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DETERMINATION OF MOISTURE IN FOOD FLOURS. A COMPARATIVE THERMOGRAVIMETRIC AND NMR STUDY, PART 2

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ABSTRACT

The percentage moisture content of food flours has been determined by TG analysis and measurement of T_1 (spin–lattice) and T_2 (spin–spin) NMR relaxation times, and the results are compared. The experimental precision of both the methods and the correlation are evaluated for ten different commercial flours.

INTRODUCTION

As part of a research program aimed at an exhaustive evaluation of the analytical applications of the chemical thermoanalysis methods (TG and DSC) to the study of natural and commercial matrices, we have performed various characterizations and comparisons of these thermal methods with other analytical methods, especially for samples of pharmaceutical interest [1–4]. More recently we have considered vegetable matrices; in this case, TG and NMR were compared as techniques for the determination of the water content of various seeds of commercial interest [5]. The results encouraged us to extend the research to food matrices of commercial interest. In this work we have employed both TG and NMR for the analysis of the moisture content of various commercially available food flours. These matrices were chosen as being most suitable for comparing the analytical results of TG and NMR methods for various reasons: (1) the food flours are natural matrices of great commercial importance; (2) the determination of their moisture content is of technical and economic interest; (3) they are matrices suitable for analysis by thermal methods (research of this kind is well documented [6]); (4) recently, other researchers at this university have demonstrated [7] that the application of NMR relaxation techniques to the water content determination of food flours is possible with satisfying results. Research,

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aimed at the experimental establishment of a correlation between these two important methods, therefore appeared to be a worthwhile undertaking, both from the analytical and the applications point of view.

EXPERIMENTAL

The flours examined (wheat meal, hard corn meal, semolina, rye flour, ground rice, corn flour, potato starch, chick pea flour, soya flour and powdered chestnuts) were all commercial products, stored in sealed tin foil, at room temperature.

The TG and DTG curves, of these flours were obtained with a Mettler TG 50 thermobalance, coupled with a Mettler TC10A-TA processor system and a Swiss dot-matrix printer. The heating rate used was $10\,^{\circ}C\ min^{-1}$; the atmosphere was an air stream with a flow rate of $100\ ml\ min^{-1}$.

NMR measurements were taken at 25 °C on a pulsed low-resolution spectrometer (Minispec P20), produced by Bruker, Karlsruhe, Germany, operating at 20 MHz for protons and equipped with an analog computer B-AC5 from the same company.

The longitudinal magnetization decay was detected by a $180\,^{\circ}$–t–$90\,^{\circ}$ pulse sequence. The curve was obtained by plotting the function $\ln(M_0 - M_t)$ vs. time (t), where M_0 is the equilibrium nuclear magnetization and M_t is the magnetization detected at time t. The slope of this curve gave the longitudinal relaxation time T_1. The transverse magnetization decay was detected by a $90\,^{\circ}$–t–$180\,^{\circ}$ pulse (spin–echo sequence). The curve was obtained by plotting the echo amplitude vs. time $2t$. The slope of this curve gave the transverse relaxation time T_2. Each reported value was the average of three separate measurements.

The 180° and 90° pulses were empirically adjusted by varying their respective widths (ca. 18 μs and 9 μs on the Minispec P20). The time delay between two consecutive measurements was 1 s to allow the nuclear magnetization to recover its equilibrium value.

The quantitative determination of the water content in the samples, was performed as previously reported [8]. The percentage water content was obtained by comparison with food flour samples with known water content.

The bound water (BW) and the free water (FW) percentages could be differentiated as a result of the double exponential nature of the water spin–echo decay curve. The following comparison of the fast and slow components of T_2 was obtained.

