Test Set of Gaseous Analytes at Hanford Tank Farms

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ABSTRACT

DOE has stored toxic and radioactive waste materials in large underground tanks. 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 to monitor the open air space above these tanks.

In developing this infrared spectra monitor as a safety alert instrument, it is important to know what hazardous gases, called the Analytes of Concern, are most likely to be found in dangerous concentrations. The monitor must also consider other gases which could interfere with measurements of the Analytes of Concern. The total list of gases is called the Test Set Analytes because they form the basis for testing the pollution monitor in future field tests at the DOE Hanford Site.

Prior measurements in 54 tank headspaces have detected 102 toxic air pollutants (TAPs) and over 1000 other analytes. The hazardous Analytes are ranked herein by a "Hazardous Atmosphere Rating" which combines their measured concentration, their density relative to air, and the concentration at which they become dangerous. The top 20 toxic air pollutants, as ranked by the Hazardous Atmosphere Rating, and the top 20 other analytes, in terms of measured concentrations, are analyzed for possible inclusion in the Test Set Analytes. Of these 40 gases, 20 are selected.

To these 20 gases are added the 6 omnipresent atmospheric gases with the highest concentrations, since their spectra could interfere with measurements of the other spectra. The 26 Test Set Analytes are divided into a Primary Set and a Secondary Set. The Primary Set, *gases which must be detectable by the monitor*, includes the 6 atmospheric gases and the 6 hazardous gases which have been measured at dangerous concentrations. The Secondary Set gases need not be monitored at this time.

The infrared spectra, barring atmospheric interferences, indicates that:

- *The pollution monitor will detect all 26 Test Set Analytes by thermal emission*
- *The pollution monitor will detect 15 Test Set Analytes by laser absorption*

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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".

Figure 1 -- A typical underground double-shell waste storage tank is very large and contains toxic vapors which can vent to the open atmosphere.

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, called the Thermal Emission, Laser Absorption (TELA) 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 — there are simply too many — and since all of the candidate gases are not equally dangerous, a focused list of analytes is determined from the most comprehensive list of gases measured in the tank headspaces. To keep the pollution monitor development effort within reasonable limits the list must not be too large but must include gases which exist in relatively high concentrations in the Hanford tank headspaces and in the Hanford above-ground air.

It is this selected set of analytes, the “Analyte Test Set”, 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 to be in the headspaces. To this list of hazardous gases are added those gases whose concentrations are sufficiently high that their spectra may interfere with the measurements of the hazardous gas spectra. The open-path atmospheric monitor is being designed under this contract to detect the hazardous analytes at concentration levels below those which would adversely affect the health of personnel in the area.

Chapter 2 examines gas measurements in the Hanford tank headspaces. In particular, the twenty toxic air pollutants (TAPs) with the highest measured concentrations and the twenty TAPs with the highest danger rankings are listed. The chapter concludes with twenty additional gases which have the highest mass densities and with sixteen naturally occurring atmospheric gases. Each hazardous gas is rated according to the danger it presents.

From this information an Analytes Test Set of twenty-six gases is determined in Chapter 3. Chapter 4 details the hazards which the selected gases present to exposed personnel. These hazards include fire & explosion dangers from sixteen Analytes plus health effects from twenty-two Analytes.

Chapter 5 divides the twenty-six Analytes into a Primary Test Set and a Secondary Test Set. *The Primary Test Set of twelve Analytes must be monitored* whereas the Secondary Test Set of fourteen Analytes need not be monitored at this time. It is also shown that fifteen Analytes can likely be detected with the active lidar (laser absorption) and all twenty-six gases can likely be detected with the passive filter (thermal emission) operation of the TELA Monitor.

2. TANK HEADSPACE MEASUREMENTS

At least four Analytes of Concern lists have been compiled for the Hanford tank headspaces.¹⁻⁴ These four sources identified 47 hazardous vapors which have been detected in at least two tanks and 15 more which have detected in only one tank. From these lists we compiled an early version of an Analytes of Concern Test List which we detailed in a DOE Topical Report⁵ on this contract and included as part of a paper⁶ delivered at the 1996 Instrument Society of America Analysis Division Symposium.

In a visit to Hanford in June 1996, Jim Huckaby⁷ provided two comprehensive lists of analytes which have had their concentrations measured in the Hanford tank headspaces. The first list includes 102 toxic air pollutants and the second list includes 1068 "Tank Chemicals". The lists have a few duplications. The TAP list is composed of particularly hazardous vapors. These two lists were used for the analysis in this report.

