1984; Camaioni et al. 1996a). However, hydrolytic reactions transform the intermediates formed in the radiolytic reactions including nitrite and nitrate esters, nitroso and nitro compounds, acetals and ketals and their related nitrogen derivatives, oximes and hydroxamates, amides, and nitriles into alcohols, aldehydes and ketones, and sodium carboxylates (Ashby et al. 1993, 1994; Barefield et al. 1995, 1996; Camaioni et al. 1994, 1995, 1996b, 1997, 1998; Camaioni and Autrey 2000).

The principal reaction pathways in Figure 4-1 guide the discussion in the next sections. The three routes for the formation of reactive inorganic radicals and ions are shown at the top of the figure. The reactions of these substances with the organic compounds which form free radicals or reactive intermediates are illustrated in the center of the figure. The ensuing radical recombination and ionic reactions that produce families of organic intermediates and the array of ionic reactions that convert these intermediates into end products or into remnant molecules that repeat the cycle are sketched at the bottom of the figure.

**Figure 4-1. Principal Reaction Pathways for the Oxidation of Organic Compounds**

The rate of decomposition of each organic molecule is the sum of rates of the reactions occurring along the different reaction channels. The rates of the individual reactions depend on the composition of the waste under consideration (i.e., concentrations of reagents in the tank, temperature, radiation dose, etc.). The initial radiolytic reactions are temperature independent, but the ensuing radical and ionic reactions are temperature dependent. The thermally-induced free radical reactions have appreciable activation energies and occur rather slowly at temperatures below 50 °C. The base-catalyzed hydrolysis reactions of amides and the reactions of hydroxide ion with aldehydes proceed quite rapidly under typical storage conditions. The aluminate ion-promoted hydrogen transfer reactions are slower. There appear to be subtle differences in the reactions that occur in different phases of the waste, but this feature of the waste chemistry has not been investigated.

The relative rates and products of these reactions will be examined in Section 4.2 prior to the more complete examination of the chemical reaction pathways in Section 4.3.

## 4.2 PRODUCT DISTRIBUTIONS AND RELATIVE RATES OF OXIDATION

### 4.2.1 Product Distributions and Relative Rates for Complexants

**4.2.1.1. Products.** The work on the identification of the organic constituents in waste, which was discussed in Section 3.0, has been complemented by targeted laboratory investigations of the products formed from pure substances during thermal and radiolytic reactions in simulants. The complexants have received much attention since these substances account for most of the TOC.

Delegard (1987) reported glycolate ion thermally decomposes in waste to yield hydrogen, nitrous oxide, nitrogen, ammonia, and oxalate ion. More recent work has demonstrated formate and carbonate ions are also produced from this substance (Camaioni et al. 1997, 1998). Citrate ion decomposes thermally to give oxalate and acetate ions as the end products (Ashby et al. 1993, 1994). The thermal reaction is catalyzed by hydroxide ion. The thermal decomposition reactions of HEDTA and EDTA provide the same principal products. Delegard (1987) reported HEDTA degraded thermally to produce the same gases obtained from glycolate ion and organic fragmentation products including ED3A and oxalate ion. Ashby et al. (1994) found thermal aging of HEDTA ion also produced *s*-ED2A, IDA, glycinate, and formate ions. Camaioni et al. (1997, 1998) have confirmed and significantly extended the results of the previous investigators. Barefield et al. (1995, 1996) provided a detailed accounting of the thermal decomposition of trisodium HEDTA in simulated waste mixtures for reactions that were carried out for 7000 hours. ED3A is the most abundant remnant at this stage of the thermal reaction, and the yield of formate ion greatly exceeds the yield of oxalate ion.

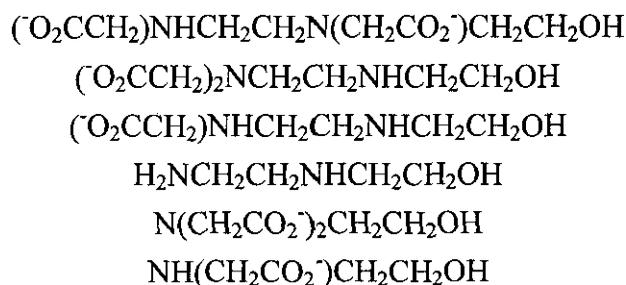
Very similar product distributions are obtained from the complexants during the radiolysis of simulants. The results obtained by Camaioni et al. (1998) are summarized in Table 4-1.

**Table 4-1. Principal Products of the Radiolysis of Complexants in Simulants**

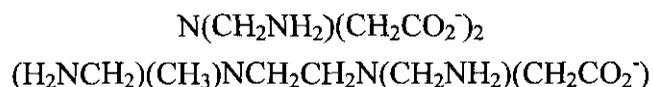
Compound		Definitely Identified	Possibly Present	Definitely Absent
EDTA	Major Products	ED3A, s-ED2A, IDA, Formate		HEDTA
	Minor Products	Acetate, glycolate, Glycinate	<i>μ</i> -ED2A, NTA	
HEDTA	Major Products	s-ED2A, IDA, Formate	NTA	
	Minor Products	Glycinate	<i>μ</i> -ED2A	
<i>μ</i> -ED2A	Major Products	IDA, Formate	EDMA	NTA
	Minor Products	Glycinate		
s-ED2A	Major Products	IDA, Formate		
	Minor Products	Glycinate		
NTA	Major Products	IDA, Formate		
	Minor Products	Glycinate		
IDA	Major Products	Glycinate, Formate		Acetate, Glycolate
Glycinate	Major Products	Formate, Oxalate		
Glycolate	Major Products	Formate, Oxalate		

Source: Camaioni et al. 1998

This work showed that the radiolysis and thermal reactions of the complexants and their remnants provide the same products, but in somewhat different amounts. Many other products are obtained in low yield. To illustrate, the radiolysis of HEDTA yields several compounds, in which the hydroxyethyl fragment is preserved (Ashby et al. 1994; Camaioni et al. 1998).

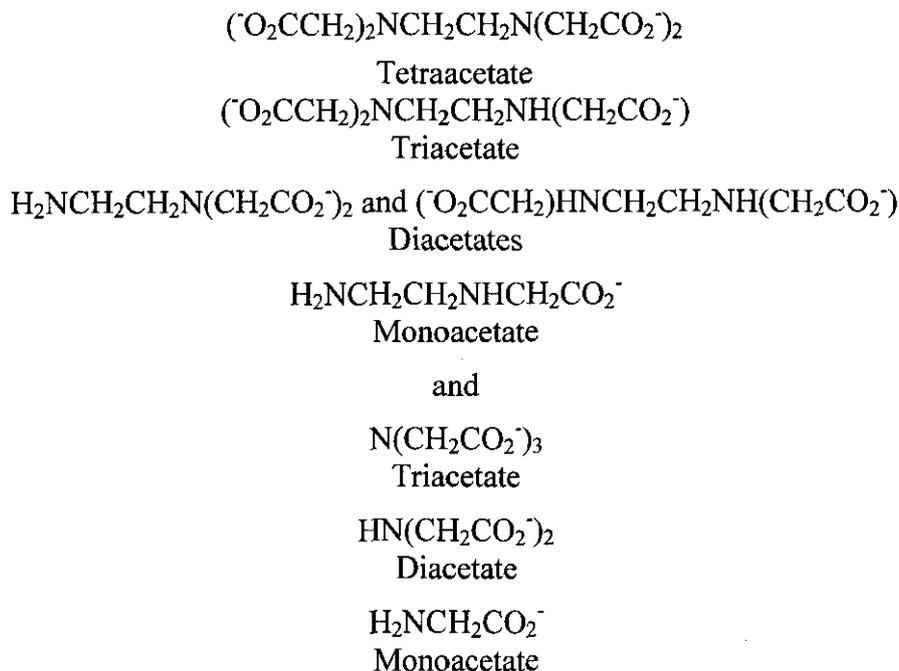


The radiolysis and thermolysis of NTA also gave N-(methylamino)iminodiacetate and a related dimeric compound (Toste 1998).



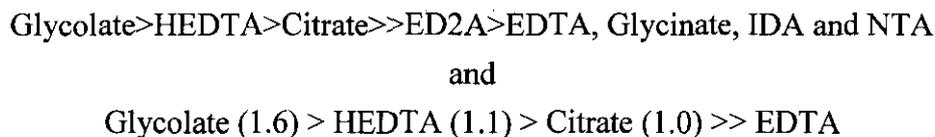
The observations of Ashby, Camaioni, and Toste imply the wastes contain a broad array of complexant derivatives, some of which are present in significant amounts and others of which

are present in very low concentrations. The degradation reactions of the complexants generally proceed sequentially by removing one methanocarboxyl,  $\text{CH}_2\text{CO}_2$ , fragment in each step as illustrated for EDTA and NTA.



The methanocarboxyl,  $\text{CH}_2\text{CO}_2$ , fragment yields both oxalate ion or formate and carbonate ion. All of the substances shown in these sequences have been detected in tank wastes or in simulants (Campbell et al. 1994, 1995a, 1995b, 1996a, 1996b, 1997; Ashby et al. 1994; Barefield et al. 1995, 1996; Camaioni et al. 1996a, 1996b, 1997, 1998; Evans et al. 1999; Mahoney et al. 1999).

**4.2.1.2. Relative Rates.** The thermal reactions occur quite slowly and are difficult to investigate in the laboratory, and only a few rates and relative rates have been determined. Barefield et al. (1995, 1996) observed that glycolate ion was thermally decomposed more rapidly than the other complexants in simulants at 90 and 120 °C. They estimated the half life of this substance to be less than one year at 60 °C. Camaioni et al. (1996b, 1997, 1998, Camaioni and Autrey, 2000) provided the order of reactivity:



The radiolytic reactions proceed much more readily and their relative rates can be readily determined by competition experiments. The results for the radiolysis of 10 compounds in simulants containing 2 M sodium hydroxide and either 3.75 M sodium nitrate and 1.25 M sodium nitrite or 2.00 M sodium nitrate and 2.00 M sodium nitrite are shown in Table 4-2 (Camaioni et al. 1997, 1998; Meisel et al. 2000).

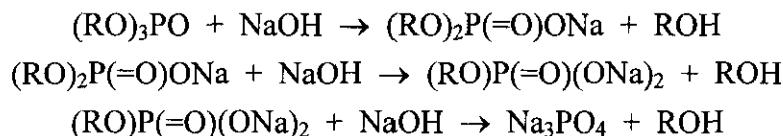
**Table 4-2. Relative Rates of Disappearance of Organic Complexants and Remnants during Radiolysis (Camaioni et al. 1997 1998; Meisel et al. 2000)**

Organic Compound	Relative Rate Per Molecule
EDTA	6
HEDTA	13
<i>u</i> -ED2A	3
<i>s</i> -ED2A	13
NYA	8
IDA	12
Glycinate	7
Glycolate	5
Formate	1
Citrate	0.6
Acetate	0.4

The nitrogen-containing members of the EDTA family are between 6 and 13 times more reactive than formate ion. Glycolate ion is also more reactive than formate ion, but citrate and acetate ion are less reactive. The most reactive compounds are about 35 times more reactive than the least reactive compound investigated. In addition, Meisel and Camaioni found that nitrogen dioxide reacts more rapidly with glycinate ion than formate ion and that nitrogen dioxide reacted more rapidly with IDA, NTA, and glycinate ion than with formate ion (Meisel et al. 2000).

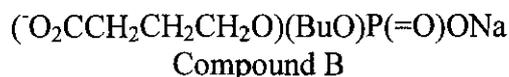
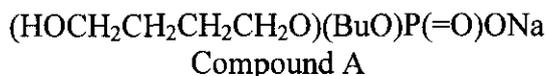
#### 4.2.2 Product Distributions and Relative Rates for Diluents and Phosphate Esters

**4.2.2.1. Products.** No targeted investigations were needed to define the products of the thermal reactions of the hydrocarbon diluents because the rates of their thermal reactions are imperceptible. The products of the thermal hydrolytic reactions of the phosphate esters are very well established in the chemical literature (Cox and Ramsey 1964; Wolfenden et al. 1998). The rates of reaction of the trialkyl, dialkyl and monoalkyl phosphates are very different, but they eventually hydrolyze to liberate an alcohol and a less alkylated phosphate as shown in the equations where R represents either the butyl or 2-ethylhexyl group,



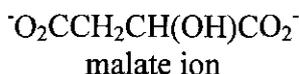
The product distributions obtained in the radiolytic reactions of the phosphate esters have been investigated by several research teams because of their importance in the PUREX process (Wilkinson and Williams 1961; Davis 1984). In targeted work, Camaioni et al. (1996a) investigated the radiolysis of dibutylphosphate ion (DBP) in alkaline solution in the presence and absence of sodium nitrate and sodium nitrite. Monobutyl phosphate forms and decomposes to phosphate ion under the same conditions. Camaioni et al. (1996a) showed phosphorous was also present in other dialkyl and monoalkyl phosphates. These new and more highly substituted

dialkyl and monoalkylphosphates are created by the introduction of hydroxyl or carbonyl groups into the butyl fragments of DBP and monobutylphosphate ion (MBP) during radiolysis. The structures of the products were not identified, so two of the many possible products are shown to illustrate the nature of these products.



It is pertinent to mention that the hydrolysis of Compound A could lead to a cyclic ether, tetrahydrofuran, and Compound B could lead to a cyclic lactone, dihydro-2(3H)-furanone. Both of these compounds have been detected in the wastes. Camaioni et al. (1996b) also detected sodium acetate, formate and oxalate among the reaction products but the sum of the carbon contained in these products and in the phosphates was smaller than the amount of carbon in the starting material. This difference originates because alkanes and alkenes are also formed. Davis (1984) pointed out that the radiolysis of tributyl phosphate produced methane, ethane, and propane and ethene and propene. Although unreported, cyclopropane is also usually produced in reactions of this kind.

Camaioni et al. (1996a) also investigated the radiolysis 1-butanol and sodium butyrate, two known reaction products, under the same conditions. These substances decomposed much more rapidly than the phosphate esters. The product mixture contained residual 1-butanol together with sodium formate, acetate, and propionate, as well as sodium malate, malonate, and oxalate.



These oxidized products account for less than 50% of the available carbon. Although the other products were not identified, related work established that inorganic carbonate ion is produced and that other oxidized and fragmented organic molecules are formed. Spinks and Woods (1990) point out the radiolysis of low molecular weight alcohols in water and in other media provides high yields of hydrogen and the corresponding aldehyde, and lower yields of alkanes, cycloalkanes, alkenes and alkynes, and other oxygen-containing compounds.

This work shows the mono-, di- and tributyl phosphates and 1-butanol are important sources of the fragmented molecules known to be in the wastes, i.e. methane, ethane, propane, butane, ethene, propene, the butenes, cyclopropane, butadiene, ethyne, propyne, the butynes, methanol, ethanol, 1-propanol and 2-propanol, butanal, acetone, and 2-butanone.

These observations are entirely compatible with the general features of the chemical literature (Gyorgy 1981; Davis 1984; Spinks and Woods 1990; Tabata et al. 1991; Bugaenko et al. 1993). These authors indicate the radiolysis of pure paraffinic hydrocarbons yields fragmented molecules and dimers together with hydrogen and other low molecular weight compounds.

Dimeric hydrocarbons, for example, the substances that would be obtained by the recombination of two dodecanyl radicals to produce a compound with 24 carbon atoms are rarely observed in the Hanford Site wastes. When the reactions are carried out in the presence of low concentrations of oxygen, the product spectrum changes and radiolysis provides fragmented alkanes and alkenes and oxidized molecules including alcohols, aldehydes and ketones, and carboxylic acids as discussed more completely in Section 4.3.3.

**4.2.2.2. Relative Rates.** Attempts to determine the relative reactivity of the hydrocarbons quantitatively under the heterogeneous conditions prevailing in the waste tanks have not been completely successful (Camaioni et al. 1995, 1996b). However, Camaioni showed that dodecane was essentially inert compared to EDTA and stearate ion (Camaioni et al. 1996b).

EDTA > Stearate Ion >> Dodecane

This observation and the other work on butyrate ion imply the hydrogen-rich, water soluble carboxylate ions undergo radiolysis during interim storage, but that water-insoluble compounds, like dodecane, are much less reactive.

Much greater success was realized in the investigations of the hydrolytic and radiolytic reactions of the phosphates. The known rate constants for hydrolysis of dialkyl esters are several orders of magnitude smaller than the rate constants for the hydrolysis of the corresponding trialkyl esters, and the rate constants for the hydrolysis of monoalkyl esters are also several orders of magnitude smaller than the rate constants for the dialkyl esters (Cox and Ramsay 1964; Wolfenden et al. 1998). The rates of hydrolysis of tributyl phosphate have been measured under heterogeneous conditions in the presence of 1M sodium hydroxide at temperatures from 30 to 100 °C by Burger (1955). The observed rate data were fit to the following expression by Camaioni et al. (1996a),

$$\ln(R) = 54.8 - 2.55 \times 10^4(1/T) + 2.69 \times 10^6(1/T)^2$$

where T is the temperature in °K and R is the rate in mg of tributyl phosphate hydrolyzed per liter per hour. The rate of disappearance of TBP was approximately 15 mg per hour per liter of 1 M sodium hydroxide at 65 °C. The reaction rate was about 60% slower when kerosene, one of the hydrocarbon diluents, was added to the reaction system. The slower reaction in the presence of kerosene can be reasonably attributed to the fact that tributyl phosphate dissolves in kerosene, where, in the absence of hydroxide ion, hydrolysis does not occur. Camaioni et al. (1996a) found that changes in the concentrations of inorganic ions had no appreciable influence on the reaction rate.

The radiolytic reactivity of sodium bis(2-ethylhexyl)phosphate has not been established. However, the oil that was isolated from a layer of sludge in tank 241-C-106 contained Hydrocarbon/TBP/(2-ethylhexyl)phosphates) in a ratio 5/10/85 compared to 40/28/4 in the original process solvent (Stauffer and Stock 1999). The major increase in the relative content of the (2-ethylhexyl)phosphates is understandable because the hydrocarbons are much more volatile than the bis phosphate and TBP is much more readily hydrolyzed. These substances disappear to leave the non-volatile and hydrolytically inert (2-ethylhexyl)phosphates. The observations also

imply that bis(2-ethylhexyl)phosphate is not rapidly degraded by radiation. The resistance to radiolysis is related to its very low solubility in aqueous solution.

In summary, the rate of hydrolysis of TBP in alkaline solution is sufficient to alter its concentration significantly during interim storage, but the rates of hydrolysis of the dialkylphosphate ions and the monoalkyl phosphate ions are negligible. The three soluble butylphosphates undergo radiolysis in the aqueous phases of the waste. Although direct evidence is lacking, the available results imply that sodium bis(2-ethylhexyl)phosphate undergoes radiolysis much more slowly than the other compounds and persists in the wastes.

