Naval Research Laboratory Industrial Chemical Analysis

Thomas E. Sutto, Ph.D.
Naval Research Laboratory
Washington, D.C.
Industrial Chemical Analysis
001-202-404-2097
thomas.sutto@nrl.navy.mil

Background

1. Testers/Scientists working with ITF-40 chemicals recognized that some chemicals were reacting/changing upon releasing them into the atmosphere for T&E.
2. Examples
   - Diborane-rapidly decomposed in air
   - Ethylene or propylene oxide-detonated/decomposed in air
   - Boron trifluoride, phosphorus trichloride, phosphoryl trichloride, sulfur trioxide
     - All fumed, chemically changed to HF, HCl, HCl, Sulfuric Acid, respectively
3. Naval Research Laboratory originally tasked to develop a prioritization approach[1] for an ongoing program of record by Joint Program Manager for Individual Protection.

1. Documented in NRL/FR/6364--09-10,182

Previous ITF-Efforts

International Task Force -25→ (1994)

International Task Force -40→ Current List (2003)

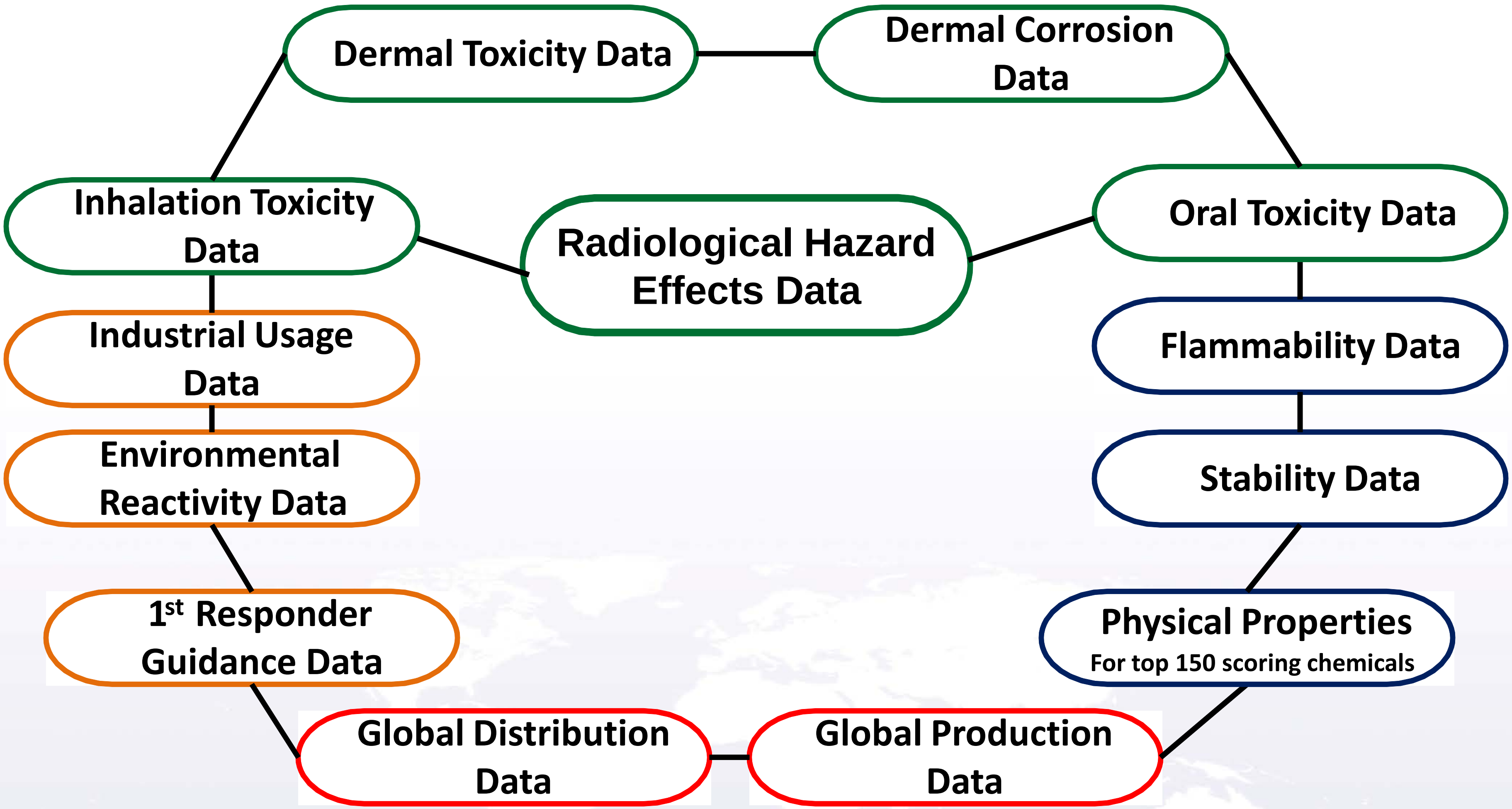
Limitations:

