Use of the Reciprocal Calculation Procedure for Setting Workplace Emergency Action Levels for Hydrocarbon Mixtures and their Relationship to Lower Explosive Limits

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This paper proposes a novel use of the reciprocal calculation procedure (RCP) to calculate workplace emergency action levels (WEALs) for accidental releases of hydrocarbon mixtures. WEALs are defined here as the concentration in air that area monitors should alarm at to provide adequate warning and be sufficiently protective of health to allow at least enough time to don respiratory protective equipment (RPE) and escape. The rationale for the approach is analysed, and ways of defining suitable substance group guidance values (GVs) for input into the RCP are considered and compared. WEAL GVs could be based on: $3 \times$ RCP GVs (i.e. using the $3 \times$ rule), the $5 \times$ RCP GVs (i.e. using the $5 \times$ rule for calculating ceiling values), emergency exposure limits, or immediately dangerous to life or health values (IDLHs). Of these, the method of choice is to base WEAL GVs on health-based IDLH values, which were developed for emergency situations in the workplace. However, IDLHs have only been set for 11 hydrocarbons, so the choice of GVs is also informed by comparison with possible GVs based on the other approaches.

Using the proposed GVs, WEALs were calculated for various hydrocarbon mixtures, and the way they vary with the composition of the mixture was examined. Also, the level of health protection given by the current practice of setting emergency area alarms in the oil and gas industry at 10% of the lower explosive limit (LEL) was tested by comparing this with the WEAL. In the event of an accidental release, this comparison suggests that, provided that aromatics constitute <50% of the mixture, an alarm set at 10% LEL should provide adequate warning and be sufficiently protective of health to allow at least enough time to don RPE and escape.

In the absence of better information or specific acute toxicity concerns (such as the presence of hydrogen sulphide), it is proposed that the WEALs be used as a guide for assessing the adequacy of area alarm levels in respect of warning of an acute health risk. This work is exploratory (e.g. other rationales for setting GVs are possible) and the approach needs testing on further real-life samples. Although not explored here, the RCP approach may also lend itself to the calculation of in-house short-term exposure limits for hydrocarbon mixtures and other mixtures where the acute toxic end points of the components are similar.

Keywords: alarms; emergency; hydrocarbons; LEL; reciprocal calculation procedure

INTRODUCTION

Hydrocarbons and hydrocarbon mixtures are commonly encountered in upstream and downstream processes in the oil and gas extraction and production industry. Fatalities from acute over-exposure have occurred from accidents in industrial settings and purposeful solvent sniffing for recreational purposes. Concern was raised again in the UK Oil and Gas industry following the death of two workers on an offshore installation in 2003.
However, toxicity is not generally used as a lead risk when designing area monitoring and setting emergency alarm levels to warn of hydrocarbon releases in the oil and gas sector, except where ‘sour’ streams containing hydrogen sulphide are present or where individually toxic materials, such as benzene, are concentrated. Instead, because hydrocarbon mixtures are generally highly flammable, the lead risk is that of fire and explosion, and monitoring methods for emergency alarms are usually defined by reference to the lower explosive limit (LEL). In accordance with Health and Safety Executive (HSE) guidance (HSE, 2004), the lowest alarm level for leak detection purposes is typically set at no more than 10% LEL (based on some calibration gas). However, it is not clear how well such area alarms are protective of human health nor is there any currently agreed way of setting health-based alarms for mixtures of hydrocarbons.

To be practicable, any method of setting general area alarms to protect against the acute toxic effects of hydrocarbons needs to align with the fact that fire and explosion risks are likely to continue to be a dominant feature in the petroleum industries.

It is argued here that an adaptation of the reciprocal calculation procedure (RCP) (HSE, 2005) is a pragmatic way of deriving in-house health-based workplace emergency action levels (WEALs) for mixtures of hydrocarbons. For this paper, WEALs are defined as the air concentration at which area monitors should alarm to provide adequate warning, and be sufficiently protective of health, to allow at least enough time to don respiratory protective equipment (RPE) and escape. This paper gives the rationale for such use of the RCP, applies the procedure to calculate WEALs for various hydrocarbon mixtures, and explores how these vary with composition. Further, by comparing these WEALs with 10% LELs for mixtures, it tests the level of health protection given by the current practice of setting area emergency alarms on this basis.

THE ACUTE TOXICITY OF HYDROCARBONS AND THEIR MIXTURES

To give context to the rationale for using the RCP for defining emergency alarm levels, the acute toxicity of hydrocarbons needs to be considered.

Background

The toxicity of individual hydrocarbons and mixtures has been reviewed many times and for a variety of reasons, including providing general reviews of toxicity and hygiene aspects (examples include Amoruso et al., 2008; Cavender, 1994a,b,c); setting occupational exposure limits (OELs) in the workplace (NIOSH, 1977a,b; ACGIH, 2009); unusual situations, such as spacecraft (McCoy, 2008; Wong, 2008) and submarines (NRC, 2008); setting emergency exposure limits (EELs) to protect populations in major emergencies (Cavender, 2006; ECETOC, 2006; Rusch, 2006; SCAPA, 2010); and setting immediately dangerous to life and health limits (IDLHs) (NIOSH, nd).

General acute toxicity

Although hydrocarbons have relatively low acute inhalational toxicity, several general trends are apparent:

- For straight chain alkanes, concentration of inhaled chemical that kills 50% of the exposed population (LC50s) fall (Cavender, 1994a) and anaesthetic potency increases (Liu et al., 1993; Fang et al., 1996) with increasing chain length. This trend in increasing toxicity is ultimately limited by decreased volatility and the fact that higher molecular weight alkanes do not easily pass the blood-brain barrier (Nilsen et al., 1988; Salvayre et al., 1988).

- Branched alkanes appear to be less potent than corresponding straight chain isomers; however, the data are limited and the observations mixed (Cavender, 1994a). Branched alkanes with approximately C10–C15 carbons (so-called isoparaffins) are practically non-toxic by oral, dermal, and inhalation routes (Mullin and Ader, 1990).

- Acute toxicity and anaesthetic potency of cycloalkanes increases with molecular weight and branching (Henderson and Johnston, 1931; Henderson and MacDonald, 1937; Cavender, 1994b; Fang et al., 1996).

