


Chemical Sciences Division

Self-Assessment Report

Hazard Analysis of Chemicals Used In CSD Research Groups

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Executive Summary

As a vital component of the forthcoming Work Planning and Control (WP&C) system it was essential to assess to what degree Chemical Sciences researchers are able to generate suitable hazard analysis of chemicals. Chemicals are frequently used in their experiments. From assessment, it was observed that a significant number of Chemical Sciences Division (CSD) researchers were not using existing resources to determine the hazards of chemicals being used. Hazard analysis is an essential step in the process controlling safe utilization of chemicals.

Chemical hazards analysis was done by researchers within a framework called: Task Specific Job Hazard Analysis (TSJHA). Researchers prepare a TSJHA, which is reviewed by their Principle Investigator/Work Lead and the CSD safety coordinator (DSC). After several iterations, the mutually agreed upon document becomes the topic for a discussion session that includes the researcher(s), PI/Work Lead and the CSD DSC. Point by point approval is covered so it is clear that all parties understand the procedures to follow and most importantly, why. People are asked to sign the TSJHA document to authorize the intended work.

Many times EHSS Subject Matter Experts are also included in these TSJHA approval conference sessions. The aim is to gather their critique of the TSJHA process. The question is, has sufficient material been included in the TSJHA hazard analysis to assure a responsible hazard and control document has been created?

Introduction

For more than two years the DSC has been asked by many CSD researchers whether a particular chemical was safe to use in their experiments. At first, conditions under which the chemical(s) were being used in the experiments were not clearly stated. It was observed that many of the researchers did not realize what hazards and dangers they might be exposing themselves and other laboratory occupants to when using a particular chemical(s).

In an evolutionary manner, a process was gradually developed and tested which follows the outline of a well-known but not that often used technique: Task Specific Job Hazard Analysis (TSJHA). TSJHA is essentially a classic ISM procedure. Step 1 – Define Scope of Work; Step 2 – Identify Hazards; Step 3 – Apply appropriate controls to mitigate hazards; and Step 4 – Perform the work. Application of TSJHA hazard analysis is confined to those substances used within a single experiment, hence the designation – Task Specific application.

Elements in a typical TSJHA would include:

- 1) Statement of Scope of Work. What are you doing?
- 2) Identification of hazards associated with the chemical(s) being used. Consideration of hazards may include not only the primary health and/or flammability dangers, but also the secondary hazards that might be created by inappropriate material handling. For example, accidental combustion of a chemical may generate a new hazardous exposure condition from the combustion products.

Starting point for the chemical hazard analysis is use of the ChemWatch Material Data Safety Sheets (MSDS). ChemWatch MSDSs are employed UC system wide and are supported by LBNL. At the top of any ChemWatch MSDS, in Section 1 – Chemical Product and Company Identification - is a –National Fire Protection Association – NFPA - graphic representation of the hazard for a chemical in consideration of:

- 1) Health Hazard (blue color in a NFPA diamond).
- 2) Flammability (red color in a NFPA diamond).

- 3) Instability (Yellow color in a NFPA diamond).
- 4) Special Chemical Sensitivities (White color in a NFPA diamond).

This NFPA rating system is principally directed towards needs of fire fighters or other emergency responders and reflects an estimation of acute hazards, without any inclusion of chronic effects or use.

Section 2 – Hazards Identification – contains the ChemWatch hazard rating system which is divided into five categories.

- 1) Flammability
- 2) Toxicity
- 3) Body Contact
- 4) Reactivity
- 5) Chronic effects

Like the NFPA system, this ChemWatch system rates each category from 0-4, with 0 being minimal, and 4 being extreme. This rating system is more reflective of actual conditions that can be expected in an actual laboratory environment. The ChemWatch MSDS “quick” hazard rating system cartoon follows the guidelines for what will likely become an internationally accepted rating system. This is the much preferred choice for a systematic first indicator of degrees of hazard for any particular substance. Whenever a 3 or 4 rating in any rating category occurs for a chemical, special considerations are contemplated in WC&P, which may include EHSS (Environmental, Health Safety and Security) - SMEs (Subject Matter Expert), as well as divisional expertise, in evaluation of the chemical hazard. For investigations done on the floor of the ALS ESS (Experimental Safety Sheets – ALS requirement) are included.

The above described rating systems are only a “quick and dirty” indicator of hazards when using the chemical. Much additional and useful safety information is found in the body of the MSDS associated with a particular chemical. The next item of interest is a quite useful data: the Chemical Abstract Service (CAS) Registry Number (RN). This special sequence of numbers uniquely identifies the compound under consideration. It is also very useful for performing any Google searches for additional information. CAS numbers are found in Section 3 of a MSDS.

Sections 4, 5, 6 and 7 are concerned with First Aid Measures, Fire Fighting Measures, Accidental Release Measures and Handling and Storage information, respectively. While important topics are contained in these sections, the content doesn’t have a direct bearing on preparing a TSJHA hazard analysis of a chemical.

MSDS Section 8 – Exposure Controls/Personal Protection – contains valuable safety information. Exposure controls limits are frequently found as adopted by the American Conference of Governmental Industrial Hygienists (ACGIH). The “threshold limit value” – TLV – quoted is defined and explained in an Appendix Y addendum contained in all of these TSJHAs. Other data such as odor detection limits, glove and eye protection, etc... is also listed in Section 8.

Section 9 – Physical and Chemical Properties – contains useful information such as: Upper and Lower explosive limits; melting, boiling and flash points, and vapor pressures.

Section 10 – Chemical Stability – lists prominent incompatibles of the substance under consideration with other chemicals.

Section 11 – Toxicological Information – repeats some of the information already developed in Section 8. However, this section also contains TLV values for Carcinogens. The values are expressed as being either A1, A2, A3, A4, or A5. A definition of these ACGIH TLV values is included in an Appendix Z, which is included

in many of these example TSJHAs. An A1 notation indicates the substance is a “confirmed human carcinogen”; a value of A5 means “not suspected as a human carcinogen”.

Infrequently Section 16 – Other Information – may contain tid-bits of useful safety information. This section appears to be a spot for listing new information that has not yet been incorporated in a periodically revised and updated MSDS.

Researchers are asked to provide a first draft of a new TSJHA which incorporates pertinent safety information gathered from these MSDSs sections. Learning which parts of these verbose MSDSs are essential as a vital part of learning how to effectively use these materials. Sections 1, 2, 3, 8, 9, 10, 11 and sometimes 16 are the key parts of a MSDS to examine. Additionally it is expected that a Google search is done using CAS RN and keywords to determine if any readily available information exists about the chemical behavior of the compound of interest.

The TSJHA draft goes through numerous reviews and revisions by both the PI/Work Lead and the DSC. When the TSJHA is ready, a conference is held which includes the researcher(s), the PI/Work Lead and the DSC. EHSS personnel are frequently invited to this TSJHA approval session.

Current Requirements

Chemical Hygiene and Safety Plan

ROLES AND RESPONSIBILITIES

Division Directors shall ensure that:

- Resources are provided to line managers to identify, evaluate and control chemical hazards associated with existing and proposed work performed within their Division to ensure that ES&H can be integrated into day-to-day operations.

Supervisors, Managers, and Work Leads

Supervisors, Managers, and Work Leads are part of the safety line management chain from each worker to the Laboratory Director. Supervisors and Managers are part of the formal management chain, and they have the responsibility for adhering to all EH&S policies and safe work practices. Work leads (who may be non-management) derive authority from formal laboratory managers and/or supervisors to ensure that day-to-day work, operations, and activities in their assigned area(s) and activities are conducted safely and within established work authorizations. Supervisors, managers and work leads are collectively referred to as “safety line management.”

Supervisors, Managers and Work Leads are required, among many other requirements, to:

Integrate ES&H into resource planning, funding, prioritizing, scheduling, and implementation of work conducted under their purview.

- Inform employees, contractors, students, and visitors about Berkeley Lab’s EH&S policies and procedures and ensure that they are aware of the existence and availability of [chemical hazard information and resources](#).
- **Provide specific training on the hazards and safety precautions related to each employee's assigned work.**

Employees, Workers, Subcontractors, and Casual and Participating Guests

For purposes of safety, LBNL does not distinguish between career employees, subcontractors, and guests/visitors. All personnel are required to:

- Work safely by observing safety standards, guidelines, and procedures, and by using good judgment based on training and expertise.
- Complete a [Job Hazard Analysis](#), follow the required controls, and complete required training. For use of chemicals in the workplace researcher is required to complete the EHSS training course - **EHS 348 Chemical Hygiene and Safety Training**.

Assessment Scope

Study and consideration of TSJHA samples detailed in the Appendix section form the basis for conducting this: Hazard Analysis of Chemicals used in CSD Research groups. Each completed example TSJHA demonstrates a point for each researcher's TSJHA.

Assessment Results

Findings:

None noted.

Observations:

#1 - Appendix A – *TSJHA for Use of Formic Acid in Dissociative Electron Attachment to Gas Molecules Experiment Apparatus*, is an earlier example of the TSJHA development process. If the document is diagrammed it is realized that the structure follows a pattern: PPE requirements (page 13 of 87); Scope Description (13 of 87); Analysis of Hazards (13 of 87); Mitigation of Hazards (13-14 of 87); concluded with a signature authorization sign off (15 of 87). This TSJHA is textual without the benefit of any photos or diagrams. What work the researcher intends to be authorized to do involving formic acid is clearly covered in the text. Reducing exposure to formic acid fumes is achieved by working with a laboratory hood system, temperature control of the sample and specially designed sample containment equipment which connects to the building air exhaust system.

What is missing are photos and/or drawings which would aid in understanding how the experiment is setup, how the additional safety equipment is incorporated and operates, and photos illustrating how sample temperature control is an essential part of the experiment. Photos, taken at a later time, demonstrate many of the essential steps in this experimental process. These are displayed on pages 16-22 of 87.

Also missing are any visual representations of NFPA and/or ChemWatch hazard ratings, in particular for health and for flammability. Quoting the NFPA values and other exposure hazard values in the text doesn't stand out. For a first attempt at generating a satisfactory TSJHA research work authorization this document was a good attempt. An hour long meeting with the researchers, the PI/Work Lead and the CSD Safety Coordinator discussing the safety and exposure information within this TSJHA was done before the TSJHA authorization was completed. This form of On-the-Job (OJT) training was well received by the experimenters and their line management, who felt the Job-Hazard-Analysis efforts expended, was very beneficial in establishing and maintaining effective hazard controls.

#2 – Appendix B – *TSJHA for Use of Sodium Azide (NaN₃), under Acidic Conditions, in Electrospray Ionization (ESI) Mass Spectrometry Experiments* – was generated two years later than the TSJHA in Appendix A. Many new graphic and tabular informational features are included in this TSJHA. The first safety information item one notices is the extreme health hazard for this chemical. In both ChemWatch and NFPA pictorial health hazard ratings are 4; indication of a serious health hazard chemical.

"OSHA mandates employers to identify higher hazard work that requires prior approval. At LBNL this is accomplished with the Activity Hazard Document (AHD). An AHD is a formal work authorization which lists controls and procedures to reduce the risks associated with a higher-hazard activity to an acceptable level. AHDs are incorporated into the [Job Hazards Analysis](#) by reference. The PI /Supervisor must identify and

evaluate all potential hazards associated with a proposed project or activity and develop measures to reduce these hazards to an acceptable level. **He/she must also determine whether an AHD is needed.** The AHD is required to be completed before work is initiated. When reviewed and approved, the AHD becomes the principal safety document for that higher-hazard portion of the research project or activity. The AHD is reviewed by EH&S health and safety professionals and line management. Work under an AHD is authorized by the responsible Division Director with EH&S concurrence.

The LBNL protocol for determining the proper level of work authorization is delineated in [PUB-3000, Chapter 6, "Safe Work Authorizations."](#)

All AHDs are developed, reviewed, and approved through the Laboratory's [Activity Hazard Document Database](#).

Examples of activities requiring AHDs include:

- Activities requiring the use of gloveboxes for safety reasons
- Work that uses toxic or pyrophoric gases. ([PUB-3000, Chapter 13, "Gases,"](#) may be consulted for further guidance regarding controls for toxic and pyrophoric gases).
- **Activities that involve reactive or explosive chemicals.**
- Work that uses chemicals possessing lethal or incapacitating toxicity or chemicals that have an [LD₅₀](#) of 0.5 mg/Kg or less.
- Other activities with chemicals for which an EH&S Industrial Hygienist determines that an AHD is required.

Below are several lists of chemicals that correspond to these work activities. Note these lists are NOT inclusive. Consult sources such as [Material Safety Data Sheets](#) (MSDSs) must be consulted to determine hazardous properties of chemicals:

Reactive and Explosive Substances: from LBNL Chemical Hygiene and Safety Plan

aluminum hydride	picric acid
benzoyl peroxide	Potassium
cesium	rubidium
copper azide	sodium
lead azide	sodium azide
lithium	triethyl aluminum
phosphorus (white)	trimethyl aluminum

Above information taken from LBNL: Chemical Hygiene and Safety Plan (CHSP) – Section devoted to defining need for an Activity Hazard Document (AHD).

The key item in the CHSP write up is the provision which allows the PI/Work Lead discretion in determining whether an AHD is needed. In this TSJHA example –Appendix B - the hazard analysis of using sodium azide under acidic conditions indicated within the boundaries presented in the "Scope of Work" statement that minimum and very well controlled hazards would be expected.

First: Sodium Azide was not used as a 100% concentrated powder. The stock solution was 1 milliliter of 0.1 Molar concentration. Dilutions were taken from this stock solution that were a thousand to 10 thousand fold more dilute. Since the acidified sodium azide (hydrogen azide) was to be mixed with radioactive elements for injection into an ESIMS apparatus this azide material would always be contained within a glovebox. Use of a glovebox is mandated under terms of a RWA which permits mixing potential complexing ligands with radioactive materials solutions. Any hydrogen azide that would be generated, as a consequence of acidification, would be exhausted through the HEPA filtered exhaust system. Personnel exposure to the potentially serious health effects of hydrogen- or sodium azide would be very well controlled and minimized.

This TSJHA serves the purpose of familiarizing the researchers and PIs/Work leads with the value of conducting their own hazard analysis. They become familiar with the numerous and readily available safe-use information sources. They then can utilize this safety information to make reasonable judgments about the need for formal authorization documents (i.e., AHDs).

This TSJHA contains the complete text for Appendix Y – **Threshold Limit Value (TLV)** and Appendix Z. – **Threshold Limit Values (TLV) – Carcinogens**.

#3 – Appendix C – *TSJHA for Use of Bromobenzene in Transient Absorption Experiment* – is a practice TSJHA to assess the ability of a graduate student researcher to construct a suitable Job-Hazard-Analysis for safe use of bromobenzene in laser-vacuum chamber experiments. This relatively benign chemical, brominated benzene, was chosen to replace the initial selection: bromine. After acquainting the researcher with the hazards to health and equipment from using bromine, a decision was made to substitute a different chemical: bromobenzene. This compound could supply the sought after information about variable UV laser induced gas-phase reactions for bromo-X bond materials.

The degree to which Material Safety Data Sheets (MSDSs) for these two chemicals were understood was a troubling indicator of an incomplete ability to evaluate hazards that could arise from employing them in complex experiments. It was decided to employ this use of bromobenzene as an opportunity to develop a familiarity with performing TSJHAs using MSDSs and other informational resources. ChemWatch MSDSs appear, at first, to be overwhelming in the volume of information being presented. It was the intent of using this practice TSJHA to strengthen this particular researcher's skills in learning how to evaluate workplace chemical hazards and how to extract pertinent information. This TSJHA also serves as an example that can be used to develop and broaden other associates competence for doing similar hazard analyses.

In the process of creating this TSJHA it also became apparent that most of the safety-based suggestions which are included in the Chemical Hygiene EHSS Training Course:EHS0348 were in need of being actively reviewed or developed by including descriptions of On-the-Job training points. These training points are frequently included in Activity Hazard Document authorizations and are nearly always presented in essentially "boiler-plate" formatted statements. What was needed was to expand concretely on the skeletal elements presented in the formal EHSS Chemical Hygiene training. Connections between the EHSS training and how to actually implement these practices were made by using these "talking points" in the subsequent discussion held between researcher(s), PI(s)/Work Lead(s) and Safety Coordinator before a work authorization was concluded.

Other concepts presented in this TSJHA include:

A) Idea of identifying systemic safety behavioral trends as related chemical members are contrasted and compared. Bromobenzene can be classified as a member of mono-substituted chemicals which have benzene as the parent. Physical properties, which control the chemical safety, will vary systemically across the substituted benzene molecules.

B) A detailed presentation of how NFPA hazard ratings are determined is presented. Criteria for each of the four hazard classifications are discussed. Presumably similar evaluations are used for the ChemWatch hazard ratings. The difference between the two systems reflects the emphasis given to acute and chronic exposure to chemicals.

C) Extensive discussion of suitable Personal Protection Equipment (PPE), especially for selection of gloves. The idea is developed that glove selection can be based, in general, by considering the three cases:

- When prolonged or frequently repeated contact may occur, a glove with a protection class of 5 or higher (breakthrough time greater than 240 minutes according to EN 374) is recommended.
- When only brief contact is expected, a glove with a protection class of 3 or higher (breakthrough time greater than 60 minutes according to EN 374) is recommended.
- Contaminated gloves should be replaced immediately.

Glove selection, beyond using the ubiquitous purple colored nitrile gloves (available from the ALS stock room), was developed.

D) Accident information, contained in the red and white Emergency Response Guide flip chart (SWIMS), was also covered.

4) Appendix D – *TSJHA of Joint Aerosol Experiments for Jan-Feb 2012* – identifies the hazards and covers the controls for these hazards in a series of related experiments being carried out by a collaborative team that includes LBNL Chemical Dynamics Beamline personnel, UCB personnel and UC Davis experimenters. The experimental setup and procedure described within is the first stage of a two part experiment to prepare and eventually examine aerosol filter samples at the ALS beam line (9.0.2). Using the TSJHA document format is a convenient and effective mechanism for getting these diverse groups “on the same page” for conducting this work. OJT is strongly emphasized and is much more effective for establishing and maintaining control over the hazards, as noted, in this TSJHA as compared to the value received from completing generalized EHSS training classes (e.g., EHSS0348 – Chemical Hygiene).

The majority of researchers in this TSJHA are not from LBNL. They are collaborators interested in doing this particular experiment and will not necessarily be involved or interested in working at LBNL beyond this task. They are not much interested in establishing a LBNL computer login and consequently are not equipped to fulfill the traditional JHA safety qualification and work authorization route.

Acknowledgement of understanding what workplace controls and practices are necessary to ensure working safely at LBNL would be certified by signature of this TSJHA. It should be noted that additional review of the TSJHA controls is performed by ALS personnel through their extensive inspections using the Experimental Safety Sheet (ESS) process. ESS evaluations are considered an essential part of maintaining all ALS work area safety by ALS safety personnel.

5) Appendixes E and F – *TSJHA for Silicon Tetrachloride [SiCl₄] Transient Absorption Experiment* and *TSJHA for Thiophene (C₄H₄S) in Transient Absorption Experiments* – were prepared by the same researcher team included in Appendix C. Good progress has been made in using ChemWatch MSDS resources. The only improvements noted included:

A) For the silicon tetrachloride TSJHA the benefit of a Google search using the compound CAS number and the keyword “hydrolysis” was very useful. Immediately an article entitled “Theoretical Study of the Reaction Mechanism and Role of Water Clusters in the Gas-Phase Hydrolysis of SiCl₄” was found on the first Google search page results. It was suspected that silicon tetrachloride would be quite sensitive to reacting with any water in the room or hood air supply. Reaction with water would produce hydrogen chloride, an irritating and

toxic chemical. This would be an example where the secondary chemical hazards are more serious than those hazards associated with the primary chemical.

The article, however, had useful information than the general reactivity of SiCl_4 in air at room temperature is remarkably slow. Hydrolysis of the compound doesn't become a serious safety hazard until temperatures exceed at least 200°F .

Nonetheless silicon tetrachloride should be considered a hazardous and toxic compound. Any accidental releases are considered serious.

B) For thiophene, ChemWatch MSDS did not quote any limits on what the dangerous levels of exposure are to either thiophene vapors or thiophene liquid. Again, a Google search using the CAS number found the thiophene MSDS from Aldrich. Unlike several years ago, Aldrich MSDSs are now much improved. Preparation date for thiophene ChemWatch MSDS is Mar 22, 2009; the equivalent Aldrich MSDS is Jan 7, 2012. Important hazardous exposure level information missing from the ChemWatch MSDS was found in the Aldrich MSDS. Hazardous exposure levels for oral LD50, Inhalation LC50, Dermal LD50 and Subcutaneous LD50 values, where LD50 (Lethal Dose-half of exposed sample will die) and LC (Lethal Concentration) were recorded. Additionally, in the physical properties section the important lower and upper explosive limits were quoted. These two sets of hazard data indicated thiophene is a highly flammable compound and is not a particularly health hazardous compound. These additions from Aldrich are found in Appendix A in the TSJHA.

C) Aldrich MSDS also indicated another new hazard rating system is now available. This system is called: **United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS).** Application of GHS system for thiophene produces results as indicated.

GHS Classification:

Flammable liquids (Category 2)

Acute toxicity, Oral (Category 4)

Acute toxicity, Inhalation (Category 3)

Skin irritation (Category 2)

Serious eye damage (Category 1)

Specific target organ toxicity - single exposure (Category 3)

Inspection of the GHS classification categories strongly suggests you should not drink thiophene. It is also probably not good to inhale the material. This GHS system will likely gain increasingly more importance in the future. It appears that Aldrich has already adopted the GHS ratings for their chemical MSDSs.

