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Calculation of Water Activity in Surface Mould-Ripened Soft Cheeses from their Chemical Composition

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ABSTRACT

The water activity (A_w) of 24 samples of 12 different brands of Brie cheese and another 12 of Camembert cheese was measured at 20°C by four methods (psychrometric, cryoscopic, dew-point hygrometric and isopiestic equilibration). The cheeses were also analysed chemically for their moisture, salt (NaCl), ash and non-protein nitrogen (NPN) contents. A linear regression analysis of data pairs of the variables [NaCl], [Ash] or [NPN] (in g/100 g moisture) and A_w *(average values of the four methods) yielded the following relations*

$$A_w = 0{\cdot}9813 - 0{\cdot}0045\ [NaCl]$$
$$A_w = 0{\cdot}9769 - 0{\cdot}0019\ [Ash]$$
$$A_w = 0{\cdot}9793 - 0{\cdot}0101\ [NPN]$$

On the other hand, a multiple linear regression analysis of sets of g ash/100 g moisture, g NPN/100 g moisture and average A_w *at 20°C led to the equation*

$$A_w = 0{\cdot}996 - 0{\cdot}0029\ [Ash] - 0{\cdot}0106\ [NPN]$$

All four equations can be used alone or in conjunction to predict the water activity of surface mould-ripened soft cheeses. The differences between the calculated and measured (average) A_w *values were similar to those yielded by the four measurement methods used.*

INTRODUCTION

Their search for potential relations between water activity (A_w) and the chemical composition of various types of cheese enabled Rüegg & Blanc

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(1977) to establish that the water activity of the cheeses they dealt with was essentially dependent on their moisture, salt (NaCl), ash and non-protein nitrogen (NPN) contents, as well as on the pH. Later, Rüegg (1985) reported a general equation for the calculation of water activities above 0·90 in cheeses based on the five above-mentioned parameters. After applying it to a large variety of cheeses, Marcos *et al.* (1985) found it to be highly precise and quite accurate for all varieties with A_w values above 0·90, with the exception of those ripened by moulds, the calculated activities of which were about two-hundredths higher than their experimental values. Fernández-Salguero *et al.* (1986) established more specific and accurate equations for prediction of the water activity of blue cheeses from their chemical composition; however, no equations are to date available for the reliable prediction of the A_w of white surface mould-ripened soft cheeses (Esteban & Marcos, 1990). In order to fill this gap, we determined the water activity of a number of brands of Brie and Camembert cheeses by four different measurement methods (Marcos *et al.*, 1990) which were analysed chemically in the present work in order to search for statistical relations between the water activity and the compositional parameters directly affecting it with a view to establishing specific equations allowing the accurate estimation of the A_w of white surface mould-ripened soft cheeses.

MATERIALS AND METHODS

Cheese samples

Samples of 12 brands of Brie cheese and another 12 of Camembert cheese used in previous work (Marcos *et al.*, 1990) were stored at −24°C in air-tight containers for subsequent chemical analysis after measuring their pH and water activity (A_w) at 20°C by four different methods, namely psychrometric, cryoscopic, dew-point hygrometric and isopiestic equilibration.

Chemical analyses

The moisture content of the 24 samples was determined according to the British Standard Institution's recommended method (1963), while the salt (NaCl) content was measured by the Volhard method as modified by Kosikowski (1982). The ash content was determined by the AOAC method (1980), and that of non-protein nitrogen (NPN), soluble in 11·5% trichloroacetic acid (TCA), was determined according to Lenoir (1962). Each sample was assayed in duplicate.

Statistical analysis

We used the least-squares linear regression method to calculate constants a and b, and the coefficient of determination (r^2) of the equation $y = a + bx$ from data pairs of the variables x (NaCl, Ash or NPN content, expressed in g/100 g moisture), and y (average A_w measured at 20°C by the four methods used). On the other hand, we used the least-squares multiple linear regression technique to determine coefficients a, b and c and the square of the multiple correlation coefficient (R^2) of the equation $z = a + bx + cy$ from sets of data points of the variables x (g ash/100 g moisture), y (g NPN/100 g moisture) and z (average A_w measured at 20°C by the four methods).

