

Flammability of gas mixtures Part 1: Fire potential

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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.

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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

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

The T_{ci} 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 T_{ci} 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 (T_{ci} values) using explosion diagrams. For mixtures of flammable gas, nitrogen and air, the explosion ranges have been determined experimentally and the T_{ci} 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

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

substances and transport regulations refer to the ISO 10156 for flammability test and calculation methods (see Table 1).

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, GGVSsee, etc. (Klasse 2 “Gase”)	Chemikaliengesetz, Gefahrstoffverordnung

Table 3
Apparatus parameters of the compared standard test methods for explosion limit determination at atmospheric pressure

	DIN 51649-1	EN 1839 (T)	EN 1839 (B)	ASTM E 681-01
Ignition vessel	Glass cylinder, $\varnothing = 60$ mm, $H = 300$ mm	Glass cylinder, $\varnothing = 80$ mm, $H = 300$ mm	Closed spherical or cylindrical vessel, $V > 5$ dm ³	Glass flask, $V = 5$ dm ³
Ignition source	High voltage spark; duration, 0.5 s; power app., 10 W	High voltage spark; duration, 0.2 s; power, app. 10 W	Fused (exploding) wire, $E = 10$ – 20 J or high voltage spark; duration, 0.2 s	High voltage spark; duration, 0.5 s; power app., 10 W
Criterion	Visually, flame detachment	Visually, flame detachment and propagation of > 100 mm or halo of $H > 240$ mm	Pressure rise $\geq 5\%$ + pressure rise caused by the ignition in air	Visually, flame spread as far as 13 mm from the wall (horizontal or vertical)
Number of repetition tests	5	4	4	1
Step size	0.1 mol% ($EL \leq 10$ mol%), 0.2 mol% ($EL > 10$ mol%)	10% rel. ($EL \leq 2$ mol%), 0.2 mol% ($EL > 2$ mol%)	10% rel. ($EL \leq 2$ mol%), 0.2 mol% ($EL > 2$ mol%)	Arbitrary, to be stated if more than 10% rel.
Explosion limit	Last non-ignition point	Last non-ignition point	Last non-ignition point	Average value between last non-ignition point and first ignition point

not a part of the explosion range. Instead the lower explosion limit (LEL) is the highest concentration of a flammable gas in a gaseous mixture, in which a flame just fails to propagate after ignition. On the other hand, American standards and US authors [13,15,16] define the explosion limit as the limiting fuel concentration enabling the flame to propagate through the mixture. Explosion limits are often measured as average values between the last “non-ignition point” and the first “ignition point”. Depending on the step size selected for mixture preparation this difference can cause significant deviations. Nevertheless, from the point of safety, it is recommended to use the more conservative European definition with the last “non-ignition” concentration as explosion limit.

The two types of the most frequently used test methods for the determination of explosion limits are the “open vessel” and the “closed vessel” methods. In most cases, the open vessel methods use vertical glass tubes (or flasks), opened to the air prior to ignition, in which a flame detachment and propagation is observed visually in a pressureless, homogeneous gas mixture. ASTM E-681, DIN 51649-1 and EN 1839(T) are typical examples. The closed vessel methods, e.g. ASTM E 918, ASTM E 2079 and EN 1839(B) require pressure resistant autoclaves (bombs) as ignition vessels. The criterion is not the flame propagation, but a pressure rise after ignition. The US literature recommends a pressure rise of 7% as threshold condition. Possibly this criterion is chosen because it corresponds to an overpressure of 1 psia per atmosphere of initial pressure. In Germany, a 10% pressure rise was applied until replacement by the new European standard recommending a 5% criterion.

In general, the explosion limits are affected by the apparatus and material parameters. The most important are:

Material parameters:

1. Flammable mixture composition, type and amount of inert gas, fuel and oxidizer;

2. Initial temperature, initial pressure;
3. Flow state.

Apparatus parameters:

4. Determination procedure (step size, criterion);
5. Type and size of the ignition vessel (closed, open, dimensions, material);
6. Ignition source (type, power, duration and location);
7. Direction of flame propagation.

