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Rules and Guidelines to Facilitate Professional Judgments

By Mark Stenzel, CIH, FAIHA and Susan Arnold, CIH, FAIHA

Introduction

Exposure assessments provide the basis for many of the decisions that industrial hygienists must make in the practice of their profession. Examples of the decisions and determinations requiring an exposure assessment include the following:

- Assessing compliance with health based or regulatory exposure limits
- Management of a chemical approval program that must be completed prior to the introduction of an agent in the workplace and includes the following components:
    - required engineering and administrative controls
    - proper procedures and work practices
    - required personal protective equipment (PPE) including respirator requirements
    - hazard communication and other training requirements
    - proper disposal of any waste material generated by the process
- Impact of a process change
- Impact of the introduction of a new process
- Adequacy of existing engineering controls or the expected performance of new controls to protect workers' health
- Medical surveillance and health monitoring requirements
- Investigations
    - process hazard reviews
    - impact of upsets or process failures
    - support emergency planning
    - formal studies
    - prevalence studies that assess if adverse medical outcomes may be associated with work place determinants such as process area, job performed, and agents present, etc.
    - epidemiology morbidity or mortality studies
    - illness cluster
    - toxic tort alleging harm from current or past exposures.

Many of these exposure assessments (> 95%) must be made with no quantitative measurements because decisions must be made prior to the introduction of the agent into the workplace, or in the case of retrospective exposure assessments no opportunity exists to go back in time and collect measurement data. Some are hypothetical such as process hazard reviews, emergency planning or impact of process failures and upsets. Also in the case of illness clusters, it may not be known today that an agent has a specific ability to cause adverse health outcomes. The judgments must be timely. In many cases, a judgment is needed in minutes or hours rather than days that are usually needed to collect quantitative measurements. Finally, the collection of quantitative measurement is very costly and time consuming. A conscious decision must be made regarding the allocation of resources across all the requirements associated with maintaining a comprehensive industrial hygiene program. The quality exposure assessment program should be a balance between quantitative measurements, modeling and qualitative judgments that all compliment and reinforce each other.

To support all the above decisions and determinations, a comprehensive exposure assessment strategy is needed such at the AIHA's® Exposure Assessment Strategy (the Strategy) that assesses all exposures, to all agents, for all workers. It is not usually that an IH must assess hundreds or even thousands of scenarios and that the scenarios can gradually change over time necessitating reassessments.

In Chapter 6, Approaches to Improving Professional Judgments, the authors present the results of formal studies that demonstrate even experienced IHs perform poorly when asked to properly assign the correct exposure control category (ECC) even when the IHs have quantitative measurements.(1,2) The IH's performance in making judgments can be improved significantly with training in the interpretation of quantitative measurements. When IH has no quantitative measurements, their ability to identify the correct ECC is near that expected by chance with the exception that they tend to under estimate exposures. The authors of Chapter 6 go on to present data that if IHs focus on a few basic determinants of exposure using a very discipline approach (Check List), the proper assignment of ECC can be made with a proficiency comparable to that achieved with quantitative data and training. Even when IHs have quantitative measurements it is important that the qualitative and semi-quantitative assessment methods be applied to evaluate and calibrate their professional judgments. In this way, knowledge and experience gleaned from situations where quantitative measurements are available can be used to improve their judgments when measurements are not available.

This chapter will expand upon the rules and guidelines presented in Chapter 6 and discuss other exposure determinants that can be used with more complex exposure scenarios such as those involving mixtures. Several case studies will be included to illustrate how to apply the rules and software (EXCEL spreadsheets) are provided to perform the calculations. The spreadsheets compliment the IC Checklist Tool but includes some features that are not in the Checklist Tool and also provides more flexibility to customize assessments when working on complex scenarios. The spreadsheets require a working knowledge of EXCEL whereas The Checklist Tool does not.

Chapter 6 presents three fundamental heuristics that have broad application. They include the Rule-of-Ten (ROT), the Vapor Hazard Ratio (VHR) and the Particulate Hazard Ratio (PHR). The ROT and the VHR apply to agents that are volatile, semi-volatile liquids, and a limited number of solids that have an appreciable vapor pressure at the conditions of interest. Exposure concentration is expressed in parts per million (ppm) or parts per billion (ppb). If two agents have the same exposure concentration (e.g., 100 ppm) they would both have the same number of molecules in a unit volume of air but if the agents had a different molecular weight, their mass per unit volume air would differ. Concentration expressed in ppm can be calculated using Equation 26.1.

