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Thermogravimetry (TG) applied to the analysis of Cabrales cheese

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Abstract

TG was used in the study of Cabrales cheese in order to obtain information on the changes linked to a weight loss in the substance. In the same way the water activity in the samples was obtained.

INTRODUCTION

Cabrales cheese is a blue-veined soft paste cheese which is fatty, semi-hard and with denomination of origin. It is produced by craftsmen in the area of Cabrales, Asturias (Spain) from whole milk which has not been submitted to any homogenisation or similar process, together with rennet and salt. The milk used may be cows' milk or mixtures with sheep's and/or goats' milk (the cheese made from the milk mixtures is only made in spring and summer).

The rennet used is generally natural rennet, although in some cases industrial rennet is used (*Penicillium roqueforti*) although this is not necessary because *Penicillium* forms naturally during the ripening of the cheese in caves. The curd, arranged in circular moulds (the normal size being 25 cm in diameter by 7–15 cm in height) is left to set for 15–30 days according to the size of the cheese, and is later taken to natural caves where the ripening takes place. If the ripening is from one to three months the cheese is still considered to be fresh, if between three and six months to be mature, and if the cheese is in the cave for more than six months it is considered to be pasty or mellow.

The kind of milk used in the making of Cabrales cheese does not have a notable influence on the average composition of fat, proteins, etc. of the cheese [1] cows' milk is used in the greatest proportion. However

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this does influence the flavour of the product, which also depends on the pH of the curd and on the ripening. Cows' milk gives body, goats' milk gives bite and sheep's milk gives aroma and mildness.

In this work TG was used in the study of Cabrales cheese. This technique has been used by other authors to determine water and ash in an Italian soft cheese [2] and in various foodstuffs including powdered milk [3].

The purpose of applying TG in the analysis of Cabrales cheese is to obtain information on the changes which are linked to a loss in weight of the substance, such as dehydration, decomposition volatilization, etc.

From the data obtained in the determination of the humidity and ash, a calculation was made for each sample of cheese analysed of the activity of the water, given the importance of this factor in fixing the limits below which the proliferation of microorganisms is impossible. As is shown in ref. 4, the growth of microorganisms stops in the areas: bacteria, $A_W = 0.91$ (non-halophilous species); yeasts, $A_w = 0.88$; moulds, $A_w = 0.80$; halophilous species, $A_w = 0.75$.

EXPERIMENTAL

The samples of Cabrales cheese were purchased in commercial establishments. In each case the cheese bore the wrapping ordered by the Regulating Council for Denomination of Origin for this purpose and a label showing the identification number of the craftsman and the types of milk used.

The samples analysed were as follows: samples 1 and 2 are cheeses made from cows' milk; samples 3 and 4 are cheeses made from cows' milk and sheep's milk; samples 5 and 6 are cheeses made from cows', goats' and sheep's milk.

TABLE 1

Contents of protein and fat, and pH of Cabrales cheeses [a]

Sample	Milk type [b]	Proteins (wt.%)	Fat (wt.%)	pH
1	c	25.31	35	6.91
2	c	29.06	33.75	5.97
3	c + s	23.56	32.67	5.57
4	c + s	24.68	36.25	5.86
5	c + s + g	25.86	33.67	5.9
6	c + s + g	30.05	30.67	5.94

[a] As shown in ref. 1, the range of values found in Cabrales cheese is: protein, 20.63–28.09 wt.%; fat, 25.65–38.69 wt.%; pH, 5.45–7.20. [b] c = cows'; s = sheep's; g = goats'.

In each sample (Table 1) the content of protein and fat, and the pH were determined in order to check if the values of the analytical parameters were within the range of values outlined in ref. 1 for Cabrales cheese.

The determination of protein was carried out as described in ref. 5 and fat by the butirometric acid method, according to Van Gilik [6].

An Orion potentiometer and a "Ross" No. 8163 electrode especially designed for solids were used.

The water and ash content were determined thermogravimetrically by heating at a speed of 10.0° C min^{-1}, the thermograms being recorded in an atmosphere of nitrogen and air, by heating in ovens at 105°C (water) and a muffle furnace at 550°C (ash).