- Aromatic hydrocarbons are more acutely toxic (Bruckner and Peterson, 1977) and have greater anaesthetic potency (Liu et al., 1993; Fang et al., 1996) than alkanes or cycloalkanes containing the same number of carbon atoms. These properties increase with molecular weight in the aromatic series but the increase is not as marked as for the alkanes (Furnas and Hine, 1958; Cavender, 1994c; Fang et al., 1996).

- Acute toxicity of saturated and aromatic hydrocarbons is essentially additive (see below).

Observations on effects at concentrations below those causing anaesthesia or death, though fewer in number and more subjective, tend to follow the same pattern. Examples include the concentrations of
alkanes, cycloalkanes, and aromatics causing loss of the righting reflex in rodents (Fuhner, 1921; Lazarow, 1929; Stoughton and Lamson, 1936) fall with increasing molecular weight and the concentration of aromatics needed to induce ‘marked’ motor activity in rats also falls with increasing molecular weight (Molnar et al., 1985).

**Acute effects of hydrocarbons significant for setting WEALs**

In acute/emergency situations, inhalation is usually the major route of exposure, so, for detection and warning purposes airborne concentrations are of interest. However, if an exposed individual’s clothing is wetted by the hydrocarbons released, this may provide a significant source of both inhalation and percutaneous exposure.

Particularly important are toxic effects that occur rapidly (i.e. over minutes) and which may be IDLH or impede the ability to escape. Hydrocarbon vapours have four such acute effects: asphyxiation, central nervous system (CNS) toxicity, cardiotoxicity, and upper respiratory tract and other sensory (eyes, nose) irritation.

**Asphyxiation.** At high concentrations, volatile hydrocarbons can act as simple asphyxiants by displacing oxygen in the air. Indeed, the gaseous alkanes methane to butane were historically regarded as simple asphyxiants so no OELs were set for them. However, even these may have significant physiological effects at concentrations that are unlikely to cause asphyxiation (Drummond, 1993) and various authorities have now set OELs for alkanes in the range methane to n-butane (e.g. ACGIH, 2009; HSE, 2005).

**CNS toxicity.** Inhalation of hydrocarbon vapours can induce CNS toxicity. Depending on the substance, the exposure concentration and the period of exposure, symptoms range from subtle behavioural effects, through headache, lassitude, ’intoxication’ (which can include giddiness, inappropriate behaviour, excitability, vertigo, nausea, confusion, and delirium) to stupor/unconsciousness and, if not removed from exposure, death by respiratory or cardiac arrest. This constellation of effects is apparent across a range of species, including mammals and rodents (Cavender, 1994a,b,c; ACGIH, 2009) and even insects, such as fruit flies (Allada and Nash, 1993). Some hydrocarbons, particularly aromatics such as benzene (IPCS, 1999), have both excitatory and depressive CNS effects. Onset of CNS effects can be very rapid, and the risk in emergency situations can be exacerbated because the early ‘intoxication’ symptoms can impair self-rescue.

**Cardiotoxicity.** Some hydrocarbons sensitize the myocardium to endogenous adrenaline (Nahum and Hoff, 1934; Chenoweth, 1946; Krantz et al., 1948; Reinhardt et al., 1971; Clark and Tinston, 1973; Aviado et al., 1977), including the induction of cardiac arrhythmias, ventricular tachycardia, and cardiac arrest. Cardiotoxicity has been implicated in sudden deaths that have occurred during the intentional inhalation of very high concentrations of hydrocarbon solvents for recreational purposes (Ramsey et al., 1989). Similar effects could occur in emergency situations where high exposure is accompanied by stress and exercise, and perhaps hypoxia, leading to an increase in adrenaline production. CNS effects occurring below such concentrations may also impede the ability to escape.

Clark and Tinston (1973) noted that the more potent a chemical’s CNS effects the more potent it is in causing cardiac sensitization. They also concluded that cardiac sensitization is unlikely to occur in man in the absence of CNS effects so that symptoms, such as dizziness, could act as a warning.

**Respiratory tract and other irritation effects.** As judged by body movements, respiratory changes observed in mice exposed to alkanes correspond to sensory irritation, which increases in severity and sensitivity with increasing carbon chain length (Swann et al., 1974; Kristiansen and Nielsen, 1988). n-Heptane’s RD50 (vapour concentration that depresses respiration rate of mice by 50%) is 17 400 p.p.m. (72 300 mg m⁻³ at 20°C). n-Heptane is the only straight chain alkane in the range C7–C11 that induces sufficient sensory response to reduce respiration by 50% relative to controls (Kristiansen and Nielsen, 1988).

There is little information available on the cycloalkanes, though cyclohexane is described as ‘somewhat’ irritating to the eyes and nose (ACGIH, 2009).

The aromatics are more significant irritants than the alkanes, and their effect increases with molecular weight, e.g. from toluene to n-hexylbenzene the RD₅₀ falls from over 3000 p.p.m. (11 471 mg m⁻³ at 20°C) to ~126 p.p.m. (848 mg m⁻³ at 20°C) (Toxnet, nd). To put these RD₅₀ values into context, the RD₅₀ for ammonia, chlorine, and acrolein in the mouse are reported to be 303, 2.3, and 1.7 p.p.m., respectively (Toxnet, nd). The hydrocarbons are comparatively mild irritants, except for aromatics with side chains longer than C5 that have RD₅₀ around that of ammonia, however, the former are liquids with relatively low vapour pressure while ammonia is a gas.

**Lead toxic effects of hydrocarbons for setting WEALs.** Of the acute effects discussed above, CNS
toxicity is probably the most significant in emergency situations for the following reasons:

- CNS effects impeding escape will occur well below the concentrations necessary for asphyxiation or cardiotoxicity and, in some situations, early CNS effects may act as warnings. Furthermore, it is conservative to assume that the risk to the CNS may escalate rapidly. This assumption is supported by the observation that the dose–response for anaesthesia is steep for some hydrocarbons (Stoughton and Lamson, 1936), solvents (HSE, 1993, 1994), and inhalational anaesthetics (De Jong and Eger, 1975).

