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ORIGINAL RESEARCH ARTICLE

Characterization of Ecuadorian feldspar by instrumental analytical techniques and statistical calculation of uncertainty for the reliability of results

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ABSTRACT

The present study has as objective the analysis and characterization of a sample of an Ecuadorian feldspar, by means of XRD, SEM and TGA techniques, for the microstructural analysis of mineral phase and chemical composition. Qualitative and quantitative X-ray diffraction analysis by Rietveld refinement revealed that this feldspar is composed of 33.31% Albite, 15.70% Quartz and a large percentage by weight of 50.99% amorphous material. To validate these results, the uncertainty of the measurement was investigated and calculated by statistical analysis of standard deviation, giving as results an uncertainty error of ±0.87 wt%, ±0.23 wt% and ±0.89 wt% respectively for the percentages by weight of the minerals found in this analysis. The result by SEM shows the presence of Albite in the feldspar exhibiting laminar twinning and characterized by randomly dispersed spherical quartz and plagioclase inclusions.

Keywords: characterization; feldspar; rietveld; DRX; SEM; FT-IR; TGA

1. Introduction

Feldspars are the most abundant mineralogical group in the earth’s crust, the name feldspar corresponds to an extensive group of minerals formed by aluminum silicates combined in its three forms: potassium, sodium and calcium, the chemical formula of feldspar is xAlSiO8 where the x can be Sodium (Na), Potassium (K) or Calcium (Ca)[1], feldspars are divided into two major groups: orthoclase (potassic feldspars) which are monocyclic such as orthoclase and plagioclase (calcium and sodium feldspars) which are triclinic such as albite[1]. If the structural state of the feldspar is known, it is possible to deduce important aspects about its internal composition.

The fundamental tool used to characterize the feldspar structure is X-ray diffraction (XRD) of the powdered material and refinement of the feldspar structure by programs using the Rietveld method.

The Rietveld method is a refinement technique that has the ability to determine more accurately the structural parameters of the sample, from the construction of a theoretical model that fits the experimental diffraction pattern, using the least squares method. The theoretical model includes structural aspects such as: crystalline structure, space group, position of the atoms in the unit cell, etc. Likewise, microstructural factors that contemplate the concentration of the phases present, crystal size and microstrain are included in the

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theoretical model[2]. Finally, the instrumental factor is also included, which considers the effect of the optics of the X-ray diffraction equipment on the measurement and whose effect is the broadening of the diffraction peaks.

XRD is a widely applied technique for the characterization of crystalline materials. The method has been traditionally used for qualitative, quantitative phase analysis and for crystal structure determination, using the Rietveld method[2], which is a powerful tool for obtaining structural, microstructural information and quantitative phase analysis from powder diffractograms. This Rietveld method basically consists of a refinement of the crystal structure, from powder diffraction data, for the quantitative analysis of crystalline samples.

For the accuracy of the Rietveld refinement[3] it is essential that the powder diffraction data are collected properly, in addition to taking into account the geometry of the diffractometer, the quality of the instrument alignment and calibration, the most appropriate radiation (e.g., conventional XRD, synchrotron or neutron XRD), wavelength, proper sample preparation and thickness, slit size, relative intensity or 2θ values, and counting time required[4]. As well as preferential orientation effects[5,6], which can lead to incorrect intensity measurements, if the intensities show a strong hkl dependence (e.g., all 00l reflections are strong and all hko reflections are weak), preferential orientation of the crystallites should be suspected, in the case of feldspars and quartz, the directions [001] and [011] respectively, are used as the special axes for preferential orientation corrections[7].

The accuracy and precision in the practice of crystallographic refinement by the Rietveld method will depend on the estimated standard deviation (standard uncertainty) of the number of observations analyzed by this method, since the measurement of the percentage by weight of phases existing in the analyzed material only provides an estimate of the value of the quantity to be measured. Since the value of a measurand is an unknowable quantity, its deviation from the measurement result (error) is also unknown, then the standard uncertainty is an estimate of the standard deviation, i.e., the positive square root of the variance, of the probability distribution of the possible values of the measurand. Uncertainty reflects the lack of exact knowledge of the value of the measurand because of random and systematic effects, including deficiencies in the model relating observations to the measurand[8].

This study investigates the accuracy and reliability of the quantitative analysis by the Rietveld method of a sample of Ecuadorian feldspar, as well as the way to prepare the sample for a correct observation, and the study of measurement uncertainty calculation (uncertainty by standard deviation) for the elemental analysis of feldspar by XRD.