This list is not exhaustive. The worldwide published explosion limit data show, that for fixed material parameters the influence of the apparatus parameters leads to significant deviations of the experimental values.

In the following, the new European methods are compared with the German DIN 51649-1 and the US standard ASTM E 681-01. Therefore, the four standard apparatus were assembled and the explosion limits were examined for selected flammable gases and gas mixtures with different burning velocities. The German DIN 51649-1 test apparatus is also recommended by ISO 10156. The experimental parameters are summarized below:

All gas mixtures were prepared according to the partial pressures of the single components. For both tube methods (DIN 51649-1 and EN 1839 (T)), this was done in a separate 14-dm³ mixing vessel (explosion pressure resistant) at 2.0 bar (abs.). The error of mixture preparation was estimated to be smaller than one step size (0.2 mol%), as recommended in the EN 1839 standard. The ignition vessels were purged with about 12 dm³ of test mixture before firing the igniter. For the other two methods (ASTM E 681-01 and EN 1839 (B)), the components of test sample mixtures were filled directly into the ignition vessel and were homogenized by stirring before igniting.

For the ignition tests according to DIN 51649-1, EN 1839 (T) and ASTM E-681, a high voltage spark igniter was

Table 4
Explosion limits of hydrogen, ethylene, methane and ammonia in air [19,20]

	DIN 51649-1 (mol%)	EN 1839 (T) (mol%)	EN 1839 (B) (mol%)	ASTM E681-01 (mol%)
LEL (H ₂ -air)	3.8	3.6	4.2	3.75
UEL (H ₂ -air)	75.8	76.6	77.0	75.1
LEL (H ₂ -40% N ₂ -air)	3.6	3.6	4.4	3.65
UEL (H ₂ -40% N ₂ -air)	38.2	38.4	38.2	37.3
LEL (C ₂ H ₄ -air)	2.3	2.4	2.6	2.15
UEL (C ₂ H ₄ -air)	33.0	32.6	27.4	33.3
LEL (C ₂ H ₄ -40% N ₂ -air)	2.4	2.4	2.6	2.35
UEL (C ₂ H ₄ -40% N ₂ -air)	8.4	8.2	6.9	8.05
LEL (CH ₄ -air)	4.2	4.3	4.9	3.8
UEL (CH ₄ -air)	16.6	16.8	16.9	16.9
LEL (CH ₄ -40% N ₂ -air)	4.3	4.5	5.1	4.15
UEL (CH ₄ -40% N ₂ -air)	6.5	6.4	5.7	6.35
LEL (NH ₃ -air)	14.3	14.3	14.2	13.3
UEL (NH ₃ -air)	31.7	32.5	39.4	32.9
LEL (NH ₃ -20% N ₂ -air)	15.4	15.2	16.2	14.1
UEL (NH ₃ -20% N ₂ -air)	19.8	20.4	21.3	20.9

applied, as described in the standards. For the experiments according to EN 1839 (B), a spherical 14 dm³ stainless steel autoclave was used equipped with a fuse wire igniter in the centre. The igniter was fired by means of special electronic equipment. This igniter consists of two insulated electrodes at a distance of 5 mm, holding a nickeline wire with a diameter of 0.12 mm at their ends. The ignition energy is provided by a 1.5 kV A/230 V insulating transformer, which is connected to the igniter by an electronic switching unit. The ignition energies were determined to be about 15 J for a burning time of 3.5 ms by measuring voltage and current. This type of igniter is recommended by EN 1839 (B) and by several EN and ASTM standards [13,15–18]. The selected concentration steps for the ASTM E 681-1 tests amounted to 0.2 mol% for all experiments (Table 3).

The results of the ignition tests are shown in Table 4. All reported limits are given as mole fractions in per cent.

