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APPLICATION OF THERMAL ANALYSIS TO THE STUDY OF SEVERAL SPANISH PEATS

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Thermogravimetry and differential thermal analysis have been applied to the study of peats from the main Spanish basements.

The results obtained show that the degree of transformation of the organic matter increases as the depth of the peat increases.

The intensity of the weight loss corresponding to the first exothermic effect (directly related to the carbohydrate content of the sample, and inversely related to the content of humic compounds) is, in the case of the peats with a high degree of transformation, strongly influenced by the nature of their humic acids.

On the other hand, the displacement of this exothermic effect towards lower temperatures is directly related to the ash content of the samples.

It is well known that thermogravimetry and differential thermal analysis are useful techniques in the study of minerals and organic compounds. Valuable information can also be obtained with these techniques in the study of the nature of soil organic matter and of other materials having potential application as fuels.

Because of the complex qualitative and quantitative compositions, soil organic matter undergoes pyrolytic decomposition in different stages. The characteristics of the constituents can be related to the stage in which their transformation takes place.

Studies by several authors coincide in pointing out that hygroscopic moisture is lost at low temperatures (around 100°), this being recognized in the curves by a slight weight loss and by a slight endothermic effect.

At somewhat higher temperature (up to 300°), the destruction takes place of the less condensed components, such as the polysaccharides or the more thermolabile components of the humic acids (functional groups and aliphatic compounds). Finally, at about 500°, thermal effects are attributed to the pyrolysis of the more condensed materials, such as the aromatic components of lignin and the "nuclear" region of the humic acids. Hoffman and Schnitzer [1] have studied humic and fulvic acids by TG, and have pointed out that the extent and intensity of the first exothermic effect is inversely related to the degree of humification of the corresponding samples.

Stewart et al. [2] have studied different samples of peat, and observed that the content of slightly transformed materials was proportionally related to the intensity of the first exothermic effect, concluding that the degree of humification of the peats increased with depth in the peat profile.

In the present investigation, the above criteria are applied to results obtained by thermal techniques from several representative Spanish peats. Some of these peats have a high degree of decomposition (sapric type), and show organoleptic properties that are very homogeneous along the profile. A clear differentiation of the materials from the different depths could not be established either by the criteria of Von Post or by fibre content determination. An investigation of the degree of peat transformation would thus require long quantitative and qualitative physicochemical determinations. We attempt to simplify the effort by means of thermoanalytical determinations, which preclude the need for laborious separations and extractions.

Materials and methods

Materials

The samples studied here are from different depths of three peat horizons from the basements of Mazagón, Daimiel, Torreblanca and Padul.

Samples M1, M-2 and M-3.

Locality and situation: Peat "Las Madres". Término de Moguer (Huelva, Spain).
Altitude: 15–20 m above sea-level.
Geological formation: Quaternary polygenic material.
Vegetation: Cladium mariscus, Dyropteris sp., Phragmites communis, Erica sp., Typha sp.
Depth in the horizon of the studied samples: M-1: 22–44 cm, M-2: 45–80 cm, M-3: 80–100 cm.

Samples D-1, D-2 and D-3.

Locality and situation: Finca Zoacorta (Ojos del Guadiana). (Daimiel. Ciudad Real. Spain)
Altitude: 560 m above sea-level.
Geological formation: Pontian karstic limestones.
Vegetation: Cladium mariscus, Phragmites communis.
Depth in the horizon of the studied samples: D-1: 0–90 cm, D-2: 90–150 cm, D-3: 150–200 cm.

Samples T-1, T-2 and T-3.

Locality and situation: Peat of Torreblanca. Castellón de la Plana, Spain.
Altitude: Sea-level.
Geological formation: Coastal lagoon formation.
Vegetation: Eliminated.
Depth in the horizon of the studied samples: T-1: 0–50 cm, T-2: 50–100 cm, T-3: 100–200 cm.

Samples P-1, P-2 and P-3.

Locality and situation: Peat of Padul (Granada, Spain).

Altitude: 760 m above sea level.

Geological formation: Neogenic basin that underwent strong subsidence.

Vegetation: Eliminated.

Depth in the horizon of the studied samples: P-1: 10 – 50 cm, P-2: 50 – 100 cm, P-3: 100 – 140 cm.

Methods

Derivative thermogravimetric curves and differential thermal analysis curves were obtained on a CHYO thermobalance model $TRDAH_3$ with a recorder incorporated. 200 mg of sample was diluted at 12.5% into calcined Al_2O_3, the latter being used as a reference for DTA. At a heating rate of 10°/min, the sensitivity of the recorder was set at 5 mg/min for DTG and at 250 μV for DTA.