2.1 Ecology-Affecting Toxic Air Pollutants

The Huckaby list of toxic air pollutants includes 102 vapors rated not by their hazardous properties but by their measured concentration relative to their ASIL value. This value is the *Acceptable Source Impact Limit* which, in a peculiar line of reasoning by the Washington State Department of Ecology, is based on environmental effects — not on health or danger effects. In particular, the ASIL is that concentration which does not significantly impact the public environment. For example, if the concentration of carbon tetrachloride is 1.07×10^{-5} ppm in the general air surrounding the Hanford Site, then any carbon tetrachloride released by the Hanford Site cannot significantly change this concentration. In particular, the limit applies to a 24 hour average at outdoor campgrounds and to annual averages at residential areas. Four aspects of this limit are:

- ASIL values are generally extremely low and therefore very hard to measure
- ASIL values are measured where they impact the public
- ASIL values have little connection to the hazard they present to the public
- ASIL values have no connection to the hazard presented to Hanford personnel

The second aspect means that TAP concentrations must be below ASIL values where they impact the public, e.g., on public roads or farms nearest the Hanford Site. The last two aspects are evident when ASIL concentrations are compared to hazardous concentrations.

Table 1 lists the twenty TAPs which have been measured in a tank headspace with the highest concentrations relative to their ASIL values. The Chemical Abstract Service (CAS) Registry number is given for each analyte. The third column gives the number of tanks in which the analyte has been measured. The average and maximum concentrations measured in the tanks are in the fourth and fifth columns. The last two columns give the ASIL value and the ratio of the maximum measured concentration relative to the ASIL concentration, respectively.

Table 1 - Hanford tank TAPs with the highest concentrations (relative to ASIL values).

TAP	CAS #	No. of Tanks	Average ppm	Max. ppm	ASIL ppm	Max. / ASIL
N-Nitrosodimethylamine	62-75-9	12	3.70E-2	8.96E-2	2.35E-8	3.82E+6
Butadiene	106-99-0	12	5.36E-2	1.90E-1	1.64E-6	1.16E+5
Carbon tetrachloride	56-23-5	8	5.16E-2	3.47E-1	1.07E-5	3.25E+4
Benzene	71-43-2	46	3.59E-2	6.93E-1	3.77E-5	1.84E+4
Methylene chloride	75-09-2	36	1.20E-1	1.88E+0	1.61E-4	1.17E+4
Ammonia	7664-41-7	54	2.23E+2	1.14E+3	1.44E-1	7.93E+3
Tributyl phosphate	126-73-8	24	2.96E-1	5.22E+0	6.72E-4	7.77E+3
Ethylene oxide	75-21-8	1	2.89E-2	2.89E-2	5.57E-6	5.19E+3
Polychlorinated Biphenyls	1336-36-3	5	4.50E-6	1.59E-3	3.77E-7	4.22E+3
Ethylene dibromide	106-93-4	1	4.50E-6	2.39E-3	5.87E-7	4.07E+3
Chloroform	67-66-3	8	4.83E-3	1.68E-2	8.84E-6	1.90E+3
Dioxane	123-91-1	4	9.47E-3	1.68E-2	8.89E-6	1.89E+3
Acetaldehyde	75-07-0	16	9.06E-2	3.76E-1	2.51E-4	1.50E+3
Cyanide	57-12-5	49	5.78E-1	1.40E+1	1.60E-2	8.73E+2
Perchloroethylene	127-18-4	24	9.74E-3	1.14E-1	1.62E-4	7.02E+2
Biphenyl	92-52-4	3	1.93E-4	4.38E-1	6.83E-4	6.41E+2
Acrylonitrile	107-13-1	1	2.81E-3	2.81E-3	6.92E-6	4.06E+2
n-Butyl alcohol	71-36-3	52	2.79E+0	6.29E+1	1.65E-1	3.81E+2
2,6-Di-tert-butyl-p-cresol	128-37-0	2	3.27E-1	6.52E-1	3.66E-3	1.78E+2
Acetonitrile	75-05-8	49	5.71E-1	1.44E+1	1.31E-1	1.10E+2

The entries in Table 1 show that 54 tank headspaces have been sampled and that most of the analytes occur in many tanks. Furthermore, the ASIL values have a wide variation, from the extremely low value of 2.35×10^{-8} ppm for n-nitrosodimethylamine to 1.31×10^{-1} ppm for acetonitrile. With these low values, it is not surprising that the maximum concentrations measured in the tank headspaces exceed the ASIL values.