RESULTS

A series of the thermogravimetric analyses were performed (in an air stream with flow rate $100\ ml\ min^{-1}$; heating rate, $10\,^{\circ}C\ min^{-1}$) on ten

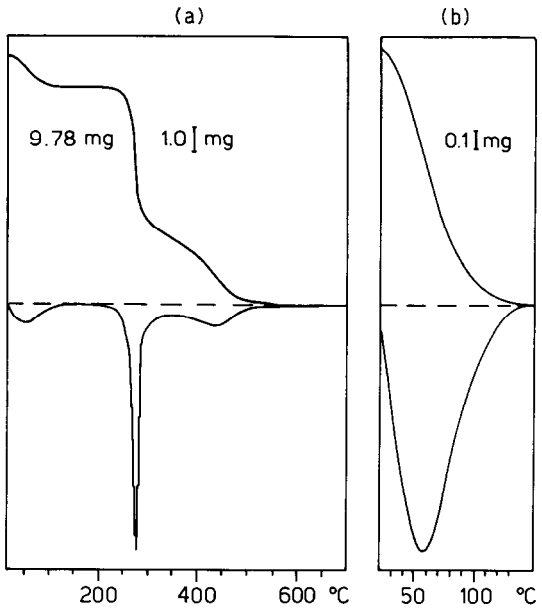

Fig. 1. TG and DTG curves for analysis of wheat meal. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

different commercially available flours. The TG and DTG curves, in the temperature range 20 °C to 120 or 170 °C (Figs. 1(b)–10(b)), yielded reliable data (standard deviation SD in the range 1–2.5% of the mean; see Table 1) for the percentage moisture loss of the samples. In Table 2, the percentage data for all samples derived from TG are compared with those obtained from the NMR relaxation times, T_1 and T_2. In Fig. 11, the correlation between the two methods is shown for all the samples. The NMR experimental data and the wt.% free water detected were summarized in Table 3. In Figs. 12–14, three typical FIDs (free induction decays), obtained for three different flours, are shown.

The ash as well as the water content is important from the commercial point of view. This too can be determined, but by TG measurement alone. The heating temperature range is extended to 650–700 °C (see TG curves in Figs. 1(a)–10(a) and relative thermal data in Table 4). The values of ash percentages obtained by TG methods at various temperatures between 550 and 700 °C are reported in Table 5 for all the food flours. The reproducibility of the measurements is also indicated (last columns of Table 1) for two different samples of the flours, to allow the precision of the techniques to be evaluated.

These experiments, more than those in the past [2–5,9], have shown that thermogravimetry allows rapid and precise determination of the water content in the real matrices. The standard deviations as percentages of the

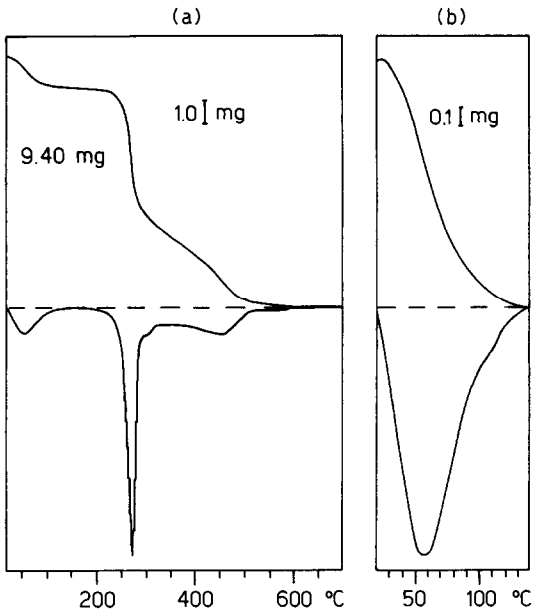

Fig. 2. TG and DTG curves for analysis of hard corn meal. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

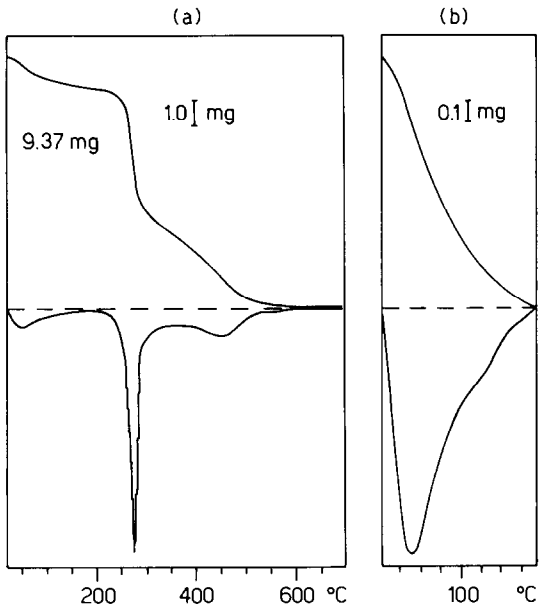

Fig. 3. TG and DTG curves for analysis of semolina. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

