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QUANTITATIVE EVALUATION OF Na_2CO_3 and NaCl CONTENT IN THE CLAYS OF THE EX-LAKE OF TEXCOCO (VALLEY OF MEXICO) BY MEANS OF THERMOGRAVIMETRY

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The clays of the ex-lake of Texcoco (Valley of Mexico) have a variable content of Na_2CO_3 and NaCl, which are usually evaluated by means of chemical methods. The experimental method presented in this article for the evaluation of these salts is thermogravimetric analysis.

In studies made by Zeevaert [1], Marsal and Mazari [2], Girault [3] and Lo [4], in order to classify, from a mineralogical point, the clays of the Valley of Mexico, it was established that most of the minerals from the samples analyzed are of amorphous character and cannot be catalogued in any crystalline mineralogic group. Due to this fact, they classify them in the group of allophane minerals. The characteristics of allophane minerals have been widely studied by Ross and Kerr [5].

The dehydration curves for allophane minerals, H_2O content as a function of temperature, are very different to those obtained for crystalline clays.

The clays of the ex-lake of Texcoco have a variable content of humidity, organic material, Na_2CO_3, NaCl and $NaHCO_3$. The evaluation of these salts is usually made by chemical methods.

The results obtained for the quantitative evaluation of Na_2CO_3 and NaCl contained in these clays are presented in this article. The technique used was thermogravimetric analysis and it is based on the decomposition of Na_2CO_3 and evaporation of NaCl. It will be noted that the decomposition temperature for pure Na_2CO_3 occurs in a range from 900 to 1200°. However, when it is mixed with the minerals from the clay, it combines with them, and a shift in the temperature decomposition occurs, this range is from 500 to 800°.

It is very important to note that in the evaluation of Na_2CO_3 in samples that contain $NaHCO_3$ an error is obtained, consisting in a higher percentage for Na_2CO_3, according to the reaction:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

This error is corrected if it is considered that $NaHCO_3$ decomposes in a very definite temperature range, from 130 to 210°.

Experimental

Equipment. The equipment used in this work was a Thermal Analyzer Du Pont Model 990, the module employed was a thermobalance (Model 951). The operation range of the equipment is from ambient to 1200°. The signal provided by the transductor of the cell is plotted in a X, Y, Y′ recorder, obtaining simultaneously the TG curve for the weight loss, as well as the rate of weight loss (DTG), both as a function of the temperature of the sample.

Description of the technique

Once the appropriate conditions were found in order to obtain TG curves on which it was easy to observe the weight loss, it was found that on the TG curves is very simple to determine such losses, but it is difficult to establish precisely the starting and ending points of the different decomposition stages, as it is seen on the TG curve of Fig. 1. If it is observed the DTG curve of the same figure, it is seen that it presents very well defined peaks, which correspond to the different decomposition stages; due to the fact that the X axis is common to both curves, the initiation and termination points of such peaks define the starting and ending limits for the different stages. The abscissas of the initiation and termination points of the peaks are defined as those for which the DTG curve tends to move from or return, respectively, to a "base line".

