STRUCTURAL CHARACTERIZATION, THERMAL AND MORPHOLOGICAL ANALYSIS OF MATERIALSAT ECOLOGICAL PARK THE POMA-COLOMBIA

CARACTERIZACIÓN ESTRUCTURAL, ANÁLISIS TÉRMICO Y MORFOLÓGICO DE MATERIALES EN PARQUE ECOLÓGICO LA POMA- COLOMBIA

S. Hidalgo*, D.A. Landinez Tellez*, J. Roa-Rojas*

ABSTRACT

Hidalgo, S., D. A. Landinez Téllez, J. Roa-Rojas. Structural characterization, thermal and morphological analysis of materialsat ecological park the Poma-Colombia. Rev. Acad. Colomb. Cienc., 37 (1): 12-16, 2013. ISSN 0370-3908.

This place hosts rock shelters with cave paintings. The materials studied include: clays, substrates and pigment in cave painting, these materials were analyzed under various experimental techniques suitable for structure determination, thermal and morphological analysis. To determine the basic composition the X-ray fluorescence energy dispersive (XRFED) was used. This is versatile, fast and nondestructive sampling technique used in archeological field, because it uses little sample and is not invasive. For identification of the clays, the technique of X-ray Diffraction (XRD) is employed in order to demonstrate the present phases. To observe the thermal behavior two methods were applied, differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). These two techniques allow determining any event associated with a change in thermal properties of a material with respect to temperature or time. Finally in the morphological analysis, the study of grain size to the clay fraction was performed by scanning electron microscope (SEM).

Keyword: Rock art, pigment, characterization techniques.

RESUMEN

Este trabajo realiza un estudio de materiales en el Parque ecológico la Poma ubicado en Soacha-Cundinamarca este lugar alberga abrigos rocosos con pinturas Rupestres. Los materiales que se estudiaron son: arcillas, sustratos y pigmento en Pintura Rupestre estos materiales se analizaron bajo varias técnicas experimentales adecuadas para la determinación estructural, análisis térmico y morfológico. En cuanto composición básica para ello se utilizo la fluorescencia de rayos X por energía dispersiva (EDXRF) es una técnica de muestreo versátil,

* Grupo de Física de Nuevos Materiales, Departamento de Física, Universidad Nacional de Colombia - A.A. 5997, Bogotá D.C, Colombia. E-mail: shidalgof@unal.edu.co.

rápida y no destructiva utilizada en el campo arqueológico ya que se utiliza poca muestra y no es invasiva, para la identificación en la arcillas se aplico Difracción de rayos X(DRX) para evidenciar las fases presentes, para ver el comportamiento térmico se aplicaron dos métodos la calorimetría diferencia de barrido (DSC) y análisis Termogravimétrico (TGA) estas dos técnicas permite determinar cualquier tipo de evento asociado a un cambio de propiedades térmicas de un material respecto a la temperatura o al tiempo, para la parte de morfología realizamos estudio de tamaño de grano a la fracción arcilla.

Palabra clave: Arte rupestre, pigmento, técnicas de caracterización.

1. Introduction

The characterization of materials in artistic representations presents a great difficulty, due to the raw materials employed in their elaboration and degradation processes, which may lead to a large number of substances. Also, the historical value usually associated to samples from artistic origin imposes reserves about the amount of available sample for study,

The study of cave paintings has been focused on understanding the forms and figures represented and the relationships that these keep with a general set of symbols, in which there is an interest in the meaning and forms represented. The Archaeometric analyzes done in these paintings do not evidence in depth aspects as raw materials used and processes performed.

Knowing this information about composition and manufacturing processes of material allows to the obtained information be associated with other already archaeological events ocurred. In addition the results obtained under the techniques which pigment is studied, will guide the conservation and restoration of cave paintings. As it is necessary, in principle, conceiving the cave paintings on a broader concept of integrity in other scientific disciplines. Likewise, it is considered that the way to make plans of preservation of the pictographs is to advance in the characterization studies of the pigments.

In Latin America are still incipient studies on the application of characterization in cave paintings. Some few reported in scientific literature, as developed in the archaeological and physicochemical study of cave paintings in Hob. Which aims to present new evidences of cave representations and nondestructive techniques used on some samples [1].

The research on materials, laboratories and relationships that can be seen in these fields are quite scarce. Only recently a report has been done in this field. The GIPRI's work has become a pioneer in the development of this research. Specifically the work of Judith Trujillo Tellez. This thesis titled Paintings Archaeometry: "La Piedra de La Cuadricula" is the first work developed in archaeometric analysis of the cave paintings of cundiboyacense plateau in infrared spectrometry laboratories of the National Museum of Natural History in Paris [2].