Conclusion

This self-assessment titled - Hazard Analysis of Chemicals used in CSD Research groups – covers the application of a hazard analysis tool called Task Specific Job Hazard Analysis (TSJHA). Examples of TSJHAs are presented, which serve as a model for work authorization with a specific chemical or with a specific project. This analysis technique was introduced and applied to pertinent work involving a subset of CSD researchers located in laboratories at LBNL. TSJHAs ensure that the project associated with a researcher-PI/Work Lead is examined inclusively enough to fulfill completely On-the-Job (OJT) requirements.

Resources for preparation of TSJHAs were identified. Emphasis is given to ChemWatch MSDSs, but it was shown that a simple Google search on the chemical or project under consideration could produce very useful supplementary information. A new hazard characterization system was uncovered - **United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS).**

Each TSJHA was well received by the members involved with the specific work. Associated hazards of working with the chemical or project, under consideration, had not necessarily been appreciated. Acquainting

them with these hazards and developing suitable controls to mitigate these hazards was quite welcomed. The TSJHA discussion meeting was a positive experience for all parties involved. Questions about hazards or potential hazards were increasingly forthcoming as the discussion went on. It is gratifying to see a genuine enthusiasm develop for implementing safe work practices as the group discussion progressed. Meeting members were appreciative when answers to controlling hazards were focused on during these OJT like discussion meetings.

TSJHAs are not the only answer for providing safety hazard analyses for laboratory based research. Other methodologies exist that will be developed in the upcoming Work Planning and Control (WP&C) system. But for division researchers who don't work daily in a chemical laboratory, or work with a substance on a one time only basis, TSJHAs offer a suitable alternative to preparing more elaborate Activity Hazard Documents.

Also TSJHAs may have a resemblance to the now mandated Standard Operating Procedures (SOP) for work authorization that are currently being demanded for a majority of UCB located Chemical Sciences Division supported members. Examples of TSJHAs within are constructed along classic ISM principles and it is expected that a similar model will evolve for the UCB SOPs. Chemical Sciences Division may have a diverse but also an integrated approach to establishing and maintaining safe work practices at both LBNL and UCB laboratory work places.

Appendixes

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Appendix A

Task Specific Job Hazard Analysis for Use of Formic Acid In Dissociative Electron Attachment to Gas Molecules Experiment Apparatus

Location(s):	2-104	Analysis By:	Jerry Bucher	Date:	06-08-2010
				Expires:	
Division:	CSD	Work Leader:	Ali Belkacem	Frequency:	One-time
Category:	Task-based			JHA Number:	
Job Title:	Dissociative Electron Attachment to Gas Molecules Experiment Using Formic Acid Vapor				

REQUIRED PERSONAL PROTECTIVE EQUIPMENT:

Safety glasses, or chemical goggles for the transfer of formic acid to the sample holder and about the laboratory
Latex, nitrile, butyl or neoprene gloves
Lab Coat
Long pants
Closed-toe shoes
see notes below for transferring formic acid from storage container to sample holder

SCOPE DESCRIPTION:

This experiment is labeled: Dissociative Electron Attachment to Gas Molecules Experiment. This Task-Specific JHA covers the hazard associated with the gases used for experiments in this apparatus. The vacuum system contains the gas inlet system and a “soft” electron gun. The gun generates, in a controlled and selectable manner, electrons within an energy range of 3-20 electron volts. The electrons are directed parallel to, and are collimated by, a magnetic field of 25 Gauss generated by a pair of low-voltage Helmholtz coils. This electron beam intersects the moderately collimated gas beam with right angle geometry. Pulse generated electrons attach to the neutral gas molecules (e.g., NH_3 , CH_4 , HCOOH) to make anions. These excited gas molecules will in turn dissociate into new species. Species will include anionic components which can be collected and measured at selective detectors, which exclude free electrons coming from the gun generator.

In a fume hood (Bldg. 2-102), high-purity formic acid will be transferred (typically 5 mL for one experimental run) from appropriate chemical storage to a sample holder (capacity 100 mL) cooled in dry ice or liquid N_2 below the freezing point of formic acid. The sample holder connects directly to a variable leak valve that controls the flow of formic acid vapor to an inlet to the vacuum chamber. All components of the sample holder and vacuum system are glass or stainless steel. Dissolved impurities in the formic acid sample will be removed by one or two freeze-pump-thaw cycles, using dry ice or liquid N_2 outside the sample holder to freeze the formic acid sample, evacuating the sample to ~ 0.1 torr and then allowing the sample to melt at room temperature.

To ensure a steady flow of vapor, heating tape protected by a ground fault circuit interrupter (GFCI) (voltage limit <50 V) is used on the needle, gas lines and leak valve to maintain progressively higher temperature of surfaces downstream of the sample holder. This will also ensure that the formic acid monomer/dimer fraction is

adequate ($T > 375\text{ K}$ should ensure that the monomer/dimer fraction is > 100). The line at the vacuum chamber inlet contains an active pressure gage which allows real time monitoring of tubing pressure from the experimental chamber's control computer screen. At the chamber inlet a reduction in tube diameter is made by incorporating a length of 0.005" inner diameter (0.01" outer diameter) SS hypodermic-needle tubing. Gas pressures of approximately 2 torr ($\sim 0.04\text{ psi}$) are established and maintained during the time period an experimental operation is happening.

The vapor pressure of formic acid is 34 Torr at $20\text{ }^{\circ}\text{C}$ and the variable leak valve will restrict the flow of vapor so that the gas pressure in most of this vacuum system will be kept at pressures below approximately 2 torr. A plastic enclosure, vented to the pump exhaust system, surrounding the sample holder will contain any accidental leak that may occur at the reservoir. The experiment gas is a column of effusively expanding gas directed into and through the experimental chamber. Pumping is done by a conventional vacuum pump. Pump exhaust is piped to an exhaust manifold which is connected to the Bldg. 2 southwest sector exhaust system ($\sim 26,000\text{ ft}^3/\text{min}$).

The principal hazard in using formic acid is associated with accidental leaks of corrosive gases from the connecting gas supply lines plumbing hardware. Formic acid is a flammable (NFPA flammability rating 2) and highly irritating (NFPA health hazard rating 3) compound, particularly if inhaled or ingested. The permissible exposure limit (PEL) for formic acid is 5 ppm, and the IDLH level is 30 ppm. The American Industrial Hygiene Association (AIHA) detection limit is quoted as $20\text{-}40\text{ mg}/\text{m}^3$ (10-20 ppm). Volume of the tubing in this setup is $\sim 0.0005\text{ ft}^3$. At 2 torr pressure this means ~ 70 milligrams of formic acid vapor is present in the tubing during experimental operations. Letting this quantity of formic acid escape into the room ($\sim 4300\text{ ft}^3$) would produce a 0.2 ppm HCOOH concentration, which is well below the PEL and detection limit. A catastrophic rupture of the sample holder and the vented enclosure could be detected by smell. Under static conditions the 5 mL of formic acid in the sample holder (STP) would be approximately 26 ppm if it leaked into the laboratory, which is well above the PEL and very close to the IDLH value. If the sample holder is ruptured or spilled in the laboratory outside of the fume hood, the laboratory must evacuate immediately and emergency services must be contacted. In addition, if the odor of formic acid (smells like red ants) is detected, the laboratory should be evacuated, and EH&S must be contacted.

The other hazard associated with formic acid is exposure during transfer from the storage container into the sample holder. This operation will be performed in a fume hood as noted above. Latex, nitrile, butyl or neoprene gloves are appropriate for work with formic acid. Disposable gloves are acceptable as splash protection provided they are removed and replaced with fresh gloves if contaminated by formic acid. Other required PPE are chemical safety goggles, lab coat, long pants, and closed toe shoes.

Following the LBNL Emergency Response Guide, the emergency response procedure for a formic acid spill is to follow S.W.I.M.S.: Stop and think, stop the spill, assess the situation; Warn others, alert people nearby, call x7911 if there is a medical emergency or a danger to life, health or the environment; Isolate the area, restrict access to those involved in the cleanup, keep doors closed; Monitor yourself carefully and completely for contamination or exposure; Stay in or near the area until help arrives, avoid spreading the contamination to other areas, have a person who is knowledgeable of the incident available to assist emergency personnel. A minor spill of $< 5\text{ mL}$ within the fume food can be cleaned up by a researcher or student provided that there is no risk of injury or release to the environment. If the spill is $> 5\text{ mL}$ or outside the fume hood, all workers should leave the immediate area, control access to the area (post a sign to the door warning of the situation) and call x6999 for assistance. If there is a danger to life, health or the environment call x7911. All workers should review the LBNL Emergency Response Guide periodically to familiarize themselves with the emergency procedures.

Task #	Description	Hazard(s)	Control(s)
--------	-------------	-----------	------------

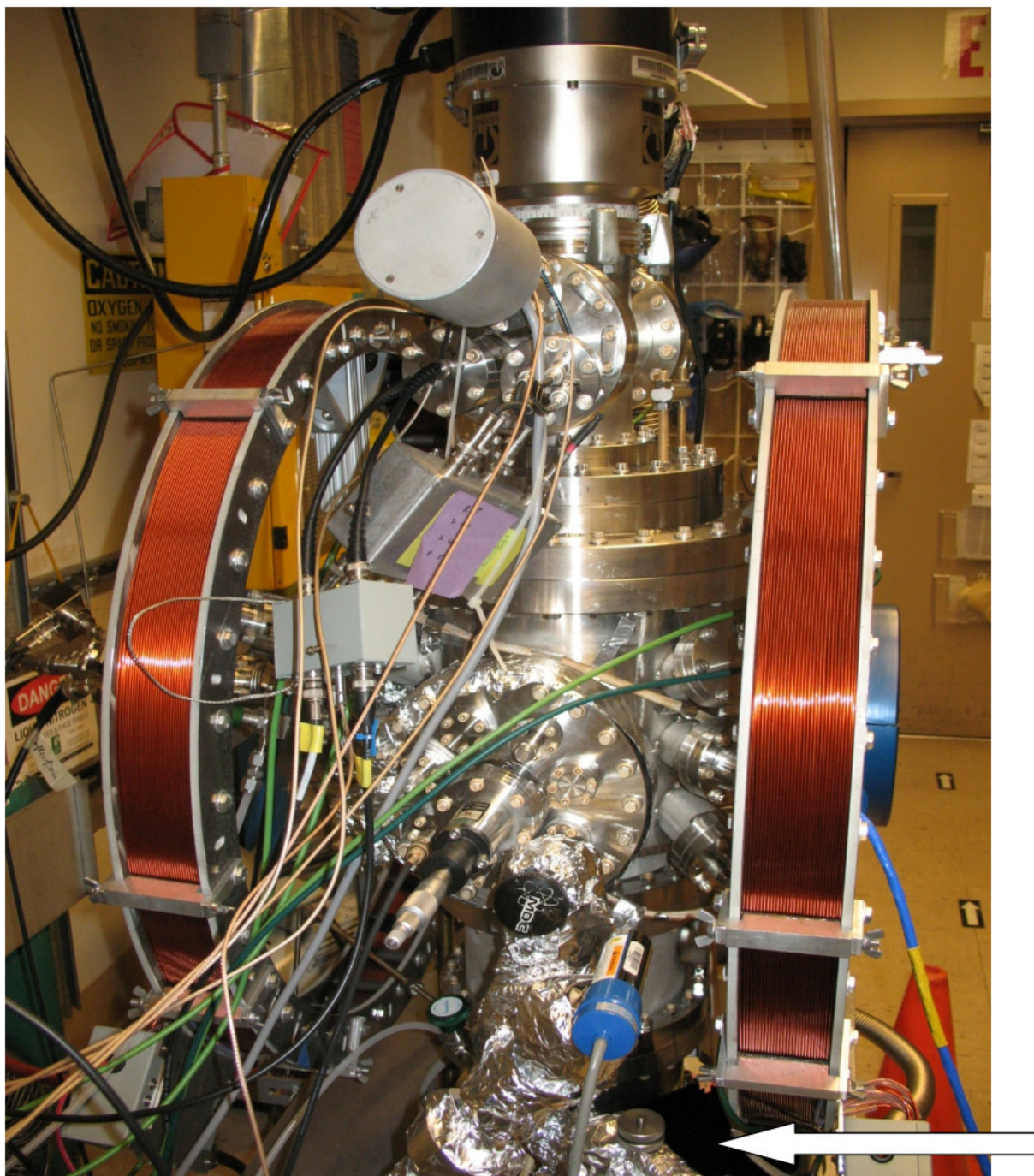
1	Transfer 5 mL of formic acid from storage to the sample holder under a fume hood. Securely mount the sample holder to the vacuum system and perform freeze-pump-thaw procedure. Install vented enclosure over the sample holder once it is in position.	Exposure to formic acid liquid or vapor is possible.	Perform operations in the fume hood. Wear appropriate PPE (gloves, safety glasses and lab coat. Disposable latex gloves are acceptable. Remove and replace gloves immediately if contaminated by formic acid). In case of spill, remove any contaminated PPE or clothing immediately to avoid skin contact and contain the spill under a fume hood. Ensure a new copper or clean viton gasket is installed on the sample holder flange.
2	Establish the ~2 torr working HCOOH pressure by adjusting the variable leak valve. Monitor by using the pressure gage readout at entrance of vacuum chamber gas inlet.	If ~2 torr HCOOH working pressure is maintained no health hazard will be experienced. A breakage or spill of > 10 mL of formic acid would exceed the IDLH.	The fairly strong stench of formic acid indicates leaving the room is necessary. In the event of any spill outside the fume hood, evacuate the laboratory and contact appropriate emergency help by consulting the 2008-2010 EMERGENCY RESPONSE GUIDE. Notify your Supervisor/Worklead.

AUTHORIZED WORKER(s) INFORMATION:

WORKER ID NUMBER:	WORKER NAME	WORKER SIGNATURE ¹	SUPERVISOR AUTHORIZATION ²
026170	Daniel Slaughter		
009576	Hidehito Adaniya		
222451	Ali Belkacem (Sup.)		
115200	Jerome J Bucher (DSC)		

¹ Worker signature indicates concurrence with the analysis and agreement to work in accordance with this authorization.

² Supervisor signature above authorizes the work subject to the controls specified.



Picture 1 – Dissociative Electron Attachment to Gas Molecules Experiment Apparatus

Arrow indicates approximate formic acid sample attachment point.



Picture 2. Sample Holder

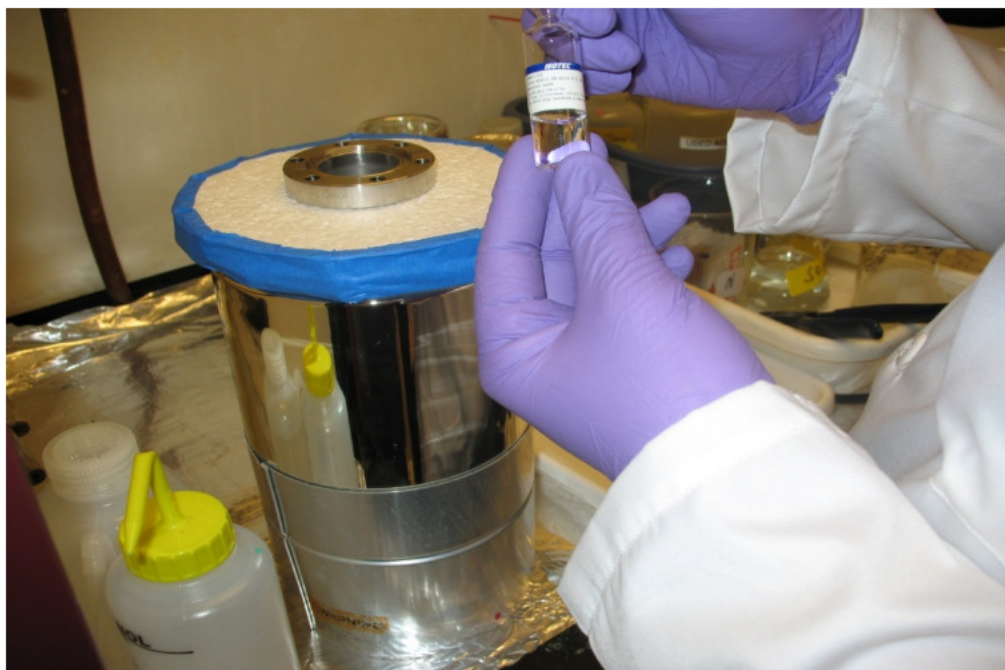
2.75 inch flange glass body. Approximately 100 ml capacity.



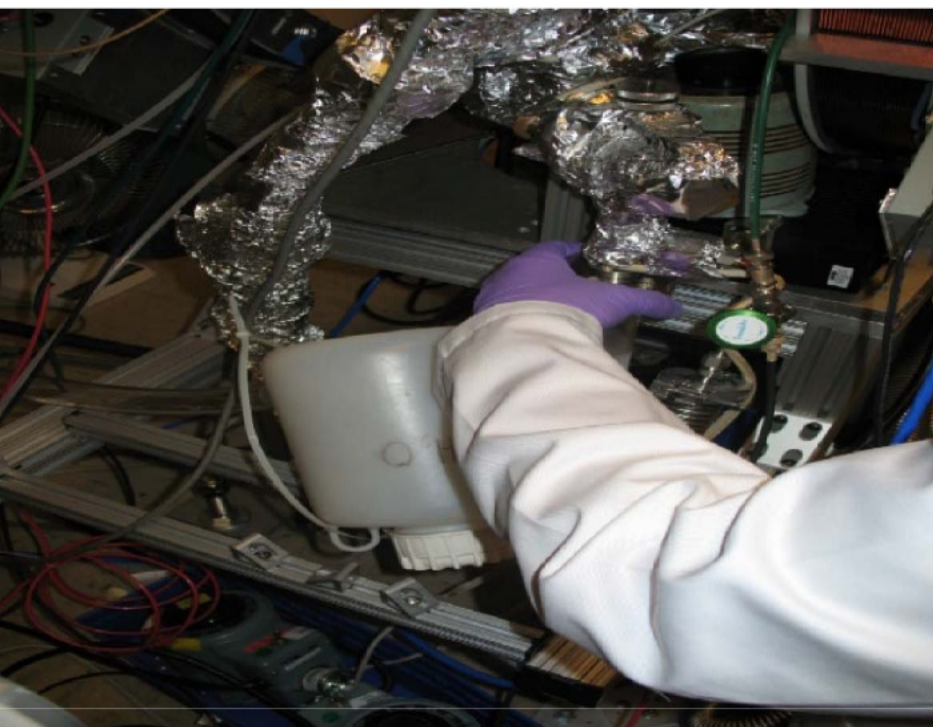
Picture 3. End On view of sample holder. Six hole attachment flange



Picture 4. Researcher in PPE. Note gloves, lab coat and safety goggles. Prepared to fill the sample holder with formic acid in internally accessible adjacent laboratory hood – 2-102.



Picture 5. Sample holder cooling in a dewar in preparation for filling with 5 ml sample of formic acid.

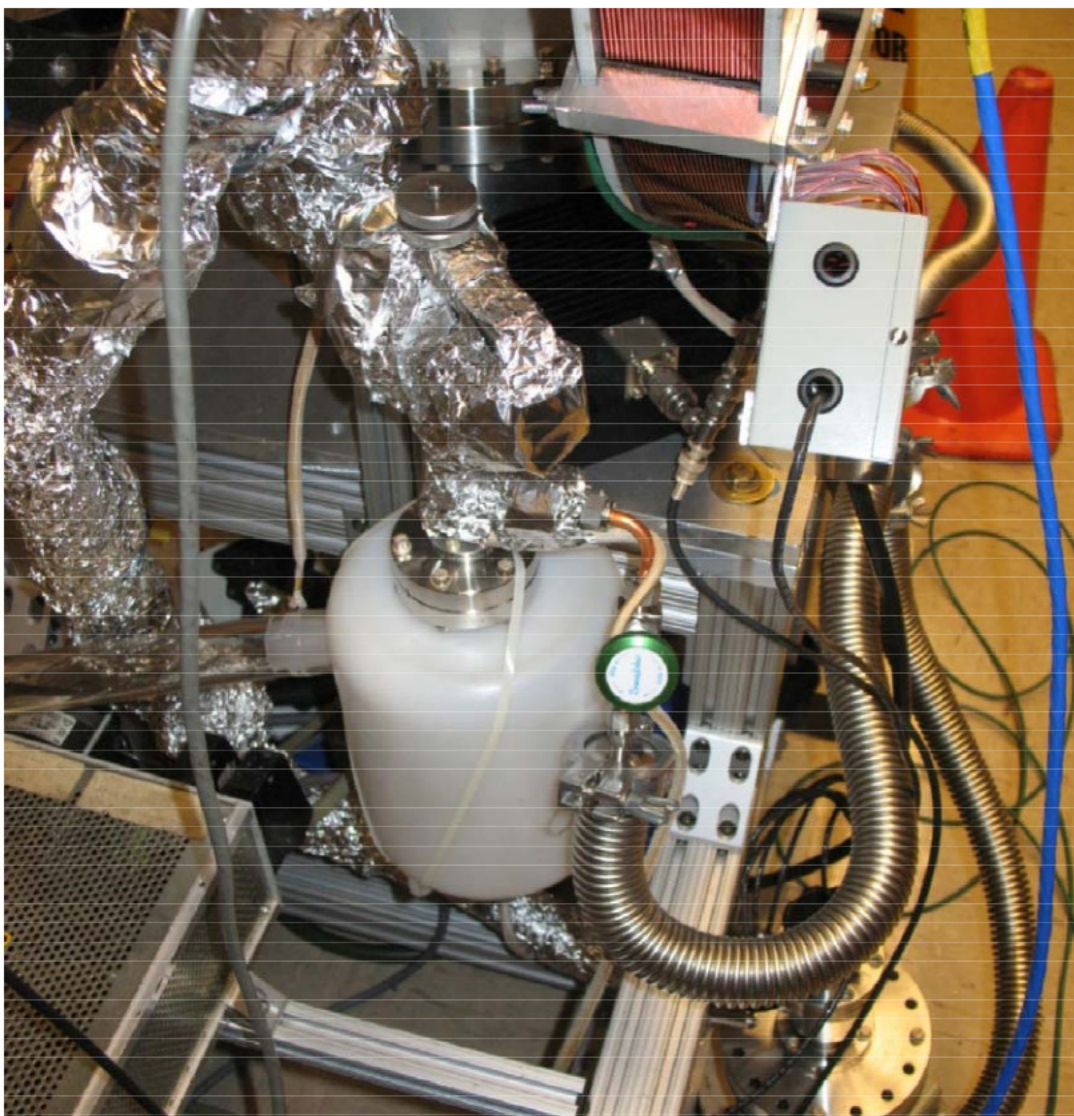


Picture 6. Mounting of sample holder to experimental device. Formic acid contents are frozen to reduce vapor pressure



Picture 7. Introduction of filled and fully attached sample into either liquid nitrogen or dry ice.