Saturated Vapor Concentration (SVC) = [Vapor Pressure of the Agent in mm of Hg / 760 mm of Hg (atmospheric pressure)] * 1,000,000 (26.1)

For example if an agent has a VP = 10 mm of Hg, then the saturated vapor concentration

$$SVC_{Agent} = (10 \text{ mm of Hg} / 760 \text{ mm of Hg}) * 1{,}000{,}000 = 13{,}160 \text{ ppm} \quad (26.2)$$

For agents that are particulates, aerosols or fibers the PHR is used as the heuristic. The exposure metric is milligrams per cubic meter (mg/m^3) or micrograms per cubic meter (µg/m^3) and relate to mass being present rather than molecules.

Following is a discussion of each heuristic.

Rule-of-Ten (ROT)

The Rule-of-Ten correlates the fraction of saturated vapor pressure with the level of control and is summarized in the attached Table 26.1. The Rule of Ten is premised on the incremental reduction in the maximum potential airborne concentration of a volatile chemical resulting from incrementally higher levels of containment. For every step change in containment (through the use of engineering controls), the maximum concentration is reduced by an order of 10. The basis of the rule is empirical observation of exposure scenarios where quantitative measurements were available.

The fraction of saturation is an approximate of the 95th percentile. It should not be considered an absolute exposure level but rather provide the IH with a reasonable exposure estimate.

Table 26.1 – Rule of Ten

Level of Control	*Fraction of Saturation Vapor Concentration (SVC)*
Confined Space – Virtually no circulation	1/10th of Saturation
Poor – Limited Circulation	1/100th of Saturation
Good – General ~ 6 air turnovers/hr.	1/1,000th of Saturation
Capture	1/10,000th of Saturation
Containment	1/100,000th of Saturation

For example, benzene has a saturated vapor pressure at 25°C of 95.2 mm of Hg and atmospheric pressure is 760 mm of Hg. The saturated vapor pressure (VP) of benzene at 25°C is calculated in the following manner:

Saturated VP of Benzene =

$$(95.2 \text{ mm of Hg}/760 \text{ mm of Hg}) \times 1{,}000{,} 000 = 125{,}000 \text{ ppm benzene} \quad (26.3)$$

Therefore: If benzene were used in a room with good general ventilation, exposures would be expected on the order of 125 ppm. Most IH's who have worked with exposure scenarios associated with benzene know that benzene requires containment engineering controls to reduce exposures to the order of magnitude of the OEL (1 ppm PEL, OSHA, 0.5 ppm TLV®, ACGIH®).

In the case of another chemical methyl ethyl ketone (MEK), a common chemical used in solvents, paints, and coatings, has a vapor pressure of 89.7 mm of Hg (25°C), a value comparable to benzene. Analogous to the benzene example above, it can be shown to have a saturated vapor of 118,000 ppm. In this case good general ventilation would result in exposures on the order of 120 ppm which is below MEK's OELs (200 ppm, OSHA and ACGIH®). The Rule-of-Ten illustrates why MEK is acceptable in the solvents, paints, and coating applications where benzene is not.

The ROT is especially useful in situations where a formal OEL has not been established because the outcome of apply the rule is an estimate of exposure rather than the assignment of an ECC related to the OEL.

The ROT is a very good screening tool that can be applied very quickly for example as the exposure assessment portion of the chemical approval process.

Vapor Hazard Ratio (VHR)

The VHR is an indication of an agent's potential to exceed accepted levels. With vapors, the significance of exposure is related to both tendency for a material to vaporize and the level of concentration in the air that may cause harmful effects. The VHR is the measure of a PURE agent's ability to volatilize (expressed as vapor pressure) divided by the material's Occupational Exposure Level (OEL) expressed Equation 26.4.

$$\mathrm{VHR}_{\mathrm{Agent}} = \mathrm{VP}_{\mathrm{Agent}} / \mathrm{OEL}_{\mathrm{Agent}} \tag{26.4}$$

Where:

$\mathrm{VHR}_{\mathrm{Agent}}$ is the Vapor Hazard Ratio of Agent

$\mathrm{VP}_{\mathrm{Agent}}$ is the vapor pressure of pure Agent

$\mathrm{OEL}_{\mathrm{Agent}}$ is the occupational exposure limit of Agent

For example, benzene with a vapor pressure of 95.2 mm of Hg at 25°C and with a TLV® of 0.5 ppm which using Equation 26.4 results in a VHR of 190.

