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The use of natural earths in picture: study and differentiation by thermal analysis

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Abstract

The composition of commercially available ochres and siennas were studied by thermal analysis (TG and DTG) and XRD analysis. The significant parameters found on the thermoanalytical curves enable the classification of the ochres tested. Depending on the matrix of the sample, ochres can be classified into: ochres containing kaolinite and ochres containing sulphate. A relationship between the matrix and the source of the sample may be established.

Keywords: Ochres differentiation; Siennas differentiation; TG; DTG; Painting analysis; Works of art

1. Introduction

Among the existing painting materials, natural earths have been widely used because of their availability, high colouring capacity and stability under varied weather conditions. These earths are inorganic pigments, known as ochres, siennas (raw and burnt), umbers, green earths and other. They exhibit different properties and quality from a pictorial point of view. Their origin may be very different (Spain, France, Italy, Germany, etc.).

Natural earths have been studied by means of infrared spectroscopy, Raman spectroscopy (1), X-ray diffraction (2) or SEM microscopy (3). No references are found, in the literature, on the use of thermal analysis in the characterisation of earth pigments. The results obtained by thermal analysis have been supported by XRD analysis.

The contribution to the characterisation of earths is one of the main aims of our working group. The interest of this study lies in the fact that the former characterisation in an artwork may shed light on its author, provenance or the working technique used by an artist, workshop or even the place of origin. Therefore, the present paper represents an attempt towards the characterisation of the painting materials used and the relationship with their source. For these purpose, the differences between several sorts of ochres and siennas have been studied.

2. Experimental

2.1. Materials, instrumentation and operating conditions

Different natural earths which can be found in works of art were analysed. The samples were obtained from Caremi (Sevilla, Spain). The supplier describes the natural earths as permanent pigments of different colours constituted basically by iron oxide. Table 1 gives provenance and characteristics of the samples studied.

Calcium sulphate dihydrate, calcium sulphate hemihydrate, goethite, kaolinite and calcium carbonate were also obtained from Caremi (Sevilla, Spain) and used as standards.

For thermal analysis (TG–DTG), the samples were dried at room temperature (in dessecator with silica gel blue) for at least 48 h. The thermal analyses were performed with a thermobalance from TA instruments (SDT 2960) with temperature and weight precision of 0.1 °C and 0.1 μg, respectively. The sample was varied between 5 and 10 mg and weighted on ceramic pans. TG–DTG experiments were carried out in flowing dry nitrogen atmosphere ($100\,\mathrm{ml\,min^{-1}}$) with a temperature gradient of $10\,^{\circ}\mathrm{C\,min^{-1}}$ up to 1200 °C. X-ray

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Table 1
Sort, colour and provenance of the samples

Sample	Sort	Colour	Provenance
O1840	Ochre Jtcles	Light yellow	France
O1850	Ochre Tfles	Dark red	France
O1880	Ochre Jfles	Dark yellow	France
O1870	Ochre Jcles	Light yellow	France
O1890	Ochre Jals	Orange	France
O1910	Ochre Havane	Orange	France
O1920	Ochre Soforouge	Orange	France
O1930	Ochre M	Dark yellow	Spain
O1960	Ochre	light yellow	Spain
O1995	Ochre	Red	Andalucía (Spain)
O2245	Ochre	Brown	France
O2280	Washed ochre	Dark yellow	Spain
O2425	Ochre Avana	Green yellow	France
O2426	Ochre Sahara	Green yellow	France
S0340	Burnt sienna	Red	Tuscanny (Italy)
S0342	Natural sienna	Dark yellow	Tuscanny (Italy)
S2005	Natural sienna	Dark yellow	Italy
S2021	Natural sienna	Dark yellow	Italy
S2040	Burnt sienna	Red	Spain
S2055	Burnt sienna	Red	Italy

diffraction (XRD) was performed on a Siemens D5000 powder diffractometer equipped with a primary beam monochromator and Cu Kα radiation. The step size used was 0.050 Å (within the angle range 3–60°). The step time was established in 2 s.

3. Results and discussion

3.1. Thermal analysis

Simultaneous TG–DTA curves of studied samples, performed in nitrogen atmosphere were carried out. Derivative thermogravimetry (DTG) and differential thermal analysis (DTA) curves happened to be comparable. Although the results of the latter method reveal even those changes of state which are not accompanied by a loss of mass, the curves by the former method are more reproducible and are characteristic for each compound. The peak temperature (PT) of the DTG curve represents the temperature at which the rate of mass-change is maximum. The number of steps, the temperature ranges and the relative weight losses represent the most significant parameters of this research.

