CHEMICAL ENGINEERING TRANSACTIONS
VOL. 77, 2019
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Genserik Reniers, Bruno Fabiano

ISBN 978-88-95608-74-7; **ISSN** 2283-9216
DOI: 10.3303/CET1977165

Quality Management in the Determination of Safety Characteristics

Christoph Cesana[a], Manfred Eiche[b], Mischa Schwaninger[b]

[a]Cesana AG, Bettingen, Switzerland
[b]TÜV SÜD Process Safety, Basle, Switzerland
mischa.schwaninger@tuev-sued.ch

Safety characteristics for a substance from different sources may differ significantly. Round robin tests have shown that in nearly all cases this is not due to negligence or carelessness by the laboratory staff. Rather, the fluctuations are due to the complex nature of the properties described by the safety characteristics and to unprecise testing standards.
The authors recommend initiating or intensifying initiatives to facilitate quality control in safety testing laboratories, like routine round robin test for many more methods and provision of suitable reference materials for tests, where such materials could help improve data quality.

1. Introduction

Safety characteristics are essential for process risk assessments and development of safety concepts. The outcome of the respective tests depends – sometimes very strongly – on the test method or even the testing equipment. Therefore, the determination of safety characteristics has been standardized (ISO/IEC 80079-20-2, VDI 2263-1, and many others) to obtain consistent data. In addition, requirements for testing laboratories have been defined in ISO/IEC 17025:2017 and in the GLP Principles (Directive 2004/9/EC, Directive 2004/10/EC).
However, despite these efforts, safety characteristics of given substances from different sources may still show significant variations. This is an entirely undesirable situation regarding the important role of these data for the safety in the process industry.

2. Causes

The following problems hinder compliance with the principles mentioned in ISO 17025 and GLP in the determination of safety data.

2.1 The nature of Safety Characteristics

In contrast to basic physical properties such as melting point or density or chemical analysis of mixtures safety data are complex combinations of basic substance properties. For example, the layer ignition temperature of powders depends on the decomposition/oxidation properties, the particle size, the humidity, the bulk density and many others. Standardization of tests is therefore not straightforward.
Safety tests are often attempts to “simulate” a situation in the plant rather than to determine fundamental substance properties. The Test for Spontaneous Decomposition is an example (VDI 2263-1).

2.2 Unprecise Testing Standards

As a result of historical developments, completely different tests are permitted for classification of materials (UNDG Classification). In other area, harmonisation has brought some progress towards unified testing standards. However, descriptions of test methods leave often room for variations, which may have an important effect on the test result.

Paper Received: 4 October 2018; Revised: 19 April 2019; Accepted: 15 July 2019

Please cite this article as: Cesana C., Eiche M., Schwaninger M., 2019, Quality Management in the Determination of Safety Characteristics, Chemical Engineering Transactions, 77, 985-990 DOI:10.3303/CET1977165

2.3 Subjective Assessment

Some test methods, like the combustibility test and the falling hammer test, are based on visual or acoustic observations of lab personnel. However, an objective documentation, which would require video or sound recording is usually not available.

2.4 Lack of Traceability

Traceability is not given in many cases. The GLP and ISO standards require that the calibration of sensors is traceable to national measurement standards. For testing equipment this would mean to ensure traceability at the level of components (e.g. for the MIE: capacitance of capacitors and voltage applied, inductance of the circuit, time delay, etc.), an effort, which goes far beyond current practice.

2.5 Reproducibility is not determined

Reproducibility is not checked: Many testing methods are so complex and expensive, or they require such large amounts of sample material, that tests are not repeated. Therefore, reproducibility, e.g. expressed as standard deviation, is largely unknown.

3. How to improve the situation?

It is evident that all acknowledged principles defined in ISO 17025 have to be applied to achieve correct and reproducible results:

- employment of qualified personnel
- training of lab personnel
- validation of test methods
- regular checks and maintenance of equipment
- internal and external audits to control adherence to these principles

Due to the nature of Safety Data some elements are of particular importance and deserve a special attention:

3.1 Round Robin Tests

CaRo Test

The comparison of data measured in different laboratories is an acknowledged method to improve data quality. The most traditional round robin test for determination of the Minimum Ignition Energy and the Explosion Characteristics of Powders is the “CaRo” Test. Since 1993 these world-wide round robin tests are carried out on a now annual basis. The CaRo test helps the participating laboratories to confirm the correct functioning of their equipment and the validity of their procedures, or, to identify deficiencies. In addition, it gives an idea of the inherent variation of the results and prevents their over-interpretation.

