

## SUPPLEMENT 7

### Beginning the Hazard Analysis Process

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## **SUPPLEMENT 7**

# **Beginning the Hazard Analysis Process**

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**Alan Cummings, Dynamac Inc.**

*Editor's Note: The first step in preparing to deal with hazardous materials incidents is to identify the types and possible sources of accidental releases. This supplement outlines the steps a community should take to analyze those facilities that use hazardous materials and the transportation corridors that bring hazardous materials into the community. Included is an item-by-item review of a material safety data sheet and instructions on using the information presented in it. Our thanks to authors William J. Keffer and Alan Cummings for submitting this paper for inclusion as a supplement to the Hazardous Materials Response Handbook.*

### **Background**

Several recent federal studies show that there are between 5 million and 6 million known chemicals, with this number growing at the rate of about 6000 chemicals per month. Furthermore, a recent computer review by the Chemical Abstract Service of the complete list of known chemicals indicates that a first responder might reasonably be expected to encounter any of 1.5 million of these chemicals in an emergency, with 33,000 to 63,000 of them considered hazardous. To complicate matters, these hazardous chemicals are known by 183,000 different names. Fortunately, not all of these chemicals are equally common.

The U.S. Department of Transportation (DOT) and the U.S. Environmental Protection Agency (EPA) have used several measures of toxicity and volume of production to develop a shortened list of chemicals that are considered hazardous when transported in

commerce. This list contains approximately 2700 chemicals, all of which are listed in 40 CFR 172.101 and the 1996 *Emergency Response Guidebook for Hazardous Materials Incidents*.

The Occupational Safety and Health Administration (OSHA) regulates about 400 chemicals on the basis of occupational exposures. This list is found in the NIOSH (National Institute of Occupational Safety and Health) *Pocket Guide to Chemical Hazards*.

Even this abbreviated list can be intimidating to local response personnel hoping to develop a comprehensive hazard analysis for their community. Further complicating their job is the fact that, according to a study by the National Academy of Sciences, National Research Council (NRC), there is so little known about seven-eighths of the 63,000 hazardous chemicals that not even a partial assessment can be made of their health hazards. Some conclusions drawn from the NRC study are as follows:

1. *Pesticides*—Of the 3350 pesticides classified as important chemicals, information sufficient to make a partial assessment of the health hazard is only available on about 1100 to 1200 (34 percent) of them.

2. *Drugs*—Of the 1815 drugs or drug ingredients noted, about 36 percent have enough information for a partial assessment.

3. *Food Additives*—For the 8627 food additives listed, there is partial information on 19 percent.

4. *Other Chemicals*—For the remaining 48,500 industrial chemicals, there is enough information on just 10 percent to develop a partial assessment.

These two points (the lack of a generally accepted name for chemicals considered hazardous and the lack of data for assessing the risk) create an obstacle for emergency response personnel and community officials who are charged with developing a viable, effective local hazardous materials management system. Without a contingency plan, however, based on effective and accurate hazard analysis prior to an emergency, it would be difficult and time-consuming to develop the necessary information in the midst of an emergency. In order to bring what appears to be an insurmountable task into perspective, the local response community must get involved in the hazard analysis process.

The *hazard analysis process* is the process of identifying chemicals present in the community (either at fixed facilities or passing through transportation corridors) and evaluating the hazards that the chemicals present and the vulnerability of the community and systems to the release of that chemical. A hazard analysis can be performed by any individual or small group that understands the principles of risk assessment. Risk is determined by estimating the consequences of a problem and the probability that the problem will occur.

The goal of this supplement is to provide a summary of the sources of information and some methodology for use by local agencies and hazardous materials teams to improve their understanding of the hazardous materials problem in the community. This is information that can be used in both planning and emergency response operations. This supplement will also introduce the use of the material safety data sheet (MSDS) in the hazard analysis process.

## **Hazard Analysis Data Sources**

The purpose of hazard analysis is to gather data on the locations, quantities, chemical and physical properties, and health hazards of chemicals most likely to be released in a community. This process may seem monumental from two aspects: (1) the sheer numbers of chemicals out there, and (2) the lack of information in a usable form available on these chemicals. In attempting to pare down the list to a workable size and gather data on the location and identity of the chemicals found in and being transported through the community, a variety of information sources may be used.

1. *Historical records of chemicals having the most frequent instances of release on a national level.* For example, all previous studies have shown that the most commonly released hazardous chemical is commercial vehicle fuel (gasoline). The EPA commissioned a national study<sup>1</sup> in 1985 to look at hazardous chemicals and the sources of their release. More recent reviews of various state and local incident report summaries verify that the figures that follow are still correct. The original survey covered 6928 incidents nationwide involving chemicals other than fuel. The source of releases study indicated that 74.8 percent were fixed facility (in-plant) incidents and 25.2 percent were in-transit incidents.

The fixed facility incidents were distributed as follows:

- 20.7 percent storage
- 19.4 percent valves and pipes
- 14.1 percent process
- 17.9 percent unknown
- 27.8 percent other

The in-transit incidents were distributed by mode as follows:

- 54.5 percent truck
- 14.1 percent rail
- 3.8 percent water
- 3.1 percent pipeline
- 2.5 percent other

Perhaps the most useful data from this national study is the information on the chemicals most commonly involved in the 6928 incidents—49.5 percent of the incidents involved only 10 chemicals:

- 23.0 percent polychlorinated biphenyls (PCBs)
- 6.5 percent sulfuric acid
- 3.7 percent anhydrous ammonia
- 3.5 percent chlorine
- 3.1 percent hydrochloric acid
- 2.6 percent sodium hydroxide
- 1.7 percent methanol/methyl alcohol
- 1.7 percent nitric acid
- 1.4 percent toluene
- 1.4 percent methyl chloride

