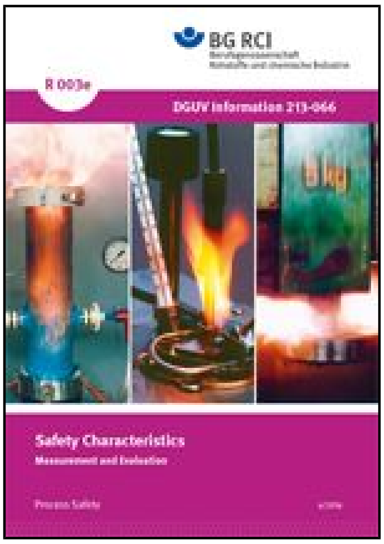
Process Safety

Safety Characteristics

Measurement and Evaluation



R 003e
DGUV Information 213-066
Edition 4/2016
(Translation of the German edition 4/2016 (including editorial changes made in the reprint 7/2017),
replaces the English edition 2/2007)

Inhaltsverzeichnis dieses Ausdrucks

Cover sheet . . . 4
1 Introduction . . . 4
Objective and target group . . . 4
Determining and applying safety characteristics . . . 4
Legal information . . . 5
Assignment of safety characteristics to safety concepts . . . 6
2 Explosive and potentially explosive substances . . . 10
2.1 Thermal sensitivity . . . 13
2.1.1 Steel tube test (Koenen test) . . . 13
2.1.2 Dutch pressure vessel test . . . 15
2.2 Mechanical sensitivity . . . 16
2.2.1 Impact sensitivity (fallhammer test) . . . 16
2.2.2 Friction sensitivity (friction test) . . . 19
2.3 Detonation properties . . . 20
2.3.1 Trauzl test (lead block test) . . . 20
2.3.2 Steel tube test (UN gap test) . . . 21
2.3.3 Steel tube test . . . 22
2.4 Deflagration properties . . . 23
2.4.1 Time/pressure test (UN Test C.1) . . . 23
2.4.2 Deflagration test (UN Test C.2) . . . 24
2.4.3 Deflagration test (VDI 2263-1) . . . 24
3 Flammable gases and vapours . . . 25
3.1 Explosion limits and limiting oxygen concentration . . . 25
3.2 Maximum explosion pressure and maximum rate of pressure rise . . . 28
3.3 Limiting pressure of stability (limiting ignition pressure) . . . 29
3.4 Minimum ignition energy . . . 30
3.5 Gap width preventing flame propagation (Maximum experimental safe gap) . . . 31
3.6 Aerosols . . . 32
3.7 Chemically unstable gases . . . 34
4 Flammable liquids . . . 35
4.1 Flash point . . . 35
4.2 Explosion points . . . 39
4.3 Sustained combustibility (UN Test L.2) . . . 39
4.4 Auto-ignition temperature . . . 40
5 Flammable solids . . . 42
5.1 Burning class . . . 42
5.2 Burning rate (UN Test N.1) . . . 44
5.3 Smouldering point . . . 45
6 Substances which, in contact with water or moist air, emit flammable gases . . . 46
6.1 UN Test N.5 . . . 46
7 Selfigniting substances . . . 47
7.1 Test for pyrophoric properties (UN Test N.2 and N.3) . . . 48
7.2 Test for self-ignition with linear rate of heating (Grewer oven test) . . . 50
7.3 Relative self-ignition temperature for solids . . . 52
7.4 Test for self-ignition with adiabatic hot-storage tests . . . 53
7.5 Test for self-ignition at a constant temperature (hot-storage test) . . . 55
7.6 Minimum ignition temperature of a dust layer with a one-sided thermal load . . . 57
8 Combustible dust clouds . . . 57
8.1 Dust explosibility . . . 58
8.2 Maximum explosion (over)pressure and maximum rate of pressure rise . . . 60
8.3 Explosion limits and limiting oxygen concentration . . . 62
8.4 Minimum ignition energy . . . 62
8.5 Minimum ignition temperature of a dust cloud . . . 64
9 Electrostatic properties . . . 66
9.1 Conductivity . . . 67

9.2 Volume resistivity 68
9.3 Volume resistance 68
9.4 Leakage resistance/resistance to earth 68
9.5 Surface resistance 69
10 Oxidising properties 69
10.1 UN Test O.1 70
10.2 UN Test O.2 71
10.3 UN Test O.3 71
11 Thermal stability of substances/exothermic chemical reactions 71
11.1 Thermal stability of substances/exothermic chemical reactions 71
11.1.1 Differential thermal analysis and differential scanning calorimetry 72
11.1.2 Calvet calorimeter 74
11.1.3 Microcalorimeter 76
11.1.4 DTA-analogous tests in the gram range, pressure and volume measurements 77
11.1.5 Thermogravimetry 77
11.2 Reaction calorimetry 78
11.3 Adiabatic calorimetry 80
11.3.1 Dewar methods 81
11.3.2 Methods with a controlled adiabatic jacket 82
11.4 Heat accumulation storage test (UN Test H.1) 84
Bibliography 85
Picture credits 92
Miscellaneous 93

The paper at hand is focussed on essential items of individual regulations and rules and for this reason it does not mention all measures required for a particular case. Moreover, the state of the art or the legal basis may have changed since the Code of Practice was issued.

This paper has been compiled with great care by the subcommittee “Verfahrenstechnik und Druckanlagen“ of the expert committee “Rohstoffe und chemische Industrie“ of the DGUV. However, this does not absolve the employer or an authorised person from the duty and responsibility of checking the information to be complete, correct and up to date.

The Act on the Protection at work uses the term “employer“, the Social Security Code VII and the Accident Prevention Regulations of the Accident Insurance Institutions say “entrepreneur“. Both terms are not completely identical, because an entrepreneur does not necessarily employ workers. This fact is irrelevant for the topic treated in this paper, and the term “entrepreneur“ is used here.

1 Introduction

Prerequisite to the safe execution of chemical and physical procedures is an understanding of the thermal properties of the chemicals being handled. Users must have a thorough knowledge of the way in which starting materials and auxiliaries, intermediates, byproducts, end products and residues behave under normal process conditions, as well as when deviations occur from normal processes. Safety characteristics provide an insight into potential fire and explosion hazards posed by substances[1] as well as their reactive properties and so represent an important bedrock for commensurate safety concepts. Untoward events during handling of explosive, combustible[2] or thermally sensitive substances often have their cause in the fact that their properties have not been properly researched.

Objective and target group

This paper aims to acquaint senior representatives from production, research, project management and applications technology as well as persons whose duty is to monitor site safety with the pertinent safety characteristics, the methods by which these are measured and ways in which they are put into practice. Its purpose is to raise an awareness of the day-to-day issues for which a knowledge of the data can be important.

The list of test procedures presented in this document is not exhaustive. The procedures are touched upon only briefly and are often subject to additional formal and standardised general conditions which will not be dealt with here. The paper is not to be seen, therefore, as a guide to performing the tests.

---

[1] The term “substances“ should be construed as also including “mixtures“. The various instructions for performing tests include such terms as “sample“, “test material“, “test substance“ and “material“. For consistency the term “substance“ is used here throughout.

[2] The term “combustible“ is sometimes used colloquially to describe substances that are “flammable“ in the sense of Regulation (EC) No 1272/2008 (CLP Regulation) and the transport regulations, as well as substances that are known to be oxidisable. Rules and regulations such as TRGS 510 draw a clear distinction between “flammable“ and “combustible“. In this paper an indication is given of what the term “combustible“ should be construed as meaning.

Determining and applying safety characteristics

Safety characteristics provide quantitative or qualitative information concerning substance properties important for assessing the hazards associated with chemical substances and reaction mixtures and for establishing constructive, technical and organisational measures.

With a few exceptions, safety characteristics are not physical constants but depend rather on the method of measurement used and on ambient conditions. Normally, therefore, the method used is quoted in addition to the numerical values that were determined. A standard method should be used wherever possible in order to enable the results from various test facilities to be compared with one another.

Furthermore, test results usually depend on the composition, purity and possibly the physical consistency of the substances. Changing the source of supply or altering the manufacturing process including workup (possibly leading to modification of the crystalline form or a change in particle size or to a qualitatively or quantitatively different byproduct content) can also change the safety characteristics of substances. In order to study actual characteristics, it is better to use the substances and commercial products that are employed in the production facility rather than highly pure analytical substances.

Adopting safety characteristics from the literature is only appropriate for substances that fully meet a given specification. For all other substances it is necessary to determine the relevant parameters, usually through experimentation.

Test results must be interpreted based on solid chemical and physical expertise and on thorough acquaintance of the person performing the assessment with the operating conditions. There is no way around making experience-based decisions and bearing responsibility for them.

This paper describes the most important safety characteristics that characterise the fire and explosion hazards presented by substances and the ways in which reaction mixtures behave. In addition to defining the parameters and describing the methods used to determine them, it presents the criteria used to support transformation of the results into operational safety concepts. Practical work sometimes calls for a need to maintain a safety margin from the limit values found.

The tests presented herein are normally satisfactory for recognising the hazard potential of a substance or reaction mixture and for setting safe working and processing conditions. Not all safety characteristics need to be measured in order to achieve this aim. What tests are needed in a given case depends, on the one hand, on the applicable regulations and, on the other, on the chosen safety concept.

For companies that only occasionally need to perform those tests and may not wish to purchase the necessary apparatus and equipment, BG RCI provides contact to institutions and other companies which are able to perform the tests against reimbursement of cost.

Legal information

The test methods mentioned in this publication are to a large extent part of the UN Manual of Tests and Criteria[3], a subset of the UN Recommendations on the Transport of Dangerous Goods (the so-called “Orange book“).

Under the German Hazardous Substances Act, since June 1, 2015 Regulation (EC) No 1272/2008 (the CLP Regulation) has been the only regulation controlling the classification, labelling and packaging of hazardous substances. The classification of the CLP Regulation is based on the UN Manual of Tests and Criteria and contains new hazard classes and, in some cases, modified/different classification criteria. Since, however, not all hazardous properties are covered in the CLP Regulation in the same way as in the chemicals legislation previously applied,

---

[3] See Appendix No 79

reference is made at several points in this paper to Council Regulation (EC) No 440/2008, which does incorporate the test methods of the previous chemicals legislation.

Further sources of information are the relevant DIN, EN and ISO standards as well as EC directives and VDI guidelines. In most instances, the legal basis of the tests is mentioned in the descriptions of the individual methods, though no claim is made that these are complete or exhaustive. Numerous national and international committees have developed their own test methods and procedures and made them binding for their own particular purposes, frequently with the support of national or international legislation.

Figure 1: Determination of burning rate and oxidising properties

Figure 2: Ignition in an Erlenmeyer flask during determination of ignition temperature

Assignment of safety characteristics to safety concepts

Explosive substances	Section 2
Information on the thermal and mechanical sensitivity and on detonation and deflagration properties	
Thermal sensitivity	Section 2.1
Mechanical sensitivity	Section 2.2
Detonation properties	Section 2.3
Deflagration properties	Section 2.4
Flammable gases and vapours	Section 3
Safety concept: Avoidance of explosive atmospheres	

Explosion limits	Section 3.1
Limiting oxygen concentration	Section 3.1
Safety concept: Avoidance of effective ignition sources	
Limiting pressure of stability	Section 3.3
Minimum ignition energy	Section 3.4
Maximum experimental safe gap	Section 3.5
Electrostatic parameters as appropriate	Section 9
Safety concept: Constructive explosion protection	
Maximum explosion overpressure	Section 3.2
Maximum rate of pressure rise	Section 3.2
Maximum experimental safe gap	Section 3.5
Information on aerosols and chemically unstable gases	
Aerosols	Section 3.6
Chemically unstable gases	Section 3.7
Flammable liquids	**Section 4**
Safety concept: Avoidance of ignition	
Flash point	Section 4.1
Explosion points	Section 4.2
Auto-ignition temperature	Section 4.4
Information concerning fire spread	
Sustained combustibility	Section 4.3
Also pay attention to	
Emission of flammable gases and vapours	Section 3
Self-ignition behaviour	Section 7
Thermal stability	Section 11
Combustible solids	**Section 5**

Information concerning fire behaviour	
Burning class	Section 5.1
Burning rate	Section 5.2
Smouldering point as appropriate	Section 5.3
Also pay attention to	
Ignitability in contact with water or moist air	Section 6
Self-ignition behaviour	Section 7
Dust explosion hazards	Section 8
Thermal stability	Section 11
Substances which, in contact with water or moist air, emit flammable gases	**Section 6**
Information on emission of flammable gases	
UN Test N.5	Section 6.1
Self-igniting substances	**Section 7**
Safety concept: Avoidance of ignition	
Pyrophoric properties	Section 7.1
Self-ignition temperature	Section 7.2–7.5
Minimum ignition temperature of a dust layer with a one- sided thermal load	Section 7.6
Also pay attention to	
Thermal stability	Section 11
Dust clouds	**Section 8**
Safety concept: Avoidance of explosive atmospheres	
Dust explosibility	Section 8.1
Explosion limits	Section 8.3
Limiting oxygen concentration	Section 8.3
Safety concept: Avoidance of effective ignition sources	
Minimum ignition energy	Section 8.4

Minimum ignition temperature of a dust cloud	Section 8.5
Safety concept: Constructive explosion protection	
Maximum explosion overpressure	Section 8.2
Maximum rate of pressure rise	Section 8.2
Also pay attention to	
Electrostatic parameters	Section 9
Thermal stability	Section 11
Electrostatic parameters	**Section 9**
Protection concept: Avoidance of effective ignition sources	
Conductivity	Section 9.1
Resistivity	Section 9.2
Vertical resistance	Section 9.3
Leakage resistance	Section 9.4
Surface resistivity	Section 9.5
Oxidising substances	**Section 10**
Information on oxidising ability	
UN Test O.1 to O.3	Sections 10.1–10.3
Also pay attention to	
Thermal stability	Section 11
Thermal stability of substances/Exothermic chemical reactions	**Section 11**
Information on thermal stability	
Thermal analysis	Section 11.1
Adiabatic calorimetry	Section 11.3
Heat accumulation storage test	Section 11.4
Information concerning reaction heat and accumulation of reactants	
Reaction calorimetry	Section 11.2

Protection concept: Pressure relief	
Adiabatic calorimetry	Section 11.3

2 Explosive and potentially explosive substances

For the purposes of this publication, substances are considered to be

- **explosive** if they belong to the “Explosives“ hazard class according to the CLP Regulation or if they return a positive result in Test Series 1 of the UN test manual. The following tests are performed:
  - Propagation of Detonation when unconfined
    (see Section 2.3.2 “UN gap test“, UN Test 1 (a))
  - Thermal sensitivity under confinement
    (see Section 2.1.1 “Koenen test“, UN Test 1(b))
  - Ability to deflagrate under confinement
    (see Section 2.4.1 “Time/pressure test“, UN Test 1(c) (i))

The explosive properties of self-reactive substances and organic peroxides are investigated through similar tests in Test Series A, C and E of the UN Manual of Tests and Criteria.

Explosive substances include, inter alia, any “solid or liquid substance or mixture of substances which is in itself capable by chemical reaction of producing gas at such a temperature and pressure and at such a speed as to cause damage to the surroundings“[4].

According to the CLP Regulation and UN Manual of Tests and Criteria, assignment to the “Explosives“ hazard class can be waived if the organic substance or homogeneous mixture of organic substances, having been checked in a screening test employing a suitable colorimetric procedure (see Section·11.1), has an exothermic decomposition energy of < 500 J g^{-1} and this decomposition occurs below 500 °C. In addition to this criterion there are others which permit assignment to be waived but are too numerous to mention here.

- **potentially explosive** if, within the meaning of Council Regulation (EC) No 440/2008 (Test Method A.14), they return a positive result in one of the three tests quoted there concerning thermal sensitivity or mechanical sensitivity with respect to shock or friction.
  The tests investigate the following:
  - explosion upon heating in a steel tube with an orifice of at least 2 mm
    (see Section 2.1.1 Steel tube test (Koenen test))
  - explosion or ignition due to an impact of 40 Nm or less
    (see Section 2.2.1 Impact sensitivity (fallhammer test))
  - explosion, ignition or crepitation due to friction energy of not more than of 360 N
    (see Section 2.2.2 Friction sensitivity (friction test))

  There is no direct link between these properties. A substance which is sensitive to heat will not necessarily also be sensitive to mechanical stress and vice versa.
  The tests do not need to be performed if available thermodynamic data (e. g. heat of formation, heat of decomposition) and/or the absence of certain reactive groups from the structural formula indicate unequivocally that the substance is incapable of rapidly decomposing with emission of gases or heat (i. e. the substance does not pose an explosion risk in the sense of Test Method A.14). Liquids not need to be subjected to the friction sensitivity test.

---

[4] See Annex 1 Section 2.1.1.2 of the CLP Regulation

The chemical structure of a substance provides early indication of its potential hazards. Table 1 gives examples of chemical groups that may be suspected of being explosive or potentially explosive in organic compounds in particular. Special care must be taken when handling these substances.

Table 1: Examples of functional groups that may be suspected of being explosive or potentially explosive

Chemical group 5[5]	Examples
Unsaturated C-C bond	Acetylenes, acetylides, 1,2-dienes
C-metal and N-metal compounds	Grignard reagents, organolithium compounds
O-O compounds	Organic peroxides, hydrogen peroxide, persulfates
N-O compounds	Hydroxylamines, nitrates, nitro compounds, nitroso compounds, N-oxides, 1,2-oxazoles
N-N compounds	Azides, aliphatic azo compounds, diazonium salts, hydrazines, triazoles, tetrazoles, sulfonylhydrazides
N-halogen compounds	Chloramines, fluoramines
O-halogen compounds	Chlorates, perchlorates, iodosyl compounds

As well as the individual substances listed above, mixtures of oxidising and combustible substances may be explosive or potentially explosive depending on their composition.

Classification

Categorising and assigning the substances to the individual hazard classes and hazard categories based on the CLP Regulation is a complex affair. The system of pictograms, signal words and hazard statements used is shown in Tables 2 and 3.

Table 2: Hazard categories in the “Explosives“ hazard class. Divisions 1.5 and 1.6 are not shown in the table, as they do not fall under the Sprengstoffgesetz (German Explosives Act).

Hazard category	Labelling		
Unstable, explosive	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H200 Unstable, explosive.
Division 1.1	**Pictogram:**	**Signal word:** Danger	**Hazard statement:** H201 Explosive; mass explosion hazard.

---

[5] not a definitive list

			
Division 1.2	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H202 Explosive, severe projection hazard.
Division 1.3	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H203 Explosive; fire, blast or projection hazard.
Division 1.4	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H204 Explosive; fire or projection hazard.

Table 3: Hazard categories in the “Self-reactive substances and mixtures“ hazard class and the “Organic peroxides“ hazard class

Hazard category	Labelling		
Typ A	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H240 Heating may cause an explosion.
Typ B	**Pictogram:**  	**Signal word:** Danger	**Hazard statement:** H241 Heating may cause a fire or explosion.
Typ C and D	**Pictogram:**	**Signal word:** Danger	**Hazard statement:** H242 Heating may cause a fire.

			
Typ E and F	**Pictogram:** 	**Signal word:** Warning	**Hazard statement:** H242 Heating may cause a fire.
Typ G	**No pictogram, signal word or hazard statement**		

Note

In Germany the handling, transport and trading of solid or liquid substances that have the potential to explode as a result of thermal, mechanical or other stresses is subjected to the Sprengstoffgesetz (German Explosives Act). This requires involved persons to hold permits and certificates of competence allowing them to handle and transport explosive and potentially explosive substances. Other regulations and ordinances include, for instance, regulations relating to the Sprengstoffgesetz (German Explosives Act), the Sprengstofflager-Richtlinien (which regulate the storage of explosives) and the regulations of the German Social Accident Insurance Institution relating to the handling of explosive and potentially explosive substances.

If a substance has proven to be or is suspected of being explosive according to Council Regulation (EC) No 440/2008 (Test Method A.14), in Germany this must be reported immediately to the Federal Institute for Materials Research and Testing (BAM) and a sample must be provided if required.

Figure 3: Experiment being conducted at the BAM test facility

2.1 Thermal sensitivity

Several test methods are used to determine the sensitivity of solid and liquid substances to the effect of intense heat under high confinement. The most commonly used test methods are the Steel tube test (Koenen test) and the Dutch pressure vessel test.

2.1.1 Steel tube test (Koenen test)

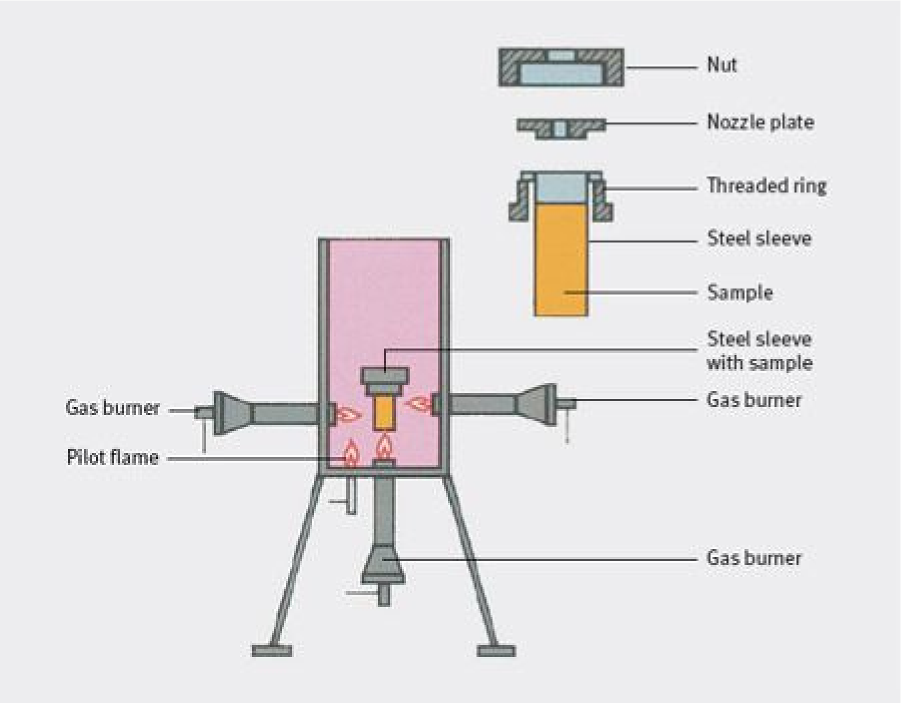
Determination procedure

The substance to be tested is heated in a cylindrical steel tube (capacity approx. 30 ml), which is closed by a plate with a defined orifice. Heating is carried out by means of four specially arranged gas burners so that the temperature of the tube increases at a defined rate to approx. 700 °C to 800 °C. If this causes the substance to release gases in such a short time that there is an abrupt pressure rise, the tube is either fragmented or simply deformed to a greater or lesser extent depending on the orifice diameter.

Varying the orifice diameter allows the maximum diameter (limiting diameter) at which the substance explodes at least once in three tests to be determined.

The test is described as UN Test 1(b) for classifying explosives and as UN Test E.1 for classifying self-reactive substances and organic peroxides. The test has to be carried out in an enclosed area (e. g. a bunker).

Figure 4: Steel tube test



Evaluation of results

An explosion is defined as the fragmentation of the tube into at least three parts.

Figure 5: Left: intact steel tube before the test. Right: deformed or shattered tubes after the test

The limiting diameter is the evaluation criterion with respect to thermal sensitivity under confinement. If the limiting diameter is ≥ 2 mm, the substance is considered to be explosive according to Council Regulation (EC) No 440/2008 (Test Method A.14) and the Sprengstoffgesetz (German Explosives Act).

If the limiting diameter is ≥ 1 mm, the substance has explosive properties according to UN Test 1(b). Other sets of rules quote different limiting diameters.

2.1.2 Dutch pressure vessel test

Determination procedure

The Dutch pressure vessel test uses as test device a solid pressure vessel which is closed by a bursting disc and a plate with defined orifice. The vessel is heated with a flame. The limiting diameter is determined by rupture or non-rupture of the bursting disc.

The test is described as UN Test E.2 for classifying self-reactive substances and organic peroxides.

Figure 6: Pressure vessel used in the Dutch pressure vessel test

Evaluation of results

The substance is placed in one of four categories depending on the way the disk ruptures as described in Table 4.

