

Preparation and characterization of phosphate rock as quality control material

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Received: 8 June 2017 / Accepted: 11 October 2017
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Abstract A quality control material for inorganic constituents present in a phosphate-bearing rock used to manufacture phosphate fertilizers was produced and characterized according to the ISO Guide 80. The evaluation of the estimated minimum mass, homogeneity, and stability of the material was performed using microwave-assisted digestion and inductively coupled plasma optical emission spectrometry (ICP-OES) as an in-house validated technique for determination of Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, V, and Zn. Phosphorus mass fraction determination was done by laser-induced breakdown spectroscopy. The accuracy of the measurement results was confirmed by analyzing the certified phosphate rock and fertilizer certified reference materials according to NIST SRM 694 and SRM 695. One-way analysis of variance (ANOVA) was applied to the measurement data, and the homogeneity and stability of the material presented averages within the 95 % confidence interval. The results from the preparation and with collaborative trial allowed the calculation and estimation of the consensus value and its expanded measurement uncertainties, obtained by combining the uncertainty contributions from characterization (u_{char}), between-bottle homogeneity (u_{bb}), short-term

stability (u_{sts}), and long-term stability (u_{lts}) for each evaluated analyte mass fraction.

Keywords Phosphate rock · Quality control material · ICP-OES · Analysis of variance · Uncertainty

Introduction

According to data from the Brazilian Ministry of Agriculture (MAPA), agricultural activities represent 23 % of total Brazilian economic output so far in 2017. Moreover, in recent years there has been an expansion not only of crops and livestock, but also the production of inputs such as fertilizers and soil amendments, which can have negative environmental impacts [1–3]. These impacts need to be controlled, and one of the ways to do this is by using accredited measurement procedures, to guarantee the accuracy of the measurement result [4]. To assure metrological traceability and desired reliability, laboratories must have quality and certification procedures [4–6]. Such measures include the use of validated methods of analysis and internal quality control procedures involving reference material (RM) and certified reference material (CRM), as well as external quality assurance procedures such as participation in collaborative trials [7].

The importance of CRMs is incontestable. However, the main problem is that there are very few CRMs available to meet the demands in all sectors, especially agricultural and food products, which are among those most needing CRMs [8, 9].

Reference materials that have properties with comparable chemical composition for analysis are necessary to evaluate some merit values for method validation. Finding a RM analogous to the evaluated sample with analytes

Electronic supplementary material The online version of this article (doi:10.1007/s00769-017-1295-3) contains supplementary material, which is available to authorized users.

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having concentration levels of the same order of magnitude, is a difficult task especially for agricultural products produced in tropical climates, with characteristics different from those produced in temperate areas, where suppliers of the commercial reference materials are usually located [10]. As an effort to obtain more appropriate control of measurement results, Embrapa, the Brazilian Agricultural Research Corporation, is developing agriculture reference materials with a close correspondence, with analyte and matrix, suitable for data quality control of inorganic constituents [11].

This paper describes the preparation and characterization of a phosphate rock quality control material (QCM) developed according to the ISO Guide 80 [12], including the results obtained in an interlaboratory comparison regarding the mass fraction of fifteen analytes. The ISO Guide 80 described the QCM “to have a RM representing as closely as possible routine samples, suitable for quality control; to have a suitable day-to-day RM to complement a commercially available CRM, and no suitable CRM exists.” The QCM production follows the details in ISO Guides 34 and 35 [12–14]. The sample preparation and interlaboratory comparison were performed at Embrapa Pecuária Sudeste with auxiliary input from outside laboratory experts. Participating laboratories were essential for reference values achievement of QCM. To evaluate the homogeneity and stability of the resulting materials, a fit-for-purpose method for the determination of Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, V, and Zn was validated in-house. The results obtained during the preparation and interlaboratory comparison allowed the chemical characterization, uncertainties regarding of each stage for preparation of QCM and the expanded uncertainties for each evaluated analyte.

