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VACUUM THERMOGRAVIMETRY OF TEXTILES: A STUDY OF KERATIN FIBRES*

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ABSTRACT

Reported is the construction and characterisation of instrumentation specifically designed with the requirements for the study of textile materials as the major objective. Those experimental factors which can influence the observed TG curves of fibres are considered, and the optimum procedures required to achieve reproducible observations are defined. In terms of the display of the thermogravimetric data, alternative methods are examined and a novel derivative thermogravimetric presentation suggested to yield the maximum amount of reliable information from the raw data. A method for obtaining this presentation is outlined.

The utility of the DTG presentation of vacuum thermogravimetric data to differentiate between different keration fibre types is noted.

INTRODUCTION

The use of thermoanalytical procedures to characterise keratin in both fibrous and non-fibrous forms has previously been described[1]. Differential thermal analysis observations with keratin fibres indicate that with predried fibres, heated under continuous evacuation, broad endotherms "peaking" above 250°C can be associated with the occurrence of thermal degradation processes[2]. The profiles of these endotherms were dependent upon the keratin studied. The optimum conditions established for the observation of reproducible DTA curves are not conducive to the clear unequivocal identification of any of the chemical changes which form part of the endothermic profile. Thermogravimetry appears to represent the ideal thermoanalytical tool for such an examination. To the present time TG has only been employed to a limited extent for such characterisation[2]. By the use of TG, physical changes which "complicate" the DTA degradation profile are removed. Thermogravimetry also allows the presentation of the substrate such that diffusion away from

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the sample of degradation products can be facilitated, thus reducing the possibilities for secondary reactions while narrowing the recorded temperature span of individual degradation steps.

Thermogravimetric studies on textile fibres have not been the subject of the same attention as studies with polymers in general. With thermoplastic materials TG observations above the melting point will be independent of the original physical form, however, with the natural fibres and the non-thermoplastic man-made fibres such an assumption cannot be justified. By their very nature, textile fibres can present difficulties as TG substrates. Apart from influences associated with the particular geometric form of fibrous elements in the presented sample, the basic anisotropic characteristics of fibres, as well as their unique often heterogeneous structures, must affect the TG observations. The significance of experimental factors in their effects on the TG curves of textiles should receive careful examination.

Of textile fibres, wools and hairs are amongst the most complex and heterogeneous at both the molecular and structural levels. The observed DTA curves of keratin fibres are particularly sensitive to the employed experimental conditions, and preliminary observations support the existence of similar dependencies in thermogravimetry. An assessment of the influence of experimental parameters on the TG curves of keratin is a prerequisite before any meaningful interpretation of such curves can be attempted. Such substrates would provide also a timely sensitive substrate for the identification of the controls necessary in sample presentation to achieve reproducible TG studies of textiles.

INSTRUMENTATION

Keratin fibres are particularly sensitive to oxidative and hydrothermal effects and, in order to restrict observation to purely thermal degradations, the use of

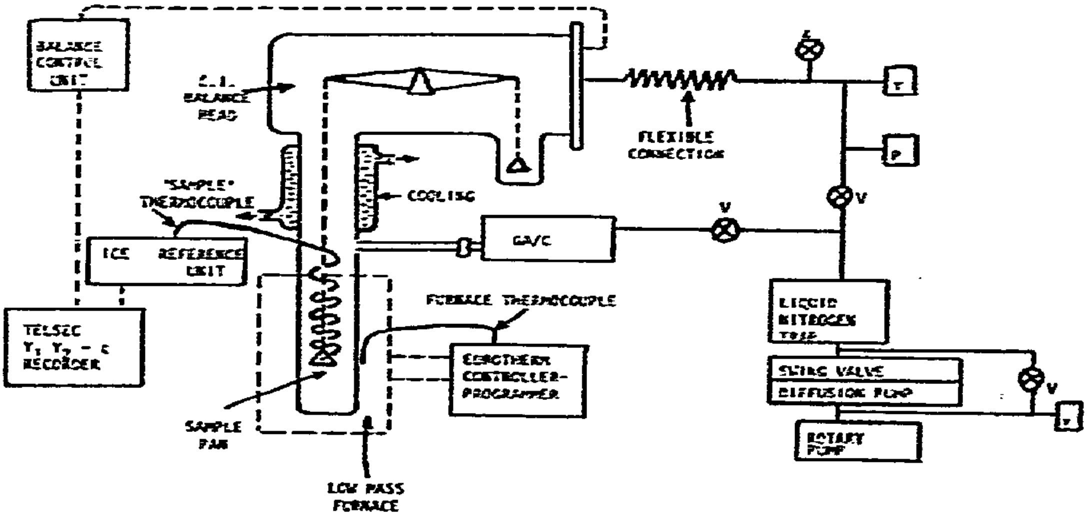


Fig. 1. A schematic representation of the TG system.

continuous evacuation with the heating of rigorously predried samples as practised in previous DTA reports was attempted. A CI Microforce Mark II balance with evacuable glass envelope was used in conjunction with a "universal attachment" and quartz sample tube. This balance of 1 g capacity and switchable ranges of 25 μg to 100 mg was more than adequate to handle the sample sizes envisaged as necessary for representability. An outline of the constructed system is shown in Fig. 1. The balance head and the sample environment could be evacuated by two different routes. Preliminary evacuation and fast pump down was achieved from the balance head through a half inch copper pipe linked to the basic cold trap–diffusion pump–rotary pump system. Penning and thermocouple gauges were sited close to the balance head to provide an assessment of the effective vacuum in the balance. Once the desired vacuum level had been attained, a valve sited between the balance head and the cold trap was closed and evacuation was continued through a quarter inch o.d. line fitted to the "universal attachment". In this quarter inch line between the "universal attachment" and the basic pumping system can be "Cajon" coupled to various evolved gas detection/

