Industrial accidents causing multicomponent clouds

SAFETY

Part II: Methodological proposals for determining airborne dispersal and planning zones

This article is a continuation of the first part published in number 119 of this review. This dealt with the acute effects on human beings caused by airborne emissions of toxic clouds from industrial accidents and also evaluated the effects of the cloud components using the Hazard Index. This second article proposes methodologies for determining, on the one hand, the dose-defining parameters and the threshold limit values of the cloud components and, on the other, the criteria for setting up the planning zones in the event of multicomponent clouds. Use of the ALOHA software and modelling of the mixture as a pure representative substance enables us to draw up the «characteristic curve» of any component of the cloud.

By E. GONZÁLEZ FERRADÁS*. Doctor in Chemistry. Professor of the University of Murcia. Department of Chemical Engineering. Chemistry School. Campus de Espinardo, University of Murcia (ferradas@um.es), E. GONZÁLEZ DUPERÓN. Doctor in Chemistry. Associate professor of Murcia University. Research fellow, J. RUÍZ GIMENO. Chemist. Professor of the University of Murcia, B. GIMÉNEZ FRANCÉS. Chemical engineer. Research fellow.

This article is the second in a series on the characteristics and impacts of the airborne emission and dispersion of toxic multicomponent clouds after industrial accidents, especially in chemical factories or the like, either due to a direct leak of gases or after fires of complex, plastic or phytosanitary products or substances, etc.

The first article, published in number 119 of this review [1] dealt with the main toxicological effects of breathing in these clouds, especially those that produce acute effects on human beings; it proposed the Hazard Index (HI) methodology for quantitative assessment of the toxic incidence of each group of components that would produce the same effect. This index weights the toxic contribution of each cloud component by means of the Hazard Quotient (HQi), defined by the equation:

\[
HQ_i = \frac{E_i}{AL_i}
\]

(Equation 1)

where \(D_i\) is the actual exposure of component \(i\) throughout the cloud’s whole trajectory and \(AL_i\) is its acceptable level. Once the Hazard Quotients have been determined for all the cloud components we then obtain the Hazard Index for each group of isoeffect components, by means of:
where j, k...x are the components making up each isoeffect group of the cloud of n components, thereby verifying:

\[ i+j+...+x \geq n \]  \hspace{1cm} (Equation 5)

If each cloud component has a single toxic effect the sum i+j+...+x is equal to the number of toxic components of the cloud (n). Conversely, if one or more of the substances may have more than one effect, the sum i+j+...+x is greater than n.

Whenever, at a given distance from the source of the accident (d_x) and in the direction the cloud is moving, the hazard index of one of the isoeffect groups reaches unity (for example, HI_x = 1), this marks the distance where the effect defined by the acceptable values (or threshold limit values) of the components of group x of the mixture (AL_x) occurs.

The above parameters are all defined and determined in this article, which also proposes a simplified method for calculating the Panning Zones (intervention and alert) for these mixtures pursuant to the criteria laid down by Royal Decree (Real Decreto) 1196/2003 of 19 September [2], for pure substances.

**Emissions of multicomponent toxic clouds: general approach**

First and foremost we need to describe the initial accidental causes that might give rise to a leak of gases, the most important characteristics of the emissions of multicomponent clouds and the general behaviour of airborne dispersion.

The initial or primary causes might be broken down into two groups: on the one hand the breakage or overspill of containers storing, transporting or processing liquid or gaseous mixtures and, on the other, the clouds formed after fires of complex materials (substances or products), whether solid, liquid or gases.

- In the first case especially serious accidents may arise as a result of leaks from storage recipients and high-capacity pipes (given the huge levels that might be involved); in chemical reactors where all components would participate (initial, final, intermediate and even the catalyster itself); in furnaces considered to be critical elements given the possibility of producing huge emissions of high-temperature vapours and fires, and in equipment producing separation operations (distillation, absorption or extraction columns, mixture, sedimentation and crystallisation recipients ...).

- As for emissions from fires, these may involve the combustion of material that, in its normal state, is non hazardous (such as many plastics or stable polymers) or intrinsically hazardous (phytosanitary or agrochemical
products, monomers and other substances or preparations with hetero-atoms, etc.). This case presents two main differences with respect to the former: firstly, the formation of toxic substances other than the precursors and, secondly, the dispersion mechanism, conditioned in this case by the intense convective emission fuelled by the high temperature produced in the exothermic combustion reaction.