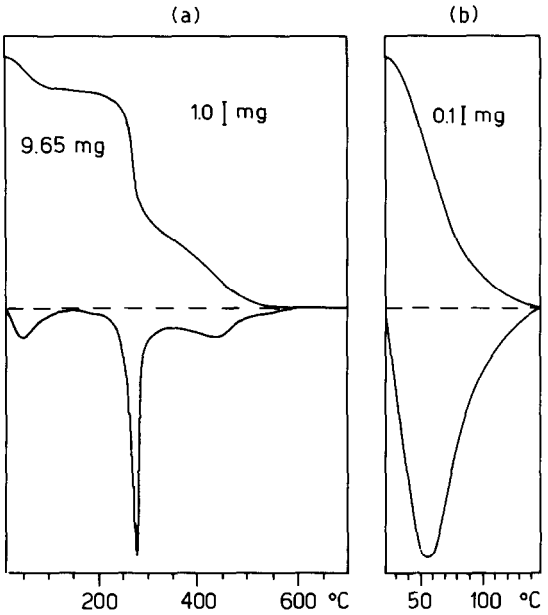

Fig. 4. TG and DTG curves of analysis of rye flour. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

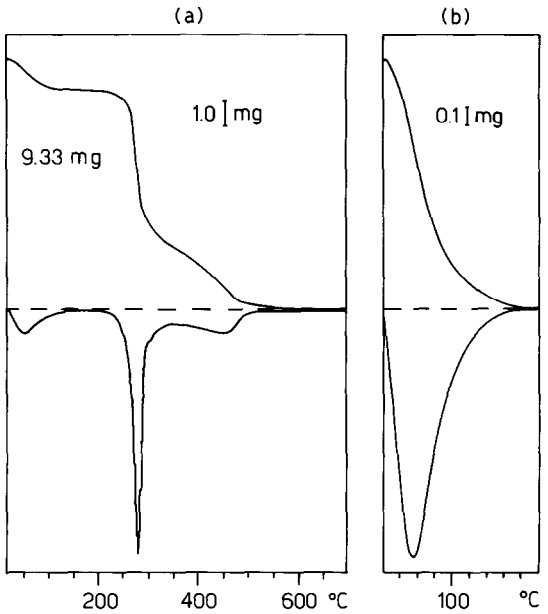

Fig. 5. TG and DTG curves for analysis of ground rice. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

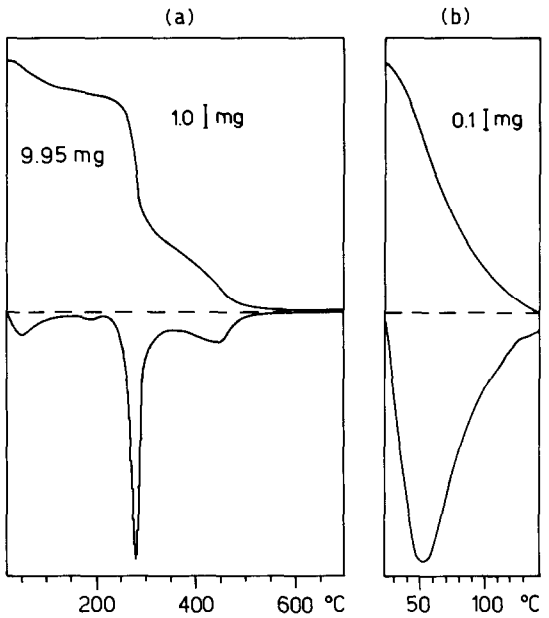

Fig. 6. TG and DTG curves for analysis of corn flour. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

