# Interlaboratory Comparison of Analytical Results a Measure of Quality Control

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An ***Interlaboratory Comparison*** is an external way of assuring quality control among laboratories. It allows the participants to detect unsuspected errors and deficiencies in their methodology. Recently, the Technological Centre of Ceramic and Glass (CTCV) in Portugal conducted an interlaboratory comparison among eight laboratories that employ the granulometric analysis technique. Each laboratory was asked to submit results of analysis of silica flour performed with the Micromeritics SediGraph™ 5100. The results were calculated by CTCV according to ISO 5725 – Part 2 standard, and the z-score to determine the testing performance of each participant laboratory.

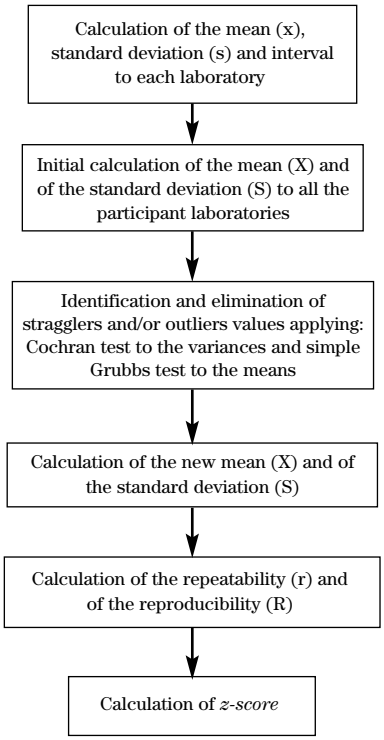
***Granulometric analysis*** is a technique for characterizing pulverized materials and is applied to the determination of the particle size distribution of a wide range of materials. Granulometric analysis by X–ray sedimentation is a technique based on the measurement of the sedimentation velocity of particles dispersed in a fluid that allows, by Stokes' law, the calculation of the diameter of the sphere with the same sedimentation speed of the particle. What is obtained is not a geometrical diameter, rather a hydrodynamical or equivalent spherical diameter. This is known as Stokes diameter, which is the diameter of a sphere whose characteristic property has the same value as that of the particle being tested. [1]

The equipment used in this interlaboratory comparison was Micromeritics' SediGraph 5100. The sedimentation technique using the SediGraph is an incremental technique and is based in the study of the concentration change with time in a zone of measurement described by its depth in the sedimentation cell. At time zero, the suspension is homogeneous and the concentration is 100%. At any time later, the relative concentration (when compared with the concentration at time zero) is equal to the cumulative mass fraction smaller than the Stokes diameter calculated for the smallest particle that could have settled below the measurement zone.

The measure of the mass distribution of particle size in the cell containing the suspension is determined using a source of X–Ray of low energy and a suitable detector. The X–Ray source and the detector remain stationary while the cell moves vertically between them subjecting different measuring zones to the X-Ray.

## Methodology of Calculation

The calculation method used to measure the results of the participant laboratories is indicated in the following flowchart (to each parameter analyzed):



The z-score measures the deviation of the result of each laboratory from the "true" value, by comparison with a reference standard deviation and is given by the formula:

$$Z = \frac{x - X}{S} \qquad (1)$$

where:

$x$ =mean value of the results of the participant laboratory

$X$ = value assumed to be true (it employed the mean of the results of all participants, after excluding the outlier values.)

$s$ =standard deviation of the mean of the results, after exclusion of the stragglers and/or outliers values

The interpretation for the z-score is the following:

| | |
|---|---|
| $\|Z\| \leq 2$ | Gratifying results |
| $2 < \|Z\| \leq 3$ | Questionable results |
| $\|Z\| \geq 3$ | Degratifying results |