Table 4: Categorisation of thermally sensitive substances according to the Dutch pressure vessel test

Result	Categorisation
Rupture of the disc with an orifice of 9.0 mm or greater and a sample mass of 10 g	Violent
No rupture of the disc with an orifice of 9.0 mm, but rupture of the disc with an orifice of 3.5 mm or 6 mm and a sample mass of 10 g	Medium
No rupture of the disc with an orifice of 3.5 mm and a sample mass of 10 g, but rupture of the disc with an orifice of 1 mm or 2 mm and a sample mass of 10 g or rupture of the disc with an orifice of 1 mm and a sample mass of 50 g	Low
No rupture of the disc with an orifice of 1 mm and a sample mass of 50 g	No

The results of both tests (UN Test E.1 and UN Test E.2) must be used for assessment of self-reactive substances and organic peroxides according to the UN Manual of Tests and Criteria.

This test is not required for tests according to Council Regulation (EC) No 440/2008.

2.2 Mechanical sensitivity

Various test methods may be used to test mechanical sensitivity with respect to impact and friction. The most commonly used test methods are the fallhammer test and the friction test. Friction sensitivity is investigated in solid and past-like substances, while impact sensitivity is investigated additionally in liquids.

2.2.1 Impact sensitivity (fallhammer test)

Determination procedure

40 µl of the substance is enclosed in a shock device consisting of two coaxial steel cylinders, one on top of the other, and a hollow steel cylinder as guide ring. This shock device is placed on an anvil and subjected to the impact of different drop weights. The impact energy can be varied both through the selection of drop height and through the selection of drop weight. The lowest impact energy just sufficient to cause an explosion is determined.

Figure 7: Fallhammer

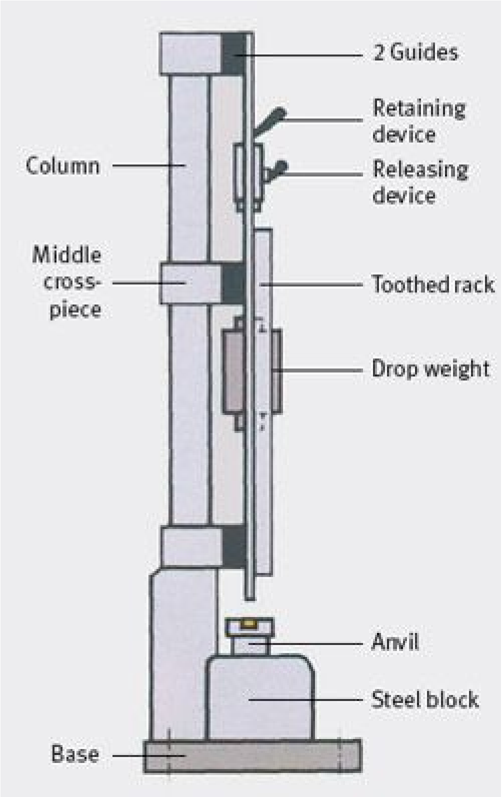
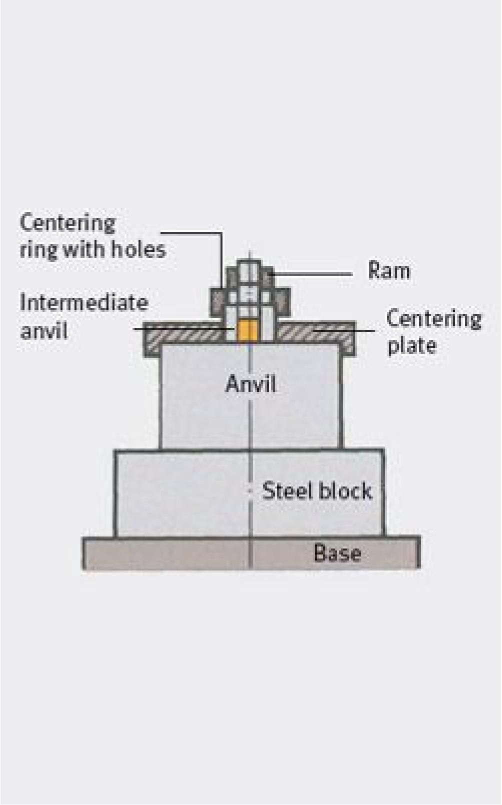


Figure 8: Anvil of the fallhammer apparatus



Evaluation of results

An explosion has occurred if a bang is heard or ignition can be seen when the drop weight strikes the shock device. In order to avoid subjective judgement by the operator in border cases, some test institutes have introduced an impulse sound level measurement as an objective criterion.

If an explosion occurs at an impact energy of ≤ 40 J, the substance is considered to be explosive according to Council Regulation (EC) No 440/2008 (Test Method A.14) and the Sprengstoffgesetz (German Explosives Act).

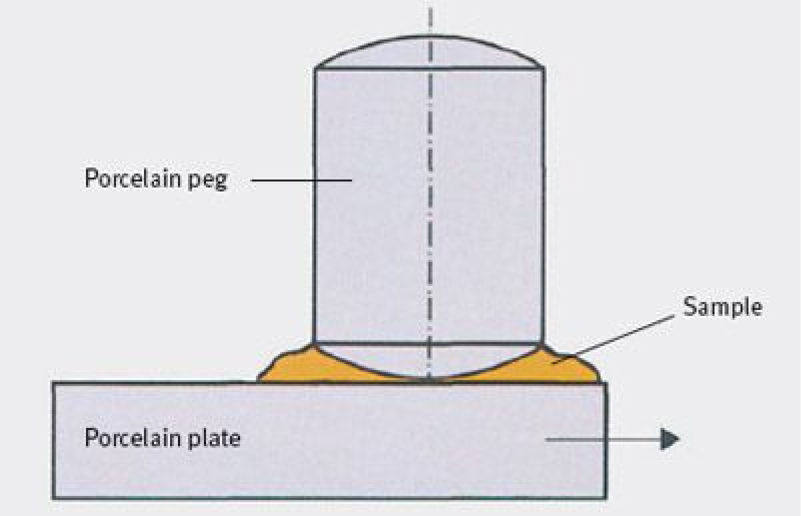
Figure 9: Fallhammer test

2.2.2 Friction sensitivity (friction test)

Determination procedure

A porcelain plate with 10 µl of test substance is moved by an electric motor beneath a stationary porcelain peg with rough spherical end surfaces. To-and-fro movements over a distance of 1 cm are executed with different peg loads. It is observed whether an explosion is caused by the friction process (e. g. crepitation, bang, ignition).

Figure 10: Friction test



Evaluation of results

If an explosion occurs at an impact energy of ≤ 360 N, the substance is considered to be explosive according to Council Regulation (EC) No 440/2008 (Test Method A.14) and the Sprengstoffgesetz (German Explosives Act).

Note

The number of chemically defined explosive substances which are sensitive to friction is fairly small. Virtually all friction-sensitive substances are also sensitive to impact. In this case the friction test is not routinely performed.

2.3 Detonation properties

It is sometimes assumed that substances which are neither thermal sensitive nor sensitive to mechanical stress and are thus not “explosive“ according to Council Regulation (EC) No 440/2008 and are exempt from categorisation under the Sprengstoffgesetz (German Explosives Act) will also not detonate. Experience shows, however, that some energetic substances (e. g. 2,4-dinitroanisole) are explosive under detonation impact conditions and are able to propagate a detonation. Dangerous Goods Regulations and the CLP Regulation require that a test be performed for sensitivity to detonation impact and ability to propagate a detonation.

The Trauzl test (see Section 2.3.1) is used to measure the explosive power of a substance. It can also be used to rule out the detonation properties of a substance.

In order to determine whether a substance is able to propagate a detonation under confinement, it is placed in steel tubes of various dimensions and subjected to the detonation impact of various booster charges. The UN gap test (see Section 2.3.2) examines whether a detonation impact is propagated within a larger amount of the substance, causing it to decompose explosively. In the case of self-reactive substances and organic peroxides the steel tube test (see Section 2.3.3) is used for this purpose.

According to the UN Manual of Tests and Criteria, if preliminary tests have been performed on organic substances showing them to have a decomposition energy < 800 J g^{-1}, then there is no need to perform the test for propagated detonation nor the test for sensitivity towards a detonation impact.

2.3.1 Trauzl test (lead block test)

Determination procedure

The apparatus consists of cylindrical lead blocks of diameter = height = 20 cm. At the centre of the lead block is a hole 2.5 cm in diameter with a volume of 61 cm^3. 10 ml of substance is placed in the hole, which is topped up with dry, fine sand. The sample is detonated, using a standard detonator placed at the centre of the substance, with pentaerythritol tetranitrate (penta, PETN) as explosion initiator. Following careful cleaning, the volume increase (bulging) of the 61 cm^3 cavity is measured and normalised to a 10 g quantity of substance.

Figure 11: Schematic diagram of the BAM Trauzl test apparatus

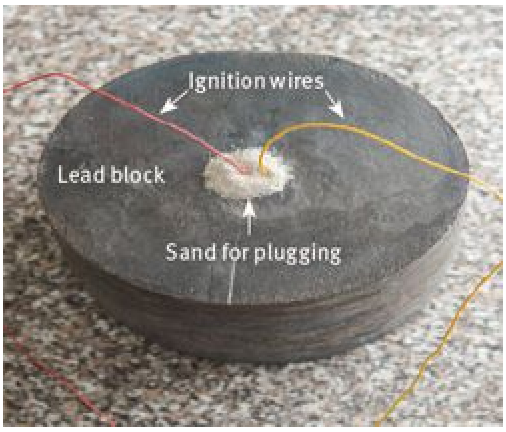


Figure 12: Time of explosion

Evaluation of results

If the bulging of the lead block amounts to less than 10 cm^3 per 10 g of substance, then the substance being tested can be assumed not to have any detonation properties. If the bulging is 10 cm^3 per 10 g of substance or more, then its detonation properties must be investigated more rigorously.

Note

The test method is also used to evaluate the explosive power of organic peroxides and self-reactive substances as part of the categorisation procedure according to the hazardous substances and dangerous goods legislation.

2.3.2 Steel tube test (UN gap test)

Determination procedure

The test sample is contained in a seamless drawn steel tube (length 400 mm, wall thickness 4 mm, internal diameter 40 mm, volume approx. 500 ml), closed at the bottom with two layers of 0.08 mm thick polyethylene sheet. A 3.2 mm thick witness plate is mounted at the upper end of the steel tube.

The tube is placed in a vertical position and detonation is induced through a booster charge with a diameter of 50 mm consisting of 160 g Cyclotrimethylentrinitramin (RDX) with 5 % wax, or Nitropenta/Trinitrotoluol 50/50.

A distinction is made between two different test procedures:

- UN Test 1 (a): The booster charge is placed in direct contact with the test substance.
- UN Test 2 (a): A 50 mm thick Polymethylmethacrylat (acrylic glass) separator is placed between the booster charge and the test substance.

Evaluation of results

If the tube is completely fragmented or a hole is punched through the witness plate, the substance is capable of propagating a detonation.

Note

Energy-rich reaction mixtures (e. g. nitrating mixtures or peroxide-containing mixtures) may have detonation properties and can be tested using this test method.

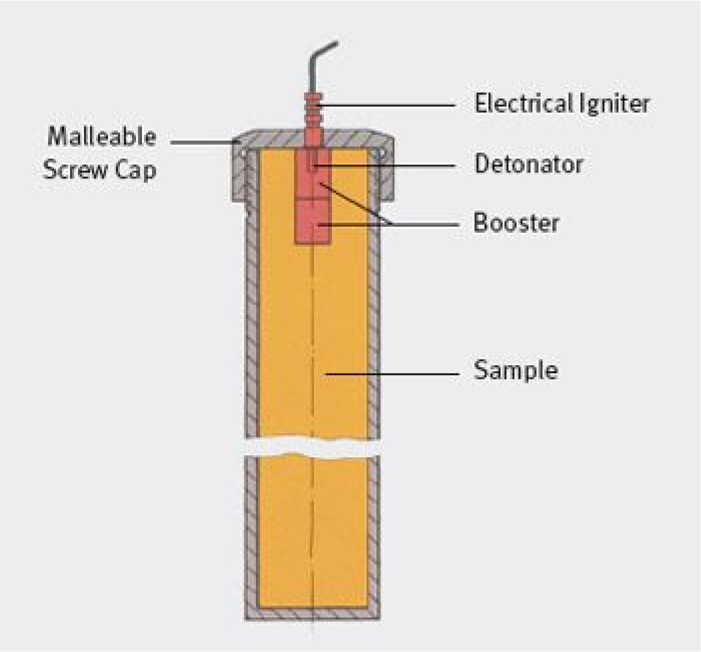
2.3.3 Steel tube test

Determination procedure

The test sample is placed in a seamless drawn steel tube (length 500 mm, external diameter 60 mm, wall thickness 5 mm). The tube is closed by a malleable screw cap made of cast iron or by an appropriate plastic cap. The booster consists of a cylindrical pellet of 50 g Cyclotrimethylentrinitramin (RDX)/wax 95/5.

The test is described as UN Test A.1 for classifying self-reactive substances and organic peroxides.

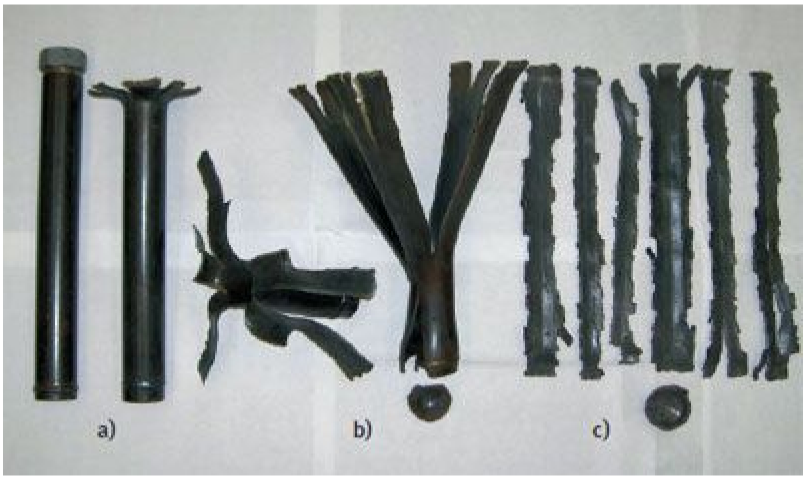
Figure 13: 2“ steel tube for testing for detonation sensitivity (based on UN Test A.1)



Evaluation of results

Test criterion for detonation impact propagation is the length over which the steel tube has fragmented.

Figure 14: Fragmentation after a 2“ steel tube test
a) No propagation
b) Partial propagation
c) Complete propagation



<u>Note</u>

The ability of a substance to propagate a detonation depends, inter alia, on the tested diameter, on the initiator, on the extent of confinement and on cavitation (gas inclusions). Investigation in the cavitated state (see Annex 3 of the UN Manual of Tests and Criteria) is recommended for evaluating process steps involving energy-rich substances.

2.4 Deflagration properties

A substance is capable of deflagrating if, after local application of a sufficiently strong ignition source, even in the absence of (atmospheric) oxygen, it undergoes complete decomposition with an advancing reaction zone (at a rate below the speed of sound). The resultant maximum pressure is roughly equivalent to 10 times the initial pressure.

Factors such as temperature and pressure can have a bearing on deflagration properties. In experiments within a closed system the confined degradation gases influence the pressure increase and p_{max}, providing important information on chemical reactions within the closed reactor.

The ability of self-reactive substances and organic peroxides in particular to propagate deflagration under confinement is tested by means of the time/pressure test (UN Test C.1) and the deflagration test (UN Test C.2).

2.4.1 Time/pressure test (UN Test C.1)

<u>Determination procedure</u>

The test apparatus consists of the small cylindrical autoclave with a capacity of about 17 ml which is filled with 5 g of the test substance. At the lower internal end of the vessel is the ignition system consisting of an electric fusehead and a pyrotechnic booster. The vessel is closed by a screw fitting containing a rupture disc with a response pressure of about 25 bar. Ignition is initiated and the time/ pressure profile is recorded.

The test is also described as UN Test 1(c) (i) and 2(c) (i).

Evaluation of results

For assessment the time interval for the pressure to rise from 7.9 bar to 21.7 bar is measured (see Table 5, the numerical values are obtained by converting the even-numbered psi results).

Table 5: Categorisation of deflagrating substances

Result	Categorisation according to UN Test C.1	Categorisation according to UN Test 1 (c) (i) and 2(c) (i)
Time difference between 7.9 bar and 21.7 bar < 30 ms	Yes, rapidly	Rapid deflagration
Time difference between 7.9 bar and 21.7 bar $\geq$ 30 ms	Yes, slowly	Capable of deflagrating
21.7 bar not achieved	No	No signs of explosion hazard through deflagration

2.4.2 Deflagration test (UN Test C.2)

Determination procedure

In UN Test C.2 the test substance, which has been heated to a temperature of 50 °C, is ignited in an open Dewar vessel of about 300 ml capacity and an internal diameter of about 5 cm at the top at atmospheric pressure by means of a gas burner. The passage of the reaction front is monitored visually and/or through the response of two thermocouples located a defined distance away and the deflagration rate is obtained through time measurement.

Evaluation of results

The substances are categorised according to the rate at which they deflagrate (see Table 6)

Table 6: Categorisation of deflagrating substances according to UN Test C.2

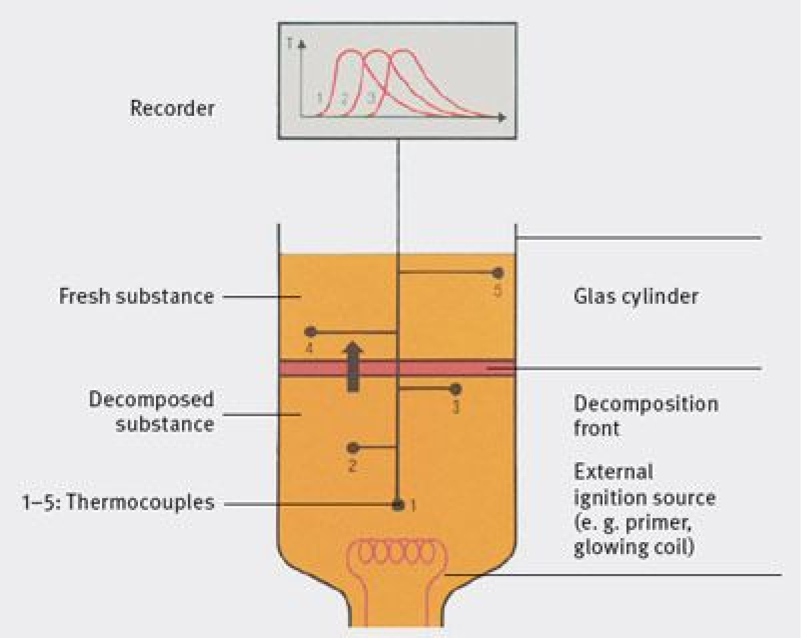
Deflagration rate	Categorisation
> 5.0 mm s^{-1}	Yes, rapidly
Between 0.35 mm s^{-1} and 5.0 mm s^{-1}	Yes, slowly
< 0.35 mm s^{-1}	No

2.4.3 Deflagration test (VDI 2263-1)

Determination procedure

A similar test for solids is performed using the VDI 2263-1 method at atmospheric pressure in a glass tube (diameter about 5 cm, length about 20 cm), which is closed at the bottom and in which several thermocouples are arranged centric at varying elevations. The glass tube is filled with substance to just below its upper edge. Local decomposition is initiated with a glow plug or an ignition mixture consisting of lead oxide and silicon (7/93), in an initial test series at the upper end of the tube and in a second test series at the lower end. The passage of the reaction front is monitored visually or through the response of the thermocouples.

Figure 15: Determination of deflagration properties according to VDI 2263-1



Evaluation of results

The test substance is capable of deflagration if decomposition propagates fully. In this case special measures are required, e. g. prevention of local overheating.

3 Flammable gases and vapours

The hazards of handling flammable gases and vapours are associated with the way in which these substances react explosively with an oxidising agent (generally the oxygen of air). Temperatures in excess of 1 000 °C and pressure increases to approximately 8 to 10 times the initial pressure may be encountered.

Even higher pressures may be encountered either with oxidising agents stronger than air, such as pure oxygen, or when detonation occurs.

The test methods described below are used for risk assessment and for determining the conditions under which the hazards can be safely kept under control.

3.1 Explosion limits and limiting oxygen concentration

Definition

Self-propagating combustion in mixtures of flammable gases and vapours with air (oxygen) can only occur within a certain concentration range. The limiting concentrations at which it can just no longer occur are referred to as the lower (LEL) and upper (UEL) explosion limit. At a concentration below the lower explosion limit the mixture is too “lean“ (it contains not enough fuel), while at a concentration above the upper explosion limit the mixture is too “rich“ (it contains too much fuel, i. e. too less oxygen) to allow a flame to propagate following ignition.

The limiting oxygen concentration (LOC) is the maximum oxygen concentration in a mixture of a flammable substance and air and an inert gas, in which an explosion will not occur, determined under specified test conditions.

Reason for determining the parameter

The explosion limits are relevant data for the registration of new chemical substances in the case of gases and for compiling the necessary safety data sheets. Together with the limiting oxygen concentration they are used within the explosion protection concept when the “Avoidance of explosive atmosphere“ concept is selected.

Determination procedure

Various standardised methods are used to determine explosion limits (see Table 7).

Table 7: Standards for determining explosion limits

Area of application	Standard
Atmospheric pressure, temperature up to 200 °C	DIN EN 1839
Atmospheric pressure, temperature up to 150 °C	ASTM E681
Elevated pressure and temperature	ASTM E918

The limiting oxygen concentration is determined according to DIN EN 1839 based on the explosion limits of three-substance mixtures (flammable gas/inert gas/air).

For determination of explosion limits according to DIN EN 1839, mixtures of flammable gas/inert gas and air are prepared with various percentages of flammable gas and subjected to ignition trials. Normally, a spark gap or wire igniter is used to induce ignition. The criterion for ignition observed in a glass tube (“tube method“) is detachment of the flame from the electrodes, linked with an upward movement of at least 10 cm (see Figure 16). In a closed pressure-resistant vessel (“bomb method“) the ratio of final pressure to starting pressure > 1.05 is used.

Figure 16: Determination of the explosion limits of ammonia (tube method) according to DIN EN 1839

The measurement of parameters at elevated pressures and temperatures > 200 °C is generally carried out in non-standardised apparatus.

Evaluation of results

Explosion limits and limiting oxygen concentrations are dependent on the determination method used, which is why literature values that were not determined by a standardised method have to be evaluated for the particular case in question.

Classification

According to the CLP Regulation, the existence of explosion limits for a gas results in its assignment to a category within the “Flammable gases“ hazard class (see Table 8).

Table 8: Hazard categories in the “Flammable gases“ hazard class

Hazard category	Labelling		
Category 1	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H220 Extremely flammable gas.
Category 2	**Pictogram:** No pictogram	**Signal word:** Warning	**Hazard statement:** H221 Flammable gas.

The classification of flammable gases as per the dangerous goods transport legislation is also based on explosion ranges.

Note

The explosion range (characterised by LEL, UEL, LOC) increases with rising pressure and rising temperature. It is also dependent on the inert gas that is added. The same applies to oxidising agents other than air.

3.2 Maximum explosion pressure and maximum rate of pressure rise

Definition

The explosion pressure is the highest pressure measured in a closed vessel upon deflagration of a defined mixture of flammable gas and air (or flammable gas, inert gas and air) under defined test conditions.

The maximum explosion pressure is the highest explosion pressure value encountered through varying the content of flammable gas in air.

In analogy, the maximum rate of pressure rise is the highest value obtained for the slope of the pressure/time curve of an explosion. It is determined by varying the amount of flammable gas.

Reason for determining the parameter

The maximum explosion pressure and the maximum rate of pressure rise are needed to draft the explosion protection concept when the “Constructive explosion protection“ concept is chosen. The parameters are used to design the “Explosion- resistant design“, “Explosion pressure relief“ and “Explosion suppression“ measures.

Determination procedure

The testing apparatus according to DIN EN 15967 consists of a closed spherical pressure vessel (volume > 5 l) or a cylinder (length = diameter, volume > 5 l) equipped with a fast pressure measuring system. The ignition source is placed at the centre of the vessel.

The pressure measuring system serves to record the pressure/time curve following ignition of an explosive mixture. For determination of the maximum explosion pressure and the maximum rate of pressure rise the amount of the flammable gas in the gas/air mixture is varied stepwise over a sufficiently broad range.

