Gaseous Analytes of Concern at Hanford Tank Farms

Topical Report

March 1, 1996

Work Performed Under Contract No.: DE-AR21-95MC32087

U.S. Department of Energy
Office of Environmental Management
Office of Technology Development
Washington, DC

For

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Electronic Sensors and Systems Division
Northrop Grumman Corporation
Pittsburgh, Pennsylvania 15235-5098

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CONTENTS

Abstract.....	iv
1. Introduction.....	1
2. Analytes of Concern Lists.....	4
3. Formulas and Densities.....	7
4. Vapor Pressures.....	10
5. Fire and Explosion Hazards.....	13
6. Health Hazards.....	16
7. Hazard Ratings.....	19
8. Infrared Spectra.....	23
9. Analytes of Concern Test List.....	26
10. References.....	29

ABSTRACT

Large amounts of toxic and radioactive waste materials are stored in underground tanks at DOE sites. When the vapors in the tank headspaces vent to the open atmosphere a potentially dangerous situation can occur for personnel in the area. An open-path atmospheric pollution monitor is being developed for DOE to monitor the open air space above these tanks.

In developing this monitor it is important to know what hazardous gases are most likely to be found in dangerous concentrations. These gases are called the Analytes of Concern. At the present time, measurements in eight tanks have detected thirty-one analytes in at least two tanks and fifteen analytes in only one tank. In addition to these gases, Carbon tetrachloride is considered to be an Analyte of Concern because it permeates the ground around the tanks. These Analytes are described and ranked according to a Hazard Index which combines their vapor pressure, density, and approximate danger level. The top sixteen ranked analytes which have been detected in at least two tanks comprise an "Analytes of Concern Test List" for determining the system performance of the atmospheric pollution monitor under development. A preliminary examination of the infrared spectra, barring atmospheric interferences, indicates that:

The pollution monitor will detect all forty-seven Analytes!

1. INTRODUCTION

In the process of manufacturing nuclear reactor fuel at the DOE Hanford Reservation and Savannah River sites, large amounts of toxic and radioactive waste materials have been generated and stored in hundreds of large underground tanks such as the one shown in Figure 1. These waste materials include the solvents used in the various recovery and decontamination processes, radiation-induced decay products, and numerous chemical reaction products from the stored chemicals. The tanks are grouped together into a few areas called "tank farms".

Since the mid-1940s employees working in the vicinity of these tanks have occasionally reported health problems such as headaches, burning sensations in the nose and throat, nausea, and impaired pulmonary function. These problems may have arisen from vapors released from the tanks. The open-path atmospheric pollution monitor being developed under this DOE contract is to monitor the open air above these tank farms whenever personnel are present and to sound an alarm whenever potentially harmful gases approach dangerous levels of concentrations.

In developing this monitor for personnel safety it is important to know the specific harmful gases which must be monitored. Several lists of candidates have been developed from measurements in the vapor headspaces of several tanks. However, since no monitor can efficiently and effectively detect all of the candidate gases, and since all of the candidate gases are not equally dangerous, a focused list of analytes is determined from these candidate lists. It is this selected set of analytes, the "Analytes of Concern Test List", that will be addressed during the performance of this contract. This list results from a selection process explained herein which addresses relative risk of vapors known or suspected to be in the headspaces. The open-path atmospheric monitor should be designed to detect these analytes at concentration levels below those which would adversely affect the health of personnel in the area.

Table 1 contains the Analytes of Concern Test List derived in the following sections. Of the sixteen Test Analytes, nine will be identified by the laser absorption measurement mode of the pollution monitor and all sixteen by the thermal emission measurement mode. The list is expected to change from time to time as more measurements are conducted in the tank headspaces or as additional chemical reactions change the vapor compositions in those headspaces.

Table 1. Analytes of Concern Test List.

Analyte	Detection by Thermal Emission	Detection by Laser Absorption
Benzene	yes	yes
Vinylidene chloride	yes	yes
Nitrogen dioxide	yes	
Carbon tetrachloride	yes	
Butadiene	yes	yes
Chloroform	yes	
Methylene chloride	yes	
Carbon monoxide	yes	
Ammonia	yes	yes
Nitric oxide	yes	
n-Hexane	yes	yes
Trichlorofluoromethane	yes	yes
2-Hexanone	yes	
Toluene	yes	yes
Acetonitrile	yes	yes
Pentane	yes	yes

2. ANALYTES OF CONCERN LISTS

Several Analytes of Concern lists have been compiled by different investigators:

1. The *Osborn List* is a compilation by Jerry Osborn in the TWRS Safety Department and was the earlist one.¹
2. *Tank List 1* is the result of measurements taken in Tank 241-C-103 by Mahlum, Young, and Weller.²
3. *Tank List 2* is from more recent measurements in Tank 241-C-103 by Huckaby and Story.³
4. The *M & M Report* is a set of compilations from measurements.⁴ Tables 3-1 and C-1 list the vapors that have been detected or suspected of being emitted from one or more of eight tanks.