- **Primarily Toxicity Based Assessment**
- **Reactivity not fully considered.**
- **Flammability not fully considered**

Solution:

1. Create a more up-to-date, comprehensive database
2. Define an algorithm to assess reactivity/flammability
3. Redefine probability to simple mathematical relationship
4. Develop and apply a Class Based Analysis

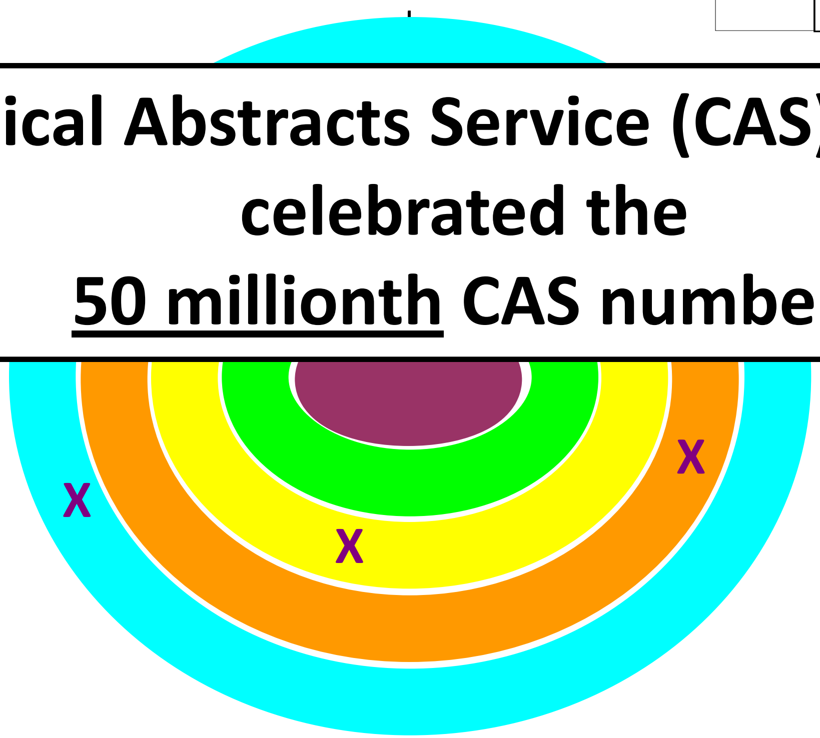
Database Development



Why a Class Based Analysis?

Global Chemicals Chart

1	50 Million CAS Chemicals
2	430 NRL ICA Chemicals



Chemical Abstracts Service (CAS) recently celebrated the <u>50 millionth</u> CAS number.