Results and discussion

Analytical characteristics of the peats which may be of interest for interpretation of the results from thermal analysis are given in Table 1.

Figures 1 to 4 show DTG and DTA curves from the peat samples, and Table 2 gives the percentages corresponding to each significant effect.

Table 1

General analytical characteristics of the peats

Sample	Fiber content, weigth	%C	C/N	% ash	% 1st eff. HA	THE, %C	F/H	C. H %C
M-1	66.74	45.51	24.33	22.2	61.5	49.63	0.17	3.24
M-2	52.49	47.37	26.17	18.4	45.5	62.21	0.22	3.19
M-3	6.96	20.69	19.52	63.2	26.3	70.66	0.38	1.55
D-1	68.91	46.67	33.34	30.7	45.5	35.55	0.49	5.80
D-2	57.68	35.66	32.42	33.3	44.5	38.05	0.50	1.80
D-3	55.77	31.85	24.50	32.7	43.9	58.90	0.30	2.08
T-1	15.47	36.69	20.38	28.1	45.0	54.57	0.32	2.43
T-2	16.32	35.09	19.49	27.1	37.9	60.48	0.33	3.38
T-3	17.02	44.25	24.58	19.2	43.2	64.04	0.46	4.88
P-1	5.37	43.60	21.40	22.2	44.4	73.62	0.53	1.41
P-2	1.82	47.20	27.30	16.7	40.0	53.63	0.55	1.60
P-3	1.32	47.50	22.11	11.3	35.4	51.50	0.73	2.01

%1st eff HA: area of the first exothermic effect in the humic acids (%) THE: Total humic extract (% respective to total C); F/H: Fulvic acids/humic acids ratio; C.H.: Percentage of carbohydrates in respect to the weight of peat

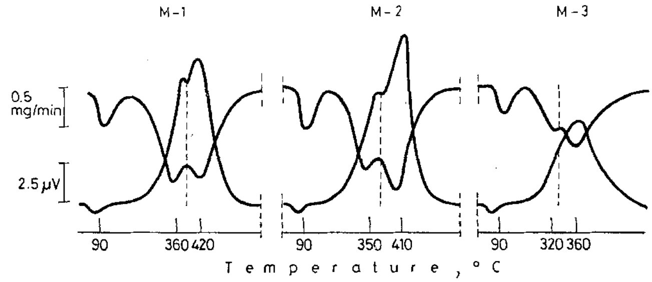

Fig. 1. TG and DTA curves from samples taken at different depths. Peat from Mazagón

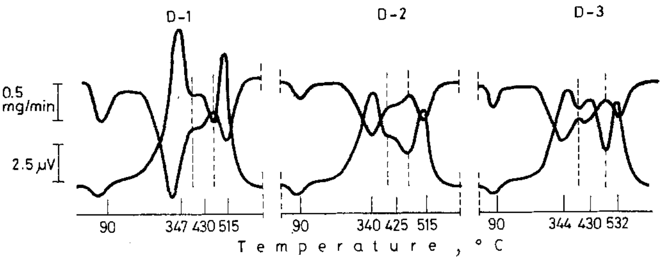

Fig. 2. TG and DTA curves from samples taken at different depths. Peat from Daimiel

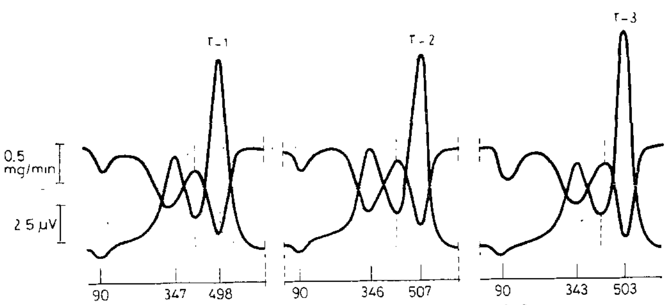

Fig. 3. TG and DTA curves from samples taken at different depths. Peat from Torreblanca

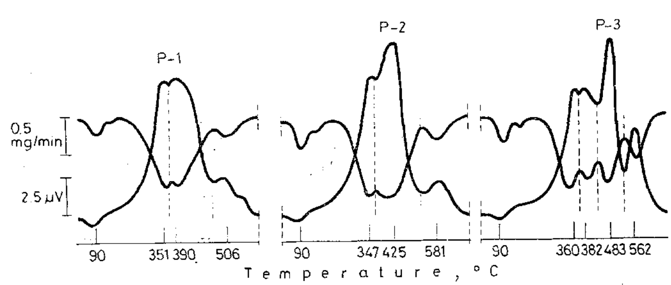

Fig. 4. TG and DTA curves from samples taken at different depths. Peat from Padul