Identification is based on comparison of the recorded TG–DTA curves with those of reference materials. For this purpose, calcium sulphate dihydrate, calcium sulphate hemihydrate, goethite, kaolinite and calcium carbonate, in the same thermal conditions as the samples, were recorded and used as standards since these are the most common compounds to be found according to the literature [1–3].

The revelant thermogravimetric data for the ochres and siennas tested are reported in Tables 2 and 3, respectively.

Thus, the temperature range 30–100 °C is induced by hygroscopic water (i.e. physically adsorbed water).Within the 70–130 and 110–180 °C ranges, the weight loss due to the crystallisation water of calcium sulphate hemihydrate and dihydrate, respectively, takes place [4]. The weight loss between 200 and 350 °C corresponds to the transformation of goethite ($Fe_2O_3 \cdot nH_2O$) into hematite (Fe_2O_3). The most common clay minerals (kaolinite, illite, smectite) show relatively strong endothermic effects within the range 500–650 °C. Thus, kaolinite shows a broad intense endothermic peak within the 500–700 °C range (with a characteristic PT = 510 °C on the DTG curve) and a very sharp exothermic peak around 1000 °C [5]. Within the 400–800 °C range, other clay mineral (such as illite and smectite) may show weight losses. Calcium carbonate decomposes in the 700–900 °C range. The weight loss at temperatures higher than 1100 °C is usually related to the decomposition of calcium sulphate (also named insoluble anhydrite) [6].

Table 2
Data from TG–DTG curves for ochres

Sample	30–100 °C		100–200 °C		200–350 °C		350–550 °C		550–900 °C	
	WL[a] (%)	PT[b] (°C)	WL (%)	PT (°C)	WL (%)	PT (°C)	WL (%)	PT (°C)	WL (%)	PT (°C)
O1840	0.61	–	0.24	–	0.94	310	6.38	506		
O1850	0.87	–	0.34	–	0.36	–	1.90	510, 618		
O1870	0.67	–	0.22	–	2.94	326	5.85	512, 632		
O1880	0.78	–	0.22	–	2.99	310	6.72	525, 626		
O1890	0.85	–	0.29	–	2.99	320	6.48	527, 649		
O1910	0.63	–	0.24	–	1.82	324	10.69	518, 701		
O1920	1.14	–	0.54	–	1.22	310	7.46	523, 665		
O1930	0.37	–	14.22	132	1.82	277			0.73	677
O1960	0.33	–	18.42	130	1.27	289			1.99	673
O1995	2.15			97	0.35	–			2.56	667
O2245	0.62	–	0.50	–	1.81	316	4.21	525, 634		
O2280	1.16	–	0.32	–	2.69	328	6.78	520, 659		
O2425	1.36	–	6.35	128	1.14	300			14.96	739
O2426	0.96	–	0.40	–	3.07	326	6.92	514, 653		

[a] Weight loss.

[b] Peak temperature of the DTG curve and represents the temperature at which the rate of mass-change is at a maximum.

Table 3
Data from TG–DTG curves for siennas

Sample	30–100 °C		100–200 °C		200–350 °C		350–550 °C		550–900 °C	
	WL[a] (%)	PT[b] (°C)	WL (%)	PT (°C)	WL (%)	PT (°C)	WL (%)	PT (°C)	WL (%)	PT (°C)
S0340	4.96	68	1.69	–	1.43	281	3.71	479	6.16	706
S0342	4.97	54	2.05	–	6.85	268	2.55			
S2005	0.85	–	0.55	–	5.34	285	2.18	492	1.85	643
S2021	3.57	–	2.11	114	3.89	256	4.34	409	4.5	734
S2040	0.24	–	8.77	130	0.48	–	–	17.13	740	
S2055	2.32		0.75	–	0.48	–	8.99			417, 765

[a] Weight loss.

[b] Peak temperature of the DTG curve and represents the temperature at which the rate of mass–change is at a maximum.