This is necessary step to remove excess water, as received from manufacturer, from the sample by doing several cycles of freeze-thaw-pump.



Picture 8. Final experiment configuration with protective shroud (plastic bottle attached to Vacuum pump exhaust line. Micro leak valve regulates the amount of formic acid delivered.

Appendix B

Task Specific Job Hazard Analysis for use of Sodium Azide, Under Acidic Conditions, In Electrospray Ionization (ESI) Mass Spectrometry Experiments

Location(s):	70A-2217 & 70A-1129 (HERL)	Analysis By:	Jerome Bucher, John K. Gibson	Date:	March 23, 2012
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				Expires:	
Division:	Chemical Sciences	Work Leader:	John K. Gibson (LBNL #018936)	Frequency:	Limited-Time
Category:	Task-based			JHA Number:	
Job Title:	Electrospray Ionization (ESI) Mass Spectrometry experiments with sodium azide (NaN ₃)				

REQUIRED PERSONAL PROTECTIVE EQUIPMENT:

Personnel must wear long pants and closed toe footwear. Safety glasses, a lab coat and disposable gloves must be worn when handling sodium azide. Skin and personal clothing at the wrist must be covered by PPE when working with sodium azide. It is recommended to make the sample in the fume hood.

SCOPE DESCRIPTION:






Sodium azide (NaN₃) is used to produce uranium azide ions in the gas phase. These ions are expected to form uranium nitride species upon (T)CID (Threshold Collision-Induced Dissociation) of the parent ions. For Electrospray Ionization (ESI) experiments, the concentration of sodium azide solution is 200-800 µM in water (0.5-1.0 mL). A purchased solution (0.1M, 1mL) will be diluted in laboratory in 70A-2217. The diluted solution will be taken to the HERL (Heavy Element Research Laboratory), where it is mixed with an acidic dilute uranium (VI) (or thorium (IV), neptunium (VI), plutonium (IV, VI)) solution (200 µM, pH=1-8) for ESI experiments. The ESI/MS and CID experiments are performed with an Agilent 6340 QIT/MS unit, with the ESI source housed within a radiological-containment glove box. When the experiments are finished, the mixed uranium and NaN₃ (with certain amount of HN₃, depending on the pH) solutions are collected into a capped liquid radioactive waste container for disposal.

Sodium Azide and Hydrazoic Acid

Sodium Azide – NaN₃ - CAS# 26628-22-8 - **Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS**

Section 2 - HAZARDS IDENTIFICATION

CHEMWATCH HAZARD RATINGS

	Min	Max	
Flammability:	0		
Toxicity:	4		
Body Contact:	4		
Reactivity:	2		
Chronic:	2		
			Min/Nil=0 Low=1 Moderate=2 High=3 Extreme=4

NFPA



PRODUCT USE - Used for air bag inflation

Heating may cause an explosion.

Contact with acids liberates very toxic gas.

Very toxic in contact with skin and if swallowed.

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

Source	Material	TWA ppm	TWA mg/m ³	STEL ppm	STEL mg/m ³	Peak ppm	Peak mg/m ³	TWA F/CC	Notes
US ACGIH Threshold Limit Values (TLV)	sodium azide (Sodium azide as Hydrazoic acid vapor)					0.11			TLV® Basis: Card impair; lung dam
US ACGIH Threshold Limit Values (TLV)	sodium azide (Sodium azide as Sodium azide)						0.29		TLV® Basis: Card impair; lung dam

See Appendix Y for explanation of US ACGIH Threshold Limit Values - TLV

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Solid.

Mixes with water.

Contact with acids liberates very toxic gas.

State	Divided solid	Molecular Weight	65.02
Melting Range (°F)	527 (decomposes)	Viscosity	Not Applicable
Boiling Range (°F)	Not applicable.	Solubility in water (g/L)	Miscible
Flash Point (°F)	Not available.	pH (1% solution)	Not available
Decomposition Temp (°F)	Not Available	pH (as supplied)	Not applicable
Autoignition Temp (°F)	Not available.	Vapour Pressure (mmHG)	Not available.
Upper Explosive Limit (%)	Not available.	Specific Gravity (water=1)	1.85
Lower Explosive Limit (%)	Not available.	Relative Vapour Density (air=1)	2.2

APPEARANCE

Colourless hexagonal crystals with characteristic odour. Soluble in water and in liquid ammonia; hydrolyses in water to form hydrazoic acid. Slightly soluble in alcohol; insoluble in ether.

Section 10 - CHEMICAL STABILITY**CONDITIONS CONTRIBUTING TO INSTABILITY**

Presence of heat source

Presence of shock and friction

Presence of incompatible materials.

Product is considered stable.

Hazardous polymerisation will not occur.

STORAGE INCOMPATIBILITY

■ Inorganic azides:

react with hot water

may explode on contact with antimony, arsenic, caesium sulfide, metals, silver, sodium, phosphorus

concentrated solutions in organic solvents may explode on shaking

decompose explosively at elevated temperatures (above 275 C).

High nitrogen compounds are often unstable or explosive; the tendency is exaggerated by attachment of azide or diazonium groups, or a high-nitrogen heterocyclic nucleus.

High-nitrogen chemical families include

azides

diazoazoles

diazonium salts

hydrazinium salts

Protect from light.

Section 11 - TOXICOLOGICAL INFORMATION

sodium azide

TOXICITY AND IRRITATION

No data for this material.

CARCINOGEN

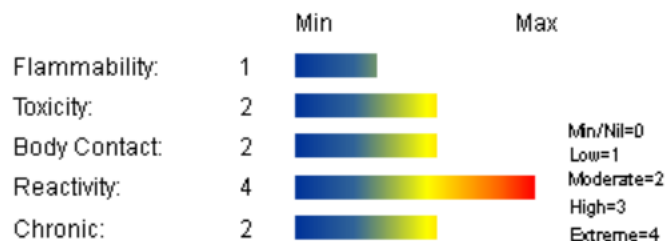
Sodium azide as Sodium azide	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A4
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See Appendix Z for definition of “Carcinogen Category” rating

Hydrazoic Acid – HN_3 CAS# 7782-79-8 Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

Section 2 - HAZARDS IDENTIFICATION

CHEMWATCH HAZARD RATINGS



NFPA



PRODUCT USE

- In the preparation of heavy metal azides for shell detonators.

Explosive when dry.

Extreme risk of explosion by shock, fire, friction or other sources of ignition.

Contact with acids liberates toxic gas.

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

The following materials had no OELs (Occupational Exposure Limits) on our records

hydrazoic acid: CAS:7782-79-8

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Liquid.

Mixes with water.

Contact with acids liberates toxic gas.

State	Liquid	Molecular Weight	43.03
Melting Range (°F)	-112	Viscosity	Not Available
Boiling Range (°F)	99	Solubility in water (g/L)	Miscible
Flash Point (°F)	Not available	pH (1% solution)	Not available
Decomposition Temp (°F)	Not available.	pH (as supplied)	Not applicable
Autoignition Temp (°F)	Not available	Vapour Pressure (mmHG)	Not available
Upper Explosive Limit (%)	Not available	Specific Gravity (water=1)	1.09
Lower Explosive Limit (%)	Not available	Relative Vapour Density (air=1)	>1

Volatile Component (%vol) 100

Evaporation Rate

Not available

APPEARANCE

Colourless, volatile liquid with obnoxious odour; mixes with water. pKa 4.72. Weakly acidic. As the lowest weight azide in the series, hydrazoic acid is extremely endothermic.

Section 10 - CHEMICAL STABILITY

CONDITIONS CONTRIBUTING TO INSTABILITY

Presence of heat source

Presence of shock and friction

Presence of incompatible materials

STORAGE INCOMPATIBILITY

Contact with acids produces toxic fumes

Hydrazoic acid is quite safe in dilute solution but is violently explosive and of variable sensitivity in concentrated solutions (17-50%) or pure states.

Whenever possible, a low boiling solvent (ether, pentane), should be added to its solutions to prevent inadvertent concentration by evaporation and recondensation. If this is not possible, no unwetted part of the apparatus containing its solutions should be kept at a temperature appreciably below its boiling point (37 deg. C.). The pure acid has often been isolated by distillation, but appears to undergo rapid sensitisation on standing so that after an hour, faint vibrations or speech are enough to initiate detonation. The solid acid (-80 deg. C.) is also unstable.

Trimethylsilyl azide serves as a safe and stable substitute for hydrazoic acid.

A laboratory explosion seems likely to have been caused by the use of a huge (90-fold) excess of azide in too-concentrated solution and at too low an ambient temperature, leading to condensation of highly concentrated hydrazoic acid. This penetrated into a ground glass joint, and explosion was initiated on removal of the stopper. It is claimed that hydrazoic acid may be distilled without fear of explosion if the trapping of the liquid azide in ground joints is prevented by thorough pregreasing of all joints

Inorganic azides:

react with hot water

may explode on contact with antimony, arsenic, caesium sulfide, metals, silver, sodium, phosphorus

concentrated solutions in organic solvents may explode on shaking

decompose explosively at elevated temperatures (above 275 C).

WARNING:

May decompose violently or explosively on contact with other substances.

This substance, or one of its components, is one of the relatively few compounds which are described as "endothermic" i.e. heat is absorbed into the compound, rather than released

from it, during its formation.

The majority of endothermic compounds are thermodynamically unstable and may decompose explosively under various circumstances of initiation.

Many but not all endothermic compounds have been involved in decompositions, reactions and explosions and, in general, compounds with significantly positive values of standard heats of formation, may be considered suspect on stability grounds.

BREThERICK L.: Handbook of Reactive Chemical Hazards.

High nitrogen compounds are often unstable or explosive; the tendency is exaggerated by attachment of azide or diazonium groups, or a high-nitrogen heterocyclic nucleus.

High-nitrogen chemical families include

azides
diazoazoles
diazonium salts
hydrazinium salts

Protect from light.

Section 11 - TOXICOLOGICAL INFORMATION

hydrazoic acid

TOXICITY AND IRRITATION

No data for this material.

AUTHORIZED WORKER(s) INFORMATION:

WORKER ID NUMBER:	WORKER NAME	WORKER SIGNATURE ¹	SUPERVISOR AUTHORIZATION ²
	(Work Leader)		

¹ Worker signature indicates concurrence with the analysis and agreement to work in accordance with this authorization.

² Supervisor signature above authorizes the work subject to the controls specified.

Appendix Y

Threshold limit value (TLV)

From Wikipedia, the free encyclopedia

The threshold limit value (TLV) of a [chemical substance](#) is a level to which it is believed a worker can be exposed day after day for a working lifetime without [adverse health effects](#). Strictly speaking, TLV is a reserved term of the [American Conference of Governmental Industrial Hygienists](#) (ACGIH). However, it is sometimes loosely used to refer to other similar concepts used in [occupational health](#) and [toxicology](#). TLVs, along with biological exposure indices (BEIs), are published annually by the ACGIH.

The TLV is an estimate based on the known [toxicity](#) in [humans](#) or [animals](#) of a given chemical substance, and the reliability and accuracy of the latest sampling and [analytical methods](#). It is not a static definition since new research can often modify the [risk assessment](#) of substances and new [laboratory](#) or [instrumental analysis](#) methods can improve analytical [detection limits](#). The TLV is a recommendation by ACGIH, with only a guideline status. As such, it should not be confused with exposure limits having a regulatory status, like those published and enforced by the [Occupational Safety and Health Administration](#) (OSHA). The OSHA regulatory exposure limits [permissible exposure limits](#) (PELs) published in 29CFR 1910.1000 Table Z1 are based on recommendations made by the ACGIH in 1968, although other exposure limits were adopted more recently. Many OSHA exposure limits are not considered by the [industrial hygiene](#) community to be sufficiently protective levels. The [National Institute of Occupational Safety and Health](#) (NIOSH) publishes recommended exposure limits (RELs) which OSHA takes into consideration when promulgating new regulatory exposure limits.

Definitions

The TLV for chemical substances is defined as a concentration in air, typically for inhalation or skin exposure. Its units are in [parts per million](#) (ppm) for [gases](#) and in milligrams per cubic meter (mg/m³) for [particulates](#) such as [dust](#), [smoke](#) and [mist](#). The basic formula for converting between ppm and mg/m³ for gases is $\text{ppm} = (\text{mg/m}^3) * 24.45 / \text{molecular weight}$. This formula is not applicable to airborne particles.

Three types of TLVs for chemical substances are defined:

1. Threshold limit value - [Time weighted average](#) (TLV-TWA): average exposure on the basis of a 8h/day, 40h/week work schedule
2. Threshold limit value - [Short-term exposure limit](#) (TLV-STEL): spot exposure for a duration of 15 minutes, that cannot be repeated more than 4 times per day
3. Threshold limit value - [Ceiling limit](#) (TLV-C): absolute exposure limit that should not be exceeded at any time

There are TLVs for physical agents as well as chemical substances. TLVs for physical agents include those for [noise](#) exposure, [vibration](#), [ionizing](#) and [non-ionizing radiation](#) exposure and [heat](#) and [cold](#) stress.

Similar concepts

The TLV is equivalent in spirit, although the materials covered, values recommended, and definitions used can differ, to the following concepts.

WEEL ([Workplace environmental exposure level](#)) created by a committee of the American Industrial Hygiene Association [AIHA](#)

Similar concepts used in other countries include:

Australia

- OES Occupational exposure standard [\[1\]](#)

France

- VME ([Valeur Moyenne d'Exposition](#))
- VLE ([Valeur Limite d'Exposition](#))

Germany

- AGW ([Arbeitsplatzgrenzwert](#))
- MAK ([Maximale Arbeitsplatz-Konzentration](#))

Netherlands

- MAC ([Maximaal Aanvaarde Concentratie](#))

Malaysia

- PEL ([Permissible exposure limit](#))

Poland

- NDN ([Najwy sze Dopuszczalne Nat enie](#))

Russia

- (_____)

Appendix Z

Threshold Limit Values (TLV) - Carcinogens

Designations - Explanatory Notes:

American Conference of Governmental Industrial Hygienists				
A1	A2	A3	A4	A5
Confirmed human carcinogen	Suspected human carcinogen	Animal carcinogen. The agent is not likely to cause cancer in humans except under uncommon or unlikely routes or levels of exposure.	Not classifiable as a human carcinogen	Not suspected as a human carcinogen

California Environmental Protection Agency

Yes - substances "Known to the State to cause cancer" included on list of carcinogens (Proposition 65 list)

European Union		
Category 1	Category 2	Category 3
Substances known to be carcinogenic to man	Substances which should be regarded as if they are carcinogenic to man	Substances which cause concern for man owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment

International Agency for Research on Cancer				
Group 1	Group 2A	Group 2B	Group 3	Group 4
The agent is carcinogenic to humans	The agent is probably carcinogenic to humans	The agent is possibly carcinogenic to humans	The agent is unclassifiable as to carcinogenicity in humans	The agent is probably not carcinogenic to humans
National Toxicology Program				
Group 1		Group 2		
"Known Carcinogen" (Sufficient information from human studies to indicate causal relationship)		"Reasonably Anticipated" (Limited evidence of carcinogenicity in humans; or sufficient evidence of carcinogenicity in experimental animals)		

Substances Assessed For Carcinogenicity (pdf files):

This list, (current to April 2002), consists of substances assessed for carcinogenicity by the American Conference of Governmental Industrial Hygienists (ACGIH), the California Environmental Protection Agency

(Cal-EPA), the International Agency of Research on Cancer (IARC), the European Union (E.U.), and the National Toxicology Program (NTP).

[A to M](#) (PDF Version - 760K)

[N to Z](#) (PDF Version - 510K)

References / Related Sites:

Canada

Statistics Canada:

[Canadian Cancer Registry](#)

Europe

International Labour Organization:

["List of Substances with Risk and Safety Phrases Used in the Countries of EU"](#)

International Agency for Research on Cancer

IARC Monographs:

["IARC Monographs on the Evaluation of Carcinogenic Risks to Humans"](#)

IARC assessment list:

["Overall Evaluations of Carcinogenicity to Humans"](#)

United States

ACGIH:

www.acgih.org

California EPA, Proposition 65:

[List of Chemicals Known to the State of California to Cause Cancer](#)" (PDF Version - 150K)

Civil Service Employee Association (CSEA):

["Cancer-Causing Chemicals in the Workplace, 1998"](#).

National Toxicology Program:

["9TH Report on Carcinogens Revised January 2001"](#)

NTP Lists:

["Known Human Carcinogens"](#)

["Reasonably Anticipated To Be Human Carcinogens"](#)

OSHA

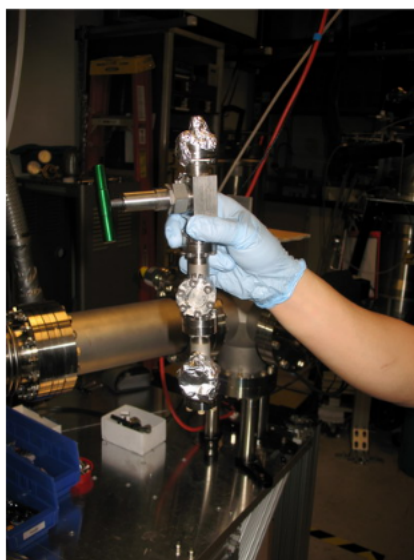
["Carcinogens"](#)

Appendix C

Task Specific Job Hazard Analysis for use of Bromobenzene In Transient Absorption Experiment

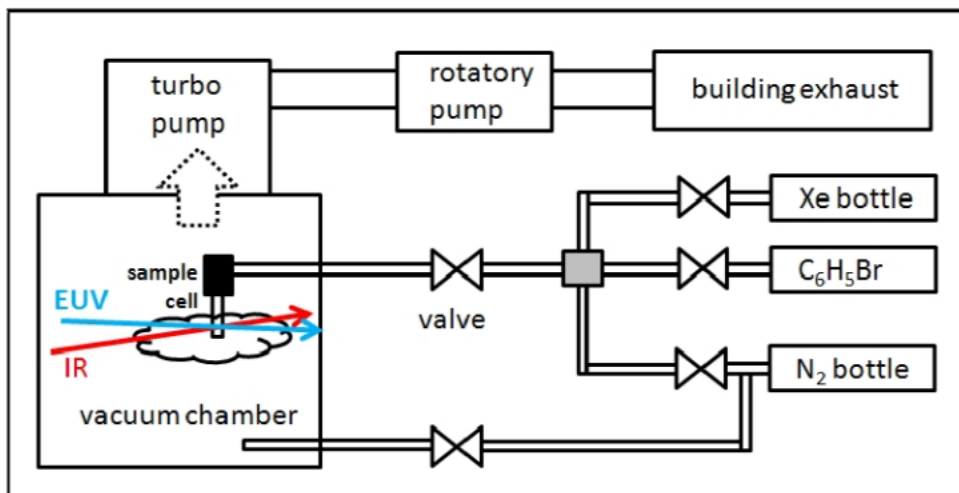
Location(s):	2-308	Analysis By:	Jerome Bucher (LBNL # 115200)	Date:	2011/05/11
				Expires:	
Division:	Chemical Sciences	Work Leader:	Oliver Gessner (LBNL # 809652)	Frequency:	Limited-time
Category:	Task-based			JHA Number:	[from system]
Job Title:	Bromobenzene transient absorption experiment				

SCOPE OF WORK DESCRIPTION:



Bromobenzene is transferred to a stainless steel sample container (see photo), which is detached from the vacuum chamber. The pump-probe scan lasts over 6 hr. The continuous flow rate of sample at 10 torr into vacuum chamber is $0.025 \text{ cm}^3/\text{sec}$. Estimated weight of sample in the experimental container is approximately 45 gram. Density of liquid is 1.495 g/cm^3 . This is equal to 30 mL of bromobenzene and occupies 1/3 of the steel sample container volume. When transferring the sample, the stainless steel container will be placed in the fume hood. The unused part of the chemical will be stored in the fume hood in its original glass container.

Proper PPE - nitrile glove, protection class 3 or higher (breakthrough time greater than 60 minutes according to EN 374, see PPE section further down), safety glasses, close toe shoes, long pants and lab coat-will be worn. Using a glass pipet and funnel, a slow and careful transferring of bromobenzene will be achieved. After sample transfer is completed, the stainless steel sample container will be installed unto the experiment apparatus (see figure 1). [Sample container and tube manifolds will be checked for leaks.](#)



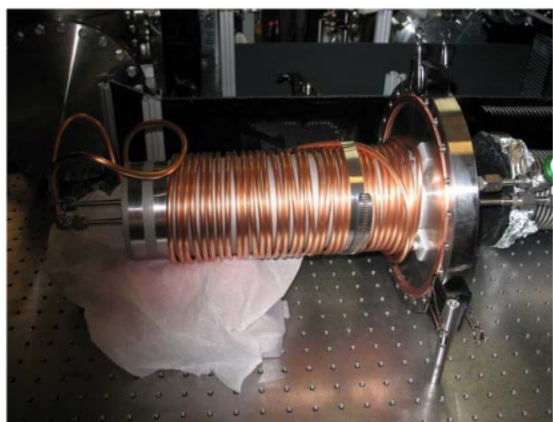
Vapor pressure of bromobenzene is 4 torr at 77 °F (25 °C) and 10 torr at 104 °F (40 °C). Sample container temperature will be varied from 77 to 104 °F. Temperature is monitored by a thermocouple with 0.1 degree accuracy. The maximum temperature reached will be 104 °F. The

sample container is heated by a heating tape on the outside of the sample container.

