Validation of Rock Testing Methods in Determination of Apparent Density

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Abstract. Research on the physical properties of rock materials and aggregates used for construction should be based on standardized methods. Whereas scientific research is focused more on the development of new methods, testing and evaluation of new properties, etc. In case of own testing procedures and standardized but modified methods, they should be validated before being put into use. Validation is the confirmation of the ability to designate that method and tests its usefulness. In order to investigate the method's possibilities, the following assessment methods can be used: calibration or precision evaluation using reference standards or reference materials, systematic evaluation of factors affecting the result, resistance of the test method to variability of controlled parameters, comparison of test results obtained by various methods, inter-laboratory comparisons, and uncertainty of measurement. The paper presents mathematical formulas allowing to evaluate the precision of research methods and the consistency of results, which are the basis for validation of research methods. In the practical part of the article, own method of apparent density testing, was validated based on the analysis of repeatability, internal laboratory reproducibility and between laboratory reproducibility.

Keywords: validation, rock testing methods, physical properties

1 Introduction

Testing of physical properties of rock material used in construction should be based on standardized methods. The assessment of results obtained during such tests makes it easier to determine whether individual raw materials or products comply with declared requirements. In addition to normalised test methods, the literature mentions other ways to determine the properties of rock, stone products or aggregate [1, 2, 3]. Proprietary research procedures, even those based on known rules, also standardized but modified methods, widened or applied out of range, should be validated prior to use [4]. The validation is a process that allows a verification and confirmation and provides an objective proof that requirements pertaining to a research method have been complied with and that the obtained result will be reliable, dependable and consistent [4, 5, 6]. This means that it has to be proven that it is possible to determine the parameters characterising a given method, and then use

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such a determination to conclude if the method is useful and meets the requirements. The validation is always a balance between costs, risk and technical capabilities of a laboratory. The validation of chemical methods is widely described in the references [7, 8, 9]. In the case of validation of physical properties testing, particularly of rock materials, the literature does not give too much detail. It is difficult to find specific examples of compatibility assessment of test results, accounting for dispersion and the necessity to perform tests on a few or even a few dozen specimens from the same batch. The unique character of testing the physical and mechanical properties of rock lies in the fact that there is a large variability of rock parameters within a single formation or even a deposit. The standards require that individual tests be made on a specific number of specimens representing a material, and the results be given as an arithmetic mean or a higher/lower expected value, accounting for the dispersion of results and the specimen size.

The paper presents mathematical formulas allowing for an evaluation of the precision of research methods and the consistency of results which are a basis of the testing method validation. The practical part uses an example of apparent density determination in a validation of a proprietary method based on the analysis of repeatability, intralaboratory reproducibility and interlaboratory reproducibility.

2 Testing Method Design and Assessment Criteria

The development of a testing procedure should particularly account for a correct identification and scope of a given property and description of the object to be tested. The requirements for the measuring instruments should be defined in terms of the equipment and environment conditions, the instruments need to be calibrated, and standards and reference materials should be used, if applicable. The research procedure description must also indicate the data to be recorded and the data analysis method, criteria for the evaluation of results, and the algorithm to estimate the uncertainty of results [4, 10].

The following assessment methods can be used to verify the test method applicability:

- calibration or precision assessment using standards or reference materials;
- regular assessment of factors affecting the result;
- research method resistance to variability of controlled parameters;
- comparison of results obtained with different methods;
- interlaboratory comparison;
- results of uncertainty evaluation.

According to the requirements of PN-EN ISO/IEC 17025:2018-02, it is possible to use one assessment method or a combination of methods. The value of parameters characterising the research method accuracy generally depends on the type of tested objects or materials and on the value level of the measured property. The parameters characterising the method accuracy include the dispersion of results and conformity of results with the measured value [6, 7, 9, 10 - 12].