Of the 6928 incidents, 468 involved human injury or death. The same 10 chemicals just listed accounted for 35.7 percent of the death and injury events, though not at the same rate as they occurred:

- 9.6 percent chlorine
- 6.8 percent anhydrous ammonia
- 5.6 percent hydrochloric acid
- 4.7 percent sulfuric acid
- 2.8 percent PCBs
- 2.4 percent toluene
- 1.9 percent sodium hydroxide
- 1.5 percent nitric acid
- 0.4 percent methyl alcohol
- 0.1 percent methyl chloride

When the data for occurrence and injury are viewed for chemicals like chlorine and PCBs, it is apparent that the release and injury data are different. That is, although PCBs were involved in more incidents, chlorine, when released, posed a greater threat to humans. Determining this potential for causing injury to humans is the area of hazard assessment that takes the most effort on the part of the local response community. Gathering this information in a systematic manner cannot be done in the midst of an incident.

2. *Summaries of previous incidents from emergency management and environmental response organizations at the local, state, regional, and federal levels.* For example, EPA Region VII and states in the region have comprehensive, computerized records of all reported incidents by county since 1977. These records are available to any jurisdiction on request.

3. *Local fire and police department records.* These files may disclose many incidents involving hazardous materials.

4. *Local yellow pages and the state industrial directory.* These sources will show most local fixed facilities that manufacture, store, or use chemicals. The EPA has prepared a variety of industry-specific summaries for certain commercial and industrial facilities that outline which types of hazardous chemicals may be encountered. Copies of the summaries may be obtained from EPA by calling the national RCRA (Resource Conservation and Recovery Act) Industry Hotline toll free at 800-424-9346. Additional area-specific release

incident information may be obtained from the emergency response program of the EPA Regional Offices from data collected by the Oil and Hazardous Materials National Response Center.

Once the chemicals in a community have been identified in name and quantity (either for contingency planning or emergency response), there are several national data bases for evaluating the hazard, vulnerability, and risk presented by those chemicals.

**Poison Control Centers.** If the chemical is a consumer product, the quickest way to get comprehensive hazard information is through the regional poison control center.

**Manufacturer's technical medical staff.** If the chemical is an industrial bulk chemical, effective assistance is generally available from CHEMTREC (Chemical Transportation Emergency Center) through the technical medical staff of the company that manufactures the chemical. Dial 800-CMA-8200 for non-emergency situations and 800-424-9300 for emergencies.

**Agency for Toxic Substances and Disease Registry (ATSDR).** If the chemical is a mixture or a waste, if a second opinion is required, or if the chemical is unknown, a good source of information for public exposure risks is the agency at the Centers for Disease Control called the Agency for Toxic Substances and Disease Registry.

When contacting any of these sources, remember there is a lack of full information on health assessment for many chemicals. Answers and information from any of the sources listed may be qualified, and each local response group, as part of their contingency planning, should locate a competent medical authority to work with the response community and assist in obtaining and interpreting health effects data.

## **Material Safety Data Sheets (MSDSs)**

The recent state and federal legislation on hazard communication, right-to-know, and mandatory local notification for certain hazardous chemicals will assist in developing pre-emergency and on-scene hazard assessments of the chemicals in the community. This legislation is bound to make the MSDS one of the best sources of information on chemical hazards. (See Figure S7-1 for an example of an MSDS.)

BURDICK & JACKSON, INC.  
1953 SOUTH HARVEY STREET  
MUSKEGON, MI 49442 USA

ACETONE

REVISION DATE: DECEMBER, 1993

REVISION NO: 1

MATERIAL SAFETY DATA SHEET

INFORMATION/EMERGENCY TELEPHONE NUMBER 616.726.3171  
CHEMTREC TELEPHONE NUMBER 800.424.9300  
CANADIAN EMERGENCY TELEPHONE NUMBER 613.996.6666

I. IDENTIFICATION

CHEMICAL NAME: ACETONE MOLECULAR WEIGHT: 58.08  
CHEMICAL FAMILY: KETONE FORMULA: C3H6O  
SYNONYMS: DIMETHYL KETONE  
DOT PROPER SHIPPING NAME: ACETONE  
DOT HAZARD CLASS: FLAMMABLE LIQUID, HAZARD CLASS 3, P.G. II  
DOT IDENTIFICATION NUMBER: UN1090 CAS NUMBER: 67-64-1

II. PHYSICAL AND CHEMICAL DATA

BOILING POINT, 760 MM HG 56.29 C  
VAPOR PRESSURE AT 20 C: 184.5 MM HG  
% VOLATILES BY VOLUME: CA 100  
FREEZING POINT: -94.7  
VAPOR DENSITY: 2.0  
SPECIFIC GRAVITY (H2O=1): @ 20 C 0.79  
EVAPORATION RATE: (BUAC=1) CA 12  
SOLUBILITY IN WATER: @ 20 C COMPLETE  
STABILITY: STABLE  
HAZARDOUS POLYMERIZATION: NOT EXPECTED TO OCCUR.  
APPEARANCE AND ODOR: CLEAR, COLORLESS LIQUID WITH A PENETRATING,  
SWEET ODOR.  
CONDITIONS TO AVOID: HEAT, SPARKS, OPEN FLAME, OPEN CONTAINERS, AND  
POOR VENTILATION.  
MATERIALS TO AVOID: STRONG OXIDIZING AGENTS AND STRONG ACIDS AND  
BASES.  
HAZARDOUS DECOMPOSITION PRODUCTS: INCOMPLETE COMBUSTION CAN GENERATE CARBON  
MONOXIDE AND OTHER TOXIC VAPORS