The numerical entries in Table 1, and in all other tables in this report, are given to three significant figures or less. Chemical names 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 Neal⁸ is given. Molecular formulas are ordered by the Hill system⁸ (order of symbols is carbon, hydrogen, and then alphabetical by element).

2.2 Health-Affecting Toxic Air Pollutants

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).⁹ Nearly all workers may be repeatedly exposed to the TWA value, day after day, for a normal 8-hour workday and a 40-hour workweek, without adverse effects.

To determine a meaningful and quantifiable hazardous rating for each chemical vapor, we note that the higher the vapor pressure, the more likely the chemical will be present at high concentrations in the air. Furthermore, the higher the density the more likely the chemical will pool, or collect, in low places and the less likely it will be

dispersed by wind. A particularly dangerous chemical would have both a high vapor pressure (expressed in ppm) and a high density (relative to dry air which has an average mass of 28.96 amu), as well as a low TWA value (in ppm) resulting from deleterious health effects. Based on these relationships, we define an unitless "**Hazardous Atmosphere Rating (HAR)**" for each chemical as:

$$HAR = (Concentration) * (Relative Density) / TWA \quad (1)$$

Note that gases with HAR values greater than 1.0 are potentially dangerous and that gases with HAR values less than 1.0 are not normally dangerous.

This rating equation is ideally suited to the open atmosphere in which there is no wind and the chemical vapor is in equilibrium with its liquid source. However, to be applicable to the Hanford tanks, the concentration in Eq. 1 should be the *measured* concentration in the tank since that will be the concentration* in any vapor release from the tank. In fact, whenever the vapor concentration is known from measurements, that is the value which should be used in Eq. 1.

Table 2 lists the twenty TAPs with the highest HAR values. The TWA values are predominately from reference 9 with a few from the R. J. Lewis Desk Reference¹⁰. Maximum concentrations measured in the tanks are used because the HAR values then represent the greatest danger from the tanks. Of the twenty TAPs listed, twelve also appear in Table 1. The largest to smallest HAR values differ by a factor of 3000, indicating a large variation in the potential danger these chemicals present.

Table 2 - Hanford tank TAPs with the highest HAR values.

TAP	CAS #	No. of Tanks	Average ppm	Max. ppm	TWA ppm	Max. HAR
Tributyl phosphate	126-73-8	24	2.96E-1	5.22E+0	0.2	240.00
Polychlorinated Biphenyls	1336-36-3	5	4.50E-6	1.59E-3	8E-5	191.00
Ammonia	7664-41-7	54	2.23E+2	1.14E+3	25	26.80
Biphenyl	92-52-4	3	1.93E-4	4.38E-1	0.2	11.70
2,6-Di-tert-butyl-p-cresol	128-37-0	2	3.27E-1	6.52E-1	1	4.96
n-Butyl alcohol	71-36-3	52	2.79E+0	6.29E+1	50	3.22
Cyanide	57-12-5	49	5.78E-1	1.40E+1	5	2.52
Acetonitrile	75-05-8	49	5.71E-1	1.44E+1	40	0.51
2-Hexanone	591-78-6	43	3.63E-2	6.44E-1	5	0.44
Carbon tetrachloride	56-23-5	8	5.16E-2	3.47E-1	5	0.37
Trimethylamine	75-50-3	1	6.88E-1	6.88E-1	10	0.28
Carbon disulfide	75-15-0	2	4.60E-1	8.65E-1	10	0.23
Diphenylamine	122-39-4	7	6.41E-3	3.31E-2	1	0.19
Benzene	71-43-2	46	3.59E-2	6.93E-1	10	0.19
1,3-Butadiene	106-99-0	12	5.36E-2	1.90E-1	2	0.18
Methyl ethyl ketone	78-93-3	40	4.83E-1	1.32E+1	200	0.16
Phenyl ether	101-84-8	2	1.32E-2	2.60E-2	1	0.15
Methylene chloride	75-09-2	36	1.20E-1	1.88E+0	50	0.11
Methylacrylonitrile	126-98-7	1	4.02E-2	4.02E-2	1	0.09
Ethyl acetate	141-78-6	3	3.70E+0	1.09E+1	400	0.08

*At least until it is dispersed by convection, diffusion, or wind

2.3 Other Tank Vapors

A comprehensive survey of tank vapors has detected 1068 chemicals.⁷ The twenty vapors with the highest mass densities, excluding TAPs listed in Tables 1 and 2, are listed in Table 3. This list includes most of the normally present atmospheric gases. The variation in concentrations is very large.

