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Pacific Northwest
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Recommendations for Sampling and Analysis of Hanford Waste Tank Vapors

August 2018

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U.S. DEPARTMENT OF
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Richland, Washington 99352

Executive Summary

This report addresses recent analytical advances in air analysis as applied to improvements in the identification and detection of volatile organic compounds in waste storage tanks at the Hanford tank farms. Past analysis has indicated that some compounds are not well identified or current analytical techniques and instrumentation are not sensitive enough. This includes improved detection of Chemical (or Compounds) of Potential Concern (COPC) and identification of unknown components in Hanford tank vapors.

It has been recommended that an annual review of the COPCs be performed to include all newly available data. The annual review of the COPC listing and the screening values will, in turn, dictate that the sampling and analytical methodologies currently employed be reviewed as well. This annual review, or Data Quality Objectives if desired, of the sampling and analytical protocols should identify any development needs. There should be an oversite committee with representation from a variety of analytical chemistry disciplines, the laboratories performing the analyses, and independent entities.

The goals for sampling will be influenced by the Integrated Sampling Data Quality Objectives effort that was completed in 2018. This effort must develop a comprehensive sampling strategy that takes into consideration a wide variety of factors.

There are two clear objectives with divergent temporal requirements: 1) the desire for near real-time monitoring of COPCs and 2) surveillance of any long-term exposures including newly identified compounds. Certainly, sorbent tube sampling does not provide real-time monitoring, but it will most likely provide more detailed analytical results. Thermal desorption tube sampling is used extensively at Hanford with widely varying sampling times and locations, making it difficult to directly compare results to other previous laboratory analyses or from real-time monitors. In addition, desorption tubes typically only afford the analytical laboratory one attempt at the analysis. This is made even more difficult in that the laboratory often does not receive details regarding the sample acquisition parameters in advance of analysis. For example, the laboratory has no way of knowing if a sample represents a large air volume containing high levels of interfering compounds. Communication of sampling information to the laboratory needs to be improved. In addition, continuing the use of sorbent tube sampling must include a re-adsorption loop at the laboratory or some other means to allow for repeat analysis of a given sample. This critical enhancement to the analytical procedure will increase the dynamic range of the methods and allow for quantification within the calibration range of instruments. This is needed because constituents in tank waste vapors can be present in a wide range of concentrations, and the target limits of detection vary greatly. Although the method can suffer from lower sensitivity, greater use of solvent dissolution of the sorbent tubes rather than thermal desorption is another option that allows for repeat analysis and can extend the dynamic range of the method. Newer, more sensitive instrumentation would help to support this approach.

A tank farm vapor dose reporting program, similar to the existing radiological program, would require a personal dosimeter. We envision development of a sampling “badge” that may consist of several sorbents and may employ multiple desorption methods such as thermal and solvent-based approaches. The importance of high-dynamic-range analytical capability will be necessary allowing for construction of doses for many compounds with wide incidence and detection limit requirements. However, the correct sorbent for a given compound cannot always be anticipated when attempting to identify new compounds. For this reason, the use of SUMMA canister sampling should be used in all instances where identification of unknown compounds is sought, and it could be used as a confirmational method or as a replacement for thermal or solvent desorption sampling if desired. Consideration also should be given to the potential presence of highly reactive compounds. While these compounds may be short lived, they also may create the greatest irritation response. Thermal desorption sampling in particular may be inappropriate for these

species, and online methods may be the most desirable approach. Co-locating multiple sampling media and analytical field instruments should be implemented where possible to provide confirmational data. Personnel SUMMA samplers are available and could be used to validate, or as a supplement to, the badge sorbent.

To further aid in the comparability of results, it is important that sampling locations are precise and consistent. Therefore, it is recommended that some form of fixture be used when repeatedly sampling at a given location. This should include samples taken from tank risers. In addition to help correlate these data to real-time monitors, precise and consistent sampling locations will be beneficial when developing dispersion models where data are obtained under varying meteorological conditions.

The error associated with sampling usually far exceeds that of analytical method uncertainty. To reduce burdensome schedule impacts and costs, this should be considered carefully when establishing analytical quality-control criteria, especially for newly developed methods or implementing additions of target compounds to existing methods. However, the error of the analytical method can increase significantly when attempting to quantify Tentatively Identified Compounds[1] because no standard material is used and response factors can vary. There are currently 22 COPCs that are quantified in this manner, and authentic standard material for these compounds should be obtained.

Past and current laboratory analyses of Hanford tank vapors have used gas chromatography mass spectrometry (GC–MS) with electron impact ionization at 70eV[2] and unit mass resolution. Higher-resolution chromatography is desired in an effort to attain a separation and thereby obtain individual compound mass spectra. Split injections onto smaller diameter columns will improve chromatographic resolution and also narrow the peak width, thereby improving separation and detection limits and increasing the likelihood of obtaining clean mass spectra. This should ease the time burden on analytical staff and improve identification of unknown compounds. Although counterintuitive, this also is a more robust analytical method. Even more resolution may be achieved by employing multidimensional chromatographic methods.

A vacuum ultraviolet detector could be added to existing GC–MS systems. This non-destructive detector would be used for confirmation and to elucidate functional groups, isomers, etc. The detector would help analysts determine if the eluting chromatographic peaks are co-eluting and, when passed on to the mass spectrometer, indicate if clean mass spectra can be obtained. Other de-convolution strategies also should be evaluated.

Finally, the newest mass spectrometers offer improved sensitivity over even recent models. In addition, significant mass resolution is readily available that would markedly improve identification of unknown compounds. A gas chromatograph coupled with a high-resolution mass spectrometer is highly recommended. The Q-Orbitrap instrument offers the greatest impact for analysis. Even new time-of-flight mass spectrometers offer significant resolution improvement and provides greater sensitivity and time resolution over older quadrupole instruments, which is important toward supporting very high chromatographic resolution. Increasing the mass resolution of the current proton-transfer reaction mass spectrometry system used in field monitoring would improve the selectivity. Other methods to increase the selectivity of this system also should be explored such as selected ion flow tube mass spectrometry. Most of these instruments can be considered to be portable or benchtop units although currently available commercial units would certainly benefit by reductions in size.

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[1] Tentatively Identified Compounds are those that can be detected by an analytical method but the concentration cannot be confirmed without additional analytical testing.

[2] An electronvolt (eV) is a unit of energy equal to approximately 160 zeptojoules (symbol zJ) or 1.6×10 joules (symbol J). By definition, it is the amount of energy gained (or lost) by the charge of a single electron moving across an electric potential difference of one volt.

To complete the spectrum of analysis and search for unknowns, an ultra-high-pressure liquid chromatography electrospray high-resolution mass spectrometer should be considered. While providing alternative nitrosamine and aldehyde analysis, it also would support solvent desorption, thus extending the polarity search range of unknown compounds.

Finally, data transfer and storage of analytical data should be closely evaluated. Streamlining these processes will reduce the burden on analysts and ensure data integrity.

Acronyms and Abbreviations

amu	atomic mass units (symbol of u), also referred as Daltons
CI	chemical ionization
COPC	chemical of potential concern
CVST	chemical vapor solutions team
DOE	Department of Energy
DQO	Data Quality Objectives
EI	electron ionization (formally known as electron impact ionization)
EPA	U.S. Environmental Protection Agency
ESI	electrospray ionization
eV	electronvolt
GC	gas chromatography
GC×GC	multidimensional gas chromatography
GC–MS	gas chromatography–mass spectrometry
GC–MS–MS	gas chromatograph–mass spectrometer–mass spectrometer
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectrometer
ISA	International Society of Automation
LC–MS–MS	liquid chromatograph mass spectrometer mass spectrometer (also referred to as a triple quadrupole)
MRM	multiple reaction monitoring
NCD	nitrogen chemiluminescence detection
NCI	negative chemical ionization
NIST	National Institute for Standards and Technology
NIOSH	National Institute of Occupational Safety and Health
NPIP	N-Nitrosopiperidine
PCI	positive chemical ionization
PNNL	Pacific Northwest National Laboratory
pptv	parts per trillion per volume
PTRMS	proton-transfer reaction mass spectrometer
SIM	single (or selected) -ion monitoring
SIFT	selected ion flow tube mass spectrometry
TD	thermal desorption
TIC	Tentatively Identified Compound
TOF–MS	time-of-flight mass spectrometer
VOC	volatile organic compound
VUV	vacuum ultraviolet

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1.0 Introduction

Vapor sampling is a multidisciplinary topic. A variety of factors must be considered to obtain an accurate representation of the vapors present within a given tank headspace. Added to that are the dynamic environmental conditions to be considered when monitoring for these compounds once released into the open air. A list of the current Chemicals of Potential Concern (COPCs) is given in Table 1.

For example, vapors do not always remain in that phase. Temperature and humidity conditions in many of the Hanford waste tank headspaces are considerably different than the conditions outside the tanks. Once released, vapors typically can encounter significant temperature and humidity changes. Particularly in colder months, the high humidity and warm tank vapor can condense and form an aerosol. A fraction of the volatile species may condense and in the process of doing so demonstrate greater preference toward polar compounds such as ammonia, alcohols, ketones, and aldehydes into the aqueous droplets due to their solubilities (Huckaby 2006). A number of factors, including meteorological conditions, then can determine where these droplets or compounds reside in the open air. Non-polar species such as the normal paraffin hydrocarbon vapor fraction will condense as separate droplets. Both the aqueous and non-aqueous droplets may then fall close to or even onto the ground, or they may be re-established in the vapor phase and quickly mix with moving air. Unfortunately, the importance of these factors are often underestimated and an oversimplified sampling approach can be undertaken (Lodge 1989).

When all of the data needs from the various data users are considered and the complexities understood, sampling properly can seem an insurmountable undertaking or one that is so involved that the costs may appear unrealistic. A practical sampling program must therefore find some middle ground. An example of such compromise is the time granularity of sampling and analytical results. One stakeholder may feel that vapor monitoring should occur instantaneously and continuously. There could be a good scientific basis for this temporal resolution requirement. However, existing technology availability may not allow for such swift analytical turnaround; for example, a 1-hour granularity may be the best that can be achieved with existing technology.

Therefore, a process must be developed that tries to accommodate the shorter time interval. Perhaps with significant data, a correlation of the presence and concentration between compounds can be made. This approach may allow monitoring of a compound or group of compounds that require less analytical rigor to represent the entire compound set. This is the approach of the Leading Indicators work now underway at Hanford.

However, these correlations should be considered carefully and initially established at the source term within the headspace so the influence of other conditions (e.g., meteorological conditions) is minimized. Such simplification concessions must initially be made with an understanding of the contributing errors, which requires a significant and broad-spectrum data set. A broad-spectrum data set refers to one in which all pertinent data are collected such as temperature and humidity as well as compounds and concentrations. Only then can reasonable approximations of the compounds present and their concentrations be represented with sufficient accuracy to later make informed exposure decisions.

Even when great care is taken, the compounding of errors associated with sampling usually far exceeds errors introduced during analysis (Nune et al. 2016). So one of the practical factors often overlooked is the requested accuracy of the analytical method.

Expectations of instrument performance or compound behavior (via recovery measurements) should be developed based on a statistical evaluation of actual results produced by the analytical method. Certainly initial target performance criteria must be used, but these can be arbitrary or, at best, based on previous experience with another similar method. These criteria should be updated as early as possible based on applicable quality assurance directives during method development activities. If artificial control limits are implemented, the analytical laboratory can expend significant time and effort trying to achieve them when in fact realistic control limits or another method is required.

Table 1. Chemicals of Potential Concern

	Agent List	Chemical Abstracts Service Registry Number	Occupational Exposure Limit	Units
Inorganic Compounds				
1	Ammonia	7664-41-7	25	ppm
2	Nitrous Oxide	10024-97-2	50	ppm
3	Mercury	7439-97-6	25	ug/m3
Hydrocarbons				
4	1,3-Butadiene	106-99-0	1	ppm
5	Benzene	71-43-2	0.5	ppm
6	Biphenyl	92-52-4	0.2	ppm
Alcohols				
7	1-Butanol	71-36-3	20	ppm
8	Methanol	67-56-1	200	ppm
Ketones				
9	2-Hexanone	591-78-6	5	ppm
10	3-Methyl-3-butene-2-one	814-78-8	0.02	ppm
11	4-Methyl-2-hexanone	105-42-0	0.5	ppm
12	6-Methyl-2-heptanone	928-68-7	8	ppm
13	3-Buten-2-one	78-94-4	0.2	ppm
Aldehydes				
14	Formaldehyde	50-00-0	0.3	ppm
15	Acetaldehyde	75-07-0	25	ppm
16	Butanal	123-72-8	25	ppm
17	2-Methyl-2-butenal	1115-11-3	0.03	ppm
18	2-Ethyl-hex-2-enal	645-62-5	0.1	ppm
New	2-Propenal	107-02-8	0.1	ppm
Furans and Substituted Furans				
19	Furan	110-00-9	1	ppb
20	2,3-Dihydrofuran	1191-99-7	1	ppb
21	2,5-Dihydrofuran	1708-29-8	1	ppb
22	2-Methylfuran	534-22-5	1	ppb
23	2,5-Dimethylfuran	625-86-5	1	ppb
24	2-Ethyl-5-methylfuran	1703-52-2	1	ppb
25	4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1	ppb
26	3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	1	ppb
27	2-Pentylfuran	3777-69-3	1	ppb
28	2-Heptylfuran	3777-71-7	1	ppb
29	2-Propylfuran	4229-91-8	1	ppb
30	2-Octylfuran	4179-38-8	1	ppb
31	2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	1	ppb
32	2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	1	ppb

Agent List		Chemical Abstracts Service Registry Number	Occupational Exposure Limit	Units
Phthalates				
33	Diethyl Phthalate	84-66-2	5	mg/m3
Nitriles				
34	Acetonitrile	75-05-8	20	ppm
35	Propanenitrile	107-12-0	6	ppm
36	Butanenitrile	109-74-0	8	ppm
37	Pentanenitrile	110-59-8	6	ppm
38	Hexanenitrile	628-73-9	6	ppm
39	Heptanenitrile	629-08-3	6	ppm
40	2-Methylene butanenitrile	1647-11-6	0.3	ppm
41	2,4-Pentadienenitrile	1615-70-9	0.3	ppm
Amines				
42	Ethylamine	75-04-7	5	ppm
Nitrosamines				
43	N-Nitrosodimethylamine	62-75-9	0.3	ppb
44	N-Nitrosodiethylamine	55-18-5	0.1	ppb
45	N-Nitrosomethylethylamine	10595-95-6	0.3	ppb
46	N-Nitrosomorpholine	59-89-2	0.6	ppb
Organophospates and Organophosphonates				
47	Tributylphosphate	126-73-8	0.2	ppm
48	Dibutylbutylphosphonate	78-46-6	0.007	ppm
Halogenated Hydrocarbons				
49	Chlorinated Biphenyls	Varies	1	mg/m3
50	2-Fluoropropene	1184-60-7	0.1	ppm
Pyridines				
51	Pyridine	110-86-1	1	ppm
52	2, 4-Dimethylpyridine	108-47-4	0.5	ppm
Organonitrites				
53	Methyl nitrite	624-91-9	0.1	ppm
54	Butyl nitrite	544-16-1	0.1	ppm
Organonitrates				
55	Butyl nitrate	928-45-0	2.5	ppm
56	1,4-Butanediol, dinitrate	3457-91-8	0.05	ppm
57	2-Nitro-2-methylpropane	594-70-7	0.3	ppm
58	1,2,3-Propanetriol, 1,3-dinitrate	623-87-0	0.05	ppm
Isocyanates				
59	Methyl Isocyanate	624-83-9	20	ppb
Organometallic				
New	Dimethyl Mercury	593-74-8	0.01	mg/m3

2.0 Integrated Vapor Data Quality Objectives Effort

Currently, there is a significant effort to determine what data are desired from sampling and analysis of Hanford tank vapors. The variety of data users are represented in a Data Quality Objective (DQO) type of approach to address each topic area. The multistep process is an attempt to capture the data needs by gathering stakeholders and clearly defining the problem, considering the decision logic, addressing data inputs and defining boundaries and constraints, evaluating error tolerance, and finally developing the design. The overall goal is actually a process to ensure the appropriate samples and analysis produce data that meets the needs of everyone involved.

Underscoring the complexities of sampling, the current DQO effort involves the following nine subgroups:

1. International Society of Automation (ISA) (to verify calculations and assumptions for placement of monitoring equipment in accordance with ISA TR84.00.07)
2. Leading Indicators
3. Dispersion Modeling
4. Abatement Design
5. Fugitive Emissions/Source Apportionment
6. Aerosols
7. Technology Maturation
8. Industrial Hygiene Technical Basis Update
9. Environmental Compliance.