RESULTS AND DISCUSSION

The physical parameters (A_w and pH) previously determined for 24 samples of different brands of Brie and Camembert cheeses are listed in Table 1, together with the three chemical parameters (salt, ash and non-protein nitrogen contents) determined at a later stage and referred to the moisture content (g/100 g H_2O).

As can be seen, there were rather small differences between the physical and chemical data of the different samples and brands, and even between cheese varieties—the greatest differences were encountered in the NPN content as a result of the different degree of proteolysis of the samples.

The water activities found are quite reliable as they are the averages of measurements made by four methods relying on different principles (Marcos *et al.*, 1990). The remaining data in Table 1 were required to apply Rüegg's equation (1985)

$$A_w = 0{\cdot}945 - 0{\cdot}0056\ [\text{NPN}] - 0{\cdot}0059\ [\text{NaCl}] \\ - 0{\cdot}0019\ ([\text{Ash}] - [\text{NaCl}]) + 0{\cdot}0105\,\text{pH} \qquad (1)$$

for calculation of the water activity of the cheeses, where the concentration of all the components involved, like in all the equations that will follow, is expressed in g/100 g moisture.

Application of eqn (1) to the data in Table 1 resulted in A_w values exceeding their experimentally measured counterparts by 0·01–0·04 A_w units, the average predictions being over 0·02 A_w units above the average experimental measurements (Table 2), consistent with earlier findings (Marcos *et al.*, 1985).

Obviously, eqn (1) is not valid as such for soft cheese varieties and requires some refinements as the salt concentration in cheese moisture alone results in lower A_w values in most samples (Table 2), closer to their measured

TABLE 1
Some Physical and Chemical Data of Surface Mould-Ripened Soft Cheeses

Sample[a]	A_w[a]	*pH*[a]	*[NaCl]*[b]	*[Ash]*[b]	*[NPN]*[b]
1	0·964	6·97	2·89	5·71	1·40
2	0·968	7·00	3·26	5·84	1·19
3	0·955	6·95	3·39	6·20	2·02
4	0·967	7·31	2·80	4·72	1·75
5	0·970	5·91	3·46	6·99	0·58
6	0·966	6·89	4·13	6·20	0·78
7	0·959	7·32	3·72	5·00	1·77
8	0·965	7·62	3·18	5·14	1·87
9	0·961	6·60	4·35	6·89	1·29
10	0·972	6·64	3·15	5·38	0·86
11	0·968	7·24	3·18	5·01	1·10
12	0·971	7·12	4·23	4·71	1·15
13	0·945	7·26	3·69	5·64	2·63
14	0·962	7·36	3·26	5·86	1·82
15	0·962	7·29	3·65	5·45	1·39
16	0·975	6·76	2·93	4·74	0·90
17	0·971	6·24	3·30	4·90	0·63
18	0·970	6·79	3·84	5·53	0·81
19	0·966	7·54	2·86	6·58	1·37
20	0·966	7·46	2·82	5·02	1·49
21	0·976	6·56	2·71	6·38	0·98
22	0·966	6·50	4·12	6·28	1·11
23	0·978	6·71	3·05	4·79	1·56
24	0·966	7·65	3·05	4·91	0·80

[a] Data from Marcos *et al.* (1990).
[b] In g/100 g moisture.

counterparts (average 0·015 A_w units higher), by applying the equation reported by Marcos *et al.* (1981):

$$A_w = 1 - 0{\cdot}005\,65\ [\mathrm{NaCl}] \tag{2}$$

In addition to the salt concentration in the aqueous phase, the water activity of ripened cheese is also depressed by the aqueous concentration of other inorganic (calcium, phosphorus) and organic species (mainly NPN from proteolysis) of low molecular weight.

