# Calibration-Round-Robin CaRo24
# Final Report



## 1. Conclusion

According to international standards the 20-l-apparatus and the 1-m3-vessel for the determination of Pmax and Kmax and the apparatus for determination of the minimum ignition energy must be calibrated at regular intervals (at least every 12 months, or following any significant maintenance or repair).
For this purpose, an international calibration round test (calibration round robin = CaRo) has been carried out periodically since 1993.

A dust has been selected, prepared and supplied to **34** test laboratories all over the world.
The mean values of the explosion indices, measured by the participating laboratories, have been calculated as reference values. The testing laboratories have been informed about the evaluation with a certificate.
This report presents the results of this calibration method and describes the evaluation procedure.

**CaRo24 – Reference values for the Explosion Indices Pmax, Kmax, LEL/MEC and LOC**

| | | |
|---|---|---|
| **Pmax** | [bar] | **8.2** ±10% (7.3 ... 9.0) |
| **Kmax** | [bar·m/s] | **246** ±10% (222 ... 271) |
| **LEL (CEN)** | [g/m$^3$] | **33** (20 ... 45) |
| **MEC (ASTM)** | [g/m$^3$] | **46** (40 ... 53) |
| **LOC** | [O2%] | **11.5** (10 ... 13) |

**CaRo24 – Reference values for the Minimum Ignition Energy MIE**

| Es / 3 | Es | Es • 3 |
|---|---|---|
| **0.7 mJ** | **2.1 mJ** | **6.2 mJ** |



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## 1.1 Participants:

Further details about participants who have agreed to a publication, can be found in section 4.

| | Pmax, Kmax (35) | | MZE (30) | |
|---|---|---|---|---|
| | 20-l | 1 $m^3$ | MIKE | others |
| Australia | 1 | | 1 | |
| Austria | 1 | | 1 | |
| Canada | 1 | | | 1 |
| China | 3 | | 2 | 1 |
| Germany | 8 | 2 | 7 | |
| Hungary | 1 | | | 1 |
| India | | | 2 | |
| Slovenia | 1 | | | |
| South Africa | 1 | | | |
| Switzerland | 4 | | 6 | |
| Taiwan | 1 | | | |
| United Kingdom | 2 | | 1 | 1 |
| USA | 8 | 1 | 5 | 1 |
| Total: | **32** | **3** | **25** | **5** |

## 1.2 Test substance:

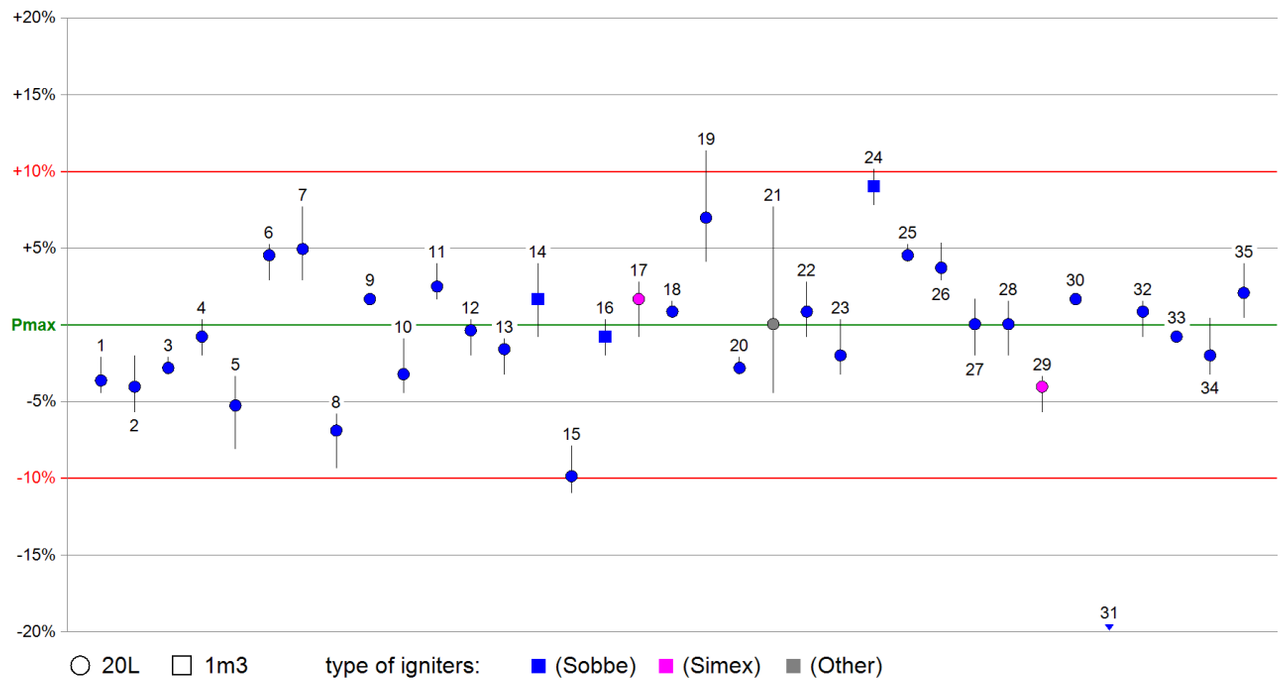
For correct calibration the CaRo24 test sample has been milled, homogenized, packed under nitrogen and shipped in an air tight package. Therefore the sample has to be tested „as delivered“.