Experimental

Reagents, solutions, and samples

All reagents used were of analytical grade, and the solutions were prepared using high-purity water (18 M Ω cm resistivity), obtained from a Milli-Q[®] water system (Millipore, Billerica, MA, USA). All glassware, including amber glass bottles to package samples and polypropylene flasks, was washed with soap and soaked for 24 h in 10 % by volume HNO₃, rinsed with deionized water, and dried in a laminar flow hood. High-purity nitric acid prepared at 65 % by volume (Carlo Erba Reagenti, Milan, Italy) by sub-boiling distillation system (BSB-939-IR, Berghof, Eningen, Germany) and 30 g/dL H₂O₂ (Synth, Diadema, SP, Brazil) were used for sample preparation.

The measurement calibration solutions (As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, V, and Zn) were prepared from mono-element solutions containing 1000 mg L⁻¹ (TecLab, Jundiaí, SP, Brazil). These solutions are traceable to NIST reference solutions. Liquid argon was used as purge and plasma gas (99.999 % purity, White Martins, Sertãozinho, SP, Brazil). Western phosphate rock, SRM 694, and trace elements in multi-nutrient fertilizer, SRM 695, from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were the CRMs used to accuracy evaluation.

For the QCM production, 10 kg of phosphate rock (apatite) from Morocco, a commercial product purchased from a local market in São Carlos, São Paulo state, Brazil, was used.

Instrumentation

The sample was ground in a stainless steel multi-use laboratory grinder (Marconi model MA 630/1, Piracicaba, Brazil). According to the Brazilian Manual of Official Analytical Methods for Fertilizer and Correctives for phosphate fertilizers [15], after grinding the material was placed in an electromagnetic stirrer equipped with 150 μ m mesh sieve (Bertel, Caieiras, SP, Brazil), homogenized in a “Y” shaped polytetrafluorethylene coated bowl (Model MA 201/5MO Marconi, Piracicaba, Brazil), and randomly bottled after division in a PT-100 rotary divider (Retsch Technology, Haan, Germany). Grain size distribution smaller than 150 μ m was determined with an Analysette 22 device (MicroTec Plus, Fritsch, Idar-Oberstein, Germany).

The phosphate rock acid digestion was performed using a microwave cavity oven with perfluoroalkoxy alkanes (PFA) in closed vessels (Ethos 1, Milestone, Sorisole, BG, Italy) equipped with sensors for pressure and temperature control.

The determination of analytes concentration in solution was performed by ICP-OES with an iCAP 6000-series dual-view emission spectrometer (Thermo Fisher Scientific, Waltham, MA, USA), operating in radial and axial view mode and equipped with simultaneous CID detector and Echelle grating.

Preparation of the quality control material

The original/starting sample of phosphate rock was divided into two buckets and homogenized using the “Y” shaped blender/homogenizer. Approximately 5 kg of the sample was placed into each bucket and stirred for 20 min. This procedure was repeated three times to ensure homogeneity of the sample. Then, fractions of the sample were randomly placed by a rotary divider in 100 previously demineralized amber glass bottles (100 g) with screw caps and packaged

in zippered metallized polyethylene terephthalate/low-density polyethylene stand-up pouches (metallized PET/LDPE). The material in one randomly selected bottle was subjected to particle size distribution testing.

Sample preparation and mass fraction determination

The mass fractions of the analytes were determined based on dry mass, involving the removal of adsorbed moisture by heating 1 g of the sample for 2 h at 105 °C. The samples were immediately transferred to desiccators containing freshly dried silica gel and stored in their original, tightly sealed bottles away from intense heat sources.

