Planning Proficiency Test RV-2019-02 for Cement

FLX-RV-2019-02-Sample01, FLX-RV-2019-02-Sample02

Bedburg-Hau, 01st October 2019

Coordinator of PT
Charlotte Winkels-Herding

Statistics and Report
Susan Aschenbrenner

New registration deadline: 15th November 2019

Important Information

Costs for the participants

The participants will be billed a total of **400 Euro** (EXW Bedburg-Hau, Germany) for all 2 samples for this proficiency test (PT).

Analysis

Sample pre-treatment

The cements provided might contain sulfide. Therefore, it is important to determine the sulfate content independently from the total sulphur content.

All results expressed should be from original sample material!

The samples must be annealed at 950 °C to a constant mass before being analysed (1 hour is usually sufficient.
The observed loss on ignition might be negative because of sulfide content!
After ignition it should be analyzed immediately to avoid any absorbance of moisture.

Parameters to determine

Al2O3, CaO, Cr2O3, Fe2O3, K2O, MgO, Mn2O3, Na2O, P2O5, SiO2, SO3, SrO, TiO2, ZnO, LOI, Sulfide, Sulfate

- **Participation is also permitted even when not all of the parameters can be determined.**
- **Each sample must be analysed two times, and every value must be reported to three decimal places (0.000).**

Preferred method of analysis

- **XRF with fusion as the sample preparation method (ISO 29581-2:2010)**
- **Every other traceable method, such as ICP, wet chemistry, etc.**

Recommended sample preparation for total sulphur content:

- **DIN 51085:2015-01**

Recommended sample preparation for Sulfate and Sulfide (EN-196-2:2013):

- **Sulfate: from original sample by gravimetry with BaSO4**
- **Sulfide: from original sample by iodometry**

Other methods, e.g., XRF using “pressed pellets” as the sample preparation method or XRF with the “standardless analysis” method, which are not traceable can also be used. These values will not be included in the evaluation. They will, however, be shown as informational values in the report and laboratory comparison.

Application

To receive the samples, they must be ordered as **RV-2019-02** by 15th November 2019.

Shipment

The samples will be shipped in November 2019.

Sending in the results

The results must be submitted by 15th December 2019, at the latest. You will receive a link, with which you can download a pre-prepared Excel Table and later upload it (completed) for the submission of your data. We assume that you will use one method for one parameter. Thus, you will receive one lab code. However, if you want to use, e.g., two methods for the same parameter, you must request an additional lab code (at no charge).

Report

We intend to complete the report by the end of January 2020.

Introduction

X-ray fluorescence analysis is a frequently used technique for the analysis of oxidic materials.

However, for the calibration of XRF instruments, dedicated standard material is needed. As a worldwide supplier for XRF laboratories, FLUXANA has developed a number of services to support XRF users. One of these services is the production of new reference materials and the organization of proficiency tests (PT).

In 2011, FLUXANA introduced its own quality management.

In February 2014, FLUXANA received accreditation from the German DAKKS according to DIN EN ISO/IEC 17025:2005 for the test laboratory in Bedburg-Hau.

The production of reference materials and the performance of proficiency tests is not yet accredited. However, the proficiency tests are conducted following the corresponding norms.

All evaluations are performed in agreement with DIN EN ISO/IEC 17043:2010, DIN EN ISO 17034:2017 and ISO Guide 35:2017.

Proficiency test provider / Address for ordering the samples

FLUXANA GmbH & CO.KG
Borschelstraße 3
47551 Bedburg-Hau, Germany
pt@fluxana.de

Coordinator: Charlotte Winkels-Herding, QM
Responsible for evaluation and data processing: Susan Aschenbrenner, PT

Subcontractors

This reference material sample was produced from commercial products. Material was taken directly from the production stream.
Analysis performed by PT Participants.

Proficiency test items

The materials were delivered and homogeneously distributed into 50 ml bottles by FLUXANA. The bottles were then vacuum packed for storage.

Test item	Description
FLX-RV-2019-02-Sample01	Cement (with Sulfate and Sulfide)
FLX-RV-2019-02-Sample02	Cement (with Sulfate and Sulfide)

Homogeneity and stability

The material was used as delivered. A homogeneity and stability study of the materials was performed based on ISO Guide 35:2017 and DIN ISO 13528:2015.

Metrological traceability

In agreement with internationally valid standards, the analytical procedures (e.g., ICP or any other wet chemical procedure) used by the participants to determine the certified values in the previous proficiency test had to be traceable. Other methods were not permitted.
In this proficiency test, only XRF results will be used to determine the statistical data. Concentration values determined with other methods can also be submitted; they will be shown in the evaluation and, as with all other values, the z-scores calculated.