As regards the first-case emission (without combustion), the duration of the leak depends mainly on the physical state, composition, quantity and storage conditions (pressure and temperature) at the moment of the accident, the geometry and volume of the equipment concerned, the position and size of the orifice or leak zone and the effectiveness of the intervention. Prima facie the leak is considered to be «instant» when the container breakage is total (catastrophic) or the size of the orifice formed by the breakage or exit zone is appreciable in relation to the total volume of the equipment or isolatable section. In other conditions the leak occurs over a more or less lengthy period; it is then considered to be continuous and generally tails off over time.

**Airborne emissions of multicomponent toxic clouds may arise from direct leaks from container equipment or as a result of fires of complex products**

Once the leak has occurred, the flow dynamics and composition of the cloud depend largely on the physical state of the product, viz:

- **Gases** are emitted as such without any variation in their composition.
- **Spills of «non boiling» liquids,** kept at a temperature below the equilibrium vapour pressure at atmospheric pressure, will form a puddle, emission then occurring by evaporation. The vapour composition generally differs from the liquid’s. Initially, therefore, the vapourised phase will be enriched in the lightest components. Any thoroughgoing assessment of the emission will depend on knowledge of the liquid-vapour equilibrium pressure of the mixture components, producing a complex flow of variable composition. Each case will therefore call for its own particular approach, simplifying procedures to suit, depending on the composition and vapour pressure of the components, extension of the spill, environmental conditions, effectiveness of the intervention, etc).
- **The leak of liquid gases** kept at more or less high pressures poses diverse problems. If the breakage is catastrophic the product would suffer a sudden evaporation (flash), producing, a priori, vapour and liquid according to the thermodynamic principles and laws of vapour-liquid equilibrium. Once again, the vapour phase (with higher concentrations of lighter products) would form a cloud whose composition is different from the original mixture and the remaining liquid (with concentration of the heavier components) would spread over the ground and evaporate, boosting the initial emission. In most cases the initial flash effect would produce an aerosol (gas and droplets), whereby the initial mass emitted into the air is higher than that obtained by theoretical calculations, which assume a clean separation of liquid and vapour phases.

On the other hand, if the leak orifice is small, the emission or spill
is considered to be continuous, tailing off over time, and the physical state of the leak will be determined by the position of the orifice in the container. If it is in the upper part of the container, occupied by the vapour, the emission will be gaseous (barring the so-called «champagne effect», when rapid evaporation of the liquid causes foam to be sent out with the gas). If the container is insulated the evaporation of the gas inside will cool down the liquid remaining in the container until it reaches the equilibrium temperature; this will occur when the inside pressure (the mixture's vapour pressure) equals the atmospheric pressure; from that moment on the emission can be said practically to cease. If the container is not totally insulated the development of the leak will depend on the characteristics of the particular product, the heat transfer surface area and outside thermal conditions. Conversely, if the leak orifice is in the zone occupied by the liquid phase a spill will occur with a continuous flash effect with similar evaporation behaviour to that already described for the catastrophic break. The two-phase leak would continue until the level of the liquid inside the container falls below the leak orifice, whereupon the emission would behave as described above. The calculation of the leak and emission of the abovementioned cases is dealt with in the specialist literature, particularly the publications of Lees [3], Casal [4], Santamaría et al. [5], TNO [6] and AIChE [7].

After the leak the airborne emission will form a multicomponent cloud, instant or continuous, usually denser than the air (heavy cloud). In the initial moments, therefore, the cloud will spread along the ground and its development will depend on the lie of the land and weather, aspects sufficiently dealt with in articles or monographs, such as those published by Hanna, et al [8] or the General Directorate of Civil Protection (Dirección General de Protección Civil), Madrid [9]. The airborne dispersion pattern and the toxicological characteristics of the cloud’s components will determine the scope of its effects. The main meteorological parameters impinging on the dispersion of these emissions are those making up the so-called stability matrices, i.e.: the stability classes and wind speeds and directions. Ceteris paribus, for risk analysis and for planning ahead of possible accident scenarios, two stability-wind speed combinations are normally used: the most frequent in the zone under consideration and the worst-case scenario producing the greatest scope of the effects. For emissions with temperatures equal to or below the ambient temperature, the worst-case scenario usually corresponds to the Pasquill stability class F and wind speeds of 1 to 2 m/s.