Evaluation of results

Normally the maximum explosion pressure is only volume-dependent to a very minor degree. For most organic gases and vapours in mixture with air, the maximum explosion pressure under initial atmospheric conditions (temperature between 20 °C and 25 °C; pressure between 980 mbar and 1020 mbar) is approximately 8 bar to 10 bar. It increases in proportional to the absolute initial pressure and is inversely proportional to the absolute initial temperature. Higher pressures may occur when using oxidising agents more powerful than air (e. g. pure oxygen or chlorine) and in case of detonations.

The maximum rate of pressure rise is volume-dependent. For mixtures with air, the product of the maximum rate of pressure rise and the cube root of the volume in question is constant (cubic law):

$$\left(\frac{\mathrm{dp}}{\mathrm{dt}}\right)_{\max} \cdot \mathrm{V}^{1/3} = \mathrm{konst.} = \mathrm{K_G}$$

The K_G value is the maximum rate of pressure rise related to a volume of 1 m^3. Transfer of the KG value to different sizes of apparatus is strictly speaking only possible when the geometries are similar. The K_G value increases with the initial pressure and with the turbulence of the unburned mixture.

Classification

This parameter is not used for classification according to the hazardous substances and dangerous goods legislation.

Note

Rates of pressure rise are highly dependent on the quantity of oxidising agent used and the geometry of the apparatus, an important consideration when the results are transferred to process scale.

3.3 Limiting pressure of stability (limiting ignition pressure)

Definition

The limiting pressure of stability (limiting ignition pressure) is the pressure below which the decomposition of a chemically unstable gas, vapour or mixture without the presence of air (oxygen) can just no longer be initiated under defined experimental conditions.

Reason for determining the parameter

The limiting pressure of stability needs to be known when explosion protection measures are being devised for handling chemically unstable gases (such as acetylene).

Determination procedure

The limiting pressure of stability is normally determined in the instruments used to determine the explosion limits at elevated pressures.

Determination involves placing the pure chemically unstable component or a mixture of chemically unstable components with other gases or vapours in the ignition vessel and subjecting it to ignition experiments. The conditions (initial pressure, initial temperature and the nature and energy of the ignition source) must be selected to accord with the pertinent safety issues.

Use of the test method described in Section 35 of the UN Manual of Tests and Criteria for classifying chemically unstable gases is in many cases an inadequate way of determining the limiting pressure of stability.

Evaluation of results

On account of the fact that the number of parameters that can potentially influence the result is so large, it takes a good deal of experience to devise a safety concept based on the limiting pressure of stability.

Classification

See “Chemically unstable gases“ (Section 3.7).

Note

The limiting pressure of stability depends on

- the temperature of the gas or vapour,
- the geometry of the experimental apparatus and
- the nature and energy of the ignition source.

Accordingly, extremely disparate limiting pressures of stability can be obtained for a substance under the varied conditions (see Table 9). As a consequence, it is always necessary to quote the experimental conditions under which the limiting pressure of stability was determined.

Table 9: Limiting ignition pressure of gases and vapours depending on the temperature, ignition vessel and ignition source. As ignition source an arc discharge was used, generated by an isolating transformer in accordance with EN 1839.
Geometry of the 6.5 l cylinder: inner diameter 187 mm, height 235 mm
Geometry of the 9.1 l cylinder: inner diameter 200 mm, height 290 mm
Geometry of the 91 l cylinder: inner diameter 415 mm, height 1160 mm

Gas or vapour	Temperature	Ignition vessel	Ignition energy	Limiting pressure of stability
Ethyne (Acetylene)	20 °C	9,1 l Cylinder	50 J	1,0 bar abs
	20 °C	9,1 l Cylinder	20 J	1,4 bar abs
1-Propyne (Methylacetylene)	30 °C	6,5 l Cylinder	60 J	2 bar abs
	30 °C	91 l Cylinder	60 J	2 bar abs
1,2-Butadiene	90 °C	6,5 l Cylinder	20 J	5,5 bar abs
	90 °C	91 l Cylinder	20 J	5 bar abs
	210 °C	6,5 l Cylinder	20 J	3 bar abs
Dinitrogen monoxide (Laughing gas)	50 °C	20 l Kugel	20 J	4 bar abs
	160 °C	20 l Kugel	20 J	1 bar abs
Nitric oxide	170 °C	91 l Cylinder	65 J	1 bar abs

3.4 Minimum ignition energy

Definition

The minimum ignition energy (MIE) is the minimum amount of electrical energy stored on a capacitor, which, upon discharge, is sufficient to ignite the most ignitable mixture of an explosive atmosphere under specified test conditions.

Note

For flammable gases and vapours in air, MIE is predominantly in the range 0.1 mJ to 1 mJ (the minimum ignition energies needed to ignite acetylene, carbon disulfide and hydrogen are lower). As the energy of commonly occuring ignition sources is above the range stated above, it is normally not necessary to determine the MIE of flammable gases and vapours.

MIE decreases with increasing pressure, increasing temperature and with oxidising agents that are more powerful than air.

Classification

This parameter is not used for classification according to the hazardous substances and dangerous goods transport legislation.

3.5 Gap width preventing flame propagation (Maximum experimental safe gap)

Definition

The gap width preventing flame propagation is the maximum width of an annular gap of defined length (25 mm) which, when a gas/air mixture is ignited, prevents a flame from passing through it, for all concentrations of the tested gas or vapour in air. If this gap width is determined under atmospheric conditions (temperature between 20 °C and 25 °C; pressure between 980 mbar and 1020 mbar) it is referred to as the maximum experimental safe gap (MESG).

Reason for determining the parameter

The propagation of an explosion from one area of a plant to another can be prevented if both areas are separated by a sufficiently narrow safe gap. The dimensions of this gap are established based on the maximum experimental safe gap.

Determination procedure

The maximum experimental safe gap is determined according to IEC 60079-20-1 in a specially designed apparatus. The flame transmission through the annular gap into the outer gas/air or vapour/air mixture after the gas/air or vapour/air mixture of the same composition located in the inner part of the apparatus has been ignited by means of an electrical ignition source is observed. The gap distance and the concentration of the gas/air or vapour/air mixture are varied until ignition of the external gas/air or vapour/air mixture is just prevented.

Evaluation of results

The maximum experimental safe gap is used to classify flammable substances, explosion-protected electrical and non-electrical equipment and autonomous protective systems (e. g. flame arresters) into explosion groups and explosion subgroups (see Table 10).

Table 10: Explosion groups and explosion subgroups

Maximum experimental safe gap (MESG) according to IEC 60079-20-1	Explosion group	
	Explosion-protected Equipment IEC 60079-20-1	Autonomous protective systems ISO 16852 *Explosion subgroup*
≥ 0.9 mm	IIA	
0,5 mm ≤ NSW ≤ 0.9 mm	IIB	
NSW ≥ *0.85 mm*		*IIB 1*
NSW ≥ *0,75 mm*		*IIB 2*
NSW ≥ *0.65 mm*		*IIB 3*

NSW ≥ *0.5 mm*		*IIB*
< 0,5 mm	IIC	

In potentially explosive atmospheres, electrical and non-electrical equipment may only be operated when it can be shown that it complies with the applicable requirements.

Classification

This parameter is not used for classifications according to the hazardous substances and dangerous goods transport legislation.

Note

The maximum experimental safe gap decreases with increasing temperature, increasing pressure and with oxidising agents that are more powerful than air. Vice versa, the maximum experimental safe gap may also increase depending on the operating environment.

The parameter is used exclusively to categorise substances, equipment and autonomous protective systems. It is not an absolute measure for setting the size of the flame-proof gap of an apparatus or of the channels or gaps in autonomous protective systems. If end-of-line flame arresters are intended not only to prevent the propagation of an explosion into the interior of a system but also to withstand a fire on the outside, they must also be tested for endurance burning.

3.6 Aerosols

Definition

For the purposes of this section, aerosols or aerosol dispensers are non-refillable receptacles containing a gas, compressed, liquefied or dissolved under pressure, with or without liquids or solid substances.

Reason for determining the parametern

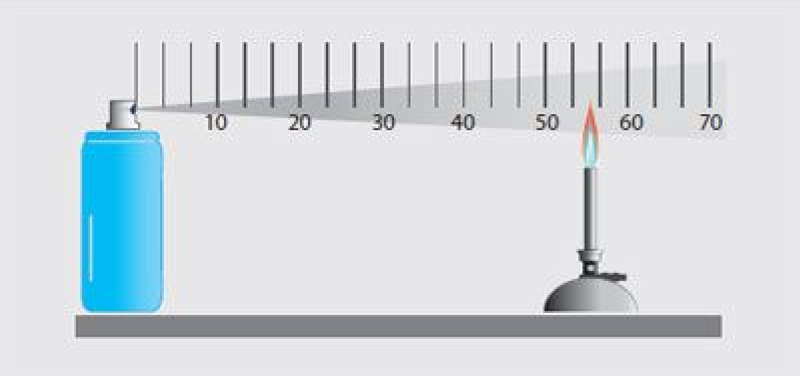
Following classification of the pressurised receptacles plus contents as an entity, a need arose to introduce the ignition distance test and the enclosed space ignition test for spray aerosols and the foam flammability test for foam aerosols to enable the flammability of the aerosol contents to be determined based on relevant criteria.

Determination procedure

The flammability of flammable aerosols is tested according to Section 31 of the UN Manual of Tests and Criteria.

In the ignition distance test (see Figure 17) a flame is used to ignite the spray as it emerges from the aerosol. The aim is to measure the maximum distance from the flame (ignition distance) at which ignition and sustained combustion of the spray can be observed.

Figure 17: Experimental setup for the ignition distance test



In the enclosed space ignition test (see Figures 18 and 19) the contents of an aerosol dispenser are sprayed through an orifice into a metal cylindrical container (enclosed space) having a capacity of 200 l. A burning candle as ignition source is positioned inside the cylindrical container. In this test the period that elapses from the start of spraying to ignition within the container (time equivalent) is measured and, through weighing of the aerosol dispenser, the mass of the sprayed contents (deflagration density) is measured.

Figure 18: Container for the enclosed space ignition test

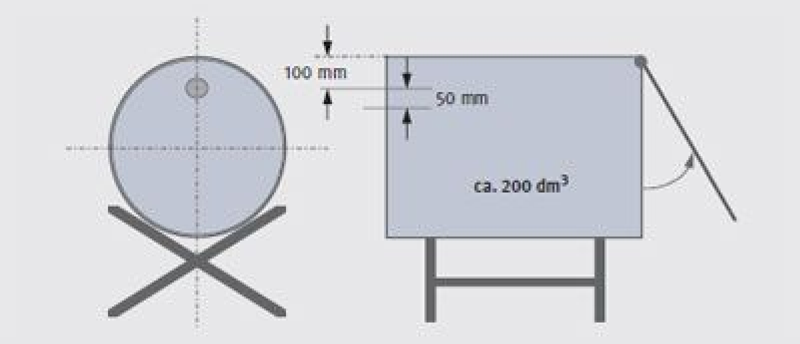
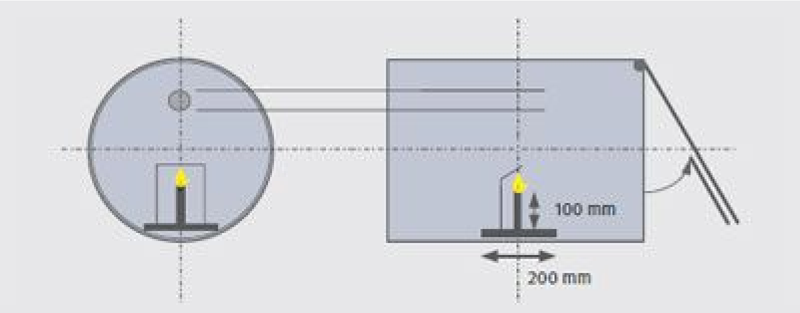


Figure 19: Candle in its metal holder



In the foam test a defined quantity of foam is applied to a watch glass and ignited. The flame height and flame duration are measured.

Evaluation of results

Evaluation is performed based on the flammable component contents and the heat of combustion of the aerosol mixture, and on the test results.

Classification

Classification is performed according to the CLP Regulation into a category within the “Aerosols“ hazard class (see Table 11).

Table 11: Hazard categories in the “Aerosols“ hazard class

Hazard category	Labelling		
Category 1	**Pictogram::** 	**Signal word:** Danger	**Hazard statement:** H229 Pressurized container: may burst if heated. H222 Extremely flammable aerosol.
Category 2	**Pictogram** 	**Signal word:** Warning	**Hazard statement:** H229 Pressurized container: may burst if heated. H223 Flammable aerosol.
Category 3	Not classifiable as a flammable aerosol → no labelling		

Note

If an aerosol contains more than 1 % flammable components or the mixture has a heat of combustion $\geq$ 20 kJ g^{-1} ist, it should be tested for flammability or assigned to Category 1 (extremely flammable aerosol).

3.7 Chemically unstable gases

Definition

Chemically unstable gases represent a special case among the flammable gases. They are able to react explosively even in the absence of air and without any other reactant. In the same way as in explosions, the decomposition of unstable gases can result in pressure increases of up to 12 times the initial pressure.

Reason for determining the parameter

The purpose of determining the chemical instability of gases and gas mixtures is to identify decomposition properties.

Determination procedure

The test method is described in Section 35 of the UN Manual of Tests and Criteria. The gas being tested is fed into a pressure-resistant, rust-free stainless steel autoclave under regulated temperature and pressure. The autoclave is fitted with a rupture disc. The gas is ignited using an exploding wire igniter.

Evaluation of results

Whether a decomposition reaction took place is deduced from the pressure increase achieved.

Classification

If gases react even in the absence of air, the CLP Regulation places them in a category within the “Unstable gases“ hazard class. They are not given an additional hazard pictogram because, with them being categorised as a flammable gas, they have already been assigned the GHS02 “Flame“ pictogram (see Table 12).

Table 12: Hazard categories in the “Unstable gases“ hazard class

Thermal stability	Pressure	Categorisation and labelling	
Chemically unstable at 20 °C	1 bar	**Hazard category:** Category A	**Signal word:** Danger
			Hazard statement: H230 May react explosively even in the absence of air.
Chemically unstable at more than 20 °C	1 bar or more	**Hazard category:** Category B	**Signal word:** Danger
			Hazard statement: H231 May react explosively even in the absence of air at elevated pressure and/or temperature.

Note

Normally there will be certain functional groups such as triple bonds, neighbouring or conjugated double bonds, halogenated double bonds or stretched rings pointing to possible chemical instability. The best-known gases in this group are acetylene and ethylene oxide.

A special case among the unstable gases is posed by nonflammable gases which are categorised as oxidising, yet are unstable (e. g. ozone, nitrous oxide (laughing gas) or chlorine dioxide).

4 Flammable liquids

When flammable liquids are being handled, hazards may arise if, for example, flammable gases or vapours are emitted which are explosive when mixed with air (oxygen)[6] or if a fire is started through the action of a local ignition source.

The safety characteristics described in this section provide indications regarding such hazards, which may need to be backed up with further investigations according to Section 3 “Flammable gases and vapours“.

---

[6] Especially when flammable liquids are atomised or sprayed.

4.1 Flash point

Definition

The flash point of a flammable liquid is the lowest temperature at which a liquid emits a flammable gas or flammable vapour in such a quantity, under specified test conditions, that contact with an ignition source immediately produces a flame which propagates across the entire surface of the liquid.

Reason for determining the parameter

The flash point is a central parameter for assessing the fire and explosion hazards of liquids. It is the basis for categorising and labelling flammable liquids and is an essential element of many product specifications.

Determination procedure

There are many standardised methods for determining the flash point (see Table 13). The essential differentiating features are the different types of cups, the use of a stirrer and the various possibilities of heating to the various temperature ranges.

Table 13: Commonly used methods for determining flash point

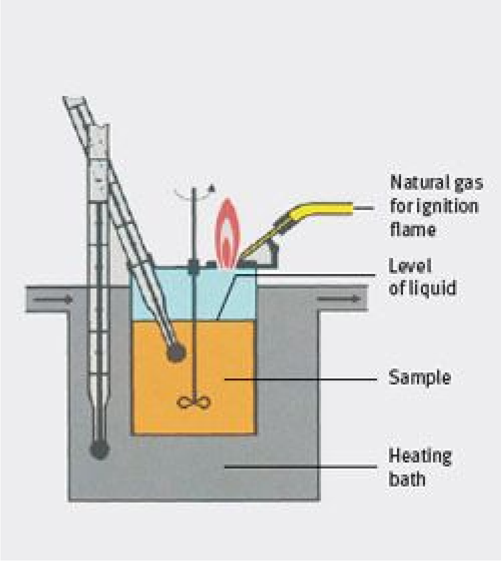
Standard	Area of application	Temperature range	Characteristics
DIN EN ISO 13736 Abel closed cup method	Flammable liquids Not suitable for waterbased varnishes and paints	–30 °C to 70 °C	• Closed cup • “Nonequilibrium method“ • Low heating rate • Sample volume approx. 75 ml • Ratio of vapour phase/liquid phase approx. 0.75
DIN EN ISO 2719 Pensky-Martens closed cup method	Flammable liquids Not suitable for waterbased varnishes and paints	40 °C to 370 °C	• Closed cup • “Nonequilibrium method“ • Higher heating rate • Sample volume approx. 75 ml • Ratio of vapour phase/liquid phase approx. 0.75
DIN EN ISO 3679 Rapid equilibrium closed cup method	Flammable liquids	–30 °C to 300 °C	• Closed cup • “Equilibrium method“ • Isothermal • Sample volume 2 ml • Ratio of vapour phase/liquid phase approx. 9
DIN EN ISO 2592 Cleveland open cup method	Flammable liquids	> 75 °C	• Open cup • “Nonequilibrium method“ • High heating rate

	Not suitable for waterbased varnishes and paints		• Sample volume approx. 50 ml • Ratio of vapour phase/liquid phase approx. 0.5

The substance is heated at the prescribed heating rate in a closed or open cup or temperature equilibration is awaited. At defined intervals or once the temperature has equilibrated, attempts are made to ignite the vapour/air mixture above the liquid by using a pilot flame.

Figure 20: Flash point test in a closed cup (a large flame only occurs way above the flash point)

Figure 21: Flash point tester



Evaluation of results

The flash point enables the explosion hazard to be assessed (TRGS 721, DGUV Information 113-001 (Explosionsschutz-Richtlinien (EX-RL), guidelines on explosion protection)). The flash point is also the basis for the explosion protection measures that need to be taken with regard to the storage of flammable (flash point ≤ 60 °C) and combustible (flash point ≤ 370 °C) liquids. For a flash point ≤ 5 °C, the technical rules for the storage of hazardous substances in stationary containers (TRGS 509) or the storage in nonstationary containers (TRGS 510) demand additional requirements.

It must be kept in mind that explosive vapour/air mixtures can also occur below the flash point. In the case of pure substances the difference can be up to 5 K, and in mixtures even up to 15 K. In particular when liquids are dispersed, sprayed or atomised in the form of droplets, the formation of an explosive atmosphere must be anticipated even at temperatures below the flash point.

The flash points measured in closed cups are generally lower than those measured in open cups. Also, the flash points measured in closed cups using the different methods can differ. In the case of liquids having only a low or slightly volatile content of flammable substances, it is even possible that a flammable vapour/air mixture will not form in an open cup while, in a closed cup, a reproducible flash point may be found. In difficult cases it is advisable to carry out additional tests (e. g. determination of the lower explosion point in a closed system, see Section 4.2).

Classification

According to the CLP Regulation, the flash point together with the Initial boiling point form the basis for assignment to a category within the “Flammable liquids“ hazard class (see Table 14).

Table 14: Hazard categories in the “Flammable liquids“ hazard class

Flash point	Onset of boiling	Categorisation and labelling	
< 23 °C	≤ 35 °C	**Hazard category:** Category 1	**Signal word:** **Danger**
		Pictogram: 	**Hazard statement:** H224 Extremely flammable liquid and vapour.
< 23 °C	> 35 °C	**Hazard category:** Category 2	**Signal word:** Danger
		Pictogram: 	**Hazard statement:** H225 Highly flammable liquid and vapour.
≥ 23 °C, ≤ 60 °C[**]	≥ 35 °C[*]	**Hazard category::** Category 3	**Signal word:** Warning
		Pictogram:	**Hazard statement:**

[**] The CLP Regulation assigns gas oils, diesel and light heating oils having a flash point between 55 °C and 75 °C to category 3.

[*] Liquids with a flash point > 35 °C do not have to be assigned to category 3 if UN Test L.2 for sustained combustibility returned a negative result (see section 4.3). Other hazardous properties remain unaffected.

			H226 Flammable liquid and vapour.

<u>Note</u>

Determining the flash point of halogenated hydrocarbons in automated flash point testers can prove problems. Visual observation is thus preferred. Halogenated hydrocarbons of low flammability such as dichloromethane form explosive mixtures with air (oxygen), but have no flash point.

Mixtures of substances hardly to ignite and combustible substances can have flash points that are significantly below the flash point of the combustible components.

For mixtures of substances with markedly different vapour pressures, reproducible determination of the flash point is difficult.

Substances that are solid at room temperature may exhibit a flash point at a temperature above their melting point. It can be measured using one of the methods stated.

4.2 Explosion points

<u>Definition</u>

The lower/upper explosion point (LEP or UEP) is the temperature of a flammable liquid at which the concentration of the saturated vapour in air equals the lower/upper explosion limit.

<u>Reason for determining the parameter</u>

The explosion points are used to appoint the explosion limits: the lower and upper explosion points permit a statement to be made regarding the temperature range within which explosive mixtures may arise.

The lower explosion point provides a more precise indication than the flash point regarding the temperature above which the formation of explosive mixtures must be anticipated.

<u>Determination procedure</u>

The substance is heated in a closed vessel according to EN 15794. Once temperature equilibrium has been attained, an attempt is made to ignite the vapour/air mixture above the liquid using a series of induction sparks. The temperature at which a flame detaches from the electrode tips to a height of at least 10 cm is referred to as the lower/upper explosion point.

<u>Classification</u>

This parameter is not used for classifications according to the hazardous substances and dangerous goods transport legislation.

<u>Note</u>

The lower explosion point is generally lower than the flash point. Halogenated hydrocarbons of low flammability such as dichloromethane form explosive mixtures with air (oxygen) and therefore have explosion points but no flash point.

4.3 Sustained combustibility (UN Test L.2)

Definition

Sustained combustibility describes the property of a substance of being able, after its vapour phase has been ignited using an external ignition source, to continue burning for a defined time.

Reason for determining the parameter

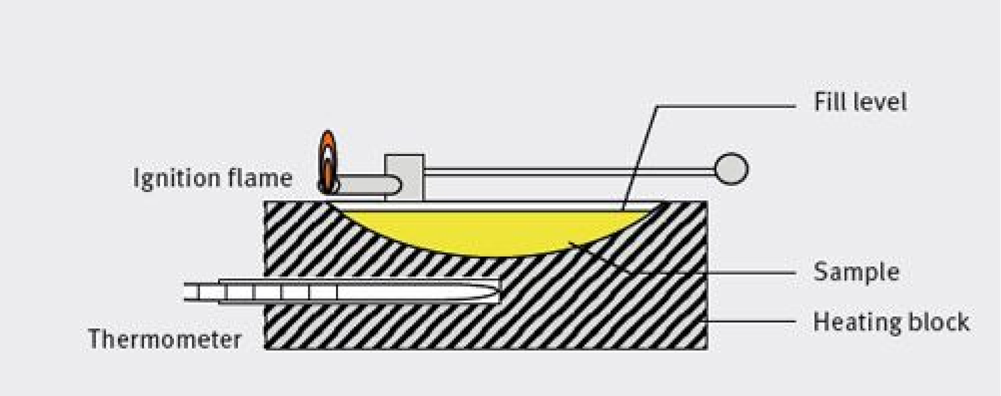
The test exempts a liquid having a flash point > 35 °C according to the CLP Regulation from the need to be placed in hazard category 3 of the “Flammable liquids“ hazard class.

Determination procedure

The test is conducted according to UN Test L.2 or EN ISO 9038. UN Test L.2 mentions two defined test temperatures, while EN ISO 9038 does not explicitly list any test temperatures.

2 ml of substance is heated in a metal block with a concave depression for a defined time to a defined temperature. With the substance having been in contact with an ignition source, observe whether the substance, if it did ignite, continues burning for a defined period without any contact with the ignition source.

Figure 22: Determination of sustained combustibility



Classification

If the test returns a negative result, flammable liquids with a flash point > 35 °C do not need to be categorised as flammable according to the CLP Regulation.

Note

Substances that have been exempted from categorisation on the basis of this test may nevertheless form an explosive atmosphere.