Table 3 - Additional Hanford tank vapors with the highest mass densities.

Gas	CAS #	No. of Tanks	Min. ppm	Average ppm	Max. ppm	Max. mg/m ³
Carbon dioxide	124-38-9	49	0.368	211.00	1560.0	2800.00
Nitrous oxide	10024-97-2	50	3.280	234.00	958.0	1720.00
Butyraldehyde	123-72-8	44	0.000	1.46	53.3	157.00
Hydrogen	1333-74-0	38	10.500	247.00	827.0	68.20
Tridecane	629-50-5	51	0.000	0.31	4.4	32.80
Acetone	67-64-1	61	0.008	0.94	10.8	25.70
Dodecane	112-40-3	50	0.000	0.23	3.5	24.10
Carbon monoxide	630-08-0	14	0.110	2.37	17.0	19.40
3-Butene-1-ol	627-27-0	2	0.026	3.12	6.2	18.20
Trichlorofluoromethane	75-69-4	59	0.001	0.21	3.2	17.90
2-methyl-Pentane	107-83-5	15	0.001	0.54	4.3	15.10
Tetradecane	629-59-4	41	0.000	0.17	1.8	14.70
7-Methyl-tridecane	26730-14-3	14	0.001	0.19	1.5	11.80
Undecane	1120-21-4	46	0.000	0.11	1.8	11.30
4,6-Dimethyl-dodecane	61141-72-8	7	0.003	0.38	1.2	9.60
Ethanol	64-17-5	43	0.000	0.47	5.0	9.44
Hexane	110-54-3	50	0.000	0.15	2.5	8.66
Methane	74-82-8	12	0.073	3.87	13.1	8.59
Furan, tetrahydro-decahydro-2-methyl-Napthalene	109-99-9	38	0.000	0.13	2.0	5.83
	2958-76-1	12	0.001	0.17	1.4	8.31

2.4 Atmospheric Gases

In measuring pollutant vapors in the open atmosphere, all monitors must contend with the omnipresent atmospheric gases which can significantly interfere with the measurement of pollutant concentrations or even their detection. Table 4 lists the atmospheric gases with nominal concentrations above 1 ppb. The gases fall naturally into two separate categories: (Category 1) atomic and homonuclear diatomic molecules, and (Category 2) all other molecules. Atmospheric gases in the first category are given in the left side of the table¹¹ and gases in the second category are given in the right side. This distinction is important because the Category 1 gases are so spatially symmetric that they do not have a permanent electric dipole. Without a permanent electric dipole, infrared transitions are very weak or nonexistent. Thus, Category 1 gases can be neglected.

Category 2 gases include all molecules of interest. The concentrations given here are from the U.S. Standard Model Atmosphere, 1976,¹² as presented by Anderson et al.¹³ for sea level conditions. As such, the concentrations given should be considered as nominal, or representative.

Table 4 - Category 1 (very weak infrared spectra) and Category 2 (extensive infrared spectra) atmospheric gases.

Category 1 Gases			Category 2 Gases			
Name	Formula	Nominal ppb	Name	Formula	CAS #	Nominal ppb
Nitrogen	N ₂	780 840 000	Water	H ₂ O	7732-18-5	7 750 000
Oxygen	O ₂	209 480 000	Carbon dioxide	CO ₂	124-38-9	330 000
Argon	Ar	9 340 000	Methane	CH ₄	74-82-8	1 700
Neon	Ne	18 200	Nitrous oxide	N ₂ O	10024-97-2	320
Helium	He	5 200	Carbon monoxide	CO	630-08-0	150
Krypton	Kr	1 100	Ozone	O ₃	10028-15-6	27
Hydrogen	H ₂	500	Formaldehyde	CH ₂ O	50-00-0	2
Xenon	Xe	100	Hydrogen chloride	HCl	7647-01-0	1

3. SELECTION OF ANALYTE TEST SET

It would be too expensive and time-consuming to test the TELA Monitor by measuring all the gases in the above tables. In down-sizing this list of gases, two choices are obvious: (1) eliminate all Category 1 gases since they do not effectively absorb in the infrared and (2) eliminate all gases which were measured in only one or two tanks since they are not very common.

