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APPROACH FOR HOMOGENEITY ASSESSMENT OF GEOLOGICAL REFERENCE MATERIALS

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Abstract: Materials of mineral origin are typically heterogeneous in composition. The material processing for the production of ore and mineral reference materials – RM at CETEM is described. The raw material was submitted to a several processing stages to ensure that individual RM unit meets the requirements for homogeneity and stability for its intended use. After material processing, an experimental homogeneity study was carried out in a subset of twenty RM units, selected from each RM batch, measured by an appropriate measurement procedure, in triplicate, under repeatability conditions, according to a randomized completed block design. This approach aimed to compare the dispersion of results for different RM units with the dispersion under repeatability conditions and determine the between-unit variance, which could then be used to calculate the uncertainty associated with heterogeneity. The evaluation of the experimental homogeneity data for the bauxite certified reference material BXBA-4 is given as an example.
Keywords: geological reference material, material processing, assessment of homogeneity, experimental homogeneity study.

INTRODUCTION

The term certified reference material – CRM is defined in ISO Guide 30 (ISO, 2015) as "material sufficiently homogeneous and stable, characterized, by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability". A CRM is suitable for use in calibrating a measurement system, evaluating measurement procedures, assigning values to similar matrix materials, and in quality control.

The Centro de Tecnologia Mineral – CETEM is accredited as a producer of ores and minerals certified reference material, in accordance with the ISO 17034 standard (ISO, 2016), by the American Association for Laboratory Accreditation - A2LA, a recognition of competence maintained since June 2011. ISO 17034 requires the assessment of the homogeneity of the reference material - RM, packaged in its final form, in order to ensure its suitability for the intended use.

The present work aims to describe the approach adopted by CETEM to ensure "sufficient homogeneity" of the CRM produced.

SAMPLING AND HETEROGENEITY

Sampling of particulate materials such as ores and concentrates is, in the proper sense, a selective process implemented on a given lot in order to reduce its bulk without altering, too much, its other characteristics. In the wider sense, sampling is a multistage operation involving "preparation stages" alternating with "selection stages" also referred to as "sampling stages" ending up with the extraction of one or several analysis samples. The word "preparation" covers all non-selective operations undergone by the lot and the successive samples, such as transfer, crushing, grinding, pulverizing, mixing, drying, etc, in order to bring it at the place and under the form convenient for the next "selection stages". Both sampling and preparation stages are error-generating with the consequence that the "total sampling error" is the sum of the "sampling errors" and "preparation errors" (GY, 1982).

Sampling errors exist because all materials are essentially heterogeneous. Heterogeneity is a primary structural property of all materials of mineral origin. There are two categories of heterogeneity: (i) the constitution heterogeneity and (ii) the distribution

heterogeneity. The constitution heterogeneity is related to the fragments of a lot under a given state of comminution. It is an intrinsic property of the lot and cannot vary, unless we proceed with a comminution. Mixing and homogeneization have no influence on constitution heterogeneity. On the other hand, the distribution heterogeneity is related to the way in which the fragments are distributed along the lot. If groups or fragments selected from the lot don´t have the same average composition, the lot has a heterogeneous distribution. Distribution heterogeneity can be diminished by homogeneization or mixing, or it can be increased by promotion segregation (PITARD, 1993).

MATERIAL PROCESSING

The material processing aims to ensure that the material meets the requirements for homogeneity and stability of the RM for its intended use. The bulk material is submitted to a several processing stages to obtain individual RM units containing sufficient material for multiple measurements with mass and maximum particle size suitable for carrying out chemical tests.

CETEM's Certified Reference Material Program – PMRC laboratory is dedicated to the mineral samples reference material processing, being fully equipped for handling large amounts of material, preventing from contamination among samples as well as from outside sources, and a qualified technical team that is committed to ensuring the quality of the reference materials produced.

The raw material, after stabilization by drying in the air or in an oven, was subjected to one or more stages of crushing, pulverizing and sieving to pass a 0.075 mm screen (0.150 mm for bauxite). A thorough homogenization of the dry powdered material batch was carried out, prior and during the sampling scheme by means of quartering and several passages of the material through a rotary divider. Sampling is made by taken every element of the cross-section of the flowing stream of material at the discharge of a conveyor intercepted at regular intervals by an intermittent cutter, in accordance with Pierre Gy's theory (GY, 1976). Final samples were split into RM units containing around 100 g of powdered material, which were properly packaged and uniquely identified. Figures 1 and 2 show respectively a partial view of the PMRC laboratory and the rotary dividers used in the increment sampling process.