### 4.3 REACTION PATHWAYS FOR ORGANIC OXIDATION

Chemical reaction models are discussed in this section. These models underpin the discussion of the formation of volatile and semivolatile compounds of interest in industrial hygiene work. The radical reactions are discussed prior to the ionic organic reactions because many of the compounds produced through thermally or radiolytically initiated radical reactions are subsequently decomposed in ionic processes.

#### 4.3.1 Radiolytic and Thermal Initiation

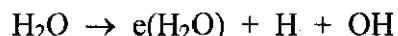
The radiation chemistry of the Hanford Site wastes is dictated by the relatively high concentrations of cesium-137 and strontium-90. The alpha particle producing nuclides are not abundant and their contribution to the radiation chemistry is small. Cesium-137 exists predominantly in aqueous solution and strontium-90 in insoluble sludges. These substances undergo radioactive decay producing beta and gamma radiation and electrons through several different reaction channels (Spinks and Woods 1990; Meisel et al. 1993; Kocher 1987).

Sr-90 with a half life of 28 years emits a 0.546 MeV beta having an average energy of 0.196 MeV and the short lived daughter Y-90 emits a 2.284 MeV beta having an average energy of 0.934 MeV. The average energy deposited per disintegration is 1.13 MeV. Cs-137 with a half life of 30 years decays via two beta emissions. One occurs with a probability of 0.946 and has a maximum energy of 0.512 MeV and an average energy of 0.157 MeV and the other occurs with a probability of 0.054 and has a maximum energy of 1.173 MeV and an average energy of 0.415 MeV. The average energy deposited during these two disintegrations is 0.171 MeV.

Beta and gamma radiation at the energy emitted by cesium-137 and strontium-90 have essentially the same consequences (Meisel et al. 1991a, 1991b, 1993), and the chemistry of the process can be investigated conveniently by using cobalt-60 sources.

The emitted particles transfer energy to water producing electronically excited molecules and ion pairs in widely separated spurs (Spinks and Woods 1990). It is convenient to consider the radiolytic reactions of the solvents and solutes as direct or indirect processes. The distinction is especially appropriate when the compounds of interest are solutes at low concentration. In these circumstances, the solvent and the other solutes at high concentration absorb the radiation and the reactive products of these direct processes are responsible for the indirect chemical reactions of the solute. It has been shown that the organic solutes in Hanford Site waste absorb no more

than about 1% of the direct radiation (Stock 2001). The direct processes involve the excitation and ionization of water molecules and the other solutes at high concentration such as nitrate ion. The reaction cascade results in the prompt formation of solvated electrons, hydrogen atoms, and hydroxyl radicals in the initial reactions.



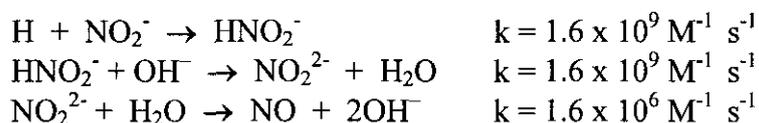
These substances react indirectly with the organic solutes in water.

Thermal initiation also occurs. The organic constituents are oxidized when waste simulants are heated in the absence of radiation. These reactions proceed by free radical reactions and by ionic processes. It is relatively easy to isolate and to identify the chemical processes responsible for the ionic reactions. To illustrate, the high concentration of hydroxide ion in the waste is a major factor in the promotion of the ionic decomposition reactions of citrate ion in the absence of radiation, and the high concentrations of hydroxide and aluminate ions are important for the ionic decomposition of glycolate ion in the absence of radiation. These ionic processes are not sensitive to the concentration of oxygen, and have significant activation energies.

The evidence for the occurrence of thermally initiated free radical processes is less direct, but it is compelling. First, the thermal formation of methane has a relatively high activation energy implying that bond-breaking, free radical forming reactions are required for initiation (Bryan and Pederson, 1994, 1995; Pederson and Bryan 1996; Bryan et al. 1996, 1997; 2004; King and Bryan 1998, 1999; King et al. 1997; Person 1996, 1998). Second, the rates and product distribution observed for thermal reactions of complexants in simulants are very sensitive to oxygen (Barefield et al. 1995, 1996; Person 1996, 1998; Camaioni et al. 1995, 1996b, 1997, 1998; Bryan et al. 2004). Ionic reactions are not usually sensitive to the oxygen content. Third, the reactions of nitrite ions often lead to the formation of radicals including nitric oxide and nitrogen dioxide. These substances are known to be effective oxidants in the radiolytic reactions of the complexants and solvents. These considerations strongly suggest that the thermal reactions occur through radical processes initiated by the decomposition of nitrite ion as well as through the ionic reactions.

**4.3.1.1. A Quantitative Kinetic Model for the Initial Reactions.** The radiolytic reactions are initiated inhomogeneously in spurs (tracks) when the beta and gamma particles transfer energy to the water and the other solutes to excite and ionize them (Spinks and Woods 1990). The free radicals and other reactive intermediates formed in the spurs diffuse and then react homogeneously in solution. Kinetic models have been developed for the description of the inhomogeneous, and the results of these models have been coupled with models for the chemical reactions that occur subsequently and homogeneously in solution. The development of the model and its applicability for the Hanford Site wastes, which has been carried out at Argonne National Laboratory and Pacific Northwest National Laboratory, has been reviewed (Stock 2001), and the commentary in this report will be restricted to a discussion of reactions that lead to the reactive substances that are responsible for the formation of volatile and semivolatile organic compounds.

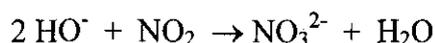
The model requires rate constants for many elementary free radical reactions. Fortunately, many reactions have been studied and the rate data have been critically examined and summarized by Buxton et al. (1988). In addition to this body of knowledge, Meisel and Camaioni et al. (Meisel et al. 1991a, 1991b, 1993, 1997; Camaioni et al. 1995, 1996b, 1997, 1998; Camaioni and Linehan 1999; Camaioni and Autrey 2000; Fessenden et al. 2000; Cook et al. 2001) have carried out targeted investigations to provide other necessary information to describe chemical transformations of the hydrogen atoms, hydroxyl radicals and solvated electrons produced from the radiolysis of water in alkaline solutions with high concentrations of sodium nitrite and sodium nitrate. The model implies that hydrogen atoms and nitrate dianions are rapidly replaced by oxidizing radicals including nitric oxide and nitrogen dioxide. Hydrogen atom reacts rapidly with nitrite ion to form nitric oxide. The reaction has been recently shown to proceed through a dihydroxylamine and the dianion of nitrite ion (Lyman et al. 2002; Hug et al. 2004)



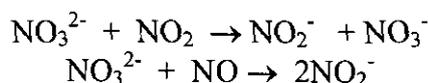
The solvated electron reacts with the nitrate ion to yield the dianion of nitrogen trioxide which rapidly decomposes to form nitrogen dioxide.



The half-life of the nitrate dianion in water is approximately 15 microseconds. However, the nitrate dianion is considerably more stable in alkaline solution because of the favorable equilibrium constant for the reaction between hydroxide ion and nitrogen dioxide (Meisel et al. 2000; Fessenden et al. 2000).



The substance is consumed in reactions with nitrogen dioxide and nitric oxide. The nitrogen oxides play a major role in the oxidation reactions of the organic solutes.



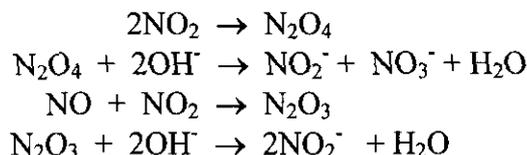
At elevated pH, hydroxyl radical reacts with hydroxide ion to produce water and the oxide anion radical. This anion radical reacts with nitrite ion to give nitrogen dioxide and the dianion of nitrogen trioxide, which also converts to nitrogen dioxide (Fessenden et al. 2000).



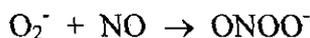
At lower pH, the hydroxyl radical reacts with nitrite ion to give nitrogen dioxide at an even faster rate.



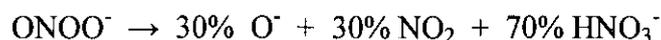
As a consequence of high sodium nitrite and sodium nitrate concentrations, the original very reactive components produce two oxidizing agents, nitric oxide and nitrogen dioxide. However, these substances are also consumed in the waste. They combine to give anhydrides that hydrolyze in aqueous solution to form nitrite or nitrate ion.



The concentration of nitrogen dioxide is augmented by the radiolytic formation of peroxyxynitrite ion. Edwards and Plumb (1994) and Hurst and Lyman (1999) have reviewed the chemistry of this ion. It is produced in biological systems by the reaction between superoxide anion and nitric oxide.



The substance is also formed by the radiation of solid sodium nitrate and in solutions containing nitrate ion. The G value for the formation of the ion in aqueous solutions of lithium nitrate at pH 13 is 0.65 molecules/100eV. This substance, although thermodynamically unstable relative to nitrate ion, persists in the solid and is responsible for the color of irradiated sodium nitrate. The ion is less stable in aqueous solution (Stern et al. 1996; Fukuto and Ignarro 1997; Lyman and Hurst 1998; Merenyi et al. 1999). Complexed transition metal ions catalyze the decomposition (Zhang and Bush 2000; Shimanovich et al. 2001). The decomposition reaction yields about 30% nitrogen dioxide and oxygen anion radical and 70% nitrate ion.



Accordingly, the direct radiation of nitrate ion in solution or the solid provides additional nitrogen dioxide. The kinetics of the competitive processes for the formation and decomposition of nitric oxide and nitrogen dioxide infer the steady-state concentrations of these oxidizing radicals are more than sufficient to dictate the chemistry.

Extensive information about the radiolysis of water provides a sound technical basis for the establishment of the rate constants for the initiation reactions. There is much less information available about the thermal chemistry of nitrite ion under the complex reaction conditions applicable for Hanford Site wastes. The free radical reaction and the ionic reactions occur competitively, but pathways of initiation of the free radical reactions have not been established, and the thermal reaction has not been explicitly modeled. However, the thermally initiated radical process is, like radiolysis, an oxidation reaction, and in the absence of definite evidence it is reasonable to postulate that nitric oxide and nitrogen dioxide also participate in the thermally initiated processes. Therefore, although the initiation reactions in the thermal reaction cannot be quantitatively analyzed, the ensuing reactions in radiolysis and thermolysis are similar.

The rate constants for the competing reactions between hydroxyl radical and its anion with the inorganic constituents are very large, but the rate constants for their reactions with organic molecules are also very large as illustrated for the hydrogen atom abstraction reaction of formate ion by hydrogen atom (Buxton et al. 1988) and the electron transfer reaction of hydroxyl radical with glycinate ion (Bonifacic' et al. 1998; Camaioni et al. 1998; Hug et al. 2000; Hug and Fessenden 2000; Stefanic et al. 2001; Armstrong et al. 2004)



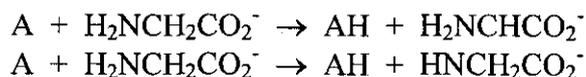
Preliminary tests of the model have been carried out successfully. Its ability to account for quite subtle differences in the reactions patterns of formate ion under different conditions is impressive (Camaioni et al. 1998). The model has also been used to describe the oxidation of glycinate ion, an important substance produced from the EDTA family of complexants. Recent investigations of the radiolytic reactions of glycinate ion (Bonifacic' et al. 1998; Camaioni et al. 1998) conclude the reaction occurs predominantly by electron transfer reactions with hydroxyl radical and nitrogen dioxide to provide the intermediate anion zwitterion pair. The rate constant for the decomposition of this substance to aminomethyl radical and carbon dioxide is greater than  $10^8 \text{ s}^{-1}$ ; however, the rate of conversion of the zwitterion into the nitrogen centered radical in an acid-base reaction is also very fast. The nitrogen centered radical is formed in preference to the more thermodynamically stable carbon centered radical.

The concept that two reaction channels, hydrogen atom abstraction and electron transfer, are available for the initiation of the oxidation reactions will be used to formulate a more general chemical model for the free radical oxidation reactions of the complexants, hydrocarbon diluents, and phosphate esters in the following sections.

### 4.3.2 Radical Reactions of the EDTA Family

The EDTA family includes the anions of the two original acidic complexants,  $\text{H}_4\text{EDTA}$  and  $\text{H}_3\text{HEDTA}$ , and the many related anions that are formed in the waste including the ED3A, the ED2A derivatives, NTA, IDA, and glycinate ion. The most important initiation reactions involving either hydrogen atom abstraction, or electron transfer were introduced in the previous section. The subsequent reactions leading to product formation are examined in this section. The reactions of glycinate ion, the structurally simplest member of the family, are discussed to describe the general reaction patterns of the complexants.

**4.3.2.1. Initiation by Hydrogen Atom Abstraction.** The hydrogen abstraction reactions from the two possible positions in glycinate ion are shown in the equations.



The reagent, A, represents the entire family of available free radical reagents including hydrogen atom, hydroxyl radical, oxygen anion radical, nitric oxide, nitrogen dioxide, the carbon and

nitrogen centered radicals in the reaction system, and inorganic substances. The corresponding products, AH, are hydrogen, water, hydroxide ion and so forth. The organic products are the nitrogen and carbon center derivatives of glycinate ion. Although the strengths of the carbon-hydrogen and nitrogen-hydrogen bonds in glycinate ion in solution have not been published, the nitrogen-hydrogen bonds in amines are stronger than the carbon-hydrogen bonds in amines and, the formation of the carbon centered radical is thermodynamically favored.

The kinetic model discussed in the previous section centers on the reactions of hydrogen atom, hydroxyl radical and its anion, nitric oxide and nitrogen dioxide. The large rate constant for the reaction of hydrogen atom with nitrite ion and the usually high concentration of nitrite ion in the waste ensures that hydrogen atoms are rapidly consumed. This reaction and other reactions that consume hydrogen atom reduce the rates of the abstraction reactions that lead to molecular hydrogen. On the other hand, the steady-state concentrations and reactivity of hydroxyl radical and its anion are sufficient to make hydrogen atom abstraction reactions from glycinate ion and the other members of the EDTA family plausible. The rate constant for the reaction of nitrogen dioxide with glycinate ion is about  $75 \text{ M}^{-1}\text{s}^{-1}$  (Meisel and Camaioni 1998, 2001). This rate constant is many orders of magnitude smaller than the rate constants for the reactions with hydroxyl radical and its anion, and other carbon and nitrogen centered organic radicals. These comparisons imply that the hydrogen abstraction reactions of the complexants are dominated by the more reactive radicals such as hydroxyl radical and its anion.

The reactions between glycinate ion and other members of the EDTA family with carbon centered radicals produce carbon centered radicals (Bonifacic' et al. 1998). Two products are formed by the hydrogen atom abstractions of EDTA.



But the product diversity increases for HEDTA which forms six different carbon-centered radicals by the abstraction of one of the six different hydrogen atoms (bold).



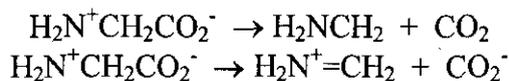
**4.3.2.2. Initiation by Electron Transfer.** The electron transfer initiation reactions of glycinate ion provide the neutral zwitterion.



The reagent, A, represents the same family of available free radical reagents discussed in Section 4.3.2.1. The corresponding products, A<sup>-</sup>, are hydride ion, hydroxide ion, oxide ion, nitroxyl anion, nitrite ion, and so forth. Few rate constants for the relevant electron transfer reactions have been measured, but elementary considerations of the thermodynamic requirements for electron transfer from many of these substances eliminates their serious consideration. For example, neither the transfer of the electron from hydrogen atom to form hydride ion nor from a carbon centered radical to form a carbanion is thermodynamically reasonable. In contrast, experimental work with glycinate ion and EDTA strongly infers that

hydroxyl radical and its anion and nitrogen dioxide react by electron transfer to provide pairs containing the zwitterion and hydroxide ion and nitrite ion, respectively (Bonifacic' et al. 1998; Hobel and von Sonntag 1998; Camaioni et al. 1998; Meisel et al. 2000).

The zwitterionic intermediate may decompose in a unimolecular process to form a primary radical and liberate carbon dioxide or produce two ionic intermediates.



The reaction leading to the aminomethyl radical and carbon dioxide is thermodynamically much more favorable than the reaction leading to the ionic products. The rate constant for the decomposition of zwitterion of glycinate is greater than  $10^8 \text{ s}^{-1}$  (Bonifacic' et al. 1998). Values greater than  $10^6 \text{ s}^{-1}$  have been reported for the decomposition of other amino acids (Su et al. 1997). The decarboxylation channel is, therefore, an important process, particularly for the nitrogen-containing complexants in the waste, leading to a family of primary free radicals. The primary radical formed through the electron transfer and decarboxylation for EDTA is shown.

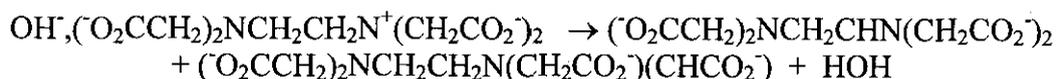


A second reaction channel is available to the zwitterion ion. The electron transfer reaction of hydroxyl radical produces an anion radical pair (a comma is employed to designate an ion pair) consisting of the basic hydroxide ion and the acidic zwitterion. Proton transfer from carbon and nitrogen to the hydroxyl anion gives the carbon and nitrogen centered radicals.



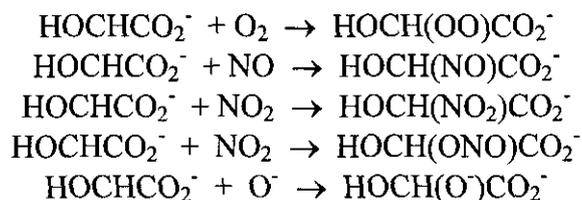
Experimental work with glycinate ion strongly suggests the nitrogen centered radical is formed preferentially even though it is the thermodynamically less stable radical.

Nitrogen centered radicals cannot be produced in this manner from the EDTA zwitterion or the other tertiary amines, for example, HEDTA and NTA. The acid base reactions of these substances lead exclusively to the formation of carbon centered radicals as illustrated by the reaction of EDTA.

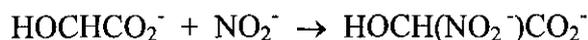


In conclusion, it is notable that the high alkalinity of the waste provides a reaction medium enabling the formation of carbon and nitrogen centered free radicals from the complexants containing nitrogen atoms by quite indirect electron transfer routes involving radicals that may otherwise be incapable of hydrogen atom abstraction reactions.

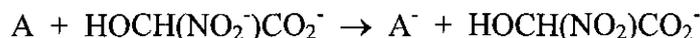
**4.3.2.3. Propagation Reactions.** The radical intermediates formed either by hydrogen atom abstraction, electron transfer, or decarboxylation combine with oxygen and other reagents including nitric oxide and nitrogen dioxide, and possibly hydroxyl radicals and their anions. Five plausible reactions of the glycolate radical are shown in the equations to illustrate this chemistry.



