

**THERMOGRAVIMETRIC ANALYSIS OF SOME SPICES  
AND COMMERCIAL FOOD PRODUCTS.  
COMPARISON WITH OTHER ANALYTICAL METHODS  
FOR MOISTURE CONTENT DETERMINATION (PART 3)**

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**ABSTRACT**

Some commercial food products, such as starch, flour, dry alimentary small paste, toasted coffee and powdered milk, were analysed by thermogravimetry. The results of the water content were compared with the values obtained using the Karl–Fischer method and those obtained from the measurement of  $T_1$  (spin–lattice) and  $T_2$  (spin–spin) nuclear magnetic resonance (NMR) relaxation times. The percentage ash content was also determined and the glucidic fraction was estimated in some samples.

**INTRODUCTION**

In recent years chemical research has been applied to the field of food products. Many analytical methods devoted to the control of foodstuffs have been set up in order to protect man against the sophistication and adulteration of food products. The mass media has contributed to the creation of public awareness. As a result, the number of scientific journals devoted to this subject has increased rapidly.

The analysis of foodstuffs is performed both by traditional and modern methods; the latter include chromatography and spectrophotometry. We believe that other methods can be advantageously applied to the analysis of foodstuffs, and therefore we have investigated the use of electrochemical and thermoanalytical methods. In particular, in the field of electrochemistry we have recently developed a method to determine lecithin in eggs, chocolate and cakes, etc. [1]. In thermoanalysis, we have developed purity and quality control methods, the former with particular reference to pharmaceutical products [2–4] and the latter with reference to foodstuffs [5]. We have

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recently performed an experimental comparison between the accuracy of values determined by nuclear magnetic resonance (NMR) and thermogravimetry (TG) of the moisture content in seed products of commercial interest [6] and in various food flours [5]. In this paper the final results of this research are presented. They refer to starch, flours, dry alimentary small paste, powdered milk, some spices, tea, coffee, cocoa, etc. A comparison is also made with the results obtained using the Karl–Fischer method.

## EXPERIMENTAL

The spices and foodstuffs examined (starch, dry alimentary small paste, toasted ground coffee, toasted ground barley, tea, tobacco, black pepper, powdered milk, toasted ground cocoa (treated with potassium carbonate and containing traces of natural flavouring) were all commercial products; other products examined (chick-pea flour, powdered chestnuts) were the same as used in a previous paper [5].

The TG and DTG curves of all these samples were obtained using a Mettler TG 50 thermobalance, coupled to a Mettler TC 10A-TA processor system and a printer plot (Swiss Matrix). The heating rate used was  $10^{\circ}\text{C min}^{-1}$ ; the atmosphere was air, with a flow rate of  $100\text{ ml min}^{-1}$ .

NMR measurements were taken at  $25^{\circ}\text{C}$  on a pulsed low-resolution spectrometer (Minispec P20; Bruker, Karlsruhe, F.R.G., operating at 20 MHz for protons and equipped with an analog computer (B-AC 5; Bruker, Karlsruhe, F.R.G.). The pulse sequence used and all other details of operation for the detection of the longitudinal relaxation time  $T_1$ , the transverse relaxation time  $T_2$  and for the quantitative determination of the percentage water content were the same as described previously [5].

The measurements of the percentage moisture content by the Karl–Fischer method were performed using an automatic titration apparatus (Mettler DL 18) with a glass cell thermostatted by forced water circulation (thermostat Julabo 50, Schelbach). These measurements were carried out at  $25.0 \pm 0.5^{\circ}\text{C}$  and  $50.0 \pm 0.5^{\circ}\text{C}$  with magnetic stirring. The adopted “stir time” (during

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Fig. 1. TG and DTG curves for analysis of starch (curves a, b, c), minced dry alimentary small paste (curves a', b', c') and toasted ground barley (curves a'', b'', c''). a, a', a'', full TG and DTG curves in the temperature range  $20\text{--}700^{\circ}\text{C}$ ; b, b', b'' and c, c', c'', TG and DTG curves (on an expanded scale) of the water loss process and the second step respectively (flowing air,  $100\text{ ml min}^{-1}$ ; heating rate,  $10^{\circ}\text{C min}^{-1}$ ).

