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VACUUM THERMOGRAVIMETRY OF TEXTILES: PROCEDURES AND USE WITH CELLULOSIC FIBRES

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Extensive thermoanalytical studies of wool and hairs (Ref. 1,2) have demonstrated that vacuum thermogravimetric techniques provide observations from which differentiation of keratin fibres can be achieved (Ref. 2). With fibrous substrates that undergo no significant physical change prior to those changes which result in the observed weight losses, variations of substrate morphology are reflected in characteristic behaviours recorded in the TG curves. The potential significance of fibre anisotropy and geometric form in influencing the TG curves has been demonstrated with reference to protein fibres (Ref. 3). Recognition of these influences must always be considered when identifying optimum experimental procedures and interpreting the reproducible observations. With those sample systems (such as keratins) where numerous processes, concurrent and consecutive in both time and temperature, contribute to the observed weight change, recognition of characteristic differences was facilitated by the presentation of data as the rate of "normalised sample weight change" as a function of "sample" temperature (Ref. 2,3). A large proportion of all commercial textile raw materials are based on cellulose. We here report the extension and refinement of those techniques used successfully with protein fibres to the examination of cellulose textile fibres.

EXPERIMENTAL

Materials

Definitive samples of Egyptian cottons (Giza and Dandara) were obtained from the NRC Cairo and examined as representative of the major class of cellulosic fibres. The preliminary purification of these fibres and the preparative procedures employed in their presentation for thermogravimetry are described in Table 1. Previous observations with keratins had shown that the degree of subdivision was a parameter requiring strict control. Reduction of the lengths of fibrous elements decreased anisotropic influences and yielded improved resolution in the observed DTG curves, provided that the final size was not so small that an increase in packing density resulted. Such an increase will lead to loss of resolution due to diffusion control of the escape of volatiles. Cutting of the purified fibres was achieved with a Wiley mill operated for short times (less than 5 minutes) to reduce

degradation possibilities (Ref. 4). The cut samples were sieved through standard mesh sizes into more 'uniform' length dimension lots; a representative analysis is shown in Table 2.

TABLE 1

Cotton Sampling, Purification and Preparation for Thermogravimetry

Step No.	Operation	
1	Tufts sampled at random from bulk, and combined.	
2	Repeat step 1 with the 'combined' product of 1.	
3	Product manually opened and cleaned of adventitious impurities.	
4	Analysis samples obtained as combined random tufts of product from 3.	
5	(a) Washed thoroughly with distilled water.	(b) Soxhlet extracted with benzene and ethanol (2:1 V/V) for 6 hours.
6	(a) air dried	(b) air dried
7	(a) Comminuted in 'Wiley' mill.	(b) processed as 5 (a) to 8 (a).
8	(a) Sieved to provide more uniform size lots.	

TABLE 2

Microscopic Examination of 'Wiley' mill cut "Giza" cotton

Sieve Conditions (B.S. Sieve Sizes)		Dimension of 'Pass' Sieve	Number of Fibres Examined	Fibre length:	
Pass	Held on	(μm)		Length (μm)	Standard Deviation (μm)
40	60	425	180	459	102
60	100	250	180	299	71
100	120	150	180	214	68

Apparatus and Materials

Continuous evacuation thermogravimetry was carried out, presenting the observations after computation in the form of the temperature based rate or normalised weight loss against "sample" temperature. A DuPont 950 thermobalance was connected directly to a two stage rotary oil pump. As reported elsewhere (Ref. 5) the analogue weight and temperature signals were sequentially logged and recorded on punched tape followed by off line computational processing with graph plotter presentation.

RESULTS AND DISCUSSION

Moisture is known to affect the thermally induced degradation behaviour of celluloses (c.f. Ref. 6), and rigorously dried samples were considered as essential for reproducible observations. A sequence of isothermal weight loss studies identified that a preheating of the sample with continuous evacuation at 140°C for 90 minutes was effective in achieving this aim.

The influences of sample degree of subdivision (sizes passing '20' to '100' B.S. mesh), sample size (4 to 15mg.), and heating rate (5 to 20K min^{-1}) on the quality

and reproducibility of the plotted "average" DTG curves were examined. Representative curves illustrating the affects of these parameters are presented in Fig. 1. From these observations practical standard operating conditions were defined (see Table 3). With the established optimum conditions the DTG curves of 'water washed only' and 'soxhlet extracted and washed' Giza cottons were compared. Also examined and compared were Giza and Dandara cotton types. The reproducible and representative DTG curves are displayed in Fig. 1.

TABLE 3

Standard experimental conditions for vacuum thermogravimetry of cellulosic fibres (DuPont 950 thermobalance)

Continuous evacuation at 50 torr.
Heating rate of 8K min^{-1} from 150° to 450°C.
Sample presentation
Purified fibre cut by 'Wiley' mill,
Sample to pass BS. 60 mesh but held on BS. 100 mesh sieves.
8mg sample spread out on platinum pan.
Sample 'predried' at 50 torr and 140°C for 90 minutes.