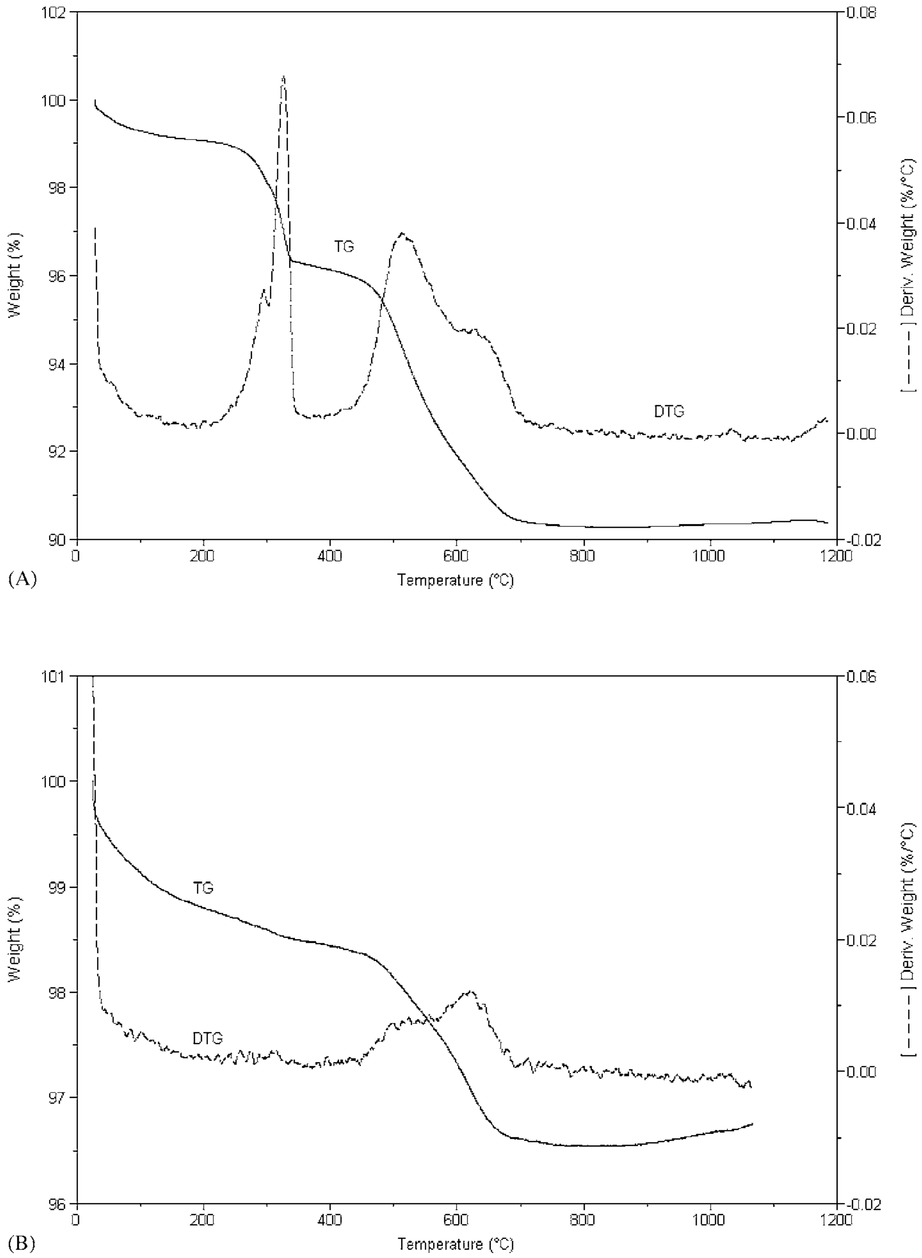

Fig. 1. TG and DTG curves of the samples: (A) O1870, (B) O1850.

The peak temperatures (PT) of the DTG curves indicate that the weight loss between 30 and 200 °C was due to the loss of hygroscopic water for all the ochres tested, except for samples O1930, O1960, O2425 and O1995 which contain calcium sulphate. In these samples, the weight loss can be attributed to bound water and clearly reveals that calcium sulphate is present in the dihydrate form in O1930, O1960 and O2425 samples (PT around 130 °C) and in the hemihydrate form in O1995 sample (PT = 97 °C).

All the ochres tested presented a PT (around 300 °C) on the DTG curves, assigned to the dehydration of goethite, except for O1850 and O1995 samples. Taking into consideration the weight losses between 200 and 350 °C, it must be pointed out that dark colours show weight losses lower than 0.4%, whereas light colours show losses higher than 1.0%.