III. FIRE AND EXPLOSION HAZARD DATA

FLASH POINT (TEST METHOD); -18 C (TAG CLOSED CUP)  
AUTO IGNITION TEMPERATURE: 465 C  
FLAMMABLE LIMITS IN AIR % BY VOLUME: LOWER LIMIT 2.6 UPPER LIMIT: 12.8  
UNUSUAL FIRE AND EXPLOSION HAZARDS: VERY VOLATILE AND EXTREMELY  
FLAMMABLE; MIXTURES WITH WATER  
CAN BE FLAMMABLE  
EXTINGUISHING MEDIA: CARBON DIOXIDE, DRY CHEMICAL,  
ALCOHOL FOAM, WATER MIST OR FOG  
1 SPECIAL FIRE FIGHTING PROCEDURES: WEAR FULLY PROTECTIVE CLOTHING  
AND SELF-CONTAINED BREATHING  
APPARATUS. HEAT WILL BUILD  
PRESSURE AND MAY RUPTURE CLOSED  
SOTRAGE CONTAINERS. KEEP FIRE-  
EXPOSED CONTAINERS COOL WITH  
WATER SPRAY.

Figure S7-1 Example of a material safety data sheet.

IV. HAZARDOUS COMPONENTS

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ACETONE	WT. % CA 100	TLV 750 PPM	CAS NO. 67-64-1
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V. HEALTH HAZARDS

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OCCUPATIONAL EXPOSURE LIMITS			CONCENTRATION IMMEDIATELY DANGEROUS TO HEALTH	
OSHA	TWA	750 PPM	OSHA/NIOSH	20,000 PPM
	STEL	1,000 PPM		
	CEILING	NOT LISTED		
ACGIH	TLV-TWA	750 PPM	ODOR THRESHOLD	
	TLV-STEL	1,000 PPM	NSC	2 PPM
			NIOSH	NOT LISTED
NIOSH 10-HOUR TWA		250 PPM		

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CARCINOGENIC DATA

ACETONE IS NOT LISTED AS A CARCINOGEN BY IARC, NTP, OSHA, OR ACGIH.

PRIMARY ROUTES OF ENTRY

ACETONE MAY EXERT ITS EFFECTS THROUGH INHALATION, SKIN ABSORPTION, AND INGESTION.

INDUSTRIAL EXPOSURE:

INHALATION:

ROUTE OF EXPOSURE/SIGNS AND SYMPTOMS  
EXPOSURE CAN CAUSE EYE, NOSE, AND THROAT IRRITATION, HEADACHE, NAUSEA, DIZZINESS AND NARCOSIS.

EYE CONTACT:

LIQUID AND HIGH VAPOR CONCENTRATION CAN CAUSE IRRITATION.

SKIN CONTACT:

PROLONGED OR REPEATED SKIN CONTACT CAN CAUSE IRRITATION AND DERMATITIS THROUGH DEFATTING OF SKIN.

INGESTION:

SYMPTOM INFORMATION IS INADEQUATE/UNKNOWN.

EFFECTS OF OVEREXPOSURE

ACETONE IS A MILD EYE AND MUCOUS MEMBRANE IRRITANT, PRIMARY SKIN IRRITANT, AND CENTRAL NERVOUS SYSTEM DEPRESSANT. ACUTE EXPOSURE IRRITATES THE EYES AND UPPER RESPIRATORY TRACT. DIRECT SKIN CONTACT PRODUCES DERMATITIS, CHARACTERIZED BY DRYNESS AND ERYTHEMA. HIGH CONCENTRATIONS PRODUCE NARCOSIS AND HYPOGLYCEMIA.

MEDICAL CONDITION AGGRAVATED BY EXPOSURE

PRECLUDE FROM EXPOSURE THOSE INDIVIDUALS SUSCEPTIBLE TO DERMATITIS.

EMERGENCY FIRST AID

INHALATION:

IMMEDIATELY REMOVE TO FRESH AIR. IF NOT BREATHING, ADMINISTER MOUTH-TO-MOUTH RESCUE BREATHING. IF THERE IS NO PULSE, ADMINISTER CARDIOPULMONARY RESUSCITATION (CPR). CONTACT PHYSICIAN IMMEDIATELY.

1EYE CONTACT:

RINSE WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES.

GET EMERGENCY MEDICAL ASSISTANCE.

SKIN CONTACT:

FLUSH THOROUGHLY FOR AT LEAST 15 MINUTES. WASH AFFECTED SKIN WITH SOAP AND WATER. REMOVE CONTAMINATED CLOTHING AND SHOES. WASH CLOTHING BEFORE RE-USE, AND DISCARD CONTAMINATED SHOES. GET EMERGENCY MEDICAL ASSISTANCE.

INGESTION:

CALL LOCAL POISON CONTROL CENTER FOR ASSISTANCE. CONTACT PHYSICIAN IMMEDIATELY. NEVER INDUCE VOMITING OR GIVE ANYTHING BY MOUTH TO A VICTIM UNCONSCIOUS OR HAVING CONVULSIONS.

Figure S7-1 Continued.