Fig. 2. TG and DTG curves for analysis of toasted ground coffee (curves a, b), minced tea (curves a', b') and toasted ground cocoa (curves a'', b''). a, a', a'', full TG and DTG curves in the temperature range  $20\text{--}700^{\circ}\text{C}$ ; b, b', b'', TG and DTG curves (on an expanded scale) water loss process (flowing air,  $100\text{ ml min}^{-1}$ ; heating rate,  $10^{\circ}\text{C min}^{-1}$ ).

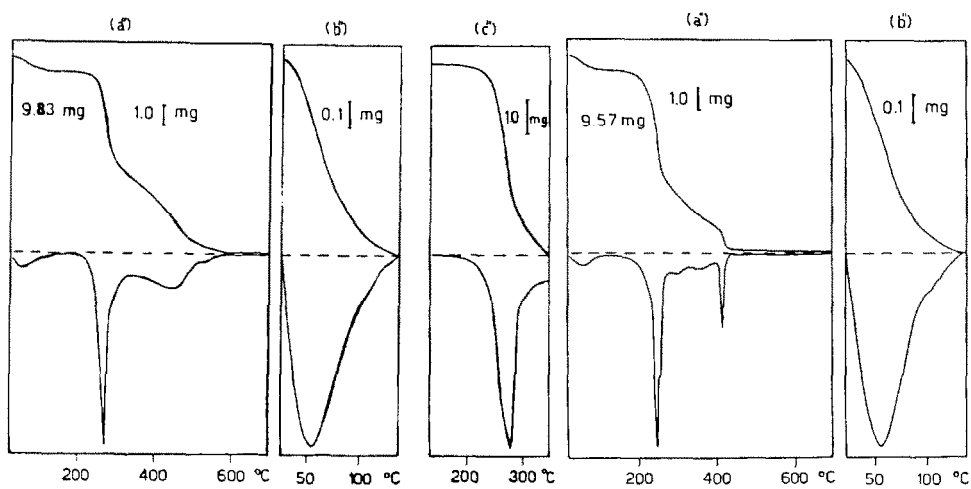
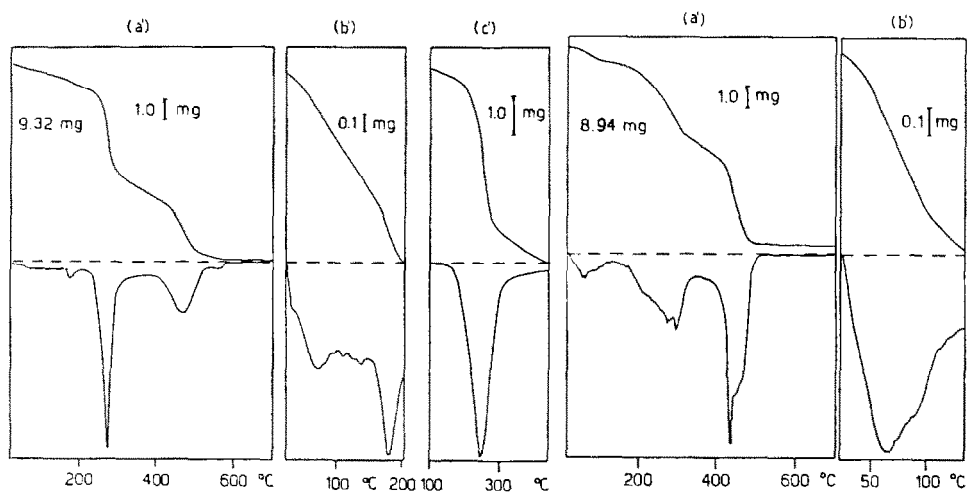
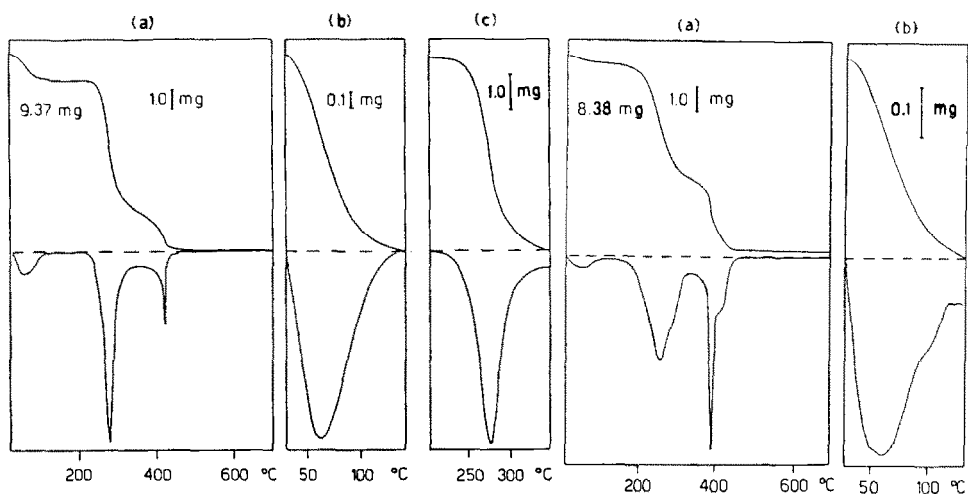