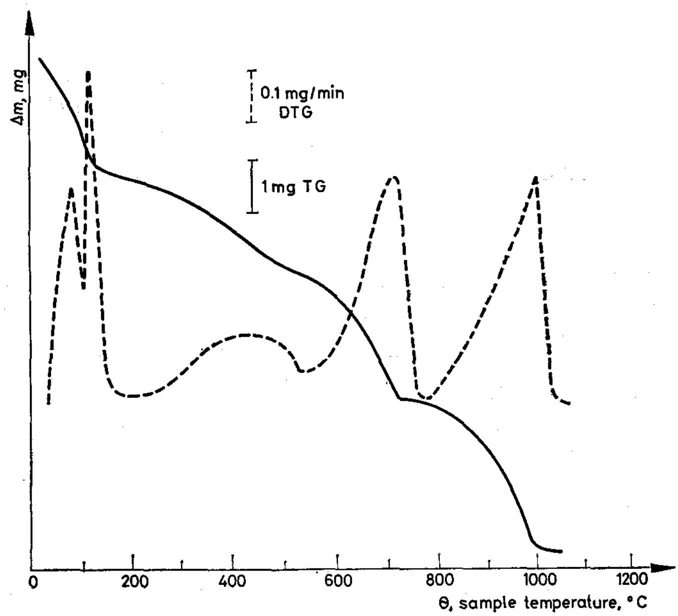

Fig. 1. TG and DTG curves for a real sample. Atmosphere: air, heating rate: 20°/min, mass: 25.5 mg, suppression: 20 mg

Commentaries on the experimental problems encountered

To obtain the definitive technique for the evaluation it was necessary to run several samples, varying the experimental conditions. When this was done the major problems encountered were:

1. Interpretation of the curve.
2. The heating rate.
3. The atmosphere that surrounds the sample.
4. The chemical interaction: Na_2CO_3 – clay.

1. *Interpretation of the thermal curves.* In order to interpret the thermal curves obtained two types of samples were defined: a) Real samples; b) Prepared samples.

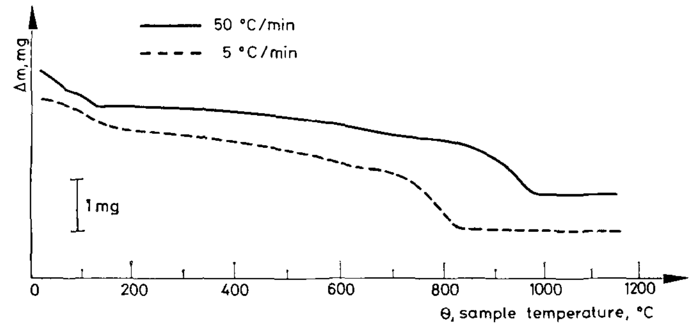

Fig. 2. TG curves that show the effect of heating rate. Atmosphere: air, suppression: none

a) *Real samples.* Real samples are defined as those which, after being taken from the ex-lake were dried and ground before being run in the thermobalance.

b) *Prepared samples.* A prepared sample is defined as a real sample, which after being washed with water to eliminate Na_2CO_3 and NaCl, was subsequently added with perfectly known quantities of these same salts.

The TG curves are interpreted by means of the prepared samples since they permit to identify precisely the different stages of weight loss.

2. *The heating rate.* In order to find the most appropriate heating rate for the evaluation, real samples were run using the following heating rates: 5, 10, 20, and 50°/min. Figure 2 shows the TG curves for the extreme cases; as it is observed, although there is a shift of the curves along the X axis, there is no appreciable variation in the value of the ordinates for a given step of the curve. The heating rate that was found to be more convenient was 20°/min.

3. *The atmosphere that surrounds the sample.* To select the type of atmosphere more convenient for the evaluation, prepared samples, perfectly identified, were run in atmospheres of air, N_2 and O_2. The experiments showed that, invariably,

the more approximate values to the added percentages were obtained in an air atmosphere.

An explanation for the difference in the values of the added percentages when N_2 and O_2 are used is as follows: in the case of N_2, the values are altered because