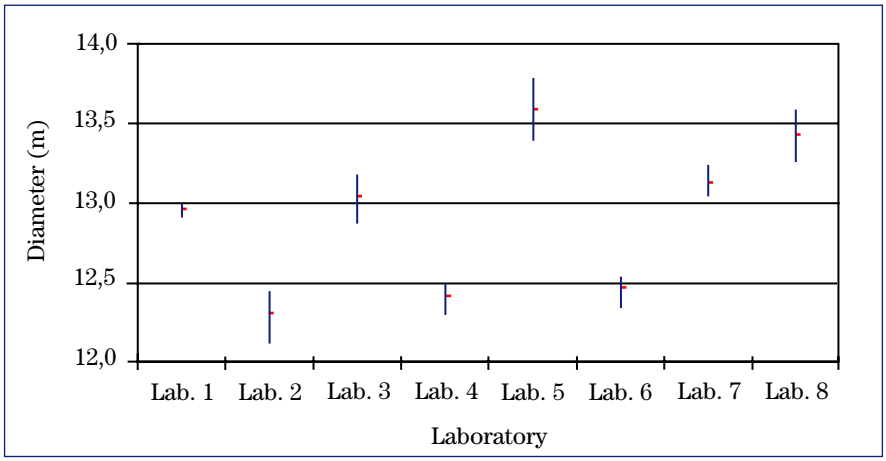



**Figure 1 – Interval of variation for the MEDIAN parameter**

## Presentation of Results

The parameters analyzed were median (diameter to 50%), d 95%, d 90%, d 75%, d 25%, d 10% and mode.

In the presentation of statistical analyses of test results that follow, all parameters, except the calculation of the z-score, are presented. Z-score is calculated only for the test medians.

## Elimination of Outlier Values

The elimination of outlier values (values appear anomalous compared to other observations in the set) was done by application of the Cochran test to the variances and by application of the simple Grubbs test to the means. The application of the Cochran test leads to the elimination of the outlier values presented in Table 2.

**Table 1 – MEDIAN Parameter (µm)**

| Laboratory | $X_1$ | $X_2$ | $X_3$ | $X_4$ | $X_5$ | Mean (x) | Standard Deviation(s) | Interval | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 12,92 | 12,94 | 12,99 | 12,97 | 12,97 | 12,96 | 0,03 | 12,92 | 12,99 |
| 2 | 12,45 | 12,38 | 12,42 | 12,15 | 12,13 | 12,31 | 0,15 | 12,13 | 12,45 |
| 3 | 12,88 | 13,16 | 12,91 | 13,07 | 13,18 | 13,04 | 0,14 | 12,88 | 13,18 |
| 4 | 12,31 | 12,46 | 12,49 | 12,39 | 12,47 | 12,42 | 0,07 | 12,31 | 12,49 |
| 5 | 13,40 | 13,79 | 13,62 | 13,58 | 13,55 | 13,59 | 0,14 | 13,40 | 13,79 |
| 6 | 12,54 | 12,54 | 12,34 | 12,45 | 12,46 | 12,47 | 0,08 | 12,34 | 12,54 |
| 7 | 13,07 | 13,08 | 13,24 | 13,19 | 13,05 | 13,13 | 0,08 | 13,05 | 13,24 |
| 8 | 13,57 | 13,35 | 13,26 | 13,59 | 13,36 | 13,43 | 0,15 | 13,26 | 13,59 |

Mean (X): 12,92 Standard Deviation ( S ) : 0,48

The application of the simple Grubbs test did not lead to the elimination of outliers. The outlier values were retained in the following calculations.

## Calculation of Repeatability and Reproducibility

The values of repeatability (r) and reproducibility (R) comprise Table 3.

**Table 2 – Stragglers and Outliers Values – Cochran test applied to variances**

| Parameter measured | Straggler value | NIL – Nº ID Lab. | Outlier value | NIL – Nº ID Lab. |
|---|---|---|---|---|
| MEDIANAd 50 (µm) | -- | -- | -- | -- |
| MODE | -- | -- | -- | -- |
| d 95 (µm) | -- | -- | 1** | Lab. 3 |
| d 90 (µm) | 1* | Lab. 3 | -- | -- |
| d 75 (µm) | -- | -- | -- | -- |
| d 25 (µm) | 1* + 1* | Lab. 2 + Lab. 8 | -- | -- |
| d 10 (µm) | -- | -- | -- | -- |

Legend: 1* - Straggler value 1** - Outlier value

**Table 3 – Repeatability and Reproducibility**

| Parameter measured | $s^2r$ | $s^2L$ | $s^2R$ | r | R |
|---|---|---|---|---|---|
| MEDIAN (µm) | 0,013 | 0,224 | 0,237 | 0,32 | 1,36 |
| MODE (µm) | 1,373 | 0,312 | 1,685 | 3,28 | 3,63 |
| d 95 (µm) | 0,283 | 0,728 | 1,011 | 1,49 | 2,82 |
| d 90 (µm) | 0,087 | 0,521 | 0,609 | 0,83 | 2,18 |
| d 75 (µm) | 0,026 | 0,308 | 0,334 | 0,45 | 1,62 |
| d 25 (µm) | 0,003 | 0,221 | 0,225 | 0,16 | 1,33 |
| d 10 (µm) | 0,007 | 0,332 | 0,339 | 0,23 | 1,63 |

