



An investigation of the statistical uncertainty analysis for results of instrumental analytical FT-IR characterization of feldspar ore

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Abstract

In the present study, the sample of an Ecuadorian feldspar was analyzed, using the FT-IR technique, for the characterization of minerals by vibrational frequency analysis. The uncertainty range of the results for FT-IR assays for Albite and Quartz compounds are within an uncertainty range of $\pm 3,8\text{cm}^{-1}$ and $\pm 6,6\text{cm}^{-1}$ respectively. To validate these results, the uncertainty of the tentative vibrational frequencies analyzed in the feldspar sample was investigated and calculated by standard deviation statistical analysis with a reliability factor of 95%.

Keywords: characterization; feldspar; FT-IR; uncertainty; minerals.

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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 their three forms: potassic, sodium and calcium, the chemical formula of feldspar is $x\text{AlSiO}_8$ where x can be Sodium (Na), Potassium (K) or Calcium (Ca) [1], feldspars are divided into two large groups: orthoclase (potassic feldspars) which are monocyclic like orthoclase and plagioclase (calcium and sodium feldspars) which are triclinic like albite [1]. If we know the structural state of the feldspar, we can deduce important aspects of its internal composition.

Among the various spectroscopic techniques recently improved, Fourier transforms infrared spectroscopy (FT-IR) in combination with X-ray diffraction (XRD) are effective tools capable of producing quantitative information to identify the substances present in the studied samples [2]. For a structural chemical identification of compounds in the analysis of feldspathic rocks, IR spectra are usually compared with reference data obtained from standard samples of known composition.

It is well known that the FT-IR absorption technique represents a very powerful tool to reveal the molecular species present in a sample from the analysis of spectral profiles. In the case of feldspar, this experimental technique allows the identification of the various constituents and thus provides information on the provenance of the mineral. Recently, FT-IR spectroscopy has been widely employed in this field in order to obtain information about structural and physical/chemical properties at the molecular level [2]. As for the analytical techniques used to give information concerning pigments, FT-IR spectroscopy is becoming one of the most appropriate experimental methods for the analysis and characterization of components in the field of materials science [3].

In the present study, the accuracy and reliability of

the quantitative analysis by FT-IR technique of a sample of Ecuadorian feldspar is investigated, as well as the way of sample preparation for a correct observation, and the study of measurement uncertainty calculation (uncertainty by standard deviation) for the elemental analysis of feldspar by FT-IR.

2. Materials and methods

2.1. Materials for quantitative analysis

Sample preparation

The sample was prepared by initially grinding to grain sizes smaller than $75\ \mu\text{m}$ [4], to be subsequently micronized in the McCrone micronizing mill with the addition of 10 ml of ethanol for 10 min [5], the result of this grinding was a kind of slurry that was dried in a convection oven at 60°C for 24 hours and then the resulting powder was sieved to grains smaller than $10\ \mu\text{m}$ to minimize the effect of micro absorption and improve the accuracy in the measured intensities [6]. Finally, the samples were prepared in pellets, about 0.5 mm thick, using small amounts of powdered sample ($\sim 2\ \text{mg}$), mixing with KBr until a homogeneous mixture was obtained [7]. The same procedure was performed for the three replicates analyzed in this study.

2.2. Analytical techniques

Fourier transform infrared spectroscopy analysis (FT-IR)

FT-IR analysis of the feldspar sample was carried out using a Perkin Elmer brand FT-IR Spectrum 100 Spectrophotometer, by KBr pellet technique, using small amounts of the feldspar powder sample ($\sim 2\ \text{mg}$) homogeneously dispersed in 200 mg of KBr powder and then pressed at 8 tons for 5 min. The pellets of approximately 13 mm diameter are held inside the sample holder and were scanned at $2\ \text{cm}^{-1}$ resolution. FT-IR absorbance measurements were performed on each sample over a wide wavenumber range ($4000\text{-}400\ \text{cm}^{-1}$), under a nitrogen environment of $1\ \text{ft}^3/\text{min}$ [8], analysis of the spectra was performed using 100 software, the same spectra



are shown in Figure 1. *Measurement uncertainty*

The uncertainty [9], 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 lies the true value of the quantity to be measured. There are two types of uncertainties 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 means. However, for small samples (smaller number of observations), statistical results based on the normal distribution are corrected by Student's t-factor. These errors may be due to uncontrollable environmental conditions, the personal judgment of the observer and the inherent instability of the measuring instrument, or any other cause of random nature. Systematic errors, on the other hand, are due to the system (including the standards used for measurement) and cannot be reduced by adopting more observations if the equipment and measurement conditions remain unchanged [10].

