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Evaluation of the moisture and ash contents in wheat mills by multistep programmed thermogravimetry

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Abstract

The determination of the moisture and ash contents in wheat mills was developed using multistep programmed thermogravimetric analysis. Preliminary research to determine the most suitable analytical conditions (carrier gas and flow rate, furnace temperature, isothermal time, type and weight of sample and size of particles) was also carried out.

Commercial flours milled from soft and hard wheats with a wide range of fibre content were analysed using both the proposed method and the Italian official methods. The same results were obtained from all these methods. Nevertheless, the thermogravimetric method has some advantages: the analysis takes place on the same sample; it requires very small samples; and it is easy and rapid.

INTRODUCTION

The determination of the moisture content of wheat flours and other milling products is important for several reasons, including the optimisation of the yield of commercial mills and the effects of spoilage during storage. Several countries also use the ash content for the classification of cereal products, and the maximum acceptable levels are established by law [1]. The Italian official methods [2,3] can be used to determine these parameters with precision and accuracy; however, they require a large sample and highly skilled personnel, and are time consuming.

Some of these constraints have been overcome by improved methodology; thus the Karl–Fisher [4], NIR [5] and NMR methods [6,7] have been developed for the moisture determination, and the dynamic thermogravimetry method [8] has been developed for the simultaneous determination of the moisture and ash contents. These methods, though more rapid and sensitive, are often less reliable than the official methods. In our opinion, thermogravimetry provides a rapid and accurate method for this kind of analysis,

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and the present study was undertaken to investigate the best experimental conditions for recording multistep programmed TG curves of flour samples. In this paper, a rapid reliable computer-assisted procedure for the simultaneous determination of the moisture and ash contents in wheat flours is proposed.

EXPERIMENTAL

Equipment

The following equipment was used: Mettler balance (± 0.0001); Brabender thermobalance ($\pm 1°$ C); Heraeus electrical oven ($\pm 5°$ C); Heraeus muffle furnace ($\pm 25°$ C); aluminium dish (width, 7.0 cm; height, 1.7 cm); Pyrex glass dish (width, 7.0 cm; height, 4.0 cm); platinum crucible (width, 4.3 cm; height, 2.8 cm); porcelain crucible (width, 5.0 cm; height, 3.0 cm); Perkin–Elmer TGS2 thermobalance; Perkin–Elmer gas selector; Perkin–Elmer 3700 Data Station equipped with the software package "TADS TGS ISO Rev. 1.00".

Materials

Commercial wheat flours were used as cereal samples classified, on the basis of the ash and cellulose contents, as fine flour (ash $\leq 0.50\%$; cellulose $\leq 0.20\%$), semolina (ash 0.70–0.90%; cellulose 0.20–0.45%), whole wheat flour (ash 1.40–1.60%; cellulose $\leq 1.60\%$), and "cruschello" (ash $> 1.60\%$).

All the samples were milled in an MCKL–Buhler experimental laboratory mill. The particle size distribution of the flours was measured. Each sample was separated into three sieve-fractions by a Buhler Plansifter (laboratory type, sieve meshes less than 60, 60, 120). Before the analysis all the samples were stored at room temperature for 60 days in polyethylene boxes. The moisture and ash contents were determined by the Italian official methods.

Moisture

(a) A 10 g sample was weighed to 0.1 mg in an aluminium dish previously dried, cooled in a desiccator and weighed after reaching room temperature. The sample was dried in an oven at $130 \pm 1°$ C to constant weight (about 90 min). The results of replicate analyses should agree within 0.15%. The percentage moisture content was reported on a wet basis.

(b) A 10 g sample was weighed to 0.1 mg in Pyrex glass dish, previously tared. The sample was dried in an oven at $105 \pm 5°$ C to constant weight (about 8 h). The results of replicate analyses should agree within 0.15%. The percentage moisture content was reported on a wet basis.