Each subgroup is essentially developing its own DQO and contributing to the currently ongoing Integrated DQO effort. Each subgroup consists of subject matter experts with relevant professional credentials and experience. The success of this enterprise is imperative toward a sampling and analysis strategy driven by the end use of the data.

3.0 Technical Considerations of Sampling

A substantial variety of factors can affect the concentration of vapor constituents not only within the tank headspace but ultimately in the open air breathing zone. These factors will be deliberated extensively during the DQO process. Not all of these factors will be addressed here but a few to be considered are listed below:

- Conditions within the tank, such as tank waste temperature, humidity, ventilation rate, etc.
- Any known tank constituents; recent or ongoing waste-disturbing activities
- Diurnal and seasonal changes
- Atmospheric pressure, temperature, and wind speed and direction.

Table 2 shows the variety of sorbent media used for vapor analysis, and the varied flow conditions used for obtaining a sample employing approved industrial hygiene or NIOSH methods. The sorbents are validated for a range of temperature and humidity conditions usually limited to those where the constituents remain in the vapor state. However as previously mentioned, vapors do not always remain in the gaseous state.

Many of the Hanford tank headspaces are considerably above ambient temperature and humidity. Once released, there may be a large temperature and humidity change that can take place. During the summer months, low humidities and high temperatures almost ensure that vapors will not condense and will remain in the gas phase. Even then, some compounds can adsorb to dust or pollens, and that process also is influenced by humidity (Lodge 1989).

Table 2. Information on the Sorbent Media used to Capture Contaminants, Flow Rates Used, Analytical Methods to Extract Analyte from Sorbent Media, and Method of Analysis to Quantify or Estimate the Concentrations of Hazardous Contaminant (from Nune et al. 2016).

Analyte	Media	Flow Rate (mL/min)	Analytical Method[a]	Instrument Used[b]	Analysis Location[c]
Acetonitrile	Charcoal Tube, SKC-226-09	100	NIOSH 1606	GC–FID	ALS
Acetonitrile	Carbotrap 300 TDU Tube	33	EPA TO-17 Modified	GC/MS	WRPS
Furans	TDU Tenax TA	33	EPA TO-17 Modified	GC/MS	WRPS
Semivolatile Organic Compounds	Carbotrap 150 TDU Tube	33	EPA TO-17 Modified	GC/MS	WRPS
VOCs	Carbotrap 300 TDU tube	33	EPA TO-17 Modified	GC/MS	WRPS
Mercury	Anasorb C300, SKC-226-17-1A	250	NIOSH-6009	CVAA	WHL
Ammonia	Anasorb 747 (sulfuric acid), SKC-226-29	200	OSHA-ID-188	IC	WHL
1,3-butadiene	Charcoal, SKC-226-37, (Parts A and B)	200	NIOSH-1024	GC–FID	ALS

Analyte	Media	Flow Rate (mL/min)	Analytical Method[a]	Instrument Used[b]	Analysis Location[c]
Aldehyde	DNPH Treated Silica Gel, SKC-226-119	200	EPA TO-11A	HPLC	ALS
Pyridine	Coconut Shell Charcoal, SKC-226-01offsite	1000	NIOSH-1613	GC–FID	ALS
Nitrosamines	Thermosorb/N	2000	NIOSH-2522 Modified	GC–TEA	CBAL
Ethylamine	XAD-7 (NBD) Chloride), SKC 226-96	200	OSHA-ID-34, 36, 40,and 41	HPLC–UV	ALS

[a] Analytical Method
NIOSH: National Institute of Occupation Safety and Health
EPA: U.S. Environmental Protection Agency
OSHA: Occupational Safety and Health Administration

[b] Instrument Used
GC–FID: Gas Chromatography–Flame Ionization Detector
GC/MS: Gas Chromatography–Mass Spectrometry
CVAA: Cold Vapor Atomic Absorption
IC: Ion Chromatography
HPLC: High-Performance Liquid Chromatography
GC–TEA: Gas Chromatography–Thermal Energy Analyzer
HPLC–UV: High-Performance Liquid Chromatography–Ultraviolet Detector

[c] Analysis Location
ALS: ALS Environmental Salt Lake City
WRPS–222S: Washington River Protection Solutions, Organic Studies Group
WHL–222S: Wastren Hanford Laboratory
CBAL: Columbia Basin Analytical Laboratory, part of the RJ Lee Group

During colder months, the high-humidity tank headspace vapor can condense when it is released into cold and perhaps humid outdoor air, leading to the formation of an aerosol. The condensed water phase of the aerosol may preferentially capture polar compounds such as ammonia, alcohols, ketones, and aldehydes into the droplets, and the non-polar compounds may remain in the gaseous state.

A number of factors including meteorological conditions, compound polarity, and volatility can then determine where these droplets or compounds reside in the open air. They may drop near to or onto the ground. They may be re-established as vapor and quickly mix with the surrounding air (Lodge 1989). For these reasons, spatial accuracy regarding sampling location is very important, particularly under highly stable meteorological conditions.

Thermal desorption (TD) tube sampling is used extensively at Hanford with widely varying sampling times and locations making it difficult to directly compare results to other previous laboratory analysis or from real-time monitors. For the previously identified reasons, it is important that consistent and precise sampling locations are used. Therefore, when sampling will be done repeatedly at a given location, the use of some form of fixture that holds the sampler each time it is used is recommended. This should include samples taken from tank risers. Consistent use of sampling locations also is important when evaluating the impact of varying meteorological conditions or validation of meteorological models.

Attempts to perform sampling isokinetically should be made even for ambient air samples. Isokinetic sampling is achieved when the sampler intake flow velocity is equal and aligned to the ambient wind velocity and direction. This helps to avoid bias of the particle or droplet size collection efficiency and perhaps limit the bias of the constituents captured as well. Isokinetic sampling is much more possible in

stack effluents in which air velocity is controlled. Sampling ambient air isokinetically is much more difficult. Unfortunately the importance of these factors is often underestimated, and an oversimplified sampling approach can be implemented.

3.1 Remote Sampling Versus At-Location Sampling

In reality, all sampling and analysis includes a sampling train; that is, some form of transfer line connected to a sample vessel or attached to the instrument in some way. In general, it is best to keep this transfer line as short as possible and at conditions which prevent sample consituent losses such as in some cases elevated temperatures. Ideally the instrument is co-located at the environment to be analyzed. Generally, this also means the time for onsite analysis is shorter than when a sample is collected and transported to the instrument.

A well-designed sampling train can deliver samples that are very representative of the true sample material. This must be validated by the use of a standard gas mixture ideally representing every COPC compound or at least the range of boiling points and polarities of vapor constituents. In addition, the matrix must be matched including temperature and humidity. For this reason, spiking material is at a significantly higher concentration, and a small volume is introduced into the actual matrix. Therefore, at-location sampling is preferred over remote sampling trains because the variabilities introduced by sampling lines are minimized. However, even at-location sampling must be validated by the use of matrix-matched spikes introduced in the field. Spiking after collection or by any other introduction mechanism is not valid for the entire sampling process.

When evaluating worker exposures that occur via inhalation, the ideal sampling location is at or near the breathing zone. If one envisions a tank farm vapor dose reporting program similar to the existing radiological program, a sampling “badge” is proposed. These sampling badges may consist of several sorbents and employ multiple desorption methods. Most likely, such exposure badges would not be available off-the-shelf or as a custom-made badge from a commercial vendor. If this is the case, applicable exposure badges may, and should, be developed. Less convenient would be the use of personal sampling tubes. Any of these devices would require certification for use on every compound to be sampled.

The correct sorbent for a given compound cannot always be predicted when attempting to identify new compounds. For this reason, the use of SUMMA canister sampling should be used in all instances where identification of unknown compounds is sought, and it may be used to replace TD sampling if desired. Consideration should be given to the potential presence of highly reactive compounds. While these compounds may be short lived, they also may create the greatest irritation response. Thermal desorption sampling may be inappropriate for these species. Co-locating multiple sampling mediums or analytical field instruments should be implemented where possible to provide confirmational data. Personal SUMMA samplers are available and could be used to validate or as a supplement toward extending the compound spectrum of the badge sorbent.

3.2 Sampling Times

Determining the sampling frequency and duration can be very difficult also. Ultimately, the Integrated Sampling DQO must decide what event may drive sampling frequency and duration. The deciding factor may be the desire to meet 15-minute and 8-hour worker exposure monitoring, and as such, one would strive to meet those sampling times. Personal vapor dosimetry could be checked in and out when entering

and exiting the tank farm. Sensitivity of the subsequent analysis is then driven by the quantity of sample passed through a TD tube or badge exposure time in the field. For a canister sample, the quantity of sample required would be determined by the laboratory performing the analysis to meet the desired detection limits.

Sampling frequency will depend largely on how the concentration of a chemical vapor changes with time due to the factors affecting the vapor discussed previously. In a worst case scenario the sampling interval also could be driven by tank release events as observed in the SY-101 tank at Hanford where hydrogen release was episodic. It is reasonable to consider that a similar buildup and release mechanism can occur for VOCs in tank waste, although no "roll-over" type event, in which the episodic release of primarily hydrogen gas saturating the waste actually causes upheaval of the waste, may be observed. Here due to the condensed phase solubility of the vapors (Huckaby 2006), the episodes may be cyclical and would be much milder although still driven by saturation of the waste with dissolved vapor. Therefore, we can assume that if releases of VOCs are episodic, it is not to the extreme of hydrogen gas.

It also is reasonable to assume that buildup and release would occur for multiple vapor components at a similar frequency because the saturation of gases would be driven by the sum of partial pressures. Based on this rationale, the formation of vapor of greatest concentration likely drives the frequency of release. For example, monitoring the concentration of ammonia versus time in a given prolonged quiescent tank should provide the same periodicity as any other vapor of similar polarity such as butanol. However, the polarity of the compound will influence where it resides; the polar compounds will reside in the liquid phase while non-polar constituents adsorb onto particles. Therefore, the sum of partial pressures is dictated by the available matrix in which the vapor resides and the rate at which gases are released is dictated by the major component formed. These factors will be highly tank dependent. However, in this consideration, the evolution of vapors would be more constant unless there were some reason for the gas-forming reaction kinetics to vary over time.

Further supporting a more continuous vapor release mechanism is the simple act of gas sparging. As the bulk gases are produced, coalesce, and buoyantly transported to the surface of the condensed phase, they act as a transport for other volatile species. Because of the highly polar nature of the condensed phase, the less polar constituents are stripped and transported more readily into a moving gas bubble. The polar volatile species certainly are stripped less efficiently.

Headspace concentrations are a function of release rate, release mechanisms, and mean residence time. Long-term continuous monitoring of ammonia and nitrous oxide in non-buoyant displacement gas release event tank headspaces revealed varying concentrations (Lockheed Martin Hanford Corporation 1998). For example, nitrous oxide headspace concentrations in the BY-105 tank ranged from 50 to 200 ppm. During this same time period, ammonia headspace concentrations ranged from 50 to 120 ppm. Correlations of vapor release were observed in that hydrogen, nitrous oxide, and methane tended to release and peak in concentration together. Ammonia tended to peak several hours later. The conclusion that must be drawn here is that to understand how headspace concentrations vary, near real-time monitoring likely is required.

3.3 Compound and Concentration Spatial Variability (stratification) within the Tank Headspace

Consideration should be given to the potential presence of highly reactive compounds. While these compounds may be short lived or thermally labile, they also may create the greatest irritation response because of their reactivity. Depending on the lifetime of these compounds, their concentrations could be higher in the region just above the waste condensed phase assuming that is where they are being produced before further reaction. Waste-disturbing activities could transport these constituents more rapidly to the ambient air prior to their opportunity to react further so the potential for exposure to them is increased. Thermal desorption sampling is likely to be inappropriate for these species so solvent desorption followed by liquid chromatography–mass spectrometry analysis may be more appropriate even though sensitivity may be reduced (discussed later in the analytical section). This is why it is valuable to co-locate sampling mediums or the sample port for analytical field instruments. It is not uncommon for a field gas chromatography–mass spectrometry (GC–MS) system to find additional or unreacted constituents when compared to TD results or even occasionally canister samples during site evaluations or air pollution surveys. Confirming data should be obtained where possible.

When tank conditions are quiescent, the waste tank headspaces tend to be relatively well-mixed by convection. Temperature differences between the waste surface and tank dome produce a corresponding difference in the density of the gas (primarily water vapor and air), which in turn induces convection within the headspace. The temperature differences are inherent to almost all of the tanks; the waste itself is heated by radioactive decay, and its surface is warmer than the tank dome. Air near the waste surface is warmed by the waste and rises, displaced by air that has been cooled by contact with the tank dome. This thermally induced convection mixes the gases and vapors vertically and horizontally throughout the convective zone.

A number of sampling and analysis studies of Hanford tank waste have been undertaken with results documented in published and unpublished (i.e., internal) reports. Published reports are included in the reference list of this report with links to online versions provided where available. Unpublished reports are identified in footnotes below. Results from studies employing numerical modeling and semi-empirical relationships have shown that transport and mixing of gases and vapors in the convection zone occur rapidly compared with their release from the waste surface, making concentration gradients within the convection zone negligible (Fauske & Associates, Inc. 1995; Antoniak and Recknagle 1997; Unpublished reports[3,4,5,6,7]). The conclusions of those studies are supported by tests performed in tanks 241-C-103 and 241-C-111 (Unpublished reports[8,9]); a tracer gas experiment conducted to evaluate the speed of mixing (Huckaby et al.1997a); and a series of multi-riser, multi-level headspace samples collected from three relatively cool tanks (Huckaby et al. 1997b; Huckaby et al. 1999).

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[3] Westinghouse Hanford Company. 1994. *Organic Evaporation in Waste Tank C-103, Rev. 0*. WHC-SD-WM-ER-344, Richland, Washington.

[4] Wood SA. 1994. "Evaluation of Mixing in the Tank 101-SY Gas Space." Internal Memorandum 23230-93-SAW-015, Westinghouse Hanford Company, Richland, Washington.

[5] Westinghouse Hanford Company. 1995. *Safety Analysis of Exothermic Reaction Hazards Associated with the Organic Liquid Layer in Tank 241-C-103, Rev. 0A*. WHC-SD-WM-SARR-001, Richland, Washington.

[6] Antoniak ZI and KP Recknagle. 1996. "Modeling Hydrogen Plume Concentrations in Single and Double-Shell Tank Dome." Letter Report TWSFG96.12, Pacific Northwest National Laboratory, Richland, Washington.

[7] Antoniak ZI and KP Recknagle. 1996. "Modeling Tracer Gas Concentrations in Single-Shell Tank 241-S-102 Dome." Letter Report TWSFG96.23, Pacific Northwest National Laboratory, Richland, Washington.

[8] Huckaby JL and MS Story. 1994. *Vapor Characterization of Tank 241-C-103, Rev. 0*. WHC-EP-0780, Westinghouse Hanford Company, Richland, Washington.

[9] Huckaby JL. 1994. *Tank 241-C-111 Headspace Gas and Vapor Sample Results, Rev. 0*. WHC-SD-WM-TP-254, Westinghouse Hanford Company, Richland, Washington.

3.4 Conclusions for Sampling

The Integrated Sampling DQO process is currently underway and may significantly impact the sampling practices used to monitor the tank vapors at Hanford. It is anticipated that the process will develop a comprehensive sampling strategy that takes into consideration a wide variety of factors in an effort to satisfy all of the stakeholders.

Annual reviews of the COPC list and their screening values will in turn dictate that the sampling and analytical methodologies employed be reviewed as well. The annual review could follow the DQO process if desired. At a minimum, review of the sampling and analytical protocols should identify any development needs. This review should be conducted by an oversight committee consisting of independent experts that represent a variety of analytical chemistry disciplines and the laboratories performing the analysis so that realistic implementation is considered during the process.

A tank farm vapor dose reporting program similar to the existing radiological program should be considered. A personal dosimeter or sampling "badge" is envisioned that may consist of several sorbents. Analysis would be performed using TD or solvent desorption methods at the laboratories. Throughput considerations may require automation of analytical methodologies as discussed in subsequent chapters.

4.0 Considerations for Analysis

This chapter addresses recent analytical advances in air analysis that are applicable to improving the identification and detection of VOCs in vapors from headspaces at the Hanford tank farms. Better detection of the COPCs and identification of unknown components in the Hanford tank vapors are included in the discussion.

Past and current laboratory analysis of Hanford tank vapors has used GC–MS with unit mass resolution and electron ionization (EI; formally known as electron impact ionization), 70 eV[10] analysis. Both TD and canister base sampling are typically used to collect grab-samples taken from the headspaces of Hanford waste tanks. Canister-based sampling also is referred to as SUMMA canister sampling, and for this report, canister-based and SUMMA sampling are the same.