Conversely, the TAP gases with high *HAR* values are the most important ones to include. From Table 2, there is a significant break in *HAR* values between cyanide and acetonitrile. We therefore include the seven TAPs from tributyl phosphate to cyanide, inclusive. We then add acetonitrile, methyl ethyl ketone, and ethyl acetate because their concentrations are sufficiently high that their spectra could interfere with those of the selected seven TAPs. To these ten we arbitrarily add those TAPs with concentrations over 10,000 times their ASIL values, i.e., the first five TAPs in Table 1. These five are the vapors of most concern for ecological reasons.

To this list of TAPs we add other gases which are not really of much interest except that their concentrations are sufficiently high that they could significantly interfere with the measurement of TAP concentrations. From Table 3 we add the eleven Category 2 gases with maximum concentrations above 3 ppm and from Table 4 we add the six Category 2 gases with nominal concentrations above 5 ppb.

Duplications reduce this list of thirty-two gases to twenty-eight gases but we must also eliminate mixtures since each component of the mixture has its own infrared spectra and must therefore be treated as a separate gas. Two mixtures are included in the above tables: polychlorinated biphenyls and cyanide. Both items, as reported in the Hanford tank headspace measurements, are really mixtures. Until their actual compositions are known, they cannot be included. However, both items include very dangerous vapors which should be included as Analytes of Concern once their compositions are known.

The final Analyte Test Set, or List, of twenty-six gases is given in Table 5. *TWA* values have not been determined for the last six analytes in Table 5, but all, excepting water, are known to be dangerous in certain concentrations. Their specific effects are given in the next chapter. Note that *maximum HAR* values were used to select the Test Set Analytes because they represent the highest danger which might be encountered. However, *average HAR* values are used to rank the Test Set Analytes because they represent the most probable danger which might be encountered.

On the average, only three Analytes occur in dangerous concentrations ($HAR > 1.0$): tributyl phosphate, ammonia, and 2,6-Di-tert-butyl-p-cresol. When maximum concentration measurements are considered (see Table 2), five Analytes occur in dangerous concentrations: the latter three gases plus biphenyl and n-butyl alcohol.

Table 5 - Analyte Test Set for TELA Atmospheric Pollution Monitor.
Analytes are ranked according to their average HAR value.

Analyte	Formula	Mass amu	Relative Density	Average ppm	TWA ppm	Average HAR
Tributyl phosphate	C ₁₂ H ₂₇ O ₄ P	266.36	9.20	2.96E-1	0.2	13.600
Ammonia	H ₃ N	17.04	0.59	2.23E+2	25	5.250
2,6-Di-tert-butyl-p-cresol	C ₁₅ H ₂₄ O	220.39	7.61	3.27E-1	1	2.490
Ozone	O ₃	48.00	1.66	2.70E-2	0.1	0.447
n-Butyl alcohol	C ₄ H ₁₀ O	74.14	2.56	2.79E+0	50	0.143
Carbon dioxide	CO ₂	44.01	1.52	3.30E+2	5 000	0.100
Carbon tetrachloride	CCl ₄	153.81	5.31	5.16E-2	5	0.055
Butadiene	C ₄ H ₆	54.10	1.87	5.36E-2	2	0.050
Ethyl acetate	C ₄ H ₈ O ₂	88.12	3.04	3.70E+0	400	0.028
Acetonitrile	C ₂ H ₃ N	41.06	1.42	5.71E-1	40	0.020
Nitrous oxide	N ₂ O	44.02	1.52	3.20E-1	50	0.010
Benzene	C ₆ H ₆	78.12	2.70	3.59E-2	10	0.010
Methylene chloride	CH ₂ Cl ₂	84.93	2.93	1.20E-1	50	0.007
Carbon monoxide	CO	28.01	0.97	1.50E-1	25	0.006
Methyl ethyl ketone	C ₄ H ₈ O	72.12	2.49	4.83E-1	200	0.006
Biphenyl	C ₁₂ H ₁₀	155.22	5.32	1.93E-4	0.2	0.005
Acetone	C ₃ H ₆ O	58.09	2.01	9.40E-1	750	0.003
2-methyl-Pentane	C ₆ H ₁₄	86.20	2.98	5.35E-1	500	0.003
Trichlorofluoromethane	CCl ₃ F	137.36	4.47	2.06E-1	1000	0.001
Ethanol	C ₂ H ₆ O	46.98	1.59	4.69E-1	1000	0.001
Water	H ₂ O	18.02	0.62	7.75E+3	---	---
Methane	CH ₄	16.05	0.55	1.70E+0	---	---
Butyraldehyde	C ₄ H ₈ O	72.12	2.49	1.46E+0	---	---
Tridecane	C ₁₃ H ₂₈	184.41	6.37	3.10E-1	---	---
Dodecane	C ₁₂ H ₂₆	170.38	5.88	2.26E-1	---	---
N-Nitrosodimethylamine	C ₆ H ₆ N ₂ O	74.10	2.56	3.70E-2	---	---

4. DANGEROUS ANALYTE PROPERTIES

Now that we have the Test Set Analytes, it is useful to briefly describe the dangerous properties of the Analytes. In particular: (1) their propensity to start or enhance fires, (2) their potential to explode, and (3) their toxicity properties. Various hazard ratings, based on these properties, are given for all the Analytes.