- Although irritants can impede escape, the sensory irritating effects of most hydrocarbons are of a relatively low order and tend to encourage the desire to escape. Irritation becomes more significant with increasing aromatic content, but many mixtures encountered in the hydrocarbon industry are relatively low in aromatics.

THE RCP

The British HSE recommends the RCP for determining ‘in-house’ OELs for vapours of mixed hydrocarbon solvents (HSE, 2005). The suitability of this method has been intensively studied (ECETOC, 1997; McKee et al., 2005).

Using the RCP, the 8-h time-weighted average (TWA) OEL for a mixture is calculated as:

\[
\frac{1}{\text{OEL}_{\text{mix}}} = \frac{\text{FR}_1}{\text{OEL}_1} + \frac{\text{FR}_2}{\text{OEL}_2} + \frac{\text{FR}_3}{\text{OEL}_3} + \ldots + \frac{\text{FR}_n}{\text{OEL}_n},
\]

where

- OEL\(_{\text{mix}}\) is the OEL for the mixture in milligrams per cubic metre
- FR\(_n\) is the fraction (w/w) of component \(n\) in the mixture i.e. \(\text{FR}_n = [\% \text{ of component } n \text{ by weight}] / 100\)
- OEL\(_n\) is the OEL or defined guidance value (GV) of component \(n\) in milligrams per cubic metre

Since it is likely that not all the components will have OELs, HSE (2005) recommends the following way of assigning GVs:

(a) divide hydrocarbons into discrete groups based on structural similarity and critical health effects;
(b) exclude from these groups compounds with specific toxicity concerns (e.g. \(n\)-hexane and benzene) for which the relevant OELs [workplace exposure limits (WELs) in the UK] should be used; and (c) assign GVs to these groups which can then be used in the RCP.

RATIONALE FOR USING THE RCP FOR CALCULATING WEALs

Application to acute effects

The additive equation was originally applied to the frequency of acute effects, such as LC\(_{50}\) (e.g. by Bliss, 1939), so there is no a priori reason why the RCP approach should not be applied to acute toxicity.

Additive effects of the acute toxicity of hydrocarbons

Acute CNS effects are considered to be additive (McKee et al., 2005), for example the potency of inhalational anaesthetics is generally additive (Eger et al., 2008). In the case of hydrocarbons, the correlation between alkanes’ anaesthetic potency and their octanol air partition coefficients is consistent with their anaesthetic effects being additive in a simple linear manner (Hau et al., 2002).

A theoretical study of additive and synergistic effects, with respect to anaesthetic mechanisms, concluded that additivity can be expected to result from drugs’ competition for a common receptor site or when drugs acting on different receptors are at concentrations much less than that associated with 50% receptor occupancy (Schafer et al., 2008). The latter may be the case for sub-narcotic CNS effects of hydrocarbons.

It is therefore reasonable to consider the acute CNS toxicity of hydrocarbons as additive, even at sub-narcotic concentrations, and hence that the RCP approach is applicable.

Interactions between hydrocarbons in mixed exposures

The most commonly observed interactions under experimental conditions are inhibition of metabolism and/or induction of metabolizing enzymes (McKee et al., 2005). However, the possibility of multiplicative (synergistic) effects between hydrocarbons is considered to be unlikely at the relatively low exposure levels typical in the occupational setting and hence not significant in the context of the RCP for 8-h TWA OELs (ECETOC, 1997; McKee et al., 2005).

Although exposures during an acute or emergency episode are potentially much higher than typical workplace exposure, the speed with which a hydrocarbon gas or vapour, and indeed other solvents, induce CNS effects suggests the involvement of the
compound rather than a metabolite. This, together with the fact that compounds will be competing for the same active, or range, of sites, suggests that multiplicative effects are unlikely during acute exposure to hydrocarbons.

The use of liquid rather than vapour compositional information in the RCP calculation

Liquid phase data, rather than vapour phase data, is considered to be adequate for RCP calculations (McKee et al., 2005) because the over representation of higher molecular weight components in the liquid phase results in a conservative result when applying the RCP. Since the acute toxicity of the hydrocarbons increases, and GVs decrease, with molecular weight, the same will be true if the RCP is applied to acute/emergency effects.

APPLICATION OF THE RCP TO CALCULATING WEALS

To apply the RCP method to setting WEALs, three questions need to be addressed and the rationale for the answers agreed:

1. What grouping of hydrocarbon components should be used?
2. How can GVs be defined?
3. What GVs should be chosen for the different groups of components?

What grouping of hydrocarbon components should be used?

The groupings of choice are those already accepted for the RCP calculation (HSE, 2005). They are representative of most hydrocarbon mixtures, and analytical reports in the oil and gas industry are often couched in similar terms, i.e. as groups of paraffins (alkanes), napthenes (cycloalkanes) and aromatics, albeit by boiling point. However, for setting WEALs, two departures from the RCP recommendations are proposed:

1. Because of their low acute toxicity compared with higher analogues, C1–C4 alkanes should be given a separate GV.
2. Components with British WELs can be included when developing GVs for an RCP for acute/emergency effects. The factors that exclude them from the RCP calculation for 8-h TWA OELs (specific toxicity concerns and the fact that the WELs must not be exceeded) are not pertinent in emergency situations.

How can GVs be defined?

Four methods for defining GVs for calculating WEALs have been considered and the results are given in Table 1.

3× existing RCP GV

HSE recommends that when no 15-min TWA short-term exposure limit (STEL) is available then 3× OEL can be used—the so-called ‘three times rule’ (HSE, 2005). This is not a health-based standard but is derived from statistical consideration and ACGIH recommend that ‘... excursions in worker exposure levels may exceed three times the Threshold Limit Value (TLV)–TWA for no more than a total of 30 min during a workday ... provided that the TLV–TWA is not exceeded’ (ACGIH, 2009). Since the RCP GVs may be regarded as surrogate OELs for groups of substances, application of the 3× rule to these is a possible approach for defining group GVs and calculating WEALs, or STELs, of hydrocarbon mixtures. The GVs calculated in this manner are given in Column 4, Table 1.