It becomes clear that a couple of explosion limits measured with the four standard test methods show significant deviations. The observations can be summarized as follows:

- The procedures according to DIN 51649-1 and EN 1839 (T) produce identical results in nearly all cases. The reason is the very similar test apparatus of both methods.
- In many cases, the ASTM method leads to similar results as DIN 51649-1 and EN 1839(T). ASTM shows the widest explosion ranges. This can be explained by the use of a 5-dm³ flask in connection with the sensitive visual criterion. However, a major disadvantage of this method is the unspecified step size in connection with the definition of the explosion limit (average value between ignition and non-ignition point). This may easily result in unsafe explosion data, if the concentration steps are not clearly stated.
- The closed vessel method EN 1839 (B) shows the highest deviations. LELs measured by this method are higher com-

pared to those from other methods. Also, a clearly lower UEL was observed for ethylene. The reason might be that the used pressure threshold criterion is less sensitive than the visual criterion. An exception was ammonia with a significant higher UEL. Possibly the large quenching distance of ammonia favouring ammonia reactions in the 14-dm³ sphere compared to smaller volumes contributes to this result.

- In general, the deviations obtained with gases, which are difficult to ignite, are higher. Typical examples are ammonia and the nitrogen mixtures. Such reactions are strongly affected by apparatus parameters.

Britton [21] evaluated explosion limit test methods in a survey paper in 2002. He recommended the ASTM E 2079 method with a 7% pressure rise criterion using a 5–20 dm³ bomb, which is comparable to the EN 1839(B) method as the most practicable one. Consequently, he did not recommend the European and German tube methods providing wider explosion ranges. Britton assumed that the preheated state of the gas mixture close to the spark is the reason for such wider ranges.

Nevertheless, for the use of explosion limits, it is necessary to know something about their applicability to practical conditions. In the field of explosion prevention, both types of explosion limits (flame propagation in a pipe or cloud and pressure rise in a closed vessel) are useful. Surely, in some cases, it is not necessary to use the more conservative flame propagation limits, e.g. for a gas mixture in a closed chemical reactor. On the other hand, it can be important to prevent the spread of a flame in a flowing gas mixture so that the flame detachment and propagation criterion is the right choice. Therefore, it is recommended to apply the flame propagation criterion for classification purposes, as given in ISO 10156, No. 4.2.

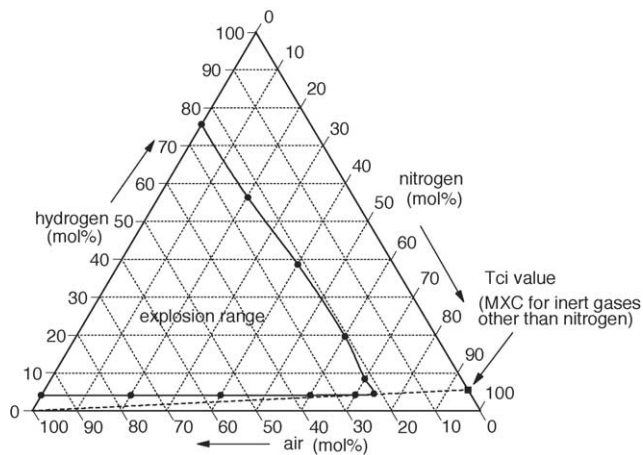


Fig. 1. Explosion diagram of the hydrogen–nitrogen–air system, measured at 20 °C and 101 kPa according to DIN 51649-1.

4. Explosion diagrams—the flammability calculation method and T_{ci} values

Explosion limits of ternary mixtures are often presented by explosion diagrams (triangular diagrams). The diagram of the hydrogen–nitrogen–air system is shown as an example in Fig. 1.

The dashed tangent represents a hydrogen–nitrogen mixture which is mixed with any content of air. The explosion range of hydrogen is not intersected by any air portions. That means this hydrogen–nitrogen mixture does not form any explosive mixtures in dilution with air. The point of the intersection of the tangent with the nitrogen axis is the so called T_{ci} value in accordance with the ISO 10156 definition. The hydrogen fraction of this point amounts to $T_{ci} = 5.5$ mol%.

If such a gas mixture of 5.5 mol% hydrogen in nitrogen would be tested according to the ISO 10156 test method by diluting it with air and making ignition tests, no flame propagation will be found.

For the determination of T_{ci} values, the explosion ranges of ternary systems must be known as demonstrated in Fig. 1. Therefore, it is necessary to measure the explosion limits of ternary gas mixtures close to the “nose” of the explosion range at high nitrogen fractions. This range of an explosion diagram is particularly influenced by apparatus parameters of the test method, as demonstrated in Section 3.