polymerizers

4. Simple Organics

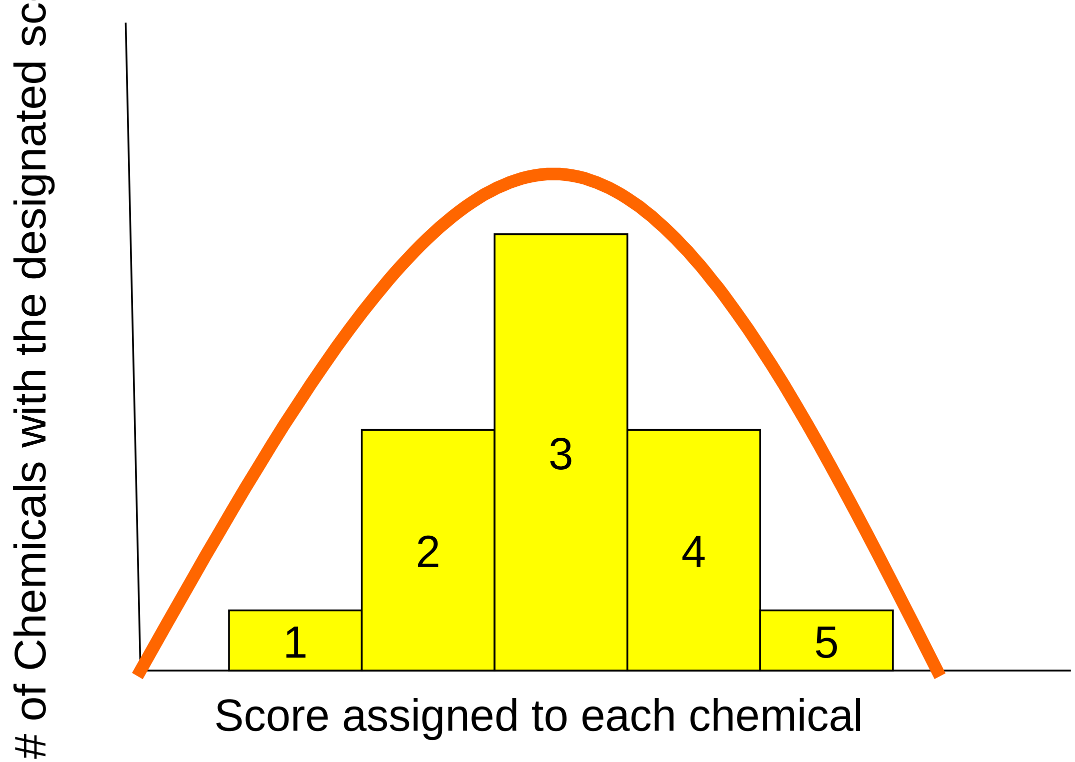
5. "ANY"-icides

Important Aspects of the Prioritization Approach

1. **Balance between toxicity and the ability of a chemical to actually manifest a toxic hazard in the operational environment (flammability/reactivity, physical state and toxicity).**
   - Assembled comprehensive data for inhalation, percutaneous, oral toxicity.
   - Introduced dermal corrosion (ability of a chemical to rapdily cause 2^{nd} degree burns) to address previously overlooked corrosive hazard of industrial chemicals
   - Assembled radiological hazard endpoints for inhalation, ocular, dermal and oral radioactive effects.
2. **Utilize up–to-date industrial data to determine Pseudo-probability function (Relative Probability Score).**
3. **Use the previously mentioned class-based analysis to assist in the downselection protocol.**

Distribution of Toxicity Scoring

Scoring system devised to ensure a Gaussian distribution



Stability-Flammability and Reactivity Considerations

Outtake from the ITF-40 Database

	OLD NFPA Values from ITF-40 (on a 0-4 pt scale)	ITF-40 hazard Score

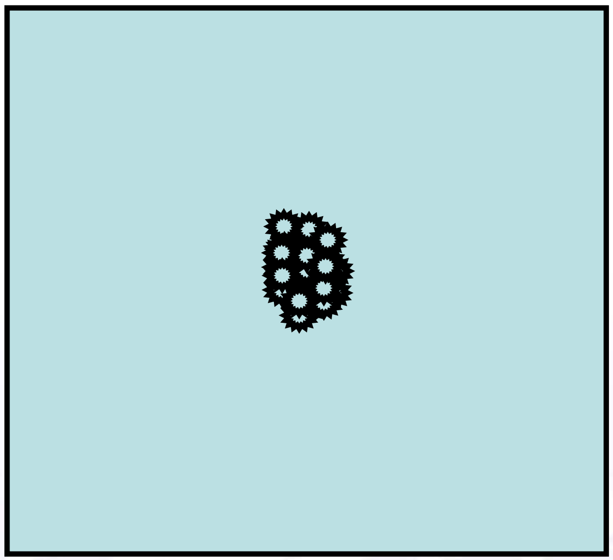
Outtake from the NRL-ICA Database

Rank (of 430)	Chemical	Reactivity Number	Reactivity Score	Flammability Number	Flammability Score	Stability Score (out of 5)
261	Diborane	3	1.25	4	0	0.625