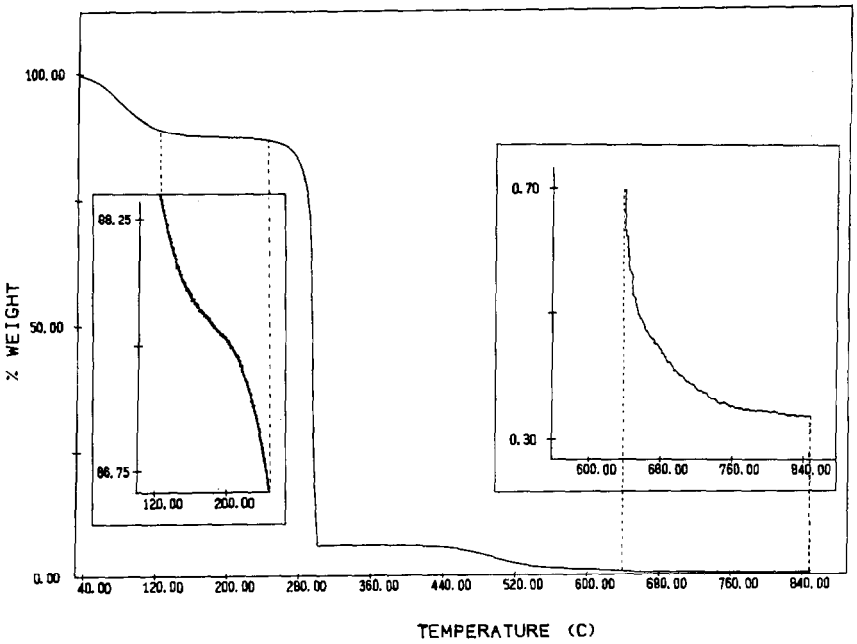

Fig. 1. TG of fine flour sample: heating rate, 10 °C min^{-1}; nitrogen dynamic atmosphere, 50 ml min^{-1}; sample weight, 20 mg; sample size, 60 mesh. The inset expansions show the interesting steps.

Ash

A 10 g sample was weighed to 0.1 mg in a platinum or porcelain ashing dish that had been ignited, cooled in a desiccator and weighed after reaching room temperature. The sample was ignited in an electric muffle furnace at 550 ± 25 °C. About 6 h later, the crucible was cooled together with any incompletely ignited sample. The crucible was filled with distilled water which was allowed to evaporate in a steam bath; the sample was then put in the furnace until constant weight was reached. The results of replicate analyses should agree within 0.02%. The percentage ash content was reported on a dry basis.

RESULTS AND DISCUSSION

Difficulties are encountered when classic dynamic thermogravimetry is applied to the determination of the moisture and ash in wheat flours. In fact, the sample does not always reach a residual constant weight which would indicate the end of the process (water loss and/or final ignited residue). In particular analyses of semolina or whole wheat flour, the TG curves show slow but continuous mass loss so that it is difficult to quantify the residual weight (Fig. 1).

TABLE 1

Moisture determination on wheat flours: the influence of flow rate of purge gas [a]

Isothermal at 30 °C	
Time (min)	Weight (%)
0.32	99.71
1.19	99.27
2.05	98.87
2.92	98.50
3.79	98.14
4.65	97.78
5.52	97.47
6.39	97.17
7.25	96.90
8.12	96.63
8.99	96.40
9.85	96.18
10.72	95.96
11.59	95.75
12.45	95.55
13.32	95.38
14.19	95.20
15.05	95.02
15.92	94.88
16.79	94.72

[a] Sample weight, 20 mg; size, 60 mesh; atmosphere of dynamic nitrogen (50 ml min^{-1}).

To find out whether multistep programmed thermogravimetry could solve these problems, an experimental critical study of those parameters which can affect the accuracy and precision of the results (carrier gas and flow rate, furnace temperature, isothermal time, the nature and weight of the sample, and the size of the particles) has been attempted. The optimum conditions for the moisture and ash determinations were considered in turn. Finally, an appropriate procedure to determine both parameters was developed. In the analysis, the weight was considered constant when the sample heated at the selected temperature for 10 min exhibited a mass loss lower than 0.02%.

Moisture

The carrier gas (N_2 and O_2) was found to have no effect on the moisture determination, whereas the flow rate and the time for loading and weighing the sample in the thermobalance crucible may affect the final result. It was observed in fact that the gas stream initiated the evaporation process even without heating (Table 1); this mass loss may not be negligible, even under the optimum experimental conditions, if the mass of the sample is low.

