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Determination of Water Activity in Brie and Camembert Cheese Varieties by Four Different Methods

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ABSTRACT

The water activity (A_w) of single samples from 12 brands of Brie cheese and 12 brands of Camembert cheese was measured at 20°C by using four methods based on different principles, namely psychrometry, cryoscopy, dew-point hygrometry and isopiestic equilibration. The average A_w values found (± standard deviation) for the Brie and Camembert cheese were 0·965 ± 0·005 and 0·967 ± 0·009, respectively. The mean difference between methods was less than 0·005 A_w units, while the mean deviation from the average A_w values was ±0·005 A_w units. The mean deviations from the average A_w for the entire population of samples of the two cheese varieties were 0·000, +0·001, +0·001 and −0·003 A_w units for the gravimetric (isopiestic), psychrometric, cryoscopic and hygrometric methods, respectively. The average pH values measured (± standard deviation) were 6·96 ± 0·44 and 7·01 ± 0·47 for the Brie and Camembert cheese, respectively.

INTRODUCTION

Camembert and Brie cheese are the best known and most significant representatives of surface mould-ripened soft cheeses judging by their world-wide popularity and the large amounts produced under many commercial brands.

The control of water activity (A_w) through salting has a selective effect on the moulds of surface mould-ripened cheeses (*Penicillium camemberti*, *Geotrichum candidum* and *Mucor*); in fact, they alter the appearance of the cheese by introducing defects such as 'toad skin' and 'cat hair', and influence the activity of *Penicillium* enzymes and the degree of proteolysis, which in

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turn affect the water activity and storage lifetime of the ripe product (Gripon, 1987).

The complexity of aroma compounds and the biochemical activity in this type of cheese may interfere with water activity measurements carried out by some methods such as those using electric hygrometers or vapour pressure manometers (Prior, 1979; Troller, 1983). Some literature A_w values, which are greater than those solely arising from the concentration of sodium chloride in the aqueous phase of the cheese (Marcos *et al.*, 1981), are obviously spurious, probably as a result of sensor contamination.

The equations developed specifically for the chemical prediction of water activity in most types of cheese were recently reviewed by Esteban and Marcos (1990), who found none suitable for the accurate determination of A_w in mould-ripened cheeses.

The primary objective of this work was to measure the water activity of a variety of brands of Brie and Camembert cheeses by four methods relying on different foundations in order to establish an accurate relationship between the A_w and chemical parameters of the cheeses in a subsequent study. The results unavoidably call for an individual and comparative discussion of the methods used for the determination of water activity.

MATERIALS AND METHODS

Cheese samples

Twelve samples of Brie cheese and another 12 of Camembert cheese of as many different brands were purchased at supermarkets in several Spanish cities. Cheeses were both imported (mainly from France) and manufactured in Spain. Retail, unprepacked samples of at least 250 g were first wrapped in polyethylene film and then in aluminium foil and subsequently taken in refrigerated isothermal bags to the laboratory, where they were frozen and stored at −24°C. For water activity measurements, the samples were thawed to take representative radial subsamples which were tempered overnight at 20°C in airtight polyethylene containers. The remaining material was homogenized with the rind, placed in sample containers and, once the pH had been measured with a Beckman 2500 digital pH-meter by inserting the combined electrode directly into the homogenized samples, the containers were closed and stored at −24°C for subsequent chemical analyses.

Measurement of water activity

The water activity (A_w) of all the cheese samples was determined simultaneously—on the same day—in a thermostated balance room at 20°C

by using two commercially available instruments and two techniques developed or modified in our laboratory. The four methods used were based on different principles.

Thermocouple psychrometer

The SC-10 Thermocouple Psychrometer/MT-3 Nanovolt-Thermometer System (Decagon Devices, Inc., Pullman, WA, USA) used was calibrated with filter paper strips dipped in saturated aqueous solutions of analytical grade salts [K_2SO_4, KNO_3, KCl and $(NH_4)_2SO_4$] of known A_w at 20°C (0·976, 0·946, 0·851 and 0·813, respectively, according to Greenspan, 1977) to determine its psychrometric constant. To speed the attainment of equilibrium, the cheese samples were spread on filter paper strips lining the side walls of the sample cups.