The explosion limits of many flammable gases and vapours according to the German and European standard and in addition many explosion diagrams with inert components are summarized in the CHEMSAFE database [22] and in a new data book [23,24]. CHEMSAFE is a German database for recommended safety characteristics, evaluated by experts of the Physikalisch-Technische Bundesanstalt (PTB) and BAM. Furthermore, this database lists safety characteristics derived from explosion diagrams, such as the so called MXC value (maximum permissible amount of combustible). In case the inert gas is nitrogen and the oxidizer is air at atmospheric conditions, MXC is identi-

cal to T_{ci} . In the meantime, many commercial users all over the world apply the CHEMSAFE database; for example, 239 in Europe, 173 in the US and Canada and 84 in Japan.

ISO 10156 proposes a method to calculate the flammability of gas mixtures using the T_{ci} values. That method is recommended for gas mixtures produced in small quantities, e.g. test gases. The application of this calculation method for the classification of gas mixtures is permissible in both, the European dangerous substances directives and in the transport regulations. A mixture can be classified as not flammable, if the following equation is satisfied:

$$\sum_{i=1}^n A_i \left(\frac{100}{T_{ci}} - 1 \right) \leq \sum_{k=1}^p B_k K_k \quad (1)$$

with A_i : fraction of flammable component i in the mixture (vol.%, mol%); n : number of flammable components; B_k : fraction of inert component k in the mixture (vol.%, mol%); p : number of inert components; K_k : coefficient of nitrogen equivalency; T_{ci} : maximum flammable gas content for which a mixture of the flammable gas i in nitrogen is not flammable in air (vol.%, mol%)

Eq. (1) is a semi-empirical one and is based on Le Chatelier’s [25] rule for the calculation of explosion limits of flammable gas mixtures. The assumption is that any flammable and inert components can be regarded as being additive. The equation was derived by transforming the equations given in ISO 10156, No. 4.6.1.

A list of T_{ci} and K_k values is provided by ISO 10156. K_k is roughly estimated by the molecular heat capacity of the inert gas. Per definition it amounts to $K_k = 1$ for nitrogen, to 0.5 for noble gases and to 1.5 for other non-flammable and non-oxidizing gases. A more detailed study about the influence of inert gases will be given in Part 2 of this paper.

5. Apparatus and test procedure for the determination of T_{ci} values

The explosion ranges of combustible–nitrogen–air mixtures at atmospheric pressure and room temperature were determined using a half-automatic test apparatus shown in Fig. 2. This apparatus is in accordance with the German DIN 51649-1. It corresponds to the testing equipment according to ISO 10156 and to test method A.11, EC Directive 67/548/EC.

The explosion vessel and ignition source were described above. A metering device with mass flow controllers (MFC) was used to purge the ignition vessel with a test mixture having the correct composition. Each channel of the MFC had to be calibrated before the ignition tests could start. For every gaseous component, a special calibration function was determined automatically by means of a precision gas meter. After calibration, the computer controlled device is able to provide any test mixture wanted for the ignition experiments. A gas volume 10-times the volume of the glass tube