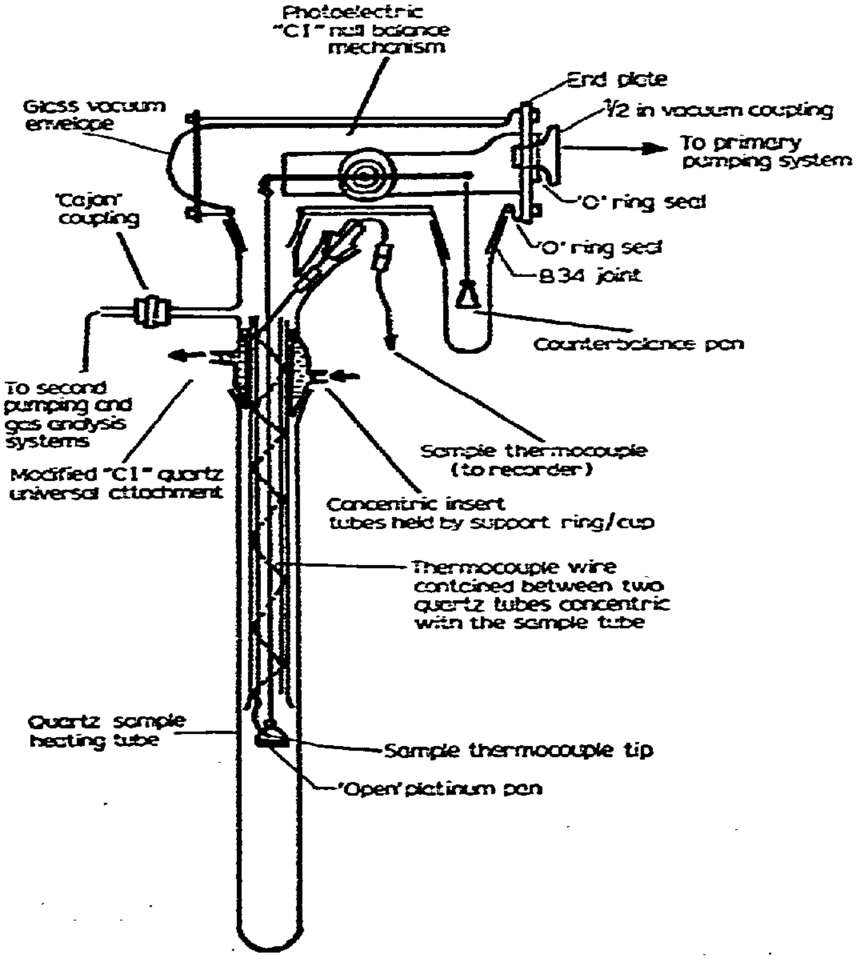


Fig. 2. The balance head and sample pan assembly.

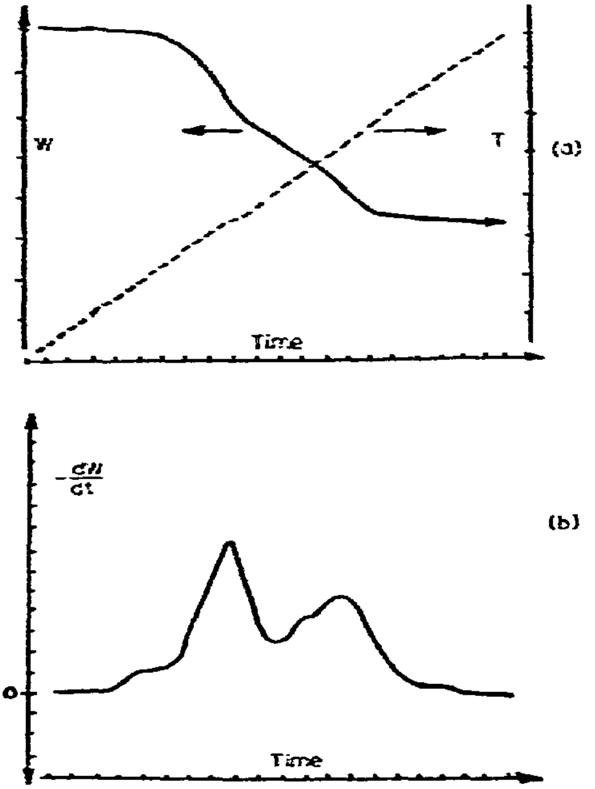
analysis facilities. The preliminary pumping was carried out through the wider bore faster pumping line to the balance head but was then discontinued to prevent the carrying of corrosive or low-volatility products onto the "exposed" balance system. The quarter inch o.d. pumping line, with any additional impedances associated with the gas detection facilities, was used to maintain the vacuum in the sample tube and to provide a "nearer to sample" access for evolved gas detection. The modified quartz "universal attachment" and sample tube assembly is illustrated in Fig. 2. Heating was achieved by a Stanton Redcroft low thermal mass furnace which experimentally generated a uniform temperature environment for an 110-mm length of the quartz sample tube in the centre of which the presented sample was suspended on an open pan. A platinum 10-mm diameter flat pan with a 2-mm rim and a weight of 625 mg was custom-made. This pan was designed for high thermal conductivity, low mass, chemical inertness and with a capacity able to support the maximum volume of fibrous sample envisaged. Following unsatisfactory trials with commercial single and multiple jointed quartz suspension rods and with fine tungsten wire, a home-made quartz filament (0.05 mm diameter) drawn from a quartz rod was used throughout this work.

Modifications to the "universal attachment" were made to accommodate the quarter inch pumping and to introduce a 1.5-mm diameter stainless-steel sheathed mineral insulated chromel–alumel extension lead. This lead was sealed (vacuum tight) with Araldite over a minimum 2-inch length into a 2-mm bore capillary terminating in a C14 conical joint. This extension lead was terminated at both ends with Spembly type IV thermocouple sockets. "Sample" temperature measurement was achieved with a 0.5-mm diameter 400 mm stainless-steel sheathed chromel–alumel thermocouple supported as illustrated in Fig. 2. The tip of the thermocouple was located immediately over the surface of the sample pan.

Temperature programming was provided by an Eurotherm digital set point three-term controller, thyristor drive unit and an Eurotherm JA06 programmer in series with the monitoring furnace thermocouple. The thyristor drive unit and controller terms were empirically adjusted to match the thermal characteristics of the furnace such that, with an empty sample pan and continuous evacuation, defined linear heating rates (as indicated by the "sample" thermocouple) were achieved.