Sampling and analysis plans specified that samples be analyzed for 61 organic target COPCs.[11] The target compounds were to be positively identified (i.e., gas chromatography retention time and mass spectra were matched to that of a known standard) and quantitatively measured (i.e., a multipoint calibration of the GC–MS was performed with known standards). Standards that include each of the target compounds should be used. Concentrations of target compounds generally were required to be accurate to within 30%. Non-target organic compounds were tentatively identified by comparing their observed mass spectra with those in the National Institute for Standards and Technology (NIST)/Wiley mass spectral library, and applying both automatic search methods and professional judgment to identify the best match (Sklarew and Mitroshkov 2006). Experience indicates this process for identification of organic compounds is fairly reliable for many compounds. Experience also may take into consideration the gas chromatographic retention times when making assignments to unknown compounds.

Confidence that any given Tentatively Identified Compound[12] has been properly identified diminishes as its concentration is reduced and as the number of possible chemical isomers increases. Concentrations of Tentatively Identified Compounds are estimated by comparing their instrument response to that of chromatographically adjacent internal standards, and generally should be considered only accurate to a factor of 2. Although examples can be found where this method of estimating the quantity of an unknown can actually be even more than an order of magnitude in error. There are currently 22 COPCs that are quantified in this manner (using the TIC method) and authentic standard material for these compounds should be obtained.

[10] An electronvolt (eV) is a unit of energy equal to approximately 160 zeptojoules (symbol zJ) or 1.6×10^{-21} joules (symbol J). By definition, it is the amount of energy gained (or lost) by the charge of a single electron moving across an electric potential difference of 1 V.

[11] At the time this report was prepared, the tank farm COPC list included 59 chemical compounds. In September 2017, dimethylmercury and 2-propenal were added to the tank farm COPC list, thereby increasing the number of COPCs to 61. Dimethylmercury requires special sampling and analysis methods. 2-Propenal is regularly addressed in Industrial Hygiene sampling as part of the aldehydes sorbent tube suite of compounds. For completeness, these two new COPCs are listed in Table 1 after COPCs #18 and #59.

[12] Tentatively Identified Compounds are those that can be detected by an analytical method but the concentrations cannot be confirmed without additional analytical testing.

4.1 Instrumentation

4.1.1 Quadrupole Gas Chromatography–Mass Spectrometry

Quadrupole GC–MS is the standard analytical technique used to detect and quantify targeted VOCs at Hanford. New GC–MS instruments have improved designs with advancements in inert sources and mass spectra detectors intended specifically for sensitivity (Wells et al. 2011). Together with the advancement in gas chromatograph columns (inertness and minimal column bleed), the standard quadrupole GC–MS is continually improving in sensitivity.

The preferred mode of acquisition for GC–MS is in full scan mode, which allows identification of non-targeted compounds and observation of the complexity of the chromatogram and potential interferences from the sample matrix (Fialkov et al.2007, Nakashima and Hayashi 2016). When improved detection limits are needed, the GC–MS is operated in single (or selected)-ion monitoring (SIM) mode. Unfortunately, SIM is only for targeted compounds and no mass spectrum is acquired. Quadrupole GC–MS systems are commonly used today and are the mainstay of laboratory mass spectrometry. However, a variety of mass spectrometers that are capable of generating searchable mass spectra are available. Table 3 compares the general specifications and costs of various commercial mass spectrometers.

Table 3. Mass Spectrometer Instrument Groups

Instrument Group	Typical Mass Range (atomic mass units [amu])	Resolution	Sensitivity	Approximate Cost (2016)
Quadrupole MS	10–2,000 amu	Low/single amu	nanogram to high picogram	$80,000
Triple-Quadrupole MS/MS	10–2,000 amu	Low/single amu	picogram to high femtogram	$180,000
Time-of-Flight (TOF) MSF	10–4,000 amu	Low or high resolution/20k	picogram	$200,000
GC-Orbitrap high-resolution mass spectrometer (HRMS)	30–3000 amu	High/50k	picogram to femtogram	$350,000
GCQ- Orbitrap HRMS	30–3000 amu	High/100k	picogram to femtogram	$450,000
GC × GC TOF	10–4,000 amu	Low or high resolution/20k	picogram	$425,000

4.1.1.1 Triple-Quadrupole Mass Spectrometry/Mass Spectrometry

Triple-quadrupole MS–MS, often noted as GC–MS–MS, is generally used for targeted compounds in multiple reaction monitoring (MRM) mode. It can produce both chemical and EI mass spectra in tandem (essentially simultaneously). Chemical ionization (CI) can be used to elucidate molecular weight by virtue of its soft ionization process, which is increasingly important for low mass compounds. Electron ionization can produce the fragmentation needed to identify compound structure. It is helpful in minimizing interferences and expands the dynamic range over that of single quadrupole GC–MS instrumentation and still satisfy the requirements of regulatory methods that may specify single quadrupole instrumentation. Selected ion monitoring and scanning analysis can be achieved simultaneously increasing sensitivity and selectivity.

4.1.1.2 Time-of-Flight Mass Spectrometry

GC−TOF instruments have better sensitivity and detection limits than conventional GC−MS quadrupole instruments. GC−MS TOF instruments are continuously in full scan mode, thereby eliminating the need for SIM mode used in GC−MS.

High-resolution TOF−MS offers immediate advantages over traditional GC−MS analysis with a quadrupole analyzer. The higher resolution allows for quantifying targeted analytes in complex mixtures. The higher resolution allows improved identification of Tentatively Identified Compounds. It also better supports faster acquisition speeds because it continuously obtains full spectra. This is necessary when extremely narrow chromatographic peaks are eluting from high-resolution separations. Higher mass resolution allows for accurate mass measurements which in turn allows for calculating the empirical formula for a mass ion. For example, 70.04186 m/z calculates to an empirical formula of C_4H_{60} for dihydrofuran. Knowing the empirical formula is an enormous help in identifying unknown constituents. This complements the NIST library search to give the analyst higher confidence in identifying unknowns. Note that many of the compounds in the COPC list have a hetero-atom of oxygen or nitrogen present in their structure which is well suited for accurate mass measurements.

4.1.1.3 Gas Chromatography−Orbitrap Mass Spectrometry

The Orbitrap technology provides higher resolution and dynamic range compared to the TOF−MS (Peterson et al. 2014). It appears to match or exceed the sensitivity of the TOF−MS instruments. Pacific Northwest National Laboratory (PNNL) has a GC−OrbiTrap MS (GC−Q-Exactive) at the William R. Wiley Environmental Molecular Sciences Laboratory. This instrument is in constant use at PNNL for identifying metabolites. It is an MS−MS with high resolution on the second mass spectrometer and is the ultimate configuration of all the GC−MS instruments. With EI and CI modes available, this instrument is a powerful tool.

The Orbitrap technology uses high-resolution, accurate mass analysis. This achieves high resolving power mass accuracy, linear dynamic range, and sensitivity that electrostatic technology provides (Silcoc et al. 2017). Resolving power up to 50,000 at m/z 272 with sub-ppm mass accuracy surpasses any high-resolution TOF instrument. Also TOF instruments lose sensitivity as resolution and/or scan speed is increased. This is not the case with Orbitrap because all the ions are being trapped.

Obtaining mass measurements with high mass accuracy is essential to providing the required selectivity in complex matrices and to increasing the confidence in compound identification and confirmation. For the former, obtaining a consistently high mass accuracy allows the use of very narrow mass extraction windows, taking full advantage of the instrument's mass resolving power. For the latter, measuring the mass of a chemical with sufficient accuracy allows the chemist to predict the elemental composition and isotopic ratios to help identify the chemical structure of the substance.

There are two types of GC-Orbitrap mass spectrometers—Q-Exactive GC and Exactive GC. The Q-Exactive instrument has a higher resolution of 100,000 @ m/z 272 while the resolution of the Exactive GC is 50,000 at m/z 272. Also, the Q-Exactive instrument has a high energy collision cell for quadrupole/Orbitrap MS−MS experiments. Table 4 provides a comparison of mass spectrometry technologies that are available and the commercial vendors. Figure 1 shows the importance of high mass resolution where a single chromatographic peak is deconvoluted to identify N-Nitrosopiperidine among interfering compounds (Krauss et al. 2010).

Table 4. Gas Chromatography/Mass Spectrometry

Type of MS	Advantages	Disadvantages	Vendors
Quadrupole MS	Proven robust quantitation tool. Meets prescribed regulatory methodology.	1) Sensitivity not as good as TOF or Orbitrap. SIM analysis improves sensitivity but loses ability to identify unknown compounds. 2) Low resolution (single amu). Lowest sensitivity.	Agilent, Bruker, Perkin Elmer, Thermo
Triple-Quadrupole MS/MS	1) Proven robust quantitation tool using MRM. 2) Very selective for most targeted (COPC) compounds. 3) Matrix interference is mostly eliminated.	1) MRM acquisition is for targeted compounds only, other compounds present are not monitored. 2) Precursor ion is generally the most abundant ion in the mass spectra which is often not the molecular ion. Sensitivity is dependent on ions available in the mass spectrum and can vary between different compounds.	Agilent, Bruker
TOF–HRMS	1) Typically much higher sensitivity than a quadrupole. 2) Full mass spectra is acquired rather than SIM mode. 3) Quicker scan speeds than quadrupole which allows for high-resolution chromatography. 4) High resolution available for mass accuracy determination of unknowns.	Not as widely accepted as a routine quantitation tool in prescribed regulatory methodology compared to GC–MS quadrupoles	SepSolve Analytical (Markes), Bruker, LECO, JEOL, Agilent,
Orbitrap HRMS	1) Same advantages as TOF but higher mass resolution. 2) Autogain allows for an improved dynamic range.	More expensive than GC–TOF instruments. Low mass range is 30 amu. Not as widely accepted as a routine quantitation tool in prescribed regulatory methodology compared to GC–MS quadrupoles	Thermo
Q-Orbitrap HRMS	1) Allows for high resolution of product scans which allows for unique libraries. 2) Higher resolution (100,000 compared to Orbitrap). 3) Extremely low noise due to pre-filtering of Q–HRMS.	More expensive than Orbitrap. Low mass range is 30 amu. Not as widely accepted as a routine quantitation tool in prescribed regulatory methodology compared to GC–MS quadrupoles	Thermo

4.1.2 Chromatographic Resolution

The success of mass spectrometry measurements of an analyte using a gas chromatograph as a way to introduce the sample is dependent on the resolution of the chromatography. Not only does this determine how well compounds are separated from one another allowing for clean spectra but it has a significant impact on the sensitivity as well.

Consider two chromatographic peaks shown in Figure 2. One peak is much wider than the other, requiring more time to elute from the column, and has considerably more area than the narrower peak. The wider peak represents the chromatographic peak from a 0.25-mm inside-diameter capillary column commonly in use today. However, the narrower peak actually delivers more mass to the detector for a short time than the broader peak.

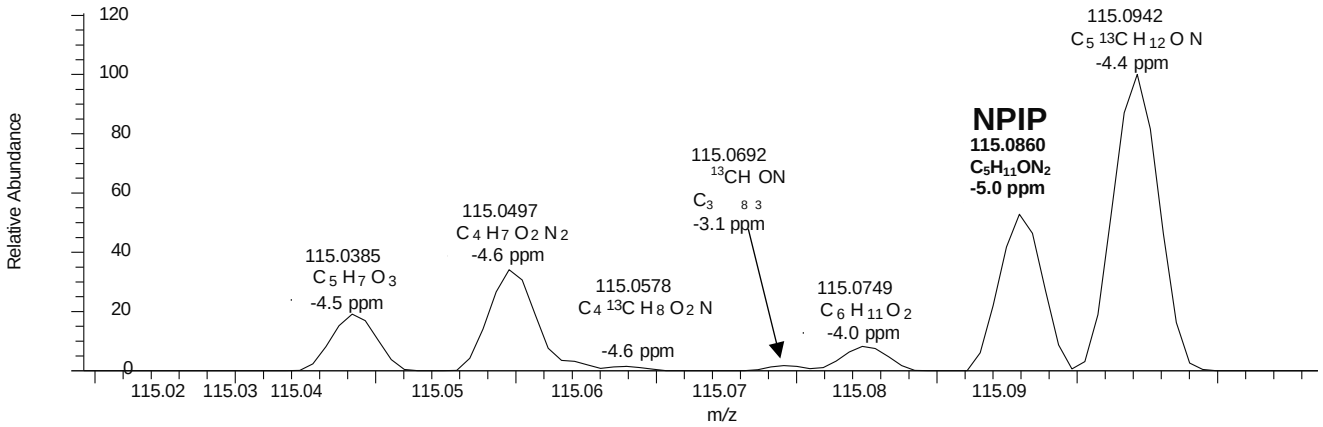

Figure 1. Zoom Section of a HRMS from an Extract of a Sewage Treatment Plant Sample Spiked with N-Nitrosopiperidine (NPIP), showing NPIP and Interfering Compounds of the Same Nominal Mass With Molecular Formula Assignments and Mass Accuracy. Mass spectrum acquired by HRMS full scan at R=30,000 using a Linear Trap Quadrupole Orbitrap.

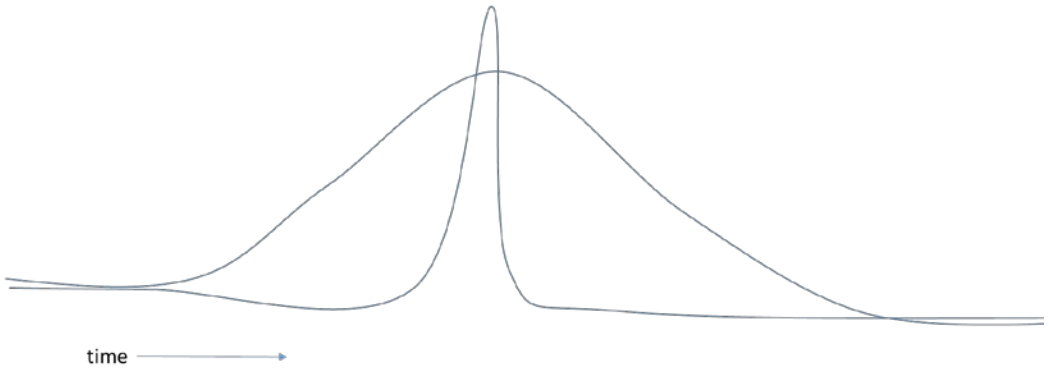

Figure 2. Comparison of Two Chromatographic Peaks

In other words, the peak height at some point is greater for the narrow peak than the broader peak. The detector sensitivity is actually greater for the narrow peak even though it represents less than a tenth of the mass introduced into the mass spectrometer compared to the broader peak. The narrower peak is indicative of smaller ID columns having diameters of 0.05 and 0.1 mm. The resolving power of these columns is much greater than the larger diameter columns.

Another consideration is how robust the column can perform over a number of analyses. Because of the added sensitivity, split injections can be used on narrower diameter columns so less material is on the column. And the improved resolution reduces the column length and the time that constituents are on the column. Therefore, a narrow column can actually be more robust while significantly improving detection limits. In extremely complex samples, even greater chromatographic resolution may be required, and multidimensional chromatography (GC × GC) may be needed.

In many cases, different isomers do not fragment appreciably from one another and cannot be distinguished by mass spectrometry even using the highest resolution instrument. There can be significant toxicity differences between isomers, thus making their separation very important. Chromatographic separation must be attained, and some of the most challenging compounds can be

isomers. A commercial GC×GC–TOF instrument is available that uses multidimensional separation. The effluent from a column is periodically switched to a second column with a different stationary phase. This technique is most successful when there are slight differences in polarity of the analytes.

4.1.3 Complementary Instruments to Gas Chromatography–Mass Spectrometry

Analytical instruments that are complementary to GC–MS are listed in Table 5, and their advantages and disadvantages then are discussed.

Table 5. Novel Complementary Instruments to GC–MS

Instrument Group	Advantages	Disadvantages
GC×GC	1) Deconvolutes complex mixtures. 2) Many homolog series can be observed for particular functional groups. For example the aldehydes.	1) Operation and maintenance are more complex. 2) Data processing can seem overwhelming to new users. 3) Background signal in GC×GC mode can show more peaks which can be confusing when managing TD blanks making source identification difficult.
GC-VUV	1) Deconvolutes overlapping peaks by the unique VUV spectrum. 2) A VUV spectrum supplements a mass spectrum for cases in which the mass spectrum is not unique for identifying unknowns. The VUV spectrum can provide functional structure of unknowns (ketone, amine, alcohols) to complement the identification by mass spectrometry. 3) Many isomers have unique absorption spectra. Spectral filters applied in software help distinguish compounds.	VUV spectra are relatively new; hence, their VUV library spectra are very limited compared to the mass spectrometry NIST library.
GC – sulfur chemiluminescence detector/nitrogen chemiluminescence detector (NCD)	High selectivity and sensitivity to nitrogen and sulfur compounds that provides additional discrimination over the tank vapor matrix that is obscuring the components of interest. A simple operational change to the NCD detector allows nitrosamine-specific detection. Sulfur- and nitrogen-specific detection may expand identification of gas chromatograph peaks.	No confirmational mass spectra unless the column effluent is split between this detector and mass spectrometer which will impact sensitivity
LC–MS–MS (triple quadrupole)	Good method for nitrosamines. A proven and reliable method for complex mixtures. Soft ionization provides molecular ion with minimal fragment ions. MRM acquisition is highly selective for targeted compounds. Collection by sorbent tube followed by solvent extraction.	Analysis is for targeted compounds only (not applicable for unknown compounds) if using MRM.
Software (isotope ratio matching)	Comparing isotope ratios with a mass spectra, molecular formulas can often be obtained even at medium or low resolution on a nominal GC–MS instrument.	Isotope patterns need to be significantly different to calculate an empirical formula. Not as reliable as HRMS.