Cryoscopic method

This was implemented by applying the cryoscopic approach to water activity measurement of non-liquid food developed by Esteban *et al.* (1987). To twenty-five grams of each cheese sample was added to 75 ml of de-ionized water and the mixture was blended, centrifuged at 2000 rpm for 5 min and allowed to stand in an ice bath for 30 min to cold-harden the upper layer of fat. The freezing points of the solute extracts from the cheeses were measured on the intermediate aqueous phase (between the bottom protein pellet and other insoluble matter and the solidified fat of the upper layer) on a standard cryoscope (original Gerber) by using a cryoscopic thermometer scaled in 0·01°C from +0·40 to −1·23°C. The calibrated thermometer was checked against de-ionized water and NaCl solutions of known molality (0·05, 0·1, 0·2 and 0·3 M) and A_w at 20°C (0·9983, 0·9966, 0·9934 and 0·9901, respectively).

The water activity of the samples was calculated by using the improved version of the equation reported by Cabezas *et al.* (1988):

$$A_w = 1{\cdot}0155 + 0{\cdot}1068 \times fp \qquad (1)$$

which relates the freezing point (fp) of the aqueous extracts of the cheese samples with the A_w of the original, non-extracted samples, measured at 20°C.

Dew-point hygrometer

The new CX-1 model manufactured by Decagon Devices, Inc. requires no calibration; yet, it was checked against de-ionized water (it provided three consecutive readings of 0·999) and some of the NaCl and saturated salt solutions used to calibrate the above methods (readings were always within ±0·003 units of the standard values).

To expedite the attainment of vapour equilibrium, the samples were spread on small circles of filter paper to cover the bottom of the sample dishes.

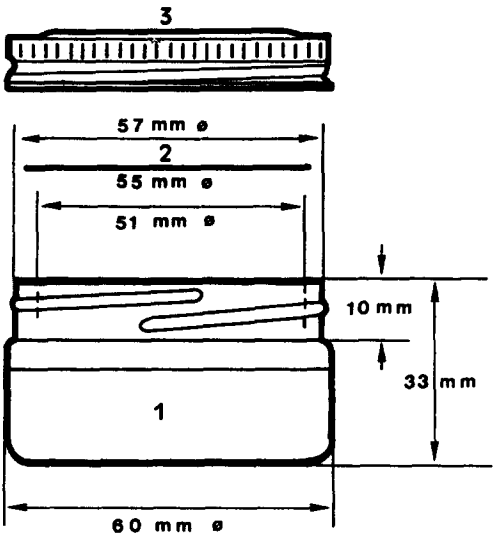

Fig. 1. Isopiestic equilibrium unit composed of (1) proximity diffusion cell containing a reference solution of known or a sample of unknown A_w, (2) circle of sorbent filter paper, and (3) airtight screw-cap with inside aluminium lining.

Gravimetric method

Flat Mason jars furnished with airtight screw-caps lined with aluminium on the inside were used as diffusion cells to hold the cheese samples and slurries of salts—those used to calibrate the psychrometer plus another two of NaCl and KI, with A_w of 0·755 and 0·699, respectively—as references of known water activity (Greenspan, 1977) and circles (diameter 5·5 cm) of untreated filter paper (Whatman No. 42) as sorbent material (Fig. 1).

The experimental procedure, applied in duplicate, involved the following steps: individual circles of filter paper were picked with forceps and weighed to 0·1 mg on a Cahn TA 450 electronic balance, after which they were exposed at 20°C in the diffusion cells over the references of known and samples of unknown A_w for 24 h. After equilibrium had been reached (95%), the circles were weighed again. The regression constants, a and b, of the linear equation

$$\log(1 - A_w) = a + b \times mg \tag{2}$$

were calculated from the moisture gains (mg) of the circles exposed over the slurries of known A_w. Then, the moisture gains of the circles exposed over the cheese samples were used to compute the A_w of the cheese samples from the equation