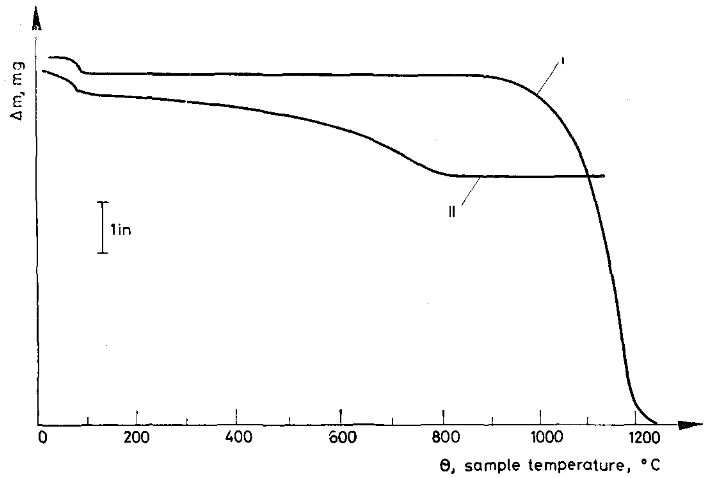

Fig. 3. TG curves showing Na_2CO_3 decomposition. Atmosphere: air, heating rate: 20°/min. Y axis sensitivities: curve I: 0.5 mg/in, curve II: 1 mg/in, suppression: none

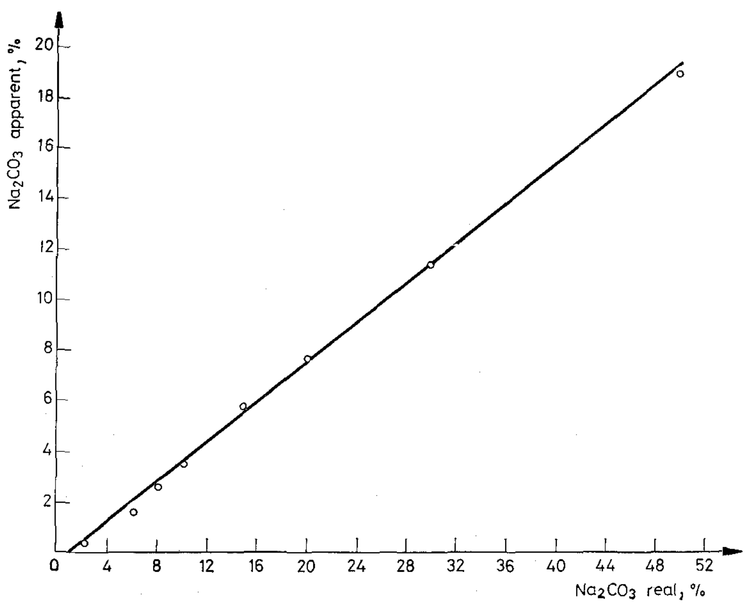

Fig. 4. Correction curve for Na_2CO_3 % weight loss

this gas inhibits the combustion of organic material contained in the samples. In the case of O_2, the values are altered because of the probable oxidation of the metals contained in the clay.

4. *The chemical interaction: Na_2CO_3–clay.* The experiments showed that the thermal decomposition of pure Na_2CO_3, for the heating rates used, occurs in the range 900 to 1200°; the temperatures for this interval are lower when the sodium carbonate and the minerals of the clay are mixed, this new range goes from

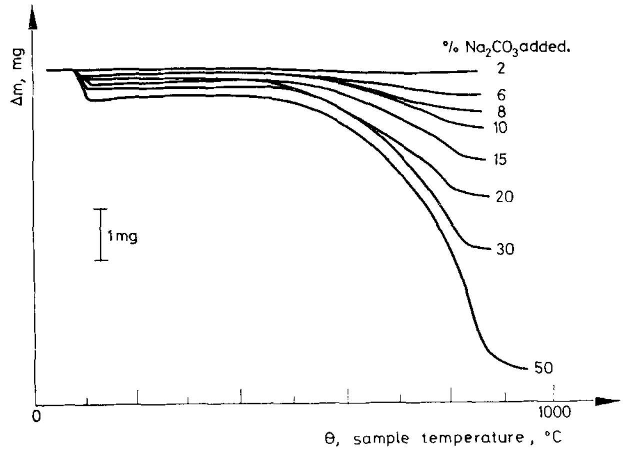

Fig. 5. Family of curves obtained for the determination of the correction curve (Fig. 4). Atmosphere: air, heating rate: 20°/min