Changes following each other very closely cannot be distinguished on the TG curves, as the corresponding stages coincide. However, the DTG curves of the same change indicate by the shape maxima that the thermogravimetric stages can be divided into two parts. Within the temperature range of 350–900 °C, two types of ochres were found: one group with weight losses below 670 °C and another group with a weight loss above this temperature. Thus, the samples O1930, O1960, O1995 and O2425 showed one only step with a PT above 670 °C, which can be assigned to the presence of calcite. On the other hand, in the remaining ochres tested, weight losses between 500 and 700 °C are detected

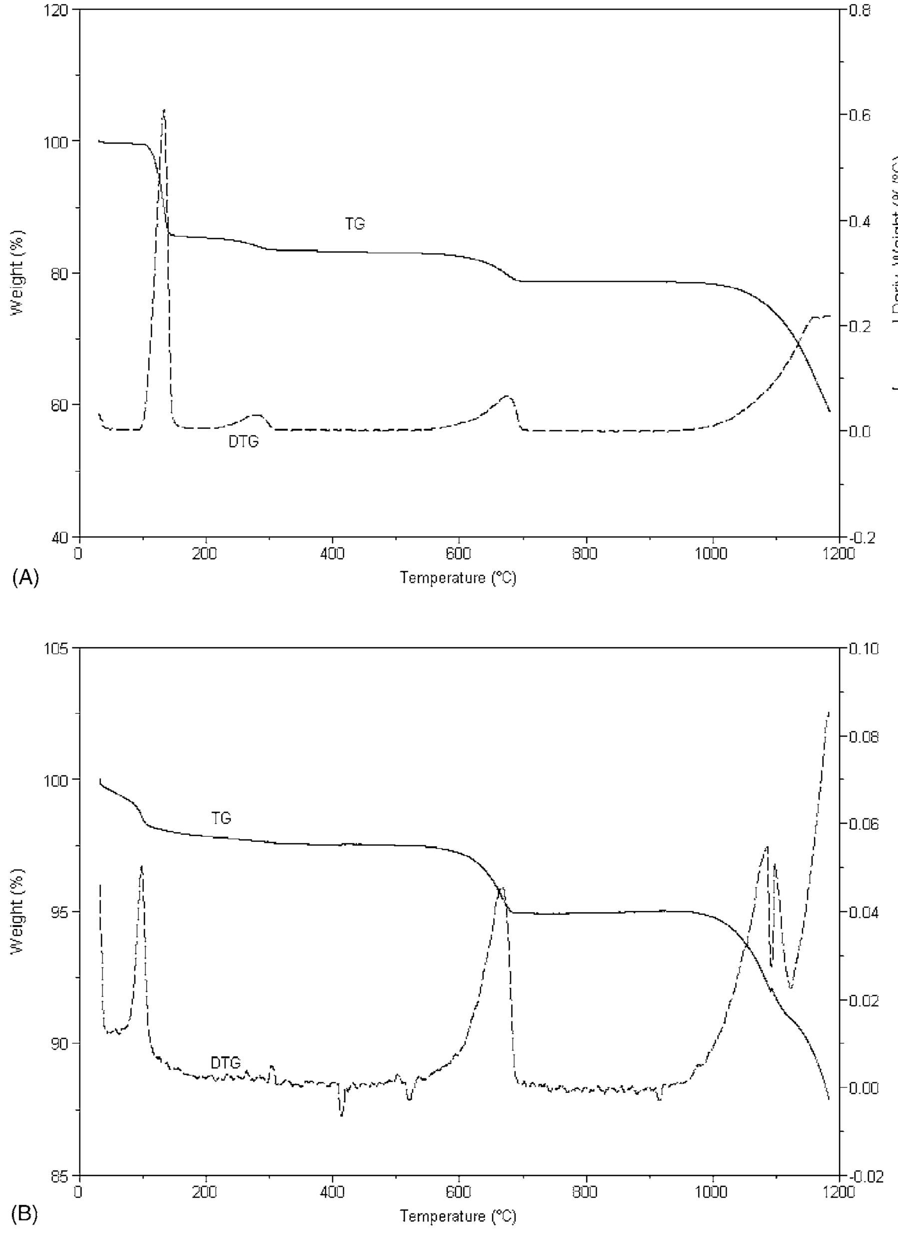

Fig. 2. TG and DTG curves of the samples: (A) O1930, (B) O1995.

and can be assigned to kaolinite and calcium carbonate (with two PT peaks on the DTG curves at 510 °C and between 610 and 670 °C, respectively). O1840 sample exhibits one only step in the temperature range of 350–900 °C which was correlated to the presence the kaolinite f (PT at 506 °C).

