New Trend In Classification Of Hazard Of Explosive Atmosphere In Laboratory Workplaces

Di Benedetto A.[1], Dolcetti G.[2], Grimaz S.[3]., Russo P.[4], Salzano E.[1]

[1]Istituto di Ricerche sulla Combustione, Consiglio Nazionale delle Ricerche
Via Diocleziano 328 - 80124, Napoli, Italy
[2]Dipartimento di Scienze e tecnologie chimiche, Università di Udine
Via Cotonificio, 108 - 33100 Udine, Italy
[3]Dipartimento di Georisorse e territorio, Università di Udine
Via Cotonificio, 114 - 33100 Udine, Italy
[4]Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno
via Ponte don Melillo - 84084 Fisciano (SA), Italy

Current EU legislation makes the classification of workplaces in hazardous zones as compulsory, in order to prevent explosions. The procedure requires in-depth knowledge about the sources of ignition and the potential sources of risk as described in the ATEX 137 Workplace Directive 1999/92/EC. To this aim, the hazard of substances is typically classified as function of specific physical and chemical properties which are relevant with respect to risk issues.

However, some other parameters which may affect the overall hazard of substances in confined or semi-confined spaces, such as the ventilation rate and the total quantity of substance have to be take into account.

In this work, we propose a new view of explosion hazard classification as function of the diffusion and residence characteristic times other than physical and chemical properties. This classification has been applied to the case of a research chemical laboratory where different chemical substances are used in small amounts.

1. Introduction

ATEX 137 (Directive 1999/92/EC) is addressed to employers operating in factories and establishments where explosive atmospheres can occur, in order to prevent and provide protection against explosions. Employers have to take technical and/or organizational measures appropriate to the nature of the operation for:
- the prevention of the formation of explosive atmospheres;
- the avoidance of the ignition of explosive atmospheres;
- the mitigation of the detrimental effects of an explosion so as to ensure the health and safety of workers.

In chemical research laboratories, a plurality of flammable substances is generally used, often in a very small quantity. Therefore, in order to survey the potential danger related to ATEX formation, it is necessary to carry out a risk assessment based on different representative and simplified scenarios.

With specific reference to Italian guidelines and standards, the CEI EN 600079-10 (CEI 30-31; CEI 31-35 and CEI 31-35/A) gives algorithms for the definition and the classification of the hazard zones in each workplace. Besides, CEI 31-35/A, in the Annex GF "Chemical Laboratories", provides that if some particular management measures are taken, no meaningful ATEX conditions are determined and therefore no

ATEX 95 (Directive 1994/9/EC) requirements for equipment and protective systems are requested in those areas.

However, only qualitative indications are given in these standards and directive. Hence, it would be useful to introduce simplified tools which allow, by quantitative evaluations, to define the boundary limit between ATEX and NO ATEX as a function of both the typology and characteristics of substances and the operative and environment conditions. To these aims, we have run simulations according to the CEI 31-30 in order to calculate the maximum allowable volume V_f of flammable substances in typical research laboratory conditions for the application of ATEX zones. The ATEX-GAS software of the TNE has been utilized for the cases described in the following sections.

1.1 Criteria of CEI 31-30

The primary source of potential ATEX is associated with the use of flammable liquids. Source releases can occur when the surface layer of these liquids is directly exposed to the air. In most cases, the liquid temperature will be below the boiling point and the vapor release rate will depend principally on the following parameters:

a. Liquid temperature
b. Vapor pressure of liquid at its surface temperature
c. Dimensions of the evaporation surface
d. Ventilation

On the basis of this parameters the CEI 30-31 standard introduces the concept of hypothetical volume V_z for the definition of the volume of flammable envelope from a source of release. More specifically, CEI 30-31 standard provides that if $Vz \leq 0.1$ m^3 than the extent of potential damage due to the sudden increase in temperature and/or pressure, as a result of the ignition of the explosive atmosphere, is negligible.

For the calculus of V_z the standard gives the following equation:

$$V_z = \frac{f \cdot (dG/dt)_{max}}{dV_0/dt} \cdot \frac{TV_0}{293 \cdot k \cdot LEL_m} \qquad (1)$$

where:

f is the efficiency of ventilation in terms of its effectiveness in diluting the explosive gas atmosphere, whit f ranging from f=1 (ideal situation) to, typically f=5 (impeded air flow)

$(dG/dt)_{max}$ is the maximum rate of release at source (kg/s)

LEL_m is the lower explosive limit (kg/m^3)

k is a safety factor applied ti the LEL_m (typically k=0.25 for primary grades of release or k=0.5 for secondary grades of release)

T is the ambient temperature (K)

dV_0/dt is the total flow rate of fresh air through the volume under consideration (kg/s)

V_0 is the entire volume served by the actual ventilation in the vicinity of the release being considered.

