

**Development of the Table of Initial
Isolation and Protective Action Distances
for the *2008 Emergency Response Guidebook***

Decision and Information Sciences Division

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Development of the Table of Initial Isolation and Protective Action Distances for the *2008 Emergency Response Guidebook*

by

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NOTATION

The following is a list of the acronyms, initialisms, and abbreviations (including units of measure) used in this document.

ACRONYMS AND ABBREVIATIONS

ABL	atmospheric boundary layer
ACGIH	American Conference of Governmental Industrial Hygienists
AEGL	Acute Exposure Guidance Level (National Research Council)
AIHA	American Industrial Hygiene Association
CAS	Chemical Abstracts Services
CASRAM	Chemical Accident Statistical Risk Assessment Model
CBL	convective boundary layer
CFR	<i>Code of Federal Regulations</i>
CWIC	crosswind-integrated concentration
DOD	U.S. Department of Defense
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
DTRA	Defense Threat Reduction Agency
EEGL	Emergency Exposure Guidance Level (National Research Council)
EEL	Emergency Exposure Level (<i>AIHA Journal</i>)
EPA	U.S. Environmental Protection Agency
ERG	Emergency Response Guidebook
ERPG	Emergency Response Planning Guideline (AIHA)
ERPG-1	ERPG Level 1
ERPG-2	ERPG Level 2
ERPG-3	ERPG Level 3
GDP	gross domestic product
GLB	Great Lakes Buoy
HCl	hydrogen chloride
HF	hydrogen fluoride
HMIS	Hazardous Materials Information System
HSE	Health and Safety Executive
IDLH	immediately dangerous to life and health (NIOSH level)
IID	Initial Isolation Distance
LC	lethal concentration
LC ₅₀	median lethal concentration (lethal to 50% of exposed population)
LC _{LO}	lowest reported lethal concentration
LD	lethal dose
LD ₅₀	median lethal dose (lethal to 50% of exposed population)
LD _{LO}	lowest reported lethal dose
LOAEL	lowest observed adverse effect level
LOC	level of concern (EPA)

NAC	National Advisory Committee
NAS	National Academy of Sciences
NIOSH	National Institute for Occupational Safety and Health
NOAEL	no observed adverse effect level
n.o.s.	not otherwise specified
NRC	National Research Council
NREL	National Renewable Energy Laboratory
SHA	Occupational Safety and Health Administration
PAD	Protective Action Distance
PAZ	Protective Action Zone
PEL	permissible exposure limit (OSHA)
RD ₅₀	concentration producing a 50% respiratory rate decrease in test animals, used to estimate severe respiratory irritation
rms	root mean square
RTECS	Registry of Toxic Effects of Chemical Substances
SBL	stratified boundary layer
SCAPA	Subcommittee on Consequence Assessment and Protective Actions (DOE)
SEB	surface energy budget
SEBMET	Surface Energy Budget Meteorological (model)
SLOT	specified level of toxicity (HSE)
STEL	short-term exposure limit (ACGIH)
TEEL	temporary emergency exposure guideline (DOE)
TIH	toxic by inhalation
TIHWR	toxic by inhalation by water reactivity
TLV	threshold limit value (ACGIH)
TWA	time-weighted average
UN	United Nations
USGS	U.S. Geological Survey
WQN	Water Quality Network

UNITS OF MEASURE

atm	atmosphere (1.01×10^5 Pa)
°C	degree(s) Celsius
cm	centimeter(s)
°F	degree(s) Fahrenheit
ft	foot (feet)
g	gram(s)
gal	gallon(s)
h	hour(s)
K	degree(s) Kelvin
kg	kilogram(s)
km	kilometer(s)
kPa	kilopascal(s)

m	meter(s)
m ²	square meter(s)
m ³	cubic meter(s)
mbar	millibar(s)
mg	milligram(s)
mi	mile(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
mmol	millimole(s)
ms	millisecond(s)
Pa	Pascal(s)
ppm	part(s) per million
rpm	revolution(s) per minute
s	second(s)
μL	microliter(s)
μm	micrometer(s)

**DEVELOPMENT OF THE TABLE OF INITIAL ISOLATION
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ABSTRACT

This report provides technical documentation on the values chosen for the Table of Initial Isolation and Protective Action Distances (PADs) in the *2008 Emergency Response Guidebook* (ERG2008). The goal was to choose PADs that would balance the need to adequately protect the public from exposure to potentially harmful substances against the need to minimize the risks and expenses that could result from overreacting to an incident involving the release of hazardous materials that are toxic by inhalation (TIH). To quantify this balance, a statistical approach was adopted, in which the best available information was used to conduct an accident scenario analysis and develop a set of up to 1,000,000 hypothetical incidents for each material in the Table. Each set accounts for differences in container types, incident types, accident severities (i.e., amounts released), locations, times of day, times of year, and meteorological conditions. Each scenario was analyzed by using detailed emission rate and atmospheric dispersion models to calculate the downwind chemical concentrations for which a “safe distance” was determined. “Safe distance” is defined as the distance downwind from the source at which the chemical concentration falls below health protection criteria. The criteria used are the National Research Council’s Acute Exposure Guideline Level 2 (AEGl-2), American Industrial Hygiene Association’s Emergency Response Planning Guideline Level 2 (ERPG-2), or equivalent guidelines. The statistical sample of safe distance values for all incidents considered in the analysis are separated into four categories: small spill/daytime release, small spill/nighttime release, large spill/daytime release, and large spill/nighttime release. The 90th-percentile safe distance values for each of these groups became the PADs that appear in the ERG2008.

SUMMARY

The transportation of hazardous materials creates numerous opportunities for the release of toxic substances into the environment as a result of traffic accidents, train derailments, equipment failures, and human error. Many of these toxic substances pose acute hazards to the general public and the emergency response personnel who are the first to arrive at the scene. To

help first responders determine whether a shipment is potentially hazardous and decide what actions should be taken if a toxic spill does occur, the Emergency Response Guidebook (ERG) is published by the U.S. Department of Transportation (DOT), Transport Canada, and Secretariat of Transport and Communications of Mexico.

The ERG provides information on fire-fighting and mitigation strategies as well as on potential health effects associated with various chemicals, which it lists under their proper shipping names and four-digit United Nations (UN) identification numbers. The ERG also provides Initial Isolation Distances (IIDs) and Protective Action Distances (PADs) for a subset of the chemicals that are toxic by inhalation (TIH) or that react with water to produce TIH gases (TIHWR). The IID identifies the radius of a zone around the release from which all people not directly involved in emergency response are to be kept away. The PAD is the downwind distance from the release that defines a zone in which persons should be either evacuated or sheltered in place, depending on the nature of the population at risk (e.g., their density, age, health) and the severity of the incident.

This report provides the technical documentation for the values in the ERG2008 Table of Initial Isolation and Protective Action Distances (hereafter referred to as “the Table”). The goal of choosing the PADs specified in the ERG2008 was to balance the need to adequately protect the public from exposure to potentially harmful substances against the need to minimize the risks and expenses that could result from overreacting to a hazardous materials incident. To quantify this balance, a “level of protection” was defined to represent the probability that the listed PAD would allow sufficient protection of the public. A 90% level of protection was selected for the ERG2008.

Quantitative analysis of the level of protection requires a statistical approach to specify the PAD. To achieve this objective, the best available information was used to analyze accident scenarios. The result was a set of up to 1,000,000 hypothetical incidents for each material. Each set accounts for differences in container types, incident types, accident severities (i.e., amounts released), accident locations, times of day, times of year, and meteorological conditions involved. Each scenario was analyzed by using detailed emission rate and atmospheric dispersion models to calculate the downwind chemical concentrations for which a “safe distance” was determined. “Safe distance” is defined as the distance downwind from the source at which the chemical concentration falls below a health protection criterion for that material. The criteria used are the National Research Council’s Acute Exposure Guideline Level 2 (AEGl-2), the American Industrial Hygiene Association’s Emergency Response Planning Guideline Level 2 (ERPG-2), or equivalent guidelines. The AEGl-2 and ERPG-2 criteria denote the highest chemical concentration at which persons will suffer no irreversible or other serious health effects that could impair their ability to take protective action. The statistical sample of safe distance values for all incidents for each material was separated into four categories: small spill/daytime release, small spill/nighttime release, large spill/daytime release, and large spill/nighttime release. The 90th-percentile safe distance values for each of these groups are the PADs that appear in the Table.

This report presents the entire methodology used to produce the Table, much of which is unchanged from the ERG2004 and companion report. Specific improvements and changes in the methodology from the ERG2004 are noted here.

1. For the ERG2008, the methodology used to select health criteria to estimate PADs was substantially modified to incorporate both final and interim AEGL-2 values when available. In this process, final AEGL-2 values are the preferred criteria, followed by ERPG-2 values, interim AEGL-2 values, and finally LC₅₀-based values. (LC₅₀ is the median lethal concentration, the concentration lethal to 50% of an exposed population.) Also, for LC₅₀- and LC_{LO}-based health criteria, acute toxicity databases were reviewed to ascertain that the correct underlying study was being used for each chemical. (LC_{LO} is the lowest reported lethal concentration.) The result was revisions in the preferred LC₅₀ values for several materials.
2. The experimental program for evaluating water-reactive materials that began for the ERG2000 was continued. For the ERG2008, an improved experimental method was developed to provide more detailed quantitative information on TIH gas evolution rates and more repeatable results. For the ERG2008, experiments were conducted on a total of 52 materials; 34 of the experiments were repeated from the ERG2000 and ERG2004 analysis, and 18 were new to the experimental program. These experiments resulted in the addition of 14 new materials, most of which are hydrochloric acid (HCl) emitters. In addition, the statistical PAD analysis for TIHWR materials was modified to include incidents in which excess water is available (such as a spill in a significant waterway) and incidents in which the amount of water that is available is restricted (such as a spill in a ditch or during a rainstorm). This latter category can sometimes result in more TIH gas evolution than the amount that results from a spill into a large waterway.
3. In the ERG2008, IIDs and PADs for generic compounds are based on the median-case (50th-percentile) compound from the pool of chemicals in the overall analysis that matches that generic description. This method is a substantial departure from the analysis method used in past versions of the ERG, in which PADs for generic materials were set as the worst-case compounds from the pool of chemicals matching the description.
4. For the ERG2008 analysis, the procedure to specify IID values was substantially modified to set a minimum distance equivalent to 15% of the daytime PAD for gases and 7.5% of the daytime PAD for liquids. This modification was made because many of the large-spill IID values appeared to be too low from a safety standpoint, as indicated by a consideration of several major accidental releases that had occurred in the last few years (e.g., Minot, North Dakota, in 2002; Festus, Missouri, in 2002; and Graniteville, South Carolina, in 2005). The net result of this modification is that the IID for gases is usually set by this minimum distance criterion rather than the

alternate LC₅₀-based value. As such, the IID values for most gases in ERG2008 are substantially higher than values used in prior editions of the ERG. Incorporating this minimum distance criterion had a much smaller effect on IIDs for liquids.

5. The ERG2008 developed several new shipment profiles tailored specifically to several high-volume chemicals. They were based on a detailed study of the supply chains for these materials.
6. The distances for weapons-related entries were recalculated and are, in many cases, lower than they were in ERG2004. For the blister and nerve agents, the maximum release amount was lowered to 25 kg. For nerve agents, adoption of the AEGL health criteria, which replaced the previous LC₅₀-based values, also reduced the distances.

1 INTRODUCTION

The transportation of hazardous materials creates numerous opportunities for the release of toxic substances into the environment due to traffic accidents, train derailments, equipment failures, and human error. Such releases can pose serious acute hazards to the general public and to emergency response personnel who are the first to arrive at the scene. To help first responders determine whether a shipment is potentially hazardous and decide what actions should be taken if a toxic spill does occur, the Emergency Response Guidebook (ERG) is published by the U.S. Department of Transportation (DOT), Transport Canada, and Secretariat of Transport and Communications of Mexico. The most recent version is the 2008 edition of the ERG (DOT et al. 2008), titled *2008 Emergency Response Guidebook* (hereafter referred to as ERG2008). The ERG provides essential information on fire-fighting, spill response, and potential public health effects. For chemicals that are toxic by inhalation (TIH) and chemicals that produce TIH gases upon reaction with water (TIH by water reactivity or TIHWR), the ERG provides Initial Isolation Distances (IIDs) and Protective Action Distances (PADs). The IID defines the radius of the zone around the spill that should be accessed solely by people who are directly involved in emergency response. The PAD is the distance downwind from the source of the release to which persons should be either evacuated or sheltered in place, depending on the severity of the incident and the nature of the population (e.g., density, age, health).

This report was prepared to document the methodology used to prepare the ERG2008 “Table of Initial Isolation and Protective Action Distances” (hereafter referred to as “the Table”). The PADs in the Table were calculated to balance the need to adequately protect the public from exposure to potentially harmful substances against the risks and expenses that could result from overreacting to a spill. In determining the PADs, this balance was quantified in terms of a level of protection; namely, the probability that the listed PAD will allow sufficient protection of the public. The level of protection adopted for the ERG was 90%. Clearly, a quantitative analysis of the level of protection requires a statistical approach, the underlying technical basis of which is described in this report, together with the pertinent chemical and incident data required for the analysis.

1.1 OVERVIEW OF THE EMERGENCY RESPONSE GUIDEBOOK

The ERG is designed for use by first responders to determine the appropriate level of action during the initial stages of an incident involving the transportation of hazardous materials. Although first responders are knowledgeable in the field of law enforcement and public protection, they are usually not experts on hazardous materials. The ERG thus provides a compact source of essential information on which to base reasonable decisions under often difficult conditions.

As noted, the ERG provides the “Table of Initial Isolation and Protective Action Distances” for TIH materials. Figure 1.1 illustrates the basic information presented in the Table and its application. To properly use the Table, a responder must first determine the following:

- United Nations (UN) identification number and/or proper shipping name of the material being transported,
- Direction of the prevailing wind,
- Whether the spill is small (60 gal or less) or large (more than 60 gal),
- Whether it is day or night, and
- Any special conditions that could preclude the use of the values given in the Table (releases of multiple tank cars, topographical anomalies, etc.).

As depicted in Figure 1.1, releases of TIH materials result in downwind concentrations of vapor that decrease with distance from the release point (assuming that the release is not buoyant). At some downwind distance, the concentration decreases to a level below which no protective action is necessary. This distance is the PAD. The Protective Action Zone (PAZ) is defined as a square region that has a side that is equal in length equal to the PAD and lies downwind and symmetrical to the accident location. Note that since the PAZ lies downwind of the spill location, the first responder must first ascertain the wind direction to correctly use the information in the ERG. Since wind direction knowledge is inherent in the PAZ definition, the PAZ does not need to be circular.

The IID specifies a circular zone surrounding the accident site. Persons not involved with the response should be kept clear of this zone. Persons in the Initial Isolation Zone may be exposed to potentially life-threatening health effects downwind of the accident site and to dangerous concentrations upwind because of variabilities in the direction of the wind. The IIDs are specified in a method analogous to that used for specifying the PADs.

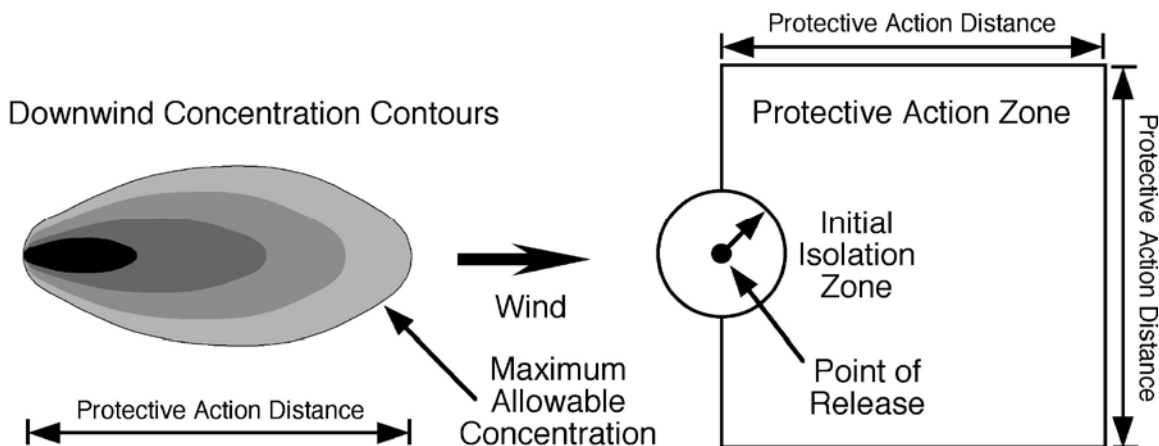


FIGURE 1.1 Illustration Showing How the ERG2008 Defines the Initial Isolation Zone and Protective Action Zone for Use by a First Responder

The range of cases for which the ERG could be used is extremely wide, covering everything from a minor leak in a compressed gas cylinder to one or more catastrophically ruptured tank cars. However, the amount of space that would be needed to address such a wide range of cases for all the TIH materials in the ERG is prohibitive. To narrow the range of cases for which a particular PAD is employed and keep the number of entries listed in the ERG reasonable, four PAD values are provided for each material. They address whether the incident involves a small or large spill and whether it occurs during the day or night. A small spill is defined as the spill from a single drum or cylinder or a small leak from a bulk container corresponding to the limits defined previously. Knowing whether a spill occurs during the day or night is very important in considering downwind dispersion of the released chemical, as discussed in Section 3. Of course, a multitude of other weather and spill variables, such as wind speed, cloud cover, and time (apart from just day or night), can greatly affect the necessary PAD for a specific incident. For this reason, we adopted a statistical approach to determine the percentage of time that a PAD will be sufficient in actual accidents.

1.2 ORGANIZATION OF THIS REPORT

Section 2 presents a detailed overview of the method used to calculate the IIDs and PADs. Included in this discussion are issues related to the TIH list and the treatment of generic compounds, mixtures, and solutions; chemical warfare agents; and water-reactive materials. Section 3 provides details on the statistical scenario analysis that was applied to the materials in the Table, as well as technical details on the consequence models used. Section 4 documents the health criteria, or threshold chemical concentrations, used to specify the IIDs and PADs. Section 5 discusses the safe distance distributions developed as a result of the analysis and describes how the PADs were determined from these distributions. Appendix A presents the Table (DOT et al. 2008). Appendixes B–D contain chemical data and details on the experiments conducted to identify and quantify the emission rates of TIHWR gases.

2 GENERAL METHODOLOGY

The methodology used in preparing the Table for the ERG2008 is illustrated schematically in Figure 2.1. The starting point for the analysis is the list of TIH materials developed by DOT and Transport Canada (see discussion in Section 2.1). This list contains a few additions to and deletions from the ERG2004 list, with most additions being water-reactive materials. For each material in the list, the authorized mode of shipping, as outlined in the *Code of Federal Regulations* (CFR), is combined with commodity flow information and historical incident data to develop a shipment profile. Shipment profiles, which are discussed in Section 2.2.1, are used in the analysis to determine the types of transportation incidents that could occur for particular materials or classes of materials.

The shipment profiles are then used to conduct a statistical analysis of accident scenarios. The result of this analysis is a set of up to 1,000,000 hypothetical incidents based on the best available statistical data. The set accounts for variability in container type, incident type, accident severity (i.e., release amount), location, time of day, time of year, and meteorology. Several of the important release parameters are selected from statistical distributions of transportation-related hazardous material releases cataloged in the Hazardous Materials Information System (HMIS) database maintained by the DOT Research and Special Programs Administration.

Each scenario is then analyzed by using detailed emission rate and atmospheric dispersion models to calculate an airborne chemical concentration footprint. The safe distance for a specific scenario is then chosen as the greatest downwind distance at which the concentration exceeds the health criteria for the chemical involved in the incident. The health criteria, which are exposure-time-dependent threshold concentrations, are based on the National Research Council's (NRC's) Acute Exposure Guideline Level 2 (AEG-L-2) or an equivalent guideline, as detailed in Section 4. The safe distance estimates for the entire set of hypothetical incidents considered in the analysis provide a distribution of safe distances that correspond to the many transportation-related releases that could occur. Incidents are then categorized by time (day, night) and spill size (60 gal or less = small, more than 60 gal = large). The PADs appearing in the ERG2008 are then selected as the 90th percentile values for these individual categories. The Initial Isolation Zones are calculated in a similar manner on the basis of health criteria for life-threatening effects.

2.1 TIH LIST

2.1.1 Background

For the purposes of our analysis, we classify materials on this TIH list into several different categories as follows: (1) pure chemicals, (2) mixtures, (3) solutions, and (4) generics (e.g., UN 1953: liquefied gas, toxic, flammable, n.o.s.). (The abbreviation n.o.s. stands for not otherwise specified.) As is explained later, generic compounds are further divided into subcategories on the basis of Hazard Zone designation, as defined in Title 49, Part 173,

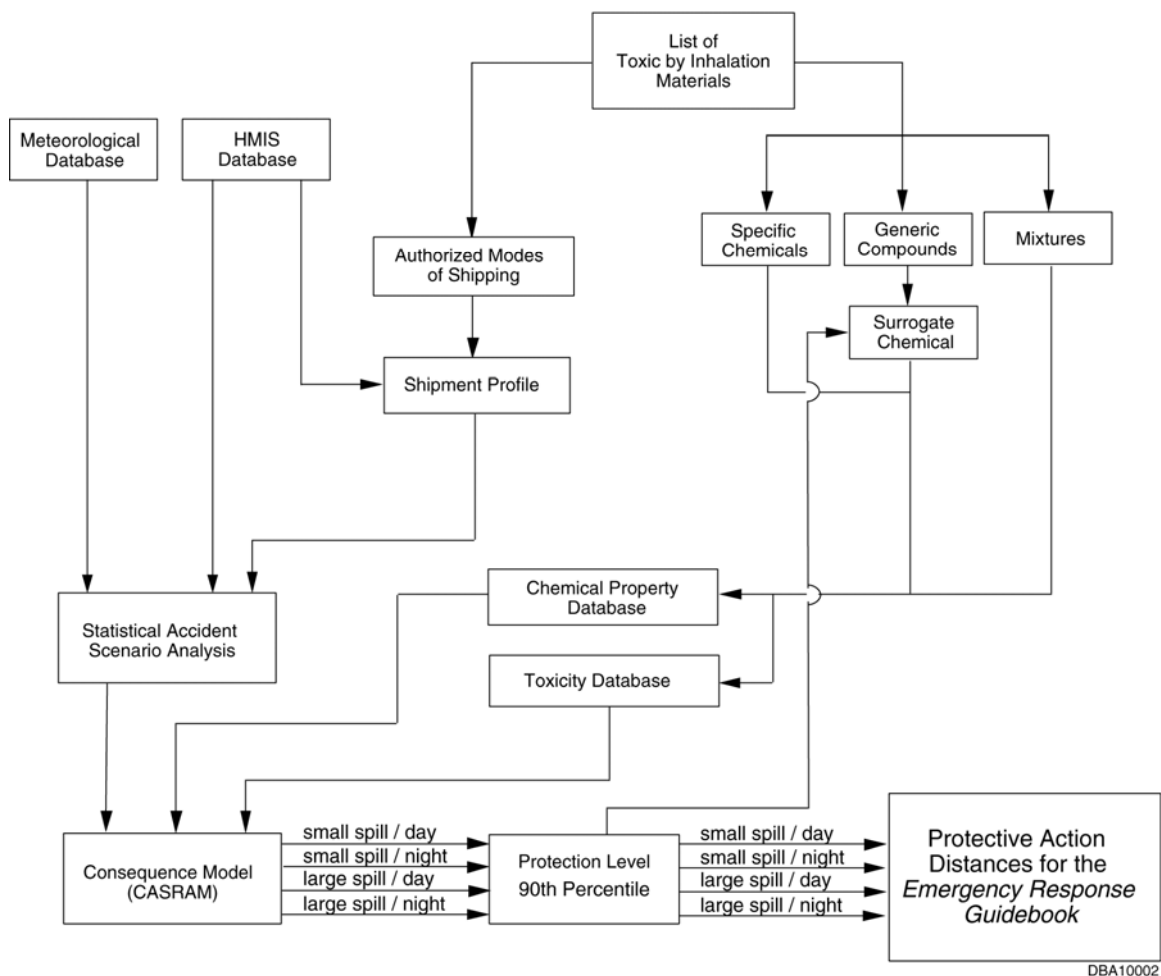


FIGURE 2.1 Schematic of the Methodology Used to Prepare the ERG2008 Table of Initial Isolation and Protective Action Distances

Section 133 of the CFR (49 CFR 173.133). TIH materials fall into four Hazard Zones for gases (A, B, C, and D) and two for liquids (A and B). The ERG2008 lists PADs for 156 single compounds, 15 mixtures, and 26 generics. In addition, 82 water-reactive materials, defined here as materials that emit a TIH gas upon contact with water, are also included in the TIH list. Of the 82 water-reactive materials in the Table, several are also TIH compounds that produce a secondary, sometimes more toxic TIH gas upon reaction with water.

Each category is handled individually. Single chemicals are specified according to a Chemical Abstracts Services (CAS) number, which is a unique numerical identifier for each chemical compound. A unique identifier is necessary to avoid problems with chemical name synonyms. It is important to note that the UN number is not a unique identifier, in that two or more chemicals may be associated with a particular UN number. One example is UN 1076, which is used for both phosgene (CAS 75-44-5) and diphosgene (503-38-8), materials with structural similarities but markedly different physical properties. Mixtures are treated by considering the individual components in the mixture. Generics are modeled by using a surrogate

compound, with the surrogate being the worst case of the materials considered for the particular generic description and hazard zone. Mixtures and generics are discussed in Section 2.3. Water-reactive materials are treated in a manner similar to that used for treating regular TIH materials, with modifications to the physical models for determining the source emission rate. The treatment of water reactivity is discussed in Section 2.4 and Appendixes C and D.

2.1.2 Changes in the TIH List for the ERG2008

There were relatively few substantive changes made in the TIH list for the 2008 Table with the exception of the addition of many new TIHWR materials. Considering water-reactive materials, 14 new materials were added to the TIHWR list. No TIHWR materials were removed. The additions were based on experimental studies conducted for the ERG2008 analysis, which built on the experimental program that was initiated for the ERG2000 and continued in 2004. The treatment of water-reactive materials is discussed in depth in Section 2.4 and Appendixes C and D. Wording revisions and synonym entry additions and deletions resulted in the addition and removal of a few entries in order to bring the names in the Table into agreement with UN naming conventions as of March 2007.

For future editions of the ERG, Argonne recommends deletion of coal gas (UN 1023) and oil gas (UN 1071). These are officially TIH materials; however, our analysis of the mixture constituents for these materials indicates that the median lethal concentration (lethal to 50% of the exposed population; LC₅₀) is well above 10,000 parts per million (ppm). Argonne recommends the addition of acrylonitrile (UN 1093) and methylamine (UN 1061). Acrylonitrile is a liquid with a vapor pressure of 11.9 kPa at 20°C, so in order to fit the criteria as a Hazard Zone B liquid, the LC₅₀ would need to be below 1,000 ppm per 49 CFR 173.333. Several references cited in developing National Institute for Occupational Safety and Health (NIOSH) “immediately dangerous to life and health” (IDLH) values indicate that the 1-h LC₅₀ may be below 1,000 ppm (see www.cdc.gov/niosh/idlh). Methylamine is a gas. The reference used to set the IDLH value indicates that 1-h LC₅₀ is below 5,000 ppm, the necessary criterion to become a Hazard Zone D gas. For reference, if acrylonitrile and methylamine were included in the Table, the large night spill PADs for them would be 0.45 and 1.47 mi, respectively.

2.2 SHIPMENT AND RELEASE SCENARIOS

To specify a level of protection as defined previously, we constructed a set of representative accident scenarios for each material on the TIH list. The first step in this process was to segregate the total transportation of the particular TIH material into a set of discrete shipments by using shipment profiles. Shipment profiles specify the bulk and package freight containers typically used in transporting the material as well as the relative frequency that each container is involved in an incident. The goal of this analysis was to assign each chemical a set of representative shipments that reflect its transportation in the United States, Canada, and Mexico. Specification of shipment profiles is discussed in Section 2.2.1. These shipment profiles were used with the Chemical Accident Statistical Risk Assessment Model (CASRAM) to

simulate tens of thousands of accidents for each chemical in a fashion similar to that used by Brown et al. (2001).

For each shipment, analyses are conducted for two types of releases: those occurring (1) during a traffic accident or a train derailment and (2) while en route from the origin to the destination but not during an accident or derailment. These release types are referred to as (1) accident-related releases and (2) en route/nonaccident releases. The latter category includes releases occurring as a result of cargo shifts, valve failures, corrosion-induced container failure, etc. Such releases are much more common than accident-related releases, as shown by the HMIS incident data for many container types (several of which are not used to transport TIH materials) summarized in Table 2.1. However, most en route/nonaccident releases are minor.

A special case within the shipment profile concept is the treatment of chemical warfare agents. These materials were first considered in the ERG2000. In 2000, entries were given for two release scenarios: (1) transportation-related release scenario and (2) weapons-related release scenario in which the material is released in a criminal or terrorist act. However, the transportation-related release scenario was removed in 2004 (but retained for those agents which have a proper shipping name and are TIH). The treatment of chemical warfare agents is outlined in Section 2.2.2.

2.2.1 Shipment Profiles

The starting point for the development of shipment profiles is 49 CFR 172.101 and associated subsections that specify the authorized shipping modes and packaging for hazardous

TABLE 2.1 Ratio of en Route/Nonaccident Releases to Accident-related Releases for Various Container Types as Derived from the HMIS Database for 1990–2005

Container Type	Ratio of en Route/Nonaccident Releases to Accident-Related Releases
111AW tank car	13
112JW and 105A tank car	24 ^a
DOT 306 cargo tank	0.2
DOT 307 cargo tank	2.2
DOT 312 cargo tank	3.3
MC 330/331 cargo tank	0.5
Small and medium drums	20
Large drums and portable tanks	7
Package freight cylinders	5

^a For the 2008ERG analysis, the ratio for 111A tank cars is used for TIH liquids transported in Type 112JW and 105A tank cars.

materials. These specifications substantially influence the amount of material that could be released in a transport-related accident and other important factors that govern the release hazard, such as the relative frequencies of each container type being involved in a release and the discharge fractions resulting from releases (the amount of material released in an incident relative to the container capacity). For example, most Division 2.3 gases under Hazard Zone A cannot be transported in bulk form. Consequently, such materials are shipped only in package freight containers (drums, cylinders). The resultant total shipping volumes are thus much less than those associated with a typical bulk shipment, even though there can be many package freight containers in a single shipment.

The shipment profiles for most chemicals fall into one of the following nine general classes:

1. Gases dominated by rail transportation,
2. Gases with mixed rail and highway transportation,
3. Gases (Hazard Zone B) dominated by highway transportation,
4. Liquids dominated by rail transportation,
5. Liquids with mixed rail and highway transportation,
6. Liquids dominated by highway transportation,
7. Bulk-forbidden gases and liquids authorized under 49 CFR 173.192,
8. Bulk-forbidden gases and liquids authorized under 49 CFR 173.302, and
9. Organophosphates authorized under 49 CFR 173.334.

Chemicals with a 49 CFR 173.245 authorization for bulk transportation are included in the bulk-forbidden classes. For these chemicals (and the ones for which bulk is forbidden), the PADs for large spills were estimated from shipments containing up to 25 cylinders or drums. A release from this number of package freight containers is equivalent to a release from a small bulk cargo tank (e.g., 1,500 kg). Larger containers were not included in this analysis because it was believed that they would add an unrealistic degree of conservatism to the results, since the probability of these materials being shipped in true bulk form appears to be very low.

Generally, a shipment was designated as being either rail- or highway-dominated on the basis of available commodity flow data (these data are for several widely shipped chemicals) and a survey of incidents from the HMIS database. If no information other than data on packing authorizations within 49 CFR was known, and if the material was authorized for bulk transport, the mixed rail and highway shipment profile was used.

For 2008, we developed several new shipment profiles tailored specifically to several high-volume chemicals identified on the basis of a detailed study of the supply chains for these materials. These materials include chlorine, ammonia, fuming sulfuric acid, hydrogen chloride, hydrogen fluoride, sodium cyanide, and sulfur dioxide. HMIS data, rail waybill data from the American Association of Railroads, and other commodity flow information, together with 49 CFR information, were used. In addition, we employed separate profiles for materials called out for specific treatment in 49 CFR, such as arsine, diborane, fluorine, hydrogen cyanide, methyl mercaptin, nickel carbonyl, nitric oxide, and tetranitromethane.

Examples of mixed rail and highway shipment profiles are provided in Tables 2.2 and 2.3 for liquids and gases, respectively. Three classes of shipments are listed for each profile: bulk rail transportation, bulk highway transportation, and package freight transportation. To provide some perspective on the relative influence of the shipment classes and release types on releases modeled in the ERG2008 analysis, the percentage of total releases represented by each type is listed for all releases, releases of 5–60 gal, and releases of more than 60 gal. When all releases are considered, en route/nonaccident incidents make up the majority of releases modeled for the shipment profiles given in Tables 2.2 and 2.3. However, in considering releases of more than 60 gal (i.e., “large spills” in the Table), accident-related incidents make up the majority of cases. For such releases, package freight incidents were the most common, and bulk highway incidents were the least. Because PADs are set by the 90th-percentile value, incidents involving bulk containers had a far greater influence on PAD values than did incidents involving package freight containers, since bulk containers usually involved larger release amounts.

2.2.2 Treatment of Chemical Agents

The 1995 Tokyo subway sarin attack and the events on and after September 11, 2001, have made the first-response community more aware of the threat from the malicious use of chemical and biological agents. For this reason, the ERG includes IIDs and PADs for various chemical agents that could be used as weapons. In addition, a separate section entitled “Criminal/Terrorist Use of Chemical/Biological/Radiological Agents” (page 354 of the ERG2008) provides information on identification, response, and decontamination strategies for personnel who must respond to a suspected release of such materials.

Table 2.4 lists 26 chemical compounds for which IIDs and PADs were calculated for cases in which the chemicals would be used as a weapon. (The table shows 36 chemical warfare agent names for the 26 compounds.) Accordingly, entries in the ERG2008 Table for these materials include the statement “when used as a weapon.” Several of these materials are also industrial chemicals that appear separately in ERG2008 as transportation-related releases. Entries for weapons-related use of chemical agents, however, are listed under the common or military name for the compound, not the chemical name. For example, for weapons-related entries, the first compound in Table 2.4 is listed as AC, whereas for transportation-related entries, this same compound is listed as hydrogen cyanide (UN 1051). These two terms refer to the same compound, but the weapons-related and transportation-related release scenarios are very different.

TABLE 2.2 Mixed Rail and Highway Shipment Profile Data for Liquids^a

Shipment	Transport Mode	Container	Shipment Amount	Release Type	Percent of Total Releases by Type, Listed by Release Amount		
					All Releases	5–60 gal ^b	>60 gal ^b
1	Rail	DOT Class 112 tank car	80,000 kg	A	3.2	1.1	24.9
				E	41.6	23.0	21.7
2	Highway	DOT 312 cargo tank	20,000 kg	A	1.6	0.7	13.6
				E	5.0	6.4	6.2
3	Highway	Ten 55-gal 5C drums	550 gal	A	2.3	3.0	14.0
				E	46.2	65.8	19.6

^a This profile covers three shipment classes and two release types, accident-related (A) and en route/nonaccident (E). Percentages are provided for the total number of incidents that occurred in the various shipment classes and release types. Percentages are given for all releases, releases of 5–60 gal, and releases of more than 60 gal.

^b Data provided are for methyl hydrazine (UN 1244). Other materials with this profile would have similar results.

TABLE 2.3 Mixed Rail and Highway Shipment Profile Data for Gases^a

Shipment	Transport Mode	Container	Shipment Amount	Re-lease Type	Percent of Total Releases by Type, Listed by Release Amount		
					All Releases	5–60 gal ^b	>60 gal ^b
1	Rail	DOT Class 105, 112 tank car	80,000 kg	A	2.5	0.8	27.9
				E	56.5	13.6	18.2
2	Highway	MC331 cargo tank	20,000 kg	A	1.2	1.2	9.9
				E	0.6	0.5	3.7
3	Highway	Fifteen 19-gal 3A or 4A cylinders	285 gal	A	4.9	9.0	27.4
				E	34.4	74.9	13.0

^a This profile covers three shipment classes and two release types, accident-related (A) and en route/nonaccident (E). Percentages are provided for the total number of incidents that occurred in the various shipment classes and release types. Percentages are given for all releases, releases of 5–60 gal, and releases of more than 60 gal.

^b Data provided are for chlorine trifluoride (UN 1749). Other materials with this profile would have similar results.

TABLE 2.4 Chemical Warfare Agents Listed in the ERG2008 Table of Initial Isolation and Protective Action Distances

UN No.	Chemical Warfare Agent Name	Chemical Compound Name	Small (kg)	Large (kg)	Type ^a
1051	AC	Hydrogen cyanide	200	30,000	SH
1076	DP	Diphosgene	30	500	AL
1076	CG	Phosgene	20	3600	SH
1556	MD	Methyldichloroarsine	30	500	AL
1556	PD	Phenyldichloroarsine	30	500	AL
1589	CK	Cyanogen chloride	30	500	AL
1694	CA	Bromobenzyl cyanides	10	500	AS
1697	CN	Chloroacetophenone	10	500	AS
1698	DM	Diphenylaminechloroarsine (10-Chloro-5,10-dihydrophenarsazine)	5	100	AS
1698	Adamsite				
1699	DA	Diphenylchloroarsine	10	500	AS
1892	ED	Ethyldichloroarsine	10	500	AL
2188	SA	Arsine	200	2000	SH
2810	H	Bis-(2-chloroethyl) sulfide	2	25	SP
2810	HD				
2810	Mustard				
2810	HN-1	Bis-(2-chloroethyl) ethylamine	2	25	SP
2810	HN-2	Bis-(2-chloroethyl) methylamine	2	25	SP
2810	HN-3	Tris-(2-chloroethyl) amine	2	25	SP
2810	L	Dichloro-(2-chlorovinyl) arsine	2	25	SP
2810	Lewisite				
2810	HL ^b				
2810	Mustard lewisite ^b				
2810	BZ	3-Quinuclidinyl benzilate	2	25	AS
2810	Buzz				
2810	CS	o-Chlorobenzylidene malononitrile	10	100	AS
2810	DC	Diphenylcyanoarsine	10	100	AS
2810	GA	Ethyl N,N-dimethylphosphoramidocyanidate	2	25	SP
2810	Tabun				
2810	GB	Isopropyl methylphosphonofluoridate	2	25	SP
2810	Sarin				
2810	GD	Pinacolyl methylphosphonofluoridate	2	25	SP
2810	Soman				
2810	GF	Cyclohexyl methylphosphonofluoridate	2	25	SP
2810	VX	O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	2	25	SP
2811	CX	Phosgene oxime	2	25	AS

^a SH = releases by shipment sabotage, AL = aerosolized liquid, AS = aerosolized solid, SP = spray or explosive release.

^b Because of uncertainties in defining the composition, HL and mustard lewisite were treated as standard lewisite (L).

Release scenarios for weapons-related incidents differ from those for transportation-related incidents because they involve deliberate releases. Two maximum release sizes were used for each material considered in the analysis. In the statistical analysis, release amounts were uniformly distributed between 50% and 100% of these maximum release amounts. Various release types were modeled, depending on the material being released. The release types are denoted in Table 2.4 by two-letter codes. The codes AL and AS refer to aerosolized liquid and aerosolized solid release mechanisms, respectively. It is assumed that AL and AS would be dispersed in aerosolized form with a 2- to 10- μm particle size. This release mechanism is used for solid materials or for materials that have very slow evaporation rates; thus, aerosolization is the only way to disseminate them effectively. The code SP refers to a spray or explosive release. This release mechanism is considered the most likely one to be used to disperse nerve and blister agents, since they are typically thick liquids not readily amenable to direct aerosolization. In the scenario used in this analysis, the spray quickly settles on the ground to a depth up to 0.25 mm and then evaporates. The evaporation rate for these materials is limited by their low vapor pressures. The code SH refers to releases by shipment sabotage. This release mechanism is used for volatile TIH materials. For example, the large release scenario for hydrogen cyanide involves the sabotage of a large bulk container such as a small rail car. Small release amounts for these materials correspond to the release of a standard gas cylinder.

There were no changes in the list of chemical warfare agents from 2004 to 2008, but the methodology to calculate the distances was substantially modified. We reset several of the small and large release amounts to bring them in line with current views on terrorist capabilities. In particular, maximum release amounts for chemical warfare agents were reduced from 100 kg to 25 kg, which is about 5 gal. In addition, release amounts for materials that have no commercial use or availability (such as BZ and CX) were set the same as those for nerve and blister agents. Another substantial change is that 75% of modeled releases were set in urban areas (versus less than 10% for transportation release scenarios). This change was made because there is clearly a greater threat to urban areas from weapons-related releases. This change reduces the resulting PAD values by 30–50%, since dispersion in urban areas is much more effective at diluting near-ground concentrations of materials released into the atmosphere, especially at night.

2.3 GENERICS, MIXTURES, AND SOLUTIONS

The Table lists a variety of compounds that are generic in nature. Two examples are liquefied gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B) (UN 3160) and toxic liquid, corrosive, organic, n.o.s. (UN 2927). Each generic compound can represent many independent chemicals that fit that description but do not have a UN number and therefore are not individually listed in the ERG2008 or the Table. In the ERG2008, IIDs and PADs for generic compounds are based on the median-case (50th-percentile) compound from the pool of chemicals in the overall analysis that matches that generic description. This method marks a substantial departure from the analysis method used in past versions of the ERG, in which the generic compound was set as the worst-case compound from the pool of chemicals matching the description.

This change was made for two reasons. First the worst-case method clearly skewed the distances for the generic compounds and imparted considerable conservatism beyond the 90th-percentile bases used in the PAD specification for individual materials. Although the various generic classes of compounds are not often used in commerce (as evidenced by HMIS records), use of the worst-case method could lead to an excessive response in a major incident. Because the distances for individual materials are already 90th-percentile values, the use of a worst case among these makes the resulting generic compound distances much more conservative than 90th-percentile distances. Use of a median distance preserves the 90th-percentile definition. The second more subtle reason is that using the worst-case chemical to fit an entire generic class resulted in many entries being more than 7 mi, which we felt diluted the importance of the larger distances for those materials that are truly most dangerous.

As an example of this process, the generic compound described as poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B) (UN 3289) is considered below. The 13 chemicals analyzed for the ERG2008 that match this category are listed in Table 2.5. Note that this list is ordered by the PAD for a large, nighttime spill. As shown, trichloroacetyl chloride (UN 2442) lies at the median of these 13 chemicals when the large spill distances are considered, meaning that half of the chemicals (6) have longer large-spill distances and half have shorter large-spill distances. For small spills, the median chemical is boron tribromide (UN 2692) (shown in bold in Table 2.5). Also provided are two entries for this generic category that reflect the variations in wording in the Table. These entries are rounded up to the nearest 0.1 mi (100 ft for Initial Isolation Zones) to reflect their appearance in the Table. Note that if the previous worst-case criteria were used, the distances for bromine would be used as a surrogate for this generic category, as was done for ERG2004.

Table 2.6 lists all the generic compounds included in the Table and provides the subset of chemicals from which their distances were calculated. Synonyms are not listed in Table 2.6, so each entry may have several corresponding entries in the Table. For categories that had fewer than three chemicals from which to pick the worst-case example, the selection pool was enlarged to include materials from the next less restrictive designation. For instance, the pool for the generic category described as compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zones C and D) included all corrosive gases in Hazard Zones C and D because no corrosive, *oxidizing* gases with those hazard zone designations were identified in the analysis pool.

Table 2.7 lists the mixtures and solutions treated in the ERG2008 analysis and indicates how they were modeled. In general, the distances for mixtures were determined by (1) selecting a surrogate compound, (2) considering the toxic effects of a single hazardous constituent, or (3) considering the toxic effects of multiple hazardous constituents. Surrogates were chosen when the mixture composition was not specified. For these cases, the surrogate was chosen as the worst-case chemical or potential composition in that mixture. As an example, consider chlorosulfonic acid and sulfur trioxide mixtures (UN 1754). In these mixtures, sulfur trioxide is the more hazardous component, primarily because of its higher vapor pressure. The addition of chlorosulfonic acid will act to lower the vapor pressure, so a 100% sulfur trioxide mixture is the worst case and was chosen for analysis. A single hazardous constituent was modeled for several cases involving mixtures in compressed gases and solutions (e.g., diborane, tetraethyl

TABLE 2.5 Chemicals Used to Determine Initial Isolation and Protective Action Distances for the Generic Material Described as Poisonous Liquid, Corrosive, Inorganic, n.o.s. (Inhalation Hazard Zone B) (UN 3289)^a

UN No.	Name of Material	Small Spills			Large Spills		
		First Isolate in All Directions (ft)	Then Protect Persons Downwind during		First Isolate in All Directions (ft)	Then Protect Persons Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
<i>Potential Surrogate Compounds</i>							
1754	Chlorosulfonic acid	26	0.03	0.04	140	0.16	0.23
1746	Bromine trifluoride	44	0.05	0.06	140	0.16	0.25
1076	Diphosgene	61	0.07	0.09	166	0.19	0.29
1082	Titanium tetrachloride	44	0.05	0.08	219	0.25	0.45
2692	Boron tribromide	61	0.07	0.2	236	0.27	0.57
1828	Sulfur monochloride	44	0.05	0.08	359	0.41	0.74
2442	Trichloroacetyl chloride	79	0.09	0.18	368	0.42	0.78
1836	Thionyl chloride	114	0.13	0.42	481	0.55	1.15
1810	Phosphorus oxychloride	123	0.14	0.31	595	0.68	1.21
1834	Sulfuryl chloride	79	0.09	0.31	516	0.59	1.28
1809	Phosphorus trichloride	96	0.11	0.38	788	0.9	1.82
1745	Bromine pentafluoride	96	0.11	0.52	770	0.88	1.94
1744	Bromine	298	0.34	1.09	1636	1.87	4.07
<i>Synonymous Entries for Generic Compound Categories</i>							
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	400	0.5	0.8
3289	Toxic liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	400	0.5	0.8

^a This table provides distance estimates for all applicable entries in the ERG2008 Table of Initial Isolation and Protective Action Distances (DOT et al. 2008). The median-case (50th percentile) distances for small spills and large spills for each column are shown in bold.

**TABLE 2.6 Summary of Generic Compounds on DOT TIH List and Corresponding Surrogates Employed for the ERG2008
(Note that a different surrogate material may be used for each release category.)**

UN Number	Proper Shipping Name	Surrogate
1953	Liquefied gas, poisonous, flammable, n.o.s.	Median cases among all TIH, flammable Hazard Zone A gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable Hazard Zone A gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable Hazard Zone B gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, flammable Hazard Zone C gases
1953	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone D gases
1955	Liquefied gas, poisonous, n.o.s.	Median cases among all TIH, Hazard Zone A gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, Hazard Zone A gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, Hazard Zone B gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, Hazard Zone C gases
1955	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, Hazard Zone D gases
1955	Organic phosphate mixed with compressed gas	Parathion and compressed gas mixture
1967	Insecticide gas, poisonous, n.o.s.	Parathion and compressed gas mixture
2810	Poisonous liquid, n.o.s.	Median cases among all TIH Hazard Zone A liquids
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH Hazard Zone A liquids
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH Hazard Zone B liquids
2810	Poisonous liquid, organic, n.o.s.	Median cases among all TIH, organic, Hazard Zone A liquids
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, organic, Hazard Zone A liquids
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, organic, Hazard Zone B liquids
2927	Poisonous liquid, corrosive, n.o.s.	Median cases among all TIH, corrosive, Hazard Zone A liquids
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, Hazard Zone A liquids
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, Hazard Zone B liquids
2927	Toxic liquid, corrosive, organic, n.o.s.	Median cases among all TIH, corrosive, organic Hazard Zone A liquids
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, organic Hazard Zone A liquids
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, organic, Hazard Zone B liquids
2929	Poisonous liquid, flammable, n.o.s.	Median cases among all TIH, flammable, Hazard Zone A liquids
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone B liquids
2929	Poisonous liquid, flammable, organic, n.o.s.	Median cases among all TIH, flammable, organic, Hazard Zone A liquids
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, organic, Hazard Zone A liquids
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, organic, Hazard Zone B liquids
3122	Poisonous liquid, oxidizing, n.o.s.	Median cases among all TIH, flammable, Hazard Zone A liquids

TABLE 2.6 (Cont.)

UN Number	Proper Shipping Name	Surrogate
3122	Poisonous liquids, oxidizing, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
3122	Poisonous liquids, oxidizing, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, oxidizing, Hazard Zone B liquids
3123	Poisonous liquid, water-reactive, n.o.s.	Median cases among all TIH Hazard Zone A liquids
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH Hazard Zone A liquids
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH Hazard Zone B liquids
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s.	Median cases among all TIH flammable liquids
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable, Hazard Zone A liquids
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable, Hazard Zone B liquids
3160	Liquefied gas, poisonous, flammable, n.o.s.	Median cases among all TIH, flammable Hazard Zone A gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, flammable Hazard Zone A gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, flammable Hazard Zone B gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, flammable Hazard Zone C gases
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, flammable Hazard Zone D gases
3162	Liquefied gas, poisonous, n.o.s.	Median cases among all TIH Hazard Zone A gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH Hazard Zone A gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH Hazard Zone B gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH Hazard Zone C gases
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH Hazard Zone D gases
3275	Nitriles, poisonous, flammable, n.o.s.	Methacrylonitrile
3276	Nitriles, poisonous, n.o.s.	Methacrylonitrile
3278	Organophosphorus compound, poisonous, n.o.s.	Methyl phosphonous dichloride
3279	Organophosphorus compound, poisonous, flammable, n.o.s.	Methyl phosphonous dichloride
3280	Organoarsenic compound, n.o.s.	Tert-butylarsine
3281	Metal carbonyls, n.o.s.	Nickel carbonyl
3287	Poisonous liquid, inorganic, n.o.s.	Median cases among all TIH, inorganic, Hazard Zone A liquids
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, inorganic, Hazard Zone A liquids
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, inorganic, Hazard Zone B liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s.	Median cases among all TIH, corrosive, inorganic, Hazard Zone A liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, corrosive, inorganic, Hazard Zone A liquids
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, inorganic, Hazard Zone B liquids

TABLE 2.6 (Cont.)

UN Number	Proper Shipping Name	Surrogate
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, corrosive, Hazard Zone B gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, corrosive, Hazard Zone C gases
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, corrosive, Hazard Zone D gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s.	Median cases among all TIH, oxidizing, corrosive, Hazard Zone A gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	Median cases among all TIH, oxidizing, corrosive, Hazard Zone A gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	Median cases among all TIH, oxidizing, corrosive, Hazard Zone B gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	Median cases among all TIH, corrosive, Hazard Zone C gases
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	Median cases among all TIH, corrosive, Hazard Zone D gases
3355	Insecticide gas, poisonous, flammable, n.o.s.	Median cases among all flammable, Hazard Zone A gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	Median cases among all flammable, Hazard Zone A gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	Median cases among all flammable, Hazard Zone B gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	Median cases among all flammable, Hazard Zone C gases
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	Median cases among all flammable, Hazard Zone D gases

TABLE 2.7 Summary of Mixtures and Solutions on DOT TIH List and How They Were Treated for the ERG2008

UN Number	Category	Proper Shipping Name	Modeled as
<i>Mixtures and Solutions Modeled as Single Toxic Species</i>			
1040	Mixture	Ethylene oxide with nitrogen	100% ethylene oxide
1051	Solution	Hydrocyanic acid, aqueous solutions, with more than 20% hydrogen cyanide	100% hydrogen cyanide
1583	Mixture	Chloropicrin mixture, n.o.s.	100% chloropicrin
1612	Mixture	Hexaethyltetraphosphate and compressed gas mixtures	20% hexaethyltetraphosphate
1613	Solution	Hydrocyanic acid, aqueous solution, with not more than 20% hydrogen cyanide	20% hydrogen cyanide solution in water
1647	Mixture	Ethylene dibromide and methyl bromide mixture, liquid	100% methyl bromide
1703	Mixture	Tetraethyl dithiopyrophosphate and gases, in solution	20% tetraethyl dithiopyrophosphate
1705	Mixture	Tetraethyl pyrophosphate and compressed gas mixtures	20% tetraethyl pyrophosphate
1744	Solution	Bromine solutions	100% bromine
1754	Mixture	Chlorosulfonic acid and sulfur trioxide mixture	100% sulfur trioxide
1911	Mixture	Diborane	7% diborane
1955	Mixture	Methyl bromide and nonflammable, nonliquified compressed gas mixtures	100% methyl bromide
1967	Mixture	Parathion and compressed gas mixtures	20% parathion
1975	Mixture	Nitric oxide and dinitrogen tetroxide mixtures	100% nitric oxide
2600	Mixture	Carbon monoxide and hydrogen mixtures	100% carbon monoxide
3294	Solution	Hydrogen cyanide, solution in alcohol, with not more than 45% hydrogen cyanide	45% hydrogen cyanide solution in alcohol
3300	Mixture	Carbon dioxide and ethylene oxide mixture, with more than 87% ethylene oxide	100% ethylene oxide
3318	Solution	Ammonia solution, with more than 50% ammonia	100% ammonia
<i>Mixtures Modeled with Multiple Toxic Chemical Species</i>			
1581	Mixture	Chloropicrin and methyl bromide mixtures	(i) 5% chloropicrin and (ii) 95% methyl bromide
1582	Mixture	Chloropicrin and methyl chloride mixtures	(i) 2% chloropicrin and (ii) 98% methyl chloride
1023	Mixture	Coal gas	(i) 48% hydrogen, (ii) 27% methane, (iii) 10% carbon monoxide, (iv) 5% carbon dioxide, and (v) 6% nitrogen
1071	Mixture	Oil gas	(i) 55% hydrogen, (ii) 25% methane, (iii) 11% carbon monoxide, (iv) 3% carbon dioxide, (v) 2% ethylene, and (vi) 2% benzene

pyrophosphate, hydrocyanic acid solutions). For each case, the worst case as specified in 49 CFR or by the description was modeled. The third class of mixtures involves compounds with more than one hazardous component. For instance, in chloropicrin and methyl bromide mixtures (UN 1581), chloropicrin is dissolved in methyl bromide up to 5% by volume. Therefore, toxic effects of both constituents are taken into account. The result is a mixture that behaves almost identically to pure methyl bromide in terms of release rate and dispersion. However, the mixture is much more toxic than pure methyl bromide as a result of the high toxicity of chloropicrin, so the PAD is longer than that for pure methyl bromide.

2.4 ANALYSIS OF WATER-REACTIVE MATERIALS

2.4.1 Background

Trucks and rail cars that transport hazardous chemicals can have accidents in which their solid or liquid cargo spills into a water-filled roadside ditch, stream, river, lake, or estuary. This presents the possibility that a material that otherwise does not pose an inhalation hazard might react with the water to produce toxic gaseous by-products. In the following discussions, materials that generate substantial quantities of toxic gases fairly rapidly after a spill into water are referred to as toxic inhalation hazards by water-reaction (TIHWR).¹ An example of a TIHWR material is silicon tetrachloride, which is not a TIH material but produces airborne hydrogen chloride (HCl) and HCl mist upon exposure to water. Even heavy rainfall at the time of an accident or airborne water vapor can cause the emission of TIH gases from this material. The well-known Chicago spill of silicon tetrachloride from a storage tank in 1976 is an example. At one point in the eight-day episode, heavy rainfall led to a significant increase in emissions and sudden damage to the surroundings because additional HCl was released into the atmosphere. The same problem, though of less magnitude (due to a smaller release amount), would occur if a truck or tank car spilled silicon tetrachloride into water or had an accident resulting a spill during a rainstorm.

Until recently, little attention was directed to materials that emit gases into the atmosphere when accidentally released into water. Kapias and Griffiths (1999) presented a limited discussion of water-reactive chemicals and the modeling of accidental releases. They used the example of silicon tetrachloride, which is a strong HCl emitter, either reacting with liquid water or scavenging atmospheric water vapor. Over the last decade, however, we have identified numerous such materials and recommended them for inclusion in the ERG as part of a long-term program for identifying TIHWR materials and quantifying their emissions.

This section provides a description of our program for identifying and classifying TIHWR materials, as well as a companion experimental program instituted to provide a quantitative basis for the TIHWR analysis. The technical aspects of how the TIH emission rates from these materials were modeled and how they were treated in the statistical analysis as part of

¹ Note that materials that evolve into flammable gases but do not otherwise pose a toxic hazard are explicitly excluded from our definition and the discussions that follow.

the ERG2008 study are detailed in Section 3.3.2.3, and additional details on the experiments and the parameters employed in the TIHWR modeling appear in Appendixes C and D.

2.4.2 Identification and Evaluation of Candidates

To compile the list of water-reactive materials for the Guidebook from the large pool of potential TIH emitters, we first screened materials by applying general principles of chemical reactivity, seeking specific reactivity information from the chemical literature and comparing such information among related compounds. Screening started with the 208 chemically distinct materials previously found by Carhart et al. (1996) to be capable of producing TIH gases if spilled into a river, lake, or other body of surface water. The 37 materials that made up the 1996 North American ERG “List of Dangerous Water-Reactive Materials” are a subset of these 208. In the analysis for the ERG2000, 16 more materials were added to the TIHWR candidate list on the basis of a review of other water-reactive lists and recommendations by DOT.

The final initial list of 224 candidate materials was carefully evaluated to determine which ones provided sufficient hazards to warrant their inclusion in the Table. The evaluation process consisted of the following steps:

1. Consideration of general patterns of reactivity,
2. Examination of the primary literature,
3. Examination of standard secondary sources such as Kroschwitz (1991–1996) and Lewis (2000), and
4. Experimental tests on compounds to estimate the yield and rate of production of toxic gases when mixed with water. These experiments both confirmed water reactivity and provided a quantitative basis for TIHWR hazard estimates.

Steps 1 through 3 were used to generate the 1996 TIHWR list. For the ERG2000, the experimental program outlined in Step 4 was initiated. This program was expanded for the ERG2004 to include over half of the TIHWR list and further expanded for the ERG2008 to encompass more than 70% of the TIHWR list. Furthermore, the set of materials under consideration for TIHWR status was expanded, thus adding several new materials to the TIHWR list.

The need for such experimental data is underscored by the fact that quantitative observations of TIH gas evolving from hazardous chemicals added to water do not exist in the chemical literature. The experimental program is outlined below.

2.4.3 Experimental Program

The experimental program consisted of a series of small-scale experiments with candidate materials. The materials were tested for the generation of gases by mixing small amounts of the material in question (about 1 millimole [mmol]) with water in a closed system. The release of gas was measured over time by observing the displacement of a nearly frictionless plunger in a gas syringe. This experimental setup was different than that used for the ERG2000 and ERG2004 analyses, in which the gas volume produced was measured by noting the displacement of manometric fluid. The experimental apparatus was changed to provide higher-quality quantitative information and results that are more reproducible, since dissolution of the progeny gases into the manometric fluid was no longer an issue. As was done before, experiments were conducted by using two different amounts of water (the stoichiometric equivalent amount and fivefold molar excess) for each material considered. These experiments are meant to approximate conditions in which (1) a material is released into a restricted water environment (or perhaps just gets wet) and (2) a material is spilled into a body of water. Most materials previously analyzed in the experiments were redone for the ERG2008, thereby providing an entirely new set of experimental data from which to estimate gas evolution.

The experimental program has not only given us useful quantitative information on the rates of evolution of TIH gases, but over the past decade, it has allowed us to delete several chemicals from the initial TIHWR list because no evolution of gas was observed. In a few cases, a reaction actually did occur, but the gas that was produced was rapidly dissolved when water was in excess. This effect might not occur when larger quantities are involved; additional experiments are required to establish whether significant amounts of TIH gases would escape under such conditions.

The experimental procedure and resulting data and analysis are fully described in Appendixes C and D.

2.4.4 Additional Selection Criteria

There are a few additional issues associated with the evaluation process that deserve special attention:

- Some potential TIHWR materials, especially generic materials, are not sufficiently described chemically to allow a complete assessment of their behavior when spilled into water. Such materials are not included on the TIHWR list unless there is a positive indication that a TIH gas might develop in a spill into water. Examples of materials that are not included on the TIHWR list at this time include pyrophoric organometallic compound, n.o.s. (UN 3203); organometallic compound solution, water-reactive, flammable, n.o.s (UN 3207); water-reactive substances, liquid, corrosive, n.o.s. (UN 3129); water-reactive solid, corrosive, n.o.s. (UN 3131); water-reactive substances, liquid, n.o.s. (UN 3148); water-reactive liquid, toxic, n.o.s.

(UN 3130); and substances which in contact with water emit flammable gases, solid, poisonous, n.o.s. (UN 3134).

- On the other hand, generic alkyl halides and chlorosilanes might generate sufficient gaseous HCl or another hydrogen halide to qualify as TIHWR materials. For this reason, aluminum alkyl halides (UN 3052); metal alkyl halides, n.o.s. (UN 3049); chlorosilanes, n.o.s. (UN 2985); chlorosilanes, flammable, corrosive, n.o.s. (UN 2986); and chlorosilanes, corrosive, n.o.s. (UN 2987) are included.
- Materials that are gaseous at ordinary temperatures (with boiling points below 0°C at atmospheric pressure) were uniformly not recommended for inclusion. An example is trifluoroacetyl chloride, which boils at -18°C. Such compounds would probably boil away too rapidly to allow a significant reaction with surface water under most atmospheric conditions.
- Liquids boiling in the range of ordinary environmental temperature (0–20°C) presented problems, because they occur as a liquid or a gas, depending on water temperature. Cyanogen chloride was rejected because it is a gas at temperatures above most of this range (boiling point 13.1°C) and because it does not require a spill into water to pose a TIH hazard. Chlorine trifluoride (boiling point 11.8°C) was rejected on similar grounds. On the other hand, BCl₃ is included despite being a gas at 20°C, because the reaction of the spilled chemical with water rapidly generates HCl gas, which is more toxic than the parent compound. Also, since its boiling point is 12.5°C, the material can remain in the liquid state when spilled into cold water. In addition, BCl₃ is frequently purveyed in solution in an organic solvent.
- Materials that undergo highly exothermic reactions with water sometimes generate acidic mists, depending on the way that they are mixed with water. The mist happens when water at hot spots of reactivity boils violently. The resulting seething and bumping kicks colloidal particles of hydrated or partially hydrated material into the air. For example, oleum (UN 1831) quite often raises a fume containing SO₃•H₂O, H₂SO₄, and related acidic species when it is mixed with water. Such a mist presents an obvious inhalation hazard. Similar mists can form when sulfur trioxide (UN 1829) and sulfuryl chloride (UN 1834) mix with water. Materials in this category were treated individually. Oleum and SO₃ were not included as TIHWR materials because spills into water would likely not lead to PADs longer than those already listed for land-based spills. Sulfuryl chloride was listed as a TIHWR material on the basis of its co-generation of gaseous HCl. Phosphorus pentoxide (UN 1807) might raise an acidic mist (of oxo-acids of phosphorus) in a spill into water. Although mists present a clear toxic inhalation hazard in certain release scenarios, the generation of mists alone is not currently a sufficient criterion for inclusion in the TIHWR table.

- Certain materials dissolve smoothly in water without generating gases under most circumstances but can decompose to evolve TIH gases if the mixing with water occurs under conditions that prevent the loss of the heat of dissolution and allow a sufficient rise in temperature. Such conditions were not attained in the water-reactivity experiments (Appendix C).
- Thermal decomposition of calcium hypochlorite (UN 1748) and lithium hypochlorite (UN 1471) generates chlorine and/or HCl (Lewis 2000), which are TIH gases. These two hypochlorites appeared as TIHWR materials in the ERG1996 but were removed as TIHWR materials in subsequent lists because the auto-heating scenario appeared too unlikely.
- A similar decomposition of sodium hydrosulfite (UN 1384), calcium hydrosulfite (UN 1923), and zinc hydrosulfite (UN 1931) can occur with water, generating sulfur dioxide and possibly hydrogen sulfide, which are TIH gases. These three hydrosulfites appear on the TIHWR list on the basis of the behavior of sodium hydrosulfite in a serious plant accident in New Jersey on April 21, 1995 (EPA and OSHA 1997).

2.4.5 Summary

As a result of the steps and considerations detailed above, 37 new materials were proposed for inclusion in the ERG2000, 14 new materials were added to the TIHWR list for 2004, and 14 more were added in the ERG2008. The full list of TIHWR materials considered in the ERG2008 is presented in Appendix C, along with a brief summary of reasons for the inclusion of each material. Appendix C also provides the parameters necessary to model TIH evolution, such as (1) shipment state, (2) TIH gas(es) evolved, (3) density of the material, (4) stoichiometric yield, (5) overall efficiency factor, and (6) rate constants. Results from the experimental program are given in Appendix D.

2.5 DETERMINATION OF INITIAL ISOLATION DISTANCES

The IID is the length of the radius of a circular Initial Isolation Zone around the accident site from which people are to be kept away. Establishment of an Initial Isolation Zone serves two purposes. First, it provides a protective barrier upwind to protect against exposures due to wind direction variations. Second, it defines a zone downwind where life-threatening effects might be expected. The latter is generally a more stringent requirement, so that purpose is used to define the IID.

The IID is calculated in a similar manner to the PAD except that a lethality health end point is a principal consideration. As such, distances are first evaluated by using the 1-h LC₅₀. The 1-h value is used in all cases (no time adjustment is made), even though exposure times are generally much shorter, since plume meander is a very transient phenomenon and people would not remain in this zone unless they became incapacitated. Earlier efforts using a 5-min exposure

time together with the ERPG-3 (or surrogate) yielded longer distances, although the methods were comparable for most materials. We use LC₅₀ values because they are experimentally derived and available for nearly all materials on the TIH list.

For the ERG2008 analysis, the procedure to specify IID values was substantially modified to set a minimum distance equivalent to 15% of the daytime PAD for gases and 7.5% of the daytime PAD for liquids. This modification was made because many of the large-spill IID values appeared too short from a safety standpoint, especially in light of some major accidental releases that occurred in the last several years (e.g., in Minot, North Dakota, in 2002; Festus, Missouri, in 2002; and Graniteville, South Carolina, in 2005). The net result of this modification is that for gases, the IID is usually set by this minimum distance criterion rather than the LC₅₀-based value. As such, the IIDs for most gases substantially increased from values used in prior editions of the ERG. As a result of incorporating this minimum distance, this criterion had a much smaller effect for liquid compounds.

An additional modification was that we binned the IID values differently than we had done for past editions, employing many fewer bins or cut points to report the distances. This was done because the vagueness of the IID definition and analysis uncertainties did not warrant such a fine gradation as that previously reported. As an example, the authors did not see additional meaning in reporting a 1,500-ft distance versus a 1,600-ft distance. The new cut points chosen were

- 30 m (100 ft)
- 60 m (200 ft)
- 100 m (300 ft)
- 150 m (500 ft)
- 200 m (600 ft)
- 300 m (1,000 ft)
- 400 m (1,250 ft)
- 500 m (1,500 ft)
- 600 m (2,000 ft)
- 800 m (2,500 ft)
- 1,000 m (3,000 ft)

It is important to note that many TIH materials are also flammable or are oxidizers. The IID is based solely on inhalation toxicity and does not account for the explosive or flammable nature of the material. As a result, there may be substantial differences between the IID that appears on the green pages and the corresponding isolation distance guidelines on the orange pages in the ERG2008. In some cases, the IID, which is based on inhalation toxicity, can be less than the suggested evacuation distance, which is based on flammability or explosion concerns.

3 STATISTICAL ACCIDENT SCENARIO ANALYSIS AND CASRAM

CASRAM (Chemical Accident Statistical Risk Assessment Model) lies at the core of the analysis for PAD determination for the 2008ERG and is the key tool we employ for both constructing accident scenarios and executing the consequence models. CASRAM predicts hazard-zone distributions (i.e., areas in which a threshold chemical concentration is exceeded) and/or affected populations resulting from releases associated with hazardous materials transportation or storage. The model utilizes a variety of statistical data for hazardous materials releases and an extensive meteorological database to statistically generate and analyze release scenarios. For a given health effect (injury, fatality, etc.), hazard-zone distributions are generated stochastically through Monte Carlo sampling of accident scenario parameters (time, location, release amount, meteorology, etc.) and detailed consequence modeling of the hypothetical releases. CASRAM is specifically designed for the *statistical* analysis of hazardous material release problems. It is this feature, in particular, that separates CASRAM from many other hazardous material release models such as ALOHA (Reynolds 1992) and SCIPUFF (Sykes et al. 1998). Rather than specifying a deterministic measure of risk, CASRAM determines the distribution of possible outcomes, thus allowing identification of the probability of a particular consequence within the limits of the statistical data.

CASRAM is primarily a routing-based risk assessment model that requires shipment attributes (e.g., materials, containers) and shipment routes as inputs. It provides distributions of affected persons as outputs (e.g., Brown et al. 2001). However, it is equally applicable to a geographically based incident distribution system. A geographically based system is required for the ERG analysis because the Table must reflect releases that occur anywhere in North America. The statistical accident scenario analysis (see Figure 2.1) combines the shipment profile information discussed in Section 2.2, meteorological observations from a preprocessed meteorological database, and statistical information from the HMIS database to provide a large distribution of incidents. These incidents are then modeled by using the consequence models within CASRAM. The overall goal of this analysis is to identify the distributions of safe distance (i.e., hazard zone length) associated with the transport within North America of all materials that are given in the Table. The PADs and IIDs in the Table are the 90th-percentile values of these safe-distance distributions.

This section first discusses the statistical scenario analysis and then the meteorological database used in the 2008ERG study. The emission rate modeling and dispersion modeling within CASRAM, which make up the consequence modeling effort to determine PADs, are then outlined.

3.1 STATISTICAL SCENARIO ANALYSIS

3.1.1 Overview of Analysis Steps

For each material in the Table, we use CASRAM to model more than 100,000 separate incidents distributed between highway and rail transportation, relevant container types (e.g., DOT Class 105 tank car, MC 330 cargo tank, 1A1 drums), and release types (e.g., accident-related, en route/nonaccident). The distribution of the incidents within the categories above are specified in the shipment profiles discussed in Section 2.2. Incidents were also distributed geographically and temporally on the basis of transportation mode and release type. Geographic and temporal effects have a large influence on meteorology, which in turn directly affects the safe distance calculation. The location of the incident affects the general climate and land use (e.g., dry desert, temperate farmland), whereas the time of day and month affect the weather at that locale.

Each release modeled in the analysis is assigned a random date, time, and location. The locations for U.S.-based accidents are chosen probabilistically on the basis of state distributions of accidents in the HMIS database. Separate distributions are used for accident-related and en route/nonaccident releases for both highway and rail. Locations for Canada and Mexico are based on population density. Date and time are assigned on the basis of month-of-year and time-of-day distributions for incidents in the HMIS database following Brown et al. (2005), where the year is assigned in a five-year window that corresponds to observations in the meteorological database (1985–1989²).