4.4 Auto-ignition temperature

Definition

The auto-ignition temperature (T_i) is the lowest temperature of a hot surface at which under specified test conditions an ignition of a flammable gas or vapour in mixture with air or air/inert gas occurs.

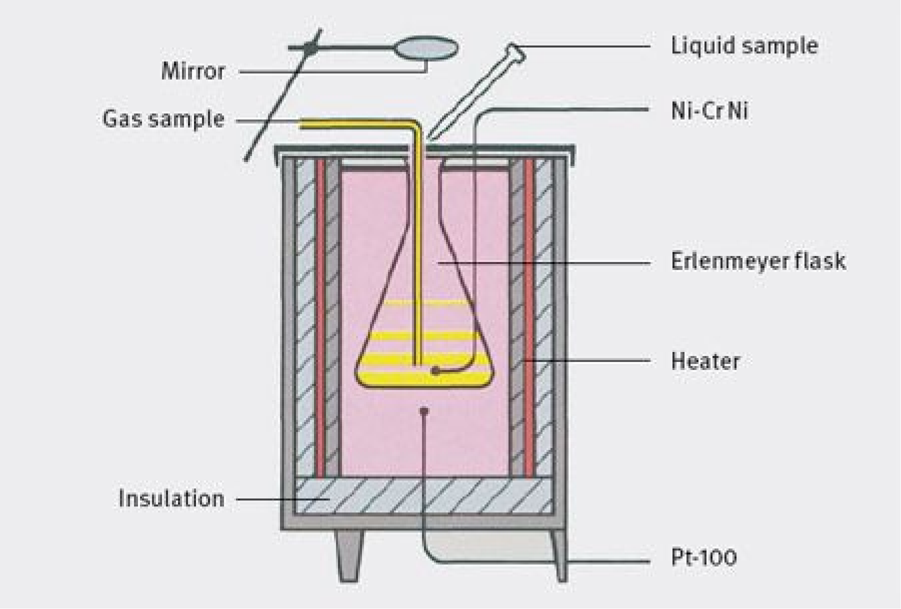
Reason for determining the parameter

The auto-ignition temperature of a substance in mixture with air is needed for registering new chemical substances, for compiling safety data sheets and for classifying combustible substances into temperature classes. The temperature classes are used, inter alia, for categorising electrical and non-electrical equipment for use in areas where there is a potential explosion hazard.

Determination procedure

The auto-ignition temperature is determined according to DIN EN 14522 or IEC 60079-20-1 in a preheated 200 ml Erlenmeyer flask in at least three test series. The auto-ignition of a gas/air or vapour/air mixture following addition of the substance in question as a function of temperature is observed.

Figure 23: Determination of ignition temperature according to DIN EN 14522



Evaluation of results

The measured auto-ignition temperature determines the temperature class and the maximum allowable surface temperature (see Table 15).

Table 15: Temperature class and maximum allowable surface temperature as a function of auto-ignition temperature

Auto-ignition temperature acc. to DIN EN 14522/IEC 60079-20-1	Temperature class	Maximum allowable surface temperature
$T_i > 450$ °C	T 1	450 °C
$300 < T_i \leq 450$ °C	T 2	300 °C

$200 < T_i \leq 300$ °C	T 3	200 °C
$135 < T_i \leq 200$ °C	T 4	135 °C
$100 < T_i \leq 135$ °C	T 5	100 °C
$85 < T_i \leq 100$ °C	T 6	85 °C
$T_i \leq 85$ °C	*)	

The temperature classes were originally developed to classify certain equipment. If hot surfaces can come in contact with explosive atmospheres, a safety margin should be ensured between the maximum surface temperature and the ignition temperature of the atmosphere. For example, according to TRBS 2152, part 3, the highest permissible temperature of a hot surface in an explosion endangered area classified as Zone I must be less than 80 % of the auto-ignition temperature (expressed in units of °C). Within explosive atmospheres, electrical and non-electrical equipment may only be operated when it has been shown that it meets the necessary criteria.

In practice the auto-ignition temperature depends on process conditions. A significant lowering of the auto-ignition temperature can be observed when there are catalytic effects, when there is a large increase in surface area, when high pressure is applied and when more powerful oxidants than air are used. Depending on the substance, increasing the pressure to 2 bar can lower the temperature by up to 300 K. Conversely, the auto-ignition temperature may also increase depending on the operating conditions.

Classification

This parameter is not used for classifications according to the hazardous substances and dangerous goods transport legislation.

5 Flammable solids

The parameters described in this section relate to flammable solids. For combustible solids, hazards posed by the formation of flammable gases upon contact with water or moist air (Section 6), self-ignition capability (Section 7) and dust explosibility (Section 8) may also exist.

Definition

A combustible solid is any substance in powder, granular or past-like form that can readily undergo combustion through contact with a source of ignition or through friction and can rapidly propagate the flames.

5.1 Burning class

Reason for determining the parameter

The burning class is a criterion for the propagation of a fire following local contact with a sufficiently strong source of ignition. The burning class is an important parameter for assessing the burning behaviour of solids on which relevant fire protection concepts are based.

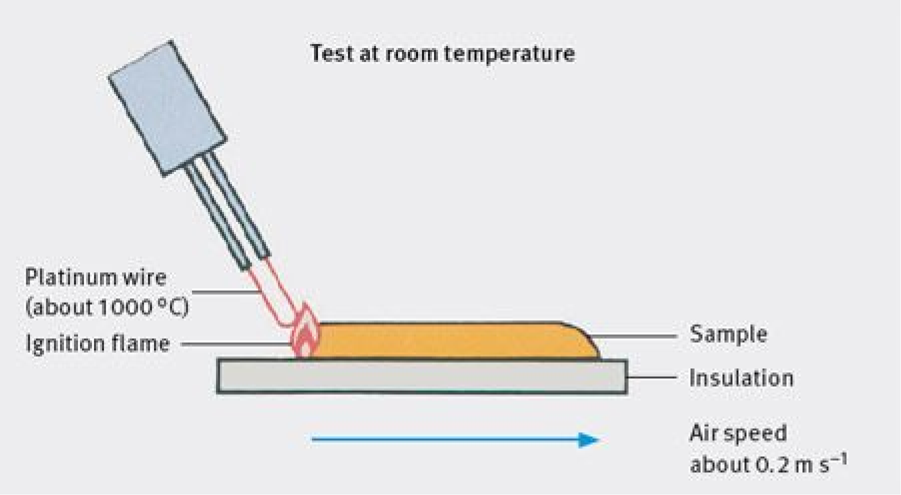
---

*) According to the CLP Regulation, substances with auto-ignition temperatures ≤ 85 °C belong in the Self-reactive substances and mixtures hazard class (see also Section 7).

Determination procedure

The burning class is determined according to VDI 2263-1 by spreading the milled (< 250 µm) and sparingly dried substance onto a heat-proof plate, covering an area measuring approximately 4 cm by 2 cm. An attempt is made to ignite the substance at one end using a glowing platinum wire (or a pilot flame). Products that melt can be mixed with kieselguhr.

Figure 24: Determination of burning class



Evaluation of results

The burning class is derived from the observed nature of the reaction (see Table 16).

Table 16: Establishment of burning class

Type of reaction		Burning class	Examples
No propagation of fire	No burning	1	Sodium chloride
	Brief burning and rapid extinction	2	Tartaric acid
	Local burning or glowing with at most only slight propagation	3	Lactose
Propagation of fire	Glowing without sparks (smouldering) or slow decomposition without flame	4	Lycopodium, tobacco
	Propagation of a naked fire or burning with spark generation	5	Sulfur
	Very rapid combustion or rapid decomposition without flame	6	Black powder

Classification

This parameter is not used for classifications according to the hazardous substances and dangerous goods transport legislation.

Note

Experience has shown that fire propagation in substances that, at room temperature, have only a slight tendency to propagate fire increases as the temperature rises, i. e. the burning class increases. Furthermore, an increase of the burning class can also be brought about by an increase of the air flow as it occurs, for example, in filters. To perform a safety assessment of processes that run at an elevated temperature level (e. g. drying processes), a test at higher temperature should be run additionally (generally at 100 °C).

5.2 Burning rate (UN Test N.1)

Definition

The burning rate describes the maximum rate of fire propagation for the combustion zone in solids.

Reason for determining the parameter

The burning rate, in the same way as the burning class, is a criterion for assessing burning behaviour. Furthermore, the parameter is relevant for classifying substances according to the hazardous substances and dangerous goods transport legislation.

Determination procedure

According to UN Test N.1 the burning rate is measured as the burning time over a distance of 10 cm for a defined powder train which is ignited at one end using a gas flame.

The test is also described in Council Regulation (EC) No 440/2008 (Test Method A.10).

Figure 25: Measurement of the burning time of a powder train

Classification

Classification is performed according to the CLP Regulation into a category within the “Flammable solids“ hazard class (see Table 17).

Table 17: Hazard categories in the “Flammable solids“ hazard class

Powdered metal	Substances other than powdered metal	Categorisation and labelling
Burning time $\leq$ 5 minutes	Burning time < 45 seconds or burning rate > 2.2 mm s^{-1} and the moistened zone does not arrest the fire	**Hazard category:** Category 1
		Pictogram: 
		Signal word: Danger
		Hazard statement: H228 Flammable solid.
Burning time > 5 minutes and $\leq$ 10 minutes	Burning time < 45 seconds or burning rate > 2.2 mm s^{-1} and the moistened zone arrests the fire for at least 4 minutes	**Hazard category:** Category 2
		Pictogram: 
		Signal word: Warning
		Hazard statement: H228 Flammable solid.

5.3 Smouldering point

Definition

The smouldering point is defined as the lowest temperature at which a solid substance emits combustible gases in such quantities that the resultant combustible gas/air mixtures can catch fire through external ignition.

Reason for determining the parameter

Determining smouldering point is advisable in the case of substances that are suspected of emitting combustible gas/air mixtures, e. g.

- in the event of incomplete combustion,
- in the event of endothermic or exothermic decomposition,
- during liberation of volatile components.

Determination procedure

There is no standardised method for measuring smouldering point. Smouldering point determination can be performed either in a flash point tester or in a special apparatus consisting of a heatable glass or steel cylinder and an ignition source (spark gap, gas flame). The Lütolf test described in VDI Guideline 2263-1 may also be used to test for flammable smouldering gases.

Classification

This parameter is not used for classifications according to the hazardous substances and dangerous goods transport legislation.

Note

Sublimable solids (such as salicylic acid) may exhibit a "flash point" sometimes referred to as a "smouldering point". Determining this is difficult owing to the sublimation properties and poor thermal conductivity of the solid substance.

Certain substances kept in closed containers may form an explosive atmosphere over a longer period below the smouldering point.

6 Substances which, in contact with water or moist air, emit flammable gases

Substances which, in contact with water or moist air, emit flammable gases may cause fire. To these substances also belong alkali metals.

6.1 UN Test N.5

Reason for determining the parameter

The parameter is relevant for labelling substances according to the hazardous substances and dangerous goods transport legislation.

Determination procedure

UN Test N.5 is conducted to check the ability of a substance to emit flammable gases if it comes into contact with water.

The test is also described in Council Regulation (EC) No 440/2008 (Test Method A.12).

Classification

Classification is performed according to the CLP Regulation into a category within the "Substances and mixtures which, in contact with water, emit flammable gases" hazard class (see Table 18).

Table 18: Hazard categories within the “Substances and mixtures which, in contact with water, emit flammable gases“ hazard class

Reactive behaviour	Categorisation and labelling
Any substance which reacts vigorously with water at ambient temperatures and generally demonstrates a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute period.	**Hazard category:** Category 1
	Pictogram: 
	Signal word: Danger
	Hazard statement: H260 In contact with water releases flammable gases which may ignite spontaneously.
Any substance which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for Category 1.	**Hazard category:** Category 2
	Pictogram: 
	Signal word: Danger
	Hazard statement: H261 In contact with water releases flammable gas.
Any substance which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for Categories 1 and 2.	**Hazard category:** Category 3
	Pictogram: 
	Signal word: Warning
	Hazard statement: H261 In contact with water releases flammable gas.

7 Selfigniting substances

In the chemical industry many substances are handled and manufactured in powder form. Self-ignition of powders and dusts is a major consideration in the safety assessment of drying processes and storage.

Self-ignition (spontaneous ignition) is the process by which a substance is able to catch fire in the presence of air (oxygen) without any external source of ignition. The heating is because of an exothermic oxidising process with air in the environment. Substances with self-ignition properties include, for instance, pyrophoric substances and self-heating substances.

- A pyrophoric substance is a substance which, even in small quantities, is liable to ignite within 5 minutes after coming into contact with air (oxygen).
- A self-heating substance is a substance which is liable to self-heat; this substance differs from a pyrophoric liquid or solid in that it will ignite only when in large amounts (kilograms) and after long periods of time (hours or days).

Note

In dust accumulations the space between the dust particles is generally filled with air. Any oxidation reaction occurring happens on the surface of all of the dust particles simultaneously. The rate of heat production is initially very low and barely discernable. When the production of heat exceeds its loss to the surroundings (which depends, inter alia, on the size and geometry of the dust layer), self-heating starts and smouldering or an open flame may ensue. The self-ignition temperature is the point at which the substance´s subcritical behaviour (rate of heat production < heat dissipation) changes to the supercritical state (rate of heat production “ heat dissipation). The process of self-heating essentially is limited to solid substances with a large surface area (e. g. dusts, bulk solids). Even at room temperature, oxidation reactions can take place on the surfaces of the particles. Furthermore, self-ignition behaviour may be seen in atmospheres other than air and in thin layers.

In processes involving high temperatures (e. g. during the drying of solids), the critical layer thickness or the volume for self-ignition may be significantly reduced.

Even organic liquids showing little volatility may exhibit self-ignition when applied to a carrier with a large surface area. This is the case, for instance, during the use of cloths to take up oils or when there are leaks in pipework surrounded by insulating material.

Substances exhibiting exothermic decomposition may lead to incorrect interpretations or to incorrect classifications. Additional measurements (e. g. using DSC, see Section 11.1.1 or storage under an inert atmosphere, see Section 7.5) are needed to permit self-heating and decomposition processes to be differentiated.

7.1 Test for pyrophoric properties (UN Test N.2 and N.3)

Reason for determining the parameter

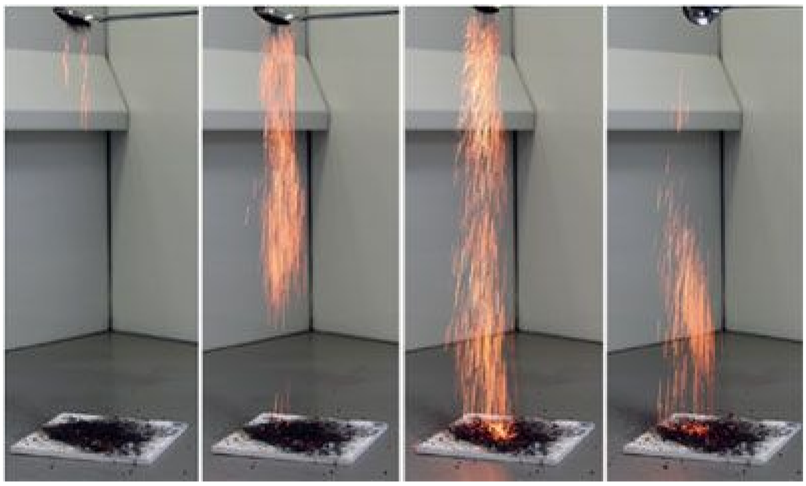
The parameter is relevant for labelling substances according to the hazardous substances and dangerous goods transport legislation.

Determination procedure

The test for pyrophoric properties is performed according to the UN Manual of Tests and Criteria (UN Test N.2 for solid pyrophoric substances, UN Test N.3 for liquid ones).
The test is also described in Council Regulation (EC) No 440/2008 (Test Method A.13).

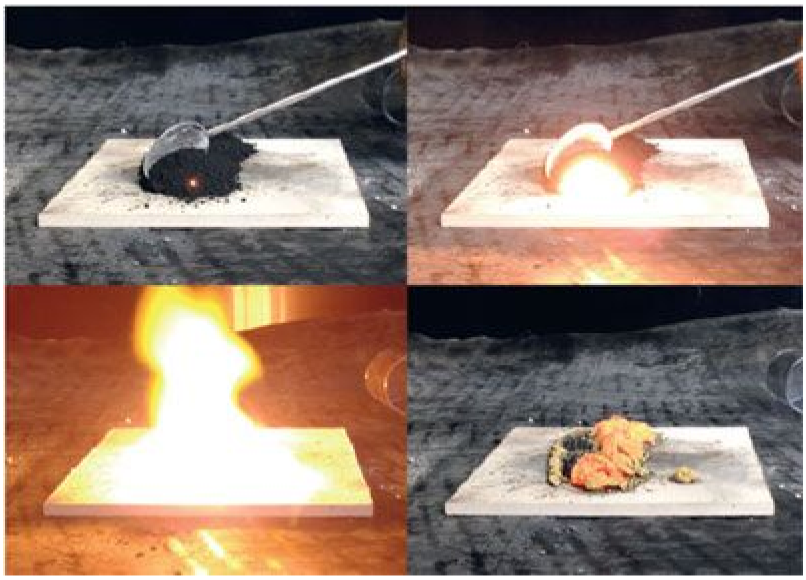
In UN Test N.2 the substance is poured from a height of about 1 m and it is observed whether the substance ignites within 5 minutes of settling.

Figure 26: Positive test for pyrogenic properties with n-iron (50–70 nm)



In UN Test N.3 the substance is added to an inert carrier and kept in contact with air at room temperature for 5 minutes. If liquid substances do not ignite, they are poured onto a filter paper and exposed to air at room temperature (about 20 °C) for 5 minutes.

Figure 27: Pyrophoric behaviour of nano scale titanium



Evaluation

If a solid or liquid substance ignites or a liquid substance ignites or chars the filter paper, it should be considered to be pyrophoric.

Classification

Classification is performed according to the CLP Regulation into Category 1 of the “Pyrophoric liquids“ or “Pyrophoric solids“ hazard class (see Table 19).

Table 19: Hazard category within the “Pyrophoric liquids“ and “Pyrophoric solids“ hazard classes

Hazard category	Labelling		
Category 1	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H250 Catches fire spontaneously if exposed to air.“

7.2 Test for self-ignition with linear rate of heating (Grewer oven test)

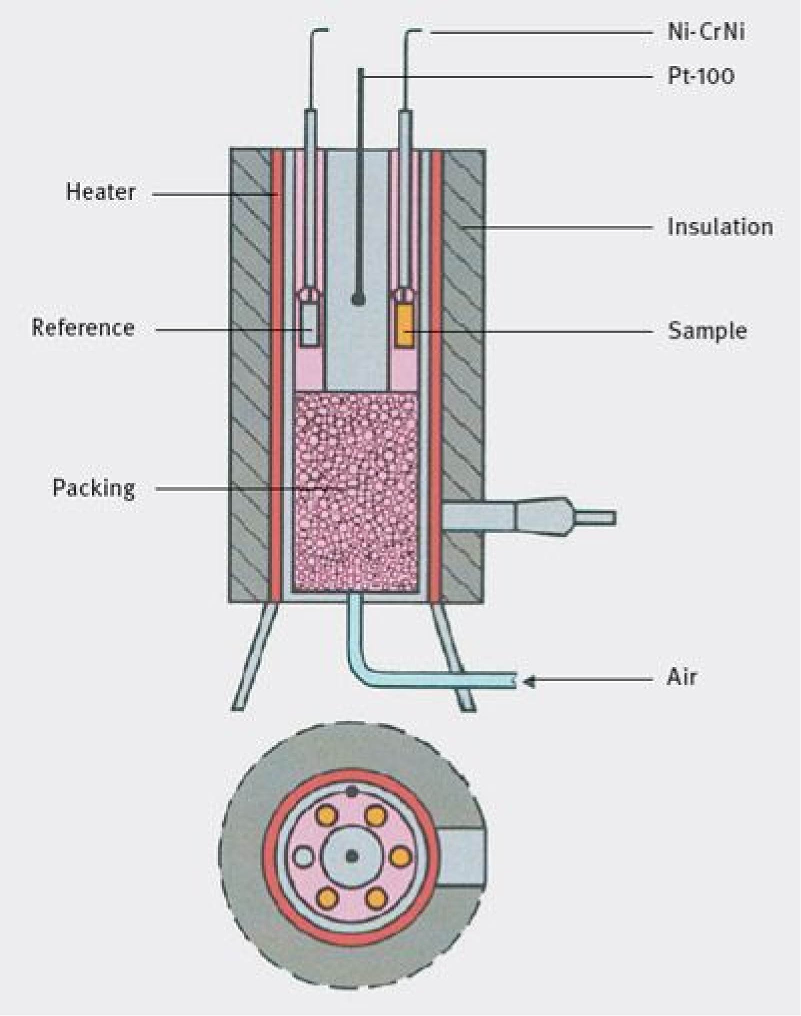
Reason for determining the parameter

The Grewer oven test is a screening test used to determine the temperature range for oxidative self-heating of a substance. According to the UN Manual of Tests and Criteria the self-ignition temperature test may also be performed as a rapid test.

Determination procedure

The substance and an equal quantity of graphite powder as reference substance are heated to 350 °C in fine-mesh wire baskets of 8 ml volume in a heated air stream at a rate of 1 K min^{-1} to 2 K min^{-1}. The oven is cylindrical, with the lower part being filled with packing while the upper part consists of a block with several cavities for sample containers. The entire test apparatus is electrically heated. 100 l to 120 l of air per hour are blown into the packing through the opening in the base. The air is heated up and comes into close contact with the substance.

Figure 28: Grewer oven

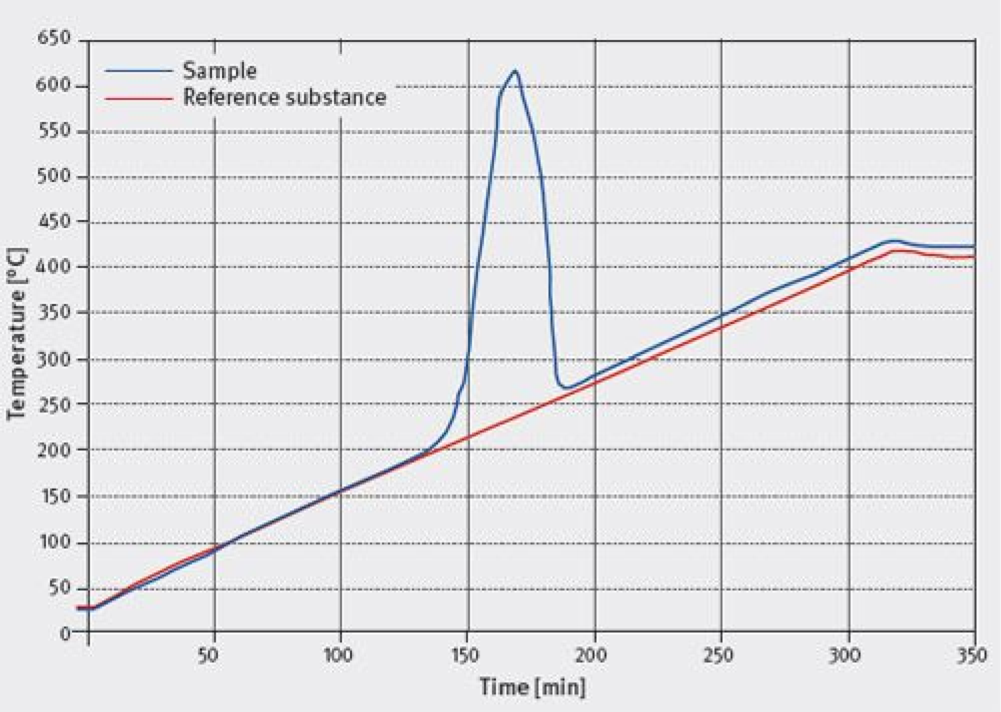


If the self-ignition behaviour of a liquid is to be investigated, an inert, solid carrier material (e. g. kieselguhr or insulating material) is soaked with the liquid.

<u>Evaluation of results</u>

An example of the results obtained from the Grewer oven experiment is shown in Figure 29.

Figure 29: Result of self-ignition temperature determination by the Grewer oven method



The ambient temperature is measured at which the temperature of the substance heated in the air stream exceeds the temperature of the reference substance. In order to measure the self-ignition onset temperature more precisely, it may be useful to calculate the 1st derivative of the curve.

Classification

This parameter is not used for classifications according to the hazardous substances and dangerous goods transport legislation.