On the manifold there are several valves connected to the sample container, which includes a nitrogen purge line and a small Xe gas cylinder. The nitrogen purge line is used to purge any residual chemical in the 1/4" stainless tube. The gas is pumped out by vacuum turbo pump and its backing rotatory vane pump. The rotatory vane pump exhaust line is directly connected to the building exhaust line. This line between the rotary vane pump and building exhaust is maintained under negative pressure, which prevents any chemical flow back into the laboratory.

After completing the experiment, the stainless steel sample container will be disconnected and placed in the fume hood. Before disconnecting any bromobenzene sample swagelok connection, N₂ gas will be used to purge the sample line for 10-15 minutes. This will flush out any residual sample in the tube and will be pumped out by the turbo pump and the associated roughing pump. Purging-and-pumping procedure will be repeated at least 3 times before the vacuum chamber system or any gas lines will be opened.

All tubing in contact with the chemicals in the manifold is stainless steel. Bromobenzene in the chamber is trapped by a LN coldtrap, placed between the turbo pump and vacuum chamber. This LN coldtrap apparatus is shown below. Pressure in the vacuum chamber is approximately 0.001 torr while the experiment is running. Pressure in the small sample cell within the vacuum chamber is ~10 torr. Most of the chemical vapor in the system will be trapped by the LN coldtrap. When the sample line is off, the pressure in the vacuum chamber is usually in the 10⁻⁷ to 10⁻⁶ torr range.



While the experiment is running, the liquid nitrogen (LN) coldtrap is used to collect bromobenzene vapor. The melting point of bromobenzene is -24 °F or -31 °C. The LN coldtrap surface is maintained around -196 °C. The trapped bromobenzene will remain a solid on the metal surface. After completing the experiment, the coldtrap will still be cold and will be moved to the fume hood. The bromobenzene on the metal surface will be melted, and washed away using acetone.

The wash solution containing bromobenzene will be collected and disposed as a chemical waste. This waste will be stored in the 2-308 SAA area. Once every half year or sooner, the chemical waste will be removed by LBNL Waste Management group.

Addendum: Coldtrap coated with condensed bromobenzene after an experimental run.



Discussion:

For purposes of assessing the chemical hazards of bromobenzene, the ChemWatch ratings are preferred. NFPA (National Fire Protection Agency) ratings are tailored for emergency responders and in particular for firefighters. The NFPA hazard ratings are acute in nature. ChemWatch hazard ratings appear to reflect the estimated hazard of working with the chemical in a workplace. Included in the ChemWatch ratings is the chronic hazard consideration (i.e., hazard of using the substance repeatedly over an extended length of time).

In this analysis a systematic examination of the parent compound: benzene and a number of mono substituted benzene molecules is made to explore whether the methodologies employed by NFPA and/or ChemWatch are consistent in generating hazard ratings for each compound. A quick glance at the health hazard ratings (blue triangle in NFPA) (toxicity and body contact blue colored bars in ChemWatch) suggest the health risk is not exceptional, except for NFPA-chlorobenzene-(hazard rating of three). Is this result reasonable? Looking a little deeper into the individual MSDSs it is noted for fluorene (Bz-F), Bz-Cl, Bz-Br and Bz-I that each compound will generate the corresponding halogen acid in the event of combustion. HF, HCl, HBr and HI could become a significant hazard. It is likely in the case of Bz-Cl that this possible combustion generated reaction was included in the health assessment for Bz-Cl, but not for the other halogenated Bz chemicals.

It is useful to calculate what concentration effects, in terms of ppm, each Bz-X compound would have in 2-308.

TABLE 1. Bz-X Physical Properties

Chemical	Density grams/cc	Molecular Weight grams/mole	Moles per cc(ml)	Gas Volume Liters-25°C per cc(ml)	ppm/cc; explosion lower limit-cc; IDLH-combustion-cc
Fluorobenzene	1.204/per ChemWatch 1.024 per literature	96.1	0.01253(CW) 0.01066 (lit)	 0.261 liters	 0.66; 1.95x10 ⁴ ; 115(HF, 30ppm)
Chlorobenzene	1.11	112.56	0.00986	0.241	0.62; 2.11x10 ⁴ ; 207(HCl, 50ppm)
Bromobenzene	1.491	157.02	0.00950	0.232	0.59; 1.01x10 ⁵ ; 129(HBr, 30ppm)
Iodobenzene	1.834	204.2	0.00898	0.220	0.56
Benzene	0.879	78.12	0.01125	0.275	0.70; 1.85x10 ⁴ ;
Toluene	0.87	92.14	0.00944	0.231	0.59; 2.20x10 ⁴ ;

The volume of gas 1 ml of Bz-X would generate at 25°C, is calculated using the Ideal Gas Law. Results are given in the last column of Table 1. A convenient online solution of the equation, with a consistent set of units, can be found at: <http://www.ajdesigner.com/idealgas/index.php> This volume is converted into a ppm/cc value that is only valid for the specific volume of 2-308

Bldg2-Room 308 has a volume of 3.92x10⁵ liters. A ml of Bz-X, uniformly spread throughout the room, would contribute between 0.56 – 0.70ppm concentration/ cc of Bz-X. Individual Bz-X values are found in the first column in Table 2.

Table 2. Amount of Bz-X Needed to Generate Lower Explosive limits

Chemical	A cc (ml) of Bz-X/2-308 room volume, ppm/cc(ml)	Explosive limits; lower limits, upper limits. %	Amount of Bz-X needed to equal Lower Explosive Limit in 2-308. cc(ml)of Bz-X in volume of 2-308
Fluorobenzene	0.66	n/a (assume 1.3)	7.7x10 ³
Chlorobenzene	0.62	1.3-7.1	8.2x10 ³
Bromobenzene	0.59	6.0-36.5	4.0x10 ⁴
Iodobenzene	0.56	n/a	-----
Benzene	0.70	1.3-7.9	7.3x10 ³

Toluene	0.59	1.3-7.0	8.6×10^3
---------	------	---------	-------------------

Clearly it is not likely an explosive mixture of bromobenzene will be generated. Using the suspect Explosive Lower Limit (ELL) value for Bz-Br over 40 liters are necessary to fill the lab with sufficient vaporized material to create a potentially explosive condition. It is likely the ELL (and EUL) bromobenzene values should resemble the pattern noted for Bz, Bz-Me and Bz-Cl. If ELL for Bz-Br was like Bz-Cl it would lower the amount needed by a factor of 4.6. In any event the enormous quantities of compound needed to effect a potential explosion will simply not be feasible to assemble in the 2-308 laboratory.

.Another property of interest for these compounds is their equilibrium vapor pressures at 20°-25° C. In Table 3 approximately room temperature values are listed for several Bz-X chemicals.

Table 3. Vapor pressures for Bz-X materials

Chemical	Vapor pressure, 20°C-25°C, mmHg	Percent of Atmosphere Pressure
Benzene	74.63 @ 20°C	9.8 %
Toluene	22 @ 20°C	2.9 %
Chlorobenzene	9.0 @ 20°C	1.2%
Bromobenzene	3.99 @ 25°C	0.5%

Both Bz-Cl and Bz-Br cannot maintain an atmosphere capable of meeting the requirement for maintaining a sufficient vapor concentration to satisfy the ELL required concentration. Both compounds would partially condense out unto 2-308 surfaces.

Along this line of inquiry, the amounts of chemicals needed to fulfill 1) Emergency Exposure Limit, 2) TWA Exposure Limit and 3) hydrogen halide (i.e., HF, HCl, HBr) IDLH limit for burning Bz-X in 2-308, under static conditions are calculated and shown in Table 3. Amounts of Bz-X Needed to Exceed Exposure Limits.

Table 4. Amounts of Bz-X Needed to Exceed Exposure Limits

Chemical	A cc (ml) of Bz-X/2-308 room volume, ppm/cc(ml)	Emergency Exposure IDLH Limit, cc(ml)	TWA Exposure Limit, cc/(ml)	Combustion Generated Hydrogen Halide, IDLH Cc(ml)
Fluorobenzene	0.66	1.5×10^3 (1000ppm)	N/A	45 (30ppm – IDLH)
Chlorobenzene	0.62	1.6×10^3 (1000ppm)	16 (10ppm)	81 (50ppm – IDLH)
Bromobenzene	0.59	1.7×10^3 (1000ppm)	17 (10ppm)	51 (30ppm – IDLH)

Iodobenzene	0.56	-----	0.02 (0.01ppm)	7 (2ppm – IDLH)
Benzene	0.70	7.1×10^2 (500ppm)	1.4 (1ppm)	-----
Toluene	0.59	8.5×10^2 (500ppm)	85 (50ppm)	-----

The amount of Bz-X material needed to create an IDLH (Immediately Dangerous to Life and Health) condition is again rather large with respect to the amounts of Bz-X chemical that would be used at any one time in an experiment in the apparatus located in 2-308.

The **flammability** hazard rating is the most prominent value in NFPA evaluations, with values of three for several components in this series. The ChemWatch **flammability** ratings are on the average a little lower than NFPA ratings, but as can be noted from Table 1 none of these compounds present a hard-to-mitigate safety element. Ten to twenty liters of vaporized compound are needed to create sufficient conditions for an explosion. Approximately 50 ml of compound would be needed to burn to create a dangerous IDLH condition.

While no definitive Odor Threshold Values for HBr are available, values for HCl are 10ppm (recognition) and 0.3 (detection). It is expected similar values would be found for HBr. Burning 5 mls of bromobenzene would yield a chemical odor somewhere between recognition and detection levels. The odor would not go unnoticed.

Combustion of bromobenzene causes the most serious chemical exposure. The concentration of HBr at the combustion source may well locally exceed IDLH criteria, but with dispersion the amount of HBr produced in the room will not present an IDLH condition, if amounts are limited (< 30ml bromobenzene in a stainless sample holder). Keep the compound away from ignition sources. Significant consequences from other types of chemical exposures from using bromobenzene appear to be diminished, if usage is not prolonged. Health effects from inhalation and possible skin absorption are easily controlled by use of laboratory hoods and chemical resistant gloves (e.g., nitrile gloves.).

Benzene



Hydrofluoric
Acid (HF)



Toluene



Hydrochloric
Acid (HCl)



Fluorobenzene



Hydrobromic
Acid (HBr)



Chlorobenzene



Hydroiodic
Acid (HI)



Bromobenzene



Iodine
(Photo
Decomposition
Product of HI)



Iodobenzene



Benzene



Toluene



Fluorobenzene



Chlorobenzene



Bromobenzene

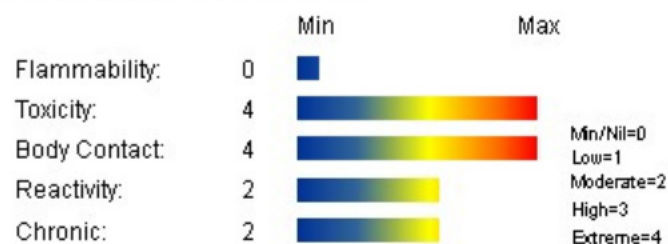


Iodobenzene



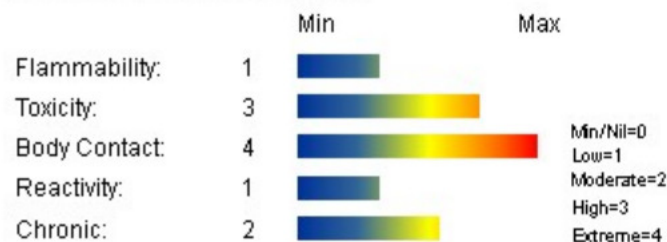
Hydrofluoric Acid (HF)

CHEMWATCH HAZARD RATINGS



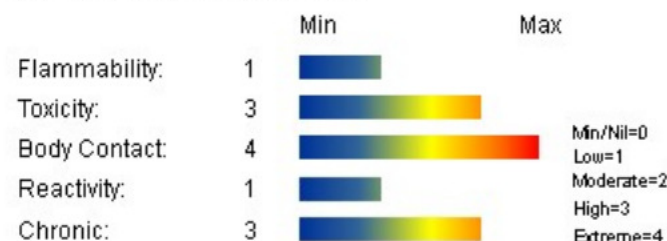
Hydrochloric Acid (HCl)

CHEMWATCH HAZARD RATINGS



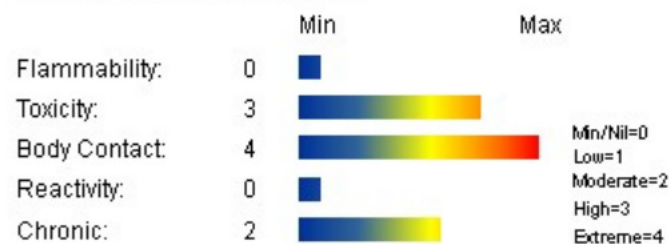
Hydrobromic Acid (HBr)

CHEMWATCH HAZARD RATINGS



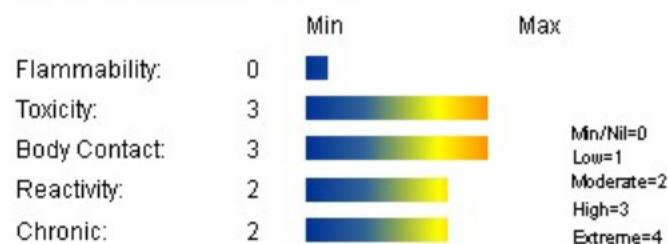
Hydrogen Iodide Acid (HI)

CHEMWATCH HAZARD RATINGS



Iodine (From photo dissociation of HI)

CHEMWATCH HAZARD RATINGS



Physical Properties taken from ChemWatch

Bromobenzene (CAS 108-86-1)
Vapor Pressure (mmHg) – 3.99@25°C
Specific Gravity (water=1) – 1.491
Upper Explosive Limit (%) – 36.5 (Questionable)
Lower Explosive Limit (%) – 6.0 (Questionable)
Chlorobenzene (CAS 108-90-7)
Vapor Pressure (mmHg) – 9.001 @20°C
Specific Gravity (water=1) – 1.11
Upper Explosive Limit (%) – 7.1
Lower Explosive Limit (%) – 1.3
Fluorobenzene (CAS 462-06-6)
Vapor Pressure (mmHg) – Not Available Aldrich – 60 @20°C
Specific Gravity (water=1) – 1.204 (Bogus) Aldrich – 1.024
Upper Explosive Limit (%) – Not Available
Lower Explosive Limit (%) – Not Available
Toluene (CAS 108-88-3)
Vapor Pressure (mmHg) – 21.977 @20°C
Specific Gravity (water=1) – 0.87 @20°C
Upper Explosive Limit (%) – 7.0
Lower Explosive Limit (%) – 1.3
Benzene (CAS 71-43-2)
Vapor Pressure (mmHg) – 74.631 @ 20°C
Specific Gravity (water=1) – 0.879 @ 20°C
Upper Explosive Limit (%) – 7.9
Lower Explosive Limit (%) – 1.3



NFPA 704 standard hazard sticker or Placard. NFPA 704 is a standard maintained by the [U.S.-based National Fire Protection Association](#). It defines the colloquial "fire diamond" used by emergency personnel to quickly and easily identify the risks posed by nearby hazardous materials. This is necessary to help determine what, if any, special equipment should be used, procedures followed, or precautions taken during the first moments of an emergency response.

Health (Blue)		Flammability (Red)	
0	Poses no health hazard, no precautions necessary (e.g., water)	0	Will not burn (e.g., argon)
1	Exposure would cause irritation with only minor residual injury (e.g., acetone)	1	Must be heated before ignition can occur (e.g., mineral oil). Flash point over 93°C (200°F)
2	Intense or continued but not chronic exposure could cause temporary incapacitation or possible residual injury (e.g., di ethyl ether)	2	Must be moderately heated or exposed to relatively high ambient temperature before ignition can occur (e.g., diesel fuel). Flash point between 38°C (100°F) and 93°C (200°F) Must be moderately heated or exposed to relatively high ambient temperature before ignition can occur
3	Short exposure could cause serious temporary or moderate residual injury (e.g., chlorine gas)	3	Liquids and solids that can be ignited under almost all ambient temperature conditions (e.g., gasoline). Liquids having a Flash point below 23°C (73°F) and having a Boiling point at or above 38°C (100°F) or having a Flash point between 23°C (73°F) and 38°C (100°F)
4	Very short exposure could cause death or major residual injury (e.g., hydrogen cyanide, phosphine, carbon monoxide)	4	Will rapidly or completely vaporize at normal atmospheric pressure and temperature, or is readily dispersed in air and will burn readily (e.g., propane). Flash point below 23°C (73°F)
Instability/ Reactivity (Yellow)		Special (White)	
0	Normally stable, even under fire exposure conditions, and is not reactive with water (e.g. helium)		The white "special notice" area can contain several symbols. The following symbols are defined by the NFPA 704 standard.
1	Normally stable, but can become unstable at elevated temperatures and pressures (e.g.		

	propene)		
2	Undergoes violent chemical change at elevated temperatures and pressures, reacts violently with water, or may form explosive mixtures with water (e.g., phosphorus , potassium , sodium)	OX	Oxidizer (e.g., potassium perchlorate , ammonium nitrate , hydrogen peroxide)
3	Capable of detonation or explosive decomposition but requires a strong initiating source, must be heated under confinement before initiation, reacts explosively with water, or will detonate if severely shocked (e.g., ammonium nitrate)	W	Reacts with water in an unusual or dangerous manner (e.g., cesium , sodium , sulfuric acid)
4	Readily capable of detonation or explosive decomposition at normal temperatures and pressures (e.g., nitroglycerine , Trinitrotoluene)		

Product Name

Bromobenzene (Synonyms – C₆H₅Br, “benzene, bromo, monobromobenzene, “phenyl bromide”, NCI-C55492

Bromobenzene CAS 108-86-1

Emergency Overview

Risk

Irritating to skin.

Flammable.

Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

2. Direct Health Effects

A. Potential Health Effects

1. Acute Health Effects

Skin

- This material can cause inflammation of the skin on contact in some persons.
- The material may accentuate any pre-existing dermatitis condition.

Inhaled

- The material is not thought to produce either adverse health effects or irritation of the respiratory tract following inhalation (as classified using animal models). Nevertheless, adverse effects have been

produced following exposure of animals by at least one other route and good hygiene practice requires that exposure be kept to a minimum and that suitable control measures be used in an occupational setting.

■ Bromobenzene is absorbed through lungs, gastrointestinal tract and intact skin. Single doses of bromobenzene have produced massive necrosis in the centrilobular regions of the liver and suggestions have been made that an epoxide which produces aromatic hydroxylation, as a labile intermediate, may be responsible for hepatic necrosis. Kidney damage has also been reported and renal activation mechanisms are suspected in bromobenzene nephrotoxicity.

The substance is also a pneumotoxin with lung damage occurring following exposures of relatively short duration.

2. Chronic Health Effects

■ Limited evidence suggests that repeated or long-term occupational exposure may produce cumulative health effects involving organs or biochemical systems.

There is some evidence that human exposure to the material may result in developmental toxicity. This evidence is based on animal studies where effects have been observed in the absence of marked maternal toxicity, or at around the same dose levels as other toxic effects but which are not secondary non-specific consequences of the other toxic effects.

B. Exposure Hazard Values

Bromobenzene (CAS 108-86-1) has no Occupational Exposure Limits (OEL) on ChemWatch records. Values from chlorobenzene (CAS 108-90-7) ChemWatch MSDS will be used as a substitute.

US - California Permissible Exposure Limits for Chemical Contaminants chlorobenzene 10ppm (TWA – Time Weighted Average, usually a nominal eight hours)

Emergency Exposure Limits

Material	Revised IDLH Value (mg/m ³)	Revised IDLH Value (ppm)
chlorobenzene	206	1,000

IDLH (Immediately Dangerous to Life and Health)

Odor Threshold

For chlorobenzene: Odor Threshold Value: 1.3 ppm (detection). Expect bromobenzene Odor Threshold Value to be at least 5 ppm (detection).

Exposure limits with "skin" notation indicate that vapor and liquid may be absorbed through intact skin. Absorption by skin may readily exceed vapor inhalation exposure. Symptoms for skin absorption are the same as for inhalation

Exposure Limits - Hydrogen Bromide:

US - California Permissible Exposure Limits for Chemical Contaminants	hydrogen bromide (Hydrogen bromide)	3 (TWA)	2	TLV Basis: upper respiratory tract irritation
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Emergency Exposure Limits – Hydrogen Bromide

Material	Revised IDLH Value (mg/m ³)	Revised IDLH Value (ppm)
hydrogen bromide	4	30

Toxicity and Irritation

Bromobenzene - unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

TOXICITY

Oral (rat) LD50: 2699 mg/kg

IRRITATION

Nil Reported

Inhalation (rat) LC50: 20411 mg/m³

CARCINOGEN

ORGANIC BROMINE COMPOUNDS

US Environmental Defense Scorecard Suspected
Carcinogens

Reference(s) P65-
MC

General Fire Hazards/Hazardous Combustible Products

- Liquid and vapor are flammable.
- Moderate fire hazard when exposed to heat or flame.
- Vapor forms an explosive mixture with air.
- Moderate explosion hazard when exposed to heat or flame.
- Vapor may travel a considerable distance to source of ignition.
- On combustion may emit toxic fumes of carbon monoxide (CO). Combustion products include: carbon dioxide (CO₂), carbon monoxide (CO), **hydrogen bromide**, other pyrolysis products typical of burning organic material.