500 to 800°. Simultaneously with this effect of lower decomposition temperatures it was observed that the weight loss for Na_2CO_3 does not correspond to a total degradation of this salt, it is assumed that this effect is due to the combination of this salt with the minerals of the clay. Figure 3 shows this. Curve I presents the thermal

Table 1

Prepared samples

Na_2CO_3	
% Real	% Apparent
2	0.36
6	1.60
8	2.60
10	3.49
15	5.75
20	7.67
30	11.33
50	19.04

decomposition of pure Na_2CO_3, curve II shows the decomposition of the carbonate in a sample prepared with the following percentages: 57.51% of washed clay, 42.49% of Na_2CO_3. The weight loss that corresponds to the carbonate was 16.35%, this weight loss, lower than the added percentage, will be called apparent loss; being retained in the sample 26.14% of the Na_2CO_3 added.

To solve this problem, that obviously will affect the value of the evaluation, the behaviour of this effect was studied. To do this, a graph for the percentage of Na_2CO_3 apparent as a function of the percentage of Na_2CO_3 (real) added, Table 1 shows the data for samples prepared with the real percentages indicated.

Figure 4 shows the graph obtained. As it is seen, the behaviour is linear for the range of interest. This curve was used to correct the percentages of Na_2CO_3 obtained for real samples, as will be seen later.

Figure 5 shows the family of curves obtained for the determination of the graph of Fig. 4.

Commentaries on the behaviour of NaCl. *The mixture:* NaCl + Na_2CO_3 + *clay and* $NaHCO_3$

NaCl did not present any problem for its direct evaluation from the TG curve except for a small shift in the temperature at which it starts to lose weight, the average for various samples is as follows:

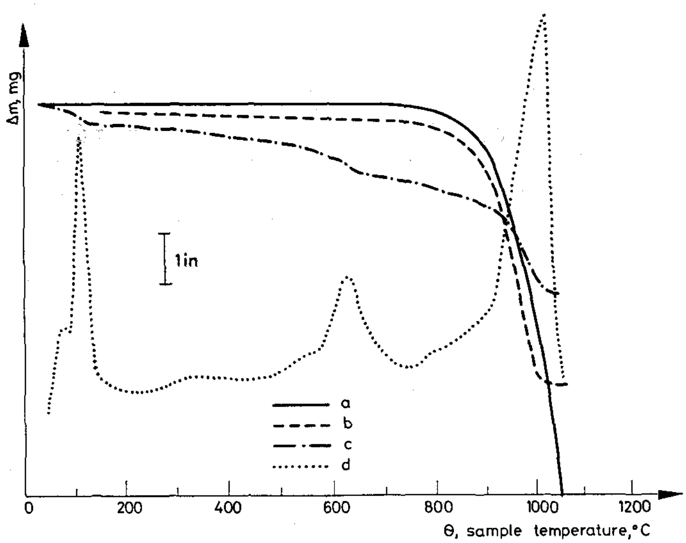

Fig. 6. TG curves showing the temperature shift for the evaporation of NaCl. Curve (a): NaCl pure, curve (b): NaCl + clay, curve (c): NaCl + Na_2CO_3 + clay, curve (d): DTG for curve (c). Atmosphere: air, heating rate: 20°/min, sensitivity: curves (a) and (b): 1 mg/in curve (c): 2 mg/in; suppression: none

Temperature (°C) at which NaCl starts to lose weight

NaCl	720	(pure)
NaCl+Clay	730	(Prepared samples)
NaCl+Na_2CO_3+Clay	740	(Prepared samples)

Figure 6 shows this effect, the DTG curve (d) for curve (c) is also included.