The instruments used were: Thermobalance (Mettler TA 4000 Thermal Analysis System); muffle and drying ovens, both time and temperature control; Buchi distiller and digester, Nos. 323 and 430 respectively.

RESULTS AND DISCUSSION

The thermogravimetric curves (Figs. 1–6) show two weight losses, which correspond to the contents of water and organic material.

The water loss, both in the air and in the nitrogen atmosphere, occurs in two partially overlapping stages, in the temperature range 25–165°C. These two stages are in agreement with the ideas suggested by Curini et al. [2], corresponding to the content of unbound water, which is lost at temperatures below 100°C, and with bound water, which is eliminated at temperatures above 100°C.

Table 2 summarizes the temperature ranges at which these weight losses take place and the percentages corresponding to each of these losses when the thermograms are carried out in air. In Table 3 the total water losses are shown as obtained by TG and by heating in an oven.

From these experiments it is deduced that TG avoids the long operational times necessary for eliminating all the water from the samples when they are heated in an oven at 105°C. Although at this temperature all the water should evaporate, some water is bound to the biological systems, and in order to reach the activation energy required to release this water, long periods of heating or much higher temperatures, are required.

Once the water has been removed the destruction of the organic material begins. This process occurs in several partially overlapping stages. The first stage is slow until temperatures nearing 280°C. The second stage occurs with a greater weight loss up to temperatures of the order of 400°C. In the third stage there is a continuous fall with a very slight slope. This stage reaches temperatures of the order of 550°C. In the thermograms recorded under nitrogen, the weight is now constant. In the

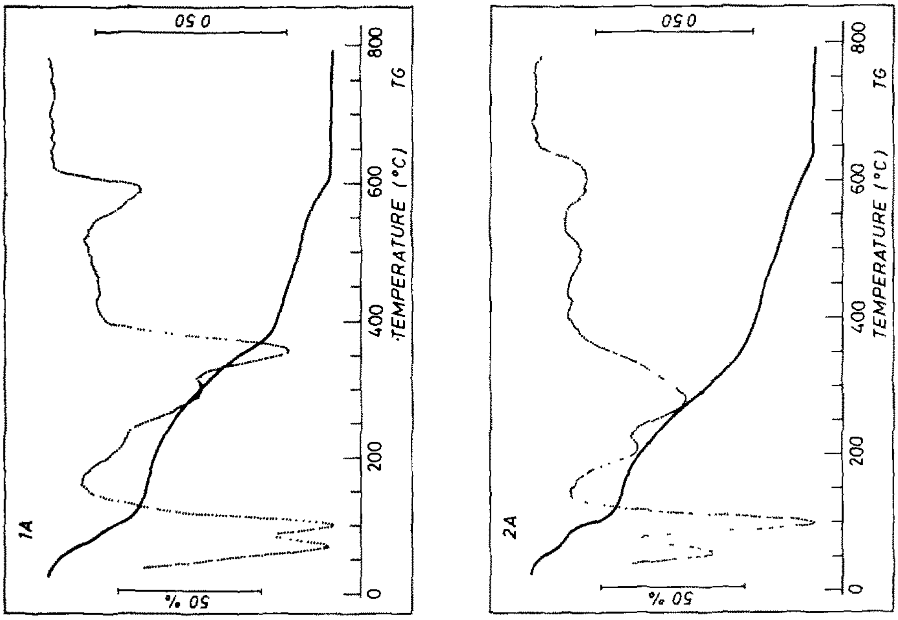

Fig. 1. TG curves for Cabrales cheeses made from cows' milk: 1A, in air; 2A, in air.