**CaRo24 = Niacin USP** (Nicotinic acid)

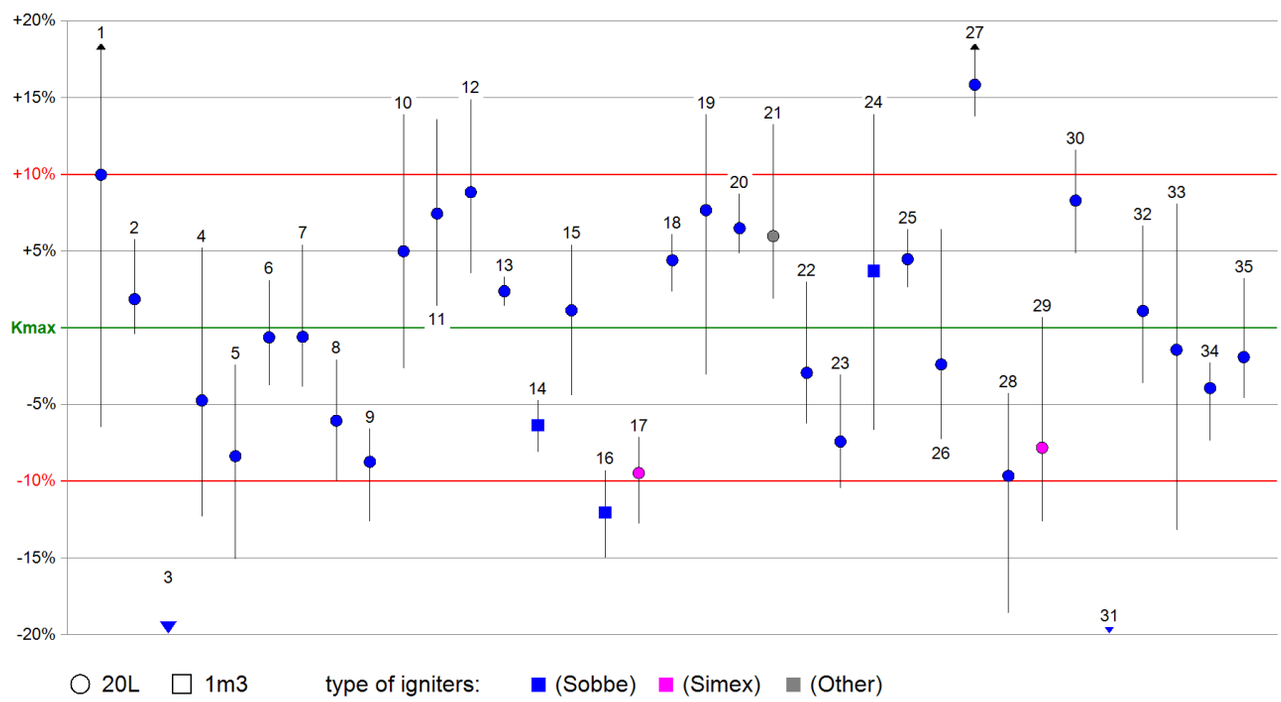
| **Particle size:** | d 10 [µm] | **d 50 = median [µm]** | d 90 [µm] |
|---|---|---|---|
| Sample 1 | 5.74 | **22.08** | 76.72 |
| Sample 2 | 5.67 | **22.67** | 83.89 |
| Sample 3 | 5.57 | **22.52** | 84.72 |
| Sample 4 | 5.72 | **22.07** | 78.25 |

