DETERMINATION OF STRUCTURAL WATER IN CERAMIC RAW MATERIALS

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1. INTRODUCTION

Water has been found present in minerals in various forms: hydration water also called H_2O^-, and is lost at temperatures around 110ºC; and crystallisation water, designated H_2O^+ or structural water, and decomposes at higher temperatures. These types of water provide different properties to materials, such as reactivity, plasticity, etc., which affect industrial processes in which they are used.

Some minerals, such as bentonites and sepiolites, present a great thirst for water due to their elevated specific surface area, which makes them suitable for a wide variety of applications, as for example, industrial absorbents, rheological additives or for waste treatment.

The H_2O^+ content is associated with loss on ignition, which is only valid in the absence of volatile components (CO_2, S^{2-}, F^-, Cl^-, etc.) and components that can be oxidised, for example, reduced Fe compounds. According to the literature, the methods most used for determining H_2O^+ in solid samples are the Penfield method and thermogravimetric analysis, but they present interference from compounds which decompose at temperatures around those of H_2O^+.

In this paper a fast and reliable method using combustion and IR detection for determining H_2O^+ in clay materials, considering both prior treatment of the materials and the measuring process. The method has been validated with certified reference materials.

2. EXPERIMENTAL PART

The materials used for conducting the study were: one bentonite, one sepiolite and one kaolin. In the first place, optimisation of sample drying was carried out, and after determining H_2O^+ using elemental analysis and thermogravimetric analysis (DTA-TG).

1) Optimisation of sample preparation

   To define the drying conditions of the materials before the H_2O^+ analysis, the samples were dried at 110ºC for 24 hours and were kept in a dryer for 14 days determining the loss on ignition of the samples periodically.

2) Measurement by combustion and IR detection with the LECO RC-412 elemental analyser

   Two calibration curves were drawn for different H_2O^+ content. Validation was achieved with the following reference materials: GBW 03118 Graphite ore and GBW 07153 Lithium Ore from the National Research Centre for Certified Reference Materials (China); Gyp-C Gypsum from DOMTAR Inc. Research Centre (Canada) and Mo-11 Anorthosite from IGEM – RAS (Russia).

Calibration	T_{max} (ºC)	Material	$C_{certified}$ (%H_2O^+)
Calibration 1	1000	GBW 03122 Kaolin	14.77
Calibration 2	1000	GBW07408 Soil	3.3

Table 1*. Calibrated for measurement by elemental analysis*

3) Thermogravimetric Analysis (DTA-TG)

   Thermogravimetric analysis was carried out on a METTLER-TOLEDO model TGA/STDA851e analyser at a maximum temperature of 1205ºC and a heating rate of 10ºC/min, using a platinum crucible in dynamic air atmosphere.

3. RESULTS

1) Optimisation of sample preparation

The results showed that it is necessary to keep the samples in a dryer and analyse them within the first 8 hours after drying, since during this time no variations in L.O.I. were observed in any of the materials analysed.

Time (days)	Loss on ignition (L.O.I) (%)		
	BENTONITE	SEPIOLITE	KAOLIN
0	7.71	11.36	11.28
8 hours	7.72	11.37	11.25
16 hours	7.91	11.82	11.22
1 day	8.12	12.59	11.20
3 days	8.72	13.06	11.20
5 days	9.53	13.82	11.25
10 days	9.99	14.62	11.26
14 days	10.85	15.05	11.28

Table 2. *Results of the tests carried out to determine the optimum storage time of the samples in the dryer*

After longer times an increase in the L.O.I. of bentonite and sepiolite is observed, while in kaolin it remains constant. This increase in the loss is directly related to the increase of the H_2O content of the materials.

2) Measurement by combustion and IR detection with the LECO RC-412 elemental analyser

Reference materials	$C_{certified}$ (% H_2O^+)	$C_{experimental}$ (% H_2O^+)
GBW 03118 Graphite ore	2.60±0.13	2.47±0.09
GBW 07153 Lithium Ore	2.29±0.15	2.22±0.08
Mo-11 Anorthosite	0.33±0.12	0.36±0.04
Gyp-C Gypsum	14.37±0.05	14.5±0.1

Table 3. *Results of the measurement of the reference materials*

SAMPLE	BENTONITE	SEPIOLITE	KAOLIN
% H_2O^+	9.8±0.1	5.9±0.1	11.3±0.1

Table 4. *Results of the measurement of samples using elemental analysis*

In the validation results there were no significant differences between the certified value and the experimental one.

3) Thermogravimetric Analysis (DTA-TG)

BENTONITE	SEPIOLITE	KAOLIN
110-200ºC $\Delta m=6.3\%$	110-200ºC $\Delta m=1.5\%$	110-200ºC $\Delta m=0.30\%$
200-900ºC $\Delta m=3.7\%$	200-900ºC $\Delta m=9.9\%$	200-900ºC $\Delta m=10.8\%$
900-1205ºC $\Delta m=0.1\%$	900-1205ºC $\Delta m=<0.1\%$	900-1205ºC $\Delta m=0.2\%$

Table 5. *Results of the measurement of the samples using DTA-TG.*

In the DTA-TG for bentonite, a loss between 110º and 900ºC of 10.0% was observed, which could correspond to with the H_2O^+ content, which was corroborated because said loss coincides with the value obtained for H_2O^+ by elemental analysis (9.8%).

In the case of sepiolite, the weight loss obtained in DTA-TG between 110 and 900ºC is 10.4%. If we compare this value with the one obtained in the elemental analyser (5.9%), a significant difference can be seen, which is due to this material containing carbonates in its composition and an overlap in the decomposition of carbonates and water. Using elemental analysis, it has been determined that the material has 5.3% of CO_2. Taking this value into account, an H_2O^+ content of 6.1% is obtained using DTA-TG, which does not present a considerable difference with the value found by elemental analysis (5.9%).

For kaolin, the loss obtained using DTA-TG between 110 and 900ºC (11.2%) corresponds to the H_2O^+content and does not differ from the value found by elemental analysis (11.3%).

4. CONCLUSIONS

1) The materials must be dried at 110ºC for 24 hours, stored, perfectly sealed, in a dryer and analysed within less than 8 hours after the drying process.
2) The measurement method using elemental analysis by combustion and IR detection is exact and fast, since it allows determination to be carried out in less than 30 minutes.
3) The DTA-TG analysis provides information about weight gains and losses of the material when it is subjected to thermal treatment, but does not enable H_2O^+ to be determined when the sample contains carbonates due to the overlap in the decomposition of H_2O^+ and CO_2.

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