Gas chromatography–vacuum ultraviolet (GC–VUV) can be a useful universal detector that also is highly selective (Bai et al. 2015). The VUV detector acquires full absorption spectra from 120 to 240 nm at sampling rates up to 100 Hz. Most gas-phase molecules exhibit strong and unique absorption spectra in the VUV region, including many isomers. The measured spectra can be matched against an existing compound-specific absorption cross-section library to rapidly identify the compounds. This fitting routine also provides the ability to deconvolute co-eluting peaks, providing a unique orthogonal separation approach. These data are integrated across the measured wavelengths and presented as a total absorption chromatogram. Extracted absorption chromatograms can be simultaneously generated using selected integration regions.

All spectral data are continuously stored, allowing these "spectral filters" to be applied post-processing. The response factors from the extracted absorption regions can be used to suppress background contributions from certain compound classes, improving the response specificity for the analytes of interest. The absorption cross section of gas-phase molecules in the VUV are hundreds of times stronger than in the infrared region, translating directly to sensitivity gains. These energies are strong enough to avoid influence by small temperature fluctuations.

Detection limits are often at picogram levels (on-column). In addition, the shapes of the absorption spectra in this wavelength region have just enough spectral richness to allow for Beer-Lambert Law driven quantitative determination and deconvolution. The VUV detector uses a flow cell and is not destructive like a mass spectrometer. This allows the detector to be used in series with a mass spectrometer, eliminating the need to have two standalone instruments and two separate sample injections. This means the signal from the detector can be used to determine if a peak eluting from the chromatographic column is indeed a single compound or a mixture. This informs the analyst about whether or not a clean mass spectrum is being obtained. In addition, in the case of tank vapor grab-samples, minimizing sample volume for an analysis is advantageous.

There is no vacuum pump to maintain or ion source to clean. Currently a small volume of purge gas is the only system requirement. Unfortunately, the purge gas dilutes the column effluent slightly but well within the flow capability of mass spectrometers. The detector has minimal moving parts and uses a long-life, user-replaceable deuterium lamp, which provides excellent reliability.

VUV is well suited for analysis of targeted and unknown compounds that are not as amendable to GC–MS. Many of the COPC components may not be baseline separated by other components in the Hanford tank vapors; that is, some components will co-elute. The co-elutions are resolved at the detector using VUV absorbance spectra and deconvolution algorithms. The resolving power is particularly powerful for the many COPCs that contain oxygen or nitrogen in their structure. In the case of the furans and substituted furans, the GC–VUV is able to resolve small VUV spectral differences in structural isomers. It is also well suited for analysis of nitrosamines and their unique VUV spectra. This detection method supplements mass spectrometry very well in the cases where unique mass spectra are not provided.

As stated before, the GC–VUV is a universal detector that is highly selective also. It also can be used to analyze gas mixtures consisting of low molecular weight hydrocarbons and inorganic gases such as ammonia, nitrous oxide, carbon dioxide, carbonyl sulfide, and water.

Recently, an ASTM standard test method (ASTM D8071 2017) was published for the use of GC–VUV to detect paraffins, isoparaffins, olefins, naphthalenes, aromatics, ethanol, and methanol in gasoline. This method quantitates compound classes, showing promise that the GC–VUV method could be adapted for analyzing compound classes on the COPC list (alcohols, aldehydes, furans, nitriles, amines, and nitrosamines).

Gas chromatography with NCD and sulfur chemiluminescence detection is a highly selective and sensitive analytical method for detecting nitrogen or sulfur containing VOCs (Xinwei 2006). The detector uses gas-phase ozone-induced chemiluminescence reactions as the basis for the detection method for the elemental content of nitrogen and/or sulfur in a sample. Because if its unique and beneficial properties of selectivity, sensitivity, and equimolarity, it is a powerful tool for selective nitrogen/sulfur detection.

NCD detection allows selective detection of nitrogen containing compounds on the COPC list (nitriles, amines, organonitrites, organonitrates, iosocyanates, and nitrosamines). In the case of nitrosamine detection, the operating conditions of the NCD can be easily changed specifically for nitrosamine compounds by lowering the pyrolyzer temperature. No hardware modifications are required.

4.1.4 Thermal Desorption Versus Solvent Desorption

Solvent desorption often is not considered in trace VOC analysis because lower detection limits are needed. In the case of TD, a larger sample amount is transferred to the GC–MS instrument compared to solvent desorption transferred to a liquid chromatograph–mass spectrometer–mass spectrometer (LC–MS–MS) system. Recent advancements in LC–MS–MS systems may have shifted this paradigm. With advances in ion funnel technology for ESI, detection limits have greatly improved and often surpass TD GC–MS. In addition, high-pressure HPLC with smaller diameter columns or reduced packing particle size has resulted in very sharp peaks as compared to the past (Anacleto et al. 1993). Triple-quadrupole LC–MS–MS has become the standard method used in drug analysis and many other applications. It enables direct, fast analysis of samples with minimal or no sample cleanup needed. LC–MS–MS is ideal for analysis of polar and reactive compounds such as nitrosamines. In cases where GC–MS is problematic for particular COPC compounds, LC–MS–MS should be considered. Additionally, HRMS is used for HPLC on a routine basis which would further improve the sensitivity and identification of compounds.

4.1.5 Mass Spectrometry Ionization Considerations

A compound must be charged or ionized to be analyzed by a mass spectrometer. Furthermore, the ions must be introduced in the gas phase into the vacuum system of the instrument. This is done easily for gaseous or heat-volatile samples. However, many (thermally labile) analytes decompose upon heating. These kinds of samples require either desorption or desolvation methods if they are to be analyzed by mass spectrometry. Although ionization and desorption/desolvation are usually separate processes, the term “ionization method” is commonly used to refer to both ionization and desorption (or desolvation) methods. Table 6 summarizes the variety of ionization methods available. The choice of ionization method depends on the nature of the sample and the type of information required from the analysis.

4.1.5.1 Electron Ionization at 70eV

This is the oldest and best characterized of all the ionization methods. A beam of electrons passes through the gas-phase sample. An electron that collides with a neutral analyte molecule can knock off another electron, resulting in a positively charged ion. The ionization process can either produce a molecular ion that will have the same molecular weight and elemental composition of the starting analyte, or more commonly in this case, it can produce a fragment ion that corresponds to a smaller piece of the analyte molecule. Appendix A contains the 70eV EI spectra of the COPCs.

Table 6. Mass Spectrometry Ionization

Subject	Pro (advantages)	Con (disadvantages)
EI at 70eV	Classical EI ionization is well established and very robust. Mass spectral library of over 250,000 chemical compounds. Library search programs often allows for tentative identification of unknowns.	Mass spectra of many of the COPCs give poor molecular ions and/or common fragment ions.
EI below 70eV	Soft ionization. Often enhances the molecular ion signal resulting in a molecular quant ion available to quantitate.	EI suffers tremendous loss in sensitivity when the ionization energy is lowered to the 10eV range. Often several orders of magnitude. New advances have dramatically improved the sensitivity at lower eV voltages making this ionization method more suitable. Distorts the mass spectra for library searches. If a molecular ion is not present at 70eV, it will not be present at lower eV values.
Positive CI (PCI)	Often enhances the molecular ion signal resulting in a quant ion available to quantitate. Well-established method. Almost all vendors provide this option on all their GC–MS models.	Loss in signal compared to 70eV EI. Not recognized as well as 70eV EI in routine quantitation.
Negative CI (NCI)	Often enhances the molecular ion signal resulting in a quant ion available to quantitate. Very selective for specific electron capturing compounds like halogen containing compounds, and in those cases, detection limits are possibly improved.	Most compounds on the COPC list are not conducive to detection by NCI. Exceptions would be the halogenated hydrocarbons (chlorinated biphenyls) and 2-fluoropropene.
Supersonic Molecular Beams	Essentially, this is cold EI. Less ion source degradation occurs. Mass spectrum can still be searched in the EI library for tentative identifications.	Only a few systems have been sold. The inventor would like to sell the technology to a larger company.
Atmospheric Pressure CI	The ionization is "soft," which means less fragmentation is observed for many compounds when compared with other techniques such as EI. Reduced fragmentation can give higher sensitivity and specificity, thereby simplifying precursor ion selection in MS–MS analyses.	Poor sensitivity relative to EI.
Field Ionization GC–MS	Soft ionization. Instrument is commonly used in petroleum industry.	Loss in sensitivity. Only one vendor (JEOL) available.
Electrospray Ionization (ESI)	Very sensitive for polar and ionic compounds. Used in HPLC.	Applicable to HPLC, but not gas chromatography.
Proton-Transfer Reaction Mass Spectrometry (PTR-MS)	Real-time analysis. Uses hydronium ions ($H_30^{+)}$ as the reagent gas. Very sensitive with detection limits reaching parts per trillion per volume (pptv) levels. Already being used on the Hanford site.	Not all VOCs are detectable. Possible false positives (matrix interference) and false negatives (ion suppression) from outdoor air background species.
Selected Ion Flow Tube Mass Spectrometry (SIFT-MS)	Real-time analysis. Very selective with detection limits reaching pptv levels. Three choices of reagent ions (H_30^+, O_2^+, or $NO^{+)}$, which allows greater selection of VOCs and confirmation.	Not all VOCs are detectable. Possible false positives (matrix interference) and false negatives (ion suppression) from outdoor air background.

Classical EI at 70eV is well established and very robust. Mass spectra for more than 250,000 chemical compounds are available in the library, and library search programs often allow for tentative identification of unknowns. Unfortunately, mass spectra of many of the COPCs give poor molecular ions and/or common fragment ions, which make tentative identification difficult.

4.1.5.2 Electron Impact Below 70eV

Lower electron voltage often enhances the molecular ion signal resulting in a molecular ion that can be used to quantitate or better identify unknowns. EI historically has suffered from tremendous loss (often several orders of magnitude) in sensitivity when the ionization energy is lowered to the 10eV level.

New advances have dramatically improved the sensitivity at lower electronvolt values, which makes this method more suitable. The large mass spectral library databases are for 70eV EI; however, the search algorithm can still be suitable for lower ionization energy spectrum. If the molecular ion is not present at 70eV, it is unlikely one will be observed at lower electronvolt values.

4.1.5.3 Positive Chemical Ionization and Negative Chemical Ionization

Both PCI and NCI often enhance the molecular ion signal resulting in an ion available to quantitate. They are both well-established ionization methods that are offered on almost all GC–MS systems. In many of the instruments, the ion source can be switched over from EI mode to chemical-ionization mode quickly even without hardware changes to the mass spectrometer.

Neither PCI nor NCI generally are used for identifying unknowns using library search programs because of limited spectral information obtained. However, they can often complement EI 70eV results by confirming molecular ions when not present in an EI mass spectrum. Another advantage is quantifying VOCs using a GC–MS–MS in MRM mode by enhancing the abundances of molecular ions. A major disadvantage of PCI is the loss in signal compared to 70eV EI, often reducing the detection limits by a factor of 10. NCI is compound-dependent. If the compound has a strongly electron withdrawing site (e.g., a halogen) in its structure, sensitivity may reach or exceed that of the EI mode. Two halogenated hydrocarbon compounds are in the COPC list—chlorinated biphenyls and 2-fluoropropene. These compounds are sensitive when analyzed using NCI. Chlorinated biphenyls are a group of compounds, and their sensitivities vary depending on the amount of chlorination. Highly chlorinated species are much more sensitive in NCI than when using EI.

4.1.5.4 Supersonic Molecular Beam Mass Spectrometry

Supersonic molecular beam mass spectrometry is essentially cold EI that results in less ion source degradation. The mass spectrum is distorted to higher masses like EI at lower ionization energy (discussed earlier in this section). The mass spectrum is often still searchable using the EI library for tentative identifications. The main advantage of this ionization approach is improved sensitivity, often meeting or exceeding the EI 70eV mode. A disadvantage is that only a few of these instruments have been sold commercially.

4.1.5.5 Atmospheric Pressure Chemical Ionization

Similar to other CI methods, this method is considered "soft" meaning that less fragmentation is observed for many compounds when compared with techniques such as EI (Peacock et al. 2016). Reduced fragmentation can simplify precursor ion selection in MRM analyses by GC–MS–MS. Again, this soft ionization suffers in loss of sensitivity as compared to the traditional EI 70eV mode.

4.1.5.6 Field Ionization Gas Chromatography–Mass Spectrometry

This ionization is based on electron tunneling from an emitter that is biased at a high electrical potential. The emitter is a filament on which fine crystalline "whiskers" are grown. When a high potential is applied to the emitter, a very high electric field exists near the tips of the whiskers. Field ionization is a soft ionization method that tends to produce mass spectra with little or no fragment-ion content. It is a proven a robust ionization method that is used often in the petroleum industry. Again, as in most all soft ionization, there is a loss in sensitivity.

4.1.5.7 Electrospray Ionization

ESI is a technique used in mass spectrometry to produce ions using a spray in which a high voltage is applied to a liquid to create an aerosol (Peacock et al. 2016). It is especially useful in producing ions from macromolecules because it overcomes the propensity of these molecules to fragment when ionized. Commercial instruments that use ESI are HPLC systems rather than gas chromatography systems. ESI LC–MS–MS is highly sensitive to polar and ionic compounds. In the case of COPCs that are difficult to analyze (nitrosamines, organonitrites, organonitrates, and isocyanate), ESI LC–MS–MS may be the best option. Air sampling would require the use of either solvent (chemical) desorption tubes or impingers.

4.1.5.8 Proton-Transfer Reaction Mass Spectrometry and Selected Ion Flow Tube Mass Spectrometry

PTR–MS and SIFT–MS are very similar ionization methods and can be used as real-time analyzers. Both methods have typical detection limits at the pptv level for certain compounds. Real-time, quantitative analysis is achieved by applying precisely controlled soft CI using reagent ions and eliminating sample preparation, pre-concentration, and chromatography.

PTR–MS uses the hydronium ion (H_3O^+) for soft ionization. This ion can be depleted by interfering scavenge species (e.g., ammonia) that are commonly found in Hanford tank vapors. Therefore, sensitivity can be dramatically reduced when a sample containing high levels of ammonia are present.

SIFT–MS uses multiple reagent ions (H_30^+, O_2^+, or $NO^{+)}$. Recently, negative reagent ions (NO_2^-, O^-, O_2^-, and OH^-) have been added to SIFT–MS. Two disadvantages of both PTR–MS and SIFT are 1) they are compound-dependent (based on proton affinity and other factors) and 2) not all VOCs will be ionized. SIFT–MS allows for greater choices of reagent ions to fine tune specific targeted analytes and therefore can be more selective than PTR-MS. Usually there are no fragment ions produced using either of these methods so compound identification relies on a single-ion mass. Therefore, like most soft ionization techniques, the resulting data must be supplemented with EI fragmentation or used with HRMS to reduce isobaric interferences.

4.2 Conclusions for Analysis

Past and current laboratory analyses of Hanford tank vapors have used GC–MS with EI at 70eV and unit mass resolution. Higher-resolution chromatography is desired in an effort to attain a separation and thereby obtain individual compound mass spectra. Split injections onto smaller diameter columns will improve chromatographic resolution and also narrow the peak width, thereby improving detection limits and increasing the likelihood of obtaining clean mass spectra. This should improve unknown compound identification. Although this may be counterintuitive, this also is a more robust analytical method. Even more resolution may be achieved by employing multidimensional chromatographic methods.

Standards containing each of the COPCs from two independent sources must be used to calibrate the instrument performing the analysis. Specialty mixes can be ordered from a number of vendors.

The addition of VUV could be added to existing GC–MS systems. This could be used as a confirmation detector and to elucidate functional groups, isomers, etc. The detector will help the analyst determine if the eluting chromatographic peaks are co-eluting and if clean mass spectra can be obtained. Other deconvolution strategies also should be evaluated such as isotope ratio matching.

