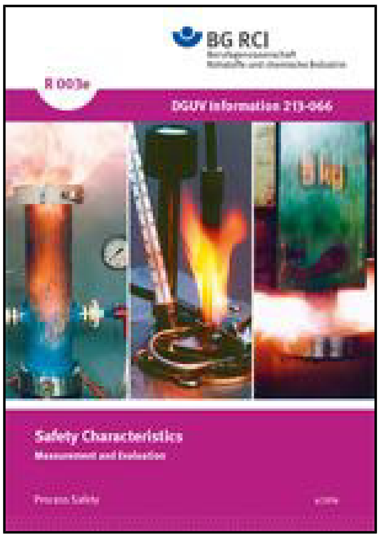
BG RCI
Berufsgenossenschaft
Rohstoffe und chemische Industrie

Process Safety

# Safety Characteristics

## Measurement and Evaluation

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# Inhaltsverzeichnis dieses Ausdrucks



 

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 | |
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| Mechanical sensitivity | Section 2.2 |
| Detonation properties | Section 2.3 |
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| Flammable gases and vapours | Section 3 |
| Safety concept: Avoidance of explosive atmospheres | |

 

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|---|---|
| Explosion limits | Section 3.1 |
| Limiting oxygen concentration | Section 3.1 |
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| Self-ignition behaviour | Section 7 |
| Thermal stability | Section 11 |
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|---|---|
| **Information concerning fire behaviour** | |
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| **Substances which, in contact with water or moist air, emit flammable gases** | **Section 6** |
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| UN Test N.5 | Section 6.1 |
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| Pyrophoric properties | Section 7.1 |
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| Minimum ignition temperature of a dust layer with a one- sided thermal load | Section 7.6 |
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| | |
|---|---|
| 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 | |
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| Thermal analysis | Section 11.1 |
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| 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.

<u>Classification</u>

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

 

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| 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** | | |

<u>Note</u>

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)