Note

If an onset temperature above 220 °C is measured in the Grewer oven test, the substance may be exempted from classification as a self-heating substance without any further investigations (see Annex 6 to the UN Manual of Tests and Criteria). If the onset of self-heating occurs at below 220 °C, further investigations must be performed (e. g. isoperibolic hot storage (UN Test N.4) or adiabatic storage).

For products that are exposed for a short time only to a heated air stream (for example in spray dryers or flash dryers) and thus do not form any significant deposits (a few millimetres at most), it is sufficient in many cases to choose a safety margin of 50 K from the self-ignition onset temperature obtained using the Grewer oven test method.

In the case of large volumes or thicknesses, it should be remembered that the onset temperature depends on the thickness. For deposits > 1 cm in thickness the test in the Grewer oven no longer suffices; in this case hot-storage tests in larger wire baskets are recommended.

7.3 Relative self-ignition temperature for solids

Reason for determining the parameter

This test provides screening information on the self-ignition behaviour of solid substances at elevated temperatures. The method is chiefly applied for comparative purposes with old data. For determining the self-ignition temperature, measurement in the Grewer oven or wire baskets (see Sections 7.2, 7.4 and 7.5) is recommended.

Determination procedure

According to Council Regulation (EC) No 440/2008 (Test Method A.16) the substance is filled at room temperature into a wire mesh cube and placed in an oven. The temperature/time curve relating to conditions in the centre of the sample is recorded while the temperature of the oven is increased to 400 °C, or to the melting point if lower, at a rate of 0.5 K min^{-1}. When the substance ignites, the sample thermocouple will show a very sharp temperature rise above the oven temperature.

Evaluation of results

The temperature of the oven at which the sample temperature reaches 400 °C by self-heating is referred to as the relative self-ignition temperature.

Classification

This parameter is not used for classifications according to the hazardous substances and dangerous goods transport legislation.

Note

The test procedure is useful as a preliminary screening test, but should not be used for substances which self-ignite at ambient conditions. The self-ignition temperatures determined using this test method are specific to the measurement procedure and should be viewed as approximate values and for comparison purposes only. For planning safe storage conditions for bulk solids it is important to establish the volume-dependent self-ignition characteristics of the substance, see Sections 7.4 and 7.5.

7.4 Test for self-ignition with adiabatic hot-storage tests

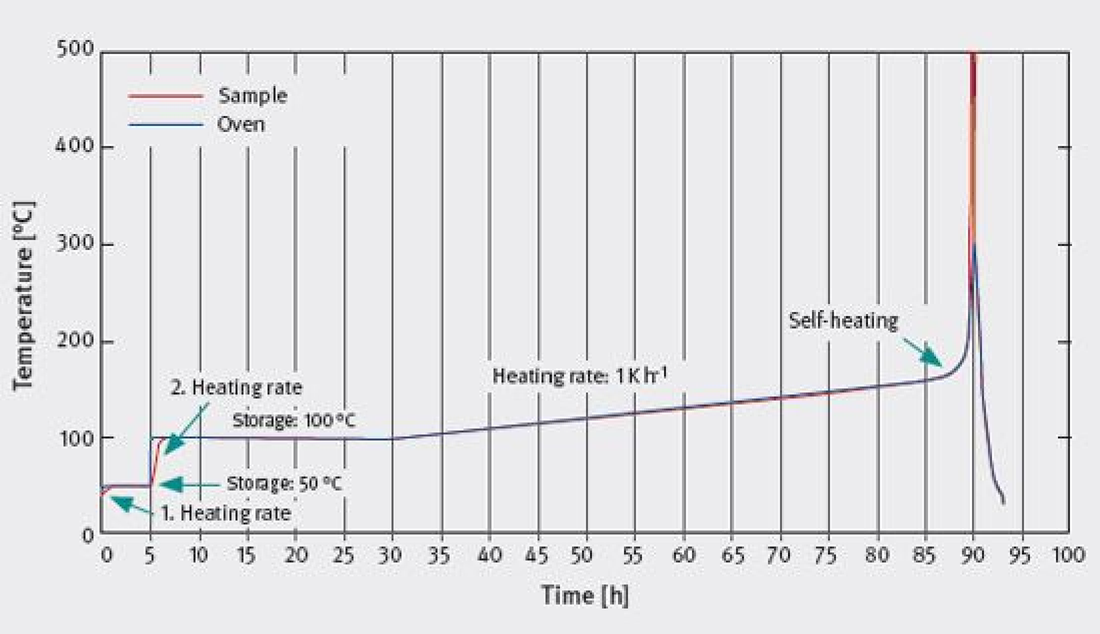
Reason for determining the parameter

The test is applied to establish the volume-dependence of the self-ignition temperature of the substance.

Determination procedure

The substance is first heated in a wire basket with a capacity of at least 400 ml at a predefined temperature for several hours in an oven with natural convection or forced circulating air. When the core temperature of the substance at this temperature rises due to self-heating, the oven temperature is raised correspondingly. This modus operandi keeps the experiment on a quasi-adiabatic course. If self-heating does not occur at the appointed temperature, the oven temperature is gradually increased at a rate of e. g. 1 K h^{-1}, until the substance starts to self-heat. From this temperature onwards the oven temperature is made to track that of the substance in order to maintain the quasi-adiabatic course of the experiment.

Figure 30: Experiment with adiabatic hot-storage tests



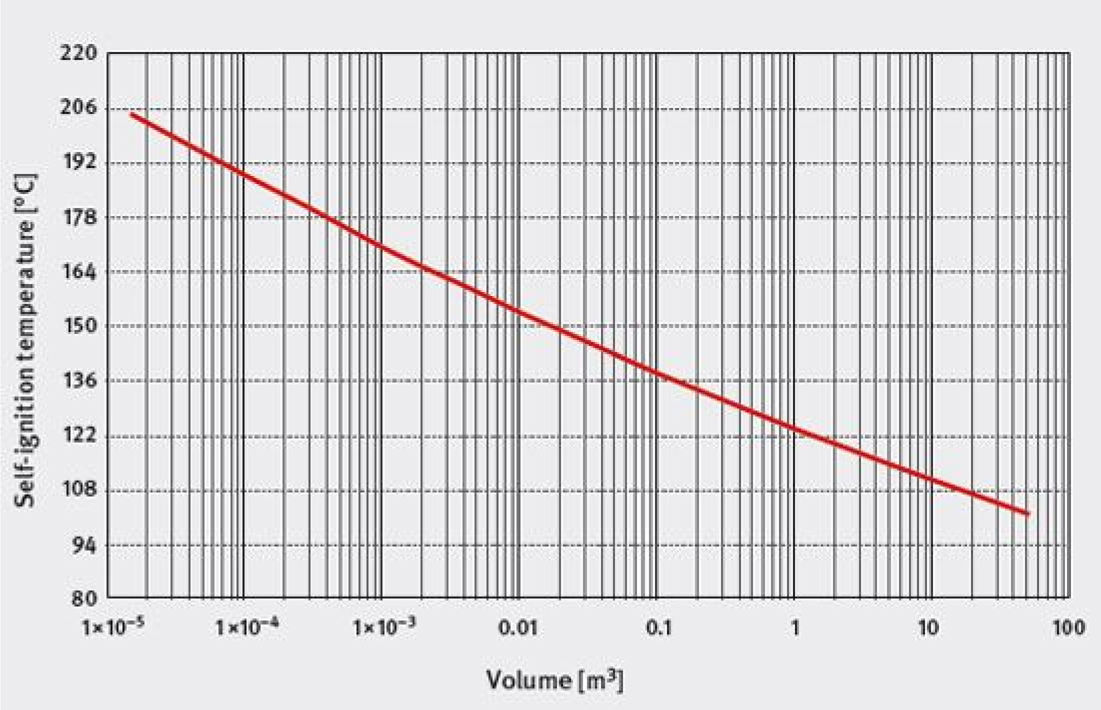
Evaluation of results

The rate of temperature increase is calculated for the temperature profile obtained. During the heating phase the experimental data can be plotted in dimensionless form as a function of time and the thermal conductivity can be so calculated.

The adiabatic temperature profile is analysed kinetically. For this the rate of temperature increase is plotted as a function of the inverse temperature of the substance. The thermal energy released during self-heating and the rate of temperature increase can be described by means of an Arrhenius plot (see also DIN EN 15188, Annex A). This Arrhenius plot reveals the activation energy E_A and the source term Q_0. Through the Frank-Kamenetskii model it is possible to use the activation energy, the source term and the thermal conductivity of the substance to calculate the self-ignition temperature for given simple geometries such as cubes, cylinders and spheres.

From the kinetic parameters of the adiabatic experiment and the thermal conductivity determined from the heating phase it is possible to calculate the self-ignition temperature for any bulk volume by applying Frank-Kamenetskii theory.

Figure 31: Volume dependence of self-ignition for a cube



The advantage of the adiabatic self-heat experiment lies in the fact that it is possible, using a single experiment, to extrapolate the self-ignition temperature for various bulk volumes.

Classification

The measurement results can be used as an exclusion criterion for classification of self-heating substances in accordance with the hazardous substances and dangerous goods transport legislation.

Note

In the case of moist substances or substances with complex reaction characteristics it is advisable to carry out additional isoperibolic heating experiments (see Section 7.5).

7.5 Test for self-ignition at a constant temperature (hot-storage test)

Reason for determining the parameter

The parameter is relevant for labelling substances according to the hazardous substances and dangerous goods transport legislation.

Determination procedure

The substance is kept in cylindrical or cube-shaped wire baskets of varying capacity in an oven at constant temperatures (isoperibolic experimental conditions). To determine volume dependence, according to the ECHA criteria[7] at least four different volumes should be investigated, with the smallest wire basket having a capacity of not less than 16 ml.

---

[7] Guidelines for labelling and packaging according to Regulation (EU) No 1272/2008 – see Annex No 83

For classification purposes, UN Test N.4 according to the UN Manual of Tests and Criteria is used. This prescribes different volumes and temperatures.

If the self-ignition behaviour of liquids is to be investigated, a solid carrier material (e. g. kieselguhr or insulating material) should be soaked with the liquid.

Evaluation of results

A rise in temperature above the storage temperature is rated as self-heating. If there is a temperature difference of more than 60 K or if there is an inflection point in the temperature profile above oven temperature, the term self-ignition is used (DIN EN 15188). The oven temperature is varied repeatedly and test series is continued until the highest oven temperature has been determined at which no ignition occurs, as well as the lowest oven temperature at which the substance still just ignites with the selected sample volume. If the results are extrapolated, the temperature difference between these two temperatures must be not more than 2 K.

The highest storage temperature at which the substance just does not ignite should be quoted as self-ignition temperature.

If the oven temperature is above the self-ignition temperature of the substance under investigation, the induction time of self-ignition can be determined. This is defined as the interval between achieving a pre-set initial temperature and achieving a temperature difference of 60 K. The induction time of self-ignition decreases with rising initial temperature and increasing product quantity. It should also be noticed that, at higher storage temperatures than those matching the respective self-ignition temperature, the induction times are considerably shorter.

Classification

Classification is performed according to the CLP Regulation into a category within the “Self-heating substances and mixtures“ hazard class (see also Table 20).

Table 20: Hazard categories within the “Self-heating substances and mixtures“ hazard class

Hazard category	Labelling		
Category 1	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H251 Self-heating; may catch fire.
Category 2	**Pictogram:** 	**Signal word:** Warning	**Hazard statement:** H252 Self-heating in large quantities; may catch fire.

Note

The self-ignition temperatures determined in this way are always lower than the temperatures measured using the Grewer method. The self-ignition temperature measured for a cubic volume of 1 l may be quoted for comparative purposes. With regard to storage of combustible dusts and deposits, however, the fact that the self-ignition temperature is quantity-dependent must be borne in mind. This temperature can be extrapolated from experiments using various quantities of substance. In order to assess how deposited and caked material behaves, the test result can often be used directly without the need for extrapolation.

7.6 Minimum ignition temperature of a dust layer with a one-sided thermal load

Definition

The minimum ignition temperature of a dust layer is the lowest temperature of a hot surface at which a dust layer ignites. Normally, the characteristic is determined for layers of 5 mm thickness.

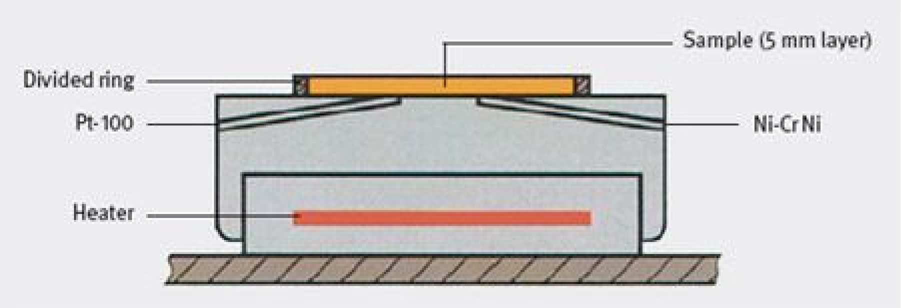
Reason for determining the parameter

The minimum ignition temperature of a dust layer is one of the relevant parameters for selecting electrical and non-electrical equipment in areas which may accumulate dust.

Determination procedure

The minimum ignition temperature of a dust layer is determined using an electrically heated plate on which, when it has heated up, the substance is distributed in a circular dust layer of 5 mm thickness. Whilst the plate temperature is kept constant, observations are made as to whether flames appear or glowing occurs.

Figure 32: Determination of minimum ignition temperature of a dust layer



Evaluation of results

In areas at risk through flammable dusts the surface temperature of areas on which dust can be deposited must be lower by at least 75 K than the minimum ignition temperature of the dust in question.

The minimum ignition temperature of a dust layer depends on the thickness of the layer and decreases as the thickness increases; also, therefore, allowable surface temperatures decrease with increasing layer thickness.

Classification

This parameter is not used for classifications according to the hazardous substances and dangerous goods transport legislation.

8 Combustible dust clouds

Combustible dusts dispersed in air (oxygen) are able to form explosive mixtures. When a sufficiently powerful ignition source is present, a dust explosion is possible, i. e. a rapid combustion reaction with advancing pressure and flame front occurs, as in a gas explosion.

A substantial hazard exists due not only to the fact that temperatures in excess of 1 000 °C occur but also that pressures rise to approximately 8 to 10 times the initial pressure (up to 13 times, occasionally, in the case of aluminium dusts). The test methods described below are used for risk assessment and for determining the conditions under which the hazards can be safely kept under control.

Classification

These parameters are not used for classifications according to the hazardous substances and dangerous goods transport legislation.

Note

According to prEN ISO 80079-20-2, the parameters of those dusts are to be measured, which are representative of the material encountered in the process in question. If this cannot be assured, the test substance must be prepared in such a way that the most critical conditions to be anticipated in practice are covered. This applies especially if the process involves altering the degree of fineness or enriching fines (e. g. through milling, suction or deposition). Wherever possible, a representative sample with the particle size of < 63 µm is investigated. Sometimes it is necessary to prepare the substance accordingly (e. g. through milling, sieving or drying).

8.1 Dust explosibility

Definition

A substance is explosive if, in a mixture with air (oxygen), a self-sustaining flame front can be triggered by an ignition source of defined energy, resulting in a rise in pressure in a closed vessel.

Determination procedure

A preliminary test can be performed according to VDI 2263-1 in the modified Hartmann apparatus.

Figure 33: Modified Hartmann tube

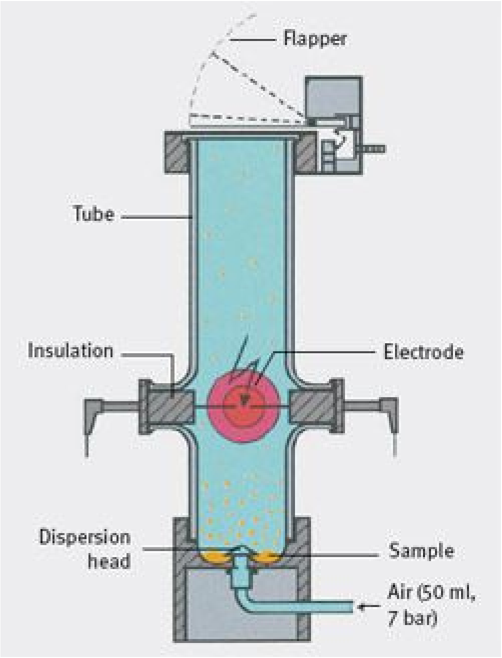


Figure 34: Ignition in a Hartmann tube

The apparatus consists of a cylindrical glass tube closed at the upper end with a movable lid. The substance under investigation (in the apparatus in a concentration of 30 g m^{-3} to 1 000 g m^{-3}) is placed at the bottom of the tube and dispersed upwards by a defined blast of air. A high-voltage generated spark gap or a glowing coil is used as ignition source. Propagation of the flame front from the ignition source is followed visually.

<u>Evaluation of results</u>

A substance is rated as dust explosive when it exhibits flame propagation within the concentration range being investigated.

Note

Combustible dusts which cannot be ignited in the modified Hartmann apparatus are relatively insensitive to ignition sources common for process plants.

However, the statement “not dust explosive“ cannot be inferred from this experiment; this verdict can only be reached following additional tests in a closed apparatus over a wide concentration range (at least from 30 g m^{-3} to 2000 g m^{-3}) (20-litre sphere apparatus, see Section 8.2).

A substance can be classified as “not dust explosive“ when

- exothermic oxidation reactions can be ruled out on account of its chemical properties,
- even with fine dust (< 63 µm), investigations of its explosibility have not resulted in an explosion,
- it does not ignite at 1 000 °C in the Godbert-Greenwald oven (see Section 8.5).

The dust explosibility of a substance is highly dependent on its form and consistency (e. g. fineness, moisture). All forms, consistencies and process conditions must therefore be considered during selection of the substance due to be tested.

8.2 Maximum explosion (over)pressure and maximum rate of pressure rise

Reason for determining the parameter

Important parameters connected with dust explosions are the following values measured during explosion of a dust/air mixture in a closed vessel at optimum concentration:

- the maximum pressure occurring p_{max} (maximum explosion overpressure),
- the maximum rate of pressure rise $(dp\ dt^{-1})_{max}$.

The maximum explosion pressure (i. e. overpressure), and maximum rate of pressure rise are used to design the constructional measures “Explosion-resistant design“, “Explosion pressure relief“ or “Explosion suppression“ (see Table 21).

Table 21: Safety concepts and parameters to be considered

Safety concept	Parameters to be considered
Explosion-resistant design	Maximum explosion (over)pressure
Explosion pressure relief	Maximum explosion (over)pressure, K_{St} value
Explosion suppression	

Determination procedure

The test apparatus consists of a closed, approximately spherical pressure container (volume e. g. 20 l, 1 m^3) and the respective control units for dispersing the dust and activating ignition. A dust cloud is created by blowing dust into the apparatus through a storage container and distributing it uniformly with the aid of a special distribution system (e. g. a rebound nozzle). The dust/air mixture is ignited at the centre of the explosion vessel by means of pyrotechnic igniters. The course of the explosion is recorded as a function of time.

Figure 35: 20 litre dust explosion sphere

Within the series of experiments the dust concentrations are varied over a wide range until the maximum values for maximum explosion overpressure and maximum rate of pressure rise have been reached.

<u>Evaluation of results</u>

The maximum rate of pressure rise is volume-dependent; the product of the maximum rate of pressure rise and the cube root of the volume in question is constant (cubic law):

$(dp\ dt^{-1})_{max} \cdot V^{1/3} = const. = K_{St}$

The K_{St} value is the maximum rate of pressure rise related to a volume of 1 m^3 (see Table 22). Applying the K_{St} value to different sizes of apparatus is, strictly speaking, only possible in geometrically similar vessels.

Table 22: Explosion classes based on K_{St} values for combustible dusts

K_{St} value	Dust explosion class
$\leq$ 200 bar m s^{-1}	St 1
between 200 bar m s^{-1} and 300 bar m s^{-1}	St 2
> 300 bar m s^{-1}	St 3

<u>Note</u>

The dust explosion class is a criterion neither of the likelihood nor of the effects of a dust explosion (all explosions are associated with sometimes substantial damage). It provides only hints with respect to the safety concept that can be selected to prevent dust explosions and how constructional measures can be applied. Special attention must be paid to the general process conditions and to the temperature-dependence of the maximum explosion pressure and the maximum rate of pressure rise.

8.3 Explosion limits and limiting oxygen concentration

Definition

The explosion limits describe the range of dust concentrations in air (oxygen) within which an explosion is possible.

The limiting oxygen concentration is the maximum oxygen concentration in a mixture of a combustible substance and air and an inert gas, in which an explosion will not occur, determined under specified test conditions.

Reason for determining the parameter

The explosion limits and the limiting oxygen concentration are required to enable the “Avoidance of explosive atmosphere“ safety concept to be implemented.

Determination procedure

The test equipment and methods are primarily the same as those described in Section 8.2.

The lower explosion limit is determined according to DIN EN 14034-3 by decreasing the concentration of dust to the point at which an attempt to ignite the dust does not result in an explosion. Owing to the inhomogeneity of dust/ air mixtures, it must be borne in mind that the lower explosion limit may still be exceeded locally, even if the mathematically calculated value for the apparatus or plant is below the limit.

The limiting oxygen concentration is determined according to DIN EN 14034-4 by adding an inert gas (generally nitrogen) to reduce the oxygen concentration in the combustible atmosphere gradually until ignition can no longer be triggered over the entire dust concentration range under the defined test conditions.

Evaluation of results

The resultant limiting oxygen concentration must be confirmed by a sufficient number of re-tests.

When the “Avoidance of explosive atmosphere“ protection measure is to be applied, it must be borne in mind that safety characteristics depend on the temperature and the inert gas used. The maximum allowable oxygen concentration can be calculated from the experimentally determined limiting oxygen concentration by subtracting a safety margin as defined in VDI 2263-2.

Note

Stating the upper explosion limit for flammable dust clouds is not appropriate since homogeneous distribution as the concentration increases cannot be guaranteed. Because it is not appropriate to develop a safety concept based on a “rich dust/air mixture“, the parameter is not determined.

8.4 Minimum ignition energy

Definition

The minimum ignition energy (MIE) is the minimum amount of electrical energy stored on a capacitor, which, upon discharge, is sufficient to ignite the most ignitable mixture of an explosive atmosphere under specified test conditions.

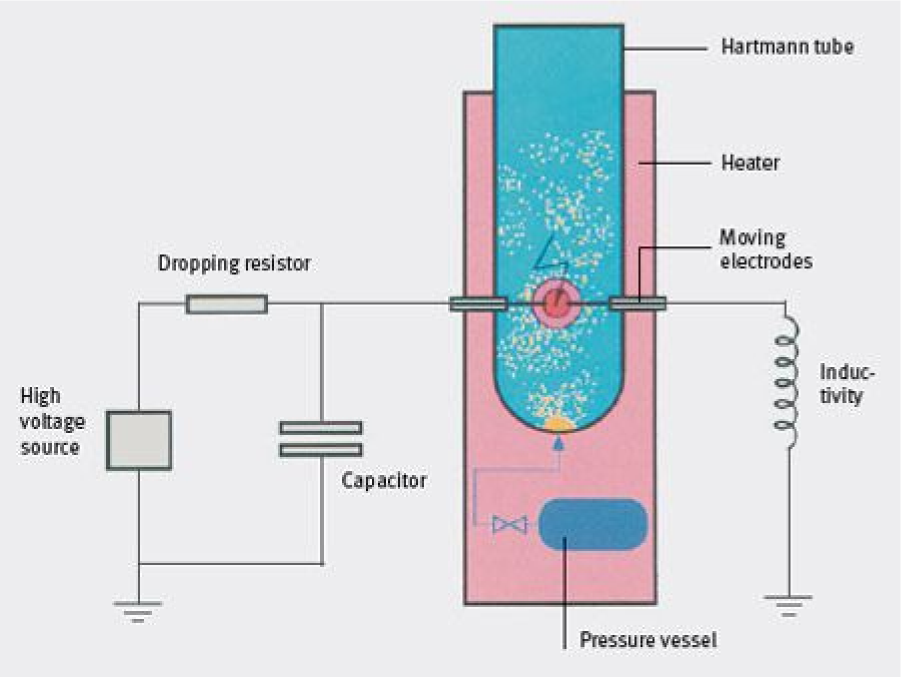
Reason for determining the parameter

The Minimum ignition energy is one criterion to estimate the effectiveness of potential ignition sources as e. g. electrostatic discharges, mechanical ignition sources or electromagnetic radiation. The Minimum ignition energy is an important parameter for developing the “Avoidance of effective ignition sources“ protection measure.

