Use of TGA-DSC thermogravimetry technology for minerals with fragments of feldspar origin under statistical validation of measurement uncertainty

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Abstract

In the present study the sample of an Ecuadorian feldspar was analyzed by the TGA-DTG technique for the thermal analysis of mass loss, resulting in the presence of three endothermic peaks, the first one at a temperature of 25 and 600ºC due to the dehydration of absorbed water with a mass loss of 0. 058%, the second peak between 600 and 878ºC and is due to water evaporation (dehydroxylation) with a mass loss of 0.23%, and the third between 878 and 1333ºC with a mass loss of 1.03%. To validate these results, the uncertainty of the mass loss measurement was investigated and calculated by standard deviation statistical analysis, giving as results an uncertainty error of ±0.02%, ±0.05%, and ±0.16% respectively with a reliability of 95% for the above-mentioned results.

Keywords: Thermogravimetry; feldspar; TGA, DTG; uncertainty; characterization.
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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 xAlSiO8 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.

The thermogravimetric analysis provides an alternative method to the standard calculation generally adopted to determine the composition of a mineral mixture; this often requires the volumetric determination of numerous elements, is time-consuming, and requires the support of a chemical laboratory which generally undertakes all the analyses for the teams performing the physical treatment tests. The physical processes adopted in such tests (flotation, magnetic separation, selective milling, cycloning, etc.) are designed to concentrate the desired component of a mineral without altering its chemical composition [2].

Thermogravimetry is a technique that has been used for the characterization of materials, mainly coal and clays. In recent years the technique has been extended to other materials. This technique in combination with other thermal methods provides a source of information not only thermal but also chemical. It is important to clarify that this method does not allow to know the chemical composition of the material under study nor to identify thermal changes that are not associated with mass variations such as crystallization or glass transition.

Thermogravimetry is based on mass changes as a result of a temperature variation or by subjecting a material to a set temperature for a defined period of time. The mass changes identified make it possible to determine under what conditions the materials decompose. The results are expressed graphically through thermograms.

Thermal methods often require complementary analyses by other techniques for a complete understanding of the processes that are occurring, even in the simplest ones. It is convenient to start by combining different thermal methods with each other as they have similar temperature and atmosphere control schedules and show the thermal processes in a complementary way. The thermal methods most commonly used simultaneously with thermogravimetry (TGA) are differential thermal analysis (DTA) and differential scanning calorimetry (DSC) giving rise to the TGA-DTA and TGA-DSC techniques. DTA curves allow the detection of exothermic and endothermic peaks (effects due to enthalpy gain/loss) that occur in the sample when subjected to controlled heating and in comparison with an inert reference material [3].

TGA is a highly accurate and sensitive method, working with very small samples, which can significantly affect the results so that the accuracy and reliability will depend on the estimated standard deviation (standard uncertainty) of the number of observations analyzed by this method. The value of a quantity to be measured is an unknowable quantity, its deviation from the measurement result (error) is also unknown, so 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. The uncertainty reflects the lack of accurate knowledge of the measurand value because of random and systematic effects, including deficiencies in the model relating observations to the measurand [4].

The present study investigates the accuracy and reliability of the TGA results of a sample of Ecuadorian feldspar, 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 TGA-DTG.

2. Materials and methods

2.1. Materials for quantitative analysis

Sample preparation

To evaluate the reliability of the TGA-DTG data for mass loss analysis at the different temperatures that such reactions occur, the sample was prepared by initially grinding to grain sizes less than 75 µm [5], and then, be micronized in the McCrone micronizing mill with the addition of 10 ml of ethanol for 10 min [6], 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 µm to ensure the homogenization of the sample [7]. Finally, between 8 to 10 mg of the sample was weighed for DTG-TGA analysis [8], and the same ratio was used for the three replicates analyzed in this study.

2.2. Analytical techniques

Thermogravimetry analysis (TGA-DTG)

The TGA-DTG analysis of the feldspar sample was carried out using a TA Instruments SDT Q-600 equipment. The analysis was performed with a nitrogen flow (with a flow rate of 100 ml/min) [8], with a temperature range from ambient to 1400ºC, at a heating rate of 10ºC/min [9,10], using an alumina crucible (Al_2O_3) as inert material. Advantage TA Universal Analysis 4.5A software was used to analyze the data obtained.