Vapor Hazard Ratio can be linked to a required level of control necessary to maintain exposure below (95th percentile) the agent's OEL. Table 26.2 associates ranges in VHR with the required level of control necessary to assure workers area acceptable. For convenience the ranges are numbered between 1 and 6.

Table 26.2 – Vapor Hazard Ratio Link to Ventilation

Vapor Hazard Ratio Scale	*Vapor Hazard Ratio (VHR)*	*Required Levels of Control*
1	< 0.05	General Ventilation ~ 3 to 6 air turnovers /hr.
2	0.05 to < 1	Good general ventilation ~ 6 to 12 air turnovers/hr. (GGV)
3	1 to < 25	GGV with capture at emission points
4	25 to < 500	Capture at points of emission with containment wherever practical
5	500 to < 3000	Containment
6	> 3000	Primary and Secondary Containment

The links between VHR and required level of control are based on empirical observations of exposure scenarios were quantitative measurements were available. Examples of the required ventilation for various agents based on their corresponding VHR include the following:

- MEK has a VP = 86.7 mm of Hg and an OEL of 200 ppm, VHR = 0.42 – requires good general ventilation ~ 6 to 12 air turnovers/hr. (GGV)
- Methylene chloride has a VP = 430 mm of Hg and an OEL of 25 ppm, VHR = 17.2 – requires GGV with capture at emission points
- Hexachlorocyclopentadiene (C56) has a VP= 0.06 mm of HG and an OEL of 0.01 ppm, VHR = 6 – requires GGV with capture at emission points
- Benzene has a VP = 95.2 mm of Hg and an OEL of 0.5 ppm, VHR=190.4 - Capture at points of emission with containment wherever practical
- Toluene has a VP = 28.4 of Hg and an OEL of 20 ppm, VHR=1.42 – GGV with capture at emission points

If two chemicals have the same VHR, they will require the same level of control to assure exposures are not excessive. The VHR can be thought of as the Rosetta Stone of IH. It allows the IH to use data from completely different chemicals to estimate exposure. Consider the following example illustrating the use of VHRs.

Example:

Assume that a plant has a good exposure assessment indicating that cyclohexane exposure is 25 ppm (95th percentile) in a specific process area. Cyclohexane's TLV® is 100 ppm and its vapor pressure at 25°C is 96.9 mm of Hg (VHR=0.96 corresponding to a vapor hazard ratio score of 2). If the plant would like to use MEK in the process instead of the cyclohexane, what MEK's exposure level will result with the substitution?

As indicated in an earlier slide MEK has a VP = 86.7 mm of Hg and an OEL of 200 ppm and therefor a VHR = 0.42.

1. Calculate the ratio of MEK and cyclohexane VHRs:
   $VHR_{MEK} / VHR_{Cyclo} = 0.42/0.96 = 0.44$ (26.5)
2. Calculate cyclohexane's exposure as a % of TLVcyclo:
   25 ppm/100 ppm = 25% (26.6)
3. MEK's has a lower VHR and therefore the % of TLV_{MEK} will be lower by the ratio of the VHR's [see (1) above]
   MEK's % TLV® = 25% * 0.42/0.96 = 10.9% (26.7)
4. MEK's expected exposure levels will be 10.9% of TLV_{MEK}
   MEK's Exposure Level = 10.9% * 200 ppm = 21.9 ppm (26.8)

It is not clear where the concept of Vapor Hazard Ratio was first formulated. Popendorf (3) defined the terms Vapor Hazard Ratio (VHR) and the log (VHR) as Vapor Hazard Index (VHI) in 1984. Dunham, et al.(4) used the VHI in an exposure assessment used to establish priorities. Popendorf used VHI in a hazard rating scheme used to evaluate suitable solvent substitutes and Stenzel(5) used VHR in a semi-quantitative exposure assessment rating scheme along with level of control and frequency and duration of tasks to classify exposure into strata defined as a fraction or multiple of the OEL. Stenzel use of the VHR concept was based on an analogous concept called an odor index which is defined as agent's vapor pressure divided by the agent's odor threshold.(6)

There are some complex exposure scenarios that require additional steps to determine the VHR or apply the ROT. These scenarios include mixtures, processes at non-ambient conditions and pressures, polymers, chemicals undergoing chemical decomposition and will be discussed later in this chapter.

