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Equations for Calculation of Water Activity in Cheese from its Chemical Composition: A Review

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ABSTRACT

This paper reviews the relations between the chemical composition of cheese and its water activity (A_w) found by linear regression analysis, including twelve regression equations proposed for the chemical prediction of such activity in different types of cheese. Equations, both applicable to all types of cheese with $A_w > 0{\cdot}90$ and others valid only for fresh, bacterial- and mould-ripened or processed cheeses, are reviewed.

INTRODUCTION

Water activity (A_w) is defined as the relationship between the vapour pressure of a given food (p) and that of pure water (p_0) at the same temperature:

$$A_w = p/p_0$$

The vapour pressure of a given food is always lower than that of pure water due to the presence of dissolved substances, so that A_w is always a fraction of unity.

As far as cheese making is concerned, water activity is dependent on the type of curdling used and influences the quality, stability and health and safety of the final product (Rüegg & Blanc, 1981; Hardy, 1984, 1985; Choisy *et al.*, 1984; Weber & Ramet, 1984; Veillet-Poncet, 1984; Rüegg, 1985; Fox, 1987).

The US FDA and international organizations, such as the Mixed

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Committee of the FAO/WHO for Codex Alimentarius, and some EEC agencies are interested in establishing limiting A_w values for different foods such as cheese. The enforcement of these rules requires the availability of appropriate methods for measurement and/or calculation of the water activity of foods—cheese in this review.

There are a number of options for determining the A_w of foods (Prior, 1979; Troller, 1983). Most of the methods available for such a purpose are applicable to cheese and each has its own advantages and disadvantages. Among the disadvantages are the high cost of some electronic instruments, the rather long times required for attainment of equilibrium in measuring the activity of a small number of samples and the lack of precision and accuracy of most of the straightforward, fast and economic methods available. Some simple methods for the determination of water activity in cheese and other foods have been modified and improved or developed in our laboratory (Marcos *et al.*, 1985*a*; Esteban *et al.*, 1987, 1989; Cabezas *et al.*, 1988).

The other general alternative to the direct measurement of the A_w of cheese lies in its calculation from chemical composition, which allows both the prediction of A_w in the assayed cheese with reasonable accuracy and its estimation from analytical data reported in the literature (composition tables, etc.).

Although there are general procedures—the Ross equation (Ross, 1975), among others—for the calculation of the vapour pressure depression brought about in foods and solutions by the occurrence of different solutes, this review only deals with empirical or semi-empirical equations specifically designed for the calculation of the water activity of cheeses on the basis of their chemical composition.

RELATIONSHIP BETWEEN THE CHEMICAL COMPOSITION AND WATER ACTIVITY OF CHEESE

The relationship between the chemical composition of cheese and A_w has been dealt with according to two different approaches. One involves the application of multiple regression analysis to the evaluation of all the factors significantly influencing the water activity of cheese; this approach has led to the development of complex equations for the calculation of water activities. The other approach, more practically than academically oriented, aims for the establishment of straightforward regression equations of the type $A_w = a + bx$ to calculate the water activity from the concentration of the chief chemical depressant of the vapour pressure in the aqueous phase of the cheese.

Rüegg and Blanc (1977) studied the relationship between the water activities of 26 varieties of European cheeses and their chemical composition, which they originally expressed as a function of the amount of dry matter. They found A_w to be essentially dependent on the moisture, total nitrogen, ash, sodium chloride, non-protein nitrogen (NPN) and pH. Rüegg (1985) proposed the following predictive equation:

$$A_w = 0{\cdot}8004 + 0{\cdot}0014 \times (H_2O) - 0{\cdot}0231 \times (NPN) - 0{\cdot}0081 \times (NaCl) + 0{\cdot}0262 \times (pH) \quad (1)$$

where moisture is expressed in g H_2O/100 g cheese and NPN and NaCl are expressed in g/100 g dry matter. This equation, applicable to cheeses with $A_w > 0{\cdot}90$, has a standard error of about 0·02.

As, by definition, water activity depends on the concentration of the solutes in the aqueous phase, Marcos *et al.* (1981) analysed 34 varieties of European cheeses and searched for correlations between their chemical composition (expressed as their moisture) and A_w; they found highly significant correlations ($p < 0{\cdot}001$) between A_w and the moisture and concentration of NaCl, NPN and NPN – formol N (nitrogen titratable in the presence of formol determined by the Sorensen method as described Lenoir (1962)) in the aqueous phase.