PRESENTATION OF DATA

With the described instrumental system, weight and temperature analogue signals are displayed on a two-pen time-based recorder. The optimal TG curve was considered to be that of sample weight as a function of "sample" temperature. The original recordings were initially redrawn in this format (see Figs. 3a and 4a). The shape of the TG curves observed with keratins identifies that many processes are occurring both consecutively and concurrently. To enable the thermal degradation profile to be used effectively, the small differences observed in the TG curves must be capable of definitive and reproducible recognition. An apparent improvement in



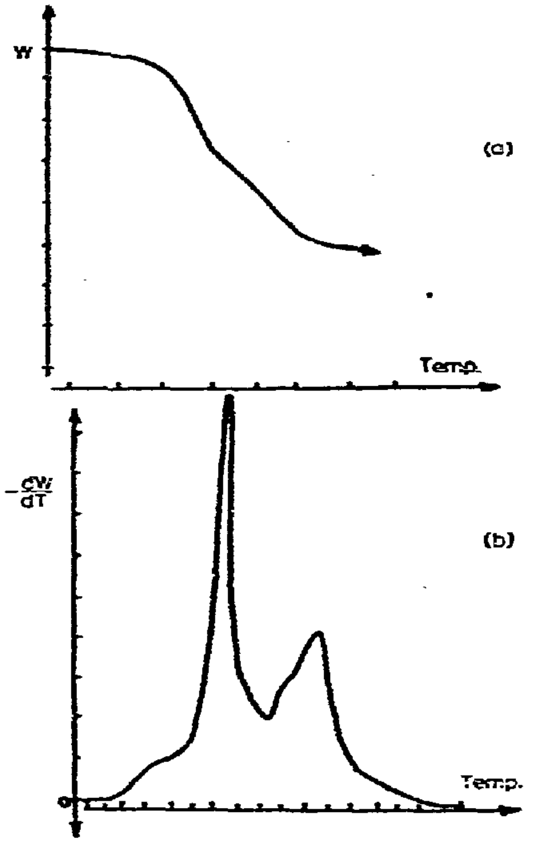


Fig. 3. A representation of time-based recordings in TG experiments. (a) Weight and temperature as a function of time. (b) $-dW/dt$, the timebased first derivative as a function of time.

Fig. 4. A representation of temperature-based recordings in TG experiments. (a) Weight as a function of temperature, the preferred TG curve. (b) $-dW/dT$, the temperature-based first derivative as a function of temperature.

clarity and resolution can be achieved by displaying the thermogravimetric data as the first derivative in a DTG curve. Where complex degradation steps are involved, the DTG curve can allow a clearer indication of the existence of individual processes and has been used in the characterisation and study of the thermal degradation of macromolecules[3]. Because of the relative simplicity of the hardwear required for direct recording, derivative thermogravimetry is commonly practised through the plotting of the rate of weight change (dW/dt) against time or temperature (see Fig. 3b). In this format, the peak "areas" reflect directly sample weight changes, if time is the ordinate. If the derivative is recorded against temperature, then the display is indicative of where the change takes place but not the extent of the change unless the "sample" heating rate can be guaranteed as strictly linear at all times. With the "time-based" first derivative, the resolution of the "peaks" increases with reduced rates of heating but concurrently the size of the "peaks" will automatically fall. A better form of the first derivative would be a continuous monitoring of the gradient of the weight–"sample" temperature TG curve, i.e., of the rate of weight change as a function of "sample" temperature dW/dT. At reduced rates of heating, inflections in the TG curve can resolve into plateaux. The revised dW/dT rate of weight change would be sharper and larger at slower heating rates, with, in a presentation against "sample" temperature, the peaks being indicative of where the changes occur and their size. In Figs. 3 and 4, representations of the described forms of the TG and DTG displays are compared.

The demands on the hardwear component specifications to achieve dW/dT directly are great. As an alternative practical procedure, the dW/dT derivative was computed directly from digitised "raw" analogue W and T data with the result plotted directly as a function of T. Manual digitisation of the analogue weight signals was carried out at equal (3 degree) "sample" temperature intervals across the whole range of the recordings. From this raw data, a concurrent smoothing was also required in order to provide a useful first derivative dW/dT. Five point-weighted smoothing and derivative calculations were combined in a procedure similar in principle to that outlined by Gorman[4]. From 5 consecutive digital values of the weight and "sample" temperature analogues, viz.:

$$(W_{N-2}, T_{N-2}) \rightarrow (W_{N+2}, T_{N+2})$$

(where $T_{N-1} - T_{N-2} = T_N - T_{N-1}$ etc. $= \Delta T$, the "sample" temperature digitisation interval), the "smoothed" first derivative dW/dT at temperature T_N is calculated from the expression:

$$(\mathrm{d}W/\mathrm{d}T)_N = [(0.25W_{N+1} + 0.125W_{N+2}) - (0.125W_{N-2} + 0.25W_{N-1})]\, \Delta T.$$

For the handling procedures employed, this expression subjectively provided the most effective, reproducible smoothed derivative with the minimum loss of resolution.

In order to eliminate the effects of variations in the specific initial sample weight analysed, a weight normalisation was carried out on the derivative analogue value. In many polymer degradation systems, it has been noted that the changes of weight at high temperature can be equally as characteristic of the original substrate as those observed at lower temperatures. Frequently with polymers also, these high temperature degradation processes involve a relatively small weight change and will therefore appear less clear in either the TG or DTG curve when compared with those observed at lower temperatures. To enhance the observability of the higher temperature processes in keratin fibre systems, normalisation was effected by the use of the instantaneous sample weight at the temperature in question. With the use of $(\mathrm{d}W/\mathrm{d}T)_N \times 1/W_N$, the "instantaneous fractional rate of weight change", those changes of weight at high temperatures, where the fractional residual weight is small, are enhanced. The consequences of this normalisation procedure are demonstrated in Fig. 5. A further advantage of this procedure is that it enables effective comparisons of data to be made independent of the temperature of entry into the TG programme. In contrast with the characteristic but sometimes indistinct inflections in the TG (weight–temperature) curve, the DTG $(-\,\mathrm{d}W/\mathrm{d}T)_N \times 1/W_N$–temperature) curve displays a series of "peaks". These "peaks" indicate those occasions at which the nett