In summary, the significant parameters found on the thermoanalytical curves allow the classification of the ochres tested. Depending on the matrix of the sample, ochres can be classified into: ochres containing kaolinite and ochres containing sulphate. In this way, the samples O1840, O1850, O1870, O1880, O1890, O1910, O1920, O2245, O2280 and O2426 belong to the first group, whereas the samples O1930, O1960, O1995 and O2425 belong to the sulphate group.

The simultaneous TG–DTG curves of each characteristic kind of ochres analysed are presented. Fig. 1 shows two ochres (O1870 and O1850) rich in kaolinite (PT at 510 °C). Two steps are observed for the sample O1870: the above-mentioned and another step in the temperature range of 200–350 °C, attributed to goethite. Whereas, this latter step does not occur in O1850 sample.

The TG–DTG curves corresponding to ochre samples containing calcium sulphate (see weight losses at temperatures higher than 1000 °C) can be observed in Fig. 2. The weight losses between 100 and 200°C exhibited by sample O1930 may be ascribed to the presence of calcium sulphate dihydrate (PT = 132 °C), whereas no significant losses are found within this temperature interval for sample O1995,

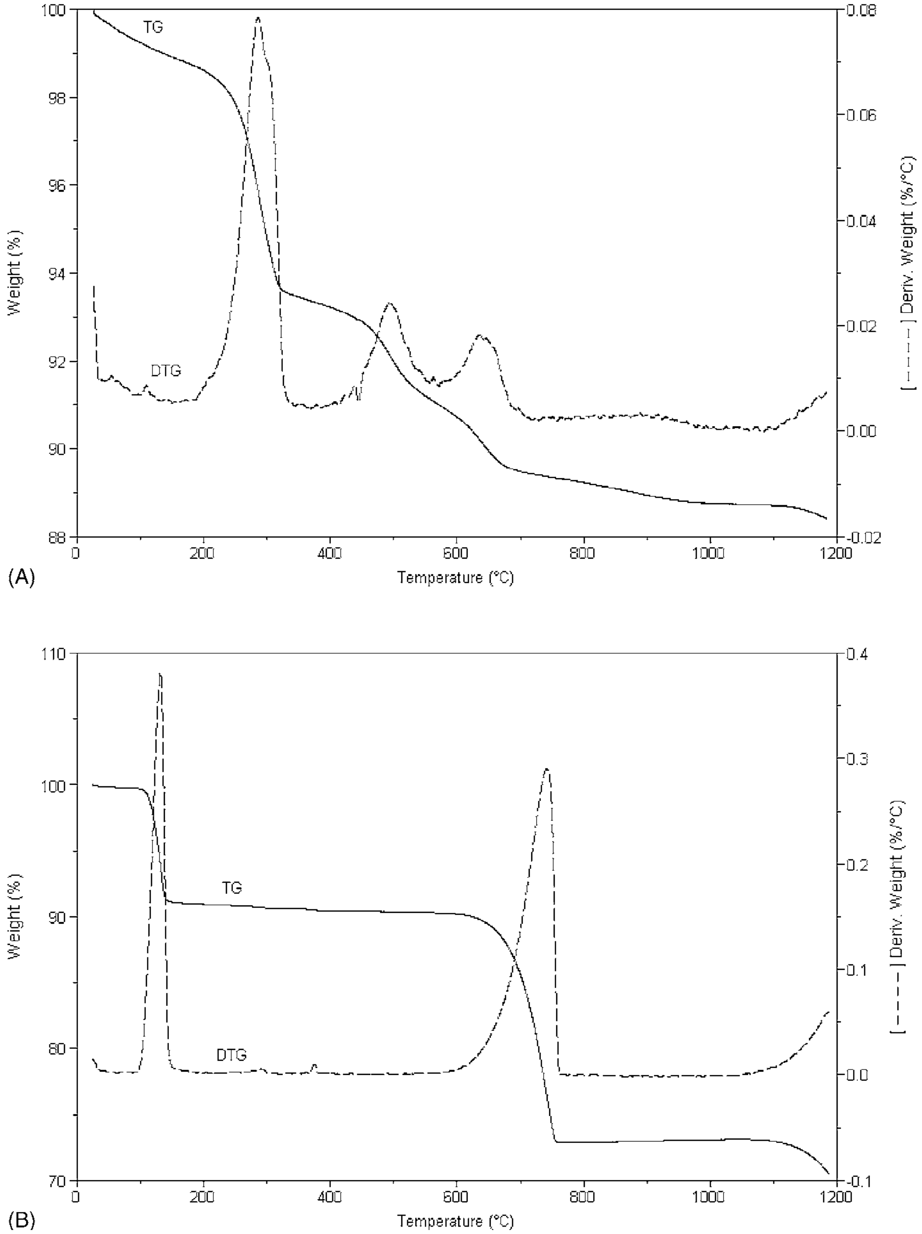

Fig. 3. TG and DTG curves of the samples: (A) S2005, (B) S2040.

Table 4
Percentages of Kaolinite, calcite and gypsum obtained from TG analysis

Sample	Kaolinite (%)	Calcite (%)	Gypsum (%)
O1840	≈70	–	–
O1930	–	1.7	67.9
O1960	–	4.5	88.3
O1995	–	5.8	–
O2425	–	34.5	30.3
S0340	–	14.7	–
S0342	–	–	–
S2021	–	10.5	10.1
S2040	–	39.0	41.9
S2055	–	9.0	–

although the PT at 97 °C of the DTG curve indicates the presence of calcium sulphate hemihydrate. Both samples also contain calcium carbonate.