Particulate Hazard Ratio (PHR)

With agents that generate airborne particulates, aerosols or fibers the appropriate heuristic is the potential hazard ratio rather than the VHR. The exposure metric is milligrams per cubic meter (mg/m^3) or micrograms per cubic meter (μg/m^3) and relates to the mass of agent or number of particles per unit volume of air rather than molecules (ppm) per unit volume used with the VHR.

$$\text{PHR} = \text{WT }\%/\text{OEL (mg/m}^3\text{)} \tag{26.9}$$

For pure materials, the WT % is equal to 100. When comparing two chemicals, the chemical with the highest PHR is considered to be the more significant hazard.

Table 26.3 – Particulate Hazard Ratio Link to Ventilation

Potential Hazard Ratio (PHR) Scale	*Agent's OEL Range (mg/m3)*	*Required Levels of Control*
1	> 5	General ventilation ~ 2 to 4 air turnovers/hr.
2	≤ 5 to 1	Good – General + fans ~ 4 to 6 air turnovers/hr.
3	≤ 1 to 0.1	Good – General + fans ~ 6 to 8 air turnovers/hr.
4	≤ 0.1 to 0.01	Capture at points of emission with containment wherever practical
5	≤ 0.01 to 0.001	Containment
6	≤ 0.001	Primary and Secondary Containment

The basis of the PHR is the potency ranges used with Performance-Based Exposure Control Limits related to pharmaceutical active ingredients published by Naumann.(7) The concepts presented by Naumann have broad application beyond the pharmaceutical industry.

An adjustment is made to the Table 26.3 if the agent is dustiness. Dustiness is related particle size, shape, electrostatic charge, moisture content and material density which results in a stable dust or aerosol in air. That is, the dust or aerosol particles do not easily settle out. A technical discussion of dustiness can be found in a NIOSH study (ECTB 154-11a [1986]) reported Cooper.(8) As a simple rule-of-thumb, the author recommends that if an agent has very fine dust droplet size the required engineering control should be increased one level. For example, is an agent had a PHR Scale value of 3, the recommended controls would be assigned as if it had PHR Scale value of 4.

Vapor Pressure (VP)

The agent's vapor pressure is used to calculate the ROT and VHR. Vapor pressures are temperature dependent. Typically VPs are reported at a standard temperature of 25°C. In adjusting the VP for temperature, the temperature of concern is the temperature of the parent liquid and not the ambient air. For example, if a worker is degreasing parts using a degreasing bath at 35°C in a room at 25°C, the VP used in the calculation of the ROT and VHR is the VP at 35°C. Considering that process temperatures are commonly not at ambient temperatures, there is a need to calculate VPs at temperatures other than those reported at 25°C.

The two most common ways to calculate vapor pressures are the Antoine's Equation and the Clausius-Clapeyron Equation.

A very good source of chemical and physical property data is the Hazardous Substance Data Bank (HSDB) located in TOXNET which is available free and maintained by NIH, U.S. National Library of Medicine (http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm).

Antoine's Equation

The relationship of VP with temperature using Antoine's Equation is defined below:

$$\log_{10}(p) = A - (B / (t + C)) \tag{26.10}$$

p = vapor pressure (mm of Hg)

t = temperature (°C)

A, B & C are constants unique to each chemical

An EXCEL spreadsheet, named Antoine-template.xls, has been provided with the constants for various materials to assist in the calculations. The spreadsheet can be updated to include other chemicals whose constants can be found in handbooks of chemistry and physics. Also, the Checklist Tool located on the AIHA® Exposure Assessment Strategy Committee (EASC) website that also provides the capability to calculate vapor pressures at non-ambient conditions using Antoine's Equation.