4.1 Fire and Explosive 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 points¹⁰ for all the Test Set Analytes are given* in Table 6, as is the U.S. Department of Transportation (DOT) Code:¹⁴

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

Dashes in the DOT Code column denote nonflammable vapors. Of the twenty-six Analytes, ten are extremely flammable and one is flammable, i.e., 42% 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 explosive combustion. Known values¹⁰ are given in Table 6 (dashes indicate no data). The "hazard concern" column grades the danger as low, moderate (Mod.), or **HIGH**, where dashes indicate a nonexplosive vapor. Of course, the danger is often increased, sometimes dramatically, if highly reacting chemicals are present. Ozone is a special case in that it becomes extremely explosive if it crystallizes or is highly concentrated through chemical reactions. Of the twenty-six Analytes, methane, carbon monoxide, and 2-methyl-Pentane 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.

Sixteen Test Set Analytes are flammable and/or explosive hazards.

* The polychlorinated biphenyls and cyanide mixtures are included in Tables 6 and 7 because they do pose a danger.

4.2 Health Hazards

Open air situations are primarily concerned with health effects. Each Test Set Analyte is categorized in Table 6 as a carcinogen, poison, or narcotic. It is also given a qualitative degree of toxicity.¹⁰ The chemical's carcinogenicity potential is denoted by "questionable (Q)" if there is minimal published evidence of possible carcinogenic activity, by "suspected (S)" if evidence is suggestive but not yet sufficient to constitute proof, and by "confirmed (C)" if it has been proven capable of causing cancer in humans. The poison or narcotic property is for the vapor form of the analyte. Technically, cyanide is not a poison but it forms the extremely poisonous HCN so quickly by so many different paths, that it is listed as a poison. Complete descriptions of the health effects and symptoms are given in reference 10 and references 14-17.

Twenty-Two Test Set Analytes are significant health hazards.

Table 6 - Hazardous properties of the Test Set Analytes.

Analyte	Fire		Explosion			Health		
	FP °F	DOT Code	LEL %	UEL %	Hazard Concern	Carcin -ogen	Toxicity	Poison/ Narcotic
Tributyl phosphate	295	---	---	---	---	---	Mod.	---
Ammonia	---	---	16.0	25.0	Mod.	---	---	P
2-6-Di-tert-butyl-p-cresol	260	---	---	---	---	Q	Mod.	---
Polychlorinated biphenyls	383	---	---	---	---	S	---	P
Ozone	---	---	---	---	---	Q	---	P
n-Butyl alcohol	95	F	1.4	11.2	Mod.	---	Mod.	---
Cyanide	---	---	---	---	---	---	HIGH	P
Carbon dioxide	---	---	---	---	---	---	---	---
Carbon tetrachloride	---	---	---	---	---	S	mild	N
Butadiene	-105	EF	2.0	11.5	Mod.	S	HIGH	---
Ethyl acetate	24	EF	2.2	11.0	Mod.	---	mild	P
Acetonitrile	42	EF	4.4	16.0	Mod.	---	Mod.	---
Nitrous oxide	---	---	---	---	Mod.	---	Mod.	---
Benzene	12	EF	1.4	8.0	low	C	Mod.	P
Methylene chloride	---	---	15.5	66.4	low	S	mild	---
Carbon monoxide	---	---	12.5	74.2	HIGH	---	mild	P
Methyl ethyl ketone	22	EF	1.8	11.5	low	---	Mod.	---
Biphenyl	235	---	0.6	5.8	low	Q	Mod.	---
Acetone	0	EF	2.6	12.8	Mod.	---	Mod.	---
2-methyl-Pentane	20	EF	1.0	7.0	HIGH	---	---	---
Trichlorofluoromethane	---	---	---	---	---	---	HIGH	---
Ethanol	56	EF	3.3	19.0	low	C	mild	---
Water	---	---	---	---	---	---	---	---
Methane	-369	EF	5.3	15.0	HIGH	---	---	---
Butyraldehyde	20	EF	2.5	12.5	low	---	Mod.	---
Tridecane	---	---	---	---	---	---	Mod.	---
Dodecane	---	---	---	---	---	Q	---	---
N-Nitrosodimethylamine	---	---	---	---	---	S	---	P