The weight loss (%) estimated from the TG and DTG curves of the siennas analysed is presented in Table 3. From the results obtained, and as far as the ochres is concerned, a classification according to the matrix (kaolinite and sulphate) may be established. In this way, samples S2021 and S2040 contain calcium sulphate dihydrate (DTG curves with PT = 114 °C and PT = 130 °C, respectively). Calcium sulphate was identified in the sample S2055, according to the weight losses at temperatures higher than 1100 °C. Samples S0342, S2005 and S2021 exhibited a weight loss, due to the dehydration of goethite, greater than that observed for ochres. This fact implies the larger amount of iron in these samples in relation to ochres. No presence of goethite was detected by TG–DTG analysis in samples S2040 and S2055. Clay minerals are the main components in S0340 and S0342 samples. In sample S2005, the weight loss between 350 and 550 °C may also be ascribed to a clay mineral.

The TG–DTG curves of two siennas, very different in composition, can be seen in Fig. 3. Fig. 3A shows a thermogram belonging to sample S2005 which contains a large amount of goethite and clay minerals, whereas curves from Fig. 3B corresponding to sample S2040 contain gypsum and calcium carbonate. Two siennas with similar composition are displayed in Fig. 4. More steps (see Table 3 for corresponding PT) can be observed in sample S2021 as was expected for raw sienna in relation to burnt sienna.

On the other hand, all siennas tested contain calcite except for sample SO342. Raw siennas show losses from 4 to 7% in the 200–350 °C range and the burnt siennas show losses lower than 1.5%.

The main components may be calculated from TG data. Table 4 shows the percentages of kaolinite ($Al_2Si_2O_5(OH)_4$), calcite ($CaCO_3$) and gypsum ($CaSO_4{\cdot}2H_2O$) for the samples tested. Bearing in mind that the samples containing kaolinite generally also contain a small percentage of calcite, the weight changes following each other are very close, and these compounds (O1850, O1870, O1880, O1890, O1910, O1920, O2245, O2280, O2426 and S2005) cannot be quantified from the TG data curves. In order to avoid the mentioned problem, a shift towards higher temperatures would be observed for calcium carbonate under CO_2 atmosphere.