## 2. Explosion Indices Pmax, Kmax, LEL/MEC, LOC

**Pmax = 8.2 bar** ±10% (7.3 ... 9.0) @ 553 g/m³

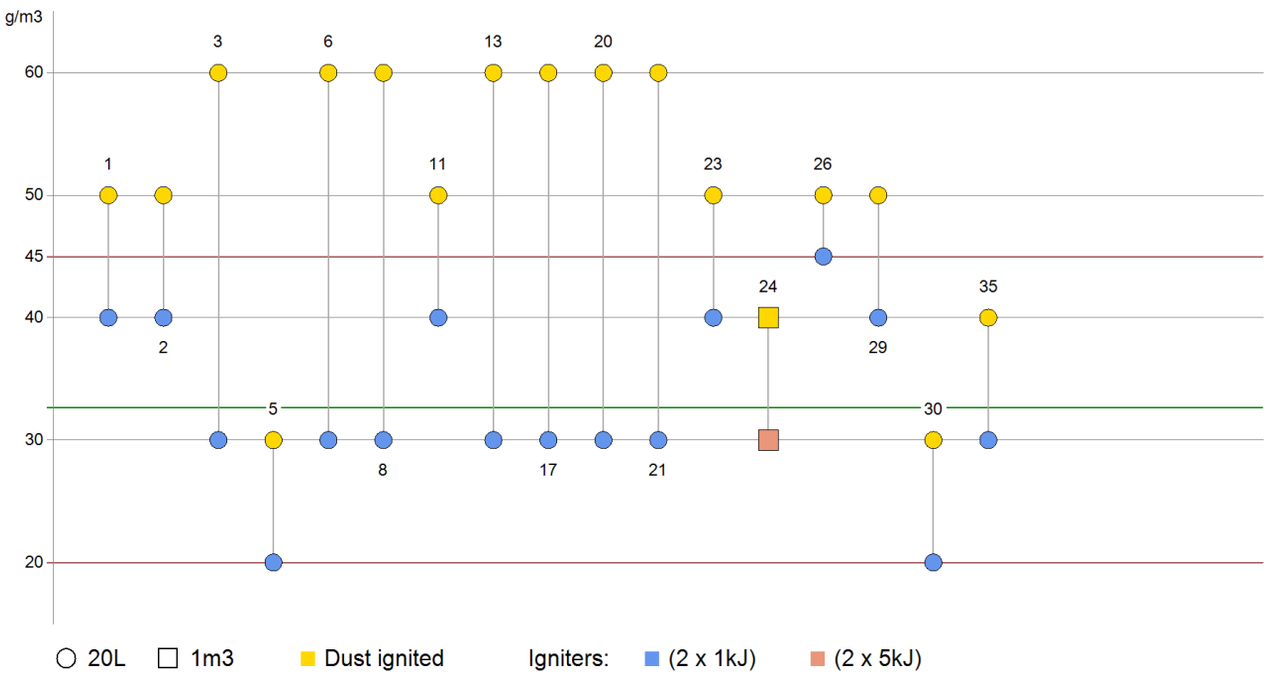



**Kmax = 246 bar•m/s** ±10% (222 ... 