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Comparison of two standard test methods for determining explosion limits of gases at atmospheric conditions

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Abstract

A comparison is made between two internationally accepted methods to determine the explosion limits of gases at atmospheric pressure and room temperature (20 l sphere — DIN 51649). Significant differences (about 1 vol.%) in the upper explosion limits (UEL) values are found for four hydrocarbons tested. A new criterion is proposed which leads to close agreement between the UEL values obtained by the two methods. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

When working with explosive gases the accurate knowledge of the explosion limits is very important. Unfortunately there are a lot of parameters that influence the explosion limits. The data collected by Coward and Jones [1] illustrates this very clearly. Even the definition of explosion limits differs from author to author. The American standards ASTM E681 [2] and E918 [3] and authors like Zabetakis [4] and Lees [5] define the explosion limits as the fuel concentrations where the flame is just capable of propagating from the ignition source through the mixture. The DIN 51649 standard [6] and authors like Bartknecht [7] and Conrad et al. [8] define the explosion limits as the fuel concentrations beyond which the mixtures are NOT ignitable.

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The parameters that influence the explosion limits can be divided in three groups:

1. the apparatus containing the gas mixture (shape and volume of the explosion vessel, ignition source, direction of flame propagation, open or closed vessel, etc.),
2. the physical condition of the gas mixture (pressure, temperature, turbulence, moisture, etc.),
3. the operator (criterion of ignition, accuracy, etc.).

A number of researchers have investigated the influence of some of these parameters. The conclusion is that almost every parameter can lead to a change of the explosion limits with several percentage points. So, it is quite clear that international normalisation of the experimental set-up and the procedure for measuring the explosion limits of gases is required.

Four different apparatuses and procedures for determining the explosion limits of gases at atmospheric conditions are internationally accepted. In the past, a lot of data was measured by the Bureau of Mines [1]. They used an open vertical glass cylinder of 5 cm diameter and 150 cm long as explosion vessel. The ignition source was an induction spark or a pilot flame and it was visually observed whether the gas mixture was explosive or not. In the ASTM E681-94 [2] the explosion vessel is a closed 5 dm³ glass sphere. The ignition source is a spark between two electrodes or a paper match head. Both sources are located at the centre of the sphere. The ASTM standard does not prescribe the required ignition energy. Again visual observation determines whether the gas mixture is explosive or not. DIN 51649 [6] is another standard which describes a test method for measuring the explosion limits. The explosion chamber is an open vertical glass tube 30 cm in height with a diameter of 6 cm. As ignition source a spark between two electrodes at the bottom of the cylinder is used. The criterion of ignition is the detachment of the flame from the ignition source. In the fourth test method the test apparatus is a 20-l steel sphere with two electrodes in the centre for spark ignition [10]. During a test the pressure inside the sphere is recorded. The criterion of ignition is based on the recorded pressure rise (i.e., the explosion pressure has to exceed a certain minimum value).

All these different test methods give rise to different results. It would be useful to know, therefore, whether the explosion limits according to one test method may be converted to the explosion limits according to another test method.

At this moment Working Group 1 of the European Commission TC 305 is working on a European standard for determining explosion limits of gases at atmospheric conditions. They consider the use of the DIN glass tube apparatus and the 20-l sphere because there exists a lot of data determined with these apparatuses. For this reason in this study these two test methods are compared and one tries to find a way to convert the data of one apparatus to the other or to modify the test method such that the two lead to the same explosion limit values.

2. Experimental apparatus and procedure

The following two apparatuses were used to conduct the testing in this study: the glass tube and the 20-l sphere.

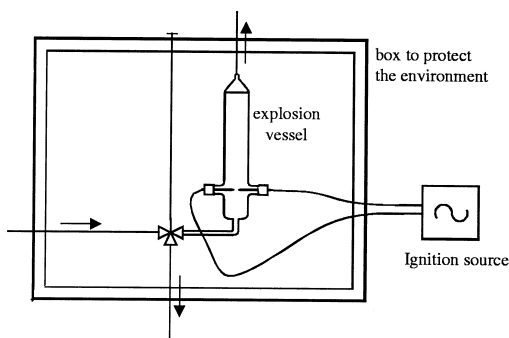


Fig. 1. Glass tube apparatus.

