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Flammability of gas mixtures Part 1: Fire potential

Volkmar Schröder*, Maria Molnarne

Bundesanstalt für Materialforschung und -prüfung (BAM), Abt. Chemische Sicherheitstechnik, Unter den Eichen 87, D-12205 Berlin, Germany

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Abstract

International and European dangerous substances and dangerous goods regulations refer to the standard ISO 10156 (1996). This standard includes a test method and a calculation procedure for the determination of the flammability of gases and gas mixtures in air. The substance indices for the calculation, the so called "*Tci* values", which characterise the fire potential, are provided as well. These ISO *Tci* values are derived from explosion diagrams of older literature sources which do not take into account the test method and the test apparatus. However, since the explosion limits are influenced by apparatus parameters, the *Tci* values and lower explosion limits, given by the ISO tables, are inconsistent with those measured according to the test method of the same standard. In consequence, applying the ISO *Tci* values can result in wrong classifications. In this paper internationally accepted explosion limit test methods were evaluated and *Tci* values were derived from explosion diagrams. Therefore, an "open vessel" method with flame propagation criterion was favoured. These values were compared with the *Tci* values listed in ISO 10156. In most cases, significant deviations were found. A detailed study about the influence of inert gases on flammability is the objective of Part 2.

Keywords: Gas classification; Flammability; Explosion limit; Test method; Calculation method

1. Introduction

One of the most important safety characteristics of gases and gas mixtures is their flammability in air. This information is necessary to prevent accidental explosions during chemical processes and to classify gases and gas mixtures for storage and transport. In many international and European regulations, a gas or gas mixture is classified as flammable if it has an explosion range in mixture with air at atmospheric conditions. Therefore, the explosion limits have to be measured. The terms explosion limit (EL) and flammable limit (FL) are interchangeable, but in Europe, it is recommended to use EL as defined in the standard EN 1127-1 [1]. Explosion limits are not independent physicochemical parameters. They are influenced by the determination method and by apparatus parameters, as most safety characteristics are. To ensure comparability, the international standardization of determination methods is particularly important.

The international standard ISO 10156 [2] includes a test method and a calculation procedure for the flammability of gases and gas mixtures. The substance indices needed for the calculation are the so called "*Tci* values", which characterise the fire potential of a flammable gas. Initially this standard was only prepared to classify gas mixtures for the selection of the correct cylinder valve outlets in combination with the newly developed ISO 5145 system of cylinder valves. The title of ISO 10156 "Gases and gas mixtures—Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets" clearly expresses this intention. In the meantime, the UN recommendations on the transport of dangerous goods and several European regulations, e.g. EC dangerous substances directives and the European transport regulations refer to ISO 10156 (1996). Therefore the ISO

* Corresponding author. Tel.: +49 30 8104 3440; fax: +49 30 8104 1217.
E-mail address: volkmar.schroeder@bam.de (V. Schröder).

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standard became particularly important in the field of explosion prevention, labelling and classifying of gases within the last years.

The Tci values and the lower explosion limits of many flammable gases and vapours are summarized in the ISO 10156 standard (see the annexes A.1–A.6 and Table 2 of ISO 10156). The listed values were taken from the available literature, without any evaluation of the test method used. Therefore many of the given explosion limits and *Tci* values are inconsistent with results of measurements, which were carried out by the University of Paderborn and by BAM [3–5] according to the test method described in ISO 10156 (1996) (DIN 51649-1). The results show that the application of the listed ISO values can result in wrong classification of gas mixtures.

In the following, the most frequently used international standard test methods for the determination of gas explosion limits are compared to evaluate their influence on tests results obtained. Furthermore, a method is shown to determine limiting values of flammability (*Tci* values) using explosion diagrams. For mixtures of flammable gas, nitrogen and air, the explosion ranges have been determined experimentally and the *Tci* values were calculated. These values have been compared with the values listed in ISO 10156.

2. International and European regulations on flammability of gases

A flammability classification with reference to the flash point, as usual for the flammable liquids, is not practicable for gases. According to the European dangerous substances regulations, e.g. Directive 67/548/EC [6], a gas or a gas mixture shall be classified as "extremely flammable" if it has an explosion range (explosion limits) in mixture with air at atmospheric conditions. In some international regulations, e.g. in the UN Recommendations on the Transport of Dangerous Goods [7] and in the corresponding European transport regulations (ADR, RID) [8,9], an exception was made for gases with lower explosion limits above 13 mol% and an explosion range (range between upper and lower explosion limit) not exceeding 12 mol%. These exceptions are especially important for ammonia and several refrigerant blends. This presents a compromise, because it is possible to get explosive atmospheres with ammonia, too. On the other hand, the high LEL of 13 mol% in air is usually not reached by smaller leakages. Nevertheless, newer tests according to DIN 51649-1 [10] resulted in explosion limits for ammonia, which do not meet the exception criterion any longer. Both, the European dangerous substances and transport regulations refer to the ISO 10156 for flammability test and calculation methods (see Table 1).

Table 2
GHS classification criteria for flammable gases [11]

Category	Criteria
1	Gases, which at 20 °C and a standard pressure of 101.3 kPa: (a) are ignitable when in a mixture of 13% or less by volume in air; or (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit
2	Gases, other than those of category 1, which, at 20 °C and a standard pressure of 101.3 kPa, have a flammable range while mixed in air

The scope of the Global Harmonization System (GHS) of classification and labelling systems for dangerous substances and goods [11] is based on the mandate by the 1992 United Nations Conference on Environment and Development (UNCED). The GHS tries to harmonize the different test methods and criteria for dangerous goods and substances worldwide, also for the flammability of gases. The GHS proposes to classify flammable gases in two categories, one category "extremely flammable", to be labelled with a flame symbol, and another group of only "flammable" gases without any additional labelling symbol (see Table 2).

Following these proposals, it is particularly important to have a suitable standard test method for the determination of flammability and explosion limits. ISO 10156 describes in No. 4.2 a test method for the flammability, but it does not give an accurate determination method for the explosion limits.

The implementation of European directives in the field of explosion prevention, which apply uniformly to all member states, required the development of a unified new European standard EN 1839 [12] for the determination of explosion limits. Two different test methods are proposed, a tube method (method T) and a bomb method (method B).

In addition to the new European standard, two frequently used national standard test methods are available for atmospheric conditions, the US standard ASTM E 681-01 [13] and the German DIN 51649-1 [10]. DIN 51649-1 was replaced by the DIN EN 1839 in January 2004.

3. Comparison of standard test methods for the determination of explosion limits

A fundamental difference between European and US methods is the definition of the explosion limit. According to the European standards [12,14], the explosion limit itself is

Table 1
International, European and German regulations for dangerous substances and goods, which refer to ISO 10156 (1996)

Regulatory areas	Transport of dangerous goods	Storage and use of dangerous substances
UN	UN recommendations on the transport of dangerous goods (Class 2 "Gases"), IMDG-Code, GHS	Global Harmonization System (GHS)
European	ADR, RID, ADNR, etc. (Class 2 "Gases")	67/548/EC, Annex V
German	GGVSE, GGVBinSch, GGVSee, etc. (Klasse 2 "Gase")	Chemikaliengesetz, Gefahrstoffverordnung