The emission rate model in CASRAM uses the shipment information and meteorology as specified above to determine the rate at which specific materials are released into the atmosphere. The first step is to estimate the discharge fraction on the basis of historical statistical distributions generated from analysis of HMIS database incidents. The emission rates of the material to the atmosphere are then calculated by using physical models for discharge, flashing, and evaporation applicable to that release. Within the emission rate model, the total amount of material spilled (discharge fraction) and median pool depth are treated stochastically.

By using the emission rates for the chemical(s) involved and the ambient meteorology, the dispersion model within CASRAM then determines the affected areas. We view the dispersion calculation as a two-step process. Step 1 involves characterizing the meteorology from the available surface observations, and Step 2 involves estimating the transport and dispersion from the applicable meteorological parameters. Step 1 is accomplished with a meteorological preprocessor, which is a series of algorithms that take raw meteorological data (e.g., wind speed, temperature, humidity, cloud cover) and site information (e.g., land cover type, roughness length) and calculate parameters necessary for estimating dispersion. While this analysis is usually closely associated with dispersion modeling, the atmospheric parameters

² More current meteorological data are not employed since the 1985–1989 window is the last 5-year period in which manual observations are available. Current National Weather Service observations are made with automated equipment that has difficulty discerning cloud amounts and precipitation type.

calculated are also used in estimating source emission rates. Traditionally, these parameters have been represented as stability classes; however, in this analysis, the turbulence of the atmospheric boundary layer was represented by more fundamental turbulence measures, such as friction velocity, surface heat flux, and inversion height. Step 2 is accomplished in CASRAM with a Lagrangian integral dispersion model for passive releases, coupled with a dense gas dispersion model to address large releases of liquefied gases where heavier-than-air plumes form. The physical relationships that make up the emission rate and dispersion models are outlined in Sections 3.3 and 3.4, respectively.

3.1.2 HMIS Database

The Hazardous Materials Information System (HMIS) database, maintained by DOT, catalogues transportation-related incidents involving the release of hazardous materials. In latter years, about 15,000 incidents per year have been catalogued for highway, rail, air, and waterway transportation. In general, 80–85% of the incidents are highway-related, and about 11–14% are rail-related. Air accidents (mainly luggage-related) make up the rest. Incidents in the database can occur (a) during an accident (i.e., during a vehicular mishap or a train derailment), (b) en route but not during an accident (e.g., due to a cargo shift or valve failure), or (c) during loading or unloading operations. For highway transportation, about 80% of the incidents in the HMIS database occur during loading and unloading, whereas for rail, about 85% are en route/nonaccident releases.

For each incident catalogued in the HMIS database, information pertaining directly to the hazardous material release is provided, including the (a) name of the chemical shipped, (b) container type and capacity, (c) number of containers shipped, (d) number of containers that fail, and (e) amount of material released. Multiple chemicals released during the same incident are recorded in the database as separate records. The database also contains information concerning the occurrence of fire, explosion, water immersion, and environmental damage, as well as the number of deaths, major and minor injuries, and number of persons evacuated. Death and injury statistics pertain only to the consequence of the hazardous material release and not to physical trauma due to the accident itself. Since this database is composed of data from actual hazardous material incidents, it is an invaluable tool in statistical analyses of hazardous material transportation incidents and the best publicly available source of information on container failures and release amounts. For the ERG analysis and other risk assessments, we use HMIS data to specify geographical incident distributions, temporal incident distributions, and discharge fraction distributions, as described in the subsections below. Further information on the HMIS database and our previous analyses can be found in Brown et al. (2001).

3.1.3 Geographic Incident Distributions

In the ERG2008 analysis, accidents are distributed across all 50 states in the United States, the southern Canadian provinces, and Mexico. Within the United States, the accident distribution is based on incident distributions in the HMIS database for 1985 through 2006, and separate geographic distributions are used for highway and rail. The distribution of

accidents among the United States, Canada, and Mexico is based on the relative gross domestic product (GDP) for 2005. GDP was selected as a measure for hazardous material incidents because of the unavailability of detailed data on hazardous material incidents for Mexico. For the United States and Canada, the relative GDP for chemical and chemical products is similar to the total GDP, but because the industry-specific GDP was not available for Mexico, and because Canadian and U.S. chemical-specific GDPs are calculated slightly differently, the total GDP was considered to be the more robust indicator. On the basis of this breakdown, 89% of incidents modeled in the 2008ERG analysis occurred in the United States, 6% occurred in Canada, and 5% occurred in Mexico. Within Canada and Mexico, incidents were distributed into regions on the basis of population. Canada was divided by province. In this process, New Brunswick, Newfoundland, Nova Scotia, and Prince Edward Island were combined as the “Atlantic Provinces,” and the Yukon and Northwest Territories were excluded because of their small populations (more than 0.5% of total Canadian population). Mexico was divided into three regions: Northern (above 22°N latitude), Central (between 18 and 22°N latitude), and Southern (below 18°N latitude, including the Yucatan Peninsula). A breakdown of the geographic distribution of incidents in the 2008ERG analysis for highway and rail transportation is provided in Table 3.1.

3.1.4 Temporal Incident Distributions

Temporal release distributions are important to specify appropriate meteorology. In some risk assessment studies, temporal variables also influence the population at risk since (1) the population density of a particular location can change throughout the day and (2) a greater fraction of people are outside during the daytime. Two temporal variables are defined in our analysis: hour of day and month of year. Concerning meteorology, the hour is critical because of the diurnal cycle of the atmospheric boundary layer, and the month is important because the season affects the temperature, wind speed, and daytime mixing height. Note that the meteorology affects not only the dispersion of the chemicals in the atmosphere but also the evaporation rate of spilled liquids in the atmosphere.

Temporal incident statistics used in CASRAM and the ERG analysis are based on HMIS database records from 1990 through 2002. Data from 2003 through 2005 were also analyzed in the course of the ERG2008 analysis, but it was determined that the additional data did not materially affect the temporal distributions, and they were therefore left unchanged from those developed for the ERG2004.

Temporal incident statistics are shown in Figures 3.1 and 3.2. The figures show the percent of incidents broken into time of day (Figure 3.1) and month (Figure 3.2). Data are shown for accident-related and en route/nonaccident releases for both highway and rail. The numbers of incidents in the statistical samples are provided in the figure legends. The incident sample differs slightly between the figures because some data fields (i.e., hour or month) are missing in a small percentage of HMIS incident records.

TABLE 3.1 Geographic Distribution of Highway and Rail Transportation Incidents Modeled in the ERG2008 Analysis, by Percentage

State	Rail	Highway	State/Province	Rail	Highway
Alabama	2.49	2.13	New Mexico	1.06	1.26
Alaska	0.18	0.10	New York	0.86	2.13
Arizona	1.34	1.37	North Carolina	2.23	2.71
Arkansas	2.57	2.87	North Dakota	0.17	0.18
California	10.63	4.25	Ohio	4.37	5.53
Colorado	1.54	1.49	Oklahoma	0.76	1.63
Connecticut	0.06	0.79	Oregon	1.49	0.93
District of Columbia	0.00	0.03	Pennsylvania	1.54	5.10
Delaware	0.12	0.20	Rhode Island	0.02	0.15
Florida	1.54	2.36	South Carolina	0.71	1.58
Georgia	2.42	2.65	South Dakota	0.02	0.20
Hawaii	0.00	0.05	Tennessee	2.35	3.29
Idaho	0.73	0.39	Texas	12.18	7.89
Illinois	5.06	4.98	Utah	2.40	1.24
Indiana	1.57	2.70	Vermont	0.01	0.14
Iowa	0.77	1.15	Virginia	1.26	1.83
Kansas	1.96	1.87	Washington	1.44	1.22
Kentucky	1.68	2.20	West Virginia	0.61	0.90
Louisiana	6.05	3.22	Wisconsin	0.29	1.50
Massachusetts	0.23	1.20	Wyoming	2.59	0.54
Maryland	0.63	1.40	----- Canada and Mexico -----		
Maine	0.12	0.27	British Columbia, Can.	0.82	0.82
Michigan	3.14	1.91	Alberta	0.63	0.63
Minnesota	0.50	1.45	Saskatchewan	0.25	0.25
Mississippi	0.86	1.60	Manitoba	0.27	0.27
Missouri	2.37	3.04	Ontario	2.51	2.51
Montana	0.54	0.30	Quebec	1.71	1.71
Nebraska	1.65	0.57	Atlantic Provinces	0.58	0.58
Nevada	0.97	0.40	Northern Mexico	1.03	1.03
New Hampshire	0.01	0.23	Central Mexico	2.69	2.69
New Jersey	0.68	1.67	Southern Mexico	0.76	0.76

3.1.5 Discharge Fraction Distributions

In the CASRAM emission model, the discharge fraction is estimated by using statistical distributions developed from an analysis of the HMIS database. HMIS records list the container type, number of containers shipped, number of containers that fail, and amount of material released. This information allowed us to statistically characterize the release amounts for containers of various types and sizes. In this process, we found that the fraction of the container capacity that is released proved to be a robust statistic in terms of both collapsing data from a wide variety of containers and ease of use in subsequent risk assessment studies. This fraction of the total container capacity that is released is defined here as the “discharge fraction.” Since the amount of material actually shipped is not currently provided in the HMIS database, the container capacity provides the best estimate of the amount shipped. As an example, consider a

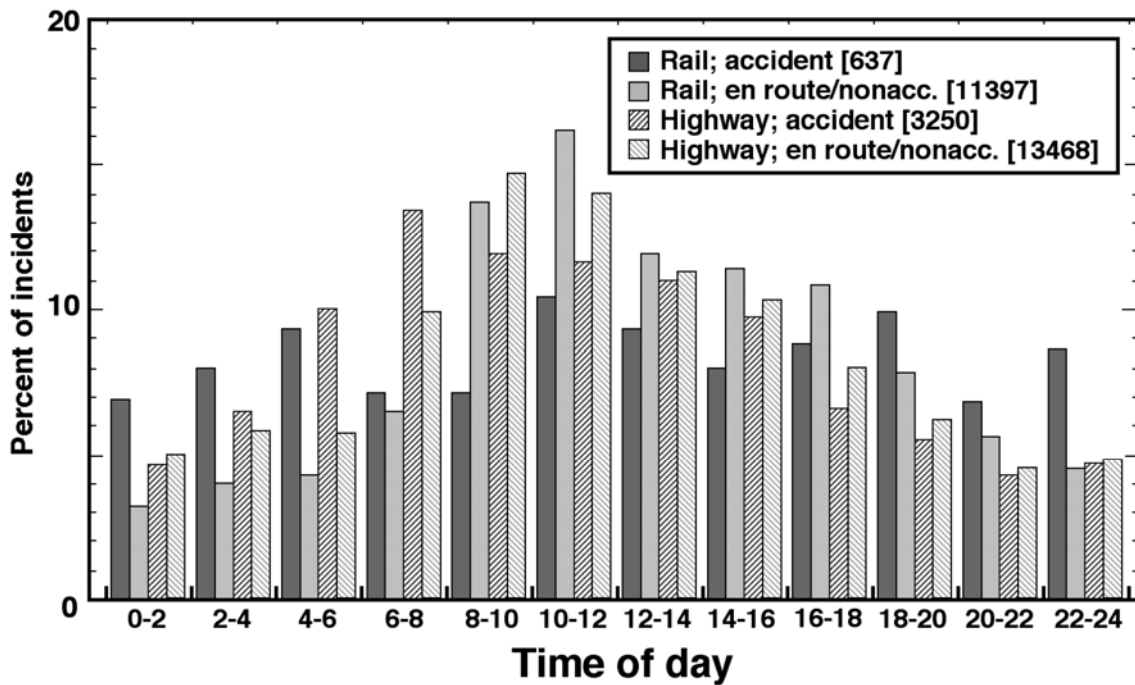


FIGURE 3.1 Hourly Distributions of Rail and Highway Transportation-Related Hazardous Material Releases Occurring during Accident-related and en Route/Nonaccident Incidents from the HMIS Database for 1990–2002

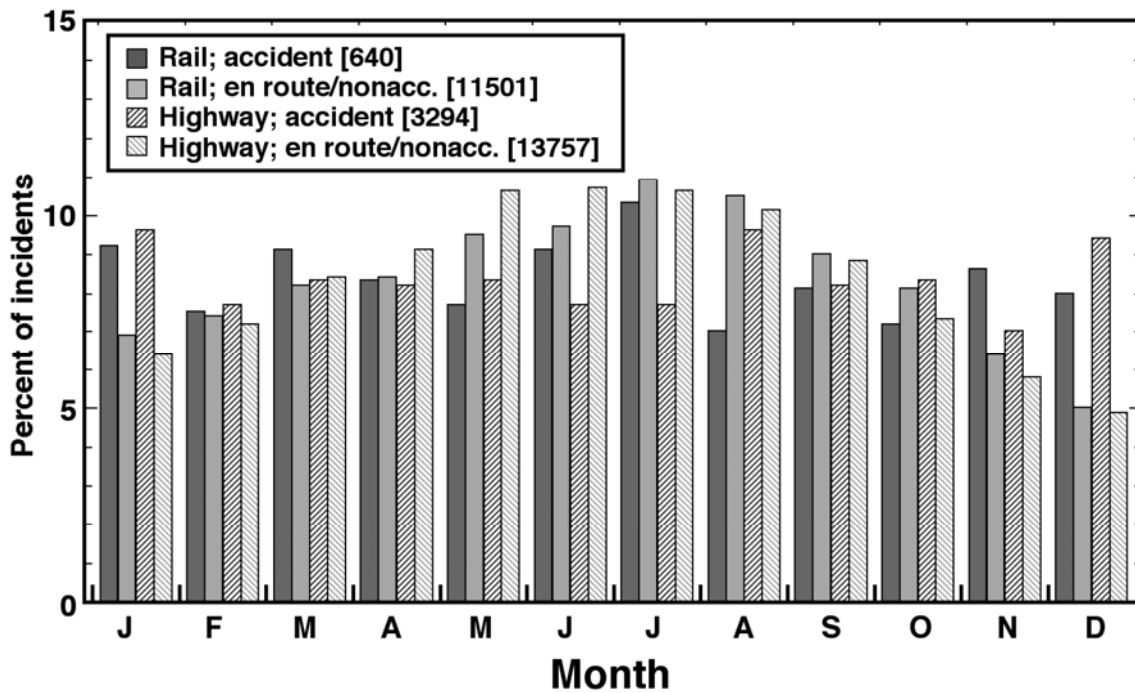


FIGURE 3.2 Monthly Distributions of Rail and Highway Transportation-Related Hazardous Material Releases Occurring during Accident-related and en Route/Nonaccident Incidents from the HMIS Database for 1990–2002

vehicular accident that involves the shipment of chlorine in a 17,000-gal Type 105A300W rail car in which 240 gal are released. The discharge fraction would be 240/17,000 or 0.014. As is discussed later, this incident would be grouped with all other incidents involving releases from pressurized rail cars (Type 105 and 112) to construct the discharge fraction distributions for accident-related releases.

In the CASRAM source model, discharge fraction statistics are segregated according to container type. In general, these container types can be classified according to whether they are used for bulk or package freight. As part of the analysis for the ERG2004, we reevaluated our previously published discharge fraction distributions (Brown et al. 2001) by using HMIS data through 2002 (Brown and Dunn 2007). Data from 2003 through 2005 were also analyzed in the course of the ERG2008 analysis, but it was determined that the additional data did not materially affect the discharge fraction distributions, so they were left unchanged from those developed for the ERG2004. The discharge fraction distributions for bulk and package freight are handled in very different ways, as described in the subsections below.

3.1.5.1 Bulk Containers

Discharge fraction statistics for bulk containers are shown in Figures 3.3 and 3.4. Figure 3.3 shows discharge fraction distributions for containers that are used for nonpressurized and low-pressure materials. Figure 3.4 shows the distributions for containers that are used for high-pressure materials. Note that not all container types shown are authorized for transport of TIH materials; these are provided for comparison and for possible use in risk assessments for other types of hazardous materials. Discharge fraction distributions are provided for the two transportation-related phases considered in the ERG analysis: accident-related and en route/nonaccident releases. Discharge fraction statistics for bulk package freight were developed for a specific container type (Type 111A tank cars, MC/DOT 312 tanks, etc.) when sufficient statistical data (i.e., data on at least 25 incidents) were available. In practice, discharge fractions for other container types for which data are insufficient could be estimated by using a surrogate for a similar container type for which data do exist. For example, the surrogate discharge fraction distribution for Type 103 tank cars would be that for Type 111A tank cars, and the surrogate for MC/DOT 338 cargo tanks would be MC/DOT 331 cargo tanks.

To facilitate their use in computational models, we developed mathematical expressions for the discharge fraction that can be employed in Monte Carlo analyses. We believe use of these functional forms is preferable to using the raw discrete distributions, as was done previously, since they eliminate discretization problems that sometimes occur in the raw distributions. Distributions for bulk containers were fit to the following functional form:

$$F(\gamma) = \min(1, e^{\zeta(\gamma)}), \quad (3.1)$$

where $\zeta(\gamma) = \sum_{n=1}^N a_n \gamma^{nb}$.

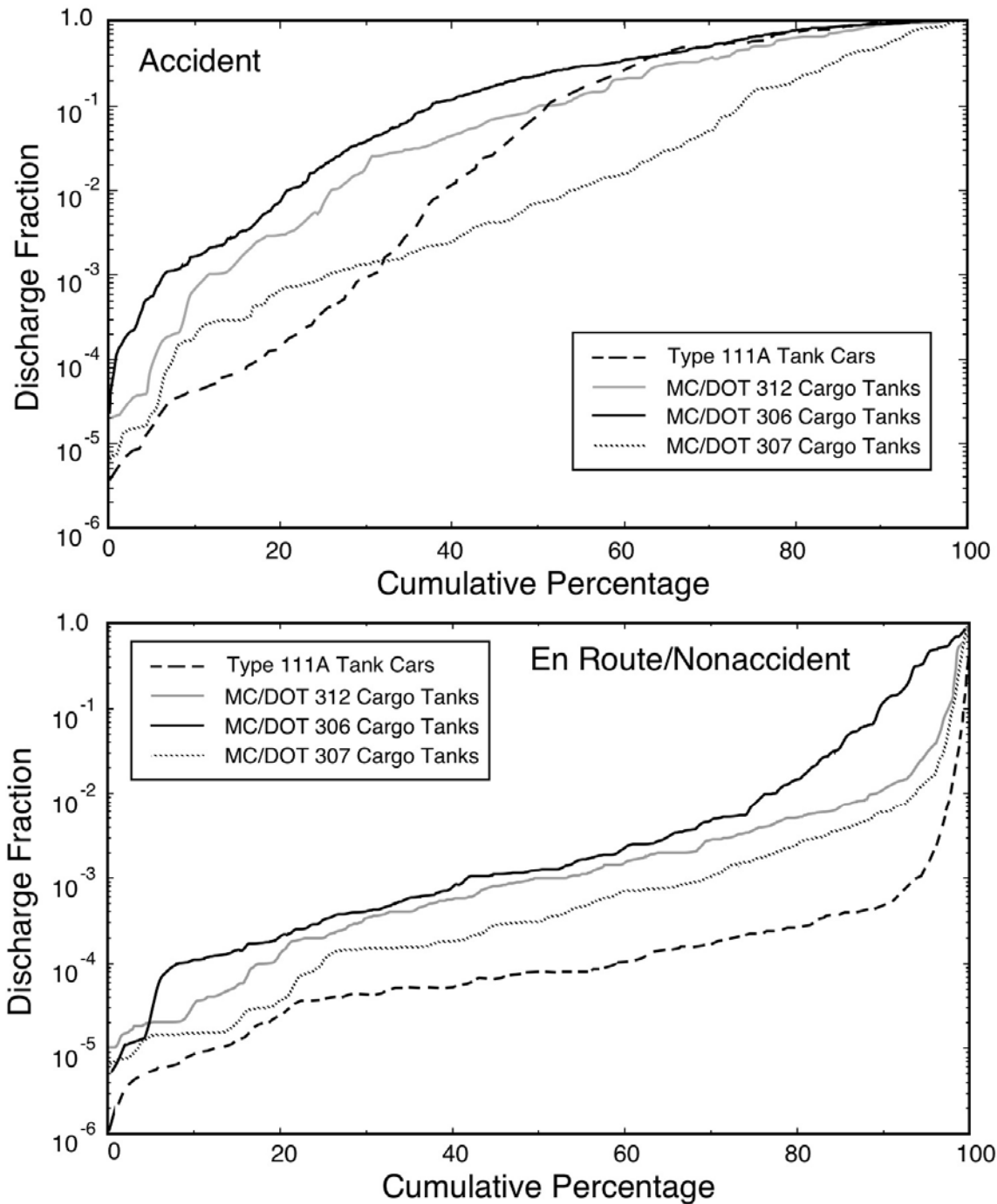


FIGURE 3.3 Discharge Fraction Cumulative Probability for Bulk Nonpressurized and Low-pressure Containers as Derived from the Analysis of the HMIS Database Used for the ERG2008 Analysis (Results are shown for accident-related and en route/nonaccident releases.)

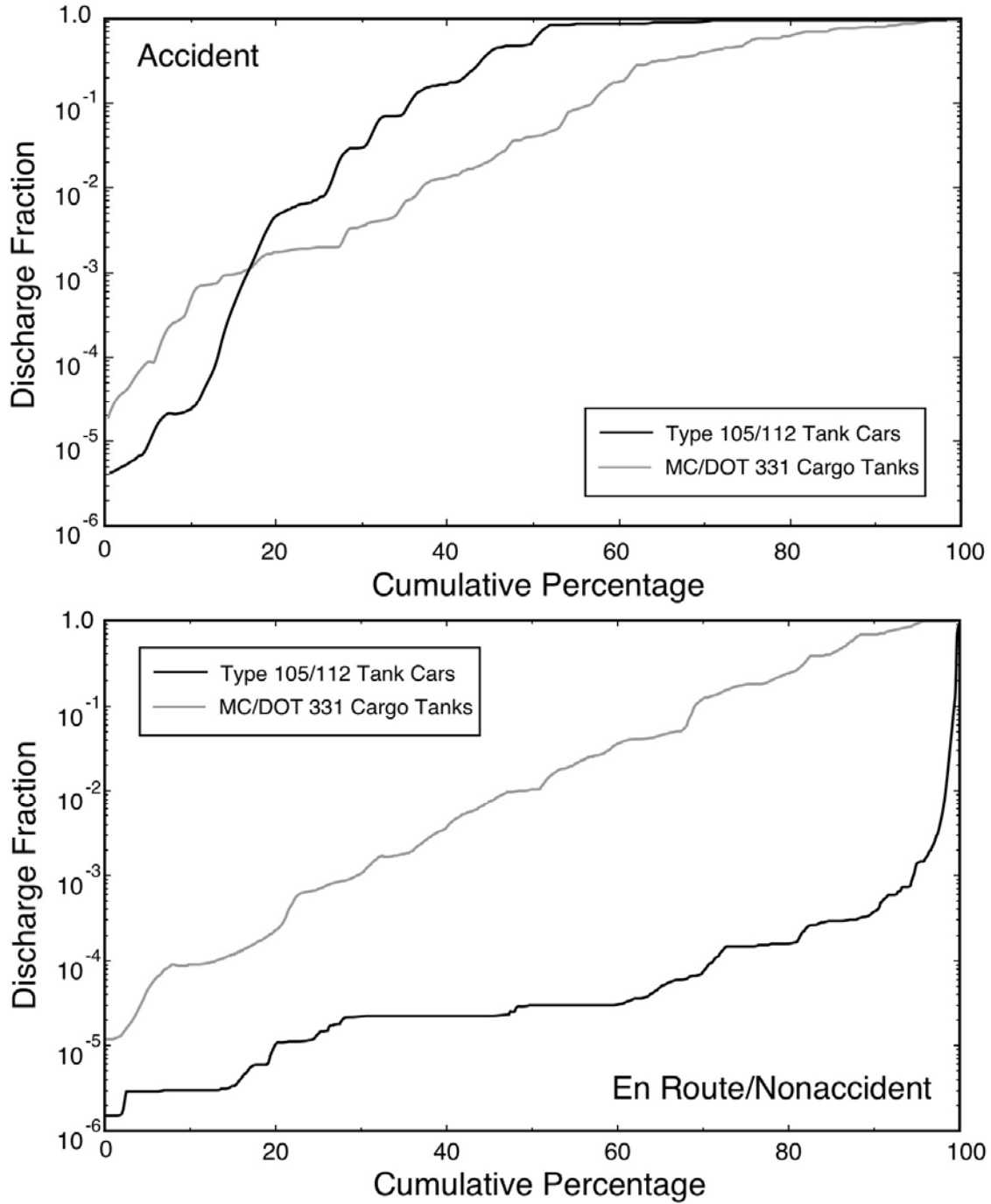


FIGURE 3.4 Discharge Fraction Cumulative Probability for Bulk Pressurized Containers as Derived from the Analysis of the HMIS Database Used for the ERG2008 Analysis (Results are shown for accident-related and en route/nonaccident releases.)

Here, F is the discharge fraction, γ is a uniform random deviate from 0 to 1, and a_i and b are coefficients that depend on container type and incident type. N , the number of coefficients a_i ($i = 1, N$) that are necessary, is either 6 or 8, depending on the complexities of the distribution, particularly near the ends. The coefficient b serves to stretch the very low probability end of the distribution and is necessary to accurately capture the frequency of rare en route/nonaccident events where a large fraction of the container capacity is released while correctly representing the remainder of the distribution. For all accident-related events, $b = 1$, and for en route/nonaccident events, b is <0.5 . The coefficients for Equation 3.1 for accident and en route/nonaccident events are listed in Tables 3.2 and 3.3, respectively.

3.1.5.2 Package Freight Containers

For package freight containers, we had previously developed discharge fraction distributions for accident-related releases that specified the total amount released as a fraction of the total container capacity (i.e., capacity of all containers combined). Discharge fraction distributions for en route/nonaccident releases were represented as the fraction of the capacity of an *individual container* in the shipment that is released (see Brown et al. 2001). One drawback of this release fraction normalization was that the distributions did not properly represent shipments that contain only a few containers. For the ERG2004 analysis, we recently revised this framework for drums and cylinders on the basis of our reanalysis of HMIS data through 2002 to specify both the (1) percentage of containers that leaked or failed and (2) discharge fraction distribution applicable to each failed container. In addition, for accident-related incidents, we specified a probability that the entire shipment was released. Since almost all cases of practical interest in evaluating inhalation hazards from package freight shipments involve drums or cylinders, we limited our discharge fraction framework for these two classes of containers.

We divide our discussion below into accident-related and en route/nonaccident releases since the methods employed to treat these cases are substantially different.

Accident-related Releases. The first step in the analysis framework is to determine the percentage of cases in which the entire shipment amount is released. Typically, only a few containers of a multiple container shipment are compromised in a traffic accident. However, in more serious accident-related events, the entire shipment can be released. A complicating factor, though, is that the probability of the entire shipment being released decreases as the number of containers in the shipment increases. Table 3.4 shows the number of accident-related incidents catalogued in the HMIS database for 1990 through 2002 involving metal drums, and it also shows the number of these cases in which more than 90% of the total shipment amount was released. In more than half of the incidents involving a single metal drum, the entire shipment contents were released; in shipments containing multiple drums, the percentage of such releases decreased to 10%. Table 3.5 shows identical information for cylinders, for which a similar trend was found. Note that the total incident counts are rather low, especially for cylinders, so there is significant statistical noise in these data.

TABLE 3.2 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions for Accident-related Releases for a Variety of Containers (Coefficients were developed from the analysis of the HMIS Database used for the ERG2008 analysis.)

Container	b	a ₁	a ₂	a ₃	a ₄	a ₅	a ₆	a ₇	a ₈
Type 111A tank cars	1	-12.2825	25.2135	-97.7815	382.86	-468.648	-106.407	513.26	-235.777
Type 105/112 tank cars	1	-13.5011	29.0148	64.2486	-235.971	223.212	-65.2201	0	0
MC/DOT 306 cargo tanks	1	-8.02475	6.20446	104.348	-325.183	284.727	149.822	-358.121	146.299
MC/DOT 307 cargo tanks	1	-12.5422	50.5658	-169.235	257.71	-84.3257	-130.654	108.216	-19.6658
MC/DOT 312 cargo tanks	1	-11.3375	43.4848	-101.806	149.477	-112.577	32.859	0	0
MC/DOT 331 cargo tanks	1	-10.8601	43.6839	-181.754	440.336	-466.95	175.992	0	0

TABLE 3.3 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions for en Route/Nonaccident Releases for a Variety of Containers (Coefficients were developed from the analysis of the HMIS Database used for the ERG2008 Analysis analysis.)

Container	b	a ₁	a ₂	a ₃	a ₄	a ₅	a ₆	a ₇	a ₈
Type 111A tank cars	0.5	0.624664	-44.0097	39.2814	150.665	-334.474	50.9987	318.078	-194.708
Type 105/112 tank cars	0.33	20.2316	-171.317	379.325	-285.744	-97.0904	46.2262	278.699	-184.156
MC/DOT 306 cargo tanks	0.33	4.67339	-71.6677	378.743	-859.395	610.244	368.827	-653.445	210.363
MC/DOT 307 cargo tanks	0.36	4.46934	-41.2228	51.6474	-6.432	-32.2012	5.55689	11.7468	-5.51775
MC/DOT 312 cargo tanks	0.4	4.15943	-39.2797	54.9507	-21.9882	-17.3163	5.09395	16.6091	-13.8431
MC/DOT 331 cargo tanks	0.5	0.338613	0.285349	-6.47588	-5.23065	0	0	0	0

TABLE 3.4 Incident Counts Involving Drums in Accident-related Releases in the HMIS Database (1990–2002), Showing the Number in Which More Than 90% of the Total Shipment Amount Was Released

Number of Drums in Shipment	Total Number of Incidents	Number with >90% Release
1	25	14
2–5	26	3
6–10	36	3
10–20	42	3
20–50	27	1
>50	37	4

TABLE 3.5 Incident Counts Involving Cylinders in Accident-related Releases in the HMIS Database (1985–2002), Showing the Number in Which More Than 90% of the Total Shipment Amount Was Released

Number of Drums in Shipment	Total Number of Incidents	Number with >90% Release
1	22	12
2–5	14	2
>5	13	3

To account for these maximum release events in a robust manner, we first select a fraction of the incidents for which the entire shipment is released. The percentages of such incidents are 10% and 25% for shipments of drums and cylinders, respectively. In practice, these are the limiting cases, as the number of containers becomes large. The increase in the percentage of total releases in which more than 90% of the shipment is released, which occurs for shipments involving small numbers of containers, is accounted for in the second analysis step detailed below.

For the remainder of the shipments, we then specify the number of failed containers N_f as

$$N_f = N_s \gamma^{N_s^a}, \quad (3.2)$$

where N_s is the number of containers shipped, γ is a uniform random deviate from 0 to 1, and a is a coefficient. In this expression, N_f is an integer that is rounded up from the value on the right-hand side.

The total amount of material released is then written as

$$F = \min\left(1, \sum_{i=1}^{N_f} [c_1 + c_2\gamma_i + c_3\gamma_i^{d_3}]\right), \quad (3.3)$$

where γ_i is a set of independent (i.e., uncorrelated) uniform random deviates from $i = 1, N_f$, and c_1, c_2, c_3 and d_3 are constants, the values of which, along with a in Equation 3.2 above, are provided in Table 3.6. Note that each failed container is treated independently in Equation 3.3.

En Route/Nonaccident Releases. From a statistical perspective, en route/nonaccident events are fundamentally different from accident-related events. Like bulk transportation, the total release amounts are typically very small compared with accident-related releases. En route/nonaccident events are also much more common, as evidenced from HMIS statistics presented previously in Table 2.1. Usually only one container is involved, even in shipments with large numbers of containers. Tables 3.7 and 3.8 provide incident counts involving drums and cylinders, respectively, from en route/nonaccident releases in the HMIS database (1990–2002), together with the number that involved only one container and, for comparison with Tables 3.4 and 3.5, the number in which more than 90% of the total shipment amount was released.

To treat the discharge fraction estimation problem for these events, we take an approach similar to the one we take for accident-related events. We first split out those events where only one container is involved. For both drums and cylinders, we set this as 75% of incidents. For the other 25% of incidents, we calculate the number of failed containers with Equation 3.2, with different values for the coefficient a . Then for all incidents, we use Equation 3.3 again, with different values for the coefficients. The coefficients for Equations 3.2 and 3.3 for en route/nonaccident releases are provided in Table 3.9.

TABLE 3.6 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions in Equation 3.3 for Accident-related Releases Involving Drums and Cylinders (Coefficients were developed from the analysis of the HMIS Database used for the ERG2008 analysis.)

Container	a	c ₁	c ₂	c ₃	d ₃
Drums	0.5	0	0	2.0	1.5
Cylinders	0.65	0	0.167	3.1	3.5

TABLE 3.7 Incident Counts Involving Drums in en Route/Nonaccident Releases in the HMIS Database (1990–2002), Showing the Number That Involved Only One Container and the Number in Which More Than 90% of the Total Shipment Amount Was Released (for Comparison with Table 3.4)

Number of Drums in Shipment	Total Number of Incidents	Number Involving One Container	Number with >90% Release
1	730	730	63
2	335	291	3
3–5	552	491	2
5–10	464	403	1
10–20	399	345	0
20–50	437	337	0
>50	705	472	0

TABLE 3.8 Incident Counts Involving Cylinders in en Route/Nonaccident Releases in the HMIS Database (1990–2002), Showing the Number That Involved Only One Container and the Number in Which More Than 90% of the Total Shipment Amount Was Released (for Comparison with Table 3.4)

Number of Cylinders in Shipment	Total Number of Incidents	Number Involving 1 Container	Number with >90% Release
1	37	37	16
2–5	45	38	0
> 5	43	28	1

TABLE 3.9 Coefficients for Calculating Discharge Fraction Cumulative Probability Distributions in Equation 3.3 for en Route/Nonaccident Releases Involving Drums and Cylinders (Coefficients were developed from the analysis of the HMIS Database used for the 2008ERG analysis.)

Container	a	c ₁	c ₂	c ₃	d ₃
Drums	0.75	0.0025	0	1.23	4.0
Cylinders	0.75	0	0.167	3.5	4.5

3.2 METEOROLOGICAL DATABASE USED TO PREPARE THE GUIDEBOOK

The meteorological database is a critical component of the ERG2008 analysis since it provides the historical meteorological data necessary to model hazardous material incidents anywhere in the United States, Canada, and Mexico. This database was generated directly from five years of observational data from 105 cities in the United States and with supplemental data from several stations in Canada and Mexico. The data were first preprocessed by using the Surface Energy Budget Meteorological (SEBMET) model (Brown 1997; Brown and Dunn 1998). This meteorological preprocessor was designed for use with statistical dispersion studies such as the ERG analyses. A meteorological preprocessor contains a series of algorithms that use routinely measured observations of wind speed, temperature, humidity, and cloud cover, along with upper-air temperature soundings, to calculate the key parameters related to the atmospheric boundary layer needed to model source thermodynamics, transport, and dispersion. The following sections first discuss the raw meteorological data used in the analysis and then provide a brief overview of SEBMET's methodology. They then describe a companion database employed to estimate water temperature for analysis of water-reactive spills.

3.2.1 Meteorological and Site Data

For the ERG analysis, CASRAM uses a meteorological database that includes hourly meteorological parameters from 105 U.S. cities in 1985 through 1989 (as illustrated in Figure 3.5) and supplemental data from several stations in Canada and Mexico. The stations were chosen to provide a roughly uniform coverage area. Raw meteorological data included yearly surface files listing hourly values of wind speed, temperature, cloud cover (height and fraction), dew point temperature, pressure, and visibility, among other variables. In addition, upper air data from 80 stations across North America were employed to evaluate the atmospheric temperature profile up to the 7,000-m altitude necessary for determining the daytime mixing height. Site characteristics determined for each station included land cover, vegetative types, the monthly leaf area index (a measure of the canopy density) for each vegetative type, roughness length, albedo, and soil types. These site-specific parameters were determined through a climatological study of the areas surrounding each site.

3.2.2 Meteorological Preprocessor

The meteorological preprocessor contains two primary components: a surface energy budget (SEB) model that determines the surface-layer turbulence parameters and an integral model that determines inversion height in convective conditions. Each component is briefly outlined below. Brown (1997) and Brown and Dunn (1998) contain additional information on the meteorological preprocessor, including details on its development and validation.



DBA10017

FIGURE 3.5 Locations of the 105 National Weather Service Stations Used for Statistical Meteorological Characterization

3.2.2.1 Surface Turbulence Parameters

The surface-layer parameters are determined by using an SEB model that consists of parameterizations of the various SEB components and well-known flux-profile relationships. The goal of this modeling approach is to isolate the sensible heat flux H from the other energy budget components. The starting point for this analysis is the SEB at the ground. When advection, photosynthesis, and snow melt are neglected, the SEB is most simply represented as follows:

$$Q^* = H + \lambda E_w + G + Q_a, \quad (3.4)$$

where

Q^* = net surface radiative heat flux,

G = conductive soil heat flux,

λ = heat of vaporization for water,

E = evaporation rate (together, λE_w is the latent heat flux), and

Q_a = anthropogenic heat flux.

The net surface radiative heat flux is the residual from the absorbed solar radiation S , incoming long-wave radiation L^+ , and outgoing long-wave radiation $\epsilon\sigma T_s^4$. It is written as follows:

$$Q^* = (1 - \alpha_s) S + L^+ - \epsilon_s \sigma T_s^4, \quad (3.5)$$

where

α_s = surface albedo,

ϵ_s = surface emissivity,

σ = Boltzmann constant, and

T_s = surface temperature.

At the surface, the short-wave balance is always positive, while the outgoing long-wave radiation generally exceeds incoming long-wave radiation. The model is constructed by parameterizing each of the components in the SEB in terms of routinely observed meteorological observations and site characteristics. A brief description of the SEB component parameterizations is presented below.

Incoming solar radiation at the surface is determined by using a variation of the Parameterization C model (Iqbal 1983). In this model, the solar radiation incident on top of the atmosphere is determined from earth-sun relationships and then adjusted via transmittance functions to account for atmospheric absorption and scattering. Separate transmittances are specified for (1) absorption due to (a) ozone, (b) water vapor, and (c) aerosols and for (2) scattering due to (a) Rayleigh particles (molecules) and (b) aerosols. In addition, the model accounts for multiple reflections of solar radiation between the ground and the atmosphere, which significantly increase solar radiation when the surface albedo is high (e.g., deserts or snow cover). Along with data on location and time, the model requires data on (1) local atmospheric pressure; (2) surface albedo; (3) visibility; (4) precipitable water content, which is derived from upper-air data; and (5) ozone amount, which is estimated from latitudinal-seasonal averages. Attenuation due to cloud cover is estimated from the opaque and total cloud cover and cloud height by a semi-empirical model that was developed by Brown (1997) from an analysis of the National Solar Radiation Database (NREL 1992).

Net long-wave radiation at the surface is determined by using data on surface temperature, emissivity, near-surface temperature profiles, and humidity profiles. In particular, incoming long-wave radiation is estimated on the basis of a semi-empirical relationship developed from parameterizing long-wave radiation estimates from a detailed narrow-band radiation model. This relationship relies on data on the near-ground temperature profile, 10-m

water vapor pressure, cloud fraction, and cloud height. Outgoing long-wave radiation is represented directly by using ground and foliage temperatures that are solved for in the model.

At the surface, the solar radiation and incoming long-wave radiation are balanced against the (1) sensible heat transfer, (2) latent heat transfer, (3) ground conduction heat transfer, and (4) outgoing long-wave radiation. To provide a physical, unified treatment valid under both daytime and nighttime conditions, SEBMET employs a two-layer canopy model that evaluates energy transfer components from both the ground and the vegetative layer. The model is formulated by writing separate energy-balance relationships for the ground and the vegetative canopy similar to Equations 3.4 and 3.5 and by parameterizing the energy transfer components in terms of available meteorological measurements and known vegetation and ground characteristics. The vegetative layer is characterized by the leaf area index and the bulk stomatal resistance, which is a measure of the latent heat transfer resistance. The key parameter is the bulk stomatal resistance, which embodies the physiological response of the vegetation to the ambient environment. In the SEBMET canopy model, this parameter is estimated by modeling the stomatal responses to (1) ambient temperature, (2) vapor pressure deficit, (3) solar radiation, and (4) moisture stress. Evaporation from the soil is considered by defining a moisture store in the soil layer that is reduced through evaporation and replenished by precipitation. The outgoing long-wave radiation is estimated directly from the canopy and ground temperatures and the canopy coverage percentage. Heat conduction into the ground is estimated by using a numerical, finite-difference algorithm that allows the dependence of soil properties and the insulating effect of overlying vegetation and snow to be explicitly treated. Such a scheme allows the ground temperature profile to be saved for use in pool evaporation calculations in the CASRAM emission rate model.

3.2.2.2 Inversion Height and Boundary Layer Height

The inversion height in convective condition is estimated with a one-dimensional model of the atmospheric boundary layer based on the Driedonks slab model (Driedonks 1982). In the Driedonks model, as in similar models, the surface turbulence fluxes u_* and H are integrated over time so the boundary layer evolves from an initial early morning height. The Driedonks model was chosen because of its comprehensive treatment of dynamics at the inversion, favorable comparison with field data, and ease of inclusion in the preprocessor.

In neutral and stable conditions, the boundary layer height is less well defined. Generally, the boundary layer height, at least in stable conditions, is taken to be the height at which surface-induced turbulence drops to a negligible value. Here, the diagnostic relations for stable conditions defined by Nieuwstadt (1981) and provided by the neutral limit ($h = 0.3u_*/f$, where f is the Coriolis force) are used, following the recommendations of Hanna and Paine (1989). (Hanna and Paine recommend that the neutral relation be used when L is greater than or equal to 100 and that Nieuwstadt's relation be used when L is more than zero but less than 100.)

3.2.3 Water Temperature for TIHWR Reaction Rates

As discussed in Section 3.3.3, the most sensitive environmental variable affecting reaction rates of spilled chemicals with water is temperature. In general, the reaction rate roughly doubles for every 10°C increase in temperature. To account for this effect in our statistical hazardous materials analysis, we developed a database for water temperature as a function of location and Julian day. We investigated the following three sources of water temperature data:

1. *Great Lakes Buoys (GLBs)*. Data were available from eight buoys scattered throughout the Great Lakes, whose reported temperatures yielded a multiyear average that was parameterized as a function of Julian day (Lesht and Brandner 1992).
2. *U.S. Geological Survey (USGS) Water Quality Network (WQN)*. The USGS gathered data on stream water temperatures for periods of up to 30 years before 1990 at about 680 water stations (the WQN data). The data were for uneven durations and taken at uneven frequencies. In the best cases, monthly temperature values were recorded for a period of 20 years or more. For most stations, the day of the month and the time of day on which measurements were recorded varied, and about one month elapsed between measurements.
3. *National Oceanic and Atmospheric (NOAA) Ocean Harbor Buoys*. Data from a series of harbor buoys along the Atlantic and Pacific Coasts were recorded for years. Data from a representative set of locations were examined and found to substantively agree with the USGS data as a function of latitude. Therefore, the harbor buoy data were not specifically used for this study.

Stations were selected to meet several criteria. We wanted the network of stations to cover the United States evenly, or, if concentrated, to represent population centers. We needed data from a period of 20 years to permit meaningful climatological modeling. In actuality, while the target was about 240 temperature values, we chose stations that had recorded between about 150 and 450 values. Locations for WQN stations and Great Lakes Buoys used in preparation of ERG2008 are shown in Figure 3.6.

We used a special parameterization of average GLB values by Julian day published by Lesht and Brandner (1992) for this study. For each WQN station or harbor buoy, the full set of values was fitted to the following equation:

$$T(J) = T_{avg} + (\Delta T) \sin \left(2\pi \frac{J - J_o}{365} \right). \quad (3.6)$$

The values of T_{avg} , ΔT , and J_o were fitted to all of the values. The GLBs were fitted with a six-parameter function given by Lesht and Brandner (1992). Because the formula has six adjustable constants and is somewhat detailed, it is not provided here. Interested readers are referred to the Lesht and Brandner (1992).

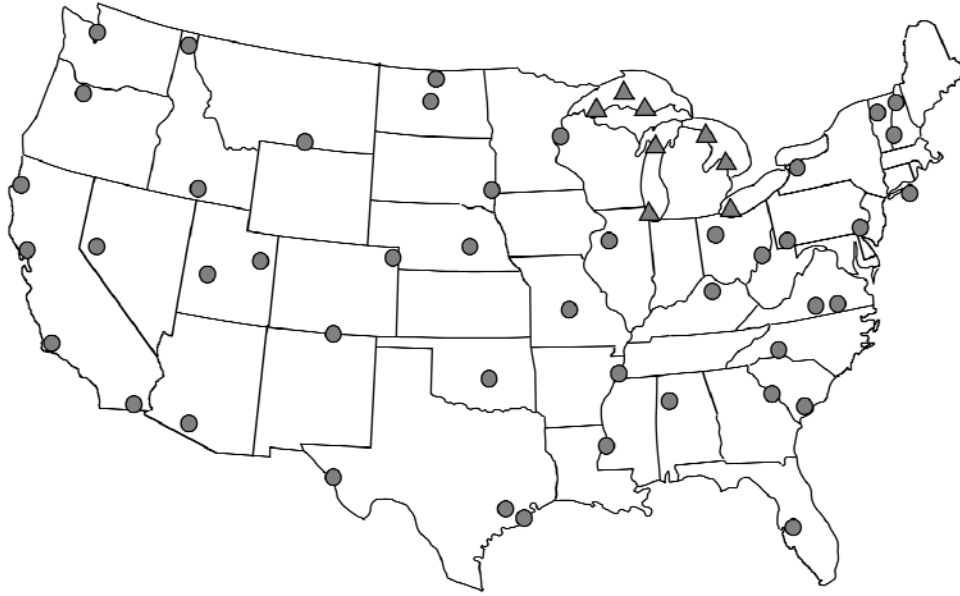


FIGURE 3.6 Water Quality Network Stations Used to Determine Variations of Average Water Temperature by Julian Day and Location (circles = 45 land-based sampling sites; triangles = 8 GLBs)

3.3 EMISSION RATE CHARACTERIZATION

3.3.1 Overview of Release Types

Materials are shipped as either (a) solids, (b) ordinary liquids, (c) compressed gases, or (d) liquefied gases. The emission rate of a chemical to the atmosphere is largely dependent on the shipment state. Because of their low volatility, solids typically exhibit low emission rates. Therefore, with the exception of certain water-reactive materials, no solid materials appear on the ERG TIH list. Release mechanisms for the other shipment states (b–d above), together with water-reactive materials, are illustrated in Figure 3.7 and discussed next.

Liquid materials are emitted to the atmosphere through pool evaporation, as illustrated in Figure 3.7a. As shall be discussed shortly, the pool evaporation rate is dependent on many factors, particularly the vapor pressure of the material. For volatile liquids (high vapor pressure), the evaporation rate is often limited by the available energy, whereas for low-volatility liquids, wind speed and atmospheric stability become very important. Highly volatile liquids evaporate very quickly, sometimes cooling the pool to more than 30°C below the ambient temperature. For certain materials, the evaporating material can cool so much that it freezes.

Compressed gases are released in a so-called “blowdown” process, as illustrated in Figure 3.7b. The blowdown process usually empties the container rapidly and, in the case of severe accidents, may result in a nearly instantaneous release. All else being equal, release rates for compressed gases are many times higher than those for ordinary liquids. Exceptions to this

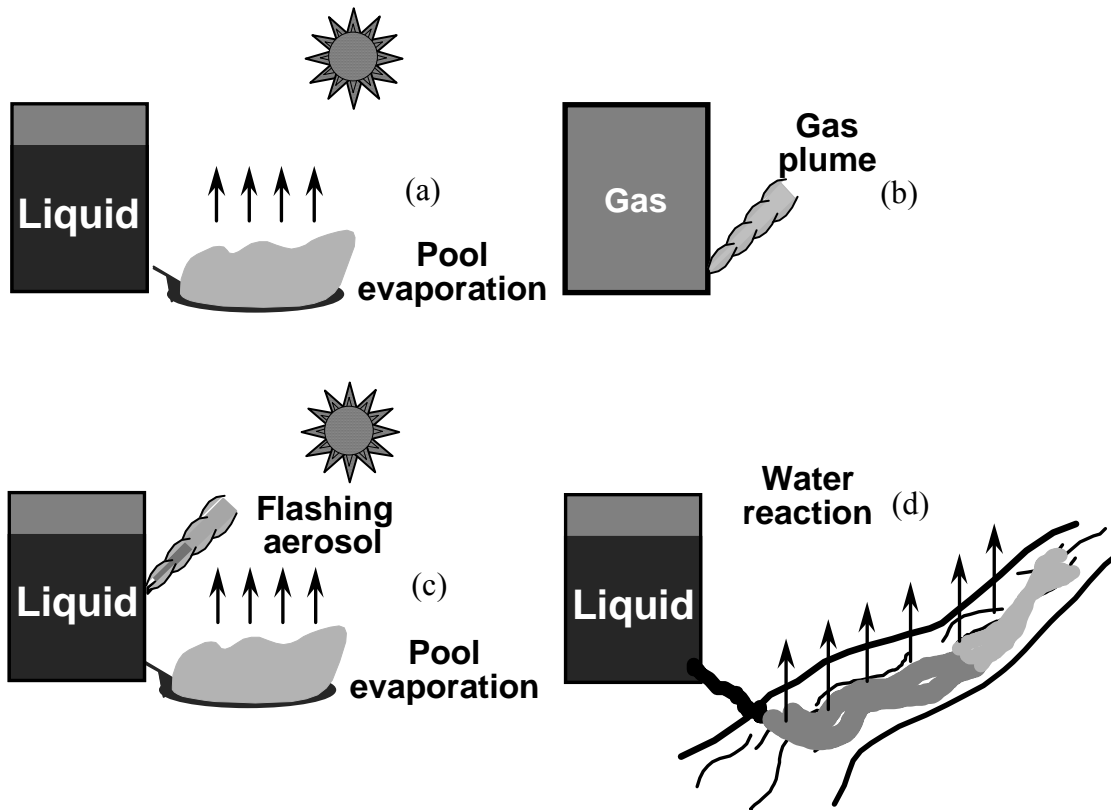


FIGURE 3.7 Important Source Types for Inhalation Risk Considered in the ERG2008 Analysis (a = ordinary liquids, b = compressed gases, c = liquefied gases, d = water-reactive materials)

rule include valve leaks and minor cracks, for which release rates may be very small. Valve leaks are the most common release mechanism for en route/nonaccident releases. With the exception of hydrogen, compressed gases are usually shipped in cylinders smaller than 100 gal.

The most catastrophic releases involve liquefied gases, as illustrated in Figure 3.7c. These materials are gases at atmospheric pressure but are liquefied through pressurization and, in some cases, refrigeration. For these materials, the release is broken into two phases. In the initial phase, denoted as the flashing and entrainment phase, a fraction of the material (usually 0–30% of the total) is instantaneously vaporized upon exiting the vessel as a result of the sudden reduction of pressure. Because of the rapid expansion of the material, much of the remaining liquid exiting the vessel is broken into tiny drops, forming an aerosol. The flashed vapor typically entrains substantial quantities of this aerosol, with the larger droplets quickly settling to the ground or “raining out.” This aerosol usually evaporates quickly when exposed to air, cooling the vapor/air mixture to the point where the density of the mixture can become considerably heavier than air. The second phase involves evaporation of the liquid that falls to the ground. Since the vapor pressures for such materials are usually well above atmospheric pressure, the evaporation phase is usually short in comparison to that for materials that are liquids at atmospheric pressure. Liquefied gases releases yield the largest overall emission rates in

comparison to liquid and compressed-gas releases and generally represent the greatest danger to the public.

An additional class of materials discussed throughout this report and treated in the ERG analysis is water-reactive materials. These materials release toxic gases to the atmosphere through the reaction of a parent chemical with water. Therefore, a water-way entry or an additional water exposure mechanism is required for them to become an inhalation hazard. The release rate of the toxic by-product to the atmosphere depends primarily on chemical reactivity, although many other factors can also influence the reaction rate. Key among these is water temperature, for higher water temperatures can greatly accelerate the reaction rate. Evidence also suggests water acidity may be important. Mixing effects also have a clear affect, for greater mixing will generally accelerate the reaction rate. Rivers are generally more turbulent than some other bodies of water and will enhance mixing and thus the TIH gas evolution rate. Also, whether the parent chemical is heavier or lighter than water (solids and some liquids) can affect the mixing rate. Finally, highly exothermic water reactions will result in faster reactions through heating and mixing and also release (typically acid) mists, which can be very corrosive and toxic.

3.3.2 CASRAM Emission Model and Its Application to the ERG2008 Analysis

The source component of CASRAM determines hazardous material release rates for each of the spill and/or vaporization scenarios described above. Information on the shipment, location, and meteorology are employed in the emission rate model to determine the amount of material spilled and the release rate. First the discharge fraction is estimated by using statistical distributions generated from analysis of HMIS database incidents, as discussed in Section 3.1.2. Then one or more physical models are employed to estimate chemical discharge rates and evaporation rates.

3.3.2.1 Assumptions Used to Develop Accident Scenarios

In developing the accident scenarios, the following assumptions were used:

- For accident-related releases from rail tank cars involving a container breach (60% of total set of such releases), the release rate of material from the container is regulated by the size of the hole, which is specified statistically according to hole size distributions presented by Raj and Turner (1993). Since no comparable data exist for highway transportation, the hole-size distributions for highway bulk containers are set to those for tank car types having similar specifications (wall thickness, insulation). Total release amounts are limited to conform to discharge fraction distributions in the HMIS database by varying the location of the hole in the container.
- For en route/nonaccident incidents and for package freight accident-related incidents, release amounts are determined directly from the HMIS database release fraction distributions. For these incidents, the release is assumed to

occur uniformly over a period of 15 min. This method overpredicts the impacts from slow leaks. However, this has no effect on values appearing in the Table, since slow vapor releases typically involve the release of small amounts of material and fall well below the 90th-percentile level of protection cutoff.

- Liquids released from the container that are not flashed or entrained with the flashed liquid form a pool of parabolic depth on the ground that expands and contracts in response to gravity-driven fluid flow and evaporation. Maximum pool depth is determined by Monte Carlo sampling for the particular incident being modeled from a clipped exponential distribution, the mean of which is set by the total volume of spilled liquid. For highway-related releases, 50% of spills are assumed to occur on paved surfaces. For rail releases, 25% of spills are assumed to occur on pavement or roadbed. All other spills are assumed to occur on natural surfaces characteristic of the accident locale. Ground temperature profiles to a depth of 1 m are provided in the preprocessed meteorological database to facilitate the ground conduction calculation, which is very important for high-volatility liquids.
- The discharge rate of water-reactive materials from their containers is varied so that 18%, 40%, 60%, and 95% of the total release amount is discharged in the first 5, 15, 30, and 60 min, respectively. The total release amounts are selected to conform with discharge fraction distributions in the HMIS database. The time-dependent emission rate of the TIH by-product from the water is calculated from the container release rate and the reaction rate of the chemical with water.
- Except for the reaction of water-reactive materials to produce TIH by-products, chemical transformation is not considered.
- The temperature of the material upon release is taken as a weighted average of the air temperature and 285 K, with the exact weight depending on the container type.

3.3.2.2 Physical Considerations

Discharge from Tanks. For liquids and liquefied gases, the first step in this process is determining the time-dependent discharge rate from the tank. Tanks punctured below the liquid line release their contents according to the Bernoulli equation (Perry et al. 1984); namely,

$$Q_t = c_o A_h \rho_l \left[2g\Delta h + 2 \left(\frac{P_t - P_a}{\rho_l} \right) \right]^{\frac{1}{2}}, \quad (3.7)$$

where

Q_l = liquid release rate (kg/s),

c_o = discharge coefficient,

A_h = hole area (m²),

ρ_l = liquid density (kg/m³),

g = gravitational acceleration (9.81 m/s²),

Δh = height of liquid above the hole (m),

P_t = tank pressure (Pa), and

P_a = atmospheric pressure (Pa).

Equation 3.7 is used to calculate the discharge rates from all bulk containers in CASRAM, where A_h is provided by the hole size distributions given by Raj and Turner (1993). Concerning the discharge coefficient c_o , experimental data show that c_o depends on the exit velocity, fluid viscosity, and hole characteristics (Perry et al. 1984). However, at high exit velocities, characteristic of the incidents modeled in CASRAM, c_o is 0.6. Therefore, we set c_o to 0.6 for all releases modeled in CASRAM. If the material is a liquid, it forms a parabolic pool (in depth) on the ground or pavement, which expands and contracts in response to gravity-driven fluid flow and evaporation. Liquefied gases, on the other hand, equilibrate to atmospheric pressure through flashing (explosive evaporation of a fraction of the released material). A fraction of the remaining material is aerosolized and entrained in the flashed vapor, and the remaining material falls to the ground and evaporates.

Pool Evaporation. Pool evaporation within CASRAM is determined by using a time-dependent, energy-budget model that accounts for the important air-pool-ground energy fluxes that govern the evaporation rate. The emission rate of material from an evaporating pool Q_e is represented as

$$Q_e = A_p E_c, \quad (3.8)$$

where

A_p = pool area (m²) and

E_c = evaporation rate from pool [kg s⁻¹ m⁻²].

Assuming that the ambient concentration of the evaporating chemical is zero, the evaporation rate is a function of the chemical vapor pressure and transfer coefficients, such that

$$E_c = h_m \frac{P_v(T_p)}{RT_p}, \quad (3.9)$$

where h_m is the mass transfer coefficient, P_v is the chemical vapor pressure at the pool temperature T_p , and R is the ideal gas constant for air. The mass transfer coefficient h_m is a function of pool size, meteorology, and chemical properties. The key variable parameter in Equation 3.9 is the pool temperature, since the vapor pressure on which the evaporation rate depends usually varies exponentially with temperature. The pool temperature (and hence the evaporation rate) is determined by using a time-dependent, energy-budget model that considers heat transfer to and from the pool via radiation, convection, conduction, and evaporation. In particular, the conductive heat flux from the ground is especially important and is often the dominant source for available energy, especially for very volatile liquids. Treating the conduction correctly, especially the initial and boundary conditions, was a principal motivation in the development of the CASRAM evaporation model.

The energy budget of the pool is a balance between solar radiation S^+ , incoming longwave radiation L^+ , outgoing longwave radiation $\varepsilon_p \sigma T_p^4$, convective heat transfer H_p , latent heat transfer of water vapor from plant material λE_{wp} , conductive heat transfer G_p , evaporative heat loss $h_{fg} E_c$, and pool energy storage $mc_p dT_p/dt$. (p subscripted variables refer to pool-specific quantities except c_p). Considering these processes, we write the pool energy budget as

$$Q_p^* = H_p + \lambda E_{wp} + G_p + h_{fg} E_c + mc_p \frac{dT_p}{dt}, \quad (3.10)$$

where Q_p^* is the net radiation given by

$$Q_p^* = (1 - \alpha_p) S^+ + L^+ + \varepsilon_p \sigma T_p^4, \quad (3.11)$$

and G_p is the ground heat flux to the pool given by Fourier's law as

$$G_p = -k_g \left(\frac{dT}{dz} \right)_{z=0}. \quad (3.12)$$

In these relationships, m is the pool mass per unit area, t is time, z is depth into the ground, ε_p is the pool emissivity, α_p is the pool albedo, k_g is the ground heat conductivity, and σ is the Boltzmann constant (5.67×10^{-8}). The necessary transfer coefficients for evaporation are provided by a chemical property database and the preprocessed meteorological database. In particular, the meteorological quantities of interest include aerodynamic resistances based on stability and wind speed, air temperature, incoming solar and longwave radiation, and the initial ground temperature profile. The relative importance of the terms in Equation 3.10 depends largely on the volatility of the chemical in the pool. For highly volatile liquids (i.e., ones that

quickly evaporate), the evaporative cooling term is large and must be balanced by the available energy provided by the net radiation, convective heat transfer, and ground conduction terms. Therefore, the amount of available energy often limits the evaporation rate for these materials. For low-volatility liquids, the evaporative cooling term is small, and the remaining terms are similar to what they would be in the absence of a pool. In these materials, evaporation is governed by the vapor pressure, wind speed, and surface turbulence characteristics.

Compressed Gas Releases. In CASRAM, compressed gas releases are modeled by using semi-empirical blowdown relationships based on compressible-flow theory. Releases are assumed to be isentropic rather than isenthalpic. The isentropic assumption is that heat transfer to the vessel is negligible, which is a reasonable approximation for most accidental releases. The isenthalpic approximation, on the other hand, requires sufficient heat transfer to maintain isothermal conditions (assuming c_p is constant).

For compressed gas releases, the release rate is calculated on the basis of hole size, tank pressure, and gas density, such that

$$Q = c_o A_h \left[P_t \rho_g \gamma \left(\frac{2}{\gamma + 1} \right)^{\frac{\gamma+1}{\gamma-1}} \right]^{\frac{1}{2}}, \quad (3.13)$$

where γ is the specific heat ratio c_p/c_v . As in the case of liquid releases, c_o is set to 0.6 for all releases.

Equation 3.13 is applicable until the tank pressure drops below a critical value, given as

$$P_r = \left(\frac{\gamma + 1}{2} \right)^{\frac{\gamma}{\gamma-1}}, \quad (3.14)$$

where P_r is ratio of the tank pressure to atmospheric pressure. After this criterion is reached, the discharge rate is given by

$$Q = c_o A_h \left[P_t \rho_g \left(\frac{2\gamma}{\gamma-1} \right) \left(P_r^{\frac{2}{\gamma}} - P_r^{\frac{\gamma+1}{\gamma}} \right) \right]^{\frac{1}{2}}. \quad (3.15)$$

Calculations are conducted iteratively by adjusting the tank pressure and density at each time step with the isentropic assumption.

Liquefied Gas Releases. Liquefied gas releases are treated by first calculating the liquid release rate from the container given by Equation 3.7. As discussed previously, this material

either flashes to vapor, is aerosolized and entrained with the vapor, or remains liquid and falls to the ground. This flash fraction f is given by

$$f = \frac{c_p(T_t - T_b)}{h_{fg}}, \quad (3.16)$$

where T_t is the tank temperature and T_b is the boiling point. This fraction of remaining material that is aerosolized and entrained into the flashed vapor is calculated by using empirical relationships based on the discharge kinetic energy of the two-phase mixture provided by Johnson and Woodward (1999). Released material that does not flash to vapor or become entrained in the vapor clouds is deposited on the ground. Evaporation of the remaining material is then estimated by using the pool evaporation algorithms.

3.3.2.3 Water-reactive Materials

For water-reactive materials, a different method is needed to estimate TIH emission rates to the atmosphere. The treatment of water-reactive materials is especially challenging for a variety of reasons. These include the following:

- Water reaction can result from spills into waterways and from other wetting mechanisms, such as rain or, in extreme cases, exposure to very high humidity.
- For waterway spills, the large variety of water body types, accident scenarios, and release characteristics adds considerable complexity to the problem.
- There is a very small amount of historical data on water entry releases, and the characterizations of water body turbulence and mixing are inadequate.
- Prior to our DOT-sponsored experimental studies, there was an almost complete lack of quantitative data with which to validate sophisticated water-reactivity models.

Our efforts to develop a robust approach for assessing the level of public protection required for TIHWR spills was initiated during the ERG1996 analysis and supplemented with an experimental program begun in the ERG2000 analysis for which 21 materials were investigated. We added experiments on 35 additional materials for the ERG2004. For the ERG2008 analysis, we developed a significantly improved experimental apparatus for investigating TIHWR materials and improved the experimental procedure, as discussed in Appendix C. We conducted experiments on 18 new materials and repeated experiments on 34 materials that had been previously investigated.

The basic formula employed to compute the release rate of TIHWR gases for most materials assumes that the reaction rate exponentially decreases with time, such that

$$Q(t) = M_o f_s \beta \lambda e^{-\lambda(t-T_{ind})}, \quad (3.17)$$

where

$Q(t)$ = time dependent release rate of TIHWR product (kg/s),

M_o = initial mass of parent chemical released into water (kg),

f_s = maximum stoichiometric yield (kg TIHWR/kg parent chemical),

β = efficiency factor for the reaction ($0 \leq \beta \leq 1$),

λ = first-order rate coefficient (s^{-1})

T_{ind} = induction time (s).

In the CASRAM source model, Equation 3.17 is discretized to yield values for ΔQ for each parcel of a parent chemical ΔM_o released into a water body. The time-dependent total evolution rate of TIH product(s) from the spill is then the sum of the individual releases arising from each parcel, where the time in Equation 3.17 is that elapsed since each parcel entered the water.

The key empirical parameters necessary to apply Equation 3.17 are β and λ , since the stoichiometric yield is easily calculated. As discussed below, an additional parameter, the induction time T_{ind} in Equation 3.17, accounts for the autocatalytic nature of the reactions for a small class of silanes. When T_{ind} is >0 , $Q(t)$ is 0 for all times until T_{ind} . Experimental data for β and λ are not available in the chemical literature. In our past efforts, an extensive search of the chemical literature yielded only qualitative descriptions of water reactivity for most of the TIHWR materials identified over the previous decade of ERG analyses. Such descriptions allow only a crude estimate of β and λ , accurate to a factor of 2 at best. Moreover, troubling inconsistencies in these qualitative descriptions were sometimes found in different literature sources. In several cases, the descriptions disagreed with the direct experience of at least one of the authors. Furthermore, we could not find any examples in which the deliberate release of a bulk chemical into a relatively large amount of water had been followed by the measurement of TIHWR production amounts.

To help provide a quantitative basis for the TIHWR analysis, we conducted a series of direct experiments on more than 70 potentially water-reactive chemicals beginning in 1999 (for the ERG2000 analysis) and continuing through the current analysis. These experiments were small in scale, which led to some substantial issues in trying to scale the results up to the size of transportation spills. Nevertheless, the experiments greatly increased the accuracy of estimates

for β and also provided a direct measure of λ , which is even more difficult to estimate from the qualitative descriptions.

In experiments conducted in 2003 and again in 2006, we found that Equation 3.17 was not adequate for fully describing the reaction for a narrow class of silanes that exhibit apparent autocatalytic reactions. For nine of these materials in our experimental series, there appeared to be an initial induction period characterized by a slow constant release rate, such that

$$Q(t) = M_o \frac{m_i}{T_{ind}}, \quad (t \text{ is } \leq T_{ind}) \quad (3.18)$$

where m_i is an initial production coefficient and T_{ind} is the induction time. For these materials, the gas evolution starts slowly and then greatly accelerates after the initial induction period, indicating the reaction is likely autocatalytic. For the ERG2004, we developed a combined evolution equation from Equations 3.17 and 3.18. However, for simplicity in treating the full range of cases treated in the ERG2008, we opted to ignore the slow initial constant release described by Equation 3.18 and instead simply use Equation 3.17 with an induction time offset. For calculations of practical interest, this simplification has no effect on the resulting hazard estimates, since release rates during the induction period are very small when compared with those after the induction period

A review of the literature on TIHWR chemicals showed that only two water body characteristics seemed likely to influence their reactions in water: acidity and temperature. For a few chemicals, the presence of acidity was reported to increase the speed and degree of the reaction. However, the characterization of these effects is not well-developed. Because of this situation, and the difficulty of obtaining water acidity data for natural water bodies, we do not attempt to account for water acidity variations in the ERG analysis. The effect of temperature is substantially stronger than the effect of acidity, however, and it is also simpler to treat in a quantitative fashion. The reaction rate of many materials roughly doubles with every 10°C increase in temperature. Fortunately, the temperature of natural water bodies is well-characterized by a network of water quality stations and buoys, as discussed in Section 3.2.3. The temperature dependence of the primary rate constant λ was included in the analysis via the Arrhenius equation, written as

$$\lambda = \lambda_o \exp \left[-6610 \left(\frac{1}{T_w} - \frac{1}{T_o} \right) \right], \quad (3.19)$$

where T_o is a reference temperature (20°C for our analyses) and T_w is the water temperature determined by the procedures outlined in Section 3.2.3. The chemical-specific constant λ_o was determined experimentally. In applying this relationship, the rate constant λ for a given hypothetical spill was specified by finding T_w on the Julian day of the simulated accident at the nearest WQN or GLB station. Then the Arrhenius formula was applied to the rate constant listed as the constant λ_o in Table C.1 in Appendix C.

3.4 ANALYSIS OF ATMOSPHERIC DISPERSION

In the atmospheric dispersion modeling phase of the problem, the hazardous material release rate and meteorology are used to estimate chemical concentrations downwind of the release. When plume buoyancy is insignificant (i.e., passive dispersion), downwind concentrations are linearly related to the (a) release rate in the event of a continuous release or (b) release amount in the event of an instantaneous release. The dispersion of the material is strongly dependent on the meteorology. In relative terms, dispersion is very good during daytime with no cloud cover (i.e., maximum surface heating) and very poor during nighttime with clear skies and light winds. Given the same emission rate, ground-level material concentrations downwind of a near-surface release can vary by three orders of magnitude between these two extremes. For moderate-to-high wind speeds and/or overcast conditions, atmospheric dispersion falls between these two limiting cases.

The dispersion method used in the ERG2008 is very similar to that employed in preparation of the ERG2004, with the only differences being minor adjustments to the horizontal dispersion coefficients and a more thorough treatment of dispersion in urban areas. For passive dispersion, we use the vertical dispersion model of Brown (1997), which is applicable for calculating ground-level concentrations from near-ground releases. For heavier-than-air or so-called dense gas releases, we use relationships from the DEGADIS model. The dense gas model is employed for liquefied gas releases in which the cooling of the plume and aerosol entrainment increase the plume density to the point where the passive dispersion assumption is no longer valid. For many liquefied gases, especially those that are highly toxic, the use of a dense gas dispersion model in the initial phases of the plume trajectory calculation does not have a significant impact on the final PAD estimates. For a narrow class of less toxic liquefied gases, such as ammonia, incorporation of a dense gas model has a more substantial effect.

We discuss some general concepts about atmospheric dispersion modeling of hazardous material releases in Section 3.4.1, then describe the CASRAM dispersion model as applied to releases of both passive and dense gases.

3.4.1 Overview of Atmospheric Dispersion

3.4.1.1 Diurnal Aspects of Plume Dispersion

The physical processes governing the development and maintenance of the atmospheric boundary layer (ABL) are very different during day and night, leading to boundary layers with extremely different sizes and characters. These marked differences substantially influence the ability of the ABL to disperse pollutants released near the ground, thereby giving rise to the pronounced differences in downwind concentrations and therefore in PAD values appearing in the Table. This section briefly describes the characteristics that distinguish the daytime and nighttime ABLs and elucidates how these variations lead to the differences in PAD values between the two cases.

The unstable or convective boundary layer (CBL), typical of daytime conditions, is shown in Figure 3.8a. The boundary layer structure is a result of the surface heating caused by solar radiation. This heating destabilizes the lower layers of the ABL, producing large convective cells. These convective cells extend vertically to the lowest temperature inversion, and they efficiently transport heat, momentum, and any material contaminants released into the atmosphere. As the day progresses, the temperature inversion marking the top of the boundary layer rises from near the ground to between 0.5 and 4 km above the surface as a result of the entrainment of stably stratified air above the inversion into the cooler air of the boundary layer below.