5× existing RCP GV

ACGIH recommends that worker exposure should never exceed a value of 5× TLV (ACGIH, 2009). Using the RCP GVs as surrogate OELs and applying the 5× rule to them is a possible approach for defining group GVs and WEALs. The GVs calculated in this manner are given in Column 5, Table 1.

Emergency exposure limits

EELs provide action levels to inform the risk assessment planning for, and responding to, chemical emergencies. Only US authorities have defined EELs for any hydrocarbons, viz emergency response planning guidelines (ERPG) set by the American Industrial Hygiene Association (Cavender, 2006); acute exposure guideline levels (AEGLs) set by the US Environmental Protection Agency (Rusch, 2006); and temporary emergency exposure limits (TEELs) set by the US Department of Energy (SCAPA, 2010). Background information on these EELs, including definitions and differences between them, can be found on the SCAPA website (SCAPA, 2010). Collectively, EELs are referred to as protective action criteria (PACs) and an annually updated compilation of all US PACs is available (SCAPA, 2010).

Definitions of EELs vary somewhat, but usually include three or four exposure thresholds ranging from ‘detectability’ (i.e. odour) to ‘potential or certain fatalities’, defined over one or more time periods
The definition of threshold Level-2 EELs, for irreversible (but not fatal) effects, includes serious (e.g. ‘slowly reversible’) toxic effects, escape impairment and the possible need for medical attention. Given this definition, EELs are suitable candidates for defining RCP GVs for WEALs, with the proviso that they are intended for application to the population as a whole, including in some definitions susceptible individuals, rather than the workplace.

Data on PAC-2 thresholds is available for 38 hydrocarbons containing up to 9 carbon atoms (SCAPA, 2010). Only 13 of these values have been formally peer-reviewed: 2 ERPGs (benzene and toluene) and 11 AEGLs (8 of which are aromatics). The remainder are TEELs derived from secondary data sources (such as existing exposure limits) using a peer-reviewed algorithm (DOE, 2010). Table 2 Column 6 lists possible GVs based on the PAC-2 data.

### IDLH values

IDLHs set by the US National Institute of Occupational Safety and Health (NIOSH) are suitable candidates for defining RCP GVs. In setting these, the ability of a worker to escape without loss of life or irreversible health effects is considered, along with severe eye or respiratory irritation and other deleterious effects that could prevent escape, e.g. disorientation or in-coordination (NIOSH, nd; NIOSH, 2005). Although, in most cases, egress from a particular worksite can probably be made in <30 min, IDLH values are based on the effects that might occur as a consequence of a 30-min exposure as a safety margin.

Because concentrations of flammable vapours in excess of 10% LEL are considered to be a hazardous atmosphere in confined spaces, current IDLHs for hydrocarbons default to this value unless a health-based value is smaller (NIOSH, nd). However, IDLH documentation still indicates what health-based values would be set but for the default. Such health-based IDLHs are available for 11 hydrocarbons (5 alkanes; 1 cycloalkane; and 5 aromatics). Since the number of data points is limited, a pragmatic approach is taken to derive suitable GVs, which is informed by the pattern of GV values suggested by the other possible methods noted above. The IDLH-based GVs are given in Column 7 Table 1, and the rationale used in their derivation is given in Table 2.

### What GVs should be chosen for the different groups of components?

The multiplication rules are not health-based and are designed to be applied in controlled conditions in the context of not exceeding the relevant 8-h TWA OEL. WEAL GVs based on the $3 \times$ rule would be particularly conservative in emergency situations, where the expected response to an alarm would be the donning of RPE and immediate escape. GVs derived from the $5 \times$ rule and from the health-based IDLHs are, however, similar.
Table 2. Proposed GVs (milligrams per cubic metre) for WEAL calculations based on IDLH values.

<table>
<thead>
<tr>
<th>Group</th>
<th>Components</th>
<th>Proposed GVs (mg/m$^3$)</th>
<th>Rationale for WEAL GVs (IDLH values are quoted from NIOSH (nd) and conversions from p.p.m. to mg/m$^3$ are at 20°C and 1 atmosphere)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(C1–C4)</td>
<td>18 000</td>
<td>The only health-based IDLH for an alkane in this group is for propane and this is &gt;10 000 p.p.m. (&gt;18, 291 mg m$^{-3}$). Given that the average PAC-2 for these alkanes which is designed to protect the general population is 18 000 mg m$^{-3}$ for Group 1 is considered conservative.</td>
</tr>
<tr>
<td>2</td>
<td>(C5–C6)</td>
<td>10 000</td>
<td>Health-based IDLH values of ‘at least 5000 p.p.m.’ (14 962 mg m$^{-3}$) and 2500 p.p.m. (8935 mg m$^{-3}$) are quoted for $n$-pentane and $n$-hexane, respectively. The average of these is 11 000 mg m$^{-3}$. It is proposed to round this down to give a GV for Group 2 of 10 0000 mg m$^{-3}$.</td>
</tr>
<tr>
<td>3</td>
<td>($\geq$C7)</td>
<td>5000</td>
<td>A GV for the group of alkanes of $\geq$C7 can be derived in three ways and Approach 3 is proposed. 1. Use the IDLH of the lowest member, i.e. $n$-heptane (3113 mg m$^{-3}$), this makes the Group 3 value the same as that proposed for Group 6 (aromatics), which does not reflect the relative acute toxicities of these groups. 2. Use the average of the health-based IDLH values for $n$-heptane and $n$-octane (14 215 mg m$^{-3}$), i.e. 9000 mg m$^{-3}$. This provides insufficient differentiation from Group 2. 3. Use 50% of the value of the GV for Group 2 (i.e. 5000 mg m$^{-3}$). This is considered a reasonable compromise since the ratio Group3:Group2 is 0.66 and 0.35 for values derived from the 5× rule and PAC-2s, respectively.</td>
</tr>
<tr>
<td>4</td>
<td>(C3–C6)</td>
<td>10 000</td>
<td>The only compound in Group 4 to have an IDLH is cyclohexane, i.e. 3000 p.p.m. (10 000 mg m$^{-3}$) and it is proposed to set the GV for Group 4 at this value. The average PAC-2 value is actually higher for this group than for Group 3 so there may be some conservatism in this choice. It also has the pragmatic advantage of making calculation of a WEAL possible when analytical data does not separate the alkanes and cycloalkanes of Groups 2 and 4.</td>
</tr>
<tr>
<td>5</td>
<td>($\geq$C7)</td>
<td>5000</td>
<td>There are no IDLH values for cycloalkanes of chain length greater than C6. It is proposed to set the GV for Group 5 at 50% of the GV for Group 4 to parallel the fall in values proposed for Groups 2 and 3. Again, this makes calculation of a WEAL possible when analytical data does not separate the alkanes and cycloalkanes of Groups 3 and 5.</td>
</tr>
<tr>
<td>6</td>
<td>(Single ring)</td>
<td>3000</td>
<td>One GV of 3000 mg m$^{-3}$ is proposed for all single ring aromatics. This is derived from the average (3142 mg m$^{-3}$) of health-based IDLH values for the five aromatics that have them: viz benzene 500 p.p.m. (1621 mg m$^{-3}$); toluene 500 p.p.m. (1912 mg m$^{-3}$); xylenes 900 p.p.m. (3965 mg m$^{-3}$); cumene 1500 p.p.m. (7482 mg m$^{-3}$); and ethylbenzene 800–2000 p.p.m. (used 1000 p.p.m., i.e. 4406 mg m$^{-3}$). The assigned health-based IDLHs for the aromatics do not align well with their acute toxicities in animals (Cavender, 1994c) or their anaesthetic potencies in man (Fang et al., 1996). The IDLHs for benzene and toluene may be conservative or those for cumene and ethylbenzene optimistic. Either way it suggests that the average of all the available IDLH is a reasonable value for the Group 6 GV.</td>
</tr>
</tbody>
</table>
Although EELs are health-based, they are more conservative than would be necessary in the workplace because they are intended to protect the general public, including, in some definitions, the vulnerable.