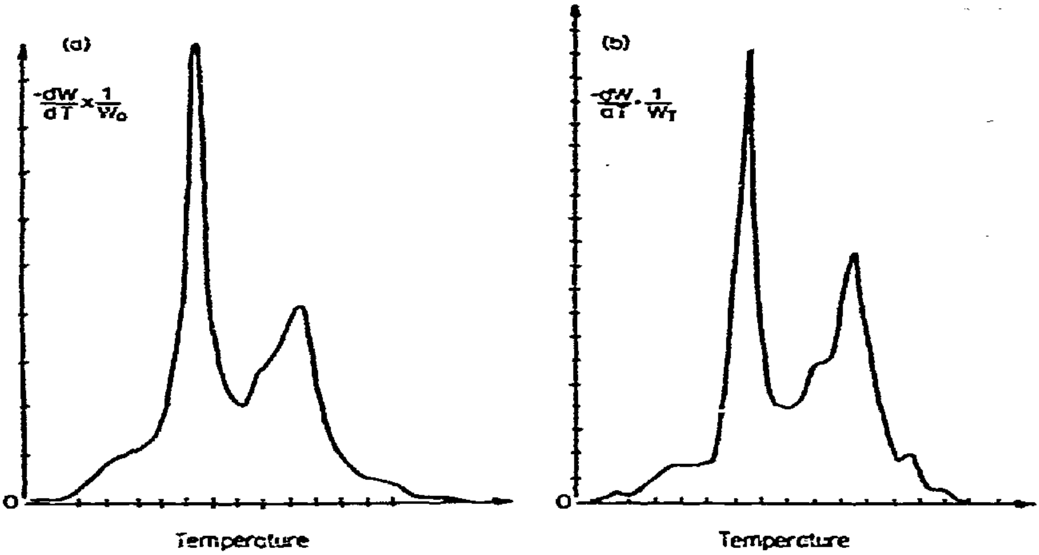


Fig. 5. Derivative thermogravimetry (DTG). A comparison of: (a) The temperature based first derivative and (b) The instantaneous rate of fractional weight loss $[-(dW/dT)_X \times 1/W_X]$.

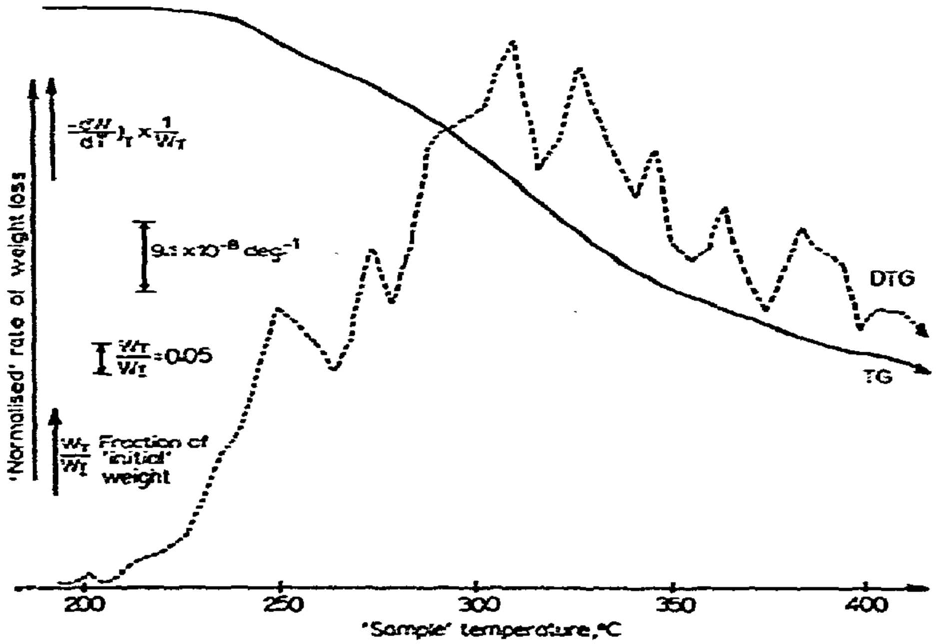


Fig. 6. Vacuum Thermogravimetry: Merino Wool 70's quality. A comparison of TG and normalised DTG observations obtained under standard conditions.

rate of weight change passes through a maximum. A single "peak" does not necessarily identify a single weight-change process. In normal use, the DTG curve represents the averaged data from at least three separate TG experiments. Figure 6 illustrates the TG and normalised DTG curve for a keratin fibre (Merino wool).

EXPERIMENTAL RESULTS

The form of the observed TG curve can be influenced by many experimental and instrumental factors. The current objectives are to identify the influence of those features which are associated with the presentation of fibrous samples, and in particular with the presentation of keratin fibres. These objectives cannot be achieved without equal consideration being given to the other factors. By restricting concern to the effects of thermal degradation on an open pan, those factors which require to be examined are as listed in Table I.

Temperature control/measurement

The "sample" temperature was recorded as that close to the surface of the pan, and control was optimised as described above. The only independent assessment of these factors was by comparison of the TG curves of finely powdered "spread out" calcium oxalate monohydrate observed with this system and on a DuPont 950 thermobalance but operated with otherwise identical conditions.

Data recording/presentation

The influences of the method of display has been discussed and identified. In the consideration of the experimental factors, observations were assessed from the special normalised DTG presentations.

System characteristics

Control tests were carried out with a constant "load" on the balance system of 50 mg, achieved with an empty pan by appropriate reduction of the counter-balance weights. The analogue weight signal was recorded and replotted as a function of "sample" temperature. In this manner, the effect of heating rate on the observed "sample weight" was assessed. With continuous evacuation and a stable pressure in

TABLE I

VACUUM THERMOGRAVIMETRY ON AN OPEN PLATINUM PAN: FACTORS INFLUENCING RECORDED OBSERVATIONS

1. Instrumental:	(a)	System Characteristics
	(b)	Temperature control
	(c)	Temperature measurement
2. Experimental:	(a)	Data recording/presentation
	(b)	Heating rate
	(c)	Sample presentation:
		(i) physical form
		(ii) mass
		(iii) disposition on the pan
		(iv) state of subdivision
	(d)	Miscellaneous:
		(i) heats of reaction
		(ii) condensation of low volatility products.