A series of preliminary in-house experiments were undertaken to evaluate the adequate sample preparation and quantification methods and to define the material's homogeneity and stability. We used two CRMs (SRM 694 and SRM 695) to estimate the measurement bias. The CRMs and the QCM of phosphate rock were submitted to microwave-assisted digestion using HNO₃ and H₂O₂. Sample masses of approximately 200 mg were accurately weighted directly in PFA digestion vessels to receive 6.0 mL of a solution of 7 mol L⁻¹ HNO₃ and 2.0 mL of 30 g/dL by volume of H₂O₂ in each bottle. The digestion of the samples was performed according to the following heating program with power, final temperature, ramp duration: (1100 W, 200 °C, 20 min), (1100 W, 200 °C, 20 min), and (0 W, 10 min) [16]. The digestion flasks cooled down to room temperature, and the solution was quantitatively transferred to volumetric vials and diluted with ultrapure water to a final volume of 20.0 mL. This procedure was performed in triplicate. The samples were centrifuged for 5 min at 200 g, and the supernatant was separated for mass fraction determination by ICP-OES.

Homogeneity testing

The influence of the sample mass on the homogeneity of the QCM was evaluated by analyzing seven replicates of different masses, ranging from 100 mg to 200 mg with precision of ± 0.001 mg, and the results were evaluated based on the standard deviation of the measurement results. For the between-bottle homogeneity assessments [17], ten bottles of QCM were randomly taken and each one analyzed in triplicate. For the within-bottle homogeneity evaluation, ten subsamples were collected from one bottle of QCM prepared and analyzed in seven replicates [14]. In these tests, the variation represents the random variation of the prepared material batch. Statistical evaluation of results was obtained using ANOVA, and the homogeneity was evaluated by the Fisher test (*F* test). All experiments were performed to determine the mass fractions of the elements

Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, V, and Zn.

Short- and long-term stability of the quality control material

To evaluate the short-term stability, three bottles of the QCM were randomly selected and submitted to extremes of humidity and temperature. The samples were placed inside a large glass jar with a platform allowing filling of water in the bottom. This apparatus remained in an oven for 30 days, with controlled temperature of 40 °C and 100 % relative humidity. The samples were analyzed in triplicate before and at the end of the experiment (after 30 days) for the mass fraction determination of the elements [17, 18].

Long-term stability was also analyzed with the use of three bottles randomly selected and stored at room temperature [17]. The quantification of the analytes was performed monthly in triplicate during 9 months for all analytes except for P, which was analyzed for 3 months.

Results and discussion

Grain size distribution

Figure 1 shows the sample size homogeneity and particle size distribution profile, indicating that around 9 kg of the sample presented particle sizes of about 150 μm, after milling in the multi-use laboratory grinder.

Method validation

The measurement procedure was applied for homogeneity and stability studies, previously validated in-house. The performance parameters evaluated included selectivity, linearity and working range, limits of detection (LOD) and quantification (LOQ), trueness, method repeatability and

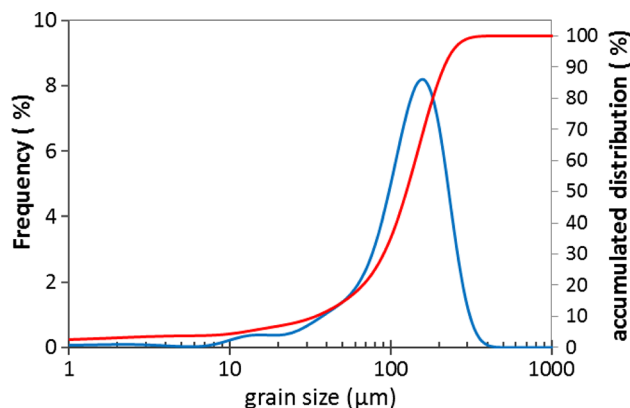


Fig. 1 Phosphate rock QCM grain size distribution

stability of the extracts. Each day of the validation, a blank (no matrix) was prepared and analyzed to check for any possible reagent or material cross-contamination.