These four sources identify forty-seven gases: thirty-two gases, designated as the Analytes of Concern, which have been detected in at least two tanks and fifteen gases, designated as Analyte Candidates, which have been detected in only one tank. The Analytes of Concern are considered more dangerous because, everything else being equal, these gases are more likely to be present in the head space of any given tank. The Analytes of Concern Test List will be a subset of the Analytes of Concern since they are more likely to be present for open-air measurements when the pollution monitor being developed on this contract is field tested at the DOE Hanford Laboratory.

Tables 2 and 3 list the forty-seven vapors which have been detected or suspected of being emitted from tanks. The number of tanks which emitted the vapors are given for the M & M Report while a + indicates detection. Tank Lists 1 and 2 are from

Table 2. Analytes of Concern ordered by frequency of occurrence.

Gas	Osborn List	Tank List 1	Tank List 2	M & M Report	Total No. of Tanks
Carbon tetrachloride					8
Benzene		+	+	6	7
Acetone	+	+	+	4	6
n-Butyl alcohol	+	+	+	4	6
Toluene	+			5	6
m-Xylene			+	5	6
o-Xylene			+	5	6
p-Xylene			+	5	6
Butadiene		+	+	4	5
n-Hexane		+	+	4	5
Trichloroflouromethane			+	4	5
Vinylidene chloride	+	+	+	3	5
Ammonia	+	+	+	2	4
Heptane			+	3	4
2-Hexanone	+		+	2	4
Methylene chloride	+	+	+	2	4
Nonane			+	3	4
Octane			+	3	4
Pentane			+	3	4
Acetonitrile		+	+	2	3
Butane			+	2	3
2-Butanone			+	2	3
Carbon monoxide			+	2	3
Chloroform			+	2	3
Methyl propyl ketone			+	2	3
Nitrogen dioxide	+		+	1	3
Tributyl phosphate	+	+	+	1	3
Dodecane	+	+	+		2
Ethyl butyl ketone			+	1	2
Naphthalene			+	1	2
Nitric oxide			+	1	2
Tetrahydrofuran			+	1	2

the same tank. The chemical names listed are the Occupational Safety and Health Administration (OSHA) names when known. When the OSHA name is not known the preferred name according to Howard and Neal is given.⁵ In the original lists, Sulfur oxides and Nitrogen trioxides were said to represent all Sulfur/Oxygen gases and all Nitrogen/Oxygen gases, respectively. We take this general statement to mean all O_xS and all NO_x. Carbon tetrachloride, while not detected in the tanks, is included in Table 2 as an Analyte of Concern because it permeates the soil around all the tanks and is therefore a common vapor in the open atmosphere of the tank farms.

Table 3. Candidate Analytes.

Gas	Osborn List	Tank List 1	Tank List 2	M & M Report	Total No. of Tanks
2-Butoxyethanol				1	1
n-Butyl acetate			+		1
Butyraldehyde		+	+		1
Butyronitrile	+				1
Carbon disulfide			+		1
Dipropylketone			+		1
Ethyl acetate			+		1
Nitrate	+				1
Ozone			+		1
Propionitrile		+	+		1
Sulfate		+	+		1
Sulfur dioxide		+	+		1
Sulfur trioxide		+	+		1
Tridecane		+	+		1
Vinyl acetate	+				1

3. FORMULAS AND DENSITIES

Table 4 contains the Chemical Abstract Service (CAS) Registry Number for the forty-seven Analytes in Tables 2 and 3 along with the molecular formulas ordered by the Hill system⁵ (order of symbols is carbon, hydrogen, and then alphabetical by element). The Candidate Analytes are italicized. The molecular weights are also given from which the density, relative to air* at the same temperature and pressure, is determined. The density relative to air is an important parameter because chemicals with a relative density less than 1.0 tend to rise and are easily dispersed in air. Conversely, chemicals with a relative density larger than 1.0 tend to "flow" or "pool" around ground level and low places, thus forming dangerous pockets of hazardous vapors. This pooling becomes less probable from top to bottom in the tables, i.e., from Tributyl phosphate to Ammonia. Thus, the darker the shading, the less likely the Analyte will hug the ground and pool in low places.

* With an average molecular weight of 28.964 amu for dry air.

Table 4. Analytes ordered by relative density.