Fires of chemical products usually produce many toxic compounds whose emission rates are difficult to calculate due to the sheer number of factors impinging on the combustion process

The formation of multicomponent toxic clouds in industrial fires is a complex matter due to the sheer number of factors, circumstances and parameters involved. The most important are:

- The combustion process in fires is not uniform. It varies according to the location of the material (indoors or outdoors), type of storage, packaging, stacking height; all these factors vary the inflow of air to the burning material.
- In fires of solids and liquids it is the surface areas exposed to the air that are burnt. The inner areas of the material, therefore, with hardly any input of air, are more prone to pyrolysis than combustion in response to the high temperatures, giving rise to unburnt material and a very diverse range of combustion products.
- Many different substances may be formed and emitted in
fires, depending on the composition of the burning material, some of them with high toxicity levels. In recent decades the results of many studies have been published on the toxic components formed in fires, the most important being the monographs published by Purser [10], Babrauskas [11], Anderson [12] and Stec et al. [13]. Other studies paid special attention to the combustion of polymers and plastics, especially after the discovery of the emission of dibenzo-p-dioxins and furans in fires of chlorine-containing materials. Christmann et al [14], Theisen et al [15], Mannson et al [16], Vikelsæ et al [17], Katami et al [18], Zhu et al [19] and Valavanidis et al [20], among others, have all published studies on fires involving PVC and other chemical substances containing diverse heteroatoms, such as heavy metals. Also worthy of particular mention are the studies published by Risø National Laboratory (Denmark) [21,22,23] on the combustion and pyrolysis of phytosanitary projects, detecting very toxic components that depend on the composition of the burning material and oxygen supply. Table 1 shows the most important combustion or pyrolysis materials of the listed substances. This may be extrapolated to other chemical substances containing the indicated heteroatoms.

To analyse the risks involved in these accidents we need to know beforehand the quantitative composition of the products formed. Often, this information is not available due to the sheer diversity of the materials and mixtures that might be involved in accidents of this type and the variability of the compositions obtained, even in controlled experiments.

Conservative best guesses are therefore normally used. For example, in its EFFECTS Plus version 5.5 software [24], TNO uses the following criteria on the products formed on the basis of the heteroatoms involved in the fire:

- All the sulphur is converted into sulphur dioxide.
- All the halogens –fluoride, chloride and /or bromide – turn into their corresponding hydrazides –HF, HCl and HBr.
- Thirty five percent of the initial nitrogen content in the original product is assumed to turn into nitrogen dioxide.

<table>
<thead>
<tr>
<th>Heteroatoms contained in materials, carbon derivatives and nitrogen in the air</th>
<th>Toxic components in smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>Sulphur dioxide, Carbonyl sulphide</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Hydrogen chloride, phosgene, dioxins and furans</td>
</tr>
<tr>
<td>Fluoride and bromide</td>
<td>Hydrogen fluoride and bromide</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Nitrogen oxides and hydrogen cyanide</td>
</tr>
<tr>
<td>Metals</td>
<td>Stable oxides and salts of the metals</td>
</tr>
<tr>
<td>Carbon derivatives</td>
<td>Carbon monoxide and a great variety of substances ranging from very light (for example formaldehyde or acrolein) to very heavy (polycyclic</td>
</tr>
</tbody>
</table>
As for the emission, the aforementioned software uses a rate of 25 g/s m\(^2\) referring to the original burning product. The surface area included in the emission rate is the surface exposed to the fire; for example, if the burning product is a solid stacked on the floor, forming a metre cube with sharp edges, the burning surface area is 5 m\(^2\), i.e., only five of the sides because the sixth, standing on the floor, is not exposed directly to the fire; in this case the initial product consumption rate would be 125 g/s.

The abovementioned consumption rate and criteria can then serve for estimating the emission mass flow rates of the possible products formed.

The emission and dispersion of fire-generated products behaves very differently from direct leaks from non-burning material in terms of flow dynamics. Convective emission forms in fires due to the high combustion temperature. The resulting cloud of low-density gases and smoke may rise to a considerable height (hundreds of metres), mixing in its rise with the surrounding air until its temperature falls and density increases, gradually coming to match that of the air. The maximum height reached by the smoke depends on the characteristics of the emission (mainly the volume flow rate and temperature) and weather conditions, particularly the stability class and wind speed. After peaking in height the subsequent dispersion depends mainly on the stability class. The most unstable class (Pasquill A) is the most unfavourable due to the vertical air turbulence, typical of this situation, which breaks up the plume and may force it down to ground level (a phenomenon known as «plume fumigation»), thereby affecting vulnerable receptors at or near ground level, mainly living beings and other ambient elements. The stable atmospheric classes, on the other hand, hardly alter the plume once it has reached its top height, so that it forms an almost cylindrical flow that is blown by the wind almost unchanged over large distances (kilometres). By the time the plume finally falls to the ground its impact may be negligible due to its low concentration.