TABLE 2

Moisture determination on wheat flours: the influence of isothermal temperature [a]

Sample [b]	TG		Italian offical method
	105 °C	130 °C	
Fine flour	13.55 ± 0.02 (35–40 min) [c]	13.60 ± 0.02 (18–24 min)	13.60 ± 0.02
Semolina	14.20 ± 0.03 (85–90 min)	14.20 ± 0.02 (45–50 min)	14.20 ± 0.02
Whole wheat flour	12.90 ± 0.04 (90–105 min)	12.95 ± 0.03 (55–60 min)	13.00 ± 0.04
"Cruschello"	11.50 ± 0.05 (115–130 min)	11.50 ± 0.04 (75–80 min)	11.50 ± 0.04

[a] Each value (%, wet basis) is the average of five determinations; the error is the mean deviation.
[b] 20 mg (weight) and 60 mesh (size).
[c] Time to reach a constant weight.

The heating rate does not affect the results of the analysis, nor does the isothermal temperature between 105 and 130 °C. Nevertheless, the sample reaches constant weight more rapidly at 130 °C than at 105 °C (Table 2).

The characteristics of the sample (weighed mass and size of particles) affect the isothermal time (Table 3).

Semolina and whole wheat flour, after an initial rapid mass loss, reach constant weight more slowly than fine flour, probably as a consequence of their compact structure (Fig. 2). The accuracy and reproducibility of replicate determinations are in agreement with values from the official methods.

Ash

The ash determination must be carried out in an oxidising atmosphere (O_2). Nevertheless, the sample was first heated to 500 °C in a nitrogen atmosphere to avoid too rapid combustion (the sample may be projected out of the crucible). The nitrogen atmosphere was then replaced by an oxygen stream at the same flow rate until the analysis was complete.

Some isothermal steps gave a rapid oxidative reaction and the best accuracy and reproducibility of the results. The data collected in Table 4 show that the residues obtained at 550 and 650 °C have a constant weight in agreement with those found with the official method. In contrast, on heating the sample at 750 or 850 °C the reaction is more rapid but the residue does not reach constant weight and the value found is lower than the expected one. The mass loss observed could be due to the decomposition of the residue during the thermogravimetric analysis, which does not occur during the normal muffle heating at 550 °C. This hypothesis was confirmed by the

TABLE 3

Moisture determination on wheat flours: the influence of mass and size of particles [a]

Sample	Isothermal at 130 °C						Italian official method
	60 mesh			20 mg			
	20 mg	10 mg	5 mg	< 60 mesh	60 mesh	120mesh	
Fine flour	13.60 ± 0.02 (18–24 min) [b]	13.55 ± 0.06 (16–20 min)	13.45 ± 0.25 (15–18 min)	13.60 ± 0.03 (20–25 min)	13.60 ± 0.02 (18–24 min)	13.60 ± 0.03 (16–22 min)	13.60 ± 0.02
Semolina	14.20–0.02 (45–50 min)	14.18 ± 0.05 (40–45 min)	14.10 ± 0.25 (38–45 min)	14.16 ± 0.04 (48–55 min)	14.20 ± 0.02 (45–50 min)	14.15 ± 0.03 (40–45 min)	14.20 ± 0.02
Whole wheat flour	12.95–0.03 (55–60 min)	12.90 ± 0.08 (52–56 min)	12.80 ± 0.30 (40–44 min)	12.90 ± 0.04 (58–65 min)	12.95 ± 0.03 (55–60 min)	12.92 ± 0.04 (52–56 min)	13.00 ± 0.02
"Cruschello"	11.50 ± 0.04 (75–80 min)	11.48 ± 0.08 (72–75 min)	11.45 ± 0.30 (70–76 min)	11.53 ± 0.05 (80–83 min)	11.50 ± 0.04 (75–80 min)	11.50 ± 0.05 (74–78 min)	11.50 ± 0.02

[a] Each value (%, wet basis) is the average of five determinations; the error is the mean deviation.
[b] Time to reach constant weight.