Fig. 1.

Fig. 2.

which the sample, in methanol, is stirred before performing the titration) was 500 s. The Karl–Fischer titrant was Hydranal no. 34805 (Riedel-De Haen AG, Seelze-Hannover); the solvent was dried methanol G.R. (Merck, Darmstadt). Sodium tartrate dihydrate was used for checking the concentration of the Karl–Fischer reagent solution.

## RESULTS

The TG and DTG curves of all the samples were recorded using the same experimental conditions as described previously [5,6]; the curves are reported in Figs. 1–3 (curves a, a' and a''); the related thermal data are summarized in Table 1. The TG and DTG curves of two samples (chickpea-flour and powdered chestnuts) are not shown as they have already been presented in ref. 5. The thermogravimetric curves of commercial starch, dry alimentary small paste and toasted ground barley show the characteristic behaviour previously observed for the flour samples [5]. Three main weight losses are observed. The first step is the loss of water (the most important step in this research). In Figs. 1–3 (curves b, b' and b'') this process is shown on an expanded scale. For the samples powdered milk, tobacco and cocoa, for which more than three processes are observed, the thermogravimetric data are collected in three main steps (the last two steps are divided into substeps (see Table 1)).

In the case of starch it can be observed (Fig. 1(a)) that decomposition mostly occurs in one step around 275°C. This step is also found between 270 and 300°C in all substances which contain a percentage of starch and other glucidic polymers, such as flours (see also previous paper [5]), dry alimentary small paste and cellulose (as observed in a study on the thermogravimetric analysis of fresh and archaeological woods [7]). This step is also shown on an expanded scale for some samples (Fig. 1 curves c, c' and c''). In Fig. 4, the percentages of thermogravimetric residue (ash) obtained between 500 and 900°C for all the samples are reported. From this figure the temperature range within which the percentage of residue remains constant can be obtained (i.e. when the oxidative decomposition of the organic substance, including the carbon residues, is complete. The decomposition of some salts and the transformation of some oxides are generally irrelevant).

The NMR experimental data and the free water detected (wt.%) are summarized in Table 2. The typical free induction decays (FIDs) obtained for the samples examined are very similar to those of the food flours reported in ref. 5.