271) @ 795 g/m³

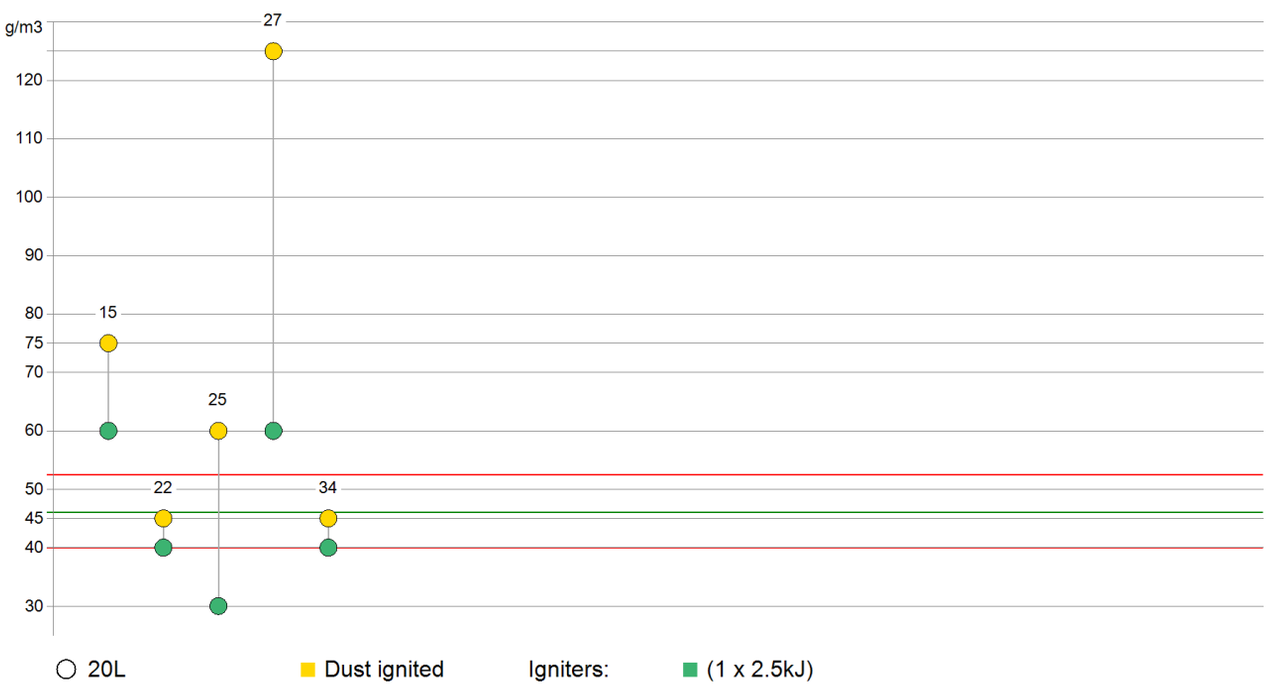



The individual results are drawn in relation to the arithmetic mean of all results and in chronological sequence (number of certificate).