2. Method

2.1 Materials for quantitative analysis Sample Preparation

To evaluate the reliability of the XRD data for quantitative phase analysis the sample was prepared by initially grinding to grain sizes smaller than 75 μm[9], to be subsequently micronized in the McCrone micronizing mill with the addition of 10 ml of ethanol for 10 min[7], the result of this milling was a kind of slurry that was dried in a convection oven at 60 °C for 24 h and then the resulting powder was sieved to grains smaller than 10 μm to minimize as much as possible the effect of micro absorption and improve the precision in the measured intensities[7]. Finally, the samples for the X-ray powder diffraction experiments were prepared by the side loading method to minimize the effect of preferential orientation[10].

2.2 Analytical techniques

2.2.1 Conventional Bragg-Brentano X-ray powder X-ray diffraction measurements

XRD analysis of the feldspar sample was carried out using a PANalytical X'Pert PRO diffractometer equipped with a conventional X-ray tube (Cu-Ka radiation) with an accelerating voltage of 40 kV and current tube of 30 mA and multichannel X`Celerator detector with anti-scattering protection. The diffraction spectrum was collected in the step-by-step mode between 5°–80° 2θ), with a scanning speed of 0.5 s/step and a step size of 0.02°[11].

2.2.2 Quantitative phase-refinement analysis Rietveld

From the diffractogram of the analyzed sample, the qualitative mineralogical composition was established, characterizing all the minerals present in the sample. The quantification of the experimental data was performed using the Rietveld Method[2], using the X'Pert HighScore Plus software[12], which is a crystal structure refinement program based on the least squares fitting method to optimize the information provided in the diffraction patterns.

2.2.3 Measurement uncertainty

Uncertainty[13] can be defined as a parameter associated with the result of a measurement that characterizes the dispersion of the values that can be attributed to the measurement itself. Uncertainty is therefore a range within which the true value of the quantity to be measured lies. There are two types of uncertainties due to random errors and systematic errors.

A random error varies unpredictably in both magnitude and sign when a large number of measurements of the same quantity are made under essentially the same conditions. These errors follow the Gaussian (normal) distribution with zero mean. However, for small samples (smaller number of observations), statistical results that are based on the normal distribution are corrected by Student's tt factor. These errors may be due to uncontrollable environmental conditions, personal judgment of the observer and the inherent instability of the measuring instrument or any other cause of a random nature. Systematic errors, on the other hand, are due to the system (including the standards used for measurement) and cannot be reduced by taking more observations if the equipment and measurement conditions remain unchanged[14].

The Guide for the Expression of Uncertainty in Measurement (GUM)[15,16], with the purpose of establishing in general rules for evaluating and expressing the uncertainty of a measurement result, establishes uncertainty components that can be classified into two categories according to their method of evaluation, known as Type A and Type B, see below. The purpose of this classification is to indicate the two fundamentally different methods of evaluating uncertainty components. This is in contrast to the traditional classification of uncertainty as the result of a combination of random and systematic effects. The categorization of uncertainty component assessment methods rather than the components themselves avoids the traditional ambiguities associated with attempts to distinguish between random and systematic effects. The result of a Type A evaluation of an uncertainty component can be referred to as a Type A standard uncertainty, that of a Type B evaluation as a Type B standard uncertainty[8]. Both types represent standard deviations. These rules are intended to be applicable to a wide spectrum of measurements, having as main sources of uncertainty the following influences that can affect measurements:

Repeatability
Resolution
Reproducibility
Sample preparation
Reference Standard uncertainty

Reference Stability Standard
Environmental factors
Specific measurement contributors
Alignment, scale, evaporation, mismatch, etc.

One of the characteristic features of the GUM is its designation of all contributions to uncertainty as either type A or type B. There are no other categories. Type A uncertainty estimates are derived from statistical analyses of test data. Any uncertainty contributor that is not derived from a statistical analysis of the test data is a Type B uncertainty contributor (derived from systematic errors). Type A and Type B uncertainty contributions[17], once determined, are both "typical uncertainties".