An example of a dispersing plume in a typical CBL is pictured in Figure 3.8b. Experimental observations, most notably those of Willis and Deardorff (1976), have indicated that vigorous convection, which typifies the CBL, results in a “rising centerline” phenomenon. In this process, energetic thermals lift the plume or cloud off the ground faster than it disperses downward. This consequence of dispersion in a fully convective boundary layer is primarily responsible for the rapid decay of material concentrations downwind from ground-level sources when the release occurs in the middle of the day.

In the absence of solar heating, the nighttime ABL structure is driven by cooling at the surface as heat is radiated to space. This situation leads to the development of a stably stratified boundary layer (SBL), which is typically much shallower and less energetic than its unstable counterpart, as illustrated in Figure 3.9a. The surface cooling strongly stratifies the low-level air, thereby creating a tenuous balance between the turbulence produced by wind shear and turbulent energy dissipation. The rapid dissipation of turbulent energy greatly limits the vertical eddy size and restricts vertical mixing.

Dispersion in a typical SBL is pictured in Figure 3.9b. The vertical stability and shallow depth profoundly affect dispersion processes by confining material contaminants to a thin layer near the ground. In very stable conditions, such as those represented in the 90th-percentile level of safe distance distributions, the SBL is usually less than 100 m deep. When a contaminant is released into the SBL, it diffuses to its maximum vertical extent in a relatively a short distance, forcing most of the dispersion to occur two-dimensionally along the ground. This plume confinement allows comparatively high concentrations to be observed near the surface at considerable distances from the release site, leading to PADs that are further from the source than are necessary for daytime incidents.

3.4.1.2 Effects of Dense Gas on Plume Dispersion

The discussion of atmospheric dispersion to this point has been confined to passive dispersion (i.e., cases in which the density of the ambient plume does not affect its dispersion). However, in many cases of practical interest, the effect of a high-density (relative to air) hazardous chemical discharge becomes important in considering impacts within 1 to 2 km of the release point. So-called dense gas effects result not only from the properties of the material released but also from the methods of storage and the conditions of the release. Most cases of interest have focused on combustibles or toxic compounds that have boiling points below

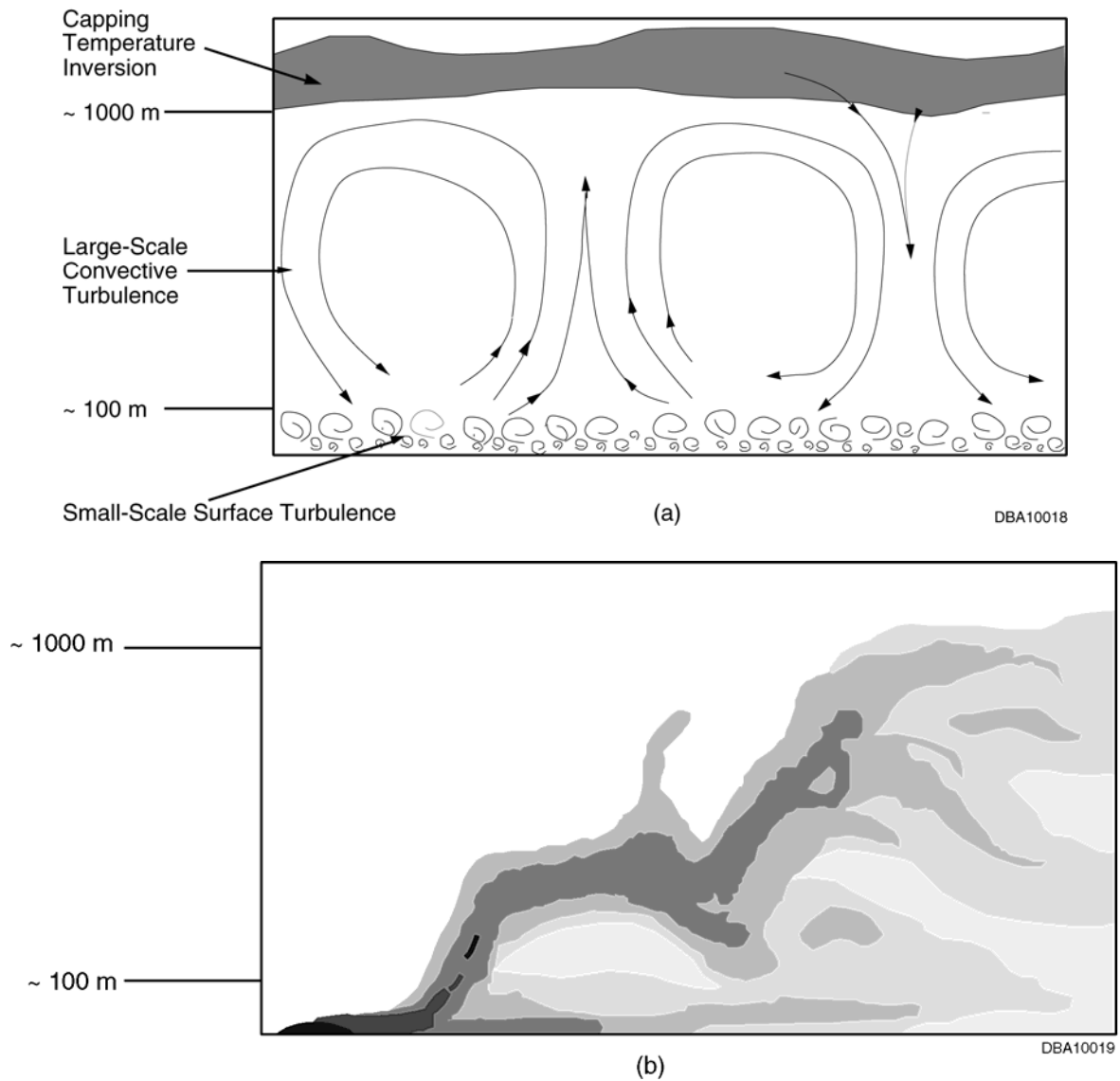
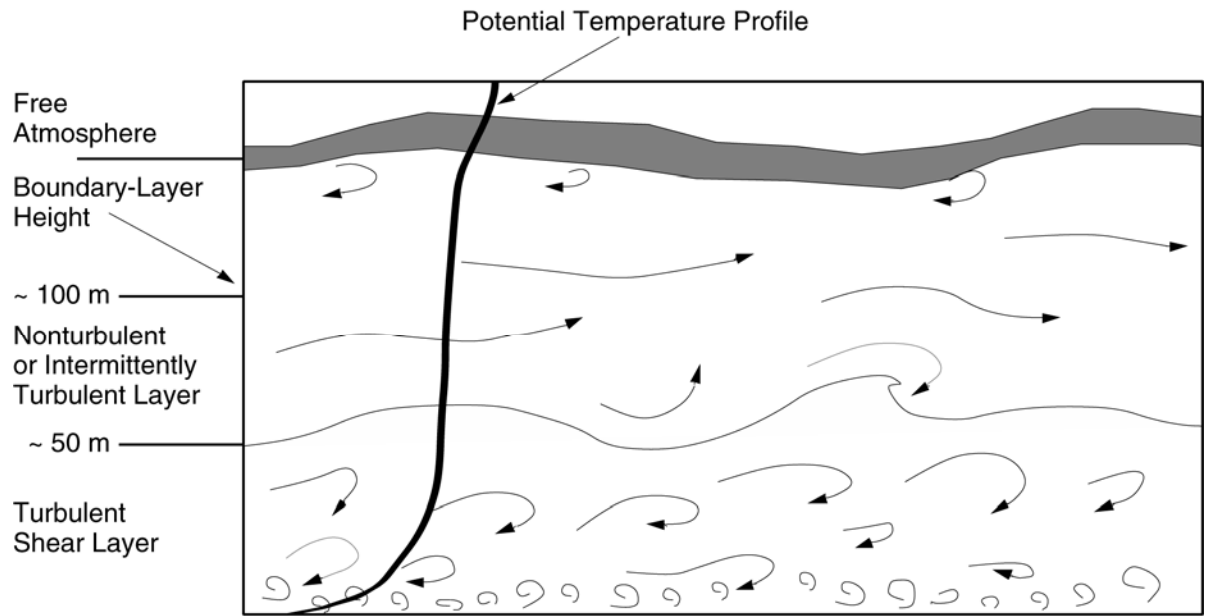
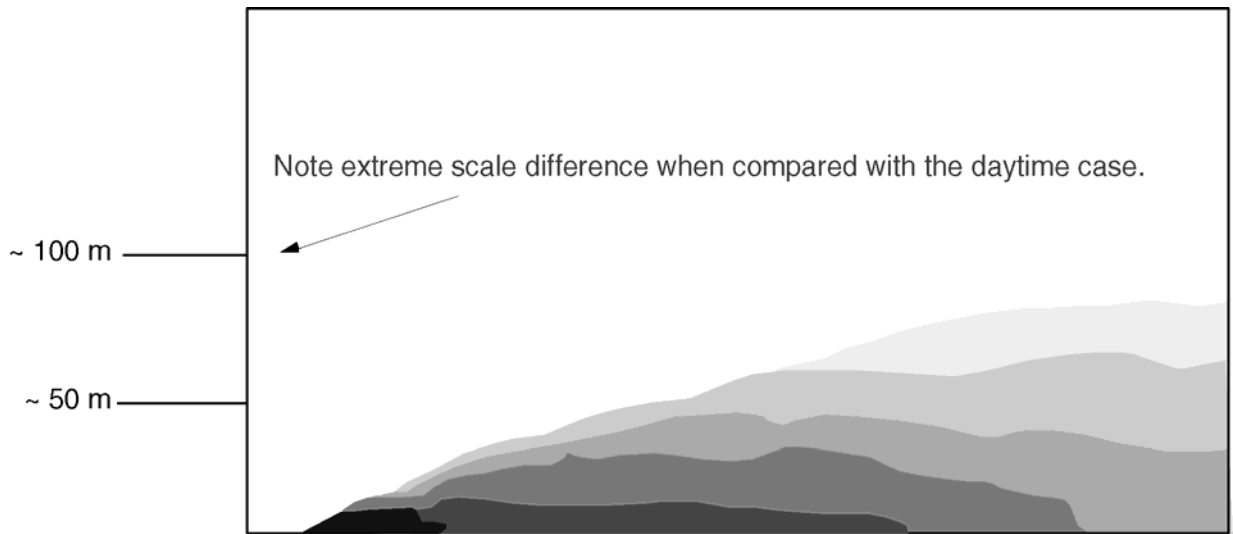


FIGURE 3.8 Typical Daytime Convective Boundary Layer Showing (a) an Instantaneous Wind Field and (b) an Instantaneous Material Concentration Field from a Ground-level Release (Characteristic heights of about 1,000 m for the boundary layer and about 100 m for the surface layer are provided for reference.)



(a)

DBA10020



(b)

DBA10021

FIGURE 3.9 Typical Nighttime Stable Boundary Layer Showing (a) an Instantaneous Wind Field and (b) an Instantaneous Material Concentration Field from a Ground-level Release (Characteristic heights of about 50 m for the surface shear layer and about 100 m for the boundary layer are provided for reference.)

ambient temperature. These compounds are commonly transported or stored as liquids and then maintained in liquid phase (1) at or near their saturation temperature at atmospheric pressure by refrigeration and insulation (i.e., refrigerated liquid) or (2) at ambient temperature by pressurization (i.e., pressurized liquid or liquefied gas). For transportation incidents, cases that could lead to significant dense gas effects fall into one or more of the following broad categories:

- Chemicals with a high molecular weight when compared with air (e.g., chlorine, arsine) coupled with a large release quantity or high release rate (i.e., much greater than 1 kg/s);
- Refrigerated chemicals with a relatively low molecular weight when their temperature upon release is cold relative to the ambient temperature (e.g., a cold methane release evolving from the boiling of refrigerated liquefied natural gas);
- Pressurized liquids containing chemicals with a low to moderate molecular weight that, although they are less dense than air at their boiling point, cool rapidly and entrain aerosol generated in the release process, thereby creating a denser-than-air plume; and
- Chemicals that undergo molecular association (hydrogen fluoride [HF]) and/or transform to secondary hazardous compounds because of their ambient water-vapor reactivity (e.g., sulfur trioxide [SO₃]/oleum, nitrogen tetroxide [N₂O₄]). (These are not necessarily the same group of compounds that are water-reactive as defined in this report.)

Several major effects can be observed during the dispersion of a ground-level, dense gas cloud that do not occur during the dispersion of a neutrally buoyant cloud. One is that there is much less vertical turbulent mixing between the dense gas cloud and the ambient atmosphere because of the strong stable density stratification of the cloud relative to the surrounding ambient air. Another is the presence of gravity-induced flow resulting from horizontal density gradients. These two effects result in a shallower and much wider cloud than the cloud that results from an analogous neutral density release. In addition, the movement of the dense gas cloud on uneven terrain can follow the downhill slope independent of the wind direction, and the cloud can become trapped in valleys or low spots. The magnitudes of these dense gas effects depend on the size of the release, local meteorological conditions, and physical properties of the chemical release.

As the dense plume travels downwind, the plume warms through ambient heating (e.g., from sunlight, ground heating) and entrainment of warmer air. At some downwind distance, the density of the plume will decrease to the point where the density can no longer retard the vertical dispersion of the plume by ambient turbulence, and the plume will subsequently disperse as a passive cloud.

3.4.2 CASRAM Dispersion Model

3.4.2.1 Passive Dispersion

Like many other dispersion models, CASRAM separates the dispersion calculation into two components: horizontal dispersion and vertical dispersion. In CASRAM, vertical turbulent dispersion is treated with a Lagrangian-integral model parameterized in terms of mean plume height, average advection velocity, and a dimensionless travel time. These parameters are expressed as integral equations written in terms of plume travel time and atmospheric boundary layer parameters. Continuous releases are treated as plumes, and instantaneous releases are treated as puffs. Horizontal turbulent dispersion is represented via Gaussian relationships that are parameterized in terms of the Lagrangian time scale and lateral wind direction fluctuations. Plume calculations are straight line in nature, since terrain effects are not currently considered in CASRAM.

The concentration relationship for continuous plume releases from point sources is represented in terms of the crosswind-integrated concentration (CWIC), chemical mass release rate Q , and traditional Gaussian expression for the horizontal plume spread. The ground-level concentration distribution is represented as follows:

$$C(x, y, z = 0) = \frac{Q\hat{C}_y(x, z = 0)}{\sqrt{2\pi}\sigma_y} \exp\left[-\left(\frac{y}{\sqrt{2}\sigma_y}\right)^2\right], \quad (3.20)$$

where

\hat{C}_y = CWIC normalized by the release rate,

σ_y = lateral plume spread, and

y = lateral distance from the plume centerline.

For releases with finite width, corresponding to large pool releases or dense gas releases as they become passive, the following expression is used:

$$C(x, y, z = 0) = Q\hat{C}_y(x, z = 0) \left(\operatorname{erf}\left[\frac{y_o - y}{\sqrt{2}\sigma_y}\right] + \operatorname{erf}\left[\frac{y_o + y}{\sqrt{2}\sigma_y}\right] \right). \quad (3.21)$$

Peak concentration averages resulting from instantaneous releases are calculated according to the relationship

$$C(x, y, z = 0) = \frac{M\hat{C}_y(x, z = 0)}{\sqrt{2\pi}\sigma_y T} \operatorname{erf} \left[\frac{UT}{2\sqrt{2}\sigma_y} \right] \exp \left[- \left(\frac{y}{\sqrt{2}\sigma_y} \right)^2 \right], \quad (3.22)$$

where

M = total release amount,

T = averaging time, and

U = 10-m wind speed.

The subsections below first present the methodology for determining vertical dispersion (i.e., for determining C_y as a function of downwind distance). They then discuss the determination of σ_y , thus providing horizontal dispersion.

Vertical Dispersion. The vertical dispersion model in CASRAM is a natural extension of the surface-layer, similarity-based model of van Ulden (1978). The van Ulden approach centered around an exact solution of the advection-diffusion equation. When written in terms of the CWIC form and neglecting stream-wise diffusion, it reads as follows:

$$U(z) \frac{\partial C_y}{\partial z} = \frac{\partial}{\partial z} \left[K_z(z) \frac{\partial C_y}{\partial z} \right], \quad (3.23)$$

where K_z is the vertical diffusivity for a scalar. The solution van Ulden advances is written in terms of the mean plume height \bar{z} , the average plume advection velocity \bar{U}_p , the power-law wind speed coefficient m , and the diffusivity coefficient n . The coefficients m and n are defined such that

$$U(z) = u_o z^m \quad (3.24)$$

and

$$K_z(z) = k_o z^n, \quad (3.25)$$

where u_o and k_o are constants representing the wind speed and diffusivity at 1 m. The advection-diffusion equation subject to the above power-law relationships yields an exact solution (see Roberts 1923; Calder 1949). The work of van Ulden (1978) extends this analysis by using the power-law coefficients to determine the concentration profile shape a priori (from the Roberts analysis) and then formulates integral relationships for the mean plume height and average advection velocity in terms of the more physically correct similarity functions for wind speed and diffusivity. The van Ulden (1978) solution reads

$$\hat{C}_y(x, z) = \frac{A}{\bar{z}U_p} \exp\left[-\left(\frac{Bz}{\bar{z}}\right)^s\right], \quad (3.26)$$

where

$$A = \frac{s\Gamma(2/s)}{\Gamma(1/s)^2}, \quad (3.27)$$

$$B = \frac{\Gamma(2/s)}{\Gamma(1/s)}, \quad (3.28)$$

and s is a shape parameter given by $1 - m - n$. In Equations 3.27 and 3.28, Γ represents the gamma function.

In applying this model, van Ulden (1978) parameterized the mean plume height and average advection velocity by using surface-layer similarity functions for wind speed and diffusivity. In a subsequent study, Gryning et al. (1983) extended this analysis by adding a sophisticated relationship to determine the shape parameter s as a function of stability and downwind distance. The relationships for s were determined through analysis of numerical solutions for the advection-diffusion equation for a wide range of conditions. In a detailed model-data comparison that used CWIC data from the Prairie Grass experiments (Barad 1958), Gryning and colleagues demonstrated the utility of the Lagrangian empirical model in representing the concentration profile as well as in estimating ground-level concentrations. This model provided an excellent description of dispersion in the surface layer. However, its application is limited to dispersion problems where the plume is confined to the surface layer. When the plume rises above the surface layer, the concentration profile given by Equation 3.26 as well as the similarity relationships for \bar{z} and $\overline{U_p}$ lose validity. For problems of practical interest, this rather severe constraint strongly limits the applicability of Equation 3.26.

Brown (1997) modified the original van Ulden work to correct this limitation. In this revised formulation, the normalized ground-level concentration is expressed as

$$\hat{C}_y(x, z = 0) = \frac{A'(\tilde{s})F(x; u_*, z_i, H_s)}{z_u \overline{U_p}}, \quad (3.29)$$

where z_u is defined such that

$$U(z_u) = \overline{U_p}, \quad (3.30)$$

and

$$A'(\tilde{s}) = \frac{1.6\tilde{s}\Gamma(2/\tilde{s})}{\Gamma(1/\tilde{s})^2}. \quad (3.31)$$

Here, A' takes the same functional form as A in van Ulden's model, except that it is multiplied by 1.6 to account for the ratio of \bar{z} to z_u and depends on a modified shape parameter denoted as \tilde{s} .

The main departure of this approach from the models of van Ulden and Gryning et al. is in the boundary-layer function F . This empirical function is added to treat dispersion within the greater ABL outside the surface layer. As previously noted, the van Ulden model was developed by using the quasi-exponential concentration profile. For surface-layer dispersion, this assumed form for the concentration profile adequately represents the concentration profiles observed in field studies, most notably the Prairie Grass experiments. However, once the plume is influenced by boundary-layer effects outside of the surface layer, the concentration profiles depart significantly from the exponential form. In unstable conditions, this departure is particularly pronounced, since the plume centerline can actually lift off the ground, creating a maximum concentration aloft. In stable conditions, the opposite effect is observed, in which the concentration profile is flattened as a result of the rapid decrease in turbulent energy with height. The transition function F allows us to adapt this methodology, which was originally developed to model surface-layer dispersion, in order to treat dispersion throughout the entire ABL.

Brown (1997) developed relationships for z_u , \tilde{s} , and F by using a parametric analysis of a Langevin-equation Monte Carlo dispersion model validated with data from field and laboratory experiments. In applying the CASRAM vertical dispersion model, \tilde{s} is a function of meteorology and therefore does not vary with distance, and F is represented as a function of travel time and meteorology. The heart of the calculation lies in z_u , which is calculated by using integral relationships represented as a function of travel time. Numerical integration of this relationship provides z_u as a function of downwind distance, which, together with \tilde{s} and F , allows the evaluation of Equation 3.24 and ultimately Equation 3.20, 3.21, or 3.22.

Horizontal Dispersion. Under horizontal homogeneous conditions, the Gaussian model correctly represents lateral concentration distributions. In CASRAM, the lateral spread from nonbuoyant releases can be related to the standard deviation of the horizontal wind fluctuations and is determined by using relationships originally proposed by Draxler (1976). Here, σ_y is given by

$$\sigma_y = \sigma_v f_y \left(\frac{t}{T_d} \right), \quad (3.32)$$

where

σ_v = standard deviation of transverse velocity,

t = transit time (estimated by using wind speed at 3 m and distance),

T_d = dispersion time scale related to the Lagrangian time scale, and

f_y = a nondimensional function of travel time.

The empirical form of f_y is estimated through evaluating field data. Several forms of f_y have been proposed (Irwin 1983; Gryning and Lyck 1984), but the empirical expression that provides the best overall fit with available field data is the form proposed by Draxler (1976). His function is given by

$$f_y = \frac{1}{1 + 0.9\sqrt{t/T_d}} \quad (3.33)$$

For surface releases, a T_d of 300 s is used for unstable conditions and a maximum of 300 s or $0.001 t^2$ s is used for stable conditions. The appeal of Draxler's relation is that it is developed from diffusion data from many experiments and that it is consistent with Taylor's limit for both small ($\sigma_y \sim t$) and large ($\sigma_y \sim t^{1/2}$) travel times (Taylor 1921).

Equation 3.32 requires the standard deviation of transverse velocity σ_v . In the absence of observational data, σ_v is determined by using the interpolation equation of Panofsky et al. (1977)

$$\sigma_v = u_* \left(12 - 0.5 \frac{z_i}{L} \right)^{1/3} \quad (3.34)$$

during unstable conditions and the proportionality relation of Panofsky and Dutton (1984)

$$\sigma_v = 1.92 u \quad (3.35)$$

during stable conditions.

In very stable conditions, Equation 3.35 fails to adequately represent σ_v , since wind speed and friction velocity become very small. For instance, if the friction velocity is about 0.015 m/s, indicative of a wind speed of about 0.5 m/s with $z_o = 0.1$ m on a clear night, Equation 3.35 predicts $\sigma_v = 0.03$ m/s. At a distance of 1 km from the source, this value of σ_v yields $\sigma_y = 36$ m from Equation 3.32. Considering the 2,000-s travel time, such a narrow plume width at ground level is not realistic when the meandering nature of stable boundary layer flows is considered. To overcome this problem, we assign a minimum value of 0.15 m/s for σ_v on the basis of observations presented by Hanna and Chang (1992).

3.4.2.2 Dense Gas Dispersion

A dense gas algorithm was added to the CASRAM methodology as part of the ERG2000 study after a detailed review of available dense gas models. The review identified five dense gas models that were well documented and would be applicable within the CASRAM framework: DEGADIS (Havens 1988), HEGADAS (Post 1994), SLAB (Ermak 1990), SCIPUFF (DTRA 1999), and TSCREEN (EPA 1992). On the basis of many considerations, the most

important being accuracy and ease of incorporation into the CASRAM framework, we opted to rely on the empirical entrainment parameterizations within the DEGADIS formulation for the CASRAM heavy gas dispersion model. As of this writing, DEGADIS is undergoing a major revision, so future applications of CASRAM for ERG-related studies will likely incorporate an updated version of this formulation.

Like the passive gas dispersion model used in CASRAM, the dense gas algorithm is integral in nature. The initial conditions are specified by the vapor release rate Q_v and aerosol release rate Q_a from the container, which are calculated from the CASRAM emission rate model. The first step is evaluating the volumetric flow rate of vapor exiting the container \dot{V}_{sv} , which is given by

$$\dot{V}_{sv} = \frac{Q_v}{\rho_v}, \quad (3.36)$$

where ρ_v is the density of the chemical vapor at the boiling point. The initial volumetric flow rate of the cloud \dot{V}_{ci} is taken as

$$\dot{V}_{ci} = (1 + \beta_{ei})\dot{V}_{sv}, \quad (3.37)$$

where β_{ei} is the entrainment parameter at the source taken as two. This is a rough estimate that depends on many factors. However, the model results at distances more than 10 to 20 m from the source are not sensitive to β_{ei} .

The initial cloud is assumed to have a flat, cylindrical shape (rectangular in two dimensions) with a width of $2r_i$ and height h_i , where $r_i = h_i$. To estimate the cloud dimensions from the volumetric flow rate, one must solve the relationship

$$h_{ci} = \frac{\dot{V}_{ci}}{2U_p r_i}, \quad (3.38)$$

where

$$\overline{U_p} = u(z = 0.6h_{ci}). \quad (3.39)$$

The solutions of Equations 3.38 and 3.39 are necessarily iterative and subject to the constraint that h_{ci} is more than 1.5 m.

The initial cloud density is then defined in terms of the sum of the mass flow rates of the “flashed” vapor and aerosol plus the entrained air as

$$\rho_{ci} = \frac{Q_v + Q_a + \beta_{ei}\dot{V}_{sv}\rho_a}{\dot{V}_{ci}}, \quad (3.40)$$

where the last term on the right side of the numerator accounts for the mass of air initially entrained into the plume.

After release, the cloud spreads horizontally under the influence of its negative buoyancy while it grows vertically through entrainment of air from above. Note that dense gas plumes are marked by a horizontal growth rate that is much higher than the vertical growth rate. The horizontal gravity spread is assumed to depend on the cloud advection speed and Richardson number for continuous releases and is computed in a form equivalent to the model of Raj (1985) such that

$$\frac{dr}{dx} = \frac{\beta_e u_*}{U_p} \sqrt{Ri_*} . \quad (3.41)$$

Here, β_e is an entrainment parameter taken as 1.15 and Ri_* is the local cloud Richardson number given by

$$Ri_* = \frac{gh_c(\rho_c - \rho_a)}{\rho_a u_*^2} . \quad (3.42)$$

Vertical cloud growth is governed by vertical entrainment of air into the cloud, which can be conveniently defined in terms of cloud advection speed and entrainment velocity v_e in the integral equation

$$\frac{dh_c}{dx} = \frac{v_e}{U_p} , \quad (3.43)$$

where the vertical entrainment velocity is as used in the DEGADIS model; namely,

$$v_e = \frac{0.4u_*}{0.88 + 0.099Ri_*^{1.04}} . \quad (3.44)$$

Equations 3.41 and 3.43 make up a coupled set of differential equations that are solved at successive points downwind of the source. The solution proceeds until the critical Richardson number Ri is less than 50. This critical Richardson number is defined differently than the local cloud Richardson number and is given by

$$Ri_c = \frac{U(h_c)(\rho_c - \rho_a)g h_c}{\rho_a u_*^3} . \quad (3.45)$$

After this Richardson number criterion is met, we initialize the passive gas dispersion model by matching the cloud height and assuming a uniform concentration across the width of the cloud of $2r$. Therefore, the parameter y_o in Equation 3.21 is set to r .

4 HEALTH CRITERIA

Over the past 20 years, various health criteria have been used to develop Initial Isolation Zones and PADs. Early efforts employed occupational exposure guidelines, such as the threshold limit values (TLVs) established by the American Conference of Governmental Industrial Hygienists (ACGIH). Beginning in 1990, the Emergency Response Planning Guidelines (ERPGs) developed by the American Industrial Hygiene Association (AIHA) were used as the criteria for evaluating the health significance of accidental releases and hence formed the basis for defining PADs. Use of the ERPGs was based on a number of factors, including the high quality of the documentation, the consensus approach upon which the values are derived, and the consideration of exposure to the general population. In the late 1990s, the AEGL values for chemicals, developed by a committee of federal, state, and private sector scientists in a manner similar to that used for ERPG development, began to be available. For ERG2008, final AEGL values are considered to be the preferred health criteria; however, ERPG values are also used for chemicals that do not have available AEGL values. In addition, for substances without AEGL or ERPG values, data on acute inhalation lethality in animals are used to develop the PADs. The acute inhalation data consist of LC₅₀ values (concentrations determined to be lethal to 50% of animals exposed) or LC₂₀ values (the lowest reported lethal concentrations).

The development of and definitions for the various health criteria used as the basis for chemical-specific PADs are described in Section 4.1, as are the findings of any expert panel reviews of the methods to identify health criteria for PAD development. Other considerations, such as data sources and exposure duration adjustments, are discussed in Section 4.2. The final health criteria used in ERG2008 for each of the substances considered (which include mainly TIH chemicals but also include some components of mixtures and some pesticides) are listed in Appendix B.

As part of the ongoing process of identifying the best applicable health criteria for the TIH chemicals, the published studies on health criteria used to evaluate accidental releases were reviewed. For the current 2008 revision of the ERG, the health criteria used to develop the PADs were reviewed to incorporate the most recent available values, and health criteria were identified for newly listed TIH substances. Also, for LC₅₀- and LC_{LO}-based health criteria, acute toxicity databases were reviewed to ascertain that the correct study was being used for each chemical, based on the methods discussed in Section 4.2.

4.1 REVIEW OF HEALTH CRITERIA DEVELOPMENT

4.1.1 Acute Exposure Guideline Levels

AEGLs are developed under the auspices of the NRC's National Advisory Committee for AEGLs for Hazardous Substances (NAC/AEGL Committee). The AEGLs are intended to describe the risk to humans resulting from once-in-a-lifetime, or rare, exposure to airborne chemicals. The NAC/AEGL Committee develops these guidelines to help both federal agencies

(e.g., DOT, NIOSH, U.S. Environmental Protection Agency [EPA], U.S. Department of Defense [DoD], U.S. Department of Energy [DOE], and Occupational Safety and Health Administration [OSHA]) and local authorities, as well as private companies, deal with emergencies involving spills or other catastrophic exposures. The NAC/AEGL Committee is composed of scientists representing federal, state, and local agencies and organizations from the private sector with an interest in emergency planning, prevention, and response programs for acutely toxic chemicals.

After AEGL values are drafted and approved by vote by the NAC/AEGL Committee, they are considered “proposed” and are published in the *Federal Register* for review and public comment (EPA 2007). Once public comments have been addressed and the NAC/AEGL Committee has voted again on the specific values, they are considered “interim” and submitted to the National Academy of Sciences (NAS)-NRC AEGL Subcommittee for review and comment. When concurrence with the NAS-NRC Subcommittee is reached, the AEGL values are considered final and published by NAS-NRC.

The AEGL values are developed for exposure times of 10 min, 30 min, 60 min, 4 h, and 8 hr and for three effect categories. The values are intended to be applicable to the general population, including infants and children and other individuals who may be sensitive and susceptible. Definitions are as follows:

- AEGL-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.
- AEGL-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.
- AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

The AEGL levels are based on no observed adverse effect levels (NOAELs) in human populations when possible (NRC 2001); however, it is often necessary to use data from animal studies. If no studies with multiple exposure levels and an identified NOAEL are available, a lowest observed adverse effect level (LOAEL) is used as the starting point for the guideline level. Uncertainty factors of 1, 3, or 10 are generally used to ensure that the guidelines are protective. Uncertainty factors are used to account for interspecies variability, intraspecies variability, use of LOAEL data when no NOAEL level is available, and other database deficiencies. The uncertainty factors used for each priority chemical are described in chemical-specific AEGL documentation.

As of April 2007 (the deadline for inclusion in the ERG2008 analysis), the NRC had published final AEGLs for 31 chemicals, interim AEGLs for 99 chemicals, and proposed AEGLs for 64 chemicals (NRC 2007). For the development of PADs, only final and interim AEGL-2 values for 1-h and 15-min exposure periods were used.

4.1.2 ERPGs

ERPGs are developed by the AIHA through a rigorous peer review process that emphasizes human experience to the extent that such information is available. However, as is done for the AEGLs, data from animal studies are often used as the basis for the ERPG concentrations. Similar to the AEGLs, ERPGs are defined for three effect levels, as follows:

- ERPG-1 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing adverse health effects other than mild, transient ones or without perceiving a clearly defined objectionable odor.
- ERPG-2 is the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.
- ERPG-3 is the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 h without experiencing or developing life-threatening health effects.

In 2007, the AIHA published ERPG concentrations for 132 different chemicals (AIHA 2007). Typically each year, the AIHA adds about 7–10 chemicals to the list and modifies previously published values for another 7–10 materials.

4.1.3 Comparisons of AEGLs, ERPGs, and Other Health Criteria

As industry and federal agencies have increased emergency preparedness efforts over the last few decades, several chemical-specific health criteria levels have been developed by various groups using differing methodologies, leading to some uncertainty over which values and methods to use for emergency planning. Some of the criteria developed include the AEGLs and ERPGs discussed above; NIOSH immediately dangerous to life and health (IDLH) levels; EPA levels of concern (LOCs) used to evaluate releases of extremely hazardous substances and help make the consequence analyses required to comply with requirements of Section 112 R of the Clean Air Act (EPA 1996); temporary emergency exposure guidelines (TEELs) developed by the DOE Subcommittee on Consequence Assessment and Protective Actions (SCAPA); and occupational health guidelines. The IDLH, LOC, and TEEL values are discussed briefly in this section; occupational health guidelines are not relevant for deriving PADs and are not further discussed, except as related to LOC levels.

4.1.3.1 IDLH Values

The IDLH concentration is defined as “an atmospheric concentration of any toxic, corrosive or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere” (NIOSH 2008). IDLH values were originally developed in the 1970s for about 400 substances; these values have since been updated. For the procedure described by NIOSH to develop IDLHs, human data are preferred. However, many of the IDLHs are based on adjusting the results of acute inhalation lethality data in animals to a 30-min exposure duration. Since IDLH values are developed for an exposure duration of 30 min and for healthy adult workers, they would be expected to be higher than ERPG-2 or 1-h AEGL levels, which are developed for an exposure duration twice as long and are protective for most of the general population.

4.1.3.2 LOC Values

The LOC, as originally defined by EPA et al. (1987), is “the concentration of an extremely hazardous substance (EHS) in the air above which there may be serious irreversible health effects or death as a result of a single exposure for a relatively short period of time.” In the EPA procedure to derive LOC values, the IDLH divided by 10 was the preferred value (EPA et al. 1987). Since IDLHs were developed for the purpose of selecting respirators in the event of an emergency in the workplace, the tenfold uncertainty factor is intended to account for the greater sensitivity of the general population versus the worker population. When IDLHs were unavailable, estimated IDLHs based on $LC_{50}/100$, LC_{LO} , $LD_{50}/100$, or $LD_{LO}/100$ were used. (LD means lethal dose.) As a third choice, ACGIH TLV values — 8-h TLV TWA (time-weighted average), TLV STEL (short-term exposure limit), and TLV ceiling values — and NRC Emergency Exposure Guidance Levels (EEGLs) were also used to derive a number of LOCs (see Section 4.4, Glossary, for definitions). AIHA ERPGs were cited as alternative criteria to use to develop LOCs. However, because only 15 draft ERPGs were available at the time the LOC guidance was developed, ERPGs did not form the basis for any LOC.

There are similarities in the procedure used by the EPA to develop LOCs and the procedure used by DOT to develop health criteria for deriving Initial Isolation Zones and PADs, most notably that many LOC levels and DOT 1-h protective levels are based on adjusted LC_{50} or LC_{LO} values divided by 100. There are also several important differences in these two procedures. In the DOT approach, AEGLs and ERPGs are the preferred choice for deriving health criteria. We believe this to be a sounder approach, since these values are considered by many authorities to be the best available criteria for evaluating accidental releases. Also, in the DOT procedure, when it was necessary to use acute lethality data in animals, a critical review of the available data was performed, which included a scheme for selecting the best study when multiple studies were available. In the DOT approach, when LC_{LO} data were employed, use of a hundredfold instead of a tenfold uncertainty factor was maintained. This recommendation was based on the concept that a significant number of LC_{LO} values represent concentrations that result in significantly high mortality, including 100% mortality.

In the approach described in the EPA's guidance document for off-site consequence analysis (EPA 1996), ERPGs were recommended as the preferred values, followed by LOC values. Since AEGLs and ERPGs are also used as the first priority in the DOT scheme, followed by the time-adjusted LC₅₀/100, and since many LOCs are based on LC₅₀/100, the two approaches are quite similar. However, as described above, there are differences in the methods used to select the acute lethality data.

4.1.3.3 TEEL Values

TEEL values are available for more than 3,000 chemicals. They have been developed for chemicals that do not have AEGL or ERPG values available, and they are considered temporary values subject to change as new or better information becomes available. The method for deriving TEEL values (Craig et al. 2000) is of interest because it has some similarities to the methods described here for deriving health criteria levels for generating PADs for the DOT ERG. However, for substances without AEGL or ERPG values, TEEL-2 levels (TEEL definition is the same as the ERPG-2 definition, but for a 15-min exposure duration) are based on a fairly complex hierarchy of emergency planning and occupational guideline levels, whereas the PAD health criteria levels are based on a simpler use of acute inhalation toxicity data (i.e., LC₅₀ and LC_{LO} values; see Section 4.2.2).

The TEEL developers also conducted studies examining the statistical relationship between ERPG levels and some other planning levels, including the IDLH values and EPA LOC values (Craig et al. 1995). For example, the mean, coefficient of variation, and coefficient of determination of the ratios of ERPG-2 criteria to other health criteria were calculated. The analysis included ERPG data for 35 chemicals. The developers found that NIOSH IDLH values overestimated ERPG-2 values (mean ratio = 2.48). A good correlation was observed between ERPG-2 values and EPA LOCs.

The study by Craig et al. (1995) confirms the validity of using LC₅₀ values divided by a factor of 100 as surrogates for ERPG values, as was done for deriving health criteria for the TIH chemicals (see Section 4.2.2.4). This conclusion is based on the good correlation between the EPA LOC and ERPG-2 values. Since many EPA LOC values were derived by dividing the IDLH by 10, and since many IDLHs were derived by dividing an LC₅₀ value by 10, a relationship between the ERPG-2 value and LC₅₀/100 is inferred. For the TIH chemicals, it is assumed in this document that the relationship also holds true for the ratio of AEGL-2 to LC₅₀/100, although no studies have been done to confirm this assumption.

4.1.4 Expert Panel Review

In 1995, an independent panel of expert toxicologists convened to make recommendations on the identification of health criteria for the 1996 version of the ERG. The panel made a number of recommendations for improving the consistency of the criteria. They recommended that the use of occupational health guidelines based on cancer or systemic effects should be avoided, because their use resulted in significant differences from other published

health criteria. The panel also recommended using acute inhalation toxicity data (e.g., LC₅₀ values) in place of occupational health guidelines to improve the consistency of the health criteria. These recommendations were implemented to identify the health criteria for the ERG2000 and ERG2004, and currently no occupational health guidelines are used in the development of health criteria for the PADs. The panel cautioned that the inconsistent use of acute inhalation toxicity data has a high potential of introducing bias. To increase consistency, a scheme that considers species, exposure duration differences, and data sources was developed and implemented, as described in Section 4.2.

In addition, the panel recommended identifying new potential sources of information for developing the health criteria. For example, additional acute toxicity data may be found in the documentation of the AIHA ERPGs. These documents cite proprietary data not included in the open literature. Also, the panel recommended making more use of ERPG values by using existing ERPGs for closely related analogs for which there are limited toxicity data and no ERPGs.

The recommendations from the expert panel, and information gained from the studies and analyses described above, were incorporated into an updated procedure for developing the health criteria used to calculate Initial Isolation Zones and PADs. This procedure was applied in developing the health criteria for the ERG2008, as outlined in the following section, with the main modification being the incorporation of final and interim AEGL values.

4.2 PROCEDURE USED TO DEVELOP HEALTH CRITERIA

The most significant change to the health criteria development method for the ERG2008 was the adoption of final AEGL-2 values as the preferred health criteria. These values, as well as ERPG-2 values, interim AEGL-2 values, and acute inhalation lethality data, were used to identify the health criteria used to determine PADs. The ranking of AEGL and ERPG values and the use of acute inhalation data to derive health criteria are described below.

4.2.1 Use of AEGL and ERPG Data

When final AEGL values were available for the chemical of interest, the 60-min, 30-min, and 10-min final AEGL-2 values were employed. If no final AEGL value was available, the ERPG-2 value was used as the health criterion, with a twofold factor used to estimate a 15-min health criterion (use of the twofold factor is explained in Section 4.2.2 below). If final AEGL or ERPG values were unavailable, then interim AEGL-2 values were used if available. In several instances in which AEGLs or ERPGs were available for a closely related structural analog to the chemical of interest, the AEGL or ERPG value for the structural analog was used for the chemical of interest.

4.2.2 Use of Acute Inhalation Lethality Data in Animals

When neither final or interim AEGLs nor ERPGs were available, health criteria were derived by using median lethal concentration (LC₅₀) data from acute inhalation studies on animals, adjusted to approximate 1-h AEGL or ERPG values. When LC₅₀ data were not available, lowest reported lethal concentration (LC_{LO}) data were used. Factors considered in selecting and using the LC₅₀ and LC_{LO} data included species, experimental exposure duration, data source, and adjustment factor, as discussed below.

4.2.2.1 Species Considerations

Data from studies using rats and mice are preferred for several reasons. Studies conducted with these species tend to use standardized protocols. Also, there is a wealth of comparative lethality data on rats and mice and much less comparative data on other species. Data on primates are rare, so using these data would limit the ability to compare responses across chemicals. However, acute lethal responses in this species might more closely simulate human responses. Therefore, if such data were available, they would be included after the data for rats and mice but before data for other species. The amount of comparative data on rabbits is limited. Results for this species are not as representative as data for primates, and so they appear lower in the ranking scheme. The entire order of species preference used (from highest to lowest) for both LC₅₀ and LC_{LO} data was rat, mouse, primate, dog, cat, guinea pig, and rabbit. In one case (i.e., bromoacetone), only an LC_{LO} value for humans was available; this value was used to develop the health criteria for bromoacetone.

4.2.2.2 Experimental Exposure Duration Considerations

The most commonly reported acute lethality studies are for 1-h and 4-h exposure durations. Therefore, use of data from studies in the range of these durations provides a measure of consistency in estimating health criteria. There is also a tendency for 1-h and 4-h LC₅₀ values to have been calculated by using standard protocols. For developing the ERG2008, health criteria based on data from 1-h exposures were preferred, since data from this duration require no adjustments. However, data from studies using exposure durations from 10 min to 6 h were used, because many chemicals did not have data for 1-h exposures.

For exposures less than 30-min long, concerns about chamber equilibration time (T₉₉) increase. For exposures more than 4-h long, concerns that effects other than acute lethal effects might influence the study results increase. Also, LC_{LO} data are considered inferior to LC₅₀ data, because there is no information on the slope of the dose response curve from these studies.

Data from exposures other than 1-h exposures were adjusted to predict results for 1-h exposures. To develop an approach for making the adjustments, various reports published by investigators who have examined the relationship between exposure duration and acute mortality response were reviewed (Doe and Milburn 1983; Haber 1924; Klimisch et al. 1987; Ten Berge et al. 1986).

In the simplest case, where the inhaled substance accumulates in the body and is not rapidly destroyed or excreted, the dose accumulated is directly proportional to the concentration c and the exposure time t , and uptake is linear. This concept, known as Habers's rule or law, would result in the following relationship:

$$W = c t, \quad (4.1)$$

where W is a constant dose specific for any given effect. This relationship is applicable for many reactive gases or highly lipid-soluble vapors over a limited range of concentrations and time.

However, many other relationships are possible. For example, for chemicals that are excreted as fast as they are inhaled and for which accumulation does not occur until a certain threshold concentration is reached, the following generalized dose-response equation applies:

$$W = (c - a)t^b, \quad (4.2)$$

where a is the threshold concentration and b is derived from experimental data.

For a significant percentage of chemicals, the following relationship has been observed:

$$LC_{50} \text{ (for } T_1) = LC_{50} \text{ (for } T_o) [T_o/T_1]^{1/n} \quad (4.3)$$

where

- T_1 = modeled exposure time (e.g., 1 h),
- T_o = experimental exposure time, and
- n = constant.

Klimisch et al. (1987), citing Doe and Milburn (1983), found that for many chemicals, n centers around a value of 0.5. Ten Berge et al. (1986) determined that for 18 of 20 chemicals studied, n values were greater than 0.3.

For deriving the health criteria, acute lethality data for exposure durations T_o longer than 1 h were normalized by using the following quadratic dose-response function:

$$LC_{50} \text{ (1 hour)} = LC_{50} (T_o) \left(\frac{T_o}{1 \text{ hour}} \right)^{0.5}. \quad (4.4)$$

This approach is conservative, in that it predicts lower LC_{50}/LC_{LO} values than does Habers's rule. Acute lethality data for exposure durations T_o of less than 1 h were conservatively predicted by using a linear dose-response function (i.e., Habers's rule):

$$LC_{50} \text{ (1 hour)} = LC_{50} (T_o) \left(\frac{T_o}{1 \text{ hour}} \right). \quad (4.5)$$

4.2.2.3 Data Source Considerations

The source of the data is another important consideration. Information from main-stream, peer-reviewed toxicology and industrial hygiene journals is preferable to information from auxiliary, non-peer-reviewed sources. The publication date may also be important. Many studies conducted before 1950 did not include analytical verification of concentrations. Information from foreign journals tends to contain more transposition errors, especially as cited in the *Registry of Toxic Effects of Chemical Substances* (RTECS). RTECS is a widely used toxicity database that was built and maintained by NIOSH from 1971 through 2001 but is now maintained and updated by a private company under contract to NIOSH (MDL Inc. 2008).

On the basis of these considerations, recent peer-reviewed U.S. data sources were preferred for the selection of health criteria for PAD development. However, for several chemicals, the only available lethal concentration data were dated, came from foreign sources, or consisted of industry data that had not been through the peer review process. Nonetheless, these data had often been in use for a number of years without reports of discrepancies between the reported lethality concentrations and toxicity experienced in industrial use. For example, such data are reported fairly often in the RTECS database and also in another standard source of lethality data for chemicals, *Sax's Dangerous Properties of Industrial Materials* (Lewis 2000). Therefore, the use of these nonsuperior data for some chemicals was retained for the ERG2008; their use was considered preferable to having no PAD values for those chemicals.

The data sources for the chemical-specific health criteria given in Appendix B include AEGL values (NRC 2007), ERPG values (AIHA 2007), and LC₅₀ and LC_{LO} data from several sources including Sax (Lewis 2000), RTECS data, and data from miscellaneous sources. Chemical-specific source data can be obtained upon request to the authors.

4.2.2.4 Adjustment Factors

As described in Section 4.1, the 1-h LC₅₀/100 or the time-adjusted LC₅₀/100 are reasonable estimators for AEGL-2 or ERPG-2. Therefore, 1-h or adjusted 1-h LC₅₀ or LC_{LO} values were divided by 100 to estimate 1-h protective health criteria.

Members of the AIHA ERPG Committee indicate that when 1-h ERPGs are extrapolated to values of shorter duration, there is concern that the potential effects of peak, high-level exposures should be minimized. A default value of 2 was suggested for these purposes. Therefore, to estimate 15-min protective health criteria from 1-h values, a factor of 2 was employed in estimating the 15-min criteria from the 1-h criteria (rather than the factor of 4 that would be used if direct linear extrapolation were used).

4.2.3 Use of Data for Structurally Similar Substances

When health criteria were not available for a chemical of interest, corresponding data for a structural analog were used. For example, for certain isocyanates for which there were no acute

lethality data, data for n-butyl-isocyanate were used. Similarly, data for boron trifluoride were used for boron tribromide. Health criteria were based on structural analog data for about 10% of the TIH chemicals in the ERG2008.

4.3 SUMMARY

By building on past efforts, an updated procedure was developed to provide health criteria for use in determining Initial Isolation Zones and PADs. The new procedure incorporated AEGL values and additional ERPG values published since 2004 and expanded the use of existing AEGLs and ERPGs by applying them to structural analogs that otherwise had limited or no available acute toxicity data. The method developed for the ERG2004, involving increased use of acute lethality data and increased consistency in data selection, was continued.

A summary of the basis for health criteria for the 164 chemicals included in the ERG2008 analysis appears in Table 4.1. Documentation of the health criteria for individual chemicals is presented in Appendix B. For 29 chemicals (18%), AEGL values or AEGLs for structurally similar chemicals formed the basis of the health criteria. For 48 chemicals (29%), ERPGs or ERPGs for a structurally similar chemical formed the health criteria basis. For 78 chemicals (48%), LC₅₀ values or LC₅₀ values for a structurally similar chemical were used to develop the health criteria. For 9 chemicals (5%), LC_{LO} values formed the basis of the health criteria. For 1 chemical, oral toxicity data were used to estimate an inhalation LC₅₀ and to derive the health criteria.

Through continued efforts of the NAC/AEGL Committee and the AIHA ERPG Committee, new AEGLs and ERPGs are developed annually. The NAC/AEGL Committee also finalizes interim AEGLs and completes the public review process necessary for proposed AEGLs to be considered interim AEGLs. ERPGs for additional chemicals are being provided at a rate of 7 to 10 per year, and already published values are occasionally revised. Not all of the chemicals on the AEGL and ERPG lists appear in the Table of Initial Isolation Zones and PADs, since many of the chemicals do not meet the specific toxicity and physical criteria for listing in the Table. However, when new AEGL or ERPGs become available for chemicals on the DOT table, the values will be incorporated into the development of Initial Isolation Zones and PADs in future editions of the ERG.

4.4 GLOSSARY FOR CHAPTER 4

ACGIH 8-hour TLV TWA: American Conference of Governmental Industrial Hygienists 8-hour threshold limit time-weighted average value (or simply 8-h TLV) (ACGIH 1995). This is the time-weighted average concentration to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

TABLE 4.1 Summary of the Basis for Health Criteria Used to Prepare the ERG2008

Basis of Health Criteria	No. of Materials	Percentage
Final AEGL for chemical of concern	17	
Interim AEGL for chemical of concern	9	
Final AEGL for structurally similar chemical	2	
Subtotal for AEGLs	28	18
ERPG for chemical of concern	39	
ERPG for structurally similar chemical	9	
Subtotal for ERPGs	48	29
LC ₅₀ for chemical of concern	71	
LC ₅₀ for structurally similar chemical	7	
Estimated LC ₅₀ ^a	1	
Subtotal for LC ₅₀ values	79	48
LC _{LO} for chemical of concern	9	5
Total	164	100

^a For one chemical (hexaethyltetraphosphate), inhalation toxicity data were not available, and the health criterion was estimated as the median of four LD₅₀ values by using standard assumptions to convert to air concentrations.

ACGIH TLV STEL: American Conference of Governmental Industrial Hygienists short-term exposure limit (ACGIH 1995). This is the concentration to which workers can be exposed continuously for a short period of time without suffering from (1) irritation, (2) chronic or irreversible tissue damage, or (3) narcosis of sufficient degree that it would increase the likelihood of accidental injury, impair self-rescue, or materially reduce work efficiency, provided that the daily TLV time-weighted average (TWA) is not exceeded.

ACGIH TLV Ceiling: American Conference of Governmental Industrial Hygienists threshold limit value ceiling (ACGIH 1995). This is the concentration that should not be exceeded during any part of the working exposure.

AEGLs: National Research Council Acute Exposure Guidance Levels. These levels are described in the text.

AIHA EEL: American Industrial Hygiene Association Emergency Exposure Level published in the *American Industrial Hygiene Association Journal* (Frawley et al. 1964). This is the concentration of a contaminant that can be tolerated without adversely affecting health but not necessarily without acute discomfort or other evidence of irritation or intoxication. The level is

intended to provide guidance in managing single, brief exposures to airborne contaminants in the working environment.

ERPGs: American Industrial Hygiene Association Emergency Response Planning Guidelines (AIHA 2007). These are described in the text.

EPA LOC: U.S. Environmental Protection Agency level of concern (EPA et al. 1987). This is the concentration of an extremely hazardous substance in the air above which there may be serious irreversible health effects or death as a result of a single exposure for a relatively short period of time.

LC₅₀: This is the median (50%) lethal concentration; it is a lethal concentration to 50% of the exposed population.

LC_{LO}: This is the lowest reported lethal concentration.

NIOSH IDLH: National Institute for Occupational Safety and Health immediately dangerous to life and health level (NIOSH 2008). This is the minimum concentration of a toxic, corrosive, or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere.

NRC EEGL: National Research Council Emergency Exposure Guidance Level (National Research Council 1984–1987). This is the concentration of a substance in air (as gas, vapor, or aerosol) that will permit continued performance of specific tasks during rare emergency conditions lasting for periods of 1 to 24 h.

OSHA PEL Ceiling: Occupational Safety and Health Administration permissible exposure limit ceiling (OSHA 1989). This is the concentration that should not be exceeded during any part of the workday.

5 SUMMARY

Sections 2–4 of this report detail the statistical methodology for developing safe distance distributions, the consequence models used in the analysis, and the health criteria that define the safe distance. This section summarizes the results and discusses the presentation of the distances in the Table (which is contained in Appendix A). It then concludes with some potential extensions of this analysis for situations when more information (in addition to the gross spill size and whether it is day or night) is immediately available.

5.1 SAFE DISTANCE DISTRIBUTIONS AND PROTECTIVE ACTION DISTANCES

The statistical accident scenario and consequence analysis set forth in previous sections resulted in a set of up to 1,000,000 hypothetical incidents for each material appearing in the Table. This set of incidents accounts for variability in container type, incident type, accident severity (i.e., release amount), location, time of day, time of year, and meteorology. Each of these scenarios was evaluated by using detailed emission rate and atmospheric dispersion models to calculate downwind chemical concentration footprints, with the safe distance for each incident defined as the distance downwind from the source at which the chemical concentration falls below the health protection criteria. The safe distance estimates for the entire set of hypothetical incidents considered in the analysis provide a safe distance distribution that corresponds to a wide spectrum of potential transportation-related releases. In the final step of the analysis, these incidents are categorized according to whether they occur during the day or night and whether they involve small (≤ 60 gal) or large (> 60 gal) spills.

Examples of safe distance distributions for two chemicals are given in Figures 5.1–5.8. The first four figures show safe distance distributions for chlorine, a Hazard Zone B gas. Distributions are separated according to spill size (large or small) and time of day (day or night). Figures 5.5–5.8 provide corresponding results for a water-reactive material, calcium phosphide, which emits phosphine when spilled into water. In all eight figures, the 50th, 70th, 80th, 90th, and 95th percentiles are identified. The PADs in the guidebook correspond with the 90th-percentile values for the individual categories. Tables 5.1 and 5.2 provide safe distance estimates at several percentiles for the chlorine and calcium phosphide distributions shown in the figures. Tables 5.3 and 5.4 provide corresponding data for two additional chemicals, phosphorous chloride (a Hazard Zone B liquid) and ammonia (a Hazard Zone D gas). Results for phosphorous chloride in Table 5.3 are for land-based releases only. A separate set of safe distance distributions was developed for spills of phosphorous chloride into water.

As demonstrated in these examples, the safe distance distributions exhibit substantial tails, denoting the presence of low-probability/high-consequence events. A comparison of the 50th- and 90th-percentile values reveals that the 90th-percentile values are often a factor of 4 above the 50th-percentile values. Clearly, use of the 90th-percentile value for the PAD affords a substantial level of protection for most incidents. The 95th and 99th percentiles do show that the PADs will not be sufficient for all incidents, however. The 99th-percentile events, corresponding

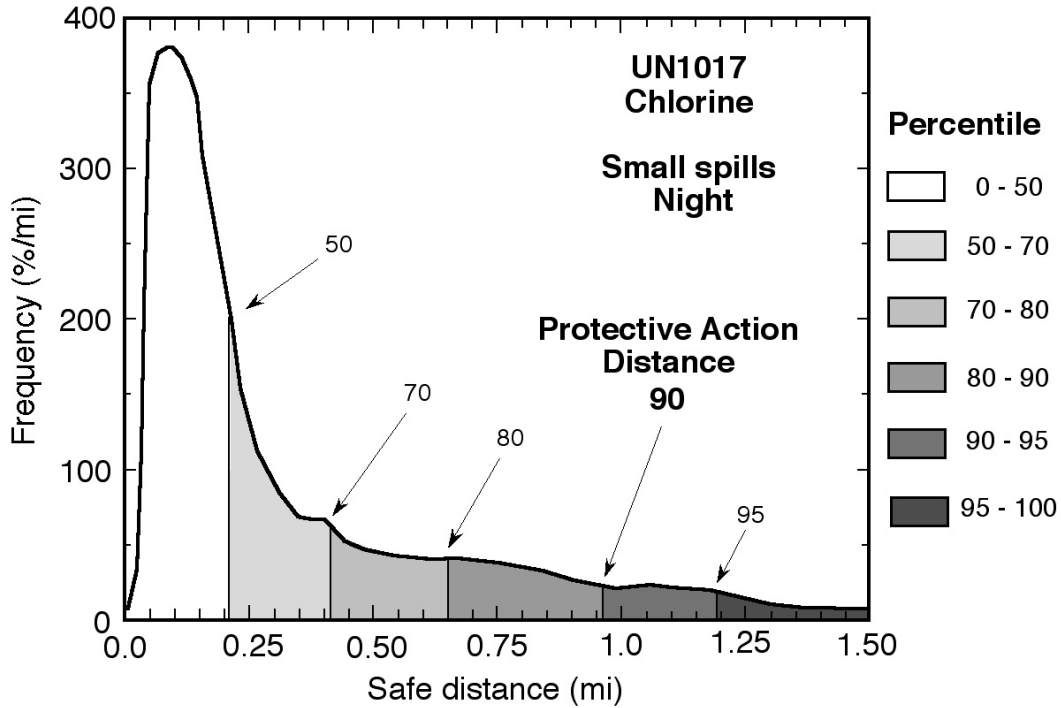


FIGURE 5.1 Frequency of Safe Distances for Small Nighttime Chlorine Spills as Determined in the ERG2008 Analysis

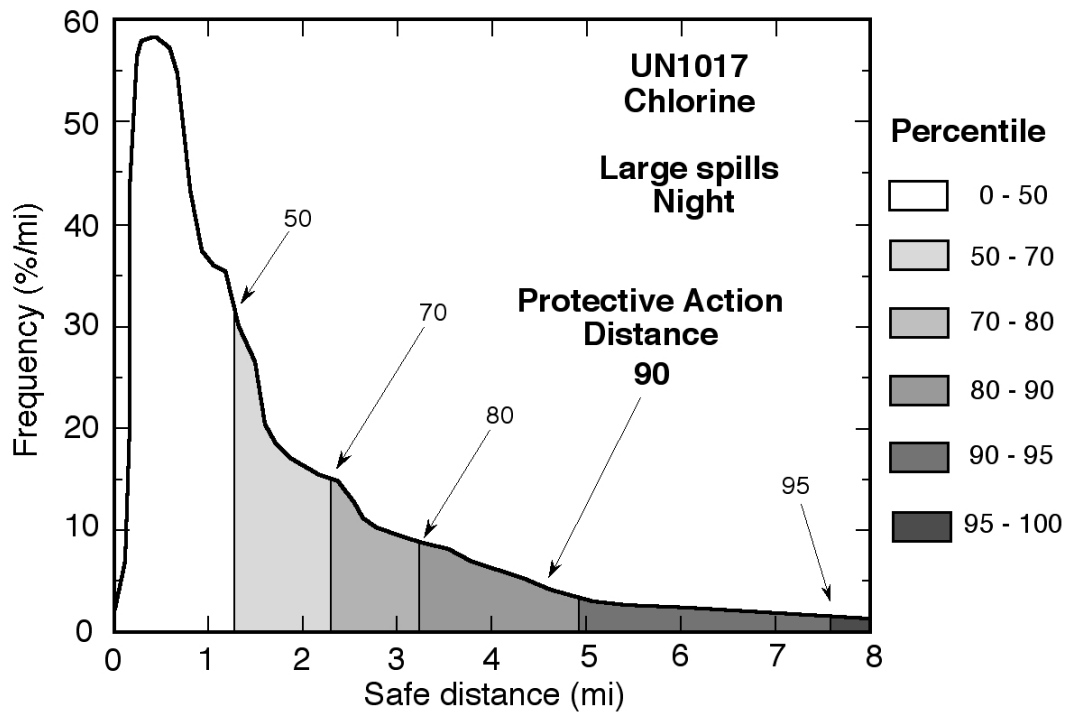


FIGURE 5.2 Frequency of Safe Distances for Large Nighttime Chlorine Spills as Determined in the ERG2008 Analysis

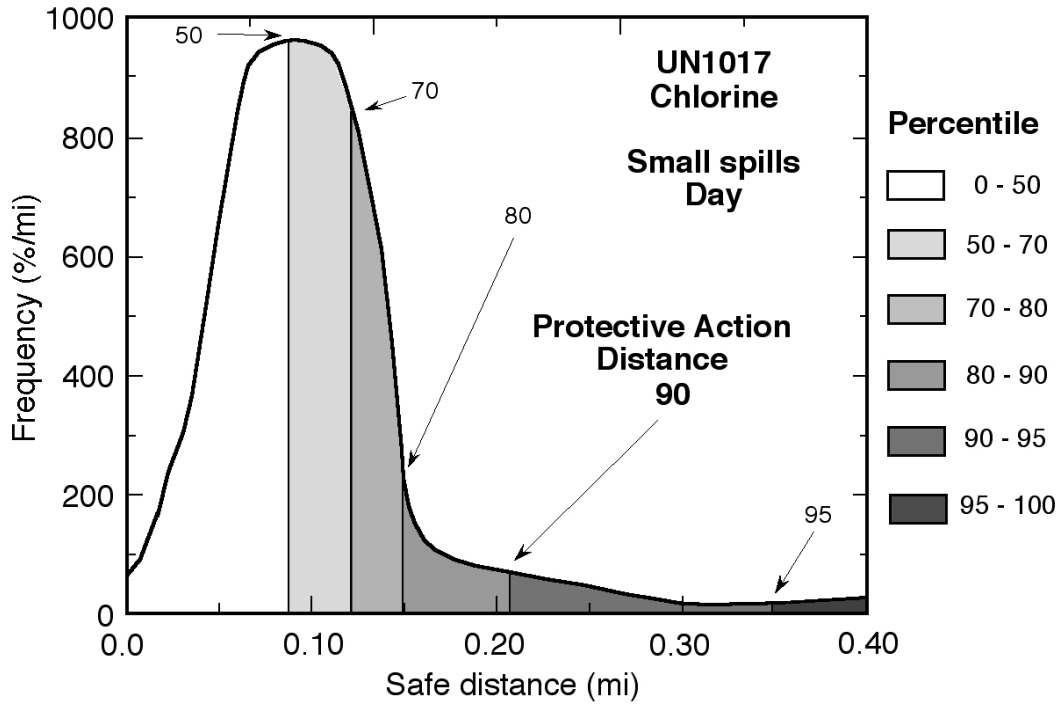


FIGURE 5.3 Frequency of Safe Distances for Small Daytime Chlorine Spills as Determined in the ERG2008 Analysis

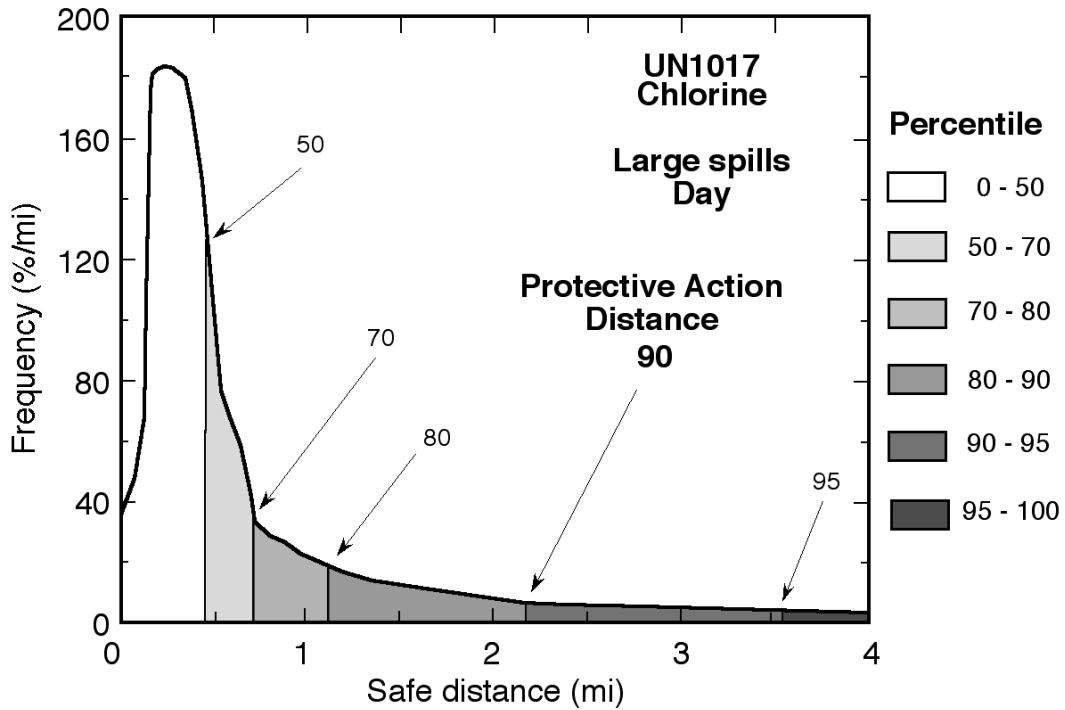


FIGURE 5.4 Frequency of Safe Distances for Large Daytime Chlorine Spills as Determined in the ERG2008 Analysis

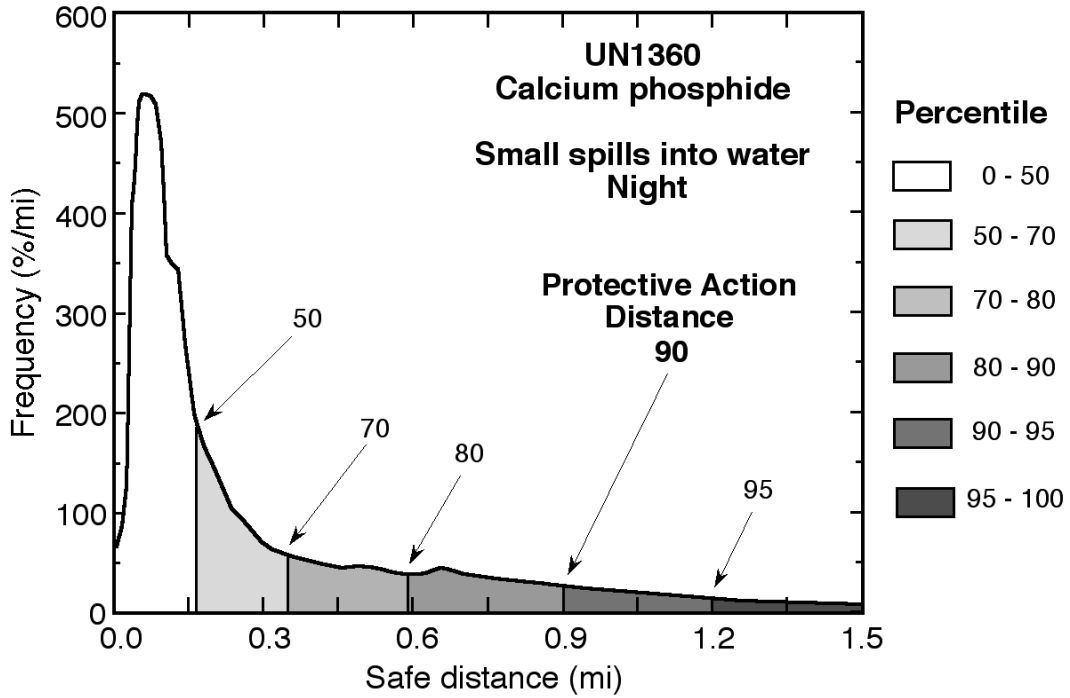


FIGURE 5.5 Frequency of Safe Distances for Small Nighttime Calcium Phosphide Spills into Water as Determined in the ERG2008 Analysis

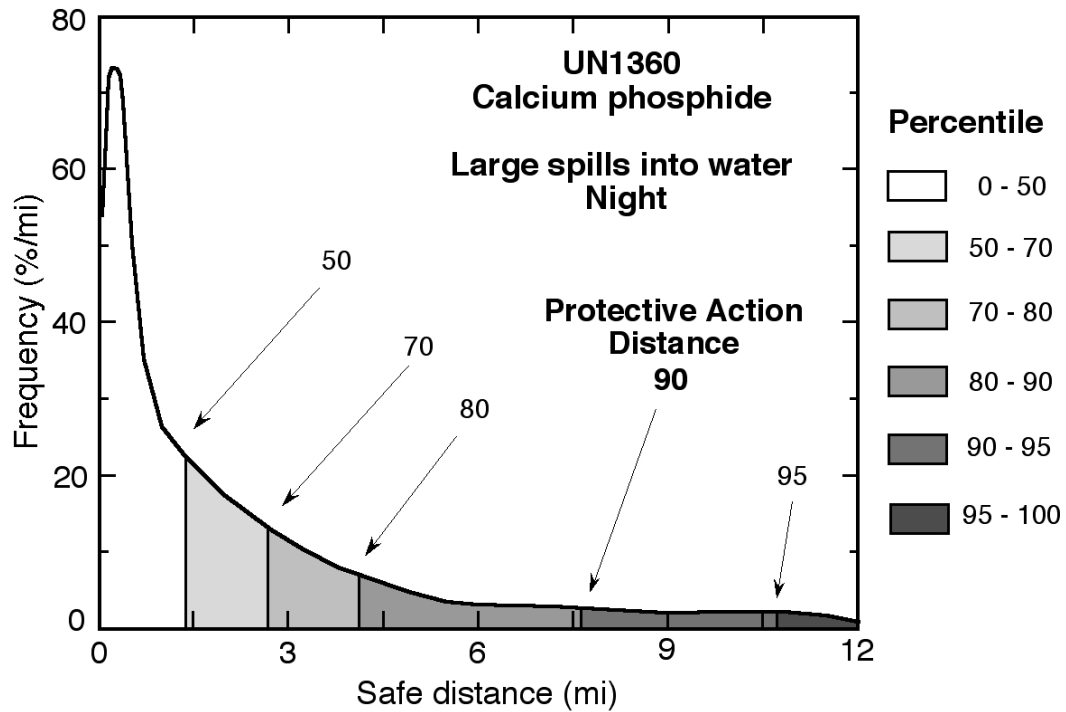


FIGURE 5.6 Frequency of Safe Distances for Large Nighttime Calcium Phosphide Spills into Water as Determined in the ERG2008 Analysis

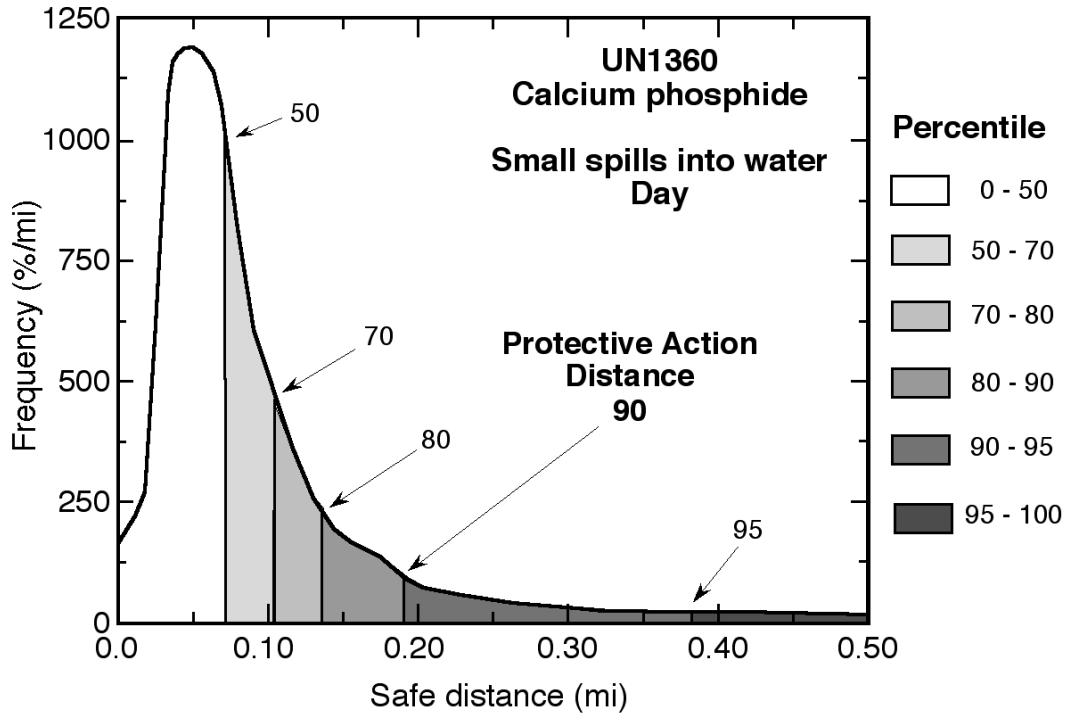


FIGURE 5.7 Frequency of Safe Distances for Small Daytime Calcium Phosphide Spills into Water as Determined in the ERG2008 Analysis

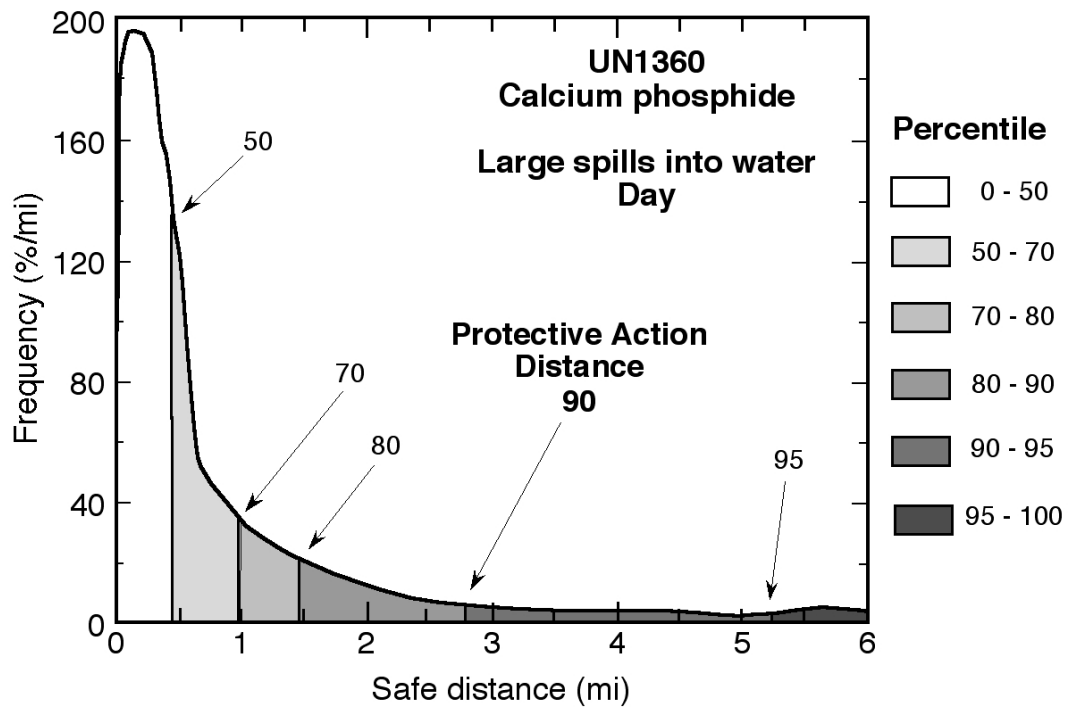


FIGURE 5.8 Frequency of Safe Distances for Large Daytime Calcium Phosphide Spills into Water as Determined in the ERG2008 Analysis

TABLE 5.1 Safe Distances at Several Percentiles for Chlorine (UN 1017) Releases as Determined in the ERG2008 Analysis

Release Size	Time	Safe Distance (mi) for Given Percentile					
		50	70	80	90	95	99
Small	Day	0.09	0.12	0.17	0.21	0.35	1.04
	Night	0.21	0.43	0.65	0.96	1.03	1.81
Large	Day	0.42	0.68	1.09	3.58	2.83	10.2
	Night	1.25	2.23	3.17	4.96	7.95	15.2

TABLE 5.2 Safe Distances at Several Percentiles for Calcium Phosphide (UN 1360) Releases into Water as Determined in the ERG2008 Analysis

Release Size	Time	Safe Distance (mi) for Given Percentile					
		50	70	80	90	95	99
Small	Day	0.07	0.10	0.13	0.19	0.36	1.05
	Night	0.16	0.35	0.58	0.90	1.20	1.95
Large	Day	0.45	0.93	1.39	2.73	5.39	11.79
	Night	1.46	2.71	3.89	7.59	10.82	15.58

TABLE 5.3 Safe Distances at Several Percentiles for Land-based Phosphorous Trichloride (UN 1809) Releases as Determined in the ERG2008 Analysis

Release Size	Time	Safe Distance (mi) for Given Percentile					
		50	70	80	90	95	99
Small	Day	0.05	0.07	0.09	0.11	0.15	0.42
	Night	0.09	0.15	0.22	0.38	0.54	0.89
Large	Day	0.21	0.37	0.57	0.90	1.21	2.82
	Night	0.46	0.84	1.18	1.83	2.74	5.85

TABLE 5.4 Safe Distances at Several Percentiles for Ammonia (UN 1005) Releases as Determined in the ERG2008 Analysis

Release Size	Time	Safe Distance (mi) for Given Percentile					
		50	70	80	90	95	99
Small	Day	0.01	0.01	0.01	0.02	0.03	0.09
	Night	0.02	0.03	0.05	0.09	0.12	0.22
Large	Day	0.08	0.15	0.23	0.44	0.67	2.03
	Night	0.21	0.50	0.77	1.39	2.29	5.36

to worst-case releases in worst-case meteorology, can result in safe distances that exceed the PAD by roughly a factor of 4 for daytime releases and a factor of 2 for nighttime releases. However, using the 99th-percentile criterion to define the PAD would result in extreme overreaction to the vast majority of incidents first responders face. The 90th-percentile criterion was selected to strike a reasonable balance between adequately protecting the public from exposure to potentially harmful substances and avoiding the needless risks and expense associated with overreaction.