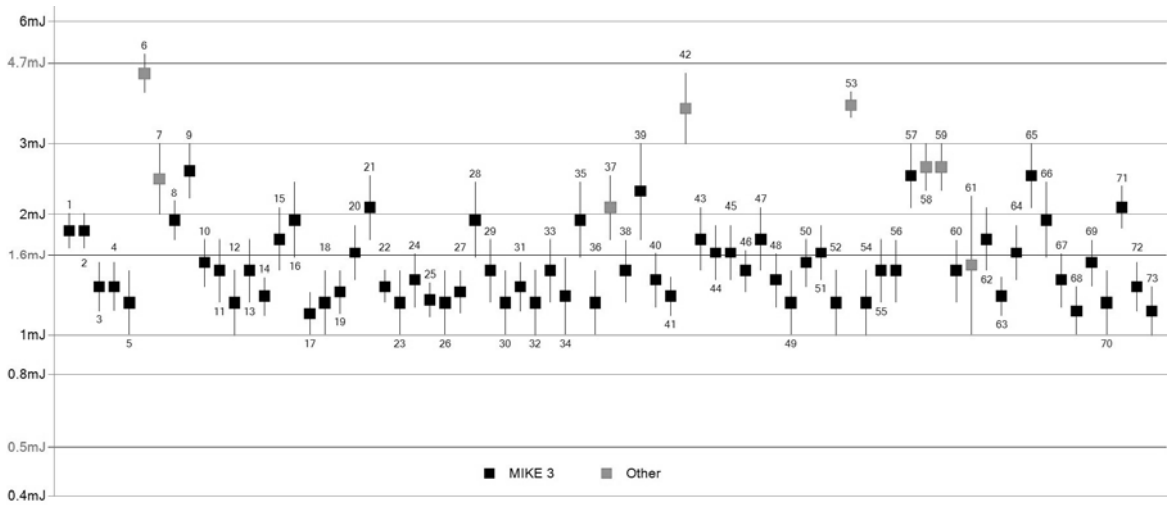

Figure 1: Results of the CaRo17 for Minimum Ignition Energy

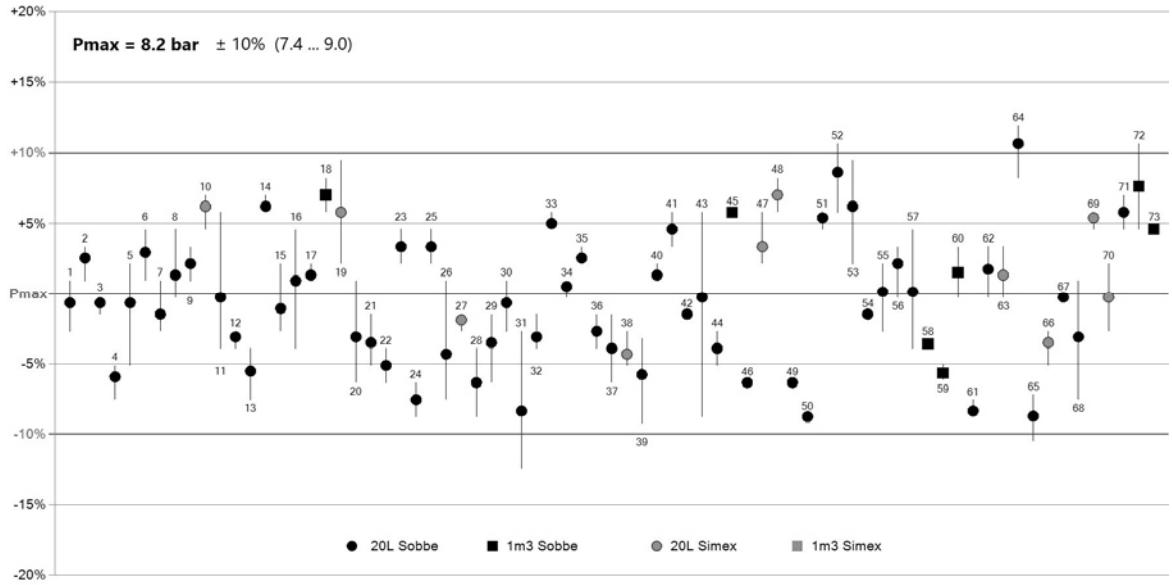

Figure 2: Results of the CaRo17 for Pmax, measured with 20 L sphere and 1 m3 vessel.

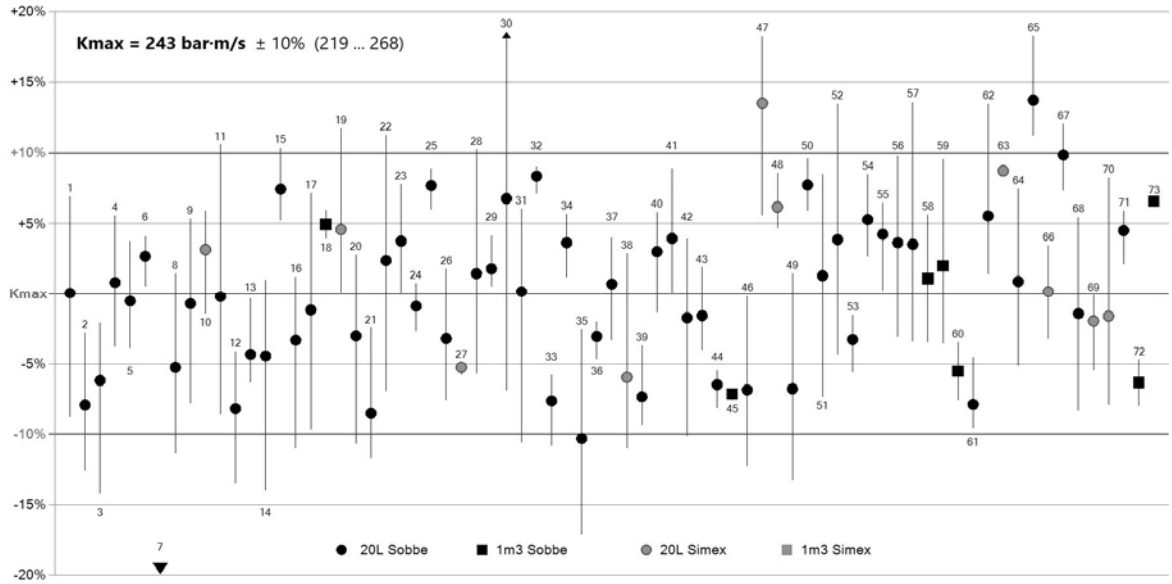

Figure 3: Results of the CaRo17 for Kmax, measured with 20 L sphere and 1 m3 vessel.

While the CaRo Test is initiated by the supplier of the testing equipment, some other round robin tests are organized by working groups.

Other Round Robins Tests

Special emphasis should be put on the interlaboratory comparison programme organized by the BAM centre for quality assurance for testing of dangerous goods and hazardous substances (CEQAT-DGHS). The thoroughly assessed data submitted by the laboratories has led to major improvements of several test methods. A recent example is the determination of the spontaneous ignition behaviour of dust accumulations according to DIN EN 15188. Whereas in a first round robin test in 2002, extrapolated self-ignition temperatures for 1000 m^3 of Lycopodium varied between -13 °C and 45 °C, a range of 58 °C, the latest follow-up test in 2015/16 with improved test conditions showed a measurement uncertainty not higher than 10 °C for the same extrapolated self-ignition temperatures of 1000 m³ for 4 different samples (Frost et al., 2016).