The measurement of bias of the method used for the elemental quantification by ICP-OES and LIBS was confirmed by analyzing the western phosphate rock (NIST 694) and trace elements in multi-nutrient fertilizer (NIST 695) CRMs. The analysis of these CRMs was performed using the same procedure as applied to the samples of QCM. The results of the paired *t* test at 95 % confidence demonstrated that this method is statistically satisfactory for the determination of all elements involved in the certification process.

Results of homogeneity testing

All samples were analyzed under repeatability condition to assure that all samples were quantified against the same calibration. To evaluate the minimum mass allowing quantification of all analytes investigated here (Al, As, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, V, and Zn), samples of various masses in the range from 100 mg to 200 mg of the same randomly chosen bottle were evaluated. ANOVA was applied to the real data matrix at 5 % significance, as recommended by ISO Guide 35 [14]. It was possible to observe a decrease in relative standard deviation (RSD) value with the increase in mass used for analysis (Table 1). According to the ANOVA results, the elements showing critical *F* value smaller than calculated *F* value did not present significant differences between the evaluated masses, which indicates that the use of any of the portions

studied in the test will not contribute significantly to the uncertainty values. However, the minimum mass was defined to homogenize the obtained data, using the lowest RSDs, and thus, the mass of 200 mg was established for subsequent studies. It should be emphasized that according to the ISO Guide 33 [19], the researcher should be aware that using test portion that does not meet or exceeds the minimum sample mass specified can significantly increase the contribution of QCM inhomogeneity to the uncertainty of the specified property, to the point where the statistical parameters of the certification are not valid [10]. Table 1 reports the mass fractions of the evaluated analytes in the QCM obtained with different sample masses analyzed by ICP-OES, after sample decomposition.

During the development of QCM, the homogeneity test should be designed to ascertain the variance due to the possible inhomogeneity of the analytes in the packed material. To determine the homogeneity of the QCM, all data are statistically evaluated by using ANOVA. The null hypothesis H_0 is used when there is no significant difference at the 95 % confidence interval between the values of measurements in each of the ten sample bottles, and the alternative hypothesis H_1 is used when there is a significant difference. Also, the results need to be within a confidence interval of 95 % between the values of the determinations in each of the ten bottles sampled. When the critical *F* value is greater than the calculated *F* value, the null hypothesis is accepted and the material is considered homogeneous. In turn, when the critical *F* value is smaller than the calculated *F* value, the null hypothesis is rejected and the material is not classified as homogeneous. We

Table 1 Mass fraction (mean \pm standard deviation (SD); $n = 3$; mg kg^{-1}) for analytes in the phosphate rock quality control material obtained with different sample masses (m_s)

Analytes	$m_s = 100$ mg		$m_s = 150$ mg		$m_s = 200$ mg	
	Mean \pm SD	RSD (%)	Mean \pm SD	RSD (%)	Mean \pm SD	RSD (%)
Al	2514 \pm 56	2.21	2568 \pm 66	2.58	2581 \pm 48	1.87
As	13.07 \pm 0.29	3.52	13.49 \pm 0.27	2.01	13.49 \pm 0.13	0.99
Ca	37.76 \pm 5.51	14.60	36.47 \pm 1.10	3.03	33.90 \pm 2.59	7.64
Cd	17.33 \pm 0.42	2.63	17.33 \pm 0.34	1.98	16.81 \pm 0.18	1.07
Cr	176.8 \pm 3.8	2.14	178.9 \pm 4.5	2.49	176.6 \pm 2.6	1.45
Cu	30.23 \pm 0.62	2.06	29.2 \pm 0.54	1.83	29.05 \pm 0.33	1.15
Fe	1366 \pm 34	2.48	1386 \pm 37	2.68	1341 \pm 20	1.46
K	938 \pm 15	1.65	886 \pm 16	1.79	867 \pm 14	1.59
Mg	2137 \pm 49	2.28	2096 \pm 51	2.43	2040 \pm 20	0.98
Mn	8.43 \pm 0.77	9.08	9.03 \pm 0.75	8.27	9.25 \pm 0.90	9.68
Na	4586 \pm 101	2.21	4613 \pm 106	2.30	4618 \pm 74	1.59
Ni	32.89 \pm 0.76	2.32	33.81 \pm 0.80	2.37	34.14 \pm 0.49	1.42
V	164.7 \pm 3.3	2.01	163.1 \pm 3.4	2.06	160.4 \pm 1.9	1.16
Zn	231.2 \pm 4.9	2.14	234.0 \pm 4.6	1.97	230.7 \pm 2.5	1.09