3. Personal Protection Equipment (PPE)

- A. Safety Glasses with side shields. Alternative: Chemical goggles.
- B. Nitrile Gloves: See discussion below.
- C. Clothing to cover legs.
- D. Closed-toe shoes

A. Eye

Safety Glasses with side shields

Chemical goggles.

Contact lenses pose a special hazard; soft lenses may absorb irritants and all lenses concentrate them

Eyewash unit.

Ensure there is ready access to a safety shower, (within ten-second access).

B. Hands Protection - Gloves

Suitability and durability of glove type is dependent on usage. Important factors in the selection of gloves include: such as:

- frequency and duration of contact,
- chemical resistance of glove material,
- glove thickness and dexterity

Select gloves tested to a relevant standard (e.g. Europe EN 374, US F739).

When prolonged or frequently repeated contact may occur, a glove with a protection class of 5 or higher (breakthrough time greater than 240 minutes according to EN 374) is recommended.

When only brief contact is expected, a glove with a protection class of 3 or higher (breakthrough time greater than 60 minutes according to EN 374) is recommended.

Contaminated gloves should be replaced immediately.

Gloves must only be worn on clean hands. After using gloves, hands should be washed and dried thoroughly.

Hand Protective Material CPI *. Gloves

VITON	A
TEFLON	A
PVA	B
NITRILE	C

* CPI - ChemWatch Performance Index

A: Best Selection

B: Satisfactory; may degrade after 4 hours continuous immersion

C: Poor to Dangerous Choice for other than short term immersion

NOTE: As a series of factors will influence the actual performance of the glove, a final selection must be based on detailed observation. - * Where the glove is to be used on a short term, casual or infrequent basis, factors such as "feel" or convenience (e.g. disposability), may dictate a choice of gloves which might otherwise be unsuitable following long-term or frequent use. A qualified practitioner should be consulted.

SUITABILITY and DURABILITY of glove type is dependent on usage. Important factors in the selection of gloves include: such as:

- frequency and duration of contact,
- chemical resistance of glove material,
- glove thickness and dexterity

Select gloves tested to a relevant standard (e.g. Europe EN 374, US F739).

When prolonged or frequently repeated contact may occur, a glove with a protection class of 5 or higher (breakthrough time greater than 240 minutes according to EN 374) is recommended.

When only brief contact is expected, a glove with a protection class of 3 or higher (breakthrough time greater than 60 minutes according to EN 374) is recommended.

Contaminated gloves should be replaced.

GUIDE 4010 Chemical protection - Nitrile



Chemical protection glove in nitrile

Thickness 0.52 mm, Length 32 cm

Produced in a very pliable and elastic nitrile material
 Environmentally friendly alternative to PVC/vinyl
 Fleece lined for comfortable use
 Food industry approved
 Silicone free

Areas of use: Industry and heavier cleaning work with both mechanical and chemical risks. Its flexibility also makes it suitable for precision and assembly work with chemicals involved.

Complies with CE Category 3 in accordance with EN 374:2003/EN388 - 3100.

Supreno* EC Powder-Free Nitrile Gloves, Microflex*

Supplier: Microflex



[Supreno* EC Powder-Free Nitrile Gloves, Microflex*](#)

Soft, durable nitrile formulation delivers improved strength and comfort.

Gloves are suitable for high-risk applications and feature an extended cuff to protect the wrist and forearm. Interior polymer coating makes gloves easy to don. Textured fingers allow for reliable grip in wet and dry conditions.

Online chlorination. Ambidextrous. Powder-free. Beaded cuff. Color: blue.

Gloves meet or exceed the emergency medical glove requirements of NFPA 1999.

Click to Enlarge

Caution: Components used in making these gloves may cause allergic reactions in some users. Follow your institution's policies for use.

Ordering Information: Gloves are packaged 50 gloves per dispenser box.

Order from VWR - online

www.vwrsp.com/catalog/product/index.cgi?catalog_number=32916-670&inE=1&highlight=32916-670

			32916-670		4547178	46181504
46181504	46181504	46181504	46181504			

[ORDER](#)
[SPECIFICATIONS](#)

ORDER

[ADD TO BASKET](#) [VIEW SHOPPING BASKET](#)

Size	Supplier No.	Cat. No.	Unit	Price	Quantity
Large	SEC-375-L	32916-674	Case of 10	\$163.64	<input type="text" value="0"/>
			Pack of 50	\$18.05	<input type="text" value="0"/>
Medium	SEC-375-M	32916-672	Case of 10	\$163.64	<input type="text" value="0"/>
			Pack of 50	\$18.05	<input type="text" value="0"/>
Small	SEC-375-S	32916-670	Case of 10	\$163.64	<input type="text" value="0"/>
			Pack of 50	\$18.05	<input type="text" value="0"/>

X-Large	SEC-375-XL	32916-676	Case of 10	\$163.64	<input type="text" value="0"/>
			Pack of 50	\$18.05	<input type="text" value="0"/>
XX-Large	SEC-375-XXL	32916-678	Case of 10	\$163.64	<input type="text" value="0"/>
			Pack of 50	\$18.05	<input type="text" value="0"/>

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SPECIFICATIONS

Cuff Thickness 4.7 mil

Finger Thickness 7.9 mil

Length 29.5 cm (115/8")

Palm Thickness 5.9 mil

C-D. Legs/Feet

When handling corrosive and hazardous liquids in LBNL labs.
wear trousers or overalls, outside of shoes (boots), to avoid direct contact of spills with legs and to
avoid spills entering shoes (boots).

4. Physical Properties – Bromobenzene

Liquid.

Does not mix with water.

Sinks in water.

State	Liquid	Molecular Weight	157.02
Melting Range (°F)	-24 (-31 °C)	Viscosity	Not Available

Boiling Range (°F)	313 (156 °C)	Solubility in water (g/L)	Immiscible
Flash Point (°F)	124 (51 °C)	pH (1% solution)	Not applicable.
Decomposition Temp (°F)	Not Available	pH (as supplied)	Not applicable
Autoignition Temp (°F)	1051	Vapor Pressure (mmHg)	3.99 @ 25°C
Upper Explosive Limit (%)	36.5	Specific Gravity (water=1)	1.491
Lower Explosive Limit (%)	6.0	Relative Vapor Density (air=1)	5.41
Volatile Component (%vol)	100	Evaporation Rate	Not available

APPEARANCE

Clear liquid with aromatic odor; does not mix well with water (0.045 g/100g H₂O).

5. Waste

Any hazardous waste that is generated will be disposed of in an SAA, and picked up as directed in accordance with Pub 3092. The SAAs are located in a cabinet under the hood in 2-308 laboratory.

6. Emergency Procedures

Authorized laboratory personnel will be familiar with the Building-2 Emergency Plan, location of emergency equipment, and emergency procedures for fires, earthquakes and evacuations. Evacuation can occur through the two doors located on either side of the lab. There is an emergency over-ride of the access controls, so that people from outside can enter and assist if needed. In the event of a fire, personnel will leave the area and summon the Lab's Fire Operations by dialing 7-911 or by pulling the fire alarm and then follow the building's emergency exit plan.

In the event of a chemical splash to the skin or eyes, personnel will wash off the material for 15 minutes and then get transported to Health Services (Bldg 26, ext 6266) for evaluation and treatment. Use the sink to wash material off of hands. Use the emergency eyewash safety shower located in the hallway for eye and body exposure.

A. Extinguishing Media

- Water spray or fog.
- Foam.
- Dry chemical powder.
- BCF (where regulations permit)
- Carbon dioxide.

B. Chemical Spill Cleanup Requirements: You can clean up a chemical spill if ALL of the following requirements are met:

You are NOT a high school student, a college student or a guest participating in an internship program. There is no potential for release to the environment. Note: Care must be taken to avoid spreading or tracking chemical contamination to other areas.

There are no personal injuries resulting from the spill.

The cleanup procedures are known and you have the proper spill cleanup materials.

You have the proper PPE to protect yourself during the cleanup.

The spill can be cleaned up safely by two people in one hour or less.

The spill does NOT involve elemental mercury. Special cleanup and monitoring procedures are required for mercury spills. Moreover, mercury contamination is easily tracked to other areas.

If ALL of the above requirements are not met or if you have any doubts about your ability to safely and effectively clean up the spill, then:

Leave the immediate area,

Close the door,

Stay close by and control access. Post the entrance with a warning such as Spill: Do Not Enter and

Call extension 6999 for assistance.

C. Other Considerations:

Restrict access to the affected area. This reduces potential exposure and minimizes the spread of chemical contamination.

Wear the proper PPE to protect yourself. The minimum includes a lab coat (or coveralls), chemical goggles and chemically resistant gloves rated for the chemical(s) of concern. Consult the Chemical Hygiene and Safety Plan for selecting and using eye/face protection and gloves.

Control or eliminate ignition sources (open flames, electrical components) when cleaning flammable liquid spills.

For mixed (i.e., radiological and chemical) spills, follow the SWIMS guidelines: Stop your work and the spill, Warn others (contact the assigned RCT or call the Urgent Radiation Safety Assistance x 7277), Isolate the spill, Monitor yourself and the area (if appropriate), and

Stay in the general area until help arrives.

Inform your supervisor of all spills and all clean ups.

Use an emergency eyewash/safety shower for eye or body exposure. A sink may be used to wash chemicals off hands. Personnel experiencing eye, skin or inhalation exposure must report to Health Services (extension 6266) for an evaluation. Ensure that you can provide Health Services with the Material Safety Data Sheet or the name of the material(s) involved in the spill.

Laboratories and shops must have an adequate number of spill kits for the hazardous materials that are either stored or handled in the areas. These are commercially available through vendors such as VWR Scientific and Sigma-Aldrich which are accessible through Procurement. It is important to note that absorbents and other materials used for spill cleanup need to be "inert" to the spilled material. For this reason, combustible materials such as saw dust and paper towels are generally inappropriate substitutes for the materials contained in spill kits.

A copy of the LBNL's red and white Emergency Response Guide flip chart must be posted in each Laboratory area.

In the event of a hazardous chemical, biological, radiological spill or release, remember — S.W. I. M. S.

S **TOP** all work. Observe and think.

W **ARN** others in the area and report the incident.

I **SOLATE** the area and restrict access.

M **ONITOR** yourself. Check skin, clothing and shoes. Observe physiological reactions.

S **TAY** in the immediate area and notify your supervisor.

AUTHORIZED WORKER(s) INFORMATION:

WORKER ID NUMBER:	WORKER NAME	WORKER SIGNATURE¹	SUPERVISOR AUTHORIZATION²
	(Work Leader)		

¹ *Worker signature indicates concurrence with the analysis and agreement to work in accordance with this authorization.*

² *Supervisor signature above authorizes the work subject to the controls specified.*

Appendix D

Task Specific Job Hazard Analysis of Joint Aerosol Experiments for Jan-Feb 2012

Work being performed in ALS facility inside CSD assigned laboratory

Date: January 6, 2012

Subject: Working Planning for Joint
Aerosol Experiments during Jan.-Feb.
2012

Supervisor: Kevin Wilson

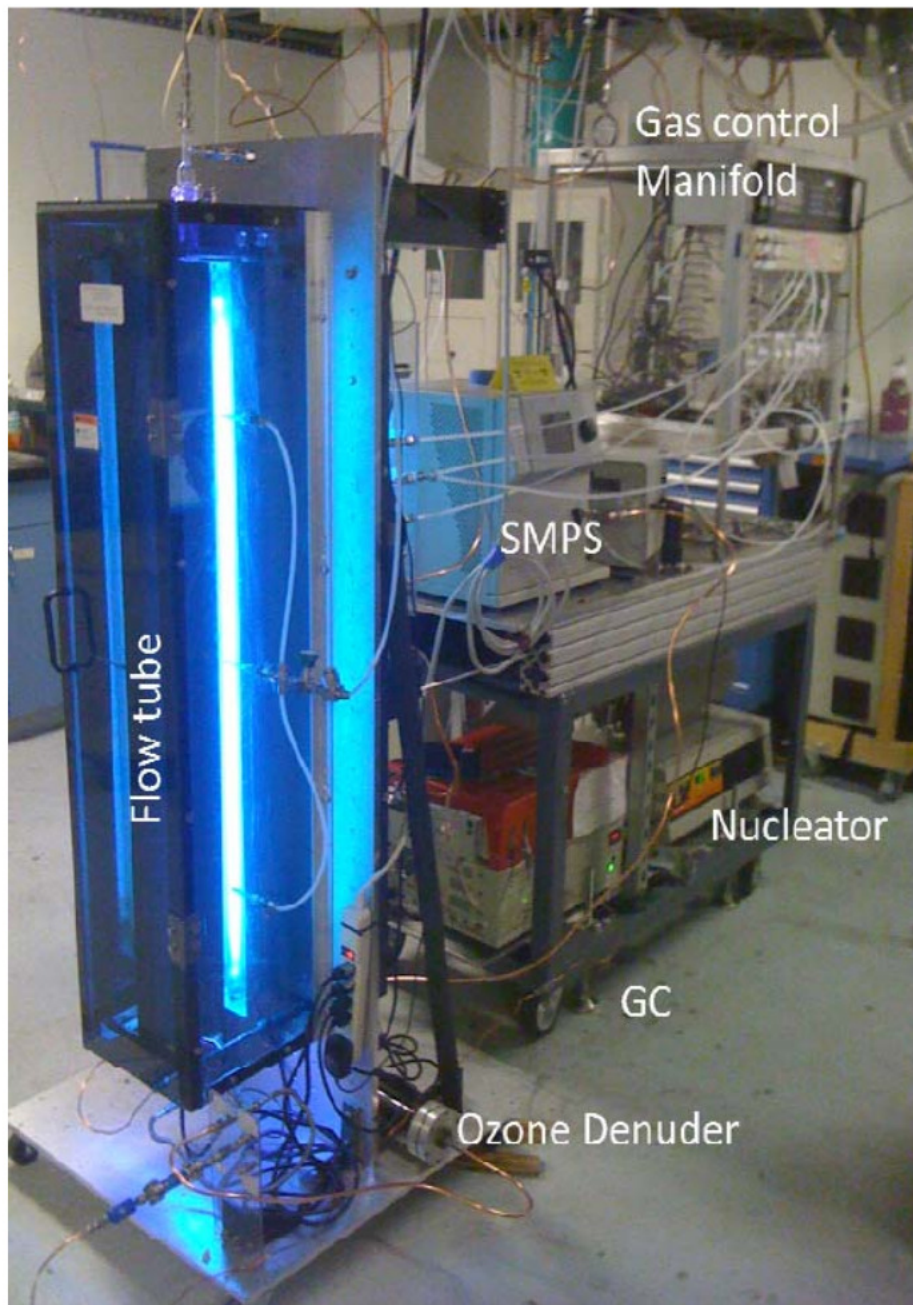
Location: Building 6-2263

Background: Flow tube oxidation experiments will be setup in 6-2263 in order to collect aerosol filter samples to be analyzed during Wilson and Goldstein beamtime (9.0.2) starting in March 2012. These experiments will be conducted by members of the Chemical Dynamics Beamline (Kevin Wilson, Theo

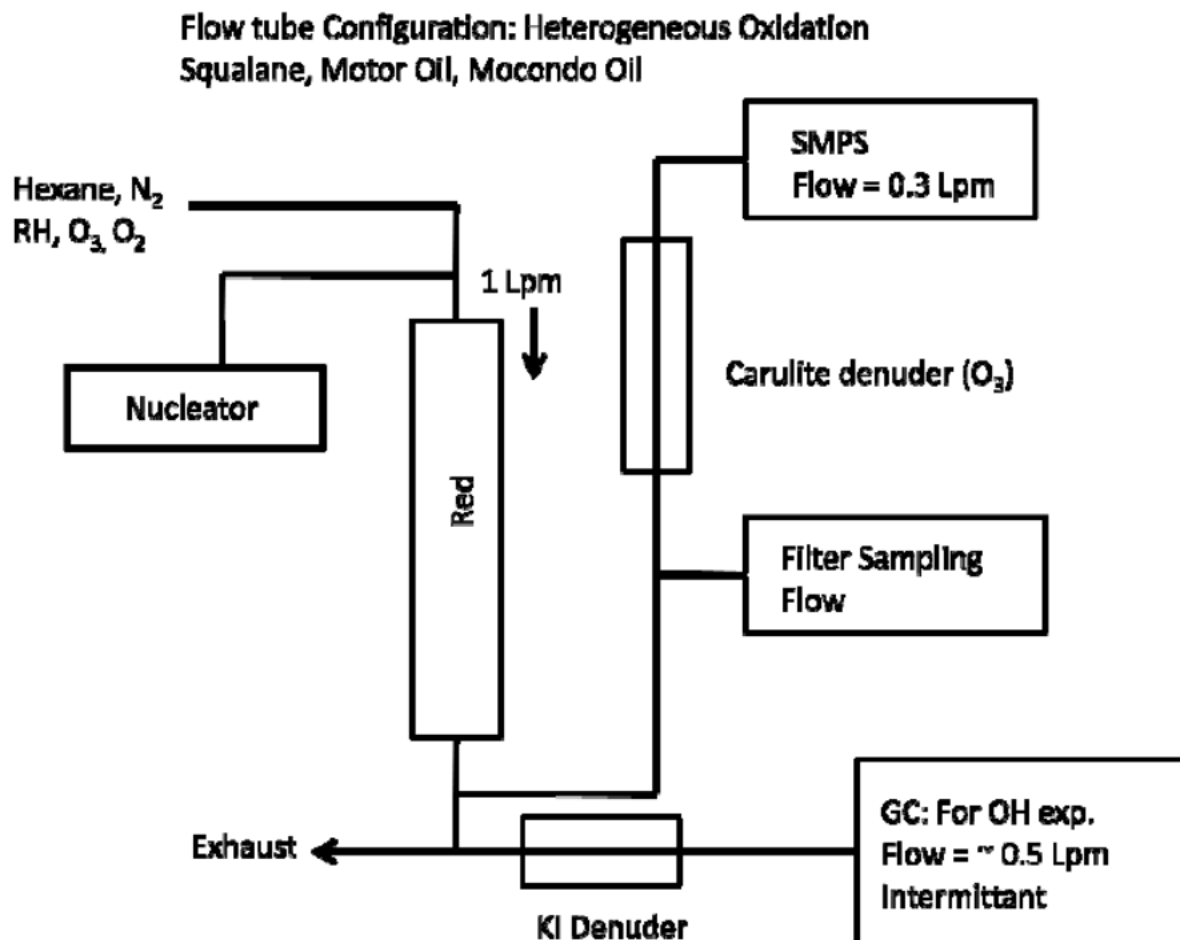
Nah), the Allen Goldstein Group (Gabriel Isaacman, Dave Worton, Arthur Chan, Chris Ruehl) as well as Chris Cappa and Katie Kolesar (U.C. Davis). With the exception of Wilson and Nah, all other personnel are users of the ALS and are badged by the user office. They receive general ALS training as part of this process (access to controlled areas). The flow tube oxidation experiments (the techniques as well as hardware) are extensively reviewed during the ESS inspections by the ALS and are documented under experiment number ALS-01431. A brief overview of the flow tube set up is provided below as well as a description of potential hazards and mitigation measures.

Cappa and the Goldstein groups will be bringing filter collection devices (vacuum pump, filters and filter holders) to sample the flow, which are minor additions to the overall experimental apparatus. Ruehl will be bringing a new instrument for cloud condensation nuclei studies, which contains an enclosed Class 3b laser. This particular piece of equipment will be reviewed by Ken Barat (LSO), as well as Jerry Bucher (CSD Safety Coordinator) before used.

Experimental Description: The flow tube oxidation apparatus consists of a 1 meter long quartz tube surrounded by two sets of 254 nm Hg lamps. Organic aerosols, formed either by nucleation of the vapor in an



oven (nucleator) or by reaction of a gas phase precursor (e.g alpha pinene), are entrained in N₂. O₂ and H₂O are mixed with ozone(O₃), which is photolyzed by the lamps to generate hydroxyl radicals. Trace concentrations of hexane (ppb) are added to the flow tube to measure OH exposure via a gas chromatograph (GC). Changes in the aerosol size are measured using a commercial scanning particle sizer (SMPS). The flow tube is run at 1 liter per minute at atmospheric pressure and filter samples will be collected by direct part of the flow from the flow tube into the appropriate collectors. See experimental schematic and photograph of setup.



Hazards and Mitigation:

Wilson will provide a briefing on the safety requirements of working in lab 6-2263 as well as provide OJT to the participants listed below. Once this is completed and Wilson is satisfied that the participants are aware of the hazards and mitigations strategies, they will review this document and sign below, after which Wilson will give them card key access to 6-2263. During this experimental period no other laser experiments will be conducted in 6-2263. Wilson will periodically review the experimental progress and setup to ensure the continuous safe operation of the setup during the two months of time.

Exposure to UV light (254 nm): The lamps are contained in a plexiglass housing to eliminate exposure of personnel to UV lights. This configuration has been previously reviewed by Ken Barat (LSO) as part of the ALS ESS safety procedure.

Compressed Gases: Safety glasses are required at all times when working in Lab 6-2263. The hydrogen (H₂) cylinder (GC) is physically segregated from the O₂ cylinder by placing it inside the toxic gas cabinet located in the lab. All gas lines have been “snooped” by Theo Nah under the supervision of Kevin Wilson on Jan 5, 2012.

Chemicals: Ozone is generated by either a pen ray lamp or commercial corona discharge instrument.

An ozone monitor is connected to the flow tube to monitor ozone concentrations at all times. The ozone is scrubbed from flow exiting the flow tube using a Carulite denuder and then passed into the house exhaust line. This configuration eliminates potential ozone exposure to personnel and equipment (SMPS).

Aerosol will be formed using squalane, motor oil (10-30W) and oil from the Macondo well from the Deepwater Horizon gulf oil spill. Aerosol of these materials are generated in an oven (nucleator) and entrained in nitrogen. All flows containing aerosols are either filtered to remove particles or directed into the house exhaust system to prevent exposure.