Uncertainties are based on repeated measurements of a controlled process and are described by the familiar normal (or "Standard") probability distribution that produces a mean and standard deviation for the whole. In crystallography as elsewhere, the measured values Y are usually derived from a number of other observed quantities $x_1, x_2, x_3, \ldots, x_n$, each of which is also a source of uncertainty:

$$Y = f(x_1, x_2, x_3, \ldots, x_n) \tag{1}$$

The best estimate of the expected value of an independent random variable of n observations $x_1, x_2, x_3, \ldots, x_n$, obtained under the same measurement conditions is the arithmetic mean of n observations given as:

$$\bar{x} = \sum_{p=1}^{p=n} x_p / n \tag{2}$$

The standard deviation of the mean $\bar{x}$ is $s(\bar{x})$ and is given by:

$$s(\bar{x}) = \left\{ \frac{\sum_{p=1}^{p=n} \left(x_p - \bar{x}\right)^2}{n(n-1)} \right\}^{1/2} \tag{3}$$

From the standard deviation of the means $s(\bar{x})$ of sample size n, the population standard deviation was calculated by multiplying by the Student's t factor. The value of Student's t for desired 95% confidence level, taking $n - 1$ as the degree of freedom. The standard random uncertainty u_r due to the single input magnitude is given as:

$$U = u_r = \left\{ \frac{\sum_{p=1}^{p=n} \left(x_p - \bar{x}\right)^2}{n(n-1)} \right\}^{1/2} \tag{4}$$

The calculated uncertainty has to be reported together with the result x and is considered as follows, (Result): ($x \pm U$) (units), where the reported uncertainty is an expanded uncertainty as defined in the International Vocabulary of Basic and General Metrology Terms (VIM) (JCGM, 2008).

3. Results and discussion

It can be seen in **Figure 1a** that the sample preparation was not adequate since the intensity of a characteristic peak is too high, this is due to the preferential orientation of the crystals, in **Figure 1b** on the other hand it can be seen that the preferred orientation was eliminated with a new sample preparation as mentioned above.

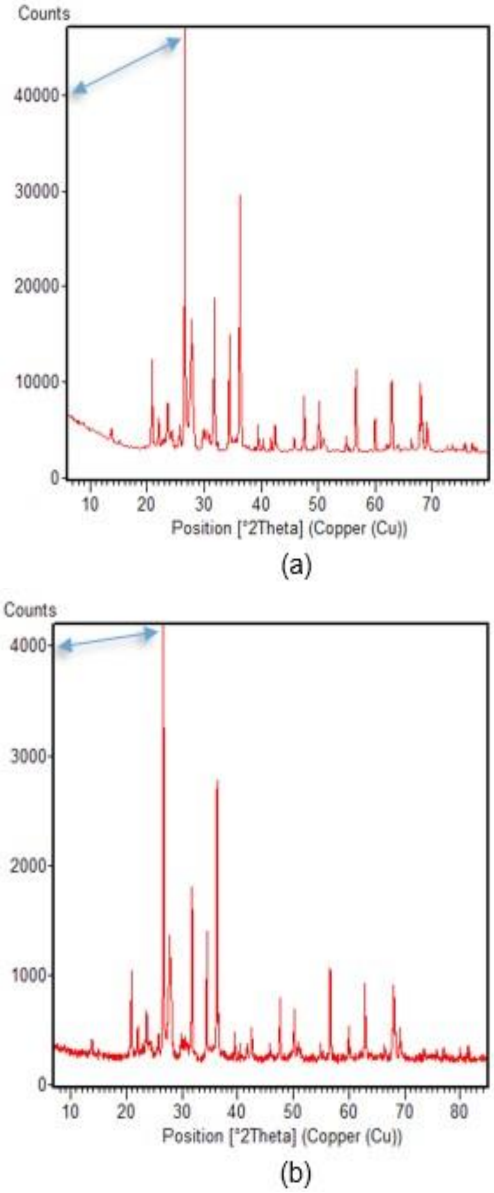


Figure 1. Diffractogram of the analyzed feldspar sample. **(a)** Sample analysis without sample preparation to avoid preferential orientation; **(b)** Diffractogram with a sample prepared to <10 μm without preferential orientation.