$$A_w = 1 - 10^{(a + b \times mg)} \tag{3}$$

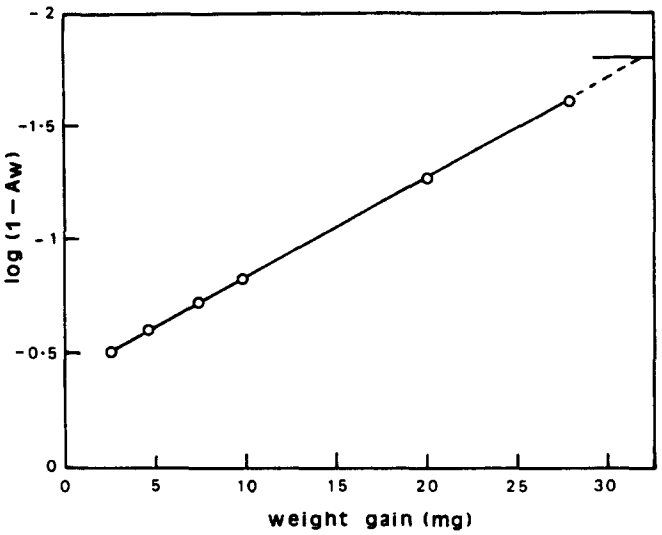

Fig. 2. Linear relationship between the moisture gain of untreated filter paper equilibrated over slurries of known A_w and $\log(1 - A_w)$.

The best fit of regression eqn (2) is shown in Fig. 2. The regression constants were $a = -0{\cdot}4039$ and $b = -0{\cdot}0446$, and the correlation coefficient was $r = 0{\cdot}993$. Thus, the actual equation used to compute the water activity of the cheese samples was:

$$A_w = 1 - 10^{(-0{\cdot}4039 + -0{\cdot}0446 \times mg)} \tag{4}$$

RESULTS AND DISCUSSION

Tables 1 and 2 list the water activities found for the 12 commercial brands of Brie and Camembert cheese tested, respectively. All values were rounded to three decimal places to equalize the water activity expressions of the four methods. The average A_w values and standard deviations of the four methods are also included in both tables.

The psychrometric method used, with a reported accuracy of $\pm 0{\cdot}005\, A_w$ units below 0·97 and $\pm 0{\cdot}0001$ units above 0·97, is based on wet-bulb temperature depression (resolution, $1{\cdot}7 \times 10^{-5}$°C) and dry bulb temperature measurements (to 0·1°C). Wet-bulb readings were obtained with a thermocouple of chromel and constantan wires (diameter 25 μm) whose junction was covered with a wetted tiny ceramic bead. After calibration, two successive readings were made for each cheese sample. The differences between the replicate readings differed usually by less than $0{\cdot}001\, A_w$ units, whereas the $\pm 0{\cdot}001$ unit differences found for some samples reveals that the ranges of the two readings differed between 0·002 and $0{\cdot}001\, A_w$ units. The

TABLE 1
Water Activity (A_w) of Brie Cheese Measured at 20°C by Four Different Methods

Sample	*Psychrometric*	*Cryoscopic*	*Hygrometric*	*Gravimetric*	*Mean ± SD*
1	0·968	0·959	0·963	0·967	0·964 ± 0·010
2	0·966	0·971	0·963	0·972	0·968 ± 0·004
3	0·950	0·949	0·951	0·966	0·955 ± 0·008
4	0·968	0·971	0·963	0·965	0·967 ± 0·004
5	0·969	0·979	0·966	0·966	0·970 ± 0·006
6	0·967	0·967	0·965	0·963	0·966 ± 0·002
7	0·961	0·953	0·960	0·960	0·959 ± 0·004
8	0·962	0·967	0·960	0·971	0·965 ± 0·005
9	0·961	0·968	0·950	0·963	0·961 ± 0·008
10	0·969	0·977	0·964	0·976	0·972 ± 0·006
11	0·970	0·970	0·965	0·967	0·968 ± 0·002
12	0·971	0·971	0·974	0·968	0·971 ± 0·002
Mean	0·965	0·967	0·962	0·967	0·965 ± 0·005
SD	±0·006	±0·009	±0·006	±0·004	±0·005

high reproducibility of consecutive readings was probably partly due to a bias from the operator in taking the second one under the subjective influence of the first. If second readings on each sample were recorded after finishing the first set of readings, the differences found would presumably be greater. Neither microbial metabolism nor volatile compounds appeared to interfere with the performance of the method.