## VI. SAFETY MEASURES AND EQUIPMENT

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VENTILATION:	ADEQUATE VENTILATION IS REQUIRED TO PROTECT PERSONNEL FROM EXPOSURE TO CHEMICAL VAPORS EXCEEDING THE PEL AND TO MINIMIZE FIRE HAZARDS. THE CHOICE OF VENTILATION EQUIPMENT, EITHER LOCAL OR GENERAL, WILL DEPEND ON THE CONDITIONS OF USE, QUANTITY OR MATERIAL, AND OTHER OPERATING PARAMETERS.
RESPIRATORY:	USE APPROVED RESPIRATOR EQUIPMENT. FOLLOW NIOSH AND EQUIPMENT MANUFACTURER'S RECOMMENDATIONS TO DETERMINE APPROPRIATE EQUIPMENT (AIR-PURIFYING, AIR-SUPPLIED, OR SELF-CONTAINED BREATHING APPARATUS).
EYES:	SAFETY GLASSES ARE CONSIDERED MINIMUM PROTECTION. GOGGLES OR FACE SHIELD MAY BE NECESSARY DEPENDING ON QUANTITY OF MATERIAL AND CONDITIONS OF USE.
SKIN:	PROTECTIVE GLOVES AND CLOTHING ARE RECOMMENDED. THE CHOICE OF MATERIAL MUST BE BASED ON CHEMICAL RESISTANCE AND OTHER USER REQUIREMENTS. GENERALLY, NEOPRENE OR RUBBER OFFERS ACCEPTABLE CHEMICAL RESISTANCE. INDIVIDUALS WHO ARE ACUTELY AND SPECIFICALLY SENSITIVE TO ACETONE MAY REQUIRE ADDITIONAL PROTECTIVE EQUIPMENT.
STORAGE;	ACETONE SHOULD BE PROTECTED FROM TEMPERATURE EXTREMES AND DIRECT SUNLIGHT. PROPER STORAGE OF ACETONE MUST BE DETERMINED BASED ON OTHER MATERIALS STORED AND THEIR HAZARDS AND POTENTIAL CHEMICAL INCOMPATIBILITY. IN GENERAL, ACETONE SHOULD BE STORED IN AN ACCEPTABLY PROTECTED AND SECURE FLAMMABLE LIQUID STORAGE ROOM.
OTHER:	EMERGENCY EYEWASH FOUNTAINS AND SAFETY SHOWERS SHOULD BE AVAILABLE IN THE VICINITY OF ANY POTENTIAL EXPOSURE. GROUND AND BOND METAL CONTAINERS TO MINIMIZE STATIC SPARKS.

## VII. SPILL AND DISPOSAL DATA

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SPILL CONTROL      PROTECT FROM IGNITION. WEAR PROTECTIVE CLOTHING AND USE APPROVED RESPIRATOR EQUIPMENT. ABSORB SPILLED MATERIAL IN AN ABSORBENT RECOMMENDED FOR SOLVENT SPILLS AND REMOVE TO A SAFE LOCATION FOR DISPOSAL BY APPROVED METHODS. IF RELEASED TO THE ENVIRONMENT, COMPLY WITH ALL REGULATORY NOTIFICATION REQUIREMENTS. CERCLA REPORTABLE QUANTITY: 5,000 POUNDS.

1WASTE DISPOSAL:      DISPOSE OF ACETONE AS AN EPA HAZARDOUS WASTE. CONTACT STATE ENVIRONMENTAL AGENCY FOR LISTING OF LICENSED HAZARDOUS WASTE DISPOSAL FACILITIES AND APPLICABLE REGULATIONS. HAZARDOUS WASTE NUMBER: U003 (IGNITABLE, TOXIC); D001 (IGNITABLE).

HAZARD CLASSIFICATION		CHEMICAL LISTINGS
IMMEDIATE HEALTH:	YES (IRRITANT)	EXTREMELY HAZARDOUS SUBSTANCES: NO
DELAYED HEALTH:	NO	CERCLA HAZARDOUS SUBSTANCES: YES
FIRE:	YES	TOXIC CHEMICALS: YES
SUDDEN RELEASE:	NO	
REACTIVE:	NO	

ACETONE IS SUBJECT TO THE REPORTING REQUIREMENTS OF SECTION 313 OF TITLE III OF THE SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT OF 1986 (SARA) AND 40CFR PART 372. THIS PRODUCT DOES NOT CONTAIN ANY OTHER TOXIC CHEMICAL ABOVE 1% CONCENTRATION OR A CARCINOGEN ABOVE 0.1% CONCENTRATION.

*Figure S7-1 Continued.*

KEY

CA APPROXIMATELY

NA NOT APPLICABLE

C CEILING

STEL SHORT TERM EXPOSURE LEVEL (15 MINUTES)

TLV THRESHOLD LIMIT VALUE

TWA TIME WEIGHTED AVERAGE

BUAC BUTYL ACETATE

CERCLA COMPREHENSIVE ENVIRONMENTAL RESPONSE, COMPENSATION AND LIABILITY ACT OF 1980.

NSC NATIONAL SAFETY COUNCIL ("FUNDAMENTALS OF INDUSTRIAL HYGIENE," 3RD ED., 1988).

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*Figure S7-1 Continued.*

Personnel from the Chemical Manufacturers Association (CMA), the sponsor of CHEMTREC, have available more than one million different MSDSs and are receiving more all the time. Access to these MSDSs for research and emergency use can be arranged with CMA or through any CMA member company in your area. For most local communities, it will be necessary to work with hard copies of the MSDSs and begin with the 10 most commonly released chemicals. Later, one can add to that list based on the results of the local hazard analysis that determined additional unique or peculiar local hazards.

All local response groups have access to MSDSs by local industry, as required by SARA, Title III, so it is helpful to become familiar with them. However, remember that MSDSs may not contain a complete description; they are not a cure-all and require some systematic way to approach their use. Most MSDSs deal with information for a pure substance. Since many releases are of dilute solutions, the MSDS would overstate the hazard. In any case, becoming familiar with the type of information presented on the MSDS and how that information will be of assistance in making a hazard assessment is essential—whether for pre-emergency planning or when responding to an emergency.