Although there are few IDLHs for hydrocarbons, and the information on which they are based is quite old, they are health based and meant to be applied in the workplace. For these reasons, GVs derived from them are considered more suitable when defining action levels for emergency situations than those based on the multiplication rules or on EELs.

### APPLICATION OF THE RCP FOR CALCULATING IN-HOUSE WEALS

#### Examples of WEALs for various mixtures

Illustrative examples of WEALs derived from published data, from invented mixtures, and from analytical data for a ‘condensate’ and some crude oils are given below.

**Published data.** As an example, consider white spirit, which consists of 52% alkanes ≥C7 (GV 5000), 27% cycloalkanes ≥C7 (GV 5000), and 21% aromatics (GV 3000) (Table 3).

Thus, using: 1/WEAL$_{mix} = FR_1/GV_1 + FR_2/GV_2 + FR_3/GV_3 + \ldots + FR_n/GV_n$,

$$1/\text{WEAL}_{mix} = (52/100)/5000 + (27/100)/5000 + (21/100)/3000$$

$$\text{WEAL}_{mix} = 4000 \text{mg/m}^3 \text{ (rounded to the nearest 1000).}$$

**Invented mixtures.** These mixtures were invented to examine how the composition influences the WEAL and how the WEAL compares with the LEL (Table 4).

**Condensate and some crude oils.** The highest molecular weight components in the headspace analysis of the ‘condensate’ were n-octane and ethylbenzene, and in the crude oil, n-nonane and trimethylbenzene (Table 5).

Crude oils 2–5 come from four different offshore fields and show a range of analytical and physical characteristics. Analyses are based on percentage by weight of paraffins (alkanes), napthenes (cycloalkanes), and aromatics in defined boiling ranges. None of the samples contained methane and the boiling ranges used were as follows:

- gases (i.e. C2–C4 alkanes);
- C5 – 95°C (i.e. alkanes: C5, C6, and some C7 isomers; cycloalkanes: C5 and C6 isomers; aromatics: benzene);
- 95–175°C (i.e. alkanes: C7 to about C10; cycloalkanes: C7 to C9; aromatics from toluene up to about the butylbenzenes); and
- 175–232°C (includes hydrocarbons of 12 or 13 carbons). Only the total weight of material in this boiling range was available. Therefore to calculate a WEAL including components in this range, it is assumed that the relative proportions of alkanes, cycloalkanes, and aromatics are the same as in the boiling range 95–175°C.

The substances in these boiling ranges are mainly aligned with the GV substance groups: the exception is that the analytical boiling range C5—95°C includes some C7 isomers. However, for calculating the WEAL, these boiling ranges have been taken to represent the substance groups and hence defines the GVs. Although this will introduce some error, given the inherent assumptions in the RCP approach and the rounding down used in the calculations, this should not be too important.

For data calculations, up to a certain cut-off point (e.g. 175°C), the total weight is normalized to 100% and the higher molecular weight materials are ignored.

### FLAMMABILITY OF HYDROCARBON MIXTURES

The LEL of a mixture (LEL$_{mix}$) of $n$ hydrocarbon gases can be calculated as (Branan, 2005):

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Table 3. Examples of WEAL calculations using some published data.

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Description</th>
<th>WEAL mg/m$^3$ (to nearest 100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>52% alkanes ≥C7; 27% cycloalkanes ≥C7; and 21% aromatics</td>
<td>White spirit$^a$</td>
<td>4400</td>
</tr>
<tr>
<td>72.7% C5–C8 alkanes/cycloalkanes; 7.5% C9–C15 alkanes/cycloalkanes; and 18.9% aromatics</td>
<td>C8–C13$^b$ (Mineral spirit)</td>
<td>5900</td>
</tr>
<tr>
<td>15.9% C5–C8 alkanes/cycloalkanes; 83% C9–C15 alkanes/cycloalkanes; and 1.1% aromatics</td>
<td>C8–C13$^b$ (Deearomatized solvent)</td>
<td>5300</td>
</tr>
<tr>
<td>100% C5/C6 alkanes/cycloalkanes</td>
<td>C6 aliphatic solvent$^b$</td>
<td>8000</td>
</tr>
<tr>
<td>100% C8–C10 aromatics</td>
<td>C9 Aromatic Solvent$^b$</td>
<td>3000</td>
</tr>
</tbody>
</table>

$^a$From HSE (2005).