Analyte	CAS Number	Formula	Weight amu	Relative Density
Tributyl phosphate	126-73-8	$C_{12}H_{27}O_4P$	266.36	9.20
Tridecane	629-50-5	$C_{13}H_{28}$	184.41	6.37
Dodecane	112-40-3	$C_{12}H_{26}$	170.38	5.88
Carbon tetrachloride	56-23-5	CCl_4	153.81	5.31
Trichlorofluoromethane	75-69-4	CCl_3F	137.36	4.74
Naphthalene	91-20-3	$C_{10}H_8$	128.18	4.43
Nonane	111-84-2	C_9H_{20}	128.29	4.43
Chloroform	67-66-3	$CHCl_3$	119.37	4.12
2-Butoxyethanol	111-76-2	$C_6H_{14}O_2$	118.20	4.08
n-Butyl acetate	123-86-4	$C_6H_{12}O_2$	116.18	4.01
Ethyl butyl ketone	106-35-4	$C_7H_{14}O$	114.21	3.94
Dipropyl ketone	123-19-3	$C_7H_{14}O$	114.21	3.94
Octane	111-65-9	C_8H_{18}	114.26	3.94
m-Xylene	108-38-3	C_8H_{10}	106.18	3.67
o-Xylene	95-47-6	C_8H_{10}	106.18	3.67
p-Xylene	106-42-3	C_8H_{10}	106.18	3.67
Heptane	142-82-5	C_7H_{16}	100.23	3.46
2-Hexanone	591-78-6	$C_6H_{12}O$	100.18	3.46
Vinylidene chloride	75-35-4	$C_2H_2Cl_2$	96.94	3.35
Sulfate	14808-79-8	O_3S	96.06	3.32
Toluene	108-88-3	C_7H_8	92.15	3.18
Ethyl acetate	141-78-6	$C_4H_8O_2$	88.12	3.04
n-Hexane	110-54-3	C_6H_{14}	86.20	2.98
Vinyl acetate	108-05-4	$C_4H_6O_2$	86.10	2.97
Methyl propyl ketone	107-37-9	$C_5H_{10}O$	86.15	2.97
Methylene chloride	75-09-2	CH_2Cl_2	84.93	2.93
Sulfur trioxide	7446-11-9	SO_3	80.06	2.76
Benzene	71-43-2	C_6H_6	78.12	2.70
Carbon disulfide	75-15-0	CS_2	76.13	2.63
n-Butyl alcohol	71-36-3	$C_4H_{10}O$	74.14	2.56
2-Butanone	78-93-3	C_4H_8O	72.12	2.49
Butyraldehyde	123-72-8	C_4H_8O	72.12	2.49

Pentane	109-66-0	C ₅ H ₁₂	72.15	2.49
Tetrahydrofuran	109-99-9	C ₄ H ₈ O	72.12	2.49
Butyronitrile	109-74-0	C ₄ H ₇ N	69.12	2.39
Sulfur dioxide	7446-09-5	O ₃ S	64.06	2.21
Nitrate	14797-55-8	NO ₃	62.00	2.14
Acetone	67-64-1	C ₃ H ₆ O	58.09	2.01
Butane	106-97-8	C ₄ H ₁₀	58.14	2.01
Propionitrile	107-12-0	C ₃ H ₅ N	55.09	1.90
Butadiene	106-99-0	C ₄ H ₆	54.10	1.87
Ozone	10028-15-6	O ₃	48.00	1.65
Nitrogen dioxide	10102-44-0	NO ₂	46.01	1.59
Acetonitrile	75-05-8	C ₂ H ₃ N	41.06	1.42
Nitric oxide	10102-43-9	NO	30.01	1.04
Carbon monoxide	630-08-0	CO	28.01	0.97

4. VAPOR PRESSURES

Table 5 gives the known vapor pressures of the Analytes at 25°C. Most of the vapor pressures have been calculated from the Antoine constants provided by Dean.⁶ Values for Butyronitrile and Dipropylketone are from Ohe,⁷ and the value for Ethyl butyl ketone (3-Heptanone) is an average of Jordan's values⁸ for 2-Heptanone and 4-Heptanone. The calculated values agree well with available measured data.⁹ The vapor pressure of Nitrate is not known* but is probably similar to Nitrogen trioxide. Similarly, the vapor pressure of Sulfate is not known but is probably similar to Sulfur trioxide.

The higher the vapor pressure the more volatile, and potentially dangerous, a chemical is. A particularly dangerous chemical would have both a high vapor pressure and a high relative density. Again, the darker the shading, the less dangerous the chemical, all other things being equal.

* Estimated values in the tables are enclosed in square brackets.

Table 5. Analytes ordered by Vapor Pressure.