Although cotton has an extremely high α cellulose content there are other materials associated with the raw fibre of which wax, largely as a coating, is the most significant. This wax, similar to carnauba, affects properties and can be removed by organic solvents such as provided by the soxhlet extraction (Ref. 7). Perkins et al., have reported changes in degradation behaviour from DTA and TG studies in both air and nitrogen (Ref. 8) in line with the current observations of more rapid and later weight loss occurring over a narrower temperature range with the extracted fibre. Other "impurities" as well as wax vary with different cottons. Variations are also known to occur in the content and distribution of the levels of cellulose order, as well in the orientation of that order. There is considerable evidence that changes in thermal degradation behaviour result from each of these variable features. One would anticipate that DTG curves of different cotton types would exhibit characteristic variation. The varieties currently examined confirm this conclusion and suggest that these procedures could be usefully extended to discriminate between cellulosic fibres of (a) different types and (b) the products of different treatments.

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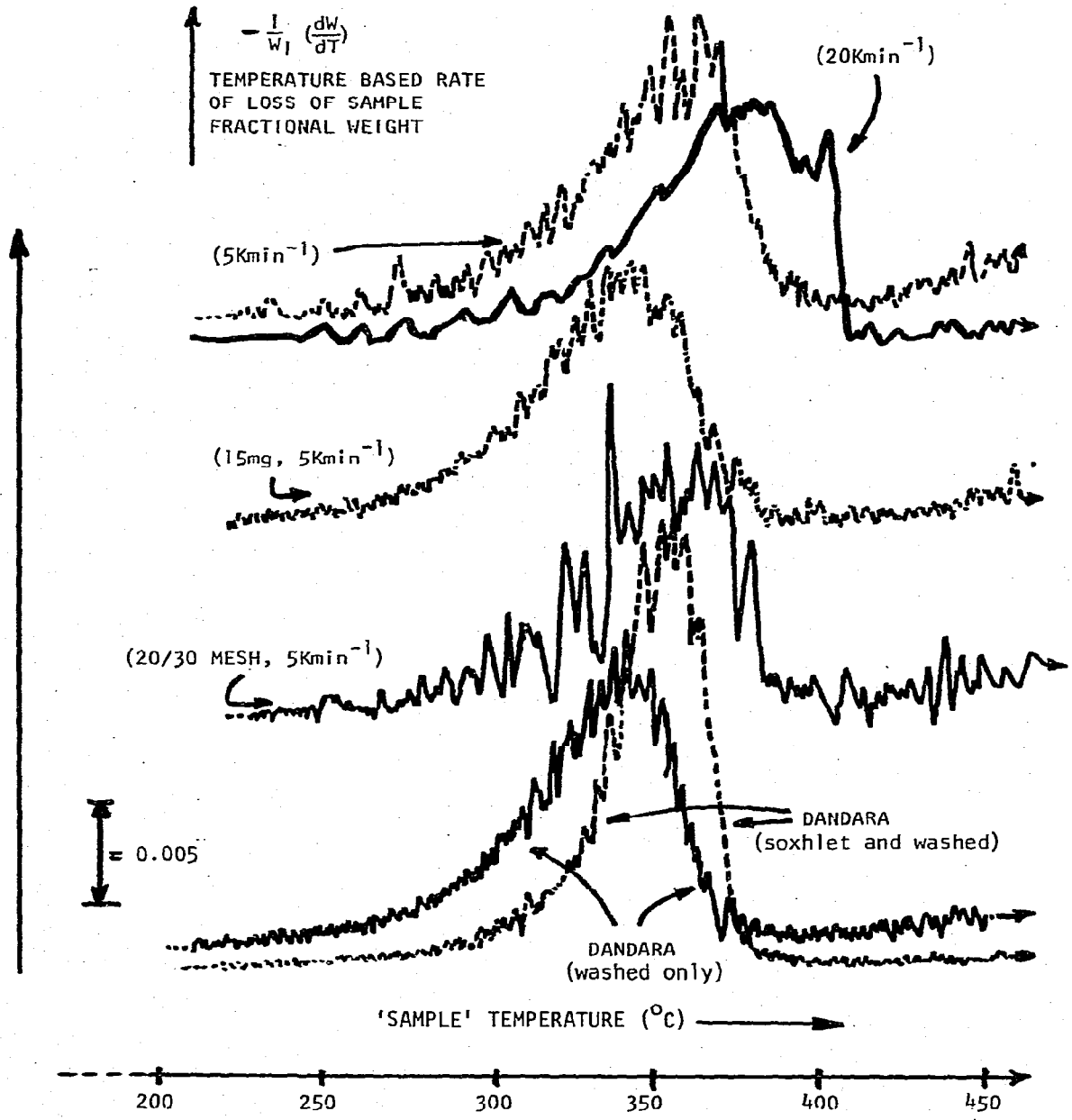

FIGURE 1. VACUUM THERMOGRAVIMETRY OF CELLULOSE FIBRES
('Giza' Cotton, Standard Conditions, Except where Indicated)