4.3 Hazard Ratings

Several measures of the danger from a chemical exist. One of the most-used measures is the *Time-Weighted Average (TWA)* noted above. 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 should never be exceeded. These measures for the Test Set Analytes are given in Table 7.^{9,10} Tributyl phosphate and ammonia are the only Analytes with average tank headspace concentrations exceeding their *TWA* value. However, n-butyl alcohol and biphenyl Analytes plus the polychlorinated biphenyls and cyanide mixtures have maximum tank headspace concentrations which exceed their *TWA* value. In other words, six Analytes have had dangerous concentration levels measured within the tanks. However, the other Analytes cannot be ignored because they could become concentrated in the open atmosphere due to wind conditions or chemical reactions.

Table 7 - Hazard ratings of the Test Set Analytes.

Analyte	Average ppm	Average HAR	TWA ppm	STEL ppm	HR	HAP
Tributyl phosphate	2.96E-1	13.600	0.2	---	3	
Ammonia	2.23E+2	5.250	25	35	3	
2,6-Di-tert-butyl-p-cresol	3.27E-1	2.490	1	---	2	
Polychlorinated biphenyls	4.50E-6	0.567	8E-5	---	3	---
Ozone	2.70E-2	0.447	0.1	0.1	3	
n-Butyl alcohol	2.79E+0	0.143	50	50	3	
Cyanide	5.78E-1	0.104	5	---	3	---
Carbon dioxide	3.30E+2	0.100	5 000	30 000	1	
Carbon tetrachloride	5.16E-2	0.055	5	10	3	1
Butadiene	5.36E-2	0.050	2	4.4	3	10
Ethyl acetate	3.70E+0	0.028	400	---	3	
Acetonitrile	5.71E-1	0.020	40	60	3	10
Nitrous oxide	3.20E-1	0.010	50	---	2	
Benzene	3.59E-2	0.010	10	32	3	10
Methylene chloride	1.20E-1	0.007	50	126	3	1
Carbon monoxide	1.50E-1	0.006	25	200	3	
Methyl ethyl ketone	4.83E-1	0.006	200	300	3	1
Biphenyl	1.93E-4	0.005	0.2	---	3	1
Acetone	9.40E-1	0.003	750	1000	3	
2-methyl-Pentane	5.35E-1	0.003	500	1000	3	
Trichlorofluoromethane	2.06E-1	0.001	1000	1000	2	
Ethanol	4.69E-1	0.001	1000	---	3	
Water	7.75E+3	---	---	---	0	
Methane	1.70E+0	---	---	---	3	
Butyraldehyde	1.46E+0	---	---	---	3	
Tridecane	3.10E-1	---	---	---	2	
Dodecane	2.26E-1	---	---	---	3	
N-Nitrosodimethylamine	3.70E-2	---	---	---	3	1

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. As noted before, a useful measure is the "*Hazardous Atmosphere Rating (HAR)*" which is the product of the concentration (in ppm) and the density (relative to air) divided by the *TWA* value (in ppm). The *HAR* values given in Table 7 indicate that tributyl phosphate, ammonia, and 2,6-Di-tert-butyl-p-cresol are particularly dangerous.

Table 7 includes two other hazard ratings. The Hazard Rating (HR) is a four number rating system which roughly identifies the level of the toxicity or hazard:

<i>HR = 3</i>	<i>The material is explosive, highly flammable, or highly reactive</i>
<i>HR = 2</i>	<i>The material is flammable or reactive</i>
<i>HR = 1</i>	<i>The material is combustible or presents some reactivity hazard</i>
<i>HR = 0</i>	<i>The material is not dangerous</i>

Not surprisingly, over 80% of the Analytes have HR values of 3, i.e., very dangerous.¹⁰

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 7, is a five number rating system which goes from 1 (least dangerous) to 100,000 (most dangerous) in multiples of 10. Of the ten HAPs included in Table 7, three are listed as fairly dangerous (HAP = 10), five are listed as slightly dangerous (HAP = 1) and two have not been assigned a weighting factor (---).¹⁴ Interesting enough, *some of the most dangerous Toxic Air Pollutants are not classified as Hazardous Air Pollutants*, probably due to their low concentrations in atmospheres normally encountered by the general population.