Analyte	Vapor Pressure Torr
Nitric oxide	2.596(+6)
Carbon monoxide	4.994(+5)
Ozone	6.842(+4)
Nitrogen dioxide	4.825(+4)
Carbon disulfide	9.591(+3)
Ammonia	7.377(+3)
Sulfur dioxide	2.942(+3)
Nitrate	[2.479(+3)]
Butadiene	2.105(+3)
Butane	1.821(+3)
Nitrogen tetroxide	9.073(+2)
Trichlorofluorometha	7.971(+2)
Vinylidene chloride	5.910(+2)
Pentane	5.319(+2)
Methylene chloride	4.400(+2)
Sulfur trioxide	2.599(+2)
Sulfate	[2.599(+2)]
Acetone	2.309(+2)
Chloroform	1.941(+2)
Tetrahydrofuran	1.621(+2)
n-Hexane	1.514(+2)
Vinyl acetate	1.148(+2)
Butyraldehyde	1.109(+2)
Carbon tetrachloride	1.053(+2)
Benzene	9.518(+1)
Ethyl acetate	9.463(+1)
Acetonitrile	9.234(+1)
2-Butanone	9.043(+1)
Propionitrile	4.605(+1)
Heptane	4.570(+1)
Methyl propyl ketone	3.530(+1)
Toluene	2.844(+1)

<i>Butyronitrile</i>	2.003(+1)
Ocatane	1.395(+1)
<i>n-Butyl acetate</i>	1.080(+1)
p-Xylene	3.757(+0)
m-Xylene	3.300(+0)
o-Xylene	6.617(+0)
n-Butyl alcohol	6.173(+0)
2-Hexanone	6.006(+0)
Nonane	4.232(+0)
Ethyl butyl ketone	1.350(+0)
Dipropyl ketone	1.175(+0)
2-Butoxyethanol	7.179(-1)
Naphthalene	1.819(-1)
Dodecane	1.132(-1)
Undecene	3.320(-2)

5. FIRE AND EXPLOSION HAZARDS

The fire hazard for open air situations is determined by the flash point (FP) which is the temperature to which a material must be heated before the vapors will ignite by a free flame in the presence of air. The known flash points¹¹ for all the Analytes are given in Table 6, as is the U.S. Department of Transportation (DOT) Code:¹²

<i>Extremely Flammable (EF)</i>	$70^{\circ}\text{F} < \text{FP}$
<i>Flammable (F)</i>	$70^{\circ}\text{F} \leq \text{FP} \leq 100^{\circ}\text{F}$
<i>Combustible (C)</i>	$100^{\circ}\text{F} \leq \text{FP} \leq 200^{\circ}\text{F}$
<i>Nonflammable (NF)</i>	$200^{\circ}\text{F} < \text{FP}$

Of the forty-seven Analytes, nineteen are extremely flammable and seven are flammable, i.e., slightly over half are potential fire hazards, although this hazard is minimized in the open air where the concentrations cannot build up.

The explosion hazard potential is given by the Lower Explosive Limit (LEL) and the Upper Explosive Limit (UEL) which are the lowest and highest percentages of the chemical in air that, in the presence of a spark or flame, can cause an explosive combustion. The known values¹¹ are also given in Table 6 with a qualitative assessment (the "hazard concern") of the explosive danger. Of course, the danger is often increased, sometimes dramatically, if highly reacting chemicals are present. Of the forty-seven Analytes, eight are particularly dangerous. However, all the explosive limits are so high that the danger in open air must be considered to be very low under most circumstances.

Table 6. Analytes ordered by fire and explosive hazards.

Analyte	Fire		Explosion		
	FP °F	DOT Code	LEL %	UEL %	Hazard Concern
<i>Carbon disulfide</i>	-22	<i>EF</i>	1.3	50.0	severe
Octane	56	<i>EF</i>	1.0	4.7	severe
Pentane	<-40	<i>EF</i>	1.5	7.8	severe
<i>Vinyl acetate</i>	18	<i>EF</i>	2.6	13.4	severe
n-Hexane	-9	<i>EF</i>	1.2	7.5	very high
Butane	-76	<i>EF</i>	1.9	8.5	high
Acetone	0	<i>EF</i>	2.6	12.8	moderate
Acetonitrile	42	<i>EF</i>	4.4	16.0	moderate
<i>Ethyl acetate</i>	24	<i>EF</i>	2.2	11.0	moderate
Heptane	25	<i>EF</i>	1.0	6.7	moderate
Methyl propyl ketone	45	<i>EF</i>	1.5	8.2	moderate
Tetrahydrofuran	1	<i>EF</i>	1.8	11.8	moderate
Toluene	40	<i>EF</i>	1.3	7.0	moderate
Vinylidene chloride	0	<i>EF</i>	7.3	16.0	moderate
o-Xylene	63	<i>EF</i>	1.0	6.0	moderate
Benzene	12	<i>EF</i>	1.4	8.0	low
Butadiene	-105	<i>EF</i>	2.0	11.5	low
<i>Butyraldehyde</i>	20	<i>EF</i>	2.5	12.5	low
<i>Propionitrile</i>	36	<i>EF</i>	3.1		low
2-Hexanone	95	F	1.2	8.0	high
<i>n-Butyl acetate</i>	72	F	1.4	7.5	moderate
n-Butyl alcohol	95	F	1.4	11.2	moderate
Nonane	88	F	0.8	2.9	moderate
m-Xylene	77	F	1.1	7.0	moderate
p-Xylene	77	F	1.1	7.0	moderate
<i>Butyronitrile</i>	79	F			
Naphthalene	174	C	0.9	5.9	moderate