The latest mass spectrometers offer improved sensitivity over even relatively recent models. Significant mass resolution is readily available that would markedly improve identification of unknown compounds. GC–HRMS is highly recommended. The instrument that offers the greatest impact for analysis is the Q-Orbitrap. Even the TOF–MS instrument offers a significant resolution improvement and provides greater sensitivity and time resolution, which is important for supporting very high chromatographic resolution. Most of these instruments are benchtop units.

A variety of ionization capabilities are offered with currently available mass spectrometers. The ionization method should be selected carefully because there are advantages and tradeoffs for each method.

Completing the spectrum of analysis and search for unknowns, an ultra-high-pressure liquid chromatography electrospray HRMS should be considered. While providing alternative nitrosamine and aldehyde analyses, this instrument also would support solvent desorption that would in turn extend the polarity search range of unknown compounds. Desorption tubes typically only give the laboratory one attempt at the analysis. This is made even more difficult in that the laboratory often does not receive details regarding the sample acquisition parameters in advance of analysis. For example, the laboratory has no way of knowing if the sample represents a large air volume containing high levels of interfering compounds. Communication of sampling information to the laboratory needs to be improved. In addition, continuing the use of sorbent tube sampling must include a re-adsorption loop at the laboratory or some other means to allow for repeat analysis of a given sample. This critical enhancement to the analytical procedure will increase the dynamic range of the method and allow quantification within the instruments calibration range. This is needed because constituents in tank waste vapors can be present in a wide range of concentrations and the target limits of detection vary greatly. Although the method can suffer from lower sensitivity, greater use of solvent dissolution of the sorbent tubes rather than TD is another option that allows for repeat analysis and can extend the dynamic range of the method. Newer, more sensitive instrumentation would help to support this approach.

A tank farm vapor dose reporting program, similar to the existing radiological program, would require a personal dosimeter. A sampling “badge” is envisioned that may consist of several sorbents and employ solvent desorption methods. The importance of high-dynamic-range analytical capability will be necessary allowing to construct the dose for many compounds with wide incidence and detection limit requirements.

Finally, data transfer and storage of analytical data should be closely evaluated. Streamlining these processes reduces the load on analysts and ensures data integrity.

5.0 References

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Appendix A

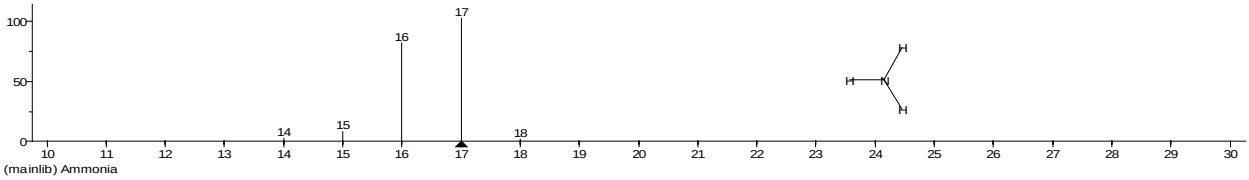
Electron Impact 70eV Mass Spectra of the Chemicals of Potential Concern

Appendix A

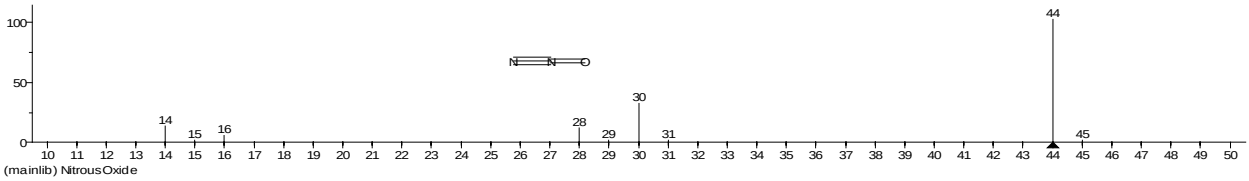
Electron Ionization 70eV Mass Spectra of the Chemicals of Potential Concern

A.1 Inorganics

	Inorganics			
1	Ammonia	7664-41-7	25	ppm
2	Nitrous Oxide	10024-97-2	50	ppm
3	Mercury	7439-97-6	25	ug/m3



Name: Ammonia
Formula: H_3N
MW: 17 CAS#: 7664-41-7 NIST#: 6 ID#: 28 DB: mainlib

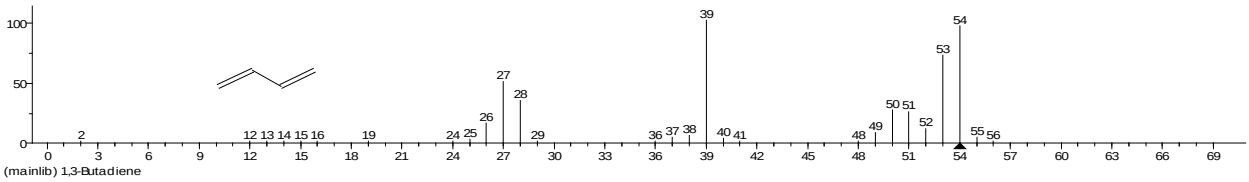


Name: Nitrous Oxide
Formula: N_2O
MW: 44 CAS#: 10024-97-2 NIST#: 70 ID#: 13255 DB: mainlib

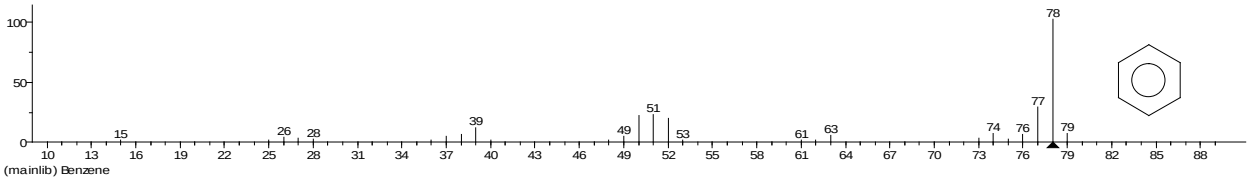
Mercury: NIST mass spectra was not found for elemental mercury

A.2 Hydrocarbons

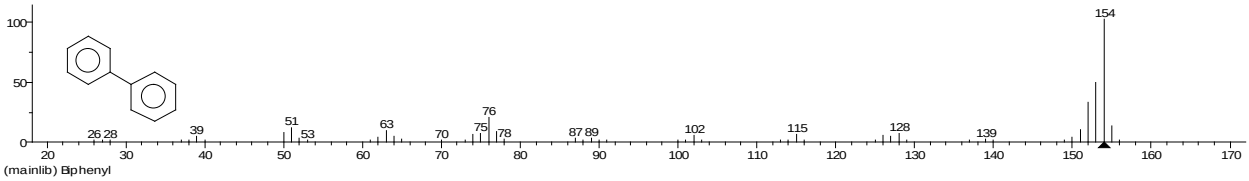
	Hydrocarbons			
4	1,3-Butadiene	106-99-0	1	ppm
5	Benzene	71-43-2	0.5	ppm
6	Biphenyl	92-52-4	0.2	ppm



Name: 1,3-Butadiene
Formula: C_4H_6
MW: 54 CAS#: 106-99-0 NIST#: 18901 ID#: 1561 DB: mainlib



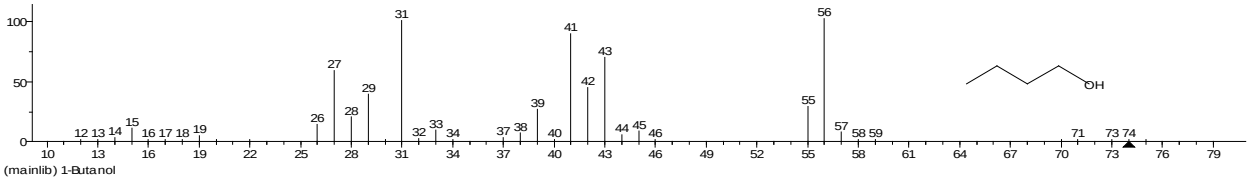
Name: Benzene
Formula: C_6H_6
MW: 78 CAS#: 71-43-2 NIST#: 114388 ID#: 37960 DB: mainlib



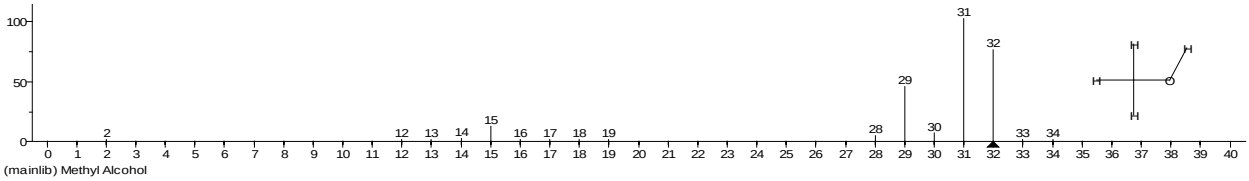
Name: Biphenyl
Formula: $C_{12}H_{10}$
MW: 154 CAS#: 92-52-4 NIST#: 114218 ID#: 99714 DB: mainlib

A.3 Alcohols

	Alcohols			
7	1-Butanol	71-36-3	20	ppm
8	Methanol	67-56-1	200	ppm



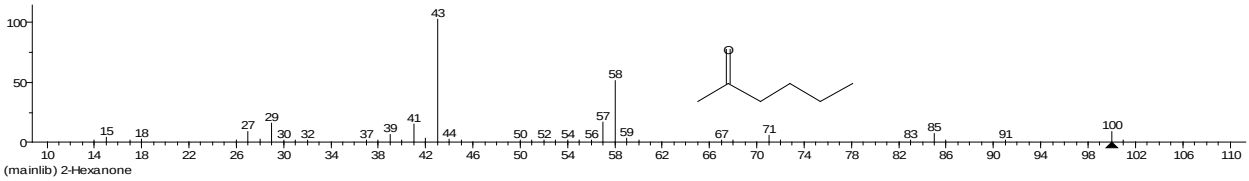
Name: 1-Butanol
Formula: $C_4H_{10}O$
MW: 74 CAS#: 71-36-3 NIST#: 133176 ID#: 18821 DB: mainlib



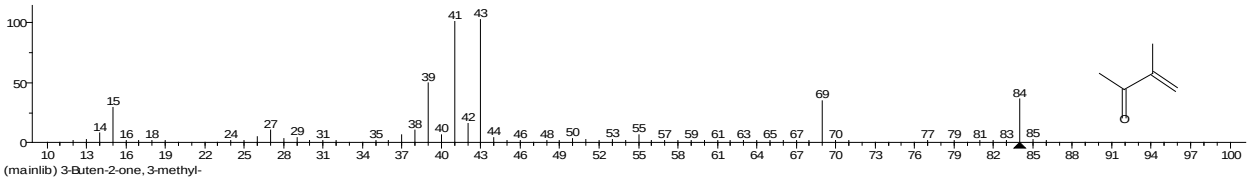
Name: Methanol
Formula: CH_4O
MW: 32 CAS#: 67-56-1 NIST#: 229809 ID#: 1305 DB: mainlib

A.4 Ketones

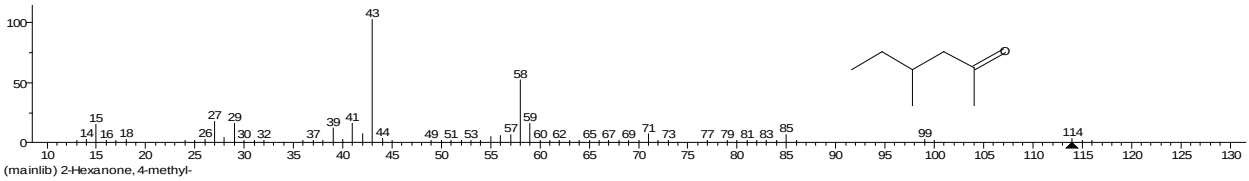
	Ketones			
9	2-Hexanone	591-78-6	5	ppm
10	3-Methyl-3-butene-2-one	814-78-8	0.02	ppm
11	4-Methyl-2-hexanone	105-42-0	0.5	ppm
12	6-Methyl-2-heptanone	928-68-7	8	ppm
13	3-Buten-2-one	78-94-4	0.2	ppm



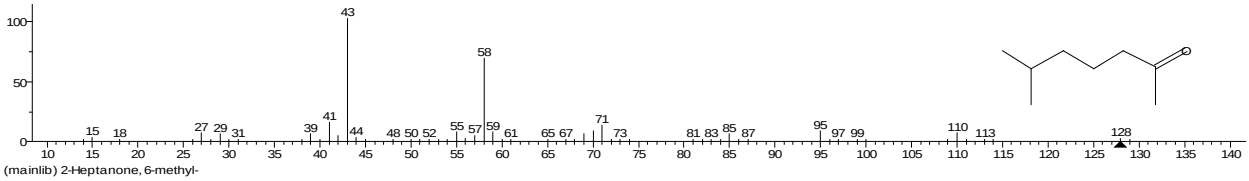
Name: 2-Hexanone
Formula: $C_6H_{12}O$
MW: 100 CAS#: 591-78-6 NIST#: 228824 ID#: 7265 DB: mainlib
Synonyms:
1.n-Butyl methyl ketone
2.Butyl methyl ketone
3.Hexan-2-one
4.Methyl butyl ketone



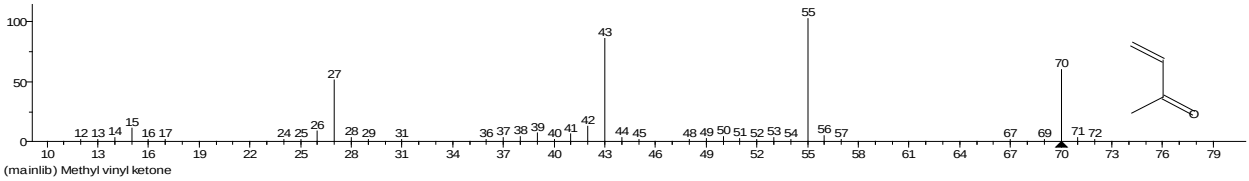
Name: 3-Buten-2-one, 3-methyl-
Formula: C_5H_8O
MW: 84 CAS#: 814-78-8 NIST#: 513 ID#: 5244 DB: mainlib



Name: 2-Hexanone, 4-methyl-
Formula: $C_7H_{14}O$
MW: 114 CAS#: 105-42-0 NIST#: 69040 ID#: 7219 DB: mainlib



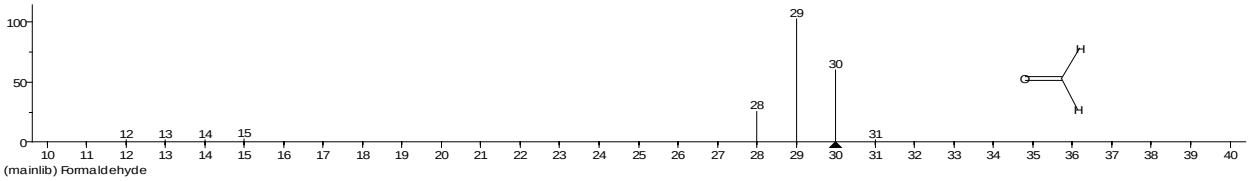
Name: 2-Heptanone, 6-methyl-
Formula: $C_8H_{16}O$
MW: 128 CAS#: 928-68-7 NIST#: 231897 ID#: 7238 DB: mainlib



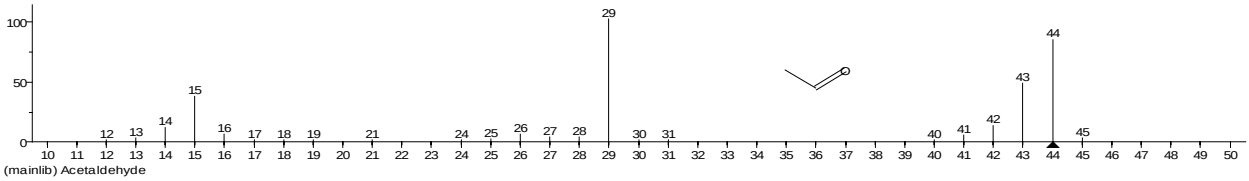
Name: Methyl vinyl ketone
Formula: C_4H_6O
MW: 70 CAS#: 78-94-4 NIST#: 230322 ID#: 17089 DB: mainlib
Synonyms:
1.3-Buten-2-one
2.Vinyl methyl ketone
3.1-Buten-3-one
4.2-Butenone

A.5 Aldehydes

	Aldehydes			
14	Formaldehyde	50-00-0	0.3	ppm
15	Acetaldehyde	75-07-0	25	ppm
16	Butanal	123-72-8	25	ppm
17	2-Methyl-2-butenal	1115-11-3	0.03	ppm
18	2-Ethyl-hex-2-enal	645-62-5	0.1	ppm
new	2-Propanal	107-02-8	0.1	ppm