Participant accreditation

It is important to know whether the participant laboratory works under ISO 17025 accreditation. Therefore, we will ask this information for each parameter. Which values were determined under accreditation will be shown anonymously in the final report.

Number of participants

The minimum number of participants is 10.

Potential major sources of errors

- Care must be taken to ensure that the material is annealed before the analysis.

Recommended rules for the analysis

1g of sample that has been annealed to a constant mass (typically 1 hour at 950 °C) and 8g flux should be weighed into a platinum crucible (with 5% gold) and mixed. Then a normal fusion should be performed manually or with an automatic machine.

When using the electrical fusion machine from FLUXANA, the program A0 is recommended. When using the gas fusion machine from FLUXANA, the program P0 is recommended.

Evaluation

According to DIN EN ISO/IEC 17043:2010-05, we will use robust statistical methods in agreement with DIN ISO 13528:2015, ISO/TS 20612:2007 and DIN 38402-45:2014-06.

Advantages of using robust statistics

Statistical methods are robust in the sense that any outliers have only a limited effect on the overall result. Steps were taken to ensure that the results are still meaningful, even if the proportion of outliers is 1/3. Robust statistics are also preferable for small populations.

Outliers

Outliers in the statistical sense are typically not detected when using robust statistical methods because the robust A+S algorithms were found to work better than the classical approach (which is outlier detection plus arithmetic mean and classical s.d. formula). Outliers shown in the evaluation are only based on z-scores and marked with yellow or red colours.

Number of measurements

All participants are requested to perform two measurements, for some methods up to six measurements are recommended. This is necessary to perform the repeatability standard deviation for the laboratories. Participants who send only one or more than two values must first ask for permission. Otherwise, they will be excluded.

Publication of the results

All participants will be informed about the results of the PT with a report. Which results were delivered by which laboratory will be kept confidential. All laboratories are encoded, and the code is only known to the organizer and the individual laboratory. The final report will be published on the FLUXANA website. First, a preliminary report will be sent out for verification by the participants. Within one month, the final report will be published.

Laboratory performance

Each participant will receive a performance evaluation report based on z-scores. The diagram shows the relative difference to the assigned values

Further Information

For this proficiency test, the participants' results must be submitted to the organizer using only the "Result Sheet" Excel table, which must not be altered. Paper sheets or other Excel tables will only be accepted in special cases in prior agreement with the organizer. In this way, we want to improve the data quality and avoid any transmission errors.

Statistical Evaluation used for this PT

Calculation of Mean m

The mean m for all laboratories is calculated using the Hampel estimator (ISO/TS 20612:2007 9.2.3) based on the laboratory means µ using traceable methods only.

Calculation of reproducibility standard deviation s_R

The reproducibility standard deviation s_R is calculated using the Q-method (ISO/TS 20612:2007 9.2.3).

Calculation of repeatability standard deviation s_r

The repeatability standard deviation s_r is also calculated using the Q-method.

Calculation of robust standard deviation s*

The robust standard deviation s* is calculated from the laboratory means µ using the Q-method.

Calculation of uncertainty U_{s_R} (according to Nordtest TR 537 ed 3.1.)

The **uncertainty** U_{s_R} for a confidence interval of P=95% (k=2) can be calculated from the **reproducibility standard deviation** s_R (factor 1.25 for average median, robust statistics) and the number of participating laboratories p:

$$U_{s_R} = 2 * 1.25 * \frac{s_R}{\sqrt{p}}$$

Calculation of uncertainty U_{s^*} (according to ISO 13528:2015)

The **uncertainty** U_{s^*} for a confidence interval of P=95% (k=2) can be calculated from the **robust standard deviation** s* (factor 1.25 for average median, robust statistics)) and the number of participating laboratories p:

$$U_{s^*} = 2 * 1.25 * \frac{s^*}{\sqrt{p}}$$

The **uncertainty** U_{s^*} only takes the between laboratories uncertainty into account while the **uncertainty** U_{s_R} also includes the within laboratories uncertainty. Therefore U_{s_R} is recommended for use in accredited laboratories.

Laboratory performance

Laboratory proficiency assessment is based on z-scores.
The **z-score** z is calculated from all laboratory means μ:

$$z = \frac{m - \mu}{s_R}$$

m	Mean value for all laboratories (assigned value)
μ	Mean value of individual laboratory
s_R	Reproducibility standard deviation

Assessment on z-scores:

$\|z\|$ <= 2.0	indicates “satisfactory” performance = generates no signal
2.0 < $\|z\|$ < 3.0	indicates “questionable” performance = generates a warning signal
$\|z\|$ >= 3.0	indicates “unsatisfactory” performance = generates an action signal

Z-scores with 3 >= $|z|$ >= 2 are highlighted with a yellow color, z-scores with $|z|$ >= 3 are highlighted with a red color.