<i>2-Butoxyethanol</i>	160	C			
<i>Dipropylketone</i>	120	C			
Dodecane	160 ⁶	C			
Ethyl butyl ketone	115	C			
<i>Tridecane</i>	174 ⁶	C			
Carbon monoxide		NF	12.5	74.2	severe
Ammonia		NF	16.0	25.0	moderate
Methylene chloride		NF	15.5	66.4	low
Carbon tetrachloride		NF			
Chloroform		NF			
Nitric oxide		NF			
Nitrogen dioxide		NF			
Ozone		NF			
<i>Sulfur dioxide</i>		NF			
<i>Sulfur trioxide</i>		NF			
Tributyl phosphate	295	NF			
Trichloroflouromethane		NF			
2-Butanone					
Nitrate					
Sulfate					

6. HEALTH HAZARDS

Open air situations are primarily concerned with health effects. A measure of the danger from a chemical is given by the *Threshold Limit Value—Time-Weighted Average* (TWA) in parts per million by volume at 25°C and 760 Torr as specified by the American Conference of Governmental Industrial Hygienists (ACGIH). Nearly all workers may be repeatedly exposed to the TWA value, day after day for a normal 8-hour workday and 40-hour workweek, without adverse effect. Supplemental measures are the *Short-Term Exposure Limit* (STEL) and the *Ceiling Limit* (CL). Workers can experience for fifteen minutes the STEL value without adverse effects, provided the TWA is not exceeded. The CL concentration is that value which should never be exceeded.

Table 7 contains established TWA and STEL values.* The TWA values in brackets are postulated to be the same as similar compounds, e.g., the Dodecane and Tridecane TWAs to be the same as the Tributyl phosphate value, the Butyraldehyde TWA to be the same as n-Butyl alcohol, and the Butyronitrile TWA to be the same as the Propionitrile value. Furthermore, when the STEL value is known but not the TWA value, 80% of the STEL value is assigned to the TWA value.

Table 7 also states if a chemical is a poison or a narcotic and its qualitative degree of toxicity.¹¹ The chemical's carcinogenicity potential is denoted by "confirmed" if it has been proven capable of causing cancer in exposed humans, by "suspected" if the

*All entries in Table 7 are from reference 11 unless noted otherwise. The TWA and STEL concentrations are the ACGIH values, except for the values in { } which are OSHA values. When the STEL value is not known, the CL value, if known, is given in parentheses.

evidence is suggestive but not yet sufficient to constitute proof, and by "questionable" if there is minimal published evidence of possible carcinogenic activity. Complete descriptions of the health effects and symptoms are given in references 10-14.

Table 7. Analytes ordered by TWA.

Analyte	Carcinogen	Toxicity	Poison/ Narcotic	TWA ppm	STEL ppm
<i>Ozone</i>			Poison	0.05 ¹⁰	0.2 ¹⁰
Tributyl phosphate		Moderate		0.2	
Dodecane	Questionable			[0.2]	
<i>Tridecane</i>				[0.2]	
Benzene	Confirmed		Poison	0.3 ¹⁰	5
<i>Sulfur dioxide</i>	Questionable		Poison	2	5
<i>Sulfur trioxide</i>			Poison	[2]	
<i>Sulfate</i>				[2]	
Nitrogen dioxide		Moderate	Poison	3	5
<i>Nitrate</i>				[3]	
Carbon tetrachloride	Suspected	Mild	Narcotic	5	30
2-Hexanone		Mild		5	
Vinylidene chloride	Suspected		Poison	5	20
<i>Propionitrile</i>		Moderate		6	
<i>Butyronitrile</i>		Moderate	Poison	8	
<i>Carbon disulfide</i>		Mild	Poison	10	{12}
Chloroform	Suspected		Poison	10	
Naphthalene	Questionable		Poison	10	15
<i>Vinyl acetate</i>	Suspected			10	10
Butadiene	Suspected			10	
<i>n-Butyl acetate</i>		Mild		20 ¹⁰	200
<i>2-Butoxyethanol</i>		Moderate	Poison	25	
Carbon monoxide		Mild		25	