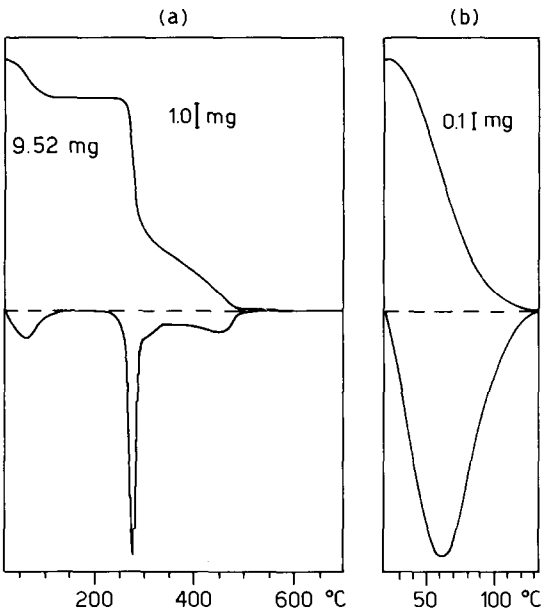

Fig. 7. TG and DTG curves for analysis of potato starch. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

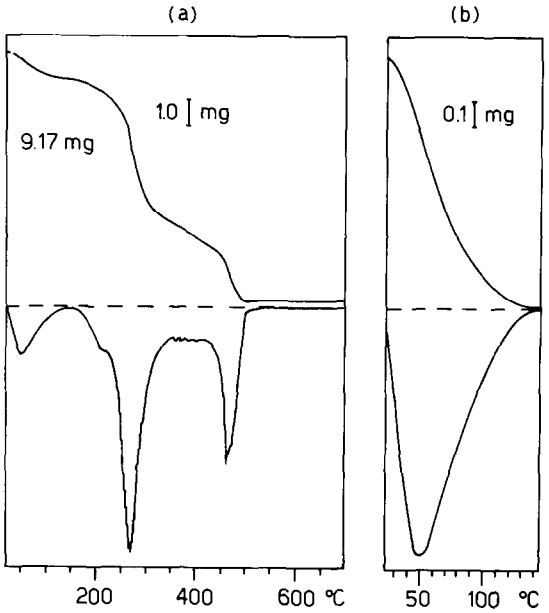

Fig. 8. TG and DTG curves for analysis of chick pea flour. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

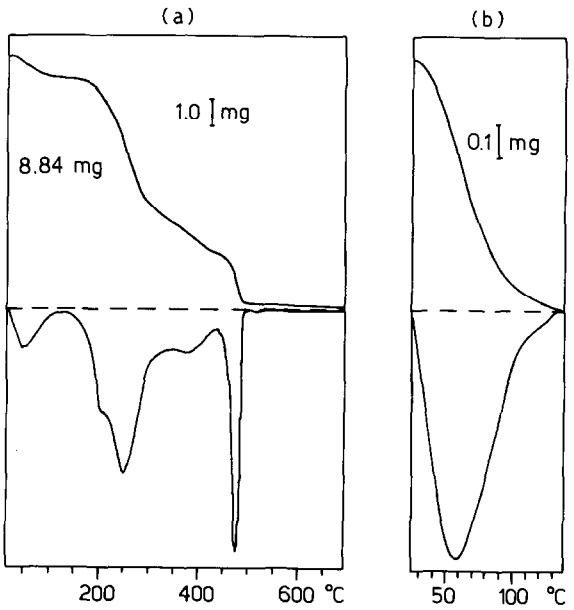

Fig. 9. TG and DTG curves for analysis of soya flour. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In flowing air 100 ml min^{-1}; heating rate 10 °C min^{-1}.