The air dispersion of multicomponent clouds can be modelled as if it were a pure substance representative of the mixture

The air dispersion of multicomponent clouds

The prime objective of this study is to propose a simplified procedure for determining the airborne concentrations of each component of the cloud and the times at which they pass each point of the cloud’s trajectory. To do so the following hypotheses and criteria are established:

1. The qualitative (components) and quantitative (mass, flow and duration) emission, all commented on in the above section, are assumed to be known.
2. To facilitate the calculation, the composition of any continuous emission is considered to hold steady throughout the whole episode, otherwise we need to work with constant mean compositions.
3. During the dispersion the cloud’s composition is
homogenous, i.e., there is no transfer to other media (wet or dry fallout) nor any transformation or separation of the components, either as a consequence of reactivity, physical state (gaseous or in particulate form) or of different molecular masses. This last working hypothesis is realistic given that in ambient air the turbulent dispersion mechanisms predominate over the molecular diffusion mechanisms (Fick’s law of diffusion); in other words the mixture within the cloud itself, provoked by the air’s dynamics, is more efficient than that provoked by movements driven by molecular gradients.

4. No procedures have yet been published for calculating the air dispersion of these mixtures and there are hence no computerised models for processing this phenomenon. That being so, we propose using software dealing with the air dispersion of pure substances, selecting for our purposes the ALOHA software (version 5.4.1.2) [25] on the grounds of the following advantages.

- It has been developed by the US Environmental Protection Agency (EPA) and enjoys widespread prestige among all experts in this field.
- It allows new substances to be phased in; this is crucial for the methodology proposed herein.
- It has a module for determining leaks through the commonest sources (pipelines and tanks).
- The presentation of results is best suited to the calculation proposal of this study.
- It is free and of open access.

5. To be able to work with ALOHA [25] it is essential to model the mixture as though it were a pure substance. Using this software the dispersion of various substances has been studied, assessing the influence of their properties on the concentration profiles throughout the cloud’s trajectory, as laid down in the programme database. The only significant variable that came to light from these experiments was the density of the substance in gaseous state. The criterion has been adopted of modelling a Substance Representative of the Mixture (SRM) with a weighted gas-phase density with respect to the component densities. The other properties may also be the weighted substances or those of the majority component of the mixture.

6. Bearing in mind the working hypotheses of continuous emission of a constant composition (hypothesis 2) and cloud homogeneity (hypothesis 3), the following ensues:

- 6.1 That the mass fractions of any component i in the cloud \( X_i \) hold steady throughout the trajectory, which implies:
  \[
  X_{i,0} = X_{i,d} = X_i = \text{cte.} \quad \text{(Equation 6)}
  \]
  where the subindices 0 and d correspond to the source of the emission and to any distance from said source, respectively.

- 6.2 That the concentrations of any component i of the mixture and of the SRM at any point of the trajectory (d) and at a given time (t) are related by:
  \[
  C_{i,d,t} = X_i C_{SRM,d,t} \quad \text{(Equation 7)}
  \]
  In particular, the following is verified for maximum concentrations (max) of i and of SRM at any point of the trajectory (d):
  \[
  C_{i,\text{max},d} = X_i C_{SRM,\text{max},d} \quad \text{(Equation 8)}
  \]

To clarify the above, Figure 1 shows the concentration
profiles of the SRM and one of the components (i) for instant emissions (figure 1.a) and continuous emissions (figure 1.b) at point d of the cloud’s trajectory.

To determine the impact of airborne toxic clouds we need to know the maximum concentration at each point of the cloud’s trajectory and the time that point is passed.

In relation to the figures 1.a and 1.b the parameters ti, tf and t (which is the difference t_f - t_i) are the times at which the cloud arrived at, left and passed by, respectively, each point d of the trajectory.

Para determinar el impacto de nubes tóxicas en aire es necesario conocer en cada punto de su recorrido la concentración máxima y su tiempo de paso.

For each point of the cloud’s trajectory ALOHA [25] gives graphic information on the concentration-time profiles for the SRM, as shown in figure 1. From this information what we have called a "characteristic curve" can be built up for each component, defined by the following parameters:

- d: distance to the source of the accident.
- C_{\text{max},d}: maximum concentration of component i at d, obtained from equation 8.
- Δt: time when component i passed by point d, coinciding with the time of the SRM.

