How to perform safely explosivity, combustibility and thermal stability tests of nanoparticles and highly active substances

Pablo Lerena, Georg Suter
Swiss Institute for the Promotion of Safety and Security,
WRO-1055.5.27, CH-4002 Basel, Switzerland, pablo.lerena@swissi.ch

The standards for the determination of safety characteristics of powders have been defined more than 30 years ago. Today, they are well established and have proven their feasibility and practical applicability in industrial practice.
However with the appearance of an increasing number of powders with high physiological activities (e.g. from pharmaceutical production) and with the development of nano-powders with yet unknown health hazards, the traditional testing methods have to be modified to meet the increasing requirements of industrial hygiene, because these testing methods often involve open handling of the test items.
Within the EU project NANOSAFE the Swiss Safety Institute in Basel has developed a number of such new test procedures and has validated them against the existing standards.

1. Basic Principle

The following basic principle is applied to achieve a high degree of protection of lab technicians against exposure to potentially toxic powder.

Open handling of the powders is limited to the transfer of the powder from the shipping container (e.g. the powder flask) either to

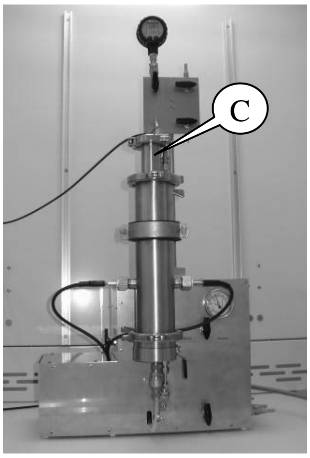
- the container, in which the test is carried out later or
- an intermediate container, from which the sample can be transferred into the test apparatus in an entirely closed way.

The remaining open handling is carried out in working stations equipped with laminar flow chambers. The personnel wear adapted personal protection equipment. A risk analysis was performed to assess if the measures are sufficient also in case of deviations form the normal operating conditions.
After the test, the residual material is either

- destroyed and washed out by a "cleaning in place" (CIP) installation
- disposed directly in the (closed) test container
- removed from the testing equipment inside the special room under laminar flow

For the implementation of this principle, it was necessary to redesign certain test methods and/or equipments.

2. Hartmann Tube



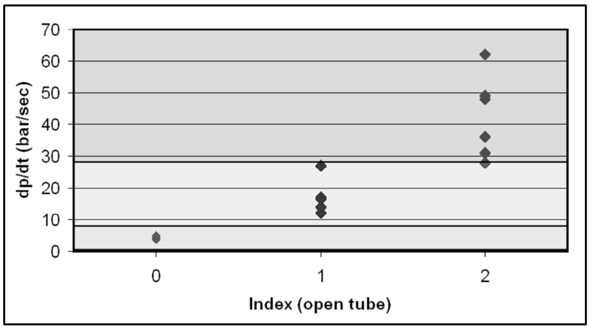
Closed Hartmann Tube, with capsule for powder transfer (C)

Traditionally a preliminary assessment of the dust explosion risk is made based on a screening Test in the modified Hartmann Tube [1]. The powder is filled into the tube (a vertical glass tube with a volume of 1.2L). A raised dust cloud is produced by pushing air through a nozzle in the bottom of the tube. At the same time, a permanent electric spark (10kV, 4mm spark gap, energy approx. 1-10J) is fired in the center of the tube. A dust explosion in the tube is detected by an electronic sensor coupled to the movable lid on top of the tube. Depending on the opening angle, the explosion is rated "1" or "2". In addition it is visually observed, if a dust fire (i.e. combustion without pressure build-up) occurs.

Obviously some sample material is ejected from the tube during this test and contamination of the surrounding lab installation can hardly be avoided.

Therefore a new closed tube made of steel was developed, similarly to the original Hartmann tube [2]. A weighted sample is transferred from the shipping flask into a small capsule under laminar flow. Then the capsule is closed and flanged tightly on the tube. The valve between the capsule and the tube is opened and the powder falls into the tube. Then a permanent spark is switched on between the electrodes, the tube is evacuated to and a dust cloud is produced by blowing air into the tube from a reservoir which was filled to d defined pressure before, such that - without explosion - the pressure inside the tube reached 1 bar.

In case of an explosion the pressure exceeds 1 bar depending on the explosion characteristics of the powder. The explosion overpressure is detected by a pressure sensor. The correlation between the traditional ratings "1" and "2" and the pressure increase rate observed in the closed tube is shown in the figure to the right.



Although the pressure curve can be exactly observed in this tube, it is not possible yet to determine Kst and Pmax values, as these are not identical to those obtained in the standard 20L sphere [2]. Instead of a permanent spark, a hot coil may be used as an ignition source.

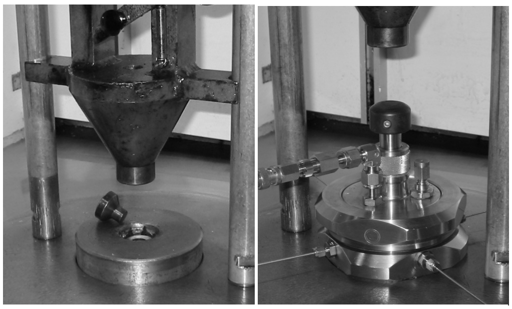
The tube is cleaned by first burning the residues in a propane explosion and then flushing the tube with water through a sphere nozzle.

3. Minimum Ignition Energy

MIKE-3 is a standard equipment for the determinations of the Minimum Ignition Energy [3]. Again the explosion is carried out in an open glass tube, similar the Hartmann tube. Instead of the permanent spark, a single spark with well defined energy is fired in this test, synchronized with the creation of the dust cloud.