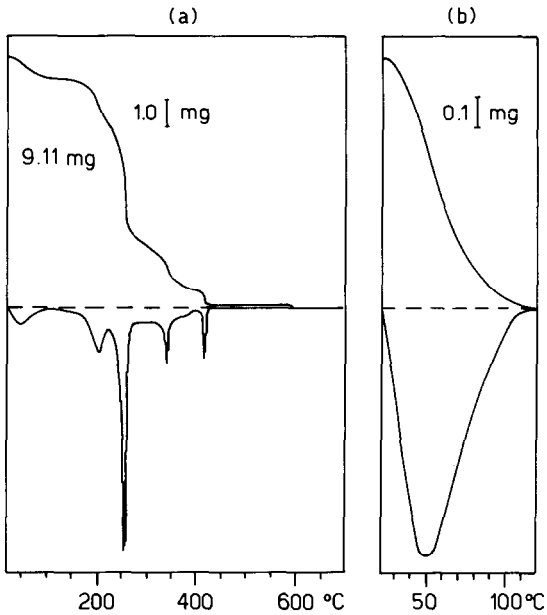

Fig. 10. TG and DTG curves for analysis of powdered chestnuts. (a) Full TG and DTG curves in the temperature range 20–700 °C; (b) TG and DTG curves (in an expanded scale) relative only to the water loss process. In air flowing 100 ml min^{-1}; heating rate 10 °C min^{-1}.

TABLE 1

Precision of the analysis of moisture and ashes in food flours. Ashes content (wt.%), obtained by TG and moisture content (wt.%), by TG and NMR

Nature of the flour	% water by thermogravimetric method			% water by NMR method			% ashes by thermogravimetric method (at 650 °C)		
	Found	Mean	% Relative SD	Found	Mean	% Relative SD	Found	Mean	% Relative SD
Soya flour	7.70			7.70			6.19		
	7.74			7.45			6.04		
	7.87	7.81	1.1	7.45	7.43	2.4	6.34	6.26	2.7
	7.85			7.30			6.23		
	7.88			7.25			6.49		
Hard corn meal	13.10			13.70			0.67		
	12.56			13.40			0.65		
	12.35	12.58	2.4	13.40	13.45	1.1	0.62	0.65	3.5
	12.56			13.45			0.65		
	12.35			13.30			0.68		

TABLE 2

Percentage by weight of moisture in the flours examined: comparison between the results by TG and NMR. Reported values are the mean of at least three determinations

Nature of the flour	TG (a)	NMR (b)	$\left(\frac{a-b}{a}\right)\%$
Wheat meal	13.0	13.3	−2.3
Hard corn meal	12.6	13.5	−7.1
Semolina	12.0	11.5	+4.2
Rye flour	12.7	13.1	−3.1
Ground rice	13.1	12.9	+1.5
Corn flour	11.4	12.5	−9.6
Potato starch	14.7	14.0	+4.8
Chick pea flour	10.4	13.0	−25.0
Soya flour	7.8	7.4	+5.1
Powdered chestnuts	8.5	10.5	−23.5

mean range between 1% and 2.5% and so are of the same order as for NMR data (Table 1). This result practically confirms the results of our previous work [5], performed on commercial seed samples. Thermogravimetric analysis on the flours is undoubtedly more accurate than the same technique applied to samples of a different nature [5,9]. Flours can be considered as homogeneous matrices, and so sampling, even if the weights required are small, is easily performed. Finally, as can be seen easily in the thermograms of Figs. 1(b)–10(b), in the case of flours, the thermogravimetric step of the

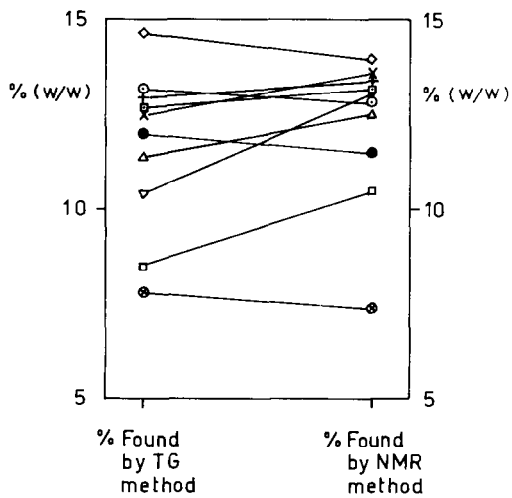

Fig. 11. Correlation of the results by TG and NMR for water content (wt.%) of ten different flours: wheat meal (+), hard corn meal (×), semolina (●), rye flour (□), ground rice (○), corn flour (△), potato starch (◇), chick pea flour (▽), soya flour (⊗), powdered chestnuts (■).