Ammonia			Poison	25	35
Nitric oxide			Poison	25	
Acetonitrile		Moderate		40	60
n-Butyl alcohol		Moderate		[40]	(50)
Butyraldehyde		Moderate		[40]	
n-Hexane		Slight		50	
Methylene chloride	Suspected	Mild		50	
Toluene		Mild		50	
Dipropylketone		Moderate		50	
Ethyl butyl ketone		Moderate		50	
m-Xylene		Mild		100	150
o-Xylene		Mild		100	150
p-Xylene		Mild		100	150
2-Butanone				200 ¹⁰	300 ¹⁰
Methyl propyl ketone		Mild		200	250
Nonane		Mild		200	
Tetrahydrofurn		Mild	Narcotic	200	250
Octane			Narcotic	300	375
Ethyl acetate			Poison	400	
Heptane			Narcotic	400	500
Pentane			Narcotic	600	750
Acetone		Moderate		750	1000
Butane		Mild		800	
Trichloroflouromethane			Poison	[800]	1000

7. HAZARD RATINGS

The exact degree of danger posed by a chemical is scenario dependent: is the chemical inhaled or absorbed through the skin? Is it near an open flame? Can it pool in a low or enclosed location where it can reach explosive concentrations? However, it is useful to rank chemicals relative to each other based on their hazardous properties under normal atmospheric conditions.

To determine a meaningful and quantifiable hazardous rating we note that the higher the vapor pressure, the more likely the chemical will be present in the air. Furthermore, the higher the density the more likely the chemical will pool and the less likely it will be dispersed. A particularly dangerous chemical would have both a high vapor pressure and a high relative density, as well as a low TWA resulting from deleterious health effects. Based on these relationships, we can postulate for each gas a "*Hazardous Atmosphere Rating (HAR)*" as the ratio of the vapor pressure-density product to the TWA. Thus, the HARs have units of Torr/ppm.

HARs are given in Table 8 along with the vapor pressure, relative density, and TWA values from previous sections. The highest vapor pressure is 760 Torr since we are concerned here with open air situations. The higher the HAR, the more dangerous the chemical — all other things being equal. Thus, Ozone, Benzene, the nitrogen oxides, and the sulfur oxides are particularly dangerous, as are Vinylidene chloride, Carbon disulfide, Butadiene, and Carbon tetrachloride. The Ozone HAR is anomalously large and would seem to indicate that its exposure limit (TWA) is about twenty times too low relative to the danger it poses in the open atmosphere.

Table 8 also includes two other hazard ratings. The Hazard Rating (HR) in column 6 is a three number rating system which roughly identifies the level of the toxicity or hazard:

HR = 3 The material is explosive, highly flammable, or highly reactive

HR = 2 The material is flammable or reactive

HR = 1 The material is combustible or presents some reactivity hazard

Not surprisingly, over 80% of the Analytes have HR values of 3, i.e., very dangerous.¹¹

The other hazardous rating is based entirely on the chemical's toxicity and is restricted to the Environmental Protection Agency's list of Hazardous Air Pollutants (HAPs). This HAP weighting factor, the last column in Table 8, is a five number rating system which goes from 1 (least dangerous) to 100,000 (most dangerous) in multiples of 10. Of the fifteen HAPs included in the forty-seven Analytes, four are listed as fairly dangerous (HAP = 10) and eleven are listed as slightly dangerous (HAP = 1).¹²

Table 8. Analytes ordered by Hazardous Atmosphere Rating.

Analyte	Pressure Torr	Relative Density	TWA ppm	HAR	HA	HAP
<i>Ozone</i>	760	1.7	0.05	25,230.0	3	
Benzene	95	2.7	0.3	856.6	3	10
<i>Sulfur dioxide</i>	760	2.2	2	839.8	3	
<i>Nitrate</i>	760	2.1	3	542.1	3	
<i>Sulfate</i>	260	3.3	2	431.4		
Nitrogen dioxide	760	1.6	3	402.8	3	
Vinylidene chloride	591	3.4	5	396.0	3	10
<i>Sulfur trioxide</i>	260	2.8	2	358.7	3	
<i>Carbon disulfide</i>	760	2.6	10	199.9	3	1
Butadiene	760	1.9	10	142.1	3	10
Carbon tetrachloride	105	5.3	5	111.8	3	1
Chloroform	194	4.1	10	80.0	3	1
<i>Vinyl acetate</i>	115	3.0	10	34.1	3	1
Nitric oxide	760	1.0	25	31.6	3	
Carbon monoxide	760	1.0	25	29.5	3	
Methylene chloride	44	2.9	50	25.8	3	1
Ammonia	760	0.6	25	17.9	3	
<i>Propionitrile</i>	46	1.9	6	14.6	3	
n-Hexane	151	3.0	50	9.0	3	1
<i>Butyraldehyde</i>	111	2.5	40	6.9	3	
<i>Butyronitrile</i>	20	2.4	8	6.0	3	
Trichlorofluoromethane	760	4.7	800	4.5	2	
2-Hexanone	6	3.5	5	4.2	3	
Dodecane	0	5.9	0.2	3.5	3 ¹³	
Acetonitrile	92	1.4	40	3.3	3	10
<i>n-Butyl acetate</i>	11	4.0	20	2.2	3	
Pentane	532	2.5	600	2.2	3	
Tetrahydrofuran	162	2.5	200	2.0	3	