The minimum content of an MSDS is mandated by OSHA in the United States. There is a major effort underway to introduce a new 16-element international MSDS as a substitute for the traditional MSDS. Many companies have started to change to this 16-element format, which is much more user-friendly for response personnel. Each MSDS currently must contain the following sections:

1. The chemical name, chemical formula, common synonyms, chemical family, and manufacturer's name and emergency telephone number
2. Hazardous ingredients and regulatory exposure limits, if any

3. Physical data
4. Fire and explosion hazard data
5. Health hazard data
6. Reactivity data
7. Spill or leak procedures
8. Special protection information
9. Special precautions

Response and/or planning personnel are encouraged to review the MSDSs for at least the 10 most commonly released chemicals (previously listed) and gasoline. They should obtain current MSDSs from companies in their community (even though there are several sources of generic MSDSs, including some where the information is computerized) to establish and maintain good working relationships with local companies.

When reviewing these 11 MSDSs, personnel should take note of the different ways information is presented and the lack of uniform presentation, which can be confusing. Preparers are not required to use the standardized content in the format suggested by OSHA. The varying presentations give insight on the use of MSDSs and factors to be considered in interpreting them. The depth of information furnished in MSDSs varies depending on the extent of what is known about the chemical, as well as the management attitude of the company providing the information.

### **MSDS Section 1—Materials Identification**

This section identifies the chemical by name, synonyms, and/or chemical family name(s). The manufacturer's name and emergency telephone number are listed in order to obtain additional data and assistance. In some cases preparers may choose to emphasize the health hazards, precautionary measures, and emergency contacts at the top of the MSDS.

### **MSDS Section 2—Ingredients and Hazards**

Absolute clarity in describing all ingredients of a material and their hazardous components is essential; however, experience indicates that this information does not always appear in the MSDS. Most of the 11 reviewed MSDSs will address pure substances or aqueous dilutions, with the notable exception of that for gasoline. For example, when discussing chlorine and its hazards, an MSDS preparer would assume chlorine to be the pure chemical in the gaseous form; however, we are more likely to encounter chlorine as a solid (HTH—commonly used in swimming pools) or as commercial bleaches (a liquid that is fairly dilute). Most commercial bleaches for domestic use contain from 30,000 to 50,000 parts per million (ppm) sodium hypochlorite as a source of chlorine.

Upon reviewing the ingredients and hazards of anhydrous ammonia and ammonium hydroxide, we see

that anhydrous ammonia is a colorless gas with an extremely pungent odor and that ammonium hydroxide is a clear, colorless liquid. Although their forms are different and their ability to impinge on exposures when released is different, the hazard is the same. Ammonia is intensely corrosive to human tissue, whether it is inhaled, contacts the skin, or is ingested. OSHA regulates workplace exposures of ammonia at 50 ppm (permissible exposure limit, PEL) while the American Conference of Governmental Industrial Hygienists (ACGIH) recommends a level of 25 ppm (threshold limit value, TLV). Additionally, OSHA regulations state that at concentrations of 300 ppm in air, the material becomes immediately dangerous to life and health (IDLH).

The OSHA system is designed to provide working conditions for reasonably healthy adult humans for 8-hour exposures for 40 hours per week for 40 years. The data are not directly applicable to general populations. Obviously, anyone with preexisting respiratory ailments would be expected to be more affected by irritants and by those chemicals that affect the central nervous system (CNS). The limits are not applicable to children, especially those in the first year of life, since their metabolism and nervous system responses are significantly different from those of adults or older children. *Emergency Response Planning Guidelines* prepared by the American Industrial Hygiene Association provide additional exposure guidelines for use when determining concentrations of concern for released chemicals.

All of the OSHA limits are for airborne concentrations and vary widely among the substances listed. It is important to note that the ratio of exposure limit to IDLH concentration also varies widely. The greater the range between these two numbers, the greater the safety factor for an exposed person to avoid permanent harm or death.

One important area of information not available from this section is how the liquids and the solid on the preceding list become airborne concentrations and how fast this occurs. For this information, we will have to look elsewhere on the MSDS.

### **MSDS Section 3—Physical Data**

In the process of hazard assessment, the ability to evaluate physical data combined with health hazard data is essential. The common physical properties provided on the reviewed MSDS include boiling point, freezing point, specific gravity, vapor pressure, vapor density, solubility, and appearance. Other parameters may be provided at the discretion of the company completing the sheets.

1. *Boiling point.* The temperature at which a liquid turns to a vapor. Since the ambient temperature of this planet ranges from around -20°C to 50°C (-10°F to

120°F), any chemical with a boiling point below the ambient temperature will rapidly become a gas when released from its container. This is certainly the case for chlorine and anhydrous ammonia. Other materials with boiling points only slightly above normal ambient temperature will, if confined in a container, rapidly expand and pressurize that container with the potential for a rapid release if heated even slightly. Other materials, such as PCBs and sodium hydroxide pellets, will be unaffected by the heat of normal structural fires but could be affected by the application of water to that fire. Sodium hydroxide pellets, for example, will dissolve in water to form a corrosive liquid.

2. *Freezing point.* Temperature at which the liquid form of a chemical will turn into the solid form.

3. *Melting point.* Temperature at which the solid form of a chemical will turn into the liquid form. The preceding two physical parameters may be of limited use to response personnel for most chemicals. There are several chemicals for which control measures such as freezing are effective and where dry ice, for example, may be used to mitigate a release. Similarly, there are some chemicals where the property changes under structural fire temperatures may be significant and may seriously alter the hazard to response personnel. Exposure of low melting point solids and most liquids to fire temperatures may result in production of toxic materials in the smoke plume.

4. *Specific gravity.* Density of a chemical compared to the density of water. If the specific gravity is less than one, the chemical will float on water. If the specific gravity is greater than one, the chemical will sink. In either case, it is important for response personnel to consider the property of solubility concurrently with specific gravity. These properties for the 11 chemicals are listed in Table S7-1.