2.1. Glass tube apparatus

Fig. 1 shows the glass tube apparatus. It is built in accordance with DIN 51649 [6] and with the draft European standard prEN1839 [9]. The explosion test vessel is a vertical glass cylinder 30 cm in height and with an inner diameter of 6 cm. The top end of the tube is open. Before each test the tube is purged at least 10 times its internal volume with the gas mixture to evacuate remains of prior tests. As ignition source an induction spark between two electrodes is used. The electrode gap is 5 mm and they are located 6 cm above the bottom of the tube. The ignition arc is generated by a high-voltage transformer (15 kV) and is maintained for 0.5 s. The ignition energy released is approximately 5 J [9], which is sufficiently high to ignite a combustible mixture.

The criterion used to judge whether a mixture is explosive or not is the detachment of the flame from the spark gap (Fig. 2). It is not necessary that the flame propagates over the full height or the full diameter of the tube, but the flame has to exist without the arc. This process of “flame detachment” is visually observed in complete darkness. The lower explosion limit is the highest gas concentration of a mixture in which the flame is not capable of propagating away from the ignition source. Correspondingly the upper explosion limit is the lowest gas concentration (above stoichiometric concentration) of a mixture in which the flame is no longer able to propagate away from the ignition source.

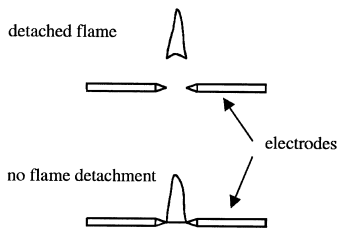


Fig. 2. Flame detachment.

2.2. 20-l sphere

Fig. 3 shows the experimental apparatus with the 20-l sphere. The explosion vessel consists of a closed steel sphere with an internal volume of 20 dm³. This sphere is the standard apparatus for testing dust explosions and is described in VDI 2263 [10]. The advantage of this set-up is that the same apparatus can be used to test gas and dust explosions. Before each test the sphere is evacuated and purged with the gas mixture. The mixture is ignited with an induction spark drawn between electrodes located at the centre of the sphere. The electrodes are 5 mm apart. A high voltage transformer (25 kV) generates a continuous arc of 4 s duration. This corresponds with an ignition energy of approximately 10 J. So, the period of the arc is longer than the explosion duration. The arc by itself does not generate a pressure rise. The pressure history during a test is recorded with a piezo-electric pressure transducer. The occurrence of an explosion is evaluated by the recorded pressure increase after the ignition, as described in ASTM E918 [3]. A test showing a pressure rise of 7% or more is called an explosion. The explosion limits are defined by the min–max criterion [3]. The min–max criterion defines the upper explosion limit (UEL) as the average between the highest explosive fuel concentration (U_1) and the lowest non-explosive fuel concentration (U_2) and the lower explosion limit (LEL) as the average between the lowest explosive fuel concentration (L_2) and the highest non-explosive fuel concentration (L_1).

2.3. Procedure

First a buffer vessel is filled with the required homogeneous fuel/air mixture. Two different mixing procedures were used depending on the fuel. The methane/air mixtures are produced by using two mass flow controllers (MFC) to control the flow rate of each gas. These separated flows are mixed in a static mixing chamber in order to homogenise the mixture. This method ensures the best accuracy but is useless for mixing the other