Figure 1. Partial view of the PMRC laboratory

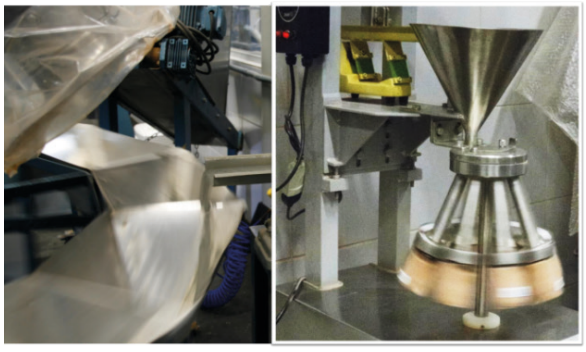

Figure 2. Rotary dividers used in the Increment sampling process

ASSESSMENT OF HOMOGENEITY

Homogeneity can refer either to variation of property value between separate units of the RM, or to variation within each unit. It is always necessary to assess the between-unit variation. After material processing, the magnitude of between-unit differences is expected to be small or even negligible

comparing to the uncertainty arising from the characterization of the material using two or more methods of demonstrable accuracy using a network of competent laboratories. However, it is recommended to perform an experimental homogeneity study in order to compare the dispersion of results for different RM units with the dispersion under repeatability conditions and determine the between-unit variance, which can then be used to calculate the uncertainty associated with heterogeneity (ISO, 2017).

To undertake an experimental homogeneity study, a subset of twenty units was selected from each RM batch using a random stratified sampling scheme. Three subsamples were taken from each unit and individually prepared for measurement under repeatability conditions. In this design, the variance within units includes the variation due to subsampling, preparation and measurement and none of these effects will contribute to the estimated between-unit variance. Figure 3 shows the layout of the between-unit homogeneity study.

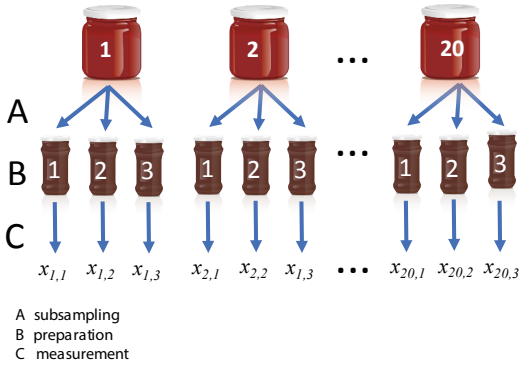

Figure 3. Layout of a between-unit homogeneity study

As all RM units could not be measured, in triplicate, in a single day, due to time constraints or instrumental constraints, the measurements were conducted in three days, each RM unit being measured once in each day, according to the homogeneity study measurement scheme shown in Table 1.

Measurement sequence	Day 1	Day 2	Day 3
	Unit/ replica	Unit / replica	Unit / replica
1	CQ1 / replica 1	CQ1 / replica 2	CQ1 / replica 3
2	134 / replica 1	4439/ replica 2	455/ replica 3
3	675 / replica 1	4285 / replica 2	921 / replica 3
4	1078 / replica 1	3956 / replica 2	1199 / replica 3
5	1498 / replica 1	3855 / replica 2	1636 / replica 3
6	2064 / replica 1	3548 / replica 2	2175 / replica 3
7	2320 / replica 1	3324 / replica 2	2651 / replica 3
8	2814 / replica 1	3048 / replica 2	3048 / replica 3
9	3324 / replica 1	2814 / replica 2	3548 / replica 3
10	3855 / replica 1	2651 / replica 2	3956 / replica 3
11	4285 / replica 1	2320 / replica 2	4439 / replica 3
12	455 / replica 1	2175 / replica 2	134 / replica 3
13	921 / replica 1	2064 / replica 2	675 / replica 3
14	1199 / replica 1	1636 / replica 2	1078 / replica 3
15	1636 / replica 1	1498 / replica 2	1498 / replica 3
16	2175 / replica 1	1199 / replica 2	2064 / replica 3
17	2651 / replica 1	1078 / replica 2	2320 / replica 3
18	3048 / replica 1	921 / replica 2	2814 / replica 3
19	3548 / replica 1	675 / replica 2	3324 / replica 3
20	3956 / replica 1	455 / replica 2	3855 / replica 3
21	4439 / replica 1	134 / replica 2	4285 / replica 3
22	CQ2 / replica 1	CQ2 / replica 2	CQ2 / replica 3

Table 1. Homogeneity study measurement scheme

Fused pellet / XRF measurement procedure was chosen mainly due to its good precision during the expected duration of each measurement run i.e. a small repeatability standard deviation. However, this procedure is not suitable for every property of interest. In the case of the bauxite RM, in order to include almost every property of interest in the homogeneity study, measurement procedures requiring extensive, multi-stage, sample preparation were also used as caustic digestion / titrimetry (available alumina), caustic digestion / flame atomic absorption spectrometry (reactive silica), caustic digestion – combustion– oxidation / infrared spectrometry (total organic carbon) and

drying / thermal gravimetric analysis (loss of mass at 1000 ºC). Table 2 shows the measurement procedures used and the properties of interest studied experimentally, for each CRM.