**Table S7-1** Exposure Limits for Common Chemicals

Chemical Name	Physical State (Ambient Temperatures)	Inhalation Exposure Limit	IDLH
Ammonium hydroxide	Liquid	25 ppm (NIOSH) 50 ppm (OSHA)	300 ppm
Anhydrous ammonia	Gas	25 ppm (NIOSH) 50 ppm (OSHA)	300 ppm
Chlorine	Gas	C 0.5 ppm (NIOSH)	10 ppm
Gasoline	Liquid	300 ppm (ACGIH) 500 ppm (OSHA) 10 ppm benzene	
Hydrochloric acid	Liquid	C 5 ppm	50 ppm
Methyl alcohol	Liquid	200 ppm (NIOSH)	6000 ppm
Nitric acid (<70%)	Liquid	2 ppm (NIOSH/OSHA)	25 ppm
PCBs	Liquid	0.5 mg/m <sup>3</sup> (ACGIH)	
Sodium hydroxide	Solid	2 mg/m <sup>3</sup>	200 mg/m <sup>3</sup>
Sulfuric acid (93%)	Liquid	1 mg/m <sup>3</sup>	80 mg/m <sup>3</sup>
Toluene	Liquid	100 ppm (NIOSH) 200 ppm (OSHA)	500 ppm

Toluene, gasoline, and methyl alcohol are all flammable or combustible liquids with similar TLV levels. A glance at their respective solubilities, however, shows that mitigation techniques would have to be substantially different due to their solubility. That is, methyl alcohol is completely miscible in water, whereas the others are relatively insoluble. Not only would fire-fighting methods differ, but additional attention would have to be paid to the solubility when environmental damage is possible. Many chemicals that are listed as only slightly soluble can still cause significant environmental toxicity to plants or aquatic life. Because the toxicity of methyl alcohol is 250 ppm and toluene 1180 ppm, for example, each presents a serious environmental hazard if significant runoff is allowed to occur.

Most MSDSs do not provide environmental risk information; therefore, this information will have to be sought from other sources. One excellent source for environmental risk information for many common chemicals is the EPA's OHM-TADS (Oil & Hazardous Materials—Technical Assistance Data System). Access to this system can be gained through any EPA regional office.

5. *Vapor density.* Density of a gas compared to the density of air. If the vapor density is less than one, the material will rise in still air and dissipate. If the vapor density is greater than one, the vapor will attempt to sink in still air and potentially collect in low spots and valleys.

6. *Vapor pressure.* Pressure exerted by vapors against the sides of the container. Vapor pressure is very temperature dependent. The lower the boiling point of the liquid, the greater the vapor pressure it will exert at a given temperature. In more common terms, the higher the vapor pressure, the more rapidly the material will change from the liquid form to a vapor when released to the environment and the higher the equilibrium concentration with air will be.

The data contained in Table S7-2 were found on MSDSs reviewed by the author. However, it is apparent that errors do creep into the MSDS listings (as shown in the sulfuric acid listing presented here). Also, MSDS listings vary in the depth of detail provided—from rough estimates or general statements for some materials to multiple listings for others.

**Table S7-2** Examples of Physical Data Found on MSDSs

Chemical	Boiling Point (°C)	Specific Gravity	Solubility	Vapor Pressure (@ 20°C)	Vapor Density
Ammonium hydroxide	36	0.9	Infinite	115 mmHg	1.2
Anhydrous ammonia	-33	0.68	Soluble	23 atm	0.6
Chlorine	-34	2.4	0.7%	4800 mmHg	2.49
Gasoline	38-204	0.7-0.8	Insoluble	—	3-4
Hydrochloric acid	53	1.18	Infinite	190 mmHg	1.27
Methyl alcohol	64.5	0.8	Miscible	97 mmHg	1.1
Nitric acid (68%)	122	1.41	Complete	62 mmHg	2.3
PCBs	360-390	1.5	0.01 ppm	<1 mmHg	—
Sodium hydroxide	1390	2.13	111 gm/100 gm	—	—
<b>Sulfuric acid (93%)</b>	<b>310</b>	<b>1.84</b>	<b>Infinite</b>	<b>&lt;0.3 mmHg @ 25°C</b>	<b>3.4</b>
Toluene	232	0.86	0.05 gm/100 gm	22 mmHg	3.14

If you can picture a room in which a release occurs from its container, and then look at the range of vapor pressures for the most commonly released substances, it will be apparent that both chlorine and anhydrous ammonia will present an almost instantaneous vapor (inhalation) hazard. Since both of these chemicals are soluble to some extent, a fog line may be helpful in suppression of volatilization or reduction of concentrations, even when the release is continuous. However, when the intent is to reduce vapor production, the water from the hose lines should not enter pooled materials like ammonia or chlorine. For materials like sodium hydroxide and PCBs, a vapor hazard is not likely to exist under most real-world conditions.

The physical properties of a chemical will help personnel determine how the chemical will behave when released from its container.

**MSDS Section 4—Fire and Explosion Data**

Most of the MSDSs reviewed contain specific information for the fire fighter on the physical characteristics of the chemicals when involved in a fire. These characteristics, as summarized in Table S7-3, should be made familiar to most fire personnel.