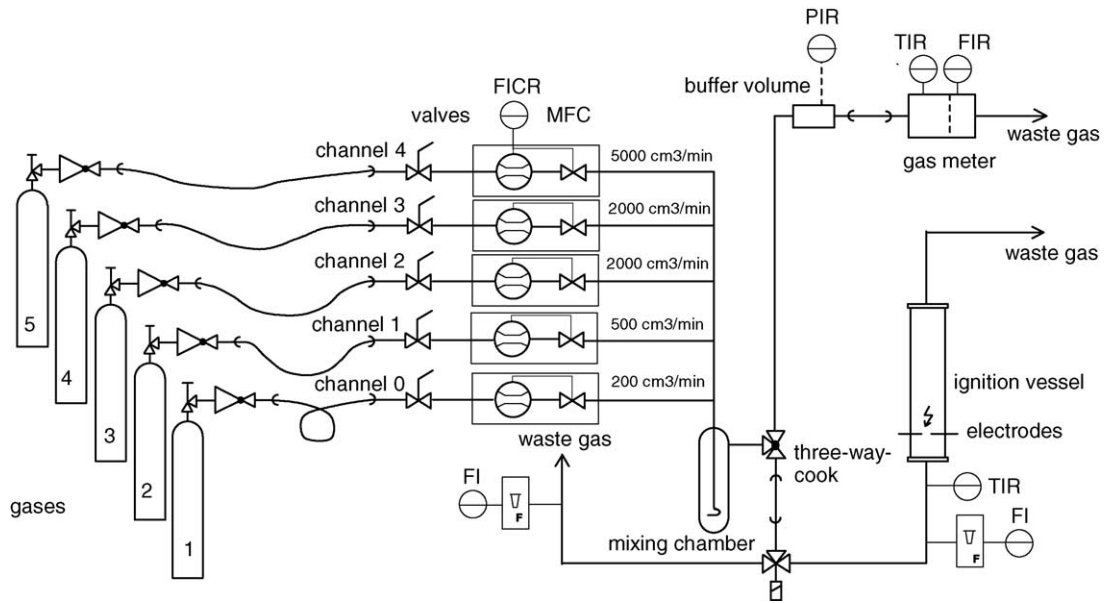


Fig. 2. Testing device for determining the explosion limits of gaseous samples.

was used to purge the vessel before the next test. Ignition tests were always carried out in the flow-free test mixture. The criterion of flammability was whether or not a flame detachment from the ignition source and propagation occurred after ignition. This was observed visually. The combustible content was increased in intervals until the explosion limit was reached. For combustible fractions less than 10 mol%, these intervals amounted to 0.1 mol%. For combustible frac-

tions above 10 mol%, tests were carried out with intervals of 0.2 mol%. If for a particular mixture, flame detachment just failed to take place, five repeated tests were carried out. The explosion limits given in this paper are the limiting percentages of the combustible component which just not lead to a reaction. The accuracy of the gas mixtures produced by means of MFC was checked by gas chromatography. For each ternary system, one sample mixture was analysed.

Table 5
T_{ci}-values calculated from explosion diagrams of different sources (20 °C, 101 kPa)

Flammable gas	ISO 10156 [2], <i>T_{ci}</i> (mol%)	BAM [3], <i>T_{ci}</i> (mol%)	Uni Paderborn [4], <i>T_{ci}</i> (mol%)	CHEMSAFE (recommended values) [22], <i>T_{ci}</i> (mol%)	Deviation between ISO and CHEMSAFE (%rel.)
Methane	14.3	8.5	9.5	8.7	+64
Ethane	7.6	4.5	4.6	4.5	+69
Propane	6.0	3.7	4.0	3.7	+62
<i>n</i> -Butane	5.7	3.6	3.8	3.6	+58
Isobutane	5.7	3.4	3.6	3.4	
Ethylene	6.0	4.1	4.3	4.1	+46
Propylene	6.5	4.2	4.0	4.2	+58
1-Butylene	5.5	3.3	–	3.3	+66
Hydrogen	5.7	5.4	5.6	5.5	+4
Carbon monoxide (pure and dry)	–	24.5	–	24.5	–
Carbon monoxide (con- taminated with hydro- gen or moist)	20	15.2	–	15.2	+32
Difluoroethane (R152)	4.6	8.7	–	8.7	–47
Chlorodifluoroethane (R142b)	5.5	26.3	–	26.4	–79
Ammonia	–	–	–	40.1	–
Acetylene	4.0	–	–	3.0	+33
Ethylene oxide	3.1	–	–	4.8	–35

6. Results and discussion

The explosion ranges of frequently used flammable gases in mixture with air and nitrogen were measured by the University of Paderborn [4,5] and BAM [3] applying the DIN 51649-1 (ISO 10156) test method. Furthermore, in the CHEMSAFE database [22], numerous ternary diagrams are available which were measured according to the DIN standard and which are recommended by German experts. For the calculation of T_{ci} values (see also Fig. 1), the special computer code TRIANGLE [26] was applied. This computer code yields a spline interpolation using experimentally determined points (explosion limits) and the T_{ci} values deduced. This program was developed for the standardized evaluation of explosion diagrams for ternary mixtures (triangular diagrams).