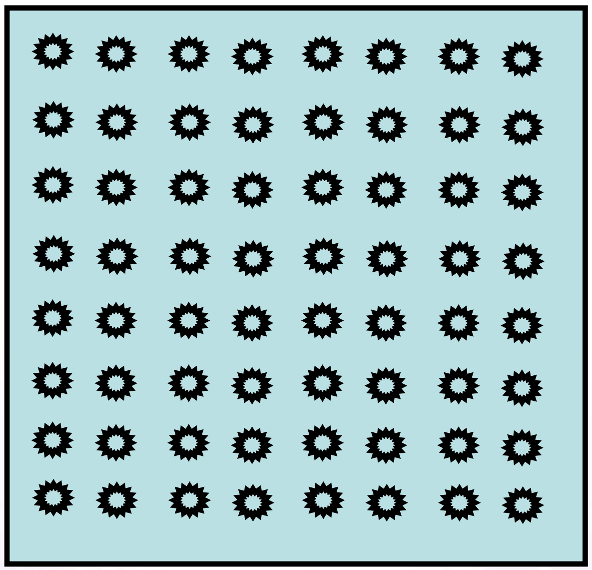
Diborane-B_2H_6

Relative Probability Score

Consider two 100 yard grids. Each with 64 land mines.
Field A has them located in the middle.
Field B has them evenly distributed.



Field A



Field B

The probability of encountering a mine is dependent not only on the number of mines but also on the distribution of mines.

Relative Probability Score

Based on mathematical probability-amount and distribution.

- **For amount-DWCP (Directory of World Chemical Producers) – the total # of countries producing a chemical**
- **For distribution-DWCP -the total # of distribution sites of a chemical world-wide**

Any chemical with a probability score of 1 or 0 is not selected as critical due to extremely low probability of encounter.

Prioritization Approach

Toxic (Operational) Hazard Score

Stability Score (From NFPA F and R)

Toxicity Score

Physical State Score

Total = 15. Any chemical with a score greater than 10 is selected as critical

Relative Probability Score

Global Production Value

Global Distribution Value

Total = 10. Any chemical with a score greater than 1 is selected as critical

Critical Inhalation/Ocular Hazard List

Critical Inhalation Ocular List			
Rank	**Chemical**	**Rank**	**Chemical**
1	Chlorine	19	Nitrogen dioxide
2	Ammonia	20	Phosphorus trichloride
3	Hydrogen chloride	21	Fluorotrichloromethane
4	Sulfuric acid	22	Hydrogen sulfide
5	Hydrogen fluoride	23	Molybdophosphoric acid
6	Formaldehyde	24	Toluene-2,4-diisocyanate
7	Mercury	25	Fluorine
8	Nitric acid	26	Malathion
9	Sulfur dioxide	27	Parathion
10	Phosgene	28	Acetylene tetrabromide
11	Hydrogen bromide	29	o-Anisidine
12	Nitric oxide	30	Sulfur trioxide
13	OMPA	31	Phosphine
14	Boron trifluoride	32	Arsine
15	Methyl bromide	33	Ethylene dibromide
16	Phosphoryl Trichloride	34	Pentachlorophenol
17	Chlorine dioxide	35	Azinphosmethyl
18	Bromine	36	1,1,2,2-Tetrachloroethane

Oxidizer	Reducer	Self-Polymerizing	Simple Organic	"ANY"-icide

Critical Percutaneous Hazard List

Critical Percutaneous List

Rank	Chemical	Rank	Chemical
1	Ammonia (as NH4OH)*	14	Hydrogen sulfide
2	Hydrogen chloride*	15	OMPA
3	Sulfuric acid *	16	Tetrachloroethylene
4	Formalin (formaldehyde)	17	Cadmium
5	Nitric acid *	18	Deltamethrin
6	Hydrogen fluoride*	19	Phosphine
7	Mercury	20	Ethylamine
8	Hydrogen bromide *	21	Methylamine
9	Potassium cyanide	22	Parathion
10	Tetrafluoroboric acid	23	Ethylene dibromide
11	Methyl bromide	24	Aldicarb
12	Boron trifluoride	25	Dichloroethyl ether
13	Fluorotrichloromethane	26	Nitrogen trifluoride

Oxidizer	Reducer	Self-Polymerizing	Simple Organic	"ANY"-icide

Downselection Process

1. Select highest scoring chemicals from each class
2. Eliminate chemicals which react to generate an alternate threat
   - Phosphoryl Trichloride and Phosphorus Trichloride generate HCl gas when released into the environment).
   - Nitric oxide (NO) converts to nitrogen dioxide in the environment. Nitrogen dioxide and nitric acid releases generate mix of nitric acid aerosol and nitrogen dioxide.
   - Chlorine dioxide generates HCl when released into the environment.