Measurement uncertainty

Uncertainty [9,10], 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. Therefore, the uncertainty is a range, within which lies the true value of the quantity to be measured. 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 based on the normal distribution are corrected by Student's t-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. In contrast, systematic errors 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 [11].

The Guide for the Expression of Uncertainty in Measurement (GUM)[12,13], 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[4]. 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 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." Uncertainty is based on repeated measurements of a controlled process and are described by the familiar normal (or "Standard") probability distribution that yields a mean and standard deviation for the ensemble. In thermal analysis 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:

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

The standard deviation of the mean $\underline{x}$ is $s(\underline{x})$ 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

It can be observed in Figure 1, the DTG curves three endothermic peaks and one exothermic peak. The temperature ranges, the mass loss of these changes and the analysis of each of these peaks are shown in the TGA and DTG curves in Figure 2.

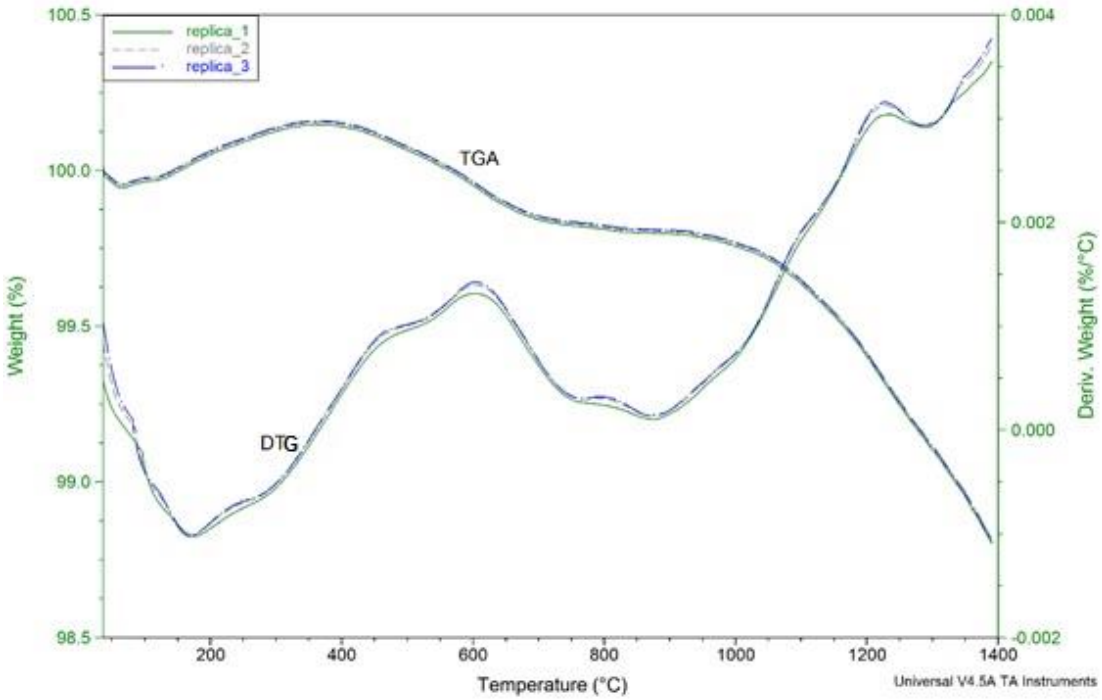

Figure 1. TGA-DTG curves of the thermal analysis of Feldspar.