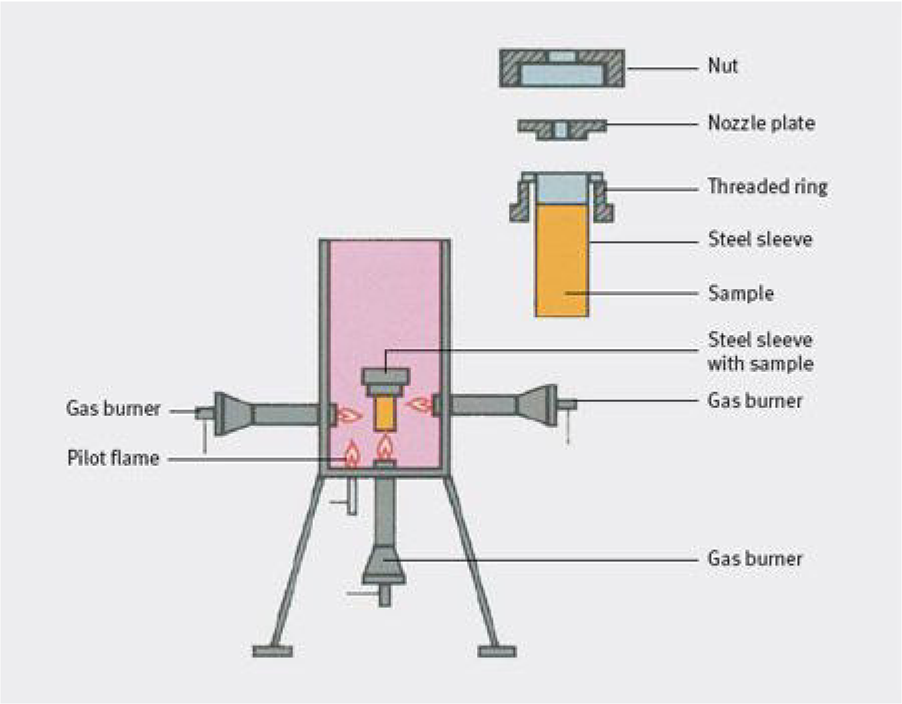
Determination procedure

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

<u>Evaluation of results</u>

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

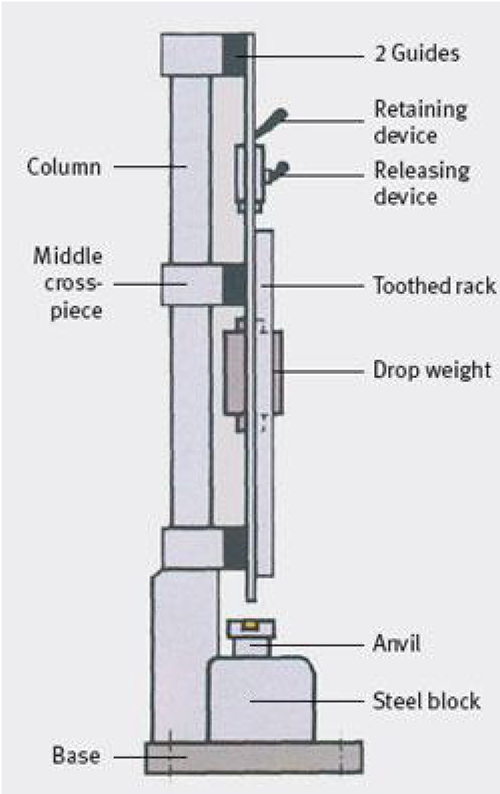
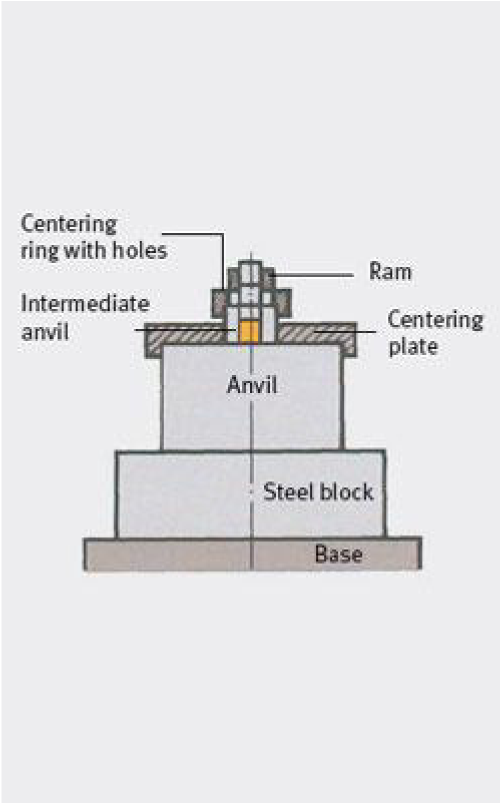


Figure 8: Anvil of the fallhammer apparatus




## 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).

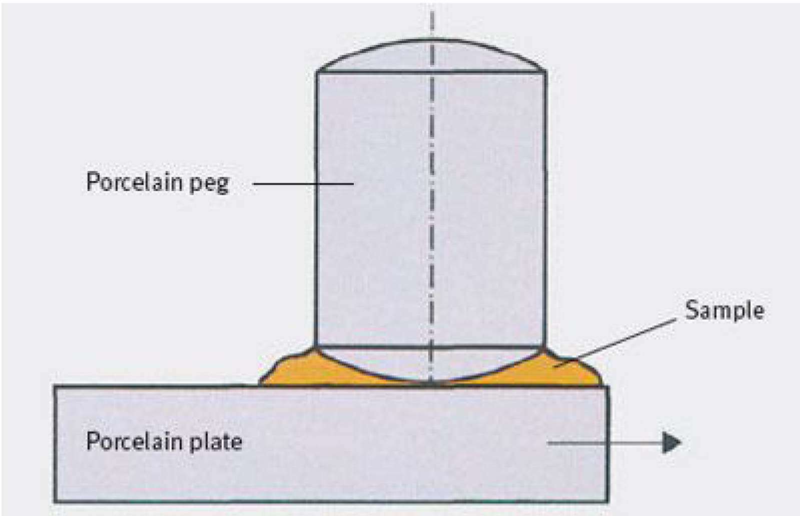
Figure 9: Fallhammer test


## 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.