In terms of measures of the dispersion of results, one can mention precision and resistance. The test result precision is evaluated based on repeatability and reproducibility. The repeatability is a degree of conformity of the results of successive measurements of the same magnitude, conducted in the same measurement conditions. The repeatability conditions include the same measurement procedure, the same observer, the same measuring instrument used in the same conditions, the same place and repetition at short time intervals. Reproducibility, on the other hand, is a degree of conformity of the results of measurements of the same magnitude performed at different measurement conditions, including e.g. measurement methods, personnel, measuring equipment, reference standards, place, application conditions and time. There is an interlaboratory reproducibility (results obtained in different laboratories) and intralaboratory reproducibility (results obtained in one

laboratory). The resistance is a measure of the test method capability of providing identical results despite slight changes of the method parameters. The resistance testing involves identification of method parameters which can significantly affect the measurement results, and examination of the impact of small, intentional changes of these parameters on the obtained results. The tested parameters can include environment parameters (e.g. temperature) and/or test method parameters (e.g. a reagent volume).

The parameters characteristic for the assessment of results conformity with the measured magnitude include the method bias (correctness) and selectivity. The test method bias is a difference between the expected test result and the accepted reference value. The selectivity means the method's ability to respond to a correct measured value in the presence of factors that prevent a correct determination. This is a qualitative parameter, and knowing it is particularly important in testing chemical properties. Other method parameters are also important in chemical tests, such as limit of quantification, limit of detection and linearity. The last, very important parameter used to assess the test method is the measurement uncertainty which describes the measured value dispersion.

3 Determination Methods of Apparent (Bulk) Density of Rock Materials

The apparent (volumetric) density is the ratio of the mass of a dried specimen to the specimen total volume including pores.

$$\rho_b = \frac{m_d}{V_b} \tag{1}$$

where:

m_d - dried specimen mass, kg,

V_b-specimen total volume including pores, m^3.

Knowing the rock volumetric density is very important and used, for example, in the determination of other physical and mechanical properties or horizontal and vertical pressures in the rock mass. References [1, 2, 3] mention many apparent density determination methods. Depending on the rock type and condition (firm, cohesive or loose), the following rock volume determination methods can be used:

- displacement of a non-wetting liquid (e.g. mercury) by the specimen:
- direct method on regular specimens,
- covering the specimen with paraffin and immersion in water,
- previous specimen saturation with water,
- testing the specimens of intact cohesive rock in a ring,
- loose rock testing in a cylinder.

The paper analyses the volumetric density determination results obtained with the use of the proprietary procedure and the following standardized methods:

- for natural stone according to PN-EN 1936:2010 [13],
- for stone materials according to PN-B-04100:1966 [14],
- for aggregates according to PN-EN 1097-6:2013 [15].

According to PN-EN 1936:2010 [13], the volumetric density is determined on regular specimens cut with a diamond saw (cylinders, cubes or prisms) of a minimum volume of 60 cm^3. In addition, the area-to-volume ratio should be from 0.08 mm^{-1} to 0.20 mm^{-1}.The test is performed using the hydrostatic method on specimens previously saturated with water. Air is removed from the specimens prior to saturation by maintaining the 2.0±0.7 kPa pressure in the vacuum vessel. The method from PN-B-04100:1966 [14] also refers to cubic or

cylindrical specimens of the side (diameter) equal to 50 mm. The specimen volume is calculated from averaged side (diameter) values. PN-EN 1097-6:2013 [15] is for aggregate testing, however aggregates with grain size above 31.5 mm can be treated as small rock fragments. The method recommended in this standard - the so-called wire-basket method - is based on the hydrostatic method, but all weighing takes place for the entire volume of a given aggregate.

Regardless of the shape and type of the stone material, the volume in the hydrostatic method is determined according to the Archimedean principle as the volume of displaced liquid and i.e. equal to:

$$V_b = \frac{m_s - m_h}{\rho_{rh}} \tag{2}$$

where:

m_s - mass of material totally saturated with water in air, kg,

m_h - mass of material totally saturated with water in water, kg,

ρ_{rh} - water density at test temperature, kg/m^3.