2. Experimental details

In this paper we study samples of clay materials from Ecological Park La Poma, whose geographical coordinates are 4° 31'56 .74" N and 74 ° 16'49 .08" W respect to Bogota at a height of 2600 meters. In this place several rock shelters are found along with paintings. This article will include results of some samples as a pigment and substrate rock, collected on a rock shelter called the Grid stone see Figure 1, which is located in the inside the park.

Figure 1. Photographs Grid stone wall the Poma Park.
Source: Researchers o frock art in Colombia.

Samples were taken following the protocols of sampling of rupestre sites. This indicates extract small rock samples to not affect the rock panel, 6 samples were taken from different materials, three of them are clays of the area denoted in the paper like (M1 , M2, M3) with different colors and textures, one rock fragment the grid stone (rock) and one of paint not exceeding 2 cm^2 denoted (pigment), the GIPRI group in an field trip several years ago found a reddish rock that also link to the study as a possible candidate for pigment raw material (M5).

2.1. *Techniques*

Fluorescence Spectrometer for X-ray, has been developed especially for mineral analysis in the field and other industrial and scientific applications.

Some characteristics of X-ray fluorescence portable (XRF) analysis make it an ideal method for researching of cultural relics and archaeological finds. Therefore, it has become a standard method used in archeometry. Paintings, manuscripts, ceramics, metalwork, glass, and many other objects are analyzed in order to recognize their materials, production technologies and origin, and to identify counterfeit [3], for this technique all samples were studied.

Thermogravimetry (TG) was used to determine the loss mass experienced by the solid sample subjected to the action of temperature. Furthermore, to determine the endothermic and exothermic reactions the differential scanned calorimetry was used (DSC), for the study a differential scanning calorimeter was used, TA Instruments DSC Q100, whose the temperature accuracy is ± 0.05°C previously calibrated with a Indian standard, an atmosphere of nitrogen was used with a controlled flow of 50ml/min.

The XRD analysis helped to characterize and quantify the mineral phases present in the samples of clays, there are two methods of XRD: Powder Method, used to make a characterization and quantification of mineral phases in general, and the aggregate oriented method, used to make a good characterization and semi-quantification of clay mineral phases, the X-ray diffraction analysis was performed with analytical X'Pert PRO MPD diffractometer, located in the department of Physics at the National Unive rsity. diffractograms were analyzed using X'Pert HighScore.

Before applying the technique of clay for samples oriented XRD, in some cases it is necessary the cleaning and preconcentration of the clays present in the sample [4].

These preparatory steps are briefly described below.

- Treatment with acetic acid to remove carbonates: It may be necessary to dissolve the carbonates in some limestones and sediments before the clay minerals can be identified.
- Removal of organic material with hydrogen peroxide: The presence of organic compounds, which causes a large hump in the diffraction patterns of powder X-ray, can obscure the maximas of diffraction of the mineral species.
- To prepare oriented aggregates of the fine fraction, the total sample is treated by homogenization and dispersion with distilled water. Then the fine fraction is separated by decantation recovering the finest fraction to verify particle size which is what we used to prepare oriented aggregates, we used the scanning electron microscope (SEM).

3. Results and discussion

3.1. *X-Ray Fluorescence*

The X-ray fluorescence, shows a high content of oxides of Aluminum and Silicon, as shown in Table.1 and 2. Lower values than 1% were not taken into account because their low percentage of concentration.

Table 1. Chemical element by X-Ray Fluorescence and concentration percentagesin clay sample M1, M2, and M3.

	Percent concentration (%)		
Compuesto / Elemento	**M1**	**M2**	**M3**
Si02	68,78	52,92	47,44
TiO2	-	1,10	0,94
Al203		25,81	26,79
Fe2O3	4,00	7,79	7,65
K20	2,05	-	-

Table 2. Chemical elements and percent concentration in samples (M5), substrate and pigment, Portable x-ray Fluorescence.

	Percent concentration (%)			
Element	**Symbol**	**M5**	**rock**	**Pigment**
Silicon	Si	-	24,33252	4,52926
Potassium	K	-	-	-
Calcium	Ca	1,71633	-	7,61755
Titanium	Ti	0	7,3547	-
Iron	Fe	98,28366	12,73902	75,56346
Strontium	Sr	-	18,6709	6,42859
Nickel	Ni	-	12,56221	-
Zirconium	Zr	-	24,34061	5,86111

For the pigment, the substrate and the M5 sample, the portable X-ray fluorescence technique was applied. In the pigment an iron (Fe) and zirconium (Zr) were found as potential chromophores. On the other hand for the substrate, elements such as silicon (Si) and zirconium (Zr) were found in equal proportions.