The same test can also be carried out in the closed tube described above. However the lowest energy which can be reliably applied is 10mJ, because the electrodes in the closed tube are not movable.

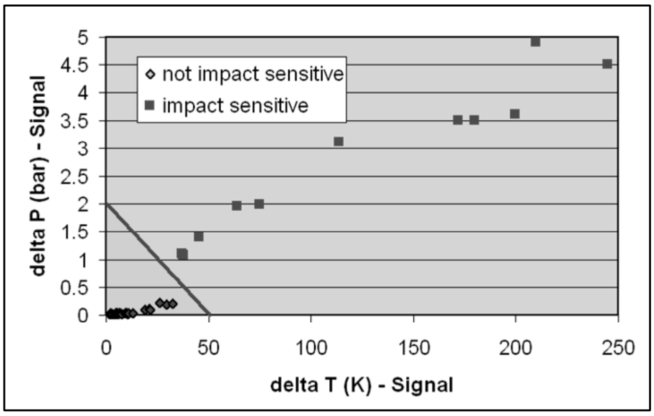
4. Impact Sensitivity



Left: Open falling hammer socket; Right: closed autocalve with thermocouples and pressure sensor

The impact sensitivity is determined with a falling hammer [1]. Samples of approx. 100mg are packed into small pieces of aluminum foil. The resulting "capsules" are exposed to the impact of a falling hammer. Ten essays, each with a fresh sample, are carried out. If in this series a detonation is detected, the tests are repeated without aluminum foil, because the foil acts as a sensitizer. A detonation is identified acoustically either by auditory perception or with a microphone, in which case a detonation is defined as a reaction causing a peak noise level 5db above the base value obtained with inert materials.

During this test some sample material is dispersed all around the impact point, which is critical for toxic or otherwise hazardous material. Based on an earlier design [4] a closed socket was developed for this test. The sample is placed inside this socket under laminar flow protection. Then the socket is tightly closed and put under the falling hammer. The test is carried out and the reaction of the sample is detected by a pressure sensor measuring the gas which eventually is produced upon impact. In addition four temperature sensors are used to indicate an exothermic reaction.

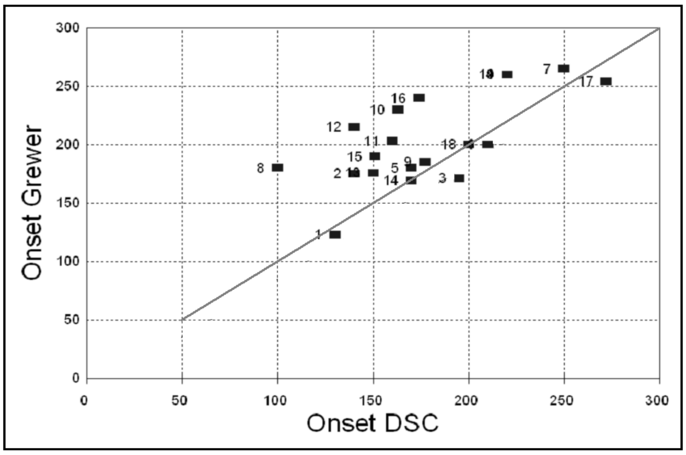


Sample results obtained from impact tests are shown in the figure above: an increase in temperature above 50 K and/or pressure above 2 bar indicates that the solid is impact sensitive.

After the test the socket is cleaned in a workbench inside a special cleaning room.

5. Tests for Self-Heating or Self Ignition

Left: Wire basket for traditional self-ignition tests (Grewer); rigth DSC crucible for the new method



Self-Ignition Temperatures of Powder Deposits are relevant for e.g:

- the determination of the maximum surface temperature permitted in Ex-Zones
- the definition of temperature limits in drying processes (fluidized beds, spray driers)
- the maximum storage temperature in bulk containers and
- the classification of solid for transport (division 4.2)

The standard testing procedures include isothermal tests in wire baskets, which include the open handling of significant amounts of sample material. A widely applied screening test for self-ignition has been developed by Grewer [5]. This test method involves only rather small baskets and is widely used. Correlations with tests in larger scales or with the smoldering test for dust deposits according to EN 50281 have been derived [6].
In order to avoid the potential for spreading dangerous powder in the laboratory, a test method for self-ignition based on a dynamic DSC run has been developed. A few Milligrams of the powder are filled under laminar flow into a DSC crucible, which then is closed under 5bar of pure oxygen. This high oxygen pressure ensures a sufficiently high sensitivity of the method for oxidation processes, and it has been shown that onset data can be correlated with the traditional dynamic test in the Grewer oven as shown in the figure above.

6. Powder Bulk resistivity

For the assessment of electrostatic hazards, it is necessary to determine the bulk resistivity of powders. According to DIN IEC 93 this is done by filling the powder into a cell consisting of a metallic base plate, a highly insulating PTFE ring wall and a movable metallic top electrode. The resistance between the top electrode and the base plate is measured and the resistivity is calculated by taking into consideration the geometrical factors (cross section and thickness of the powder).

In view of highly hazardous substances, the critical issue is again the open handling during filling and emptying the cell.

In the new approach, a one-way cell is used. As with the traditional cell, the powder has to be filled into the cell, consisting of a base plate tightly fixed to the PTFE ring wall. The electrode is then screwed into a thread in the PTFE, such that the powder is completely sealed between the base plate and the top electrode. After the measurement the entire cell is disposed. This eliminates the risks associated with emptying and cleaning the cell.

7. Conclusions

A series of modified test methods for the determination of safety characteristics of powders with health hazards have been developed. The methods are based on a reduction of open handling steps during sample preparation, testing and cleaning. It has been demonstrated that the data obtained by these methods are in good agreement with those obtained from conventional standard methods.

8. References

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