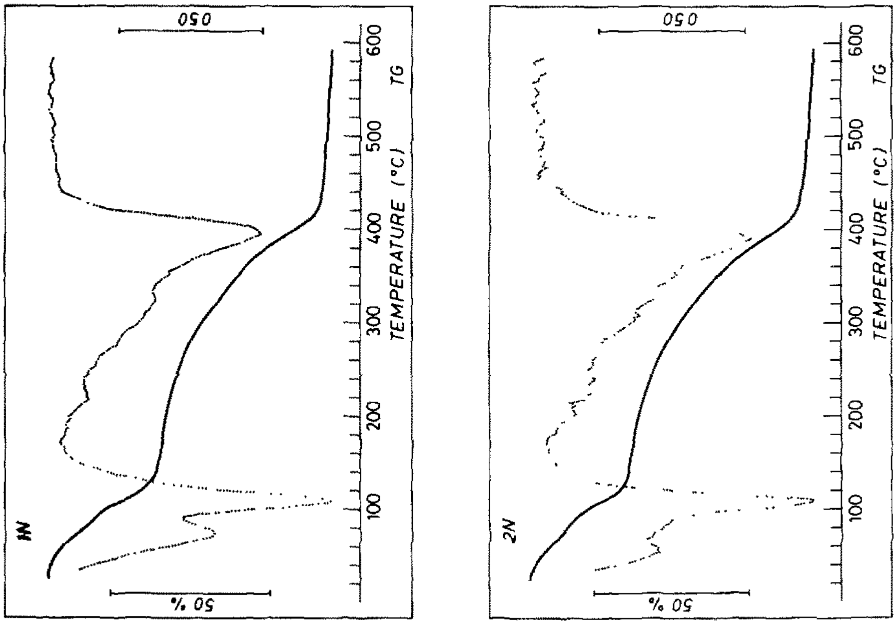

Fig. 2. TG curves for Cabrales cheeses made from cows' milk; 1N, in nitrogen; 2N, in nitrogen.

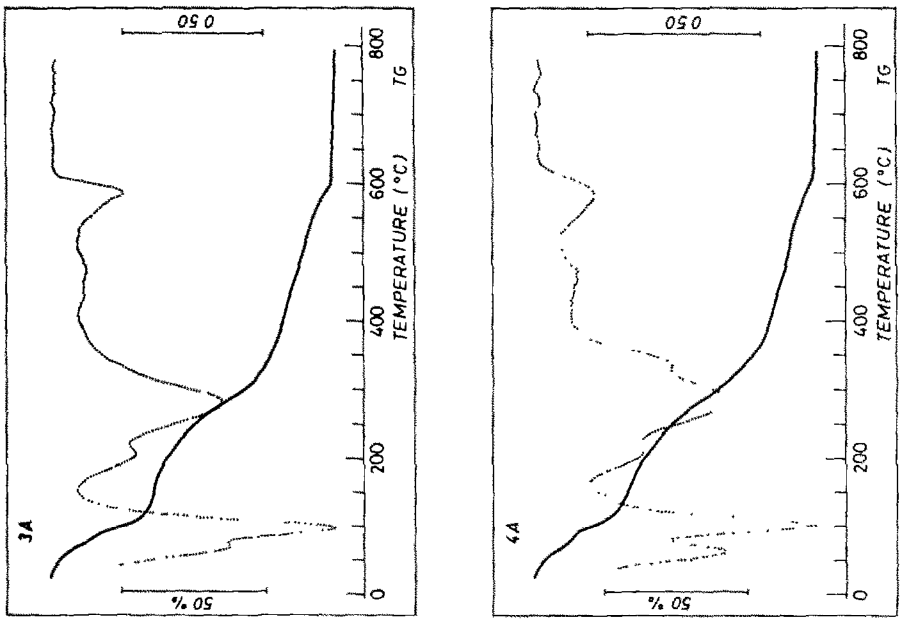

Fig. 3. TG curves for Cabrales cheeses made from cows' milk and sheep's milk. 3A, in air; 4A, in air.