The proprietary procedure is also based on the hydrostatic method, but it differs from the method referenced in the standard [13] in that it is used for testing specimens of irregular (any) shape fragments chipped away from an undisturbed rock. In addition, prior to weighing, the specimens are saturated to obtain constant mass under the atmospheric pressure (the difference in two successive weighings24-hours apart must not exceed 0.1% of the initial mass). Regular specimens from standardized methods will always have the area-to-volume ratio as small as possible, and a smooth surface created by cutting with a diamond saw. On chipped specimens, on the other hand, the surface area will be highly diversified, and the surface will be very rough, sometimes not free of cracks. This results in the collection of a much larger amount of water on the surface and consequently can distort the specimens' volume. The specimens' saturation with water (vacuum in the standard method, and pressure saturation in the proprietary method) does not affect the volume because in both cases the surface pores are closed and do not allow a further specimen saturation during the weighing on a hydrostatic scales. The vacuum specimen saturation is relevant only in the assessment of open porosity.

4 Measures of test method compatibility assessment

The following methods have been applied to check the test results: repeatability and intralaboratory reproducibility, and interlaboratory comparisons taking into account the measurement uncertainty [6, 7, 11, 12].

The repeatability standard deviation is one of the measures of the method accuracy and is determined based on the results of independent repeated measurements of the same object. The repeatability standard deviation is calculated based on many series of results. *J* series with *K* independent repetitions of measurements of the same magnitude were conducted. The measurements in each individual series were performed under the repeatability conditions, but they related to different objects with similar properties (many specimens from the same rock type). The tests were performed using the PN-EN 1936:2010 method on regular specimens, and on irregular specimens according to the test method to be validated. The standard deviation evaluation s_{rj} was calculated for each series based on the obtained x_{jk} results.

$$S_{rj} = \sqrt{\frac{1}{K-1}\sum_{k=1}^{K}\left(x_{jk} - \bar{x}_j\right)^2} \tag{3}$$

where:

$\bar{x}_j$- arithmetic mean from the *j*-th series results under the repeatability conditions.

Then, the repeatability standard deviation (4) and the repeatability limit *r* (5) were calculated:

$$S_r = \sqrt{\frac{1}{J}\sum_{j=1}^{J} S_{rj}^2} \tag{4}$$

$$r = 2.8 \cdot S_r \tag{5}$$

The absolute difference between two results obtained under the repeatability conditions should not be greater than the repeatability limit *r* determined with the 95% probability.

The reproducibility standard deviation was determined for variable conditions but within the same laboratory (intralaboratory reproducibility). Again, *J* series (2 test methods) with *K* independent repetitions of measurements of the same magnitude were conducted. The assessment was performed for the volumetric density testing with the use of various instruments, i.e. the volumetric density test results according to PN-B-04100:1966 [14]) were compared with the results obtained with the use of hydrostatic (proprietary) method. Similar to the repeatability, the standard deviation evaluation S_{Rk} (6) and the reproducibility standard deviation S_R (7) were calculated:

$$S_{Rj} = \sqrt{\frac{1}{K-1}\sum_{k=1}^{K}\left(x_{jk} - \bar{x}_j\right)^2} \tag{6}$$

where:

$\bar{x}_j$ - arithmetic mean from the *j*-th series results under the reproducibility conditions

$$S_R = \sqrt{\frac{1}{J}\sum_{j=1}^{J} S_{Rj}^2} \tag{7}$$

Again, the absolute difference between two results obtained under the reproducibility conditions should not be greater than the reproducibility limit *R* (8):

$$R = 2.8 \cdot S_R \tag{8}$$

The t-Student's test was also used to evaluate the method correctness under the intralaboratory reproducibility conditions. The obtained results were used to calculate mean volumetric density values using the proprietary method $\bar{x}_A$ and the standardized method $\bar{x}_B$, and then the difference $\Delta\bar{x}$. The *t* statistics were calculated to evaluate the statistical significance of this difference (9).