5.2 PRESENTATION OF THE TABLE IN THE GUIDEBOOK

Appendix A provides the Table of Initial Isolation and Protective Action Distances as it appears in the ERG2008 (DOT et al. 2008), with one important modification discussed below. The PADs in the Table are the 90th percentiles of the safe distance distributions presented in the previous section. As discussed in Section 2, three distinct types of materials are listed in the Table. The first are TIH materials released in transportation-related incidents. The second are water-reactive materials that emit TIH gases when spilled into water. These entries are denoted by the phrase “when spilled in water.” For TIH materials that emit a secondary TIH product when spilled in water, two entries are listed; they correspond to spills in water and on land. The third are chemical warfare agents released in a malicious manner. These entries are denoted by the phrase “when used as a weapon.” Some chemical warfare agents, such as arsine and hydrogen cyanide, are TIH industrial chemicals as well and contain additional entries for transportation-related releases.

In all cases, the PADs have been rounded *up* to the next 0.1 mi. Appendix A differs from the presentation in the ERG2008 in that distances are not limited to 7 mi (or 11 km). These “unclipped” values are provided to more accurately show the relative risk of the high-hazard materials for which PADs can exceed 7 mi. IIDs are rounded up and binned as described in Section 2.5. Note that many of the IIDs for liquefied gases are substantially larger in the ERG2008 than in the ERG2004 because of a change in the methodology, as discussed in Section 2.5.

5.3 EXTENSIONS OF THE ERG ANALYSIS

One key limitation of PAD estimates in the ERG is that the only information taken into account is the spill size (large or small) and whether it is day or night. Clearly, the distributions in Figures 5.1–5.8 show wide variability in PAD estimates, and the data used to construct them contain a great amount of additional information that could be very useful in emergency response situations as well as a wide variety of other analyses. Factors that could be easily ascertained by emergency response personnel are whether the incident is a highway or rail incident, whether a vehicular accident or derailment is involved (as opposed to an en route/nonaccident event), and what the general wind conditions (e.g., high or low wind speed), temperature, and cloud cover (clear or overcast) are. Each of these factors can affect the safe-distance estimate by a factor of 3 or more.

Examples of additional information that can considerably narrow the safe-distance distributions are shown in Figures 5.9–5.12. Figures 5.9 and 5.10 are for chlorine. This analysis was described in the Argonne documentation for the ERG2004 and in Brown and Dunn (2007) and is repeated here. Note that the underlying analysis for chlorine was modified for the ERG2008 by including more detailed shipment profiles and incorporating AEGL health criteria and minor changes to the source and dispersion models used within CASRAM. The relative benefit of using more detailed information, however — as illustrated in this example — remains the same. In these figures, the distributions are shown with the ordinate on a log scale to emphasize differences at higher percentiles. The percentiles of the distributions are shown as circles superimposed on the curves. Figure 5.9 compares safe-distance distributions for large, daytime chlorine spills from rail-transported tank cars and highway-transported cargo tanks. Since rail cars contain approximately four times more chlorine than do highway vehicles, safe-distance estimates are higher at all percentiles for tank cars than for highway cargo tanks. At the 50th, 70th, 80th, and 90th percentiles, safe distances for rail releases falling under the definition of a large spill as found in the ERG (>60 gal) are about double those for corresponding highway cargo tank releases.

Figure 5.10 compares two wind-speed cases, representing low-wind (2–3 m/s) cases and high-wind (7–9 m/s) cases. It demonstrates the profound influence of wind speed on atmospheric dispersion and, consequently, safe distances. Above the 70th percentile, safe distances for low-wind-speed cases greatly exceed those for high-wind-speed cases. For high-wind-speed cases, a 5-mi safe distance would provide protection 99.5% of the time, whereas this distance would be sufficient only 65% of the time for low-wind-speed cases.

Figure 5.11 compares safe-distance distributions for two different times of year. It shows results for a volatile liquid, fuming nitric acid. Higher temperatures characteristic of summer increase the pool evaporation rate and therefore increase safe distances. Again, we see about factor-of-2 differences between percentiles for summer and winter cases. These distributions could be refined much further if the ERG analysis considered a particular location rather than the full range of locations.

The last example is Figure 5.12, which shows the effect of increased information on safe-distance estimates for a rail chlorine spill involving more than 1,000 gal. Each factor listed in the

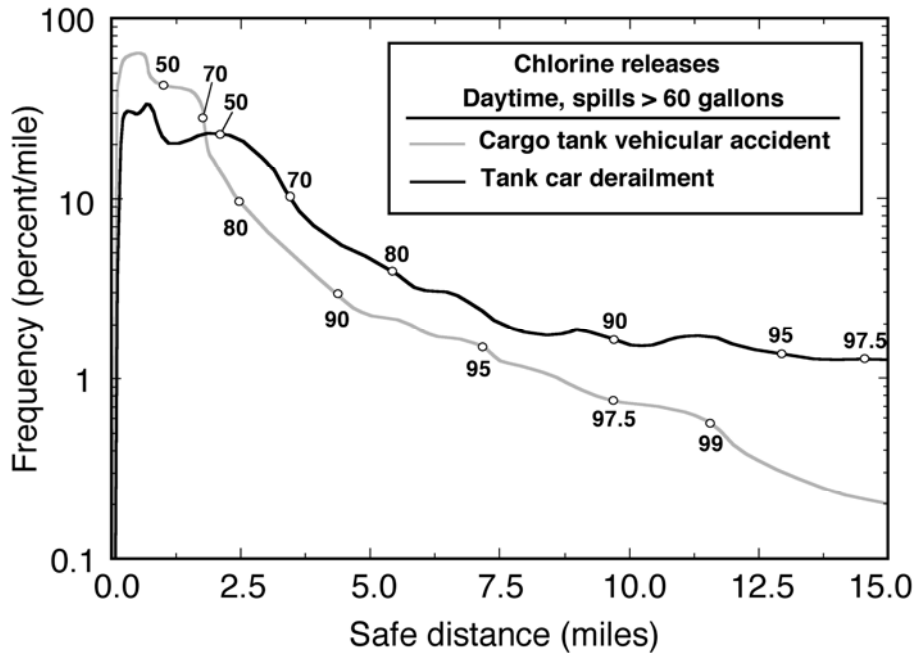


FIGURE 5.9 Frequency of Safe Distances for Large Daytime Chlorine Spills Resulting from Vehicular Accidents and Tank Car Derailments (Percentiles are denoted by open circles superimposed on the curves. These are a subset of cases shown in Figure 5.3.)

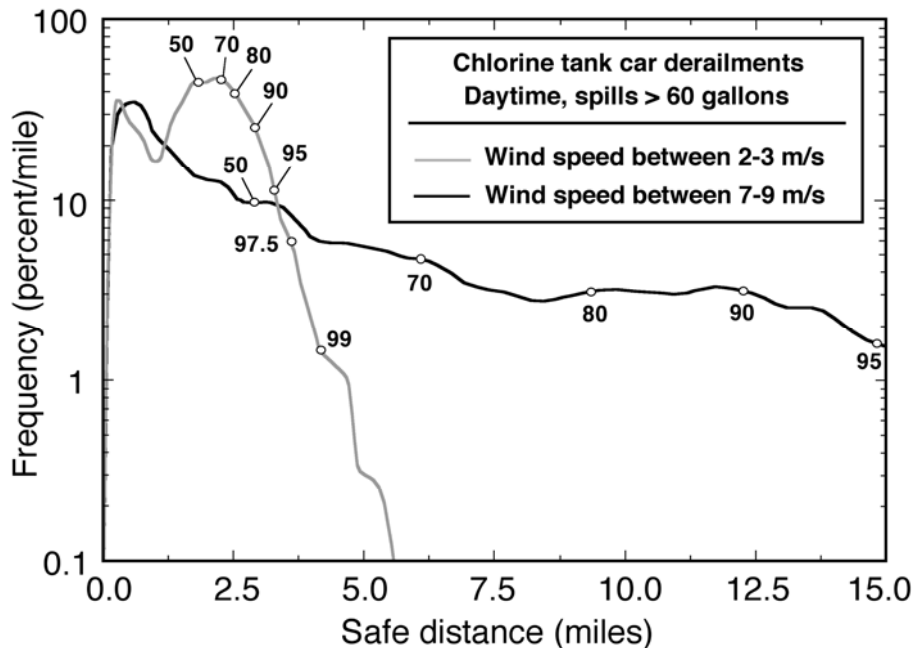


FIGURE 5.10 Frequency of Safe Distances for Large Daytime Chlorine Spills for Different Wind Speed Ranges (Percentiles are denoted by open circles superimposed on the curves. These are a subset of cases shown in Figure 5.9.)

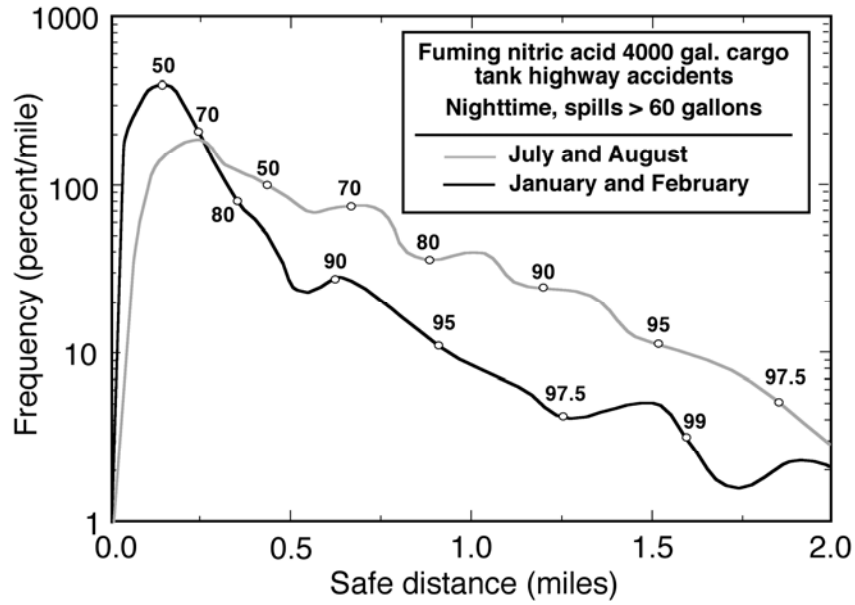


FIGURE 5.11 Frequency of Safe Distances for Highway Accidents Involving 4,000-gal Cargo Tanks of Fuming Nitric Acid in Summer and Winter Conditions (This shows the effects of seasonal climatology. Percentiles are denoted by open circles superimposed on the curves.)

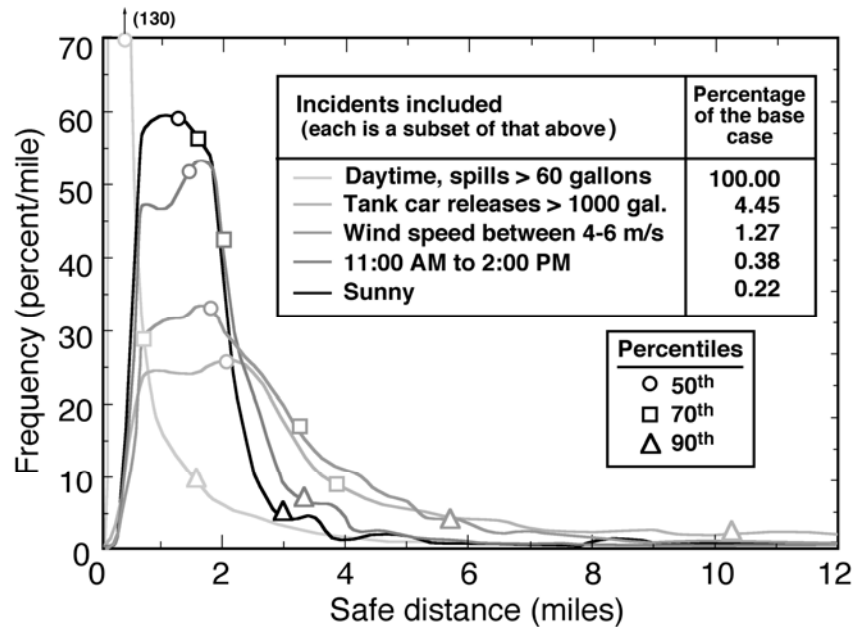


FIGURE 5.12 Frequency of Safe Distances for a Chlorine Tank Car Release of More Than 1,000 gal, Occurring from 11 a.m. to 2 p.m. on a Sunny Day with the Wind between 4 and 6 m/s (This shows the effect on the safe-distance distribution as each constraint is imposed. Percentiles are denoted as shown in the legend. The percentage of the base case, as given in Figure 5.3, is also provided.)

figure could be easily determined by personnel arriving at the accident scene. The first curve shown is the large spill daytime distribution illustrated in Figure 5.3. This distribution encompasses more than 422,451 safe-distance estimates from our statistical analysis. Next, the estimate is narrowed down to tank car spills involving more than 1,000 gal. These incidents constitute 4.45% of the original distribution.

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APPENDIX A:

**TABLE OF INITIAL ISOLATION AND PROTECTIVE ACTION DISTANCES
IN THE *2008 EMERGENCY RESPONSE GUIDEBOOK***

TABLE A.1 Initial Isolation and Protective Action Distances for TIH Materials as Determined in the ERG2008 Study

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1005	Ammonia, anhydrous	100	0.1	0.1	500	0.5	1.4
1005	Anhydrous ammonia	100	0.1	0.1	500	0.5	1.4
1008	Boron trifluoride	100	0.1	0.4	1000	1.2	3.0
1008	Boron trifluoride, compressed	100	0.1	0.4	1000	1.2	3.0
1016	Carbon monoxide	100	0.1	0.1	500	0.5	1.7
1016	Carbon monoxide, compressed	100	0.1	0.1	500	0.5	1.7
1017	Chlorine	200	0.3	1.0	2000	2.2	5.0
1023	Coal gas	100	0.1	0.1	200	0.2	0.3
1023	Coal gas, compressed	100	0.1	0.1	200	0.2	0.3
1026	Cyanogen	100	0.1	0.5	500	0.7	2.2
1026	Cyanogen gas	100	0.1	0.5	500	0.7	2.2
1040	Ethylene oxide	100	0.1	0.1	500	0.5	1.6
1040	Ethylene oxide with Nitrogen	100	0.1	0.1	500	0.5	1.6
1045	Fluorine	100	0.1	0.2	500	0.5	1.9
1045	Fluorine, compressed	100	0.1	0.2	500	0.5	1.9
1048	Hydrogen bromide, anhydrous	100	0.1	0.3	1000	1.0	2.8
1050	Hydrogen chloride, anhydrous	100	0.1	0.2	200	0.2	0.9
1051	AC (when used as a weapon)	300	0.2	0.7	3000	2.4	4.5
1051	Hydrocyanic acid, aqueous solutions, with more than 20% Hydrogen cyanide	200	0.1	0.4	1250	1.0	2.5
1051	Hydrogen cyanide, anhydrous, stabilized	200	0.1	0.4	1250	1.0	2.5
1051	Hydrogen cyanide, stabilized	200	0.1	0.4	1250	1.0	2.5
1052	Hydrogen fluoride, anhydrous	100	0.1	0.3	1000	1.1	2.2
1053	Hydrogen sulfide	100	0.1	0.3	1000	1.3	3.9
1053	Hydrogen sulphide	100	0.1	0.3	1000	1.3	3.9
1062	Methyl bromide	100	0.1	0.1	500	0.4	1.4
1064	Methyl mercaptan	100	0.1	0.2	600	0.8	2.6
1067	Dinitrogen tetroxide	100	0.1	0.2	1250	0.7	1.9
1067	Nitrogen dioxide	100	0.1	0.2	1250	0.7	1.9
1069	Nitrosyl chloride	100	0.2	0.7	2500	2.6	7.3
1071	Oil gas	100	0.1	0.1	200	0.2	0.3
1071	Oil gas, compressed	100	0.1	0.1	200	0.2	0.3
1076	CG (when used as a weapon)	600	0.7	2.5	3000	4.7	8.6
1076	Diphosgene	100	0.1	0.1	100	0.2	0.3
1076	DP (when used as a weapon)	100	0.2	0.5	600	0.7	1.6
1076	Phosgene	300	0.4	1.6	1500	2.0	6.1
1079	Sulfur dioxide	200	0.2	0.7	1250	1.3	3.6
1079	Sulphur dioxide	200	0.2	0.7	1250	1.3	3.6
1082	Trifluorochloroethylene, stabilized	100	0.1	0.1	200	0.3	0.6
1092	Acrolein, stabilized	300	0.7	2.0	3000	7.9	12.1
1098	Allyl alcohol	100	0.1	0.1	200	0.4	0.7
1135	Ethylene chlorohydrin	100	0.1	0.2	200	0.5	0.7
1143	Crotonaldehyde	100	0.1	0.1	200	0.3	0.5
1143	Crotonaldehyde, stabilized	100	0.1	0.1	200	0.3	0.5
1162	Dimethyldichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.3

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1163	1,1-Dimethylhydrazine	100	0.1	0.4	300	0.8	1.5
1163	Dimethylhydrazine, unsymmetrical	100	0.1	0.4	300	0.8	1.5
1182	Ethyl chloroformate	100	0.1	0.1	200	0.3	0.4
1183	Ethylchlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.4
1185	Ethyleneimine, stabilized	100	0.1	0.3	300	0.7	1.4
1196	Ethyltrichlorosilane (when spilled in water)	100	0.1	0.2	1000	0.5	1.7
1238	Methyl chloroformate	100	0.2	0.4	500	0.8	1.6
1239	Methyl chloromethyl ether	100	0.2	0.7	600	1.5	3.2
1242	Methyldichlorosilane (when spilled in water)	100	0.1	0.2	200	0.5	1.6
1244	Methylhydrazine	100	0.2	0.4	500	1.0	1.5
1250	Methyltrichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.3
1251	Methyl vinyl ketone, stabilized	500	1.0	2.3	3000	10.7	12.6
1259	Nickel carbonyl	500	0.9	3.1	3000	7.8	10.8
1295	Trichlorosilane (when spilled in water)	100	0.1	0.2	200	0.5	1.4
1298	Trimethylchlorosilane (when spilled in water)	100	0.1	0.1	100	0.3	0.7
1305	Vinyltrichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.3
1305	Vinyltrichlorosilane, stabilized (when spilled in water)	100	0.1	0.2	200	0.4	1.3
1340	Phosphorus pentasulfide, free from yellow or white Phosphorus (when spilled in water)	100	0.1	0.1	200	0.2	0.9
1340	Phosphorus pentasulphide, free from yellow or white Phosphorus (when spilled in water)	100	0.1	0.1	200	0.2	0.9
1360	Calcium phosphide (when spilled in water)	200	0.2	0.9	1500	2.8	7.6
1380	Pentaborane	200	0.4	1.4	1250	2.9	5.5
1384	Sodium dithionite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1384	Sodium hydrosulfite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1384	Sodium hydrosulphite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1397	Aluminum phosphide (when spilled in water)	200	0.3	1.2	2000	3.6	9.4
1412	Lithium amide (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1419	Magnesium aluminum phosphide (when spilled in water)	200	0.3	1.1	2000	3.3	8.8
1432	Sodium phosphide (when spilled in water)	100	0.2	0.8	1250	2.2	6.6
1510	Tetranitromethane	100	0.2	0.2	200	0.4	0.6
1541	Acetone cyanohydrin, stabilized (when spilled in water)	100	0.1	0.1	300	0.2	0.7
1556	MD (when used as a weapon)	100	0.1	0.4	500	0.4	1.4
1556	Methyldichloroarsine	100	0.1	0.2	200	0.3	0.5
1556	PD (when used as a weapon)	100	0.1	0.1	100	0.1	0.1
1560	Arsenic chloride	100	0.1	0.2	300	0.7	1.1
1560	Arsenic trichloride	100	0.1	0.2	300	0.7	1.1
1569	Bromoacetone	100	0.2	0.5	300	0.7	1.5
1580	Chloropicrin	100	0.3	0.6	500	1.2	2.1
1581	Chloropicrin and Methyl bromide mixture	100	0.1	0.4	1000	1.3	3.7
1581	Methyl bromide and Chloropicrin mixture	100	0.1	0.4	1000	1.3	3.7
1582	Chloropicrin and Methyl chloride mixture	100	0.1	0.3	200	0.2	1.1
1582	Methyl chloride and Chloropicrin mixture	100	0.1	0.3	200	0.2	1.1
1583	Chloropicrin mixture, n.o.s.	100	0.3	0.6	500	1.2	2.1
1589	CK (when used as a weapon)	200	0.3	1.0	2000	2.5	5.0

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1589	Cyanogen chloride, stabilized	300	0.3	0.9	1250	2.0	4.3
1595	Dimethyl sulfate	100	0.1	0.1	200	0.3	0.5
1595	Dimethyl sulphate	100	0.1	0.1	200	0.3	0.5
1605	Ethylene dibromide	100	0.1	0.1	100	0.2	0.3
1612	Hexaethyl tetraphosphate and compressed gas mixture	300	0.5	1.7	1250	2.2	5.1
1613	Hydrocyanic acid, aqueous solution, with not more than 20% Hydrogen cyanide	100	0.1	0.1	300	0.3	0.7
1613	Hydrogen cyanide, aqueous solution, with not more than 20% Hydrogen cyanide	100	0.1	0.1	300	0.3	0.7
1614	Hydrogen cyanide, stabilized (absorbed)	200	0.1	0.4	500	0.4	1.1
1647	Ethylene dibromide and Methyl bromide mixture, liquid	100	0.1	0.1	500	0.4	1.4
1647	Methyl bromide and Ethylene dibromide mixture, liquid	100	0.1	0.1	500	0.4	1.4
1660	Nitric oxide	100	0.1	0.4	300	0.4	1.4
1660	Nitric oxide, compressed	100	0.1	0.4	300	0.4	1.4
1670	Perchloromethyl mercaptan	100	0.2	0.2	300	0.5	0.9
1680	Potassium cyanide (when spilled in water)	100	0.1	0.1	300	0.2	0.8
1680	Potassium cyanide, solid (when spilled in water)	100	0.1	0.1	300	0.2	0.8
1689	Sodium cyanide (when spilled in water)	100	0.1	0.1	300	0.3	0.9
1689	Sodium cyanide, solid (when spilled in water)	100	0.1	0.1	300	0.3	0.9
1694	CA (when used as a weapon)	100	0.1	0.3	300	0.4	1.7
1695	Chloroacetone, stabilized	100	0.1	0.2	200	0.4	0.7
1697	CN (when used as a weapon)	100	0.1	0.1	200	0.2	0.9
1698	Adamsite (when used as a weapon)	100	0.1	0.2	200	0.2	0.9
1698	DM (when used as a weapon)	100	0.1	0.2	200	0.2	0.9
1699	DA (when used as a weapon)	100	0.1	0.4	600	0.6	2.4
1716	Acetyl bromide (when spilled in water)	100	0.1	0.2	200	0.4	1.1
1717	Acetyl chloride (when spilled in water)	100	0.1	0.2	300	0.6	1.8
1722	Allyl chlorocarbonate	300	0.8	1.8	2000	4.9	7.9
1722	Allyl chloroformate	300	0.8	1.8	2000	4.9	7.9
1724	Allyltrichlorosilane, stabilized (when spilled in water)	100	0.1	0.2	200	0.4	1.2
1725	Aluminum bromide, anhydrous (when spilled in water)	100	0.1	0.2	100	0.2	0.8
1726	Aluminum chloride, anhydrous (when spilled in water)	100	0.1	0.2	200	0.4	1.3
1728	Amyltrichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.2
1732	Antimony pentafluoride (when spilled in water)	100	0.1	0.3	500	0.8	2.5
1741	Boron trichloride (when spilled on land)	100	0.1	0.2	300	0.4	1.0
1741	Boron trichloride (when spilled in water)	100	0.1	0.3	300	0.8	2.4
1744	Bromine	200	0.4	1.1	1000	1.9	4.1
1744	Bromine, solution	200	0.4	1.1	1000	1.9	4.1
1744	Bromine, solution (Inhalation Hazard Zone A)	200	0.4	1.1	1000	1.9	4.1
1744	Bromine, solution (Inhalation Hazard Zone B)	100	0.3	0.7	500	1.2	2.1
1745	Bromine pentafluoride (when spilled on land)	100	0.2	0.6	500	0.9	2.0
1745	Bromine pentafluoride (when spilled in water)	100	0.1	0.4	500	0.8	2.6
1746	Bromine trifluoride (when spilled on land)	100	0.1	0.1	100	0.2	0.3

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1746	Bromine trifluoride (when spilled in water)	100	0.1	0.3	300	0.7	2.4
1747	Butyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1749	Chlorine trifluoride	200	0.3	1.1	1250	1.7	4.5
1752	Chloroacetyl chloride (when spilled on land)	100	0.2	0.4	500	0.9	1.5
1752	Chloroacetyl chloride (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1753	Chlorophenyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1754	Chlorosulfonic acid (when spilled on land)	100	0.1	0.1	100	0.2	0.3
1754	Chlorosulfonic acid (when spilled in water)	100	0.1	0.3	200	0.6	1.8
1754	Chlorosulfonic acid and Sulfur trioxide mixture (when spilled on land)	200	0.2	0.6	1000	1.8	3.6
1754	Chlorosulfonic acid and Sulfur trioxide mixture (when spilled in water)	100	0.1	0.3	200	0.6	1.8
1754	Chlorosulphonic acid (when spilled on land)	100	0.1	0.1	100	0.2	0.3
1754	Chlorosulphonic acid (when spilled in water)	100	0.1	0.3	200	0.6	1.8
1754	Chlorosulphonic acid and Sulphur trioxide mixture (when spilled on land)	200	0.2	0.6	1000	1.8	3.6
1754	Chlorosulphonic acid and Sulphur trioxide mixture (when spilled in water)	100	0.1	0.3	200	0.6	1.8
1754	Sulfur trioxide and Chlorosulfonic acid mixture (when spilled on land)	200	0.2	0.6	1000	1.8	3.6
1754	Sulfur trioxide and Chlorosulfonic acid mixture (when spilled in water)	100	0.1	0.3	200	0.6	1.8
1754	Sulphur trioxide and Chlorosulphonic acid mixture (when spilled on land)	200	0.2	0.6	1000	1.8	3.6
1754	Sulphur trioxide and Chlorosulphonic acid mixture (when spilled in water)	100	0.1	0.3	200	0.6	1.8
1758	Chromium oxychloride (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1762	Cyclohexenyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.3	0.9
1763	Cyclohexyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.3	0.9
1765	Dichloroacetyl chloride (when spilled in water)	100	0.1	0.1	100	0.2	0.6
1766	Dichlorophenyltrichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.4
1767	Diethyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1769	Diphenyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.4
1771	Dodecyltrichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	0.9
1777	Fluorosulfonic acid (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1777	Fluorosulphonic acid (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1781	Hexadecyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.4
1784	Hexyltrichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	0.9
1799	Nonyltrichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	1.0
1800	Octadecyltrichlorosilane (when spilled in water)	100	0.1	0.1	100	0.3	0.9
1801	Octyltrichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	1.0
1804	Phenyltrichlorosilane (when spilled in water)	100	0.1	0.1	200	0.3	1.0
1806	Phosphorus pentachloride (when spilled in water)	100	0.1	0.2	100	0.3	1.0
1808	Phosphorus tribromide (when spilled in water)	100	0.1	0.2	200	0.4	1.2
1809	Phosphorus trichloride (when spilled on land)	100	0.2	0.4	500	0.9	1.9
1809	Phosphorus trichloride (when spilled in water)	100	0.1	0.2	200	0.5	1.7
1810	Phosphorus oxychloride (when spilled on land)	100	0.2	0.4	300	0.7	1.3

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1810	Phosphorus oxychloride (when spilled in water)	100	0.1	0.2	200	0.5	1.4
1815	Propionyl chloride (when spilled in water)	100	0.1	0.1	100	0.2	0.5
1816	Propyltrichlorosilane (when spilled in water)	100	0.1	0.2	200	0.4	1.3
1818	Silicon tetrachloride (when spilled in water)	100	0.1	0.2	300	0.6	1.8
1828	Sulfur chlorides (when spilled on land)	100	0.1	0.1	200	0.5	0.8
1828	Sulfur chlorides (when spilled in water)	100	0.1	0.1	100	0.2	0.8
1828	Sulphur chlorides (when spilled on land)	100	0.1	0.1	200	0.5	0.8
1828	Sulphur chlorides (when spilled in water)	100	0.1	0.1	100	0.2	0.8
1829	Sulfur trioxide, inhibited	200	0.2	0.6	1000	1.8	3.6
1829	Sulfur trioxide, stabilized	200	0.2	0.6	1000	1.8	3.6
1829	Sulfur trioxide, uninhibited	200	0.2	0.6	1000	1.8	3.6
1829	Sulphur trioxide, inhibited	200	0.2	0.6	1000	1.8	3.6
1829	Sulphur trioxide, stabilized	200	0.2	0.6	1000	1.8	3.6
1829	Sulphur trioxide, uninhibited	200	0.2	0.6	1000	1.8	3.6
1831	Sulfuric acid, fuming	200	0.2	0.6	1000	1.8	3.6
1831	Sulfuric acid, fuming, with not less than 30% free Sulfur trioxide	200	0.2	0.6	1000	1.8	3.6
1831	Sulphuric acid, fuming	200	0.2	0.6	1000	1.8	3.6
1831	Sulphuric acid, fuming, with not less than 30% free Sulphur trioxide	200	0.2	0.6	1000	1.8	3.6
1834	Sulfuryl chloride (when spilled on land)	100	0.1	0.4	300	0.6	1.3
1834	Sulfuryl chloride (when spilled in water)	100	0.1	0.1	200	0.3	1.2
1834	Sulphuryl chloride (when spilled on land)	100	0.1	0.4	300	0.6	1.3
1834	Sulphuryl chloride (when spilled in water)	100	0.1	0.1	200	0.3	1.2
1836	Thionyl chloride (when spilled on land)	100	0.2	0.5	300	0.6	1.2
1836	Thionyl chloride (when spilled in water)	100	0.2	0.9	1000	2.1	4.7
1838	Titanium tetrachloride (when spilled on land)	100	0.1	0.1	200	0.3	0.5
1838	Titanium tetrachloride (when spilled in water)	100	0.1	0.1	200	0.4	1.2
1859	Silicon tetrafluoride	100	0.1	0.3	300	0.3	1.2
1859	Silicon tetrafluoride, compressed	100	0.1	0.3	300	0.3	1.2
1892	ED (when used as a weapon)	100	0.1	0.2	500	0.5	1.2
1892	Ethylidichloroarsine	100	0.1	0.2	200	0.4	0.6
1898	Acetyl iodide (when spilled in water)	100	0.1	0.2	200	0.3	0.9
1911	Diborane	200	0.2	0.8	1000	1.1	2.7
1911	Diborane, compressed	200	0.2	0.8	1000	1.1	2.7
1923	Calcium dithionite (when spilled in water)	100	0.1	0.2	100	0.2	0.8
1923	Calcium hydrosulfite (when spilled in water)	100	0.1	0.2	100	0.2	0.8
1923	Calcium hydrosulphite (when spilled in water)	100	0.1	0.2	100	0.2	0.8
1929	Potassium dithionite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1929	Potassium hydrosulfite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1929	Potassium hydrosulphite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1931	Zinc dithionite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1931	Zinc hydrosulfite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1931	Zinc hydrosulphite (when spilled in water)	100	0.1	0.1	100	0.2	0.7
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
1953	Compressed gas, flammable, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
1953	Compressed gas, flammable, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
1953	Compressed gas, poisonous, flammable, n.o.s.	300	0.4	1.5	2500	2.7	5.6
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
1953	Compressed gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
1953	Compressed gas, toxic, flammable, n.o.s.	300	0.4	1.5	2500	2.7	5.6
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
1953	Compressed gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
1955	Compressed gas, poisonous, n.o.s.	300	0.3	1.3	2500	2.7	5.6
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.3	2500	2.7	5.6
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	2.0
1955	Compressed gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
1955	Compressed gas, toxic, n.o.s.	300	0.3	1.3	2500	2.7	5.6
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.3	2500	2.7	5.6
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	2.0
1955	Compressed gas, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
1955	Organic phosphate compound mixed with compressed gas	300	0.7	2.1	1500	2.7	6.0
1955	Organic phosphate mixed with compressed gas	300	0.7	2.1	1500	2.7	6.0
1955	Organic phosphorus compound mixed with compressed gas	300	0.7	2.1	1500	2.7	6.0
1967	Insecticide gas, poisonous, n.o.s.	300	0.7	2.1	1500	2.7	6.0
1967	Insecticide gas, toxic, n.o.s.	300	0.7	2.1	1500	2.7	6.0
1967	Parathion and compressed gas mixture	300	0.7	2.1	1500	2.7	6.0
1975	Dinitrogen tetroxide and Nitric oxide mixture	100	0.1	0.4	300	0.4	1.4
1975	Nitric oxide and Dinitrogen tetroxide mixture	100	0.1	0.4	300	0.4	1.4
1975	Nitric oxide and Nitrogen dioxide mixture	100	0.1	0.4	300	0.4	1.4
1975	Nitric oxide and Nitrogen tetroxide mixture	100	0.1	0.4	300	0.4	1.4
1975	Nitrogen dioxide and Nitric oxide mixture	100	0.1	0.4	300	0.4	1.4
1975	Nitrogen tetroxide and Nitric oxide mixture	100	0.1	0.4	300	0.4	1.4
1994	Iron pentacarbonyl	300	0.6	1.3	1500	3.5	5.5
2004	Magnesium diamide (when spilled in water)	100	0.1	0.2	200	0.4	1.5
2011	Magnesium phosphide (when spilled in water)	200	0.3	1.0	1500	3.0	8.5
2012	Potassium phosphide (when spilled in water)	100	0.2	0.7	1250	2.0	5.9
2013	Strontium phosphide (when spilled in water)	100	0.2	0.7	1250	1.9	5.9
2032	Nitric acid, fuming	100	0.1	0.2	500	0.4	0.7
2032	Nitric acid, red fuming	100	0.1	0.2	500	0.4	0.7
2186	Hydrogen chloride, refrigerated liquid	100	0.1	0.2	1500	1.7	6.3
2188	Arsine	600	0.7	2.5	3000	4.4	7.5
2188	SA (when used as a weapon)	1250	1.3	3.4	3000	5.7	9.3
2189	Dichlorosilane	100	0.1	0.6	2500	2.6	6.4
2190	Oxygen difluoride	2500	3.3	7.0+	3000	17.9	19.1
2190	Oxygen difluoride, compressed	2500	3.3	7.0+	3000	17.9	19.1
2191	Sulfuryl fluoride	100	0.1	0.3	1000	1.1	3.1
2191	Sulphuryl fluoride	100	0.1	0.3	1000	1.1	3.1
2192	Germane	100	0.1	0.5	500	0.5	1.8
2194	Selenium hexafluoride	200	0.3	1.2	1500	1.8	4.0
2195	Tellurium hexafluoride	600	0.8	2.7	3000	5.9	9.3
2196	Tungsten hexafluoride	100	0.1	0.5	500	0.6	1.8
2197	Hydrogen iodide, anhydrous	100	0.1	0.2	500	0.6	2.0
2198	Phosphorus pentafluoride	100	0.2	0.7	600	0.8	2.4
2198	Phosphorus pentafluoride, compressed	100	0.2	0.7	600	0.8	2.4
2199	Phosphine	300	0.4	1.5	2500	2.7	5.6
2202	Hydrogen selenide, anhydrous	600	0.8	2.9	3000	5.4	9.4
2204	Carbonyl sulfide	100	0.1	0.4	1500	2.1	5.4
2204	Carbonyl sulphide	100	0.1	0.4	1500	2.1	5.4
2232	Chloroacetaldehyde	100	0.1	0.3	300	0.5	0.9
2232	2-Chloroethanal	100	0.1	0.3	300	0.5	0.9
2308	Nitrosylsulfuric acid (when spilled in water)	100	0.1	0.3	1000	0.5	1.6
2308	Nitrosylsulfuric acid, liquid (when spilled in water)	100	0.1	0.3	1000	0.5	1.6
2308	Nitrosylsulfuric acid, solid (when spilled in water)	100	0.1	0.3	1000	0.5	1.6
2308	Nitrosylsulphuric acid (when spilled in water)	100	0.1	0.3	1000	0.5	1.6
2308	Nitrosylsulphuric acid, liquid (when spilled in water)	100	0.1	0.3	1000	0.5	1.6
2308	Nitrosylsulphuric acid, solid (when spilled in water)	100	0.1	0.3	1000	0.5	1.6

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
2334	Allylamine	100	0.1	0.4	500	1.1	1.9
2337	Phenyl mercaptan	100	0.1	0.1	100	0.2	0.3
2353	Butyryl chloride (when spilled in water)	100	0.1	0.1	100	0.2	0.6
2382	1,2-Dimethylhydrazine	100	0.1	0.3	300	0.6	1.1
2382	Dimethylhydrazine, symmetrical	100	0.1	0.3	300	0.6	1.1
2395	Isobutyryl chloride (when spilled in water)	100	0.1	0.1	100	0.2	0.4
2407	Isopropyl chloroformate	100	0.1	0.2	200	0.5	0.9
2417	Carbonyl fluoride	100	0.1	0.5	500	0.5	1.9
2417	Carbonyl fluoride, compressed	100	0.1	0.5	500	0.5	1.9
2418	Sulfur tetrafluoride	300	0.4	1.6	2500	2.9	6.4
2418	Sulphur tetrafluoride	300	0.4	1.6	2500	2.9	6.4
2420	Hexafluoroacetone	200	0.2	0.9	3000	5.2	11.1
2421	Nitrogen trioxide	100	0.1	0.2	300	0.2	0.8
2434	Dibenzylchlorosilane (when spilled in water)	100	0.1	0.1	100	0.1	0.4
2435	Ethylphenyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.2	0.7
2437	Methylphenyldichlorosilane (when spilled in water)	100	0.1	0.1	100	0.1	0.4
2438	Trimethylacetyl chloride	100	0.1	0.2	200	0.4	0.7
2442	Trichloroacetyl chloride	100	0.1	0.2	200	0.5	0.8
2474	Thiophosgene	200	0.4	1.3	1000	1.9	3.3
2477	Methyl isothiocyanate	100	0.1	0.1	200	0.3	0.5
2480	Methyl isocyanate	500	1.1	3.3	3000	14.3	16.5
2481	Ethyl isocyanate	500	1.0	2.4	3000	11.3	14.6
2482	n-Propyl isocyanate	300	0.8	1.7	2500	6.0	8.8
2483	Isopropyl isocyanate	300	0.8	1.9	3000	7.4	10.2
2484	tert-Butyl isocyanate	300	0.7	1.6	2500	5.8	8.3
2485	n-Butyl isocyanate	200	0.5	1.1	1250	3.0	4.3
2486	Isobutyl isocyanate	200	0.5	1.1	1250	3.0	4.6
2487	Phenyl isocyanate	100	0.3	0.4	500	1.0	1.6
2488	Cyclohexyl isocyanate	100	0.2	0.2	300	0.6	0.9
2495	Iodine pentafluoride (when spilled in water)	100	0.1	0.4	500	0.8	2.6
2521	Diketene, stabilized	100	0.1	0.1	100	0.2	0.3
2534	Methylchlorosilane	100	0.1	0.4	1000	1.0	2.7
2548	Chlorine pentafluoride	200	0.2	0.9	1250	1.4	4.1
2600	Carbon monoxide and Hydrogen mixture	100	0.1	0.1	500	0.5	1.7
2600	Carbon monoxide and Hydrogen mixture, compressed	100	0.1	0.1	500	0.5	1.7
2600	Hydrogen and Carbon monoxide mixture	100	0.1	0.1	500	0.5	1.7
2600	Hydrogen and Carbon monoxide mixture, compressed	100	0.1	0.1	500	0.5	1.7
2605	Methoxymethyl isocyanate	100	0.3	0.4	500	1.0	1.6
2606	Methyl orthosilicate	100	0.1	0.1	100	0.2	0.3
2644	Methyl iodide	100	0.1	0.1	300	0.2	0.5
2646	Hexachlorocyclopentadiene	100	0.1	0.1	100	0.3	0.3
2668	Chloroacetonitrile	100	0.1	0.1	100	0.2	0.3
2676	Stibine	200	0.2	1.1	1500	1.7	4.5
2691	Phosphorus pentabromide (when spilled in water)	100	0.1	0.2	100	0.3	1.0
2692	Boron tribromide (when spilled on land)	100	0.1	0.2	200	0.3	0.6
2692	Boron tribromide (when spilled in water)	100	0.1	0.4	300	0.6	1.9
2740	n-Propyl chloroformate	100	0.1	0.2	200	0.5	0.8

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
2742	sec-Butyl chloroformate	100	0.1	0.1	100	0.2	0.4
2742	Isobutyl chloroformate	100	0.1	0.1	100	0.2	0.3
2743	n-Butyl chloroformate	100	0.1	0.1	100	0.2	0.3
2806	Lithium nitride (when spilled in water)	100	0.1	0.2	200	0.4	1.4
2810	Buzz (when used as a weapon)	100	0.1	0.1	100	0.1	0.3
2810	BZ (when used as a weapon)	100	0.1	0.1	100	0.1	0.3
2810	CS (when used as a weapon)	100	0.1	0.4	300	0.3	1.3
2810	DC (when used as a weapon)	100	0.1	0.4	300	0.3	1.3
2810	GA (when used as a weapon)	100	0.1	0.1	300	0.4	0.4
2810	GB (when used as a weapon)	200	0.3	0.8	2500	1.4	2.8
2810	GD (when used as a weapon)	200	0.3	0.5	1250	1.1	1.5
2810	GF (when used as a weapon)	200	0.2	0.2	500	0.6	0.7
2810	H (when used as a weapon)	100	0.1	0.1	200	0.2	0.3
2810	HD (when used as a weapon)	100	0.1	0.1	200	0.2	0.3
2810	HL (when used as a weapon)	100	0.1	0.2	300	0.3	0.7
2810	HN-1 (when used as a weapon)	100	0.1	0.1	200	0.2	0.4
2810	HN-2 (when used as a weapon)	100	0.1	0.1	200	0.2	0.3
2810	HN-3 (when used as a weapon)	100	0.1	0.1	100	0.1	0.1
2810	L (Lewisite) (when used as a weapon)	100	0.1	0.2	300	0.3	0.7
2810	Lewisite (when used as a weapon)	100	0.1	0.2	300	0.3	0.7
2810	Mustard (when used as a weapon)	100	0.1	0.1	200	0.2	0.3
2810	Mustard Lewisite (when used as a weapon)	100	0.1	0.2	300	0.3	0.7
2810	Poisonous liquid, n.o.s.	200	0.5	1.1	1000	1.8	3.6
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
2810	Poisonous liquid, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2810	Poisonous liquid, organic, n.o.s.	200	0.5	1.1	1250	3.0	4.6
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1250	3.0	4.6
2810	Poisonous liquid, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2810	Sarin (when used as a weapon)	200	0.3	0.8	2500	1.4	2.8
2810	Soman (when used as a weapon)	200	0.3	0.5	1250	1.1	1.5
2810	Tabun (when used as a weapon)	100	0.1	0.1	300	0.4	0.4
2810	Thickened GD (when used as a weapon)	200	0.3	0.5	1250	1.1	1.5
2810	Toxic liquid, n.o.s.	200	0.5	1.1	1000	1.8	3.6
2810	Toxic liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
2810	Toxic liquid, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2810	Toxic liquid, organic, n.o.s.	200	0.5	1.1	1250	3.0	4.6
2810	Toxic liquid, organic, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1250	3.0	4.6
2810	Toxic liquid, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2810	VX (when used as a weapon)	100	0.1	0.1	200	0.2	0.3
2811	CX (when used as a weapon)	100	0.1	0.4	300	0.3	1.4
2826	Ethyl chlorothioformate	100	0.1	0.1	200	0.3	0.5
2845	Ethyl phosphonous dichloride, anhydrous	100	0.2	0.5	500	1.0	1.8
2845	Methyl phosphonous dichloride	100	0.3	0.8	600	1.6	2.8
2901	Bromine chloride	100	0.2	0.6	1250	1.5	4.0

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
2927	Ethyl phosphonothioic dichloride, anhydrous	100	0.1	0.1	100	0.1	0.2
2927	Ethyl phosphorodichloridate	100	0.1	0.1	100	0.2	0.2
2927	Poisonous liquid, corrosive, n.o.s.	200	0.5	1.1	1000	1.8	3.6
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
2927	Poisonous liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2927	Poisonous liquid, corrosive, organic, n.o.s.	300	0.8	1.8	2000	4.9	7.9
2927	Poisonous liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone A)	300	0.8	1.8	2000	4.9	7.9
2927	Poisonous liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2927	Toxic liquid, corrosive, n.o.s.	200	0.5	1.1	1000	1.8	3.6
2927	Toxic liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
2927	Toxic liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2927	Toxic liquid, corrosive, organic, n.o.s.	300	0.8	1.8	2000	4.9	7.9
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone A)	300	0.8	1.8	2000	4.9	7.9
2927	Toxic liquid, corrosive, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2929	Poisonous liquid, flammable, n.o.s.	200	0.4	1.4	1250	2.9	5.5
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.4	1250	2.9	5.5
2929	Poisonous liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2929	Poisonous liquid, flammable, organic, n.o.s.	300	0.7	1.6	2000	4.9	7.9
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	300	0.7	1.6	2000	4.9	7.9
2929	Poisonous liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2929	Toxic liquid, flammable, n.o.s.	200	0.4	1.4	1250	2.9	5.5
2929	Toxic liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.4	1250	2.9	5.5
2929	Toxic liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2929	Toxic liquid, flammable, organic, n.o.s.	300	0.7	1.6	2000	4.9	7.9
2929	Toxic liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone A)	300	0.7	1.6	2000	4.9	7.9
2929	Toxic liquid, flammable, organic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
2977	Radioactive material, Uranium hexafluoride, fissile (when spilled in water)	100	0.1	0.2	200	0.3	1.4
2977	Uranium hexafluoride, fissile containing more than 1% Uranium-235 (when spilled in water)	100	0.1	0.2	200	0.3	1.4
2978	Radioactive material, Uranium hexafluoride (when spilled in water)	100	0.1	0.2	200	0.3	1.4

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
2978	Uranium hexafluoride (when spilled in water)	100	0.1	0.2	200	0.3	1.4
2978	Uranium hexafluoride, non fissile or fissile-excepted (when spilled in water)	100	0.1	0.2	200	0.3	1.4
2985	Chlorosilanes, flammable, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
2985	Chlorosilanes, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
2986	Chlorosilanes, corrosive, flammable, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
2986	Chlorosilanes, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
2987	Chlorosilanes, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
2987	Chlorosilanes, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
2988	Chlorosilanes, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
2988	Chlorosilanes, water-reactive, flammable, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
3023	2-Methyl-2-heptanethiol	100	0.1	0.1	200	0.3	0.5
3023	tert-Octyl mercaptan	100	0.1	0.1	200	0.3	0.5
3048	Aluminum phosphide pesticide (when spilled in water)	200	0.3	1.2	2000	3.6	9.3
3049	Metal alkyl halides, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	0.8
3049	Metal alkyl halides, water-reactive, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	0.8
3049	Metal aryl halides, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	0.8
3049	Metal aryl halides, water-reactive, n.o.s. (when spilled in water)	100	0.1	0.1	200	0.3	0.8
3052	Aluminum alkyl halides (when spilled in water)	100	0.1	0.1	200	0.3	0.8
3052	Aluminum alkyl halides, liquid (when spilled in water)	100	0.1	0.1	200	0.3	0.8
3052	Aluminum alkyl halides, solid (when spilled in water)	100	0.1	0.1	200	0.3	0.8
3057	Trifluoroacetyl chloride	100	0.2	0.7	2500	2.9	8
3079	Methacrylonitrile, stabilized	100	0.1	0.1	200	0.3	0.5
3083	Perchloryl fluoride	100	0.1	0.4	1500	2.0	5.2
3122	Poisonous liquid, oxidizing, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3122	Poisonous liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3122	Poisonous liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3122	Toxic liquid, oxidizing, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3122	Toxic liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3122	Toxic liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3123	Poisonous liquid, water-reactive, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3123	Poisonous liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3123	Poisonous liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3123	Toxic liquid, water-reactive, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3123	Toxic liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3123	Toxic liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3123	Toxic liquid, which in contact with water emits flammable gases, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3123	Toxic liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3123	Toxic liquid, which in contact with water emits flammable gases, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3160	Liquefied gas, poisonous, flammable, n.o.s.	300	0.4	1.5	2500	2.7	5.6
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3160	Liquefied gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3160	Liquefied gas, toxic, flammable, n.o.s.	300	0.4	1.5	2500	2.7	5.6
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3160	Liquefied gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3162	Liquefied gas, poisonous, n.o.s.	300	0.3	1.3	2500	2.7	5.6
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.3	2500	2.7	5.6
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	2.0
3162	Liquefied gas, poisonous, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3162	Liquefied gas, toxic, n.o.s.	300	0.3	1.3	2500	2.7	5.6
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.3	2500	2.7	5.6

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	600	0.6	2.0
3162	Liquefied gas, toxic, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3246	Methanesulfonyl chloride	100	0.1	0.1	100	0.1	0.2
3246	Methanesulphonyl chloride	100	0.1	0.1	100	0.1	0.2
3275	Nitriles, poisonous, flammable, n.o.s.	100	0.1	0.1	200	0.3	0.5
3275	Nitriles, toxic, flammable, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, poisonous, liquid n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, poisonous, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, toxic, liquid, n.o.s.	100	0.1	0.1	200	0.3	0.5
3276	Nitriles, toxic, n.o.s.	100	0.1	0.1	200	0.3	0.5
3278	Organophosphorus compound, poisonous, liquid, n.o.s.	100	0.3	0.8	600	1.6	2.8
3278	Organophosphorus compound, poisonous, n.o.s.	100	0.3	0.8	600	1.6	2.8
3278	Organophosphorus compound, toxic, liquid, n.o.s.	100	0.3	0.8	600	1.6	2.8
3278	Organophosphorus compound, toxic, n.o.s.	100	0.3	0.8	600	1.6	2.8
3279	Organophosphorus compound, poisonous, flammable, n.o.s.	100	0.3	0.8	600	1.6	2.8
3279	Organophosphorus compound, toxic, flammable, n.o.s.	100	0.3	0.8	600	1.6	2.8
3280	Organoarsenic compound, liquid, n.o.s.	100	0.1	0.5	500	1.3	3.0
3280	Organoarsenic compound, n.o.s.	100	0.1	0.5	500	1.3	3.0
3281	Metal carbonyls, liquid, n.o.s.	500	0.9	3.1	3000	7.8	10.8
3281	Metal carbonyls, n.o.s.	500	0.9	3.1	3000	7.8	10.8
3287	Poisonous liquid, inorganic, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3287	Poisonous liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	500	0.4	0.7
3287	Toxic liquid, inorganic, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3287	Toxic liquid, inorganic, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3287	Toxic liquid, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	500	0.4	0.7
3289	Poisonous liquid, corrosive, inorganic, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3289	Poisonous liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.5	0.8
3289	Toxic liquid, corrosive, inorganic, n.o.s.	200	0.5	1.1	1000	1.8	3.6
3289	Toxic liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3289	Toxic liquid, corrosive, inorganic, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.5	0.8

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3294	Hydrogen cyanide, solution in alcohol, with not more than 45% Hydrogen cyanide	100	0.1	0.2	600	0.3	1.2
3300	Carbon dioxide and Ethylene oxide mixture, with more than 87% Ethylene oxide	100	0.1	0.1	500	0.5	1.6
3300	Ethylene oxide and Carbon dioxide mixture, with more than 87% Ethylene oxide	100	0.1	0.1	500	0.5	1.6
3303	Compressed gas, poisonous, oxidizing, n.o.s.	300	0.3	1.3	2500	2.7	5.6
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.3	2500	2.7	5.6
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	1500	1.7	4.5
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3303	Compressed gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3303	Compressed gas, toxic, oxidizing, n.o.s.	300	0.3	1.3	2500	2.7	5.6
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.3	2500	2.7	5.6
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	1500	1.7	4.5
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3303	Compressed gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3304	Compressed gas, poisonous, corrosive, n.o.s.	500	0.4	1.6	2500	2.9	6.4
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	500	0.4	1.6	2500	2.9	6.4
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	1250	1.5	4.0
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1.1	2.2
3304	Compressed gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3304	Compressed gas, toxic, corrosive, n.o.s.	500	0.4	1.6	2500	2.9	6.4
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone A)	500	0.4	1.6	2500	2.9	6.4
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	1250	1.5	4.0
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1.1	2.2
3304	Compressed gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s.	300	0.4	1.6	2500	2.9	6.4
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2500	2.9	6.4
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	2500	2.6	6.4

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3305	Compressed gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3305	Compressed gas, toxic, flammable, corrosive, n.o.s.	300	0.4	1.6	2500	2.9	6.4
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2500	2.9	6.4
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	2500	2.6	6.4
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3305	Compressed gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s.	300	0.4	1.5	2500	2.7	5.6
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	1500	1.7	4.5
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3306	Compressed gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s.	300	0.4	1.5	2500	2.7	5.6
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	1500	1.7	4.5
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3306	Compressed gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3307	Liquefied gas, poisonous, oxidizing, n.o.s.	300	0.3	1.3	2500	2.7	5.6
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.3	2500	2.7	5.6
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	1500	1.7	4.5
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3307	Liquefied gas, poisonous, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3307	Liquefied gas, toxic, oxidizing, n.o.s.	300	0.3	1.3	2500	2.7	5.6
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone A)	300	0.3	1.3	2500	2.7	5.6
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	1500	1.7	4.5
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3307	Liquefied gas, toxic, oxidizing, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3308	Liquefied gas, poisonous, corrosive, n.o.s.	500	0.4	1.6	2500	2.9	6.4
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone A)	500	0.4	1.6	2500	2.9	6.4
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	1250	1.5	4.0
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1.1	2.2
3308	Liquefied gas, poisonous, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3308	Liquefied gas, toxic, corrosive, n.o.s.	500	0.4	1.6	2500	2.9	6.4
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone A)	500	0.4	1.6	2500	2.9	6.4
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	1250	1.5	4.0
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.3	1000	1.1	2.2
3308	Liquefied gas, toxic, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s.	300	0.4	1.6	2500	2.9	6.4
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2500	2.9	6.4
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	2500	2.6	6.4
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3309	Liquefied gas, poisonous, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s.	300	0.4	1.6	2500	2.9	6.4
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.6	2500	2.9	6.4
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.6	2500	2.6	6.4
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3309	Liquefied gas, toxic, flammable, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s.	300	0.4	1.5	2500	2.7	5.6
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	1500	1.7	4.5
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3310	Liquefied gas, poisonous, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s.	300	0.4	1.5	2500	2.7	5.6

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone B)	200	0.2	0.6	1500	1.7	4.5
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3310	Liquefied gas, toxic, oxidizing, corrosive, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3318	Ammonia solution, with more than 50% ammonia	100	0.1	0.1	500	0.5	1.4
3355	Insecticide gas, poisonous, flammable, n.o.s	300	0.4	1.5	2500	2.7	5.6
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3.0
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3355	Insecticide gas, poisonous, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3355	Insecticide gas, toxic, flammable, n.o.s	300	0.4	1.5	2500	2.7	5.6
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone A)	300	0.4	1.5	2500	2.7	5.6
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.5	1250	1.2	3
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone C)	100	0.1	0.2	1000	0.8	2.6
3355	Insecticide gas, toxic, flammable, n.o.s. (Inhalation Hazard Zone D)	100	0.1	0.1	500	0.5	1.7
3361	Chlorosilanes, poisonous, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
3361	Chlorosilanes, toxic, corrosive, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
3362	Chlorosilanes, poisonous, corrosive, flammable, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
3362	Chlorosilanes, toxic, corrosive, flammable, n.o.s. (when spilled in water)	100	0.1	0.1	300	0.3	1.0
3381	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3381	Toxic by inhalation liquid, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3382	Poisonous by inhalation liquid, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3382	Toxic by inhalation liquid, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3383	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.4	1250	2.9	5.5
3383	Toxic by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone A)	200	0.4	1.4	1250	2.9	5.5

TABLE A.1 (Cont.)

UN ID No.	Name of Material	Small Spills			Large Spills		
		First Isolate in all Directions (ft)	Then Protect Downwind during		First Isolate in all Directions (ft)	Then Protect Downwind during	
			Day (mi)	Night (mi)		Day (mi)	Night (mi)
3384	Poisonous by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3384	Toxic by inhalation liquid, flammable, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3385	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3385	Toxic by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3386	Poisonous by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3386	Toxic by inhalation liquid, water-reactive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3387	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3387	Toxic by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3388	Poisonous by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3388	Toxic by inhalation liquid, oxidizing, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.2	200	0.4	0.6
3389	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3389	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone A)	200	0.5	1.1	1000	1.8	3.6
3390	Poisonous by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3390	Toxic by inhalation liquid, corrosive, n.o.s. (Inhalation Hazard Zone B)	100	0.1	0.1	200	0.3	0.5
3456	Nitrosylsulfuric acid, solid (when spilled in water)	100	0.1	0.3	600	0.5	1.6
3456	Nitrosylsulphuric acid, solid (when spilled in water)	100	0.1	0.3	600	0.5	1.6
3461	Aluminum alkyl halides, solid (when spilled in water)	100	0.1	0.1	200	0.3	0.8
9191	Chlorine dioxide, hydrate, frozen (when spilled in water)	100	0.1	0.1	100	0.2	0.4
9192	Fluorine, refrigerated liquid (cryogenic liquid)	100	0.1	0.2	500	0.5	1.9
9202	Carbon monoxide, refrigerated liquid (cryogenic liquid)	100	0.1	0.1	500	0.5	1.7
9206	Methyl phosphonic dichloride	100	0.1	0.1	200	0.3	0.4
9263	Chloropivaloyl chloride	100	0.1	0.1	100	0.2	0.2
9264	3,5-Dichloro-2,4,6-trifluoropyridine	100	0.1	0.1	100	0.2	0.2
9269	Trimethoxysilane	100	0.1	0.3	500	0.7	1.3

APPENDIX B:
CHEMICALS ANALYZED IN THE ERG2008 ANALYSIS

APPENDIX B:

CHEMICALS ANALYZED IN THE ERG2008 ANALYSIS

Table B.1 lists the 164 chemicals analyzed in the *2008 Emergency Response Guidebook* (ERG2008) analysis in alphabetical order by U.S. Department of Transportation (DOT) name. Most of these materials are toxic by inhalation (TIH) materials; however, several are surrogates for generic table entries (e.g., 2-amino-2-methylpropanenitrile) or mildly toxic components of mixtures (benzene, methyl chloride, etc). For reference, the Chemical Abstract Services (CAS) number, boiling point, vapor pressure at 20°C, and toxicological data are provided. Additional chemical data used in the analysis include critical temperature, critical volume, melting point, and the following temperature-dependent properties: heat of vaporization, liquid density, specific heat of the liquid, viscosity, and surface tension.