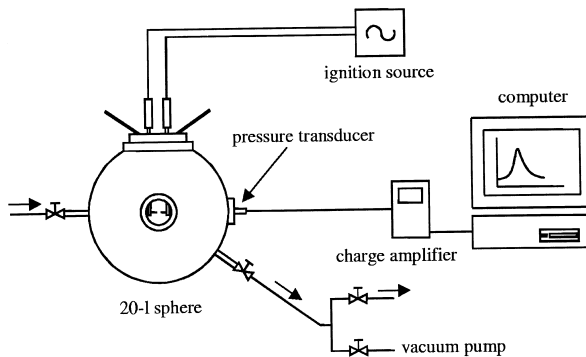


Fig. 3. 20-l sphere.

chemicals because their saturation pressure at room temperature is too low to use the MFCs. These gas mixtures are produced by introducing the gas and the air consecutively in the buffer vessel according to their required partial pressures. After filling of the vessel the mixture is circulated through a mixing loop at least 10 times to obtain complete mixing. The relative error of the fuel concentration of the gas mixtures in both methods is between 1% and 3%.

The 20-l sphere and the glass tube apparatus are purged and filled with the mixture of the buffer vessel. Then the mixture is tested in each set-up according to their procedures (cf. previous subsections). When the mixture did not ignite in the glass tube apparatus a second test was performed with the same mixture from the buffer vessel as dictated by the DIN standard. If there was still enough mixture in the buffer vessel also a third test was performed.

This procedure is repeated with another fuel concentration until the explosion limits are found. All experiments were performed with dry air at atmospheric pressure and room temperature and the results are found in Ref. [11].

The advantage of this procedure is that the gas mixture tested in both apparatuses is identical. Therefore, the results can be compared with each other without taking into account the concentration error.

3. Results and discussion

3.1. Results

The lower explosion limit (LEL) and the upper explosion limit (UEL) of four hydrocarbon gases (methane, ethane, propane, butane) have been measured. Table 1 shows the results. For each gas the explosion range according to the DIN 51649 is wider than the explosion range measured in the 20-l sphere. Especially the UEL differs with the method used.

3.2. Correlation between the explosion limits of both apparatuses

Figs. 4 and 5 show the LEL and UEL values of Table 1. The explosion limits according to the glass tube method are given in the ordinate and the explosion limits

Table 1
Explosion limits of methane, ethane, propane and butane

Gas	20-l sphere				Glass tube	
	LEL _{7%} (vol.%)	UEL _{7%} (vol.%)	LEL _{2%} (vol.%)	UEL _{2%} (vol.%)	LEL _{DIN} (vol.%)	UEL _{DIN} (vol.%)
Methane	4.85 ± 0.11	15.1 ± 0.3	4.58 ± 0.11	15.9 ± 0.3	4.60 ± 0.06	16.2 ± 0.2
Ethane	2.53 ± 0.09	13.8 ± 0.2	2.46 ± 0.09	14.1 ± 0.2	2.39 ± 0.05	14.8 ± 0.2
Propane	1.93 ± 0.07	9.4 ± 0.2	1.85 ± 0.07	10.2 ± 0.2	1.82 ± 0.04	10.5 ± 0.2
Butane	1.55 ± 0.04	8.1 ± 0.2	1.38 ± 0.04	8.6 ± 0.2	1.34 ± 0.03	8.9 ± 0.2

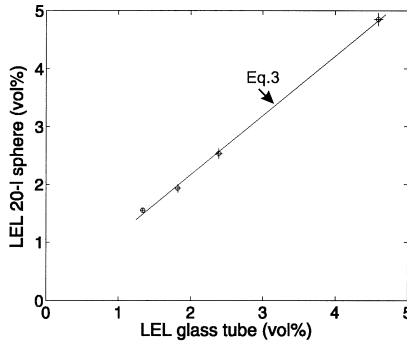


Fig. 4. Correlation for the LEL.

according to the 20-l sphere method are given in the absciss. The small horizontal and vertical lines through the data points correspond with the inaccuracies of the concentrations. The figures indicate a linear correlation between the explosion limits of both methods. By means of a regression procedure one obtains as correlation:

$$LEL_{7\%} = 1.03LEL_{DIN} + 0.11 \tag{1}$$

$$UEL_{7\%} = 0.98UEL_{DIN} - 0.76 \tag{2}$$

The constants are determined by the method of least squares. With these correlations the explosion limits according to the glass tube method can be converted to the explosion limits according the 20-l sphere method and vice versa.