Determination procedure

The determination is performed according to DIN EN 13821 or prEN ISO 80097-20-2. The modified Hartmann apparatus is typically used as test equipment. The ignition energy provided by a capacitor discharge across a spark gap is in the range up to 1 000 mJ. Higher minimum ignition energies can be achieved in closed apparatus by means of pyrotechnic igniters (see Section 8.2).

Figure 36: Determination of minimum ignition energy in dusts



With variation of the apparatus parameters (ignition energy, ignition delay time, occasionally temperature) and the dust concentration, the lowest spark energy is determined at which the most ignitable dust/air mixture ignites as well as the highest spark energy at which it fails to ignite within ten attempts. Minimum ignition energy should generally be quoted in the form of these pairs of values.

Evaluation of results

The minimum ignition energies of explosive dust clouds are as a rule 100 to 1 000 times higher than the corresponding values for gases and vapours (see Table 23). Minimum ignition energy is decisively influenced by the fineness of the dust, its surface properties, its temperature and its moisture content. Minimum ignition energy decreases with decreasing particle size and with increasing temperature. This effect should be noted in particular when drying processes are involved.

Table 23: Categorisation of dusts according to minimum ignition energy

MIE	Categorisation of dusts
≥ 10 mJ	Normal ignition sensitivity
3 mJ ≤ MZE < 10 mJ	Particular ignition sensitivity
< 3 mJ	Extreme ignition sensitivity

If the minimum ignition energy is less than 10 mJ, the test may be repeated without inductance. An ignition test without inductance gives mostly higher values of the minimum ignition energy. The resulting values can be used with the “Avoidance of effective ignition sources“ approach if prolonged spark discharges can be excluded in practice.

8.5 Minimum ignition temperature of a dust cloud

Definition

The minimum ignition temperature of a dust cloud is the lowest temperature of a hot surface, as determined under specified experimental conditions, at which the most ignitable mixture of dust and air (oxygen) ignites.

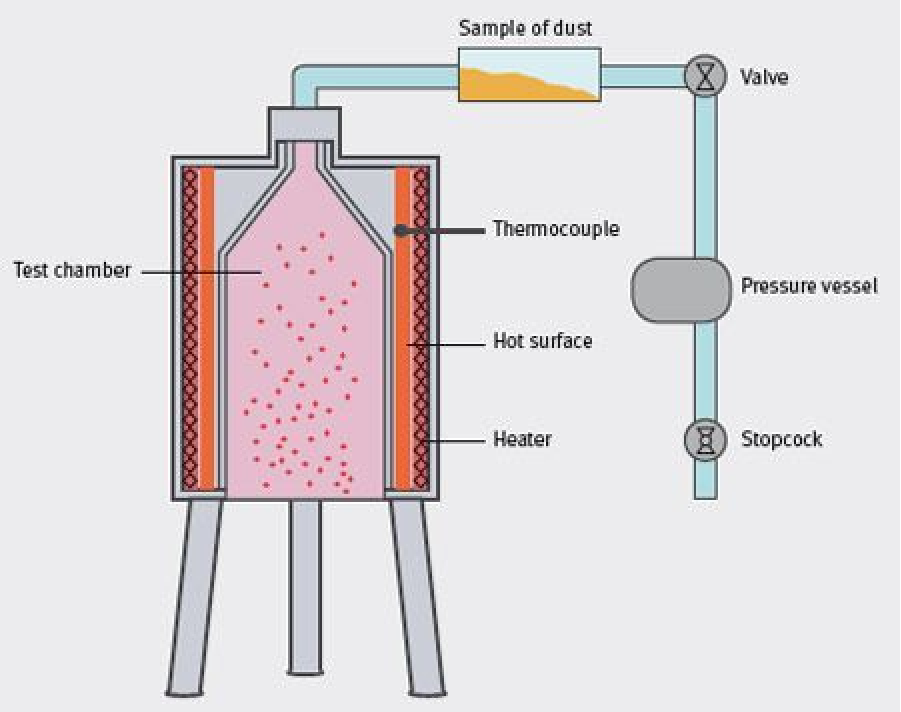
Reason for determining the parameter

The ignition temperature of a dust is used to establish the maximum allowable surface temperature of electrical and non-electrical equipment for use in areas where a dust explosion hazard exist.

Determination procedure

The ignition temperature is determined by the DIN EN 50281-2-1 method using a Godbert-Greenwald oven (GG oven). The apparatus consists of a vertical electrically heated pipe oven with a maximum working temperature of approximately 850 °C to 1 000 °C. The temperature of the inner wall of the pipe oven is recorded. The substance is blown with air from the top vertically into the oven and the reaction behaviour is observed visually.

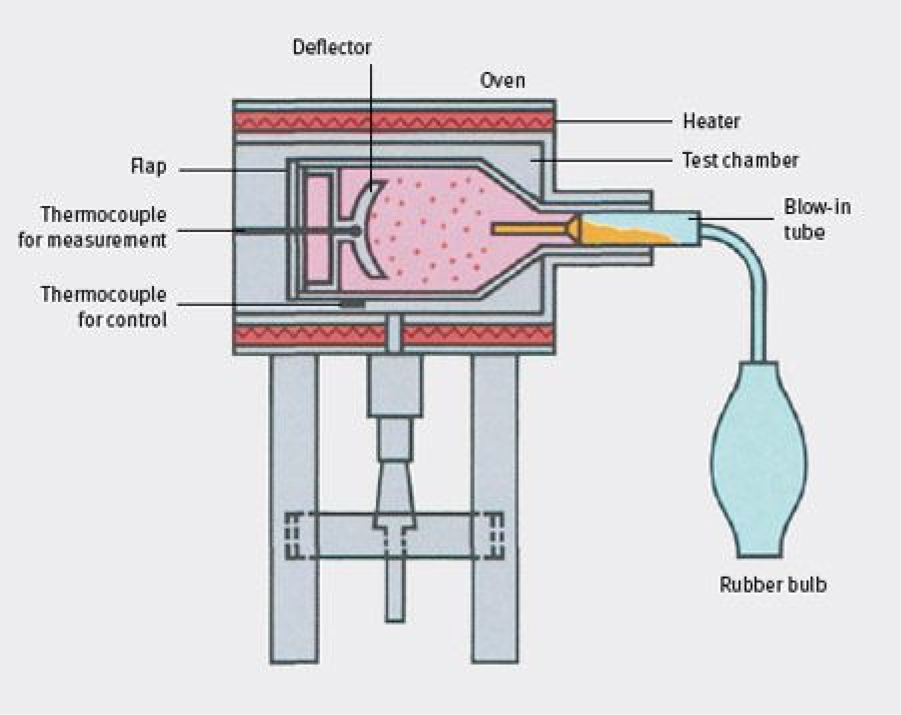
Figure 37: Godbert-Greenwald oven



Tables of values published in the literature mostly contain the minimum ignition temperature as determined in a BAM oven according to VDI 2263-1. The BAM oven is an electrically heated pipe oven (maximum working temperature approximately 600 °C) arranged horizontally. Roughly in the centre of the oven is a vertical deflection surface the temperature of which is measured. The substance is blown with air from the face of the oven against the deflection surface and the reaction behaviour is observed visually. The BAM oven will also detect smoulder reactions, generally yielding lower minimum ignition temperature values as compared to the Godbert-Greenwald oven.

prEN ISO 80079-20-2 states that either apparatus may be used to determine the minimum ignition temperature. The maximum test temperature prescribed therein is 600 °C, though testing at higher temperatures in the GG oven is allowed.

Figure 38: BAM oven



<u>Evaluation of results</u>

The minimum ignition temperature is stated as the lowest temperature at which the dust/air mixture can still just be ignited, producing a flame and/or a bang. The appearance of individual sparks is not classed as ignition.

The surface temperature of electrical and non-electrical equipment for use in areas where a dust explosion hazard exists is not allowed, during continuous operation, to be higher than two-thirds of the ignition temperature stated in °C. Where dust accumulations occur simultaneously, the minimum ignition temperature of the dust accumulation (for a 5 mm dust layer this is the same as the layer ignition temperature, see Section 7.6) must be taken into account.

For most dusts the minimum ignition temperature is between 200 °C and 600 °C, being highly dependent on the particle size distribution and moisture content of the sample.

9 Electrostatic properties

This area of explosion protection is covered specifically in TRGS 727 (see also IEC TS 60079-32-1) and exemplified there by means of selected procedures.

<u>Reason for determining the parameter</u>

If the safety concept “Avoidance of effective ignition sources“ is applied to prevent gas and dust explosions, the parameters listed below can be used to assess the extent to which a potential hazard due to electrostatic discharges exists and whether suitable protective actions must be taken to prevent hazardous electrostatic charging. Charging is hazardous if it gives rise to discharges capable of igniting an explosive atmosphere or a readily flammable substance or material.

The following safety characteristics are most commonly used to assess electrostatic behaviour:

- for substances (i. e. gases, liquids or solids): conductivity or, its reciprocal, volume resistivity,

- for materials (e. g. steel, glass, plastics, wood, paints, finishes and coatings): volume resistance and volume resistivity,
- for objects (e. g. pipelines, hoses, containers, pumps): leakage resistance and surface resistivity.

Table 24: Selection of standards for determining electrostatic properties

Parameter	Standard (selection)	Example
Conductivity	DIN 51412-1	Petroleum products
Volume resistivity	DIN IEC 60093 (VDE 0303 Part 30)	Semi-finished plastic articles
Volume resistance	DIN EN 1149-2	Textiles
Leakage resistance	DIN EN 61340-2-3	Hoses
Surface resistance	DIN IEC 60093 (VDE 0303 Part 30)	Plastic funnels
	DIN EN 1149-1	Workwear, textiles

Classification

These parameters are not used for classifications according to the hazardous substances and transport of dangerous goods legislation.

Note

Electrostatic charging of substances, materials or objects may occur

- through friction or grinding of solids or separation of objects,
- through pouring, flowing, stirring or spraying of liquids or powders and
- through flowing of gases and vapours that contain minute quantities of finely distributed liquids or solids.

Mechanical separation processes always lead to a separation of electrical charges. The electrical charges that remain on the surfaces of substances, materials or objects impart an “electrostatic charge“ to them. In addition, persons or objects in the vicinity of charged objects may also become charged through electrostatic induction.

Every charging process is opposed by a discharging process. How fast discharging takes place is dependent on the electrical properties of the substance, material or object as well as possibly existing contact with ground potential. Relaxation time is the time needed for an electrical charge to dissipate e. g.

- from a surface,
- from inside a liquid,
- a bulk material or
- a mist or dust cloud

to a level equivalent to 1/e (i. e. approximately 37 %) of its original value. Relaxation time is a measure of the ability of a substance, material or object to release its accumulated electrical charges.

9.1 Conductivity

Determination procedure

Electrical conductivity is mainly used to characterise liquids and is commonly expressed in pS m^{-1} (1 pS = 1 picoSiemens = $10^{-12}\ \Omega^{-1}$). The parameter is measured

- in liquids of low or medium conductivity (e. g. petroleum products) according to DIN 51412-1,
- in liquids with high conductivity (e. g. acids and alkalis) according to DIN EN 27888.

Evaluation of results

Hazardous charging may occur, for instance, in

- organic liquids with a conductivity below 50 pS m^{-1},
- other liquids with a conductivity below 100 pS m^{-1} and
- liquids containing undissolved solid or liquid matter with a conductivity below 10,000 pS m^{-1}.

9.2 Volume resistivity

Determination procedure

Volume resistivity, also known as specific electrical resistance, is a measure of the chargeability of solid substances and materials. It is determined according to DIN IEC 60093 (VDE 0303 Part 30) as the electrical resistance of a test piece 1 m in length and with a cross-section of 1 m^2 of the substance or material under investigation.

Evaluation of results

Substances and objects consisting of materials whose volume resistivity is more than $10^9\ \Omega m$ are insulating.

9.3 Volume resistance

Determination procedure

Volume resistance is often used instead of volume resistivity to assess the chargeability of thin materials and objects (e. g. textiles or films). It is measured according to DIN IEC 60093 (VDE 0303 Part 30) or, for textiles, according to DIN EN 1149-2.

Evaluation of results

Solids and objects whose volume resistance is $> 10^8\ \Omega$ are insulating.

9.4 Leakage resistance/resistance to earth

Determination procedure

Leakage resistance, also known as resistance to earth, is the electrical resistance measured between an object and earth. It is measured in operating condition based on DIN EN 61340-2-3.

Evaluation of results

A conductive object with a resistance to earth below 10^6 Ω is electrostatically earthed (grounded).

9.5 Surface resistance

Determination procedure

Surface resistance is a measure of the chargeability of materials and objects. The electrical resistance between two electrodes fixed on the surface of an object is measured. The electrodes are of narrow width and a length of 10 cm arranged parallel to each other in a distance of 1 cm.

Evaluation of results

Materials and objects are considered as

- conductive, if the surface resistivity is $\leq 10^4$ Ω,
- dissipative, if the surface resistivity – measured at 23 °C and 50 % relative humidity – is between 10^4 Ω and 10^9 Ω,
- isolating, if they are neither conductive nor dissipative.

As a rule, surface resistivity increases considerably as relative humidity decreases.

10 Oxidising properties

Oxidising substances are those which are not necessarily combustible themselves but, in contact or when mixed with flammable substances, can increase the fire hazard and the intensity of a fire by releasing oxygen or undergoing other oxidising processes.[8]

Reason for determining the parameter

Tests are performed in order to measure the oxidation potential of a solid or liquid substance. They are used for classifications according to the hazardous substances and dangerous goods transport legislation.

The classification procedure does not need to be applied for organic compounds if:

- the substance does not contain any oxygen, fluorine or chlorine, or
- the substance does contain oxygen, fluorine or chlorine, but these elements are chemically bonded only to carbon or hydrogen.

The classification procedure does not need to be applied for inorganic compounds if the substance does not contain any oxygen or halogen atoms.

Note

---

[8] This was referred to in the past as a fire-promoting property, see Council Regulation (EC) No 440/2008.

For classification according to the hazardous substance legislation, formerly a test was used corresponding to the Council Regulation (EC) No 440/2008 (test methods A.17 or A.21). In part this testing procedure differs considerably, both in nature of procedure and in produced results, from the tests specified in the UN Manual of Tests and Criteria. Any transfer of results of formerly carried out tests must be carefully verified.

It must be ensured in the case of the UN tests that the reference mixture and test substance are measured in the same apparatus, with the same reference substance and within the same period. As the classification criteria (rate of pressure rise, burning time and burning rate) are potentially influenced by numerous factors (e. g. factors specific to the apparatus), comparing the results obtained with the results for reference substances in the literature is neither appropriate nor permissible.

Oxidising substances, when mixed with combustible substances, can exhibit explosive properties. Safety measures must therefore be observed throughout testing.

Evaluation of results

A solid substance is classified as oxidising when, in a mixture with cellulose, it has a higher oxidation potential than a defined reference mixture.

Classification

Classification is performed according to the CLP Regulation into a category within the “Oxidising solids“ or “Oxidising liquids“ hazard class (see Table 25).

Table 25: Hazard categories within the “Oxidising solids“ or “Oxidising liquids“ hazard class

Hazard category	Labelling		
Category 1	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H271 May cause fire or explosion; strong oxidizer.
Category 2	**Pictogram:** 	**Signal word:** Danger	**Hazard statement:** H272 May intensify fire; oxidizer.
Category 3	**Pictogram:** 	**Signal word:** Warning	**Hazard statement:** H272 May intensify fire; oxidizer.

10.1 UN Test O.1

Determination procedure

To classify solids according to UN Test O.1, various mixtures of potassium bromate and cellulose are used as reference. The substance is mixed with cellulose in two different mixing ratios and formed into a truncated conical pile with a base diameter of 7 cm. This conical pile is ignited with an ignition wire. The time from when the power is switched on to when the main reaction ends (e. g. when burning ceases) is recorded. This period is referred to as the burning time. The test should be performed repeatedly and the mean burning time calculated. The substance is classified by comparing the mean burning time of the substance mixtures with those of the reference mixtures.

10.2 UN Test O.2

Determination procedure

To classify liquids according to UN Test O.2, various mixtures of oxidising substances and cellulose are used as reference. The substance is mixed in a 1 to 1 ratio with cellulose and the mixture ignited in a closed apparatus with an ignition wire. The pressure within the closed apparatus rises through heating and through thermal oxidative decomposition of the cellulose. The time taken for the pressure to rise from 7.9 bar to 21.7 bar is measured several times and the mean time interval is noted. In this test the rate of pressure rise is taken as the measure for oxidising properties. The substance is classified by comparing the mean rate of pressure rise of the substance mixtures with those of the reference mixtures.

10.3 UN Test O.3

Determination procedure

For classifying solids UN Test O.3 is recommended, in which various mixtures of calcium peroxide and cellulose are used as reference. The burning tests are conducted in the same way as in UN Test O.1, likewise using a truncated conical pile with a base diameter of 7 cm. Following ignition of the mixture with an ignition wire, its mass loss with time is recorded. The mass loss between 80 % and 20 % of the initial mass per unit time is the burning rate, which is taken as the measure for oxidising properties. The substance is classified by comparing the mean burning rates of the substance mixtures with those of the reference mixtures.

11 Thermal stability of substances/exothermic chemical reactions

Various methods are available for measuring the thermal hazard potential of reactive chemicals and chemical reactions. These can be roughly differentiated according to three measurement principles: thermal analysis, calorimetry and adiabatic calorimetry/heat accumulation experiments. Not all of the methods need to be applied in order to elaborate an appropriate safety concept. The experimental volume should fit the hazard potential and the existing operating conditions. In addition, the significance of the applied measurement technique must be taken into account when results are interpreted. The combination and interpretation of results with regard to the thermal stability of substances and exothermic chemical reactions is described in Leaflet R 004 “Thermische Sicherheit chemischer Prozesse“.

11.1 Thermal stability of substances/exothermic chemical reactions

Various safety characteristics can be measured through thermal analysis (see Table 26).

Table 26: Safety characteristics measured through thermal analysis

	Symbol	Unit
Decomposition energy/Heat of reaction	Q_R	J g^{-1}
Temperature of measurable start of decomposition	T_{Onset}	°C
Adiabatic temperature rise	ΔT_{ad}	K
Adiabatic induction time	τ_{ad}, TMR_{ad}	s, min, h or d
Heat capacity	c_p	J g^{-1} K^{-1}

11.1.1 Differential thermal analysis and differential scanning calorimetry

Both methods, differential thermal analysis (DTA) and differential scanning calorimetry (DSC), are used to investigate the thermal behaviour of a substance based on a defined temperature program. In DTA the temperature difference between the substance and a reference system is measured; in DSC the heat flow difference. DSC is mostly used owing to the widespread availability of instruments.

Both methods enable information on the thermal behaviour of substances, substance mixtures and reaction mixtures to be obtained with relatively little effort.

Determination procedure

Various types of crucibles (e. g. open, closed, pressure resistant up to several hundred bar) made of a number of different materials (e. g. aluminium, stainless steel, glass, gold, corundum) are available as sample vessels. To measure the heat flow quantitatively it is necessary to use pressure resistant closed crucibles.

Figure 39: Opened DSC measuring cell with sample and reference crucibles (gilded high pressure crucibles)

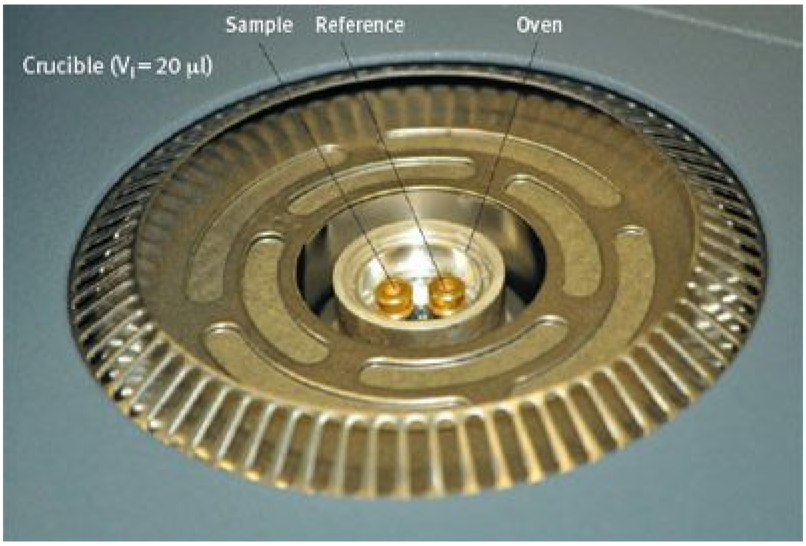
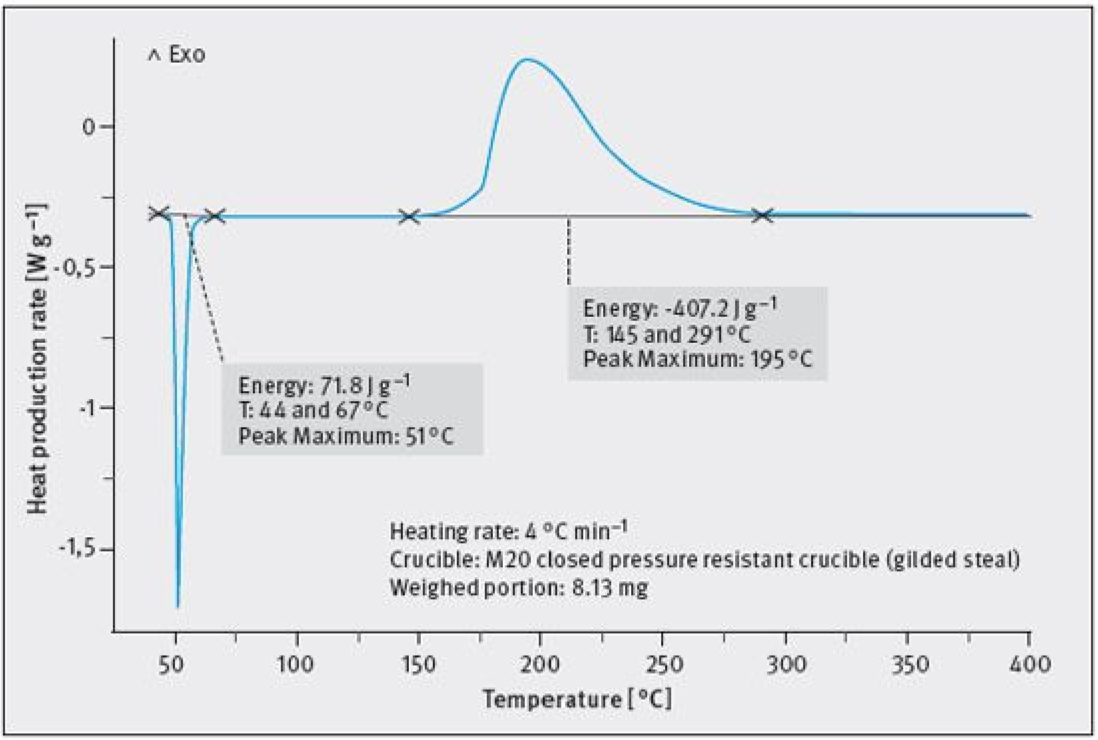


Figure 40: Thermogram of a DSC measurement



For reliable measure a reaction between crucible material and substance must be excluded. When processes are being investigated in which gaseous reaction products are generated or where reaction products evaporate, the various crucible types (closed or open) may yield entirely different results. Endothermic processes such as evaporation might override or obscure exothermic processes when open crucibles are used. Pressure resistant crucibles, in contrast, are able to inhibit such endothermic processes and allow complete measurement of exothermic processes, a very important factor for assessment of thermal stability. It has to be considered, nevertheless, that in pressure resistant crucibles a vapour pressure rise due to increased temperatures may influence the course of the reaction, especially in terms of reaction equilibrium.

Special DSC pressure cells, where the whole measuring system is located in an adjustable pressure vessel, permit studies under a defined pressure and atmosphere (e. g. inert gas or reactive gases such as hydrogen or oxygen).

Depending on the instrument used, samples of between 1 mg and 50 mg can be analysed. The advantage of minimal material requirement is accompanied by the fact that the measurements have to be carried out in batch mode and without stirring (only a small number of measuring cells allow spontaneous dosing or mixing of components). If the chemical reaction cannot be properly controlled, the outcome may be faulty interpretation of quantitative results. Especially when suspensions or inhomogeneous mixtures are being analysed, care must be taken to collect a representative sample. Typical temperature programs involve linear heating rates from 1 to 10 K min^{-1} or isothermal mode.