The percentage moisture contents in some samples were also obtained using the Karl–Fischer method. Finely powdered solid samples were used. The release of water by the samples (Fig. 5(a)) is dependent on the stir time

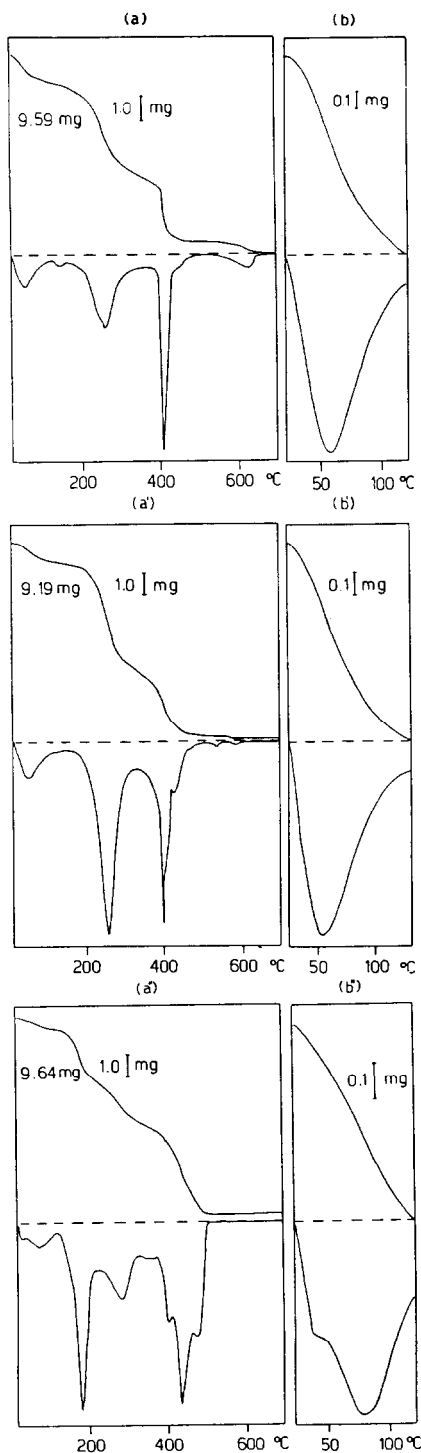


Fig. 3. TG and DTG curves for analysis of minced tobacco (curves a, b), minced black pepper (curves a', b') and powdered milk (curves a'', b''). a, a', a'', full TG and DTG curves in the temperature range 20–700 °C; b, b', b'', TG and DTG curves (on an expanded scale) of the water loss process (flowing air, 100 ml min<sup>-1</sup>; heating rate, 10 °C min<sup>-1</sup>).

TABLE 1

Thermal analysis of some foodstuffs, spices and other commercial products

Nature of the sample	First step (H <sub>2</sub> O loss)		Second step		Third step			
	Loss (%)	PDT <sup>a</sup>	Loss (%)	PDT <sup>a</sup>	Loss (%)	PDT <sup>a</sup>		
Starch	12.8	23	65.1	200	20.8	342		
		59		275		418		
		145		342		500		
Minced dry alimentary small paste	11.3	23	52.9	205	35.0	365		
		178		275		468		
		200		365		600		
Toasted ground barley	7.0	23	53.6	170	35.6	347		
		54		272		437		
		140		347		600		
Toasted ground coffee	4.8	24	54.9	140	35.3	337		
		59		262		391		
		130		337		500		
Minced tea	7.8	24	38.2	130	48.2	347		
		66		297		434		
		125		347		510		
Toasted ground cocoa	7.0	24	53.6	143	10.0	402		
		54		247 (a)		415		
		137		280		450		
				20.9		280		
						300 (b)		
Minced tobacco	11.7	22	2.6	125	27.0	370		
		55		145 (a)		408 (c)		
		120		164		500		
				39.2		164	4.8	500
						260 (b)		630 (d)
Minced black pepper	9.3	24	52.0	150	32.0	335		
		52		225		399		
		130		335		600		
Powdered milk	5.5	24	23.8	125	44.1	333		
		80		182 (a)		435		
		123		223		510		
				19.1		223		
						284 (b)		
		333						

<sup>a</sup> Procedural decomposition temperature. (a), (b), (c), (d): substeps.