**Table S7-3** Examples of Fire and Explosion Data

Chemical	Flash Point	Autoignition Temperature	Flammable Range	Extinguishing Media
Ammonium hydroxide	—	—	—	—
Anhydrous ammonia	NA	651°C	16-27%	Shut off gas
Chlorine	NA	NA	NA	NA
Gasoline	-45°F	536-853°F	1.5-7.6%	Dry chemical, water spray
Hydrochloric acid	NA	NA	NA	NA
Methyl alcohol	52°F	385°F	6-36.5%	Water spray
Nitric acid	NA	NA	NA	NA
PCBs	NA	NA	NA	NA
Sodium hydroxide	NA	NA	NA	NA
Sulfuric acid	NA	NA	NA	NA
Toluene	40°F	480°F	1.3-7.1%	Dry chemical

In addition to these normal fire characteristics, the chemicals have other fire-related hazards, some of which are reported in the fire and explosion section. The following examples are:

1. Chlorine and anhydrous ammonia are generally stored in pressure containers, and the violent rupture of these containers represents a significant hazard, in addition to their toxicity.
2. Many of the chemicals listed generate toxic vapors or mists when involved in a fire, thus representing an additional hazard.
3. Hydrochloric acid, nitric acid, sodium hydroxide, and sulfuric acid are such vigorous oxidizers or reducers that, although they are not flammable hazards themselves, they react with metals to produce hydrogen gas, which is extremely flammable.

### **MSDS Section 5—Health Hazard Information**

This section of the MSDS presents information on the routes of exposure (inhalation, ingestion, dermal) and, in some cases, the severity of these risks (low, moderate, high). This information is essential for the selection of appropriate personal protective equipment and safety procedures for response actions at incidents. Some of the MSDSs reviewed highlighted the major hazards in Section 1 on the sheets, while others give a more detailed formal listing of the hazards in this section. Some sheets list the NFPA 704 rating for the specific chemical (use of the 704 system by local industry should be encouraged, as it provides local emergency response personnel a basis for quick judgments about the severity of personal exposure). A brief summary of the hazards for each chemical as contained in the MSDSs reviewed is listed in Table S7-4. *More than one source should always be used to clearly identify all of the hazards associated with the chemical of concern.*

**Table S7-4** Examples of Hazards Listed on MSDSs

Chemical	Hazards as Listed in the MSDSs
Ammonium hydroxide	Corrosive, severe eye and skin irritant
Anhydrous ammonia	Corrosive, severe eye and skin irritant
Chlorine	Corrosive, life threatening toxic effects possible at concentrations of 25 ppm on short exposures
Gasoline	Flammable, irritant, CNS effects, some evidence of carcinogenicity, also numerous chronic effects
Hydrochloric acid	Corrosive, may be fatal if ingested
Methyl alcohol	Flammable, may be fatal if ingested
Nitric acid (68%)	Corrosive, strong oxidizer at higher concentrations
PCBs	Very long lasting material, some evidence of liver damage, carcinogenic risk, adverse reproductive effects
Sodium hydroxide	Corrosive, may be fatal if swallowed, causing severe burns
Sulfuric acid (93%)	Corrosive, causes severe burns, may be fatal if swallowed, harmful if inhaled
Toluene	Flammable, chronic skin irritant, various systematic effects on CNS, liver, kidneys

The most common hazard of the chemicals listed is their corrosive effect on nearly every part of the human body. The effects of chlorine and sulfuric acid are very similar. What makes chlorine a greater risk is the volatility of the liquid when released compared to the acid, which is already a liquid at ambient temperatures and volatilizes very slowly.

### MSDS Section 6—Reactivity Data

Generally, four areas of information are presented in this section, and all are potentially useful to those responding to a hazardous chemical emergency.

1. *Stability.* Is the material stable at ambient temperature and pressure or at normal storage conditions? Most of the chemicals reviewed are stable and not liable to undergo spontaneous changes.

2. *Polymerization.* Will the chemical change through polymerization at normal conditions of storage and temperature? For chemicals that spontaneously polymerize, this frequently leads to generation of heat and potential container failure.

3. *Decomposition.* What new chemicals and what hazards will be created by the thermal decomposition of the chemical? Important information is included in this section for officials concerned about the exposures of

response personnel and general population if the chemical is exposed to fire. For example, formaldehyde may be formed from fire involving methyl alcohol, oxides of nitrogen from anhydrous ammonia, and from most of the other chemicals, oxides of carbon that may increase the hazards from simple asphyxiation.

4. *Incompatibles*. What materials may cause violent reactions with the chemical? Note especially the MSDS for gasoline.

Predicting the potential violent reactions of the estimated 6 million chemicals in the world requires some idea of the likelihood of any of these chemicals coming in contact with each other. Many of the chemicals reviewed are potent acids or bases, and they will certainly be incompatible with chemicals of widely differing pH. For example, the sheet for sulfuric acid lists water as being incompatible. The mixing of sulfuric acid (96 percent) with water (at pH of 7) releases enough heat to cause a violent reaction.

### **MSDS Section 7—Spill or Leak Procedures**

This section contains suggested steps for handling releases of the chemical in question. The information provided is usually similar to the 1996 DOT *North American Emergency Response Guide*. It is important to note the order in which the material is presented. If the material is extremely flammable, but not particularly toxic, initial advice will usually be to control ignition sources. If the material is extremely toxic, initial advice will generally be to evacuate.

### **MSDS Section 8—Special Protection Information**

On many MSDSs now in use, this section is not very specific. Hopefully, improvements will be made that recommend specific respiratory and clothing information. It is important to know that none of the impervious clothing is suitable for all chemicals. For example, polyethylene protective clothing is not recommended for concentrated sulfuric acid but is suitable for more dilute solutions.

Special problems may be created for first responders by those materials that adversely affect normal fire fighter protective clothing. These materials (i.e., chlorobenzene, methyl iodide, etc.), for which breakthrough times are less than one tank of air, may not offer any useful protection to the responder. Once a hazard analysis is completed and response organizations are at the point of their contingency planning where they are selecting response equipment, it is suggested that they obtain copies of the various protective clothing vendors' performance information, especially for the multilayer garments, and also talk with other responders about the selection and use of specific protective clothing ensembles.