TABLE B.1 Chemicals Analyzed for the ERG2008 (abbreviations are defined at end of table)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC ₅₀ or LC _{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Acrolein	107-02-8	56.1	52.7	29.69	62	0.15	0.3	ERPG
Acrylonitrile	107-13-1	53	77.4	11.4	392	35	70	ERPG
Aldicarb	116-06-3	N/A	N/A	N/A	1	0.01	0.02	LC ₅₀
Allyl alcohol	107-18-6	58.1	97.1	2.491	330	4.2	4.2	AEGL-I
Allyl chloroformate	2937-50-0	120.5	112.9	6.194	7	0.07	0.14	LC ₅₀
Allyl isothiocyanate	57-06-7	99.2	150.7	0.516	635	6.4	13	LC ₅₀ -S
Allylamine	107-11-9	57.1	53.4	25.69	572	3.3	3.3	AEGL-I
2-Amino-2-methylpropanenitrile	19355-69-2	84.1	159.5	0.099	112	1	2	LC ₅₀
Ammonia	7664-41-7	17	-33.5	854.5	7,338	150	300	ERPG
Arsenic trichloride	7784-34-1	181.2	130.1	1.113	56	0.56	1.1	LC _{LO}
Arsine	7784-42-1	77.9	-62.5	1475	30	0.17	0.3	AEGL-F
Benzene	71-43-2	78.1	80.1	9.983	26,458	150	300	ERPG
Bis-(2-chloroethyl) ethylamine	538-07-8	170.1	193.9	0.023	3.6	0.036	0.072	LC ₅₀
Bis-(2-chloroethyl) methylamine	51-75-2	156.1	174.9	0.039	7.8	0.078	0.157	LC ₅₀
Bis-(2-chloroethyl) sulfide	505-60-2	159.1	216.9	0.010	6.5	0.02	0.09	AEGL-F
Boron tribromide	10294-33-4	251.5	89.0	7.336	387-S	3.9	7.8	LC ₅₀ -S
Boron trichloride	10294-34-5	117.2	12.5	132.2	2541	25	50	LC ₅₀
Boron trifluoride	7637-07-2	67.8	-99.8	4,264	387	30 mg/m ³	60 mg/m ³	ERPG
Bromine	7726-95-6	159.8	58.8	22.87	310	0.5	1	ERPG
Bromine chloride	13863-41-7	115.4	4.9	220.0	290	3	6	LC ₅₀
Bromine pentafluoride	7789-30-2	174.9	40.9	42.88	299-S	3	6	LC ₅₀
Bromine trifluoride	7787-71-5	136.9	125.9	0.774	299-S	3	6	LC ₅₀
Bromoacetone	598-31-2	137	135.9	11.431	95	1	2	LC _{LO}
n-Butyl chloroformate	592-34-7	136.6	137.9	0.765	323-S	3	6	LC ₅₀
sec-Butyl chloroformate	17462-58-7	136.6	127.9-E	1.051-E	323	3	6	LC ₅₀ -S
n-Butylisocyanate	111-36-4	99.1	115.0-S	1.755-S	105	0.05	0.1	ERPG
tert-Butyl-isocyanate	1609-86-5	99.1	86.0	4.888-E	22	0.05	0.1	ERPG-S
tert-Butylarsine	117791-53-4	134	44.4-E	40.35-E	147	1.5	3	LC ₅₀
Carbon monoxide	630-08-0	28	-191.5	2,792	4,590	350	700	ERPG
Carbon tetrachloride	56-23-5	153.8	76.7	12.138	19,000	100	200	ERPG
Carbonyl fluoride	353-50-4	66	-84.6	5,211	360	3.6	7.2	LC ₅₀
Carbonyl sulfide	463-58-1	60.1	-50.2	1,124	924	9.2	18	LC ₅₀
Chlorine	7782-50-5	70.9	-34.1	679.7	293	2	2.8	AEGL-F

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TABLE B.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC ₅₀ or LC _{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Chlorine pentafluoride	13637-63-3	130.4	-13.9	332.1	122	1	2	ERPG-S
Chlorine trifluoride	7790-91-2	92.4	11.8	148.0	299	1	2	ERPG
Chloroacetaldehyde	107-20-0	78.5	84.9	3.522	200	2	4	LC ₅₀
Chloroacetone	78-95-5	92.5	120.1	1.567	262	2.6	5.2	LC ₅₀
Chloroacetonitrile	107-14-2	75.5	126.0	1.087	500	5	10	LC _{LO}
Chloroacetyl chloride	79-04-9	112.9	106.0	2.522	660	0.5	1	ERPG
Chloromethyl methyl ether	107-30-2	80.5	59.5	21.14	441	1	2	ERPG
p-Chlorophenyl isocyanate	104-12-1	153.6	199.0	0.069	18	0.36	0.72	LC ₅₀
Chloropicrin	76-06-2	164.4	111.9	3.190	28	0.3	0.6	ERPG
Chloropivaloyl chloride	4300-97-4	155	147.9	0.189-E	126	1.3	2.6	LC ₅₀
Chlorosulfonic acid	7790-94-5	116.5	153.9	0.309	929 mg/m ³	10 mg/m ³	20 mg/m ³	ERPG
Crotonaldehyde	4170-30-3	70.1	104.9	3.121	380	10	20	ERPG
Cyanogen	460-19-5	52	-21.2	489.7	350	3.5	7	LC ₅₀
Cyanogen chloride	506-77-4	61.5	12.9	135.0	80	0.4	0.8	ERPG
Cyclohexyl isocyanate	3173-53-3	125.2	169.0	0.094	15	0.05	0.1	ERPG-S
Cyclohexyl methylphosphonofluoridate	329-99-7	180.2	238.9	0.006	1.25	0.0024	0.0062	AEGL-F
Diamylamine	2050-92-2	157.3	203.0	0.013	126	1	2	LC _{LO}
Diborane	19287-45-7	27.7	-92.6	3438	80	1	2	AEGL-F
Dichloro-(2-chlorovinyl) arsine	541-25-3	207.3	463	0.055	2.4	0.024	0.048	LC ₅₀
Dichlorosilane	4109-96-0	101	8.4	154.2	215	2	4	LC ₅₀
3,5-Dichloro-2,4,6-trifluoropyridine	1737-93-5	202	177.5-S	0.104-S	62	0.6	1.2	LC ₅₀
Diketene	674-82-8	84.1	126.1	1.064	750	5	10	ERPG
1,1-Dimethyl hydrazine	57-14-7	60.1	63.4	16.38	504	3	18	AEGL-F
1,2-Dimethyl hydrazine	540-73-8	60.1	87.1	7.230	680	3	18	AEGL-F
Dimethyl sulfate	77-78-1	126.1	188.9	0.069	17	0.17	0.34	LC ₅₀
Diphosgene	503-38-8	197.8	127.9	0.553	74	0.74	1.5	LC ₅₀
Ethyl chloroformate	541-41-3	108.5	92.9	2.121	145	5	10	ERPG
Ethylchlorothioformate	2812-73-9	124.6	131.9	0.685-E	138-S	1.4	2.8	LC ₅₀ -S
Ethylchlorothiolformate	2941-64-2	124.6-S	131.9-S	0.685-S	138-S	1.4	2.8	LC ₅₀ -S
Ethyl dichloroarsine	598-14-1	174.9	155.9	0.281	36	0.36	0.72	LC ₅₀
Ethyl N,N-dimethylphosphoramido-cyanidate	77-81-6	162.3	239.9-E	0.005-E	2.5	0.0053	0.013	AEGL-F
Ethyl isocyanate	109-90-0	71.1	61.6	24.50	15	0.067	0.4	AEGL-F-S
Ethyl phosphonothionic dichloride	993-43-1	162.9	176.9	0.026-E	52	0.52	1	LC ₅₀

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TABLE B.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC ₅₀ or LC _{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Ethyl phosphonous dichloride	1498-40-4	130.9	113.0-E	4.762-E	62	0.62	1.2	LC _{LO}
Ethyl phosphorodichloridate	1498-51-7	162.9	166.9	0.040-E	43	0.43	0.86	LC ₅₀
Ethylacrolein	922-63-4	84.1	92.9	5.392-E	578	5.8	12	LC ₅₀
Ethylene chlorohydrin	107-07-3	80.5	128.7	0.699	66	0.66	1.3	LC ₅₀
Ethylene dibromide	106-93-4	187.9	131.4	1.357	691	6.9	14	LC ₅₀
Ethylene oxide	75-21-8	44.1	10.5	146.3	5,840	50	100	ERPG
Ethylenimine	151-56-4	43.1	55.9	22.18	80	4.6	33	AEGL-I
Fluorine	7782-41-4	38	-188.3	4,160	185	5	10	ERPG
Germanium tetrachloride	10038-98-9	214.4	83.9	9.51	7,100	71	142	LC ₅₀
Germanium tetrahydride	7782-65-2	76.6	-88.2	3,870	440	4.4	8.8	LC ₅₀
Hexachlorocyclopentadiene	77-47-4	272.8	239.1	0.0052	3	0.03	0.06	LC ₅₀
Hexaethyltetraphosphate	757-58-4	506.2	GS	GS	85-E	0.9	1.8	LC ₅₀ -E
Hexafluoroacetone	684-16-2	166	-27.3	584.19	476	1	2	ERPG
Hydrogen bromide	10035-10-6	80.9	-66.8	2,182	2,860	28.6	57	LC ₅₀
Hydrogen chloride	7647-01-0	36.5	-85.1	4,206	3,124	22	100	AEGL-F
Hydrogen cyanide	74-90-8	27	25.8	81.63	71	7.1	7.1	AEGL-F
Hydrogen fluoride	7664-39-3	20	19.6	102.7	1,300	24	95	AEGL-F
Hydrogen iodide	10034-85-2	127.9	-35.6	691.0	2,860	28.6	57	LC ₅₀
Hydrogen selenide	7783-07-5	81	-42.1	911.1	5	0.2	0.4	ERPG
Hydrogen sulfide	7783-06-4	34.1	-60.4	1781	712	30	60	ERPG
Iron pentacarbonyl	13463-40-6	195.9	102.8	3.142	57	0.06	0.077	AEGL-I
Isobutyl chloroformate	543-27-1	136.6	128.1	0.751	299	3	6	LC ₅₀
Isobutyl isocyanate	1873-29-6	99.1	115.0	1.755	28-S	0.05	0.1	ERPG-S
Isopropyl chloroformate	108-23-6	122.6	104.9-S	4.698-S	299	3	6	LC ₅₀
Isopropyl isocyanate	1795-48-8	85.1	82.9	7.372	28-S	0.05	0.1	ERPG-S
Isopropyl methylphosphonofluoridate	107-44-8	140.1	157.9	0.283	1.22	0.006	0.015	AEGL-F
Methacrylonitrile	126-98-7	67.1	90.4	7.541	656	13	15	AEGL-I
Methanesulfonyl monochloride	124-63-0	114.6	162.4	0.190	325	3.3	6.6	LC ₅₀
Methanesulfonyl dichloride	3518-65-8	149	178	0.121	325-S	3.3	6.6	LC ₅₀ -S
Methoxymethyl isocyanate	6427-21-0	87.1	165.7-E	0.250-E	28-S	0.05	0.1	ERPG-S
Methyl bromide	74-83-9	94.9	3.6	184.3	1007	50	100	ERPG
Methyl chloride	74-87-3	50.5	-24.3	495.4	5,133	400	1,500	ERPG
Methyl chloroformate	79-22-1	94.5	70.9	11.20	88	2	4	ERPG

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TABLE B.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC ₅₀ or LC _{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Methyl hydrazine	60-34-4	46.1	87.6	4.997	68	0.9	5.3	AEGL-F
Methyl iodide	74-88-4	141.9	42.5	44.33	448	50	100	ERPG
Methyl isocyanate	624-83-9	57.1	38.9	50.18	15	0.067	0.4	AEGL-F
Methyl isothiocyanate	556-61-6	73.1	118.9	3.205	635	6.4	13	LC ₅₀
Methyl mercaptan	74-93-1	48.1	6.0	169.8	1340	25	50	ERPG
Methyl phosphonic dichloride	676-97-1	132.9	162.9-E	0.040-E	52	0.5	1.0	LC ₅₀
Methyl phosphonous dichloride	676-83-5	116.9	81.9-E	11.89-E	62	0.62	1.2	LC ₅₀
Methyl phosphonic difluoride	676-99-3	100.0	98	3.685	780	7.8	16	LC _{LO}
Methyl silicate	681-84-5	152.2	120.9	1.613	500	5	10	LC ₅₀
Methyl vinyl ketone	78-94-4	70.1	81.5	9.274	5	0.05	0.1	LC ₅₀
Methylamine	74-89-5	31.1	-6.3	295.7	708	100	200	ERPG
Methylchlorosilane	993-00-0	80.6	8.8	149.6	600	6	12	LC ₅₀
Methyldichloroarsine	593-89-5	160.9	135.9	1.034	68	0.68	1.4	LC ₅₀
Nickel carbonyl	13463-39-3	170.8	42.5	43.50	18	0.036	0.1	AEGL-I
Nitric acid	7697-37-2	63	83.0	6.401	67	6	12	ERPG
Nitric oxide	10102-43-9	30	-151.8	5,093	1,708	17	34	LC ₅₀
Nitrogen dioxide	10102-44-0	46	21.0	96.04	115	15	30	ERPG
Nitrogen fluoride oxide	13847-65-9	87.1	-129.1-E	3,979-E	48	0.5	1.0	LC ₅₀
Nitrogen trioxide	10544-73-7	76	2.0	218.3	115-S	15	30	ERPG-S
Nitrosyl chloride	2696-92-6	65.5	-5.3	270.4	293	2.9	5.8	LC ₅₀ -S
tert-octyl mercaptan	141-59-3	146.3	155.9	0.488	102	1	2	LC ₅₀
O-Ethyl S-(2-diisopropylaminoethyl) methylphosphonothiolate	50782-69-9	267.4	297.9	0.00005	0.06	0.00027	0.00065	AEGL-F
Oxygen difluoride	7783-41-7	54	-145.0	2,789	2.6	0.026	0.052	LC ₅₀
Parathion	56-38-2	291.3	GS	GS	14	0.14	0.28	LC ₅₀
Pentaborane	19624-22-7	63.2	58.4	22.70-E	12	0.12	0.24	LC ₅₀
Perchloromethyl mercaptan	594-42-3	185.9	148.0	0.642	11	0.3	0.53	AEGL-I
Perchloryl fluoride	7616-94-6	102.4	-46.7	1,060	770	7.7	15	LC ₅₀
Phenyl isocyanate	103-71-9	119.1	165.7	0.250	16	0.05	0.1	ERPG-S
Phenyl mercaptan	108-98-5	110.2	169.2	0.142	66	0.66	1.3	LC ₅₀
Phosgene	75-44-5	98.9	7.6	159.3	10	0.3	0.6	AEGL-F
Phosphine	7803-51-2	34	-87.8	3,517	22	0.5	1	ERPG
Phosphorous oxychloride ^a	10025-87-3	153.3	105.5	3.273	66	0.7	1.4	LC ₅₀
Phosphorous pentafluoride	7647-19-0	126	-84.6	56,888	260	2.6	5.2	LC ₅₀

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TABLE B.1 (Cont.)

DOT Name	CAS #	Mol. Weight	Boiling Point (°C)	Vapor Pressure at 20°C (kPa)	LC ₅₀ or LC _{LO} (ppm)	1-h Protective (ppm)	10-min or 15-min Protective (ppm)	Basis
Phosphorous trichloride	7719-12-2	137.3	76.1	12.82	208	2	2.5	AEGL-I
Phosphorous trifluoride	7783-55-3	88	-101.3	6,902	420	4.2	8.4	LC ₅₀
Pinacolyl methylphosphonofluoridate	96-64-0	182.2	197.9	0.037	1.25	0.0022	0.0057	AEGL-F
n-Propyl chloroformate	109-61-5	122.6	104.9	4.698	319	3.2	6.4	LC ₅₀
n-Propyl isocyanate	110-78-1	85.1	82.9	5.274	44	0.05	0.1	ERPG-S
Selenium hexafluoride	7783-79-1	193	-34.7	2,854	50	0.5	1	LC ₅₀
Silicon tetrafluoride	7783-61-1	104.1	-95.2	3,205	922	9	18	LC ₅₀
Stibine	7803-52-3	124.8	-18.5	286.1-E	20	0.5	1	ERPG
Sulfur chloride pentafluoride	13780-57-9	162.5	-21.2	442.0-S	100	1	2	LC _{LO}
Sulfur dioxide	7446-09-5	64.1	-10.1	336.5	2,520	3	6	ERPG
Sulfur monochloride	10025-67-9	135	137.9	0.944	150*	1.5	3	LC ₅₀
Sulfur tetrafluoride	7783-60-0	108.1	-40.4	1,785	40	0.4	0.8	LC _{LO}
Sulfur trioxide	7446-11-9	80.1	44.8	26.5	106 mg/m ³	10 mg/m ³	20 mg/m ³	ERPG
Sulfuryl chloride	7791-25-5	135	69.4	14.811	318	3.2	6.4	LC ₅₀
Sulfuryl fluoride	2699-79-8	102.1	-55.4	1,964	1,982	20	40	LC ₅₀
Tellurium hexafluoride	7783-80-4	241.6	-38.2	709.6	10	0.1	0.2	LC _{LO}
Tetraethyl dithiopyrophosphate	3689-24-5	322.3	GS	GS	6	0.06	0.12	LC ₅₀
Tetraethyl pyrophosphate	107-49-3	290.1	GS	GS	1.5-S	0.06	0.12	LC ₅₀ -S
Tetrafluorohydrazine	10036-47-2	104	-74.3	2,515	900	9	18	LC ₅₀
Tetramethyl tin	594-27-4	178.8	77.9	17.92-E	58	0.6	1.2	LC _{LO}
Tetranitromethane	509-14-8	196	125.8	1.121	36	0.52	0.66	AEGL-I
Thionyl chloride	7719-09-7	119	75.7	12.77	500	2	4	ERPG
Thiophosgene	463-71-8	115	72.9	15.04	25	0.3	0.6	AEGL-F-S
Titanium tetrachloride	7550-45-0	189.7	135.9	1.253	1,300 mg/m ³	20 mg/m ³	40 mg/m ³	ERPG
Trichloroacetyl chloride	76-02-8	181.8	118.0	2.189	128	1.3	2.6	LC ₅₀
Trifluoroacetyl chloride	354-32-5	132.5	-17.9	356.2-S	208	2.1	4.2	LC ₅₀
Trifluorochloroethylene	79-38-9	116.5	-27.9	531.4	2,000	100	200	ERPG
3-Trifluoromethyl phenyl isocyanate	329-01-1	187.1	179.6	0.33	43	0.43	0.86	LC ₅₀
Trimethoxy silane	2487-90-3	122.3	80.9	20.40-E	84	2	4	ERPG
Trimethylacetyl chloride	3282-30-2	120.6	106.9	2.866	250	2.5	5	LC ₅₀
Tris-(2-chloroethyl) amine	817-09-4	204.5	255.9	0.00094	2.99	0.03	0.06	LC ₅₀
Tungsten hexafluoride	7783-82-6	297.8	17.4	111.8	217	2.2	4.4	LC ₅₀

Footnote and definitions of abbreviations appear on next page.

TABLE B.1 (Cont.)

- ^a Only interim AEGL-3 values for phosphorous oxychloride are available, because AEGL documentation did not recommend development of AEGL-2 values. Therefore, the PAD value was based on an LC₅₀ level.

Abbreviations

- AEGL = Acute Emergency Guideline Level established by the National Research Council
AEGL-F = final AEGL
AEGL-I = interim AEGL
E = estimated value
ERPG = Emergency Response Planning Guideline established by the American Industrial Hygiene Association
GS = solid or liquid in solution with gas
LC₅₀ = median lethal concentration in animals exposed via inhalation
LC₅₀-E = LC₅₀ estimated from oral toxicity data
LC_{LO} = lowest lethal concentration reported in an animal study
N/A = not applicable
S = data are for a structurally similar chemical

APPENDIX C:
ADDITIONAL DETAILS ON WATER-REACTIVE MATERIALS

APPENDIX C:

ADDITIONAL DETAILS ON WATER-REACTIVE MATERIALS

This appendix provides detailed information on the water-reactive materials listed in the Table of Initial Isolation and Protective Action Distances. Section C.1 begins with a detailed discussion of how we use the experimental data listed in Appendix D to determine the key parameters necessary to model TIHWR releases. Then Section C.2 provides information on these parameters for all the TIHWR materials considered in the ERG2008. Finally, Section C.3 explains why we selected various materials to include on the TIHWR list on the ERG2008 Table and reviews changes from previous recommendations.

C.1 ANALYSIS OF EXPERIMENTAL DATA: EXTRACTION OF KEY PARAMETERS

As discussed in Section 3.3, we model the evolution of a TIHWR gas by using the first-order rate equation with an induction time offset

$$M(t) = M_{st} \beta (1 - e^{-\lambda(t-T_{ind})}), \quad (C.1)$$

where M_{st} is the stoichiometric mass that could evolve and $M(t)$ is the total mass of TIH gas actually emitted from the spill by time t . The parameter λ is the first-order rate constant for the process, and β is an empirically determined efficiency factor defined from Equation D.1 as

$$\beta = \frac{M_{\infty}}{M_{st}}, \quad (C.2)$$

where M_{∞} is the maximum mass of TIH gas that evolves from the water at long times and T_{ind} is an induction time as described below. Note that more product may be formed than the amount that actually evolves from the water as a result of the dissolution of the gas in the water, as discussed in Section C.1.3. We generally determine these parameters by least-squares fitting from the amount of TIH gas emitted as a function of time, as observed in our experiments.

Throughout the course of our experimental program for the 2000, 2004, and 2008 ERGs, we observed four general types of behavior. They are described in the following subsections to provide context for understanding the data used in our TIHWR analysis.

C.1.1 No Emissions

Some experiments did not produce any TIH gases with either the stoichiometric amount of water (Method A) or with a five-fold molar excess (Method B), even though we had descriptive evidence that the TIH gases were quite reactive with water. A related class of materials exhibited slow emissions when Method A was used but no emissions when Method B

was used because of sequestration of the evolved gas by the excess water. Examples of these materials include hexadecyltrichlorosilane (UN 1781) and phosphorus oxybromide (UN 1939). Note that not all of the materials that failed to exhibit significant evolution of TIH gases in the experiments were removed from the TIHWR list, as discussed in Section C.3.3.

C.1.2 Simple First-Order Process

Many experiments showed the simple first-order process described above in Equation C.1 with no induction time ($T_{ind} = 0$). Typical examples of the first-order process can be seen in Appendix D in the data for methylchlorosilane (UN 1242) and methyltrichlorosilane (UN 250). For these materials, we used the actual observed maximum mass of gas evolved, M_{∞} , divided by the stoichiometric maximum, M_{st} , to determine β . Using a least-squares fit for M_{∞} gave almost identical results in all cases. λ was determined by using a least-squares fit as well.

C.1.3 First-Order Process with Dissolution

Several experiments showed an apparent first-order process in which the evolved TIH gas dissolved back into the water, thus serving as a removal mechanism. This process was especially apparent when Method B was used, which involved a five-fold molar excess of water. Classic examples of such cases are shown in Appendix D for nitrosylsulfuric acid (UN 2308) and in the Method B results for acetyl bromide (UN 1716). Because the TIH gas was kept in contact with water in the experimental apparatus in a closed environment, dissolution was promoted. In a natural environment, the TIH gas that would be produced would likely bubble out of the water quickly and dilute in the atmosphere, thus avoiding significant dissolution. For this reason, M_{∞} was determined by using a least-squares fit of the data up to the peak measured evolution amount to obtain the completion fraction β , rather than by simply using the observed maximum that occurred as dissolution overcame the rate of evolution. Admittedly, this procedure could overestimate the source term for atmospheric dispersion of the TIH gas, but it was chosen because it offered the most reasonable solution for determining the model parameters from the experimental data.

C.1.4 Autocatalytic Reactions

In a few of the experiments, we observed a more complex reaction pattern, in which a polymeric by-product formed during the first stages. This slowed the reaction of the remaining material with water. All of these cases involved silanes. Classic examples are cyclohexyltrichlorosilane (UN 1763) and octadecyltrichlorosilane (UN 1800). In these reactions, slow emissions of gas at a constant rate ensued for a period of 2–10 min. At that point, the reactions appeared to autocatalyze, and then they subsequently followed what appeared to be a normal first-order reaction process. In these cases, we used a three-parameter fit. The values of M_{∞} and λ were given their normal meaning, but the time was measured from T_{ind} , a new parameter that indicated when the autocatalysis began strongly.

In previous analyses (Brown et al. 2005), we had also separately considered the mass of gas that had evolved during the interval from $t = 0$ to $t = T_{ind}$ defining an induction mass m_i . The formal relationships are as follows:

$$M(t) = m_i \frac{t}{T_{ind}} \quad (t \leq T_{ind}) \quad (C.3)$$

$$M(t) = m_i + M_{st} \beta' (1 - e^{-\lambda(t-T_{ind})}), \quad (t > T_{ind}) \quad (C.4)$$

where

$$\beta' = \beta - \frac{M_i}{M_{st}}.$$

In compiling the experimental data for the ERG2008, however, we found that we could simplify the analysis and determination of model parameters from the experimental data by ignoring the slow initial constant release described by Equation C.3 and instead simply use Equation C.1 with an induction time offset. For calculations of practical interest, this practice has no discernable effect on the hazard predictions.

C1.5 Summary

We applied least-squares fits to the data shown in Appendix D to provide β , λ , and T_{ind} as represented in Equation C.1 for experimental trials of both Method A and Method B. These parameters were subsequently used in CASRAM to model time-dependent emissions of TIH gas for cases in which a water-reactive substance spills into water or becomes wet during a spill (e.g., because of rain). Note that we used data from both Method A (stoichiometric water added) and Method B to model TIHWR incidents in order to account for cases in which water was limited and cases in which excess water was available. Model parameters for materials for which experimental data are not available are estimated on the basis of qualitative descriptions in the literature and/or chemical similarities to materials for which data do exist, as described in Section C.2. In the future, larger-scale experiments should verify that these millimole results do indeed give a good approximation of an actual large-scale spill.

C.2 KEY PARAMETERS EMPLOYED IN THE TIWHR ANALYSIS

Supplementary information on all water-reactive materials in the ERG2008 TIHWR list is provided in Table C.1. Table C.2 provides updated parameters for 12 materials for which experiments were conducted after February 2007, which was the cutoff for inclusion in the ERG2008. We opted to perform these additional trials to provide a more complete data set from using the new experimental method. All of these latter trials were repeats of experiments conducted for ERG2000 or ERG2004. These data were not used for ERG2008 but should replace data in Table C.1 for all future analyses.

TABLE C.1 Supplementary Information on Water-reactive Materials in the ERG2008 TIHWR List^a

UN No.	Name	St	Dens	Prod	Experiments Conducted				Method A			Method B		
					00	04	08	S.Y.	β	λ (min ⁻¹)	T_{ind} (s)	β	λ (min ⁻¹)	T_{ind} (s)
1162	Dimethyldichlorosilane	L	1.06	HCl	X	X	X	0.565	0.54	0.15	0	0.25	0.93	0
1183	Ethyl dichlorosilane	L	1.09	HCl			X	0.565	0.74	0.68	0	0.33	2.03	0
1196	Ethyltrichlorosilane	L	1.24	HCl		X	X	0.669	0.63	0.24	31	0.39	1.55	5
1242	Methyldichlorosilane	L	1.11	HCl		X	X	0.634	0.45	1.50	0	0.40	6.0	0
1250	Methyltrichlorosilane	L	1.27	HCl	X	X	X	0.732	0.18	0.20	0	0.23	0.50	0
1295	Trichlorosilane	L	1.34	HCl			X	0.808	0.31	1.83	0	0.21	24	0
1298	Trimethylchlorosilane	L	0.85	HCl	X	X	X	0.336	0.25	0.20	0	0.27	0.55	0
1305	Vinyltrichlorosilane	L	1.26	HCl			X	0.677	0.47	0.17	0	0.23	3.76	0
1339	Phosphorus heptasulfide	S	2.19	H ₂ S				0.685	0.15	0.23	31	0.15	0.12	71
1340	Phosphorus pentasulfide	S	2.09	H ₂ S			X	0.767	0.15	0.23	31	0.15	0.12	71
1360	Calcium phosphide	S	2.51	PH ₃	X	X	X	0.374	0.35	0.045	0	0.35	0.045	0
1384	Sodium hydrosulfite ^b	S	2.20	SO ₂	X			0.735	0.05	0.10	0	0.03	0.10	0
1397	Aluminum phosphide	S	2.40	PH ₃				0.588	0.35	0.045	0	0.35	0.045	0
1412	Lithium amide	S	1.18	NH ₃		X		0.742	0.19	1.0	0	0.16	3.0	0
1419	Magnesium aluminum phosphide	S	2.20	PH ₃				0.530	0.35	0.045	0	0.35	0.045	0
1432	Sodium phosphide	S	1.74	PH ₃				0.342	0.35	0.045	0	0.35	0.045	0
1541	Acetone cyanohydrin	L	0.93	HCN		X		0.318	0.20	0.060	0	0.05	0.060	0
1680	Potassium cyanide	S	1.52	HCN			X	0.415	0.20	0.060	0	0.05	0.060	0
1689	Sodium cyanide	S	1.60	HCN			X	0.551	0.20	0.060	0	0.05	0.060	0
1716	Acetyl bromide	L	1.66	HBr		X	X	0.658	0.43	8.20	0	0.43	8.20	0
1717	Acetyl chloride	L	1.11	HCl		X	X	0.464	0.70	6.38	0	0.70	6.38	0
1724	Allyltrichlorosilane	L	1.21	HCl		X	X	0.623	0.50	0.94	0	0.21	2.38	0
1725	Aluminum bromide	S	2.64	HBr	X		X	0.910	0.20	30	0	0.20	30	0
1726	Aluminum chloride	S	2.44	HCl	X			0.820	0.20	30	0	0.20	30	0
1728	Amyltrichlorosilane	L	1.13	HCl		X	X	0.532	0.63	0.067	91	0.30	0.22	27
1732	Antimony pentafluoride	L	2.99	HF		X		0.462	0.40	0.60	0	0.40	0.60	0
1741	Boron trichloride^c	L	1.35	HCl			X	0.934	0.61	9.73	0	0.55	5.14	0
1745	Bromine pentafluoride ^{b,c}	L	2.47	HF				0.572	0.40	0.60	0	0.40	0.60	0
1746	Bromine trifluoride ^{b,c}	L	2.80	HF				0.438	0.40	0.60	0	0.40	0.60	0
1747	Butyltrichlorosilane	L	1.16	HCl		X	X	0.571	0.25	0.015	300	0.17	0.060	120
1752	Chloroacetyl chloride	L	1.50	HCl	X	X	X	0.323	0.67	0.060	0	0.07	0.39	0
1753	Chlorophenyltrichlorosilane	L	1.25	HCl			X	0.445	0.36	0.11	24	0.10	0.37	0

TABLE C.1 (Cont.)

UN No.	Name	St	Dens	Experiments Conducted					Method A			Method B		
				Prod	00	04	08	S.Y.	β	λ (min ⁻¹)	T_{ind} (s)	β	λ (min ⁻¹)	T_{ind} (s)
1754	Chlorosulfonic acid	L	1.76	HCl		X	X	0.313	0.64	3.75	0	0.64	19.8	0
1758	Chromium oxychloride	L	1.91	HCl		X		0.471	0.06	0.067	0	0.06	0.067	0
1762	Cyclohexenyltrichlorosilane	L	1.23	HCl				0.507	0.50	0.025	265	0.24	0.060	144
1763	Cyclohexyltrichlorosilane	L	1.30	HCl		X	X	0.503	0.50	0.025	265	0.24	0.060	144
1765	Dichloroacetyl chloride	L	1.53	HCl			X	0.247	0.60	0.15	48	0.11	0.74	4
1766	Dichlorophenyltrichlorosilane ^d	L	1.56	HCl		X		0.421	0.25	0.059	180	0.40	0.50	0
1767	Diethyldichlorosilane	L	1.05	HCl		X	X	0.464	0.45	0.019	0	0.26	0.048	0
1769	Diphenyldichlorosilane	L	1.22	HCl		X	X	0.288	0.23	0.071	180	0.08	0.13	60
1771	Dodecyltrichlorosilane	L	1.03	HCl		X	X	0.360	0.47	0.054	0	0.32	0.64	23
1777	Fluorosulfonic acid	L	1.73	HF			X	0.200	0.09	0.028	0	0.05	6.0	0
1781	Hexadecyltrichlorosilane	L	1.25	HCl			X	0.304	0.44	0.026	125	0.10	0.060	0
1784	Hexyltrichlorosilane	L	1.30	HCl		X	X	0.498	0.71	0.021	32	0.19	0.28	0
1799	Nonyltrichlorosilane	L	1.30	HCl		X		0.418	0.20	0.060	0	0.50	0.037	0
1800	Octadecyltrichlorosilane	L	1.30	HCl		X	X	0.282	0.28	0.034	600	0.34	0.25	420
1801	Octyltrichlorosilane	L	1.30	HCl		X	X	0.442	0.38	0.027	0	0.27	0.24	0
1804	Phenyltrichlorosilane	L	1.33	HCl		X	X	0.517	0.50	0.50	0	0.17	0.27	0
1806	Phosphorus pentachloride	S	1.60	HCl		X	X	0.875	0.34	0.53	0	0.11	1.28	0
1808	Phosphorus tribromide	L	2.86	HBr	X		X	0.897	0.65	0.061	0	0.65	0.061	0
1809	Phosphorus trichloride ^c	L	1.57	HCl	X		X	0.796	0.56	1.25	0	0.25	4.8	0
1810	Phosphorus oxychloride	L	1.67	HCl	X	X	X	0.713	0.23	0.10	0	0.23	6.0	0
1815	Propionyl chloride	L	1.06	HCl			X	0.394	0.70	1.11	12	0.06	7.74	0
1816	Propyltrichlorosilane	L	1.30	HCl	X	X	X	0.616	0.73	0.20	31	0.27	0.33	5
1818	Silicon tetrachloride ^c	L	1.48	HCl		X	X	0.858	0.49	2.88	0	0.30	1.81	0
1828	Sulfur chlorides ^{b,c}	L	1.62	HCl			X	0.540	0.45	0.027	78	0.09	0.39	0
1834	Sulfuryl chloride ^{b,c}	L	1.63	HCl	X		X	0.540	0.35	0.051	0	0.28	0.080	0
1836	Thionyl chloride ^{b,c}	L	1.63	SO ₂	X			0.538	1.00	2.75	0	1.00	2.75	0
1838	Titanium tetrachloride ^c	L	1.73	HCl	X	X		0.769	0.20	1.35	0	0.13	1.35	0
1898	Acetyl iodide	L	2.07	HI			X	0.753	0.52	7.42	0	0.48	37.2	0
1923	Calcium hydrosulfite ^b	S	2.20	SO ₂				0.761	0.05	0.10	0	0.03	0.10	0
1929	Potassium hydrosulfite^b	S	2.20	SO ₂				0.621	0.05	0.10	0	0.03	0.10	0
1931	Zinc hydrosulfite ^b	S	2.20	SO ₂				0.662	0.05	0.10	0	0.03	0.10	0
2004	Magnesium diamide	S	1.39	NH ₃				0.604	1.00	60	0	1.00	60	0
2011	Magnesium phosphide	S	2.06	PH ₃				0.505	0.35	0.045	0	0.35	0.045	0

TABLE C.1 (Cont.)

UN No.	Name	St	Dens	Prod	Experiments Conducted				Method A			Method B		
					00	04	08	S.Y.	β	λ (min ⁻¹)	T_{ind} (s)	β	λ (min ⁻¹)	T_{ind} (s)
2012	Potassium phosphide	S	2.50	PH ₃				0.230	0.35	0.045	0	0.35	0.045	0
2013	Strontium phosphide	S	2.68	PH ₃				0.210	0.35	0.045	0	0.35	0.045	0
2308	Nitrosylsulfuric acid (liquid)	L	1.89	NO ₂	X		X	0.362	0.43	4.94	0	0.43	4.98	0
2353	Butyryl chloride	L	1.03	HCl			X	0.342	0.62	0.48	8	0.14	1.48	0
2395	Isobutyryl chloride	L	1.03	HCl			X	0.342	0.71	0.17	21	0.05	2.4	0
2434	Dibenzylchlorosilane	L	1.30	HCl			X	0.263	0.23	0.071	180	0.08	0.13	60
2435	Ethylphenyldichlorosilane	L	1.30	HCl			X	0.355	0.43	0.011	528	0.41	0.021	86
2437	Methylphenyldichlorosilane	L	1.30	HCl		X	X	0.382	0.17	0.034	0	0.05	0.10	0
2495	Iodine pentafluoride	L	3.75	HF				0.451	0.40	0.60	0	0.40	0.60	0
2691	Phosphorus pentabromide	S	3.60	HBr		X	X	0.940	0.24	2.38	0	0.24	2.38	0
2692	Boron tribromide ^c	L	2.65	HBr		X	X	0.969	0.64	3.94	0	0.64	3.94	0
2806	Lithium nitride	S	1.27	NH ₃		X		0.489	1.00	18	0	1.00	18	0
2977	Uranium hexafluoride, fissile	S	4.68	HF				0.341	0.20	0.60	0	0.20	0.60	0
2978	Uranium hexafluoride, non-fissile	S	4.68	HF				0.341	0.20	0.60	0	0.20	0.60	0
3048	Aluminum phosphide pesticide	S	2.40	PH ₃				0.588	0.35	0.045	0	0.35	0.045	0
3456	Nitrosylsulfuric acid (solid)	S	1.89	NO ₂				0.362	0.33	6.0	0	0.75	6.0	0
3052	Aluminum alkyl halides	S	1.60	HCl				0.500	0.05	5.0	0	0.05	5.0	0
9191	Chlorine dioxide, hydrate, frozen	S	1.40	Cl ₂				0.084	0.05	5.0	0	0.05	5.0	0

^a Names in bold are new additions to the TIHWR list in 2008. Column headings are defined as follows: St = normal state during shipment (solid, liquid), Dens = density (g/cm³), Prod = Primary TIH product produced (see Note b below), Experiments Conducted = ERG edition (2000, 2004, or 2008) for which experiments on the compound were performed, S.Y. = stoichiometric yield of TIH gas (kg of TIH gas/kg of spilled parent), β = efficiency factor (average fraction of S.Y. produced), λ_0 = primary rate constant at 20°C (min⁻¹), and T_{ind} = initial induction period (s).

^b Multiple TIH gases are produced; the most hazardous (in terms of production rate and toxicity) are shown.

^c Parent chemical is TIH gas.

^d Experiments performed on the closely related compound 4-(chloromethyl)phenyltrichlorosilane were assumed to apply to this compound.

TABLE C.2 Updated TIHWR Parameters for 12 Materials for Which Experiments Were Completed after the ERG2008 TIHWR List Was Finalized in February 2007 (These are all repeated experiments from the ERG2000 or ERG2004.)

UN No.	Name	Method A			Method B		
		β	λ (min ⁻¹)	T_{ind} (s)	β	λ (min ⁻¹)	T_{ind} (s)
1242	Methyldichlorosilane	0.60	5.1	0	0.39	3.5	0
1250	Methyltrichlorosilane	0.43	0.39	0	0.37	2.6	0
1298	Trimethylchlorosilane	0.35	0.29	0	0.47	0.40	0
1360	Calcium phosphide	0.12	0.30	0	0.11	0.21	0
1725	Aluminum bromide	0.05	0.70	0	0.05	0.70	0
1747	Butyltrichlorosilane	0.67	0.030	76	0.28	0.19	53
1752	Chloroacetyl chloride	0.57	0.04	127	0.09	0.31	41
1754	Chlorosulfonic acid	0.72	15	1	0.59	15	0
1769	Diphenyldichlorosilane	0.23	0.038	191	0.36	0.084	114
1800	Octadecyltrichlorosilane	0.29	0.024	152	0.40	0.18	76
2437	Methylphenyldichlorosilane	0.69	0.0065	0	0.27	0.14	43
2691	Phosphorus pentabromide	0.12	2.2	0	0.11	0.14	40

C.3 SUPPLEMENTARY DETAILS IN SUPPORT OF MATERIALS APPEARING IN TABLE C.1

Most materials appear in the ERG2008 TIHWR list (and consequently in Table C.1) either because TIH gases evolved from them at reasonable rates in the experiments described in Appendix D or because the chemical literature says that TIH gases evolve from them. Sections C.3.1–C.3.3 give reasons that these materials are included on the TIHWR list. Section C.3.4 briefly describes why other materials were never included on the list or deleted from it.

C.3.1 Materials from Which TIH Gases Evolved during Experiments

The ERG2008 TIHWR list contains 62 materials from which TIH gases evolved during the experimental program described in Appendix D and in Brown et al. (2005). These are listed in Table C.1. The availability of experimental data is noted in Table C.1.

C.3.2 Materials Described as TIHWR in the Literature

The ERG2008 TIHWR list includes 23 materials on the basis of the descriptions of their water reactivity in the chemical literature. These are listed in Table C.3.

TABLE C.3 Chemicals Reported to Be Water-reactive in the Scientific Literature

UN No.	Name	Comment	Reference
1397	Aluminum phosphide	Slowly evolves PH ₃ in contact with water.	Lewis (2000)
1419	Magnesium aluminum phosphide	Evolves PH ₃ in contact with water.	Lewis (2000)
1432	Sodium phosphide	Is known to evolve PH ₃ in contact with water.	Lewis (2000)
1680	Potassium cyanide	Is included on the basis of its chemical similarity to sodium cyanide.	
1745	Bromine pentafluoride	Explodes on contact with water. Products of this rapid reaction include HF and possibly Br ₂ .	Lewis (2000)
1746	Bromine trifluoride	Smokes in air and decomposes violently in water. Products of reaction include HF and possibly Br ₂ .	Budavari (1996); Lewis (2000)
1923	Calcium hydrosulfite	Is included by analogy to sodium hydrosulfite.	
1931	Zinc hydrosulfite	Is included by analogy to sodium hydrosulfite.	
2004	Magnesium diamide	Reacts violently with water, evolving NH ₃ .	Budavari (1996)
2011	Magnesium phosphide	Phosphides tend to decompose to PH ₃ upon contact with moisture or acids.	Lewis (2000)
2012	Potassium phosphide	Phosphides tend to decompose to PH ₃ upon contact with moisture or acids.	Lewis (2000)
2013	Strontium phosphide	Phosphides tend to decompose to PH ₃ upon contact with moisture or acids.	Lewis (2000)
2495	Iodine pentafluoride	Violently reacts with water. Products include HF.	Lewis (2000)
2977	Uranium hexafluoride, fissile	Is rapidly hydrolyzed by water and reacts vigorously with water. Products include HF.	Cotton and Wilkinson (1966); Lewis (2000)
2978	Uranium hexafluoride, non-fissile	Is rapidly hydrolyzed by water and reacts vigorously with water. Products include HF.	Cotton and Wilkinson (1966); Lewis (2000)
2985	Chlorosilanes, n.o.s. ^a	Most chlorosilanes generate HCl at some rate upon contact with water.	
2986	Chlorosilanes, flammable, corrosive, n.o.s.	Most chlorosilanes generate HCl at some rate upon contact with water.	
2987	Chlorosilanes, corrosive, n.o.s.	Most chlorosilanes generate HCl at some rate upon contact with water.	
2988	Chlorosilanes, water reactive, flammable, corrosive, n.o.s.	Most chlorosilanes generate HCl at some rate if spilled into water.	
3048	Aluminum phosphide pesticide	Aluminum phosphide slowly evolves PH ₃ in contact with water. Is included despite the fact that the coating applied to the particles in the pesticide application is likely to slow the hydrolysis.	Lewis (2000)
3049	Metal alkyl halides, n.o.s.	Metal alkyl halides generally react to form hydrogen halides (HCl, HBr, HI) when mixed with water.	
3052	Aluminum alkyl halides	Aluminum alkyl halides generally react to form hydrogen halides (HCl, HBr, HI) when mixed with water.	
9191	Chlorine dioxide hydrate, frozen	Decomposes in water. Products likely to include gaseous Cl ₂ .	Lewis (2000)

^a n.o.s. = not otherwise specified.

C.3.3 Materials Included Due to Special Concerns

TIH gases did not evolve from four materials appearing in Table C.1 during the Appendix D experiments. They were still included on the TIHWR list because TIH gases might evolve from them under the right circumstances if they spilled.

1. **UN 1384 — sodium hydrosulfite.** Experiments conducted in 1999 found no evolution of gas when the chemical was mixed with room-temperature water, although both SO₂ and H₂S were detected because of their odor. This material was retained on the TIHWR list, however, because of the possibility that a substantial amount of TIH gas could evolve as a result of decomposition caused by the confined heat of dissolution in restricted amounts of water in spills having the proper geometry (such as a heap on a puddle). Of particular note is the following statement from the EPA/OSHA Joint Chemical Accident Investigation Report of an accident on April 21, 1995, at Napp Technologies, Inc., in Lodi, New Jersey: “Sodium hydrosulfite is unstable in the presence of water, heat or humid air, giving off sulfur dioxide gas and other sulfur products in an exothermic reaction. Once initiated, the decomposition process of sodium hydrosulfite supports continued decomposition due to the generation of heat in the exothermic reaction.”
2. **UN 1541 — acetone cyanohydrin.** Experiments conducted in 2003 found no evolution of gas when the chemical was mixed with room-temperature water. This material was retained on the TIHWR list, however, because of its chemical similarity to sodium cyanide. A May 20, 1998, spill of sodium cyanide into a river in Kyrgyzstan led to evolution of gaseous HCN, as discussed below.
3. **UN 1689 — sodium cyanide.** Experiments conducted for the ERG2008 found no evolution of gas when the chemical was mixed with room-temperature water. Despite the negative result, this compound was retained on the TIHWR list because of the conclusions found in Cleven and van Bruggen (2000). This report on a large spill of sodium cyanide into a river in Kyrgyzstan in May 1998 stated that “...a large part of the dissolved cyanide must have been rapidly transformed into HCN, which will have been released into the air.” The report continues that people “...must have been at considerable risk for life-threatening disease through inhalatory uptake of HCN (gas).” Several deaths were attributed to either dermal or inhalatory contact with HCN in this incident.
4. **UN 1726 — aluminum chloride (anhydrous).** Experiments in 1999 found no evolution of gas when the chemical was mixed with room-temperature water. This chemical was retained on the TIHWR list, however, because the small scale of the experiment might have masked its TIHWR character. Aluminum chloride is cited in Carson and Mumford (1994) as generating HCl in contact

with water: “Reacts with air moisture to form corrosive HCl gas. Violent reaction when a stream of water hits a large amount.”

C.4 MATERIALS NO LONGER RECOMMENDED AS TIHWR MATERIALS

Ten materials previously recommended by Argonne and the University of Illinois at Chicago as TIHWR materials were removed from the current TIHWR list. (Note that not all of these materials actually appeared in previous editions of the ERG.) Here are the reasons.

1. **UN 1433 — stannic phosphide.** No evolution of TIH gas was observed in the experiments (see Appendix C).
2. **UN 1714 — zinc phosphide.** No evolution of TIH gas was observed in the experiments (see Appendix C).
3. **UN 1736 — benzoyl chloride.** No evolution of TIH gas was observed in the experiments (see Appendix C). However, literature sources do mention TIH gas evolution; for example, see Carson and Mumford (1994): “Reacts strongly with water or water vapor, producing heat and toxic, corrosive fumes.”
4. **UN 1749 — chlorine trifluoride.** This material reacts explosively with water to generate HF and possibly Cl₂. The compound is gaseous above 11.8°C and was therefore treated as a TIH gas in its own right.
5. **UN 1807 — phosphorus pentoxide.** This material reacts explosively with water to generate water-soluble phosphoric acid. It had been previously included on the TIHWR list by analogy to SO₃ — because of the possibility that this very rapid, exothermic reaction might raise a toxic acidic mist in a spill. However, since phosphoric acid is not a TIH material, DOT chose not to include phosphorus pentoxide on the TIHWR list.
6. **UN 1831 — fuming sulfuric acid (oleum).** Oleum is a solution of sulfur trioxide in sulfuric acid. It fumes strongly in moist air (Lewis 2000) and reacts with water and water vapor to form sulfuric acid mists (NIOSH Substance Profile; see <http://ntp.niehs.nih.gov/ntp/roc/eleventh/profiles/s164sulf.pdf>). The reaction is quite exothermic. However, oleum is already a TIH material, and spills into water would likely not lead to PADs in excess of those already listed for land-based spills.
7. **UN 1829 — sulfur trioxide.** Like oleum, this compound reacts with water and water vapor to form sulfuric acid mists (NIOSH Substance Profile). However, it was excluded from the TIHWR list for the same reasons that oleum was excluded.

8. **UN 1939 — phosphorus oxybromide (solid).** This compound reacted with water, in a manner similar to that of phosphorus tribromide in 2003 experiments. However, it was excluded from the TIHWR list because the HBr apparently dissolved into the excess water as rapidly as it was formed.
9. **UN 2442 — trichloroacetyl chloride.** This compound was reacted with water in the experiments, but it was not included on the TIHWR list because no evolution of gaseous HCl was observed (see Appendix C).
10. **Sodium methylcarbamodithioate (metam sodium) (no UN number).** This material has a known history of water reactivity, but it was excluded from the TIHWR list because it does not have a UN number.

APPENDIX D:
EXPERIMENTAL PROGRAM CONDUCTED TO SUPPORT
THE WATER REACTIVITY ANALYSIS

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APPENDIX D:

EXPERIMENTAL PROGRAM CONDUCTED TO SUPPORT THE WATER REACTIVITY ANALYSIS

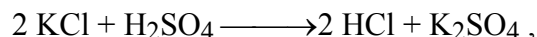
This appendix gives the details of laboratory work undertaken in 2006 and 2007 to extend the experimental basis for estimates of (1) the amounts of toxic inhalation hazard (TIH) gases that might evolve when water-reactive materials are spilled into water and (2) the rates at which such gases might evolve. Experiments in 1999 and 2000 developed preliminary information on 21 materials in support of the 2000 edition of the Emergency Response Guidebook (ERG2000; Brown et al. 2000). Experiments in 2003 and 2004 in support of ERG2004 (Brown et al. 2005) added 35 new materials and repeated or extended observations on 10 materials from the first group. The work reported on here was conducted in support of ERG2008 and covered 52 materials. Of these, 18 were new and 34 had been worked with previously.

D.1 GENERAL DESCRIPTION

Small (millimole or mmol) amounts of water-reactive substances were stirred in contact with water in a closed, nonrigid system at near-constant temperature and pressure. The evolution of gas caused the system to expand, and the change in volume was recorded. For a pure gas (or for a mixed gas of known composition), the change in volume as time went on was proportional to the mass of new gas that was generated. If no concurrent reactions (such as dissolution) occurred to remove gas, then the rate of change of the volume was the rate of the gas-generating reaction.

D.1.1 Previous Apparatus and Previous Results

Previous experiments used the displacement of a manometric fluid to indicate the volume of gas that evolved from reactions of the different materials with water. Evolving gas pushed the fluid from a reservoir up a calibrated glass tube. The level of fluid in the tube was observed and noted at appropriate intervals. This apparatus was reconstructed¹ in 2006 but proved difficult to calibrate. The problem was the tendency of the manometric fluid to dissolve significant quantities of the TIH gas despite being freshly saturated with that gas. In particular, dissolution occurred when *n*-octane was employed as the manometric fluid and when the TIH gas was hydrogen chloride. Repeated experiments, in which 2.00 mmol of HCl was generated by the reaction between potassium chloride and concentrated sulfuric acid as follows:



¹ The original setup became unavailable after the death of Miroslav Krumpolc, who had performed most of the previous experiments.

and in which *n*-octane that had been freshly saturated with HCl was used as the manometric fluid, gave volumes of HCl(g) that ranged between 40.0 and 48.0 mL. The volume of 2 mmol of an ideal gas at 24°C and 1 atm is 48.77 mL.

These difficulties prompted these major modifications of the experimental method for 2006 and 2007:

- A gas syringe replaced the manometric fluid.
- The acquisition of volume data was computerized.
- The temperature and pressure of the reaction system were recorded (also automatically) concurrently with the volume.

The changes eliminated concerns about dissolution of the TIH gases in the manometric fluid, made it possible to record volumes at shorter intervals and over longer periods than was done previously, and eliminated the need to assume that the temperature and pressure of the reaction system remained constant throughout the reaction.²

Equipment for the acquisition of volume, temperature, and pressure data was acquired commercially from ScienceScope.³ Figure D.1 shows the experimental setup. The chemical reaction under study took place in the two-necked 25-mL, round-bottomed flask clamped in position at the far left. This flask contained an egg-shaped stirring bar and was positioned above a stirring plate. Gas from the reaction passed from the reaction flask through a filter (the round-bottomed flask containing a wad of glass-wool) into a 60-mL gas syringe, which is seen resting horizontally on two lab-jacks near the center of Figure D.1. The jacks allowed adjustments to eliminate binding between the walls of the syringe and the piston, which was lubricated with a light coating of silicone oil (not grease). Leads conveyed data from the volume sensor (the green tube) to the data interface (the blue box). Other connections fed data from a thermocouple (clamped in contact with the exterior of the reaction flask) and an aneroid barometer (sitting on the base of the rightmost ring-stand) to the interface. The interface passed *V*, *P*, *T*, and *t* (volume, pressure, temperature, and elapsed time) data to a computer (not visible). The Tygon tube to the left furnished dry nitrogen through a gas needle to purge the system of moisture and air before an experimental run. The nitrogen exited through the oil-filled bubbler at the rear.

² The temperature of the reaction system in the experiments reported here never varied more than 0.8°C (0.27%) during the course of a run; the pressure rarely changed more than 1 mbar (0.1%). Thus, the assumption in previous work that the temperature and pressure were constant was valid to about 0.4%.

³ ScienceScope, Abington House, 146 London Road West, Bath BA1 7DD, UK, Phone: 011 44 870 225 6175.

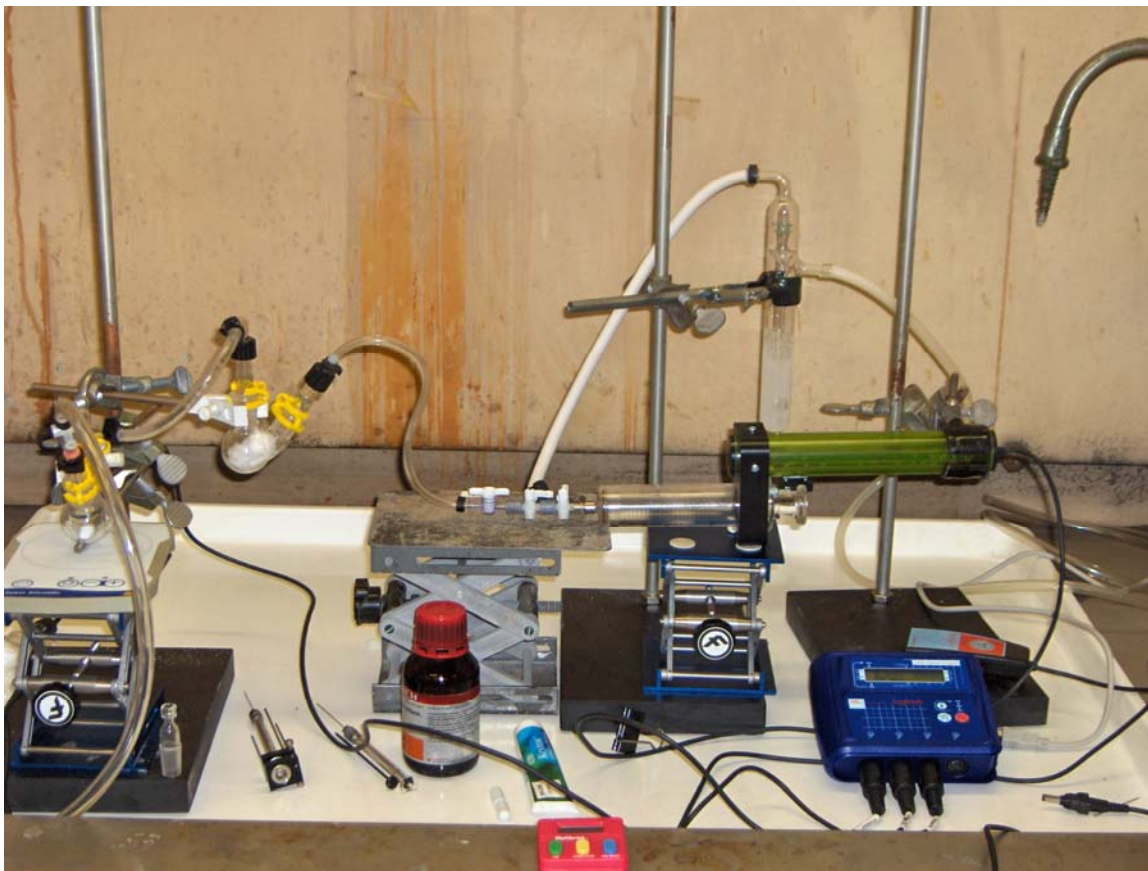


FIGURE D.1 Apparatus Used to Measure the Amounts and Rates of Evolution of TIH Gases

D.1.2 Use of the New Apparatus

To conduct an experimental run involving a liquid material and water, we

1. Put the stirring bar in the reaction flask;
2. Manually confirmed that the piston in the gas syringe moved freely, positioning the syringe in the empty position when finished;
3. Closed the valve to the gas syringe and opened the valve connecting the reaction flask to the bubbler;
4. Closed the open neck of the reaction flask with a rubber septum;
5. Purged the system for 5–10 minutes with dry nitrogen supplied through a gas needle inserted through the rubber septum;
6. Turned off the flow of nitrogen and withdrew the gas needle;

7. Used a microliter syringe to inject the desired quantity of the first reactant through the septum onto the stirring bar, avoiding splashing onto the walls of the flask;
8. Started the stirring motor at the minimum rate and turned up the rate cautiously to the maximum rate that avoided splashing onto the walls of the reaction flask (not exceeding 200 revolutions per minute or rpm);
9. Closed the valve between the system and the bubbler while opening the valve between the reaction flask and the gas syringe; and
10. Injected the desired quantity of the second reactant from a microliter syringe through the septum while simultaneously starting the data collection program.

Extra-long needles helped in delivering the reactants directly to the stirred region at the bottom of the flask without splashing. This apparatus and the data collection program supplied by the vendor allowed accumulation of P , V , T versus t data at intervals as brief as 125 ms over periods that lasted as long as several hours.

D.1.3 Calibration of the Pressure and Temperature Measurements

Pressure measurements were checked against a mercury barometer in the range of ordinary room pressure and found to agree to within 1 mbar. Temperature measurements were checked against a mercury-in-glass laboratory thermometer in the range of 18 to 24°C and found to agree to within 0.05°C. No corrections were applied to the pressure and temperature data.

D.1.4 Calibration of the Volume Measurements

The accuracy of the volume sensor was checked by injecting measured volumes of dry nitrogen from a calibrated 10-mL syringe into the closed system and noting the volume that the sensor reported to the data interface. Five runs consisting of five successive injections of 10.00-mL portions of nitrogen gave these results:

Total Volume Injected (mL)	Mean Volume Reading, (mL)	Standard Deviation, σ (mL)
0	0	0
10.00	9.48	0.04
20.00	19.14	0.05
30.00	29.15	0.06
40.00	39.27	0.10
50.00	49.74	0.15

The sensor reported consistently low volumes. The error ranged from 5.2% at 10 mL to 0.52% at 50 mL. The error was assumed to apply to all volume measurements and was corrected for by linear interpolation within each of the five 10-mL intervals of volume. Specifically, the following equations were used to compute corrected volumes from observed volumes

$$V_{corr} = \left(\frac{10.00 - 0.00}{9.48 - 0.00} \right) V_{obs} + 0.000 \text{ mL} \quad \text{if } 0 < V_{obs} \leq 9.48 \text{ mL}$$

$$V_{corr} = \left(\frac{20.00 - 10.00}{19.14 - 9.48} \right) V_{obs} + 0.186 \text{ mL} \quad \text{if } 9.48 < V_{obs} \leq 19.14 \text{ mL}$$

$$V_{corr} = \left(\frac{30.00 - 20.00}{29.15 - 9.14} \right) V_{obs} + 0.879 \text{ mL} \quad \text{if } 19.14 < V_{obs} \leq 29.15 \text{ mL}$$

$$V_{corr} = \left(\frac{40.00 - 30.00}{39.27 - 29.15} \right) V_{obs} + 1.196 \text{ mL} \quad \text{if } 29.15 < V_{obs} \leq 39.27 \text{ mL}$$

$$V_{corr} = \left(\frac{50.00 - 40.00}{49.74 - 39.27} \right) V_{obs} + 2.493 \text{ mL} \quad \text{if } 39.27 < V_{obs} \leq 49.74 \text{ mL}$$

$$V_{corr} = V_{obs} + 0.260 \text{ mL} \quad \text{if } 49.74 < V_{obs}$$

The fractions in these equations are the slopes of straight-line segments spanning each interval.

In a separate series of calibration experiments, single injections of 50.00 mL of dry nitrogen from a calibrated syringe gave an average volume reading in five trials of 49.73 mL ($\sigma = 0.18$ mL). This result was essentially identical to the result from five successive 10.00-mL injections.

D.1.5 Measurements of Amount

Solid substances were weighed out to the nearest milligram by using an analytical balance. Liquid substances were measured out to the nearest microliter by using microliter syringes of suitable capacity. The required volumes of liquids were calculated by using the densities and relative molar masses tabulated in Table D.1.

TABLE D.1 Compounds Studied

UN	Compound	Molecular Formula	Purity (min assay) (%)	Molar Mass	RT Density	Amt. Used (μL)	Stoic Factor	TIH Gas
1162	Dimethyldichlorosilane	(CH ₃) ₂ SiCl ₂	99	129.06	1.064	121	2	HCl
1183	Ethylchlorosilane	(C ₂ H ₅)HSiCl ₂	98	129.06	1.092	120	2	HCl
1196	Ethyltrichlorosilane	(C ₂ H ₅)SiCl ₃	99	163.51	1.238	132	3	HCl
1242	Methyldichlorosilane	(CH ₃)HSiCl ₂	99	115.03	1.105	105	2	HCl
1250	Methyltrichlorosilane	(CH ₃)SiCl ₃	99	149.48	1.273	118	3	HCl
1295	Trichlorosilane	HSiCl ₃	99	135.45	1.340	101	3	HCl
1298	Trimethylchlorosilane	(CH ₃) ₃ SiCl	97	108.64	0.854	130	1	HCl
1305	Vinyltrichlorosilane	C ₂ H ₃ SiCl ₃	97	161.49	1.270	131	3	HCl
1340	Phosphorus pentasulfide	P ₄ S ₁₀	99	444.55	2.09 (s) ^a	444 mg	5	H ₂ S
1360	Calcium phosphide	Ca ₃ P ₂	100	182.19	Solid	182 mg	2	PH ₃
1680	Potassium cyanide	KCN	99	65.12	1.52 (s)	66 mg	1	HCN
1687	Sodium azide	NaN ₃	99	65.01	1.85 (s)	65 mg	1	HN ₃
1689	Sodium cyanide	NaCN	99	49.01	1.6 (s)	50 mg	1	HCN
1716	Acetyl bromide	CH ₃ COBr	99	122.95	1.663	75	1	HBr
1717	Acetyl chloride	CH ₃ COCl	98	78.50	1.104	73	1	HCl
1724	Allyltrichlorosilane	CH ₂ CHCH ₂ SiCl ₃	95	175.52	1.211	149	3	HCl
1725	Aluminum bromide	AlBr ₃		266.69	3.21 (s)	267 mg	3	HBr
1728	Amyltrichlorosilane (pentyltrichlorosilane)	C ₅ H ₁₁ SiCl ₃	99	205.59	1.142	180	3	HCl
1741	Boron trichloride	BCl ₃	99	117.17	1.346	87	3	HCl
1747	Butyltrichlorosilane	C ₄ H ₉ SiCl ₃	99	191.56	1.160	165	3	HCl
1752	Chloroacetyl chloride	ClCH ₂ COCl	98	112.94	1.418	81	1	HCl
1753	Chlorophenyltrichlorosilane	ClC ₆ H ₄ SiCl ₃	97	246.00	1.42	179	3	HCl
1754	Chlorosulfonic acid	HSO ₃ Cl	99	116.52	1.753	67	1	HCl
1763	Cyclohexyltrichlorosilane	C ₆ H ₁₁ SiCl ₃	98	217.60	1.232	176	3	HCl
1765	Dichloroacetyl chloride	Cl ₂ CHCOCl	98	147.39	1.532	96	1	HCl
1767	Diethyldichlorosilane	(C ₂ H ₅) ₂ SiCl ₂	97	157.12	1.050	154	2	HCl
1769	Dipenyldichlorosilane	(C ₆ H ₅) ₂ SiCl ₂	97	253.20	1.204	217	2	HCl
1771	Dodecyltrichlorosilane	C ₁₂ H ₂₅ SiCl ₃	98	303.78	1.020	304	3	HCl
1777	Fluorosulfonic acid	HSO ₃ F	100	100.06	1.840	54	1	HF
1780	Fumaryl chloride	C ₂ H ₂ (COCl) ₂	95	152.96	1.410	114	2	HCl
1781	Hexadecyltrichlorosilane	C ₁₆ H ₃₅ SiCl ₃	90	359.89	0.990	399	3	HCl
1784	Hexyltrichlorosilane	C ₆ H ₁₃ SiCl ₃	97	219.62	1.107	198	3	HCl
1800	Octadecyltrichlorosilane	C ₁₈ H ₃₇ SiCl ₃	90	387.94	0.984	433	3	HCl
1801	Octyltrichlorosilane	C ₈ H ₁₇ SiCl ₃	97	247.67	1.070	231	3	HCl
1804	Phenyltrichlorosilane	C ₆ H ₅ SiCl ₃	97	211.55	1.321	162	3	HCl
1806	Phosphorus pentachloride	PCl ₅	95	208.24	1.60 (s)	218 mg	5	HCl
1808	Phosphorus tribromide	PB ₃	99	270.68	2.85	96	3	HBr
1809	Phosphorus trichloride	PCl ₃	98	137.33	1.574	89	3	HCl
1810	Phosphorus oxychloride	OPCl ₃	99	153.33	1.675	92	3	HCl
1815	Propionyl chloride	C ₃ H ₅ COCl	98	92.53	1.060	87	1	HCl
1816	Propyltrichlorosilane	C ₃ H ₇ SiCl ₃	98	177.53	1.195	151	3	HCl
1818	Silicon tetrachloride	SiCl ₄	99	169.90	1.483	116	4	HCl
1828	Sulfur chlorides	S ₂ Cl ₂	98	135.03	1.678	80	2	HCl
1834	Sulfuryl chloride	SO ₂ Cl ₂	97	134.96	1.670	83	2	HCl
1898	Acetyl iodide	C ₂ H ₃ OI	95	169.95	1.06	170	1	HI
2308	Nitrosylsulfuric acid sol.	HO ₃ SONO	40	127.07	1.612	197	1	NO ₂
2353	Butyryl chloride	C ₃ H ₇ COCl	98	106.55	1.026	104	1	HCl
2395	Isobutyryl chloride	C ₃ H ₇ COCl	99	106.55	1.02	106	1	HCl
2435	Ethylphenyldichlorosilane	C ₇ H ₅ (C ₆ H ₅)SiCl ₂	99	205.16	1.18	170	2	HCl

TABLE D.1 (Cont.)

UN	Compound	Molecular Formula	Purity (min assay) (%)	Molar Mass	RT Density	Amt. Used (μL)	Stoic Factor	TIH Gas
2437	Methylphenyldichlorosilane	$\text{CH}_3(\text{C}_6\text{H}_5)\text{SiCl}_2$	98	191.13	1.176	166	2	HCl
2691	Phosphorus pentabromide	PBr_5	95	430.49	Solid	452 mg	5	HBr
2692	Boron tribromide	BBr_3	99	250.52	2.650	94	3	HBr

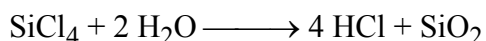
^a (s) = solid.

D.1.6 Two Experimental Protocols

Materials were reacted with water in two ways:

- **Method A.** After the nitrogen purge, 1.00 mmol (typically) of the material was injected into the reaction flask through an inlet covered with a rubber septum and stirred. A chemically equivalent amount of water was then rapidly injected. Equivalency was determined from a chemical equation written to represent the anticipated reaction.⁴

For example, 1.00 mmol (115 μL , 170 mg) of tetrachlorosilane (SiCl_4) was injected into the reaction flask followed by 2.00 mmol (36.0 μL , 36.0 mg) of H_2O . This 1:2 molar ratio ensured that both reactants would be consumed entirely if the reaction



went to completion. Method A was designed to verify the evolution of gases, measure their yield, and estimate the rate of their production.

- **Method B:** The material was added to the water (rather than the reverse), and a fivefold molar excess of water was used. For example, 10.0 mmol of H_2O was put in the reaction flask and stirred, and then 1.00 mmol of SiCl_4 was rapidly injected. This method was intended to model an actual spill more realistically.

Multiple runs (usually three, but as many as seven) were carried out on each material using each method.

⁴ This reaction, of course, is not necessarily the only chemical reaction that occurred, nor is it even a reaction that occurred at all.

D.1.7 Addition of Reactive Solids to Water

Several of the materials studied are solids. In Method A, solids were simply weighed out and transferred into the reaction flask to await the injection of water. Method B required the addition of the solid materials to water. This was hard to do while keeping the system gas-tight. A powder-dumping device was constructed to assist. A small spoon was fashioned by trimming away the top half of the cylindrical squeeze bulb of a 5-mL Beral pipet. A long stainless steel pin was then passed down the length of the pipet tube, out the tip, and through the center of a rubber septum from the inside. The protruding point of the pin was capped with a cork. To use the powder-dumper, a three-neck 25-mL flask (rather than the usual two-neck flask) was used to contain the reaction. After the stirring bar and the appropriate amount of water were put in the flask, the measured mass of solid material, in powdered form, was transferred into the spoon of the device, which was then cautiously inserted through the third neck in such a way that the contents of the spoon were positioned directly above the water. The device was kept in position by fitting the septum to the neck of the flask. The system was purged with nitrogen through the remaining pair of necks. Rotating the pin (using the cork as a handle) inverted the spoon and dumped the solid into the stirred water to start the reaction. This could be done with one hand while the data collection program was initiated with the other.

D.1.8 Stirring

The rate of mixing often controls the rate of heterogeneous chemical reactions. In these experiments, an attempt was made to avoid effects arising from incomplete mixing by stirring the reaction mixture as actively as possible. The stirring rate was set at the highest rate possible while avoiding splashing the reaction mixture onto the sides of the reaction flask. This rate was in the range of 180 to 200 rpm.

The by-products of the reactions were often solid or gelatinous. They sometimes slowed or stopped the motion of the stirring bar, as noted in the following text, which sometimes caused the evolution of gas to slow (compared to the expectation that was based on the assumption of first-order kinetics). The Method A data on butyltrichlorosilane (UN 1747) are typical.

D.1.9 Binding of the Piston in the Gas Syringe

In some runs, the piston of the gas syringe failed to move freely. The symptom was a period of no volume change followed by a sudden increase. These runs were discarded.

D.1.10 Scope of the Experimental Work

Gas evolution experiments were performed on 52 substances. Of the 52, 34 had been studied previously. The additional experiments on the 34 provided more detailed data on the rate of evolution of gases during the early stages of the reactions and allowed comparisons to be

made of the results from using the old experimental apparatus and the results from using the new apparatus.

D.1.11 Purity of Materials

The nominal purities of the materials under study appear in Table D.1. Most were not chemically pure. All were used as received.

D.2 EXPERIMENTAL RESULTS AND DISCUSSION

The results consist principally of yield curves, graphs of the change in the volume ΔV of the reaction system as a function of the time t after the water-reactive material was mixed with water. Attempts, mostly successful, were made to interpret the results by fitting a simple first-order kinetic equation to each yield curve by the method of least squares. The parameters obtained from these fits provided the basis for estimating the yields of gas from the reactions and the rates at which gas evolved.

D.2.1 Adjusting Volumes to a Set of Reference Conditions of Temperature and Pressure

All volume measurements were adjusted to eliminate the effect of minor fluctuations in the temperature and pressure of the reaction system during the experimental runs or from one day to the next. Temperature and pressure data were recorded alongside the volumes to provide the necessary basis for these adjustments. Volumes were adjusted to their ideal-gas values at 20.0°C (293.15 K, 68°F) and 1 atm (1013.25 mbar) by using the following equation:

$$\Delta V_{adj} = \Delta V_{corr} \left(\frac{293.15 \text{ K}}{(273.15 + T_{obs}) \text{ K}} \right) \left(\frac{P_{obs} \text{ mbar}}{1013.25 \text{ mbar}} \right).$$

The subscript *corr* (corrected) on the right side of this equation refers to the calibration correction that is discussed in the preceding section.

Adjustments amounted to no more than 0.4%, which is negligible. In previous work, variations of room temperature and pressure during the runs were, in fact, neglected.

D.2.2 Fitting Kinetic Models to the Volume Data by the Method of Least Squares

The evolution of gas in the majority of the experiments followed first-order kinetics reasonably closely. It was modeled by least-squares adjustment of the three parameters a , λ_0 , and c in the equation

$$\Delta V = a(1 - e^{-\lambda_0 t}) + c \tag{D.1}$$

to fit the data. The λ_0 here is a first-order rate constant (with units of reciprocal time), and a and c are volumes. Fits was carried out by using two different least-squares fitting programs.⁵ The two gave identical results. Final values of the three parameters, together with the root mean square deviation or r.m.s.d. (in which $f(t)$ represents the function being fitted to the data) appear in Table C.1. The r.m.s.d signifies the goodness of fit (the smaller the better):

$$\text{r.m.s.d} = \sqrt{\frac{\sum_{i=1}^n [(\Delta V)_i - f(t_i)]^2}{n}} .$$

In some reactions, the volume of gas spiked to a maximum and then diminished. This behavior could not be modeled by using Equation D.1. It was, however, successfully modeled in several cases by using the five-parameter equation

$$\Delta V = a(1 - e^{-\lambda_0 t}) - b(1 - e^{-\lambda_1 t}) + c . \quad (\text{D.2})$$

The first term on the right-hand side of this equation accounts for the production of gas by a first-order reaction; the second term (with its minus sign) accounts for the consumption of gas by a competing first-order process.

D.2.3 Obtaining Rate Constants and Yields from Least-Square Parameters

The first-order rate constant equals λ_0 , the least-squares parameter in the exponential in Equation D.1. This parameter was computed in reciprocal seconds and converted to reciprocal minutes for the sake of consistency with previous work.

At infinite time, the term in parentheses in Equation D.1 becomes equal to 1, and the volume change is

$$\Delta V_{\infty} = a + c .$$

Pictorially, this quantity equals the final volume attained along the plateau portion of the yield curves. It equals the experimental yield of a particular TIH gas if that gas is the sole gas that is produced in the experiment.

⁵ The two-dimensional data modeling facilities at <http://zunzun.com/> and the modeling facility available within the data-plotting program PLOT (see <http://plot.micw.eu/>).