Marcos (1987) reported an alternative equation for the prediction of water activity in mould-ripened cheeses (blue and soft varieties included),

$$A_w = 1{\cdot}0076 - 0{\cdot}0079\ [\mathrm{Ash}] \tag{3}$$

TABLE 2

Differences Between the Experimental A_w Values of Surface Mould-Ripened Soft Cheeses and the A_w Values Calculated from their Chemical Compositions According to Various Predictive Equations

Sample	*Differences (× 10^{-3} A_w units) between $(A_w)_{calc}$ and $(A_w)_{exp}$*						
	Eqn (1)	*Eqn (2)*	*Eqn (3)*	*Eqn (4)*	*Eqn (5)*	*Eqn (6)*	*Eqn (7)*
1	24	20	−2	−4	2	1	1
2	21	14	−7	−1	−2	−1	−1
3	26	26	4	11	10	4	2
4	25	17	3	2	1	−5	−3
5	7	10	−18	−4	−6	3	0
6	19	11	−7	−3	−1	5	4
7	29	20	9	6	8	2	4
8	27	17	2	2	2	−5	−4
9	16	14	−8	1	3	5	2
10	15	10	−7	−5	−5	−1	−1
11	25	14	0	−1	−1	0	2
12	16	5	−1	−9	−3	−3	−1
13	36	34	18	20	21	8	7
14	26	20	−1	5	4	−1	−2
15	27	17	3	3	4	3	4
16	25	8	−5	−7	−7	−5	−2
17	13	10	−2	−4	−3	2	4
18	16	8	−6	−6	−4	1	2
19	27	18	−10	3	−2	0	−3
20	33	18	2	3	1	−2	0
21	9	9	−19	−7	−11	−7	−9
22	13	11	−8	−3	−1	2	0
23	7	5	−8	−10	−10	−14	−12
24	33	17	3	2	2	5	7

which yielded A_w values within $\pm 0{\cdot}02\, A_w$ units of their experimentally measured counterparts (Table 2).

The lack of an accurate equation for the prediction of the water activity of surface mould-ripened cheeses (Esteban & Marcos, 1990), prompted us to use the data in Table 1 to search for relations between the chemical composition and water activity of this type of cheese.

By using the linear regression technique we arrived at the following relations:

$$A_w = 0{\cdot}9813 - 0{\cdot}0045\ [\text{NaCl}] \qquad r^2 = 0{\cdot}10 \qquad (4)$$

$$A_w = 0{\cdot}9769 - 0{\cdot}0019\ [\text{Ash}] \qquad r^2 = 0{\cdot}04 \qquad (5)$$

$$A_w = 0{\cdot}9793 - 0{\cdot}0101\ [\text{NPN}] \qquad r^2 = 0{\cdot}52 \qquad (6)$$

TABLE 3
Differences from the Average Water Activity (A_w) Yielded by Each Method[a]

Sample	*Differences from average* ($\times 10^{-3}$ A_w *units*) *Method*			
	Psychrometric	*Cryoscopic*	*Hygrometric*	*Gravimetric*
1	4	−5	−1	3
2	−2	3	−5	4
3	−5	−6	−4	11
4	1	4	−4	−2
5	−1	9	−4	−4
6	1	1	−1	−3
7	2	−6	1	1
8	−3	2	−5	6
9	0	7	−11	2
10	−3	5	−8	4
11	2	2	−3	−1
12	0	0	3	−3
13	10	−13	−3	5
14	0	5	−5	0
15	6	−7	−9	0
16	4	2	0	−8
17	5	5	−5	−6
18	1	2	2	−5
19	3	0	−4	0
20	−2	1	−2	2
21	−2	3	−9	6
22	2	6	0	−8
23	2	3	−3	−1
24	3	1	−1	−3

[a] From Marcos *et al.* (1990).

where the coefficients of determination (r^2) are not very large because of the small differences (variability) between the data pairs noted earlier. However, application of these equations to the data in Table 1 resulted in differences between the calculated and measured A_w values (Table 2) similar to those found between the four measurement methods (Marcos *et al.*, 1990) and the average values yielded by them (Table 3), except for one odd sample (number 13), which gave differences of 0·02 A_w units on application of eqns (4) and (5).