obtained calculated F values smaller than the critical F value (2.39 at 0.05 significance) for all the evaluated elements, demonstrating there were no significant differences between the variances obtained using a sample mass of 200 mg (Table 1).

The uncertainty due to inhomogeneity arising from between-bottle, within-bottle, and homogeneity tests, for all the quantified elements, is shown in Table A1 in Electronic Supplementary Material (ESM) to this article.

Results of short- and long-term stability of the quality control material

The stability of the trace element content was tested to determine the suitability of this material as QCM. The short-term stability study simulates handling conditions, ensuring that the material will not degrade due to changes in temperature and humidity during transport, for example. Temperature variation is a key factor in the deterioration of the material, and therefore, the flasks with the material were kept at different temperatures and analyzed at various time intervals to verify possible changes in the material's properties.

The single-factor ANOVA with a significance level of 5 % ($\alpha = 0.05$) was used in the analyses to check the short-term stability of the QCM. From the obtained results, it can be seen that all analytes presented no statistically significant differences and can be considered stable. These data are shown in Table A2 in ESM.

The long-term stability simulates the shelf life, to verify whether the QCM can be stored under defined conditions, such as at room temperature. Stability tests are also used to estimate the contribution of measurement uncertainty associated with material stability as well as to define storage and transport conditions.

Also, the single-factor ANOVA with a significance level of 5 % ($\alpha = 0.05$) was used for analyses to check the stability of the QCM in long-term storage. The results presented no statistically significant differences and can be considered stable. These data are shown in Table A3 in ESM.

The stability of the QCM was assessed by regression analysis of the data obtained from each measurement versus time in months, as described in the ISO Guide 35:2006 [14]. According to this, a significant slope indicates the parameter changed with time, i.e., degree of instability, while the absence of a significant slope means the material is stable during the evaluated period. The associated uncertainties were considered [20].

Consensus value

The QCM was characterized by a consensus value obtained from an interlaboratory comparison. A bottle of prepared material and a form with the instructions to carry out the

determinations were sent to 17 laboratories that accepted the invitation to participate in the interlaboratory comparison. The laboratories, all with ISO 17025 certification, belong to network of MAPA (Brazilian Ministry of Agriculture) and were selected according to their competence. The laboratories used their own validation procedures, with six replicates, and sent the results to us on a pre-established schedule. An attempt was consciously made to get good results, using three independent measurement procedures for sample preparation (HNO_3 7 mol L⁻¹, H_2O_2 and microwave-assisted digestion, ultrasonic digestion or official methods of MAPA for each analyte [15]) as well as different detection techniques. Table 2 shows the different sample preparation and analysis techniques used for each analyte.

The statistical analysis was conducted based on ISO/IEC 17043:2010 [21], using the z -score for the accuracy assessment, as described in the ISO Guide 35 [14]. Some outliers (data points far above or below the mean value of what is being observed or measured) were found and removed to obtain the consensus value. The Grubbs test at 95 % confidence level was employed to identify potential outliers among individual replicate results or bottle averages [22].

By applying the z -score, it was possible to observe reproducibility problems (interlaboratory variation) for some analytes and laboratories, with results outside those established for the statistical parameters. These results were excluded from the uncertainty calculation associated with the characterization of the QCM after both the Grubbs test and z -score confirmed they were outliers.

After removing outliers, the Horwitz [23] and Thompson [24] models were adopted for the estimation of the standard deviation for the proficiency assessment (σ_p).