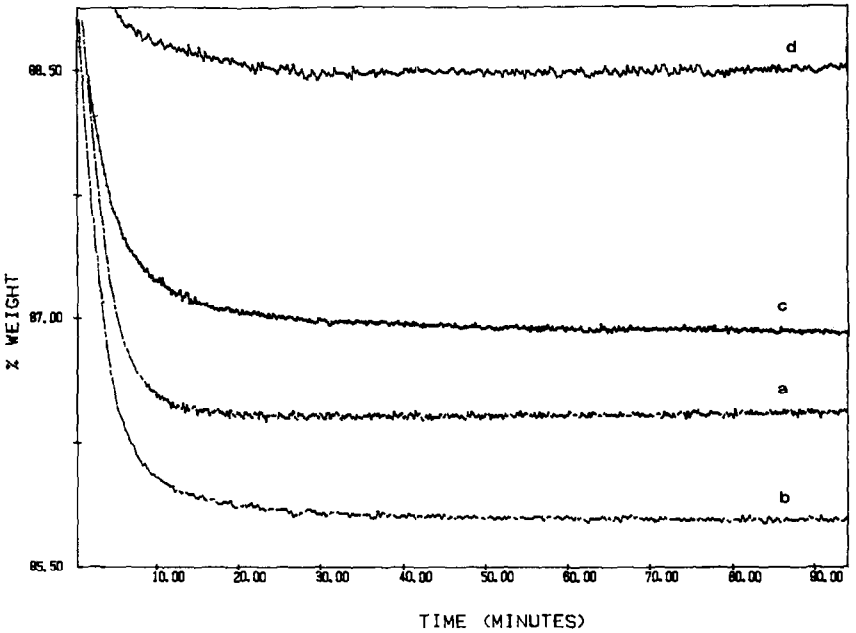

Fig. 2. Multistep programmed TG of fine flour (curve a), semolina (curve b), whole wheat flour (curve c) and "cruschello" (curve d). Heating rate, 50 °C min^{-1}; isothermal temperature, 130 °C; nitrogen dynamic atmosphere, 25 ml min^{-1}; sample weight, 20 mg; sample size, 60 mesh.

observation of a significant mass loss in a sample heated at 750 °C and/or 850 °C soon after it reached a constant weight at 650 °C.

The heating rate does not affect the results, although fine flour reaches constant weight at 650 °C more rapidly than semolina or whole wheat flour (Fig. 3).

The effects of the mass and size of the particles are the same as those observed in the moisture determination (Table 5).

Multistep program

In the light of these results, a multistep program was established for the simultaneous, rapid, accurate and precise determination of the moisture and ash contents of food flours. This program controls all the parameters of the thermogravimetric analysis.

TG runs (Fig. 4) were performed on samples of 15–20 mg (60–120 mesh) in dynamic nitrogen up to 500 °C, and then, using a gas selector, in an oxygen stream. The flow rate affects the two determinations in opposite ways, but to keep the base line stable the same flow rate was selected for both gases: 25 ml min^{-1} gave a high accuracy and precision in the moisture determination and allowed a rapid attainment of constant weight in the ash

TABLE 4

Ash determination on wheat flours: the influence of isothermal temperature [a]

Sample [b]	Isothermal temperature				Italian official method
	550 °C	650 °C	750 °C	850 °C	
Fine flour	0.35 ± 0.02 (25–30 min) [c]	0.35 ± 0.02 (18–25 min)	0.33 ± 0.03 (10–15 min)	0.32 ± 0.03 (5–8 min)	0.35 ± 0.02
Semolina	0.84 ± 0.02 (30–35 min)	0.84 ± 0.02 (20–25 min)	0.81 ± 0.04 (12–15 min)	0.80 ± 0.04 (5–8 min)	0.84 ± 0.02
Whole wheat flour	1.52 ± 0.02 (32–35 min)	1.52 ± 0.02 (22–26 min)	1.48 ± 0.04 (15–18 min)	1.46 ± 0.05 (10–12 min)	1.53 ± 0.02
"Cruschello"	6.92 ± 0.03 (35–40 min)	6.91 ± 0.02 (25–30 min)	6.84 ± 0.05 (15–18 min)	6.82 ± 0.05 (12–14 min)	6.90 ± 0.02

[a] Each value (%, dry basis) is the average of five determinations; the error is the mean deviation.
[b] 20 mg (weight) and 60 mesh (size).
[c] Time to reach constant weight (at 750 and 850 °C the residue does not reach a satisfactory constant weight).