3.2 Standard Reference Materials

As a consequence of the nature of Safety Data (2.1) “calibration” cannot be done on the basis of sensor calibration. Rather an agreed outcome for a given reference material is often used as the basis for calibration. This approach is well known from other areas of laboratory testing (e.g. melting point determination, calibration of the Kofler Bench for melting point determination or calibration of DSC using the heat of melting of indium.
Unfortunately, the reference materials for safety testing are often themselves subject of relevant variations. E.g. the cellulose used for testing oxidizing solids, which may vary in particle shape and size and consequently in bulk density. The required unique material characteristics are sometimes only met if the material stems from the same supplier or even from the same batch, e.g. in case of thermal stability testing. Thus, successful testing can become dependent on material availability. Other material characteristics, such as moisture content, require standardized sample conditioning, which must be clearly specified in the test procedures.
Regarding reference materials the aspect of lab personnel training is also very important. Such materials can be crucial to improve the manual skills to perform e.g. fall hammer or friction sensitivity tests.
Though a clear demand for dedicated reference materials which can be used for laboratory internal quality control is identified. Such materials should be manufactured and distributed centrally. The authors see the demand among others for the following tests:

Table 1: List of tests for which a demand for standard reference materials is seen

Test	Guideline/ Norm	Reference material example
Self-ignition temperature	DIN EN 15188	Coal, Lycopodium
Self-heating substances	UN Test N.4	Coal, Lycopodium
Thermal stability (possible end points: Q'_r, ΔT_{ad}, q'_r @ T_{def}, V'_r)		Sodium chloroacetate, Di-tert-butyl peroxide in Toluene, Dicumylperoxide in Ethylbenzene, AIBN (2,2′-Azobis(2-methylpropionitrile))
Readily combustible solids	UN Test N.1	
Substances which in contact with water emit flammable gases	UN Test N.5	Powder of mixed metals
Ignition temperature of plastics	ISO 871, ASTM D1929	High-density polyethylene, Polycarbonate
Corrosive properties of liquids and solids	UN Test C.1	Hydrochloric acid (diluted), NaOH solution

In the above table Q'_r is the specific heat of reaction or decomposition, ΔT_{ad} the adiabatic temperature increase, q'_r @ $T_{def.}$ the specific heat release at a pre-defined temperature, V'_r the released specific gas volume

3.3 Testing Standards

Testing Standards often leave too much room for variation in the testing procedure or the design of the test set-up. In some cases this is due to incomplete understanding of relevant influence factors of the test outcome. The UN test N.5 for substances which, in contact with water, emit flammable gases, may serve as an example for this. Depending on the gas metering systems which were used in a round robin test organized by BAM in 2005, significant differences were observed on the determined gas flow rates. This resulted in a relatively high probability of incorrect classification (Kunath et al., 2009).
A round robin test for spontaneous ignition behaviour of dust accumulations according DIN EN 15188 from 2010/ 11 (Kunath et al., 2013) has shown that a more specified test setup could significantly improve the precision of the test. A mesh wire screen had to be placed in the oven to better control the air flows and thus the temperature homogeneity in the hot storage oven. In addition a defined wire basket volume ratio of 1 : 1.7 : 5 : 8 had to be used, which led to a better defined regression line in the Pseudo-Arrhenius plot of the self-ignition temperatures. Prior to these modifications several other recommendations from former round robin tests were implemented, e.g. on the oven size, the oven ventilation (enforced vs. natural convection), the type of wire baskets, the minimum sample size, as well as the measuring precision (temperature difference between tests with ignition and without ignition). The sum of these additional specifications has finally led to the previously discussed round robin test results with an uncertainty of the extrapolated self-ignition temperature for volumes of 1000 m³ of not more than 10 °C (Frost et al., 2016).
On the other hand, one should also notice that very precise test descriptions bear some risks. One of them is the risk to hinder innovation, in particular the transformation of “manual” to automated procedures. This may

be one of the reasons for the persistence of test methods with “subjective assessment” like falling hammer test, friction test and others.
The compromise may to have strict descriptions for existing methods on one hand but to be more open for innovative methods, and to provide faster pathways for innovated test methods to become new standards.
Another risk is the hindered representation of natural sample variability. As indicated in the graph below, the self-ignition temperature of a natural food ingredient could very well be extrapolated according to DIN EN 15188, based on the measurements with sample material from one batch. However, the material from another batch led to a 7 °C lower self-ignition temperature.