TABLE 3

Pulsed low-resolution NMR data, for the food flours. 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 = ± 8ms	Relaxation time T_2(μs); SD = ± 5 μs		Free water (%)
			(Fast)	(Slow)	
Wheat meal	346.7	79.23	10.74	474.4	97.8
Hard corn meal	367.8	74.01	11.79	464.9	97.5
Semolina	364.1	63.39	12.35	563.5	97.9
Rye flour	373.3	66.05	14.60	548.9	97.4
Ground rice	374.0	67.08	11.36	314.7	96.5
Corn flour	402.8	97.23	12.57	503.0	97.6
Potato starch	458.8	70.34	10.98	606.9	98.2
Chick pea flour	352.5	80.16	16.27	740.9	97.9
Soya flour	321.6	88.82	10.91	319.2	96.7
Powdered chestnuts	303.9	41.37	11.31	192.4	94.4

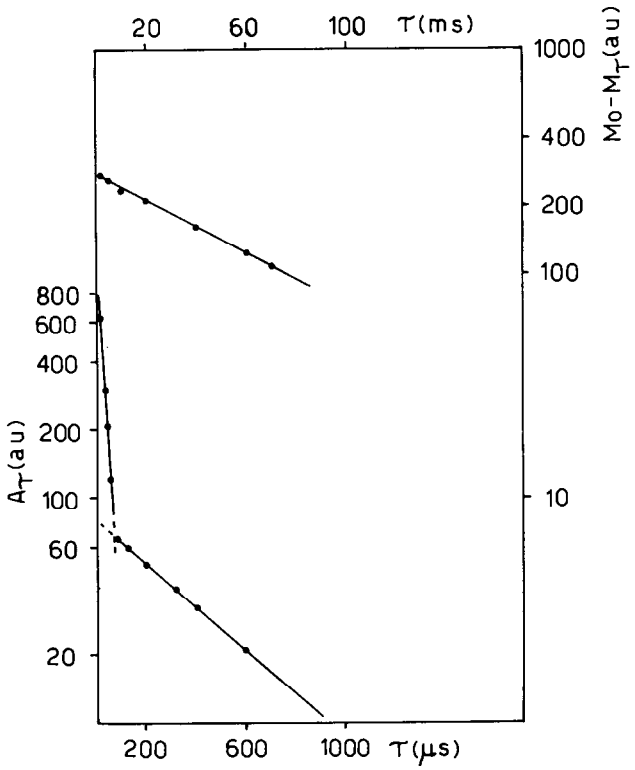

Fig. 12. Semilogarithmic plot of the longitudinal magnetic decay in the hard corn meal analysis.