The fractional yield of a substance in a chemical reaction (symbolized by β in this work⁶) equals its experimental yield divided by its theoretical yield. In terms of volumes at constant T and P ,

$$\beta = \frac{\Delta V_{\infty}}{\Delta V_{theory}} .$$

The denominator in this fraction comes from the balanced chemical equation (the theory) that represents the reaction. It is easily computed if the gas is ideal. For example, if a reaction, at completion, generates 1.000 mmol of ideal gas at 293.15 K and 1 atm pressure (the reference conditions for these experiments), then

$$\Delta V_{theory} = \frac{\Delta n_{theory}(RT)}{P} = \frac{(1.000 \text{ mmol})(0.082057 \text{ L atm K}^{-1}\text{mol}^{-1})(293.15 \text{ K})}{1 \text{ atm}} = 24.055 \text{ mL} .$$

Deviations from ideal-gas behavior were assumed to be negligible in this work.

In Equation D.2, the rate constant for the production of gas is in the exponential in the first term on the right:

$$\text{First-order rate constant for production of gas} = \lambda_0 .$$

At infinite time, both terms in parentheses in Equation D.2 become equal to 1, and the volume change at infinite time is

$$\Delta V_{\infty} = (a + c) - b .$$

The volume change in the absence of the competing process that removes gas is

$$\Delta V_{\infty} = a + c ,$$

and the fractional yield of gas at infinite time is

$$\beta = \frac{\Delta V_{\infty}}{\Delta V_{theory}} .$$

Fractional yields obtained from Equation D.2 parameters were recommended for the development of protective action distances (PADs) in several cases.

⁶ The symbol β sometimes also refers to percentage yield, the fractional yield multiplied by 100%.

D.2.4 Induction Times

The evolution of gas in the experiments did not necessarily begin at the moment of mixing. It often required an induction period. The duration of these periods could be estimated from the results of least-square fit to Equation D.1 by using the relationship

$$t_{\text{induction}} = \frac{\ln(1 + c/a)}{-\lambda_0} .$$

This equation is derived by setting ΔV equal to zero in the kinetic model and solving for t . The parameters a and λ_0 must be positive or zero. Under these circumstances, a negative c implies a positive induction time: the yield curve has an apparent negative value at $t = 0$ so that some time must pass before it gets up to $V = 0$. A positive c does not indicate a negative induction time, which is a physical impossibility, but is rather an artifact of the least-squares fitting procedure.

Induction times could not be estimated from fits to Equation D.2.

D.2.5 Half-Lives

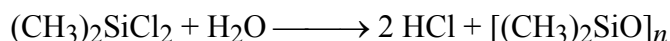
It is sometimes convenient to discuss first-order processes in terms of their half-lives. The half-life is defined as

$$t_{1/2} = \frac{\ln 2}{\lambda_0} .$$

D.2.6 Yield Curves

UN 1162, Dimethyldichlorosilane, $(\text{CH}_3)_2\text{SiCl}_2$ (Repeat of 2003 experiment)

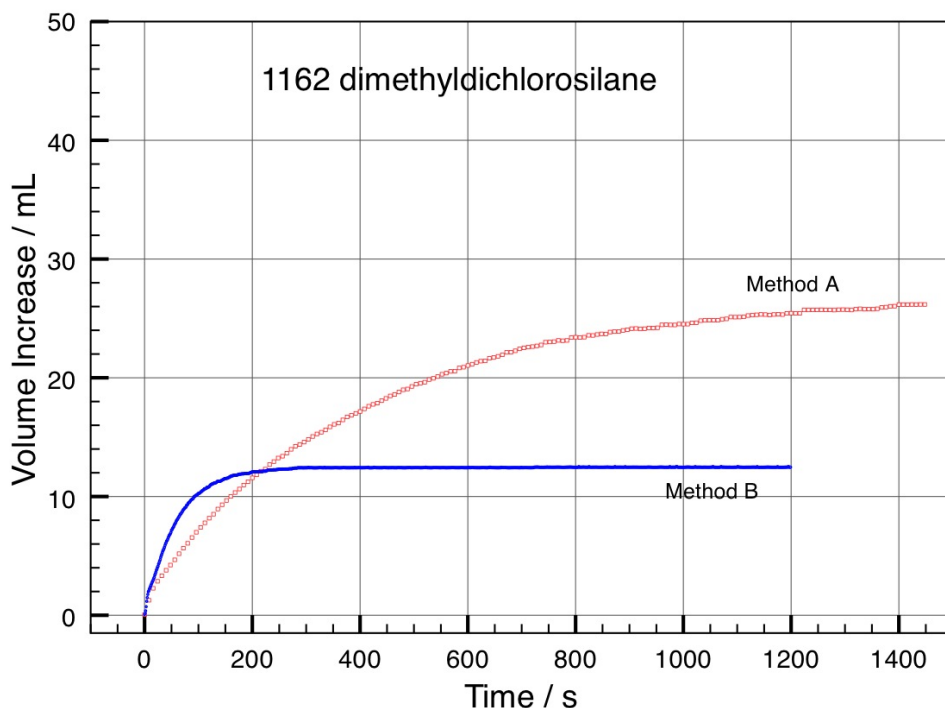
The reaction



was taken as a source of $\text{HCl}(g)$. In Method A, 1.00 mmol of water ($18.0 \mu\text{L} = 18.0 \text{ mg}$) of water was added to $121 \mu\text{L}$ of the compound. This was 1.00 mmol of compound, as computed on the basis of the purity, molar mass, and density listed in Table D.1. In Method B, the same amount of compound was added to 5.00 mmol ($90.1 \mu\text{L} = 90.1 \text{ mg}$) of water. The theoretical yield of $\text{HCl}(g)$ was 2.00 mmol. This amount of ideal gas has a volume of 48.1 mL at 20.0°C and 1 atm.

Observations: A solid by-product formed immediately upon mixing of the reactants when both Method A and Method B were used. The motion of the stirring bar was slowed but not stopped by this material.

Results: The Method A yield curve contains 182 points that were obtained by averaging the results of four runs in which P , V , and T versus t values were recorded at equal intervals for 1,448 s. The Method B yield curve contains 1,200 points, obtained by averaging the results of five runs in which data were recorded at equal intervals for 1,199 s, except that one of the five runs was terminated after 722 s.



Discussion: The fractional yields and first-order rate constants determined from the parameters that were obtained in the least-square fit of Equation D.1 to the two yield curves appear in Table C.1. The small r.m.s.d.'s show that the fit was quite good in both cases.

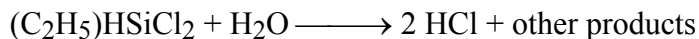
Production of $\text{HCl}(g)$ was faster by using Method B than by using Method A, but the ultimate yield of gas was less. These first of these observations is explained by the larger concentration of water present in Method B; the second is explained by quick dissolution of some of the $\text{HCl}(g)$ in the excess water.

The reaction started so promptly in most runs that some gas evolved before the clock was started. This led to positive values of the least-squares parameter c , which is the ΔV -intercept of the curve (the value of ΔV at $t = 0$). This had scant effect on the values of β and λ_0 .

The fractional yield and rate constant obtained in the Method B experiments were recommended for the development of the PAD for this material.

UN 1183, Ethyldichlorosilane, (C₂H₅)HSiCl₂ (New in 2006)

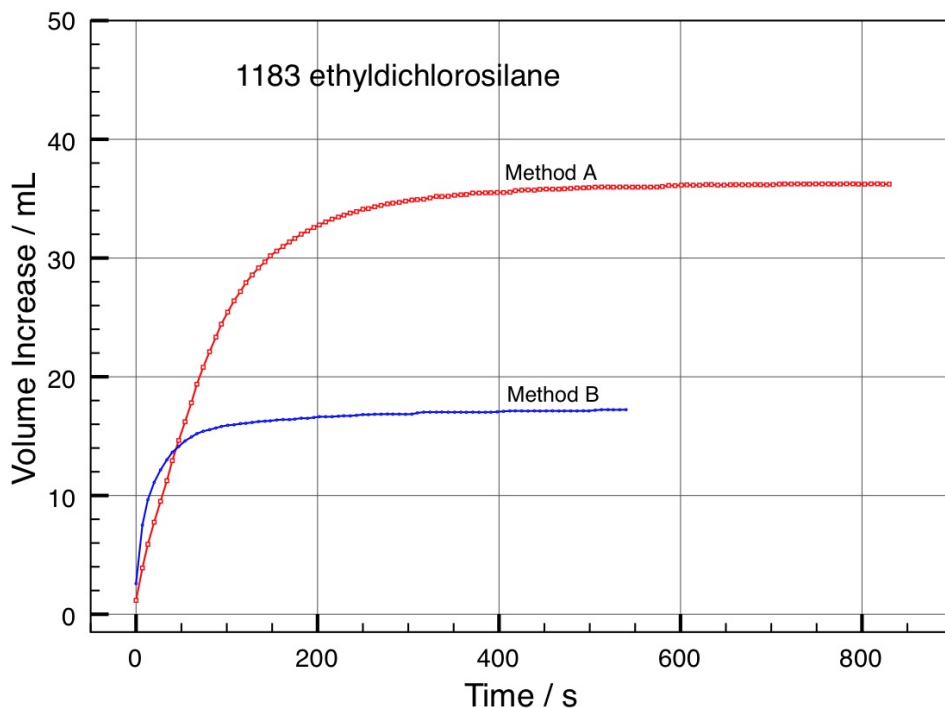
The reaction



was taken as a source of HCl(g). For the Method A runs, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 120 μL of the compound. This was 1.00 mmol, based on the purity, molar mass, and density listed in Table D.1. For the Method B runs, the same amount of the compound was added to 5.00 mmol (90.1 μL, 90.1 mg) of water. In both experiments, the theoretical yield of HCl(g) was 2.00 mmol (48.1 mL at 20.0°C and 1 atm).

Observations: No solid by-product was formed in the Method A runs. In the Method B runs, small amounts of solid formed, but they were too little to affect the motion of the stirring bar.

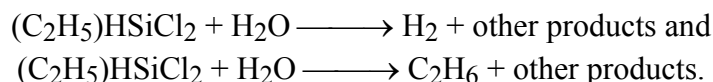
Results: The Method A yield curve consists of 124 points. Each point was obtained by averaging the results of three runs in which data were taken at equal intervals of 830 s. The Method B curve consists of 81 points, each one of which was obtained by averaging the results of three runs in which data were recorded at equal intervals for 540 s.



Discussion: These are the first experiments of this type on this compound. The fractional yields and first-order rate constants estimated from the results of the least-squares fit of Equation D.1 to the two yield curves appear in Table C.1.

Reaction began promptly upon mixing of the two reactants. The reaction was three times faster with Method B than with Method A because of the greater concentration of water in the system when Method B was used. The yield of HCl(g) was less using Method B because some of the HCl(g) dissolved in the excess water. The quality of the least-squares fit of Equation D.1 to the yield curve was good with both data sets.

It is conceivable that the compound underwent one or both of the following reactions concurrently with the reaction to generate HCl:

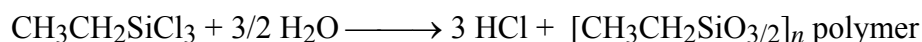


Such reactions would make the true yield of HCl(g) less than the yield concluded here.

The fractional yield and rate constant (β and λ_0) obtained in the Method B experiments were recommended for the development of PADs for this material.

UN 1196, Ethyltrichlorosilane, (C₂H₅)SiCl₃ (Repeat)

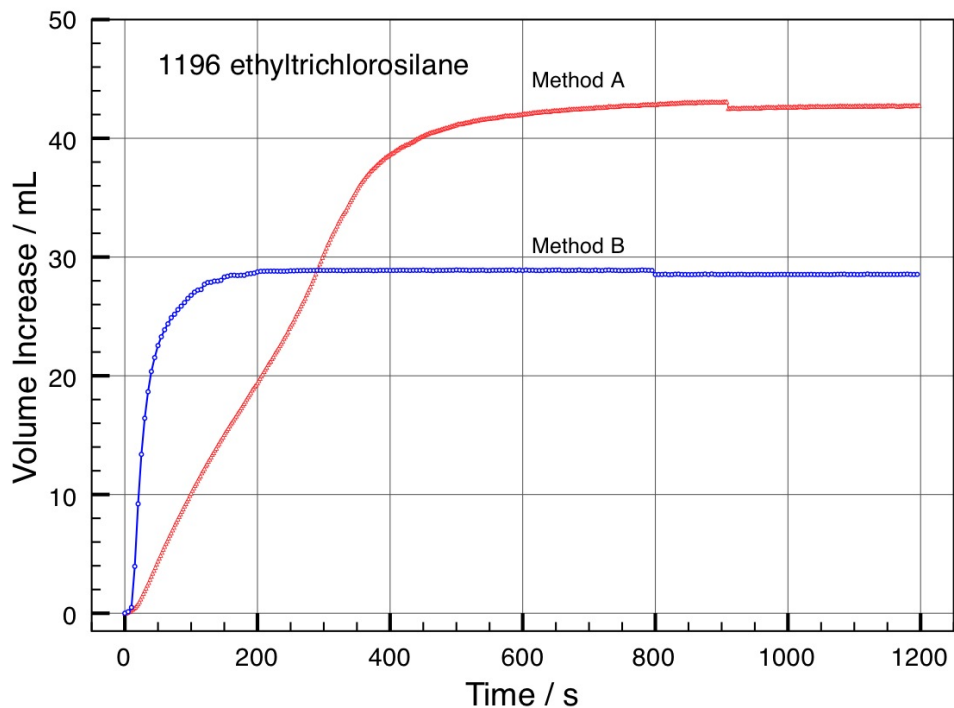
The reaction



was taken as a source of HCl(g). In Method A, 1.50 mmol (27.0 μL = 27.0 mg) of water was added to 132 μL of the compound. This was 1.00 mmol, based on the purity, molar mass, and density listed in Table D.1. In Method B, the same amount of the compound was added to 7.50 mmol (135 μL = 135 mg) of water. The theoretical yield of HCl(g) in both cases was 3.00 mmol, which had a volume of 72.2 mL at the reference conditions of 20.0°C and 1 atm.

Observations: When Method A was used, a white solid by-product formed. This material neither stopped nor noticeably slowed the motion of the stirring bar. When Method B was used, a white solid also formed. The amount of solid was greater than that from using Method A and brought the motion of the stirring bar to a stop after approximately 360 s.

Results: The Method A yield curve consists of 600 points, each of which was obtained by averaging the results of six runs (of seven attempted) in which data were recorded at the same equal intervals over 1,198 s. The Method B curve consists of 240 points obtained by average of the results from three runs (of five attempted) in which data were recorded at the same equal intervals over 1,195 s.



Discussion: The breaks in the curves at 800 s and 900 s arise from the early termination of one of the experimental runs.

The fractional yields, first-order rate constants, and induction times obtained from least-squares fits of Equation D.1 to the two yield curves appear in Table C.1. The reaction was about seven times faster when Method B was used because of the larger concentration of water, but the final yield was less because of dissolution of the product in the excess water.

The slope of the Method A curve perceptibly increased at $\Delta V \approx 25$ mL. This indicates that the reaction sped up after the first of the three Cl atoms had been hydrolyzed, a result that is plausible chemically. The Method A yield curves of 7 of the other 15 trichlorosilanes in this study had more or less similar sigmoidal shapes. The final r.m.s.d. for the fit to the Method A curve was 1.95 mL. This figure of merit was worse than for most of the other materials studied (see Table C.1). It was possible to fit the shape of the Method A yield curve more closely by using more elaborate kinetic models, but doing so did not give useful (i.e., interpretable) results.

The short, flat stretches in the yield curves near $t = 0$ indicate that the reactions did not start immediately upon mixing the reactants. The induction periods, computed as explained in Section D.2.4, were 31 s from using Method A and 4 s from using Method B.

The fractional yield and rate constant (β and λ_0) obtained in the Method B experiments were recommended for the development of PADs for this compound.

UN 1242, Methylchlorosilane, $(\text{CH}_3)\text{HSiCl}_2$ (Repeat)

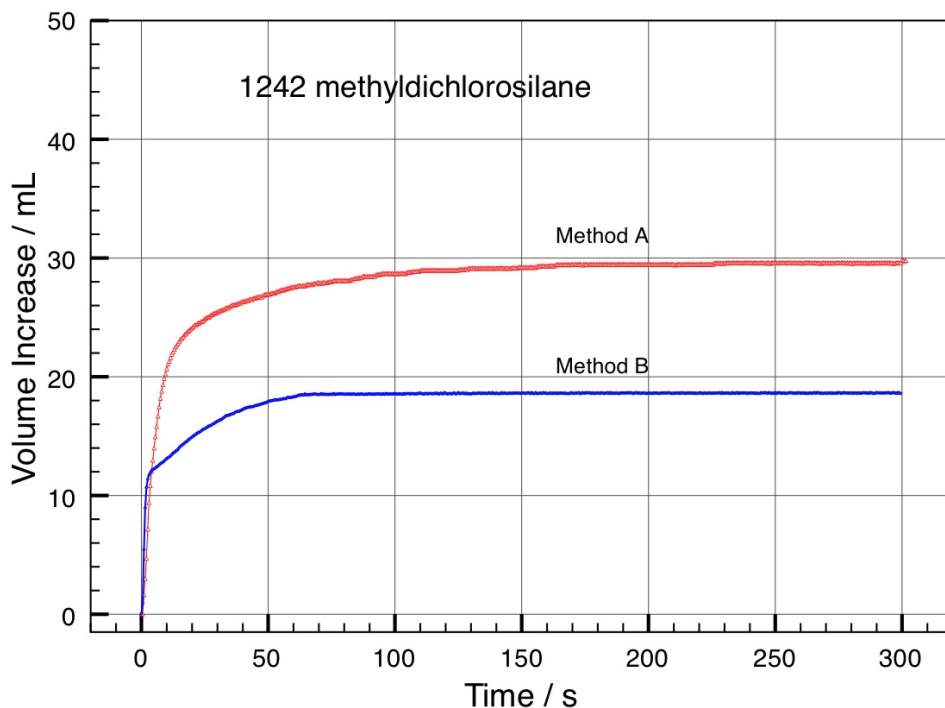
The reaction



was taken as a source of $\text{HCl}(g)$. In Method A, 1.00 mmol ($18.0 \mu\text{L} = 18.0 \text{ mg}$) of water was added to $105 \mu\text{L}$ of the compound. This was 1.00 mmol based on the density and purity listed in Table D.1. In Method B, the same amount of compound was added to 5.00 mmol ($90.1 \mu\text{L} = 90.1 \text{ mg}$) of water. The theoretical yield of HCl in both cases was 2.00 mmol or 48.1 mL at 20.0°C and 1 atm, the reference conditions of the experiments.

Observations: In all experiments, a viscous liquid by-product formed quickly. The material did not stop the motion of the stirring bar in any of the experiments, but it did slow down the motion.

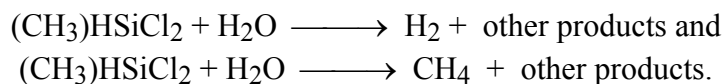
Results: The Method A yield curve consists of 300 points derived from data recorded at equal intervals over 299.5 s. The points are averages of the results from three identical runs. The Method B curve contains 300 points obtained by averaging observations gathered at equal intervals in three identical runs lasting 299.5 s.



Discussion: The fractional yields and first-order rate constants computed from the least-squares fit of Equation D.1 to the yield curves appear in Table C.1. The reaction went faster when Method B was used because of the larger concentration of water, but the yield of $\text{HCl}(g)$ was less because some of the gas dissolved in the excess water. The r.m.s.d.'s between the model

curve and the data were 0.925 mL (Method A) and 0.530 mL (Method B). Both were deemed acceptable. An abnormal drop in the reaction rate occurred in the Method B curve after about 3 s. The buildup of the viscous by-product may have caused this. This product might also have sequestered some water and so reduced the yield of HCl(g) in the Method A experiments.

It is possible that the compound underwent one or both of the following reactions concurrently with the reaction to generate HCl:

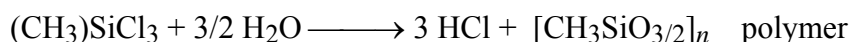


Formation of either of these gases would make the true yield of HCl lower.

The fractional yield and rate constant (β and λ_0) obtained from the Method B experiments are recommended for the development of PADs for this material. These results were not available in time for use in preparing this ERG2008. The 2003 estimates were used instead.

UN 1250, Methyltrichlorosilane, (CH₃)SiCl₃ (Repeat)

The reaction

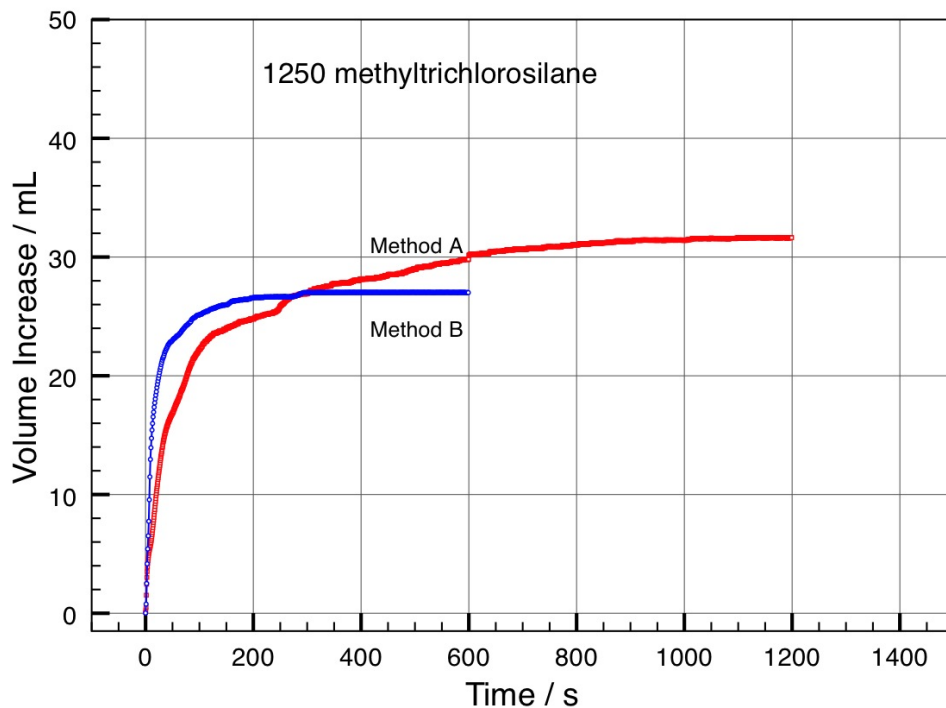


was taken as a source of HCl(g). In Method A, 1.50 mmol (27.0 μL = 27.0 mg) of water was added to 118 μL of the compound. This was 1.00 mmol, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol (135 μL = 135 mg) of water. The theoretical yield of HCl(g) in each case was 3.00 mmol or 72.2 mL at the reference conditions (20.0°C and 1 atm).

Observations: In all experiments, white solid formed immediately after the reactants were mixed. This material did not stop or noticeably slow the motion of the stirring bar.

Results: The Method A yield curve consists of 2,399 points that were obtained by averaging the results of four identical runs in which data were recorded at equal intervals for 1,199 s (however, one of the four runs was terminated after 599.5 s). The Method B curve consists of 600 points obtained by averaging the results of five identical runs in which data were recorded at equal intervals for 599 s.

Discussion: The fractional yields and first-order rate constants computed from the least-squares fit of Equation D.1 to the two yield curves appear in Table C.1. The irregularity at 600 s in the Method A yield curve is caused by the early termination of one of the four experimental runs. The other irregularities in this curve (in the range of 16 to 26 mL) have no obvious explanation. The flattening at $V = 24$ mL may reflect a slowing of the hydrolysis after the first of



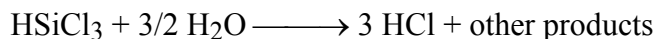
the three Cl atoms reacted away. Because of the irregularities, the r.m.s.d. of the model from Method A yield curve was high (see Table C.1), but it was judged acceptable. The r.m.s.d. for the Method B yield curve was considerably better. As with most of the other chlorosilanes, the reaction went faster when Method B was used, but the yield of HCl(g) was less.

This white solid by-product observed in the reaction flask might have sequestered water, or unreacted methyltrichlorosilane, or both, thus reducing the yield and the rate of the reaction.

The fractional yield and rate constant (β and λ_0) obtained from the Method B experiments are recommended for the development of PADs for this compound. These results were not available in time for use in preparing ERG2008, and the 2003 estimates were used instead.

UN 1295, Trichlorosilane, HSiCl₃ (New in 2006)

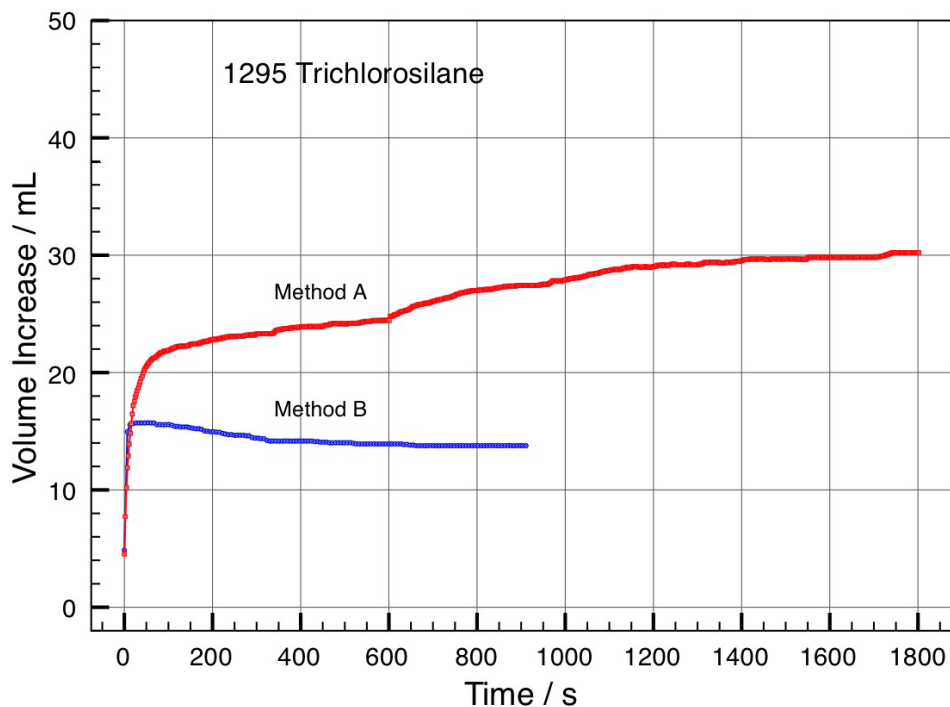
The reaction



was taken as a source of HCl(g). In Method A, 1.00 mmol (27.0 μL = 27.0 mg) of water was added to 101 μL of the liquid compound. This was 1.00 mmol, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol (135 μL , 135 mg) of water. The theoretical yield of HCl was 3.00 mmol, which had a volume of 72.2 mL at the reference conditions (20.0°C or 293.15 K and 1 atm).

Observations: In the experiments using Method A, a white solid by-product formed immediately, and in 2 min, it built up enough to stop the rotation of the stirring bar. In the experiments using Method B, a similar solid formed right away, but in enough quantity to stop the rotation of the stirring bar within a few seconds.

Results: The Method A yield curve consists of 268 volumes obtained by averaging the results from three runs in which data were recorded at nearly equal intervals for 601 s. The Method B curve contains 136 volumes obtained by averaging the results of two experimental runs in which data were obtained at nearly equal intervals for 911 s.



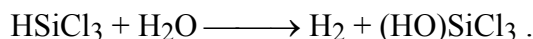
Discussion: These were the first experiments of this type on this compound. The onset of reaction was rapid in all runs. This caused nonzero volumes at $t = 0$ in both yield curves. The fractional yield and first-order rate constant obtained from fitting Equation D.1 to the Method A yield curve appear in Table C.1. The irregularities in this curve are obvious. They probably resulted from episodic evolution of gas from the reaction mixture after the stirring ceased. Despite the irregularities, the r.m.s.d. of the fit of Equation D.1 to the Method A data was acceptable (0.718 mL).

The Method B yield curve rose to a maximum (15.7 mL at $t = 54$ s) and then went down. This shape is not typical, but it was not unique either. The loss of $\text{HCl}(g)$ resulted from its dissolution in the excess water or possibly from an interaction with the by-products of the reaction. This yield curve obviously could not be modeled by using Equation D.1 (in

Section D.2.4). Attempts to model it by using Equation D.2 failed. The difficulty might have been caused by the uneven evolution of gas that was occasioned by the failure of stirring after the first few seconds. Finally, the rising and flat portions of the yield curve were used to model the evolution of gas: The first 19 points of the yield curve (collected over 121 s) were successfully fitted to Equation D.1. The fractional yield and rate constant obtained from this procedure appear in Table C.1. They were recommended for the development of PADs for this material.

The rate constant for the evolution of gas here was the largest among the 25 chlorosilanes that were studied.

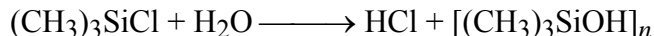
This substance might have generated dihydrogen (H₂) in some proportion alongside the HCl according to the equation



Formation of dihydrogen would make the true yield of HCl lower than estimated here.

UN 1298, Trimethylchlorosilane, (CH₃)₃SiCl (Repeat)

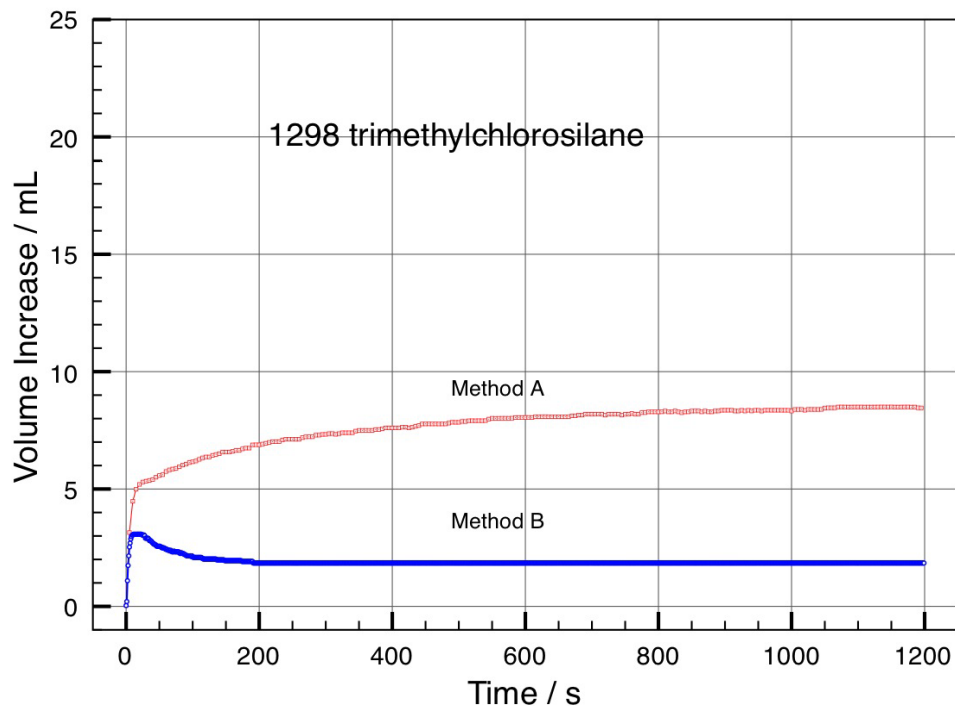
The reaction



was taken as a source of HCl(g). In Method A, 1.00 mmol of water (18.0 μL = 18.0 mg) was added to 130 μL of the compound. This was 1.00 mmol, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (90 μL = 90 mg) of water. The theoretical yield of HCl(g) in both reactions was 1.00 mmol, which had a volume of 24.1 mL at 20.0°C and 1 atm (the reference conditions).

Observations: The reaction produced a white, solid by-product from both methods of mixing. This material slowed the rotation of the stirring bar in all experiments but never stopped it.

Results: The Method A curve consists of 240 points that were obtained by averaging the results of three identical experimental runs in which data were recorded at equal intervals for 1,195 s. The Method B curve contains 1,200 points, obtained as the average of three runs in which data were recorded at equal intervals for 1,199 s.



Discussion: The fractional yield and first-order rate constant obtained from the least-squares fit of Equation D.1 to the Method A yield curve appear in Table C.1.

The Method B yield curve has an early spike. The reaction started with a burst of $\text{HCl}(g)$, after which the amount of the gas dwindled, presumably because of dissolution in the excess water. Equation D.1 could not be fitted to this yield curve, but it could be fitted to the first 23 data (collected over the first 23 s). The final parameters for this fit were

$$a = 3.43 \text{ mL}, \quad c = -0.30 \text{ mL}, \quad \text{and} \quad \lambda_0 = 18.4 \text{ min}^{-1}$$

for which the r.m.s.d. was 0.132 mL. An equally good fit (r.m.s.d. = 0.143 mL) of Equation D.2 to the entire data set was also obtained. The final parameters in Equation D.2 were

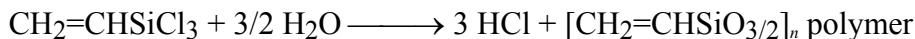
$$a = 9.50 \text{ mL}, \quad b = 8.52 \text{ mL}, \quad c = 1.86 \text{ mL}, \quad \lambda_0 = 0.40 \text{ min}^{-1}, \quad \text{and} \quad \lambda_1 = 0.375 \text{ min}^{-1}.$$

As explained in Section D.2.3, the yield that would result if none of the gaseous product dissolved in the excess water in Method B would be the sum of a and c , and the fractional yield β would be this sum divided by the theoretical yield. The fractional yield was thus 0.47.

Equation D.2 results appear under the Method B heading in Table C.1 and are recommended for the development of PADs for this material. They were not available in time for use in preparing ERG2008, so the 2003 estimates were used instead.

UN 1305, Vinyltrichlorosilane, C₂H₃SiCl₃ (Repeat)

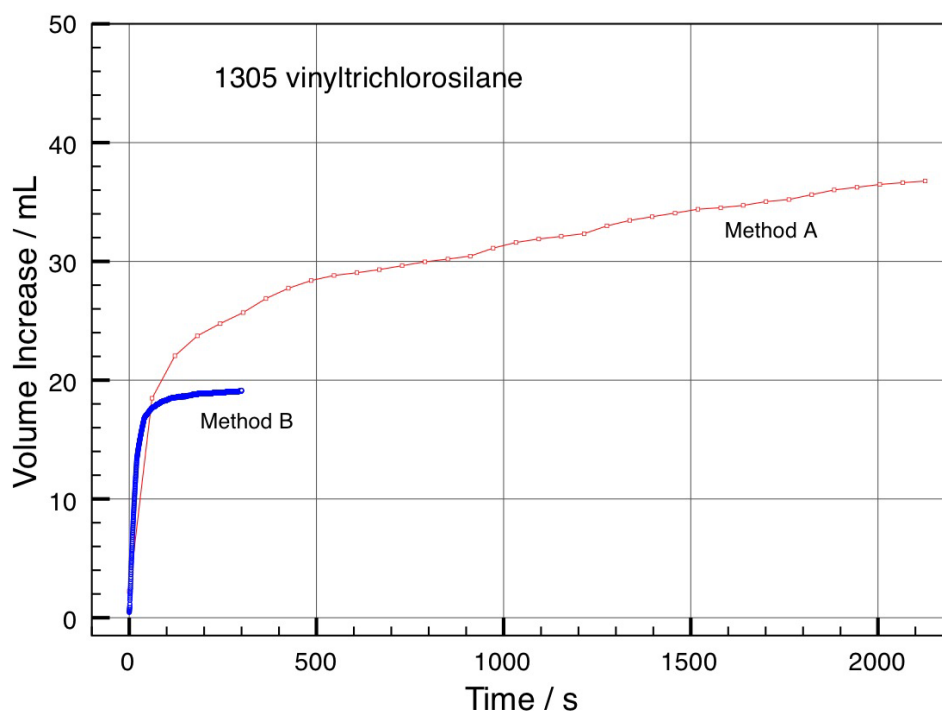
The reaction



was taken as a source of HCl(g). In Method A, 1.50 mmol of water (27.0 μL = 27.0 mg) was added to 131 μL of the compound. This amount equaled 1.00 mmol based on the density and purity listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol (135 μL = 135 mg) of water. The theoretical yield of HCl(g) in both reactions was 3.00 mmol or 72.2 mL at the reference conditions (20.0°C and 1 atm).

Observations: A white solid precipitated in all experiments. This material slowed the motion of the stirring bar in the Method A runs but did not stop it. It did stop the stirring bar in the Method B runs after approximately 20 s.

Results: The Method A curve contains 36 points that were obtained by averaging the results of three runs in which data were recorded at nearly equal intervals for 2,126 s. The Method B curve contains 1,501 points, obtained by merging (with interpolation) the average of two runs in which data were recorded at equal intervals for 120 s (601 items of data) with the average of three runs in which data were collected at equal intervals for 324 s (19 items of data).



Discussion: The fractional yields and first-order rate constants computed from the least-squares fit of Equation D.1 to the two yield curves appear in Table C.1.

The r.m.s.d. for the fit to the Method A data was 2.26 mL, which was high. The low quality of the fit was caused by the relative paucity of data and the speed-ups and slow-downs over the course of the experiment that are obvious in the plot of the yield curve. These might have been caused by the difficulties with stirring. The Method A yield curves for 7 of the 15 other trichlorosilanes that were studied had more or less similar appearances. The similarities between this Method A yield curve and the Method A curve for trichlorosilane (UN 1295) are obvious.

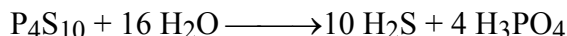
In Method B, the less-than-theoretical yield of $\text{HCl}(g)$ might have been caused by sequestration of some reactant by the thick by-product as well as by dissolution of $\text{HCl}(g)$ in the excess water.

Conceivably, some HCl was also consumed by a side-reaction involving the vinyl group.

The fractional yield and rate constant appearing under the Method B heading in Table C.1 are recommended for the development of PADs. They differ slightly from those that were recommended previously for this material for ERG2008 because of the inclusion of additional experimental runs and the application of corrections to the volume measurements that had been omitted previously.

UN 1340, Phosphorus Pentasulfide, P_4S_{10} (New in 2006)

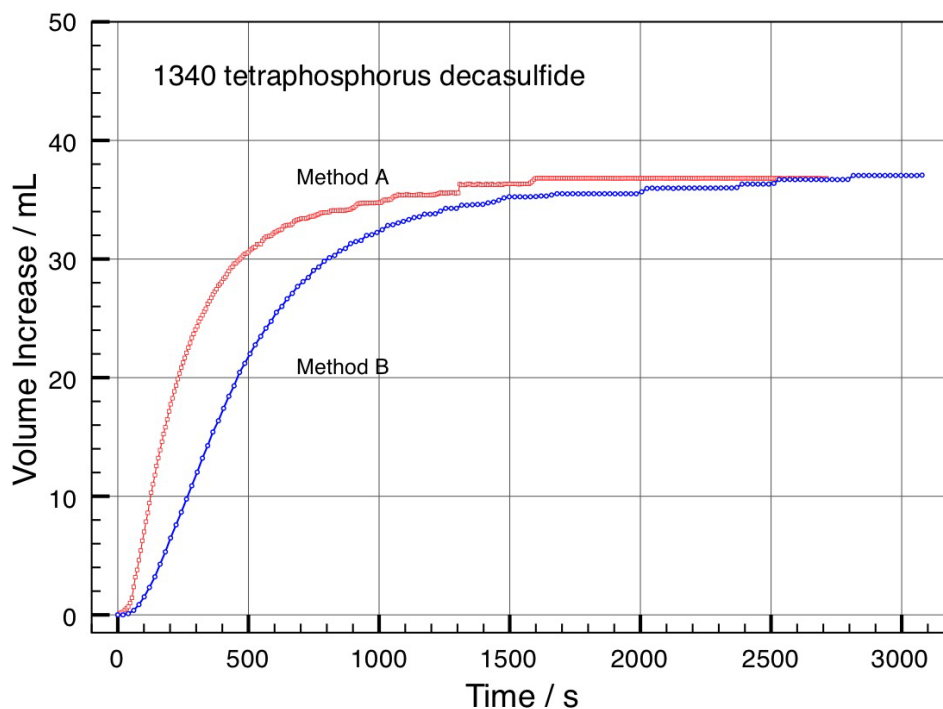
The reaction



was taken as a source of $\text{H}_2\text{S}(g)$. In Method A, 16.0 mmol (288 μL = 288 mg) of water was added to 444 mg of the compound, which is a solid. This was 1.00 mmol based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 80.0 mmol (1441 μL = 1441 mg) of water. The theoretical yield of $\text{H}_2\text{S}(g)$ in both cases was 10.0 mmol, which is 240.6 mL at 20.0°C and 1 atm pressure.

Observations: In Method A, the reaction mixture appeared to become dry almost immediately as the stirring bar continued to turn. In Method B, the reaction flask always contained a visible liquid as a white solid formed. The white solid did not noticeably hinder the rotation of the stirring bar

Results: The Method A curve consists of 403 points that were obtained by averaging the results of three runs in which P , V , and T versus t data were recorded at equal intervals. One of the runs lasted 2,713 s; the second was terminated after 1,303 s; the third was terminated after 1,478 s. The Method B curve consists of 143 points obtained as the average of three runs recorded at equal intervals for 3,078 s (but one of the runs was terminated after 2,794 s).



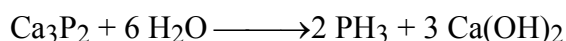
Discussion: These were the first experiments of this type on this material. The fractional yields, first-order rate constants, and induction times computed from the least-squares fitting of Equation D.1 to the two yield curves appear in Table C.1. The flat segments at the beginning of the yield curves indicate that the reaction required a period of induction. The ultimate yields of $\text{H}_2\text{S}(g)$ were the same from using the two methods. $\text{H}_2\text{S}(g)$, unlike the hydrogen halides, is poorly soluble in water. Dissolution in the excess water in Method B could not significantly lower the yield of $\text{H}_2\text{S}(g)$, and it did not.

The production of gas went faster when Method A was used than when Method B was used, contrary to the findings for most of the chlorosilanes.

The fractional yield and rate constant appearing under the Method B heading in Table C.1 were recommended for the development of PADs for this material.

UN 1360, Calcium Phosphide, Ca_3P_2 (Repeat)

The reaction

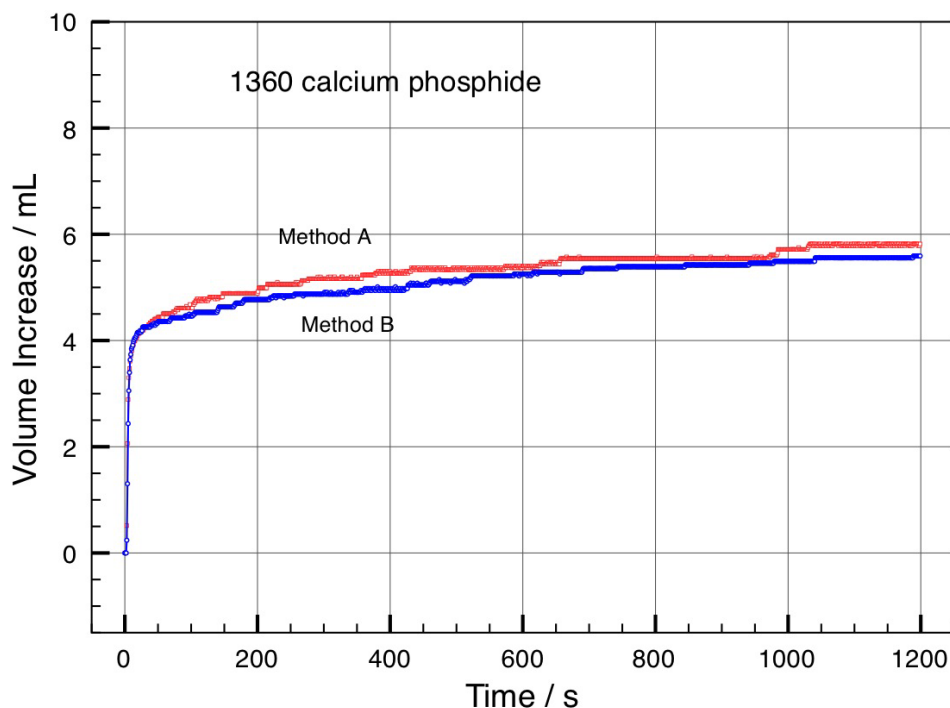


was taken as a source of $\text{PH}_3(g)$. In Method A, 6.0 mmol (108 μL = 108 mg) of water was added to 182 mg of the compound, which is a solid. This was 1.00 mmol of the compound, based upon the purity and molar mass listed in Table D.1. In Method B, 1.00 mmol of the compound was

added to 30.0 mmol (540 μL = 540 mg) of water. The theoretical yield of PH_3 in each case was 2.00 mmol, which is 48.1 mL at 20.0°C and 1 atm.

Observations: When Method A was used, the reaction mixture thickened and became difficult to stir.

Results: The Method A curve contains 1,200 points, The information was obtained by averaging the results of three runs in which data were recorded at equal intervals for 1,199 s. The Method B curve also has 1,200 points obtained as the average of three runs in which data were recorded at equal intervals for 1,199 s.



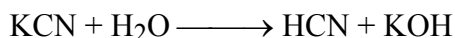
Discussion: The fractional yields and first-order rate constants computed from the least-squares fitting of Equation D.1 to the two yield curves appear in Table C.1. The rates of reaction were similar from using the two methods, and the yields of $\text{PH}_3(g)$ were almost identical. $\text{PH}_3(g)$ dissolves only poorly in water, which nearly eliminates dissolution of the gas in the excess water used in Method B. Finding the same yields with Method A and B in this case strengthened the notion that dissolution of soluble $\text{HCl}(g)$ in the excess water caused the lower yields that were usually found from using Method B on the chlorosilanes. The equality of yield in the two methods was observed with phosphorus pentasulfide, which also evolves a poorly soluble gas when reacted with water.

Chemical events in the mixture might have been more complex than suggested by the single equation. For example, gaseous diphosphine ($\text{P}_2\text{H}_4(g)$) might have formed. The extent of such a concurrent reaction could not be determined in this experiment, which measured only the volume, not the identity, of evolved gases.

The values for β and λ_0 that appear under the Method B heading in Table C.1 are recommended for the development of PADs for this material. They were not available in time to use in preparing ERG2008, and the 2003 estimates were used instead.

UN 1680, Potassium Cyanide, KCN (New in 2006)

The reaction



was taken as a source of HCN(g). In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 50 mg of the compound, a solid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (90.1 μL = 90.1 mg) of water. The theoretical yield of HCN(g) was 1.00 mmol, which is 24.1 mL of gas at 20°C and 1 atm pressure.

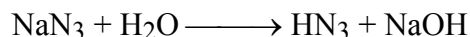
Observations: No volume change was detected with either method; no gas evolved.

Discussion: These were the first experiments of this type on this compound. This compound evolves highly toxic HCN(g) in contact with acidic solutions. The evolution of gas was not expected under the conditions of these experiments, but the experiments were performed anyway for the sake of confirmation.

The retention of the compound on the list of materials that evolve TIH gases by water reaction was recommended with a fractional yield β of 0.4 and rate constant λ_0 of 0.1 min^{-1} . These are the 2003 estimates of these quantities for this compound.

UN 1687, Sodium Azide, NaN₃ (New in 2006)

The reaction



was taken as a source of HN₃(g). In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 65 mg of the compound, a solid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (90.1 μL = 90.1 mg) of water. The theoretical yield of HN₃(g) was 1.00 mmol, which is 24.1 mL of gas at 20°C and 1 atm pressure.

Observations: No volume change was detected with either method; no gas evolved.

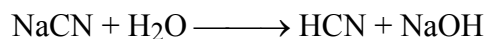
Discussion: These were the first experiments of this type on this compound. Hydrogen azide (hydrazoic acid) is a highly toxic, volatile, water-soluble liquid at room conditions (boiling point 37°C). Spills of sodium azide into acidic waters could conceivably lead to the release of

vaporous hydrazoic acid. The evolution of gas was not expected under the conditions of these experiments, but trials were performed to make sure.

The omission of this compound from the list of materials that give TIH gases by water reaction was recommended.

UN 1689, Sodium Cyanide, NaCN (New in 2006)

The reaction



was taken as a source of HCN(g). In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 50 mg of the compound, a solid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (90.1 μL = 90.1 mg) of water. The theoretical yield of HCN(g) was 1.00 mmol, which is 24.1 mL of gas at 20°C and 1 atm pressure.

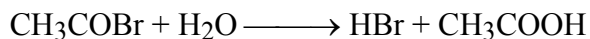
Results: No volume change was detected with either method; no gas evolved.

Discussion: These were the first experiments of this type on this compound. Despite the negative result, the retention of the compound on the list of materials that give TIH gases by water reaction was recommended. A report (Cleven and van Bruggen 2000) on a large spill of sodium cyanide into a river in Kyrgyzstan in May 1998 concluded that “a large part of the dissolved cyanide must have been rapidly transformed into HCN, which will have been released into the air.” The report said that people “must have been at considerable risk for life-threatening disease through inhalatory uptake of HCN (gas).” Several deaths were attributed to either dermal or inhalatory contact with HCN in this incident.

The retention of the compound on the list of materials that evolve TIH gases by water reaction was recommended, with a fractional yield β of 0.4 and rate constant λ_0 of 0.1 min^{-1} . These are the 2003 estimates of these quantities for this compound.

UN 1716, Acetyl Bromide, CH₃COBr (Repeat)

The reaction

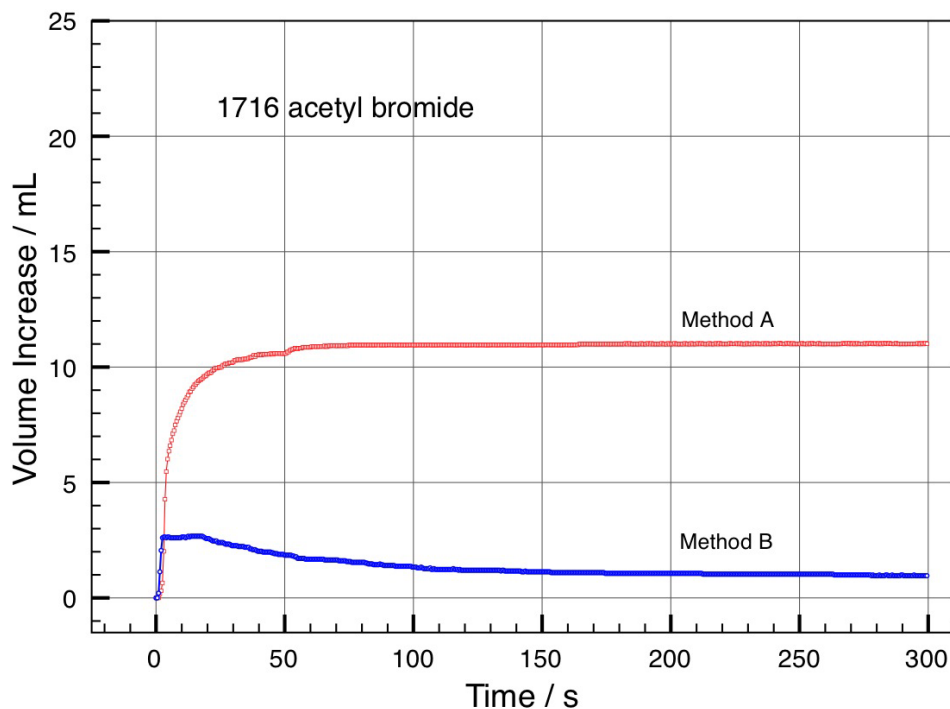


was taken as a source of HBr(g). In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 75 μL of the compound, a liquid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound

was added to 5.00 mmol (90.1 μL = 90.1 mg) of water. The theoretical yield of $\text{HBr}(g)$ was 1.00 mmol, which is 24.1 mL of gas at 20°C and 1 atm pressure.

Observations: No solid by-products were observed with either method.

Results: The Method A curve contains 300 points, obtained by averaging the results of three runs in which P , V , and T versus t data were recorded at equal intervals for 299.5 s. The Method B curve contains 300 points observed at equal intervals for 299.5 s and obtained as the average of three runs.



Discussion: The fractional yield and first-order rate constant computed from the least-squares fit of Equation D.1 to the Method A yield curve appear in Table C.1.

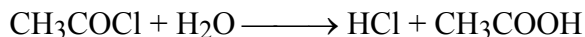
With Method B, the rate at which gas was produced was initially high, but it soon fell to zero and then became negative as $\text{HBr}(g)$ dissolved in the excess water. Equation D.1 could not meaningfully be fit to the whole of the Method A curve. Attempts to fit Equation D.2 also failed. The rising portion of the Method B curve (the first 36 points, which were collected during the first 18 s) was satisfactorily fit to Equation D.1. These results appear under the Method B heading in Table C.1. They are recommended for the development of PADs for this material. They were not available in time for use in preparing ERG2008, and the 2003 estimates were used instead.

Note that the yield curves for this compound generally resemble those of the closely related compound acetyl chloride (UN 1717).

The values for fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 are recommended for the development of PADs for this material. They were not available in time for use in preparing ERG2008, so the values derived from the 2003 experiments were used instead.

UN 1717, Acetyl Chloride, CH_3COCl (Repeat)

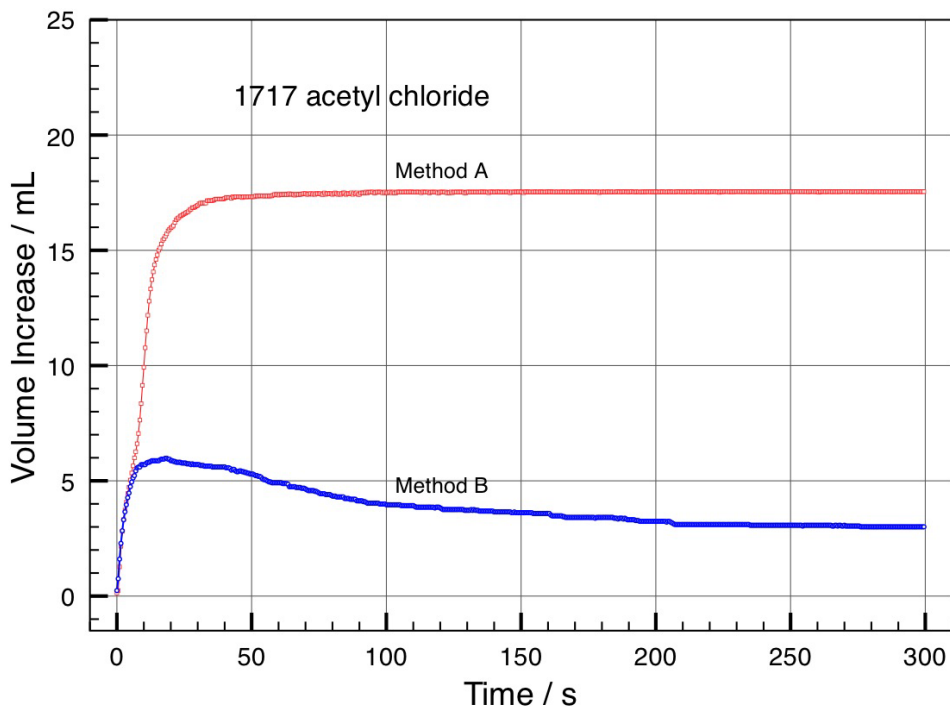
The reaction



was taken as a source of $\text{HCl}(g)$. In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 73 μL of the compound, a liquid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (90.1 μL = 90.1 mg) of water. The theoretical yield of $\text{HCl}(g)$ was 1.00 mmol, which is 24.1 mL of gas at 20°C and 1 atm pressure.

Observations: No solid by-products were observed with either method.

Results: The Method A curve consists of 600 points obtained at equal intervals as the average of three runs each lasting 300 s. The Method B curve also consists of 600 points obtained at equal intervals of time as the average of three runs lasting 300 s.



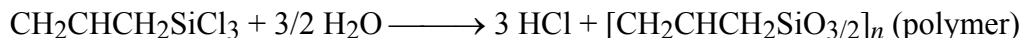
Discussion: The fractional yield and first-order rate constant computed from a least-squares fit of Equation D.1 to the Method A yield curve appear in Table C.1.

With Method B, the production of gas was initially rapid but soon went into reverse as the $\text{HCl}(g)$ dissolved in the excess water. The resulting maximum on the Method B yield curve prevented meaningful fitting of the whole of the curve to Equation D.1. Attempts to fit Equation D.2 to the data failed. Finally, the rising portion of the Method B curve (the first 38 points, which were collected during the first 18.5 s) was satisfactorily fit to Equation D.1. These results appear under the Method B heading in Table C.1. They are recommended for the development of PADs for this material. They were not available in time to prepare ERG2008, and the 2003 estimates were used instead.

The yield curves for this compound resemble those obtained for the related compound acetyl bromide (UN 1716).

UN 1724, Allyltrichlorosilane, $\text{CH}_2\text{CHCH}_2\text{SiCl}_3$ (Repeat)

The reaction



was taken as the source of $\text{HCl}(g)$. In Method A, 150 mmol (27.0 μL = 27.0 mg) of water was added to 149 μL of the compound, a liquid. This amount equaled 1.00 mmol based on the purity, molar mass, and density listed in Table D.1. In method B, 1.00 mmol of the compound was added to 7.50 mmol of water. The theoretical yield of $\text{HCl}(g)$ in each case was 3.00 mmol, which is 72.2 mL at 20.0°C and 1 atm.

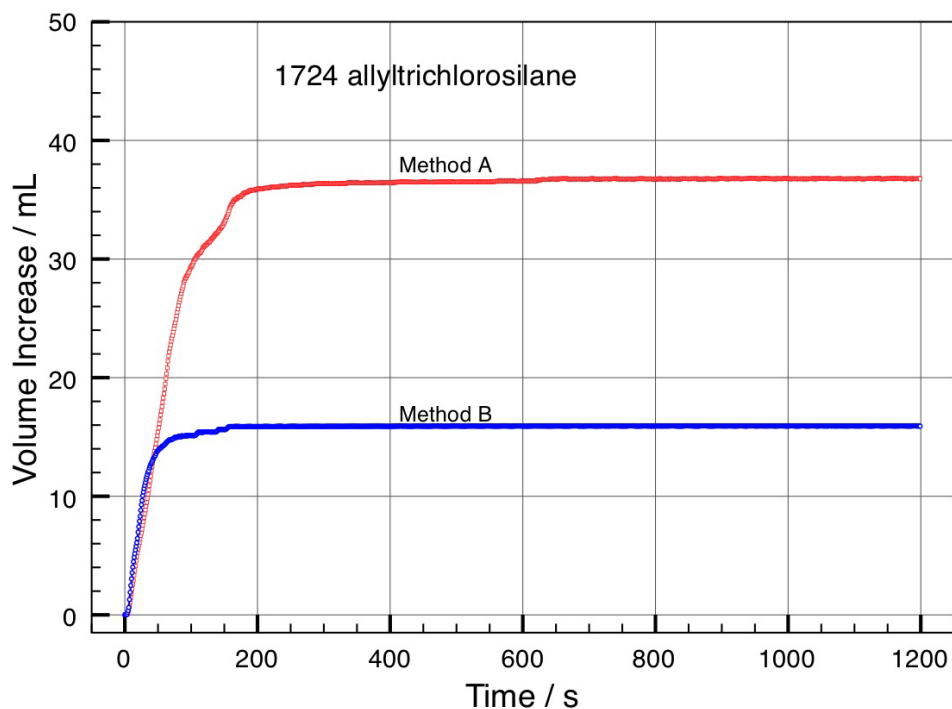
Observations: In all experiments, the reaction rapidly formed a viscous by-product that slowed but did not stop the motion of the stirring bar.

Results: The Method A yield curve contains 1,200 points that were obtained by averaging the results of five runs in which P , V , and T versus t data were recorded at equal intervals for 1,199 s. The Method B curve contains 1,200 points that were obtained by averaging the results of two runs in which data were recorded at equal intervals for 1,199 s.

Discussion: The fractional yields and first-order rate constants computed from the least-squares fitting of Equation D.1 to the two yield curves appear in Table C.1. The irregularities in the curves in the region from 100 to 200 s perhaps arose from the slowing of the stirring rate, which began at different points in time in the experimental runs. Despite the irregularities, the r.m.s.d.'s for the fits were both acceptably low.

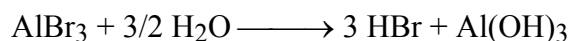
Although the two curves seem almost to overlap during the first 50 s; in fact, they do not. The rate constant obtained from using Method B was more than twice the rate constant from using Method A.

These fractional yield and rate constant appearing under the Method B heading in Table C.1 were recommended for the development of PADs for this material.



UN 1725, Aluminum Bromide, Anhydrous, AlBr₃ (Repeat)

The reaction

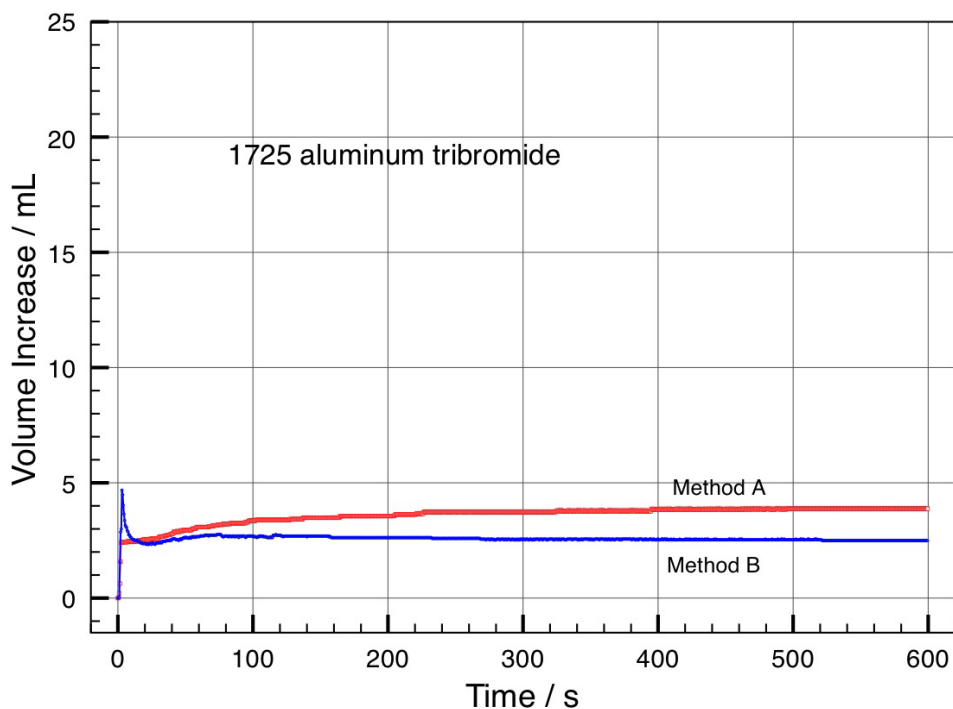


was taken as the source of HBr(g). In Method A, 1.50 mmol (27.0 μL = 27.0 mg) of water was added to 267 mg of the compound, a solid. This amount equaled 1.00 mmol on the basis of the purity listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol of water. The theoretical yield of HBr(g) in each case was 3.00 mmol, which is 72.2 mL at 20.0°C and 1 atm.

Observations: No insoluble products formed in any of the experiments. No substantial increases in temperature were recorded.

Results: The Method A yield curve contains 1,200 points that were obtained by averaging the results of four runs in which P , V , and T versus t data were recorded at equal intervals for 599.5 s. The Method B curve contains 1,200 points that were obtained by averaging the results of three runs in which data were recorded at equal intervals for 599.5 s.

Discussion: The fractional yield and first-order rate constant computed from fitting Equation D.1 to the Method A yield curve appears in Table C.1. At 3.8 mL (5.2% of the theoretical yield), the yield of gas in the Method A experiments was small. This was because HBr tends to stay associated with the Al(OH)₃ by-product; that is, the principal product of the reaction was hydrated aluminum bromide, which is not a gas.



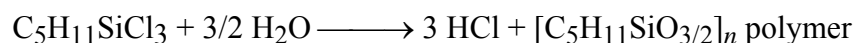
The Method B yield curve had a maximum. Eight rising points (collected during the first 3.5 s) ascended to 4.7 mL and were followed by a quick descent to a final ΔV of 2.5 mL. Equation D.1 could not be fit to the whole of this curve, and the rising portion alone did not give acceptable results when attempts were made to fit it to Equation D.1 separately.

Previous experiments (in 2003) on this material detected minimal (1 mL) increases in volume. These increases were attributed to heating from the strongly exothermic dissolution of the aluminum bromide. In the current experiment no heating was observed, but more gas evolved when both methods were used. Moreover, the possibility exists that a big spill of aluminum bromide into a restricted quantity of water might raise a dangerous acidic mist.

In the absence of a fit to the exotic-looking Method B curve, the fractional yield and rate constant from Method A are recommended as a basis for estimating PADs. These results were not available in time to use in preparing the ERG2008, and the values from 2004ERG were carried forward without change.

UN 1728, Amyltrichlorosilane, $C_5H_{11}SiCl_3$ (Repeat)

The reaction

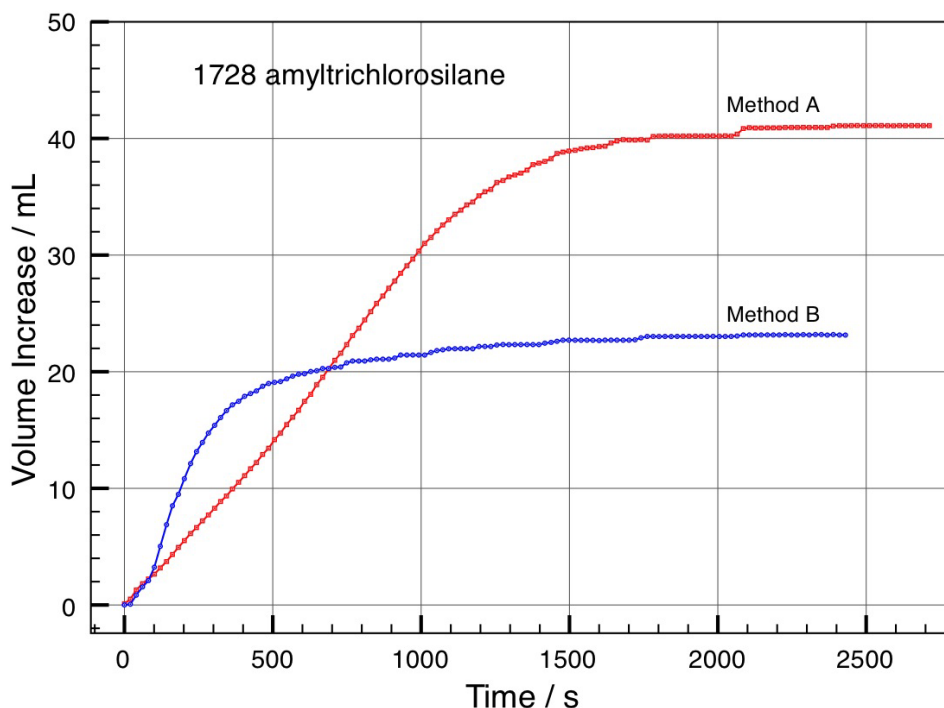


was taken as a source of $HCl(g)$. In Method A, 1.50 mmol of water was added to 180 μL of the substance, a liquid. This amount of the substance was 1.00 mmol on the basis of the density and purity listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol of

water. The theoretical yield of $\text{HCl}(g)$ in both cases was 3.00 mmol, which corresponded to 72.2 mL of gas at 20°C and 1 atm.

Observations: In Method A, the reaction slowly formed a very viscous liquid by-product that slowed, but did not stop, the motion of the stirring bar. A viscous liquid by-product also formed with Method B. It also slowed but did not stop motion of the stirring bar.

Results: The Method A curve contains 135 points that were obtained by averaging the results of three runs in which P , V , and T versus t data were recorded at equal intervals for 2,713 s. The Method B curve contains 121 points, obtained by averaging three runs in which data were recorded at equal intervals for 2,430 s.



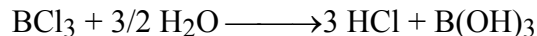
Discussion: The fractional yields, first-order rate constants, and induction times obtained from fitting Equation D.1 to the two yield curves appear in Table C.1. The r.m.s.d. for the fit to the Method A curve was 1.924 mL, which was rather large. An increase in rate after about 800 s (when about 24 mL of gas had evolved) was responsible for much of the deviation. This increase, which is visible in the yield curve, started just after 1 mol of $\text{HCl}(g)$ had formed. It might have been caused by a change in the mechanism of the reaction at that juncture. Similar speed-ups in the rate of evolution of $\text{HCl}(g)$ appeared in the Method A yield curves of 7 of the 15 other trichlorosilanes that were studied in 2006. The unexplained minor increase in volume at 2,086 s also harmed the quality of the fit.

The Method B yield curve overlaps the Method A curve for the first minute or so but then shoots upward. This acceleration in the rate of reaction was very likely a result of the problems encountered in stirring the mixture. The figure of merit for the fit of Equation D.1 to the Method B data was accordingly poor (r.m.s.d. = 1.92 mL). Nevertheless, the fractional yield and

rate constant obtained in the Method B experiments were recommended for the development of PADs for this material.

UN 1741, Boron Trichloride, BCl₃ (New in 2006)

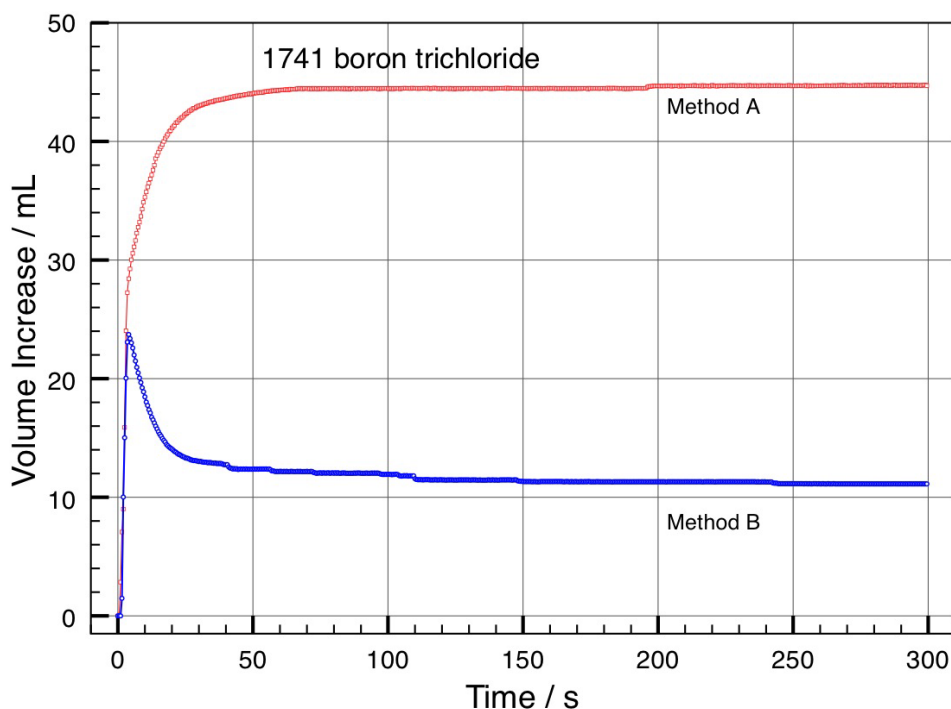
This material is gaseous at room conditions, but it was easily cooled below its boiling point of 12.5°C and handled as a liquid. The reaction



was taken as a source of HCl(g). In Method A, 1.50 mmol (27.0 μL = 27.0 mg) of water was added to 87 μL of the compound. This was 1.00 mmol of the compound on the basis of the density and purity listed in Table D.1. In Method B, 1.00 mmol was added to 7.50 mmol (135 μL = 135 mg) of water. The theoretical yield of HCl in both cases was 3.00 mmol, which had a volume of 72.2 mL at the reference conditions (20.0°C and 1 atm).