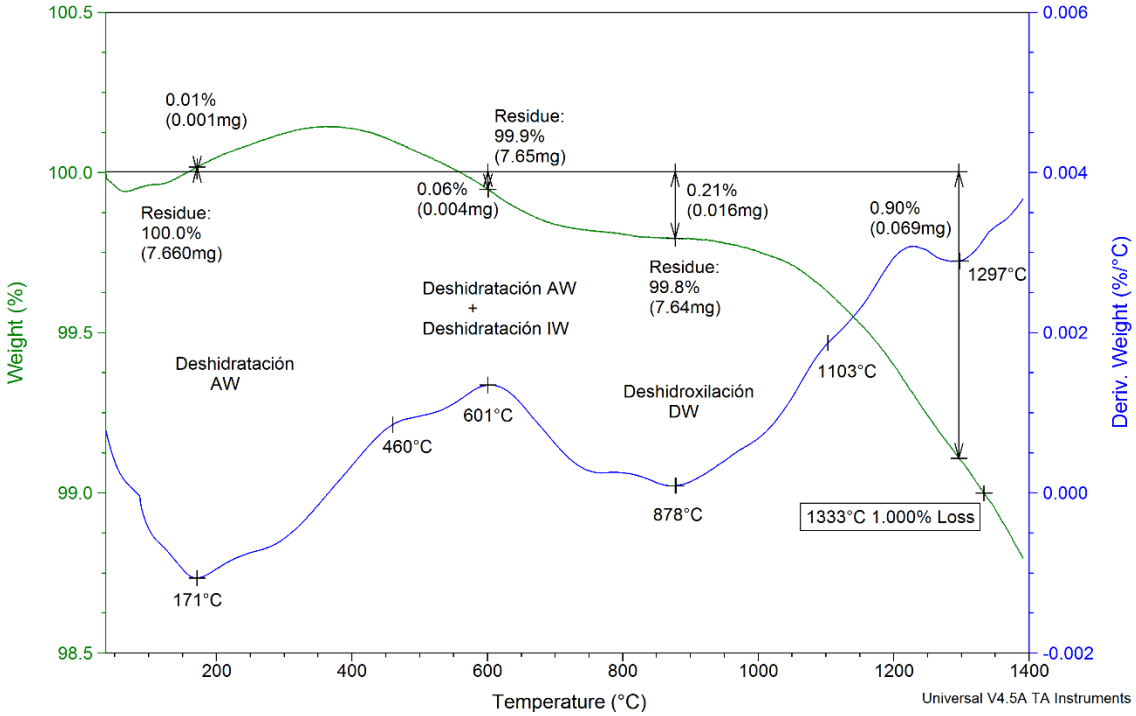

Figure 2. Analysis of TGA and DTG curves (AW absorbed water, IW intermediate water layer, DW water dehydroxylation).

The first and dominant endothermic peak is between 25 and 600°C and is due to dehydration of absorbed water (AW) and the intermediate water layer (IW) with a maximum heating rate of 171°C (dehydration) and 460°C (DW dehydroxylation) respectively. The mass loss due to dehydration is 0.06%. The mass loss of 0.21% between 600 and 878°C is due to decarbonylation.

The endothermic mass loss of 1.0% between 878 and 1333°C with a maximum rate at 1100°C originates mainly from calcination of trace amount of albite ($NaAlSi_3O_8$) [8]. The exothermic change without mass loss with a maximum rate at 1400ºC shows the recrystallization of the dehydroxylation of the sample.

The mass loss and temperature results of the three analyzed replicates are shown in Table 1, in which it can be seen that the results are close to each other, indicating a slight deviation between the values of each result.

Table 1. Temperatures and mass losses in percentage of the three samples analyzed.

Sample	Ta-Tb (°C)	% Lost Mass	Tb-Tc (°C)	% Lost Mass	Tc-Td (°C)	% Lost Mass
1	25-600	0,06	600-878	0,21	878-1333	1
2	32-601	0,049	580-879	0,25	886-1329	0,98
3	29-598	0,065	598-880	0,22	880-1330	1,1

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

	Sample mean$(\underline{X})$	Standard Deviation$S(\underline{X})$	Uncertainty U
% Mass Loss (Ta-Tb)	0,058 599,7	0,004 0,88	0,02 3,78
% Mass Loss (Tb-Tc)	0,23 879	0,012 0,57	0,05 2,45
% Mass Loss (Tc-Td)	1,03 1330,7	0,037 1,2	0,16 5,16
	(Sample1)	(Sample 2)	(Sample 3)

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 uncertainty of the results of the mass losses is in an acceptable range, these errors of uncertainty is due to the factors that affect the data collection, one of them and the most important is the amount of the sample that is placed in the crucibles and the operator who places the sample in the microbalance of the equipment, Another factor that can contribute to the uncertainty in data collection is the humidity of the sample, since if the sample has a large amount of humidity, the percentage of degradation or loss of mass would also be higher.

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