When isothermal measurements are performed, the process is analysed as a function of the reaction time. Measurements at various temperatures are required in order to obtain information regarding temperature dependence. Isothermal investigations may be helpful in analysing the reaction kinetics. Autocatalytic effects are detectable and their induction times can be measured. So-called stepwise investigations are a combination of heating and isothermal phases, in which the temperature is increased stepwise to determine the temperature range within which the onset of an exothermic process becomes measurable.

Information to such measurements are to be found also in Section 20.3.3.3 of the UN Manual of Tests and Criteria.

Evaluation of results

The reaction heat of target reactions and of secondary, subsequent or decomposition reactions can be measured by integrating the measured flow of heat with time. The amount of the reaction heat is an indication of the thermal hazardous potential and plays an essential role for the design of safety concepts. Catalytic influences can also be investigated by deliberately adding various substances.

DSC as a screening method provide the opportunity to exclude substances or mixture from a classification into a hazard class. This concerns e. g. the hazard class “Explosives“, if the organic substance or a homogeneous mixture of organic substances is shown in a screening test to have a decomposition energy of less than 500 J g^{-1} and the onset of decomposition is detected below 500 °C. Exclusion is also possible for the “Desensitised explosives“ and the “Self-reactive substances“ (when the decomposition energy is below 300 J g^{-1}) hazard classes.

DSC measurements are also used as screening measurements before test methods having an intensive substance and time requirement are employed.

In principle, every result obtained by thermal analysis exhibits a dependence on the temperature program. In the most commonly used linear heating programs the temperature range and heat flow signal are influenced by the heating rate; as the heating rate increases, the observed reaction signal shifts to higher temperatures. Further influencing factors are the experimental conditions with regard to the measuring cell and crucible (mass, thermal conduction, thermal capacity) and the mass of sample taken. Any correction requires the entire system to be calibrated.

The combination of investigation methods and the conditions to be met must always be adapted to the specific circumstances. Sometimes reliable results will only be obtained following numerous experiments carried out under a variety of different measurement conditions.

11.1.2 Calvet calorimeter

Calvet calorimeters are based on the heat flow principle and work according to the differential measurement principle, where the change in the difference in heat flow between the substance and reference substance is measured. Calvet calorimeters are used to investigate thermal stability and chemical reactions within temperature ranges between approximately –70 °C and 300 °C, and from ambient pressure up to approximately 350 bar respectively.

One of the chief features of the Calvet calorimeter is its high sensitivity (up to 0.1 mW g^{-1}), which is a result of its specific construction. A further advantage of the Calvet calorimeter is its integrated pressure measurement feature. This allows gas-generating reactions to be investigated and the quantity of non-condensable gases to be measured.

Determination procedure

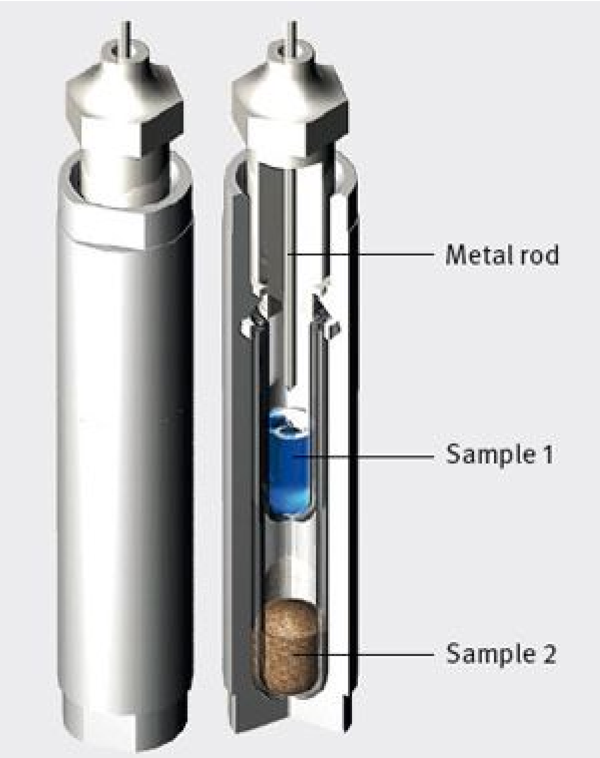
The Calvet calorimeter can be operated using a variety of different sample vessels or reactor types. Typical for Calvet calorimeter are sample quantities of up to 10 g, allowing even heterogeneous substances and substance mixtures to be representatively investigated.

For thermal stability analysis the substance (between 0.1 g and 1 g) is filled into a glass ampoule, which in turn is placed into a high-pressure measuring cell. During measurement the substance is heated at a continuous slow heating rate (e. g. 0.5 K min^{-1}) to approximately 300 °C. The heat flow signal is plotted throughout the process.

A so-called mixing cell is used to investigate synthesis reactions. The reactants are mixed by pushing a special metal rod through the predetermined breaking point at the base of the internal glass ampoule. Isothermal measurements are normally performed. A gas supply line can be installed for gas reactions. This can be used to feed gaseous components continuously into the reactor or force them in at one time. If the reaction is strongly mixture-controlled, a weak flow of inert gas, with gas bubbling and consequent thorough mixing, can be introduced.

When the reaction is complete, there is the added possibility of measuring the thermal stability of the reaction mixture. In this process the reactor contents are heated to 300 °C and the heat signal and pressure gradient are recorded.

Figure 41: Mixing cell of the Calvet calorimeter



This system allows the pressure gradient to be recorded in addition to the heat flow or reaction heat. The pressure is measured with the aid of a special metal membrane which is in direct contact with the pressure sensor. To obtain the quantity of non-condensable gases liberated during measurement, the initial pressure (at the start of measurement) is compared with the final pressure (at 30 °C). A gas volume per unit mass of sample [l kg^{-1}] can be calculated from the pressure difference. The derivative of the pressure plot yields the rate of pressure rise. The onset of gas generation can be qualitatively evaluated based on the plot for the rate of pressure rise.

If the decomposition gases are to be analysed, an adapter is used to conduct the gas from the pressurised measuring cell in a controlled manner, e. g. into a gas chromatograph/mass spectrometer (GC-MS).

11.1.3 Microcalorimeter

Microcalorimeters function as isoperibolic heat flow calorimeters, where the change in the difference in heat flow between the substance and a reference substance is measured. Microcalorimeters are used to analyse thermal stability and chemical reactions in temperature ranges between approximately 15 °C and 150 °C.

At the heart of a microcalorimeter is a thermostat unit characterised by its ability to maintain an extremely constant temperature with a deviation of less than 0.1 mK. Depending on the calorimeter unit this enables extremely high sensitivities in the range from 0.001 W kg^{-1} to 0.01 W kg^{-1} to be achieved.

Determination procedure

Microcalorimeters can be operated with various calorimeter units. In addition to static twin calorimeters with closed glass ampoules or low-pressure mini autoclaves in the volume range from 3 ml to 20 ml there are stirrerable units with 25 ml volume and a dosing feature or perfusion cells with a facility for introducing gases and vapours. Several twin calorimeters can be joined together to form multicalorimeters with up to 48 individual cells, thus enabling parallel analyses to be conducted.

Essentially, measurements are performed in isothermal mode, allowing even experiments with low heating rates of up to 2 K h^{-1} or steps in temperature to be performed. The measuring range for absolute heat flow is typically within the range from 500 nW to 20 mW.

The high sensitivity of these systems enables the thermal stability of substances in terms of the assessment of chemical processes, drying steps or storage to be investigated at considerably lower temperatures than with other methods. It is often possible to perform a measurement at or close to the process or storage temperature. The deliberate inclusion of additives enables their catalytic effect on the decomposition reaction to be studied. In perfusion cells, test substances can be perfused with air to allow oxidative processes to be analysed for assessment of self-ignition processes. By taking measurements at various temperature levels it is also possible to derive kinetic parameters such as n-th order induction times or autocatalytic reactions.

Figure 42: Microcalorimeter test ampoules

Figure 43: Multicalorimeter with six measuring cells

11.1.4 DTA-analogous tests in the gram range, pressure and volume measurements

Allowing slowly initiated decomposition reactions to be analysed, a series of sometimes extremely sensitive experimental set-ups exists specially for gramscale (from 1 g to approximately 5 g) sample quantities.

Determination procedure

Typically, glass vessels or mini autoclaves are used as sample cells. Either the difference between a sample and inert reference substance or only the temperature difference between sample and oven is detected. Owing to the increased mass of sample and sample cell, lower heating rates (typically between 0.05 K min^{-1} and 1.5 K min^{-1}) are applied compared to DSC. In general, exothermic decompositions are detected at lower temperatures compared to DSC scans, which may be important for the storage of the substance.

On the one hand the increased sample quantity is advantageous especially in the case of heterogeneous substance and reaction mixtures because representative samples can be used. On the other, proper calibration is more difficult due to an increased variety of heat transfer properties and time constants.

Evaluation of results

Pressure and volumetric measurements can be used to provide additional information. When gas releases have to be evaluated, the time- or temperature-dependent pressure or volume trends can be analysed directly or as derived rate signals in analogy with thermoanalytical signals.

In part, the influence of the atmosphere (e. g. inert gas, air) on decomposition processes can be observed using additional flushing gas equipment.

11.1.5 Thermogravimetry

Thermogravimetry (TG) is a technique in which the mass loss of a substance during physical or chemical processes is measured. As just a change in mass is measured, only processes involving volatile components (e. g. drying processes, decomposition reactions) can be evaluated.

Determination procedure

The experimental conditions that exist with this method in terms of the temperature program and crucible material are similar to the experimental conditions with DSC measurements. Here, too, the system must be calibrated.

As TG is performed in open crucibles, it is possible to vary the atmosphere (e. g. inert gas or oxygen). Coupling methods have been devised for TG instruments (e. g. DSC, IR spectrometry, mass spectrometry, gas chromatography), allowing thermokinetics to be determined or decomposition products to be analysed.

11.2 Reaction calorimetry

Various safety characteristics can be measured through reaction calorimetry (see Table 27).

Table 27: Safety characteristics measured through reaction calorimetry

	Symbol	Unit
Overall reaction heat	Q_R	$J\ g^{-1}$
Rate of heat production	$dQ_R\ dt^{-1}$	$W\ kg^{-1}$
Maximum rate of heat production	$(dQ_R\ dt^{-1})_{max}$	$W\ kg^{-1}$
Heat capacity	c_p	$J\ g^{-1}\ K^{-1}$
Degree of accumulation (equals accumulation of chemical energy)	α_{akku}	%
Adiabatic temperature rise	ΔT_{ad}	K
Maximum temperature of the synthesis reaction	MTSR	°C

Determination procedure

Reaction calorimeters can be used to investigate chemical reactions on a benchscale based on prescribed synthesis procedures under near-industrial conditions. Reaction calorimeters are generally characterised by a reaction volume of 0.1 l to 2.5 l. In most cases the reactor geometry corresponds to stirring tank reactors. Therefore they are referred to as “bench-scale reaction calorimeters“. While a reaction is in progress it is possible to add substances, run temperature gradients and change stirring parameters. Depending on the reactor type, experiments can be run unpressurised or under pressure.

The principle of reaction calorimetry is based on a heat balance of the reaction vessel. The heat production rate of the chemical reaction and the stirring power input are balanced against the removal of heat through convection (direct cooling), conduction (contact cooling), evaporation, loss of heat to the surroundings and heat accumulation by the reaction mixture. Balancing requires the system to be calibrated.

Since only overall reaction heat is measured, it is not possible to differentiate between co-occuring endo- and exothermic effects (e. g. simultaneous reactions, changes in enthalpy through phase changes, heat of mixing or solution, changes in physical state). If only a single reaction is running in the reactor, the measured rate of heat release is directly proportional to the reaction rate.

Figure 44: Heat flux reaction calorimeter

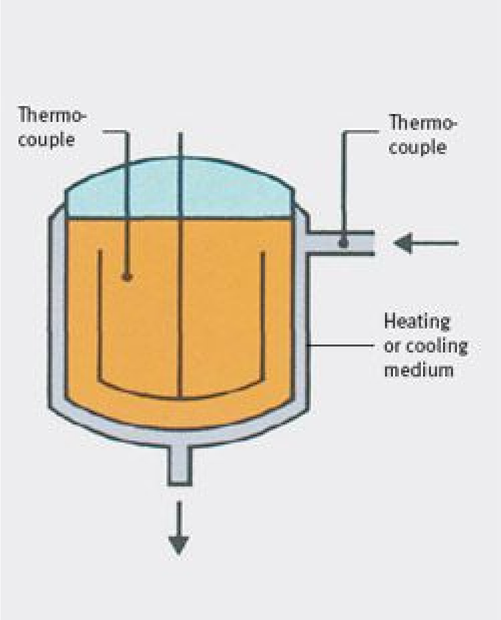


Figure 45: Reaction calorimeter

The measured maximum heat release rate is an important factor for dimensioning the cooling performance of the industrial-scale reactor. The overall heat production can be used to calculate the maximum adiabatic temperature increase. For this purpose it is important to check the degree of chemical conversion through appropriate additional methods.

Evaluation of results

To assess the thermal hazard potential posed by a reaction mixture at a given reaction time, the degree of heat accumulation must be known. This parameter allows the calculation of the corresponding adiabatic temperature rise at any time. Heat accumulation is calculated from the difference between the theoretically released heat according to the amount of fed reactants and the actual heat released up until the time point being analysed.

Reaction calorimeters are mainly operated in isothermal or isoperibolic mode.

When a reaction calorimeter is operated in isothermal mode, the temperature of the reaction mixture is kept constant by adjusting the temperature of a rapidly circulating jacket cooling medium. Therefore, isothermal reaction calorimeters are active heat flow calorimeters.

In isoperibolic mode the jacket or ambient temperature of the calorimeter is kept constant. The heat released in the reactor is both accumulated and removed via the cooling jacket. Isoperibolic calorimeters are passive heat flow calorimeters. There is no control system intervention in the heat exchange processes.

Note

In order to describe the course of the reaction, a suitable combination of reaction calorimetry with other measurement procedures is appropriate and is recommended with regard to safety concepts. Additional measurements (e. g. of pH, conductivity, pressure) may be applied along with infrared or Raman spectroscopy to measure further parameters in real time.

11.3 Adiabatic calorimetry

Adiabatic calorimetry can be used to determine various safety characteristics (see Table 28).

Table 28: Safety characteristics in adiabatic calorimetry

	Symbol	Unit
Temperature profile	$T = f(t)$	
Adiabatic temperature rise	ΔT_{ad}	K
Maximum rate of temperature increase	$(dT\ dt^{-1})_{max}$	$K\ s^{-1}$
Pressure profile	$p = f\ (t)$	
Pressure rise	Δp	bar
Maximum pressure	p_{end} , p_{max}	bar
Maximum rate of pressure rise	$(dp\ dt^{-1})_{max}$	$bar\ s^{-1}$
Adiabatic induction time	t_{ad}, TMR_{ad}	s, min, h oder d
Decomposition energy, overall heat of reaction	$Q\ R$	$J\ g^{-1}$
Rate of heat generation	$dQ_R\ dt^{-1}$	$W\ kg^{-1}$

Maximum rate of heat generation	$(dQ_R\ dt^{-1}1)_{max}$	W kg^{-1}
Maximum temperature of the synthesis reaction	MTSR	°C

Using bench-scale equipment, adiabatic calorimetry allows to characterize the behaviour of thermally unstable substances and reaction mixtures in a runaway situation. The worst-case scenario is tracked by obtaining temperature and pressure trends.

Whether the heat of the decomposition reaction, which may also occur without the presence of oxygen, exceeds the heat loss, depends, inter alia, on the size and geometry of the vessels and on the ambient temperature.

Adiabatic conditions can be realized using either a thermally insulating vessel (Dewar) or a thermally controllable adiabatic jacket. The information provided is important for the safe handling and storage of substances and mixtures.

Note

As a matter of principle, the sensitivity of the method (e. g. detectable heat flow) must fit the process considered.

11.3.1 Dewar methods

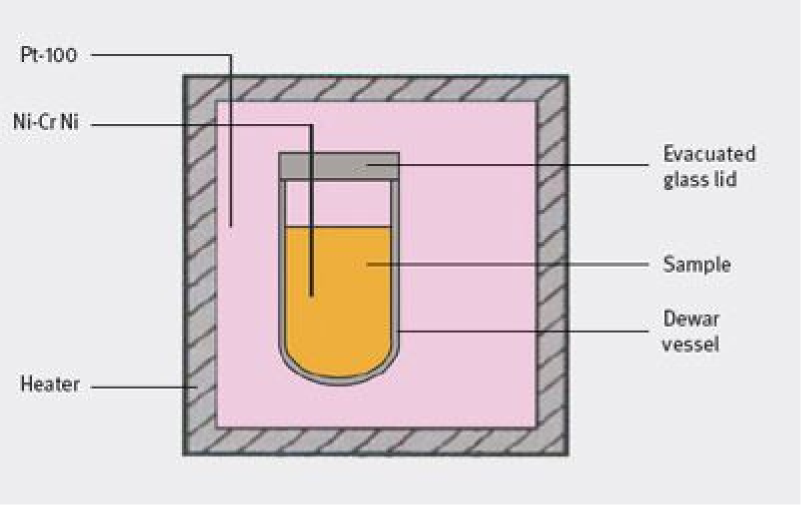
In Dewar vessels samples are held under thermally insulated conditions. When exothermic reactions occur, the generated reaction heat largely remains within the system. Dewar vessels are nearly adiabatic.

Determination procedure

The Dewar vessel is filled with substance and placed in an oven (e. g. an electrically heated aluminium block or a convection oven). The sample and oven temperatures are measured using thermocouples and recorded.

Depending on the process to be analysed, this simple setup can be extended through addition of a stirrer to blend a heterogeneous mixture or a heater to bring the sample quickly to the intended testing temperature. If the self-heating starts near or above the boiling temperature, measurement in an open Dewar vessel is inappropriate because this situation results does not reflect the worst case owing to mass and energy loss through evaporation. For such experiments Dewar vessels located in an autoclave under an inert gas atmosphere or stainless steel Dewar vessels can be used.

Figure 46: Dewar vessel



Evaluation of results

Using the first method it is possible to obtain more extensive results, whereas stainless steel Dewars are a cost-effective alternative when there is only casual demand.

11.3.2 Methods with a controlled adiabatic jacket

Determination procedure

The principle of this method is the tracking of ambient temperature according to the sample temperature when an exothermic reaction takes place. Various instruments are available with a controlled adiabatic jacket, e. g. PHI-TEC, VSP (Vent Sizing Package), AST (Adiabatic Storage Test), ARC (Accelerating Rate Calorimeter). These instruments differ in

- sample volume (ideally about 100 ml),
- construction material (glass or metal),
- ϕ-factor (the ratio of the overall thermal capacity of the sample mass plus measuring cell plus other items to the thermal capacity of the sample itself),
- temperature and pressure design limits,
- handling details (stirring, dosing, venting) and
- the software used to control and evaluate the experiment.

Adiabatic calorimeters can be used typically up to temperatures of 400 °C and pressures of up to approximately 100 bar, while special instruments (e. g. AST, ARC) can even be used up to 1 000 bar. If the assembly allows the tracking of the pressure of the outer vessel according to the pressure of the measuring cell, which is enclosed in the outer vessel, the walls of the cell can be kept very thin and the heat capacity of the cell also kept low. Heat loss to the wall are minimal, which is advantageous for analysis of the results. In the most favourable cases the ϕ-factor in these calorimeters is 1.05, which is a typical value for reaction vessels on a plant scale. Usually the value is approximately $\phi = 1.3$ and, for the ARC, between $\phi = 1.5$ and $\phi = 2.0$.

Figure 47: Adiabatic storage test apparatus

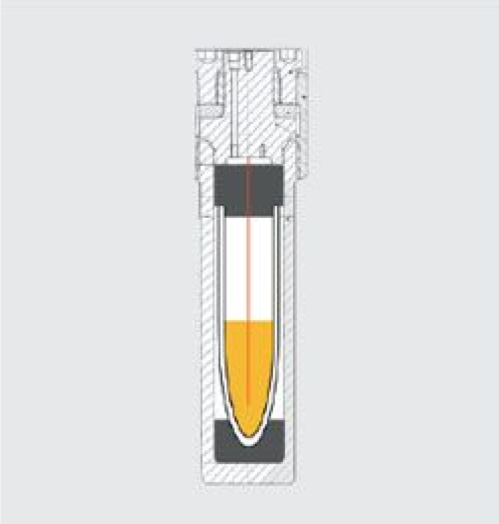
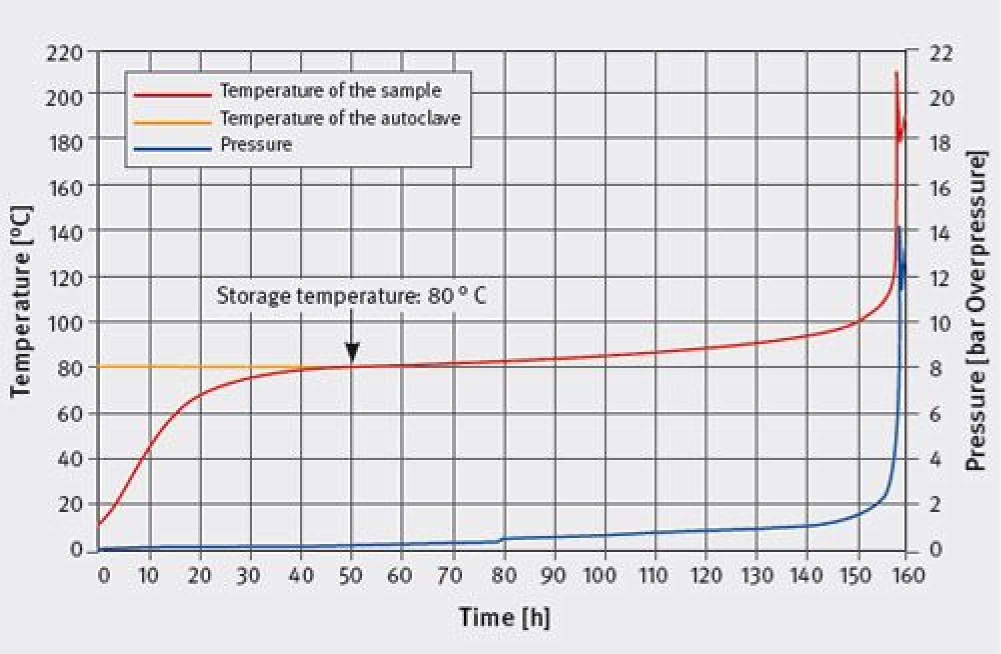


Figure 48: Pressure and temperature course with time



Evaluation of results

Figure 48 shows the pressure and temperature course of a substance which initially was heated to 80 °C (vessel temperature > sample temperature). At this temperature an exothermic reaction is initiated (with the vessel temperature being kept in line with the sample temperature), bringing the reaction mixture to a final temperature of 210 °C.

Further information can be derived from the primary measurement data, such as release of a non-condensable gas.

If the pressure rise and temperature rise rates are plotted over reciprocal temperature, a so-called Arrhenius plot is obtained.

In the simplest case the gas mass flow can be calculated from the pressure rise rate. The gas mass flow is required for proper vent sizing and design of blowdown drums and can be used to calculate propagation scenarios. Certain instruments (e. g. VSP, PHI-TEC) allow the filling status of the experimental system to be matched exactly to the in-plant status. These systems offer the benefit to use the resultant pressure rise rates for calculation and design the pressure relief systems.

The adiabatic induction time is the time period, under adiabatic conditions, between the time corresponding to the initial temperature and the time, at which the maximum reaction rate is detected. In practice, this point of maximum reaction rate is often equated with the maximum rate of temperature rise. A specific adiabatic induction time can thus be stated for each initial temperature. The adiabatic induction time can be directly derived from the experiment. Because decomposition reactions are complex, values such as ADT24 (temperature at which the adiabatic induction time to decomposition is exactly 24 hours) should ideally not be extrapolated, but measured.

11.4 Heat accumulation storage test (UN Test H.1)

Reason for determining the parameter

The classification of thermally sensitive substances according to UN transport regulations requires special heat accumulation experiments to be conducted, some of which take into account the size of the container.

Tests H.1 (SADT test for packages), H.2 (adiabatic storage test for packages, IBCs and tanks) and H.4 (heat accumulation storage test for packages, IBCs and small tanks) are recommended tests for self-reactive substances and organic peroxides. Test H.3 (isothermal storage test) is not a standard test.