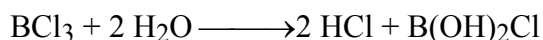
Observations: When Method A was used, a white solid formed that stopped the motion of the stirring bar within 60 s, approximately when the evolution of gas concluded. When Method B was used, considerable amount of white solid formed, but the stirring bar was not stopped.

Results: The Method A yield curve contains 600 points, obtained by averaging the results of five runs in which *P*, *V*, and *T* versus *t* data were recorded at equal intervals for 600 s. The Method B curve contains 600 points, obtained by averaging the results of five runs in which data were recorded at equal intervals for 300 s.



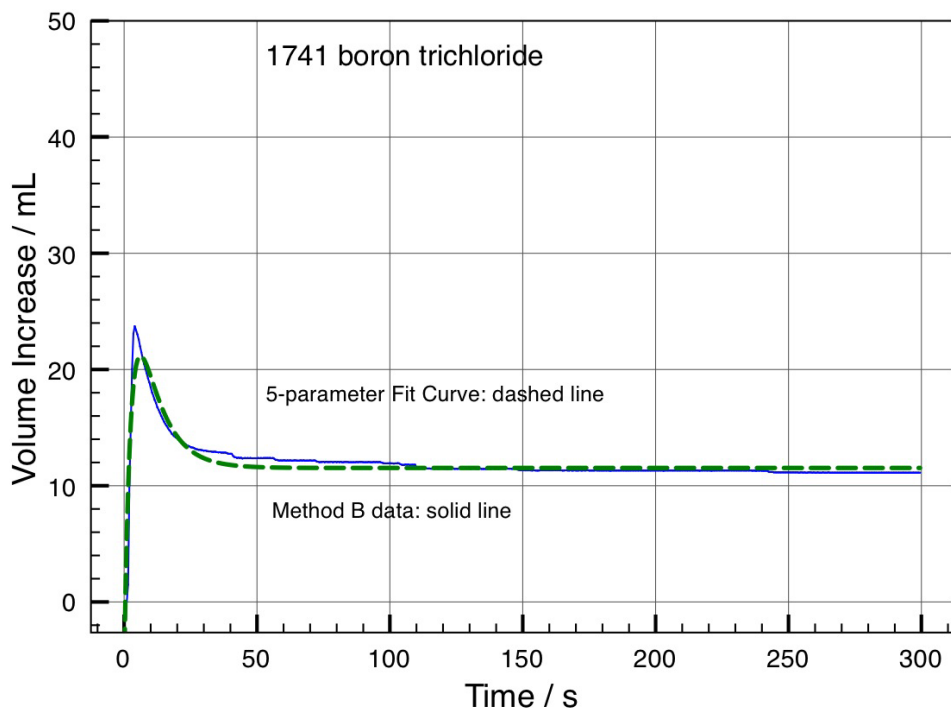
Discussion: These were the first experiments of this type on this compound. The evolved gas might have contained unreacted $\text{BCl}_3(g)$ from boiling of the BCl_3 of the (l) . Although the quick formation of quantities of solid by-product indicated that much $\text{BCl}_3(l)$ reacted right away rather than boiling first, some $\text{BCl}_3(g)$ might yet have formed. If so, its presence was presumably temporary and so did not affect the final fractional yield of HCl . The presence of $\text{BCl}_3(g)$ would certainly affect the rate of formation of HCl in some way. In the absence of information on this point, it was assumed that the evolved gas was exclusively $\text{HCl}(g)$.

The fractional yield, first-order rate constant, and induction time obtained from fitting Equation D.1 to the Method A yield curve appear in Table C.1. Nearly two-thirds of the theoretical amount of $\text{HCl}(g)$ evolved in less than a minute when Method A was used. The reaction under Method A conditions might be better represented as



in order to fit the observed stoichiometry.

The quick maximum in the Method B yield curve might have come from the evolution of $\text{BCl}_3(g)$ or the dissolution of $\text{HCl}(g)$ or from some combination of the two. It meant that the whole of the curve could not be fitted to Equation D.1. The rising portion of the Method B curve (the first 14 points, which were collected during the first 6.5 s of the run) was fitted, but only crudely (r.m.s.d. = 3.47 mL). The fractional yield β and rate constant λ_0 based on this crude fit were 0.40 and 19.5 min^{-1} . The whole of the Method B yield curve was more successfully fitted (r.m.s.d. = 0.723 mL) to Equation D.2. This fit appears as the dashed line in the following graph:

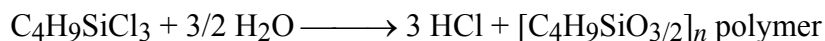


The values of the parameters in Equation D.2 that define this line were $a = 28.5$ mL, $b = 46.3$ mL, $c = 11.5$ mL, $\lambda_0 = 7.04$ min⁻¹, and $\lambda_1 = 23.3$ min⁻¹. The fractional yield β of HCl(*g*) and first-order rate constant λ_0 computed from these parameters were 0.55 and 7.04 min⁻¹. These values appear under the Method B heading in Table C.1. They differed somewhat from $\beta = 0.46$ and $\lambda_0 = 5.04$ min⁻¹, which had been obtained from a preliminary analysis of the data and supersede those values.

The yield curves for this compound resemble the curves obtained for the related compound boron tribromide (UN 2692). The method of analysis of the kinetic data that succeeded for this compound also succeeded for boron tribromide.

UN 1747, Butyltrichlorosilane, C₄H₉SiCl₃ (Repeat)

The reaction

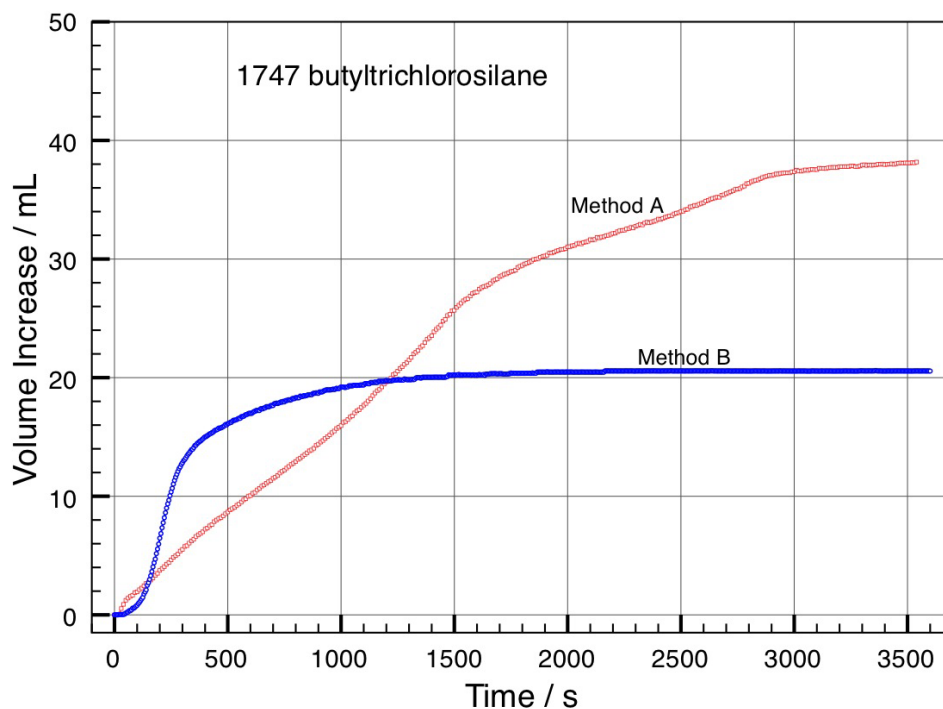


was taken as a source of HCl(*g*). In Method A, 1.50 mmol (27.0 μ L, 27.0 mg) of water was added to 165 μ L of the compound, a liquid. This was 1.00 mL on the basis of the density and purity listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol (135 μ L, 135 mg) of water. The theoretical yield of HCl(*g*) was 3.00 mmol, which had a volume (assuming ideal-gas behavior) of 72.2 mL at 20.0°C and 1 atm.

Observations: In all experiments, a very viscous liquid by-product formed. This material slowed the rate of stirring by interfering with the motion of the stirring bar. The effect was noticeable right away when both Method A and Method B were used.

Results: The Method A yield curve consists of 355 points that were obtained by averaging the results of three runs in which P , V , and T versus t data were recorded at equal intervals for 3,540 s. The Method B curve consists of 721 points obtained by averaging the results of three runs in which data were recorded at equal intervals for 3,600 s.

Discussion: The fractional yields, first-order rate constants, and induction times computed from fitting Equation D.1 to the two yield curves appear in Table C.1. The Method A yield curve had a considerable amount of unexpected structure. Its slope *increased* at about 1,250 s, which was when ΔV equaled 24 mL, the volume of 1 mmol of gas. A greater-than-expected decrease in rate at 1,650 s followed. This decrease was followed by a slow-down and speed-up between 2,300 and 2,800 s. The first of these peculiarities might have been caused by a change in the mechanism of the reaction after the first mole of Cl was hydrolyzed away from the chlorosilane. A similar structure appeared in the Method A yield curves of 8 of the other 15 trichlorosilanes that were studied. The effect might also have resulted, in whole or part, from the reduction of the stirring rate caused by the viscous by-product of the reaction. The sigmoidal character of the curve, whatever its origin, adversely affected the goodness of fit of Equation D.1 to the data. It was possible to fit the shape of the Method A yield curve more closely by using more elaborate kinetic models, but doing so did not give more useful (i.e., interpretable) results.

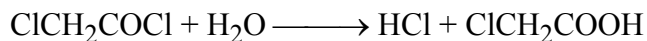


Equation D.1 was fit to the Method B data with an acceptably small r.m.s.d.. As was the case for most of the other chlorosilanes, the hydrolysis was faster with Method B than with Method A, but the yield of $\text{HCl}(g)$ was less.

The fractional yield and rate constant from the Method B experiments are recommended for developing PADs for this compound. They were not available in time to use in preparing the ERG2008, and the estimates from the 2003 experiments were used instead.

UN 1752, Chloroacetyl Chloride, ClCH_2COCl (Repeat)

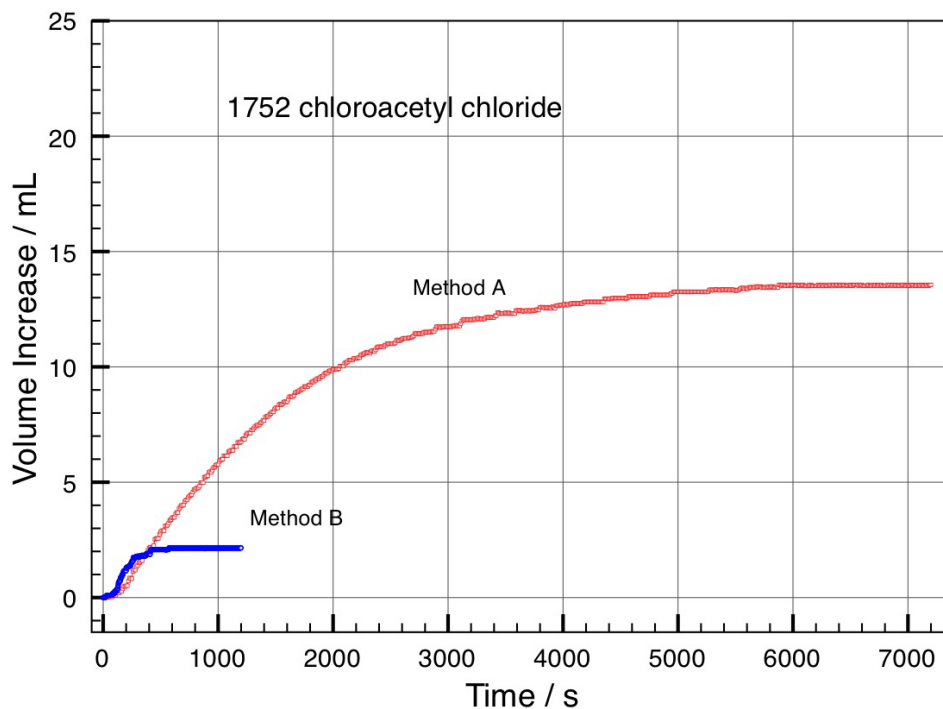
The reaction



was taken as the source of $\text{HCl}(g)$. In Method A, 1.00 mmol ($18.0 \mu\text{L} = 18.0 \text{ mg}$) of water was added to $81 \mu\text{L}$ of the compound, a liquid. This was 1.00 mmol based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol ($90.0 \mu\text{L} = 90.0 \text{ mg}$) of water. The theoretical yield of $\text{HCl}(g)$ was 1.00 mmol, which had a volume (assuming ideal-gas behavior) of 24.1 mL at the reference conditions (20.0°C and 1 atm).

Observations: The reaction took a couple of minutes to start when Method A was used. It took a briefer but still noticeable amount of time when Method B was used. No precipitates formed during any of the runs.

Results: The Method A yield curve contains 721 points, obtained by averaging the results of three runs in which P , V , and T versus t data were recorded at equal intervals for 7,200 s. The Method B curve contains 1,200 points, obtained by averaging the results of three runs in which data were recorded at equal intervals for 1,199 s.



Discussion: The fractional yields, first-order rate constants, and induction times computed from the fits of Equation D.1 to the two yield curves appear in Table C.1.

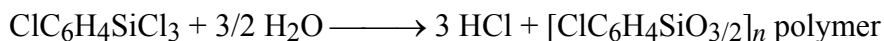
The by-product of the reaction was chloroacetic acid. This substance is a solid at room temperature that is freely soluble in water. The lack of a precipitate in the experiments was consistent with this fact.

The reaction had a brief induction time when Method A was used, but no induction time when Method B was used. It was significantly slower than the similar reaction of the related compound acetyl chloride (UN 1717), and the yield of gas was less.

The values of the fractional yield β and the rate constant λ_0 obtained from the Method B experiments are recommended for the development of PADs for this material. They were not available in time for use in preparing the ERG2008. The values derived from the 2003 experiments were used instead.

UN 1753, Chlorophenyltrichlorosilane, $\text{ClC}_6\text{H}_4\text{SiCl}_3$ (New in 2006)

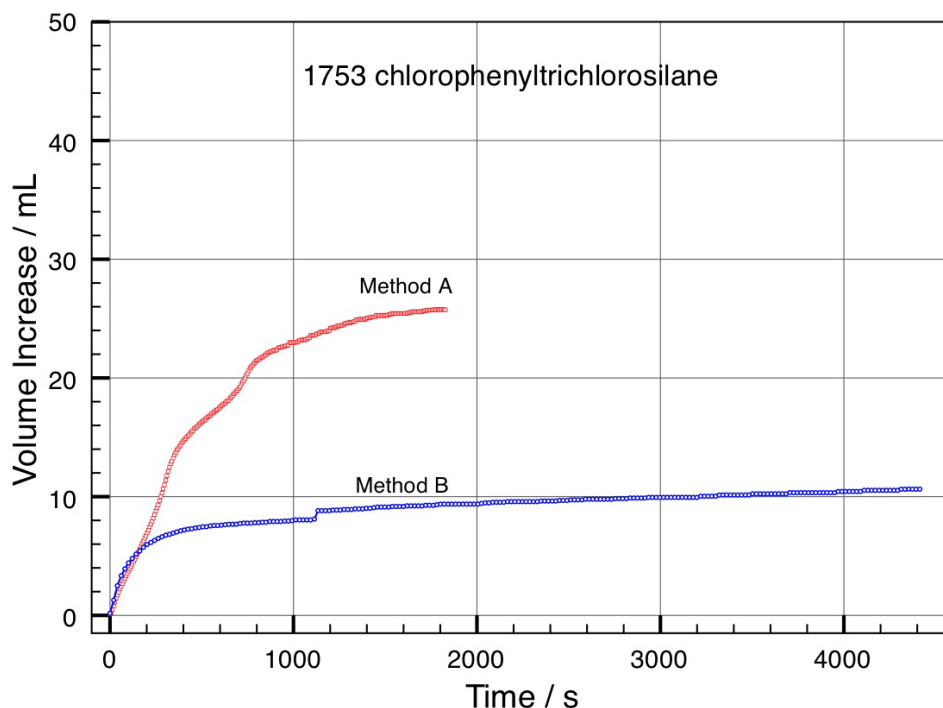
The reaction



was taken as the source of $\text{HCl}(g)$. In Method A, 1.50 mmol ($27.0 \mu\text{L} = 27.0 \text{ mg}$) of water was added to $179 \mu\text{L}$ of the compound, a liquid. This amount of the compound was 1.00 mmol on the basis of the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol of water. The theoretical yield of $\text{HCl}(g)$ in each case was 3.00 mmol, which is 72.2 mL at 20.0°C and 1 atm.

Observations: Under Method A, a white solid residue formed slowly. The stirring bar continued to spin at its usual speed on top of it. Under Method B, a white solid precipitate formed rapidly and stopped the stirring bar, usually within 120 s after mixing.

Results: The Method A yield curve consists of 272 points obtained by averaging the results of three runs in which P , V , and T versus t data were recorded at equal intervals for 1,829 s. The Method B curve consists of 319 points obtained by averaging the results of three runs in which data were recorded at equal intervals for 1,134, 3,017, and 4,414 s.



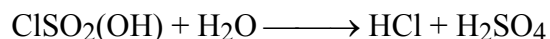
Discussion: These were the first experiments of this type on this compound. The fractional yields, first-order rate constants, and induction times computed from fitting Equation D.1 to the two yield curves appear in Table C.1. Despite the fluctuations in rate between 400 and 900 s in the Method A curve, the fit to the simple first-order kinetics

(Equation D.1) was acceptable (r.m.s.d. = 0.436 mL). Similar slow-downs and speed-ups were found in the Method A yield curves of 7 of the 15 other trichlorosilanes discussed in this work.

The jump in the Method B yield curve at 1,134 s was caused by the termination of one of the experimental runs. The average final yield of gas in the Method B experiments on this substance was among the lowest among the 25 chlorosilanes reported on here. The solid by-product of the reaction, which stopped the stirring bar in the Method B experiments, might have sequestered some HCl and so led to this result. Nevertheless, the use of the fractional yield β and rate constant λ_0 computed from the results of the Method B runs was recommended for the estimation of PADs for this compound.

UN 1754, Chlorosulfonic Acid, HSO₃Cl (Repeat)

The reaction



was taken to represent the evolution of HCl(g). For Method A, 1.00 mmol of water was added to 67 μL of the compound, a liquid. This was 1.00 mmol of the compound based on the purity, molar mass and density listed in Table D.1. For Method B, 1.00 mmol of compound was added to 5.00 mmol of water. The theoretical yield of HCl(g) was 1.00 mmol, which corresponded to 24.1 mL at 20°C and 1 atm pressure.

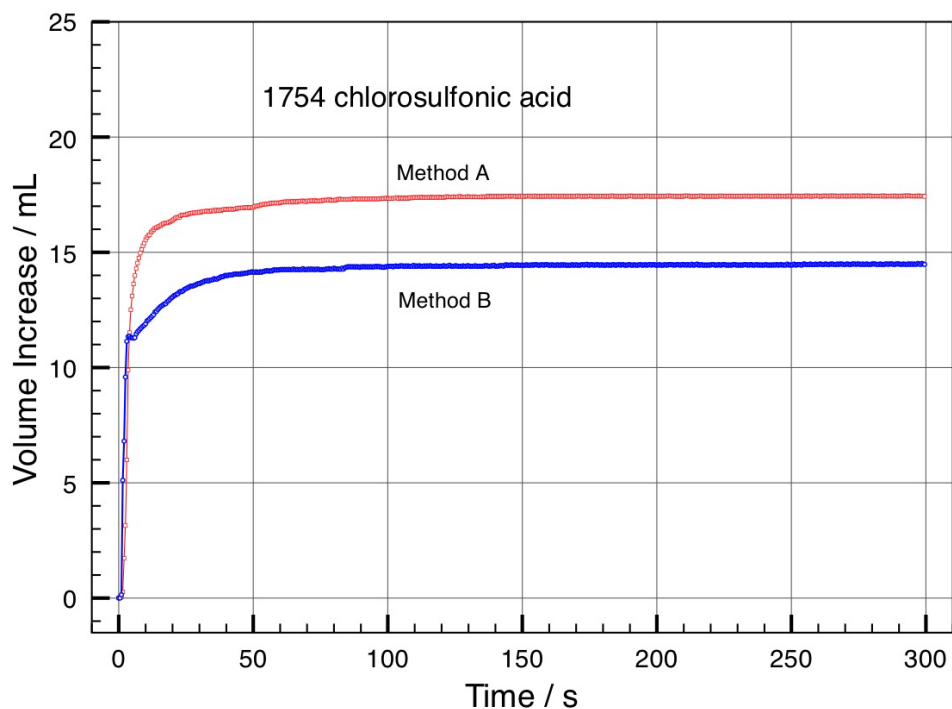
Observations: No insoluble by-products formed in any of the experiments.

Results: The Method A yield curve consists of 600 points that were obtained by averaging the results of five runs in which P , V , and T versus t data were recorded at equal intervals for 299.5 s. The Method B curve consists of 600 points that were obtained by averaging the results of five runs in which data were recorded at equal intervals for 299.5 s.

Discussion: The fractional yields, rate constants, and induction times computed from fitting Equation D.1 to the two yield curves appear in Table C.1.

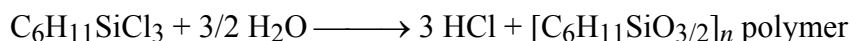
Hydrolysis proceeded at essentially the same rate when the two methods were used, but there was a smaller yield with Method B because of dissolution of HCl(g) in the excess water. The presence of the strongly acidic by-product H₂SO₄ in the reaction system lowered the solubility of HCl in the reaction mixture and so raised the yield of HCl(g) in the Method B experiments. In a real spill, the by-product H₂SO₄ would be diluted, and the yield of HCl(g) would be less.

The fractional yield and rate constant from the Method B experiments are recommended for developing PADs for this compound. They were not available in time to use in preparing the ERG2008, and the estimates obtained from the 2003 experiments were used instead.



UN 1763, Cyclohexyltrichlorosilane, $C_6H_{11}SiCl_3$ (Repeat)

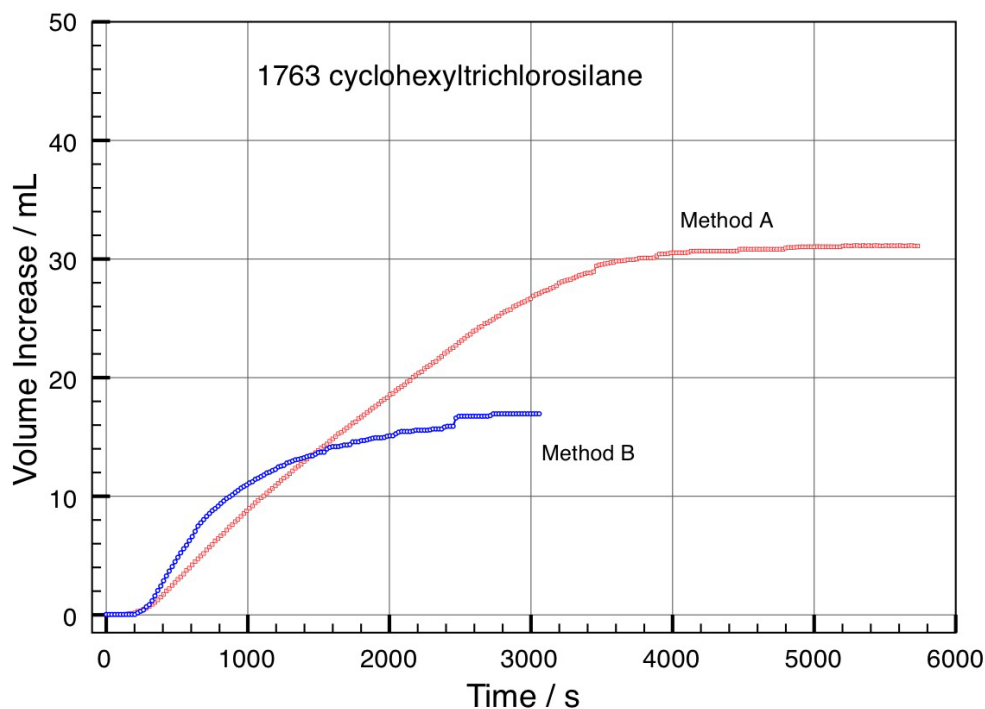
The reaction



was taken as the source of $HCl(g)$. In Method A, 1.50 mmol ($27.0 \mu L = 27.0 \text{ mg}$) of water was added to $176 \mu L$ of the compound, a liquid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol of water. The theoretical yield of $HCl(g)$ was 3.00 mmol, which corresponded to 72.2 mL of gas at the reference conditions ($20^\circ C$ and 1 atm pressure).

Observations: The reaction slowly formed a white solid in all experiments, irrespective of the method that was used. This solid did not noticeably slow the motion of the stirring bar. The production of gas did not start immediately when either method was used.

Results: The Method A yield curve contains 284 points. They were obtained by averaging the results of three runs in which data were recorded at nearly equal intervals for 5,731 s. A fourth run was rejected because yields were much lower than they were in the other three. The Method B yield curve contains 152 points, obtained as the average of three runs, two in which data were recorded at 10-s intervals for 3,058 s and one in which data were recorded at 10-s intervals for 2,450 s.



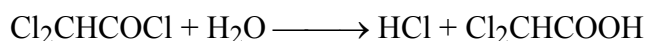
Discussion: The jump in the Method B yield curve at 2,450 s was caused by the early termination of one of the kinetic runs. The fractional yields, first-order rate constants, and induction times computed from fitting Equation D.1 to the yield curves appear in Table C.1. The Method A yield curve leveled off suddenly after about 3,600 s to a final ΔV between 30 and 31 mL. Calculations based on the parameters obtained from the least-square fit (see Section 2.3) indicate a final yield of 36.7 mL of gas. This final ΔV took the whole trend of the data set into account and so was preferred to the apparent ΔV . The final ΔV (after 7,200 s) in the 2003 experiment using Method A was 31.0 mL. The system in 2003 might still have been slowly evolving gas when the kinetic run was terminated.

The quality of the fit of Equation D.1 to the Method B yield curve was rather poor (r.m.s.d. = 1.25 mL). Nevertheless, the fractional yield and rate constant obtained in the Method B experiments were recommended for the development of PADs for this compound.

The induction time required for reaction is particularly evident in these yield curves.

UN 1765, Dichloroacetyl Chloride, Cl_2CHCOCl (New in 2006)

The reaction

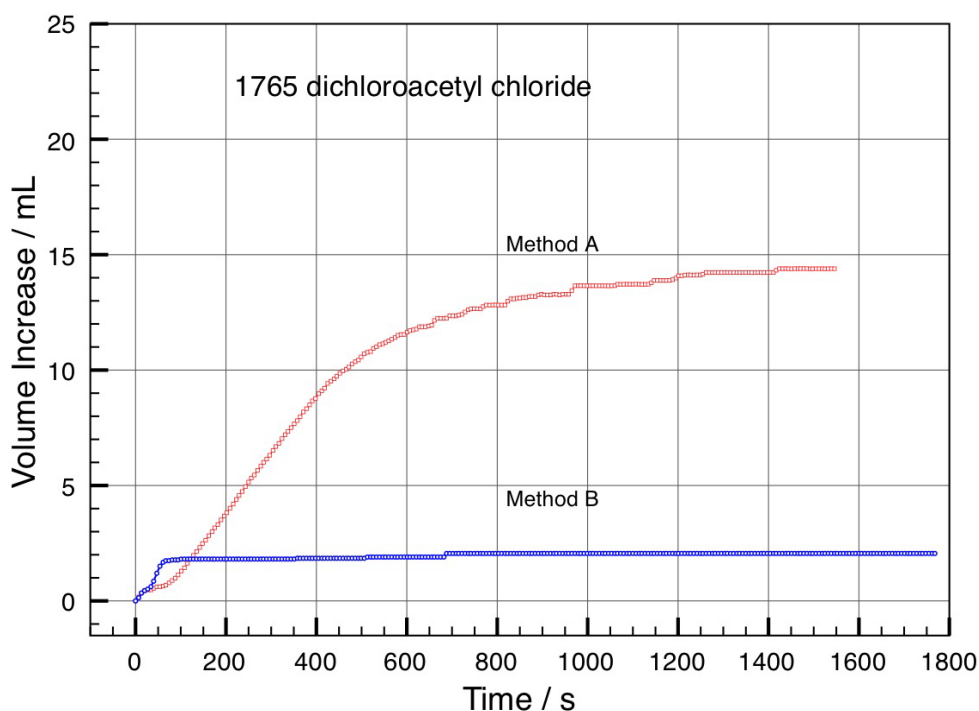


was taken to represent the evolution of $\text{HCl}(g)$ because the two Cl atoms bonded to the C atom are not hydrolyzable. In Method A, 1.00 mmol of water was added to 96 μL of the compound, a liquid. This was 1.00 mmol of the compound based on the purity, molar mass, and density listed

in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol of water. The theoretical yield of HCl(g) was 1.00 mmol, which corresponded to 24.06 mL at 20°C and 1 atm pressure.

Observations: No insoluble solids or liquids formed with either Method A or Method B. The rate of rotation of the stirring bar stayed constant. Yields were much smaller when Method B was used than when Method A was used.

Results: The Method A yield curve contains 230 points, obtained by averaging the results of three runs in which P , V , and T versus t data were recorded at equal intervals for 1,546 s. The Method B curve contains 263 points obtained as the average of three runs in which volumes were recorded at approximately equal intervals for 1,768 s.



Discussion: These were the first experiments of this type on this compound. The jumps in the curves at 900 s (Method A) and 700 s (Method B) occurred because an experimental run was terminated early. The fractional yields, first-order rate constants, and induction times computed from the fits of Equation D.1 to the yield curves appear in Table C.1. As was the case for other acid chlorides, the yield of gas was less when Method B was used than when Method A was used because some of the HCl dissolved in the excess water that is used in Method B.

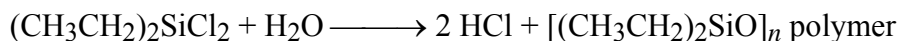
The by-product of the reaction was dichloroacetic acid, a water-miscible liquid. The lack of appearance of any by-products was consistent with the formation of this compound.

The fractional yield and rate constant obtained in the Method B experiments were recommended for the development of PADs for this compound.

Considerable similarity exists between the yield curves for this compound and those for the related compounds chloroacetyl chloride (UN 1752) and propionyl chloride (UN 1815).

UN 1767, Diethyldichlorosilane, (C₂H₅)₂SiCl₂ (Repeat)

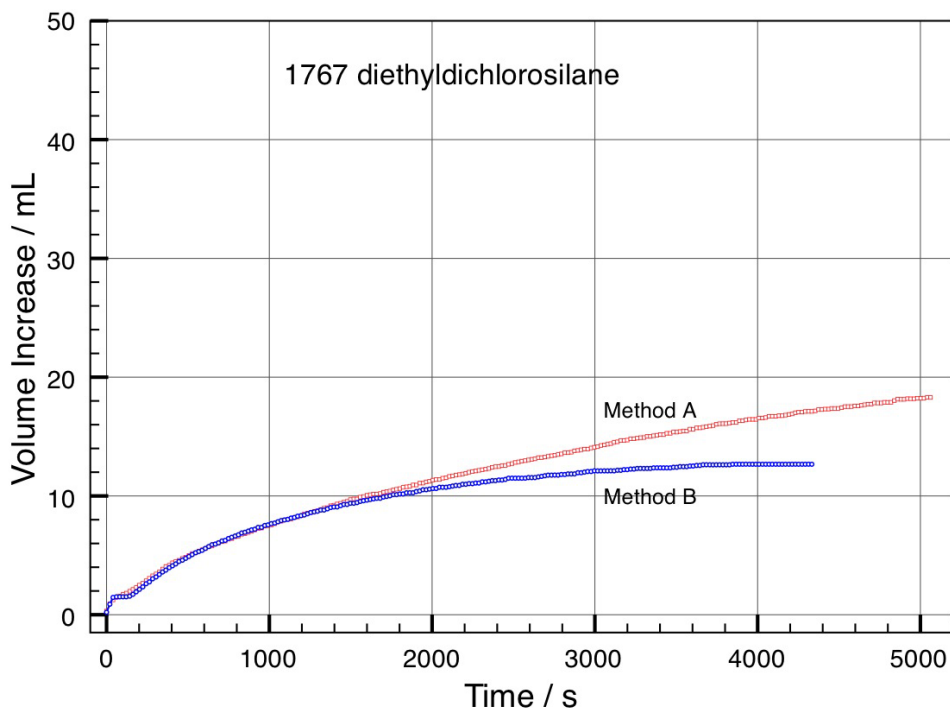
The reaction



was taken as the source of HCl(g). In Method A, 1.00 mmol of water was added to 154 μL of the compound, a liquid. This was 1.00 mmol of the compound based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol of water. The theoretical yield of HCl(g) was 2.00 mmol, which corresponded to 48.1 mL at 20°C and 1 atm pressure.

Observations: The reaction formed a very viscous liquid by-product when both Method A and Method B were used. This material slowed down the rotation of the stirring bar but did not stop it.

Results: The Method A yield curve contains 251 points obtained by averaging the results of two experimental runs in which data were recorded at equal intervals for 5,062 s. The Method B curve contains 215 points obtained as the average of two experimental runs in which data were recorded at equal intervals over 4,333 s.



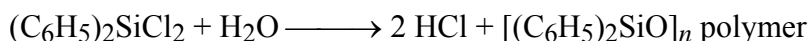
Discussion: The fractional yields and first-order rate constants computed from the parameters used to fit Equation D.1 to the yield curves appear in Table C.1. The final measured ΔV from using Method A was 18.51 mL, but the final ΔV computed from using the parameters from the least-squares fit of Equation D.1 to the data was 22.14 mL; thus, the evolution of gas evidently continued after the kinetic runs were terminated. When Method B was used, the ΔV settled to a constant value before the runs were terminated.

The rates of reaction for both methods of mixing were very nearly the same early in the experiments. Moreover, for both methods, the rate of reaction at the beginning was large but then fell considerably, and then rose it again before slowing down smoothly in the expected way. The viscous by-product probably caused this non-first-order behavior (which is obvious in the yield curves) through its effect on the stirring rate, if nothing else. Overall, the reaction was faster when Method B rather than Method A was used, but the yield was less.

The fractional yield and rate constant obtained in the Method B experiments were recommended for the development of PADs for this compound in ERG2008.

UN 1769, Diphenyldichlorosilane, $(C_6H_5)_2SiCl_2$ (Repeat)

The reaction



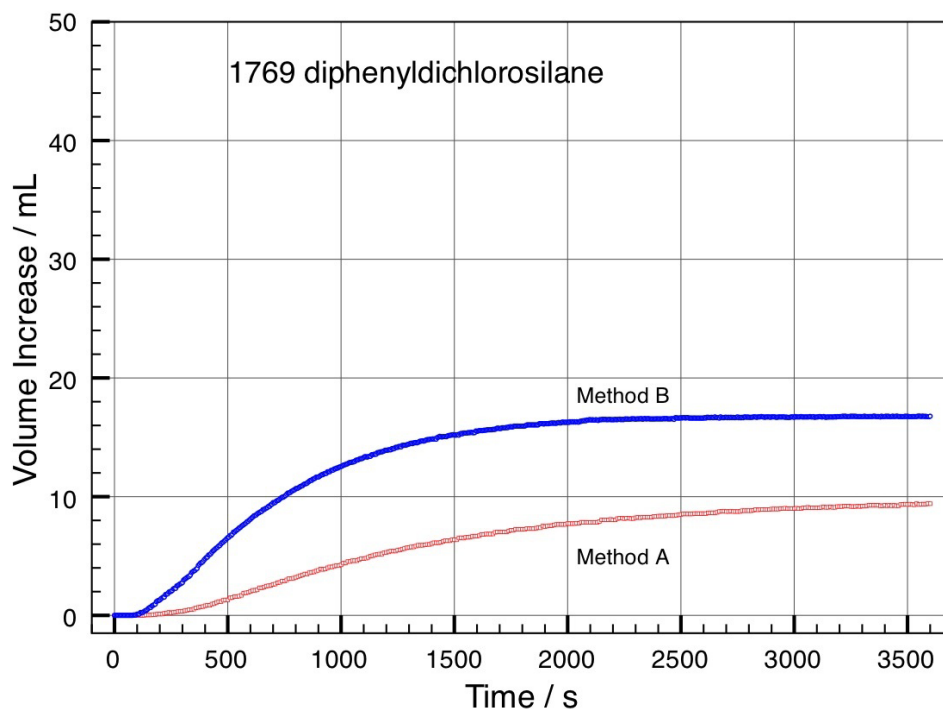
was taken as the source of $HCl(g)$. In Method A, 1.00 mmol of water was added to 217 μL of the compound, a liquid. This was 1.00 mmol of the compound based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol of water. The theoretical yield of $HCl(g)$ was 2.00 mmol, which corresponded to 48.1 mL at 20°C and 1 atm pressure.

Observations: For both methods, a solid by-product slowly formed, but this material did not noticeably slow the motion of the stirring bar. The stirring bar spun on top of the solid.

Results: The Method A curve contains 721 points obtained from observations recorded at equal intervals over 3,600 s. The values are averages of results from the three runs that were performed. The Method B curve consists of 361 observations from data recorded at equal intervals over 3,600 s. The values are averages of results from the three runs that were performed.

Discussion: The fractional yields, first-order rate constants, and induction periods computed from the fits of Equation D.1 to the two yield curves appear in Table C.1. Induction periods, which are prominent in the preceding graph, were not observed in 2003.

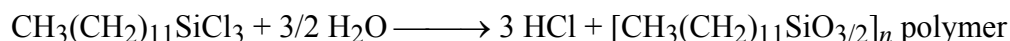
The yield of gas from using Method B exceeded the yield from using Method A; this result was a reversal of the findings for all of the other chlorosilanes, with one exception. The reason is unclear.



The values of the fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 are recommended for the development of PADs for this compound. They were not available in time for use in preparing ERG2008, so the values derived from the 2003 experiments were used instead.

UN 1771, Dodecyltrichlorosilane, $C_{12}H_{25}SiCl_3$ (Repeat)

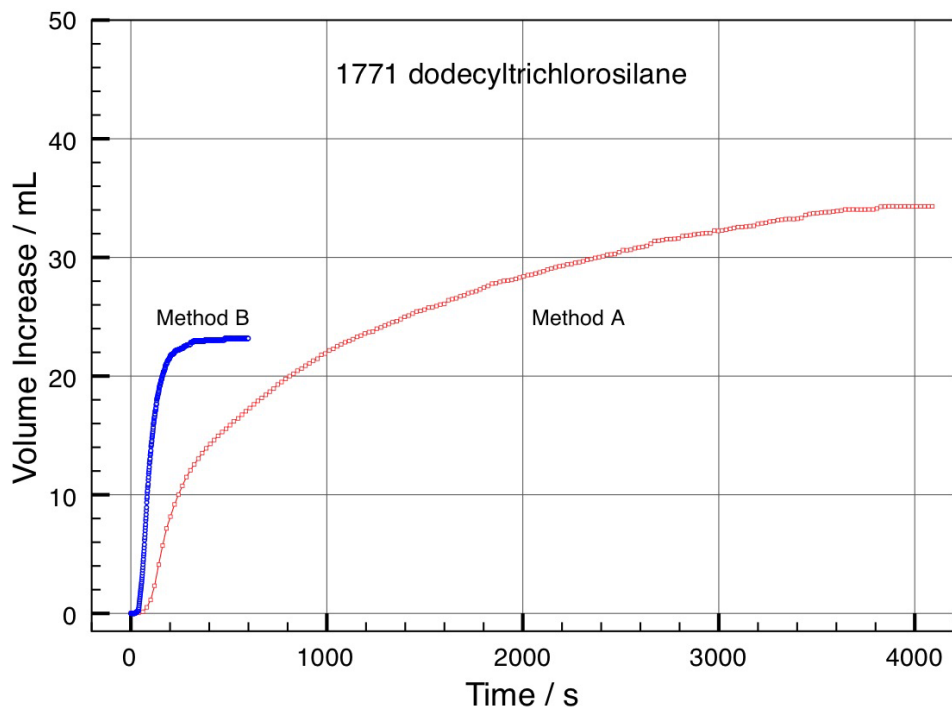
The reaction



was taken as the source of $HCl(g)$. In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 304 μL of the compound, a liquid. This was 1.00 mmol, as computed on the basis of the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol (135 μL = 135 mg) of water. The theoretical yield of HCl in both experiments was 3.00 mmol, which is 72.2 mL at 20.0°C and 1 atm.

Observations: The reaction did not start immediately for either Method A or Method B. When Method A was used, the reaction slowly formed a white solid by-product.

Results: The Method A yield curve contains 203 points obtained at equal intervals over 4,090 s. They are averages of the volumes observed in three runs. The Method B curve contains 600 points recorded at equal intervals over 599 s. The values are averages of the adjusted volumes from the three runs attempted.

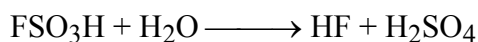


Discussion: The fractional yields, first-order rate constants, and induction times computed from fitting Equation D.1 to the two yield curves appear in Table C.1. The reaction had a brief induction period when Method B was used and no induction period when Method A was used. After this lagging start, the Method B reaction went much faster than did the Method A reaction. As it came to an end, the Method B reaction slowed abnormally quickly (compared to the prediction of first-order kinetics). The lower yield of $\text{HCl}(g)$ in Method B was caused by dissolution of $\text{HCl}(g)$ in the excess water.

The goodness of fit to the Method B curve (r.m.s.d. = 1.46 mL) was relatively poor; nevertheless, the fractional yield and rate constant from the Method B experiments were recommended for developing PADs for this compound in ERG2008.

UN 1777, Fluorosulfonic Acid, HSO_3F (New in 2006)

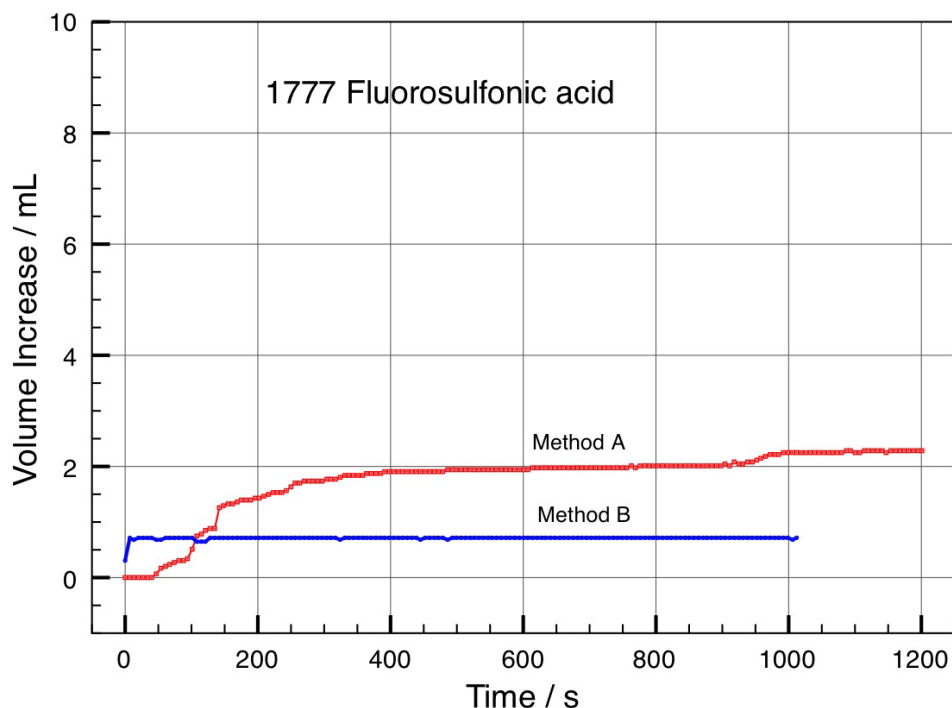
The reaction



was taken to produce $\text{HF}(g)$. In Method A, 1.00 mmol of water ($18.0 \mu\text{L} = 18.0 \text{ mg}$) was added to $54 \mu\text{L}$ of the compound, a liquid. This was 1.00 mmol of fluorosulfonic acid based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol ($90.0 \mu\text{L} = 90.0 \text{ mg}$) of water. The theoretical yield of HF in both reactions was 1.00 mmol, which was 24.1 mL at the reference conditions (20.0°C and 1 atm).

Observations: In all experiments for both methods, a small amount of white vapor formed rapidly. No precipitates formed in any of the experiments, and the motion of the stirring bar stayed at its original rate. Method A yielded more gas than did Method B, but both yields were small. No corrosion of the glass parts of the apparatus from HF was found; however, the apparatus was purged and emptied promptly after each run.

Results: The Method A yield curve contains 179 points obtained from observations recorded at equal intervals over 1,201 s. The points are averages of the volume changes observed in the three runs that were attempted. The Method B curve consists of 151 points from data recorded at equal intervals over 1,012 s. The values are averages of the volume changes observed in three runs.



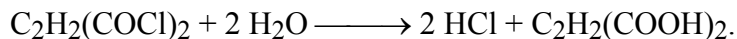
Discussion: These were the first experiments of this type on this compound. The fractional yield, first-order rate constant, and induction period computed from fitting Equation D.1 to the Method A yield curve appear in Table C.1.

No useful estimates of rate were possible from the Method B experiments because the yield curve had only one rising point. The system reached its final volume of 0.71 mL (3.0% of the theoretical) in 7 s.

The Method A results were recommended as a conservative basis for developing PADs for this material for ERG2008.

UN 1780, Fumaryl Chloride, $C_2H_2(COCl)_2$ (Repeat)

The compound is *trans*-2-butenedioyl dichloride. It is also called fumaryl dichloride and fumaroyl dichloride. The anticipated reaction was



In Method A, 2.00 mmol of water (36.0 μ L = 36.0 mg) was added to 114 μ L of the compound, a liquid. This was 1.00 mmol of compound based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 10.0 mmol (180 μ L = 180 mg) of water. The theoretical yield of HCl in both reactions is 1.00 mmol, which is 24.1 mL at the reference conditions (20.0°C and 1 atm).

Observations: No gas evolved; no precipitates formed.

Discussion: The experiment was performed by using a fresh supply of the compound because of concerns that the 2003 experiments (in which gas also did not evolve) were performed with material that was partially hydrolyzed.

The results confirmed that the compound was correctly omitted from the list of TIHWR compounds (compounds that yield toxic inhalation hazards by water reaction).

UN 1781, Hexadecyltrichlorosilane, $C_{16}H_{33}SiCl_3$ (New in 2006)

The reaction

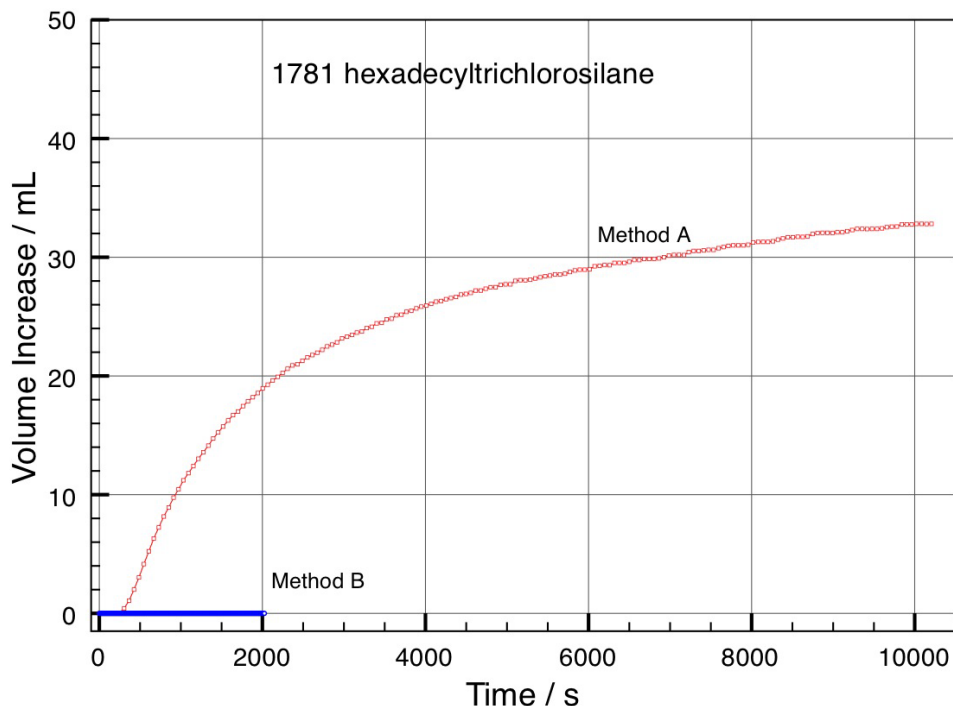


was taken to produce HCl(g). In Method A, 1.50 mmol of water (27.0 μ L = 27.0 mg) was added to 399 μ L of the compound, a liquid. This was 1.00 mmol based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol (135 μ L = 135 mg) of water. The theoretical yield of HCl in both reactions was 3.00 mmol, which was 72.2 mL at the reference conditions (20.0°C and 1 atm).

Observations: When Method A was used, a white precipitate slowly formed. It slowed the motion of the stirring bar and caused it to stop completely after approximately 5 min. This occurred in all three runs. Some time passed at the beginning of each run before the evolution of gas began. In the Method B trials, a white residue quickly formed, and the motion of stirring bar was stopped immediately. No gas evolved despite the evidence of a chemical reaction.

Results: The experimental points appear as closely spaced dots in the graphs. The Method A curve consists of 169 points, obtained by averaging the results of three runs in which *P*, *V*, and *T* versus *t* data were recorded at equal intervals for 10,206 s. The Method B curve

contains 300 points, obtained as the average of three runs in which P , V , and T versus t data were recorded at equal intervals for 2,025 s.



Discussion: These were the first experiments of this type on this compound. The fractional yield, first-order rate constant, and induction period computed from the fit of Equation D.1 to the Method A yield curve appear in Table C.1. The reaction required a substantial induction time before it started, and it was sluggish (the rate constant corresponds to a half-life of about 26 min.).

The formation of a solid in the Method B experiments meant that some kind of reaction occurred. No gas evolved, however. It is possible that the reaction occurred according to the equation, but the $\text{HCl}(g)$ was physically trapped in the solid polymeric by-product, and subsequently, after the motion of the stirring bar was stopped, productive contact between the test material and the water was greatly slowed. Or it is possible that impurities prevented or slowed the evolution of gas in some way. The available sample was only 90% pure; it had the lowest quoted purity of any material studied.

Under these circumstances, and knowing that the closely related compound octadecyltrichlorosilane (UN 1800) gave considerable volumes of gas when Method B was used, it was recommended that this compound be added on the list of TIHWR materials. The use of the fractional yield β and rate constant λ_0 obtained from the Method A runs was recommended as a conservative basis for estimating PADs for ERG2008.

UN 1784, Hexyltrichlorosilane, C₆H₁₃SiCl₃ (Repeat)

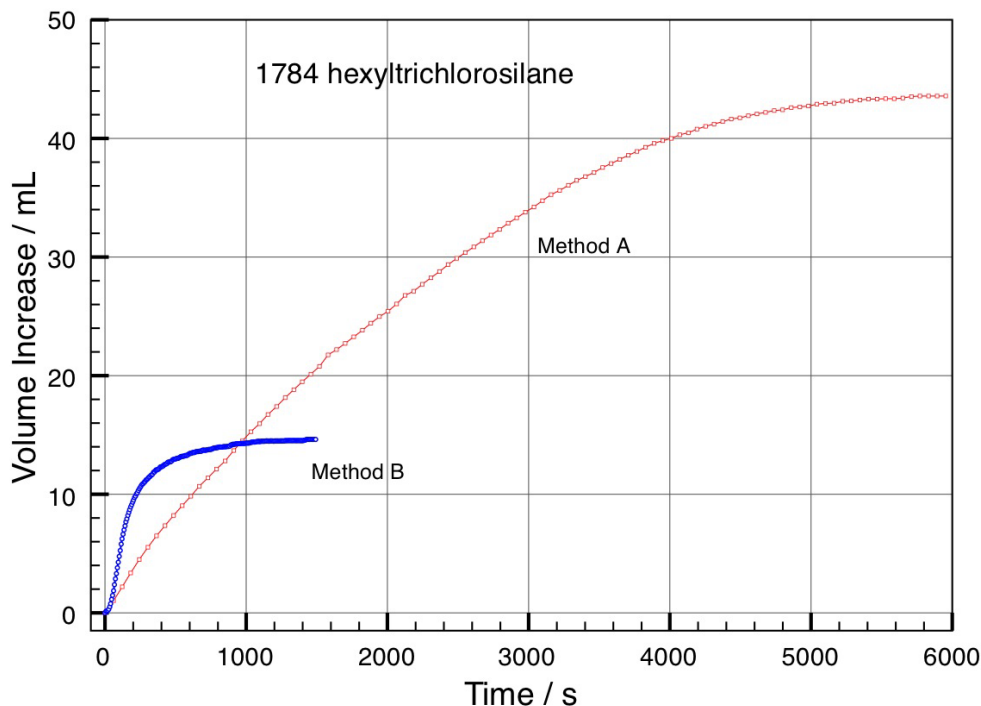
Reaction according to the equation



was taken to produce HCl(g). In Method A, 1.50 mmol of water (27.0 μL = 27.0 mg) was added to 199 μL of the compound, a liquid. This was 1.00 mmol on the basis of the density and purity listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol (135 μL = 135 mg) of water. The theoretical yield of HCl was 3.00 mmol, which had a volume of 72.2 mL at the reference conditions (20.0°C and 1 atm).

Observations: In Method A, the reaction slowly formed a solid polymeric siloxane that might have sequestered some water. In Method B, the reaction also slowly formed a solid polymeric siloxane.

Results: The Method A curve contains 99 points, obtained by averaging the results of three runs in which P , V , and T versus t data were recorded at equal intervals for 5,954 s. The Method B curve contains 222 points, obtained as the average of four runs in which data were recorded at equal intervals for 1,492 s.



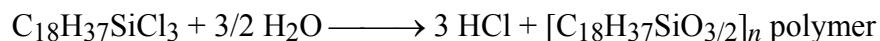
Discussion: The fractional yields, first-order rate constants, and induction periods computed from the fit of Equation D.1 to the two yield curves appear in Table C.1. The quality of the fit was good in both cases. The yield curves show that the reaction required some time to get started.

This chlorosilane is one of the 8 (out of 16 studied) in which the production of gas in the Method A experiment did not speed up at some point along the yield curve.

The use of the fractional yield β and rate constant λ_0 computed from the results of the Method A runs was recommended for estimating PADs for ERG2008.

UN 1800, Octadecyltrichlorosilane, $C_{18}H_{37}SiCl_3$ (Repeat)

Reaction according to the equation



was taken to produce $HCl(g)$. In Method A, 1.50 mmol of water ($27.0 \mu L = 27.0 \text{ mg}$) was added to $433 \mu L$ of the compound, a liquid. This was 0.988 mmol, based on the density, molar mass, and purity listed in Table D.1. In Method B, 0.988 mmol of the compound was added to 7.50 mmol ($135 \mu L = 135 \text{ mg}$) of water. The theoretical yield of HCl in reactions is 2.97 mmol or (assuming ideal-gas behavior) 71.32 mL at the reference conditions ($20.0^\circ C$ and 1 atm).

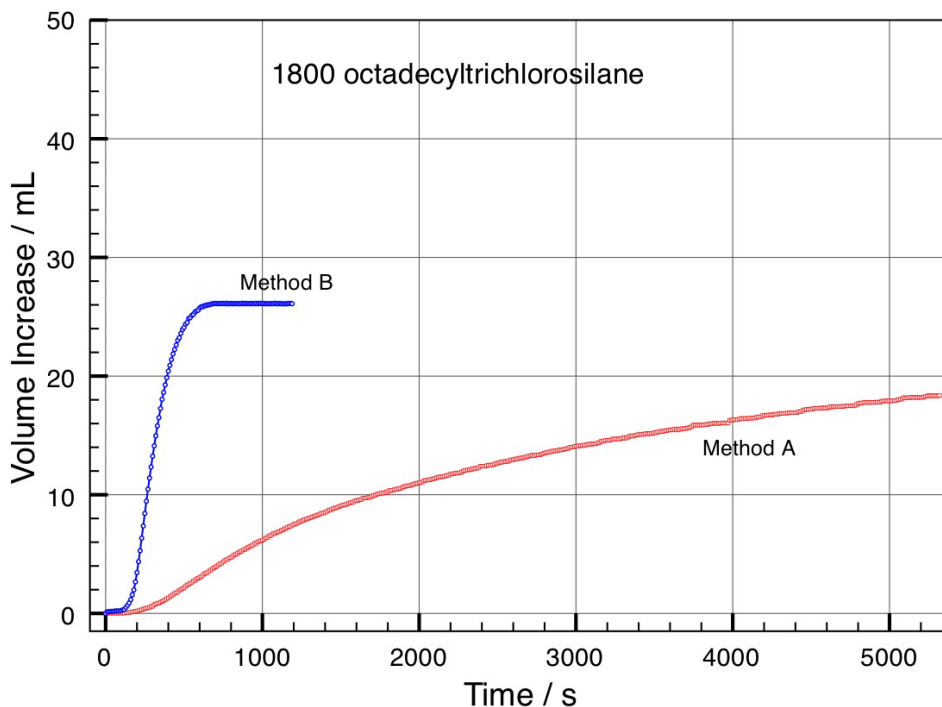
Observations: In all experiments, the evolution of gas required an induction period, and a solid by-product formed. The motion of the stirring bar was never noticeably affected by the presence of the solid.

Results: The Method A yield curve contains 533 points. They are the average of results from four runs in which data were collected at equal intervals over a period of 5,320 s. The Method B curve contains 120 points. They are the average of results from three runs in which data were collected at approximately equal intervals for 1,190 s.

Discussion: The fractional yields, first-order rate constants, and induction periods computed from fitting Equation D.1 to the two yield curves appear in Table C.1. The induction periods are evident in the flat segments at the starts of the yield curves. The fit to the Method B data was poor (r.m.s.d. = 2.55 mL). The low purity of the sample (90%) might have been the cause. Until an impurity was consumed, it might generate $HCl(g)$ faster or slower than would the substance itself.

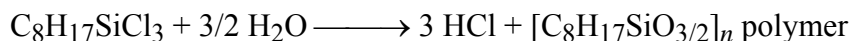
When the results from the fit of Equation D.1 to the Method A data were used to extrapolate the curve, the final ΔV was 20.7 mL. This amount significantly exceeded the highest observed ΔV . This result could be understood if all of the Method A runs were terminated before reaching a final plateau of volume. The fit curve for the Method B data gave a final ΔV of 28.5 mL when extrapolated. This amount similarly exceeded the highest observed ΔV .

The values of the fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 are recommended for developing the PADs for this material. They were not available in time for use in preparing ERG2008, so the values derived from the 2003 experiments were used instead.



UN 1801, Octyltrichlorosilane, $C_8H_{17}SiCl_3$ (Repeat)

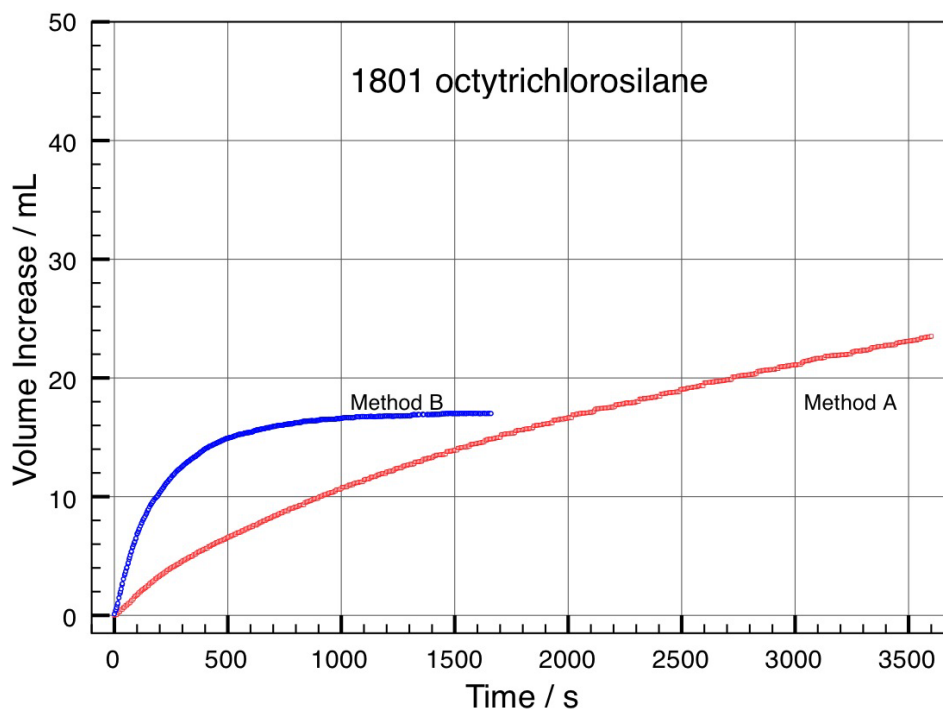
The reaction



was taken as the source of $HCl(g)$. In Method A, 1.50 mmol of water ($27.0 \mu L = 27.0 \text{ mg}$) of water was added to $231 \mu L$ of the compound, a liquid. This was 1.00 mmol of the compound, as computed using the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol ($135 \mu L = 135 \text{ mg}$) of water.

Observations: When Method A was used, a viscous liquid by-product formed slowly. When Method B was used, a solid polymer formed in the early stage of the reaction. The rate of stirring was slightly slowed by the presence of this solid.

Results: The Method A yield curve contains 721 points obtained at equal intervals over a period of 3,600 s. It represents the average of three runs. The Method B curve contains 469 points. It results from the average of six runs in which data were collected at approximately equal intervals for 1,660 s.



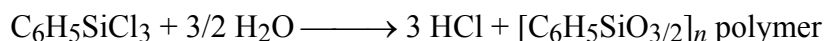
Discussion: The fractional yields and first-order rate constants computed from fitting Equation D.1 to the two yield curves appear in Table C.1. The quality of the fit was good for both sets of data.

The reaction started promptly (with no period of induction) when both methods were used. The Method A runs apparently were terminated before a constant-value plateau in the yield curve was reached. The results from the least-squares fit of the data to Equation D.1 were used to extrapolate the curve.

The values of the fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 were recommended for the developing PADs for this material.

UN 1804, Phenyltrichlorosilane, $C_6H_5SiCl_3$ (Repeat)

The reaction according to the equation

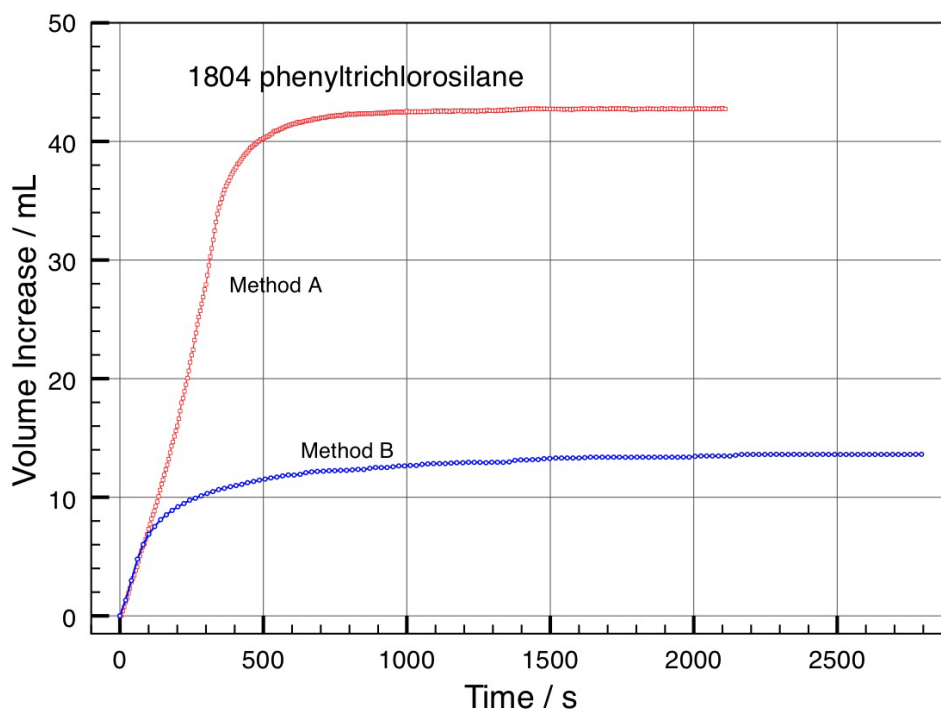


was taken as the source of $HCl(g)$. In Method A, 1.50 mmol of water ($27.0 \mu L = 27.0 \text{ mg}$) was added to $162 \mu L$ of the compound, a liquid. This was 1.00 mmol, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 7.50 mmol ($135 \mu L = 135 \text{ mg}$) of water. The theoretical yield of $HCl(g)$ in both reactions is 3.00 mmol, which occupies 72.2 mL at the reference conditions ($20^\circ C$ and 1 atm pressure).

Observations: The reaction formed a white, voluminous, solid by-product in all experiments. The buildup of this material slowed and, in some cases, stopped the motion of the stirring bar.

Results: Seven runs were performed by using Method A. Four runs in which the stirring bar was stopped by the buildup of the by-products of the reaction were discarded. These runs released smaller amounts of gas. The 421 data points plotted here are the average of three runs in which observations were made at approximately equal intervals of time for 2,110 s.

Five runs were performed by using Method B. Two runs in which the stirring bar was stopped by the buildup of the by-products of the reaction were discarded. The 139 data points in the plot are the average of three runs in which observations were made at approximately equal intervals of time for 2,794 s.



Discussion: The fractional yields and first-order rate constants computed by from the parameters obtained by fitting Equation D.1 to the two yield curves appear in Table C.1. The yield curves from the two methods are nearly superimposed during the first 100 s of the experiments. The rate constants obtained for the two methods were consequently almost equal.

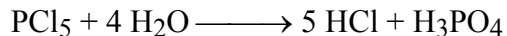
For both methods, the yield of $\text{HCl}(g)$ might have been lowered by sequestration of some reactant by the polymeric by-product.

The slope of the Method A curve increased slightly, starting at about 24 mL, before resuming its decrease. The behavior of 7 other trichlorosilanes (out of 16 studied) was similar.

The values of the fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 were recommended for developing PADs for this material for ERG2008.

UN 1806, Phosphorus Pentachloride, PCl_5 (Repeat)

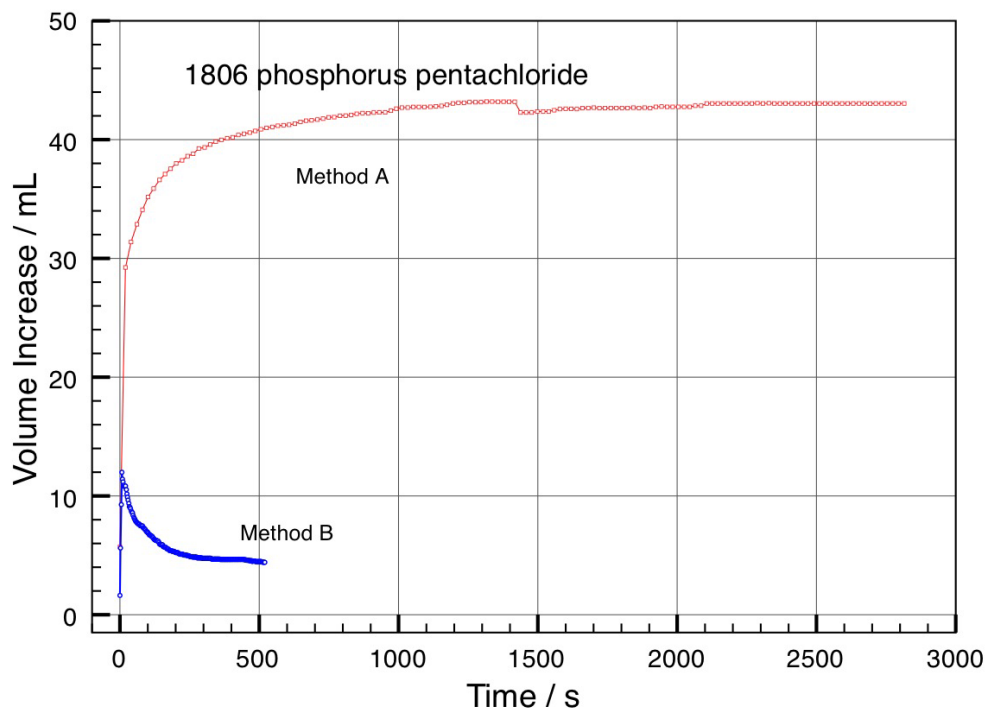
The reaction



was taken as the source of $\text{HCl}(g)$. In Method A, 4.00 mmol (72 μL = 72 mg) of water was added to 218 mg of the compound, a solid. This was 1.00 mmol of the compound, based on the purity and molar mass listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 20.0 mmol of water. The theoretical yield of $\text{HCl}(g)$ was 120.3 mL at 20°C and 1 atm pressure.

Observations: The reaction began instantly in all experiments. No insoluble solid or liquid by-products formed. When Method B was used, the visible signs of reaction subsided within the first 60 s.

Results: The yield curve for Method A has 129 points that were collected at approximately equal intervals over 2,815 s, The data were obtained as the average of results from two runs. The curve for Method B has 232 points taken at approximately equal intervals over 520 s.



Discussion: The jump at 1,400 s in the Method A yield curve was caused by early termination of one of the experimental runs. The fractional yield and first-order rate constant computed from fitting Equation D.1 to the Method A yield curve appear in Table C.1. More than one Cl atom reacted per PCl_5 molecule, but the reaction remained incomplete with respect to the theoretical yield of 5.0 mmol of $\text{HCl}(g)$ after 50 min.