$$t = \frac{|\Delta\bar{x}|}{S_{\Delta\bar{x}}} \tag{9}$$

where:

$S_{\Delta\bar{x}}$ - standard deviation of the difference of the means, equal to (10):

$$S_{\Delta\bar{x}} = \sqrt{\left(S_{RA}^2 - \frac{K_A - 1}{K_A} \cdot S_{rA}^2\right) + \left(S_{RB}^2 - \frac{K_B - 1}{K_B} \cdot S_{rB}^2\right)} \tag{10}$$

where:

S_{rA} and S_{rB} - repeatability standard deviation for methods A and B, respectively,

S_{RA} and S_{RB} - interlaboratory reproducibility standard deviation for methods A and B,

K_A, K_B - number of repetitions in each series.

If the *t* statistics value is greater than that the critical value resulting from the t-Student's distribution for the number of degrees of freedom v_A and v_B of estimators S_{RA} and S_{RB} and the agreed confidence level (usually 95%), then the bias resulting from the various test methods is statistically significant.

The E_n test calculated according to the following formula recommended by ISO [11] (11) is very often used to determine the compatibility of results obtained in different laboratories (PT testing):

$$E_n = \frac{|\bar{x}_A - \bar{x}_B|}{\sqrt{U^2(\bar{x}_A) + U^2(\bar{x}_B)}} \tag{11}$$

where:

$\bar{x}_A$, $\bar{x}_B$ - results of tests of the same specimen obtained inlaboratories A and B,

$U(\bar{x}_A)$, $U(\bar{x}_B)$ - expanded uncertainties obtained inlaboratories A and B.

If the E_n value is less than one, then the results obtained in the two laboratories are consistent.

Both the repeatability and the reproducibility developed at the method validation stage are a basis for estimating the expanded uncertainty of the test result *U(x)*. The measurement uncertainty is a parameter related to the measurement result, characterising the dispersion of values that can be reasonably assigned to the measured magnitude. Such a parameter can be a standard deviation or a coefficient of variation. The laboratory tests use a 95% confidence level and the interval around the test result is built for this probability [10].

5 Comparative Analysis of Volumetric Density Measurements

In order to validate the method proposed in the proprietary procedure, the results for specimens prepared from selected rock materials using the same method (hydrostatic), but of different shapes, were compared, i.e. the density results for regular specimens according to PN-EN 1936:2010) and the results in the test involving a direct measurement of the regular specimen sides(according to PN-66/B-04100). The determination was performed in the same laboratory, using the same equipment and personnel. The measurement accuracy measure used in the analysis was repeatability and intralaboratory reproducibility. In addition, the proficiency test was performed, involving the comparison of results from the proprietary procedure with the results from the other laboratory that measured the density according to the wire-basket method from PN-EN 1097-6:2013. The results were evaluated using the E_n test.

Table 1 includes mean values with the standard deviation estimation for the volumetric density tests of the same materials tested with the use of the standardized method on cubic specimens and with the proprietary method on irregular specimens. These data were used to calculate the repeatability standard deviation for each rock material and the repeatability limit *r*, and also in the conformity assessment. The difference between the mean values of volumetric density determined using the hydrostatic method on regular specimens and on irregular specimens for the same rock materials is in the 2 - 45 kg/m^3 range at the repeatability limits from 29 - 176 kg/m^3. The absolute difference values between the results for individual rock materials did not exceed the values of corresponding repeatability limit s_r.

Table 2 presents the results of volumetric density measurements on rock specimens under the intralaboratory reproducibility conditions.

Table 1. Results under the repeatability conditions and the conformity assessments parameters.