$^b$From McKee et al. (2005); C5–C8 were taken as Group 2.
\[
1/\text{LEL}_{\text{mix}} = \frac{\% V_1}{\text{LEL}_1} + \frac{\% V_2}{\text{LEL}_2} + \ldots + \frac{\% V_n}{\text{LEL}_n},
\]

where, \(\% V_n\) is the volume \% of component \(n\) (i.e. \(\% v/100\)) and \(\text{LEL}_i = \text{LEL}\) of component \(i\).

This is based on Le Chatelier’s principle, the generality of which suggests that it should apply to hydrocarbon vapours as well as gases.

For comparison with WEALs, the calculated \(\text{LEL}_{\text{mix}}\) values have been converted from \(\% v\) to milligrams per cubic metre at 1 atmosphere and 20°C as follows:

\[
\text{LEL}_{\text{mix}}(\text{ppm}) = \left[\text{LEL}_{\text{mix}}(\% V) \times 10,000\right]
\]

\[
\text{LEL}_{\text{mix}}(\text{mg/m}^3) = \left[\text{LEL}_{\text{mix}}(\text{ppm}) \times \text{MW}_{\text{av}}\right]/24.055,
\]

where, \(\text{MW}_{\text{av}}\) is the average molecular weight of the mixture and calculated as \(\text{MW}_{\text{av}} = 100/n_T\), where \(n_T\) is the total number of moles in 100 g of the mixture.

The \(\text{LEL}\) of hydrocarbon mixtures containing other gases, such as nitrogen, oxygen, and carbon dioxide, can also be calculated. However, all calculations in this work assume the presence of hydrocarbons only in the mixtures considered, which may give

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Comments</th>
<th>WEAL mg/m³ (to nearest lower 100)</th>
<th>10%LEL mg/m³ (to nearest lower 100)</th>
<th>Ratio WEAL:10%LEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% methane, 20% propane, 20% butane, and 10% i-butane</td>
<td>Trivial example of a mixture of hydrocarbon gases.</td>
<td>18 000</td>
<td>4500</td>
<td>4.0</td>
</tr>
<tr>
<td>70% methane, 10% pentane, 10% hexane, and 10% heptanes</td>
<td>Essentially methane with small quantities of higher alkanes.</td>
<td>12 200</td>
<td>3600</td>
<td>3.4</td>
</tr>
<tr>
<td>60% ethane, 10% hexane, 10% cyclopentane, and 20% benzene</td>
<td>Essentially ethane with small quantities of higher hydrocarbons.</td>
<td>8300</td>
<td>3300</td>
<td>2.5</td>
</tr>
<tr>
<td>10% hexane, 20% octane, 20% cycloheptane, and 50% ethylbenzene</td>
<td>The aromatic content is high (50%) and 30% of the other components are ≥C7.</td>
<td>3800</td>
<td>4400</td>
<td>0.9</td>
</tr>
<tr>
<td>100% ≥C7 (assumed MW = 112)</td>
<td>All components have GV of 5000 mg m⁻³; average MW is that of octane and LEL used for comparison is lowest in group.</td>
<td>5000</td>
<td>4200</td>
<td>1.2</td>
</tr>
<tr>
<td>25% octane, 25% cycloheptane, and 50% ethylbenzene</td>
<td>The aromatic content is high (50%) and all the components are ≥C7.</td>
<td>3700</td>
<td>4400</td>
<td>0.8</td>
</tr>
<tr>
<td>15% isobutane, 17% n-hexane, 17% n-decane, 17% methycyclopentane, 17% ethylcyclohexane and 17% t-butyl benzene</td>
<td>Each member of the RCP group is present in about the same concentration by weight and each has the ‘lowest’ known LEL in the group.</td>
<td>5900</td>
<td>4200</td>
<td>1.4</td>
</tr>
<tr>
<td>25% Group 2, 25% Group 3, 25% Group 4 and 25% Group 5.</td>
<td>Examples illustrating the effect on the WEAL of increasing the percentage of components ≥C7 in the mixture in the absence of aromatics with the other substance groups being present in equal quantities by weight. In these examples, the compounds in the substance groups with the lowest LEVs were used in the calculations.</td>
<td>6700</td>
<td>4100</td>
<td>1.6</td>
</tr>
<tr>
<td>20% Group 2, 30% Group 3, 20% Group 4 and 30% Group 5.</td>
<td></td>
<td>6200</td>
<td>4000</td>
<td>1.5</td>
</tr>
<tr>
<td>10% Group 2, 40% Group 3, 10% Group 4 and 40% Group 5.</td>
<td></td>
<td>5500</td>
<td>4000</td>
<td>1.4</td>
</tr>
<tr>
<td>5% Group 2, 45% Group 3, 5% Group 4, and 45% Group 5.</td>
<td></td>
<td>5200</td>
<td>4000</td>
<td>1.3</td>
</tr>
<tr>
<td>20% Group 2, 20% Group 3, 20% Group 4, 20% Group 5, and 20% Group 6.</td>
<td>Examples illustrating the effect on the WEAL of increasing the percentage of components ≥C7 in the mixture with the other substance groups being present in equal quantities by weight. In these examples, the compounds in the substance groups with the lowest LEVs were used in the calculations.</td>
<td>5300</td>
<td>3800</td>
<td>1.4</td>
</tr>
<tr>
<td>15% Group 2, 15% Group 3, 15% Group 4, 15% Group 5, and 40% Group 6.</td>
<td></td>
<td>4400</td>
<td>3600</td>
<td>1.2</td>
</tr>
<tr>
<td>12.5% Group 2, 12.5% Group 3, 12.5% Group 4, 12.5% Group 5, and 50% Group 6.</td>
<td></td>
<td>4100</td>
<td>3500</td>
<td>1.2</td>
</tr>
<tr>
<td>10% Group 2, 10% Group 3, 10% Group 4, 10% Group 5, and 60% Group 6.</td>
<td></td>
<td>3800</td>
<td>4400</td>
<td>0.9</td>
</tr>
<tr>
<td>5% Group 2, 5% Group 3, 5% Group 4, 5% Group 5, and 80% Group 6.</td>
<td></td>
<td>3300</td>
<td>4400</td>
<td>0.8</td>
</tr>
</tbody>
</table>
a conservative result. An example calculation (Branan, 2005) gives a lower LEL for a mixture containing hydrocarbons only compared with a similar one containing other gases.