Table 5
Main data of XRD for ochres. Principal minerals contained and semi-quantitative estimation referred to the relative peak intensity[a]

Sample	Go	He	Ma	Ka	Qu	Ca	Gy	An	Ba
O1840	+	−	−	++	++	−	−	−	−
O1850	−	+	−	++	++	+	−	−	−
O1870	+	−	−	++	++	−	−	−	−
O1880	+	−	−	++	++	+	−	−	−
O1890	+	−	−	++	++	++	−	−	−
O1910	+	−	−	++	++	++	−	−	−
O1920	−	+	−	++	++	+	−	−	−
O1930	−	−	−	−	+	−	++	−	−
O1960	+	−	−	−	−	−	++	−	−
O1995	−	+	−	−	++	−	−	++	+
O2280	+	−	−	++	++	+	−	−	−
O2245	+	+	+	++	++	−	−	−	−
O2425	−	−	−	−	−	+	++	+	−
O2426	+	−	+	++	++	−	−	−	−

[a] Go: goethite; He: hematite; Ma: maghemite; Ka: kaolinite; Qu: quartz; Ca: calcite; Gy: gypsum; An: anhydrite; Ba: bassanite. +: minority; ++: majority.

3.2. *XRD analysis*

The mineralogical characterisation by means of XRD for the ochres and siennas tested is reported in Tables 5 and 6. The terms majority and minority are referred to the relative peak intensity in the XRD spectra. X-ray powder diffraction analysis allowed to identify the crystalline substances, when their composition is higher than 5% approximately. Minerals rich in sulphate such as gypsum, anhydrite or bassanite are easily identified and they show high crystallinity and a good signal/noise relationship. Clay minerals such as kaolinite, muscovite, etc. are also identified, however, their crystallinity is lower and the signal/noise relationship is worse. Iron is always present in earths and can be present in several forms (goethite and hematite) which are also recognised by means of XRD.

In this way, the results obtained by TG–DTG are in good agreement with those obtained by XRD. In several sam-

Table 6
Main data of XRD for siennas. Principal minerals contained and semi-quantitative estimation referred to the relative peak intensity[a]

Sample	Go	He	Qu	Ca	Gy	An	Mu	Others
S0340	++	−	+	++	−	−	−	Ak (+), So (+)
S0342	++	−	+	−	−	−	−	−
S2005	+	−	+	−	−	−	++	Ka (+)
S2021	+	−	++	−	++	+	−	−
S2040	−	+	−	+	++	−	−	−
S2055	−	++	++	+	−	++	−	−

[a] Go: goethite; He: hematite; Ka: kaolinite; Qu: quartz; Ca: calcite; Gy: gypsum; An: anhydrite; Mu: muscovite; Ak: ankerite; So: sodium magnesium iron aluminium silicate hydroxide. +: minority; ++: majority.