3.3. An adapted criterion for the 20-l sphere

Fig. 6 shows the dependence of the explosion pressure rise in the 20 l sphere on the concentration near the UEL for ethane. A similar behaviour was observed for the LEL

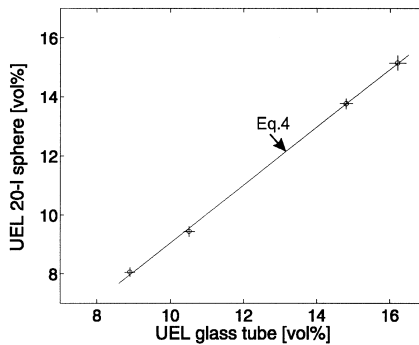


Fig. 5. Correlation for the UEL.

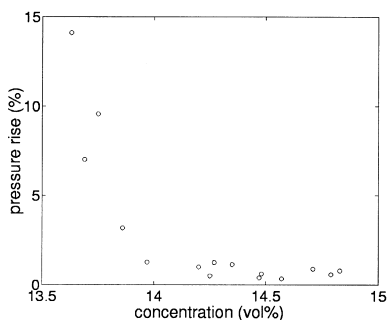


Fig. 6. Pressure rise as a function of the ethane concentration near the UEL.

and for the other hydrocarbons investigated. It is obvious from Fig. 6 that when the explosiveness criterion is decreased from 1% then the UEL will increase and approach the value obtained by the DIN method. The same is true for the LEL value.

A second reason to decrease the cut-off value of the explosion criterion is that at the explosion limits the flame propagates only upwards [1,4,11]. This means that only the part of the mixture above the ignition source reacts. The shape of the burned volume is a cone upside down with the top at the ignition source [12,13]. The volume ratio of this cone to the total volume of the sphere is small. The oxidation reactions at the limits are partially which results in lower explosion pressures. Also the flame velocity at the limits is low which results in a high heat loss during the combustion. Taking into account these previous tree arguments, the pressure rises at the limits are very small. The experimental research of Furno et al. [13] proved this statement. They measured a pressure rise of 1 to 5% at the UEL of butane and the LEL of hydrogen.

Considering the previous remarks, it is obvious that a criterion of pressure rise of 7% is too large. Therefore the criterion of ignition to evaluate the tests in the 20-l sphere is adapted. A pressure rise of 2% is chosen as cut-off criterion instead of 7%. There are two reasons for choosing this adapted criterion. First a pressure rise of 2% can be measured accurately in the 20-l sphere whereas a pressure rise of 1% cannot (cf. Fig. 6).

The second reason for choosing a criterion of pressure rise of 2% is given by Heinonen et al. [12]. They did a similar study but with two different apparatuses (ASTM E681 test apparatus and NMERI 8 l explosion sphere). During the tests in the ASTM E681 test apparatus they observed visually the flame development and they recorded the pressure rise at the same time. The gases tested were refrigerants. They concluded that visual indication of flammability (the cone method) in the ASTM test apparatus at atmospheric pressure corresponds to an explosion overpressure of slightly over 2.1 kPa. This equals a pressure rise of 2%.

In order to take into account the stochastic nature of the combustion process near the explosion limits it is proposed to interpolate the pressure rise data to 2% by means of a least squares linear approximation of the data ($EL_{2\%}$). Table 1 gives the original and adapted explosion limits according to the 20 l sphere and the explosion limits according to the DIN method.