1.2 Input data of simulations

For the simulation by ATEX-GAS, we have assumed a number of chemicals and laboratory conditions. Table 1 reports the list of the flammable substances investigated in this work and their main properties needed for the simulations.

Table 1 – Chemical properties of substances.

Chemicals	Flash point, °C	Lower Flammability Limits, %	Diffusion coefficient, m^2/h	P_{sat} at 20°C, mmHg
Acetone	-20	2.5	0.037	181
Methanol	11	6	0.057	96
Hexane	-21	1.2	0.022	132

Quite clearly, the exercise requires also the definition of working environment, as reported in Table 2. The data were obtained at fixed ventilation conditions.

Table 2 – Laboratory and Hood conditions

	Laboratory	Hood
Volume, m^3	134.4	2
Temperature, °C	20	20
Pressure, Pa	100120	100120
Q_aria, m^3/h	806	300
Number of air changes, h^{-1}	6	300

2. Methodology and Results

Results of simulations carried out according to the methodology proposed in standard CEI 31-30 are reported in Table 3 in terms of the maximum allowable volume V_f of spilled flammable substances in laboratory and inside fume cupboard (hood) as described in Table 2.

Table 3 – Results of simulations

Chemicals	V_f, m^3	
	Laboratory	Hood
Acetone	0.0025	0.0025
Methanol	0.004	0.004
Hexane	0.0035	0.0035

Starting from these results we tried to derive a general criterion in order to rationalize all the data in a classification map.

To this aim, we define three characteristic times: the diffusion time, the resident time and the dilution time. Details of these times follows.

The diffusion time t_D gives an estimation of the time required by the vapor to diffuse in the surrounding environment:

$$t_D = \frac{V^{2/3}}{D} \tag{2}$$

where V is the volume of the chamber and D is the substance diffusion coefficient. The values of D are given on Table 1 for all the substances used.

The residence time t_r allows the requirement to renew the gas in the chamber:

$$t_r = \frac{V}{Q} \tag{3}$$

where Q is the chamber ventilation volume flow rate.

Finally, the time required to keep the substance concentration, within the analyzed environment, as lower or equal to the lower flammability limit (dilution time t_d).

$$t_d = \frac{V_f}{Q_f} \tag{4}$$

where Q_f is the volume flow rate of the substance, which may be calculated from the following mass balance:

$$Q_f \frac{\rho_f}{M_f} = Q_{air} \frac{\rho_{air}}{M_{air}} LFL + Q_f \frac{\rho_f}{M_f} LFL \tag{5}$$

where ρ is the density, M is the molecular weight and LFL the lower flammability limit and subscripts "f" and "air" refer to fuel and air, respectively.

From Eq.4) the expression of the flammable substance volume flow rate becomes:

$$Q_f = \frac{Q_{air} \dfrac{\rho_{air}}{M_{air}} LFL}{\dfrac{\rho_f}{M_f} (1 - LFL)} \tag{6}$$

By arranging all the data obtained by means of the software ATEX GAS, reported in the Tables 1-3 and calculating the diffusion time (t_D), the residence time (t_R) and the dilution time (t_d), we obtained the data plotted in Figure 1, which represents a classification map in which two zones (NO-ATEX and ATEX) may be clearly distinguished.

An a-posteriori test was done here by adding the data obtained by the simulations according with CEI 31-30, utilizing the ATEX GAS software for xylene. The data of xylene are given in table 4.

Table 4 – Chemical properties of Xylene

Chemicals	Flash point, °C	LFL, %	D, m^2/h	P$_{sat}$ at 20°C, mmHg
Xylene	32	1.1	0.026	5

From test results it was found that 4 L of xilene can be considered a safe volume.