The product distributions depend upon the concentrations of the reagents and the rate constants for the different reactions. The organic radicals also react with nitrite ion (Kerber 1964; Zeldes and Livingston 1968; Leffler 1993). This process is favored by the very high concentration of nitrite ion in the waste.



The wastes contain many different inorganic substances in a mobile array of oxidation states. These substances act as electron donors and acceptors. Electron transfer to one of these acceptor molecules, A, provides the same product as reaction between the free radical and nitrogen dioxide.

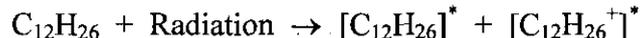


Consequently, each radical that is formed in the waste can form at least five different substances. The reaction complexity is immediately apparent.

### 4.3.3 Radical Reactions of the Hydrocarbons

**4.3.3.1. Initiation Reactions.** The radiolytic reactions of the water-insoluble hydrocarbons take place in organic layers, organic films, and micelles. The radiolysis of the hydrocarbon began during the operation of the PUREX process and has continued during interim storage. Specific transformations occurring during the PUREX process have been discussed by Davis (1984), and the general features of the chemical transformations of hydrocarbons during radiolysis have been discussed by Gyorgy (1981), Spinks and Woods (1990), Tabata et al. (1991), and Bugaenko et al. (1993). Targeted studies have not been carried out at the Hanford Site because the information in the literature is quite complete.

Hydrocarbon radiolysis begins with the formation of electronically excited molecules and ions (Spinks and Woods 1990; Bugaenko et al. 1993). The formation of an excited state of dodecane and an excited radical cation of dodecane is shown in the first equation to illustrate the process.



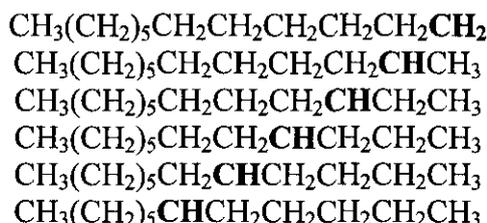
One of the several possible reaction channels (Spinks and Woods 1990) leads to proton loss and the formation an alkyl radical. The electronically excited molecules and ions undergo carbon-carbon and carbon-hydrogen bond scission as illustrated in the next equation.



Sanche and coworkers (Rowntree et al. 1991; Mozejko et al. 2003) have shown that hydrocarbons in films undergo dissociative electron attachment.



The original diluents contained many different hydrocarbons as noted in Section 2.0, and the analytical work discussed in Section 3.0 affirms that the wastes contain many hydrocarbons including original diluents such as undecane, dodecane, tridecane, and tetradecane with many different methyl derivatives, for example, 2-, 3-, 4-, 5- and 6-methyldodecane, as well as alkylated cyclopentanes, cyclohexanes, and decalins. The radiolysis of this family of hydrocarbons provides a very broad family of alkyl radicals since each hydrocarbon can be converted to several free radicals. The six radicals which are formed by hydrogen loss from dodecane and the homologous series of radicals which are formed by carbon-carbon bond cleavage are shown to illustrate the complexity.

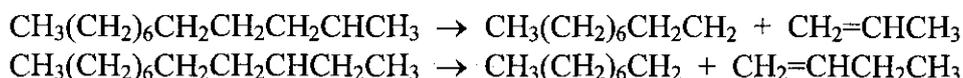


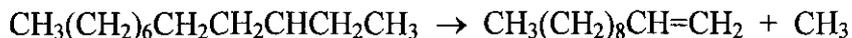
The same radicals are produced when the excited molecules decompose by the loss of a hydrogen atom or an alkyl radical or by dissociative electron attachment. The radiolysis of a complex mixture of hydrocarbons produces a complex mixture of alkyl radicals. The same large group of alkyl radicals is formed by the reactions of the hydrocarbons with the hydrogen atoms and hydroxyl radicals formed through the radiolysis of water.

**4.3.3.2. Propagation Reactions.** Alkyl radicals decompose by beta scission (Leffler 1993) to form an alkene and a hydrogen atom as illustrated for the 2-dodecanyl radical,



or to form an alkyl free radical and an alkene as illustrated for the reactions of the 2- and 3-dodecanyl radicals.

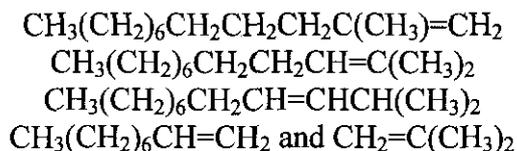




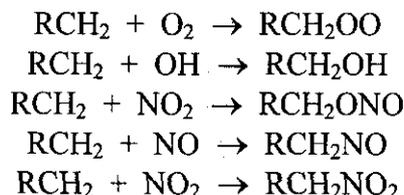
The products obtained from dodecane through  $\beta$ -scission reactions provide the same family of radicals as are obtained in the high-energy fragmentation reactions that were described in the previous section. The entire homologous series of linear radicals beginning with methyl radical and extending to 1-undecanyl radical and the entire family of alkenes beginning with ethene and extending to 1-dodecene are accounted for by these processes.

The alkyl radicals also abstract hydrogen atoms from other alkanes. The reactions of the alkyl radicals obtained in the reactions noted in the previous paragraph, i.e., methyl, ethyl, propyl, butyl, pentyl, hexyl, and so forth produce the corresponding alkanes: methane, ethane, propane, butane, pentane, hexane, and so forth to give a homologous series of alkanes.

Radical reactions generally occur without structural rearrangement, and the original normal and branched hydrocarbons in the hydrocarbon diluents yield homologous series of unrearranged radicals, alkanes, and alkenes. The  $\beta$ -scission of the radical formed at the 2-position of 2-methyltridecane gives 2-methyl-1-dodecene and 2-methyl-2-dodecene, and the  $\beta$ -scission products of the radical formed at the 3-position of 2-methyltridecane include E- and Z-2-methyl-3-dodecene and 2-methyl-1-propene and 1-nonene.

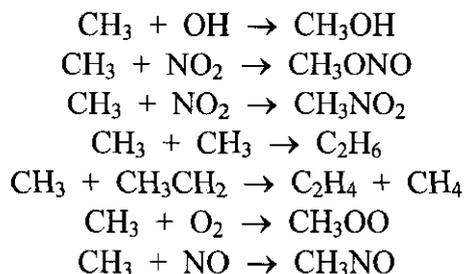


This analysis accounts for the diversity of the hydrocarbons in the wastes and implies that many other compounds such as the undetected E- and Z-2-methyl-3-dodecene are present. The homologous series of alkyl radicals, represented by  $\text{RCH}_2$ , produce homologous series of peroxy radicals, alcohols, and nitrogen derivatives in their recombination reactions with oxygen, nitric oxide, and nitrogen dioxide as discussed in Section 4.3.2.3.

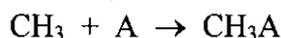


The reactions with nitric oxide and nitrogen dioxide may predominate because the concentration of hydroxyl radical is very low (Camaioni et al. 1998; Meisel et al. 2000). The same families of compounds are produced by the other alkyl radicals in the reaction mixtures leading to an array of diverse products.

The products of the reaction of methyl radical are especially interesting because of their rather high volatility. The reactions leading to ethane and ethene are added to this list for completeness.



The first five reactions lead to relatively stable products that have been analytically detected in the wastes. The hydroperoxyl radical shown in the sixth equation is reduced to form methyl hydroperoxide, which has not been analytically detected but presumably exists in the waste. The nitroso compounds shown in the seventh equation is converted into the oxime. The nitroso compound has been detected as noted in Table 3-14, but the oxime is not volatile and has not been detected in the headspaces of the waste tanks. Lastly, it is prudent to acknowledge that the understanding of waste chemistry is not so advanced as to preclude the formation of other substances derived from other recombination reactions of the methyl radical.



Reactions between the ethyl radical and the other alkyl radicals with more than one carbon and the reactive intermediates can also lead to alkenes.

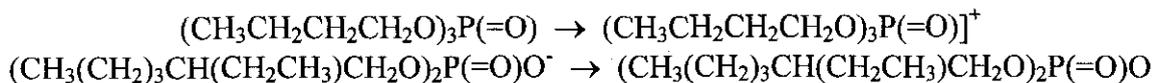


The large family of reactions converts alkyl radicals into alkenes. A reactive intermediate such as hydroxyl radical (or its anion) yields the alkene and water (or hydroxide ion), and a reactive intermediate such as methyl radical leads to the alkene and methane.

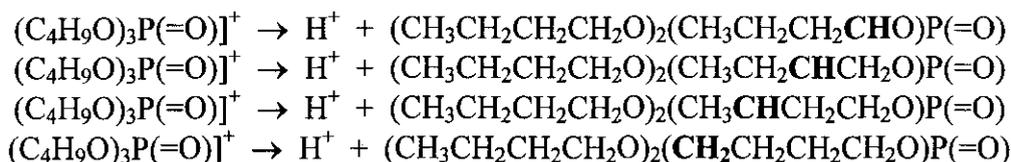
In summary, the families of alkyl radicals form families of alkenes, alcohols, hydroperoxides, nitrite esters, and nitro compounds, many of which occur in homologous series. The net result is that the original hydrocarbons are fragmented into lower molecular weight alkanes and oxidized. As these reactions proceed, the molecular dimensions are reduced and the reaction products are more water soluble and more volatile than the original hydrocarbons. The subsequent ionic reactions of the oxygenated compounds will be examined in the ensuing discussions.

#### 4.3.4 Radical Reactions of the Phosphate Esters

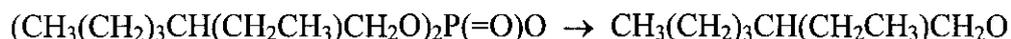
**4.3.4.1. Initiation Reactions.** The radiolytic reactions of the phosphate esters that lead to oxidized intermediate phosphate esters and fragmented molecules can be formulated in exactly the same way as the reactions of the complexants and hydrocarbons (Davis 1984). The direct radiolytic reactions proceed through excited molecules and ions. In addition, other radical reactions are initiated by electron transfer and by hydrogen atom abstraction reactions. The electronically excited cation radical formed from tributyl phosphate and the related neutral radical formed from bis(2-ethylhexyl)phosphate anion provide direct pathways to products that have been detected in the wastes.



These substances have as diverse a chemistry as the hydrocarbons, and only two reaction channels will be outlined here. Proton loss from the cation radical of tributyl phosphate provides four radicals.

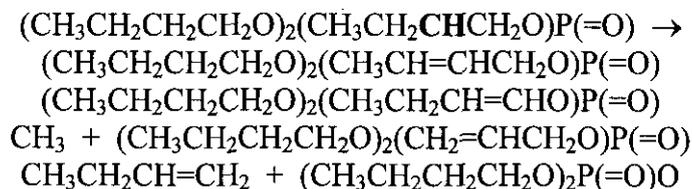


Proton loss does not occur with the neutral radical obtained from bis(2-ethylhexyl)phosphate anion. The nature of the compounds that emerged from tank 241-C-106 during sluicing implies the principal reaction of the initial radical is  $\beta$ -scission to form the alkoxy radical.

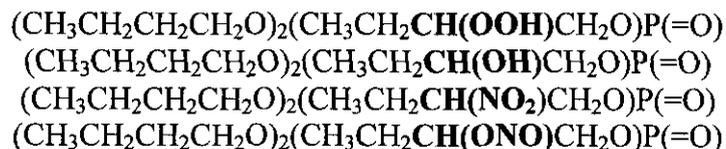


This radical decomposes to provide 3-heptyl radical and formaldehyde. The reactions of the radicals from the phosphate esters are examined in the next section.

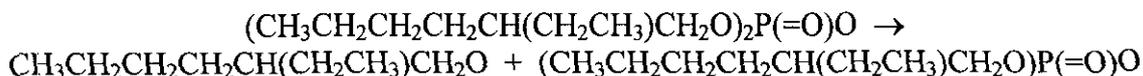
**4.3.4.2. Propagation Reactions.** The chemistry of the radicals produced by the radiolysis of the phosphate esters follows the same pathways outlined for the complexants and hydrocarbons. The  $\beta$ -scission reactions of the radicals derived from tributyl phosphate lead to simple alkenes and alkyl radicals and new phosphate esters. Many different compounds can form as illustrated in the following equations which show the formation of four new phosphate esters, methyl radical, and butene from one of the four possible initial radicals.



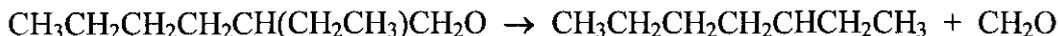
The related hydroperoxides, alcohols, nitro compounds, and nitrite esters are formed in other reactions of the radical to give the same kinds of products that are obtained from the hydrocarbons.



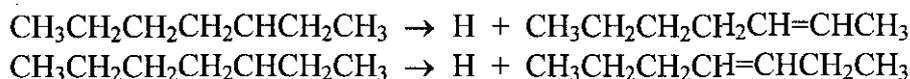
The radical derived from the bis(2-ethylhexyl)phosphate anion decomposes through  $\beta$ -scission to yield an alkoxy radical.



The alkoxy radical can decompose to 3-heptynyl radical and formaldehyde (Leffler 1993).



The energy requirements for  $\beta$ -scission are not large (Leffler 1993), and hydrogen atom loss from 3-heptynyl radical would give 2- and 3-heptenes.



Intramolecular 1,4-hydrogen atom transfer leads to the 2-heptynyl radical (Leffler 1993),



and then to the 1-, 2-, and 3-heptenes. Reactions of these intermediate radicals with the inorganic radicals give the same set of oxidized products that have already been presented.

Significant quantities of 1-butanol are formed during the hydrolysis of tributyl phosphate. Camaioni et al. (1996a) have also investigated the radiolysis of this compound. Their work and other work in the literature (Spinks and Woods 1990) imply that the same kinds of intermediates, i.e., hydroperoxides, alcohols, nitroso, and nitro compounds, are produced from this compound.

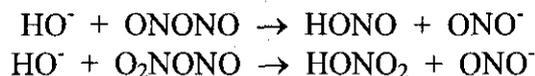
In summary, radiolysis of the butyl- and 2-ethylhexylphosphates produces many oxidized phosphate esters together with 1-butene, the 1-, 2-, and 3-heptenes.

#### 4.3.5 Reaction Pathways of Organic Intermediates

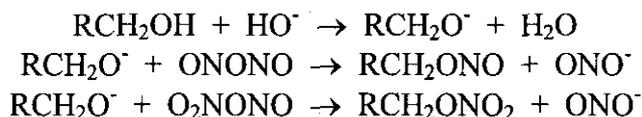
Other reaction pathways contribute to the formation of volatile and semivolatile compounds. The original complexants undergo certain base-catalyzed reactions, and many of the intermediate organic reaction products produced in the radical reactions react with water and are transformed into other more stable compounds. The intermediates with two electronegative substituents bonded to one tetrahedral carbon atom are converted by water into new substances in which the hydroxyl, nitro and nitroso groups are converted carbonyl or carboxyl groups (Jencks 1969; Lowry and Richardson 1987; Carey and Sundberg 1990; March 1992; Smith and March 2001). These reaction sequences and other ionic conversion reactions are outlined here because they account for many of the other observed products that were listed in Section 3.0.

**4.3.5.1. Reactions of Nitrate and Nitrite Esters and 1,2-Diols.** The reactions responsible for the formation of the nitrate esters that are found in many wastes have not been uniquely established by laboratory work. However, pathways for their formation, which are compatible with conventional chemical reactions, can be readily formulated. Nitrate esters could be produced in reactions between nitrogen trioxide and the organic radicals, through reactions between alkoxy radicals and nitrogen dioxide, or through reactions between the alcohols and

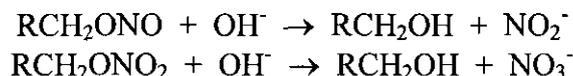
dinitrogen trioxide and dinitrogen tetroxide. The latter reaction is discussed here. The reaction model that was presented in Section 4.3.1.1 includes reactions in which hydroxide ion reacts with dinitrogen trioxide and dinitrogen tetroxide to form nitrous and nitric acid.



Similar reactions with the alkoxide ions,  $\text{RO}^-$ , which are in equilibrium with the alcohols,  $\text{ROH}$ , are, therefore, plausible pathways for the formation of nitrite and nitrate esters. The concept that these substances are formed by the reactions of the alcohols is compatible with the fact that butyl nitrate and butyl nitrite are especially prevalent in a virtually complete homologous series as shown in Table 3-14. The predominant substances would result from the reactions of 1-butanol, the abundant product of hydrolysis of the butylphosphates.

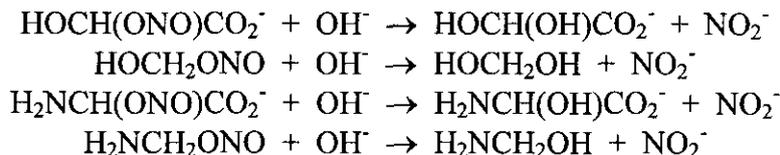


The rate constants for the hydrolysis of primary alkyl nitrates and nitrites are approximately  $5 \times 10^{-4} \text{ L mole}^{-1} \text{ s}^{-1}$  (Boschan et al. 1955; Oae et al. 1978; Challis and Shuker 1979; Camaioni and Autry 2000).

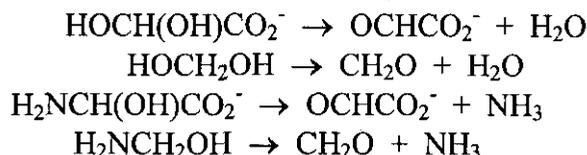


This formulation suggests the nitrite and nitrate esters, like many other compounds, are formed and hydrolyzed in a dynamic reaction system under the conditions of interim storage.

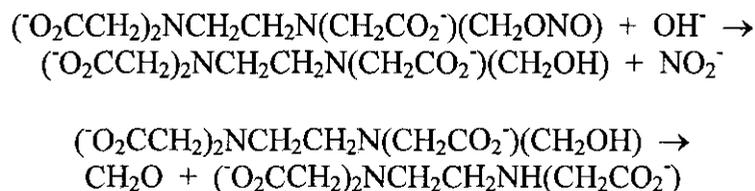
Many of the nitrite esters formed in the recombination reactions of the complexants and phosphates esters have an additional hydroxyl group bonded to the same carbon atom. The hydrolytic reactions of these compounds, for example, the derivatives of glycolate and glycinate ions, produce other unstable intermediates.



The two nitrite esters provided by glycolate ion are hydrolyzed to diols with both hydroxyl groups on the same carbon atom. The two nitrite esters formed from glycinate ion yield compounds with an amino group and a hydroxyl group bonded to the same carbon atom as illustrated by the reactions of the two glycinate ions. These compounds undergo hydrolysis to liberate the amine and formaldehyde (Lowry and Richardson 1987; Carey and Sundberg 1990; March 1992; Smith and March 2001). Formaldehyde and glyoxalate ion are obtained from the compounds under discussion.