Aerosol will also be formed within the flow via the reaction of α -pinene + ozone. α -pinene is introduced into the flow tube using a syringe pump containing ~10-100 microliters of total liquid. The concentration of α -pinene in the flow tube is on the order of 500 ppb.

Electrical: All experimental platforms and equipment when needed will be attached to the laboratory ground.

Laser: A Continuous-Flow Streamwise Thermal Gradient Chamber will be brought by Ruehl and interfaced to the flow tube system. This instrument contains a Class 3b laser which is enclosed. Another review will be conducted by Ken Barat of this instrument before becoming operational.

Participants:

Theo Nah _____ Date: _____

Kevin R. Wilson _____ Date: _____

Gabriel Isaacman _____ Date: _____

Dave Worton _____ Date: _____

Chris Cappa _____ Date: _____

Katie Kolesar _____ Date: _____

Arthur Chan _____ Date: _____

Chris Ruehl _____ Date: _____

Review:

Chemical Sciences Safety Coordinator

Jerome J Bucher _____ Date _____

LBNL Laser Safety Officer

Ken Barat _____ Date _____

Work Plan - Addendum

Date: January 17, 2012

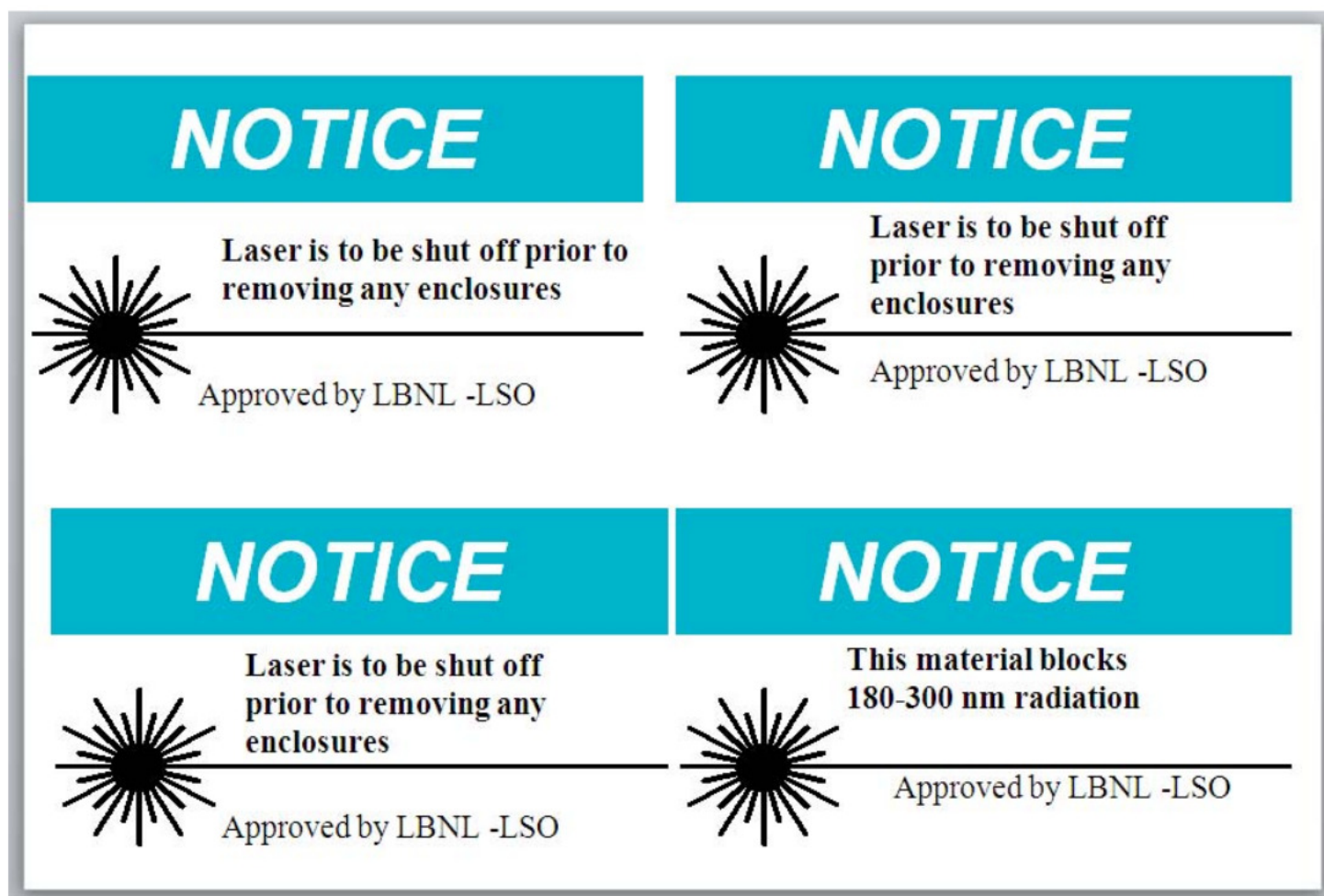
Subject: Addendum to Work Plan for Joint Aerosol Experiments During Jan. – Feb 2012.

Room: 6-2263

On January 17th at 3 pm Ken Barat reviewed the commercial laser setup inside the Continuous-Flow Streamwise Thermal Gradient Chamber with Kevin Wilson and Chris Ruehl.

The following hazard mitigation steps are to be taken before the instrument is used:

1. Better enclose the optical path at the bottom of the instrument with anodized aluminum foil or some facsimile.
2. No unattended operation of instrument when laser is running.
3. If it is necessary to open the shielding for non-laser alignment troubleshooting the laser must be powered off.
4. No laser alignment is authorized. If this is required then further review by the LSO is needed.



Appendix A – Scope of Work -Detailed

Published 11 December 2009, Science 326, 1525 (2009)

DOI: 10.1126/science.1180353

S1.1. Description of Laboratory Aging Experiments

The α -pinene SOA and squalane aging experiments shown in Figures 2c-d were conducted at the Advanced Light Source at the Lawrence Berkeley National Laboratory in Berkeley, California (S1, S2). SOA from α -pinene ozonolysis is generated by mixing α -pinene (~40 ppm, from bubbling N₂ through α -pinene) with ozone (~500 ppb, generated by passing N₂/O₂ mixture through a quartz absorption cell illuminated by a pen-ray Hg lamp) in a 130 cm long, 2.5 cm ID flow tube. The total residence time within the flow tube is ~90 s, which is sufficient to generate a high concentration of SOA particles. Upon exiting the flow tube the aerosol stream is passed through a carulite ozone denuder and an activated carbon trap to remove any remaining ozone, α -pinene, and gas phase organic products. In a separate oven, squalane aerosol is formed by homogeneous nucleation of the heated vapor above a liquid sample.

The heterogeneous oxidation of either α -pinene SOA or squalane particles by OH radicals is carried out in a second flow tube (130 cm long, 2.5 cm ID, type 219 quartz).

The aerosol stream is mixed with humidified N₂ (RH = 10-60%, controlled by a water bubbler), O₂ (5%), and variable amounts of O₃ (generated by passing pure O₂ through a corona discharge). OH radicals are generated within the reaction cell by the photolysis of ozone using light from four 130 cm long Hg ($\lambda = 254$ nm) lamps (UVP, Upland, CA) positioned along the length of the reactor, followed by reaction with water vapor. OH concentration is varied by adjusting both the RH and ozone concentration within the flow cell. The steady state OH concentrations are estimated using a kinetic modeling program fit to GC-FID measurements of the decay of hexane over a large range of precursor, RH, and ozone concentrations. The total flow through the reactor is 1.0 L min⁻¹, which corresponds to an exposure time of ~ 37 s. The temperature of the reactor was $\sim 35^\circ\text{C}$ as a result of moderate heating from the nearby UV lamps. As discussed by Smith et al. (2009), the heterogeneous reaction rate should be only very weakly dependent on temperature, and therefore the effect of the 10°C difference from room temperature should be insignificant for those experiments. Upon exiting the reactor a portion of the aerosol stream is sampled by an Aerodyne HR-ToF-AMS (S3). The remainder of the aerosol stream is sent to a differential mobility analyzer (DMA) and condensation particle counter (CPC) to measure the size and concentration of the particles. The aging experiments for diesel and biomass burning emissions shown in Figures 2e-f were carried out in the smog chamber at Carnegie Mellon University. Briefly, source emissions were injected into the smog chamber and, after an initial mixing period, photochemical aging was driven using UV lights. Further experimental details are described by (S4-S7). A quadrupole AMS (Q-AMS) (S8-S9) was used to characterize the evolving OA composition.

Supporting Online Material for Evolution of Organic Aerosols in the Atmosphere

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Appendix B – -pinene (CAS # 80-56-8)

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
alpha-pinene	80-56-8	>98

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

Source	Material	TWA ppm	TWA mg/m ³	STEL ppm	STEL mg/m ³	Peak ppm	Peak mg/m ³	TWA F/CC	Notes
US ACGIH Threshold Limit Values (TLV)	alpha-pinene (Turpentine and selected monoterpenes)	20							TLV® Basis: URT & skin irr; CNS impair; lung dam
US ACGIH Threshold Limit Values (TLV)	alpha-pinene (Diesel fuel, as total hydrocarbons)		100						TLV® Basis: Dermatitis

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Liquid.

Does not mix with water.

Floats on water.

State	Liquid	Molecular Weight	136.23
Melting Range (°F)	Not available	Viscosity	Not Available
Boiling Range (°F)	311- 313 dl-form	Solubility in water (g/L)	Immiscible
Flash Point (°F)	90	pH (1% solution)	Not applicable.
Decomposition Temp (°F)	Not Available	pH (as supplied)	Not applicable
Autoignition Temp (°F)	Not available	Vapour Pressure (mmHG)	Not available
Upper Explosive Limit (%)	Not available	Specific Gravity (water=1)	0.8592 dl-form
Lower Explosive Limit (%)	Not available	Relative Vapour Density (air=1)	>1
Volatile Component (%vol)	Not available.	Evaporation Rate	Not available

Section 11 - TOXICOLOGICAL INFORMATION

alpha-pinene

TOXICITY AND IRRITATION

ALPHA-PINENE:

■ unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

TOXICITY	IRRITATION
Oral (rat) LD50: 3700 mg/kg	Skin (man): 100% - SEVERE
	Skin (rabbit): 500 mg/24h - Moderate

■ Contact allergies quickly manifest themselves as contact eczema, more rarely as urticaria or Quincke's oedema. The pathogenesis of contact eczema involves a cell-mediated (T lymphocytes) immune reaction of the delayed type. Other allergic skin reactions, e.g. contact urticaria, involve antibody-mediated immune reactions. The significance of the contact allergen is not simply determined by its sensitisation potential: the distribution of the substance and the opportunities for contact with it are equally important. A weakly sensitising substance which is widely distributed can be a more important allergen than one with stronger sensitising potential with which few individuals come into contact. From a clinical point of view, substances are noteworthy if they produce an allergic test reaction in more than 1% of the persons tested.

The material may cause severe skin irritation after prolonged or repeated exposure and may produce on contact skin redness, swelling, the production of vesicles, scaling and thickening of the skin. Repeated exposures may produce severe ulceration.

Bicyclic terpenes are very low in acute toxicity. However, repeated dosing may have deleterious effects on the liver and kidney. Members of this category show no significant reproductive or developmental toxicity and may have a little, if any, potential to alter genetic material.

CARCINOGEN

Turpentine and selected monoterpenes	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A4
Diesel fuel, as total hydrocarbons	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A3

See Appendix Z

Section 16 - OTHER INFORMATION

LIMITED EVIDENCE

- Inhalation and/or ingestion may produce health damage*.
 - May produce discomfort of the respiratory system*.
 - Repeated exposure potentially causes skin dryness and cracking*.
- * (limited evidence).

Denmark Advisory list for selfclassification of dangerous substances

Substance	CAS	Suggested codes
alpha- pinene	80- 56- 8	N; R51/53
alpha- pinene	1330- 16- 1	R52/53
alpha- pinene	2437- 95- 8	N; R51/53
alpha- pinene	7785- 70- 8	N; R51/53
alpha- pinene	7785- 26- 4	N; R51/53

Ingredients with multiple CAS Nos

Ingredient Name	CAS
alpha-pinene	80-56-8, 1330-16-1, 2437-95-8, 7785-70-8, 7785 -26-4

Appendix C – Ozone (CAS# 10028-15-6)

NFPA



CHEMWATCH HAZARD RATINGS

		Min	Max
Flammability:	0	<div style="width: 0%; background-color: blue;"></div>	
Toxicity:	3	<div style="width: 75%; background-color: blue;"></div>	
Body Contact:	2	<div style="width: 50%; background-color: blue;"></div>	
Reactivity:	2	<div style="width: 50%; background-color: blue;"></div>	
Chronic:	2	<div style="width: 50%; background-color: blue;"></div>	

Min/Nil=0
Low=1
Moderate=2
High=3
Extreme=4

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
ozone	10028-15-6	>98

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

Source	Material	TWA ppm	TWA mg/m³	STEL ppm	STEL mg/m³	Peak ppm	Peak mg/m³	TWA F/CC	Notes
US NIOSH Recommended Exposure Limits (RELs)	ozone (Ozone)					0.1	0.2		
US ACGIH Threshold Limit Values (TLV)	ozone (Ozone Moderate work)	0.08							TLV® Basis: Pulm func
US ACGIH Threshold Limit Values (TLV)	ozone (Ozone Heavy work)	0.05							TLV® Basis: Pulm func
US ACGIH Threshold Limit Values (TLV)	ozone (Ozone Heavy, moderate, or light)	0.20							TLV® Basis:

workloads (< 2 hours))						Pulm func
US ACGIH Threshold Limit Values (TLV)	ozone (Ozone Light work)	0.10				TLV® Basis: Pulm func
US - California Permissible Exposure Limits for Chemical Contaminants	ozone (Ozone)	0.1	0.2	0.3	0.6	
US OSHA Permissible Exposure Levels (PELs) - Table Z1	ozone (Ozone)	0.1	0.2			

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Gas. Toxic or noxious vapours/gas.

State	COMPRESSED GAS	Molecular Weight	48
Melting Range (°F)	32 192	Viscosity	Not Applicable
Boiling Range (°F)	32 112	Solubility in water (g/L)	Partly Miscible
Flash Point (°F)	Not applicable	pH (1% solution)	Not applicable.
Decomposition Temp (°F)	Not applicable	pH (as supplied)	Not applicable
Autoignition Temp (°F)	Not applicable	Vapor Pressure (mmHg)	22.502 (-157.2 C)
Upper Explosive Limit (%)	Not applicable	Specific Gravity (water=1)	2.144 g/l
Lower Explosive Limit (%)	Not applicable	Relative Vapour Density (air=1)	1.65
Volatile Component (%vol)	Not applicable.	Evaporation Rate	Not applicable

APPEARANCE

Colourless to blue gas, depending on concentration. Pungent odour above 0.01 ppm. Disagreeable sulfur-like odour above 1-2 ppm. Solubility in water: 0.49% by weight

Section 11 - TOXICOLOGICAL INFORMATION

OZONE

TOXICITY AND IRRITATION

OZONE:

- unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.
- Asthma-like symptoms may continue for months or even years after exposure to the material ceases. This may be due to a non-allergenic condition known as reactive airways dysfunction syndrome (RADS) which can occur following exposure to high levels of highly irritating compound. Key criteria for the diagnosis of RADS include the absence of preceding respiratory disease, in a non-atopic individual, with abrupt onset of persistent asthma-like symptoms within minutes to hours of a documented exposure to the irritant. A reversible airflow pattern, on spirometry, with the presence of moderate to severe bronchial hyperreactivity on methacholine challenge testing and the lack of minimal lymphocytic inflammation, without eosinophilia, have also been included in the criteria for diagnosis of RADS. RADS (or asthma) following an irritating inhalation is an infrequent disorder with rates related

to the concentration of and duration of exposure to the irritating substance. Industrial bronchitis, on the other hand, is a disorder that occurs as result of exposure due to high concentrations of irritating substance (often particulate in nature) and is completely reversible after exposure ceases. The disorder is characterised by dyspnea, cough and mucus production.

NOTE: Ozone aggravates chronic obstructive pulmonary diseases. Ozone is suspected also of increasing the risk of acute and chronic respiratory disease, mutagenesis and foetotoxicity. In animals short-term exposure to ambient concentrations of less than 1 ppm results in reduced capacity to kill intrapulmonary organisms and allows purulent bacteria to proliferate [Ellenhorn etal].

CARCINOGEN

Ozone Heavy work US ACGIH Threshold Limit Values (TLV) - Carcinogens **Carcinogen Category A4**
See Appendix Z

Appendix D – Carulite “denuder” (O₃) (CAS# 1313-13-9, 1317-38-0)

Carus Carulite 200 Low Temperature Oxidation Catalyst

NFPA



CHEMWATCH HAZARD RATINGS

		Min	Max
Flammability:	0	<div><div></div></div>	
Toxicity:	2	<div><div></div></div>	
Body Contact:	2	<div><div></div></div>	
Reactivity:	2	<div><div></div></div>	
Chronic:	2	<div><div></div></div>	

Min/Nil=0
Low=1
Moderate=2
High=3
Extreme=4

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
manganese dioxide	1313-13-9	60-75
aluminium oxide	1344-28-1.	8-18
copper(II) oxide	1317-38-0	11-14

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

Source	Material	TWA ppm	TWA mg/m ³	STEL ppm	STEL mg/m ³	Peak ppm	Peak mg/m ³	TWA F/CC	Notes
US NIOSH Recommended Exposure Limits (RELs)	manganese dioxide (Silica, amorphous)		6						
US - California Permissible Exposure Limits for Chemical	manganese dioxide (Silica, amorphous Total dust)		6						

Contaminants				
US - California Permissible Exposure Limits for Chemical Contaminants	manganese dioxide (Silica, amorphous Respirable fraction)	3		(n)
US ACGIH Threshold Limit Values (TLV)	manganese dioxide ((Manganese and inorganic compounds, as Mn))	0.2		TLV® Basis: CNS impair , See Notice of Intended Changes (NIC)
US OSHA Permissible Exposure Levels (PELs) - Table Z1	aluminium oxide (alpha-Alumina - Total dust)	15		
US OSHA Permissible Exposure Levels (PELs) - Table Z1	aluminium oxide (alpha-Alumina - Respirable fraction)	5		
US - California Permissible Exposure Limits for Chemical Contaminants	aluminium oxide (Aluminum welding fumes)	5		
US ACGIH Threshold Limit Values (TLV)	aluminium oxide (Aluminum metal and insoluble compounds)	1		TLV® Basis: Pneumoconiosis; LRT irr; neurotoxicity
US - California Permissible Exposure Limits for Chemical Contaminants	aluminium oxide (Aluminum metal and oxide Respirable fraction)	5		(n)
US - California Permissible Exposure Limits for Chemical Contaminants	aluminium oxide (Aluminum metal and oxide Total dust)	10		
US ACGIH	copper(II)	1		TLV® Basis: Irr:

Threshold Limit Values (TLV)	oxide (Copper Dusts and mists, as Cu)		GI; metal fume fever
US OSHA Permissible Exposure Levels (PELs) - Table Z1	copper(II) oxide (Copper - Dusts and mists (as Cu))	1	
US - California Permissible Exposure Limits for Chemical Contaminants	copper(II) oxide (Copper salts, dusts and mists, as Cu)	1	

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Does not mix with water.

Sinks in water.

State	Divided Solid	Molecular Weight	Not Applicable
Melting Range (°F)	Not Available	Viscosity	Not Applicable
Boiling Range (°F)	Not Applicable	Solubility in water (g/L)	Immiscible
Flash Point (°F)	Not Applicable	pH (1% solution)	Not Applicable
Decomposition Temp (°F)	849	pH (as supplied)	Not Applicable
Autoignition Temp (°F)	Not Available	Vapour Pressure (mmHG)	Not Applicable
Upper Explosive Limit (%)	Not Applicable	Specific Gravity (water=1)	4.7
Lower Explosive Limit (%)	Not Applicable	Relative Vapour Density (air=1)	Not Available
Volatile Component (%vol)	Not Applicable	Evaporation Rate	Not Applicable

Section 11 - TOXICOLOGICAL INFORMATION

Carus Carulite 200 Low Temperature Oxidation Catalyst

TOXICITY AND IRRITATION

■ unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

ALUMINIUM OXIDE:

COPPER(II) OXIDE:

MANGANESE DIOXIDE:

■ No significant acute toxicological data identified in literature search.

CARUS CARULITE 200 LOW TEMPERATURE OXIDATION CATALYST:

■ None assigned. Refer to individual constituents.

MANGANESE DIOXIDE:

TOXICITY	IRRITATION
----------	------------

Oral (Rat) LD50: >3478 mg/kg

ALUMINIUM OXIDE:

COPPER(II) OXIDE:

■ Asthma-like symptoms may continue for months or even years after exposure to the material ceases. This may be due to a non-allergenic condition known as reactive airways dysfunction syndrome (RADS) which can occur following exposure to high levels of highly irritating compound. Key criteria for the diagnosis of RADS include the absence of preceding respiratory disease, in a non-atopic individual, with abrupt onset of persistent asthma-like symptoms within minutes to hours of a documented exposure to the irritant. A reversible airflow pattern, on spirometry, with the presence of moderate to severe bronchial hyperreactivity on methacholine challenge testing and the lack of minimal lymphocytic inflammation, without eosinophilia, have also been included in the criteria for diagnosis of RADS. RADS (or asthma) following an irritating inhalation is an infrequent disorder with rates related to the concentration of and duration of exposure to the irritating substance. Industrial bronchitis, on the other hand, is a disorder that occurs as result of exposure due to high concentrations of irritating substance (often particulate in nature) and is completely reversible after exposure ceases. The disorder is characterised by dyspnea, cough and mucus production.