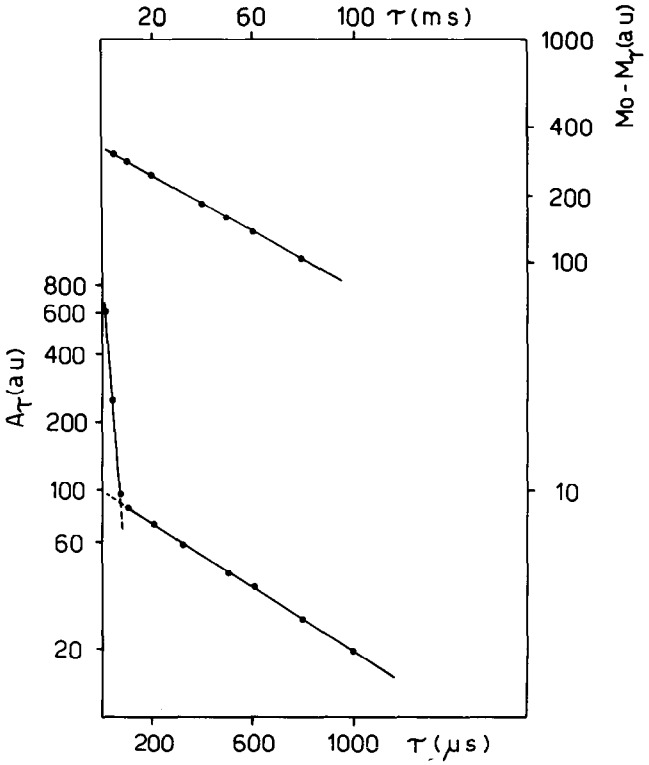

Fig. 13. Semilogarithmic plot of the longitudinal magnetic decay in the potato starch analysis.

moisture loss is generally unique and the TG peak very regular, so the quantitative analysis is made easier as the initial and final ptd of the peaks can be accurately determined.

In this research, analyses were performed in flowing air rather than in static air for the reasons described previously [5]. The correlation between moisture content values, determined by TG and NMR, on observing Table 2 and Fig. 14, is good ($\Delta\% \leqslant 5$) in the case of six of the ten samples considered, it is just acceptable in two cases ($\Delta\% \leqslant 10$); and in the other two (chick pea flour and powdered chestnuts), the correlation between the methods is not satisfactory ($\Delta\% \leqslant 25$). The poor correlation between the two techniques, in these cases, probably results from the different errors inherent in the physical principles on which the methods are based. For example, small amounts of water can be lost in the automatic recording and evaluation of the TG step and the presence of some volatile substance can contribute to the weight loss recorded by TG analysis. Similarly, the liquid/solid ratio, obtained by NMR, can be affected by small errors in the determination of the T_1 values. Another reason for the discrepancy could be a significant difference between the type of matrix in these last two samples of flour and the type of matrix in the sample, with known water content

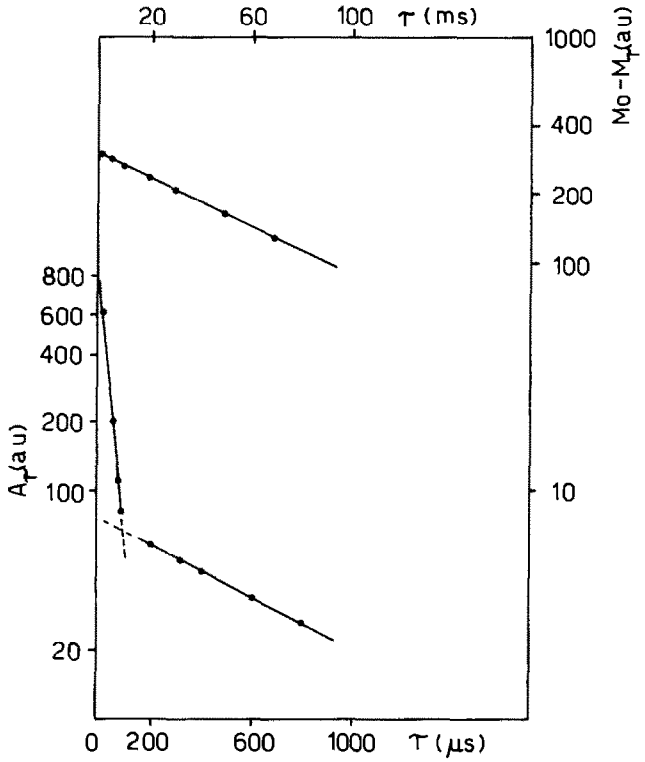

Fig. 14. Semilogarithmic plot of the longitudinal magnetic decay in the chick pea flour analysis.

used to perform the calibration by NMR. This can be confirmed by considering the thermogravimetric curves Figs. 1(a)–10(a). The first seven of these are very similar, only the last curves, particularly those of Figs. 8(a) and 10(a), show a marked difference corresponding to the cases for which the results by NMR differ more significantly from those by TG.