Rüegg (1985) proposed an alternative equation for cheeses with $A_w > 0{\cdot}87$, namely:

$$A_w = 0{\cdot}939 - 0{\cdot}0077 \times (NPN) - 0{\cdot}0064 \times (NaCl) - 0{\cdot}0024 \times (Ash - NaCl) + 0{\cdot}0127 \times (pH) \quad (2)$$

where the concentrations of the different solutes are expressed in g/100 g moisture. After omitting the data provided by cheeses with $A_w < 0{\cdot}90$, eqn (2) was modified to the improved eqn (3):

$$A_w = 0{\cdot}945 - 0{\cdot}0056 \times (NPN) - 0{\cdot}0059 \times (NaCl) - 0{\cdot}0019 \times (Ash - NaCl) + 0{\cdot}0105 \times (pH) \quad (3)$$

applicable to cheeses with $A_w > 0{\cdot}90$ and subject to a standard error slightly smaller than 0·01. This polynomial expression is not only academically interesting, but also rather precise, as Marcos *et al.* (1985*b*) showed on application to data from different types of Spanish cheeses. However, it has some practical disadvantages in that it requires five different parameters to be determined—which is more cumbersome than the direct measurement of A_w—or obtained from composition tables; in addition, the computations involved can be somewhat complex.

As the NaCl concentration in the aqueous phase of the cheese yielded the highest coefficient of correlation with A_w ($r = -0{\cdot}81$) in our study (Marcos *et al.*, 1981), we used data reported by Robinson and Stokes (1970), which relates the molality of aqueous solutions of NaCl to water activity, to arrive at the following regression equation:

$$A_w = 1{\cdot}0048 - 0{\cdot}0386m \quad (4)$$

where m is the molality of NaCl (mol/kg water). The application of eqn (4) to the molality of NaCl in the aqueous phase of the cheeses assayed, resulted in good agreement between the calculated and experimentally measured A_w values (standard error of the estimation, 0·01) for almost all fresh cheeses (with moistures equal to or higher than 40%), which indicates that, in these cheeses—which undergo little or no proteolysis—the vapour pressure depression is caused almost exclusively by the salt content in the aqueous phase. The water activities calculated for the other cheese varieties, namely ripened cheeses, were higher than those measured experimentally because of the additional depressing effect due to the presence of other solutes of low molecular weights (e.g. NPN) resulting from proteolysis.

CALCULATION OF WATER ACTIVITY IN FRESH CHEESE

As the linearity of the data reported by Robinson and Stokes (1970) is only preserved up to an NaCl molality of 1·2 (corresponding to $A_w = 0{\cdot}96$), the equation

$$A_w = 1 - 0{\cdot}033m \quad (5)$$

mathematically simpler and more accurate, was proposed by Marcos *et al.* (1981) to calculate the water activities of fresh cheeses. It was used to construct a nomograph (Marcos & Esteban, 1982)which allowed the direct graphical estimation of A_w with no arithmetical calculations. Equation (5) and its associated nomograph indicate the maximum water activity (the actual A_w value is always slightly lower because of the presence of other solutes) in fresh cheeses. The use of the diagram only requires the knowledge of the moisture and salt percentages of the cheese, which are always included in composition tables.

For greater practicality—simplified computations—eqn (5) can be transformed into:

$$A_w = 1 - 0{\cdot}005\,65 \times [(\text{g NaCl})/(100\text{g } H_2O)] \quad (6)$$

which allows calculation of the water activity of fresh cheeses from literature or experimental data of moisture and salt contents, provided the latter is not greater than 7g/100g moisture (Marcos, 1987). It even allows one to predict the A_w at any point in the cheese and any time after salting, according to the relations reported by Guinee and Fox (1983) on the diffusion of salt–water during the first phase of the diffusion process.

CALCULATION OF WATER ACTIVITY IN RIPENED CHEESE

By applying regression analysis to 82 samples of various types of cheeses with water activities in the range 0·995–0·87, a close correlation ($r = -0·89$) was found between A_w and the ash content, expressed in g ash/100g cheese moisture (Dixon, 1975).

Ash material includes both NaCl and other inorganic materials—mainly calcium and phosphorus solubilised from the caseins at an acid pH—which probably also have a strong depressing effect on water activity.