TABLE 5

Ash determination on wheat flours; the influence of sample mass and size of particles [a]

Sample	Isothermal at 650 °C						Italian official method
	60 mesh			20 mg			
	20 mg	10 mg	5 mg [b]	< 60 mesh	60 mesh	120 mesh	
Fine flour	0.35 ± 0.02 (18–25 min) [c]	0.34 ± 0.04 (15–20 min)	–	0.35 ± 0.02 (18–25 min)	0.35 ± 0.02 (18–25 min)	0.35 ± 0.02 (18–25 min)	0.35 ± 0.02
Semolina	0.84 ± 0.02 (20–25 min)	0.83 ± 0.05 (18–22 min)	–	0.84 ± 0.02 (20–25 min)	0.84 ± 0.02 (20–25 min)	0.84 ± 0.02 (20–25 min)	0.84 ± 0.02
Whole wheat flour	1.52 ± 0.02 (22–26 min)	1.50 ± 0.04 (20–25 min)	–	1.52 ± 0.02 (22–26 min)	1.52 ± 0.02 (22–26 min)	1.52 ± 0.02 (22–26 min)	1.52 ± 0.02
"Cruschello"	6.89 ± 0.02 (25–30 min)	6.87 ± 0.03 (22–26 min)	–	6.89 ± 0.02 (25–30 min)	6.89 ± 0.02 (25–30 min)	6.89 ± 0.02 (25–30 min)	6.90 ± 0.02

[a] Each value (%, dry basis) is the average of five determinations; the error is the mean deviation.

[b] Too low a sample mass compromises the reliability of the analysis.

[c] Time to reach constant weight.

TABLE 6

Flowsheet for the proposed multistep thermal analysis

	P1	P2	P3
Temperature (°C)	30	130	675
Time (min)	0	X [a]	Y [a]
Heating rate (°C min^{-1})	50	50	0

[a] Time required for the two isothermal steps.

determination. The heating rate was 50 °C min^{-1} and the isothermal temperatures were 130 and 650 °C. The flowsheet for the proposed multistep thermal analysis is outlined in Table 6, where X and Y are the times required for the two isothermal steps and depend on the characteristics of the sample. The weight was considered constant when the sample exhibited

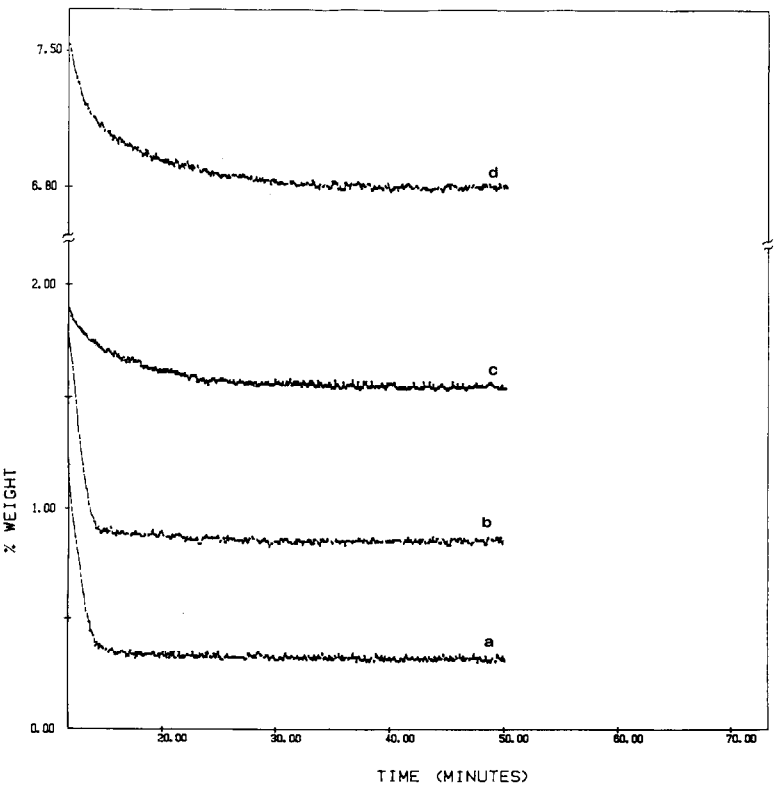

Fig. 3. Multistep programmed TG of fine flour (curve a), semolina (curve b), whole wheat flour (curve c) and "cruschello" (curve d). Heating rate, 50 °C min^{-1}; isothermal temperature, 650 °C; nitrogen and oxygen dynamic atmosphere, 25 ml min^{-1}; valve time, 9.4 min; sample weight, 20 mg; sample size, 60 mesh.