Clausius-Clapeyron Equation

If Antoine's constants are not available, an estimate of the vapor pressure can be made using the Clausius-Clapeyron Equation. This equation states that plotting $\log_{10}(p)$ vs. 1/T results in a straight line with the equation:

$$\log_{10}(p) = m(1/T) + C \tag{26.11}$$

Where:

p = vapor pressure in mm of Hg

T = temperature in degrees Absolute (K)

m = slope of the line

c = intercept of the line

If the VP is known at two points, the slope and the intercept of the line can be determined and used to calculate the VP at any other temperature. One point that can be used is the reported VP in HSDB (typically reported at 25°C). The second point that can be used is the substance boiling point. The VP of a substance at its boiling point is 760 mm of Hg. Occasionally for very high boiling substances, a boiling point is reported at a reduced pressure. For example, the HSDB may report a boiling point of 100°C at 200 mm of Hg. In this case, 200 mm of Hg at 100°C is the second point. An EXCEL spreadsheet named Claus.-Clap.-template.xls has been provided to calculate the slope of the line and the vapor pressure at any desired temperature. A problem set with answers has been provided in the supplemental materials (VP-Problem Set 1-Answers .doc) along with the corresponding EXCEL spreadsheets (VP-Set-1-SS.xls) to illustrate the use of the VP spreadsheets.

A 3rd way to estimate VP is with a simple rule of thumb which is useful but only over rather narrow temperature ranges and should be considered a crude estimate. The rule is that the VP pressure doubles with every 10°C increase in temperature. That is, if an agent's has vapor pressure of 100 mm of Hg at 25°C its VP would be approximately 200 mm of Hg at 35°C.

Mixtures

It is very common for exposure scenarios to involve mixtures rather than only pure materials. The ROT, VHR and PHR heuristics are still applicable but added calculations are necessary to determine each components new vapor pressure. In mixtures, the VP associated with each component is lower than the VP observed in pure liquids. In non-aqueous solutions, the adjusted VP for each component can be determined applying Raoult's Law and in aqueous solutions, the adjustment is made using Henry's Law. EXCEL spreadsheets are attached along with instructions and case studies to illustrate the use of Raoult's or Henry's Laws in determining adjusted vapor pressures.

Raoult's Law

The vapor pressure of any specific component of a mixture is decreased in proportion to the mole fraction of each specific component in the mixture. The following equation expresses the relationship.

$$P_A = X_A * P^0_A \qquad (26.12)$$

Where:

P_A is the vapor pressure of Component A over the solution

X_A is the mole fraction of Component A in the mixture, and

$_A$ is the vapor pressure of the pure Component A at 25°C

Raoult's Law assumes ideal gas behavior. That is, the forces between all molecules (same component and different components) of the mixture are the same. There are situations where this is not true. Reinke[(9)] includes a discussion of situations where Raoult's does not hold and provides guidance to address the deviation.

The adjusted vapor pressure from the Raoult's Law equation for each component can then be used to calculate the corresponding VHR of the component and to apply the ROT. An EXCEL spreadsheet titled "Mixture Template – Raoult's Law" is provided that can be used to complete all the calculations.

Consider a mixture with the following composition:

Table 26.4 – Mixture Example

Chemical Components	*Weight Percent (WT %)*
Toluene	40
Xylene	20
Ethyl acetate	20
Benzene	2
Methylene chloride	3
Carbon tetrachloride	15

Table 26.5 presents the pertinent columns from the Mixture – Template Raoult's Law.

Table 26.5 – Mixture Example Calculations Using Raoult's Law

		A	B	C	D	E	F	G	H	I
CAS	Chemical	WT (%)	OEL (ppm)	MW	VP mm of Hg	moles	Mole Fraction	Adjusted VP	Adjusted VHR	VHR %
Number		MSDS	look up	look up	look up	A/C	E/total E	F* D	(G/B)	(H/Max H)* 100
108-88-3	toluene	40	20	92.1	28.4	0.434	0.431	12.229	0.611	12.70%
106-42-3	xylene	20	100	106.2	8.74	0.188	0.187	1.632	0.016	0.34%
141-78-6	ethyl acetate	20	400	88.1	93.2	0.227	0.225	20.977	0.052	1.09%
71-43-2	benzene	2	0.5	78.1	94.8	0.026	0.025	2.407	4.814	100.00%
75-09-2	methylene chloride	3	25	84.9	435	0.035	0.035	15.239	0.610	12.66%
56-23-5	carbon tetrachloride	15	5	153	115	0.098	0.097	11.178	2.236	46.44%
	Total	*100.0*				*1.009*	*1.000*	*63.662*	8.339	

The following steps should be followed to use the spreadsheet. Columns are lettered in red for reference.

The third row of the Table is also in and indicates where data are found or the formula used to obtain the value in the column.