The Guide for the Expression of Uncertainty in Measurement (GUM)[11,12], 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 [13]. 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 in measurements.

- Repeatability
- Resolution
- Reproducibility
- Sample preparation
- Reference Standard Uncertainty
- Reference Stability Standard
- Environmental factors
- Alignment, scale, evaporation, mismatch, etc.

One of the characteristic features of the GUM is its designation of all contributions to uncertainty as 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 [14], 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 which produces a mean and standard deviation for the whole. In crystallography as elsewhere, the measured values Y are generally derived from a number of other observed quantities $x_1, x_2, x_3, \dots, x_n$, each of which is also a source of uncertainty:

$$Y = f(x_1, x_2, x_3, \dots, x_n) \quad (1)$$

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



$$\bar{x} = \sum_{p=1}^{p=n} \frac{x_p}{n} \quad (2)$$

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

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

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

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

The calculated uncertainty has to be reported together with the result x as follows, $(Resultado): (x \pm U) (unidades)$, where the reported uncertainty is an expanded uncertainty as defined in the International Vocabulary of Basic and General Metrology Terms (VIM) [15].

3. Results and discussions



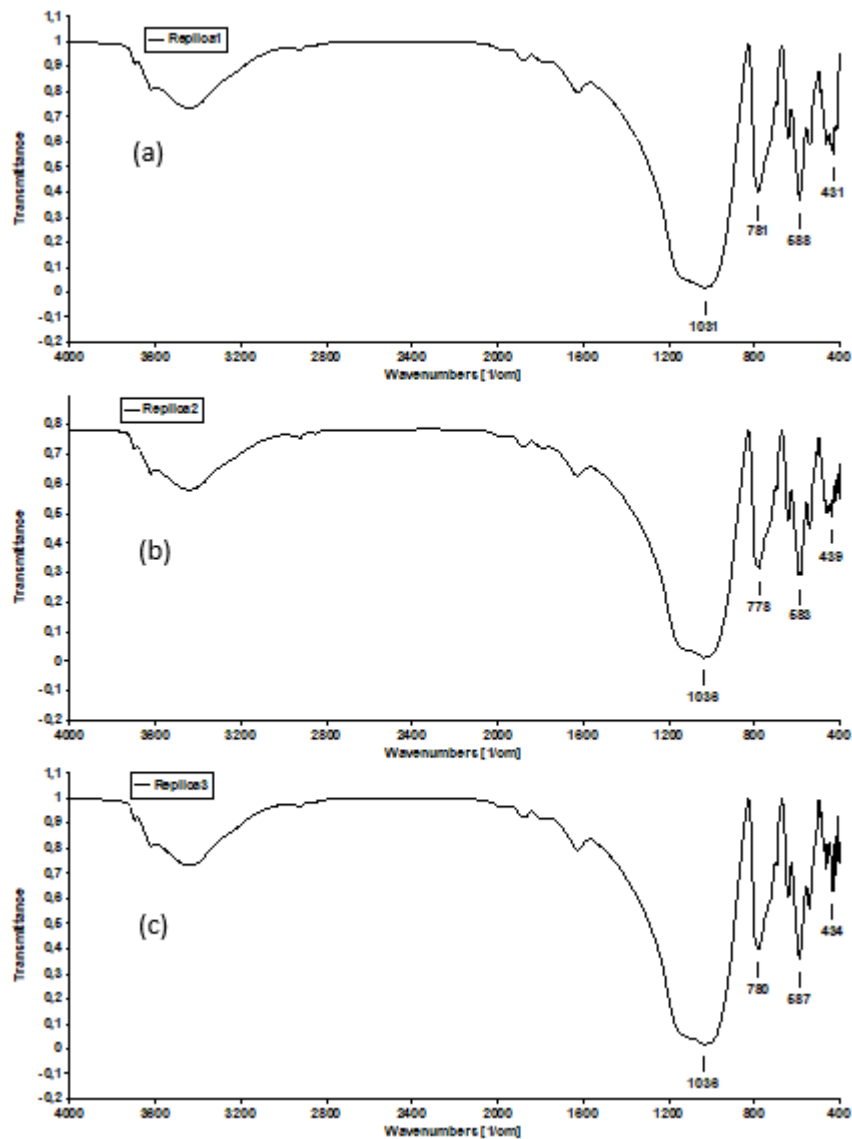


Figure 1. (a-c) FT-IR spectra.