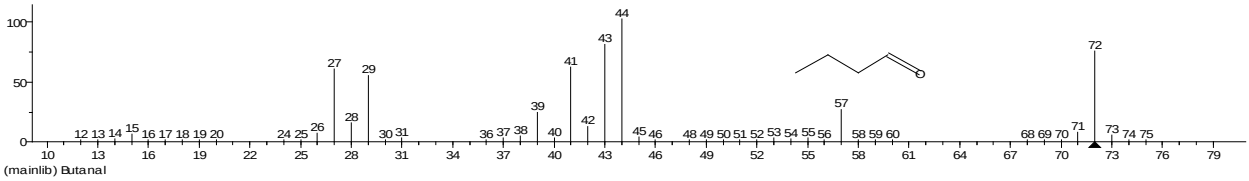


Name: Formaldehyde
Formula: CH_2O
MW: 30 CAS#: 50-00-0 NIST#: 37883 ID#: 404 DB: mainlib

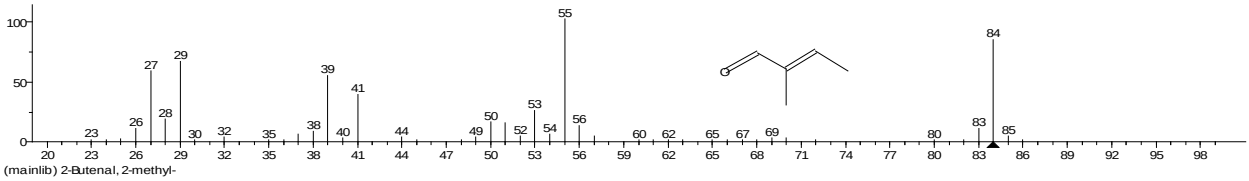


Name: Acetaldehyde
Formula: $C_2H_2H_4O$

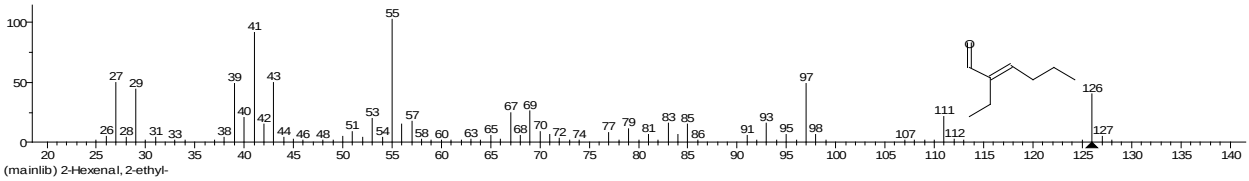
MW: 44 CAS#: 75-07-0 NIST#: 227634 ID#: 478 DB: mainlib



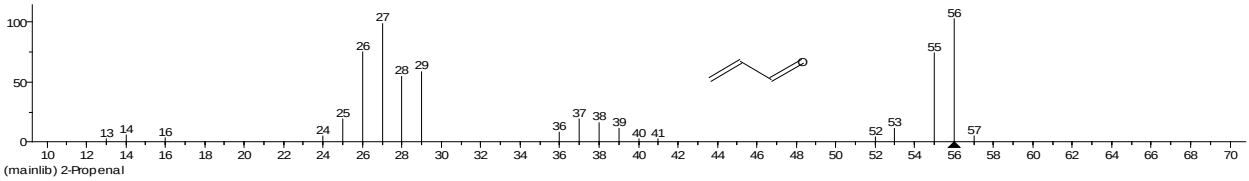
Name: Butanal
Formula: C_4H_8O
MW: 72 CAS#: 123-72-8 NIST#: 19131 ID#: 13497 DB: mainlib



Name: 2-Butenal, 2-methyl-
Formula: C_5H_8O
MW: 84 CAS#: 1115-11-3 NIST#: 150334 ID#: 18061 DB: mainlib



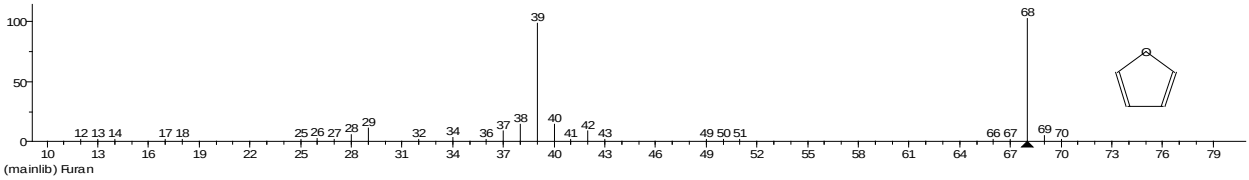
Name: 2-Hexenal, 2-ethyl-
Formula: $C_8H_{14}O$
MW: 126 CAS#: 645-62-5 NIST#: 250086 ID#: 16537 DB: mainlib
Synonyms:
1. à-Ethyl-á-propylacrolein
2. 2-Ethyl-2-hexen-1-al
3. 2-Ethyl-2-hexenal



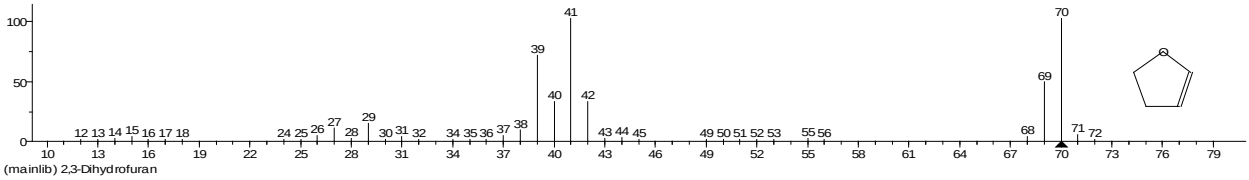
Name: 2-Propenal
Formula: C_3H_4O
MW: 56 CAS#: 107-02-8 NIST#: 114921 ID#: 18782 DB: mainlib

A.6 Furans and Substituted Furans

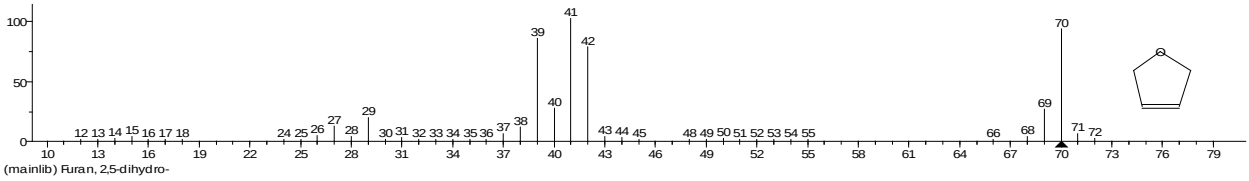
	Furans and Substituted Furans			
19	Furan	110-00-9	1	ppb
20	2,3-Dihydrofuran	1191-99-7	1	ppb
21	2,5-Dihydrofuran	1708-29-8	1	ppb
22	2-Methylfuran	534-22-5	1	ppb
23	2,5-Dimethylfuran	625-86-5	1	ppb
24	2-Ethyl-5-methylfuran	1703-52-2	1	ppb
25	4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1	ppb
26	3-(1,1-Dimethylethyl)-2,3-dihydrofuran	34314-82-4	1	ppb
27	2-Pentylfuran	3777-69-3	1	ppb
28	2-Heptylfuran	3777-71-7	1	ppb
29	2-Propylfuran	4229-91-8	1	ppb
30	2-Octylfuran	4179-38-8	1	ppb
31	2-(3-Oxo-3-phenylprop-1-enyl)furan	717-21-5	1	ppb
32	2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	1	ppb



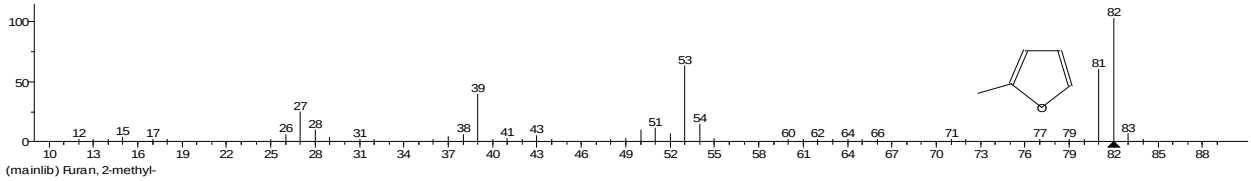
Name: Furan
Formula: C_4H_4O
MW: 68 CAS#: 110-00-9 NIST#: 228308 ID#: 27442 DB: mainlib



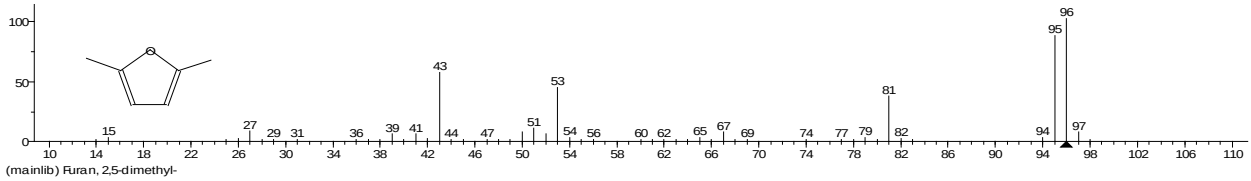
Name: 2,3-Dihydrofuran
Formula: C_4H_6O
MW: 70 CAS#: 1191-99-7 NIST#: 230218 ID#: 3160 DB: mainlib



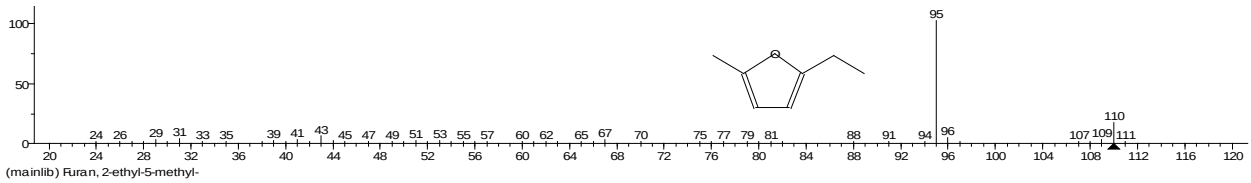
Name: Furan, 2,5-dihydro-
Formula: C_4H_6O
MW: 70 CAS#: 1708-29-8 NIST#: 227714 ID#: 3159 DB: mainlib



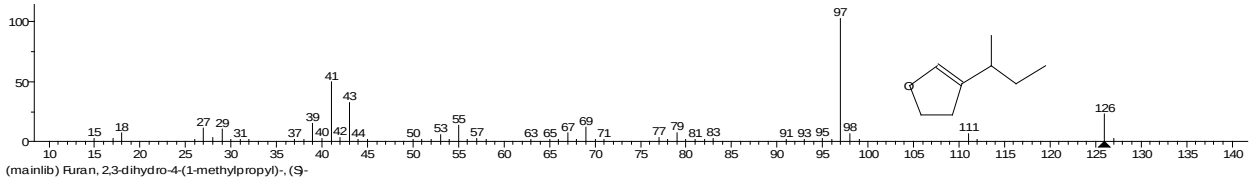
Name: Furan, 2-methyl-
Formula: C_5H_6O
MW: 82 CAS#: 534-22-5 NIST#: 229471 ID#: 40452 DB: mainlib



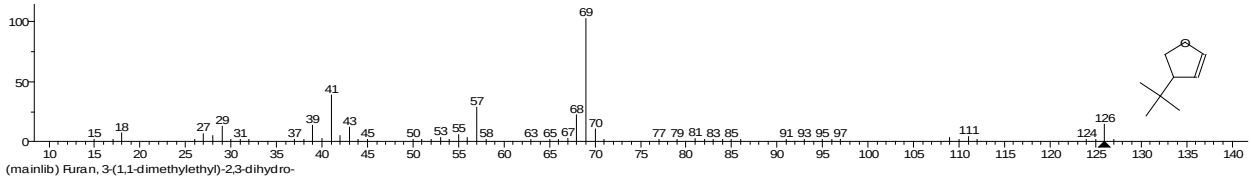
Name: Furan, 2,5-dimethyl-
Formula: C_6H_8O
MW: 96 CAS#: 625-86-5 NIST#: 233792 ID#: 54000 DB: mainlib



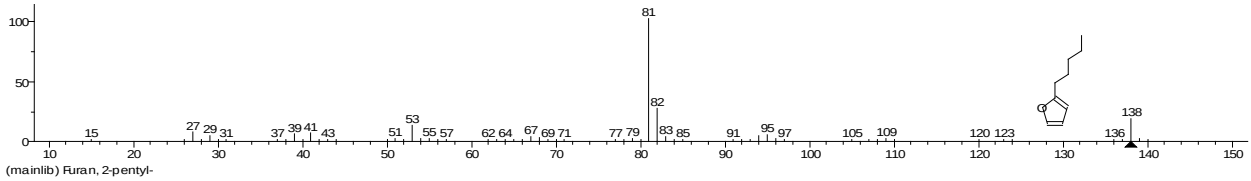
Name: Furan, 2-ethyl-5-methyl-
Formula: $C_7H_{10}O$
MW: 110 CAS#: 1703-52-2 NIST#: 249554 ID#: 53357 DB: mainlib



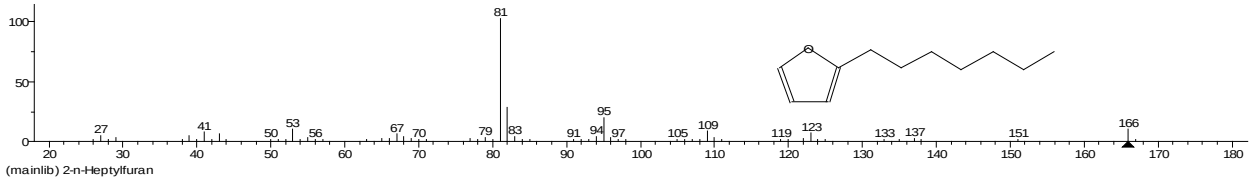
Name: Furan, 2,3-dihydro-4-(1-methylpropyl)-, (S)-
Formula: $C_8H_{14}O$
MW: 126 CAS#: 34379-54-9 NIST#: 38684 ID#: 54205 DB: mainlib



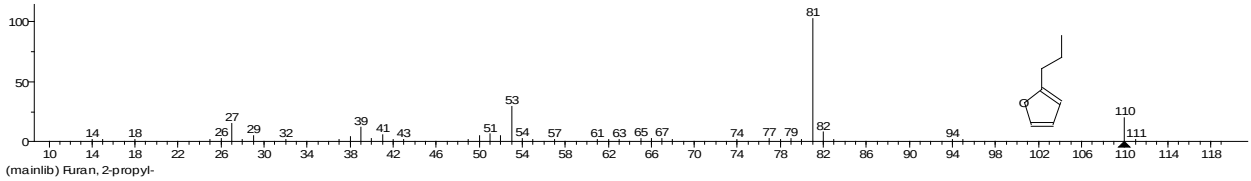
Name: Furan, 3-(1,1-dimethylethyl)-2,3-dihydro-
Formula: $C_8H_{14}O$
MW: 126 CAS#: 34314-82-4 NIST#: 38683 ID#: 28123 DB: mainlib



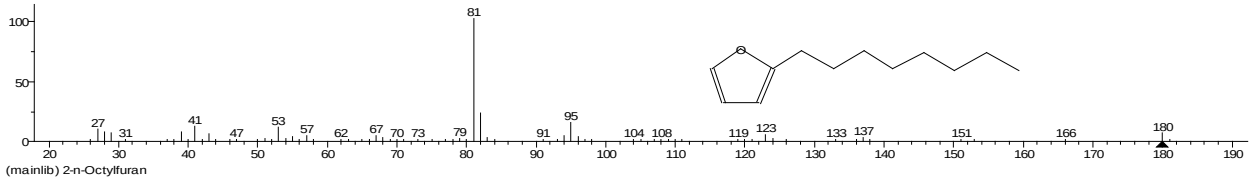
Name: Furan, 2-pentyl-
Formula: $C_9H_{14}O$
MW: 138 CAS#: 3777-69-3 NIST#: 237570 ID#: 39874 DB: mainlib