Table 2

Percentages representing the different significant thermal effects in DTG and DTA curves

M - 1	DTA	50.0	50.0		
	DTG	36.2	63.8		
M - 2	DTA	45.1	54.9		
	DTG	38.0	62.0		
M - 3	DTA	29.4	70.6		
	DTG	26.9	73.1		
D - 1	DTA	64.0	20.0	16.0	
	DTG	55.6	24.4	20.0	
D - 2	DTA	62.7	15.6	21.7	
	DTG	52.2	19.6	28.2	
D - 3	DTA	54.5	30.3	15.2	
	DTG	47.1	35.2	17.7	
T - 1	DTA	55.0	45.0		
	DTG	42.9	57.1		
T - 2	DTA	52.4	47.6		
	DTG	46.3	53.7		
T - 3	DTA	51.4	48.6		
	DTG	39.0	61.0		
P - 1	DTA	38.3	51.1	10.6	
	DTG	34.7	51.0	14.3	
P - 2	DTA	35.6	56.7	7.7	
	DTG	34.7	54.6	10.7	
P - 3	DTA	34.6	26.9	27.0	11.5
	DTG	28.8	26.9	32.7	11.6

200 250 300 350 400 450 500 550 600

Temperature, °C

Both percentages were planimetrically evaluated from the surfaces of the corresponding differential curves, excluding the moisture peaks

In the curves of the peat from Mazagón (Fig. 1 and Table 2) the percentage corresponding to the weight loss during the first effect tends to decrease as the depth in the horizon increases, so that for specimen M-3, having a high content of extractable humic compounds (respective to total C) and a low polysaccharide content (sapric type), the bulk of the organic matter corresponds to compounds whose destruction takes place at about 400°. Additionally, a high ash content results in the intensities of both effects being lower than for specimens M-1 and M-2 and, possibly, the low temperatures at which these effects occur. This will be discussed below.

The results are comparable in the case of the peat from Daimiel: the areas of the first peak are higher in the curves from the top horizons, where thermolabile compounds of the type of incompletely decomposed roots predominate. The percentage corresponding to the effect at about 341° (64%) is the highest for all the peats studied here, in correspondence with the polysaccharide content (Table 1), which is higher than in the remaining samples.

In the peats from Torreblanca and from Padul, in contrast, the different horizons are difficult to differentiate at first sight: they have a rather low fibre content, that remains practically invariable down the profile. Even then, the results from derivative thermogravimetry and from differential thermal analysis show again that the percentages for the first thermal effect decrease with depth. Characteristic features in the curves from the peat from Padul (the one having the highest degree of decomposition) are the low values for the percentage of the first effect (28 – 34%; DTG) being comparable only to the value for the sapric horizon of the peat from Mazagón, and also the elevated temperatures at which the two final effects take place, which could be attributed to the low mineral content of this sample.

In view of the above results, it is confirmed that differential thermal analysis is an adequate procedure for obtaining information on the degree of humification of organic matter. This is so even for peats of the more pronounced sapric type,

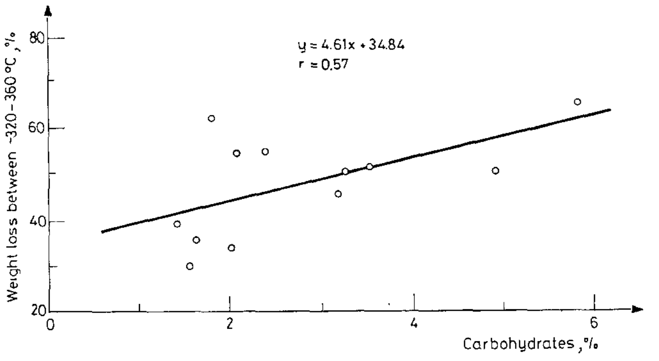

Fig. 5. Increase in the weight loss at 320—360° as a function of the carbohydrate content of the peat

where thermostable aromatic material predominates and where the contribution of polysaccharide materials is of little significance (they represent less than 10%, but in many instances no more than 3% of the total C content).

Figure 5 shows how the low content of polysaccharides is indeed related to the percentage representing the area of the first exothermic effect. On the other side (Fig. 6), the weight percent of humic substances extractable from the peat is inversely related to the intensity of this effect, because these substances have a much more thermostable character, despite the fact that a considerable amount of them is destroyed at about 400°.

When techniques of thermal analysis are applied to the study of the fraction of humic acids extracted from peats, it is observed that the percentage representing the first exothermic effect also shows a certain trend to decrease with depth in the horizon (Table 1). It appears, therefore, that in the case of highly transformed peats, the intensities of the different thermal effects are mainly influenced by the nature of the corresponding humic compounds. Independently, the influence of the content of humic acids (highly abundant in this type of peats), and of the low content of carbohydrates, must be taken into consideration.