- The IH must complete the cells in pink.
  - The components name and WT (%) [Column A] can be found on the mixtures SDS
  - The CAS Number is optional but very useful information. Many chemicals have very similar names and the same chemical may have multiple valid names. The CAS number is a unique identifier and databases such as HSDB can be searched by CAS number.
  - The information in Columns B, C and D may be on the SDS but sometimes the quality of the SDS data is questionable. The author strongly recommends that the IH use the HSDB located in TOXNET mentioned above.
- The number of moles (Column E) is determined by dividing the WT % by the components MW. For simplicity, it is assumed that there is 100 grams of mixture which will result in the WT % being equal to the number of grams of each component.
- The number at the bottom of column E (1.009) is the total number of moles in the mixture.
- The mole fraction in Column F is then determined by dividing each components number of moles by the total number of moles.
- The Raoult's Law is calculated in Column G. It is obtained by multiplying the mole fraction in Column F and the VP of the pure component found in Column D.
- Column H contains the VHR as described in the VHR section above with the exception that the Raoult's Law adjusted VP is used for the component of the mixture. The number in red at the bottom of the column (8.339) is the total of the individual VHR of the mixture.

- Column I contains the VHR %. The VHR% indicates which VHR is the highest (100%) and the relative percentage of each other VHR in the mixture. The component that has the VHR % equal to 100% is considered the controlling component.

Controlling Component

The controlling component of a mixture is the component that will have the greatest likelihood to exceed its corresponding OEL. In this case benzene is the controlling component. If benzene exposures are known (for example an exposure of 0.5 ppm, benzene's OEL), then the concentration of each other component can be calculated using the VHR % in Column I. For example, in this mixture the carbon tetrachloride VHR % is 46.4%. This means that if carbon tetrachloride exposures were measured, they would be observed to be approximately 46.4% of its OEL of 5 ppm or 2.32 ppm. If the exposure of at least one component of a mixture is measured, the IH can calculate the exposure levels of the other components. This will likely reduce the cost of monitoring because not all components of a mixture need to be monitored. Another feature is cases where a specific component is very difficult to analyze. The IH can instead select a surrogate component to measure that requires simpler analytical procedures. Finally, the example shows that the components of the mixture in greatest concentration (WT %) may not, from an exposure perspective, be the components of concern. Every component of the mixture (except benzene) would likely be adequately controlled with good general ventilation. Significant exposure could have been missed by the IH if they only considered the components of the mixture in highest WT % concentrations.

Table 26.6 is generated in the Mixture Template – Raoult's Law worksheet. It presents the expected exposure for each component of the mixture associated with each level of control.

Note that even though the mixture only contains 2% benzene, the ROT indicates that capture ventilation is needed to assure that exposures to all components of the mixture are properly controlled. This is consistent with the Adjusted Total VHR (8.339) in Table 26.5 which has a VHR Scale = 3.

Table 26.6 Mixture Example Calculations – Rule of Ten

			Degree of Ventilation – Concentration in ppm					
Chemical Information	**OEL ppm**	**VP Corrected mm Hg**	**Sat. VP**	**Very Limited**	**Poor**	**Good**	**Capture**	**Containment**
toluene	20	12.229	16090.57	1609.06	160.91	16.09	1.61	0.16
xylene	100	1.632	2147.19	214.72	21.47	2.15	0.21	0.02
ethyl acetate	400	20.977	27600.86	2760.09	276.01	27.60	2.76	0.28
benzene	0.5	2.407	3166.94	316.69	31.67	3.17	0.32	0.03
methylene chloride	25	15.239	20051.90	2005.19	200.52	20.05	2.01	0.20
carbon tetrachloride	5	11.178	14707.89	1470.79	147.08	14.71	1.47	0.15

Henry's Law

As stated above Raoult's Law assumes ideal gas behavior. That is, the forces between all molecules (same component and different components) of the mixture are the same. This is not the case with polar molecules especially aqueous solution. The water molecules are attached to specific portions of the molecules of various chemicals in solution. For these solutions, Henry's law is used to calculate the adjusted vapor pressures.

$$P = k_H * c \qquad (26.13)$$

Where:

P = the partial pressure of the chemical in water above the liquid

k_H = the Henry's constant to a specific chemical

c = is the molar concentration of the chemical in the water solution.

Consider a mixture that is made up of 10% methanol and 5% acetone in water.