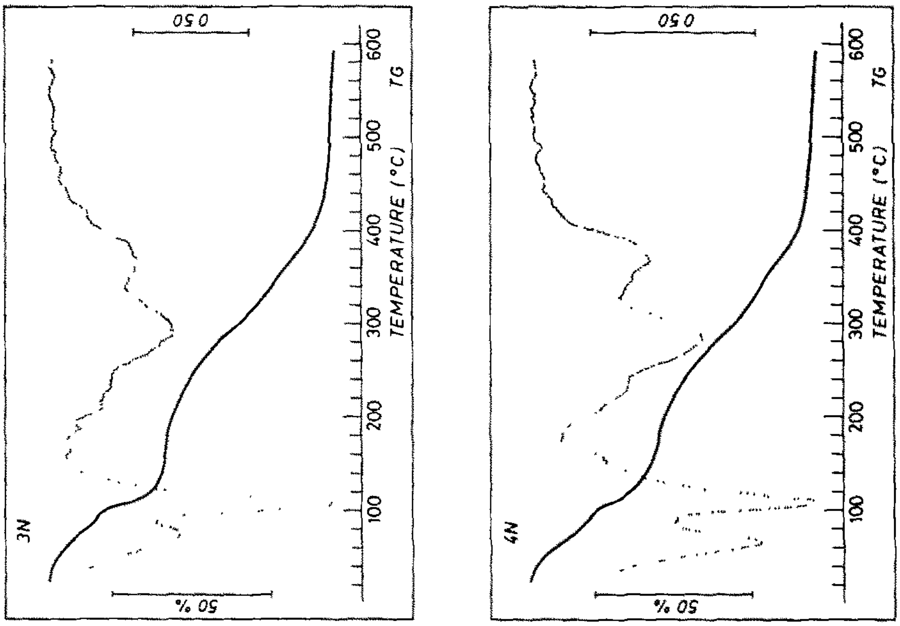

Fig. 4. TG curves for Cabrales cheeses made from cows' milk and sheep's milk: 3N, in nitrogen; 4N, in nitrogen.

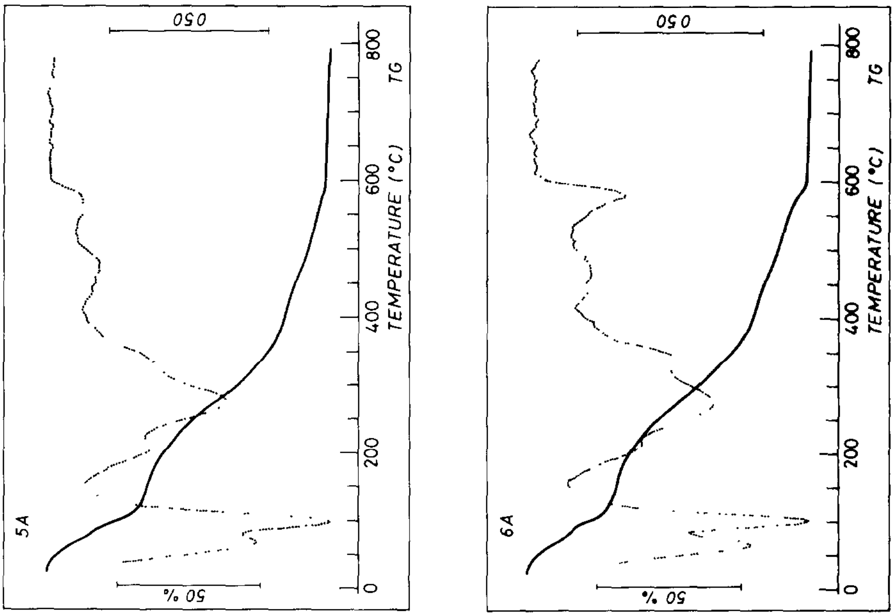

Fig. 5. TG curves for Cabrales cheeses made from cows', goats' and sheep's milk: 5A, in air; 6A, in air.