Where:

- $s^2r$: Repeatability Variance
- $s^2L$: Between – Laboratory Variance
- $s^2R$: Reproducibility Variance
- r: Repeatability
- R: Reproducibility

The values of repeatability and reproducibility presented were calculated using a factor of 2, 8, for n=2.

## Calculation of Z – score

The values of z-score to the Median (µm) parameter make up Table 4 and are presented in Figure 2.

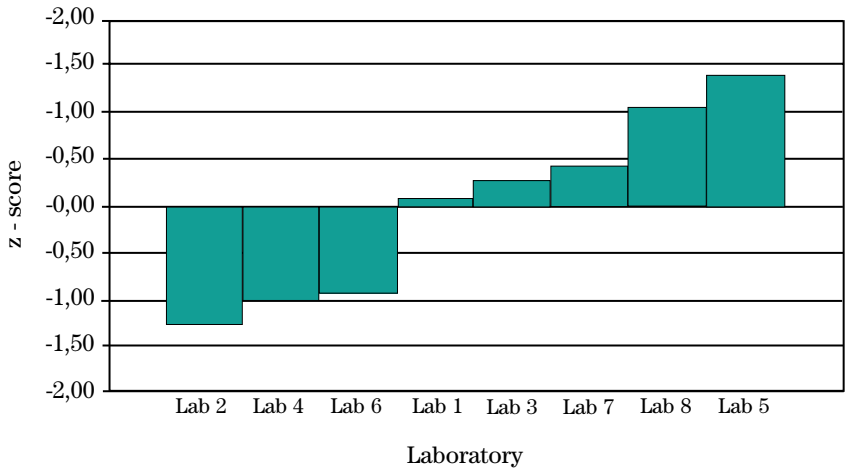
**Table 4 – *Z-score* - MEDIAN Parameter (µm)**

| NIL – Nº ID Laboratory | Mean (x) | Standard Deviation (s) | $n_i$ | *Z - score* |
|---|---|---|---|---|
| Laboratory 1 | 12,96 | 0,03 | 5 | 0,08 |
| Laboratory 2 | 12,31 | 0,15 | 5 | - 1,28 |
| Laboratory 3 | 13,04 | 0,14 | 5 | 0,25 |
| Laboratory 4 | 12,42 | 0,07 | 5 | - 1,05 |
| Laboratory 5 | 13,59 | 0,14 | 5 | 1,40 |
| Laboratory 6 | 12,47 | 0,08 | 5 | - 0,94 |
| Laboratory 7 | 13,13 | 0,08 | 5 | 0,44 |
| Laboratory 8 | 13,43 | 0,15 | 5 | 1,07 |

Mean (X): 12,92

Standard Deviation (S): 0,48

**Figure 2 – Z-score – MEDIAN (µm)**




## Final Considerations

- The 'true' value, as employed in the calculations, was calculated using the mean of the results of all the participants, after excluding outlier values. The value adopted as 'true' refers to results obtained with the SediGraph 5100 applying the test procedures to the sample analyzed.
- The values of repeatability and reproducibility represent the repeatability and reproducibility of the test method, the test conditions, and the sample employed.
- The absolute difference between two results determined in repeatability conditions must not exceed the value of r (repeatability).
- The absolute difference between two results determined in reproducibility conditions must not exceed the value of R (reproducibility).

CTCV wishes to express recognition and to thank the contribution given by IPN – Labgran, and Laboratories of Cerisol, Comital, Lusoceram, Omya Mineral Portuguesa, Sanitana e Somincor in this interlaboratory comparison of analytical results.

## REFERENCES

[1] F. M. Barreiros, P. J. Ferreira, M. G. Rasteiro, and M. M. Figueiredo "Granulometric Analysis," Chemical Engineering Department of Coimbra University

[2] International Standard Organization: Accuracy (trueness and precision) of measurement methods and results, ISO 5725: Part 2:Basic methods for the determination of repeatability and reproducibility of a standard measurement method: 1994