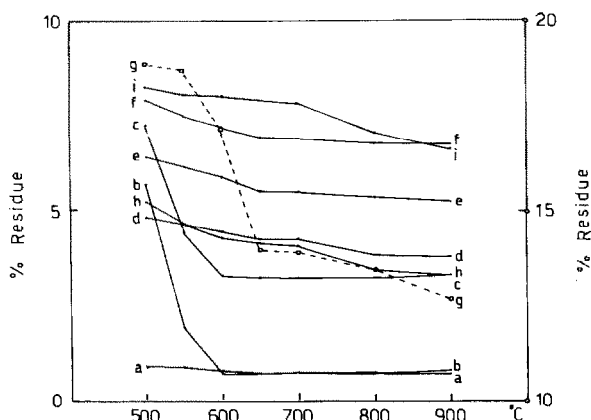


Fig. 4. Ash residue (%) at several temperatures between 500 and 900 °C found by TG analysis. Curve a, ash residue of a starch sample; curve b, dry alimentary small paste; curve c, toasted ground barley; curve d, toasted ground coffee; curve e, minced tea; curve f, toasted ground cocoa; curve g, minced tobacco; curve h, minced black pepper; curve i, powdered milk (only curve g refers to right-hand y axis).

and on the experimental temperature (Table 3). In addition, the percentage of water released is strongly affected by the granulometry of the analysed sample (Fig. 5(b)). With a sufficiently long stir time (i.e. 500 s), the experimental temperature plays a different role according to the nature of the sample. In the case of powdered samples (starch or flours) for which the water release is relatively suitable, the value of the experimental temperature is not very important (Table 3). However, in the case of powdered milk, the increase in temperature seems to be disadvantageous, producing incorrect results. For samples which release water with great difficulty (e.g. dry

TABLE 2

Pulsed low-resolution NMR data of the examined samples (wt.% values of free water obtained from data of relaxation time  $T_2$  (values are the mean of three determinations))

Nature of the flour	Weight (mg of the analysed sample)	Relaxation time $T_1$ (ms) (SD = $\pm 5$ ms)	Relaxation time $T_2$ ( $\mu$ s) (SD = $\pm 5$ $\mu$ s)		Free water (%)
			Fast	Slow	
Starch	228.9	71.65	12.94	600.33	97.9
Dry alimentary small paste	233.1	78.18	14.41	300.27	95.4
Toasted ground barley	257.6	67.71	14.52	590.66	97.6
Minced tea	243.3	73.21	8.06	495.78	98.4
Toasted ground cocoa	245.2	80.75	12.63	713.40	98.3
Tobacco	150.7	61.33	11.63	505.23	97.8
Black pepper	207.9	62.06	17.97	535.10	98.8
Powdered milk	183.9	55.65	11.81	250.55	95.5

TABLE 3

Percentage by weight of water in some foodstuffs, spices and other commercial products: comparison between the results of TG, Karl-Fischer and NMR methods (reported values are the mean of at least three determinations)

Nature of the sample	TG	Karl-Fischer		NMR (d)	$\left(\frac{a-b}{a}\right)\%$	$\left(\frac{a-c}{a}\right)\%$	$\left(\frac{a-d}{a}\right)\%$	$\left(\frac{b-d}{a}\right)\%$
	(a)	At 50 °C (b)	At 25 °C (c)					
Starch	12.8	13.7	13.1	14.7	-7.0	-2.3	-14.8	-7.3
Chick-pea flour	10.4	9.7	9.0	13.0	+6.7	-13.5	-25.0	-34.0
Powdered chestnuts	8.5	7.7	7.4	10.5	+9.4	+12.9	-23.5	-36.4
Powdered milk	5.3	7.0	5.2	5.8	-32.1	+1.9	-9.4	+17.1
Dry alimentary small paste	11.3	9.7	6.3	11.0	+14.2	+44.2	+2.7	-13.4
Toasted ground barley	7.0	6.2	5.7	9.3	+11.4	+18.6	-32.9	-50.0
Toasted ground coffee	4.8	5.3	2.7	-	-10.4	+43.8	-	-
Minced tea	7.8	8.1	4.1	7.8	-3.8	+47.4	0	+3.7
Toasted ground cocoa	7.3	7.2	7.2	9.4	+1.4	+1.4	-28.8	-30.6
Minced tobacco	11.7	10.6	10.3	12.1	+9.4	+12.0	-3.4	-14.2
Minced black pepper	9.3	7.5	7.4	11.3	+19.4	+20.4	-21.5	-50.7

Powdered samples were analysed as received; solid samples were minced if examined by TG or NMR methods, and were ground to a fine powder if analysed using the Karl-Fischer method.