CARCINOGEN

Aluminum metal and insoluble compounds	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A4
See Appendix Z			

Appendix E – KI “Denuder” (CAS# 7681-11-0)



Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
potassium iodide	7681-11-0	> 99

Section 5 - FIRE FIGHTING MEASURES

Vapor Pressure (mmHg):	99.758 @ 1080 C
Upper Explosive Limit (%):	Not applicable
Specific Gravity (water=1):	3.13
Lower Explosive Limit (%):	Not applicable

Section 8 - EXPOSURE CONTROLS / PERSONAL PROTECTION

EXPOSURE CONTROLS

Source	Material	TWA ppm	TWA mg/m ³	STEL ppm	STEL mg/m ³	Peak ppm	Peak mg/m ³	TWA F/CC	Notes
US - California Permissible Exposure Limits for Chemical Contaminants	potassium iodide (Particulates not otherwise regulated Respirable fraction)		5						(n)
US ACGIH Threshold Limit Values (TLV)	potassium iodide (Iodine and iodides Iodides)	0.01							TLV® Basis: Hypothyroidism; URT irr

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Solid. Mixes with water.

State	Divided solid	Molecular Weight	166.0
Melting Range (°F)	1333	Viscosity	Not Applicable
Boiling Range (°F)	2588	Solubility in water (g/L)	Miscible
Flash Point (°F)	Not applicable	pH (1% solution)	Not available
Decomposition Temp (°F)	Not available.	pH (as supplied)	Not applicable
Autoignition Temp (°F)	Not applicable	Vapor Pressure (mmHg)	99.758 @ 1080 C
Upper Explosive Limit (%)	Not applicable	Specific Gravity (water=1)	3.13
Lower Explosive Limit (%)	Not applicable	Relative Vapour Density (air=1)	Not applicable
Volatile Component (%vol)	Negligible	Evaporation Rate	Not applicable

APPEARANCE

Colourless or white, odourless crystals, granules or powder. Slightly deliquescent in moist air. Bitter saline taste. Soluble in water, alcohol, acetone and glycerol. Light and moisture accelerate decomposition.

Section 11 - TOXICOLOGICAL INFORMATION

potassium iodide

TOXICITY AND IRRITATION

POTASSIUM IODIDE:

■ unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

TOXICITY	IRRITATION
Oral (mouse) LDLo: 1862 mg/kg	Nil Reported

■ Contact allergies quickly manifest themselves as contact eczema, more rarely as urticaria or Quincke's

oedema. The pathogenesis of contact eczema involves a cell-mediated (T lymphocytes) immune reaction of the delayed type. Other allergic skin reactions, e.g. contact urticaria, involve antibody-mediated immune reactions. The significance of the contact allergen is not simply determined by its sensitisation potential: the distribution of the substance and the opportunities for contact with it are equally important. A weakly sensitising substance which is widely distributed can be a more important allergen than one with stronger sensitising potential with which few individuals come into contact. From a clinical point of view, substances are noteworthy if they produce an allergic test reaction in more than 1% of the persons tested.

Allergic reactions involving the respiratory tract are usually due to interactions between IgE antibodies and allergens and occur rapidly. Allergic potential of the allergen and period of exposure often determine the severity of symptoms. Some people may be genetically more prone than others, and exposure to other irritants may aggravate symptoms. Allergy causing activity is due to interactions with proteins.

Attention should be paid to atopic diathesis, characterised by increased susceptibility to nasal inflammation, asthma and eczema.

Exogenous allergic alveolitis is induced essentially by allergen specific immune-complexes of the IgG type; cell-mediated reactions (T lymphocytes) may be involved. Such allergy is of the delayed type with onset up to four hours following exposure.

CARCINOGEN

Iodine and iodides	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A4
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Appendix F – Hydrogen (gas) (CAS# 1333-74-0)

NFPA



CHEMWATCH HAZARD RATINGS

		Min	Max	
Flammability:	4			
Toxicity:	2			
Body Contact:	0			
Reactivity:	0			
Chronic:	0			

Min/Nil=0
Low=1
Moderate=2
High=3
Extreme=4

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
hydrogen	1333-74-0	> 99.5

Section 5 - FIRE FIGHTING MEASURES

Vapor Pressure (mmHg):	126760.394 cyl @ 15C
Upper Explosive Limit (%):	75.0
Specific Gravity (water=1):	Not applicable
Lower Explosive Limit (%):	4.1

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Gas.

State	Compressed gas	Molecular Weight	2.016 (H ₂)
Melting Range (°F)	32 259	Viscosity	Not Applicable
Boiling Range (°F)	33	Solubility in water (g/L)	Slight.
Flash Point (°F)	Not applicable	pH (1% solution)	Not applicable.
Decomposition Temp (°F)	Not Applicable	pH (as supplied)	Not applicable
Autoignition Temp (°F)	1060	Vapor Pressure (mmHg)	126760.394 cyl @ 15C
Upper Explosive Limit (%)	75.0	Specific Gravity (water=1)	Not applicable
Lower Explosive Limit (%)	4.1	Relative Vapour Density (air=1)	0.09 @ 0C/1 atm
Volatile Component (%vol)	100	Evaporation Rate	Not applicable
Gas group	IIC		

APPEARANCE

Colourless, odourless extremely flammable gas; slightly soluble in water.

Section 11 - TOXICOLOGICAL INFORMATION

Hydrogen - TOXICITY AND IRRITATION- No significant acute toxicological data identified in literature search

Appendix G – Squalene (CAS# 111-02-4)

Squalene - C₃₀-H₅₀, "2, 6, 10, 14, 18, 22-tetracosahexaene

NFPA



CHEMWATCH HAZARD RATINGS

		Min	Max
Flammability:	1	<div style="width: 25%; background: linear-gradient(to right, blue, green, yellow);"></div>	
Toxicity:	2	<div style="width: 50%; background: linear-gradient(to right, blue, green, yellow);"></div>	
Body Contact:	2	<div style="width: 50%; background: linear-gradient(to right, blue, green, yellow);"></div>	
Reactivity:	2	<div style="width: 50%; background: linear-gradient(to right, blue, green, yellow);"></div>	
Chronic:	0	<div style="width: 10%; background: linear-gradient(to right, blue, green, yellow);"></div>	

Min/Nil=0
 Low=1
 Moderate=2
 High=3
 Extreme=4

Section 3 - COMPOSITION / INFORMATION ON INGREDIENTS

NAME	CAS RN	%
squalene	111-02-4	>98

Section 9 - PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES

Liquid. Does not mix with water. Floats on water.

State	Liquid	Molecular Weight	410.73
Melting Range (°F)	-103	Viscosity	Not Available
Boiling Range (°F)	545 (25 mm Hg)	Solubility in water (g/L)	Immiscible
Flash Point (°F)	>230	pH (1% solution)	Not applicable.
Decomposition Temp (°F)	Not available.	pH (as supplied)	Not applicable
Autoignition Temp (°F)	Not available	Vapour Pressure (mmHG)	Not available
Upper Explosive Limit (%)	Not available	Specific Gravity (water=1)	0.858
Lower Explosive Limit (%)	Not available	Relative Vapour Density (air=1)	>1
Volatile Component (%vol)	Not available	Evaporation Rate	Not available

APPEARANCE

Oil with faint agreeable odour; does not mix with water. Soluble in ether, petroleum ether, carbon tetrachloride, acetone, and other fat solvents. Absorbs oxygen and becomes viscous in a manner similar to linseed oil.

Section 11 - TOXICOLOGICAL INFORMATION

squalene

TOXICITY AND IRRITATION

SQUALENE:

■ unless otherwise specified data extracted from RTECS - Register of Toxic Effects of Chemical Substances.

TOXICITY	IRRITATION
Oral (mouse) LD50: 5000 mg/kg	Nil Reported
Intravenous (mouse) LD50: 1800 mg/kg	

Appendix Y

Threshold limit value (TLV)

From Wikipedia, the free encyclopedia

Please see Page 29 for contents of Appendix Y

Appendix Z

Threshold Limit Values (TLV) - Carcinogens

Please see Page 31 for contents of Appendix Z

Appendix E

Task Specific Job Hazard Analysis for Silicon Tetrachloride [SiCl_4] Transient Absorption Experiment

Location(s):	2-308	Analysis By:	Jerome Bucher (LBNL # 115200)	Date:	2012/06/22
				Expires:	
Division:	Chemical Sciences	Work Leader:	Oliver Gessner (LBNL # 809652)	Frequency:	Limited-time
Category:	Task-based			JHA Number:	
Job Title:	Silicon tetrachloride [SiCl_4] transient absorption experiment				

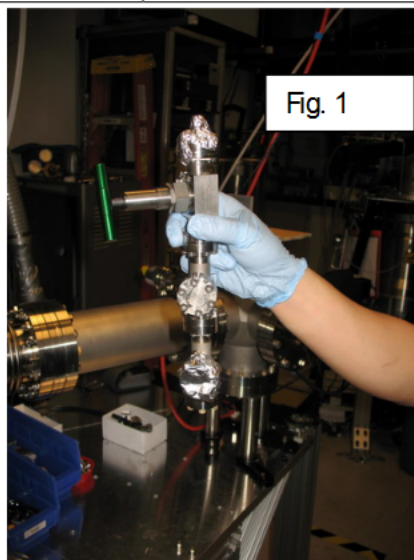


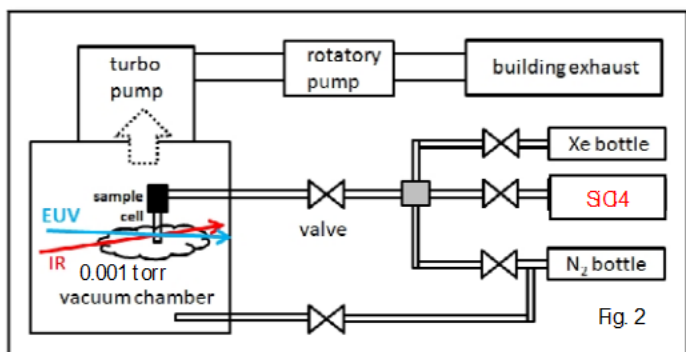
Fig. 1

SCOPE OF WORK DESCRIPTION:

Ten grams of silicon tetrachloride (ST) is used in each experiment. Approximately 6-7 milliliters of ST is transferred from the stock glass container (100g=67 ml) in the fume hood into the stainless steel sample holder – Figure 1. While transferring the sample in the fume hood, protective eyewear, lab coat and extended cuff nitrile gloves will be worn. The vapor pressure of ST at room temperature is approximately 0.3 atm (250 torr). Heating of the sample to increase vapor pressure is not necessary. The experiment is run at room temperature. Sample flow into the chamber is controlled by a needle valve. The stainless steel tubing is leak tight from the stainless steel sample holder to the absorption cell inside the vacuum chamber. Leak testing is done by sending N_2 into the stainless tubing [see Fig. 2]. The pressure in the tubing of sample line is monitored

over 2 hr for any indications of leaks before opening the sample control valve.

The duration of each pump-probe experiment is approximately 2 to 3 hrs. The gas pressure in the sample cell is 10 torr. The cell length is 5 to 10 mm. The diameter of the hole on cell is 0.2 mm. The estimated flow of sample into the chamber is 4 grams (~2.7 ml) over 2 hours of scanning. While experiment is running, the pressure in the chamber will be under 0.001 torr. Half of the pressure is from an Argon stream needed to purge the recombination mirror [0.0005 torr].



On the manifold there are several valves connected to the sample container, which includes a nitrogen purge line and a small xenon gas cylinder (see Fig. 2). The nitrogen purge line is used to purge any residual chemical in the 1/4" stainless tube. The gas is pumped out by vacuum turbo pump and its backing rotatory vane pump. The rotatory vane pump exhaust line is connected directly to the building exhaust line. This line between the rotary vane pump and building exhaust

is maintained under negative pressure, which prevents any chemical backflow into the laboratory.

After completing the experiment, the sample container will be disconnected and placed in the fume hood. Before disconnecting any ST sample Swagelok connection, N_2 gas will be used to purge the sample line for 10 to 15 minutes. This will flush out any residual sample in the tube, which will be pumped out by the turbo pump and the associated roughing pump. Purging-and-pumping procedure will be repeated at least 3 times before the vacuum chamber system or any gas lines are opened.

The concentration of ST in the exhaust is estimated to be 0.010 ppm/min [based on 4 grams of sample released over 2 hr. and the building SE (southeast) quadrant exhaust rate of 26000 ft³/min]. The time-weighted-average (TWA) permissible exposure limit (PEL) in California is not established for ST. (A TWA is the average exposure over a specified period of time, usually a nominal eight hours.) No IDLH value is found for ST. The major hazard of $SiCl_4$ is reaction with water, resulting in hydrolysis of ST to HCl and formation of mixed chloro-hydroxyl silicic acid molecules.

A value of IDLH for hydrogen chloride (HCl) of 50 ppm for irreversible effects is found. This IDLH concentration may lead to an individual's inability to take protective actions. The value of US ACGIH Threshold Limit Values (TLV) for HCl is 2 ppm. TWA-PEL for HCl is 5 ppm. The odor threshold is 0.26 ppm, with recognition value of HCl ~10 ppm. .

The overall ST sample in the container is 10 grams or 1.4liters of ST gas at STP. The worst scenario would be dispersion of the entire ST sample holder contents into the whole room as vapor. The room size is 373410 Liters. Therefore, the resulted concentration will be 0.0004 % in volume. ST is not flammable. Moreover, the 0.0004% in volume corresponds to 4 ppm x 4 – four chloride atoms per one ST molecule. This value is lower than the IDLH value for HCl (50 ppm). The 16 ppm is not lower than the California PEL-TWA value of HCl [5 ppm over 8 hours]. However, any ST vapor would be pumped out of the laboratory in less than 1 min. [Room volume divided by exhaust air flow speed 160000 L/min.] Even in the case of an exhaust failure, the strong smell of HCl [0.25 ppm] would induce an emergency response that would limit the exposure of experimenters below the PEL's.

Hydrolysis of ST is treated in great detail in a paper titled: Theoretical Study of the Reaction Mechanism and Role of Water Clusters in the Gas-Phase Hydrolysis of $SiCl_4$, *J. Phys Chem A* 2003, 107, 8705-8713. Reactive step-wise partially hydrolyzed ST species are formed which may react with metal surfaces and optical elements. Hydrolyzed ST species can also ultimately form silicon dioxide (hydrated) deposits if inhaled in sufficient quantity. Note that in the air $SiCl_4$ barely react with atmosphere when the partial pressure of $SiCl_4$ is less than 300 torr at room temperature according to "Furman, A. A. Inorganic chlorides; Chemistry: Moscow, 1980; p183". The major hazard is body contact of liquid $SiCl_4$. This is prevented by wearing personal protective equipment (PPE) while transferring sample in the fume hood.

Physical data

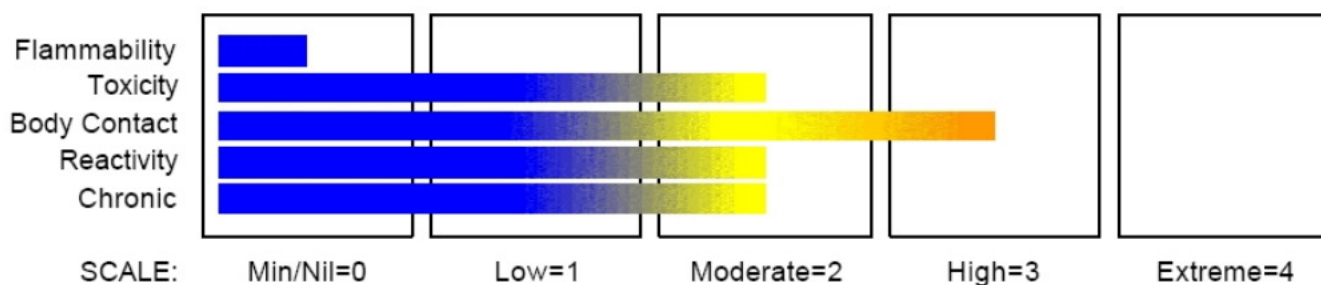
Appearance: colorless or light yellow liquid

Melting point: -70 C

Boiling point: 57.6 C at 750 mm Hg
 Vapour density: 5.9
 Vapour pressure: 250 mm Hg at 26 C
 Specific gravity: 1.48
 Odor: stench, suffocating

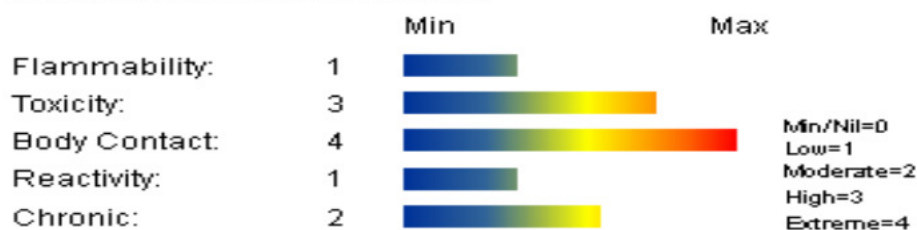
Silicon Tetrachloride - CAS # 10026-04-7 [SiCl₄]

HAZARD RATINGS



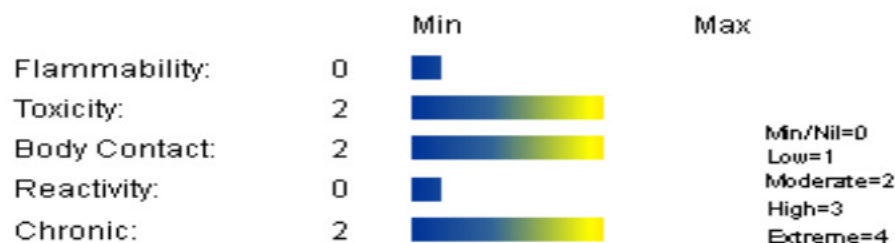
Hydrogen Chloride - CAS # 7647-01-0 [HCl]

CHEMWATCH HAZARD RATINGS



Silicic Acid - CAS # 1343-98-2 [Si(OH)₄]

CHEMWATCH HAZARD RATINGS



From examining the CHEMWATCH HAZARD RATINGS reaction of ST with water produces the most serious chemical exposure. This water-ST reaction will generate corrosive HCl molecules. A potential concentration of HCl, if all the material in the sample source (10 g of ST, 4x4 ppm- HCl = 16ppm HCl) were hydrolyzed is still well below IDLH criteria of HCl (50 ppm). And the detectable odor of HCl and ST will be sufficient to prevent staying in the laboratory. Keep the ST compound away from water sources. Avoid

inhalation of vapor, skin contact and wear proper protection equipment is necessary. Significant consequences from other types of chronic chemical exposures from using ST appear to be diminished.

Silicic acid and/or partially hydrolyzed ST do not present a serious health hazard. These species may however become deposited inappropriately on laboratory and equipment surfaces.

Health effects

CHRONIC HEALTH EFFECTS

■ Repeated or prolonged exposure to acids may result in the erosion of teeth, swelling and/or ulceration of mouth

lining. Irritation of airways to lung, with cough, and inflammation of lung tissue often occurs.

Chronic exposure may inflame the skin or conjunctiva.

Long-term exposure to respiratory irritants may result in disease of the airways involving difficult breathing and related systemic problems.

Substance accumulation, in the human body, may occur and may cause some concern following repeated or long term occupational exposure.

Chronic minor exposure to hydrogen chloride (HCl) vapour or fume may cause discoloration or erosion of the teeth, bleeding of the nose and gums; and ulceration of the nasal mucous membranes.

Repeated exposures of animals to concentrations of about 34 ppm HCl produced no immediate toxic effects.

Workers exposed to hydrochloric acid suffered from gastritis and a number of cases of chronic bronchitis have also been reported.

Repeated or prolonged exposure to dilute solutions of HCl may cause dermatitis.

Toxicity and Irritation

The same descriptive words apply to both ST and HCl exposure since the toxicity and irritation basis for both compounds is the formation of HCl in a human exposure.

“Asthma-like symptoms may continue for months or even years after exposure to the material ceases. This may be due to a non-allergenic condition known as reactive airways dysfunction syndrome (RADS) which can occur following exposure to high levels of highly irritating compound.

The material may produce moderate eye irritation leading to inflammation. Repeated or prolonged exposure to irritants may produce conjunctivitis.

The material may cause severe skin irritation after prolonged or repeated exposure and may produce on contact skin redness, swelling, and the production of vesicles, scaling and thickening of the skin. Repeated exposures may produce severe ulceration.

Carcinogen Evaluation

ChemWatch MSDSs contribute the following carcinogenic information:

Hydrochloric acid	International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs	Group	3
Acid mists, strong inorganic	International Agency for Research on Cancer (IARC) - Agents Reviewed by the IARC Monographs	Group	1
Hydrochloric acid	US ACGIH Threshold Limit Values (TLV) - Carcinogens	Carcinogen Category	A4
Silicic acid, Silicon	US - Maine Chemicals of	Carcinogen	CA Prop 65; NTP 11th

Dioxide	Concern List		ROC
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See Appendix Y and Z for explanation of ratings.

Conclusions;

It is essential when using Silicon Tetrachloride that no exposure to water can occur, except under controlled conditions. Consideration should be given to trapping ST after it has passed through the experimental chamber instead of releasing ST to the environment.

Ensure the connecting line between the sample holder and experimental vacuum chamber is not leaking.

Personal Protection Equipments (PPEs) : Extended cuff Nitrile gloves

UltraSense™ EC Powder-Free Nitrile Gloves, Microflex®

Supplier: Microflex



Ultra-soft, powder-free gloves are made from a nitrile formulation that has the fit and feel of latex and provides reliable protection against many hazardous and infectious substances. Non-stick surface resists tapes and adhesives. Ambidextrous. Textured Fingers. Extended beaded cuff.

Caution: Components used in making these gloves may cause allergic reactions in some users. Follow your institution's policies for use.