The adjusted vapor pressure from Henry's Law equation for each component can then be used to calculate the corresponding VHR of the component and to apply the ROT. An EXCEL spreadsheet titled "Mixture Template – Henry's Law" is provided that can be used to complete all the calculations. Table 26.7 provides pertinent columns of the Henry's Law spreadsheet.

Table 26.7 – Mixture Example Calculations Using Henry's Law

		A	B	C	D	E	G	H	I	J
CAS	Chemical	WT (%)	OEL (ppm)	MW	k_H (atm*L/mol)	Molarity (mol/L)	Adjusted VP (mm of Hg)	Adjusted VHR	VHR %	Henry's Law Constant (k_H) [atm*m^3/mol]
Number		MSDS	look up	look up	J*1000	(A*10)/C	D*E*760	(G/B)	(H/Max H)* 100	
67-56-1	Methanol	10.00	200	32.04	4.55E-03	3.121	10.793	0.054	51.94%	4.55E-06
67-64-1	Acetone	5.00	250	58.08	3.97E-02	0.861	25.975	0.104	100.00%	3.97E-05
7732-18-5	Water	85.00	10000	18	8.41E-06	47.222	0.302	0.000	0.03%	8.41E-09
	Total	*100*				*51.2042*	*37.0691*	*0.158*		

The following steps should be followed to use the spreadsheet.

- As with the Raoult's Law spreadsheet, complete the cells in pink. The Henry's Law constants can usually be found in the HSDB located in TOXNET. Note that these constants can be expressed in various units. Typically the units in the reference are expressed in atm*m^3/mole.
- This spreadsheets requires the units of Henry's Law constant to be expressed atm*L/mole. The conversion of the constant to required units in Column D by multiplying the values in Column J times 1000.
- Molarity (Column E) is calculated from the WT %. Water weights 1 gram per milliliter and therefore 1000 grams are needed to have a total volume of one liter. Again, if it is assumed that there is 100 grams of the mixture, the weight percent is equal to the number of grams of the component in 100 grams. The molarity in Column E is then calculated by multiplying the WT % in Column A by 10 and then dividing by the MW in Column C.
- The adjusted vapor pressure is calculated by multiplying Column D (Henry's Law constant) by Column E (Molarity) by 760 (converts atmospheres to mm of HG).
- The VHR Column H and VHR % are calculated in the same manner used in the Raoult's Law spreadsheet.

Note that acetone is the controlling component even though its composition is less than that of methanol. The adjusted VHR of 0.158 corresponds to Vapor Hazard Ratio score of 2 (good general ventilation).

The Rule-of-Ten provided in Table 26.8 looks the same as that discussed in the Raoult's Law section.

Table 26.8 Mixture Example Calculations – Rule of Ten

			Degree of Ventilation – Concentration in ppm					
Chemical Information	**OEL (ppm)**	**Adjusted VP mm of Hg**	**Sat. VP**	**Very Limited**	**Poor**	**Good**	**Capture**	**Containment**
Methanol	200	10.793	14201	1420.10	142.01	14.201	1.420	0.142
Acetone	250	25.975	34177	3417.70	341.77	34.177	3.418	0.342
Water	10000	0.302	397	39.71	3.97	0.397	0.040	0.004

Table 26.8 indicates that good general ventilation is adequate to control exposure but if the actual ventilation were poor, there would be a problem with acetone exposure.

Henry's Law constant is temperature dependent. A detailed discussion of this temperature dependence is beyond the scope of this chapter but an approximation method is provided. Henry's Law constants are usually reported at 25°C. For mixtures at less than 80°C, a reasonable estimate of Henry's Law constant for a specific chemical can be calculated using the following equation.

$$\boldsymbol{k}_{\mathrm{H(new\ temperature)}} = \boldsymbol{k}_{\mathrm{H(25°C)}} * (\mathrm{VP}_{\mathrm{(new\ temperature)}} / \mathrm{VP}_{\mathrm{(25°C)}}) \quad (26.14)$$

Where:

$\boldsymbol{k}_{\mathrm{H(new\ temperature)}}$ is the Henry's Law constant at the new temperature

$\boldsymbol{k}_{\mathrm{H(25°C)}}$ is the Henry's Law constant at 25°C

$\mathrm{VP}_{\mathrm{(new\ temperature)}}$ is the vapor pressure of the chemical at the new temperature

$\mathrm{VP}_{\mathrm{(25°C)}}$ is the vapor pressure of the chemical at 25°C

Special Cases where Raoult's Law or Henry's Law are not applicable.