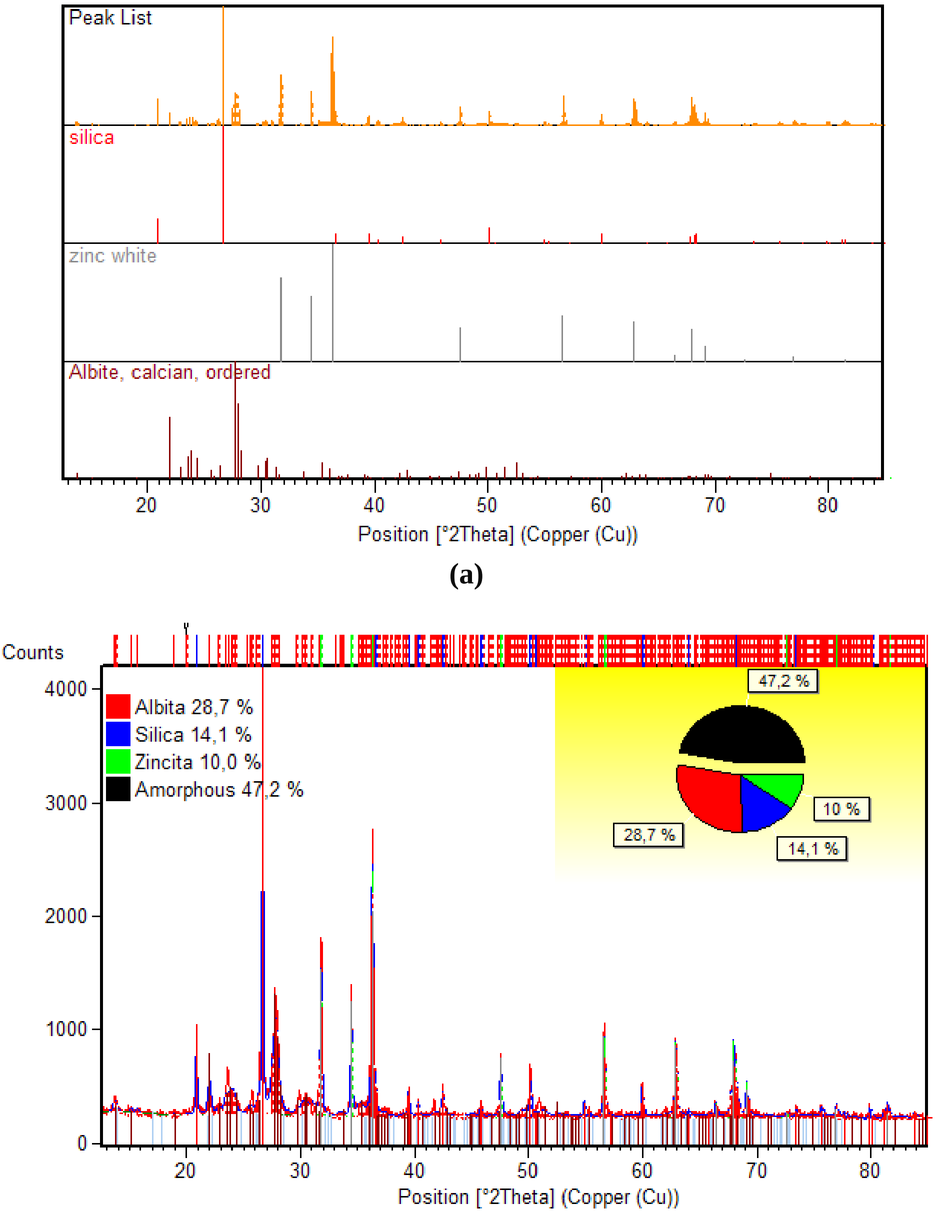
Once the elimination of the preferential orientation of the prepared samples is confirmed, the analysis of 10 powder X-ray diffraction (DRXP) samples from a randomly chosen batch of samples is performed for their respective quantification analysis of the results of the diffractograms obtained by DRXP.

For quantification, the XRD patterns shown in **Figure 2a** were used, using the PDF02 database that was possible to obtain the phase indexing of the feldspar samples. The results show that the analyzed feldspar presents an albite phase ($(Na,Ca)Al(Si,Al)_3O_8$), mixed with a low concentration of quartz (SiO_2) and a large percentage of amorphous material, the same that cannot be analyzed by XRD, this result shows that the analyzed feldspar belongs to the plagioclase group. For the quantification of the crystalline phases found, the Zincite standard was used as a known weight, in each measurement approximately 10% of Zincite was used. **Figure 2b** shows the phases found in weight percentage of one of the 10 samples analyzed and quantified by the Rietveld method with the X'Pert HighScore Plus software.

The results of the quantification of the percentage by weight of minerals found in the 10 samples of feldspar taken randomly are shown in **Table 1**, from which it can be seen that there is a deviation from the real value, for which a statistical analysis of control of means was performed (see **Figure 3**) to evaluate all the points that are within the control limits, which the mineral Albite an uncertainty error of ±0.87% in its measurements and for the mineral Silica an uncertainty error of ±0.23%, with a reliability of 95% and a Student's t factor $t = 2.26$ in both cases.

Table 1. Mineralogical composition of the 10 samples analyzed in weight percentage (M, indicates the sample analyzed).

Mineral	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10
Albita	31.9		33.5	34.1	34.5	31.6	32.2	33.1	32.8	35.4
Silica	15.7	15.6	15.4	16.3	16.1	15.8	15.5	15.8	15.6	15.2
Amorphous	52.4	50.4	51.1	49.6	49.4	52.6	52.3	51.1	51.6	49.4
Total (%)										



(a)

(b)

Figure 2. **(a)** XRD patterns for the sample analyzed from feldspar; **(b)** Quantification of the phases found in percent by weight.