## LEL (CEN) = 33 g/m³ (20 ... 45)

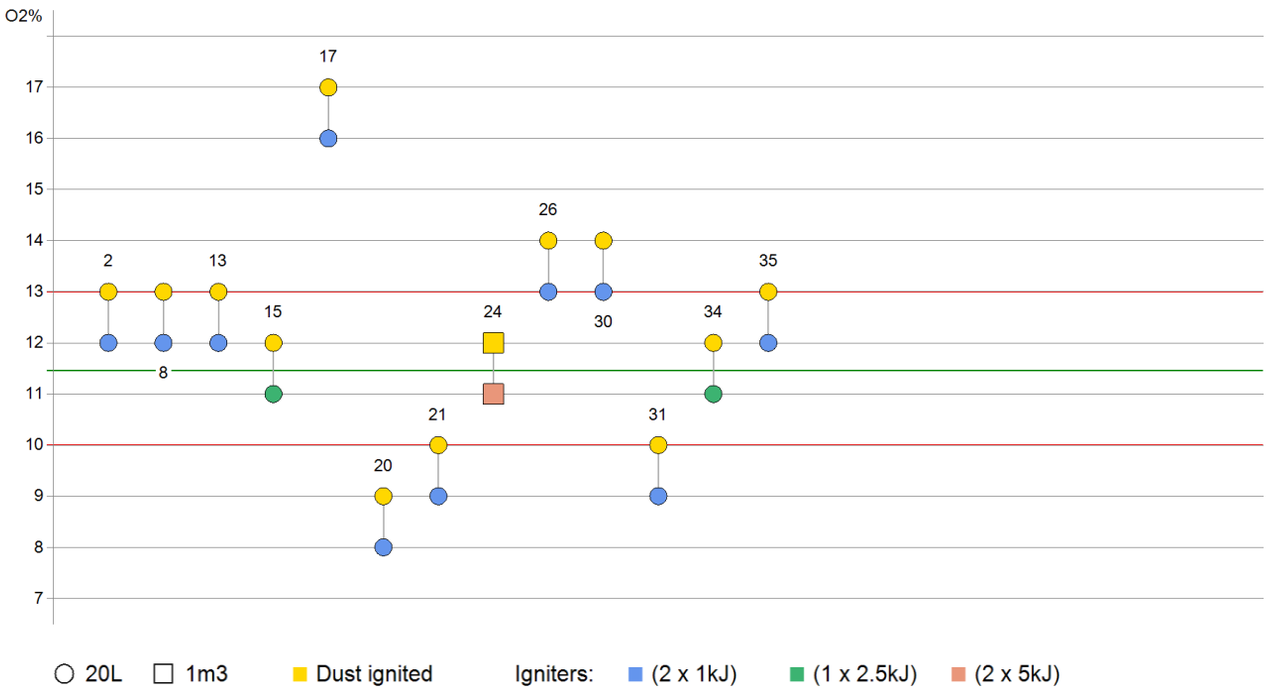



## MEC (ASTM) = 46 g/m³ (40 ... 53)




The individual results are drawn in relation to the arithmetic mean of all results and in chronological sequence (number of certificate).

**LOC = 11.5 $O_2$%** (10 ... 13)




The individual results are drawn in relation to the arithmetic mean of all results and in chronological sequence (number of certificate).

## 2.1 Test procedure:

The determination methods are defined in the “Instructions CaRo24”

## 2.2 Evaluation of Pmax and Kmax:

The explosion indices Pmax and (dP/dt)max are defined as the mean values of the maximum values of each series. Subsequently, the explosion index Kmax is calculated from the mean value (dP/dt)max.

**Scatter of Pmax and Kmax:**

The maxima of each series must not deviate by more than **10%** of Pmax resp. Kmax. Otherwise this series must be repeated!

**Calculation of the reference values:**

First the mean value of all test results (35) has been calculated. In a second step all results outside of the tolerance band are excluded prior to the subsequent calculation of the mean value.

## 2.3 Evaluation of LEL/MEC:

The highest concentration of combustible dust at which no ignition occurs in three consecutive tests is given as the lower explosion limit (LEL/MEC). For the 1m3 vessel, only 1 test per concentration is sufficient.

The test specifications in the ASTM standard differ significantly from EN 14034-3.
ASTM E1515 states: “Direct comparisons between ASTM MEC and European CEN/CENELEC LEL determinations may not be possible.”
We take this into account through separate evaluations.

**Calculation of the reference values for LEL (CEN):**

The mean value was calculated from all test results (17).
The limit values were set to match the 10g/m$^3$ step size.

Calculation of the reference values for LEL (ASTM):
The mean value from all test results (5) was formed.
The limit values were set to match the 5g/m$^3$ step size.