Estimated mass fractions in the final sample with associated uncertainties

The measurement uncertainty ensures better confidence in the validity of the measurement result. A value with its uncertainty allows evaluating the accuracy of an analytical method. Table 3 presents the uncertainty values associated with the characterization pattern (u_{char}), between-bottle homogeneity (u_{bb}), short-term stability (u_{sts}), long-term stability (u_{lts}), and expanded uncertainty, used to define the measurement uncertainty of a reference value (U_{QCM}), which was calculated as described in Eq. 1, where $k = 2$ (for 95 % confidence interval).

$$U_{\text{QCM}} = k \sqrt{u_{\text{char}}^2 + u_{\text{bb}}^2 + u_{\text{sts}}^2 + u_{\text{lts}}^2} \quad (1)$$

Estimated mass fractions of targets analytes in the final phosphate rock material were calculated from the results obtained by the interlaboratory comparison, final expanded

Table 2 Summary of procedures for reference values used by the laboratories during the interlaboratory comparison

Analyte	Sample preparation	Analytical technique
Al	AD	ICP-OES
As	AD and UD	ICP-OES, GF-AAS, INAA
Ca	OM and UD	FAAS, ICP-OES, MIP-OES
Cd	AD, OM and UD	FAAS, ICP-OES, MIP-OES
Cr	AD, OM and UD	GF-AAS, FAAS, ICP-OES, INAA
Cu	OM	FAAS, MIP-OES, ICP-OES
Fe	AD, OM and UD	FAAS, ICP-OES, INAA
K	OM and UD	FAAS, FAES, ICP-OES
Mg	OM and UD	FAAS, MIP-OES, ICP-OES
Mn	OM and UD	FAAS, MIP-OES, ICP-OES
Na	OM	FAAS, MIP-OES, ICP-OES, INAA
Ni	AD, OM and UD	FAAS, ICP-OES
P	OM and UD	Gravimetry, LIBS
V	AD	ICP-OES
Zn	OM and UD	FAAS, MIP-OES, ICP-OES, INAA

AD: acid digestion HNO_3 (7 mol L^{-1}) + H_2O_2 ; OM: [15] official methods of MAPA; UD: ultrasonic digestion; FAAS: flame atomic absorption spectrometry; ICP-OES: inductively coupled plasma optical spectrometry; MIP-OES: microwave-induced plasma optical emission spectrometry; INAA: instrumental neutron activation analysis; LIBS: laser-induced breakdown spectroscopy; GF-AAS: graphite furnace-atomic absorption spectroscopy; FAES: flameatomic emission spectroscopy

Table 3 Estimates of standard uncertainties of characterization (u_{char}), between-bottle homogeneity (u_{bb}), short-term stability (u_{sts}), long-term stability (u_{lts}), and expanded uncertainty (U_{QCM}), where $k = 2$ (for 95 % confidence interval) for the mass fraction of each element in the QCM

Analyte [mass fraction; mg kg^{-1}]	u_{char}	u_{bb}	u_{sts}	u_{lts}	U_{QCM}
Al	25.4	24.6	27.9	51.4	137
As	3.59	0.12	0.19	0.43	7.25
Ca [g (100 g)^{-1}]	2.61	0.32	0.48	0.90	5.64
Cd	1.43	0.19	0.25	0.36	3.02
Cr	5.89	1.64	2.56	6.74	18.9
Cu	6.29	0.27	0.24	0.57	12.6
Fe	8.79	9.56	16.8	22.7	62.1
K	8.72	8.18	12.5	19.2	51.7
Mg	19.2	26.0	28.9	50.1	132
Mn	3.09	0.34	1.24	0.84	6.90
Na	27.8	38.3	51.9	117	273
Ni	4.00	0.40	0.69	0.95	8.38
P [g (100 g)^{-1}]	1.94	0.09	0.14	0.31	3.94
V	2.78	1.22	2.51	2.65	9.49
Zn	2.74	3.48	3.53	2.98	12.80