TABLE 2
Water Activity (A_w) of Camembert Cheese Measured at 20°C by Four Different Methods

Sample	*Psychrometric*	*Cryoscopic*	*Hygrometric*	*Gravimetric*	*Mean ± SD*
13	0·955	0·932	0·942	0·950	0·945 ± 0·010
14	0·962	0·967	0·957	0·962	0·962 ± 0·004
15	0·976	0·955	0·953	0·962	0·962 ± 0·010
16	0·979	0·977	0·975	0·967	0·975 ± 0·005
17	0·976	0·976	0·966	0·965	0·971 ± 0·006
18	0·971	0·972	0·972	0·965	0·970 ± 0·003
19	0·969	0·966	0·962	0·966	0·966 ± 0·003
20	0·964	0·967	0·964	0·968	0·966 ± 0·002
21	0·974	0·979	0·967	0·982	0·976 ± 0·007
22	0·968	0·972	0·966	0·958	0·966 ± 0·006
23	0·980	0·981	0·975	0·977	0·978 ± 0·003
24	0·969	0·967	0·965	0·963	0·966 ± 0·003
Mean	0·970	0·968	0·964	0·965	0·967 ± 0·005
SD	±0·007	±0·013	±0·009	±0·008	±0·009

The cryoscopic procedure was applied by making single freeze-point readings of the cheese extracts as it was thought that replicate readings on the same extract or single readings on two extracts from the same cheese sample would be rather time-consuming and would not result in increased accuracy. Although the readings were made at temperatures below 0°C, the water activities of the cheese samples were referred to 20°C since the freezing points of the extracts were related with the A_w of the original (non-extracted) cheese samples, measured at 20°C with the thermocouple psychrometer (Esteban *et al.*, 1987; Cabezas *et al.*, 1988). Obviously, the cryoscopic approach has all the constraints of the reference method in addition to its own.

The hygrometric method relies on the cooled mirror (dew-point) principle for measuring water activity. The two successive readings made on each sample were of an objective nature thanks to the fact that the microprocessor fixed the digital A_w display. The average difference between consecutive readings on the Brie and Camembert cheese samples was $\pm 0{\cdot}001$ A_w units, i.e. within the reported accuracy of $\pm 0{\cdot}003$ for activities between 0·03 and 1·0. According to the manufacturer, the instrument can also accurately determine the water activity of samples containing volatiles. The average A_w values found for the Brie and Camembert cheese varieties, however, were 0·003–0·004 A_w units lower than those provided by the above methods (psychrometric and cryoscopic).

The gravimetric technique applied here was a new, simplified version of previously reported methods (Marcos *et al.*, 1985*a*; Esteban *et al.*, 1989) based on the isopiestic equilibration of untreated ashless cellulose filter paper. The principle behind the determination of water activity by this method lies in the linear relationship between the moisture gain of untreated filter paper and $\log(1 - A_w)$ over the A_w range from 0·70 to 0·98 (Fig. 2). Such a range encompasses the minimal A_w limits for the growth of micro-organisms relevant to human health and their production of toxins (Beuchat, 1981), as well as the entire A_w spectrum of almost all non-fresh cheese (Marcos *et al.*, 1985*b*). The accuracy of the method ($\pm 0{\cdot}005$ A_w at the lower limit) increases with increasing A_w and the average precision of replicate determinations is $\pm 0{\cdot}001$ A_w units over the full operative range. This modified technique does not allow extrapolations above $A_w = 0{\cdot}98$ to be made owing to the abrupt increase in the slope occurring close to $A_w = 0{\cdot}985$; neither can extrapolations below $A_w = 0{\cdot}70$ be made owing to another significant change in the slope usually occurring with most batches of filter papers between 0·70 and 0·40 arising from the fact that, in the moisture sorption isotherms, the A_w of the untreated paper cross over from the adsorption branch of the hysteresis loop to the desorption branch (unpublished results). Extrapolations above $A_w = 0{\cdot}98$ can indeed be made

by using larger pieces of filter paper and weighing them once equilibrated in a humid microenvironment (RH $\simeq$ 90%) (Esteban *et al.*, 1989), and also below $A_w = 0{\cdot}70$ (to 0·40) by using predried filter paper (McCune *et al.*, 1981; Lenart & Flink, 1983; Palacha & Flink, 1987). The filter paper obviously absorbed iodine from the reference KI solution (Lees *et al.*, 1989) and polar volatiles from the cheese samples—the smell of the equilibrated papers is similar to that of the cheese samples—but the amounts sorbed are gravimetrically insignificant in practice as shown by the high correlation coefficient ($r = 0{\cdot}9993$) obtained for the reference solutions. The average differences in the water activities between replicate samples determined by this technique were $\pm 0{\cdot}001\ A_w$ units, i.e. the same as for the consecutive readings made on the same samples with the dew-point hygrometer.