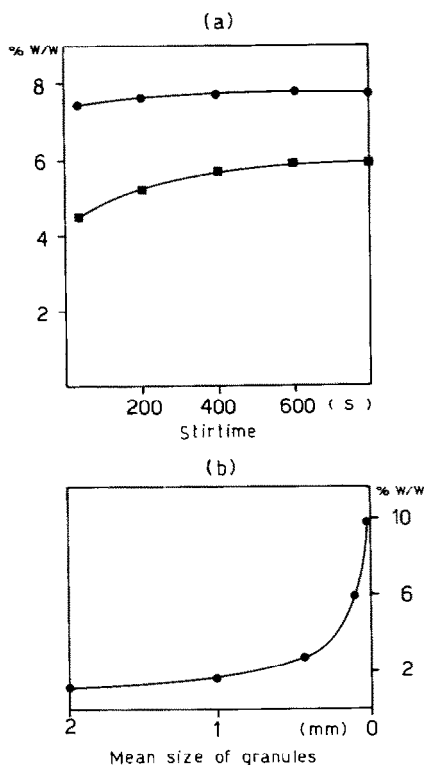


Fig. 5. (a) Water loss (%) vs. stir time (Karl–Fischer method): ●, powdered chestnuts analysed at 50 °C; ■, toasted ground barley analysed at 25 °C. (b) Water loss (%) vs. mean size of granules (Karl–Fischer method) (samples, dry alimentary small paste analysed at 50 °C).

alimentary small paste) the increase in experimental temperature from 25 °C to 50 °C has a strong positive effect as observed in Table 3. In Table 3 the values of the percentage water content obtained using the Karl–Fischer

TABLE 4

Evaluation of the precision of the analysis of the percentage water content in the samples examined by repeated measurement of a commercial starch sample

Water found by thermo-gravimetric method (%)			Water found by Karl–Fischer method (%)			Water found by NMR method (%)		
Found	Mean	% relative SD	Found	Mean	% relative SD	Found	Mean	% relative SD
12.7	12.8	0.8	13.4	13.8	1.7	14.6	14.7	0.8
12.9			13.9			14.7		
12.7			14.0			14.7		
12.8			13.7			14.5		
12.9			13.8			14.8		

TABLE 5

Comparison of the values of percentage moisture, ashes and glucidic fraction in some commercial foodstuffs obtained by TG analysis with those reported in the literature

Foodstuff	Water (%)		Ashes (%)		Glucide fraction (%) (starch + cellulose)		
	[8,9]	TG	[8,9]	TG	[8,9]	TG (corr.) <sup>a</sup>	TG <sup>b</sup>
Wheat meal	14-14.5	13.0	0.2-0.9	0.9	65-76	81	61
Corn flour	12.8	11.4	1.0	1.4	74	74	64
Ground rice	11.4-12.3	13.1	0.4-0.7	1.2	80-81	83	63
Rye flour	11	12.7	1.5	2.0	67	77	58
Dry alimentary small paste	12.5	11.3	0.7-0.9	0.7	70-75	70	53
Toasted ground coffee	≤ 3	4.8	4-6	4.2			
Tea	5-10	7.8	5-7	5.5			

<sup>a</sup> TG values corrected for the percentage of glucidic matter lost during the third step.