The «characteristic curve» of any component i is shown in figure 2, using the curve-defining parameters.
The benchmark concentrations taken to represent the "characteristic curves" of the SRM or i were the maximums at each point of the trajectory; this is the same criteria used for assessing the Planning Zones for clouds of pure toxic substances, as detailed in the technical guide (guía técnica) "Planning Zones for grave accidents of a toxic type" ("Zonas de planificación para accidentes graves de tipo tóxico") [9]. Selection of this maximum concentration instead of any other representative sample (for example, the weighted mean value) is a conservative principle offering greater guarantees of protection when setting up the Planning Zone.

**Planning Zones for Multicomponent Clouds**

Once the isoeffect groups have been drawn up following the criteria laid down in part I of this study [1] together with the "characteristic curves" of the mixture components, the Hazard Indices are then established for each group of components producing the same effect, at various distances from the source of the accident and in the direction of the wind (HIj,d), by means of

\[
HI_{j,d} = \sum_{i} \left( \frac{C_{i,\text{max},d}}{\text{TLV}_{i,d}} \right) = \sum_{i} \left( \frac{X_i C_{i,\text{SRM, max},d}}{\text{VL}_{i,d}} \right)
\]

(Equation 9)

where j refers to the number of components included in each group producing a given isoeffect and \( \text{TLV}_{i,d} = \Delta t_d \) is the threshold limit value of component i producing the level of seriousness under study for said isoeffect, taking as exposure time \( t_{exp} \) the same as the time the cloud passed by point d \( (\Delta t_d) \).

The distance \( d_{j}^* \) where \( HI_{j,d}^* \) is seen to equal 1 is where the seriousness of the effect under study would occur, as defined by \( \text{TLV}_{i,d} = \Delta t_d \). At bigger/smaller distances than \( d_{j}^* \) the seriousness of the effects is greater/less than that produced at \( d_{j}^* \). This procedure is repeated for the other groups of isoeffects (k,l,...), obtaining for each level of seriousness the distances \( d_k^* \), \( d_l^* \), ... The biggest of these distances delimits the scope of the Planning Zone (intervention or alert) of the cloud of n components.

**Figure 2.** Characteristic curve of component i.
Figure 3. «Characteristic curves» of the group of components $j$ and of its threshold limit value. The distance $d_j^*$ determines the level of seriousness delimiting the planning zone under study ($HI_{j,d_j^*} = 1$).

The procedure described above is time-consuming due to the number of repeats that might be necessary before finding the distance where the Hazard Index of each group equals one, but it can be simplified as follows:

1. For each group of components $j$ producing the level of seriousness of the isoeffect under study, a threshold limit value ($TLV_{j,\text{exp} = \Delta t}$) is defined, applicable to the whole set of said elements, as follows:

$$HI_{j,d} = \sum_{i=1}^{n} \left( \frac{X_i C_{SRJ,\text{max},d}}{VL_{i,j,\text{exp} = \Delta t}} \right) = \frac{\sum_{i=1}^{n} X_i C_{SRJ,\text{max},d}}{VL_{i,j,\text{exp} = \Delta t}}$$

(Equation 10)

From which:

$$VL_{j,\text{exp} = \Delta t} = \frac{\sum_{i=1}^{n} X_i}{\sum_{i=1}^{n} \frac{X_i}{VL_{i,j,\text{exp} = \Delta t}}}$$

(Equation 11)

Equation 11, which we have called the «characteristic curve» of the threshold value limit, enables us to operate with a single limit value for each group of $j$ components of the isoeffect under study.

2. The maximum concentrations of the «characteristic curve» of the $j$ components are calculated as follows:

$$C_{SRJ,\text{max},d} = \sum_{i=1}^{n} X_i C_{SRJ,\text{max},d}$$

(Equation 12)

and the times at which they pass a given point will be the same as the SRM at the same distances from the source of the accident.

If the «characteristic curve» of the limit value – equation 11 – and of the isoeffect group under study – equation 12 – are plotted on the same graph, as in figure 3, then the point where both curves cross defines the «characteristic data» $(d_j^*, C_{j,\text{max},d})$ and
t_{\text{exp, dj*}}) for group j. To put it another way: the distance d_{j*} is the scope of the level of seriousness assessed for group j. The procedure is then repeated for all the other groups of isoeffects (k, l, ...) ascertaining the other distances (d_{k*}, d_{l*}, ...), and taking the biggest distance as the limit of the Planning Zone (intervention or alert as the case may be).

The Planning Zones for multicomponent clouds are determined as though it were a pure substance but the maximum damage distance is chosen for all the isoeffect groups formed by the cloud’s components.

The third part of this study, coming out soon in this review, will set forth a practical example to help explain the proposed methodology.