Butane	760	2.0	800	1.9	1	
Toluene	28	3.2	50	1.8	3	1
2-Butanone	90	2.5	200	1.1	2	
<i>Tridecane</i>	0	6.4	0.2	1.1	2 ¹³	
<i>Ethyl acetate</i>	95	3.0	400	0.7	3	
Acetone	231	2.0	750	0.6	3	
Methyl propyl ketone	35	3.0	200	0.5	3	
n-Butyl alcohol	6	2.6	40	0.4	3	
Heptane	46	3.5	400	0.4	3	
m-Xylene	8	3.7	100	0.3	3	1
p-Xylene	9	3.7	100	0.3	3	1
o-Xylene	7	3.7	100	0.2	3	1
Octane	14	3.9	300	0.2	3	
Naphthalene	0	4.4	10	0.1	3	1
<i>2-Butoxyethanol</i>	1	4.1	25	0.1	3	
<i>Dipropylketone</i>	1	3.9	50	0.1	2	
Ethyl butyl ketone	1	3.9	50	0.1	2	
Nonane	4	4.4	200	0.1	3	
Tributylphosphate	0	9.2	0.2	0.0	3	

8. INFRARED SPECTRA

Having obtained a list of Analytes, it is important to determine which Analytes will be detectable by the Thermal Emission — Laser Absorption (TELA) Atmospheric Pollution Monitor being developed on this contract. The analysis presented here compares known Analyte spectra with the detection wavelengths of the TELA Monitor. In this first examination of the spectra, atmospheric interferences and system performance are not included. A detailed examination will be given in a later report where they will be included.

The TELA Pollution Monitor uses a CO₂ laser for atmospheric spectral absorption measurements in the 1090-926 cm⁻¹ region and an acousto-optic tunable filter (AOTF) for atmospheric spectral emission measurements in the 5000-714 cm⁻¹ region. From these wavelengths, Table 9 shows which Analytes have spectra within the AOTF detection range and which Analytes have spectra within the CO₂ laser detection ranges of existing CO₂ lidar systems^{16,17}. For the known infrared spectra, we use the digitized spectra data base from Infrared Analysis, Inc.¹⁸ or the FTIR vapor phase spectra published by Aldrich,¹⁹ unless otherwise noted. The specific chapter, denoted by a capital letter, in the Infrared Analysis data set is given in the last column. Barring atmospheric interferences, it would appear that:

- *The TELA Monitor can detect all 47 Analytes by thermal emission*
- *The TELA Monitor can detect 27 Analytes by laser absorption*

Furthermore, we already have 33 digitized spectra for real time analysis.

Table 9. Monitor detection of Analytes ordered by HAR.

Analyte	Detection by Thermal Emission	Detection by Laser Absorption	Digital Spectra Chapter
<i>Ozone</i>	yes	yes	F
Benzene	yes	yes	D
<i>Nitrate</i> ²⁰	yes	yes	
<i>Sulfate</i> ⁶	yes	yes	
Nitrogen dioxide	yes		M
Vinylidene chloride	yes	yes	R
<i>Sulfur trioxide</i>	yes		
<i>Sulfur dioxide</i>	yes	yes	O
<i>Carbon disulfide</i>	yes		O
Butadiene	yes	yes	A
Carbon tetrachloride	yes		P
Chloroform	yes		P
<i>Vinyl acetate</i>	yes	yes	K
Nitric oxide	yes		M
Carbon monoxide	yes		F
Methylene chloride	yes		P
Ammonia	yes	yes	E
<i>Propionitrile</i>	yes		
n-Hexane	yes	yes	C
<i>Butyraldehyde</i>	yes	yes	H
<i>Butyronitrile</i>	yes		
Trichlorofluoromethane	yes	yes	P
2-Hexanone	yes		
Dodecane	yes		
Acetonitrile	yes	yes	N
<i>n-Butyl acetate</i>	yes	yes	K
Pentane	yes	yes	B