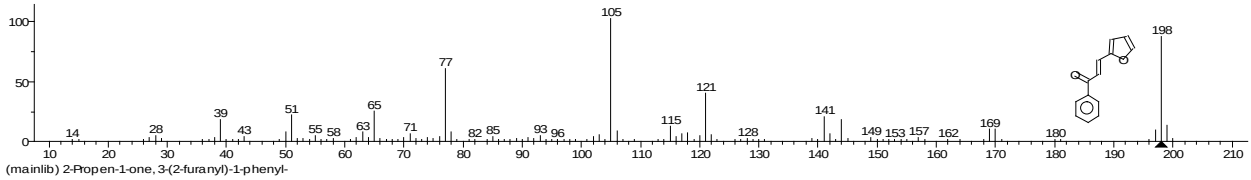
Name: 2-n-Heptylfuran
Formula: $C_{11}H_{18}O$
MW: 166 CAS#: 3777-71-7 NIST#: 118078 ID#: 39872 DB: mainlib



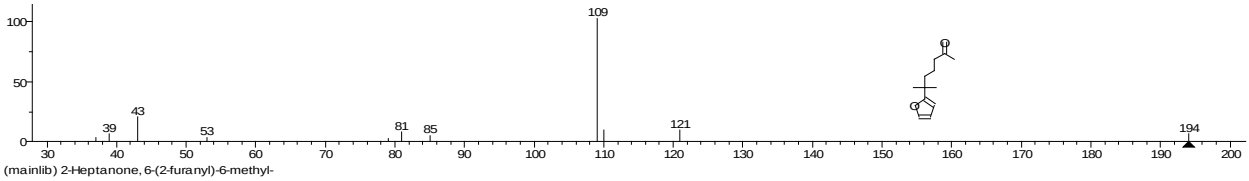
Name: Furan, 2-propyl-
Formula: $C_7H_{10}O$
MW: 110 CAS#: 4229-91-8 NIST#: 113123 ID#: 39523 DB: mainlib



Name: 2-n-Octylfuran
Formula: $C_{12}H_{20}O$
MW: 180 CAS#: 4179-38-8 NIST#: 249559 ID#: 39873 DB: mainlib



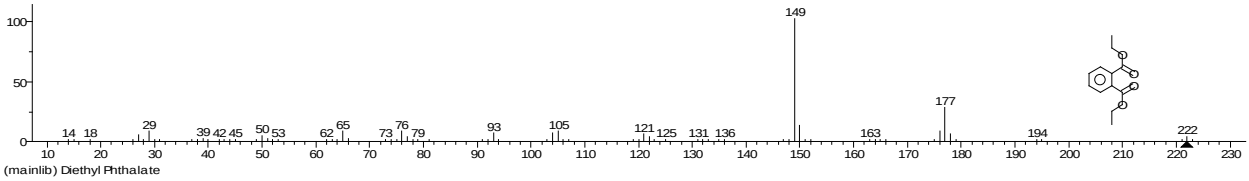
Name: 2-Propen-1-one, 3-(2-furanyl)-1-phenyl-
Formula: $C_{13}H10O_2$
MW: 198 CAS#: 717-21-5 NIST#: 8813 ID#: 62155 DB: mainlib
Synonyms:
1.Acrylophenone, 3-(2-furyl)-
2.Furfurylideneacetophenone
3.3-(2-Furyl)acrylophenone
4.(2E)-3-(2-Furyl)-1-phenyl-2-propen-1-one



Name: 2-Heptanone, 6-(2-furanyl)-6-methyl-
Formula: $C_{12}3H_{18}O_2$
MW: 194 CAS#: 51595-87-0 NIST#: 28481 ID#: 65263 DB: mainlib

A.7 Phthalates

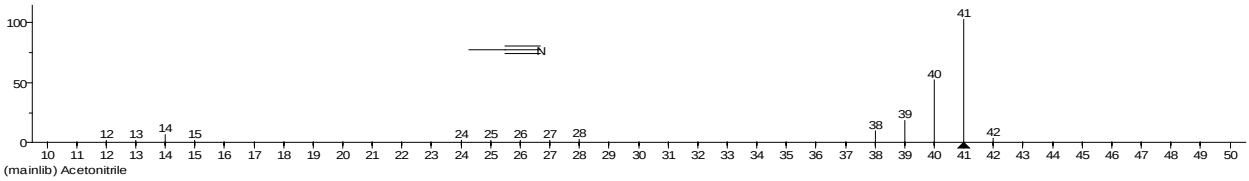
	Phthalates			
33	Diethyl Phthalate	84-66-2	5	mg/m3



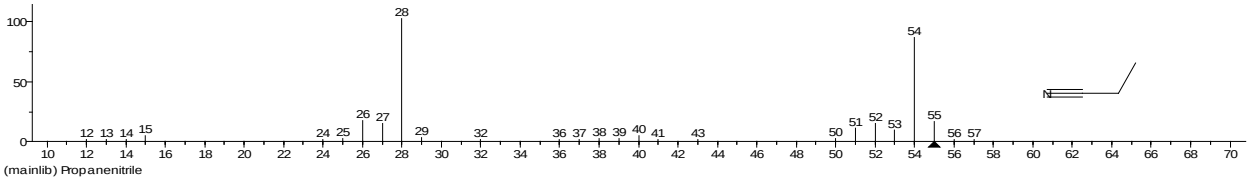
Name: Diethyl Phthalate
Formula: $C_{12}H_{14}O_4$
MW: 222 CAS#: 84-66-2 NIST#: 227685 ID#: 96325 DB: mainlib

A.8 Nitriles

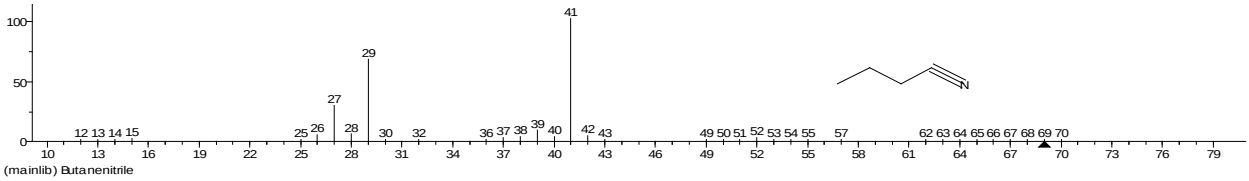
	Nitriles			
34	Acetonitrile	75-05-8	20	ppm
35	Propanenitrile	107-12-0	6	ppm
36	Butanenitrile	109-74-0	8	ppm
37	Pentanenitrile	110-59-8	6	ppm
38	Hexanenitrile	628-73-9	6	ppm
39	Heptanenitrile	629-08-3	6	ppm
40	2-Methylene butanenitrile	1647-11-6	0.3	ppm
41	2,4-Pentadienenitrile	1615-70-9	0.3	ppm



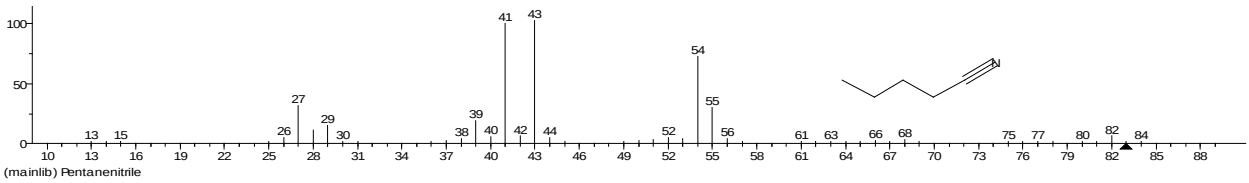
Name: Acetonitrile
Formula: C_2H_3N
MW: 41 CAS#: 75-05-8 NIST#: 228221 ID#: 2004 DB: mainlib



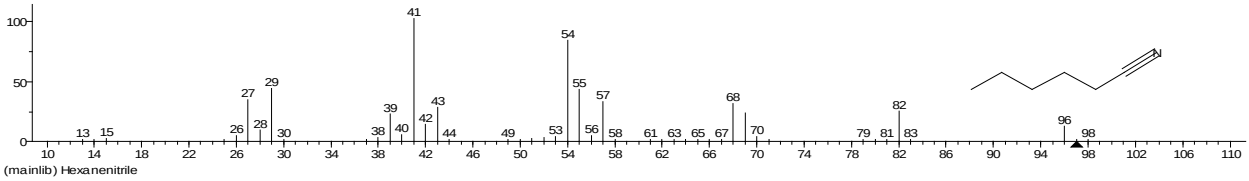
Name: Propanenitrile
Formula: C_3H_5N
MW: 55 CAS#: 107-12-0 NIST#: 227644 ID#: 182 DB: mainlib



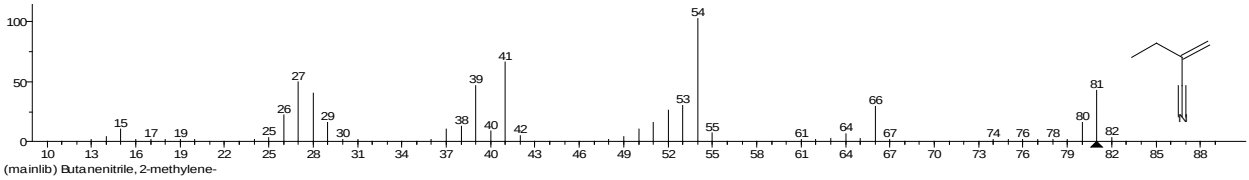
Name: Butanenitrile
Formula: C_4H_7N
MW: 69 CAS#: 109-74-0 NIST#: 228226 ID#: 1805 DB: mainlib



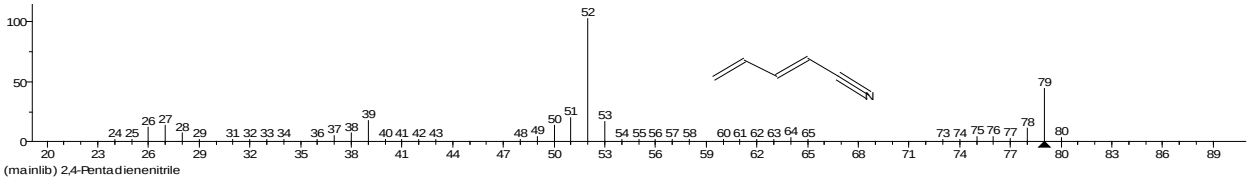
Name: Pentanenitrile
Formula: C_5H_9N
MW: 83 CAS#: 110-59-8 NIST#: 227665 ID#: 5299 DB: mainlib



Name: Hexanenitrile
Formula: $C_6H_{11}N$
MW: 97 CAS#: 628-73-9 NIST#: 228551 ID#: 2320 DB: mainlib



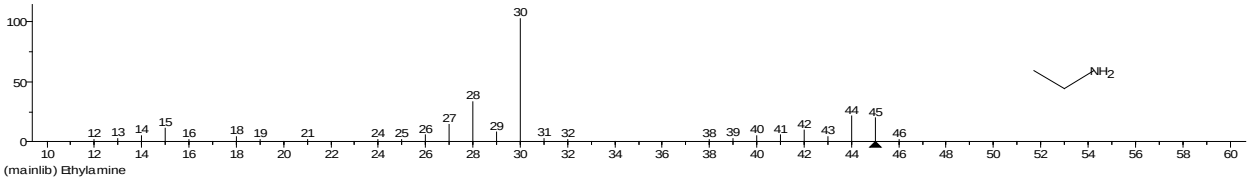
Name: Butanenitrile, 2-methylene-
Formula: C_5H_7N
MW: 81 CAS#: 1647-11-6 NIST#: 26961 ID#: 16116 DB: mainlib



Name: 2,4-Pentadienenitrile
Formula: C_5H_5N
MW: 79 CAS#: 1615-70-9 NIST#: 409 ID#: 15850 DB: mainlib

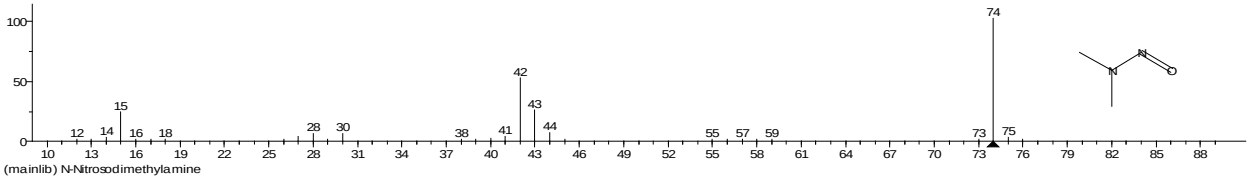
A.9 Amines

	Amines			
42	Ethylamine	75-04-7	5	ppm

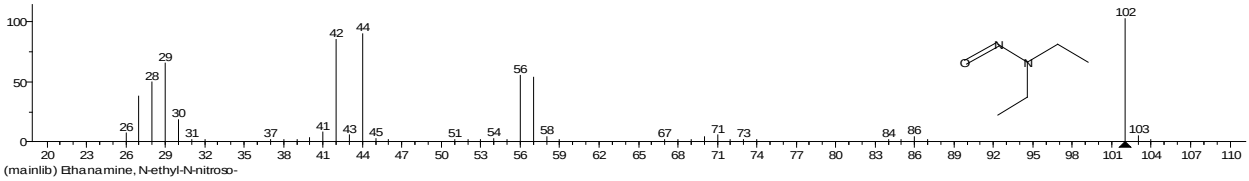


Name: Ethylamine
Formula: C_2H_7N
MW: 45 CAS#: 75-04-7 NIST#: 71 ID#: 798 DB: mainlib

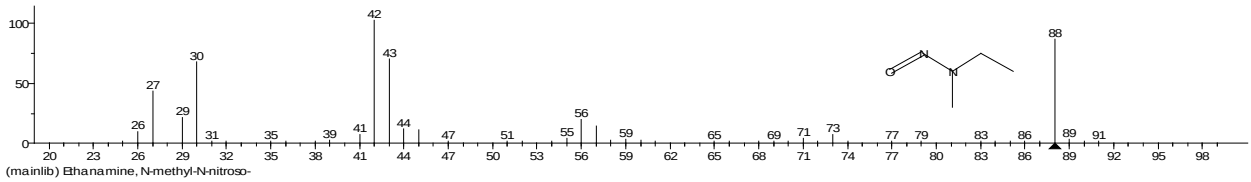
	Nitrosamines			
43	N-Nitrosodimethylamine	62-75-9	0.3	ppb
44	N-Nitrosodiethylamine	55-18-5	0.1	ppb
45	N-Nitrosomethylethylamine	10595-95-6	0.3	ppb
46	N-Nitrosomorpholine	59-89-2	0.6	ppb
	1-Butanamine, N-butyl-N-nitroso (new candidate for COPC)	924-16-3		



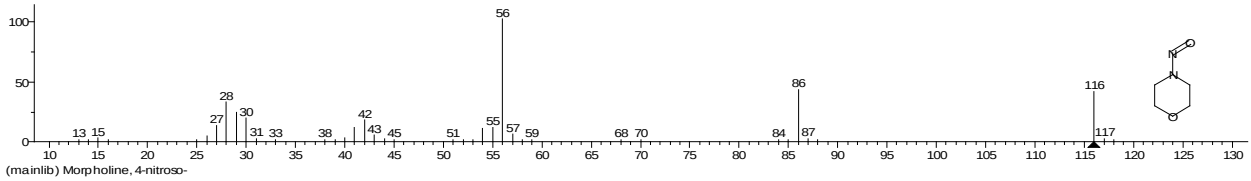
Name: N-Nitrosodimethylamine
Formula: $C_2H_6N_2O$
MW: 74 CAS#: 62-75-9 NIST#: 229457 ID#: 35070 DB: mainlib
Synonyms:
1. NDMA



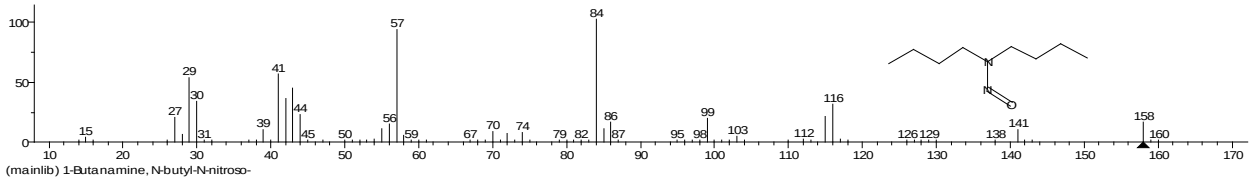
Name: Ethanamine, N-ethyl-N-nitroso-
Formula: $C_4H_{10}N_2O$
MW: 102 CAS#: 55-18-5 NIST#: 53405 ID#: 57809 DB: mainlib



Name: Ethanamine, N-methyl-N-nitroso-
Formula: $C_3H_8N_2O$
MW: 88 CAS#: 10595-95-6 NIST#: 249039 ID#: 4462 DB: mainlib
Synonyms:
1. NMEA