For the bauxite reference material, 93 % of the properties certified in the collaborative study to characterize the RM, were also included in the experimental homogeneity study. However, for reference materials with a large set of properties of interest, an experimental homogeneity study for every property may be burdensome both economically and physically and, in some cases unfeasible.

For the jarosite and tertiary mud mining waste CRM, with respectively 52 and 54 property values certified, only 46 % and 33 % of the properties certified, respectively, were included in the experimental homogeneity study. On the other hand, the homogeneity between-unit could be assessed during the RM characterization involving multiple laboratories using two or more independent methods for each property of interest, measuring different units of an RM.

EVALUATING THE HOMOGENEITY STUDY

Initially, the experimental data was inspected for measurement and processing trends. Outliers could be identified by visual inspections by using graphical consistency technique called Mandel's h and k statistics (ISO, 2019). After investigation into the cause of the outlying values, more than one such observation could be discarded.

A randomized completed block design involved twenty RM units with 3 replicates, with one replicate per unit per run and 3 runs, in random order. Two-way analysis of variance without replication was applied to estimate the within- and between-unit standard deviations independently of the run effect (MONTGOMERY, 1976).

Analysis of variance led to a between-run mean square M_{block} together with a between-unit mean square $M_{between}$ and a residual mean square M_{within}. The residual mean square is an unbiased estimate of the repeatability variance it s_r^2. The between-unit standard deviation s_{bb} was calculated as in Equation 1, where n is the number of replicates per RM unit.

$$s_{bb} = \sqrt{\frac{M_{between} - M_{within}}{n}} \quad (1)$$

There were cases where the measurement procedure were not sufficiently repeatable resulting in negative values for s_{bb}. In such cases, an alternative approach that accounts for insufficient repeatability of the measurement procedure were used (Linsinger et al., 2001). The uncertainty associated with between-unit heterogeneity u_{bb}^* was calculated as in Equation 2, where ν_{within} are the degrees of freedom of the residual mean square.

$$u_{bb}^* = \sqrt{\frac{M_{within}}{n}} \sqrt{\frac{2}{\nu_{within}}} \quad (2)$$

The largest value between s_{bb} and u_{bb}^* was used as an estimate of the between-unit heterogeneity uncertainty u_{bb}.

To check for sufficient homogeneity, the contribution of between-unit heterogeneity u_{bb} to the relative robust estimate of the standard deviation of laboratory averages from the characterization study s_d was calculated as in Equation 3.

$$u_{bb} / s_d \quad (3)$$

Table 3 shows the results of evaluation of the homogeneity study for the bauxite CRM BXBA-4.

The measurement procedure in the homogeneity study used was sufficiently repeatable, except for available alumina, Fe_2O_3 and loss of mass. In such cases, the between-

CRM	Measurement procedure	Properties studied
Bauxite	Fused Pellet/XRF	Al_2O_3, Cr_2O_3, Fe_2O_3, K_2O, MnO_2, P_2O_5, SiO_2, TiO_2, V_2O_5, ZrO_2,
	Caustic Digestion/TIT	Available alumina
	Caustic digestion/FAAS	Reactive silica
	Combustion/IR	Total organic carbon
	TGA	Loss of mass (1000 ^{O}C)
Copper ore	Fused Pellet/XRF	Al, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Si, Ti
Copper concentrate	Fused Pellet/XRF	Al, Ca, Cu, Fe, K, Mg, Mn, Na Ni, P, S, Si, Ti
Mining waste - Jarosite	Fused Pellet/XRF	Ag, Al, As, Ba, Ca, Cd, C, Cu, Fe, K, Mg, Mn, Mo, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl , Zn
Mining waste - Tertiary mud	Fused Pellet/XRF	Al, Ba, Ca, Cd, C, Cr, Cu, Fe, K, Mg, Mn, Ni, P, S, Si, Sr, Ti, Zn