Tetrahydrofuran	yes		F
Butane	yes	yes	A
Toluene	yes	yes	D
2-Butanone	yes	yes	I
Tridecane	yes		
Ethyl acetate	yes	yes	K
Acetone	yes		I
Methyl propyl ketone	yes	yes	
n-Butyl alcohol	yes	yes	J
Heptane	yes		C
m-Xylene	yes	yes	D
p-Xylene	yes	yes	D
o-Xylene	yes	yes	D
Octane	yes		C
Naphthalene	yes		
2-Butoxyethanol	yes	yes	
Dipropylketone	yes	yes	
Ethyl butyl ketone	yes	yes	
Nonane	yes		
Tributylphosphate	yes		T

9. ANALYTES OF CONCERN TEST LIST

Although forty-seven Analytes have been identified, the TELA Monitor will not be tested against all the Analytes since, within the schedule and financial constraints, this would over-emphasize spectra comparisons and under-emphasize optimization of the system design. A subset of the complete list will adequately test the TELA Monitor.

In determining a good Analytes of Concern Test List, it is important to include those Analytes which (1) are very hazardous and (2) have a relatively high probability of being present. Furthermore, the list should include some Analytes which will test the absorption spectra detection mode of the TELA Monitor in addition to the emission spectra detection mode. The HAR rating quantifies the potential hazard and the number, N_i , of tanks in which they have been detected quantifies their probability of detection. We therefore determine the Test List by ranking the Analytes by their THAR value where

$$THAR = N_i * HAR,$$

and considering only Analytes of Concern, i.e., only those Analytes which have been detected in more than one of the eight tanks used for measurements.

The Analytes of Concern Test List, the Analytes of Concern which have THAR values of 9 or higher, is given in Table 10 and all other Analytes, ordered by their THAR values, are given in Table 11. For convenience, the information from Table 9 is included in these tables. Sixteen Analytes of Concern comprise the Analytes of Concern Test List, a number which is reasonably large for test purposes. Of the

sixteen Test Analytes, nine will be identified by laser absorption spectra and all sixteen by thermal emission spectra. Furthermore, we already have digitized spectra for fifteen Test Analytes — spectra needed for real time Analyte identification — which means that detailed spectra analysis can proceed immediately. Digitized spectra measurements will be obtained in the laboratory for 2-Hexanone.

Table 10. Analytes of Concern Test List.

Analyte	THAR	Detection by Thermal Emission	Detection by Laser Absorption	Digital Spectra Chapter
Benzene	5996	yes	yes	D
Vinylidene chloride	1980	yes	yes	R
Nitrogen dioxide	1208	yes		M
Carbon tetrachloride	894	yes		P
Butadiene	710	yes	yes	A
Chloroform	240	yes		P
Methylene chloride	103	yes		P
Carbon monoxide	88	yes		F
Ammonia	72	yes	yes	E
Nitric oxide	63	yes		M
n-Hexane	45	yes	yes	C
Trichlorofluoromethane	22	yes	yes	P
2-Hexanone	17	yes		
Toluene	11	yes	yes	D
Acetonitrile	10	yes	yes	N
Pentane	9	yes	yes	B

Table 11. Other Analytes ordered by THAR.

Analyte	THAR	Detection by Thermal Emission	Detection by Laser Absorption	Digital Spectra Chapter
<i>Ozone</i>	25230	yes	yes	F
<i>Sulfur dioxide</i>	840	yes	yes	O
<i>Nitrate</i>	542	yes	yes	
<i>Sulfate</i>	431	yes	yes	
<i>Sulfur trioxide</i>	359	yes		
<i>Carbon disulfide</i>	200	yes		O
<i>Vinyl acetate</i>	34	yes	yes	K
<i>Propionitrile</i>	15	yes		
<i>Butyraldehyde</i>	7	yes	yes	H
<i>Dodecane</i>	7	yes		
<i>Butane</i>	6	yes	yes	A
<i>Butyronitrile</i>	6	yes		
<i>Acetone</i>	4	yes		I
<i>Tetrahydrofuran</i>	4	yes		F
<i>2-Butanone</i>	3	yes	yes	I
<i>n-Butyl acetate</i>	2	yes	yes	K
<i>n-Butyl alcohol</i>	2	yes	yes	J
<i>Heptane</i>	2	yes		C
<i>Methyl propyl ketone</i>	2	yes	yes	
<i>m-Xylene</i>	2	yes	yes	D
<i>p-Xylene</i>	2	yes	yes	D
<i>Ethyl acetate</i>	1	yes	yes	K
<i>Octane</i>	1	yes		C
<i>Tridecane</i>	1	yes		
<i>o-Xylene</i>	1	yes	yes	D
<i>2-Butoxyethanol</i>	0	yes	yes	
<i>Dipropylketone</i>	0	yes	yes	
<i>Ethyl butyl ketone</i>	0	yes	yes	
<i>Naphthalene</i>	0	yes		
<i>Nonane</i>	0	yes		
<i>Tributyl phosphate</i>	0	yes		T

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