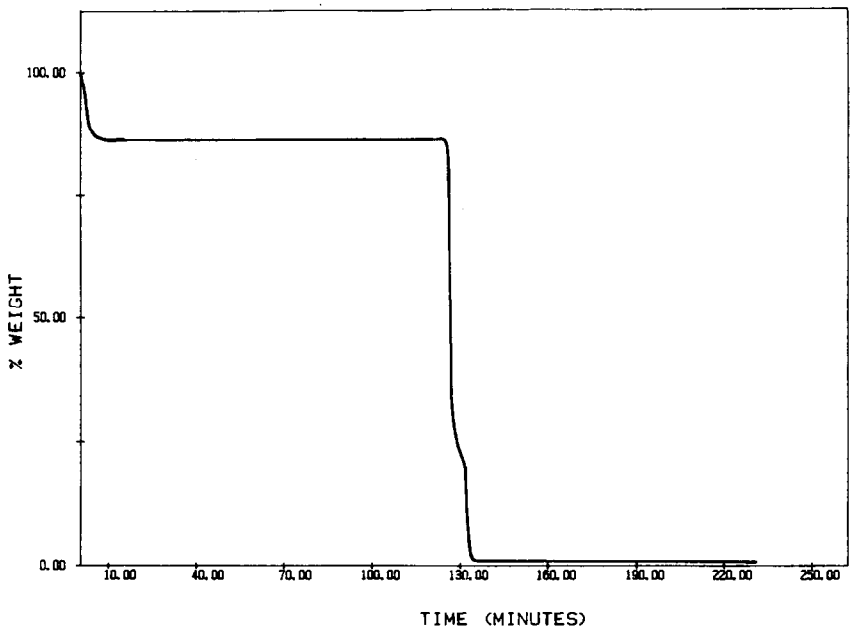

Fig. 4. Multistep programmed TG of fine flour: heating rate, 50 °C min^{-1}; isothermal temperature, 130 °C and 650 °C; nitrogen and oxygen dynamic atmosphere, 25 ml min^{-1}; valve time, 100 min; sample weight, 20 mg; sample size, 60 mesh.

a mass loss lower than 0.02% in 10 min. The time to commute the gas atmosphere in the furnace is $X + 9.4$ min.

CONCLUSIONS

The results obtained using the thermogravimetric multistep program are in accordance with those found by the official methods. Nevertheless, thermogravimetry applied to the analysis of the flours has some advantages: the moisture and the ash contents are determined on the same sample; it requires very small samples; and it is easy, rapid and very reliable. Unlike the dynamic thermogravimetric method, the proposed multistep program allows a complete separation of the water loss and ignited residue measurements so that the results of the analyses are more accurate and precise.

REFERENCES

1 E. Rizzatti and L. Rizzatti, Tutela igienico-sanitaria degli alimenti, (11th edn.), Pirola, Milano, 1977, in Italian.
2 Gaz. Uff. Rep. Ital., Parte Prima, n. 145 del 21.06.1985.
3 F. Di Stefano, F. Lintas Simoncelli, F. Muntoni and D. Renzi, Ann. ISS, 3 (1967) 245.
4 G. Seghieri, M. Mecozzi, G. Sechi and M. Benedetti, Rass. Chim., 4 (1988) 203.

5 K.H. Norris, Near Infrared Reflectance Spectroscopy. The Present and Future, 6th International Cereal and Bread Congress, AACC, Winnipeg, 16–22 September, 1978.
6 Oxford Analytical Instruments, Application Report, 4 (1985).
7 J. Chambers, N.J. McKevitt, K.A. Scudamore and C.E. Bowman, J. Sci. Food Agric., 49 (1989) 211.
8 M. Tomassetti, L. Campanella and M. Delfini, Thermochim. Acta, 105 (1986) 179.