Table 2. Measurement procedures and property of interest studied experimentally

Property	Certified value (%m/m)	s_r (%m/m)	s_{bb} (%m/m)	u^*_{bb} (%m/m)	u_{bb} (%m/m)	$u_{bb\,rel}$ (%)	s_d (%m/m)	$u_{bb}\,/\,s_d$
Available alumina	43.7	0.2	nc	0.05	0.05	0.1	0.5	0.11
Reactive silica	4.53	0.06	0.03	0.02	0.03	0.7	0.2	0.16
Al_2O_3	49.7	0.1	0.03	0.03	0.03	0,1	0.6	0.05
Fe_2O_3	12.8	0.08	nc	0.02	0.02	0.2	0.1	0.19
$SiO_{2\_}$	8.45	0.03	0.01	0.007	0.03	0.1	0.2	0.08
$TiO_{2\_}$	1.55	0.02	0.009	0.006	0.009	0.6	0.04	0.22
$ZrO_{2\_}$	0.028	0.001	0.0005	0.0004	0.0005	1.8	0.04	0.13
P_2O_5	0.195	0.0008	0.0004	0.0002	0.0004	0.2	0.006	0.07
V_2O_5	0.023	0.0007	0.0004	0.0002	0.0004	1.7	0.004	0.09
MnO_2	0.035	0.0005	0.0001	0.0001	0.0001	0.4	0.006	0.02
Total organic carbon	0.28	0.007	0.0005	0.002	0.002	0.7	0.08	0.02
Loss of mass (1000 ^{O}C)	27.3	0.3	nc	0.09	0.09	0.3	0.2	0.51

Table 3. Evaluation of the homogeneity study for the bauxite BXBA-4

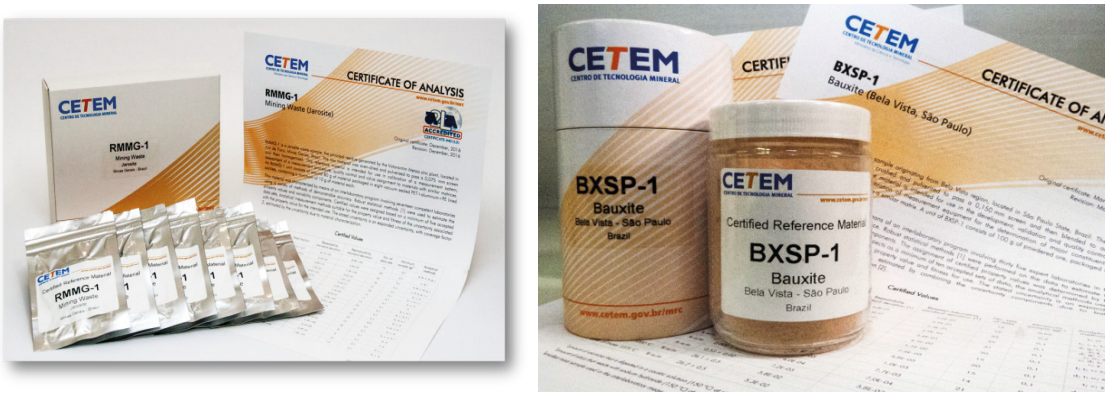

Figure 4. Units of BXSP-1 - bauxite (Bela Vista) and RMMG-1 – mining waste (Jarosite)

unit standard deviation s_{bb} couldn´t be calculated (nc) and the approach that accounts for insufficient repeatability was used to estimate the between-unit heterogeneity u_{bb}^{*} . The most conservative estimate of the between-unit heterogeneity u_{bb} , with relative values less than 2%, confirmed the efficiency of the material processing. Furthermore, except for loss of mass, the between-unit heterogeneity uncertainty u_{bb} was at most 0.2 s_d , indicating that the uncertainty due to any unit-to-unit differences is already reflected in the lab-to-lab differences, as quantified in the uncertainty of characterization.

WITHIN-UNIT HETEROGENEITY

The intended use of geological reference materials always permits the use of a small portion of the RM unit. Therefore, it is also usually necessary to provide instructions for use that control the impact of within-unit heterogeneity (ISO, 2017).

The CETEM´s CRM certificates include instructions for mixing the contents of the unit, by rolling the unit, before taking samples. It is also highlighted that the sample mass for analyses should not be less than the minimum sample size used in the material characterization and that the property value and its associated uncertainty are only guaranteed if the minimum sample size is respected.

For the bauxite, copper sulphide ore and concentrate CRMs, one unit consists of approximately 100 g of powdered material, packaged in a glass bottle. For the jarosite and tertiary mud mining wastes, one unit consists of around 90 g of material packaged in eight vacuum sealed PET+aluminum+PE lined sachets, containing a minimum of 11 g of material each. Figure 4 shows the BXSP-1 and RMMG-1 units and their respective certificates.

CONCLUSIONS

The approach adopted to evaluate homogeneity proved to be suitable for the production of geological material certified reference materials. The measurement procedures used in the experimental homogeneity studies were, in most cases, sufficiently precise for the assessment of homogeneity. Estimates of between-unit heterogeneity less than 2%, confirm the effectiveness of material processing. The contribution of heterogeneity to the characterization uncertainty, although significant, is not dominant, which indicates the adequacy of the certified values uncertainties.

AUTHORIZATION/ ACKNOWLEDGMENT

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this article.

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