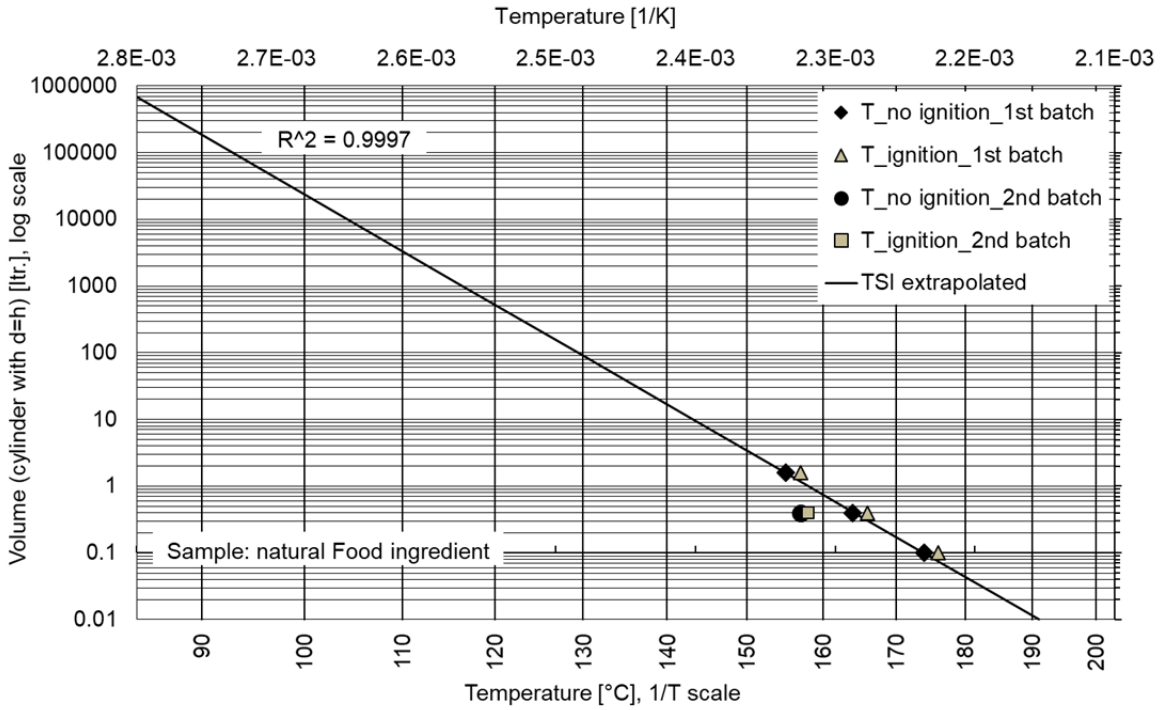

Figure 4: Pseudo-Arrhenius plot of the self-ignition temperatures of a natural food ingredient according to DIN EN 15188

The measuring precision required according to DIN EN 15188, to determine the self ignition temperature per volume in a range of 2 °C (temperature difference between tests with ignition and without ignition), does not allow to combine the measurements from the two batches. For proper evaluation of this product either a large series of tests according to DIN EN 15188 with material from several batches would be required or a smaller series of tests with a method considering a lower measuring precision, e.g. 10 °C, combining tests with material from several batches. The later must then however consider very large uncertainties for the extrapolated self ignition temperatures.

4. Conclusions

As illustrated by the examples in this paper, considerable efforts are still necessary to bring safety testing to the level required for analytical testing with respect to reproducibility and traceability.
Important elements would be

- Systematic round robin testing to reduce variability between different testing sites and to get an idea about inherent variations
- Provision of suitable and agreed reference materials for tests, where such materials could help to improve data quality
- Improvement of testing standards based on results of round robin tests
- Acceleration of testing standard revision to support continuous improvement

Acknowledgments

The authors like to thank Georg Suter, TÜV SÜD (Switzerland) for valuable discussions.

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