From the best fit of eqn (6) we constructed a nomograph (Fig. 1) in which the NPN in cheese moisture was related coincidentally with the water activity. This allows the direct graphical estimation of A_w, thereby saving some arithmetic calculations.

The better fit of the A_w values obtained from eqns (5) and (6) to their

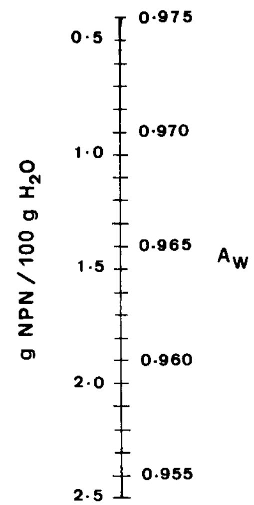

Fig. 1. Nomograph for direct estimation of the A_w of surface mould-ripened soft cheeses from the non-protein nitrogen (NPN) content in the cheese moisture.

experimental counterparts led us to apply the multiple linear regression technique to the ash and NPN contents (both expressed on a moisture basis) against the water activity in order to establish a more complex, though also more refined and accurate predictive equation, namely:

$$A_w = 0{\cdot}996 - 0{\cdot}0029\ [\text{Ash}] - 0{\cdot}0106\ [\text{NPN}] \qquad (7)$$

the square of multiple correlation coefficient of which was somewhat larger ($R^2 = 0{\cdot}60$) than the coefficient of determination ($r^2 = 0{\cdot}52$) resulting from the use of the NPN content alone (eqn (6)). The differences between measured A_w values and those calculated from eqn (7) were less than $\pm 0{\cdot}005\ A_w$ units for 83% of the samples—versus 63% with eqn (6). This figure was equal to that of the most accurate method used, namely that of the thermoelectric psychrometer, and clearly surpassed those of the other three methods (Tables 2 and 3).

The proportion of samples yielding differences not larger than $\pm 0{\cdot}005\ A_w$ units from the average experimental A_w (Table 1) values on applying the regression equations arrived at in this work (data in Table 2) and each of the four methods used (data in Table 3) were as follows:

Eqn (4)	67%	Cryoscopic method	71%
Eqn (5)	71%	Gravimetric method	75%
Eqn (6)	88%	Hygrometric method	83%
Eqn (7)	83%	Psychrometric method	92%

The next step in this work involved checking these equations for accuracy by applying them to alien literature data not used in the regression analysis.

TABLE 4
Some Physical and Chemical Data of Surface Mould-Ripened Soft Cheeses

Cheese variety	A_w	*pH*	*[NaCl]*[a]	*[Ash]*[a]	*[NPN]*[a]	*Source*
Belle des Champs	0·987	5·66	3·73	6·11	0·85	Rüegg and Blanc (1977)
Brie suisse	0·974	5·55	3·86	6·06	0·47	Rüegg and Blanc (1977)
Camembert suisse	0·990	7·39	5·33	5·87	1·03	Rüegg and Blanc (1977)
Tomme vaudoise	0·987	6·52	3·14	3·49	1·67	Rüegg and Blanc (1977)
Brie	0·954	6·32	3·56	6·20	1·66	Marcos *et al.* (1985)
Brie	0·968	7·18	4·64	4·91	1·15	Marcos *et al.* (1985)
Camembert	0·969	7·08	3·28	5·41	1·23	Marcos *et al.* (1985)
Camembert	0·972	6·95	3·37	4·67	1·19	Marcos *et al.* (1985)
Goat cheese	0·970	7·23	3·87	7·36	1·19	Marcos *et al.* (1985)
Goat cheese	0·965	7·10	4·29	5·04	2·46	Marcos *et al.* (1985)

[a] In g/100 g moisture.