Apart from the effect of inorganic solutes, the water activity of ripened cheese is also lowered by soluble nitrogen-containing compounds of low molecular weight (e.g. NPN) resulting from proteolysis. The extent and intensity of the hydrolysis of caseins differs markedly in cheeses ripened by bacteria and moulds as fungal proteases are most active.

In searching for correlations between the water activity and ash content (in g ash/100g cheese moisture) in ripened cheese, an assumption was made that, for groups of cheeses undergoing a similar degree of proteolysis (e.g. those ripened by bacteria or by moulds), the content of nitrogen-containing compounds of low molecular weight resulting from proteolysis—lower for bacteria- than mould-ripened cheeses—would proportionally affect the depression of A_w in all the cheeses within each group and therefore would not substantially affect the correlations with the ash contents in each group.

Bacterial-ripened cheese

For a batch of 20 samples of a bacterial-ripened cheese variety which comprised a wide range of moisture (20–46%) and ash content (8–25g/100g moisture)—and, presumably, different degrees of proteolysis—highly significant correlations (Marcos *et al.*, 1983) were found between the moisture and A_w ($r = 0·98$), and the ash content and A_w ($r = -0·99$), the regression equations arrived at being:

$$A_w = 0·7262 + 0·0046 \times [(\text{g } H_2O)/(100\text{g Cheese})] \quad (7)$$

and

$$A_w = 1·0234 - 0·0070 \times [(\text{g Ash})/(100\text{g } H_2O)] \quad (8)$$

From these, a nomograph was constructed to estimate A_w from either parameter or from both. Although it was originally thought that eqns (7) and (8) were only valid for the variety assayed, it was later found that eqn (8) was equally applicable to all varieties of cheese ripened by bacteria that were assessed by Marcos *et al.* (1985*b*).

Mould-ripened cheese

An empirical equation for calculation of A_w from the ash content (per 100 g moisture), similar to eqn (8), was established on the basis of the data obtained from 50 international varieties of mould-ripened cheeses (40 blue vein cheeses and 10 ripened by surface moulds). The equation in question (Marcos, 1987),

$$A_w = 1{\cdot}0076 - 0{\cdot}0079 \times [\text{g Ash})/(100\,\text{g } H_2O)] \quad (9)$$

is better suited to cheeses ripened by internal moulds (with lower water activities) than to those ripened by surface moulds, in which the differences between calculated and measured A_w values are more significant on account of their higher water activities.

By using only the 40 blue cheese samples referred to above, Fernández-Salguero *et al.* (1986) found the following two regression equations:

$$A_w = 1{\cdot}0013 - 0{\cdot}0051 \times (\text{Ash}) - 0{\cdot}0056 \times (\text{SN}) \quad (10)$$

where the ash and soluble nitrogen (SN) contents are expressed in g/100g moisture, and

$$A_w = 0{\cdot}9808 - 0{\cdot}0058 \times [(\text{g Ash})/(100\text{g } H_2O)] \quad (11)$$

The water activities of bacterial- and mould-ripened cheeses can also be estimated diagrammatically (Marcos, 1987) from their correlations with the ash contents.

Cheeses ripened by surface moulds probably allow the application of the same procedure used for the establishment of a predictive equation for A_w, similar to eqn (11)—corresponding to cheeses ripened by internal moulds—and more accurate than eqn (9).

CALCULATION OF WATER ACTIVITY IN PROCESSED CHEESE

Processed cheeses differ considerably from natural cheeses, both in their composition and in technological aspects (Carić & Kaláb, 1987). Although eqn (3) (Rüegg, 1985) is also applicable to this type of cheese, Esteban and Marcos (1989) recently found a highly significant correlation ($r = -0{\cdot}96$) between the mean ash contents (per 100 g moisture) and the A_w of six types of processed cheeses (low-fat, semi-fat, fat, extra-fat, double fat and special). The regression equation

$$A_w = 0{\cdot}9951 - 0{\cdot}0032 \times [(\text{g Ash})/(100\,\text{g } H_2O)] \quad (12)$$

applied to 40 individual samples, yielded A_w values which differed by less than 0·005 A_w units from those measured experimentally in 75% of the samples. The maximum difference between the calculated and measured values (observed in only two samples) was $\pm 0{\cdot}01$ A_w units.

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