Rock type	Test method	Number of samples	ρ_b [kg/m^3]	S_{rj} [kg/m^3]	S_r [kg/m3]	r [kg/m3]	Δx [kg/m^3]	Assess-ment
Granite	proprietary	50	2612	10	11	29	2	yes
	PN-EN 1936:2010	10	2614	11				
Cergowa sandstone	proprietary	50	2633	19	17	48	20	yes
	PN-EN 1936:2010	36	2653	15				
Basalt	proprietary	50	2890	64	63	176	32	yes
	PN-EN 1936:2010	10	2922	62				
Krosno sandstone	proprietary	8	2548	41	35	97	45	yes
	PN-EN 1936:2010	7	2593	27				

Table 2. Results under the intralaboratory reproducibility conditions and the conformity assessments parameters.

Rock type	Test method	Number of samples	ρ_b [kg/m^3]	S_{Rj} [kg/m^3]	S_R [kg/m3]	R [kg/m3]	Δx [kg/m^3]	Assess-ment
Granite	proprietary	10	2635	32	35	99	14	yes
	PN-66/B-04100	10	2621	38				
Crystalline limestone	proprietary	12	2628	32	40	111	30	yes
	PN-66/B-04100	12	2599	46				
Thick-bedded sandstone	proprietary	8	2548	41	39	108	25	yes
	PN-66/B-04100	14	2523	36				
Thin-bedded sandstone	proprietary	7	2593	27	38	106	2	yes
	PN-66/B-04100	14	2591	46				
Bazalt	proprietary	10	2922	62	62	174	18	yes
	PN-66/B-04100	10	2904	63				
Limestone	proprietary	10	2550	195	141	395	14	yes
	PN-66/B-04100	15	2564	41				

The t statistics from the t-Student's distribution were also used to assess the significance of the difference between the mean volumetric density values determined with two independent methods (Table 2). The statistics parameters for individual rock materials are given in Table 3.

The difference between mean volumetric density values tested under the reproducibility conditions is in the 2-30 kg/m^3 range, at the reproducibility limits from 99 to even 395 kg/m^3. The absolute difference values between the results for individual rock materials did not exceed the corresponding values of reproducibility limits R. In addition, the analysis of the statistical significance of difference between the results did not show the impact of the test method on the results.

The E_n test was used in the case of interlaboratory tests and its values are presented in Table 4.

Table 3. *t*-statistics.

Rock type	$S_{\Delta\overline{x}}$	*t*	Critical value from t-Student's distribution	Assessment
Granite	16	0.88	For the number of degrees of freedom from 6 - 14, it is from 2.1448 to 2.4469	No significant impact on the test results
Crystalline limestone	16	1.83		
Thick-bedded sandstone	17	1.41		
Thin-bedded sandstone	16	0.13		
Basalt	28	0.64		
Limestone	63	0.22		

Table 4. Results and conformity assessment in interlaboratory tests.

	ρ_b [kg/m^3]	S_j [kg/m^3]	$U(x_j)$	E_n	Conformity assessment
Tests according to the proprietary method	2332	45	49	0.36	The E_n<1 results obtained in two laboratories are conforming
Test according to PN-EN 1097-6:2013 at an external lab	2310	-	35		

All analysed cases of the method precision assessment gave similar results, indicating that the suggested volumetric density testing method can be used for determination of these parameters, and the obtained results conform with the results obtained with the use of standardized methods.

6 Summary

The presented analysis aimed at showing the possibility of validation of a testing method for the rock material physical properties. The methodology and the possibilities of assessment of the results obtained using different testing methods, different equipment and even in different laboratories were presented on a simple example of volumetric density determination of rock materials.

The method validation did not show significant differences between mean volumetric density values obtained with the application of various testing methods. It was proven that the initially assumed factors (specimen shape, surface roughness, saturations methods) have no significant impact on the test results. However, as the rock material is very heterogeneous, a sufficient number of specimens of the same material has to be made.

The scientific research often aims at discovering new, hitherto unknown properties, using modern equipment, or testing at unstandardized external or environmental conditions, e.g. extremely high or low temperatures. The results of tests with a method not used to date can be unreliable and inconsistent. In order to support the obtained results and to ensure their correctness, all result-affecting factors must be identified and then the test method must be validated.

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