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Size	Length	Color	Supplier No.	VWR Catalog Number	Unit	Your Price	Quantity
Large	29 cm (11 ⁷ / ₁₆ "	Custom Blue	USE-880-L	89065-284	Case of 1000	\$162.60	<input type="text" value="0"/>
					Pack of 100	\$16.26	<input type="text" value="0"/>
Medium	29 cm (11 ⁷ / ₁₆ "	Custom Blue	USE-880-M	89065-282	Case of 1000	\$121.18	<input type="text" value="0"/>
					Pack of 100	\$12.12	<input type="text" value="1"/>
Small	29 cm (11 ⁷ / ₁₆ "	Custom Blue	USE-880-S	89065-280	Case of 1000	\$121.18	<input type="text" value="0"/>
					Pack of 100	\$12.12	<input type="text" value="1"/>
X-Large	29 cm (11 ⁷ / ₁₆ "	Custom Blue	USE-880-XL	89065-286	Case of 1000	\$147.33	<input type="text" value="0"/>
					Pack of 100	\$14.73	<input type="text" value="0"/>
XX-Large	29 cm (11 ⁷ / ₁₆ "	Custom Blue	USE-880-XXL	89065-288	Case of 1000	\$162.60	<input type="text" value="0"/>
					Pack of 100	\$16.26	<input type="text" value="0"/>

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AUTHORIZED WORKER(s) INFORMATION:

ID NUMBER:	WORKER NAME	WORKER SIGNATURE¹	WORKLEAD AUTHORIZATION²
020735	Ming-Fu Lin		
809652	Oliver Gessner (Supervisor and Worklead)		
115200	Jerome Bucher (Chemical Sciences Safety Coordinator)		

¹ Worker signature indicates concurrence with the analysis and agreement to work in accordance with this authorization.

² Supervisor signature above authorizes the work subject to the controls specified.

Appendix Y

Threshold limit value (TLV)

From Wikipedia, the free encyclopedia

Please see Page 29 for contents of Appendix Y

Appendix Z

Threshold Limit Values (TLV) - Carcinogens

Please see Page 31 for contents of Appendix Z

Abstract for Hydrolysis of SiCl₄ paper.

J. Phys. Chem. A 2003, 107, 8705–8713

Theoretical Study of the Reaction Mechanism and Role of Water Clusters in the Gas-Phase Hydrolysis of SiCl₄

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University of Cincinnati, Cincinnati, Ohio 45221

Received: March 11, 2003; In Final Form: July 17, 2003

The energies and thermodynamic parameters of the elementary reactions involved in the gas-phase hydrolysis of silicon tetrachloride were studied using ab initio quantum chemical methods (up to MP4//MP2/6-311G- (2d,2p)), density functional (B3LYP/6-311++G(2d,2p)), and G2(MP2) theories. The proposed mechanism of hydrolysis consists of the formation of SiCl_{4-x}(OH)_x (x = 1–4), disiloxanes Cl_{4-x}(OH)_{x-1}Si–O–SiCl_{4-x}(OH)_{x-1}, chainlike and cyclic siloxane polymers [–SiCl₂SiO–]_n, dichlorosilane Cl₂SiO, and silicic acid (HO)₂SiO. Thermodynamic parameters were estimated, and the transition states were located for all of the elementary reactions. It was demonstrated that the experimentally observed kinetic features for the high-temperature hydrolysis are well described by a regular bimolecular reaction occurring through a four-membered cyclic transition state. In contrast, the low-temperature hydrolysis reaction cannot be described by the traditionally accepted bimolecular pathway for Si–Cl bond hydrolysis because of high activation barrier ($E_a > 107.0$ kJ/mol, $\Delta G^\ddagger > 142.5$ kJ/mol) nor by reactions occurring through three- or four-molecular transition states proposed earlier for reactions occurring in aqueous solution. The transition states of SiCl₄ with one- and two-coordinated water molecules were located; these significantly decrease the free energy of activation ΔG^\ddagger (to 121.3 and 111.5 kJ/mol, correspondingly). However, this decrease in ΔG^\ddagger is not sufficient to account for the high value of the hydrolysis rate observed experimentally under low-temperature conditions.

Appendix F

Task Specific Job Hazard Analysis for Thiophene (C₄H₄S) In Transient Absorption Experiment

Location(s):	2-308	Analysis By:	Jerome Bucher (LBNL # 115200)	Date:	2012/09/20
Division:	Chemical Sciences	Work Leader:	Oliver Gessner (LBNL # 809652)	Expires:	
Category:	Task-based			Frequency:	Limited-time
Job Title:	Thiophene (C ₄ H ₄ S) transient absorption experiment				
				JHA Number:	

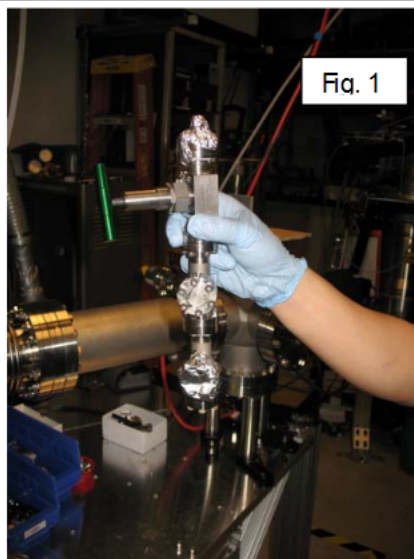


Fig. 1

SCOPE OF WORK DESCRIPTION:

Ten grams of thiophene (TP) is used in each experiment. Approximately 10 milliliters of TP is transferred from the stock glass container (100g=95 ml) into the stainless steel sample holder inside the fume hood – Figure 1. While transferring the sample in the fume hood, protective eyewear, lab coat and extended cuff nitrile gloves will be worn. The vapor pressure of TP at room temperature is approximately 0.07 atm (50 torr). Heating of the sample to increase vapor pressure is not necessary. The experiment is run at room temperature. Sample flow into the chamber is controlled by a needle valve. The stainless steel tubing is leak tight from the stainless steel sample holder to the absorption cell inside the vacuum chamber. Leak testing is done by sending Argon into the stainless steel tubing [see Fig. 2].

The pressure in the tubing of the sample line is monitored over 2 hrs for any indications of leaks before opening the sample control valve, which is located directly adjacent to the vacuum chamber.

The duration of each pump-probe experiment is approximately 4 to 6 hrs. The gas pressure in the sample cell is 10 torr. The cell length is 5 to 10 mm. The diameter of the laser entrance- and exit-holes in the gas cell is 0.2 mm. The estimated flow of sample into the chamber is 4 grams (~3.8 ml) over 4 hours. While the experiment is running, the pressure in the chamber will be less than 0.001 torr.

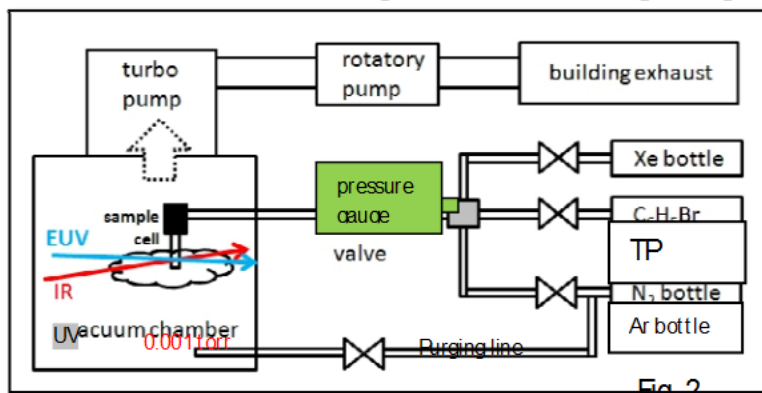


Fig. 2

Half of the pressure is from Argon that is used to purge the recombination mirror [0.0005 torr].

On the manifold there are several valves connected to the sample container, which includes an Ar purge line and a small xenon gas cylinder (see Fig. 2). The Ar purge line is used to purge any residual chemical in the 1/4" stainless tube. The experimental chamber is pumped by a turbo vacuum pump and a backing rotatory vane pump. The

rotatory vane pump exhaust line is connected directly to the building exhaust line. The line between the

rotary vane pump and the building exhaust is maintained under negative pressure, which prevents any chemical backflow into the laboratory.

After completing the experiment, the sample container will be disconnected and placed in the fume hood. Before disconnecting any Swagelok connections that are exposed to the TP sample, Argon gas will be used to purge the sample line for 10 to 15 minutes. This will flush out any residual sample, which will be pumped out by the turbo pump and the associated roughing pump. The purging-and-pumping procedure will be repeated at least 3 times before the vacuum chamber system or any gas lines are opened.

The concentration of TP in the exhaust is estimated to be 0.010 ppm [based on 4 grams of sample released over 4 hr. and the building SE (southeast) quadrant exhaust rate of 26000 ft³/min.]. The time-weighted-average (TWA) permissible exposure limit (PEL) in California is not established for TP. (A TWA is the average exposure over a specified period of time, usually a nominal eight hours.) No IDLH value is found for TP. The major hazard of TP is products of combustion. It releases CO, CO₂ and sulfur oxides (e.g., SO₂). Combustion can be avoided by storing the sample away from fire source.

The overall TP sample in the container is 100 grams or 29 liters of TP gas at STP. The worst scenario would be dispersion of the entire TP sample holder contents into the room as vapor and complete combustion to form CO and SO₂ gas. The room size is 373410 Liters. Therefore, the resulting concentration of CO and SO₂ would be 0.0078 % in volume. A volume concentration of 0.0078% corresponds to a maximum mole fraction of carbon-containing compounds of 78 ppm $\times 4 = 312$ ppm (four carbon atoms per TP molecule). This value is lower than the Emergency Exposure Guidance Levels (EEGL) value of CO (400 ppm in one hour) but higher than the TWA-PEL value (50ppm) and the TLV value (threshold limit value = 25 ppm). The IDLH value for CO is 1000 pm to 1200 pm for 1-hour exposure. For SO₂, the maximum mole fraction is 78 ppm. This value is higher than the TLV-ACGIH – Threshold exposure Limit value (0.25 ppm) (See Appendix Y) but lower than IDLH value (100 ppm). However, any TP, CO and SO₂ vapor would be pumped out of the laboratory in less than 1 min. [Room volume divided by room exhaust air flow speed of 160,000 L/min.].

A spill of the whole bottle of TP liquid (95mL) in the fume hood can be soaked up by Kimwipes and tissues. The contaminated wastes and broken glass should be placed in a plastic container made of polyethylene or polypropylene for later disposal. Secondary containment of thiophene reagent must be done at all times. The hood drain does not have a suitable lip to prevent draining of liquids spilled in the hood. While transferring the sample, a tray made of polyethylene or polypropylene will be placed beneath the sample glass bottle. If a spill on the laboratory floor happens, people in the lab need to be notified and need to evacuate. Notice whether any ignition source is near the floor spill. If possible consider covering spill with Kimwipes and/or tissues for containment and later disposal. Beforehand consider obtaining and locating nearby a quantity of bulk absorbent material, which could be poured on the spill.

Thiophene vaporizes slowly at room temperature (boiling point: 84C). The concentration of thiophene upon sudden, full vaporization of the entire 100 g storage bottle content would be 0.267 g/m³, which is much lower than the acute toxicity of inhalation LC50 value (9.5 g/m³, see Addendum A - Aldrich MSDS). Note, however, that any vaporized thiophene would be pumped out of the laboratory quickly by the room exhaust system.

Physical data

Appearance: colorless liquid

Melting point: -38 C

Boiling point: 84 C at 760 mm Hg

Vapour density: 2.9

Vapour pressure: 40 mm Hg at 12.5C

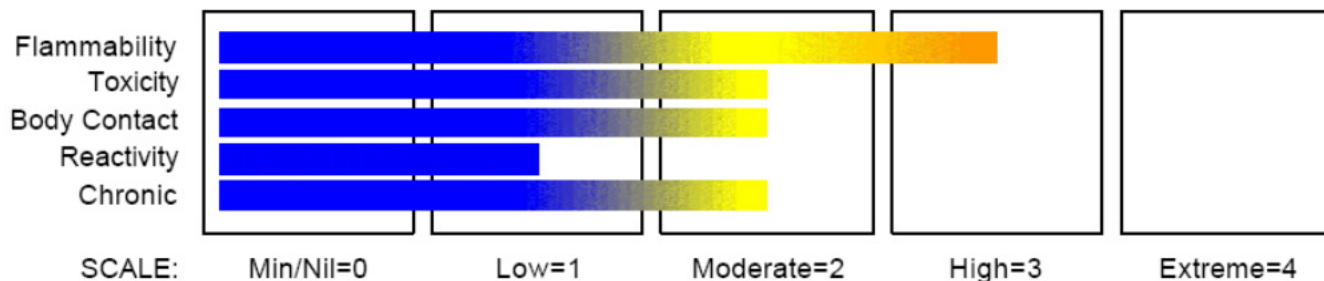
Specific gravity: 1.051

Molecular mass: 84.14 g/mol

Odor: mildly pleasant odor reminiscent of benzene. Do not mix with water!

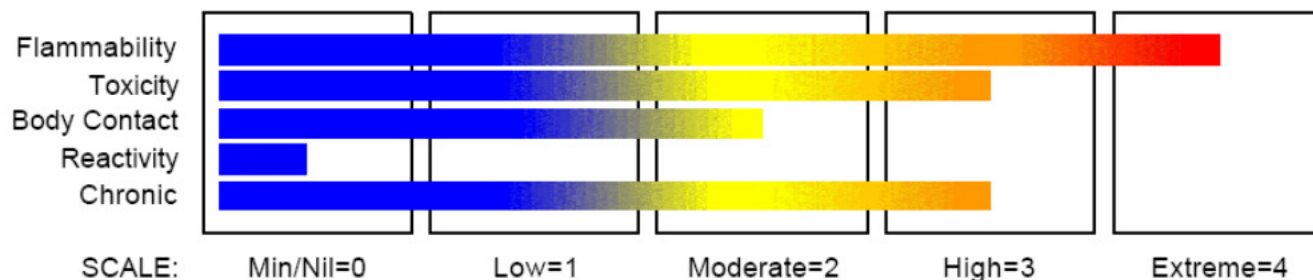
Thiophene - CAS # 110-02-1 [C₄H₄S]

HAZARD RATINGS



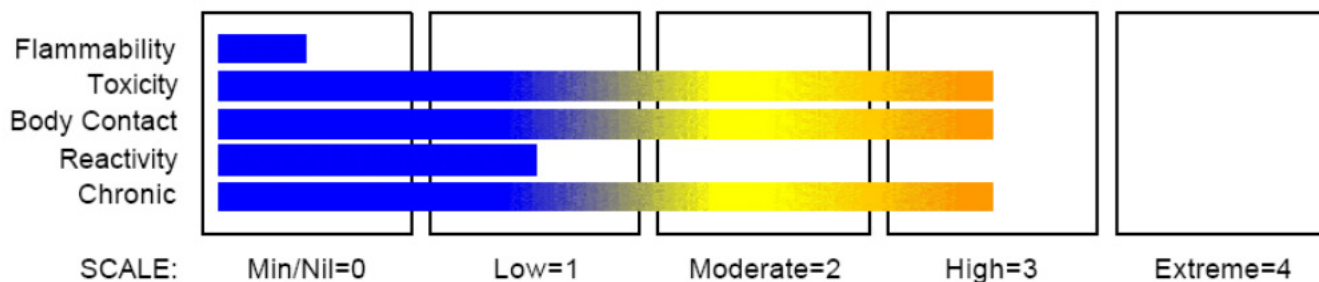
Carbon monoxide - CAS # 630-08-0 [CO]

HAZARD RATINGS



Sulfur dioxide - CAS # 7446-09-5 [SO₂]

HAZARD RATINGS



Health effects (thiophene)

CHRONIC HEALTH EFFECTS

1. Long-term exposure to respiratory irritants may result in disease of the airways involving difficult breathing and related systemic problems.
2. Harmful: danger of serious damage to health by prolonged exposure if swallowed.

This material can cause serious damage if one is exposed to it for long periods. It can be assumed that it contains a substance which can produce severe defects. This has been demonstrated via both short- and long-term experimentation.

3. Substance accumulation, in the human body, may occur and may cause some concern following repeated or long-term occupational exposure.
4. Workers engaged in the synthesis of thiophenes show changes to the nervous system, the cardiovascular system and the liver.
5. Thiophene produced tremor in animals after prolonged exposure.

TOXICITY AND IRRITATION

Asthma-like symptoms may continue for months or even years after exposure to the material ceases. This may be due to a nonallergenic condition known as reactive airways dysfunction syndrome (RADS) which can occur following exposure to high levels of highly irritating compound.

See Appendix Y for explanation of ratings

Personal Protection Equipments (PPEs): eyewear, gloves, lab coat and mask.

PERSONAL PROTECTION



AUTHORIZED WORKER(s) INFORMATION:

ID NUMBER:	WORKER NAME	WORKER SIGNATURE ¹	WORKLEAD AUTHORIZATION ²
020735	Ming-Fu Lin		
809652	Oliver Gessner (Supervisor and Worklead)		
115200	Jerome Bucher (Chemical Sciences Safety Coordinator)		

¹Worker signature indicates concurrence with the analysis and agreement to work in accordance with this authorization.

²Supervisor signature above authorizes the work subject to the controls specified.

Appendix Y

Threshold limit value (TLV)

From Wikipedia, the free encyclopedia

Please see Page 29 for contents of Appendix Y

Addendum A – Other Sources of Information

Google Search

CAS No. **110-02-1** | Sigma-Aldrich (Thiophene)

www.sigmaaldrich.com/catalog/search?term=110-02-1...

GHS Classification

Flammable liquids (Category 2)

Acute toxicity, Oral (Category 4)

Acute toxicity, Inhalation (Category 3)

Skin irritation (Category 2)

Serious eye damage (Category 1)

Specific target organ toxicity - single exposure (Category 3)

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance

Form clear, liquid
Colour light yellow

Safety data

pH no data available

Melting point/freezing point

Melting point/range: -38 °C (-36 °F) - lit.

Boiling point 84 °C (183 °F) - lit.

Flash point -1 °C (30 °F) - closed cup

Ignition temperature 395 °C (743 °F)

Autoignition temperature no data available

Lower explosion limit 1.5 %(V)

Upper explosion limit 12.5 %(V)

Vapour pressure 53 hPa (40 mmHg) at 12.5 °C (54.5 °F)

Density 1.051 g/cm³ at 25 °C (77 °F)

Water solubility no data available

Partition coefficient: n-octanol/water no data available

Relative vapour density no data available

Odour no data available

Odour Threshold no data available

Evaporation rate no data available

11. TOXICOLOGICAL INFORMATION

Acute toxicity

Oral LD50

LD50 Oral - rat - 1,400 mg/kg 1.33ml of TS/kg or 90ml of TS/150 lb

Inhalation LC50

LC50 Inhalation - mouse - 2 h - 9,500 mg/m³ 9ml of TS/m³

Dermal LD50

LD50 Dermal - guinea pig - > 20,000 mg/kg 19ml of TS/kg

Other information on acute toxicity

LD50 Subcutaneous - rabbit - 830 mg/kg 0.8ml of TS/kg

Skin corrosion/irritation

no data available

Serious eye damage/eye irritation

no data available

Respiratory or skin sensitization

no data available

Germ cell mutagenicity

no data available

Carcinogenicity

Germ cell mutagenicity

no data available

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

ACGIH: No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by ACGIH.

NTP: No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.

OSHA: No component of this product present at levels greater than or equal to 0.1% is identified as a carcinogen or potential carcinogen by OSHA.

Reproductive toxicity - no data available

Teratogenicity - no data available

Specific target organ - no data available

Appendix X – GHS Labeling

1.0 Background

The purpose of this document is to describe the United Nations Globally Harmonized System of Classification and Labeling of Chemicals (GHS), why it was developed, and how it relates to the sound management of chemicals. The [full official text](#) of the system is available on the web.

1.1 What is the GHS?

The GHS is an acronym for The Globally Harmonized System of Classification and Labeling of Chemicals. The GHS is a system for standardizing and harmonizing the classification and labeling of chemicals. It is a logical and comprehensive approach to:

Defining health, physical and environmental hazards of chemicals;

Creating classification processes that use available data on chemicals for comparison with the defined hazard criteria; and

Communicating hazard information, as well as protective measures, on labels and Safety Data Sheets (SDS).

Figure 1.1

GHS Document ("Purple Book")



Many countries already have regulatory systems in place for these types of requirements. These systems may be similar in content and approach, but their differences are significant enough to require multiple classifications, labels and safety data sheets for the same product when marketed in different countries, or even in the same country when parts of the life cycle are covered by different regulatory authorities. This leads to inconsistent protection for those potentially exposed to the chemicals, as well as creating extensive regulatory burdens on companies producing chemicals. For example, in the United States (U.S.) there are requirements for classification and labeling of chemicals for the Consumer Product Safety Commission, the Department of Transportation, the Environmental Protection Agency, and the Occupational Safety and Health Administration.

The GHS itself is not a regulation or a standard. The GHS Document (referred to as "The Purple Book", shown in Figure 1.1) establishes agreed hazard classification and communication provisions

with explanatory information on how to apply the system. The elements in the GHS supply a mechanism to meet the basic requirement of any hazard communication system, which is to decide if the chemical product produced and/or supplied is hazardous and to prepare a label and/or Safety Data Sheet as appropriate. Regulatory authorities in countries adopting the GHS will thus take the agreed criteria and provisions, and implement them through their own regulatory process and procedures rather than simply incorporating the text of the GHS into their national requirements. The GHS Document thus provides countries with the regulatory building blocks to develop or modify existing national programs that address classification of hazards and transmittal of information about those hazards and associated protective measures. This helps to ensure the safe use of chemicals as they move through the product life cycle from "cradle to grave."

See - <http://www.osha.gov/dsg/hazcom/ghs.html#3.1> for a complete description of GHS labeling