Adding these points on the graph of Figure 1 we found that they are placed in the NO-ATEX region, as it can be expected.
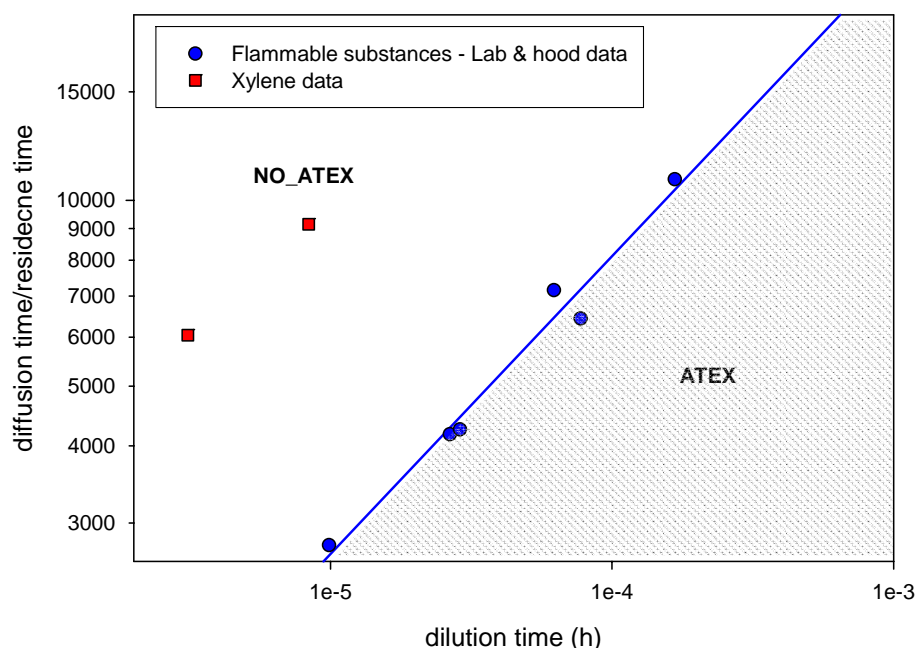
Figure 1 – ATEX / NO ATEX regions as a function of diffusion, dilution and residence time.

3. Conclusions

Current health and safety legislation requires that employer has to demonstrate that he has taken all organizational and/or technical measures to reduce the risk of harm to employees and other workers from hazardous material, so far as is reasonably practicable. For the case in which the quantities of flammable substances manipulated are small – as in the chemical laboratory – it is necessary to evaluate if some ATEX areas are generated, and specific equipments must be adopted.

The method presented in this work defines the maximum quantity of flammable substance that doesn't determine ATEX 137 zones, for which ATEX 95 directive equipment is required. In other words it permits to know the maximum volume of spillage of same flammable substances that can be tolerated without ATEX certified equipments.

The results of the proposed procedure have shown that in many cases the volume determining ATEX conditions is larger than capacity of containers generally used in laboratories. Therefore, depending on the type of substance, if containers in laboratories are smaller than 2.5 dm^3, both laboratory and hood may be classified as no-ATEX zones.

The procedure is particular useful in the design of laboratories in order to define the equipment and facilities requirements. Moreover the procedure is useful to establish the exercise limits in the management of activities in laboratory and in particular to define the maximum quantities of flammable liquids manageable without determining ATEX zone classification.

In any case, where flammable liquids or gases are handled in laboratories, it is always necessary to consider sources of ignition, even if there are no hazardous areas formally designated.

4. Acknowledgements

5. References

ATEX-GAS software, Version 2.1, TNE Tuttonormel, Torino

CEI EN 60079-10 (CEI 31-30): Costruzioni elettriche per atmosfere esplosive per la presenza di gas - Parte 10: Classificazione dei luoghi pericolosi.

CEI 31-35: Costruzioni elettriche per atmosfere esplosive per la presenza di gas - Guida all'applicazione della Norma CEI EN 60079-10 (CEI 31-30) - Classificazione dei luoghi con pericolo di esplosione per la presenza di gas, vapori o nebbie infiammabili.

CEI 31-35/A: Costruzioni elettriche per atmosfere esplosive per la presenza di gas - Guida all'applicazione della Norma CEI EN 60079-10 (CEI 31-30) - Classificazione dei luoghi con pericolo di esplosione per la presenza di gas, vapori o nebbie infiammabili: esempi di applicazione.

Directive 1999/92/EC. ATEX 137. European Union Directive on minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres

Directive 1994/9/EC. ATEX 95. European Union Directive on the approximation of the laws of Member States concerning equipment and protective systems intended for use in potentially explosive atmospheres.