For the TG analysis of the ash content of the flours, a detailed study was performed, aimed at the evaluation of the reliability of the commonly employed methods. They generally measure the ashing of a weighed amount (about 10 g) of the samples, in an oven at around 550 °C [10]. The TG curves we obtained clearly show that, for all the samples examined at this temperature the thermal decomposition of the organic substance is not yet completed but residues, probably of carbon, spoil the analytical data. A detailed investigation of the thermogravimetric data, between 550 and 700 °C (Table 5), has shown that between about 650 and 700 °C, heating in flowing air, any carbon residue is already present; moreover, at 650 °C, the transformation processes into the corresponding oxides of most salts, are generally not extensive. However, at this temperature, more reproducible (Table 1) and accurate data on the ash content of the flours can be obtained.

TABLE 4

Thermal analysis of the food flours, in an air stream (100 ml min^{-1})

Nature of the flour	H_2O loss		First step		Second step	
	Found %	Pdt [a]	Found %	Pdt [a]	Found %	Pdt [a]
Wheat meal	13.0	21	61.0	184	24.0	356
		57		278		438
		135		356		588
Hard corn meal	12.4	22	57.8	175	28.8	348
		54		274		454
		140		348		597
Semolina	12.0	23	58.8	175	27.5	362
		51		277		456
		165		362		590
Rye flour	12.7	22	58.4	148	26.1	356
		54		278		439
		148		356		583
Ground rice	13.1	22	62.6	204	22.3	364
		53		280		456
		160		364		587
Corn flour	11.4	23	64.4	144	22.6	368
		52		282		445
		144		368		567
Potato starch	14.7	23	63.3	225	20.5	362
		61		278		448
		132		362		511
Chick pea flour	10.4	23	57.5	145	28.3	366
		48		270		463
		145		366		527
Soya flour	7.8	23	65.3	139	19.7	438
		58		252		478
		139		438		510
Powdered chestnuts [b]	8.5	22	17.5 (a)	119	20.3 (c)	284
		49		203		341
		119		222		401
			44.8 (b)	222	5.4 (d)	401
				256		418
				284		439

[a] Procedural decomposition temperature.

[b] (a), (b), (c) and (d) represent substeps.

CONCLUSIONS

This research has confirmed the results of previous work on seed samples [5] by showing that the moisture content of flours can be determined by

TABLE 5
Ash residue, by TG analysis of food flours, at several temperatures, from 550 and 700 °C, as wt.%

Nature of the flour	Found % at 550 °C (a)	Found % at 600 °C (b)	$\left(\frac{a-b}{a}\right)\%$	Found % at 650 °C (c)	$\left(\frac{b-c}{b}\right)\%$	Found % at 700 °C (d)	$\left(\frac{c-d}{c}\right)\%$
Wheat meal	1.81	1.03	43.1	0.95	7.8	0.91	4.2
Hard corn meal	1.90	0.73	61.6	0.65	11.0	0.64	1.5
Semolina	3.05	1.40	54.1	1.34	4.3	1.31	2.2
Rye flour	3.59	2.10	41.5	2.05	2.4	2.04	0.5
Ground rice	2.16	1.39	35.6	1.29	7.2	1.23	4.7
Corn flour	2.25	1.42	36.9	1.39	2.1	1.38	0.7
Potato starch	0.67	0.42	37.3	0.39	7.1	0.38	2.6
Chick pea flour	3.41	3.18	6.7	3.15	0.9	3.13	0.6
Soya flour	7.05	6.72	4.7	6.49	3.4	6.46	0.5
Powdered chestnuts	2.62	2.50	4.6	2.39	4.4	2.29	4.2

both TG and NMR methods, generally with a good or acceptable correlation between the data. The ash content of these samples was also determined with great precision and rapidity by TG analysis. By NMR, some additional information about free and bound water in the samples can be obtained. Particularly in the case of flour analysis, the free water content (essentially moisture) ranged between 94 and 98% of the total water (see Table 3), in very good agreement with the behaviour of the relative TG steps (Figs. 1(b)–10(b)) typical of moisture release on heating damp samples. Lastly, it is encouraging to observe that both the water and ash (650–700 °C) contents obtained by the methods discussed in this paper are in good agreement with literature data [11] for common, wheat, rice and maize flours: i.e. (11–14%) water content and (0.5–2%) ash content.

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