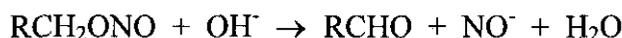


The recombination reactions of the primary radicals from HEDTA and EDTA introduce hydroxyl groups directly or indirectly through the nitrite esters. These substances exhibit the same chemistry.

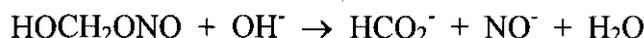


The illustration shows the conversion of EDTA into ED3A and formaldehyde. Clearly, formaldehyde, a compound of interest in industrial hygiene, can be formed from many different complexants and remnants.

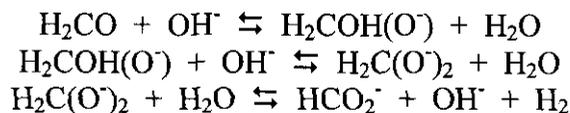
Another well known reaction occurs in competition with the simple hydrolysis reaction. At high pH, hydroxide ion abstracts a proton from the primary carbon to provide an aldehyde directly from the nitrite and nitrate esters (Boschan et al. 1955; Lowry and Richardson 1987; Carey and Sundberg 1990; March 1992; Smith and March 2001). The homologous series of esters produce a homologous series of aldehydes.



When there is a second electronegative group on the reactive carbon atom, the reaction of the nitrite ester provides formate ion.

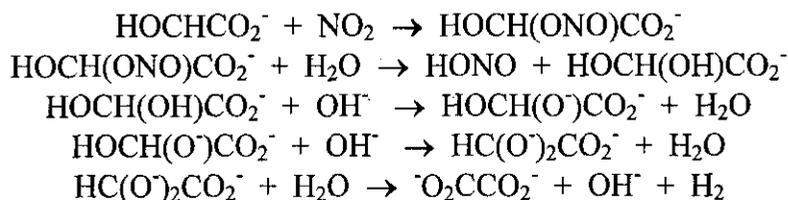


**4.3.5.2. Ionic Base-Catalyzed Oxidation Reactions.** Hydroxide-ion catalyzed transformations of aldehydes are an important source of hydrogen and carboxylate anions in Hanford Site wastes. Ashby and Barefield (Ashby et al. 1993, 1994; Barefield et al. 1995, 1996) described the importance of this variant of the Cannizzaro reaction (Lowry and Richardson 1987; Carey and Sundberg 1990; March 1992; Smith and March 2001) for the production of hydrogen and sodium formate from formaldehyde.

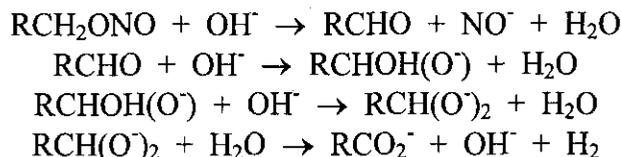


Formaldehyde, as discussed in the prior section, is an important product of the fragmentation reactions of the complexants. This substance is readily hydrated in aqueous solution and the protons of the hydrate are sufficiently acidic to be removed by hydroxide ion to form a dianion.

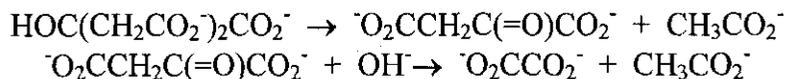
The reaction between this anion and water to form hydrogen and formate ion is the dominant decomposition pathway for formaldehyde in strongly alkaline solution (Ashby et al. 1993). The hydrate from glyoxalate ion undergoes the same reactions as formaldehyde.



Similarly, the aldehydes derived from the oxidation of the paraffinic hydrocarbons also participate in reactions that lead to sodium carboxylates.

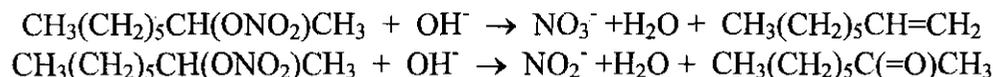


Citrate ion and certain intermediate compounds undergo another type of base-catalyzed fragmentation. Study of the decomposition of citrate ion in alkaline simulants in the absence of radiation has shown that it slowly undergoes fragmentation to acetate and oxalate ion (Ashby et al. 1994; Barefield et al. 1995, 1996). This reaction is not catalyzed by sodium aluminate. These observations are accommodated by the formulation of the base-catalyzed thermal process as a reverse Claisen reaction (Lowry and Richardson 1987; Carey and Sundberg 1990; March 1992; Smith and March 2001). The thermal relative rate data imply this reaction proceeds much more slowly than the decomposition of glycolate ion in simulated waste.



The reaction sequence accounts for the formation of acetate ion in the wastes.

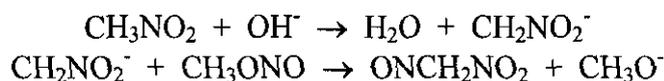
The nitrate and nitrite esters produced at the 2-, 3-, 4-, 5-, and 6-positions of the many different hydrocarbons react with hydroxide ion by  $\alpha$ -elimination to give ketones and by  $\beta$ -elimination to give alkenes. The reactions that lead to alkenes usually are more rapid than the reactions that lead to ketones. The reactions of the nitrate ester produced during the recombination reaction of 2-octanyl radical are displayed to illustrate this chemistry.



Such reactions may be responsible for the formation of some ketones. The diversity of the chemistry implies that there are more ketones present in the wastes than are presented in Table 3-9.

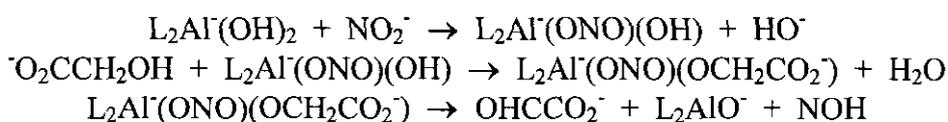
**4.3.5.3. Ionic Oxidation Reactions Catalyzed by Aluminate Ion.** Delegard pointed out the decomposition reactions of the organic complexants were promoted by aluminate, hydroxide, and nitrite ion (Delegard 1980, 1987). Ashby and Barefield also observed the thermal reactions of glycolate ion were catalyzed by nitrite, aluminate, and hydroxide ions (Ashby et al. 1994; Barefield et al. 1995, 1996).

The nature of the catalysis has not been established, and several interpretations have been advanced for it. It has been suggested that nitrite esters nitrosate the complexants to provide nitroso compounds through ionic reaction pathways (Barefield et al. 1995, 1996). These reactions are usually formulated as NO transfer reactions between an inorganic ester and a carbanion to produce a C-nitroso compound and liberate an alkoxide ion as outlined for the reaction of the anion of nitromethane with methyl nitrite.



Touser (1953) discussed the structural requirements for the reaction and pointed out electron-withdrawing groups were required for nitrosation by nitrite esters. This structural requirement implies that carbanions need to be formed. However, the negatively charged complexants are very weak carbon acids and the concentrations of the required carbanions are very low. Also, the nitrite esters are hydrolyzed in alkaline solution maintaining their concentrations at low levels. It seems doubtful that C-nitrosation reaction of a complexant, phosphate ester or hydrocarbon diluent could be accomplished under these circumstances with such low concentrations of the carbanions and the nitrite esters.

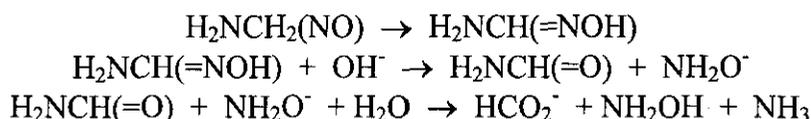
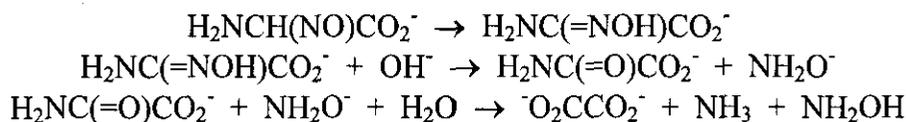
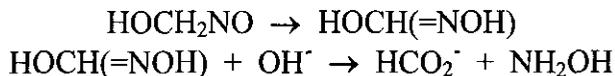
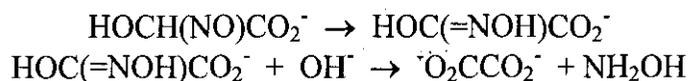
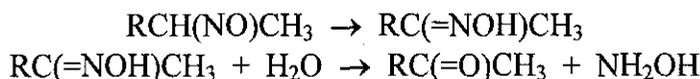
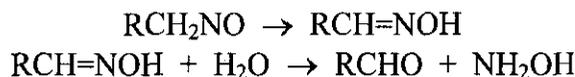
Other difficulties associated with the formulation of the reaction as a bimolecular nitrosation process have been discussed by Camaioni and Autrey (2000). Their work favors an alternative formulation that could account for the oxidation of glycolate ion. The chemistry is reminiscent of the Tischenko reaction (Jencks 1968; March 1992; Smith and March 2001) and the Oppenauer oxidation (Hudlicky' 1990; March 1992; Smith and March 2001) in which the oxidation reduction reaction is accomplished by hydrogen transfer. The simultaneous bonding of a hydroxyl group of the organic complexant and nitrite ion to an aluminate ion provides a reasonable pathway for the assembly of the required reagents. The transfer of hydrogen from the organic molecule to the nitrite ion in a conventional six-membered transition state accomplishes the oxidation-reduction reaction (Stock 1992). The reaction of glycolate ion is formulated to illustrate the process in the following equations, where L is used to represent the other ligands on the aluminum atom.



This reaction sequence provides another pathway for the transformation of a hydroxyl group in a complexant or an intermediate produced from one of the phosphate esters or diluent hydrocarbon into a carbonyl group. The occurrence of this reaction may contribute to the relatively rapid disappearance of glycolate ion from the waste (Barefield et al. 1995, 1996). More important, the

reaction provides another pathway for the formation of the broad variety of aldehydes that analytical work implies are present in the wastes.

**4.3.5.4. Reactions of C-Nitroso Compounds.** Inasmuch as nitric oxide is ubiquitous in the wastes, the reaction pathway leading to C-nitroso compounds has been postulated as an important reaction pathway (Meisel et al. 1991a, 1991b, 1992, 1993, 2000; Camaioni et al. 1997, 1998). The products of these reactions rearrange to oximes which hydrolyze providing a carbonyl compound and hydroxylamine (Jencks 1969; Lowry and Richardson 1987; Carey and Sundberg 1990; March 1992; Smith and March 2001). The conversions of the nitroso compounds obtained from a paraffinic hydrocarbon and glycolate and glycinate ions illustrate the chemistry.

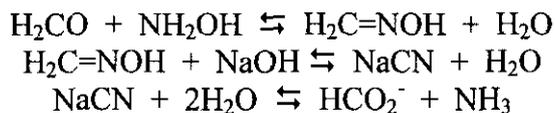


Isomerization to the more thermodynamically stable oxime occurs in the first step. Hydrolysis is shown in the next one or two reactions. The substances derived from the hydrocarbons provide aldehydes or ketones. But some complexants yield amides, hydroxamate ions or their analogues. Barefield et al. (1995) note that benzylhydroxamate hydrolyzes slowly (Brendt and Fuller 1966), whereas the simplest hydroxamate, the hydroxamate of formate ion, hydrolyzes in minutes in 2.0 M sodium hydroxide at 60 °C.



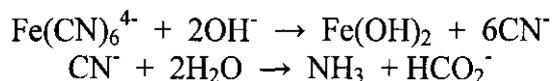
The simplest amide, formamide, is also rapidly decomposed in alkaline solution.

In a targeted investigation, Ashby et al. (1994) showed that formaldehyde reacted rapidly with hydroxylamine to form the expected oxime and that this compound then reacted to form sodium cyanide which subsequently gave formate ion and ammonia.

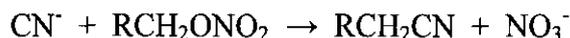


Whether the reaction occurs by dehydration or by hydrolysis, the main carbon containing products of the complexants are oxalate or formate ion. The main products of the hydrocarbons are the homologous series of nitriles that are found in the wastes. This reaction like other reactions in the oxidation reduction cascade yield hydroxylamine. It is interesting to note that the nitrogen atom from the complexant evolves as ammonia, and the nitrogen atom from nitrous oxide, i.e. nitrite ion, becomes the nitrogen atom in hydroxylamine.

These reactions are not the only source of cyanide ion. As noted in Section 2.0, large quantities of sodium ferrocyanide were used in cesium removal operations, and the wastes from these processes were discarded in the waste tanks. The complex ion is hydrolyzed to cyanide ion, and the cyanide ion is then hydrolyzed to formate ion (Robuck and Luthy 1989; Meeussen et al. 1992; Lilga et al. 1996).



Large quantities of the ferrocyanide ion were destroyed by hydrolysis to formate ion during the passage of the materials through the evaporator and during the storage of the warm wastes. Nevertheless, cyanide ion was available for reaction with activated organic compounds such as the nitrate esters. Characterization work shows that there is a homologous series of alkyl nitrates, their reactions with cyanide ion provide a path for the formation of the homologous series of organic nitriles.



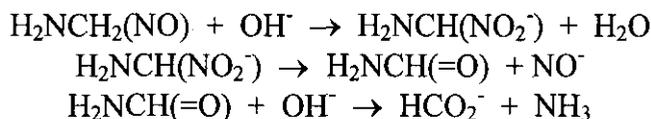
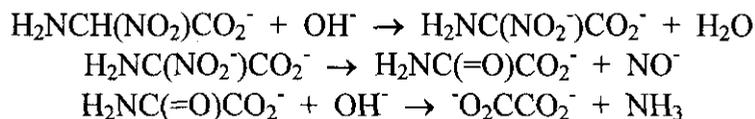
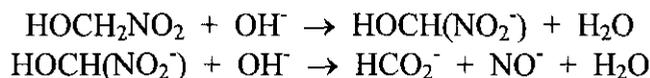
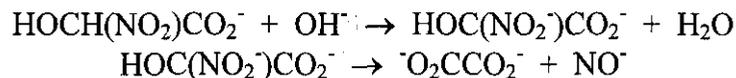
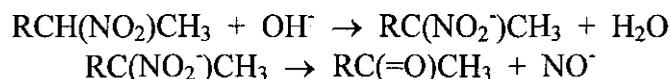
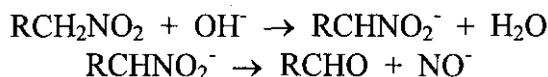
Although the wastes are alkaline and cyanide ion would be retained as the ion, the concept that weak acids are in equilibrium with their conjugate bases implies that volatile hydrogen cyanide could be released from the waste tanks.



**4.3.5.5. Reactions of C-Nitro Compounds.** The C-nitro compounds formed during the radical reactions of the complexants and phosphate esters can have two electronegative atoms bonded to a tetrahedral carbon atom and are, therefore, susceptible to the decomposition reactions discussed for other substances with two electronegative groups. However, the nitro compounds also contain acidic hydrogen atoms which can be abstracted by the hydroxide ions in the alkaline waste (Lowry and Richardson 1987; Carey and Sundberg 1990; March 1992; Smith and

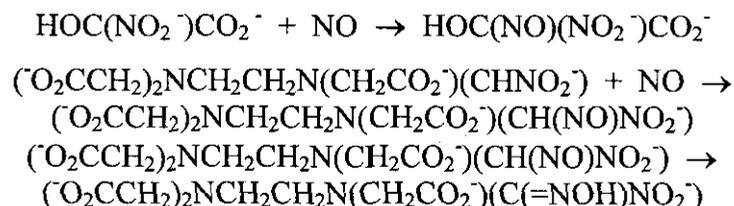
March 2001). The anionic substances are quite reactive and readily undergo several different reactions.

The decomposition of the nitro compound in aqueous media provides an oxidized organic product with a carbonyl group and the reduced nitrosyl anion, which spontaneously produces nitrous oxide (Noland 1955; Hawthorne 1957; Pinnick 1990; March 1992; Smith and March 2001). This reaction usually is carried out in acidic solution, but there are many examples of the reaction in alkaline media (Pinnick 1990). The reaction is usually formulated as shown in the equations illustrating the chemistry of the paraffinic hydrocarbons and the complexants.



These reactions are of interest not only because they provide oxidized organic compounds including aldehydes and ketones, but also because they ultimately provide nitrous oxide.

An early review of the chemistry of aliphatic nitro compounds indicates the anions readily undergo nitrosation (Touser 1953). Secondary nitro compounds yield C-nitroso compounds. The primary nitro compounds also yield C-nitroso compounds, but these substances convert to oxime derivatives. The products of the complexants have several electronegative groups bonded to a single carbon and are unstable in alkaline solution as illustrated for the secondary C-nitro derivative of glycolate ion and the primary C-nitro derivative of EDTA.

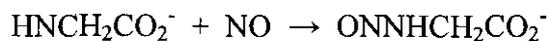


These substances are hydrolyzed to form oxidized molecules containing carbonyl groups and reduced inorganic nitrogen derivatives. The C-nitration of glycolate ion followed by C-nitrosation and electron transfer would convert glycolate ion into oxalate ion and hydroxylamine. The same sequence of reactions would convert the EDTA derivative into ED3A, carbonate ion, and hydroxylamine.

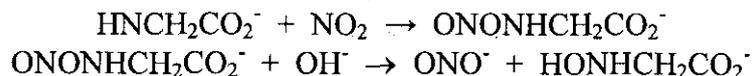
Investigations of the chemistry of nitrogen dioxide and nitric oxide have demonstrated that the salt of nitromethane reacts with both substances in alkaline solution to form even more oxidized products with two nitro groups or one nitro and one nitroso group bonded to the same carbon atom (Gilbert and Norman 1972; Gilbert et al. 1972; Madden 1988; Reszka et al. 1996). This work suggests that the nitro compounds formed in the Hanford Site waste may react similarly because of the high concentrations of nitrous oxide and nitric oxide and nitrogen dioxide. At this time, no compounds with two nitro groups or two nitroso groups or one nitroso group and one nitro group have been detected in the dome spaces of the 110 waste tanks that have been investigated; however, their volatility is limited because of their acidity and the GC/MS analysis of these compounds would be difficult to accomplish because of their high polarity.

The chemistry of these complex molecules has not specifically been investigated. But, it is evident that the initial products, which are anion radicals, would have a rich chemistry in the aqueous alkaline waste solutions. For example, the decomposition of the anion radical formed by the loss of nitrite ion would provide a nitroso derivative related to the oxime discussed in the previous section. Simple electron transfer converts the products into molecules with three electronegative atoms bonded to the same reactive carbon atom. Such compounds should have relatively short lifetimes in the waste and since the reactive carbon atom in these substances is in the oxidation state of the carbon atom in a carboxyl group, hydrolysis would produce a carboxylate anion.