The FT-IR spectra of the recorded samples in the range of 4000 to 400 cm^{-1} collected for the present study are shown in Figure 1, the tentative vibrational assignments in the IR peaks as the status of the analyzed samples are given in Table 1

and Figure 2. From the FT-IR spectra of the samples of analyzed, according to literature [7], the FT-IR absorption band around 3630 cm^{-1} is due to the hydroxyl groups persisting up to 800°C, demonstrated earlier in the TGA report.

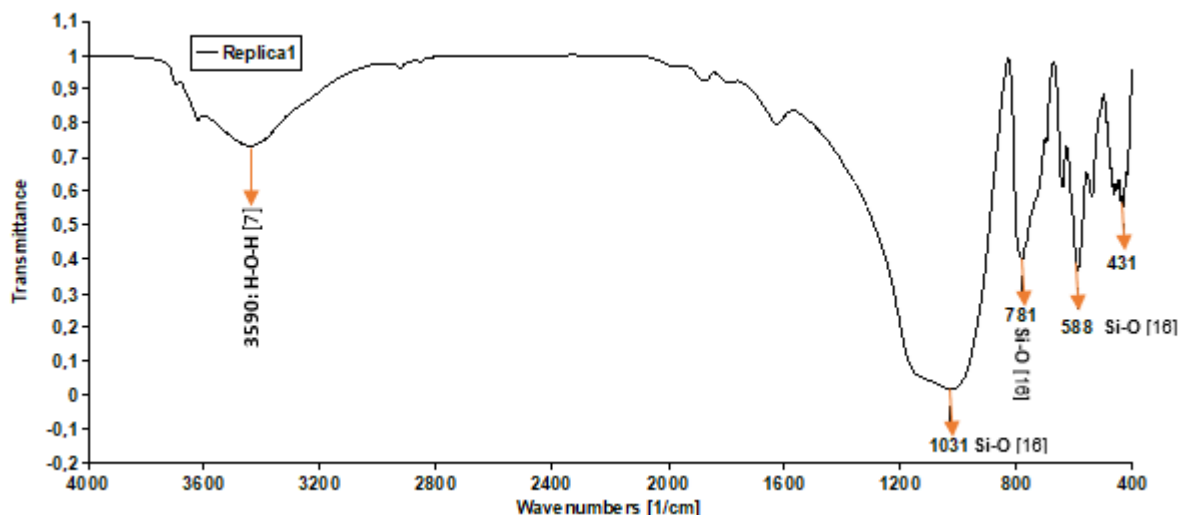


Figure 2. Typical FT-IR spectra of minerals observed from the Feldspar sample analyzed.

Table 1. Infrared absorption wavenumbers (cm^{-1}) of Feldspar samples with tentative vibrational assignments.

Replica 1	Replica 2	Replica 3	Tentative Assignments	Vibration
Wave number (cm^{-1})				
3590	3593	3589	H-O-H Water bending	
1031	1036	1036	Si-O Quartz	
781	778	780	Si-O Quartz	
588	583	587	Si-O Quartz	
431	439	434	Si-O Quartz/Albite	

Table 2 shows the results of the standard deviation calculation for the uncertainty analysis of the vibrational frequency wavenumber shift measurements of each compound found in cm^{-1} ,

with a reliability of 95% and a student's t-factor $t = 4.3$ in both cases, since there are three analyses and therefore the degrees of freedom would be $n-1$, for the selection of t .

Table 2. Results of the statistical analysis of uncertainty

Tentative Assumptions	Vibration	Sample Mean (\bar{X})	Standard Deviation $S(\bar{X})$	Uncertainty $U(\text{cm}^{-1})$
H-O-H Water flexure		3590,7	1,2	5,2
Si-O Quartz		1034,3	1,7	7,2
Si-O Quartz		779,7	0,9	3,8
Si-O Quartz		586,0	1,5	6,6
Si-O Quartz/Albite		434,7	2,3	10,0

The type of uncertainty reported in this study is a Type A uncertainty, since it was calculated statistically, and the systematic errors of the measuring instrument did not intervene.

4. Conclusions

The results of the uncertainty analysis of FT-IR assays of the minerals found are within a range of $\pm 5,2\text{cm}^{-1}$, $\pm 7,2\text{cm}^{-1}$, $\pm 3,8\text{cm}^{-1}$, $\pm 6,6\text{cm}^{-1}$ and $\pm 10\text{cm}^{-1}$, of the tentative vibrational assignments analyzed above with 95% confidence.

The calculated uncertainty is too high and is not in

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a satisfactory range, this may be caused by several factors, it may be due to poor sample preparation, the thickness of the pellet to be analyzed, the percentage of mass used for sample preparation, poor use of the equipment, etc.

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