5. PRIMARY AND SECONDARY TEST SETS

It is apparent from the hazardous ratings that not all of the twenty-six Analytes are dangerous in the concentrations which have been measured in the tank headspaces. In fact, the twenty-six Analytes can be divided into two Test Sets — a Primary Test Set which must be monitored and a Secondary Test Set which need not be monitored at this time. Furthermore, it is important to know for the operation of the TELA Monitor if the active or the passive subsystem will be able to measure the individual Analyte concentrations. This determination is obtained from a preliminary examination of the infrared spectrum of each Analyte.

5.1 TEST SETS

The twenty-six gas Analyte Test Set is reproduced in Table 8 but is divided into two segments: a twelve gas Primary Test Set and a fourteen gas Secondary Test Set.

In the Primary Test Set the first six Analytes are the atmospheric gases which could interfere with the measurements and/or occur at high concentrations within the tank headspaces. The next five Analytes are those pollutants with *HAR* values above 1.0, i.e., the dangerous Analytes. They are ranked according to their maximum *HAR* value. Although it has a low *HAR* value, carbon tetrachloride is added to this set because it was, and still is, a commonly used solvent in above-ground work such as cleaning instruments. Consequently, tank headspaces are not the only source of this pollutant. These other sources could potentially increase its *HAR* value considerably.

In the Secondary Test Set the first six Analytes are those that have *HAP* ratings. They are ranked by the *HAP* rating first and concentration second. The last eight are ranked by their *HR* ranking first and concentration second. The *HAR* values are not used to rank these Analytes because they are all below the danger level, i.e., less than 1.0.

The Primary Test Set are those twelve Analytes which must be monitored because of their potential danger or interference effects. This Set includes the ammonia and tributyl phosphate Analytes. Because they occur in virtually all the tank headspaces and are easily detected, the presence at a high concentration of either Analyte is a good indication of a venting or leaking tank.

The Secondary Test Set are those fourteen Analytes which are not dangerous at presently known concentrations in the tank headspaces. They need not be monitored at this time. However, tank compositions are continually changing due to chemical reactions and these fourteen Analytes have the greatest potential for moving into the Primary Test Set. Furthermore, the first six Analytes are of interest to the Environmental Protection Agency.

Table 8 - Detection method for prioritized Test Set Analytes.

Analyte	Detection by Thermal Emission	Detection by Laser Absorption	Digital Spectra Chapter
PRIMARY TEST SET			
Water	YES	YES	E
Carbon dioxide	YES	YES	F
Methane	YES	No	A
Nitrous oxide	YES	No	M
Carbon monoxide	YES	No	F
Ozone	YES	YES	F
Tributyl phosphate	YES	No	T
Ammonia	YES	YES	E
2,6-Di-tert-butyl-p-cresol	YES	YES	---
Biphenyl	YES	YES	---
n-Butyl alcohol	YES	YES	J
Carbon tetrachloride	YES	No	P
SECONDARY TEST SET			
Acetonitrile	YES	YES	N
Butadiene	YES	YES	A
Benzene	YES	YES	D
Methyl ethyl ketone	YES	YES	I
Methylene chloride	YES	No	P
N-Nitrosodimethylamine	YES	YES	N
Ethyl acetate	YES	YES	K
Butyraldehyde	YES	YES	H
Acetone	YES	No	I
2-methyl-Pentane	YES	No	C
Ethanol	YES	YES	J
Dodecane	YES	No	C
Tridecane	YES	No	---
Trichlorofluoromethane	YES	No	P

5.2 INFRARED SPECTRA

Having obtained a list of Analytes, it is important to determine which Analytes will be detectable by the thermal emission and which Analytes will be detected by laser absorption, i.e., which subsystem of the TELA Monitor will be usable for each Analyte. 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.

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 8 shows which Analytes have spectra within the AOTF detection range and which Analytes have spectra within the CO_2 laser detection ranges of existing^{18,19} CO_2 lidar systems. For the known infrared spectra, we use the digitized spectra data base from Infrared Analysis, Inc.²⁰ or the FTIR vapor phase spectra published by Aldrich,²¹ unless otherwise noted. The specific chapter, denoted by a capital letter, in the Infrared Analysis digitized data set is given in the last column. The digitized spectra are needed for real time analysis.

Barring atmospheric interferences, it would appear that:

The TELA Monitor can detect all 26 Analytes by thermal emission

The TELA Monitor can detect 15 Analytes by laser absorption

Furthermore, we *already* have 23 digitized spectra for these Analytes.

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