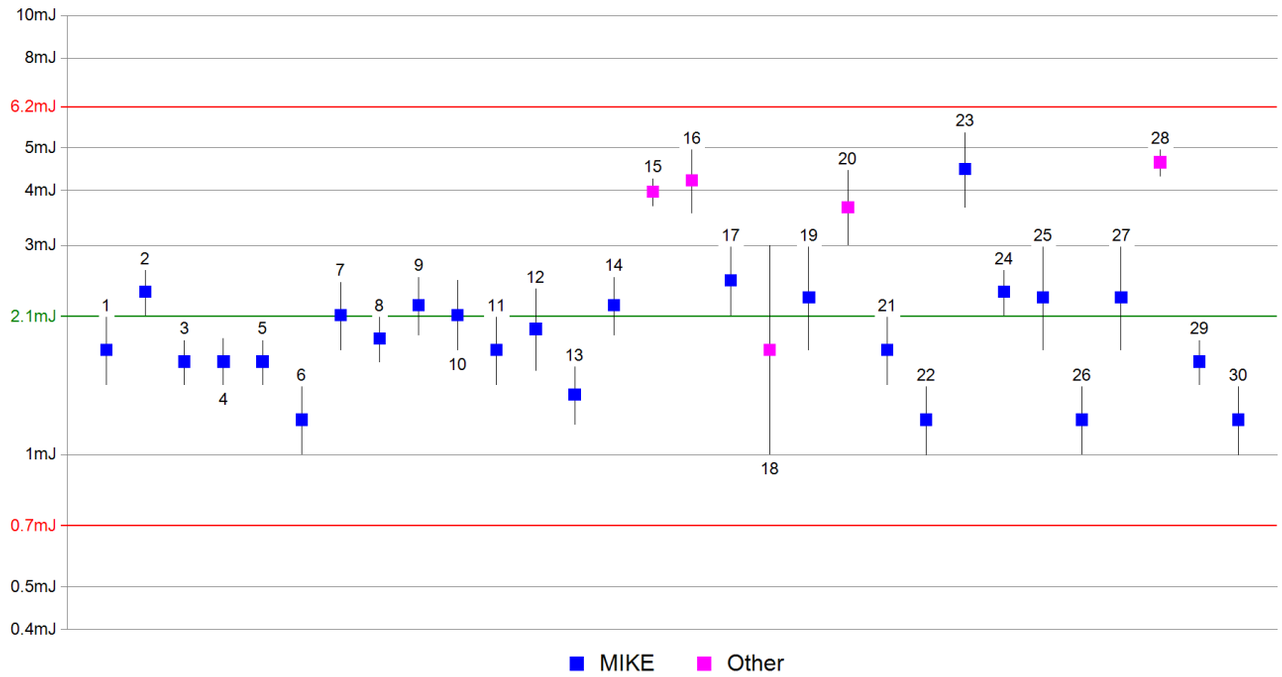
## 2.4 Evaluation of LOC:

By gradually increasing the ratio of inert gas to air and changing the dust concentration, the oxygen concentration must be lowered to such an extent that an explosion no longer occurs at any given dust concentration. The value found in this way is the limiting oxygen concentration (LOC). For tests in the 20L sphere, no explosion may occur for three consecutive tests.

**Calculation of the reference values:**

The mean value from all test results (13) was calculated.
The limit values were set to match the 1% step size.

## 3. Minimum Ignition Energy MIE




The individual results are drawn in chronological sequence (number of certificate).

### 3.1 Test procedure:

The method for determination of the MIE is described in the „Instructions CaRo24“.

### 3.2 Estimation of the statistical energy (Es):

The minimum ignition energy MIE lies, by definition, between two energy values: E1 < MIE < E2

For the purpose of comparison between different apparatuses, only one MIE value (Es) instead of the energy range (E1, E2) shall be used. This single value (Es) can be estimated by use of the probability of ignition as follows (EN 13821):

$$E_S = 10^{\log E_2 - \frac{I[E_2]\cdot(\log E_2 - \log E_1)}{(NI + I)\cdot[E_2]+1}}$$

where is: I[E2] = number of tests with ignition at energy E2

(NI+I) [E2] = total number of tests at energy E2

### 3.3 Criteria for conformity:

Conformity in the CaRo24 is given, when the Es-value of each equipment differ less than a factor of 3 to the mean (Es) of all equipment:

| Es / 3 | Es | Es • 3 |
|---|---|---|
| 0.7 mJ | 2.1 mJ | 6.2 mJ |

## 4. List of Participants

| Country | Company<br>Laboratory | Pmax<br>Kmax | LEL<br>MEC | LOC | MIE |
|---|---|---|---|---|---|
| Australia | Simtars – Resources Safety & Health Queensland | ✓ | | | ✓ |
| Austria | AUVA - STP | ✓ | | | ✓ |
| Canada | Jensen Hughes Consulting Canada Ltd. | ✓ | ✓ | | ✓ |
| China | BASF Advanced Chemicals Co., Ltd. | | | | ✓ |
| China | Shanghai Research Institute of Chemical Industry Testing Co., Ltd. | ✓ | | | ✓ |
| China | TÜV SÜD Certification and Testing (China) Co., Ltd. Shanghai Branch | ✓ | ✓ | ✓ | ✓ |
| Germany | BAM Bundesanstalt für Materialforschung | ✓ | ✓ | | ✓ |
| Germany | BASF SE | ✓ | ✓ | ✓ | ✓ |
| Germany | BGN | ✓ | ✓ | | ✓ |
| Germany | IBExU | ✓ | ✓ | ✓ | ✓ |
| Germany | IFA - DGUV | ✓ | ✓ | ✓ | ✓ |
| Germany | REMBE® Research+Technology Center GmbH | ✓ | ✓ | ✓ | ✓ |
| Germany | Zschimmer & Schwarz GmbH & Co KG | | | | ✓ |
| Hungary | University of Miskolc (DustLab) | ✓ | ✓ | ✓ | ✓ |
| India | Aarti Industries Limited | | | | ✓ |
| India | GVS Cibatech Private Limited | | | | ✓ |
| Slovenia | University of Ljubljana (Faculty of Chemistry) | ✓ | ✓ | | |
| South Africa | CSIR | ✓ | | | |
| Switzerland | Dottikon Exclusive Synthesis AG | | | | ✓ |
| Switzerland | DSM | | | | ✓ |
| Switzerland | F. Hoffmann-La Roche AG | | | | ✓ |
| Switzerland | Givaudan International SA | ✓ | | | ✓ |
| Switzerland | TÜV SÜD Process Safety | ✓ | ✓ | ✓ | ✓ |
| Switzerland | TÜV SÜD Schweiz AG | ✓ | ✓ | ✓ | |
| Taiwan | Yun Safety Tech | ✓ | | | |

| Country | Company<br>Laboratory | Pmax<br>Kmax | LEL<br>MEC | LOC | MIE |
|---|---|---|---|---|---|
| United Kingdom | BRE Global | ✓ | ✓ | ✓ | ✓ |
| United Kingdom | DEKRA Organisational & Process Safety | ✓ | | | ✓ |
| USA | Ashland Inc. | ✓ | | | ✓ |
| USA | BASF Corporation | ✓ | | | ✓ |
| USA | DEKRA Services, Inc. | ✓ | | ✓ | ✓ |
| USA | EMSL Analytical, Inc. | ✓ | ✓ | | ✓ |
| USA | Exponent, Inc. | ✓ | ✓ | ✓ | ✓ |
| USA | Fike Corporation | ✓ | ✓ | ✓ | ✓ |

## 5. Standards, History

### 5.1 Standards:

The following Standards have been applied:

- EN 13821: Determination of minimum ignition energy of dust/air mixtures
- EN 14034-1: Determination of max. explosion pressure Pmax …
- EN 14034-2: Determination of max. rate of explosion pressure rise $(dp/dt)_{max}$ …
- EN 14034-3: Determination of the lower explosion limit LEL …
- EN 14034-4: Determination of the limiting oxygen concentration LOC …
- ASTM E2019: Minimum Ignition Energy MIE of a Dust Cloud in Air
- ASTM E1226: Explosibility of Dust Clouds
- ASTM E1515: Minimum Explosible Concentration MEC of Combustible Dusts
- ASTM E2931: Limiting Oxygen Concentration LOC of Combustible Dust Clouds
- EN ISO/IEC 80079-20-2: … Material characteristics. Combustible dust methods

### 5.2 History:

Our previous world-wide round robin tests:

| | | |
|---|---|---|
| CaRo93: 77 apparatuses | CaRo07: 77 apparatuses | CaRo18: 41 apparatuses |
| CaRo96: 68 apparatuses | CaRo09: 90 apparatuses | CaRo19: 127 apparatuses |
| CaRo98: 63 apparatuses | CaRo11: 122 apparatuses | CaRo20: 41 apparatuses |
| CaRo00: 69 apparatuses | CaRo13: 112 apparatuses | CaRo21: 125 apparatuses |
| CaRo03: 93 apparatuses | CaRo15: 131 apparatuses | CaRo22: 50 apparatuses |
| CaRo05: 98 apparatuses | CaRo17: 144 apparatuses | CaRo23: 117 apparatuses |

➔ All final reports can be downloaded here:
https://www.cesana-ag.ch/Calibration.shtml

**References**

Cesana Ch., Eiche M., Schwaninger M., 2019,
Quality Management in the Determination of Safety Characteristics, CET-Paper