3.2. *Analysis Thermal*

The results of TG and DSC analysis are presented in Figure 2 and 3, they evidence similar peaks in the two studied clays, the DSC chart between (8.01°C and 9.54°C) is observed respectively, and a second endothermic peak common to all clays, between 138.61 °C and 122.89 ° C, both peaks are caused by the loss of hygroscopic or free water. This loss of water is also reflected in the thermogravimetric curves for the marked loss weight and these result from the loss of hygroscopic or free water [5], this water loss is also reflected in the thermogravimetric curves, for the marked weight loss as shown in Table 3, mass loss on clay is very small, they are thermally stable, in the M5 sample the mass loss is minimal and no marked losses.

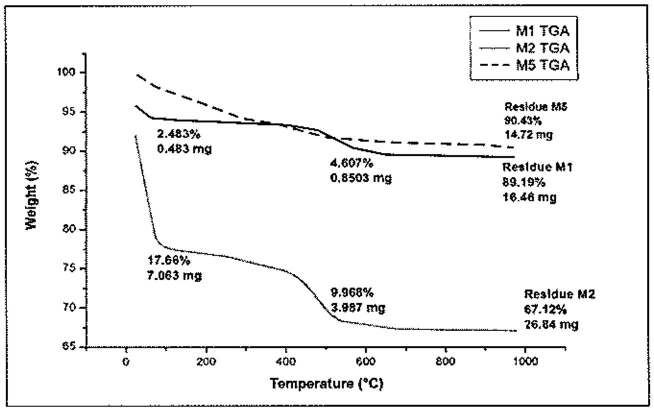

Figure 2. Graphical mass loss for the (TGA) M1 and M2.

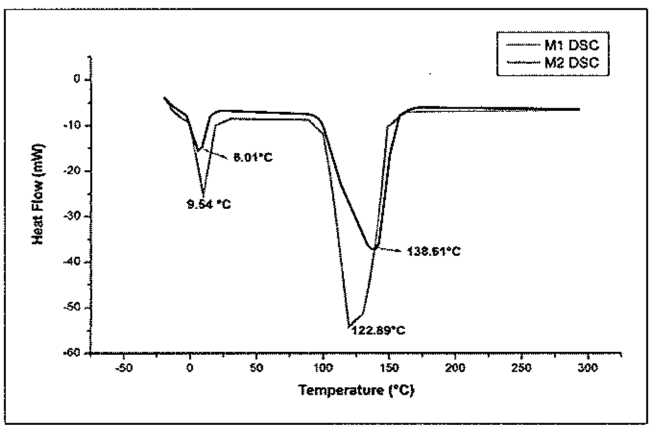

Figure 3. Scanning calorimetry differences (DSC) M1 and M2.

Table 3. Percent of mass loss between 0°C y 1000°C.

Mass	Mass initial (mg)	Mass loss (%)	Residue (mg)	Residue (%)
M1	18,456	10,81	16,46	89,19
M2	39,993	32,88	26,84	67,12
M5	16,283	5,57	1,563	90,43

3.3. *Analysis granulometric*

The obtained results for the various fractions in table 4 are given. Product average values are shown for chemical treatments performed. The counting was done in the Image J. Processing and Analysis Imagen is a public domain software, As noted, the samples M1, M2, M3 and M5 has an average value between 0.390µm- 0.559µmwhich corresponds to a clay fraction, Becomes effective chemical treatment processes carried out for the removal of impurities to find the fraction clays.

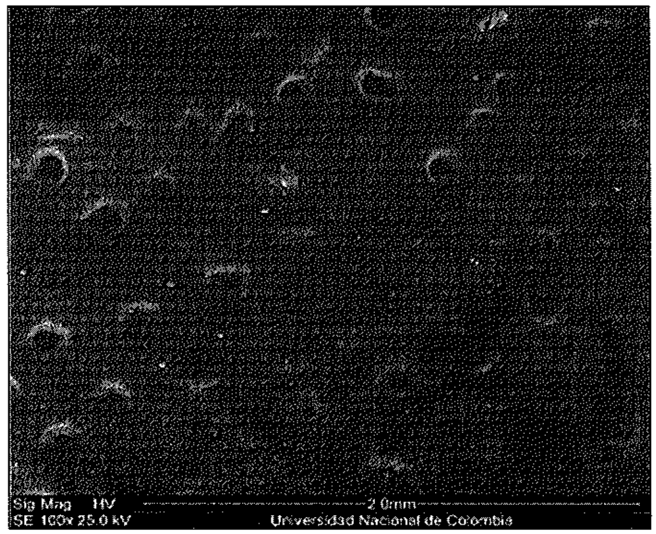

Figure 4. Clay Fraction M1, SEM image taken by.