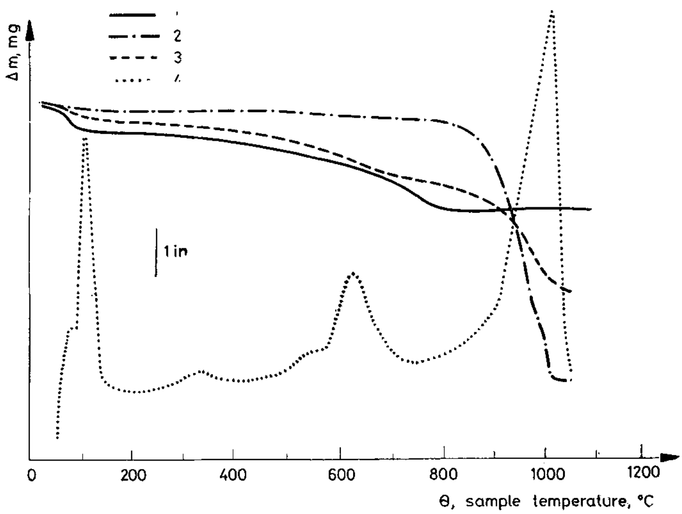

Fig. 7. TG curves for the mixtures: curve 1: Na_2CO_3 + clay; curve 2: NaCl + clay; curve 3: NaCl + Na_2CO_3 + clay; curve 4: DTG for curve 3. Atmosphere: air, heating rate: 20°/min. Sensitivity: curves (1) and (2): 1 mg/in, curve (3): 2 mg/in; suppression: none

Experimental results

The mixture NaCl + Na_2CO_3 + *clay*

In order to be valid, all that has been said to this point must hold for prepared samples with the mixture:

$$NaCl + Na_2CO_3 + clay$$

Table 2 shows an example for each case.

Figure 7 shows the TG curves for each one of the samples of Table 2.

$NaHCO_3$ *and the mixtures:* $NaHCO_3$ + *clay and* Na_2CO_3 + $NaHCO_3$ + *clay*

Even though in the real samples that were run the presence of $NaHCO_3$ was no detected, it is important to consider its thermal behaviour in order to foresee

Table 2

Sample	$\%Na_2CO_3$			%NaCl	
	Added	Apparent	Corrected	Added	Direct
Na_2CO_3+clay	42.55	16.22	42.60	— —	— —
NaCl+clay	— —	— —	— —	68.70	67.08
NaCl+Na_2CO_3+clay	35.2	13.93	34.6	28.5	28.7

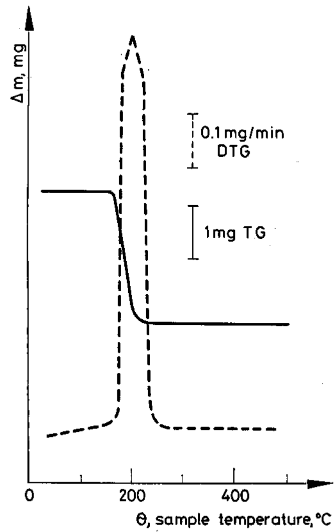

Fig. 8. Thermal decomposition of $NaHCO_3$. Atmosphere: air, heating rate: 20°/min, suppression: none

the corrections that would be necessary for samples that contain a noticeable percentage of this salt.

The experimental results for $NaHCO_3$, according to the equation:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

are shown in Fig. 8.

In the TG curve the weight loss appears for $CO_2 + H_2O$, leaving a Na_2CO_3 residue. The comparison between theoretical and experimental results is as follows:

$NaHCO_3$

	Theoretical, mg	Experimental, mg
CO_2+H_2O	2.63	2.59
Na_2CO_3	4.52	4.58

Several samples prepared with $NaHCO_3$ and clay were run in order to see if there was an interaction between them and it was observed that there is a difference in the temperatures at which $NaHCO_3$ + clay and $NaHCO_3$ pure start to lose weight, these temperatures are 145 and 170°, respectively. This difference does not affect the calculations made from the TG curves, Figure 9 shows one of the thermal curves obtained for this mixture. The comparison between theoretical and experimental results is as follows:

$NaHCO_3$+clay

	Theoretical, mg	Experimental, mg
CO_2+H_2O	3.32	3.32
Na_2CO_3	5.68	5.68

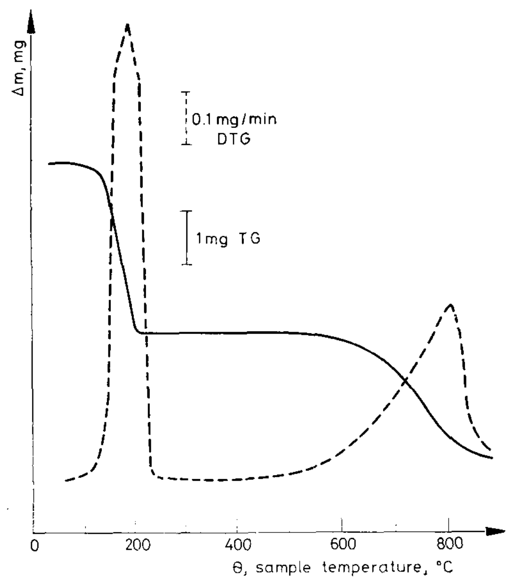

Fig. 9. TG curve for the mixture: $NaHCO_3$ + clay. Atmosphere: air, heating rate: 20°/min, mass: 18 mg, suppression: 10 mg

As it is seen, the concordance is perfect for the example presented. However, for other cases the difference is not higher than 0.01 %. Due to this fact, it was concluded that there was not chemical interaction between $NaHCO_3$ and the clay.

Now, evaluation from the TG curve of the Na_2CO_3 percentage, due to $NaHCO_3$, gives:

Na_2CO_3 from $NaHCO_3$

% Theoretical	% Experimental
31.55	34.8

From these results, it was concluded that it is possible to avoid the error that would result in Na_2CO_3 % in samples that could contain $NaHCO_3$.

Mixture of Na_2CO_3 + $NaHCO_3$ + *clay*

Figure 10 shows the TG and DTG curves for this mixture and Table 3 shows the results:

Table 3

Mixture of 20% $NaHCO_3$+20% Na_2CO_3+60% clay			
	% $NaHCO_3$	% Na_2CO_3 from $NaHCO_3$	% Na_2CO_3
Added	20	— —	20
Experimental	19.92	12.56	32.30
Corrected	— —	— —	19.67

As it is seen, from Table 3, the difference between Na_2CO_3 added and Na_2CO_3 corrected is 0.33%.

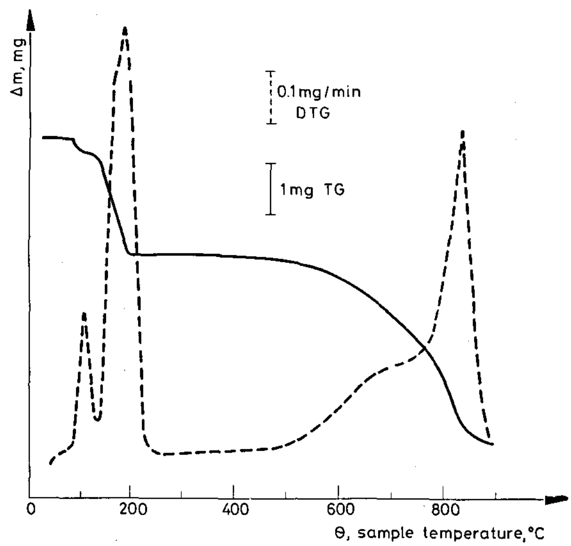

Fig. 10. TG curve for the mixture: 20% $NaHCO_3$ + 20% Na_2CO_3 + 60% clay. Atmosphere: air, heating rate: 20°/min, mass: 27.8 mg, suppression: 20 mg

Evaluation of real samples

As an example of a real sample, Fig. 11 shows the TG and DTG curves obtained for sample C (Table 4).