No attempt was made to fit Equation D.1 to the Method B yield curve, for which it was obviously an unsuitable model. Equation D.2 was successfully fit. The parameters were as follows:

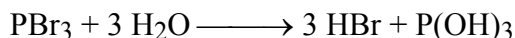
$$a = 7.44 \text{ mL}, b = -10.73 \text{ mL}, c = 4.57 \text{ mL}, \lambda_0 = 0.728 \text{ min}^{-1}, \lambda_1 = 21.1 \text{ min}^{-1}.$$

This fit was good (r.m.s.d. = 0.182 mL). The fractional yield β of $\text{HCl}(g)$ in the absence of dissolution and the first-order rate constant λ_0 for the production of $\text{HCl}(g)$ were estimated from these parameters, as discussed in Section D.2.3. These values appear under the Method B heading in Table C.1 and are recommended for developing PADs for this material.

During preliminary analysis of the Method B data, a fit of Equation D.1 to the first five points (the rising points) gave a fractional yield β and first-order rate constant λ_0 of 0.109 and 1.28 min^{-1} . These values were recommended for use in developing PADs for ERG2008. The somewhat different results cited here used the whole data set and supersede the preliminary results.

UN 1808, Phosphorus Tribromide, PBr_3 (Repeat)

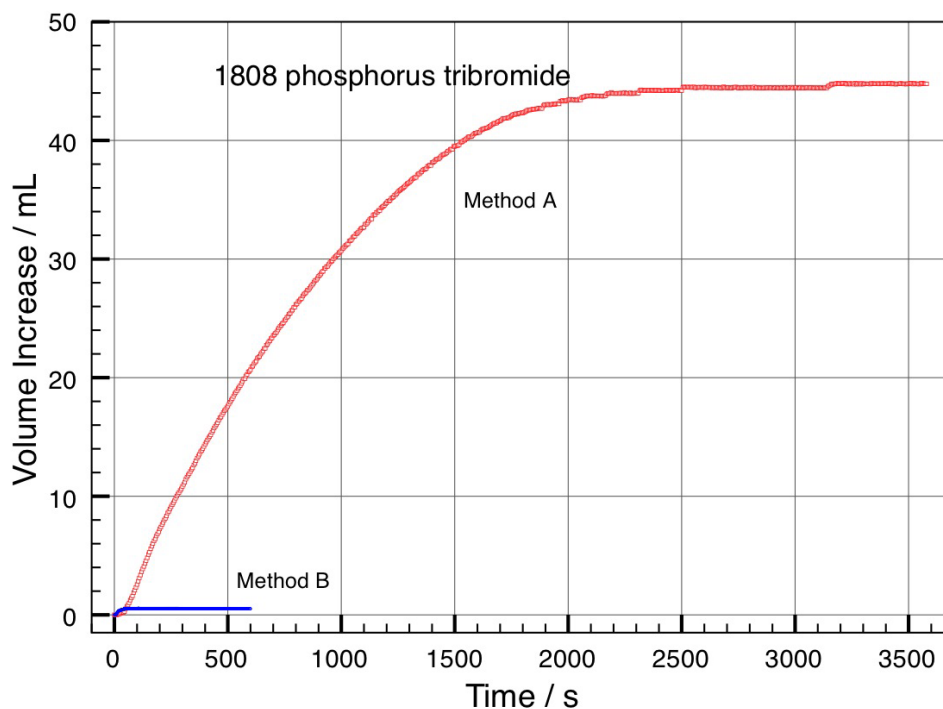
The reaction



was taken as the source of $\text{HBr}(g)$. In Method A, 3.00 mmol of water was added to 96 μL of the compound, a liquid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 15.0 mmol of water. The generation of the theoretical yield of 3.00 mmol of gas corresponded to an increase in volume of 72.2 mL at the reference conditions (20°C and 1 atm pressure).

Observations: No insoluble liquids or solids formed in any of the experiments. Very little gas evolved when Method B was used.

Results: The yield curve for Method A was obtained by averaging the results of three runs. It has 717 points that were taken at approximately equal intervals over 3,580 s. The curve for Method B also results from three runs. It has 1,200 points, obtained at approximately equal intervals over 599.5 s.

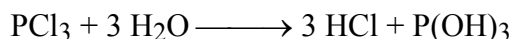


Discussion: The fractional yield and first-order rate constant computed from fitting Equation D.1 to the Method A yield curve appear in Table C.1. When Method A was used, the reaction began to generate $\text{HBr}(g)$ after about 1 min, and after an hour, close to two-thirds (65%) of the theoretical amount of $\text{HBr}(g)$ had been liberated. The final volume of gas (46.7 mL) was close to the final volume of gas in the same experiment in 2003.

When Method B was used, the volume of $\text{HBr}(g)$ never exceeded 0.56 mL. The rate and extent of dissolution of the HBr in the excess water were apparently so high that effectively no $\text{HBr}(g)$ was released. The same result was obtained in 2003. On the basis of these results, the prior recommendation to exclude PBr_3 as a TIHWR material was continued.

UN 1809, Phosphorus Trichloride, PCl_3 (Repeat)

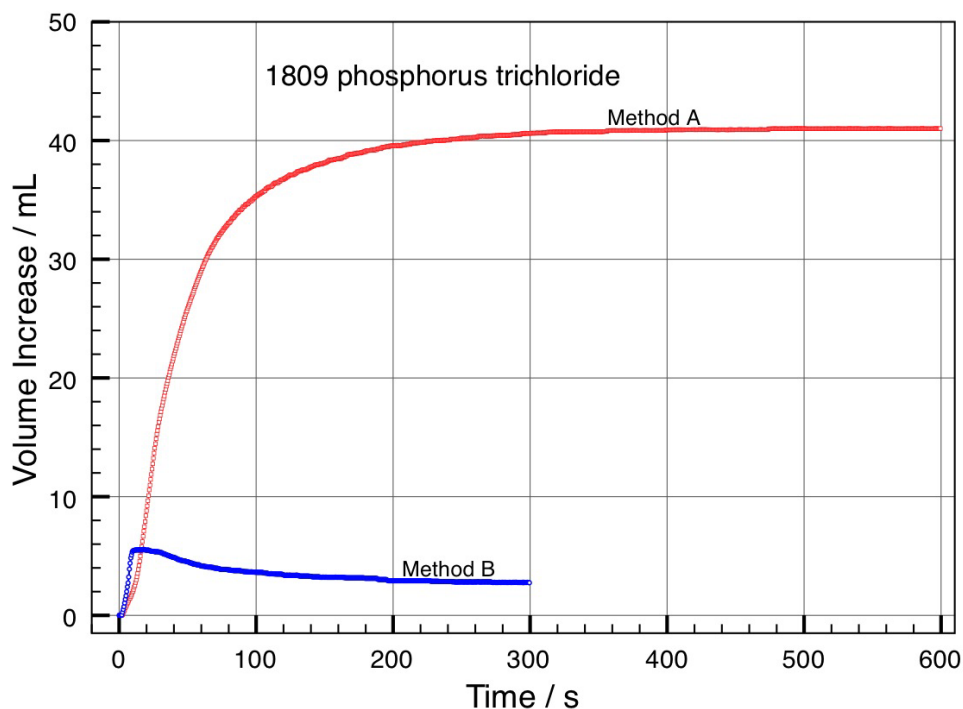
The reaction



was taken as a source of $\text{HCl}(g)$. In Method A, 3.00 mmol ($54.0 \mu\text{L} = 54.0 \text{ mg}$) of water was added to $89 \mu\text{L}$ of the compound, a liquid. This was 1.00 mmol of the compound based on the purity, molar mass, and density listed in Table D.1. In Method B, 15.0 mmol of water was added to 1.00 mmol of the compound.

Observations: When Method B was used, the volume of gas rose to a quick maximum and then fell.

Results: The yield curve for Method A is the average of five runs. It has 1,200 points that were taken at approximately equal intervals over a period of 1,200 s. The curve for Method B is also the average of five runs. It has 600 points taken at approximately equal intervals over 600 s.



Discussion: The fractional yield and first-order rate constant computed from fitting Equation D.1 to the Method A yield curve appear in Table C.1.

Much of the $\text{HCl}(g)$ that initially formed in the Method B experiments appeared to quickly dissolve in the excess water. For this reason, no attempt was made to fit Equation D.1 to the Method B yield curve. Equation D.2 was successfully fit (r.m.s.d. = 0.797 mL). The parameters were as follows:

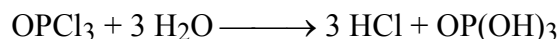
$$a = 31.15 \text{ mL}, b = -28.18 \text{ mL}, c = 0.53 \text{ mL}, \lambda_0 = 33.53 \text{ min}^{-1}, \lambda_1 = 43.30 \text{ min}^{-1} .$$

The fractional yield β of $\text{HCl}(g)$ in the absence of dissolution and the first-order rate constant λ_0 for the production of $\text{HCl}(g)$ were estimated from these parameters, as discussed in Section D.2.3. These values appear under the Method B heading in Table C.1 and are recommended for developing PADs for this material.

During preliminary analysis of the Method B data, a fit of Equation D.1 to the first 44 points (the rising points) gave a fractional yield β and first-order rate constant λ_0 of 0.084 and 8.28 min^{-1} . These values were recommended for use in developing PADs for ERG2008. The differing values for β and λ_0 in Table C.1 supersede the preliminary results.

UN 1810, Phosphorus Oxychloride, OPCl_3 (Repeat)

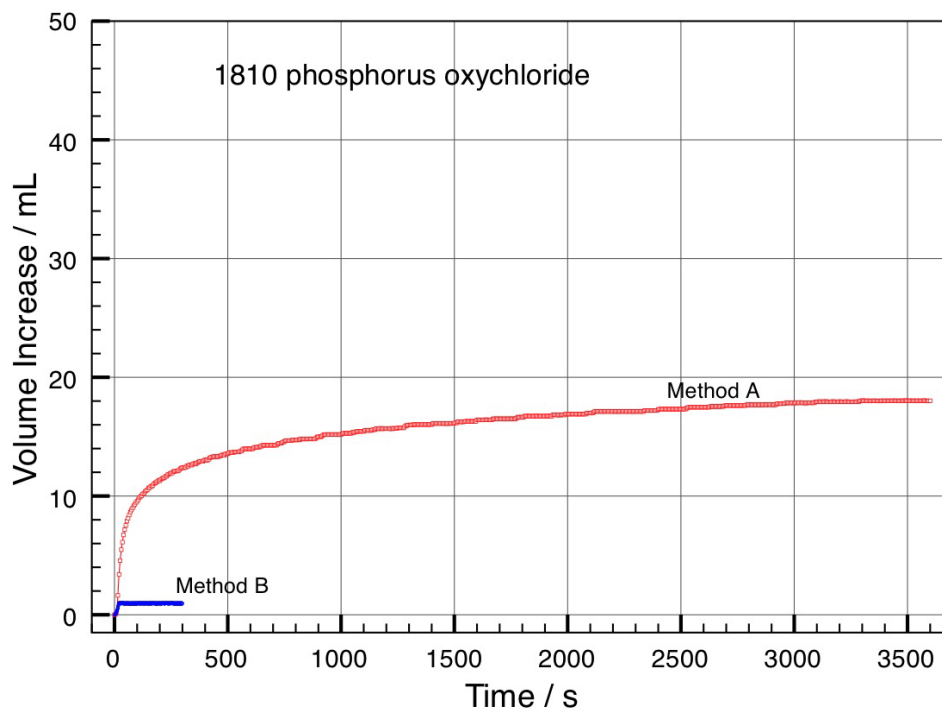
The reaction



was taken as the source of HCl. In Method A, 3.00 mmol of water was added to 92 μL of the compound. This was 1.00 mmol based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol was added to 15.0 mmol of water. The theoretical yield of $\text{HCl}(g)$ was 72.2 mL at the reference conditions (20°C and 1 atm pressure).

Observations: No insoluble liquids or solids formed in any of the experiments. Stirring continued at its initial rate throughout all of the runs.

Results: The Method A yield curve contains 721 points, obtained by averaging the results of five runs in which data were recorded at equal intervals for 3,600 s. The Method B curve contains 600 points obtained as the average of four runs in which volumes were recorded at equal intervals for 299.5 s. None of the experimental runs were terminated early.



Discussion: The fractional yield β , rate constant λ_0 , and induction time computed from the least-squares fits of the Method A yield curve to Equation D.1 appear in Table C.1. The yield of gas from using Method B was nearly zero. The fractional yield β , rate constant λ_0 , and induction time could not be computed.

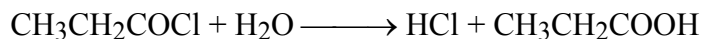
In the 2003 experiments, the volume of gas in the Method B experiment spiked to 13.6 mL in 20 s and then fell to 2.4 mL in the next 280 s. In these experiments, the volume rose

only very slightly and then stayed constant. Possibly the mixture was stirred faster in these experiments than in 2003 (the rate of stirring was not recorded in 2003). Faster stirring would increase the rate of dissolution of HCl.

The use of the β and λ_0 obtained by using Method A was recommended as a conservative basis for computing PADs for this compound.

UN 1815, Propionyl Chloride, C₃H₅COCl (New in 2006)

The reaction



was taken as a source of HCl(g). In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 87 μL of the compound, a liquid. This was 1.00 mmol of the compound based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (135 μL = 135 mg) of water. The theoretical yield of HCl(g) in both cases was 1.00 mmol, which is 24.1 mL at 20.0°C and 1 atm (the reference conditions).

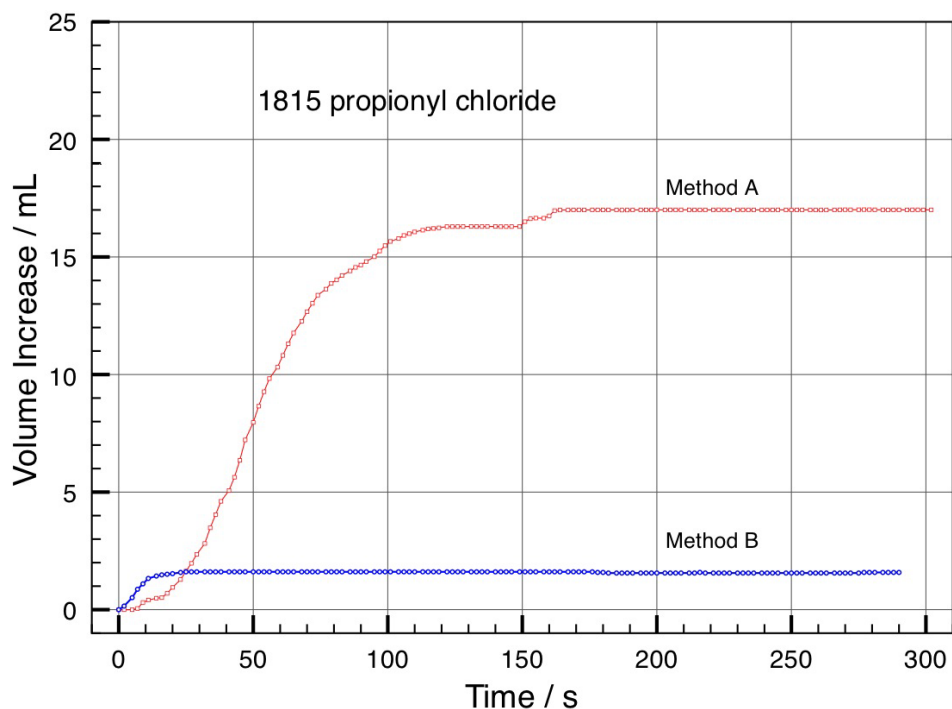
Observations: No solids formed when either Method A or Method B was used. The rate of rotation of the stirring bar stayed constant. Yields were much smaller when Method B was used than when Method A was used.

Results: The Method A yield curve contains 135 points. They were obtained by averaging the results of four runs in which data were recorded at equal intervals for 302 s. The Method B curve contains 130 points obtained as the average of three runs in which volumes were recorded at equal intervals for 290 s. None of the experimental runs was terminated early.

Discussion: These were the first experiments of this type on this compound. The fractional yields β , rate constants λ_0 , and induction times computed from the least-squares fits of the two yield curves to Equation D.1 appear in Table C.1.

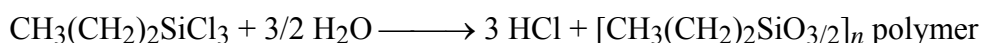
The absence of a precipitate was consistent with the formation of propionic acid, which is a water-soluble liquid, as the by-product. No explanation could be given for the jumps in volume between 150 and 165 s in the Method A curve.

The values for the fractional yield β and rate constant λ_0 that appear under the Method B heading in Table C.1 are recommended for developing PADs for this material. They were not available in time to prepare ERG2008, so the values derived from the 2003 experiments were used instead.



UN 1816, Propyltrichlorosilane, C₃H₇SiCl₃ (Repeat)

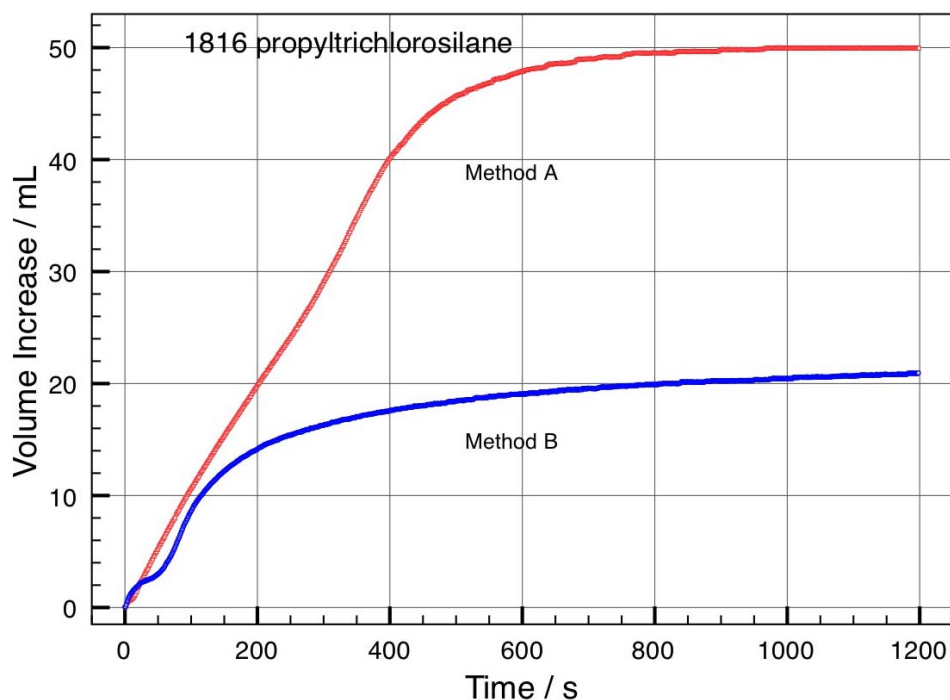
The reaction



was taken as a source of HCl(g). In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 151 μL of the compound. This was 1.00 mmol of the compound based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (135 μL = 135 mg) of water. The theoretical yield of HCl(g) in both cases was 3.00 mmol, which was 72.2 mL at the reference conditions (20.0°C and 1 atm).

Observations: In all experiments, the reaction slowly formed a white, solid polymeric by-product. The rate of stirring was not noticeably slowed.

Results: The yield curve for Method A has 1,200 points obtained as the average of triplicate runs in which data were collected at equal intervals for 1,199 s. The yield curve for Method B has 1,199 points. These represent the average of four runs in which data were collected at equal intervals for 1,198 s.



Discussion: The fractional yield β , rate constant λ_0 , and induction time computed from the least-squares fits of the two yield curves to Equation D.1 appear in Table C.1. The slope of the Method A curve increased at $\Delta V \approx 25$ mL, indicating that the reaction sped up at that point. This occurred just as the first third of the Si–Cl bonds had been hydrolyzed. Similar effects appeared in the yield curves of other trichlorosilanes. This finding suggested a real chemical phenomenon. The rate of the reaction when Method B was used slowed suddenly at about 1 min after the start of the reaction, but then it quickly sped up again. This might have been caused by the buildup of the polymeric by-product. Because of these vagaries, the fits of Equation D.1 to the two sets of data were rather poor.

The values for the fractional yield β and rate constant λ_0 that appear under the Method B heading in Table C.1 were recommended for developing PADs for this material.

UN 1818, Tetrachlorosilane, SiCl_4 (Repeat)

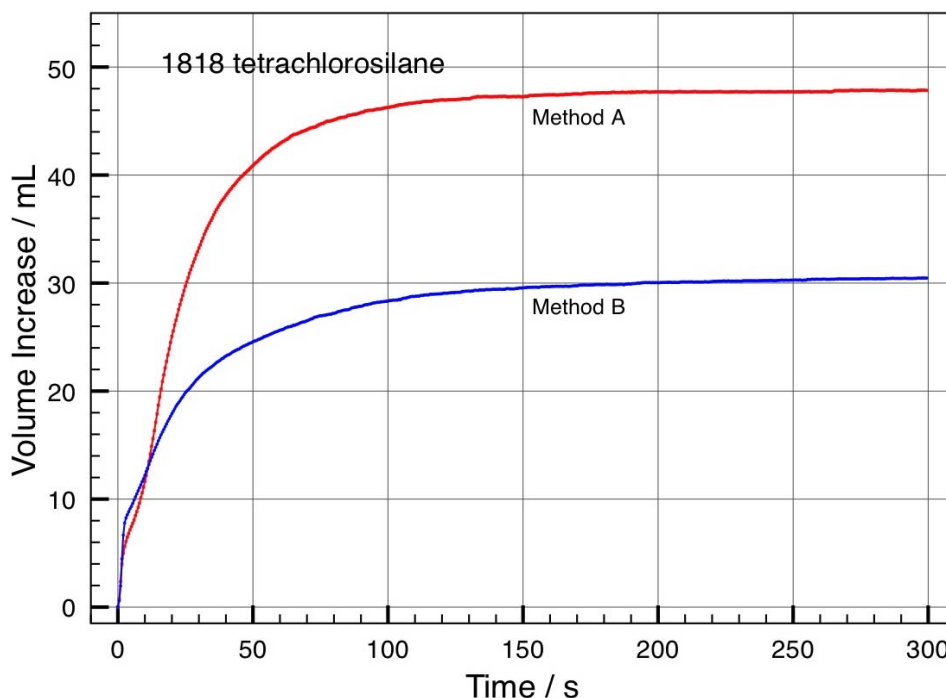
The chemical reaction



was taken as the sole source of evolved gas. In Method A, 2.00 mmol (36.0 μL = 36.0 mg) of water was added to 116 μL of the compound. This was 1.00 mmol of compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 10.0 mmol of water was added to 1.00 mmol of the compound. The theoretical yield of $\text{HCl}(\text{g})$ was 96.22 mL at 20°C and 1 atm pressure.

Observations: In all experiments, a white solid formed immediately upon mixing of the reactants. The motion of the stirring bar did not, however, get noticeably slower, because the bar spun on top of the solid.

Results: The yield curve for Method A has 300 points obtained as the average of five runs in which data were collected at equal intervals for 299.5 s. The yield curve for Method B also has 300 points. They were obtained as the average of six runs in which data were collected at equal intervals for 299.5 s.



Discussion: The fractional yields β , rate constants λ_0 , and induction times computed from the least-squares fit of Equation D.1 to the two yield curves appear in Table C.1. The slight decrease in rate that starts in the Method A curve at about 8 mL and is reversed at about 12 mL did not significantly affect the quality of the fit. The reaction started promptly when both methods were used and proceeded at about the same rate; the half-lives were 0.30 min (Method A) and 0.37 min (Method B). The shape of the Method A curve shows that the reaction slowed down soon after its start and then sped up again. The Method B curve shows that the reaction slowed sharply at about the same time after its start. Such minor deviations from first-order kinetics were common among the chlorosilanes.

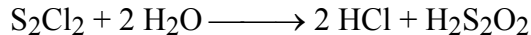
The white solid by-product is hydrated silicon dioxide $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. This material ties up water and so might have prevented or slowed the production of $\text{HCl}(g)$ in these experiments. For example, the 50% yield of HCl in the Method A experiments is perfectly explained if the x in $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ equals 2. Such sequestration of water would not limit the production of $\text{HCl}(g)$ in most spills into environmental water because the water would be available in essentially infinite excess.

The yield curve from using Method B does not reach a maximum, whereas the yield curves obtained from using Method B in 1999 and 2003 did. The 1999 and 2003 kinetic runs lasted 60 min rather than 5 min, and the maximums appeared in the 2003 runs after the first 10 min. However, dissolution of HCl(g) into the aqueous phase was more rapid than this when it occurred in experiments with other chlorosilanes. It may be that some or all of the decrease in volume in the 1999 and 2003 runs came from dissolution of HCl(g) in the manometric fluid (see Section D.1.1).

The values for fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 were recommended for developing PADs for this material for ERG2008.

UN 1828, Sulfur Chlorides, S₂Cl₂ (New in 2006)

The reaction



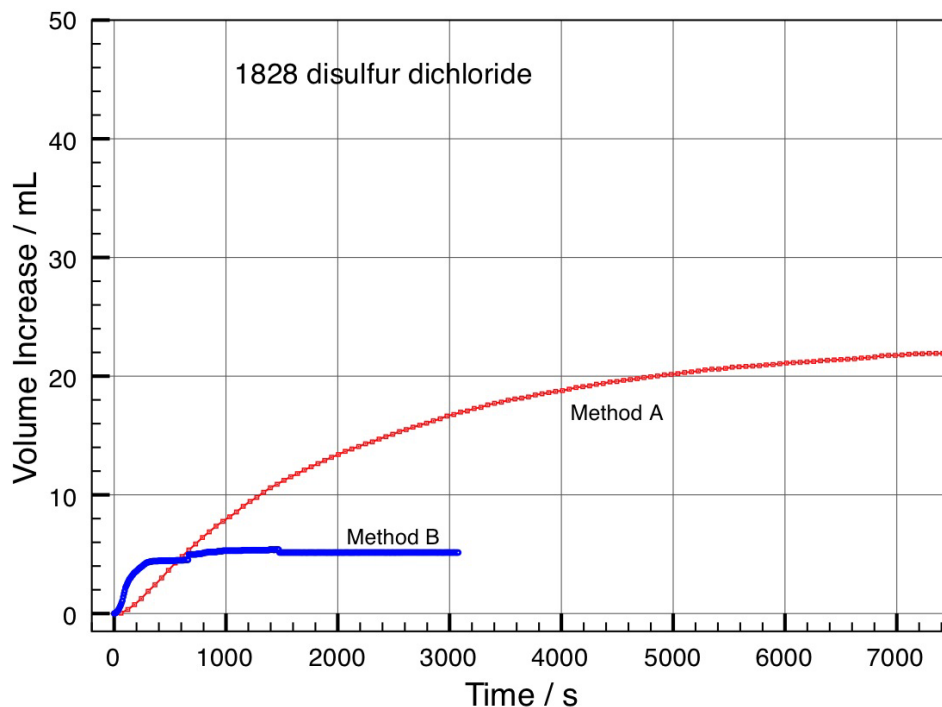
was taken as the source of HCl(g). For Method A, 2.00 mmol (36.0 μL = 36.0 mg) of water was added to 80 μL of the compound, a liquid. This was just under 1.00 mmol of the compound based on the purity, molar mass, and density listed in Table D.1. For Method B, the same amount of the compound was added to 10.0 mmol of water. The theoretical yield of HCl(g) was 48.1 mL at the reference conditions of 20°C and 1 atm pressure.

No attempts were made to analyze the product gas either qualitatively or quantitatively. The issue of the possible production of sulfur-containing gases is discussed below.

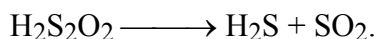
Observations: The substance was yellow before being mixed with water. In all experiments, the reaction mixture grew dark and gummy-looking as the reaction proceeded, but the rate of rotation of the stirring bar was not noticeably affected.

Results: The Method A yield curve has 123 points collected as the average of three runs at approximately equal intervals over 7,412 s. The Method B curve has 457 points collected as the average of three runs at approximately equal intervals over 3,078 s. The irregularities in the Method B yield curve arise because one of the runs terminated after 661 s, and a second ended after 1,471 s.

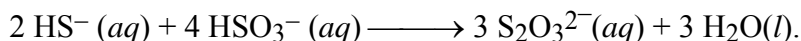
Discussion: These were the first experiments of this type on this compound. The fractional yields of HCl(g), the rate constants, and the induction times computed from the fit of Equation D.1 to the two yield curves appear in Table C.1.



It was assumed in calculating the fractional yields that the only gas that evolved was $\text{HCl}(g)$. This assumption relied on the strong possibility that polymerization reactions tied up most or all of the sulfur in nonvolatile species. Obviously, thiosulfurous acid, the by-product in the above chemical equation, might decompose to the TIH gases hydrogen sulfide and sulfur dioxide according to



However, both H_2S and SO_2 dissolve to some extent in water.⁷ Both are weak acids. The first reacts with water to give the hydrogen sulfide ion HS^- ; the second reacts with water to give the hydrogen sulfite ion HSO_3^- . These two species are known to combine to give the thiosulfate ion (Heunisch 1977):



This reaction is, in fact, supposed to involve a thiosulfurous intermediate (such as the HS_2O_2^- ion). Additional sulfur-containing species (polythionates⁸) are also known to form. The fact that the reaction mixtures darkened and thickened during the experiments suggests that some polythionates did form. Although their formation might have reduced rather than wholly prevented the evolution of the two sulfur-containing gases, it was nevertheless assumed that only the $\text{HCl}(g)$ evolved. In previous work, the three gases $\text{HCl}(g)$, $\text{H}_2\text{S}(g)$, and $\text{SO}_2(g)$ had been judged to evolve in the molar ratio 4 to 1.2 to 1.

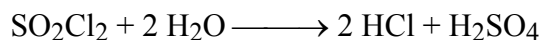
⁷ $\text{H}_2\text{S}(g)$ is sparingly soluble in water (0.25 g per 100 mL at 25°C); $\text{SO}_2(g)$ is somewhat soluble (9.4 g per 100 mL at 25°C).

⁸ Polythionates have the general formula $[\text{S}_n(\text{SO}_3)_2]^{2-}$.

Preliminary values for the fractional yield β and the rate constant λ_0 were recommended for developing PADs for this material for ERG2008. Slightly revised values appear under the Method B heading in Table C.1.

UN 1834, Sulfuryl Chloride, SO_2Cl_2 (Repeat)

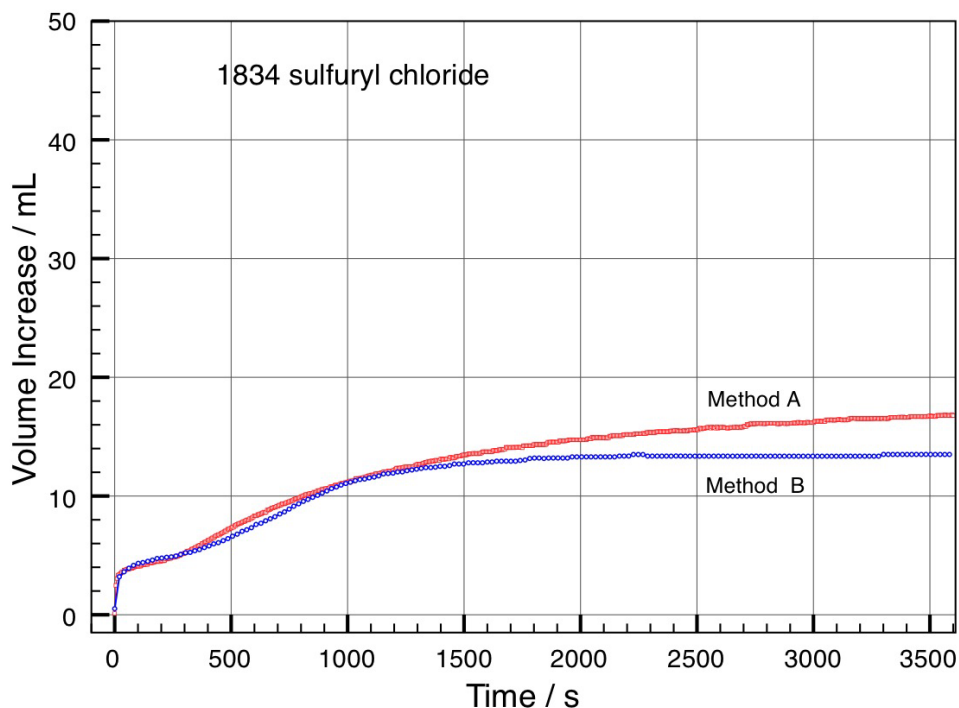
The reaction



was taken as the source of $\text{HCl}(g)$. In Method A, 2.00 mmol of water ($36.0 \mu\text{L} = 36.0 \text{ mg}$) was added to $83 \mu\text{L}$ of the compound. This was 1.00 mmol of the compound based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 10.0 mmol of water. The theoretical yield of HCl when both methods were used was 48.1 mL at 20°C and 1 atm pressure.

Observations: No insoluble solids or insoluble liquids formed during any of the experimental runs.

Results: The Method A yield curve consists of 721 points that were collected as the average of three runs in which data were taken at equal intervals over 3,600 s. The Method B curve consists of 178 points collected as the average of three runs in which data were taken at equal intervals over 3,584 s, except that one of the runs was terminated after 2,268 s.



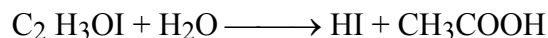
Discussion: The fractional yields β , rate constants λ_0 , and induction times computed from the least-squares fits of Equation D.1 to the two yield curves appear in Table C.1. The rate and yield of reaction were approximately the same for both methods. Both yield curves indicate that the reaction started fast, slowed, and then sped up again before finally coming to a stop. Equation D.1 has no room for such behavior, but its fit to the data was nevertheless acceptable in quality (the r.m.s.d.'s were 0.224 mL and 0.497 mL, respectively).

The absence of insoluble solids or liquids is consistent with the formation of hydrogen chloride and sulfuric acid in the reaction. The acidic by-product H_2SO_4 reduced the solubility of HCl in whatever water remained at the end of the reactions and so raised the yield of $\text{HCl}(g)$ in these experiments. In an accidental spill, the by-product H_2SO_4 would quickly be diluted, and the yield of $\text{HCl}(g)$ would be less.

The values for fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 were recommended for developing PADs for this material in ERG2008.

UN 1898, Acetyl Iodide, $\text{C}_2\text{H}_3\text{OI}$ (New in 2006)

The reaction



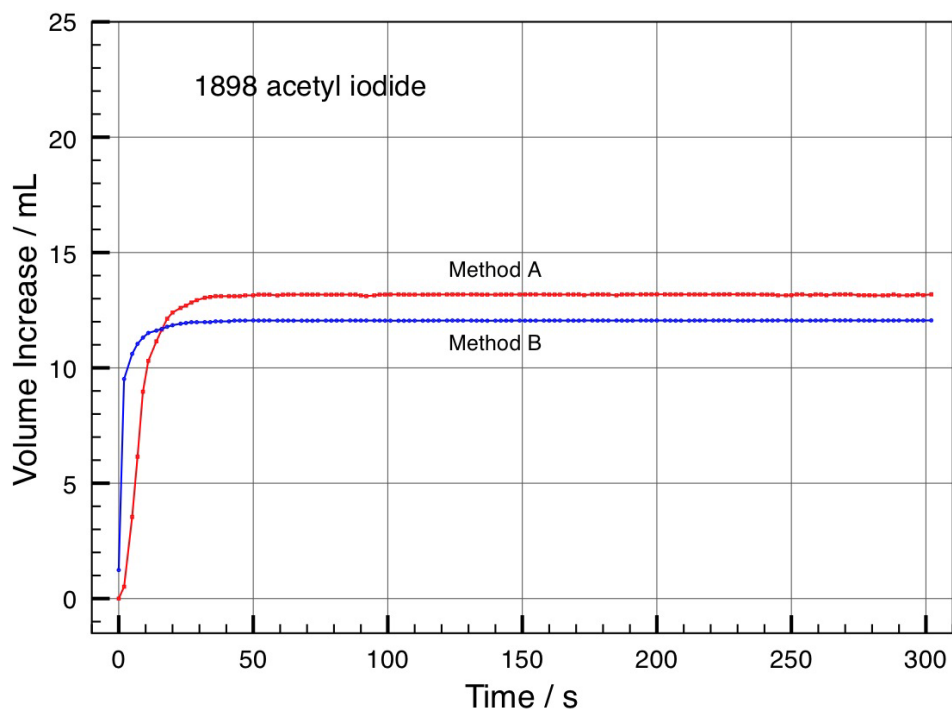
was taken as a source of $\text{HI}(g)$. In Method A, 1.00 mmol (18.0 μL , 18.0 mg) of water was added to 170 μL of the compound, a liquid. This was 1.00 mmol of compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (135 μL , 135 mg) of water. The theoretical yield of $\text{HI}(g)$ in both cases was 1.00 mmol, which is 24.1 mL at 20.0°C and 1 atm.

Observations: When both methods were used, the reaction quickly generated gas without producing insoluble by-products that might slow or stop the stirring bar.

Results: The Method A yield curve contains 135 points that were obtained by averaging the results of three runs in which data were recorded at approximately equal intervals for 302 s. The Method B curve contains 135 points, obtained as the average of three runs in which data were recorded at equal intervals for 302 s.

Discussion: These were the first experiments of this type on this compound. The fractional yields β , rate constants λ_0 , and induction times computed from least-squares fits of Equation D.1 to the yield curves appear in Table C.1.

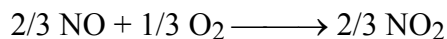
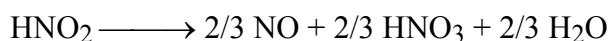
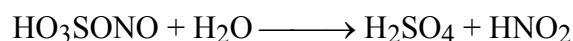
The reaction was faster when Method B was used than when Method A was used, and the yield of toxic gas was only slightly less. This result differs from the result with the acid chlorides. The reaction started quite promptly when Method B was used, and there was only a very brief induction period when Method A was used.



UN 2308, Nitrosylsulfuric Acid, 40% Solution, HO₃SONO (New in 2006)

This material was a mixture. It contained sulfuric acid (52.2% by mass) and water (7.8%) in addition to nitrosylsulfuric acid. Pure nitrosylsulfuric acid, a solid, is listed as UN 3456 and UN 2308 (pages 139 and 140 in ERG2004), but the solution is listed only as UN 2308.

The reaction sequence



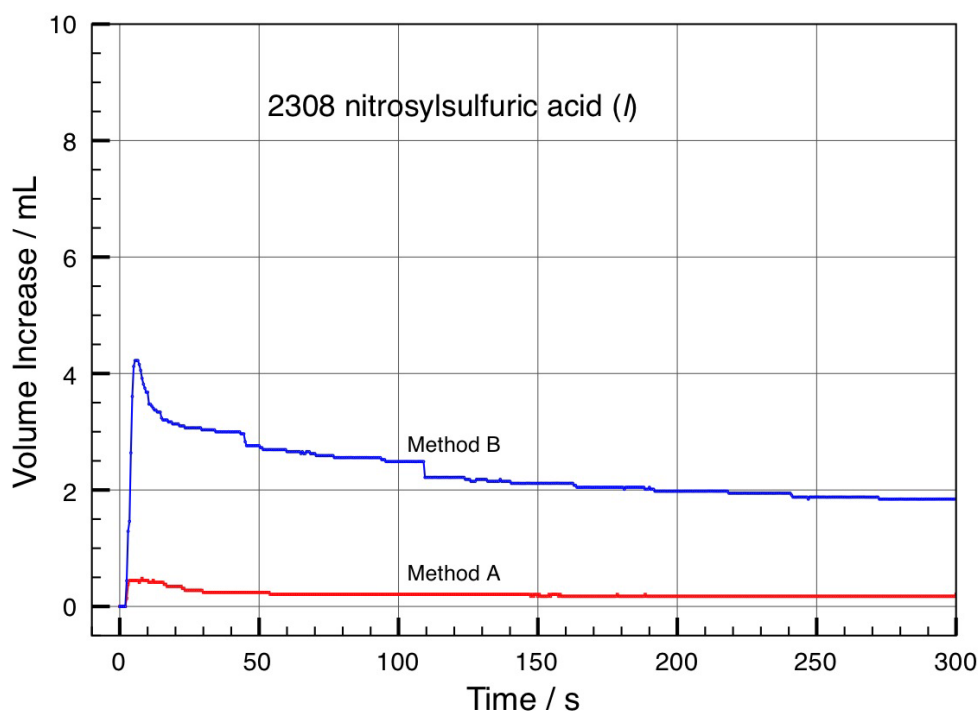
was taken as a source of the TIH gas nitrogen dioxide (NO₂). The last step is known to be quite rapid. In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 197 mL of the solution. This volume of the solution furnished 1.00 mmol of HO₃SONO based on the molar mass of the compound and the density of the solution (see Table D.1) and the composition of the solution. In Method B, 197 mL of the solution was added to 5.00 mmol (135 μL = 135 mg) of water.

The balanced equations predict the formation of 2/3 mmol of NO₂(g) from 1 mmol of nitrosylsulfuric acid. This amount of NO₂(g) occupies a volume of 2/3 × (24.11 mL) = 16.04 mL at 20°C and 1 atm (the reference conditions). However, the third step in the reaction sequence removes 1 mmol of O₂(g) from the air in the closed test system for every 2 mmol of NO₂(g) that

it generates. This step reduces the theoretical ΔV by a factor of 1/3: from 16.04 mL to 10.69 mL. Because the formation of NO_2 in the third step requires O_2 , the nitrogen purge was omitted in the experiments.

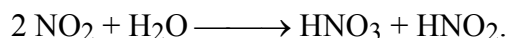
Observations: The characteristic brown-red color of $\text{NO}_2(g)$ appeared immediately in the space above the reaction mixture in all experiments. No precipitate formed in any of the experiments.

Results: The Method A yield curve consists of 601 data points obtained as the average of three runs in which measurements were taken at equal intervals for 300 s. The Method B curve contains 600 data points obtained as the average of three runs in which measurements were taken at equal intervals for 299.5 s.



Discussion: These were the first experiments of this type on this material. The volume rose to a maximum and then fell off when both methods were used. The drop-off was more rapid when Method A was used than when Method B was used. When Method A was used, the final volume of gas was essentially zero.

Nitrogen dioxide gas dissolves in water by disproportionating to yield nitric acid and nitrous acid (Cotton and Wilkinson 1966):



This reaction explains the absorption of $\text{NO}_2(g)$ after the initial spikes. The reaction produces HNO_2 , which can go back into the second step of the original reaction sequence. It suggests that the ultimate products from mixing nitrosylsulfuric acid with excess water in the presence of

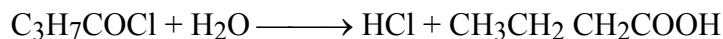
oxygen consist solely of aqueous nitric acid and aqueous sulfuric acid (and no gases). However, such a result would require that the intermediate gases remain in contact with the water, which would not happen in a spill.

The early spikes in the yield curves meant that they could not be modeled by using Equation D.1. Equation D.1 was, however, successfully fit to the rising portion of the Method B curve (the first 17 points). The results appear in Table C.1. The fractional yield β of $\text{NO}_2(g)$ listed in Table C.1 equals the “observed” ΔV (obtained by extrapolation from the rising data points) divided by 10.69 mL, the theoretical ΔV . At 0.96, it is nearly quantitative. The rate constant λ_0 is also large. Thus, $\text{NO}_2(g)$ would evolve rapidly and quantitatively under circumstances that prevented its absorption by dissolution. Dissolution reduced the final yield in Method B to 1.84 mL ($\beta = 0.17$).

No experiments were performed on solid nitrosylsulfuric acid (UN 3456) in 2006 because the material was unavailable. The 1999 experimental results on the solid were somewhat similar to these results. When Method A was used, ΔV spiked to 3 mL and then fell to 0 mL over 1,200 s. When Method B was used, ΔV spiked to 11 mL (close to 10.69 mL, the theoretical ΔV at 20°C and 1 atm) and then dropped off to 8.0 mL over 1,200 s.

UN 2353, Butyryl Chloride, $\text{C}_3\text{H}_7\text{COCl}$ (New in 2006)

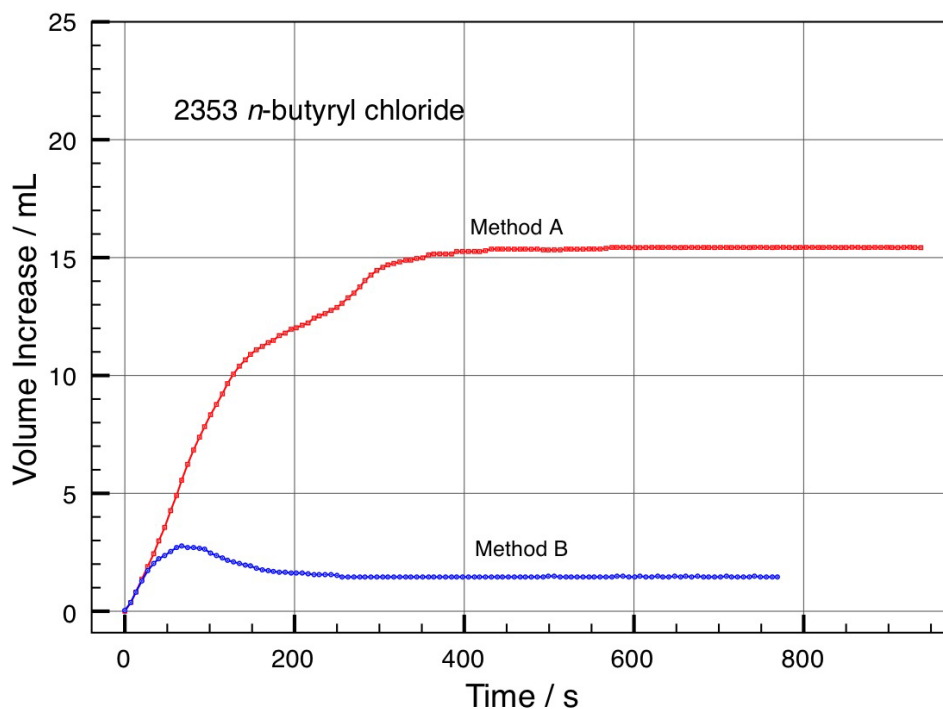
The reaction



was taken as a source of $\text{HCl}(g)$. In Method A, 1.00 mmol (18.0 μL = 18.0 mg) of water was added to 104 μL of the compound. This was 1.00 mmol based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (135 μL = 135 mg) of water. The theoretical yield of $\text{HCl}(g)$ in both cases was 1.00 mmol, which is 24.1 mL at 20.0°C and 1 atm.

Observations: In all experiments, the reaction proceeded without formation of insoluble products that might slow or stop the stirring bar. When Method B was used, some of the product gas apparently dissolved in the excess water (causing a maximum in the yield curve).

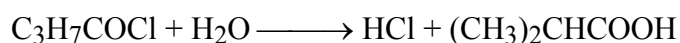
Results: The Method A yield curve consists of 140 points, obtained by averaging the results of three runs in which P , V , and T values were recorded at equal intervals of time for 952 s. The Method B yield curve consists of 115 points that were obtained as the average of four runs in which values were recorded at equal intervals for 769 s.



Discussion: These were the first experiments of this type on this compound. The fractional yield β , rate constant λ_0 , and induction time computed from a least-squares fit of Equation D.1 to the Method A yield curve appear in Table C.1. Despite the increase in rate at 12–14 mL in this curve, the quality of the fit was acceptable. Due to the maximum in the Method B yield curve, we used just the rising points (the first 14 points) in fitting Equation D.1 to determine the fractional yield, rate constant, and induction time listed in Table C.1. Doing this removed the effect of dissolution of the toxic gas in the excess water. Even so, the yield of HCl in Method B is slight.

UN 2395, Isobutyryl Chloride, C_3H_7COCl (New in 2006)

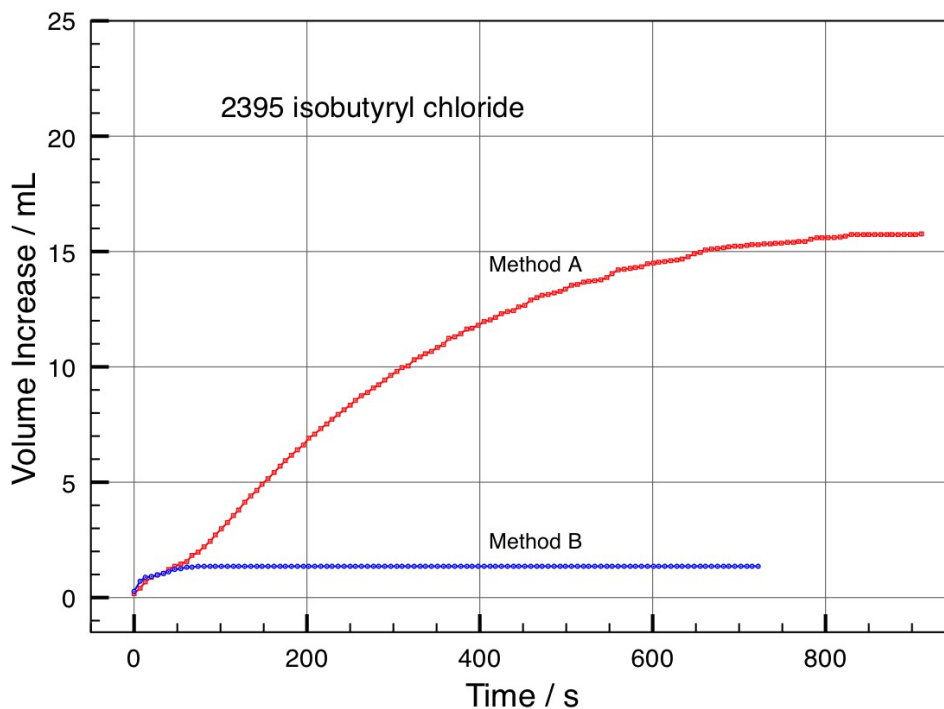
The reaction



was taken to produce HCl(g). In Method A, 1.00 mmol of water ($18.0 \mu\text{L} = 18.0 \text{ mg}$) was added to $106 \mu\text{L}$ of the compound. This was 1.00 mmol, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol ($90.1 \mu\text{L} = 90.1 \text{ mg}$) of water. The theoretical yield of HCl in both reactions is 1.00 mmol or (assuming ideal-gas behavior) 24.11 mL at the reference conditions (20.0°C and 1 atm).

Observations: In all experiments, the reaction proceeded without producing any immiscible by-products that might slow or stop the stirring bar. The volume of gas generated by using Method B was very small compared to that generated by using Method A.

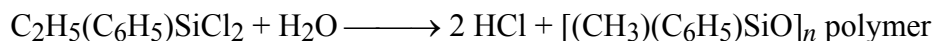
Results: The Method A yield curve contains 136 points, obtained by averaging the results of three runs in which P , V , and T values were recorded at equal intervals of time for 911 s. The Method B yield curve consists of 108 points that were obtained as the average of three runs in which values were recorded at equal intervals for 722 s.



Discussion: These were the first experiments of this type on this compound. The fractional yields β , rate constants λ_0 , and induction times computed from least-squares fits of Equation D.1 to the two yield curves appear in Table C.1. The 74% yield of $\text{HCl}(g)$ in Method A is roughly comparable to the 65% obtained by using Method A with the isomeric butyryl chloride (UN 2353), but the rate constant is only about one-third as large. The yield from using Method B on this compound is even smaller than the yield from using Method B on butyryl chloride. Also, the yield curve did not reach a maximum.

UN 2435, Ethylphenyldichlorosilane, $\text{C}_2\text{H}_5(\text{C}_6\text{H}_5)\text{SiCl}_2$ (New in 2006)

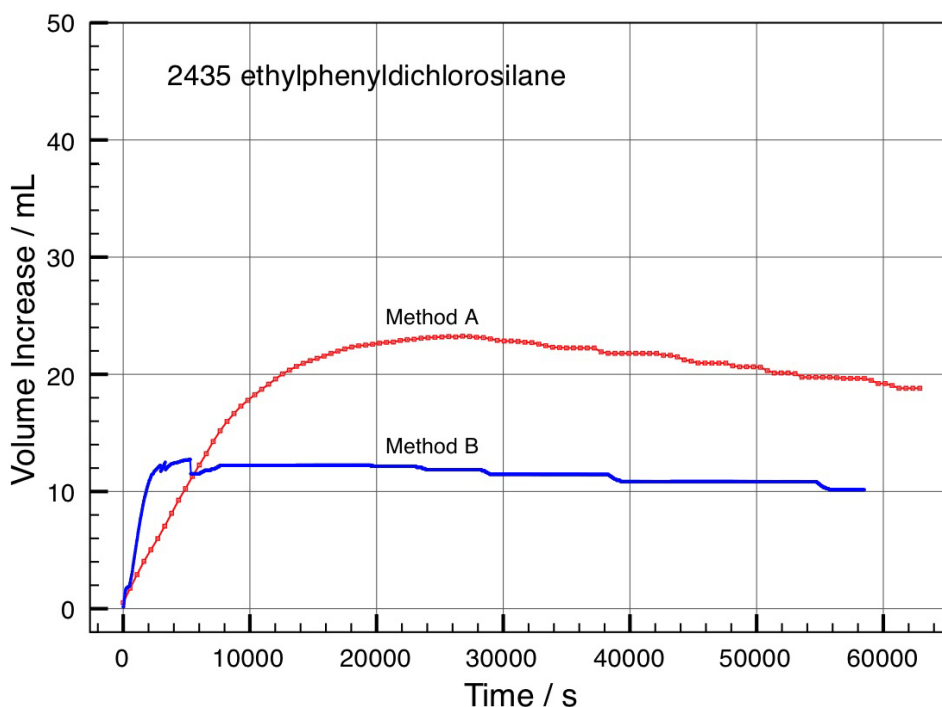
The reaction



was taken as the source of $\text{HCl}(g)$. In Method A, 1.00 mmol of water (18.0 mL = 18.0 mg) was added to 170 μL of the compound, a liquid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (90.1 mL = 90.1 mg) of water. The theoretical yield of HCl in both reactions was 2.00 mmol or (assuming ideal-gas behavior) 48.1 mL at the reference conditions (20.0°C and 1 atm).

Observations: Some solid by-product formed in all runs when both methods were used, but the rotation of the stirring bar was not noticeably slowed.

Results: The Method A yield curve contains 116 points that were obtained by averaging the results of three runs in which P , V , and T values were recorded at equal intervals of time for 62,876 s. The Method B yield curve consists of 2,890 points that were obtained as the average of four runs in which values were recorded at equal intervals for 58,502 s. One of the runs was terminated after 2,936 s, a second was ended after 3,321 s, and a third was ended after 5,305 s.



Discussion: These were the first experiments of this type on this compound. The irregularities in the first portion of the Method B yield curve were caused by the early termination of three of the four experimental runs.

The yield of $\text{HCl}(g)$ reached a maximum and then very sluggishly diminished. This result occurred in all trials when both methods were used. Although in experiments with other materials, ΔV rose to a maximum and then diminished, in this case, the contraction was uniquely slow. Dissolution of $\text{HCl}(g)$ in water was too fast in other experiments to account for such behavior when Method B was used, and this behavior was not possible when Method A was used. Absorption of $\text{HCl}(g)$ by the by-products of the reaction may have been responsible. It is unlikely that simple leakage would have reproduced itself in the triplicate Method A runs. Also, the percentage changes from the maximum ΔV after about 17 h were essentially the same for both methods: -19% (from 23.2 to 18.8 mL) for Method A and -20% (from 12.7 to 10.1 mL) for Method B.

The fractional yields β , rate constants λ_0 , and induction times were computed from the least-squares fit of Equation D.1 to the first 29,000 s of the Method A yield curve and the first

23,600 s of the Method B yield curve because loss of HCl(g) after so long a time would be immaterial in a spill scenario. These results appear in Table C.1. The yield of HCl(g) from using Method A had its maximum at 23.8 mL, corresponding to the reaction of almost exactly one-half of the available Cl.

UN 2437, Methylphenyldichlorosilane, CH₃(C₆H₅)SiCl₂ (Repeat)

The reaction



was taken as the source of HCl(g). In Method A, 1.00 mmol of water (18.0 μL = 18.0 mg) was added to 166 mL of the compound, a liquid. This was 1.00 mmol of the compound, based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 5.00 mmol (90.1 mL = 90.1 mg) of water. The theoretical yield of HCl in both reactions was 2.00 mmol or (assuming ideal-gas behavior) 48.1 mL at the reference conditions (20.0°C and 1 atm).

Observations: In all experiments, the reaction slowly formed a very viscous liquid by-product.

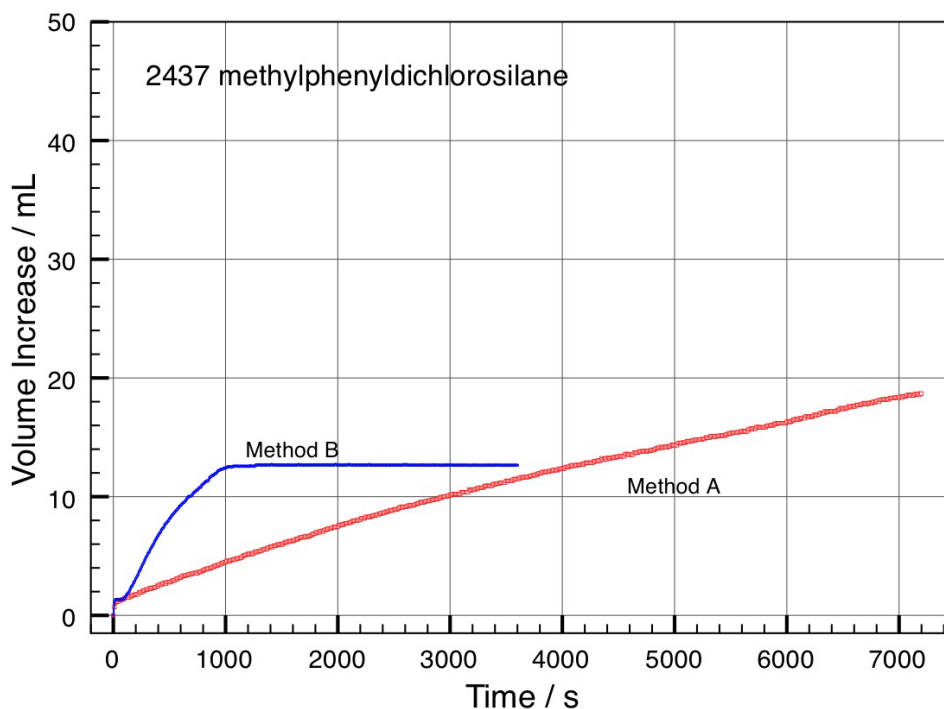
Results: The Method A yield curve contains 721 points taken at equal intervals over 7,200 s. Each point was the average of the results of three runs. The Method B curve has 361 points, each obtained as the average of two runs in which data were recorded at equal intervals for 3,600 s. One Method B run was rejected because all volumes were roughly one-third of the corresponding volumes in the other runs.

Discussion: The fractional yields β , rate constants λ_0 , and induction times computed from the fits of Equation D.1 to the two yield curves appear in Table C.1. The Method A runs were terminated before a final plateau in the yield curve was reached. The parameters from the least-squares fit of the data to Equation D.1, for which the goodness of fit was better than average (r.m.s.d. = 0.132 mL), were used to extrapolate the curve to infinite time, at which the final ΔV was 33.2 mL. (The maximum experimental ΔV reached on the Method A yield curve was only 18.7 mL.)

The reaction strongly resembled that of diethyldichlorosilane (UN 1767) in its rate and yield and in the appearance of its by-product.

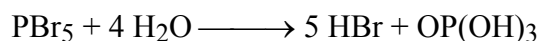
The yield of gas when both methods were used exceeded the yields in the 2003 experiments. The Method B yield in the 2003 experiments was only 2.3 mL of gas.

The values of the fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 are recommended for developing PADs for this material. They were not available in time to prepare ERG2008, so the 2003 results were used instead.



UN 2691, Phosphorus Pentabromide, PBr_5 (Repeat)

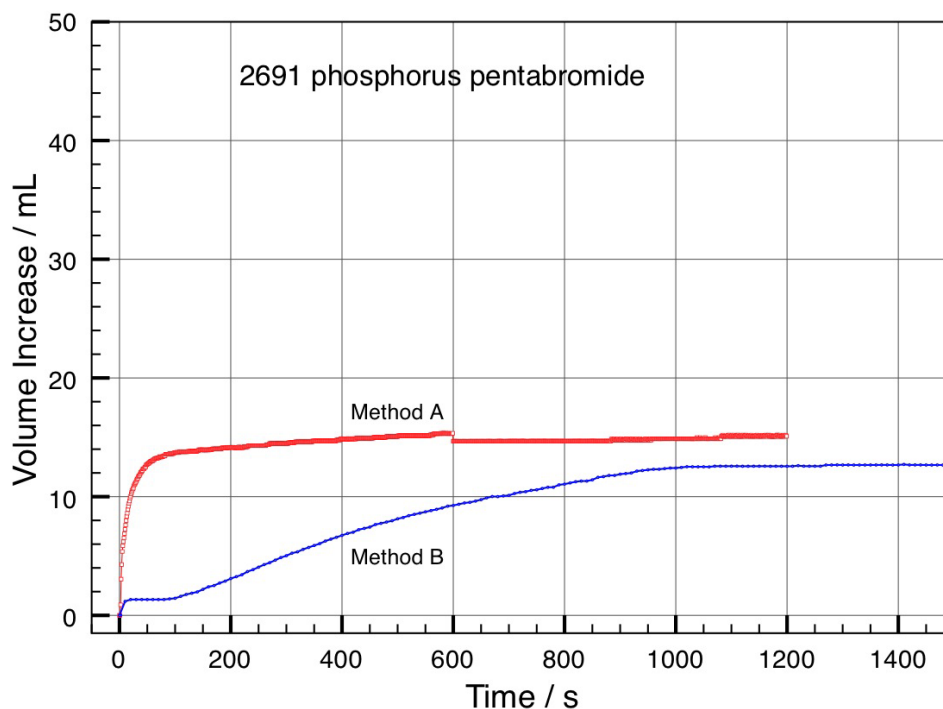
The reaction



was taken as the source of $\text{HBr}(g)$. In Method A, 4.00 mmol of water was added to 452 mg of the compound, which is a solid. This was 1.00 mmol of compound based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 20.0 mmol of water. Generation of 5.00 mmol of $\text{HBr}(g)$ corresponded to an increase in volume of 120.28 mL in the reaction system at 20°C and 1 atm pressure.

Observations: When Method A was used, the reaction was rapid and violent. A few droplets of water were spattered onto the walls of the container and out of contact with rest of the mixture. When Method B was used, $\text{HBr}(g)$ formed less rapidly.

Results: The Method A yield curve contains 1,200 points, obtained by averaging the results of three runs in which P , V , and T values were recorded at equal intervals of time for 1,199 s. Two of the runs were terminated after 599 s, however. The Method B yield curve consists of 362 points that were obtained as the average of two runs in which values were recorded at equal intervals for 3,600 s. Only the first 1,500 s of the Method B data are graphed; the rest of the curve is exactly horizontal.



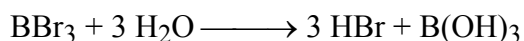
Discussion: The break in the Method A yield curve at 600 s resulted from termination of two of the Method A runs at that time. The fractional yields β , rate constants λ_0 , and induction times obtained from the least-squares fits of Equation D.1 to the two yield curves appear in Table C.1.

The reaction was substantially faster when Method A was used. This result was the reverse of the result for most of the other materials that were studied. Also, the reaction began promptly when Method A was used, but a period of induction was needed when Method B was used. The yields of gas were roughly the same when both methods were used.

The values of the fractional yield β and the rate constant λ_0 that appear under the Method B heading in Table C.1 are recommended for developing PADs for this material. They were not available in time to prepare ERG2008, so the 2003 estimates were used instead.

UN 2692, Boron Tribromide, BBr_3 (Repeat)

The reaction



was taken as the source of $\text{HBr}(g)$ for computations of mass and yield. In Method A, 3.00 mmol of water was added to 94 μL of the compound, which is a liquid. This was 1.00 mmol based on the purity, molar mass, and density listed in Table D.1. In Method B, 1.00 mmol of the compound was added to 15.0 mmol of water. The theoretical yield of 3.00 mmol of $\text{HBr}(g)$

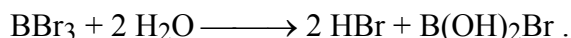
corresponds to a 72.2-mL increase in the volume of the reaction system at 20°C and 1 atm pressure (the reference conditions).

Observations: The reaction was immediate and rapid when Method A was used. No insoluble liquids or solids formed. The reaction was also quite rapid when Method B was used. Most of the HBr(*g*) that formed apparently soon dissolved in the excess water to produce HBr(*aq*).

Results: The yield curve for Method A consists of 139 points. They were obtained by averaging the results of four kinetic runs in which data were collected at equal intervals for 952 s. The yield curve for Method B consists of 134 points that were obtained as the average of three runs in which data were collected at equal intervals for 299 s. The curves are shown in the first graph.

An additional Method B yield curve was obtained in which data were collected at intervals of approximately 0.1 s rather than 2–3 s. This curve consists of 601 points obtained by averaging the results of three kinetic runs in which data were collected at approximately equal intervals for 60 s. This yield curve appears in the second graph. The Method B yield curve that appeared in the first graph is also reproduced here for the sake of comparison.

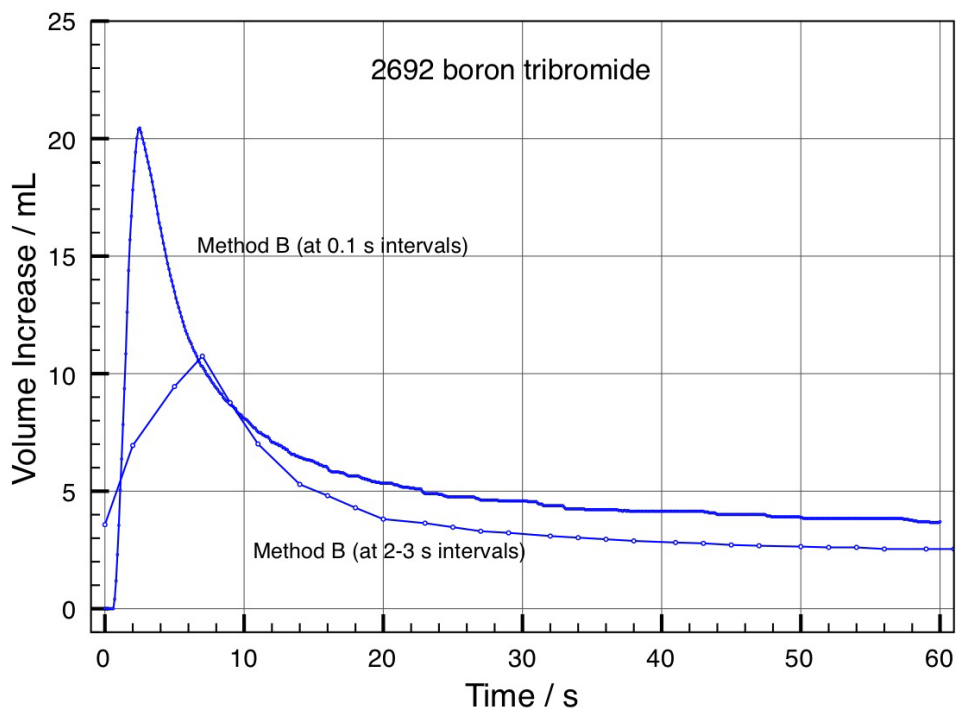
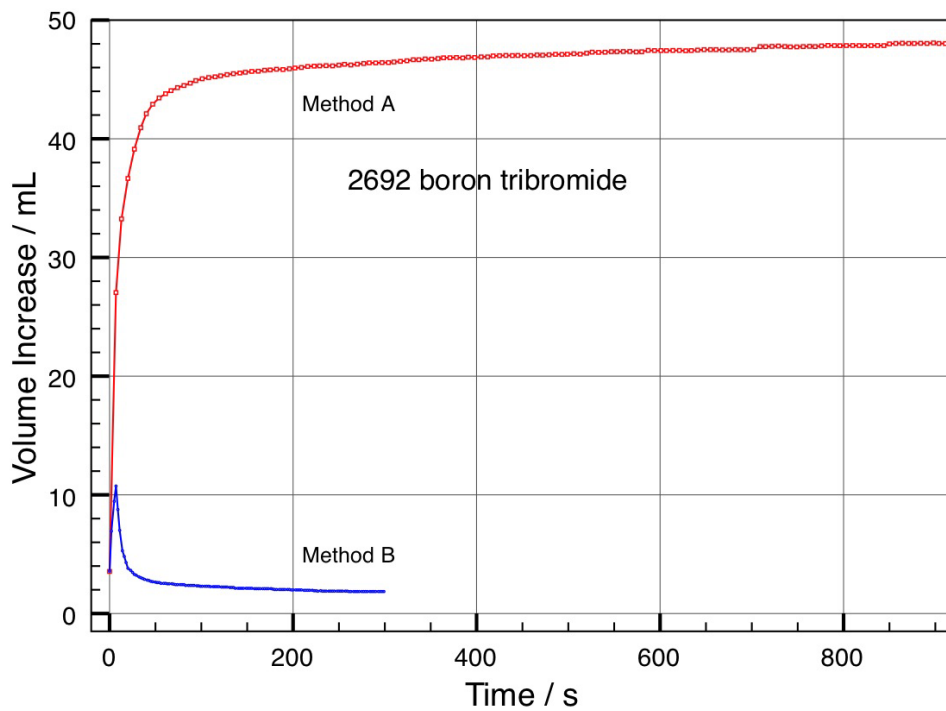
Discussion: The fractional yield, first-order rate constant, and induction time obtained by fitting Equation D.1 to the Method A yield curve appear in Table C.1. Nearly two-thirds of the theoretical amount of HBr(*g*) evolved from using Method A. The reaction under Method A conditions thus might be better represented as



The Method B yield curve in the first set of experiments spiked quickly to a maximum and then fell. This behavior was investigated more closely by performing additional runs on a shorter time scale. Equation D.2 was successfully (r.m.s.d. = 1.00 mL) fit to these additional data. The parameters were

$$a = 36.0 \text{ mL}, b = -47.5 \text{ mL}, c = 4.3 \text{ mL}, \lambda_0 = 13.1 \text{ min}^{-1}, \text{ and } \lambda_1 = 39.9 \text{ min}^{-1}.$$

The fractional yield β of HBr(*g*) in the absence of dissolution and the first-order rate constant λ_0 for the production of HBr(*g*) were estimated from these parameters, as discussed in Section D.2.3. These values appear under the Method B heading in Table C.1 and are recommended for developing PADs for this material.





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