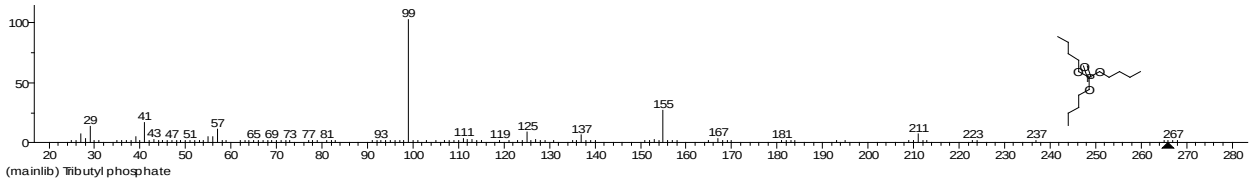
Name: Morpholine, 4-nitroso-
Formula: $C_4H_8N_2O_2$
MW: 116 CAS#: 59-89-2 NIST#: 291320 ID#: 19441 DB: mainlib
Synonyms:
1.N-Nitrosomorpholine



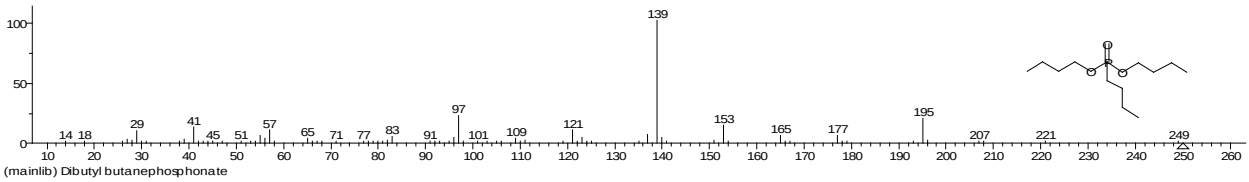
Name: 1-Butanamine, N-butyl-N-nitroso-
Formula: $C_8H_{18}N_2O$
MW: 158 CAS#: 924-16-3 NIST#: 233736 ID#: 42273 DB: mainlib

A.10 Organophosphates and Organophosphonates

	Organophosphates and Organophosphonates			
47	Tributylphosphate	126-73-8	0.2	ppm
48	Dibutylbutylphosphonate	78-46-6	0.007	ppm

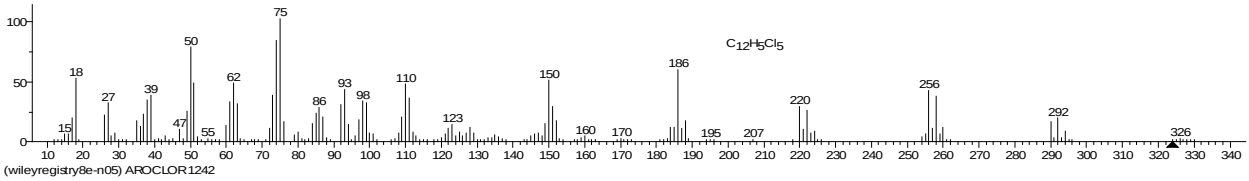


Name: Tributyl phosphate
Formula: $C_{12}H_{27}O_4P$
MW: 266 CAS#: 126-73-8 NIST#: 154673 ID#: 56489 DB: mainlib
Synonyms:
1. TBP

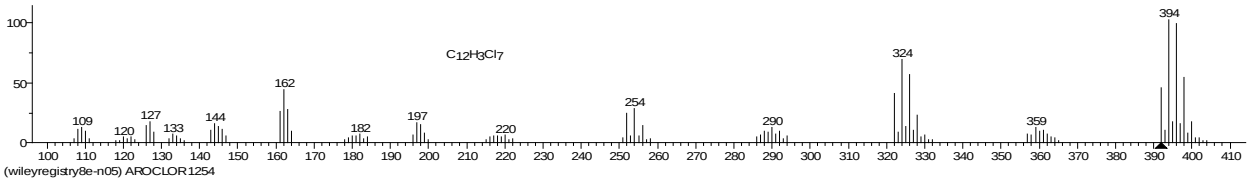


Name: Dibutyl butanephosphonate
Formula: $C_{12}H_{27}O_3P$ $C_{12}H_{27}O_3P$
MW: 250 CAS#: 78-46-6 NIST#: 118343 ID#: 88920 DB: mainlib

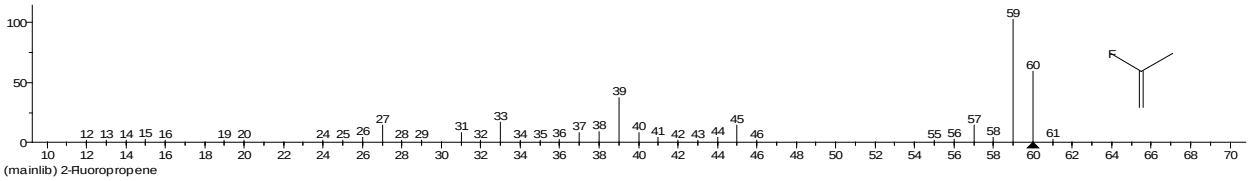
	Halogenated Hydrocarbons			
49	Chlorinated Biphenyls	Varies	1	mg/m3
50	2-Fluoropropene	1184-60-7	0.1	ppm



Name: AROCLOR 1242
Formula: $C_{12}H_5Cl_5$
MW: 324 CAS#: 53469-21-9 ID#: 119579 DB: wileyregistry8e-n05
Synonyms:
1. Polychlorinated Biphenyl (Aroclor 1242)
2. Polychlorobiphenyls (42% Chlorine)



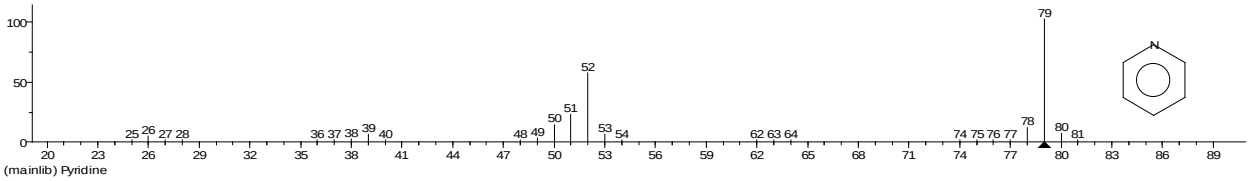
Name: AROCLOR 1254
Formula: $C_{12}H_3Cl_7$
MW: 392 CAS#: 11097-69-1 ID#: 517221 DB: wileyregistry8e-n05
Synonyms:
1. Arochlor 1254
2. Heptachlorobiphenyl
3. PCB 1254



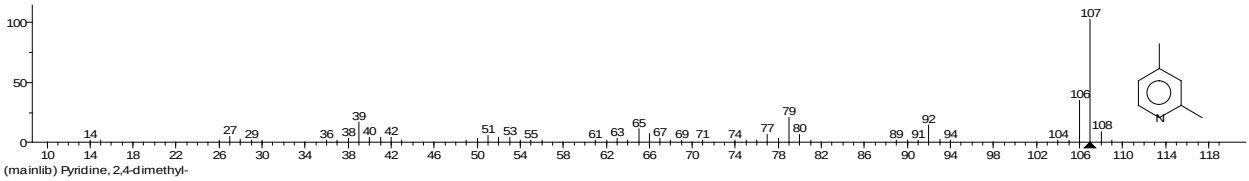
Name: 2-Fluoropropene
Formula: C_3H_5F
MW: 60 CAS#: 1184-60-7 NIST#: 152 ID#: 24872 DB: mainlib

A.11 Pyridines

	Pyridines			
51	Pyridine	110-86-1	1	ppm
52	2, 4-Dimethylpyridine	108-47-4	0.5	ppm



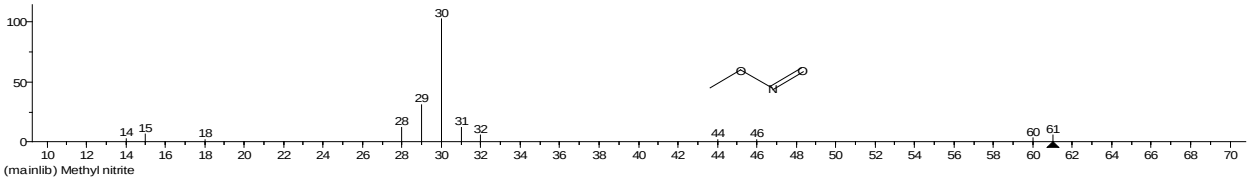
Name: Pyridine
Formula: C_5H_5N
MW: 79 CAS#: 110-86-1 NIST#: 227742 ID#: 38341 DB: mainlib



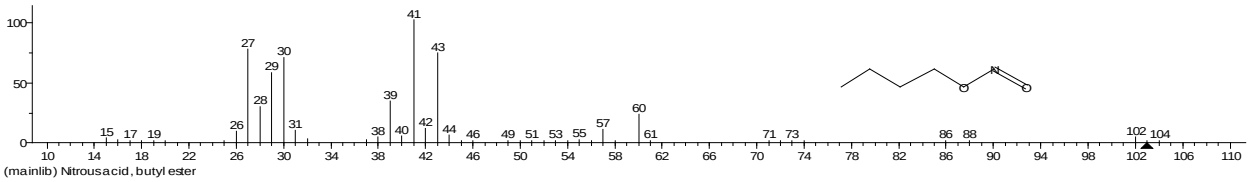
Name: Pyridine, 2,4-dimethyl-
Formula: C_7H_9N
MW: 107 CAS#: 108-47-4 NIST#: 227867 ID#: 64039 DB: mainlib

A.12 Organonitrites

	Organonitrites			
53	Methyl nitrite	624-91-9	0.1	ppm
54	Butyl nitrite	544-16-1	0.1	ppm



Name: Methyl nitrite
Formula: CH_3NO_2
MW: 61 CAS#: 624-91-9 NIST#: 19008 ID#: 817 DB: mainlib

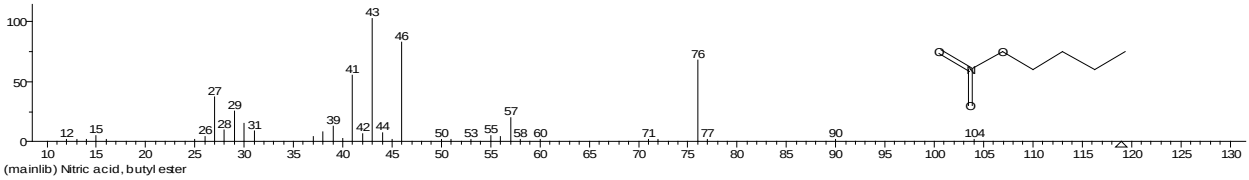


Name: Nitrous acid, butyl ester
Formula: $C_4H_9NO_2$
MW: 103 CAS#: 544-16-1 NIST#: 247736 ID#: 1783 DB: mainlib

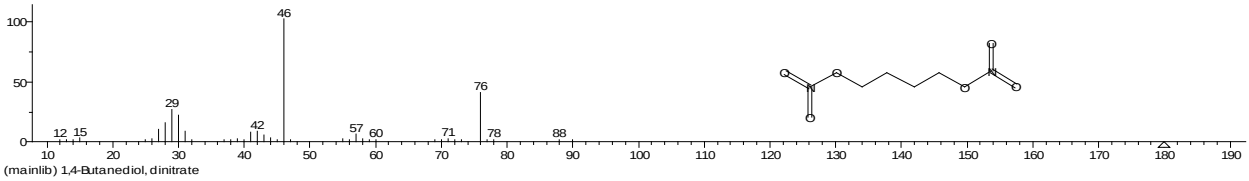
Synonyms:
1. n-Butyl nitrite
2. Butyl nitrite

A.13 Organonitrates

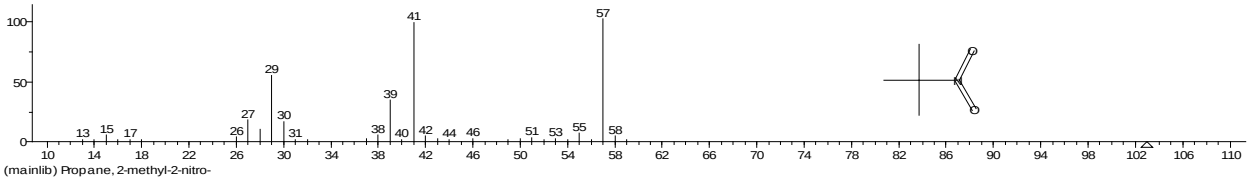
	Organonitrates			
55	Butyl nitrate	928-45-0	2.5	ppm
56	1,4-Butanediol, dinitrate	3457-91-8	0.05	ppm
57	2-Nitro-2-methylpropane	594-70-7	0.3	ppm
58	1,2,3-Propanetriol, 1,3-dinitrate	623-87-0	0.05	ppm



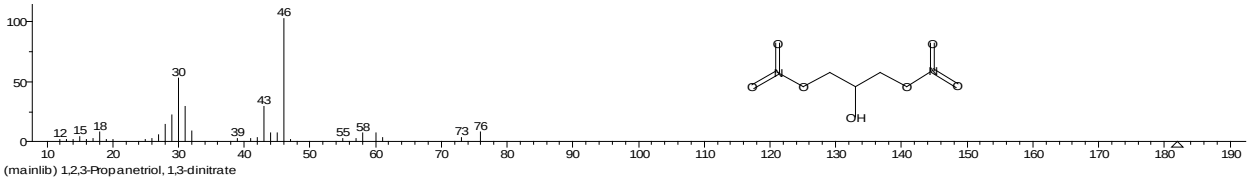
Name: Nitric acid, butyl ester
Formula: $C_4H_9NO_3$
MW: 119 CAS#: 928-45-0 NIST#: 2131 ID#: 6254 DB: mainlib
Synonyms:
1. Butyl nitrate



Name: 1,4-Butanediol, dinitrate
Formula: $C_4H_8N_2O_6$
MW: 180 CAS#: 3457-91-8 NIST#: 7517 ID#: 15553 DB: mainlib



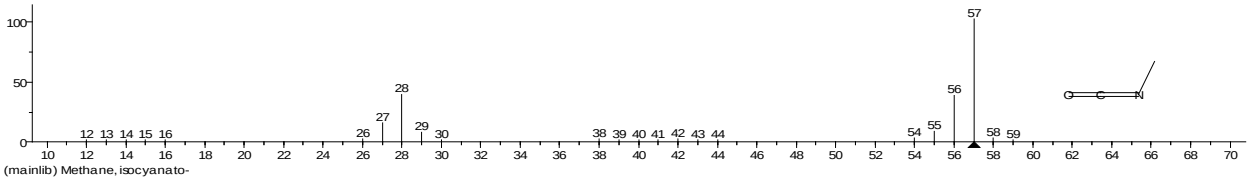
Name: Propane, 2-methyl-2-nitro-
Formula: $C_4H_9NO_2$
MW: 103 CAS#: 594-70-7 NIST#: 125413 ID#: 19955 DB: mainlib
Synonyms:
1. Trimethylnitromethane
2. 1,1-Dimethyl-1-nitroethane
3. 2-Methyl-2-nitropropane
4. 2-Nitro-2-methylpropane



Name: 1,2,3-Propanetriol, 1,3-dinitrate
Formula: $C_3H_6N_2O_7$
MW: 182 CAS#: 623-87-0 NIST#: 7697 ID#: 15493 DB: mainlib

A.14 Isocyanates

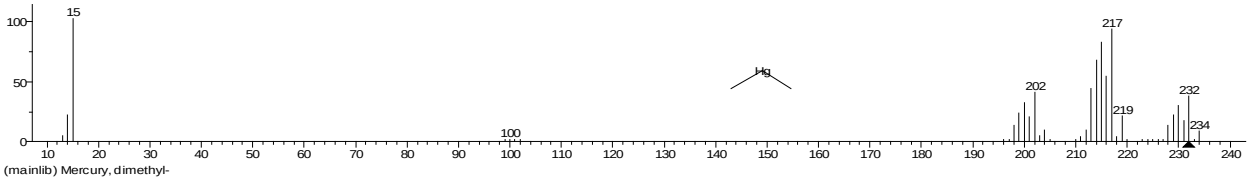
	Isocyanates			
59	Methyl Isocyanate	624-83-9	20	ppb



Name: Methane, isocyanato-
Formula: C2H3NO
MW: 57 CAS#: 624-83-9 NIST#: 291572 ID#: 19766 DB: mainlib
Synonyms:
1. Isocyanic acid, methyl ester
2. Methyl isocyanate

A.15 Dimethyl Mercury

	Organometallic	CAS No.	OEL	Units
new	Dimethyl mercury, as Hg	593-74-8	0.01	mg/m3



Name: Mercury, dimethyl-
Formula: C_2H_6Hg
MW: 232 CAS#: 593-74-8 NIST#: 34446 ID#: 24 DB: mainlib

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