The explanation for each one of the different stages of weight loss is as follows:

Step a: Loss of humidity contained in the clay.

Step b: Loss of H_2O contained in Na_2CO_3.

Step c: Loss due to the thermal degradation of organic material.

Step d: Loss due to decomposition of Na_2CO_3.

Step e: Loss due to NaCl evaporation.

Table 4 shows the comparison of the traditional and the thermogravimetric methods.

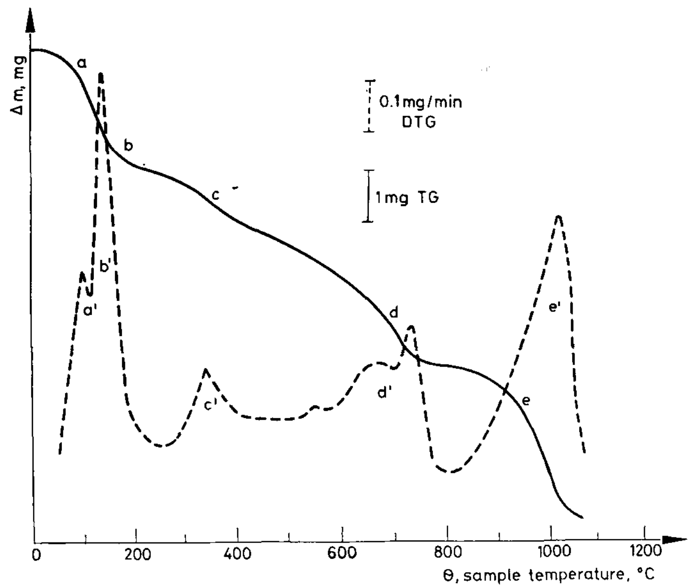

Fig. 11. TG curve for a real sample. Atmosphere: air, heating rate: 20°/min, suppression: 20 mg

Table 4

Sample	% Na_2CO_3 TG	% Na_2CO_3 Chemical	% NaCl TG	% NaCl Chemical
A	33.22	26.97	11.78	11.46
B	26.24	20.86	13.52	13.58
C	16.48	11.20	13.32	13.20
D	19.42	15.21	13.64	13.45
E	22.32	17.75	16.53	16.61

As it is seen, the differences obtained for NaCl are very small. However, the differences for Na_2CO_3 are greater. These differences are due to several experimental factors, some of them are:

1. Solubility
2. Homogeneity in samples
3. Humidity.

Conclusions

By the experiments presented here, it is possible to see that TG and DTG present an alternative method that can be very useful in the evaluation of certain salts contained in clays. The advantage of thermal analysis over other methods are:

1. More sensitivity, the measurements of mass variation have, for the sensitivities employed, an uncertainty of $\pm$ 0.05 mg.
2. More reproducible, the ability of the analyst is substituted by an electronic device.
3. More efficient, thermal methods furnish multiple information in a single experiment.

*

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Résumé — Les argiles de l'ancien lac de Texcoco (Vallée de Mexico) ont des teneurs variables en Na_2CO_3 et NaCl, qui sont en général évaluées par des méthodes chimiques. Dans cette publication, la méthode expérimentale présentée pour l'évaluation de ces sels est la thermogravimétrie.

ZUSAMMENFASSUNG — Die Ton-Arten des früheren Sees von Texcoco (Valley of Mexico) haben einen unterschiedlichen Na_2CO_3 und NaCl Gehalt, der gewöhnlich mittels chemischer Methoden ausgewertet wird. Zur Bewertung dieser Salze wird die Thermogravimetrie vorgeschlagen.

Резюме — Глины бывшего озера Тексkоко (Мексика) имеют переменное содержание Na_2CO_3 и NaCl, которые обычно оценивают химическими методами. Экспериментальным методом, представленным в этой статье, для определения этих солей, является термогравиметрия.