Table 4 Phosphate rock reference values associated with expanded uncertainties (mg kg^{-1} and g (100 g)^{-1}), where $k = 2$ (for 95 % confidence interval)

Analyte	Reference value (mass fraction; mg kg^{-1})	U_{rel} (%)
Al	2840 ± 137	5
As	15.5 ± 7.25	47
Ca	$(36.9 \pm 5.64) \text{ g (100 g)}^{-1}$	16
Cd	21.3 ± 3.02	14
Cr	289 ± 18.9	7
Cu	36.2 ± 12.6	35
Fe	1709 ± 62.1	4
K	568 ± 51.7	9
Mg	2696 ± 132	5
Mn	16.3 ± 6.90	42
Na	5350 ± 273	5
Ni	32.8 ± 8.38	25
P	$(14.3 \pm 3.94) \text{ g (100 g)}^{-1}$	27
U ^a	–	–
V	158 ± 9.49	6
Zn	277 ± 12.8	5

^aU information value (determined by INAA) 139 mg kg^{-1}

uncertainty and percentage, as shown in Table 4. The variability of the different procedures used by the laboratories, as presented in Table 2, can generate the differences among the results, which are presented in Fig. 2.

Arsenic, Cu, and Mn presented higher standard deviations between the measurements due to their low concentration in the sample, and also due to the variability of the analytical and sample preparation methods used by the laboratories. This variability generated significant differences between the results and a greater contribution to the uncertainties of characterization.

The phosphate rock quality control material (E2003a, Fosfato de Rocha) is available on Internet (<http://www2.cppse.embrapa.br/materiaisdereferencia/>). Each bottle is accompanied by a certificate and a report describing the production procedure.

Conclusions

This paper describes the production of a phosphate rock reference material produced in Brazil to be used as a quality assurance tool in laboratories that perform this kind of analysis in fertilizers samples. The experimental procedure to study the homogeneity and short- and long-term stability of prepared phosphate rock quality control material were taken into account to yield combined standard

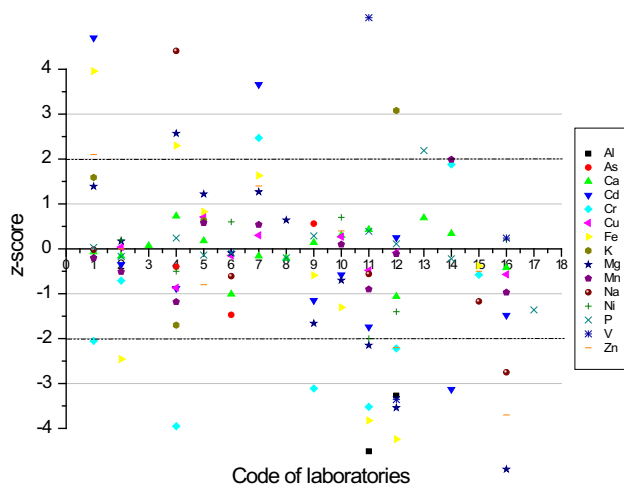


Fig. 2 z-scores obtained by the laboratories participating in the interlaboratory comparison for mass fractions of the various elements

uncertainties. From results by an interlaboratory comparison and using statistical parameters for exclusion of outliers, were determined the mass fractions of elements. The different levels of uncertainty observed reflected the experience of the laboratories and the techniques used. However, although it is indisputable that the quality of a QCM is directly dependent on low uncertainty, the uncertainties obtained mainly for As, Cu, and Mn can still be considered appropriate, considering the lower mass fraction values obtained for these analytes and that the characterization component presented the major uncertainty contribution [25]. Based on the proven characteristics of homogeneity, stability and the characterization, the produced material is adequate for quality control of laboratories.

Acknowledgements We are grateful for grants and fellowships provided by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP - 2015/14488-0), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES).

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