Although every individual method is sufficiently accurate and precise for measuring water activity in cheese, we calculated the average A_w values ($\pm$ standard deviations) of the four methods for the samples of Brie and Camembert cheese (Tables 1 and 2). These data allow one to search for a more reliable relation between water activity and the chemical composition of surface mould-ripened soft cheese, which may allow the future development of a more accurate chemical prediction of the water activity of this type of cheese than do currently available equations (Esteban & Marcos, 1989).

The differences from the average A_w values (considering the results listed in Tables 1 and 2 jointly) were 0·000, +0·001, +0·001 and −0·003 A_w units for the gravimetric, psychrometric, cryoscopic and hygrometric methods, respectively.

Table 3 lists the average differences between the A_w values obtained by the four methods for all the Brie and Camembert cheese varieties, as well as the arithmetic mean for both cheeses. The differences between methods were within $\pm 0{\cdot}005$ units for the Brie cheese and ranged between 0·006 and

TABLE 3
Average Differences between Pairs of Methods for Measurement of Water Activity

Methods	*Average A_w differences ($\times 10^{-3}$ units)*		
	Brie cheese	*Camembert cheese*	*Both cheeses*
Psy–Cry	−2	2	0
Psy–Hyg	3	6	<5
Psy–Gra	−2	5	<2
Cry–Hyg	5	4	<5
Cry–Gra	0	3	<2
Hyg–Gra	−5	−1	−3

TABLE 4
pH of Surface Mould-Ripened Soft Cheeses

Brie cheese		*Camembert cheese*	
Sample	*pH*	*Sample*	*pH*
1	6·97	13	7·26
2	7·00	14	7·36
3	6·95	15	7·29
4	7·31	16	6·76
5	5·91	17	6·24
6	6·89	18	6·79
7	7·32	19	7·54
8	7·62	20	7·46
9	6·60	21	6·56
10	6·64	22	6·50
11	7·24	23	6·71
12	7·12	24	7·75
Mean	6·96	Mean	7·01
SD	±0·44	SD	±0·47

−0·001 units for the Camembert cheese. The average differences between methods in the A_w values measured for the two cheeses (arithmetic mean) were less than 0·005 A_w units. The larger differences were related with the hygrometric method. In any case, such differences were lower than those found in other comparisons between methods (Labuza *et al.*, 1976; Stoloff, 1978; Stamp *et al.*, 1984; Fernández-Salguero *et al.*, 1989).

TABLE 5
Literature Values of Water Activity (A_w) and pH of Samples of Surface Mould-Ripened Cheese Varieties

Cheese variety[a]	A_w	*pH*	*Cheese variety*[b]	A_w	*pH*
Belle des Champs	0·987	5·66			
Brie Suisse	0·974	5·55	Brie	0·954	6·32
			Brie	0·968	7·18
Camembert Suisse	0·990	7·39	Camembert	0·969	7·08
			Camembert	0·972	6·95
			Goat cheese	0·970	7·23
			Goat cheese	0·965	7·10
Tomme Vaudoise	0·987	6·25			

[a] From von Rüegg and Blanc (1977).
[b] From Marcos *et al.* (1985*b*).

We also measured the pH of the samples, another physical parameter related with cheese stability (Table 4).

There appears to be no literature compilation of water activity and pH data on surface mould-ripened soft cheese varieties; no systematic studies, but only isolated data for individual cheese samples are available in this respect. Some reported values are listed in Table 5. The water activities measured by von Rüegg and Blanc (1977) with an electronic hygrometer seem too high compared with those listed in Tables 1 and 2. The divergence may arise from sensor contamination by cheese volatiles since the use of the electronic hygrometer on other products (canned fish) with similar A_w values (0·97–0·98) resulted in slightly lower activities than those measured with the thermocouple psychrometer and by the gravimetric method (Marcos *et al.*, 1985*a*), as shown by Fernández-Salguero *et al.* (1989) in a recent comparison between these methods.

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