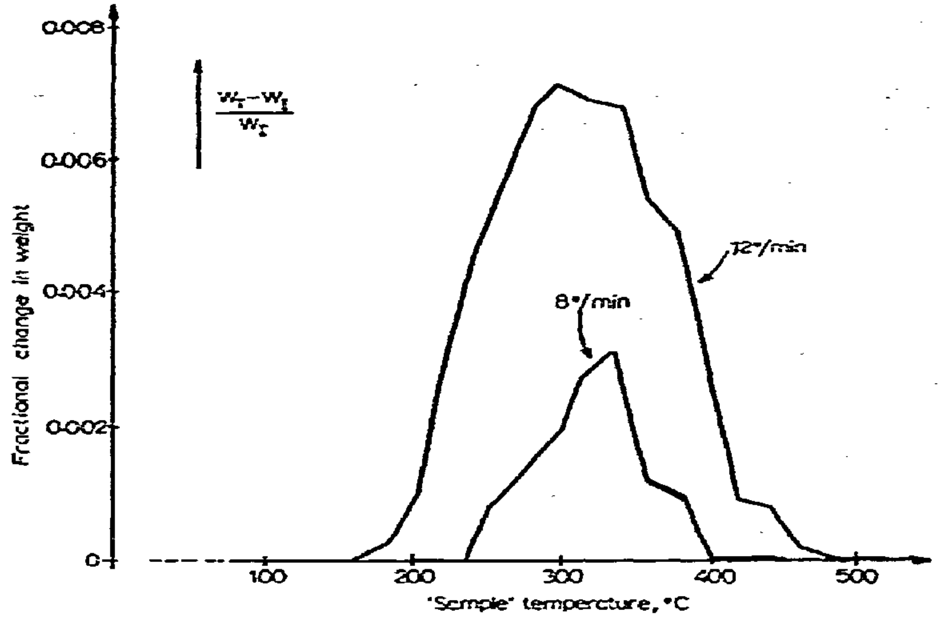


Fig. 7. Thermogravimetry: Thermal balance characteristics I. The effect of heating rate with CI balance system. (50 mg sample "loading" and at atmospheric pressure).

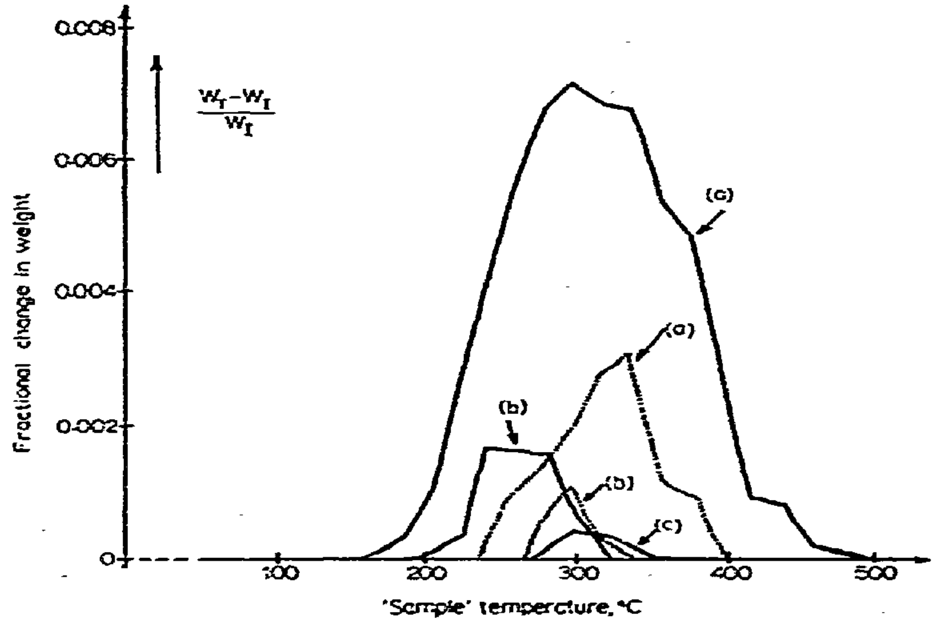


Fig. 8. Thermogravimetry: thermal balance characteristics II. The effect of pressure with CI balance system. (50 mg sample "loading", varying pressures: a = 760 torr; b = 10 torr; c = 0.01 torr and different heating rates: —, 12°C min^{-1}; ---, 8°C min^{-1}.)

the system of 0.01 torr or less, no detectable deviation in the observed weight was noted at applied heating rates from 2 to 8°C min^{-1}. At 12°C min^{-1} however, an increase in apparent weight was detected at between 250 and 350°C. The maximum recorded deviation was 0.02 mg (0.04% of the "sample weight"). The rate of weight change dW/dT was below levels capable of accurate estimation, but was of the order of 0.2 $\mu g\,°C^{-1}$. Thermogravimetry of most polymers and fibres usually involves losses in weight. In systems in which either the system volume is relatively small and/or the pumping rate is limited, a considerable rise in the balance pressure can occur if the rate of production of volatiles is sufficiently large (in terms of gram moles of volatile per minute) compared with the pumping rate. The effect of system pressure on the observed weight deviations was examined. The effects of heating rate on the apparent increases in "sample weight" were additionally assessed with a static air atmosphere (760 torr) and with dynamic but stable atmospheres of 10 torr and 0.1 torr. The observations are illustrated in Figs. 7 and 8 and summarised in Table 2. Provided the heating rate is low ($< 8°C\ min^{-1}$) and that the atmosphere can be maintained continuously at 0.1 torr or better, then no correction was considered necessary to the recorded sample weight signals. These observations indicate the care that must be taken to recognise any behavioural characteristics of the balance system which could affect the significance of recorded TG curves.

Sample presentation

A standard reference keratin fibre sample, the thermal behaviour of which was known from previous DTA investigations, was used throughout. The description and preliminary preparation of this fibre is described in Table 3. Natural wools and hairs carry a relatively high percentage of impurities noteably grease and suint[5]. Various degreasing/extraction preliminary procedures were examined, and in no case were

TABLE 2

INSTRUMENTAL CHARACTERISTICS: CI THERMOBALANCE-VACUUM SYSTEM: INFLUENCE OF HEATING RATE AND "ATMOSPHERIC PRESSURE"

Observed maximum percentage weight changes (50mg "Loading").

Atmosphere pressure (torr)	*Heating rate (°C min⁻¹)* 2	4	8	12
760	0.02	0.04	0.3	0.7
10	<0.02	0.04	0.12	0.16
0.1	<0.02	<0.04	0.04	0.04
0.01	<0.02	<0.02	<0.04	0.04

TABLE 3

KERATIN REFERENCE SUBSTRATE

(a) WOOL staple, 64's quality Merino fibre.
(b) Sample freed of attendant foreign matter and tips/roots removed.
(c) Fibrous sample soxhlet extracted for 24 h with petroleum ether and 6 h with methanol.
(d) The degreased product dried of solvent under evacuation at room temperature.

any significant differences in the DTG curves of the product fibres identified except after the use of an aqueous alkaline scouring bath. The influences of the following sample preparation parameters on the observed DTG curves were studied: predrying of the sample, state of sample subdivision (fibre length), total sample size, and the disposition of the sample on the pan.