Some agents or mixtures are not stable and a chemical reaction (or decomposition) occurs that results in a new agent not present in the original pure material or mixture. There are rules to address these situations but they require a rather detailed understanding of the chemistry involved. The authors recommend that the reader consult with technical experts such as chemists or engineers to gain an understanding of the emission characteristics and then use modelling tool such as those provided in IHMOD to develop exposure estimates.

Another case is when molecules have agent molecules entrapped in a structure such as a polymer. In this case, the entrapped chemical and the polymer are not a mixture. In many cases the manufacturer of the product will provide emission (or off gassing) rates. Again, it is best to use these rates to estimate exposures with IHMOD. It should be noted that the percent of chemical in the polymer does not limit the amount of vapor in the headspace. The chemical vapor concentration in the headspace from the off-gassing process will continue to increase until the chemicals saturated vapor pressure is reached. This can be of critical importance if there is a need for a worker to enter the headspace of a tank containing this polymer. A polymer with an entrapped chemical even at the ppm level can result in a very high exposures. Another concern can be that of an explosion. If the agent has a lower explosive limit (LEL) below the concentration in the headspace, static electricity could trigger an explosion. Typically most chemicals have LELs on the order of 1% or about 10,000 ppm.

Finally, there is the situation where a mixture may layer. The composition of the top layer is controlling the chemical concentration in air. This can happen when the components have a low solubility in the parent material such as the case of benzene in water. It is not unusual that the components are miscible to begin with then due to process conditions or reactions, the mixture layers.

Particulates, Aerosols and Fibers

Mixtures of particulates or aerosols or fibers relate to the weight percent of each component in the mixture. For example, if the total particulate is measured for a mixture and the mixture has a component that is 50%, then 50% of the total particulate result can be attributed to the component.

The controlling component is the component that results in the highest PHR value (see Equation 26.9).

As is the case with the vapor pressure spreadsheets, problems sets with answers are provided in chapter supplementary materials to illustrate the use of both the Mixture Template for Raoult's Law and Henry's Law. The Worksheets have added functionality that is not discussed here including the impact of mixtures on the interpretation of direct reading instruments measurements.

Other Determinants of Exposure

The practicing IH is likely to know and understand the issues described below. But they are mentioned in the context of Chapter 6, where a check list approach assures that they are being considered at the appropriate time in the decision making process.

Quantity

It seems intuitive that quantity should be factored into the assessment but this is not always the case. For example, if a worker is sampling a 1000 gallon reactor through a 2 foot diameter hatch or if he is sampling 100 gallon reactor through a 2 foot hatch the exposure will be the same even though the larger reactor may have a much larger quantity of material present. Another issue related to quantity is the type of packaging. Adding five 40 pound bags (200 lbs) of paraformaldehyde to a reactor may result in more exposure than adding the paraformaldehyde via a 1000 pound supper sack. With this example there is also potential exposure with disposing of the bags. Another case is sampling a process. The worker may be only catching a few ounces of material, but one also needs to take into consideration, how many times was the sample bottle rinsed to assure a good sample and where did the worker pour the rinse.

Pressure

The ROT and VHR are based on the material diffusing into the breathing zone that is pressure neutral. In some situations such as filling a drum, air from the headspace is forced out of the vessel into the breathing zone. This pressuring effect could exceed the ventilations capacity to dilute the concentration to acceptable levels. This same type of situation can occur when a volatile material is being added to reactor that already contains materials at elevated temperatures. As soon as the added material hits the hot surface of the existing material in the reactor, it will immediate try to reach its vapor pressure at the new temperature which has the effect of pressuring vapor out of the reactor hatch and into the workers breathing zone. In these cases capture or containment will likely be needed to adequately control exposures.

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Edited by
Steven D. Jahn, CIH, MBA
William H. Bullock, DHSc, CIH, CSP
Joselito S. Ignacio, CIH, CSP, MPH, REHS/RS

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American Industrial Hygiene Association
3141 Fairview Park Drive, Suite 777
Falls Church, VA 22042
Tel.: (703) 849-8888
Fax: (703) 207-3561
http://www.aiha.org
e-mail: infonet@aiha.org