In the following table, the T_{ci} values from four sources are summarized for a number of gases.

T_{ci} values are influenced by measuring errors of the explosion limits. It must be considered, that the measuring error often is in the dimension of one step size (0.1–0.2 mol%). Due to the tangent correlation this can lead to considerable higher deviations for T_{ci} (see Fig. 1).

Table 5 shows clearly the differences between the ISO values and other T_{ci} values, calculated from DIN explosion limits. The ISO values of hydrocarbons are 50–70% higher than those derived from the CHEMSAFE explosion diagrams.

7. Influence of pressure and temperature on the flammability

Actually, the flammability (combustibility) is defined for atmospheric conditions only. This suffices for transport, storage and handling (leakages, etc.). In the process safety, however, non-atmospheric conditions must be considered. This is the case in exhaust systems, furnaces and pressurized pipes and vessels. Since the explosion range usually becomes larger with higher temperatures and pressures, their effect on flammability must be taken into account. Therefore, it is not allowed to adopt a non-flammability classification of a gas to non-atmospheric conditions. In some cases it is even possible, that “non-flammable” classified substances become flammable at higher temperatures or pressures. Typical examples are partially halogenated hydrocarbons.

Fig. 3 shows the enlargement of the explosion range of the refrigerant R134a. R134a is not flammable at atmospheric conditions, but at 280 °C the explosion range touches the air line. That means R134a can form explosive mixtures with air at higher temperatures. This behaviour can be observed not only for pure materials, but also for mixtures of fluorinated hydrocarbons, the so called refrigerant blends. Usually such blends are composed in such a way that they are classified as “non-flammable” according to the refrigerant regulations. Nevertheless, at higher temperatures or higher pressures in closed devices those “non-flammable” substances are able to cause accidental fires and explosions.

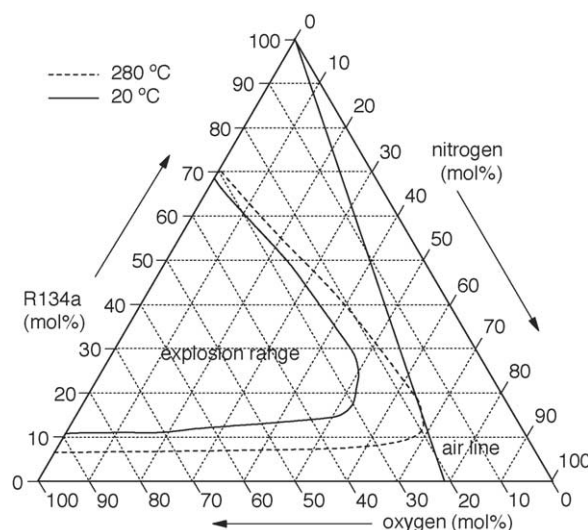


Fig. 3. Explosion range of 1,1,1,2-tetrafluoroethane (R134a refrigerant) at 101 kPa and temperatures of 20 and 280 °C [27].

8. Conclusions

The experiences in the determination of T_{ci} values can be summarized as follows:

- It is necessary to apply a standardized test method for measuring explosion limits and T_{ci} values. Three of the most used open vessel test methods, ASTM E 681-01, EN 1839(T) and DIN 51649-1 are suitable for the T_{ci} determination and yield similar results in the LEL range.
- The CHEMSAFE database contains explosion diagrams measured according to standard test methods. Therefore it is recommended to use T_{ci} values from CHEMSAFE for flammability calculations of gas mixtures.
- Applying ISO data for the calculation of the flammability may result in wrong classifications and explosion hazards.
- It is not recommended to apply the so called bomb methods for classification purposes, as given by EN 1839(B) [12] and ASTM E 2079 [18]. The pressure rise criterion of these methods is less sensitive compared to the flame propagation criterion. A classification procedure, however, shall include all dangerous situations, pressure rise in a closed vessel as well as flame propagation in a flowing mixture.

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