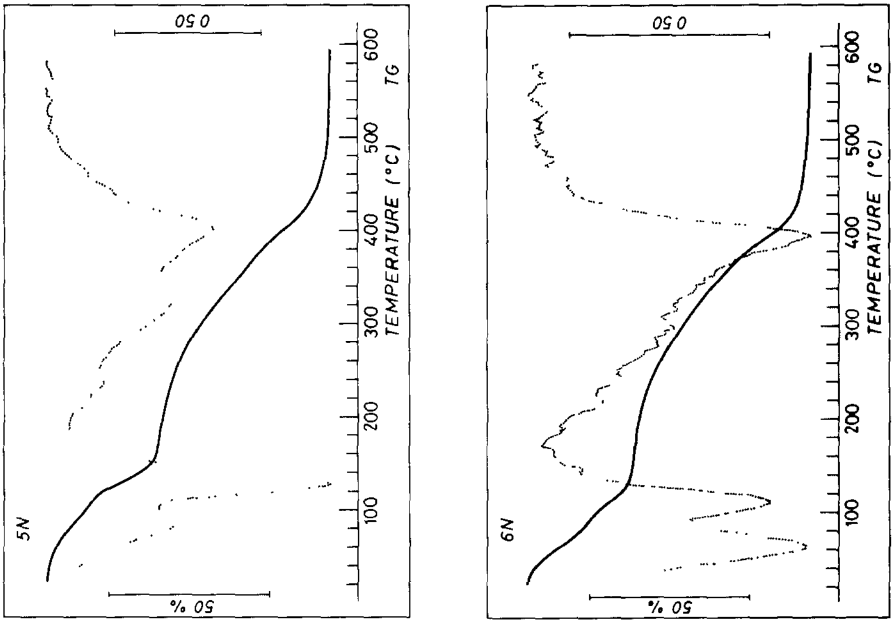

Fig. 6. TG curves for Cabrales cheeses made from cows', goats' and sheep's milk. 5N, in nitrogen; 6N, in nitrogen.

TABLE 2

Thermal analysis of Cabrales cheese

Sample	1st Loss of water		2nd Loss of water	
	Temp. range (°C)	H_2O (wt.%)	Temp. range (°C)	H_2O (wt.%)
1	25–84.6	17.06	84.6–162.3	17.07
2	25–76.3	12.47	76.3–144.2	18.80
3	25–76.3	11.72	76.3–152.6	22.66
4	25–80.5	12.57	80.5–165	21.08
5	25–80.5	14.60	80.5–151.2	19.74
6	25–83.2	13.96	83.2–155.3	16.15

TABLE 3

Percentage of water in Cabrales cheeses: comparison of TG and oven results

Sample	H_2O (wt.%)		
	TG		Oven (105°C)
	In air	In N_2	
1	34.13	34.31	34.37
2	31.27	32	32.21
3	34.38	35.78	
4	33.65	38.41	37.92
5	34.34	34.57	34.37
6	30.11	32.05	30.29

TABLE 4

Percentages of ash in Cabrales cheeses: comparison of TG and muffle results

Sample	Ash (wt.%)		
	TG		Muffle (550°C)
	In air (650°C)	In N (550°C)	
1	2.57	12.92	5.03
2	2.31	10.45	4.66
3	4.23	11.97	7.79
4	2.63	10.64	5.76
5	3.44	12.73	7.05
6	3.68	12.42	6.82

thermograms recorded in air, a fourth stage is observed, with a weight loss a little more marked than in the former, with a horizontal section appearing at temperatures in the order of 650°C.

Comparing the values obtained ash content using TG (to constant weight) with those obtained by heating in the muffle, serious discrepancies are seen (Table 4).

In the nitrogen atmosphere at 550°C higher values are observed than by heating in the muffle at the same temperature. This is due to the fact that in the residue there is still part of the carbon which was not eliminated as CO_2 because of insufficient oxygen and also because of being coated with salts which melt at this temperature.

In the thermograms carried out in the air the residue obtained at 650°C weighs less than that obtained in the muffle at 550°C. The reasons for this weight loss lie in the fact that in order to burn the carbon coated in melted salts, longer periods or higher temperatures are needed and increasing the temperature increases the volatility of some mineral compounds, especially chlorides.

The calculation of the water activity was carried out by applying the formulae suggested by Marcos for cheeses ripened with moulds, [7], i.e. $A_w = 1.0076 - 0.0079$ (g ash per 100 g H_2O); and by Marcos et al. for Cabrales cheese [8], i.e. $A_w = 1 - 0.00776$ (g ash per 100 g H_2O).

The values used for this calculation are those which have been obtained in the muffle at 550°C and in the oven at 105°C.

The results obtained (Table 5) show that the samples analysed have A_w values which make the proliferation of a large number of microorganisms impossible, so the possibility of food poisoning is minimal.

TABLE 5

Water activities A_w of Cabrales cheeses [a]

Sample	Ref. 6	Ref. 7	Average
1	0.892	0.886	0.889
2	0.893	0.888	0.890
3	0.829	0.824	0.826
4	0.888	0.882	0.885
5	0.846	0.841	0.843
6	0.830	0.825	0.827

[a] See text for formulae.

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