The SADT (Self Accelerating Decomposition Temperature) is the lowest temperature at which a substance will rise 6 K above the oven temperature. If the sample temperature does not exceed the oven temperature by 6 K in any test, the SADT is rated as being greater than the highest oven temperature used.

Determination procedure

In the SADT test (Test H.1) the substance is placed in its packaging in a temperature-controlled room and the air surrounding the package under test is maintained at a constant temperature for a period of at least ten days.

This method determines the minimum constant temperature of the ambient air at which auto-accelerative decomposition occurs for a substance in a specific package. An indication of the explosion hazard from the decomposition reaction can also be obtained.

The test must be carried out in an area that offers adequate protection against fire, explosion hazards and toxic gases. Maintenance of a distance from public roads and buildings in which persons permanently work or reside is recommended. It may be necessary to maintain greater distances if toxic gases are released during substance decomposition.

Evaluation of results

The following control and emergency temperatures are obtained through Test H.1:

Table 29: Control and emergency temperatures according to SADT

Type of container	SADT	Control temperature	Emergency temperature
Single packs and IBCs	≤ 20 °C	20 °C below SADT	10 °C below SADT
	20 °C < SADT $\leq$ 35 °C	15 °C below SADT	10 °C below SADT

	> 30 °C	10 °C below SADT	5 °C below SADT
Nonstationary tanks	< 50 °C	10 °C below SADT	5 °C below SADT

Bibliography

Laws, ordinances, and legal text of the Accident Prevention Regulations are **binding legal norms.** Deviations require permission of the competent authority or the competent Accident Insurance Institution respectively (e. g. German Social Accident Insurance Institution). Issuing a special dispensation requires compensation measures at the same safety level at least.

Technical rules affiliated to ordinances, execution instructions of Accident Prevention Regulations (DGUV Regulations), DGUV Rules, DGUV Informations, Codes of Practice, and DIN-/VDE-Standards are **not binding legal norms.** These are regarded as important standards of evaluation and rules of technology that do not need to comply with if the same safety level can be obtained otherwise.

Sources of information in the Internet
Codes of Practice of the German Social Accident Insurance Institution for the Raw Materials and Chemical Industry (Berufsgenossenschaft Rohstoffe und chemische Industrie – BG RCI) as well as a broad part of the occupational safety and health regulations issued by the German government and the German Social Accident Insurance Institutions (ca. 2,200 files – nearly all in German) can be found in the Compendium for Occupational Safety and Health of BG RCI (“Kompendium Arbeitsschutz“). The use is not free of charge. A free limited trial is available. For further information see www.kompendium-as.de.

The homepage of BG RCI (www.bgrci.de) and fachwissen.bgrci.de offer a huge amount of relevant information.

Detailed information about publications and media of BG RCI and mail order: medienshop.bgrci.de

The download-center of BG RCI offers selected Codes of Practice, appendices and forms from Codes of Practice and DGUV Rules as well as additional guidance documents: downloadcenter.bgrci.de

Accident Prevention Regulations (Unfallverhütungsvorschriften), DGUV Rules (DGUV Regeln), DGUV Principles (DGUV Grundsätze) and many DGUV Informational Publications (DGUV Informationen) are available at the homepage of the German Social Accident Insurance (Deutsche Gesetzliche Unfallversicherung): publikationen.dguv.de

Since 01.05.2014 the rules and regulations of the German Social Accident Insurance Institutions have a new classification including a new numbering.

1. EU publications in the Official Journal of the European Union

Obtainable from: Bundesanzeiger-Verlag, Postfach 10 05 34, 50445 Köln
Free download at http://eur-lex.europa.eu/de/index.htm

(1) Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006 (CLP Regulation)

(2) Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC (REACH Regulation)

(3) Commission Regulation (EC) No 440/2008 of 30 May 2008 laying down test methods pursuant to Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)

(4) Directive 2014/34/EU of the European Parliament and of the Council of 26 February 2014 on the harmonisation of the laws of the Member States relating to equipment and protective systems intended for use in potentially explosive atmospheres (recast) (ATEX directive; for equipment and protective systems placed on the market from 20 April 2016)

(5) Directive 94/9/EC of the European Parliament and of the Council of 23 March 1994 on the approximation of the laws of the Member States concerning pressure equipment and protective systems intended for use in potentially explosive atmospheres (ATEX directive; for equipment and protective systems placed on the market until 19 April 2016)

2. Laws, Regulations, Technical Rules

Obtainable from: Bookshops
Free download at www.gesetze-im-internet.de (Laws and Regulations) or www.baua.de (Technical Rules); TRAS (Technical Rules on Installation Safety) are located at www.kas-bmu.de.

(6) Gesetz über die Durchführung von Maßnahmen des Arbeitsschutzes zur Verbesserung der Sicherheit und des Gesundheitsschutzes der Beschäftigten bei der Arbeit (Arbeitsschutzgesetz – ArbSchG)

(7) Verordnung über Sicherheit und Gesundheitsschutz bei der Verwendung von Arbeitsmitteln (Betriebssicherheitsverordnung – BetrSichV) mit Technischen Regeln für Betriebssicherheit (TRBS), particularly:

(8) TRBS 2152 Part 3: Gefährliche explosionsfähige Atmosphäre – Vermeidung der Entzündung gefährlicher explosionsfähiger Atmosphäre

(9) Verordnung zum Schutz vor Gefahrstoffen (Gefahrstoffverordnung – GefStoffV) mit Technischen Regeln für Gefahrstoffe (TRGS), particularly:

(10) TRGS 407: Tätigkeiten mit Gasen – Gefährdungsbeurteilung

(11) TRGS 509: Lagern von flüssigen und festen Gefahrstoffen in ortsfesten Behältern sowie Füll- und Entleerstellen für ortsbewegliche Behälter

(12) TRGS 510: Lagerung von Gefahrstoffen in ortsbeweglichen Behältern

(13) TRGS 721: Gefährliche explosionsfähige Atmosphäre – Beurteilung der Explosionsgefährdung (identical in its content: TRBS 2152 Part 1)

(14) TRGS 727: Vermeidung von Zündgefahren infolge elektrostatischer Aufladungen

(15) BekGS 408: Anwendung der GefStoffV und TRGS mit dem Inkrafttreten der CLP-Verordnung (Bekanntmachung zu Gefahrstoffen)

(16) Gesetz über die Beförderung gefährlicher Güter (Gefahrgutbeförderungsgesetz – GGBefG)

(17) Verordnung über die innerstaatliche und grenzüberschreitende Beförderung gefährlicher Güter auf der Straße, mit Eisenbahnen und auf Binnengewässern (Gefahrgutverordnung Straße, Eisenbahn und Binnenschifffahrt – GGVSEB)

(18) Verordnung über die Beförderung gefährlicher Güter mit Seeschiffen (Gefahrgutverordnung See – GGVSee)

(19) Gesetz über explosionsgefährliche Stoffe (Sprengstoffgesetz – SprengG) with Verordnungen zum Sprengstoffgesetz (SprengV) and Sprengstofflager-Richtlinien (SprengLR)

(20) Technische Regeln Anlagensicherheit (TRAS), particularly:

(21) TRAS 410: Erkennen und Beherrschen exothermer chemischer Reaktionen

3. Accident Prevention Regulations (DGUV Regulations), DGUV Rules, DGUV Principles, DGUV Informative Publications, and Codes of Practice of BG RCI

Obtainable from: Berufsgenossenschaft Rohstoffe und chemische Industrie, Postfach 10 14 80, 69004 Heidelberg, medienshop.bgrci.de or Jedermann-Verlag GmbH, Postfach 10 31 40, 69021 Heidelberg, www.jedermann.de, verkauf@jedermann.de
Member companies of BG RCI may obtain the papers listed free of charge (until the next source is cited), as long as the quantity is appropriate to the size of company.

(22) DGUV Vorschrift 13: Organische Peroxide (former BGV B 4)

(23) DGUV Regel 113-016: Sprengarbeiten (former BGR/GUV-R 241)

Obtainable from: Carl Heymanns Verlag, Luxemburger Straße 449, 50939 Köln, www.arbeitssicherheit.de
Free download of the contents at www.exinfo.de

(24) DGUV Regel 113-001: Explosionsschutz-Regeln (EX-RL) – Sammlung technischer Regeln für das Vermeiden der Gefahren durch explosionsfähige Atmosphäre mit Beispielsammlung zur Einteilung explosionsgefährdeter Bereiche in Zonen (former BGR 104)

Obtainable from: Berufsgenossenschaft Rohstoffe und chemische Industrie, Postfach 10 14 80, 69004 Heidelberg, medienshop.bgrci.de or Jedermann-Verlag GmbH, Postfach 10 31 40, 69021 Heidelberg, www.jedermann.de, verkauf@jedermann.de
Member companies of BG RCI may obtain the papers listed free of charge (until the next source is cited), as long as the quantity is appropriate to the size of company.

(25) Merkblatt M 001: Organische Peroxide (DGUV Information 213-069, previously BGI 752)

(26) Merkblatt M 001-1: Organische Peroxide – Arbeitsschutzinformationen für Beschäftigte

(27) Merkblatt M 053: Arbeitsschutzmaßnahmen bei Tätigkeiten mit Gefahrstoffen (DGUV Information 213-080, former BGI 660)

(28) Merkblatt M 058: Organische Peroxide – Antworten auf häufig gestellte Fragen (DGUV Information 213-096, former BGI 8619)

(29) Merkblatt M 060: Gefahrstoffe mit GHS-Kennzeichnung – Was ist zu tun? (DGUV Information 213-082, former BGI 5150)

(30) Merkblatt M 060-2: GHS – Chemikalien weltweit einheitlich kennzeichnen (former BGI 5150-2)

(31) Merkblatt R 001: Exotherme chemische Reaktionen – Grundlagen (DGUV Information 213-063)

(32) Merkblatt R 002: Maßnahmen der Prozesssicherheit in verfahrenstechnischen Anlagen (DGUV Information 213-064)

(33) Merkblatt R 004: Thermische Sicherheit chemischer Prozesse (DGUV Information 213-065)

(34) Merkblatt R 005: Übertragung chemischer Synthesen vom Labor bis in den Betrieb (DGUV Information 213-068, former BGI 5002)

(35) Merkblatt R 007: Lehren aus Ereignissen – Sicherheitstechnische Erkenntnisse für die Bewertung chemischer Reaktionen und thermisch sensibler Stoffe (former BGI/ GUV-I 5153)

(36) Merkblatt R 008: Polyreaktionen und polymerisationsfähige Systeme (DGUV Information 213-097)

(37) Merkblatt T 033: Vermeidung von Zündgefahren infolge elektrostatischer Aufladungen (DGUV Information 213-060; TRGS 727)

(38) Merkblatt T 049: Explosionsschutz – Antworten auf häufig gestellte Fragen

4. DIN/EN Standards/VDE Regulations

Obtainable from: Beuth Verlag GmbH, Burggrafenstraße 6, 10787 Berlin, www.beuth.de and
VDE Verlag GmbH, Bismarckstraße 33, 10625 Berlin, www.vde-verlag.de

(39) DIN 51412-1: Testing of petroleum products – Determination of the electrical conductivity – Part 1: Laboratory method (June 2005)

(40) DIN EN 1839: Determination of the explosion limits for gases and vapours (December 2012)

(41) prEN 1839: Determination of the explosion limits and the limiting oxygen concentration (LOC) for flammable gases and vapours (June 2014)

(42) DIN EN 13821: Potentially explosive atmospheres – Explosion prevention and protection – Determination of minimum ignition energy of dust/air mixtures (March 2003)

(43) DIN EN 1149-1: Protective clothing – Electrostatic properties – Part 1: Test method for measurement of surface resistivity (September 2006)

(44) DIN EN 1149-2: Protective clothing – Electrostatic properties – Part 2: Test method for measurement of the electrical resistance through a material (vertical resistance) (November 1997)

(45) DIN EN 14034-3: Determination of explosion characteristics of dust clouds – Part 3: Determination of the lower explosion limit LEL of dust clouds (April 2011)

(46) DIN EN 14034-4: Determination of explosion characteristics of dust clouds – Part 4: Determination of the limiting oxygen concentration LOC of dust clouds (April 2011)

(47) DIN EN 14522: Determination of the auto ignition temperature of gases and vapours (December 2005)

(48) DIN EN 15188: Determination of the spontaneous ignition behaviour of dust accumulations (November 2007)

(49) DIN EN 15967: Determination of maximum explosion pressure and the maximum rate of pressure rise of gases and vapours (October 2011)

(50) DIN EN 27888: Water quality; determination of electrical conductivity (ISO 7888) (November 1993)

(51) DIN EN 50281-2-1/ VDE 0170/0171-15-2-1: Electrical apparatus for use in the presence of combustible dust – Part 2-1: Test methods; methods for determining the minimum ignition temperatures of dust (November 1999)

(52) DIN EN 60079-20-1/ VDE 0170-20-1: Explosive atmospheres – Part 20-1: Material characteristics for gas and vapour classification – Test methods and data (IEC 60079-20-1) (September 2010)

(53) DIN EN 61340-2-3/ VDE 0300-2-3: Electrostatics – Part 2-3 Methods of test for determining the resistance and resistivity of solid planar materials used to avoid electrostatic charge accumulation (IEC 61340-2-3) (December 2000)

(54) DIN EN ISO 2592: Petroleum products – Determination of flash and fire points – Cleveland open cup method (ISO 2592) (September 2002)

(55) DIN EN ISO 2719: Determination of flash point – Pensky-Martens closed cup method (ISO 2719) (September 2003)

(56) DIN EN ISO 3679: Determination of flash no-flash and flash point – Rapid equilibrium closed cup method (ISO 3679) (June 2015)

(57) DIN EN ISO 13736: Determination of flash point – Abel closed-cup method (ISO 13736) (August 2013)

(58) prEN ISO 80079-20-2: Explosive atmospheres – Part 20-2: Material characteristics – Combustible dusts test methods (ISO/DIS 80079-20-2) (October 2014)

(59) DIN IEC 60093/ VDE 0303-30: Methods of test for insulating materials; Volume resistivity and surface resistivity of solid electrical insulating materials (IEC 60093) (December 1993)

5. VDI Guidelines

Obtainable from: Beuth Verlag GmbH, Burggrafenstraße 6, 10787 Berlin, www.beuth.de

(60) VDI 2263-1: Staubbrände und Staubexplosionen; Gefahren, Beurteilung, Schutzmaßnahmen; Untersuchungsmethoden zur Ermittlung von sicherheitstechnischen Kenngrößen von Stäuben (Dust fires and dust explosions; hazards, assessment, protective measures; methods for investigating safety-related parameters of dusts) (May 1990)

(61) VDI 2263-2: Staubbrände und Staubexplosionen; Gefahren, Beurteilung, Schutzmaßnahmen; Inertisierung (Dust fires and dust explosions; hazards, assessment, protective measures; inertisation) (May 1992)

6. Other Publications

Obtainable from: ASTM International, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania, USA, www.astm.org

(62) Active Standard ASTM E681 – 09(2015): Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)

(63) Active Standard ASTM E918 – 83(2011): Standard Practice for Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure

Obtainable from: Bookshops

(64) Barton, J. and Rogers, R.: Chemical Reaction Hazards – A Guide to Safety. Publisher: Institution of Chemical Engineers (IChemE). 2nd Edition 1997. ISBN: 0-85295-341-0

(65) Brandes, E. and Möller, W.: Sicherheitstechnische Kenngrößen. Volume 1: Brennbare Flüssigkeiten und Gase. 2nd Edition 2008. Wirtschaftsverlag NW – Verlag für neue Wissenschaft GmbH, Bremerhaven. ISBN: 978-3-86509-811-5

(66) Center for Chemical Process Safety (CCPS) of the AIChE: Guidelines for Chemical Reactivity Evaluation and Application to Process Design. 1995. ISBN: 978-0-8169-0479-2

(67) Dyrba, B.: Kompendium Explosionsschutz – Sammlung der relevanten Vorschriften zum Explosionsschutz mit Fragen und Antworten für die Praxis. 2014. Carl Heymanns Verlag GmbH, Köln. ISBN: 978-3-452-25836-6

(68) Grewer, T., Roger, R.: Thermal Hazards of Chemical Reactions. Industrial Safety Series Vol. 4. 2nd edition, 2010. Elsevier Science, Amsterdam. ISBN: 9780444522269

(69) Hemminger, W. F. and Cammenga, H. K.: Methoden der Thermischen Analyse. 1989. Springer-Verlag GmbH, Berlin. ISBN: 978-3-642-70176-4

(70) Höhne, G. W. H., Hemminger, W. F., Flammersheim, H.-J.: Differential Scanning Calorimetry. 2nd Edition 2003. Springer-Verlag GmbH, Berlin. ISBN: 978-3-642-05593-5

(71) Kreysa, G., Langer, O. U. and Pilz, V.: Chemische Reaktionen – Erkennung und Beherrschung sicherheitstechnisch relevanter Zustände und Abläufe. Band 4 – Praxis der Sicherheitstechnik. 1997. Publisher: DECHEMA e.V.. ISBN: 9783926959898

(72) Molnárné, M., Schendler, Th. and Schröder, V.: Sicherheitstechnische Kenngrößen. Volume 2: Explosionsbereiche von Gasgemischen. 2nd Edition 2008. Wirtschaftsverlag NW – Verlag für neue Wissenschaft GmbH, Bremerhaven. ISBN: 978-3-86509-856-6

(73) Pilz, V. et al.: Plant and Process Safety. In: Ullmann´s Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. ISBN: 978-3527306732. Available online at: http://onlinelibrary.wiley.com/doi/10.1002/14356007.b08_311/pdf

(74) Sarge, S. M., Höhne G. W. H. and Hemminger, W.: Calorimetry: Fundamentals, Instrumentation and Applications. 2014. Wiley-VCH Verlag GmbH, Weinheim. ISBN: 978-3- 527-32761-4

(75) Schacke, H.: Fire and Explosion, Fact Finding and Basic Data, Proceedings of the First IUPAC Workshop on Safety in Chemical Production, Basel, 1990, International Union of Pure and Applied Chemistry, Blackwell Scientific Publications, University Press, Cambridge, 1991

(76) Steen, H.: Handbuch des Explosionsschutzes. 2000. Wiley-VCH Verlag GmbH, Weinheim. ISBN: 978-3527298488

(77) Steinbach, J.: Chemische Sicherheitstechnik. 1995. VCH Verlagsgesellschaft mbH, Weinheim. ISBN: 3-527-28710-8

(78) Stoessel, F.: Thermal Safety of Chemical Processes – Risk Assessment and Process Design. 2008. Wiley-VCH Verlag GmbH, Weinheim. ISBN: 978-3-527-31712-7

(79) UN Manual of Tests and Criteria: Recommendations on the Transport of Dangerous Goods – Manual of Tests and Criteria. Rev. 6, 2015. United Nations, New York and Geneva. Available online at www.unece.org/trans/areas-of-work/dangerous-goods/legal-instruments-and-recommendations/un-manual-of-tests-and-criteria/rev6-files.html The German translation „Empfehlungen für die Beförderung gefährlicher Güter – Handbuch über Prüfungen und Kriterien“ (5. revised edition, 2009. New York and Geneva. (version revised and corrected through Amendment 1 and 2 and the 2012 corrigendum, 2015)) of the Bundesanstalt für Materialforschung und -prüfung is available for download free of charge at www.bam.de/_SharedDocs/DE/Downloads/befoerderung-gefaehrlicher-gueter.html

(80) Yoshida, T., Wada, Y. and Foster, N.: Safety of Reactive Chemicals and Pyrotechnics. Industrial Safety Series Vol. 5. 1995. Elsevier Science, Amsterdam. ISBN: 978-0-444- 88656-9

Obtainable from: European Chemicals Agency, P.O. Box 400, 00121 Helsinki/Finland,
http://echa.europa.eu/de/
Free download at http://echa.europa.eu/de/guidance-documents/guidance-on-clp

(81) Guideline on labelling and packaging in accordance with Regulation (EC) Nr. 1272/2008

7. Databases and information on the Internet

(82) GESTIS database on substances of DGUV at www.dguv.de/ifa/stoffdatenbank providing information on safe handling with hazardous substances and other chemical substances at work. The database informs on important physico-chemical data as well as specific rules regarding individual substance, particularly for

classification and labelling according to GHS in compliance with the CLP Regulation. Information about 9,400 substances is available.

(83) GESTIS-STAUB-EX database at www.dguv.de/ifa/gestis-staub-ex as a project supported by the Commission of the European Union. The database contains important combustion and explosion characteristics of more than 6000 dust samples from almost any branch and serves as a base for safe handling of combustible dusts and for the planning of preventive and protective measures against dust explosions in dust-generating and processing plants. The database was elaborated in co-operation with the Federal Institute for Materials Research and Testing (BAM), the German Social Accident Insurance Institution for the Foodstuffs and Catering Industry (BGN), the Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA), the DMT-Gesellschaft für Forschung und Prüfung mbH (association for research and testing), the Expert Body for Surface Fire and Explosion Protection – Mining Test Facility (BVS) – and Henkel KGaA, Düsseldorf, Germany.

(84) Gefahrstoffinformationssystem Chemikalien GisChem at www.gischem.de of the German Social Accident Insurance Institution for the Raw Materials and Chemical Industry (BG RCI) and German Social Accident Insurance Institution for the Woodworking and Metalworking Industries (BGHM) including different modules, e. g. “GisChem-Interaktiv“ to create individual operating instructions, “Gefahrstoffverzeichnis“ (“register of hazardous substances“) or “Gemischrechner“ (“mixture calculator“) for the classification of mixtures according to CLP Regulation. GisChem provides support to small and medium-sized enterprises for safe handling with and management of hazardeous substances.

(85) CHEMSAFE database with assessed safety parameters of flammable gases, liquids and dusts for fire and explosion prevention. The database presently contains data for more than 3000 pure substances and mixtures. This database is a collaborative project of the Gesellschaft für Chemische Technik und Biotechnologie e. V. (DECHEMA e. V.), the Physikalisch-Technischen Bundesanstalt (PTB) and the German Federal Institute for Materials Research and Testing (BAM). Internet access to the database is possible via websites of the DECHEMA e. V. at www.dechema.de/Datenbanken.

(86) Explosionsschutzportal of the German Social Accident Insurance Institution for the Raw Materials and Chemical Industry (BG RCI) at www.exinfo.de with detailed information concerning explosion prevention and protection, such as expert know-how, FAQs, latest developments, accident evaluations, links to databases of combustion and explosion characteristics, important BG RCI information sheets on explosion prevention and protection, events, video download. Subscription to the Exinfo Newsletter is also available.

Picture credits
The pictures used in this paper are intended for illustration only. A product recommendation is expressly not intended by BG RCI.

Figures and illustrations were kindly provided by:

Cover picture and Figures 1, 9, 20, 25, 34:
Bayer AG
51368 Leverkusen:
www.bayer.com

Figures 2:
Physikalisch-Technische Bundesanstalt (PTB)
Bundesallee 100
38116 Braunschweig
www.ptb.de

Figures 3, 6, 16, 26, 27:
Bundesanstalt für Materialforschung und -prüfung (BAM)
Unter den Eichen 87
12205 Berlin
www.bam.de

Figures 4, 7, 8, 10, 13, 15, 21, 23, 24, 28, 32, 33, 36, 38, 44, 46:
BASF SE
Carl-Bosch-Str. 38
67056 Ludwigshafen
www.basf.com

Figures 5, 39, 40, 41 und 45:
TÜV SÜD Schweiz AG
Mattenstraße 24
CH-4002 Basel
www.tuev-sued.ch

Figures 11, 12, 29, 30, 31, 47 und 48:
consilab
Gesellschaft für Anlagensicherheit mbH
Chempark Leverkusen/Gebäude Q18L
Kaiser-Wilhelm-Allee 1
51368 Leverkusen
www.consilab.de

Figures 14:
AQura GmbH
Rodenbacher Chaussee 4
63457 Hanau-Wolfgang
www.aqura.de

Figures 17, 18, 19, 22 und 37:
Jedermann-Verlag GmbH
Heidelberg

Figures 42 und 43:
Merck KGaA
Frankfurter Str. 250
64293 Darmstadt
www.merckgroup.com

“Exotherme Reactions“ working group

Edition 4/2016
This code of practice can be ordered online at medienshop.bgrci.de
Do you have questions, suggestions, or criticisms?
If so, please contact:
In writing:
Berufsgenossenschaft Rohstoffe und chemische Industrie,

Prävention, KC Präventionsprodukte und -marketing, Referat Medien
Postfach 10 14 80,
69004 Heidelberg
E-Mail: praeventionsprodukte@bgrci.de
Contact form in the Internet:
www.bgrci.de/kontakt-schriften