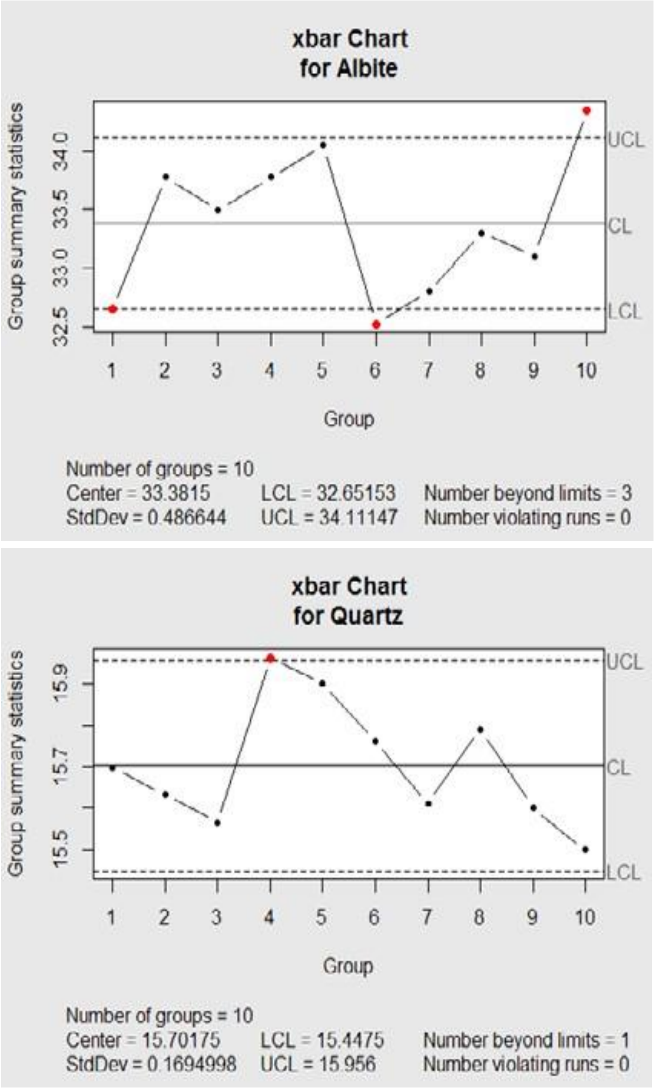


Figure 3. Control means for albite and silica minerals in the analyzed samples.

The type of uncertainty reported in this study is a Type A uncertainty, because its calculation was performed statistically and the systematic errors of the measuring instrument did not intervene.

4. Conclusions

According to the mineralogical composition obtained from the analyzed material indicates a percentage of: 33.31% of albite, 15.7% of silica and 50.99% of amorphous, therefore according to the classification mentioned by the authors Parsons, I., Gerald, J. D. F., & Lee, the material studied corresponds to calcium and sodium feldspars, since the sample has presence of Albite, exhibiting laminar twinning and characterized by inclusions of quartz and spherical plagioclase that are randomly dispersed.

The feldspar samples analyzed in this study presented preferential orientation effects, which were observed in the different diffractograms, identifying a peak with a high intensity of 40,000 (counts) in the position $2\theta = 28^{\circ}$, causing difficulties in the analysis of phase quantification, this defect was corrected with a correct preparation of the sample as mentioned at the beginning of this study, and configuring the power generation at 40 kV and 30 mA together with a divergence slit of 1/8º, with which the intensity of the peak was lowered to 4000 (counts) eliminating the effect of prefrecial orientation, which was necessary to perform for the analysis of phase quantification and for the calculation of uncertainty (see **Table 2**).

Table 2. Results of the statistical analysis of uncertainty.

Mineral	**Average of the sample ($\bar{X}$)**	**Deviation Standard $S(\bar{X})$**	**Uncertainty U (%)**
Albita	33.31	0.39	0.87 Type A
Silica	15.70	0.10	0.23 Type A
Amorphous	50.99	0.39	0.89 Type A

The results of the uncertainty analysis of the XRD-PD assays are within a range of ±0.87 wt% and ±0.23 wt% of the Albite and Silica phases respectively with a reliability of 95%. This uncertainty report guarantees the validity of the results of the quantification of the crystalline phases found in this analysis, being as main contributors to the uncertainty the sample preparation factors and the handling of the XRD equipment.

Conflict of interest

The authors declare no conflict of interest.

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