On the other hand, the proportion of cellulose and other plant residues in general, as well as the fibre content of the less decomposed peats (frequently studied by authors who collect peat from colder climates), are decisive parameters for recognizing the degree of transformation of these types of peats.

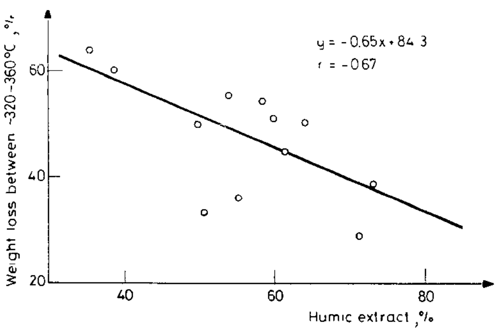

Fig. 6. Decrease in the weight loss at 320—360° as a function of the content of extractable humic substances

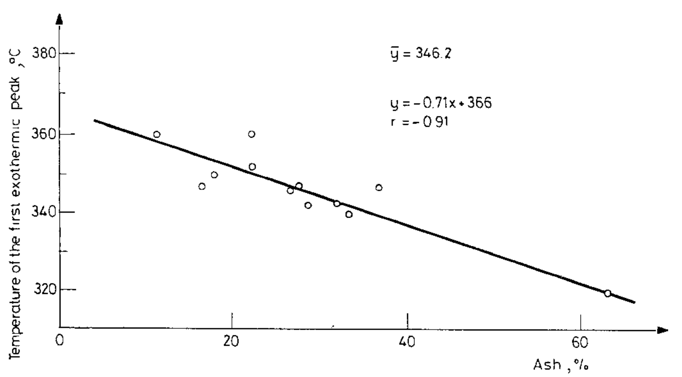

Fig. 7. Peak temperature of the first exothermic effect as a function of the mineral content of the peat

The strong qualitative influence of humic acids is best manifested in the case of the peat from Padul, where one can observe the percentages due to the first effect increasing in the sense of the more superficial horizons, despite the fact that the polysaccharide content increases and the content of extractable humic substances decreases in the deepest horizons.

The remaining variables studied (Table 1) show little correlation with the area of the first exothermic effect.

Finally, a certain correlation may be established between the mineral content of the peats and the temperature at which the different thermal effects take place. According to Hoffman and Schnitzer [1], formation of organometallic complexes promotes a significant shift of the maxima towards lower temperatures, this effect being more pronounced as the proportion of the mineral cation forming the complex increases.

Among the cases studied here, it has already been indicated that the two main peaks in the curves corresponding to the third horizon of the peat from Mazagón lie at relatively low temperatures because the mineral content of this particular sample is very high. Inversely, the low ash content of the peat from Padul can be correlated to the fact that thermal effects take place at high temperatures. The relationship between the ash content and the temperature of the first exothermic effect (Fig. 7) may be interpreted as a decrease in the second parameter due to the higher possibilities of formation of certain organomineral complexes.

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ZUSAMMENFASSUNG — Die thermogravimetrische Analyse und die Differentialthermoanalyse wurden zum Studium von Torfen aus den wichtigsten spanischen Lagerstätten eingesetzt.

Die erhaltenen Ergebnisse zeigen, daß der Umwandlungsgrad der organischen Substanz mit zunehmender Tiefe des Torfes zunimmt.

Die Intensität des dem ersten exothermen Effekt entsprechenden Gewichtsverlustes (welcher dem Kohlenhydratgehalt der Probe direkt und seinem Huminverbindungsgehalt umgekehrt proportional ist) wird im Falle von Torfen von hohem Umwandlungsgrad durch die Beschaffenheit ihrer Huminsäuren stark beeinflußt.

Andererseits ist die Verschiebung dieses exothermen Effekts in Richtung der niedrigeren Temperaturen dem Aschegehalt der Proben direkt proportional.

Резюме — Термогравиметрический и дифференциальный термический анализ был использован для изучения торфов в главных испанских подвалах. Полученные результаты показали, что степень превращения органического вещества увеличивается по мере увеличен глубины торфа. Степень потери веса на первом экзотермическом пике (прямо связанного с содержанием углеводов и в обратной степени с содержанием гуминовых соединений в образце) в случае торфов с высокой степенью превращения, сильно зависит от природы их гуминовых кислот. С другой стороны, сывиг этого экзотермического пика к более низким температурам находится в прямой зависимости от содержания золы.