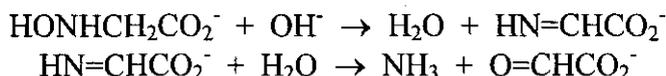
**4.3.5.6. Reactions of Compounds with Oxidized Amino Groups.** Although nitrogen centered radicals do not form from the original complexants, they can be obtained from remnants such as IDA and glycinate ion, which have primary and secondary amino groups. Recombination reactions of the nitrogen-centered radicals react with nitrite ion, nitric oxide, nitrogen dioxide, and hydroxyl radical provide the oxidized intermediate organic compounds with N-oxygen and N-nitrogen bonds. The reaction between the N-centered radical of glycinate ion and nitric oxide yields the corresponding N-nitroso compound.



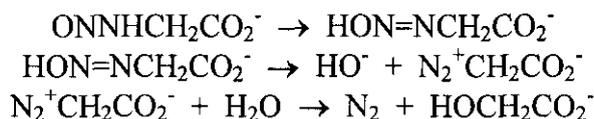
The nitrite ester obtained in the reaction with nitrogen dioxide is hydrolyzed to the hydroxyl amine. This behavior is illustrated by the reactions of the glycinate derivatives in the following equations.



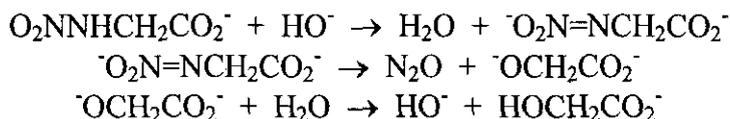
The N-hydroxyl compound obtained in this reaction is also produced in the recombination reaction with hydroxyl radical. These hydroxylamines are converted in alkaline solution into imines that hydrolyze to form ammonia and aldehydes.



The N-nitroso compound is converted into glycolate ion and nitrogen through several reactions that involve the diazohydroxide and diazonium hydroxide.

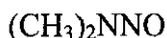


The related decomposition of the N-nitro compound, which begins with the removal of the acidic proton from nitrogen, provides glycolate ion and nitrous oxide.

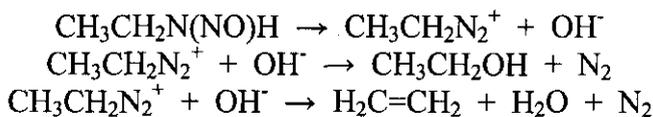


The highly unsaturated intermediates would react very rapidly with nitric oxide and nitrogen dioxide. These reaction pathways eventually lead to the same more highly oxidized substances such as glyoxalate and oxalate ion.

**4.3.5.7. Reactions of Compounds with N-Nitroso Groups.** The nitrosation of secondary amines provides stable N-nitroso compounds.



Several N-nitroso compounds of this kind were observed in liquid and solid samples as shown in Table 3-9, and N-nitrosomorpholine and N-nitrosodimethylamine were observed in headspaces as shown in Table 3-14. It is notable that N-nitrosodimethylamine has been detected in the headspaces of more than 25 tanks, while dimethylamine has been rarely detected. Apparently, N-nitrosation occurs in the alkaline liquid waste. The products of N-nitrosation of the primary and secondary amines are unstable and are converted into alcohols and alkenes. Methylamine yields methanol and ethylamine provides ethanol and ethene.



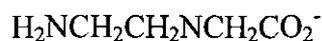
**4.3.5.8. The Formation of Nitrogen Heterocycles.** The complexants are responsible for the formation of many of the amines in the wastes. They are also responsible for the formation of some of the more prominent nitrogen heterocycles. Campbell et al. (1995b) showed that the

complexants could undergo cyclization reactions and the formation of several nitrogen-containing heterocycles can be formulated in this way. The cyclization reactions of the family of degraded complexants with amino and hydroxyl groups noted in Section 4.2.1.1 provide immediate pathways for the formation of nitrogen and oxygen heterocycles with five- and six-membered rings.

The cyclization of compound C with the elimination of water gives piperazine, and the elimination of ammonia gives morpholine. The cyclization of ED1A gives the related oxidized molecules.



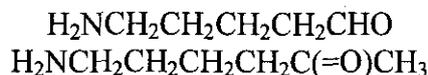
Compound C



ED1A

The elimination of water leads to dihydropyrazine, and oxidation yields pyrazine. The same compounds could in principle be formed from the hydrocarbon diluents through much longer reaction pathways.

Pyridine is another prominent heterocycle. This compound can not be produced in any reasonably direct way from the complexants because these molecules do not have five contiguous carbon atoms. There are at least two alternate modes for its formation. Pyridine is present in a polyvinylpyridine resin that was discarded into the waste tanks as noted in Table 2-4. The alternatives for the formation of pyridine and its alkylated derivatives involve rather long reaction sequences. A plausible pathway that accounts for these compounds envisions the formation of amino aldehydes and ketones. For example, a tetrahydropyridine would be produced from 5-amino-1-pentanal, and a methyltetrahydropyridine would be produced from 6-amino-2-hexanone. Hydrogen removal from these intermediates leads to the corresponding dihydropyridines and eventually to pyridine and 2-methylpyridine,



These interpretations are quite speculative, but they are not unreasonable.

**4.3.5.9. The Formation of Oxygen Heterocycles.** Several cyclic ethers including ethylene oxide and tetrahydrofuran are detected among the organic compounds in the wastes. These ethers are apparently obtained by the cyclization of the corresponding diols, ethane-1,2-diol and butane-1,4-diol. Ethane-1,2-diol is present in the wastes and the base-catalyzed cyclization reaction, although slow, is plausible. Tetrahydrofuran is readily accounted by the cyclization of 1,4-butandiol which is derived from the oxidation of TBP. The radiolytic oxidation of TBP provides Compound A as discussed previously.

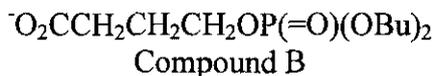
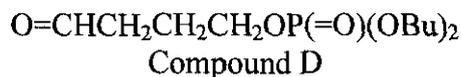


Compound A

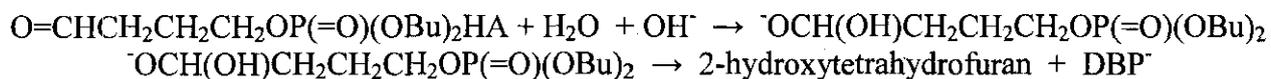
The reaction of this substance with hydroxide ion forms DBP and tetrahydrofuran.



The thermal and radiolytic oxidation of the 4-hydroxybutyldibutylphosphate lead to the corresponding aldehyde, Compound D, and thence to the carboxylate derivatives, Compound B.



Compound D can be converted in alkaline solution into 2-hydroxytetrahydrofuran. The loss of water from this substance yields 2,3-dihydro-2H-tetrahydrofuran.

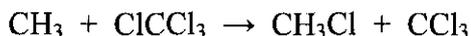


The closure of the ring in Compound B in alkaline solution leads directly to DPB and butyrolactone (dihydro-2(3H)-furanone).

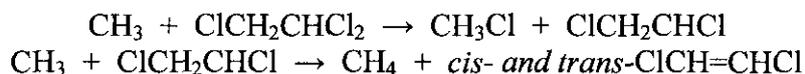


In principle, the same compounds can be derived by sequential oxidation reactions of fragments of the hydrocarbons; that formulation of the chemistry would more readily account for the formation of alkylated derivatives. However, the route to the furan family from TBP and its derivatives is much more direct.

**4.3.5.10. Halogen Compounds.** Numerous halogen compounds have been found in the headspaces of the wastes. Many of the chlorine compounds are directly related to the solvents that were employed in supporting operations. The list of compounds shown in Tables 2-3 and 2-4 includes methylene chloride, chloroform, carbon tetrachloride, tri- and tetrachloroethane, and trichloroethylene. Inasmuch as alkyl radicals readily abstract halogen atoms from compounds of this kind as illustrated by the formation of methyl chloride from carbon tetrachloride, it is surprising that more chlorine-containing compounds have not been formed.



Other unsaturated chlorocarbons have also been detected. The reactions for the formation of *cis*- and *trans*-1,2-dichloroethylene from 1,1,2-trichloroethane are readily formulated. Related processes provide the other observed compounds of this type.

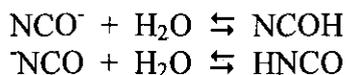


The simple alkyl chlorides are not stable in alkaline solution and would slowly be converted into the corresponding alcohols with the formation of chloride ion. Therefore, the chlorocarbons that

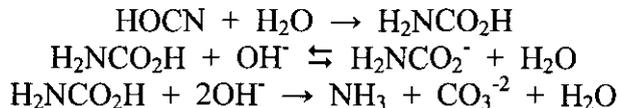
were originally present in the wastes have been substantially depleted by evaporation and by these chlorine transfer reactions.

Freons are also frequently detected in the waste tanks. No reasonable chemical model is available for their formation in the waste. Rather, these substances are most reasonably accounted for by other explanation centered, for example, on the idea that they were used in unidentified supporting operations, or as refrigerants in the vicinity of the waste tanks or sample collection equipment.

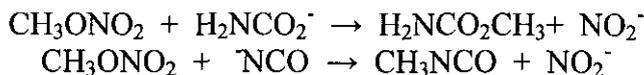
**4.3.5.11. Carbamates, Cyanates, and Isocyanates.** Ashby et al. (1993, 1994) and Stock and Pederson (1997) have suggested that cyanate ion may be an intermediate in the chemistry. If this ion is present, the conjugate acids, cyanic acid (HOCN) and isocyanic acid (HNCO), would be formed in solution. Isocyanic acid is more volatile than cyanic acid and would preferentially evolve from the waste tanks.



These cyanates and isocyanates can lead to other compounds of interest. Isocyanic acid forms a cyclic trimer, cyanuric acid ( $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$ ). The hydration of cyanate ion produces carbamic acid, and the acid reacts with hydroxide ion to give carbamate ion. These two substances react in alkaline solution to give ammonia and carbonate ion.



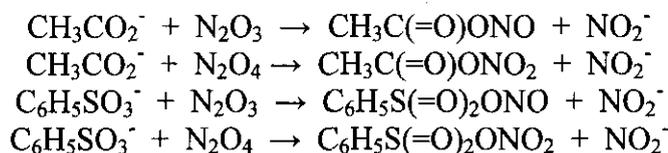
The reaction of cyanate ion or carbamate ion with one of the reactive inorganic esters such as methyl nitrate would yield methyl cyanate and methyl isocyanate.



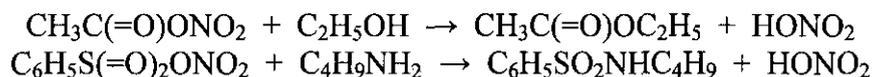
As many other compounds in the wastes, these quite reactive substances are formed and destroyed in dynamic processes, but experience shows that volatile intermediates can evolve from the waste.

**4.3.5.12. Activation by Mixed Anhydride Formation.** The very alkaline conditions in most waste tanks are unfavorable for the formation or the accumulation of esters and amides. Nevertheless, many compounds of this kind have been detected in the wastes including alkyl alkanoates and alkyl nitrites and nitrates as well as compounds such as N-butylsulfonamide. The alkyl nitrites can be accounted for by recombination reactions between alkyl radicals and the relatively abundant nitrogen dioxide, but the formation of the alkyl nitrates requires a reaction between the alkyl radical and the much less abundant nitrogen trioxide. The pathways for the formation of these compounds can be formulated more generally though mixed anhydrides.

These compounds may be formed by the reactions of the carboxylate and sulfonated ions with the nitrogen oxides as illustrated by the reactions of acetate ion and benzenesulfonate ion.



The mixed anhydrides react with the available nucleophiles in the waste. The reactions with water and hydroxide ion regenerate the carboxylate ion, but the reactions with alcohols, ammonia and alkyl amines produce metastable esters and amides (Smith and March 2001).



This interpretation accounts for the release of esters such as benzenesulfonamide and ethyl acetate. The interpretation also predicts the formation of many other esters and amides that have not been detected. Volatility and the balance between the formation rate and the rate of hydrolysis determine whether the compound emerges from the waste.

#### 4.4 SUMMARY

The results of the fundamental and targeted investigations provide a framework for the definition of the reaction pathways by which the organic complexants, phosphate esters and diluent hydrocarbons are oxidized. Indeed, the work has resulted in the formulation of a chemical model with relatively long sequences of chemical reactions that eventually lead to carbonate ion as the final product of organic oxidation. Hydrogen and nitrogen oxides are byproducts of the chemistry that leads to alkanes, alkenes, alcohols, aldehydes, ketones, nitriles, acids and bases, and heterocycles.

The chemical model for the oxidation reactions of the organic molecules centers on three distinctly different initiation processes. Two initiation pathways involve radicals produced by the radiolysis of concentrated aqueous solutions of sodium nitrite and nitrate or by the thermal decomposition of chemical substances in the waste. The initial radiolytic processes have negligible activation energies, but the rates of the thermally initiated reactions have high activation energies. The reactive inorganic radicals either abstract a hydrogen atom or an electron from the organic constituents to produce free radicals. The organic radicals subsequently recombine with nitric oxide, nitrogen dioxide and other substances to form more oxidized organic intermediates. The third initiation pathway involves reactions between the ionic inorganic substances present in the waste and the organic molecules. These reactions, which are temperature dependent, also lead to oxidized organic intermediates.

Many of the intermediate organic compounds, particularly the nitrite and nitrate esters and the C-nitroso and C-nitro compounds, provided by three different initiation pathways are more reactive than the original solvents, phosphate esters or complexants. These reactive intermediates undergo additional reactions to give relatively stable remnant molecules including

NTA, IDA, and glycinate ion, formate, and oxalate ion in the case of the complexants and homologous families of alkanes, alkenes, alcohols, aldehydes, and ketones, and nitriles in the case of the phosphate esters and diluents. The entire family of organic intermediates and the metastable end products are susceptible to the same sets of initiation reactions as the original organic compounds.

The chemical model, some elements of which have been presented in a quantitative format, is fully consistent with the results of characterization work establishing the presence of remnant molecules and metastable end products of the oxidation reaction in tank waste, as well as with the fundamental and targeted investigations carried out in the laboratory. Moreover, the model has predictive capabilities in the sense that many compounds that are very difficult to detect by routine methods such as GC/MS can be anticipated.

## **5.0 STORAGE, OPERATIONS, AND COMPOUNDS OF INTEREST**

The consequences of the storage of the wastes for 25 additional years and intrusive waste operations will be examined in this section together with discussions of new compounds and compounds of special interest.

### **5.1 COMPOSITIONAL CHANGES DURING STORAGE**

#### **5.1.1 Removal of Organic Compounds by Evaporation**

The decomposition reactions of the complexants, phosphate esters, hydrocarbon diluents and the substances that are being formed from them during storage continuously produce many fragmented volatile organic compounds. When volatile water-insoluble compounds are formed in a convective layer, they evaporate from the waste in a short time. Methane, ethane, propane, butane, and the related unsaturated compounds with similar volatility are, therefore, continuously being evolved from the waste tanks together with insoluble inorganic gases including hydrogen and nitrogen. Even substances with low volatility evolve from the convective layers (Bartley 1999), and the concentrations of the hydrocarbon diluents have already been substantially depleted from the convective layers during quiescent storage. One of the original phosphate esters, TBP, and its principal impurity, DBBP, are sufficiently volatile to appear in the headspaces of the waste tanks. But, their rates of evaporation are much lower than the hydrocarbons. More important, TBP is slowly being hydrolyzed to form a non-volatile anion, DPB, and volatile butanol. When volatile water-soluble compounds such as butanol and the other alcohols, aldehydes, ketones, nitriles, etc. are formed in convective layers, they dissolve in the aqueous phase and then slowly evaporate from the waste in accord with Raoult's Law. The reaction products of the complexants include one insoluble compound, oxalate ion, and a variety of water-soluble compounds that are retained in the convective layers as salts. The chemistry that occurs during long-term storage has already depleted the concentrations of the original complexants, but they have been replaced by other non-volatile substances including NTA, IDA, acetate, and formate ion, which are retained in solution, and oxalate ion, which precipitates. Ammonia is very soluble in waste and accumulates until a steady state concentration, which is

dictated by its rate of formation and evaporation, is realized. Nitrous oxide which has a limited solubility in water behaves in a similar fashion.

The complexants, phosphate esters, and hydrocarbons that are retained in the non-convective solid layers experience the same radiolytic and chemical reactions as the compounds in the convective layer. For example, the hydrolytic and radiolytic reactions of TBP in the solid layer also lead to the formation and retention of DPB and butanol. But slow transport essentially anchors these substances in the solid layers. Indeed, the very slow transport rates in the non-convective layers have led to the accumulation of substantial quantities of gas. Clearly, if hydrogen can be retained, the soluble and insoluble, volatile and semivolatile organic reaction products will also be retained. This feature is illustrated by the analytical work on the wastes from tanks 241-C-104, 241-AN-107, and 241-AW-101 where the solid layers have much higher concentrations of organic material than the liquid layers. The fact that the organic compounds accumulate in the solids is also well illustrated by their rapid emergence during sluicing from the solid waste in tank 241-C-106.

In summary, the organic complexants and their principal carbon-containing end-products, oxalate ion and carbonate ion, are not volatile and are retained within the waste. The hydrocarbon diluents, which were present in the convective layers, have largely evaporated. The compounds that were deposited in the solid layers are much less mobile and are often retained within the wastes even though they may be quite volatile.

### 5.1.2 Slow Oxidation and Hydrolysis Reactions

The thermal and radiolytic rates of hydrogen formation depend directly on the TOC concentration (Hu 1997; Hu et al.1998; Hu 1999; Hu 2002; Hu and Barker 2003). Person (1996, 1998) and Camaioni and his associates (Camaioni et al.1998; Camaioni and Autrey 2000) have considered the relationship between the rates hydrogen formation and the rates of oxidation of organic compounds in the wastes. The application of these ideas to the waste in tank 241-SY-101 (Stock 2001) implied that the TOC content of the tank had changed only modestly because the reactive complexants were converted to unreactive acetate and oxalate ions without the loss of organic carbon. Person (1998) evaluated the half-life for the oxidation of the complexants in tank 241-AN-105 into oxalate ion. He estimated that the half-life for this conversion ranged between 21 and 51 years. The most rapid rate of consumption of organic carbon implies that the organic substances in a waste with 3% TOC would be converted into oxalate ion at the rate of about  $1 \times 10^{-4}$  moles of TOC/kg per day. Accordingly, the concentrations of the complexants within the tanks change quite slowly as the reactive molecules such as glycolate ion and HEDTA and their remnants such as NTA, IDA, and glycinate ion are converted into oxalate ion and carbonate ion.