Sample drying. DTA observations on wool fibres have shown that keratin is particularly sensitive to hydrothermal degradation. The total removal of the equilibrium water content of the fibre (ca. 16%) was necessary in order to obtain stable DTA curves. Heating with continuous evacuation at 145°C for 2 h was identified as the condition required to remove the last traces of strongly bound water and without significant degradation of the protein[2]. When there was any residual water in the wool fibre sample, then the "peak" in the DTG curve at ca. 250°C shifted to lower temperatures. With no preliminary drying of a 10-mg wool sample heated at 4°C min^{-1}, the described DTG "peak" was observed at 240°C. With increased isothermal drying under vacuum at 140°C this "peak" gradually shifted to be observed at a limiting constant temperature of 250°C following treatment times in excess of 90 min. A 2-h predrying treatment was carried out as standard in all subsequent studies.

Fibre dimensions. The DTA curves of keratin fibres showed a marked dependence upon the dimensions of the fibre in the sample analysed[1]. Differences were particularly significant in those regions of the DTA curve which can be associated with degradation processes. Because of their geometric form, heterogeneity and anisotropic character, the need to assess the influence of the fibre dimensions of individual fibre elements on the observed DTG curve was clear. The fibre elements of different lengths without damage to or destruction of the fibre structure were obtained either: (a) by manual scissor cutting to fibre lengths of 2.0–0.5 mm or (b) by comminution in a Wiley Cutting Mill (A. H. Thomas Inc.). To avoid further the possibilities of fibre damage during mill cutting, only very small fibre loads were cut at a time in the laboratory microscale mill. Cutting to the required sizes was achieved in several stages. The cut fibres were sieved to provide a more uniform length distribution in any

TABLE 4

MICROSCOPIC EXAMINATION OF WILEY MILL CUT KERATIN (MERINO 64's) FIBRES

Cleansed Merino 64's fibre cut by Wiley Mill and sieved; that sample held on each sieve examined microscopically for fibre length.

U.S. standard sieve sizes		*Dimensions of sieve (pass) (μm)*	*No. of fibres examined*	*Fibre length*	
Sample passed through	*Held on*			*Mean (μm)*	*Standard deviation (μm)*
20	40	850	180	1380	650
40	60	425	180	750	320
60	100	250	180	465	235
100	pan	150	180	245	170

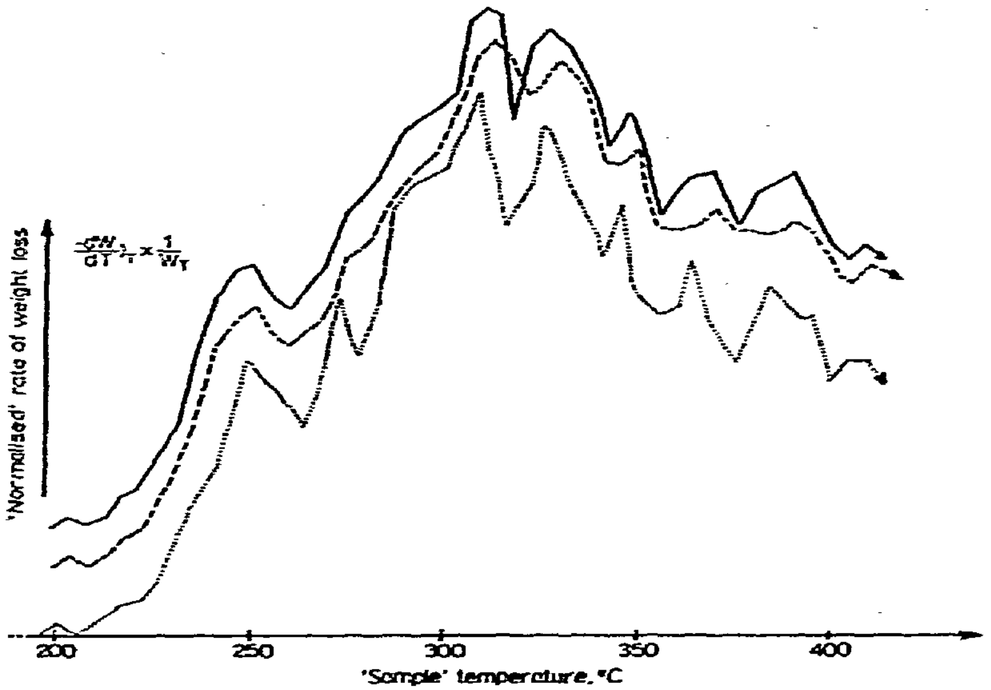


Fig. 9. Vacuum thermogravimetry: DTG of keratin fibres—Effect of "Fibre Length". 10-mg sample, predried and spread evenly over pan, heated 4 °C min^{-1} with continuous evacuation (0.01 torr). —, 20 mesh; ---, "scissor cut"; ...., 60 mesh.

TABLE 5

THE INFLUENCE OF SAMPLE PARAMETERS ON THE DTG CURVE OF KERATIN: FIBRE LENGTH
5-mg sample of Merino 64's wool, "predried", heated at 4 °C min^{-1} with continuous evacuation.

DTG "peak" positions (°C)	*Sample "fibre length" parameter*				
	Scissor cut	*Fibre cut in Wiley Mill to pass mesh size:*			
	2.0–0.5 mm	*20 mesh*	*40 mesh*	*60 mesh*	*100 mesh*
"Peak" I	202	202	202	202	202
"Peak" II	251	250	250	250	250
"Peak" III	276	275	274	274	274
"Peak" IV	311	309	308	308	308
"Peak" V	330	330	329	328	328
"Peak" VI	349	348	346	346	346
"Peak" VII	370	369	366	365	365
"Peak" VIII	391	389	387	387	387

one "size" lot. With their particular geometric form, sieving is not an efficient method for separating fibrous material into sharp classifications of length, but does provide a practical means of achieving subdivision, as is reflected by microscopic examination of the cut fibre lots (Table 4). This microscopic examination also showed that no severe damage to the fibre structure had occurred during the cutting process. In Fig. 9

is shown the effect of fibre length on the observed DTG curves of keratin. Eight "peaks" can be empirically recognised in the DTG curve of keratins and the variations in the positions of these "peaks" as a function of fibre length is presented in Table 5. For fibre "lengths" of "60 mesh" and "100 mesh" dimensions, the DTG curves are stable and reproducible. Attempts to cut the fibres shorter led increasingly to problems of "clumping" together of the fine elements with less reproducible and frequently more diffuse DTG "peaks". The "scissor cut" sample was extremely bulky and open because of the influence on packing at 2-mm lengths of fibre crimp. During degradation, sample movement occurs and frequently parts of the sample can be ejected from the pan.