**DISCUSSION**

The WEAL

The analysis above suggests that the use of an additive equation is justifiable for the acute effects of hydrocarbons and that extension of the RCP to the calculation of WEALs is logical and defensible. The calculated WEALs in Tables 3–5 also demonstrate that they follow the expected toxicity of the mixtures; for example falling with increasing concentrations of aromatics or hydrocarbons of $\geq C7$ in the mixture.

Although in some of the examples, WEALs have been calculated for mixtures, including components up to 12 or 13 carbon atoms, in practice it may not be necessary to consider components above about C9/C10.

Table 5. Examples of WEALs for a condensate and some crude oils.

<table>
<thead>
<tr>
<th>Material Analysis used</th>
<th>WEAL to nearest lower 100 (mg/m³)</th>
<th>Ratio WEAL:10% LEL$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condensate: 80.3% C3/C4 alkanes; 16% C5/C6 alkanes; 0.3% $\geq C7$ alkanes; 1.9% C5/C6 Cycloalkanes; and 1.5% aromatics</td>
<td>Headspace analysis$^b$</td>
<td>13 800</td>
</tr>
<tr>
<td>Crude 1: 85.1% C3/C4 alkanes; 11% C5/C6 alkanes; 0.4% $\geq C7$ alkanes; 2.0% C5/C6 Cycloalkanes; 0.3% $\geq C7$ Cycloalkanes; and 1.2% aromatics</td>
<td>Headspace analysis$^b$</td>
<td>14 500</td>
</tr>
<tr>
<td>Crude 2a: 11% C2–C4 alkanes; 28.3% C5/C7 alkanes; 21.5% $\geq C8$; 10.4% Cycloalkanes C5/C6; 17.9% Cycloalkanes $\geq C7$; and 11% aromatics</td>
<td>Gases to bp 149°C$^c$</td>
<td>6200</td>
</tr>
<tr>
<td>Crude 2b: 9.2% C2–C4 alkanes; 23.7% C5/C7 alkanes; 25.3% $\geq C8$ alkanes; 8.7% C5/C6 Cycloalkanes; 21.1% $\geq C7$ Cycloalkanes; and 12.2% aromatics</td>
<td>Gases to bp 175°C$^c$</td>
<td>5800</td>
</tr>
<tr>
<td>Crude 2c: 8% C2–C4; 17.5% C5/C7; 34.5% $\geq C8$; 6.4% Cycloalkanes C5/C6; 23.6% Cycloalkanes $\geq C7$; and 11.4% aromatics</td>
<td>Gases to bp 232°C$^c,d$</td>
<td>5500</td>
</tr>
<tr>
<td>Crude 3a: 5.3% C2–C4; 20.7% C5/C7; 29.5% $\geq C7$; 10.4% C5/C6 Cycloalkanes; 22.3% $\geq C7$ Cycloalkanes; and 11.8% aromatics</td>
<td>Gases to bp 149°C$^c$</td>
<td>5600</td>
</tr>
<tr>
<td>Crude 3b: 4.1% C2–C4; 16.1% C5/C7; 29.9% $\geq C7$; 8.1% C5/C6 Cycloalkanes; 26.2% $\geq C7$ Cycloalkanes; and 15.6% aromatics</td>
<td>Gases to bp 175°C$^c$</td>
<td>5200</td>
</tr>
<tr>
<td>Crude 3c: 2.6% C2–C4; 10.2% C5/C7; 38.9% $\geq C7$; 5.1% C5/C6 Cycloalkanes; 29.8% $\geq C7$ Cycloalkanes; and 13.4% aromatics</td>
<td>Gases to bp 232°C$^c,d$</td>
<td>5000</td>
</tr>
<tr>
<td>Crude 4a: 10.7% C2–C4; 30.5% C5/C7; 27.6% $\geq C7$; 9.7% C5/C6 Cycloalkanes; 13.9% $\geq C7$ Cycloalkanes; and 7.8% aromatics</td>
<td>Gases to bp 149°C$^c$</td>
<td>6400</td>
</tr>
<tr>
<td>Crude 4b: 9% C2–C4; 25.5% C5/C7; 32.6% $\geq C7$; 8.1% C5/C6 Cycloalkanes; 16.4% $\geq C7$ Cycloalkanes; and 8.5% aromatics</td>
<td>Gases to bp 175°C$^c$</td>
<td>6000</td>
</tr>
<tr>
<td>Crude 4c: 6.8% C2–C4; 19.4% C5/C7; 24.2% $\geq C7$; 6.1% C5/C6 Cycloalkanes; 24.2% $\geq C7$ Cycloalkanes; and 14% aromatics</td>
<td>Gases to bp 232°C$^c,d$</td>
<td>5500</td>
</tr>
<tr>
<td>Crude 5a: 3.3% C2–C4; 14.16% C5/C7; 22% $\geq C7$; 14.13% C5/C6 Cycloalkanes; 36.5% $\geq C7$ Cycloalkanes; and 9.9% aromatics</td>
<td>Gases to bp149°C$^c$</td>
<td>5500</td>
</tr>
<tr>
<td>Crude 5b: 2.4% C2–C4; 10.1% C5/C7; 20.3% $\geq C7$; 10.1% C5/C6 Cycloalkanes; 43.2% $\geq C7$ Cycloalkanes; and 14% aromatics</td>
<td>Gases to bp 175°C$^c$</td>
<td>5100</td>
</tr>
</tbody>
</table>

bp, boiling point.

$^a$Based on the calculated LEL of the mixture, or the known LEL range of the components in the substance groups.

$^b$From Floock (2003).

$^c$Based on bulk analysis.