The full set of data required for this purpose could only be found for ten of the cheese samples (Table 4), four of which had been analysed by Rüegg & Blanc (1977), and six by Marcos *et al.* (1985).

Application of eqns (1)–(7) to the literature data (Table 5) revealed Rüegg's equation (1977), *viz.* eqn (1), to work well with the data reported by Rüegg & Blanc (1977), although it yielded estimated A_w values exceeding those measured by Marcos *et al.* (1985) by about 0·02 A_w units, consistent with the results listed in Table 2. On the other hand, application of eqn (3), from Marcos (1987), and eqns (4)–(7), established in the present work, had the opposite effect, i.e. the calculated values were about 0·02 A_w units lower than those measured by Rüegg & Blanc (1977).

The A_w values of soft cheeses measured by Rüegg & Blanc (1977) using an electronic hygrometer were suspectedly too high (Marcos *et al.*, 1990), probably as a result of the sensor contamination by volatile substances. This suspicion was unequivocally confirmed by the fact that in three of the four samples assayed by Rüegg & Blanc (1977), the depression in the water activity caused solely by the aqueous concentration of NaCl alone (eqn (2) in Table 2) was greater (lower A_w) than its experimentally measured counterpart.

Insofar as eqn (2) is based on data from Robinson & Stokes (1970), the true water activity of the cheeses should not exceed its calculated counterpart; in fact, it should be lower as a result of the additional vapour pressure depression caused by other solutes of low molecular weights (e.g. NPN in mould-ripened cheeses). The anomalous performance of Rüegg's equation (1985) on application to this type of cheese suggests that it was established by including the data from Rüegg & Blanc (1977) in the regression analysis.

TABLE 5
Differences between the Experimental A_w Values of some Soft Cheeses and the A_w Values Calculated from their Chemical Compositions according to Various Predictive Equations

Sample	*Differences* (× 10^{-3} A_w *units) between* $(A_w)_{calc}$ *and* $(A_w)_{exp}$						
	Eqn (*1*)	*Eqn* (*2*)	*Eqn* (*3*)	*Eqn* (*4*)	*Eqn* (*5*)	*Eqn* (*6*)	*Eqn* (*7*)
Belle des Champs	−14	−8	−28	−23	−22	−16	−26
Brie suisse	0	4	−14	−10	−9	1	−13
Camembert suisse	−6	−20	−29	−33	−24	−21	−28
Tomme vaudoise	−2	−5	−7	−20	−17	−25	−25
Brie	22	26	5	11	11	9	6
Brie	18	6	1	−8	0	0	0
Camembert	20	12	−4	−2	−2	−2	−4
Camembert	17	9	−1	−6	−4	−5	−3
Goat cheese	15	8	−21	−6	−7	−3	−17
Goat cheese	14	11	3	−3	2	−11	2

Obviously, the development of predictive equations must rest on the use of reliable A_w data and chemical parameters, and so does the application of the equations proposed for the calculation of the water activity of cheeses. This is particularly true and essential whenever nitrogen fractions (SN, NPN) are involved since they are normally extracted or fractionated by a variety of procedures (Fox, 1989) which require standardization, an attempt at which was made by Kuchroo & Fox (1982).

According to Van den Berg (1986), some experimentally measured A_w data could be estimated more readily and at least with the same accuracy by using predictive equations. In fact, the results obtained in this work allow us to conclude that some straightforward equations are more precise than certain measurement methods for estimation of water activity in mould-ripened cheeses. In addition, the differences between the calculated and experimental A_w values are not much larger in many instances than are those encountered between measurement methods (Labuza *et al.*, 1976; Stoloff, 1978; Stamp *et al.*, 1984; Fernández-Salguero *et al.*, 1989).

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