It is not practical to carry out an effective assessment of the influence of fibre "diameter" on the observed DTG curves. Differences in diameter inevitably mean changes in histology and in the basic fibre type.

Sample presentation

In order to illustrate the expected need for spreading the cut fibre finely over the sample pan surface, samples of "60 mesh" cut fibre were alternatively prepared for analysis as a "tamped" (compressed) mass and as a "pyramid" in the centre of the pan. The effect of these variations on the observed DTG curve (Fig. 10) showed the anticipated reduction in resolution with both the "tamped" and "pyramid" presenta-

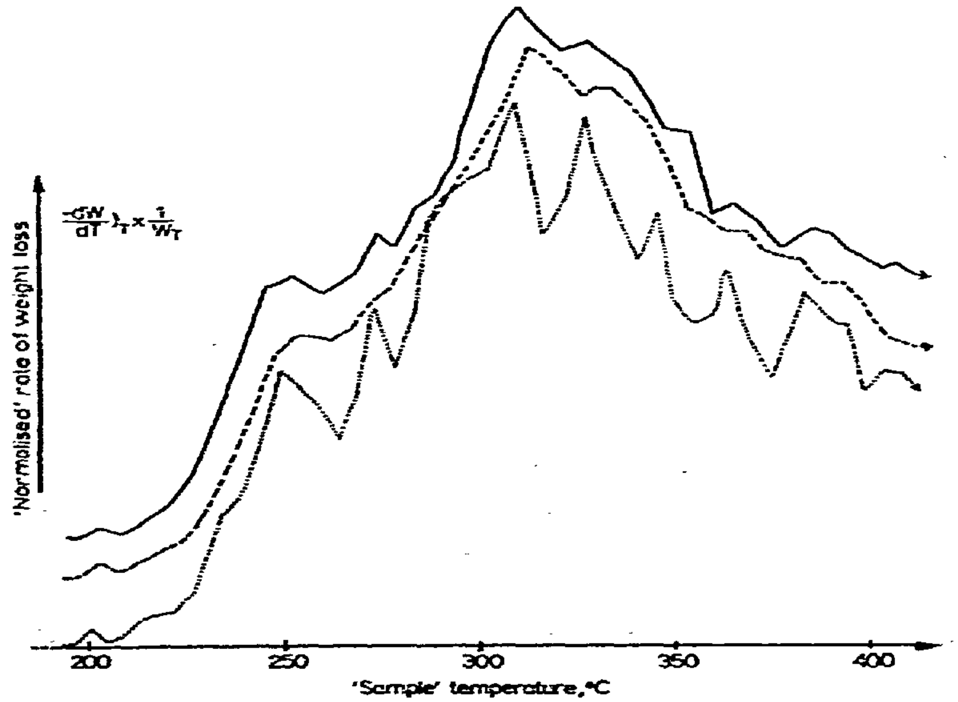


Fig. 10. Vacuum thermogravimetry: DTG of keratin fibres—Effect of "Sample Presentation". (10 mg of "60 mesh" cut fibre, predried, heated at 4°C min^{-1} with continuous evacuation, 0.01 torr.) —, "pyramid"; ---, "tamped"; ....., evenly spread.

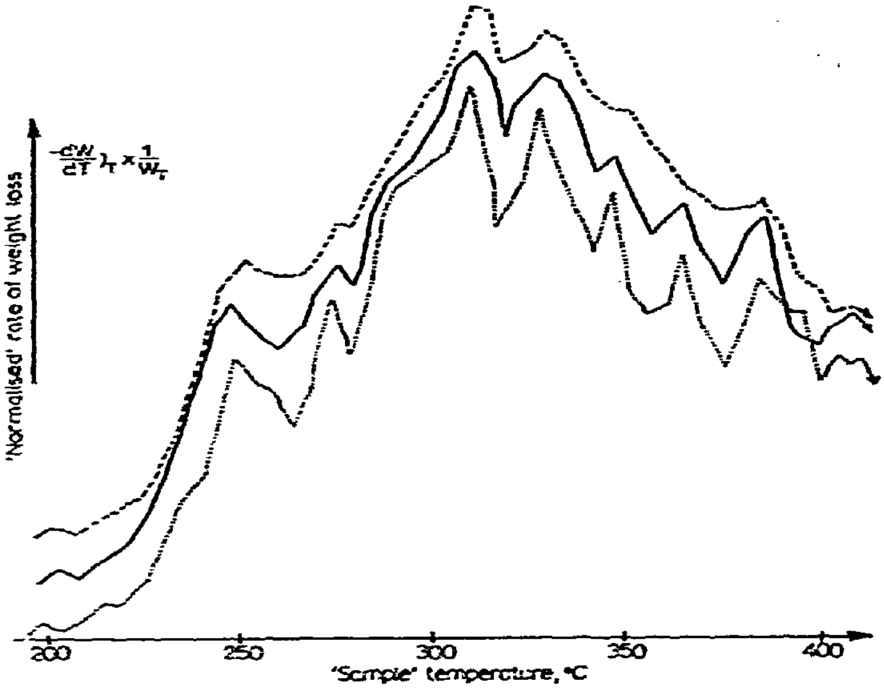


Fig. 11. Vacuum thermogravimetry: DTG of keratin fibres—Effect of "sample size". ("60 mesh" cut fibre samples, predried and spread evenly over pan, heated at 4°C min^{-1} with continuous evacuation, 0.01 torr.) —, 50 mg; ---, 100 mg; ...., 10 mg.

TABLE 6

THE INFLUENCE OF SAMPLE PARAMETERS ON THE DTG CURVE OF KERATIN: SAMPLE SIZE

Cleansed "60 mesh" fibre spread evenly over the pan and "predried" before heating at 4°C min^{-1} under continuous evacuation (0.01 torr).