The hydrolysis of TBP to DPB to butanol, which was discussed in Section 4.0, also occurs without a change in the TOC content. However, the process converts a partially water-soluble molecule into two soluble substances. The ionic DBP is not volatile and will be retained in the aqueous solution, but butanol will slowly evaporate from the waste surface with an eventual reduction in the TOC content. Additional butanol is produced by hydrolytic and radiolytic processes which convert DPB into MPB. Person did not consider these reactions or evaporative

processes in the estimation of the TOC half-life. However, the uncertainty is not large because the quantities of the non-volatile complexants are much greater than the hydrocarbons or the phosphate esters.

The rate of hydrolysis of TBP is much more rapid than the rate of hydrolysis of bis(2-ethylhexyl)phosphate as discussed in Section 4.0. Mixtures that originally contained comparable concentrations of hydrocarbon diluent, TBP and this dialkylphosphate ion now contain high relative concentrations of the water-insoluble bis(2-ethylhexyl)phosphate ion (Stauffer and Stock 1999; Stock 2001).

In summary, the oxidation reactions of the complexants in the aqueous phases of the liquid and solid layers occur slowly. No more than 50% of these materials will disappear from the wastes in the next 25 years. Hydrolysis has already depleted the concentration of TBP, the remainder will almost certainly be converted to DBP in the next 25 years. In general, water-insoluble compounds such as bis(2-ethylhexyl)phosphate ion and the long chain hydrocarbons are essentially inert toward ionic reagents such as hydroxide ion under the conditions of storage in the tank waste, and they are only slowly oxidized by direct or indirect radiolysis. Attempts to determine the relativities of paraffinic compounds under the heterogeneous conditions that prevail in the waste tanks have not been completely successful, but the available results imply that the insoluble hydrocarbons and esters retained within immobile solid layers decompose very slowly. Overall, the highly water-insoluble compounds accumulate in the solid wastes. When organic substances decompose in the supernatant layers, the volatile products emerge from the waste, when the organic substances decompose in the solid layers, the volatile products are retained.

## **5.2 OPERATIONS**

### **5.2.1 Evaporator Operations**

Evaporator 242-A will continue to be used to remove water from tank waste. The waste that is be evaporated is pumped into a recirculation loop and then passed through a heat exchanger where the waste is warmed before being passed into a vapor-liquid separator, which operates between 50 and 60 °C at approximately 60 torr. Heat is supplied by the continuous passage of a portion waste stream through the steam-heated recirculation loop. The average temperature of the waste in the recirculation loop is about 2 to 3 °C warmer than the waste in the vapor-liquid separator. The waste remains in the vapor-liquid separator for 12 to 24 hours. Between 0.15 and 2.2 g/L of Dow Corning 1520-US is added to the evaporator to prevent foaming. This substance contains 15 to 40% polydimethylsiloxane, 1 to 5% of a modified polyethyleneglycol, 1 to 5% glycerides, and 1 to 5% methylcellulose (Dow Corning 2002).

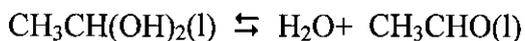
Evaporation has several effects. First, retained gases will be removed. Second, soluble and insoluble organic compounds that were present in the liquid waste will be redistributed between the vapor, the highly aqueous condensate and the salt rich residue. Third, the rates of decomposition of the residual complexants, phosphate esters and the hydrocarbon diluents and their remnants will increase because of the temperature change.

Heating the waste in a partial vacuum will release the gases including hydrogen, nitrogen, nitrous oxide, methane, ethane, and related low molecular weight compounds that were retained in waste in the feed tank. As discussed in Section 3.0, the RGS program found that the slurry from tank 241-SY-101 contained about 3% gas. However, the other liquid wastes usually retained less than 1% by volume of gas. In any event, the retained gas that will be promptly released in the evaporator will have the same composition as the gas in the feed.

If the waste had 1% retained gas, which contained 2% methane, then the passage of 100,000 liters per day through the tank would release about 20 liters (about 1 mole) of methane.

The distillation of water from the waste will simultaneously distill soluble organic compounds. Portions of these compounds will escape from the condensate and be released as gases, but most will dissolve in the condensed water that is eventually transferred to the process condensate holding tank. The concentrations of the compounds which are more volatile than water will increase in the condensate in accord with the concepts of fractional distillation. Conversely, the concentrations of the organic compounds which are less volatile than water will be depleted in the condensate. Compounds such as methanol, ethanol, propanol, butanol, acetaldehyde, propanal, butanal, acetone, butanone, 2-pentanone, methylamine, ethylamine, tetrahydrofuran, dimethylmercury, and other low molecular weight polar organic compounds will be enriched in the distillate. The volatility of these compounds is higher than in water because of the high salt content of the liquid wastes.

The relative amounts of the retained gases and volatile solutes that are released will be dictated largely by their concentrations in the liquid and their vapor pressures. However, when a volatile compound is in rapid equilibrium with another substance, additional amounts of the volatile compound will be formed and released. For example, acetaldehyde is present in liquid waste in the form of its hydrate. The evaporative removal of the volatile aldehyde will prompt the conversion of the hydrate into acetaldehyde.



If insoluble organic compounds such as hydrocarbons are present in an organic liquid phase, they will also be transferred to the condensate by steam distillation. Even substances with rather low vapor pressures will codistill with water.

The chemical reactions that fragment and oxidize organic constituents will accelerate in the evaporator in accord with the difference in concentration of the organic compounds because of the addition of the organic antifoam agent and the difference between the temperature in the feed tank and the evaporator (50 to 60 °C). The organic chemicals in the antifoam agent are neither appreciably more nor less reactive than the constituents in typical waste tanks and the difference in temperature is too small to cause the onset of unusual chemical reactions. These considerations imply the slow degradation reactions that occur in the waste tanks will simply increase in the evaporator.

Although the rates and activation energy for the decomposition of the organic compounds have not been measured directly, they can be estimated from the known rates and activation energies for the formation of hydrogen or the most abundant organic product: methane. The highest thermal rate of formation of hydrogen at 60 °C is about  $10^{-6}$  moles/kg/day, and the highest thermal rate of formation of methane at this temperature is about  $10^{-7}$  moles/kg/day (King and Bryan 1999).

The use of the highest observed rate constant for methane implies that the 100,000 L of waste in the evaporator with a density of 2.0 kg/L will produce 0.02 moles of methane each day. This is approximately 2% of the amount of methane that is stored in 100,000 L of waste.

The analysis illustrates the general observation that the amount of a chemical that is retained in a waste generally exceeds the amount that can be made during an operation that requires only a few days to complete.

### **5.2.2 Sluicing and Waste Transfer**

The extent to which gases and organic compounds are released from the wastes during transport operations obviously depends on the aggressiveness of the operation. Pumping operations disturb the wastes in the source tank and in the receiver tank, but sluicing operations are probably the most aggressive operation performed at the Hanford Site. Experience indicates that it causes the evolution of volatile gases and volatile and semivolatile organic compounds. These intrusive operations can release large amounts of undesirable materials. The outcome of such an operation is well illustrated by the sluicing operation in tank 241-C-106 (Stauffer and Stock 1999).

Previous characterization studies implied the organic material was located in the topmost sludge layer and consisted of about 318 kL (84 kgal) of a mixture of low-level waste from B Plant and washed Plutonium Uranium Extraction (PUREX) process sludge from the AR vault. The organic material originated from strontium removal operations in which glycolic and citric acid were used with bis(2-ethylhexyl)phosphoric acid and tributyl phosphate in a hydrocarbon diluent. An organic oil, which had separated from the sludge during analysis, contained sodium bis(2-ethylhexyl)phosphate with lesser quantities of butyl bis(2-ethylhexyl)phosphate and sodium butyl(2-ethylhexyl)phosphate, other phosphate esters, and residual hydrocarbons. The amounts of the oil in grab samples of sludge collected in 1996 ranged from 0.5 to 3.0 percent by volume.

Unexpectedly high concentrations of inorganic gases and volatile organic compounds were released from the ventilation stack of tank 241-C-106 during sluicing operations in November 1998. Workers experienced serious discomfort. They reported an obnoxious acrid odor and the 450 ppm of volatile organic compounds in ventilation stack 296-C-006 exceeded the level approved in the air discharge permit and the operation was terminated. Subsequent analyses of samples collected opportunistically from the stack indicated many organic compounds including heptenes, heptanones, and hydrocarbons were present. Subsequently, a process test, which avoided unnecessary worker exposure, was carried out, and analytical

samples were collected from the stack, the breathing area, and the receiver tank in December 1998.

Approximately 50 samples were collected before and during the test from the breathing areas near tank 241-C-106, the ventilation stack of this tank, and the headspace of tank 241-AY-102. Huckaby and Evans (1999) and Bonfoey et al. (1999) found about the same amounts of organic compounds were present in the absorbent traps and canisters that were collected at the same time at the same location in these tests.

The concentrations of the compounds in the breathing area before and during sluicing, although considerably attenuated by dilution in air, correlated with the observations for the substances in the ventilation stack of tank 241-C-106 (Bartley 1999). Similarly, the concentrations of the volatile organic compounds in the headspace of the receiver tank correlated with their concentrations in the stack.

**5.2.2.1. Before Sluicing.** Samples from the headspace of quiescent tank 241-C-106 had been analyzed in 1994 by Rasmussen (1994) and Jenkins and coworkers (Jenkins et al. 1995 and Ma et al. 1997). They found the organic content in the headspace was quite low, only a few parts per million. The samples that were obtained in 1998 before sluicing began provided the same results, about 45 compounds were present in the ventilation stack with concentrations greater than 5 ppb (Huckaby and Evans 1999; Bonfoey et al. 1999). This group includes 12 alkanes, two cycloalkanes, nine alkenes, ten alcohols and ethers, seven aldehydes and ketones, three nitriles, and two esters. More than 20 of the 45 compounds contain oxygen and are significantly soluble in water. Ten hydrocarbons have fewer than six carbon atoms and normal boiling points below 50 °C. The remaining compounds include four heptenes and nine paraffinic hydrocarbons. The water-soluble compounds are more efficiently transported from the sludge to the headspace than the water-insoluble hydrocarbons during quiescent intervals. Not surprisingly, only the more volatile or more abundant hydrocarbons among the many compounds now known to be present in the sludge were present at more than 5 ppb in the ventilation stack before sluicing began.

**5.2.2.2. During Sluicing.** The samples that were opportunistically collected from the ventilation stack in November 1998 during the aborted sluicing operation contained 450 ppm volatile organic compounds. The same substances evolved from the waste during operations in December and in subsequent operations and tests. The absolute concentrations differed, but the relative concentrations were not substantially different. The prominent compounds observed during sluicing are summarized in Table 5-1.

Table 5-1. Principal Compounds That Evolved during Sluicing of Tank 241-C-106

Alkanes	Conc (mg/m <sup>3</sup> )	Unsaturated Compounds	Conc (mg/m <sup>3</sup> )	Oxygenated Compounds and Ethers	Conc (mg/m <sup>3</sup> )
Propane	7	Cyclopropane		1-Butanol	3
Butane	17	Ethylcyclopropane	2	3-Heptanol	14
2-Methylbutane	2	Butylcyclopropane	23	2-Ethylhexanol	110
Pentane	9	trans-1-Butyl-2-methylcyclopropane	10	Dibutyl ether	12
2-Methylpentane	3	Cyclobutane		1,2-Diethyl-1,4-epoxybutane	35
Hexane	13	Butylcyclobutane	2	1,3-Diethyl-1,4-epoxybutane	30
2-Methylhexane	4	Cyclopentane			
Heptane	80	Ethylcyclopentane	2	Butanal	2
3-Methylheptane	86	Cyclohexane			
2,3-Dimethylheptane	2	Methylcyclohexane	2	Acetone	3
3-Ethylheptane	9	Ethylcyclohexane	2	2-Pentanone	6
Octane	20	Pentylcyclohexane	2	2-Hexanone	4
Nonane	19	1-Methyl-3-propylcyclohexane	2	3-Hexanone	
Decane	28	(2-Methylpropyl)cyclohexane	3	5-Methyl-3-hexanone	2
4-Methyldecane	8	2-Butyl-1,1,3-trimethylcyclohexane	2	2-Heptanone	22
3,7-Dimethyldecane	3	1,1,3-Trimethylcyclohexane	3	3-Heptanone	170
2,6,7-Trimethyldecane	2	Trans-Decalin	12	4-Heptanone	50
Undecane	44	2-Methyl-trans-decalin	6	3-Methyl-4-heptanone	3
2-Methylundecane	3	2,3-Dimethyl-trans-decalin	16	2-Octanone	4
6-Methylundecane	2	2,6-Dimethyl-trans-decalin	4	3-Octanone	3
2,6-Dimethylundecane	4			4-Octanone	10
Dodecane	64	2,3-Hexadiene			
6-Methyldodecane	6	2-Methyl-2,3-hexadiene	47		
2,6,10-Trimethyldodecane	7	1,6-Octadiene	4		
Tridecane	45				
7-Methyltridecane	3	1-Hexyne	2		
Tetradecane	5	2-Hexyne	2		
6-Methyltetradecane	19	2-Heptyne	22		
Tetradecane	75				
Pentadecane	8	Toluene	2		
Hexadecane	25				
Heptadecane	3				

Source: Bonfoey et al. 1999

The initiation of sluicing increased the hydrogen and nitrous oxide release rates substantially. In addition, more than 200 organic compounds representing eight different organic structural groups appeared in the ventilation stack. The mixture included normal alkanes from propane to tetradecane, linear alkenes from propene to decene and smaller amounts of linear alkadienes and alkynes, cycloalkanes with three-, five-, and six-membered rings and certain decalins, lower concentrations of aromatic compounds including benzene, toluene, and the xylenes. Several alcohols and ethers with structures topologically related to butanol and 2-ethylhexanol were found together with homologous series of linear aldehydes and ketones, an allylic nitrile and a

homologous series of linear nitriles. The heptanes, heptenes, and heptanones were especially abundant (Bonfoey et al. 1999). However, tributyl phosphate was not detected in the ventilation stack.

The sludge retained between 3 and 6% permanent gas. Disturbance of the waste released this gas, principally hydrogen, nitrous oxide, and nitrogen, and the volatile organic compounds, which were retained in void spaces and the aqueous and oil phases of the sludge. When sluicing began, the concentrations of water-soluble volatile organic compounds in the ventilation stack increased, but the concentrations of the water-insoluble compounds increased even more.

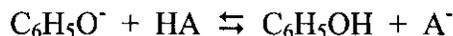
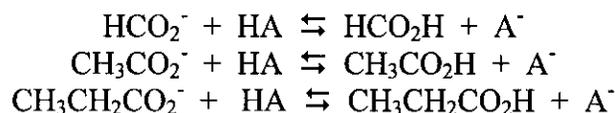
Information about the structural characteristics of the organic compounds and their chemical and radiolytic conversion reactions provides a technical basis for describing the results of vigorous sluicing. In brief, the hydrocarbons are more volatile than the phosphate esters and their concentrations were substantially depleted by evaporation during interim storage. Tributyl phosphate is partially water-soluble and was largely converted into dibutyl- and monobutylphosphate ions. Sodium bis(2-ethylhexylphosphate) is neither volatile, soluble in water, nor chemically reactive, and it was the most abundant organic compound in the tank, with the possible exception of sodium oxalate. The remaining original compounds and the molecules formed from them and retained in the waste had been partially oxidized to hydrogen-deficient hydrocarbons, alcohols, aldehydes, ketones, nitriles, and carboxylate ions. Hydrogen, nitrous oxide, nitrogen, and ammonia were simultaneously formed in the course of these reactions. Some of the retained compounds, for example, the numerous heptenes, were formed by radiolysis of sodium bis(2-ethylhexyl)phosphate. Others, for example, 1-butanol, are related to the hydrolysis and radiolysis of the mono-, di-, and tributyl phosphates. The concentration of 2-ethyl-1-hexanol is much smaller because the rates of hydrolysis and radiolysis of the corresponding ester are much slower. Methanol, ethanol, and propanol are formed as intermediates in the oxidation sequences leading to formate, acetate, and propionate ions. Most of the ethers have structures topologically related to the original phosphate esters. Overall, the organic compounds emerging from the ventilation stack during sluicing are readily related to the mixture of phosphate esters and hydrocarbons originally used for strontium removal in B Plant. The composition of the original mixture had been altered by the vaporization of hydrocarbons, the hydrolysis of tributyl phosphate, and the radiochemical conversions of the hydrocarbons and phosphate esters. The inherently slow rate of hydrolysis of bis(2-ethylhexyl)phosphate ion, the least volatile and least reactive compound in the original mixture, coupled with its insolubility in water and its very low vapor pressure led to its selective retention in the sludge. Its slow radiolytic decomposition produced the volatile organic compounds during years of interim storage in tank 241-C-106.

Lastly, a correlation of the chemical and analytical information implicates 3-octanone, as chemical marker for the oxidation of the hydrocarbon diluents. This substance has been detected in the headspaces of 50 SSTs. Similarly, 3-heptanone is a chemical marker indicative of the oxidation of the diluents and sodium bis(2-ethylhexyl)phosphate. This compound has been detected in the headspaces of 45 SSTs.

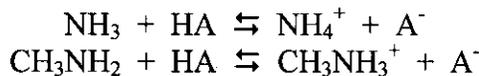
### 5.2.3 Chemical Additions

**5.2.3.1. Acid Washing.** Operations in which the waste is acidified, for example during the removal of waste residues with an aqueous solution of oxalic acid or a solution of nitric acid and oxalic acid, will substantially alter the behavior of the acidic and basic compounds in the waste. Volatile acidic substances will be released and basic substances will be converted to less volatile salts.

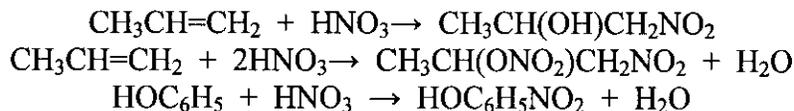
Specifically, the non-volatile carboxylate anions and phenolate ions will be converted into the corresponding volatile acids and phenols as shown in the equations where HA represents either oxalic or nitric acid.



Ammonia and the amines will be converted into ammonium ions.



Nitric acid and the nitrogen oxides that are formed by the reactions between nitric acid and the nitrite ions in solution will react with alkenes and some benzene derivatives. The alkenes and dienes and the benzene derivatives of higher reactivity, such as naphthalene, the xylenes, and phenols, readily undergo nitrosation and nitration under these conditions to provide nitroalkenes and other complex disubstituted molecules as well as nitronaphthalenes, nitroxylenes, and nitrophenols.



The rates of these reactions depend of course on the strength of the acid and the temperature of the waste.

Work at the Oak Ridge National Laboratory (Bonnesen et al. 2002) found that alkylbenzenes were oxidized by nitric acid to produce phenyl alkyl ketones as illustrated for ethylbenzene.