## MSDS Section 9—Special Precautions

Many MSDSs do not contain any information in this area. In some cases, for extremely flammable materials there is an additional warning about sparks and radiant heat; for chlorine, there is a warning about igniting other combustible materials on contact; and for many other chemicals there is a reiteration of standard storage and handling procedures.

One important area that may be covered on some MSDSs is the hazard of the chemical to animal or aquatic life. This information is frequently based on scientific testing of the compound or chemical in controlled laboratory settings. The information from this testing is presented in terminology different from the regulatory TLV and PEL information and will require additional effort before the responder can evaluate the information.

Depending on the potential use of the chemical, a series of tests may be conducted over a period of time in a manner that resembles successive elimination. Tests are run for a variety of acute and chronic effects as well as exotic effects on more and more complex animals. Initial screening is done on bacteria, which allows the testing of large numbers of individuals and numerous generations in small spaces and in a short time. Subsequent tests may be conducted with any of a wide variety of rodents, pigs, dogs, and, sometimes, primates. The sequence of the tests is shown in Figure S7-2.

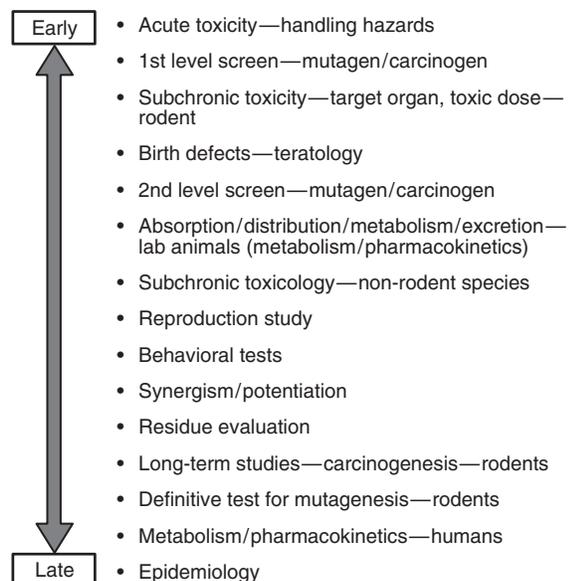


Figure S7-2 Chronology of testing.

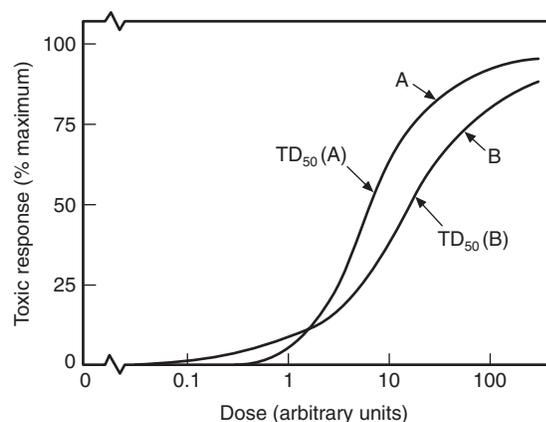
Tests are done to evaluate the physical/chemical properties of the substance, note routes of entry into the organisms being tested, and document exposure variables. The tests are used to evaluate the biological fate of the chemicals and develop a dose/response curve for the specific effects being evaluated. Hypothetical dose/response curves are shown in Figure S7-3. The most common expression of the results of these tests is

the dose or concentration at which 50 percent are affected, known as the  $TD_{50}$ . Toxicologists exhibit their skills by the accuracy with which they can extrapolate animal data to predict effects on man. In general,  $TD_{50}$  data are commonly given for pesticides and other chemicals developed for pest and weed control. An example of interpreting these data for responders is shown in Table S7-5.

**Table S7-5** *Relative Index of Toxicology*

Toxicity Rating	Probable Oral Dose	Lethal Dose for Average Adult Human
Practically nontoxic	>15 g/kg	more than a quart
Slightly toxic	5–150 g/kg	between pint and quart
Moderately toxic	0.5–5 g/kg	between ounce and pint
Very toxic	50–500 mg/kg	between teaspoon and ounce
Extremely toxic	5–50 mg/kg	7 drops to teaspoonful
Supertoxic	<5 mg/kg	a taste (less than 7 drops)

Dose/response curves deal with acute exposures, but it is important to also consider the potential for repetitive exposures at lower doses, which may accumulate in the body. This situation is called chronic exposure and is shown diagrammed in Figure S7-3. The two toluene sheets discussed earlier provide chronic exposure data indicating the potential for brain cell damage from long-term inhalation of toluene vapor.



**Figure S7-3** *Hypothetical dose/response curve of two chemicals, A and B.*

## Summary

Local government emergency response personnel can avoid much confusion if they concentrate on utilizing MSDSs in pre-emergency planning. That is, they should identify in advance the buildings or processes that store or utilize extremely toxic materials, then make basic decisions regarding “no attack” before an emergency occurs. There is a recent major effort by a new NFPA committee to develop standard recommended practices for pre-incident planning responses. This document, NFPA 1620, is still in the draft stage but could be

obtained for review by contacting the Committee Members or the NFPA Standards Administration Staff Assistant.

Once response community personnel have completed the hazard analysis and have evaluated the collected MSDS in the manner discussed here, numerous additional questions need to be answered to complete the contingency planning portion of the work. Some of the questions that the hazard analysis and contingency planning process will help answer include the following:

1. What risks will be encountered by first responders?
2. What protective equipment (respiratory and clothing) will be needed by the responders?
3. What type of support resources are likely to be necessary for mitigation supplies or medical assistance?

One useful way to clarify these questions and to provide practical guidance for the response community is to use the highest risk situation from the hazard analysis as a scenario for a hands-on drill/exercise for the participating members of the response community.

#### **Reference**

1. *Acute Hazardous Events*, Data Base Industrial Economics, Inc., Cambridge, MA 02140, December 1985.