<sup>b</sup> Uncorrected TG values.

method are compared with those obtained using NMR and TG. In Table 4 the estimated precision of all the three methods is given. In Table 5, some data from the literature concerning the percentage of moisture, ashes and glucidic fraction (essentially starch and a small percentage of cellulose) of some foodstuffs examined in this or in a previous report [5] are compared with those obtained by TG. The last two columns show the percentage weight loss related to the second step in the thermograms (see Fig. 1, curves c, c' and c''), and the same weight loss corrected for the percentage of glucidic matter lost during the third step (essentially carbon, lost as carbon dioxide). This correction was obtained from the ratio between the loss corresponding to the second and third steps in the thermogravimetric curve of starch (Fig. 1 curve a, and Table 1) (assuming no impurity was present) and the loss of the second step of each sample.

## DISCUSSION AND CONCLUSIONS

The results of Table 3 confirm that the thermogravimetric method seems to be the most versatile and generally applicable. Although the samples examined are very different in physical nature and grain size, the TG method always yields reliable results. It does not give doubtful results in any of the cases examined. This cannot be said for the other methods.

In TG analysis, the limit of accuracy of the method is represented by the determination of the final temperature of the water loss; this operation can be performed easily in some cases, i.e. for starch, powdered milk and flours, but is difficult in others, e.g. dry alimentary small paste. Nevertheless, the results obtained in this report confirm those presented previously [5,6] and the accuracy and reproducibility are quite good.

Charging of the sample in the crucible is favoured by the powdered state of the sample, as in flours and powdered milk; however, charging also occurs reliably in samples which need to be cut into small pieces, provided that the pieces are of such a dimension that they can be easily inserted into the crucible. In contrast, the results obtained using the Karl–Fischer method, are dependent on the granulometry of the sample. The quantitative determination of the ash content is particularly easy and accurate with the TG method. The results obtained in this paper fully confirm (Fig. 4) those observed previously [5] on the temperature interval for this determination; the temperature range 650–700 °C should be used and not the lower temperatures sometimes advised in the literature.

As regards the results of the percentage water content of the foodstuffs and spices obtained using the other two methods, the NMR data discussed previously [5] are confirmed. The advantage of this technique is the additional information which can be obtained about free and bound water (Table 2); its precision is of the same order as the TG method (Table 4). Nevertheless from the comparison of the NMR results with those obtained by the other two methods, it can be seen that NMR generally yields larger values especially in comparison with the Karl–Fischer method and in particular for samples such as barley, spices and cocoa (Table 3), rather than flours or dry alimentary small paste (Table 3). For toasted coffee, our NMR measurements were not reliable (Table 3). This observation seems to confirm the hypothesis, presented previously [5], that the greatest differences between the NMR data and those of the other two methods can be explained on the basis of the marked differences between the type of matrix in the analysed sample and the types of matrix in the sample with a known water content used to perform the calibration.

The Karl–Fischer method is generally considered to be a reference method for this kind of determination. In general sufficient agreement is obtained with TG (Table 3), provided that the experimental temperature is suitable, the stir time is sufficient and the sample is finely powdered (Fig. 5(b)); this last condition seems to be critical for the analysis. The agreement with the TG data is satisfactory for flours, starch, powdered milk and cocoa, but for dry alimentary small paste and pepper errors are observed, even if these samples have been finely ground in a mortar. Finally, the precision is lower for the Karl–Fischer data than for the other two methods (Table 4).

A comparison is made in Table 5 of the ash and moisture contents of some of the examined foodstuffs obtained from the literature with those obtained using TG. The agreement is satisfactory although it is unlikely that identical samples were examined in the two cases. In contrast, if the glucidic fraction (essentially starch and cellulose) data reported in the literature are compared with those determined by TG, only in some cases does the correlation seem satisfactory. In other cases the uncorrected TG data are too low and the corrected data are too high, although, in general, the corrected

data are in better agreement than the uncorrected data. The chance of obtaining the correct glucidic fraction with only one thermogravimetric test is slight. The development of a true analytical method requires the analysis of a much greater number of samples and a comparison with other values obtained with a different method of analysis. Nevertheless, it is our opinion that this work indicates the great and unexplored potential of the TG method for the analysis of foodstuffs.

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