The alkenes, dienes, and alkylbenzenes mentioned in Section 3.0 are candidates for reactions of this kind. Some of these compounds will immediately appear in the vapor space.

Acidification of the waste with nitric acid will also form N-nitroso compounds. That feature of the chemistry will be discussed in Section 5.3.3.

**5.2.3.2. Corrosion Prevention.** Hydroxide and nitrite ion must be added to the waste tanks from time to time to minimize the corrosion of the steel tank liners. The addition of hydroxide ion or nitrite ion as discussed in Section 4.0 will alter the rates of degradation of organic compounds in the waste. However, the changes in the reaction rates caused by the addition of hydroxide ion and nitrite ion will be modest because corrosion control is achieved at pH 11 with concentrations of nitrite ion that are much less than the nitrite ion concentrations in typical saltcake waste tanks.

Other substances, for example, chromate or molybdate ion, also inhibit corrosion, but there are no plans for the use of reagents of this type in the waste tanks.

## 5.3 COMPOUNDS OF SPECIAL INTEREST

### 5.3.1 Nitrogen Oxides

Nitrous oxide ( $N_2O$ ) is formed in the waste tanks in the cascade of reactions involving the inorganic nitrate and nitrite ion and the organic compounds in the wastes. This compound is not reactive with the organic or inorganic constituents of the waste. However, it is partially soluble in water, and there are now substantial amounts of the compound in the aqueous portions of the waste tanks (Mahoney et al. 1999; Mahoney 2000).

Nitric oxide (NO) and nitrogen dioxide ( $NO_2$ ) are produced during the chemical and radiolytic reactions of the inorganic ions as discussed in Section 4.0. Although these compounds react with the organic compounds in the waste, they are not completely consumed. They accumulate in the waste until a balance is achieved between their rates of formation and disappearance. The RGS program (Mahoney et al. 1999; Mahoney 2000) shows they are present in the retained gases in many tanks. Although the concentrations of these substances in the evolving gases are now rather low, their concentrations will increase as the concentrations reactive organic compounds decline. Their concentrations will also increase if the wastes are acidified.

### 5.3.2 Volatile Aldehydes

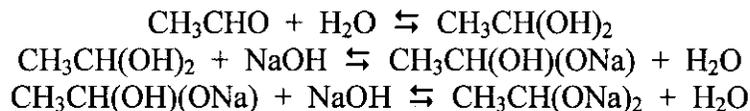
Formaldehyde and acetaldehyde are formed during the thermal and radiolytically induced oxidation reactions of the organic compounds in the wastes as discussed in Section 4.0. The ongoing oxidation reactions of the complexants and their remnants and the hydrocarbons and phosphate esters and their remnants produce formaldehyde and acetaldehyde as intermediate in the oxidation of the hydrocarbons and the phosphate esters. The aldehydes are also intermediates in the oxidation of methanol and ethanol to formate and acetate ion. Neither compound is formed from oxalate ion. The radiolytic and thermal formation rates are directly proportional to the amount of reactive organic carbon in the waste. The formation rate is, therefore, proportional to the TOC content in the liquid phase of the waste, since oxalate ion is insoluble.

Formaldehyde is very soluble in water. According to Smith and March (2001), 99.99% of the formaldehyde in water is present in the form of the hydrate at 20 °C.



It is interesting to compare the Henry's law constants for a molecule with one aldehyde functional group like formaldehyde with the Henry's law constant for a molecule with two hydroxyl groups like the hydrate of formaldehyde. The National Institute of Science and Technology Webbook (NIST 2003) has data for ethanal (one aldehyde group) with a Henry's Law constant of 14 mol/kg/bar and ethylene glycol (two hydroxyl groups) with the Henry's law constant of 4,000,000 mol/kg/bar. The huge increase in the constant reflects the fact that the molecule with two hydroxyl groups hydrogen bonds with water to form a polymolecular network that reduces mobility and volatility.

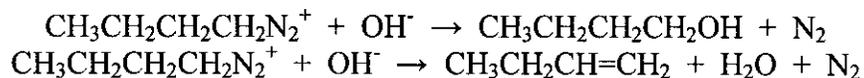
The same reactions occur with acetaldehyde.



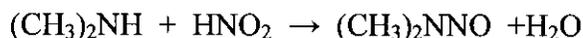
In summary, formaldehyde and acetaldehyde are formed, stored, and destroyed in dynamic chemical processes within the wastes. The soluble (reactive) organic compounds in the waste produce these compounds. Formaldehyde is almost completely converted into the hydrate and its salts in alkaline solution. The concentration of formaldehyde is suppressed by oxidation to formate ion. Acetaldehyde is only partially converted into its hydrate and salts and this compound is, therefore, more likely to appear in the headspaces of the tanks.

### 5.3.3 Amines and Nitroso Compounds

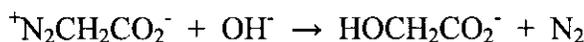
The acid-base reactions of the amines were discussed in Section 5.2.3.1. More important, acidification of alkaline solutions of nitrite ion immediately produces nitrous acid. This substance is an effective reagent for N-nitrosation. It is well known that analytical procedures that require the acidification of Hanford Site wastes cause the N-nitrosation of the amines (Klinger et al. 2000). The products of N-nitrosation of the primary amines are unstable in acid solution and are converted into alcohols and alkenes. Methylamine yields methanol and butylamine provides butanol and 1-butene.



The nitrosation of secondary amines provides stable N-nitroso compounds. Some compounds of this kind including N-nitrosomorpholine and N-nitrosodimethylamine have already been detected in the waste tanks and are listed in the tables in Section 3.0. However, the rates of formation of these substances will be much greater in acid solution.



The nitrosation of glycinate ion, an important remnant of the EDTA family, reacts in the same manner to provide glycolate ion. This chemistry rather than the discharge of glycolate ion from

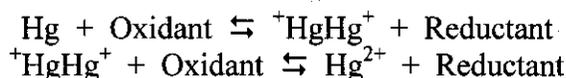


process operations is probably responsible for the current presence of glycolate ion in the wastes

### 5.3.4 Dimethylmercury and Other Organometallic Compounds

Investigations at the Savannah River Site (Wilmarth and Rosencrance 2003) show that mercury and dimethyl mercury can be present in wastes tanks that contained mercury together with organic compounds. Air samples were collected from the headspaces of waste tanks that had the highest concentrations of mercury at the Hanford Site. Frontier Geosciences, Inc. analyzed six samples from the headspaces of these tanks and found that the headspace in tank-241-C-103 contained approximately 55,750 ng/m<sup>3</sup> mercury, and tank-241-C-104 contained approximately 95,500 ng/m<sup>3</sup> mercury. Mercury was absent from blank samples and ambient air. Sampling for dimethyl mercury in Hanford Site tanks is planned, but results were not available for this report.

**5.3.4.1. Chemical Formation.** The technical work at Savannah River and Frontier Geosciences, Inc. coupled with the thermodynamic modeling implies that metallic mercury is present in the waste together with mercuric and mercurous ions (Wilmarth and Rosencrance 2003).



Both reactions are reversible. Laboratory tests showed that typical waste constituents such as nitrite and nitrate ions and organic compounds converted soluble mercuric hydroxide into mercury. Thermodynamic relationships implicate mercurous ion in this conversion as shown in the equations. Metallic mercury is volatile, and it evolves from the waste tanks into their headspaces.

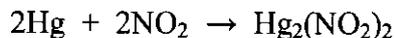


Much more mercury is evolved during evaporation of water from the wastes at the Savannah River Site because the high temperature, which can exceed 150 °C in the still, accelerates the rates of the oxidation and reduction reactions and the rate of codistillation of metallic mercury.

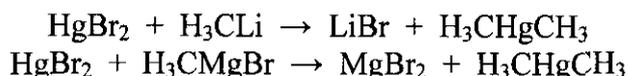
The technical work also indicates that methylmercuric ion (H<sub>3</sub>CHg<sup>+</sup>) and dimethylmercury (H<sub>3</sub>CHgCH<sub>3</sub>) are also formed when organic constituents are present in the waste tanks or in the evaporator (Wilmarth and Rosencrance 2003).

The chemistry of organomercury compounds has been reviewed frequently. An early presentation of this chemistry is provided by Aylett (1973) and more contemporary versions are presented by Smith and March (2001), Cotton et al. (1999), and Cotton and Wilkinson (1988).

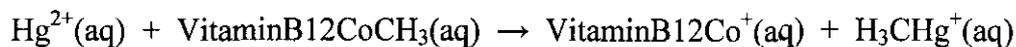
Low concentrations of mercuric ion are soluble in alkaline solutions and mercury exists as a mixture of elemental mercury, mercurous ion and mercuric ion in solution. It is pertinent that elemental mercury may be consumed in reactions with ammonia to form a polymeric material ( $\text{Hg}_2\text{NOH}$ ) or in a reaction with nitrogen dioxide to form mercurous nitrite.



Dimethylmercury is conveniently made in the laboratory by the reaction of methyllithium or methyl magnesium bromide with mercuric bromide (Smith and March 2001; Cotton et al. 1999; Cotton and Wilkinson 1988). These reactions are carried out in an inert organic solvent in the exclusion of all water because water would instantly destroy methyllithium and methylmagnesium bromide.



Methylmercuric ion ( $\text{H}_3\text{CHg}^+$ ) is produced in water or other natural environments when mercuric ion and microorganisms are present (Cotton et al. 1999; Cotton and Wilkinson 1988). The reaction between mercuric ion and the cobalt-methyl entity in vitamin B12 (methylcobalamin) is responsible (at least in part) for the formation of this substance in nature in wet environments (Baird 1995; Cotton et al. 1999; Cotton and Wilkinson 1988).



Some forms that may be present in alkaline solution are shown.

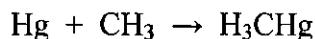


Methylmercuric ion and dimethylmercury are formed in test solutions when organic compounds are present (Wilmarth and Rosencrance 2003). Their rates of formation are temperature dependent and increase as the reaction proceeds. The tests were carried out in the relatively simple reaction systems that contained sodium hydroxide, sodium nitrite and sodium nitrate in addition to the mercuric compounds and the organic substances. The results imply that the organic compounds degrade in alkaline solution to form methyl radicals. It is pertinent to mention that rate of formation dimethylmercury was much more rapid with Dow Corning H-10 antifoam than with acetate ion (Wilmarth and Rosencrance 2003). These observations and other investigations concerning the manner in which organic compounds decompose in the wastes at the Hanford Site suggest that the organic compounds decompose to form methyl radicals and that the methyl radicals react with mercury to form methylmercury. The more rapid rate with the antifoam is readily explained by the fact that the antifoam has many methyl groups, whereas a slow thermal decarboxylation reaction is required for the formation of a methyl radical from acetate ion. The methylation of mercury may proceed more rapidly in complex waste mixtures that contain transition metals.

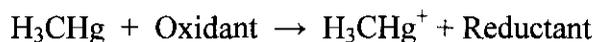
In summary, the reaction sequence for the formation of dimethylmercury can be formulated as beginning with the decomposition of the organic material to form methyl radicals.



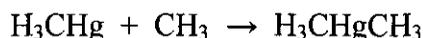
When metallic mercury is present, methylmercury ( $\text{H}_3\text{CHg}$ ) can be formed in competition with the formation of methane, methyl hydroperoxide, and nitro and nitroso methane as discussed in Section 4.0.



The same oxidation reactions sequences that occur with mercury, mercurous and mercuric ion also occur with the methylated derivatives of mercury and methylmercuric ion is formed by the oxidation of methylmercury.

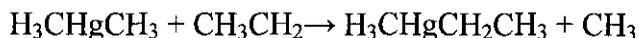


This reaction is reversible and the competitive reaction of methylmercury with methyl radical leads to dimethylmercury.

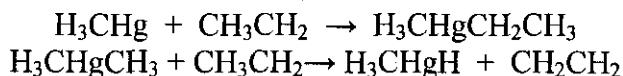


The reaction system is thermodynamically driven toward the formation of dimethylmercury (boiling point  $92.5^\circ\text{C}$ ), which evolves into the vapor phase in the evaporator or the waste tank.

The reaction pattern outlined in the previous section implies that other organomercury compounds should also be formed during the decomposition of organic compounds in the waste tanks and in the evaporators. The organic compounds that have been investigated by the Savannah River team are biased for the formation of methyl radicals because ethyl radical is not formed from acetate ion. As discussed in Sections 3.0 and 4.0, the Hanford Site wastes evolve ethane, which is produced from ethyl radical. Indeed, displacement reactions between radicals and dimethylmercury can produce complex mixtures of organomercury compounds as illustrated by the reaction between ethyl radical and dimethylmercury (Ingold and Roberts 1970).



Alternatively, methylmercury may simply combine with ethyl radical to form methylethylmercury or to abstract a hydrogen atom and form monomethylmercury and ethene.



The volatility of methylethylmercury is likely between dimethylmercury (boiling point  $92.5^\circ\text{C}$ ) and diethylmercury (boiling point  $159^\circ\text{C}$ ). These compounds are sufficiently stable to evolve from Hanford Site waste.

Organomercury compounds are generally regarded as stable compounds under ordinary conditions. For example, Aylett (1973) states that diethylmercury is only slowly decomposed in

alkaline solution. The decomposition reactions of dimethylmercury in the gas phase can be conveniently studied at about 125 °C. At that temperature, dimethylmercury decomposes to provide the products expected for a free radical reaction which include methane, ethane, methylethylmercury, hydrogen, ethene, and propene (Aylett 1973). The same products are expected for the thermal and radiolytically induced decomposition reactions in Hanford Site wastes.

### 5.3.5 Surprise Molecules

Compounds that are reactive or volatile are often difficult to detect by the usual methods of analysis. The information presented in Sections 3.0 and 4.0 provides a basis for the prediction of substances that may be present in the waste tanks but have not have been yet been detected. This feature is illustrated by the experience with formaldehyde. Chemical observations pointed to the existence of this material in waste as early as 1993 (Ashby et al. 1993; Meisel et al. 1993; Stock and Pederson 1997). This same approach has been used here to elaborate other waste constituents that for one reason or another have been over looked by the customary analytical methods. The approach begins with a consideration of one and two carbon atom compounds that also may contain oxygen or nitrogen. Some compounds of this class could, for example, be overlooked in the GC/MS approach because they are too volatile or because they are destroyed in the collection matrix.

**5.3.5.1. Organic Compounds with One and Two Carbon Atoms.** Organic compounds with one or two carbon atoms and oxygen or nitrogen or both are listed in Table 5-2. The compounds, their identification numbers, formulae, and molecular weights are given together with information about whether they have been detected in the tank wastes. Some have been detected during RGS work, others during headspace analyses. The designation "chemical" means the substance is an anticipated intermediate in one or more of the chemical reaction sequences discussed in Section 4.0.

**Table 5-2. Compounds with One or Two Carbon Atoms (Page 1 of 2)**

Name	CAS	Formula	Evidence for Presence in Waste
1,1-Dinitroethane	600-40-8	CH <sub>3</sub> CH(NO <sub>2</sub> ) <sub>2</sub>	Chemical
Acetamide	60-35-5	CH <sub>3</sub> CONH <sub>2</sub>	Chemical
Acetate ion		CH <sub>3</sub> CO <sub>2</sub> <sup>-1</sup>	Core
Acetic acid	64-19-7	CH <sub>3</sub> CO <sub>2</sub> H	GC/MS
Acetonitrile	75-05-8	CH <sub>3</sub> CN	GC/MS
Cyanide ion		CN <sup>-1</sup>	Chemical
Dimethylamine	124-40-3	CH <sub>3</sub> NHCH <sub>3</sub>	GC/MS
Dimethyl ether	115-10-6	CH <sub>3</sub> OCH <sub>3</sub>	GC/MS
1,1-Dimethylhydrazine	57-14-7	(CH <sub>3</sub> ) <sub>2</sub> NHNH <sub>2</sub>	GC/MS
Dinitromethane	625-76-3	CH <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	Chemical
Ethanal	75-07-0	CH <sub>3</sub> CHO	GC/MS
Ethanal hydrate		CH <sub>3</sub> CH(OH) <sub>2</sub>	Chemical
Ethanal oxime	107-29-9	CH <sub>3</sub> CHNOH	Chemical
Ethane	74-84-0	CH <sub>3</sub> CH <sub>3</sub>	RGS
Ethanol	64-17-5	CH <sub>3</sub> CH <sub>2</sub> OH	GC/MS
Ethene	74-85-1	CH <sub>2</sub> CH <sub>2</sub>	RGS

**Table 5-2. Compounds with One or Two Carbon Atoms (Page 2 of 2)**

Name	CAS	Formula	Evidence for Presence in Waste
Ethylamine	75-04-7	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>	RGS
Ethyl hydroperoxide	3031-74-1	CH <sub>3</sub> CH <sub>2</sub> OOH	Chemical
Ethyl nitrate	625-58-1	CH <sub>3</sub> CH <sub>2</sub> ONO <sub>2</sub>	GC/MS
Ethyl nitrite	109-95-5	CH <sub>3</sub> CH <sub>2</sub> ONO	GC/MS
Ethyl peroxyxynitrite		CH <sub>3</sub> CH <sub>2</sub> OONO <sub>2</sub>	Chemical
Ethylene oxide	75-21-8	cyclic-CH <sub>2</sub> CH <sub>2</sub> O	GC/MS
Ethyleneimine	151-56-4	cyclic-CH <sub>2</sub> CH <sub>2</sub> NH	Chemical
Ethyne	74-86-2	CHCH	RGS
Formamide	75-12-7	HCONH <sub>2</sub>	Chemical
Formate ion		HCO <sub>2</sub> <sup>-1</sup>	Core
Formic acid	64-18-6	HCO <sub>2</sub> H	Chemical
Glycine	56-40-6	H <sub>2</sub> NCH <sub>2</sub> CO <sub>2</sub> H	Chemical
Glycolate anion		HOCH <sub>2</sub> CO <sub>2</sub> <sup>-1</sup>	Core
Glycolic acid	79-14-1	HOCH <sub>2</sub> CO <sub>2</sub> H	Chemical
Glyoxylate anion		OCHCO <sub>2</sub> <sup>-1</sup>	Chemical
Glyoxylic acid	298-12-4	OCHCO <sub>2</sub> H	Chemical
Hydrogen Cyanide	74-90-8	HCN	
Methanal	50-00-0	H <sub>2</sub> CO	Special detection
Methanal hydrate	463-57-0	H <sub>2</sub> C(OH) <sub>2</sub>	Chemical
Methanal oxime	75-17-2	CH <sub>2</sub> NOH	Chemical
Methane	74-82-8	CH <sub>4</sub>	RGS
Methanol	67-56-1	CH <sub>3</sub> OH	GC/MS
Methylamine	74-89-5	CH <sub>3</sub> NH <sub>2</sub>	GC/MS
Methyl formate	107-31-3	HCO <sub>2</sub> CH <sub>3</sub>	GC/MS
Methylhydrazine	60-34-4	CH <sub>3</sub> NHNH <sub>2</sub>	GC/MS
Methyl hydroperoxide	3031-73-0	CH <sub>3</sub> OOH	Chemical
Methyl isocyanate	624-83-9	CH <sub>3</sub> NCO	GC/MS
Methyl nitrate	598-58-3	CH <sub>3</sub> ONO <sub>2</sub>	GC/MS
Methyl nitrite	624-91-9	CH <sub>3</sub> ONO	GC/MS
Methyl peroxyxynitrite		CH <sub>3</sub> OONO <sub>2</sub>	Chemical
Nitroethane	79-24-3	CH <sub>3</sub> CH <sub>2</sub> NO <sub>2</sub>	GC/MS
Nitromethane	75-52-5	CH <sub>3</sub> NO <sub>2</sub>	GC/MS
Nitrosoethane		CH <sub>3</sub> CH <sub>2</sub> NO	GC/MS
Nitrosomethane	865-40-7	CH <sub>3</sub> NO	GC/MS
N-Methylformamide	123-39-7	HCONHCH <sub>3</sub>	Chemical
N-Nitrosodimethylamine	62-75-9	CH <sub>3</sub> N(NO)CH <sub>3</sub>	GC/MS
Oxalate anion		O <sub>2</sub> CCO <sub>2</sub> <sup>-2</sup>	Core
Oxalic acid	144-62-7	HO <sub>2</sub> CCO <sub>2</sub> H	Chemical
Trinitromethane	517-25-9	CH(NO <sub>2</sub> ) <sub>3</sub>	Chemical

**5.3.5.2. One Carbon Atom Group.** Many of the compounds with one carbon atom have been observed. The exceptions are methyl hydroperoxide, the hydrate of formaldehyde, the oxime of formaldehyde, dinitro and trinitromethane, methyl peroxyxynitrite, hydrogen cyanide, and formamide.