Downselected Inhalation/Ocular Hazard Chemicals

#	Chemical	#	Chemical
1	Chlorine	8	Nitric acid-Nitrogen dioxide
2	Ammonia	9	Sulfur dioxide
3	Hydrogen chloride	10	Phosgene
4	Sulfuric acid	11	Hydrogen bromide
5	Hydrogen fluoride	12	OMPA
6	Formaldehyde	13	Methyl bromide
7	Mercury	14	Hydrogen sulfide

Chemicals in alphabetical order

Oxidizer	Reducer	Self-Polymerizing	Simple Organic	"ANY"-icide

Note that hydrogen cyanide and cyanogen chloride are alternative chemicals for this list. However, hydrogen cyanide is a highly flammable, self-reactive compound which did not have a high enough Toxic Hazard Score. Cyanogen chloride has no known industrial uses. It is recommended instead that these compounds be assessed as CWA's if warrented.

Downselected Percutaneous Hazard Chemicals

Rank	Chemical
1	Ammonia (as NH4OH)*
2	Ethylene dibromide
3	Formalin (formaldehyde)
4	Nitric acid *
5	OMPA
6	Sulfuric acid *

Chemicals in alphabetical order

Oxidizer	Reducer	Self-Polymerizing	Simple Organic	"ANY"-icide

Conclusions

1. Starting from developing a Risk Mitigation Strategy for T&E results in a short focused representative list of chemicals which:
   - Can guide further R&D efforts to produce the best systems at significant savings to cost and schedule
   - For KPP's →Provide meaningful guidance for system performance.
     - Threshold requirements-"Laws of Physics"
     - Objective requirements-Guidance to Industry about where we want to grow our capability
   - Rapidly provide predictive performance limiting capability should an untested chemical be used by adversaries
2. Up-front use of class-based analysis to fully encompass potential global hazard of industrial chemicals.

Conclusions

3. Database and prioritization approach that can be re-assessed and analyzed when required
4. Prioritization and down selection based on fundamental chemical principles that balance toxicity and the actual ability of a chemical to manifest a toxic hazard in the operational environment.
   - Flammability and reactivity considerations
5. Consideration of the corrosive hazards of industrial chemicals in the percutaneous hazard prioritization.

Acknowledgments

Karen A. McGrady, Ph.D.

Darren S. Wheeler, MBA

Joint Project Manager for Individual Protection

Backups

Path Forward

1. **Develop database of industrial chemicals**
   - Inhalation/Ocular Toxicity→ AEGL-3 1hr
   - Percutaneous Toxicity→ Dermal LD50 or Dermal Corrosion Effects
   - Current NFPA scores for Flammability & Reactivity
   - Physical State→ (Solid, Liquid or gas)
   - Data from Directory of World Chemical Producers
     - # of countries producing and total number of distribution sites globally
2. **Develop algorithm to provide a technical justification for downselection to priority industrial chemicals for inhalation/ocular and percutaneous hazard**
3. **Result: NRL Industrial Chemical Analysis-Prioritization approach adopted by TIC TIM Task Force (TTTF)**

NRL-ICA Database

1. Uses a database of 430 chemicals, with complete data sets for each.
2. Includes inhalation, percutaneous, oral and radiological toxicity(hazard) data
3. Both global and individual country (20 countries and the U.S.) production and distribution data
   - Allows for country by country as well as CONUS/OCONUS Analysis
4. Industrial Usage Database for assessing a particular industry (Uranium enrichment, semiconductor, mining, etc.)
5. Employs fundamental chemical classes to allow for class-based analysis.
   - Based on strictly defined chemical principles.

Stability Scoring

Based upon the fact that increased flammability and reactivity with air or water decrease the potential toxic threat of a chemical in the operational environment.