DTA "peak" positions (°C)	*Sample size (mg)*					
	1	*5*	*10*	*20*	*50*	*100*
I	202	202	202	202	202	202
II	250	250	250	250	250	251
III	274	274	274	274	275	276
IV	307	308	308	308	308	308
V	328	328	328	329	329	329
VI	346	346	346	347	348	*
VII	365	365	365	366	366	*
VIII	387	387	387	387	387	389

* Peak unresolved.

tions. It was noted that 15 mg of "60 mesh" cut fibre would just spread thinly over the pan surface.

Sample mass

The influence of sample size on the observed DTG curves is reflected in Fig. 11.

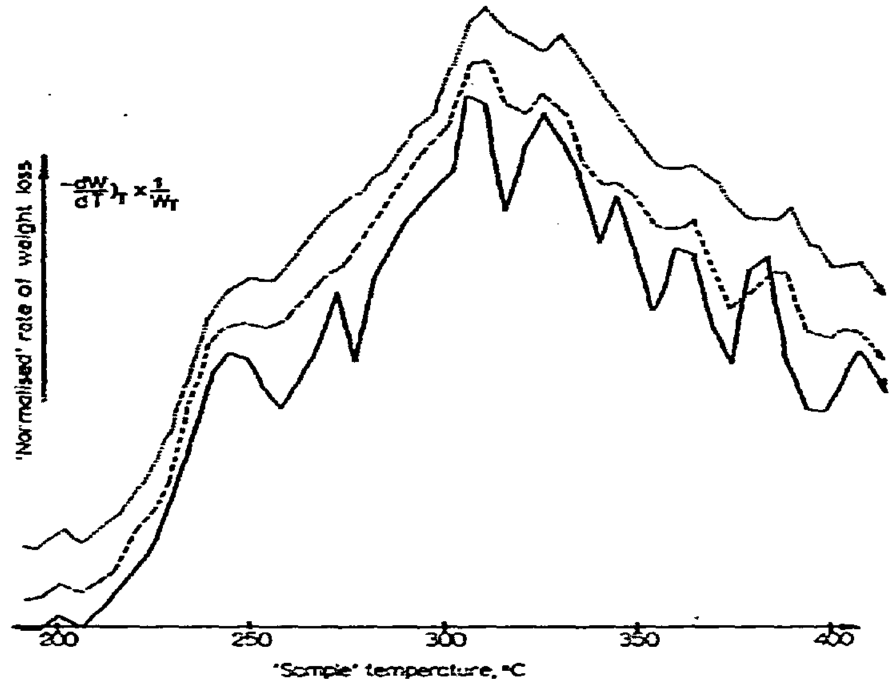


Fig. 12. Vacuum thermogravimetry: DTG of keratin fibres—effect of "heating rate". (5-mg samples of "60 mesh" cut fibre, predried and spread evenly over pan, continuous evacuation, 0.01 torr.) —, 2°C min^{-1}; ---, 8°C min^{-1}; ...., 12°C min^{-1}.

In Table 6 the positions of the 8 recognisable DTG "peaks" are recorded as a function of sample size. The breadth of the "peaks" increases with a sample size of 50 mg, and at 100 mg, two of the "peaks" are unresolved. With samples of 50 mg size, the rate of production of volatiles was such that with this experimental system, pressure rises to 1 torr were detected. At sample sizes below 5 mg, the signal-to-noise ratio of the weight analogue prevented the use of the required sensitivity commensurate with the small sample mass.

Heating rate. In the TG curve of a single-step endothermal degradation, the effect of increasing heating rate is to broaden the temperature range over which the weight loss is observed. Reduced heating rates should therefore sharpen the DTG "peak" and, in overlapping multiprocess systems, provide improved resolution. The influence of heating rates over the range 1 to 12°C min^{-1} on the DTG curves of keratin is shown in Fig. 12 and in Table 7. As anticipated the "peaks" of the DTG curve are best resolved at the slowest heating rate used (1°C min^{-1}). Because of the presentation as a temperature-based derivative, no reduction in peak size is apparent with reduced heating rates. With increasing rates of heating greater than 4°C min^{-1} the temperatures at which the DTG "peaks" are observed to shift to higher temperatures, while below 4°C min^{-1} their positions are stable (Table 7). At very slow rates, e.g., 1°C min^{-1} the time scale of the experiment and its influence on overall signal stabilities become the determining factor.

TABLE 7

THE INFLUENCE OF EXPERIMENTAL PARAMETERS ON THE DTG CURVE OF KERATIN: HEATING RATE
"60-mesh" fibre, 5-mg predried sample spread evenly over pan and heated under contuous evacuation 0.01 torr.

DTG "peak" positions (°C)	*Heating rate (°C min^{-1})*				
	1	*2*	*4*	*8*	*12*
I	202	202	202	203	203
II	249	250	250	250	251
III	274	274	274	[a]	[a]
IV	308	308	308	309	311
V	328	328	328	329	331
VI	346	346	346	[a]	[a]
VII	365	365	365	367	[a]
VIII	386	387	387	388	391

[a] "peak" not resolved.

CONCLUSIONS

Observations of the influence of instrumental and experimental factors on the recorded DTG curves of keratin show that care is essential before results can be obtained without extraneous complications and which can be the subject of meaningful discussion. The optimal practical operating conditions for vacuum thermogravimetry of keratin fibres is recorded in Table 8. With the use of these conditions reproducible DTG curves characteristic of different wool types are obtained. The "peak" positions are reproducible to ± 1 °C and their heights to 5%, despite the fact that they represent the nett profile of multiprocess losses.

Keratin fibres represent one of the most complex fibre systems, but the influences recognised here will be reflected to varying degrees with all textile fibres. An assessment of their significance must always be made in fibre studies if meaningful interpretations of TG and DTG curves are to be attempted.

TABLE 8

OPTIMUM THERMOGRAVIMETRY CONDITIONS FOR THE EXAMINATION OF KERATINS

(with C.I. Microforce Balance, Mark II)
1. Minimum balance damping, 10-mg sample weight range.
2. Open platinum pan.
3. Continuous evacuation with an initial pressure of 10^{-2} torr.
4. Heating rate of 4 °C min^{-1} from 100 to 410 °C.
5. Sample presentation:
   (a) Fibres cut by Wiley Mill to pass 60-mesh sieve.
   (b) 10-mg maximum weight of cut fibre spread over the pan.
   (c) Fibre predrying under continuous evacuation at 140 °C for 2 h.

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