Table 4: mean, standard deviation SD, Maximum, Minimum and all elements studied.

Date	Mean	SD	Minimum	Size
M1	3,93E-04	2,33E-03	1,59E-06	1343
M2	4,93E-04	1,83E-03	1,61E-06	2267
M3	5,59E-04	2,90E-03	1,61E-06	1937
M5	0,00409	0,00331	0,00178	1789

3.4. *Analysis X-ray diffraction*

X-ray diffractograms obtained for samples M1 are presented in Figure 5, based on these, one can identify the majority and minority phases which compose each of the clays, for powder samples, the clay glycol treated, and process temperature 350°C and 550°C.

The analysis took into account the higher mineral phases of the sample, in the samples studied these are: a high content of Quarzo Si O_2, Kaolinita ($Al_2Si_2O_5(OH)_4$), Hematita (Fe_2O_3) y Aluminum Phosphate (PO_4).

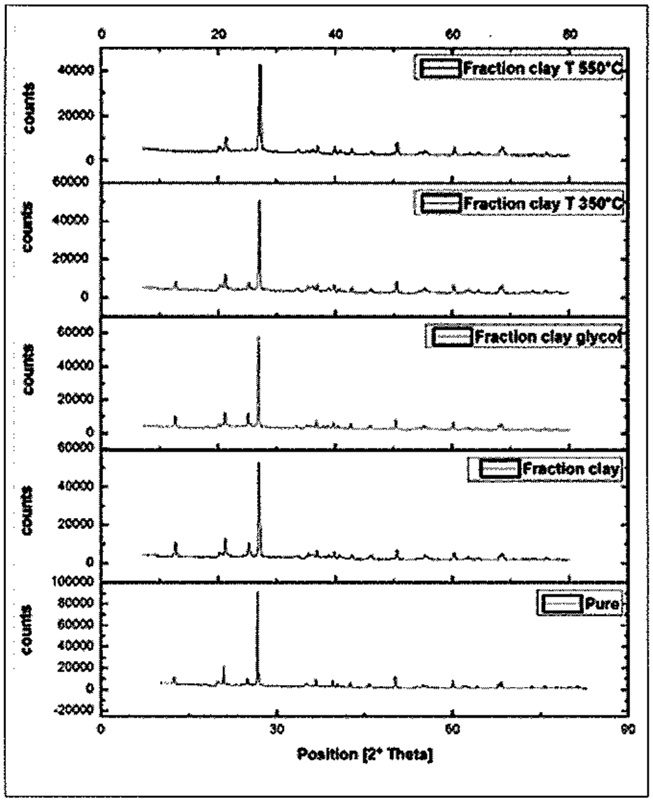

Figure 5. X-ray diffraction shows M1 powder sample, treated with glycol temperature 350 ° C and 550 ° C.

Table 5. Phase percent in samples clay treated..

	Quarzo (%)	Kaolinite (%)	Anastase (%)	Aluminium phosphate (%)	Hematita (%)
M1	31	11	1	56	1
M1 sin glicol	57	33	-	6	3
M1 con glicol	20	28	8	41	3
350 C	25	20	4	43	8
550 C	31	30	4	33	2
M2	58	36	-	-	5
M2 sin glicol	26	68	4	-	3
M2 con glicol	37	56	7	-	-
M3	37	56	7	-	-
M3 sin glicol	12	84	3	-	-
M3 con glicol	11	83	6	-	-
M5	20	-	-	21	59

4. Conclusions

The clays studied under the x-ray fluorescence technique shows the presence of oxides of Si and Al. This matches with majority mineral phases exhibited in the X-ray diffraction, These two techniques in the sample M5 presents greater amounts of iron oxides.

The x-ray fluorescence Portable technique showed a great advantage in the study of pigment and substrate, since allowed to identify separately its composition without damaging the sample, the use of this technique resulted very useful because the amount of sample studied was very small and has great wear. The presence of iron oxide in the clay and the pigment are associated like responsible for its reddish color.

Clay samples analyzed under the DSC and TGA thermal techniques exhibit thermal stability, this is evidenced by the low mass loss also associated with hygroscopic water loss.

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