$^d$The analysis for 149–175°C cut was used to represent the 175–232°C cut.
A comparison of the anaesthetic partial pressure with saturated vapour pressure of hydrocarbons suggests that at 30°C, only hydrocarbons up to about C8 are capable of producing anaesthesia (Flook, 2003). However, in principle, there may be sufficient vapour even from higher homologues to induce sub-anaesthetic effects (such as intoxication) that might impair escape. However, as previously noted higher molecular weight alkanes do not easily pass the blood-brain barrier (Nilsen et al., 1988; Salvayre et al., 1988). For example, average blood/brain ratios in the rat after 8-h exposure to air saturated with C9–C13 alkanes are: 5.77, 4.43, 3.88, 1.27, and 0.6, respectively, i.e. they fall even though lipophilicity rises (Nilsen et al., 1988). Results in Rowley et al. (1997) suggest that brain penetration is significantly compromised for compounds with a log \( \text{K}_{ow} \) (\( \text{K}_{ow} = \text{octanol/water partition coefficient} \)) greater than \( \sim 3 \). So the effect will be significant from at least \( n \)-octane, which has a log \( \text{K}_{ow} \) of 5.18 (Hau et al., 2002), and higher alkanes are likely to have more limited acute CNS effects compared with lower homologues under any given set of conditions of temperature and pressure.

Comparison of derived WEALs with the LELs of the mixtures

Table 1 compares the values of GVs based on IDLHs with the range of known LELs for components of the substance group involved. This shows that for the aromatic substances group the GV is 7–8% LEL. This in itself suggest that an alarm set at 10% LEL of a hydrocarbon mixture should be sufficiently health protective to allow the donning of RPE and escape provided that the concentration of aromatics is not too high. This is supported by comparison of WEALs with 10% LELs of the invented mixtures (Table 4), which demonstrates that the concentration of aromatics needs to increase to \( \sim 50\% \) of the total for the WEAL to be \( \leq 10\% \) LEL of the mixture.

The analyses available for crude oils (Table 5) were by hydrocarbon group and boiling range not individual substances, so it was not possible to calculate their LELs, and hence not possible to make direct comparisons with WEALs. However, the LELs for these crude will fall somewhere in the range 39 900–44 555 mg m\(^{-3}\), i.e. between the highest and lowest known LELs for the possible components from C2 (ethane) to C10 (tert-butylbenzene). On rounding, the 10% LEL value will be in the range 4000–4500 mg m\(^{-3}\) and a range can be calculated for the WEAL:10% LEL ratio. As the examples in Table 5 show the WEALs will be >10% LEL, even when a wider cut (up to 232°C) is taken to include less volatile components.

Application of the WEAL

Area monitoring provides an alarm system to give warning of hydrocarbon releases above a defined concentration (generally 10% LEL). In the absence of better information or specific acute toxicity concerns (such as the presence of hydrogen sulphide), it is proposed that WEALs be used as a guide for assessing the adequacy of area alarm levels in respect of warning of an acute health risk.

WEALs are not intended to be used as STELs, so application over a specific time period is not included in the definition. However, given that the GVs used to calculate WEALs are derived from IDLHs set on the basis of allowing 30 min for escape and that rounding down is proposed at each step, it seems plausible to assume they will provide a window of \( \sim 15 \) min for individuals to react after the alarm sounds.

The comparison made above between WEALs and LELs calculated for various invented and real mixtures suggests that 10% LEL should give adequate warning for hydrocarbons containing up to 50% aromatics. There are, however, caveats to this:

1. The GVs proposed are open to discussion since there are other possible methodologies for defining them. These include: basing the GVs on the lowest value set for an IDLH in a given RCP group and where they exist use existing IDLHs for individual components with the GVs derived in Table 2 for everything else. The former may give such low values for the WEAL that practical detection problems arise because current monitoring methods are not be sufficiently sensitive or at these settings give rise to false alarms. The latter requires the availability of more detailed analytical data, and this could pose problems where the mixtures vary over a relatively short time period.

2. The RCP approach does not apply to aerosols (HSE, 2005). Also the commonly used methods for monitoring hydrocarbon leaks (pellistors, infra-red, and photo-ionization) are based on the detection of gases/vapours. A comparison of the warning characteristics of alarms set at 10% LEL and the WEAL is justified in relation to gases/vapours but neither reflects risks from aerosols.

CONCLUSIONS

For the purposes of this paper, WEALs are defined as the concentration in air that area monitors
should alarm at to provide adequate warning and be sufficiently protective of health to allow at least enough time to don RPE and escape.

Analysis of the acute toxicity of hydrocarbons and their mixtures suggests that, in principle, the RCP method of calculating in-house OELs can be applied to calculating in-house WEALs for setting warning alarm levels for accidental releases.

It is proposed that the most appropriate GV’s for calculating WEALs are those derived from IDLH values. The fact that IDLH values are set on a 30-min basis and GV’s rounded down means that the use of WEALs as alarm levels should be conservative. They are not intended to be used as STELs, but the basis on which they are set suggests that as well as being suitable alarm levels they should give sufficient health protection to allow a window of opportunity to don RPE and escape.

WEALs calculated for exemplar mixtures show the pattern of values that are required for them to be useful in the context of providing protection in emergencies. For instance, their value decreases with increasing toxicity of the mixtures, particularly with increasing concentrations of aromatics.

WEALs calculated for both model mixtures and using a limited selection of real samples, suggest that, in general, they will be >10% LEL. This generality only begins to breakdown when the composition includes high (>50%) concentrations of aromatics or aromatics and hydrocarbons ≥C7. This is an encouraging finding since it implies that area alarms set at 10% LEL, which is the usual practice, should, in the event of an accidental release, give adequate warning and be sufficiently protective of human health to allow a window of opportunity in which RPE can be donned and escape made. Where it is reasonably practicable to set alarm levels at <10% LEL this should, of course, be encouraged for both safety and health reasons.

This paper is exploratory in nature and further discussion of the appropriateness of the GV’s proposed for calculating WEALs, the testing of the approach by application to further real-life samples, and the possible extension to STELs would be welcomed.

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REFERENCES


De Jong RH, Eger EI. (1975) MAC expanded AD₅₀ and AD₉₅ values of common inhalation anaesthetics in man. Anesthesiology; 60: 40–44.


Lazarew NW. (1929) Uber die Giftigkeit verschiedener Kohlenwasserstoffdampfe (About the toxicity of various hydrocarbon vapors). Arch Exp Pathol Pharmacol; 143: 223–33.


Rusch GM. (2006) The development and application of acute exposure guideline levels for hazardous substances. In...