Formaldehyde and its hydrate are produced by several reaction channels. Formaldehyde as already discussed is hydrated in aqueous alkaline solution. It is oxidized to formate ion in the waste solutions with the attendant formation of hydrogen. Like methyl hydroperoxide, formaldehyde and the hydrate are continuously formed and destroyed in the wastes. Although the hydration reaction is thermodynamically favored, formaldehyde is volatile and thermodynamic preference for hydration is contravened by the entropy to be gained by volatilization of the substance into a very dilute vapor. The same factor may enable the other compounds that are mentioned in the following discussion to evolve from the wastes even though other thermodynamic considerations imply they are converted to non-volatile ions.

Methyl hydroperoxide is produced in free radical recombination reactions between methyl radical and oxygen. The substance is readily oxidized to formaldehyde and its concentration in the waste will be dictated by the balance between its rate of formation and its rate of decomposition. In addition, the hydroperoxides are much more acidic than the corresponding alcohols and a portion of the hydroperoxide will be present in the alkaline wastes as the anion. The cyclic peroxide,  $\text{CH}_2\text{OO}$ , has also been implicated in waste chemistry. This substance is both very volatile and very reactive with a half life measured in seconds. It is mentioned here for completeness inasmuch as its low concentration and high reactivity mitigate its appearance in the headspaces of the waste tanks.

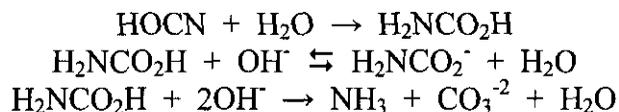
The reaction of methyl radical with nitric oxide leads to the formation of nitrosomethane. The compound has been reported to be present in the GC/MS analyses of the headspaces. It rearranges spontaneously to the oxime of formaldehyde in solution. The oxime is metastable and converts to formaldehyde and hydroxyl amine. Oximes have low volatility and many compounds of this class form highly crystalline solids.

The chemical model discussed in Section 4.0 implies that dinitromethane and trinitromethane can be produced. However, the model also implies that these compounds are destroyed by conversion to their anions in the alkaline wastes and by their oxidation to formate ion.

Methyl peroxyxynitrite is included in this listing because the radiolysis of nitrate ion is known to form the peroxyxynitrite anion and the chemical model includes recombination reactions that could lead to the methyl ester. As in the other instances discussed here, these substances are formed and destroyed in the wastes in ongoing chemical and radiochemical reactions. The chemistry of formamide and hydrogen cyanide are coupled in the same manner as the chemistry of acetamide and acetonitrile. The presence of formamide implies the presence of hydrogen cyanide and cyanide ion as discussed in Section 4.0.

Cyanate ion has also been suggested to be an intermediate in the waste chemistry. The conjugate acids, cyanic acid ( $\text{HOCN}$ ) and isocyanic acid ( $\text{HNCO}$ ), are formed in solution. Isocyanic acid is more volatile than cyanic acid. Isocyanic acid forms a cyclic trimer, cyanuric acid ( $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$ ). Isocyanic acid is a plausible constituent of the vapor even though the formation of the salt is thermodynamically favorable in solution.

The hydration of cyanate ion produces carbamic acid and the acid reacts with hydroxide ion to give carbamate ion. These two substances react in alkaline solution to give ammonia and carbonate ion.



Even though the third step in the reaction sequence is thermodynamically favorable and irreversible, it is impossible to preclude the volatilization of isocyanic acid to the headspace.

**5.3.5.3. Two Carbon Atom Group.** Many of the compounds with two carbon atom that are listed in Table 5-2 have also been observed. The exceptions are ethyl hydroperoxide, ethylene oxide, the hydrate of acetaldehyde and its oxime, the acidic forms of the acids with two carbon atoms, dinitroethane, ethyl peroxyxynitrite, and acetamide. Intermediates, which are closely related to the intermediates involved in the formation of the one carbon atom compounds are also involved in the formation of the two carbon atom compounds mentioned in the table.

The list also includes 1,1-dimethylhydrazine and 1,2-dimethylhydrazine. Although their origins are somewhat obscure, some hydrazines have been detected in the headspaces of the waste tanks.

**5.3.5.4. Organic Compounds in Homologous Series.** The analytical work has identified or tentatively identified more than 1230 compounds as discussed in Section 3.0. Some of these compounds have been detected in several samples and others have only been detected in one sample. These variations are possible because there are inherent differences between the samples from the various waste tanks, and because changes in relative concentration can lead to the selective isolation of a signal in one chromatogram that is obscured in another chromatogram. In addition, small differences in the operating conditions of the GC/MS equipment enable one analyst to resolve signals that are not uniquely observed by others. More important, even cursory inspection of the chromatograms shows there are even more organic compounds present than have been identified.

The chromatograms for the organic compounds in the headspaces of C-Farm tanks (Rasmussen 1994) indicate there are at least four unidentified compounds in the region between 10 and 25 minutes, 20 in the region between 25 and 45 minutes, and 50 in the region between 45 and 65 minutes. There are even more unidentified compounds in the region between 65 and 80 minutes. The compounds in this region include the original hydrocarbons in the diluent and many of their reaction products. There is no reliable way to even estimate the numbers of unidentified compounds in the region, but it is evident that the number is large.

Some progress toward the identification of these compounds can be made by consideration of the substances that are absent from homologous series. Many of the homologous series, which have been established by the analytical work described in Section 3.0, are systematically examined in the following paragraphs.

**1-Alkanes.** The homologous series of normal alkanes is complete from methane to cosane.

2-, 3-, 4-Methylalkanes. These homologous series are also virtually complete.

Dimethylalkanes. The 2,2-, 2,3-, and 2,4-dimethylpropanes, butanes, pentanes and hexanes form complete series, but there are few reports of the corresponding heptanes, octanes, nonanes, decanes, dodecanes, tridecanes, or tetradecanes. The undecane family is complete. The heptanes, octanes, nonanes, and decanes with these substitution patterns may account for some of the unidentified compounds that appear before the diluent in the chromatograms. The identification of the dimethylundecanes is probably the consequence of their relatively high abundance and their emergence from the chromatograph before the other components of the diluent. The failure to detect the related derivatives of the dodecanes, tridecanes, tetradecanes, and pentadecanes is probably related to their relatively low concentrations and the complexity of the chromatogram. The reason for the absence of these compounds can be traced at least in part to the fact that 2,6-dimethylalkanes are much more abundant in petroleum than the corresponding 2,2-, 2,3-, 2,4-, or 2,5-dimethylalkanes.

Other alkanes. The trimethylalkanes, especially the hexanes, heptanes and octanes are well represented. However, it is notable that many trimethyldecanes have been detected, but that there are only a few trimethylated nonanes, undecanes, dodecanes, tridecanes, or tetradecanes. The absence of the trimethyltridecanes and trimethyltetradecanes is not unexpected because these compounds have 16 and 17 carbon atoms, respectively, and would have been removed during refining.

In summary, while more than 200 alkanes have been detected, other members of homologous series have not been observed and these substances, which are present in low concentration account for some of the unidentified compounds in the GC/MS work.

Cycloalkanes. Some of the cycloalkanes in the waste tanks were present in the commercial diluents as discussed in Section 2.0. Others have been introduced into the waste by cyclization reactions as discussed in Section 4.0.

Monoalkylcycloalkanes. The cycloalkanes with linear alkyl group are rather well represented in the wastes. The homologous series of alkylcyclohexanes is complete to decylcyclohexane with the exception of the heptyl and nonyl derivatives. The methyl and ethyl derivatives of cyclopropane, cyclobutane, Cyclopentane, and cyclohexane are also complete. But, there are few higher homologues of cyclobutane and cyclopentane. The absence of the cyclobutanes is not surprising; but the absence of the cyclopentanes is unexpected, and some of the more volatile but as yet unidentified compounds may originate from the simple alkylcyclopentanes.

Dimethylcycloalkanes. The 1,2-dimethylcycloalkanes with 3-, 5-, and 6-membered rings are present in the waste. The absence of the related cyclobutanes is not unreasonable in view of the higher energy barriers for their formation. The related 1,1-dimethylcyclopropane and cyclohexane are also present. Although unreported, 1,1-dimethylcyclopentane may be present.

Other substituted cycloalkanes. Many cyclopentanes and cyclohexanes with two or three alkyl groups have been tentatively identified, and many of them have fewer than 10 carbon atoms and

would emerge from the chromatograph prior to the diluent. Many other cyclopentanes and cyclohexanes emerge with the other abundant compounds in the diluent. Although 150 of these compounds have been identified, it is reasonable to postulate that other members of this class have not yet been identified and contribute to the large signal intensity. On the other hand, cyclic compounds with seven or more atoms are unusual and their absence is not unexpected.

The alkenes are formed from the alkanes during the ongoing radiolytic and thermal reactions. Approximately 150 of these compounds have been detected in the wastes. However, they appear to be under represented.

1-Alkenes. The homologous series of 1-alkenes is complete from ethene to pentadecane.

2-Alkenes. The homologous series of 2-alkenes is not complete. In some instances, only one of the geometric isomers has been reported, and there is no technical reason for the absence of the other isomer. In addition, the fact that the 1-alkenes with 12 to 15 carbon atoms are found implies that the 2-alkenes with 12 to 15 carbon atoms should also be present. These substances have not yet been identified in the wastes.

3-Alkenes. The family of the 3-alkenes is substantially complete from 3-hexene to 3-tetradecene and both geometric isomers have been identified in some instances. However, neither the 3-nonenes, 3-decenes, nor the 3-tridecenes have been reported. There is no technical basis for their absence and it should be assumed that they are present.

4-Alkenes. Few 4-alkenes have been identified in the wastes. Again, there is no technical basis for the exclusion of these substances.

Substituted Alkenes. The same reactions that provide the 1-, 2-, 3- and 4-alkenes should also provide the related methyl derivatives. Only a limited number of alkenes with methyl substituents have been identified. For example, the relatively abundant 2-methylalkanes should provide 2-methyl-1-alkenes and E- and Z-2-methyl-2-alkenes, E- and Z-2-methyl-3-alkenes, and so forth. The low molecular weight butenes and pentenes have been reported, but few of the other compounds in this series have been detected.

Dienes and alkynes. 1,3-Butadiene and the related 1,3-pentadiene and 1,3-hexadiene have been observed in the headspaces of the waste tanks and in the condensed phase. In addition, acetylene and propyne and alkynes with four or more carbon atoms have been detected in the vapor sampling program. Although the compounds of this type are more difficult to form chemically because of the many other available reaction channels, the fact that the three dienes and some alkynes are found suggests that other molecules of this type are also present. The 1-alkynes with 5, 6, 7, and 8 carbon atoms are plausible. Like many other molecules in the waste, the reactive dienes are continuously formed and destroyed. For example, 1,3-dienes are formed from either the 1- or 3-alkenes. Inasmuch as these substances are prevalent, the dienes produced from them are plausible reaction products. However, the dienes are reactive and like many other compounds, their concentrations in the wastes depend upon the relative rates of formation and decomposition.

**Benzene derivatives.** Benzene, toluene and the xylenes probably originate from the early diluents and their use in solvents supporting plant operations and from the oxidation of the cyclohexanes. In principle, monosubstituted cyclohexanes and 1,2-, 1,3-, and 1,4-disubstituted cyclohexanes can be oxidized to monoalkyl- and dialkylbenzenes. The existence of a benzene derivatives implies that the corresponding cycloalkanes might be in the waste and the existence of a cyclohexane derivative implies that the benzene might be present. In fact, there is only limited agreement. The low concentrations of the compounds of this type whether cyclohexanes or benzenes, complicate their identification especially since most of the molecules have more than 10 carbon atoms and would coelute with the many other constituents of the diluent.

**Alcohols.** The homologous series of 1-alkanols is virtually complete. The missing members of this series, for example 1-tridecanol, are likely to also be present. Similarly, the 2-alkanol family is complete to 2-octanol, but some higher members of this series have not been detected even though there is no basis for their exclusion. Even fewer of the corresponding 3- and 4-alkanols have been reported. Similar comments can be made about the methyl derivatives of these compounds. Very few high molecular weight monomethylalkanols have been identified in the wastes. Again, the concentrations of these alcohols are minimized by their propensity for oxidation. Inasmuch as these substances also coelute with the other diluent materials, their detection presents a considerable challenge. In addition, these relatively non-volatile, polar compounds may be retained within the sampling equipment.

**Aldehydes.** The homologous series of aldehydes from ethanal to tridecanal has been observed. The 2- and 3- methylalkanals are also fairly complete for the low molecular weight compounds, but the anticipated methyl derivatives of heptanal and the higher homologues have not been reported. As in the other cases, the failure to detect the other molecules in the series may result from their low concentrations and the attendant analytical difficulties rather than to their absence from the waste. A family of unsaturated aldehydes has also been detected. The 2-butenals and the other members of this series can exist as geometric isomers and it should be anticipated that if one isomer is observed the other isomer also exists in the waste (although perhaps at lower concentration). Accordingly, other aldehydes of this kind are also present.

**Ketones.** Several homologous series have been found. The 2-, 3-, 4-, and 5-alkanone series are essentially complete from propanone to tetradecanone. Only 3-decanone, 5-tridecanone and 5-tetradecanone are absent. As in other cases, many of the anticipated methyl derivatives of the higher homologues have not been reported. Unsaturated ketones such as 3-buten-2-one, 3-penten-2-one, and 3-hexen-2-one have also been reported. The early members of this series are fairly complete, but the related heptenes, octenes, nonenes, and higher homologues are distinctly underrepresented.

**Carboxylic Acids.** Even though the carboxylic acids form carboxylate ions in alkaline solution, some acids appear in the headspaces. Early analytical work in which the carboxylate ions in the wastes were converted to their methyl esters revealed many additional compounds of this class were present. In principle, the oxidation reactions of the aldehydes should lead to the formation of the corresponding carboxylate ions in the alkaline waste. This concept implies that there are many more carboxylate ions in the liquid and solid layers than implied by the GC/MS determinations of the compounds in the headspaces of the waste tanks.

Esters. Esters have been detected in spite of the fact that they are hydrolyzed in alkaline solution. The esters are continuously formed and destroyed in the wastes and the volatile water-insoluble esters enter the stored gases and evolve from the waste tanks with the gas. The analysis of the head space leads to the selective detection of the more volatile and less soluble compounds.

Nitriles. The homologous series of nitriles is complete from acetonitrile to pentadecanenitrile with the exception of dodecanenitrile and tetradecanenitrile. As in many other instances, these compounds are not detected because of they emerge from the chromatograph in the midst of the diluent. Surprisingly, few substituted nitriles have been observed.

Amines. Many serious problems have been encountered in the detection and measurement of the concentrations of ammonia and the amines in the condensed phases and the headspaces. The relatively high abundances of these compounds in the wastes from tank 241-SY-101 imply that there are almost certainly more organic amines in the wastes than have been reported in the GC/MS investigations.

Nitrogen-Containing Compounds. The series of nitrate esters from methyl nitrate to decyl nitrate is complete with the exception of octyl nitrate. In contrast, only two nitrite esters have been detected. In principle, esters should be formed from the other alcohols in the waste tanks. On this basis, there should be many more nitrate and nitrite esters than have been observed. Some nitro compounds including nitromethane and 2-nitro-2-methylpropane have been detected. The fact that 2-nitro-2-methylpropane is observed to the exclusion of the many other nitroalkane intermediates in the reaction cascade discussed in Section 4.0, implies that this nitro compound is kinetically stable because the nitro group is bonded to a tertiary (hydrogen-free) carbon atom. This concept implies that 2-nitro-2-methylbutane, 2-nitro-2-methylpentane, and related compounds may also be kinetically stable and accumulate.

#### 5.4 SUMMARY

The wastes will slowly change their composition during the next 25 years. The volatile and semivolatile hydrocarbon will evolve from the liquid phases, but these substances will probably be retained in the solid phases of the wastes where they will continue to undergo radiolytic reactions. Tributylphosphate will be converted into dibutyl- and monobutylphosphate ions in both the liquid and solid portions of the wastes during this interval. Approximately 50% of the reactive complexant TOC will be converted to oxalate ion in the next 25 years. The organic reactions, whether ionic or radiolytic will slow as the radionuclides decay and the tanks cool.

Organic compounds that are retained in the waste feed will be distilled during evaporator operations. The residence time in the evaporator is too short and the temperature is too low to initiation reactions that have already been identified.

The wastes almost certainly contain organic compound that have not yet been detected in the wastes. Some of these substances are envisioned as reaction intermediates and others are members of incomplete homologous series. Recent experience with formaldehyde and

dimethylmercury shows that reactive compounds that are stored in the waste in non-volatile forms emerge from it. The reactive organic compounds are formed and destroyed in ongoing processes. If the compound has a volatile form, it can be released from the waste even though it is being consumed in a thermodynamically favorable reaction in the waste and even though its concentration in the waste is fleetingly small.

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