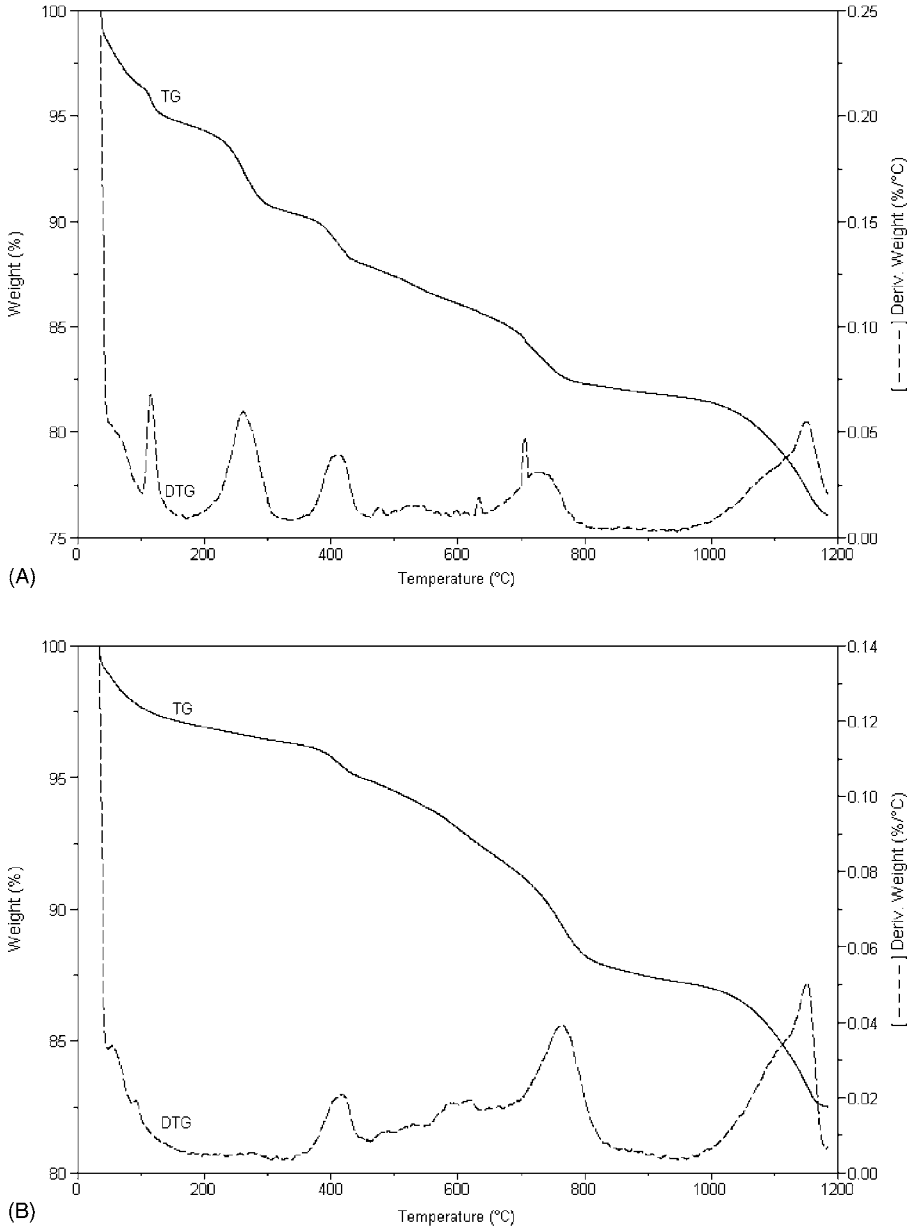

Fig. 4. TG and DTG curves of the samples: (A) S2021, (B) S2055.

ples, XRD analysis is complementary to thermal analysis as occurs in sample O1995 where anhydrite and hematite (samples O1850 and O1995) are present and may only be detected by means of XRD. In addition, in sample S2005, the clay mineral has been identified as muscovite.

Calcium sulphate was present as anhydrite in the sample S2055. XRD analysis revealed the presence of hematite in samples S2040 and S2055 in which no presence of goethite was detected by means of TG–DTG analysis.

3.3. Discussion

Earth pigments such as ochres and siennas chiefly contain iron oxides in several forms. Gettens and Stout [7] established than an ochre is a natural earth substance, consisting of silica and clay and owing its colour to iron oxide. Raw sienna is known as a special kind of yellow ochre which name comes from the homonymous town in Italy. According to Gettens and Stout [8], raw sienna contains yellow hydrous ferric oxide.

From the results obtained it must be pointed out that the colour, composition and the form iron oxide was present in natural earths cannot be considered separately as a safe criterion for the differentiation between ochres and siennas. When hematite is especially present, a red colour is exposed, whereas in cases where goethite dominates, yellow is the colour which is revealed. In both cases the earth pigment may be named as ochre or sienna. Nevertheless, in the case of French ochre (O1850, dark red) and red ochre (O1995, from Spain) both containing hematite, their matrix happened to be different.

On the other hand, raw siennas and yellow ochres may be distinguished between them, as a consequence of the greater weight loss (in the 200–350 °C interval) for siennas than for ochres. This fact is in good agreement with the literature, which describes siennas as a variety of ochres with a high content in goethite [1,2].

4. Conclusions

Differential thermal and thermogravimetric analysis are suitable for establishing characteristics of natural earths. In this way, the detection and quantification of the main components is easily achieved with a small amount of sample.

All the ochres tested contain goethite except for O1850 and O1995 samples, where iron is present as hematite. The weight loss (between 200 and 350 °C) is lower than 0.4% for dark colours, whereas light colours show weight losses higher than 1.0%.

Ochres and siennas show different visual displays on the TG–DTG curves, exhibiting different steps according to the matrix and/or diverse height of the steps. Thus, yellow ochres and raw siennas present different weight losses (200–350 °C range) even in those cases of similar matrix.

A relationship between the matrix and the source of the sample may be established. Thus, calcium sulphate is the most common component in the natural earths from Spain, whereas French ochres were basically composed of aluminosilicates.

When the quantification of kaolinite and calcium carbonate is not possible in some ochres, due to the overlapping of the steps, the use of CO_2 atmosphere should avoid this problem.

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