As shown by Table 1 the adapted limits $EL_{2\%}$ are almost the same as the explosion limits according to the DIN method. The exact correlations between the adapted explosion limits of both methods, determined by the method of least squares are:

$$LEL_{2\%} = 0.98LEL_{DIN} \quad (3)$$

$$UEL_{2\%} = 0.97UEL_{DIN} \quad (4)$$

The conclusion that there is close agreement between the visual indication of flammability and the 2% pressure rise criterion is valid not only for the four hydrocarbons tested in this study. Heinonen et al. [12] concluded the same for experiments with many different gases in different apparatuses. So, there are indications that our conclusion is also valid for other flammable gases. This is not surprising as a 2% pressure rise corresponds to a very small percentage of the total pressure rise (several 100%) which occurs during complete combustion. In other words a 2% pressure rise takes into account phenomena such as strained flames, cool flames etc.

4. Conclusions

The lower and upper explosion limits of four hydrocarbons (methane, ethane, propane and butane) at atmospheric conditions are determined with two internationally used test methods. The explosion range of each gas according to the DIN test method is wider than the explosion range measured in the 20-l sphere. A linear correlation between the explosion limits according to the DIN-method and the explosion limits of the 20-l sphere is found. The criterion of ignition is the main reason for the significant difference of the explosion range. Therefore the criterion of ignition used to evaluate the test in the 20-l sphere is adapted to a pressure rise of 2%. This leads to very good agreement between the results of the two methods.

Taking into account this result, the criterion of ignition of the 20 l sphere method should be adapted to a 2% pressure rise. The ASTM E918 standard [3] should also be adapted. The comparison between visual observation of flame propagation and pressure rise is also important for experiments in order to determine the explosion limits at increased initial pressures. Explosion tests at elevated pressures are performed in closed vessels and because of the high pressures there are practical problems to observe the flame visually.

Of course the above conclusions are based upon a limited number of experiments. Further work could be done to investigate the general applicability of the conclusions and this with respect to the type of gas, test pressures and temperatures, etc.

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References

- [1] H.F. Coward, G.W. Jones, Limits of flammability of gases and vapors, US Bureau of Mines, Bulletin 503, Washington, DC, 1952.
- [2] ASTM E681-94, Standard test method or concentration limits of flammability of chemicals, American Society for Testing and Materials, Philadelphia, 1994.
- [3] ASTM E918-83 (Reapproved 1993), Standard practice for determining limits of flammability of chemicals at elevated temperature and pressure, American Society for Testing and Materials, Philadelphia, 1993.
- [4] M.G. Zabetakis, Flammability Characteristics of Combustible Gases and Vapours, US Bureau of Mines, Bulletin 627, Washington, DC, 1965.
- [5] P.F. Lees, Loss prevention in the process industries, Butterworths, London, 1980.
- [6] DIN 51 649 Teil 1, Bestimmung der Explosionsgrenzen von Gasen und Gasgemischen in Luft, Deutsches Institut für Normung, Berlin, 1986.
- [7] W. Bartknecht, Explosionsschutz: Grundlagen und Anwendung, Springer-Verlag, Berlin, 1993.
- [8] D. Conrad, T. Grewer, B. Hentschel, T. Redeker, Development of a standard method for flammability limits of vapour-air mixtures, 7th Int. Symp. on Loss Prevention and Safety Promotion in the Process Ind., European Federation of Chem. Eng., Italy, 1992.
- [9] prEN1839, Determination of explosion limits of gases vapours and their mixtures, European Standard, 1995.
- [10] VDI 2263 Part 1, Test methods for the determination of the safety characteristics of dusts, Verein Deutscher Ingenieure, 1990.
- [11] G. De Smedt, J. Berghmans, Explosion phenomena: A test apparatus to determine the explosion limits of gases at high pressure and temperature, final report, in Dutch, K.U. Leuven, 1998.
- [12] E.W. Heinonen, R.E. Tapscott, F.R. Crawford, Methods development for measuring and classifying flammability/combustibility of refrigerants, DOE/CE/23810-50, NMERI, The University of New Mexico, Albuquerque, 1994.
- [13] A.L. Furno, E.B. Cook, J.M. Kuchta, D.S. Burgess, Some observations on near-limit flames, 13th Int. Symp. on Combustion, 1971, pp. 593.