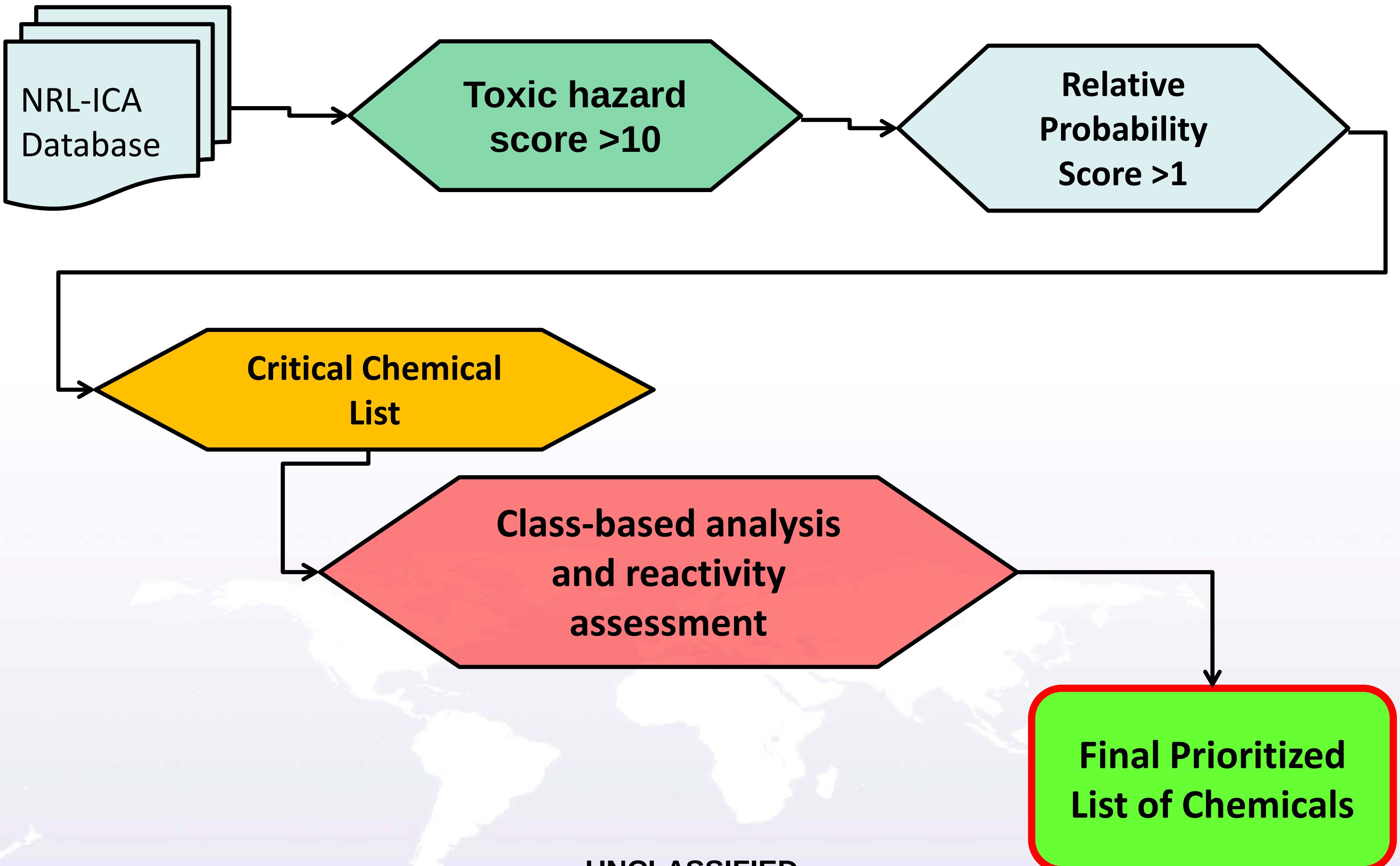
Scored as the inverse of the F and R NFPA ratings as shown below:

Ethylene Oxide; NFPA values of F = 4 and reactivity of 3.

Stability score = [(4-F value+ 4-R value)/2]* 1.25 (5 pt scaling)

Ethylene Oxide stability score is then 0.63 out of 5.

Downselection Process



ITF-40 Database Assessment

Results indicate an error rate of 57%

The Threshold and Objective Chemicals of the JSGPM System	ITF-40 Values			ITF-40 HAZARD SCORE	ACTUAL CURRENT NFPA VALUES- CORRECTIONS IN RED		
COMPOUND	H	F	I		H	F	I
Hydrogen chloride	4			4	3	0	1
Hydrogen cyanide	4	4	1	4	4	4	2
Hydrogen fluoride	4			4	4	0	1
Hydrogen sulphide	2	4	0	4	4	4	0
Methyl Isocyanate	4	3	2	4	4	3	2
Methyl Mercaptan	4	4	1	4	4	4	1
Nitric acid	3	0		3	4	0	1
Nitrogen dioxide	3			3	3	0	0
Phosgene	3			3	4	0	1
Phosphine	2	4	2	4	4	4	2
Phosphorus trichloride	4	0	0	4	4	0	2
Sulphur dioxide	2			2	3	0	0
Sulphur trioxide	4			4	3	0	2
Sulphuric acid	4			4	3	0	2
Toluene diisocyanate				0	3	1	3
Tungsten hexafluoride	2			2	4	0	1