Food Chemistry **30** (1988) 59–66

Improved Equation for Cryoscopic Estimation of Water Activity in Cheese

L. Cabezas, A. Marcos, M. A. Esteban, J. Fernández-Salguero & M. Alcalá

Departamento de Tecnología y Bioquímica de los Alimentos,
Universidad de Córdoba, Córdoba, Spain

(Received 7 October 1987; revised version received and accepted 18 December 1987)

ABSTRACT

Cryoscopes employed in dairy plants for routine quality control of milk can be used for the determination of the water activity (A_w*) of cheese according to the equation:*

$$A_w = 1{\cdot}0155 + 0{\cdot}1068\,.\,\mathrm{fp}$$

where fp *is the freezing point in °C of an aqueous extract of cheese solutes obtained under standard conditions. This linear regression equation was obtained for 139 pairs of* A_w *and* fp *measurements. The differences between the measured and calculated* A_w *values in the range 1·00–0·90 were only greater than 0·02* A_w *units in a small number (6·5%) of the samples with the lower* A_w *values. Hence this cryoscopic approach can be applied by the cheese industry as a straightforward quality control technique.*

INTRODUCTION

Esteban *et. al.* (1987) reported a new cryoscopic approach to the water activity (A_w) of non-liquid food systems based on the fact that, in most foods, A_w is depressed chiefly, and almost solely, by the aqueous concentration of low-molecular weight solutes. Such solutes can be extracted from solid foods by using water under standard conditions in order to obtain aqueous

Food Chemistry 0308-8146/88/$03·50 © 1988 Elsevier Applied Science Publishers Ltd, England. Printed in Great Britain

solutions quantitatively related to the concentrations of the solutes in the aqueous phase of the original product. The diluted aqueous phase can be readily separated from non-soluble compounds and be used for freezing point (*fp*) measurements with standard milk cryoscopes.

This new approach was applied in searching for a relation between the water activity of cheese and the freezing point of the dilute aqueous cheese extracts. A highly significant correlation was found between the freezing point of the cheese extracts and the measured A_w values, signified by the equation of the best-fit line:

$$A_w = 1{\cdot}0162 + 0{\cdot}0981 \, . \, fp$$

which was proposed for calculation of A_w from cryoscopic data as a means of controlling the quality of cheese. The water activity is a major physico-chemical factor influencing cheese manufacture and intrinsically related to curd ripening and the quality, storage stability and safety of the ripe product (Rüegg & Blank, 1981; Hardy, 1984; Choisy *et al.*, 1984; Weber & Ramet, 1984; Veillet-Poncet, 1984; Rüegg, 1985).

The aim of this work was to check the accuracy of the above equation and to refine it by statistical analysis of a large number of pairs of measurements of the water activity of the cheeses and the freezing points of their corresponding aqueous phase extracts.

MATERIALS AND METHODS

Cheese samples

A few hundred assorted cheese samples were purchased at market. The rinds were removed when needed and internal portions were ground and subjected to physical and chemical analyses for characterization (Marcos *et al.*, 1985). The remaining ground material was placed in air-tight containers and stored at −24°C for further analysis. One-hundred-and-fifty samples in all were used in the experiments.

Measurement of water activity in the cheeses

The stored ground cheese samples were thawed overnight and warmed to room temperature. Each thawed sample was thoroughly homogenized. An SC-10 Thermocouple Psychrometer/MT-3 Nanovolt-Thermometer System supplied by Decagon Devices, Inc. (Pullman, WA, USA) was used to measure the A_w of the cheese samples at 20°C. The instrument was calibrated and operated according to the instructions supplied by the manufacturer.

Measurement of the freezing point of the aqueous cheese extracts

To 25 g of thawed ground cheese were added 75 ml of de-ionized water and the mixture was blended, centrifuged at 2000 rpm for 5 min and then allowed to stand at refrigeration temperature for 30–60 min to cold-harden the upper layer of fat. The freezing points of the solute extracts from the cheeses were measured on the intermediate phase (between the bottom protein pellet and other insoluble matter and the solidified fat of the upper layer) in a standard cryoscope (original Gerber) with a cryoscopic thermometer scaled in 0·01°C from +0·40 to −1·23°C.

Statistical analysis

The equation representing the best fit between the variables x (*fp* of the aqueous phase of the cheese extracts) and y (A_w of non-extracted cheese) was obtained by linear regression according to the least-squares method.

RESULTS AND DISCUSSION

The A_w values obtained at 20°C for 150 cheese samples, together with the initial freezing points (*fp*, in °C) of their corresponding dilute aqueous extracts are listed in Table 1. As can be seen, A_w ranged from 0·994 to 0·822 and *fp* between −0·18°C and the lowest limit of the cryoscopic thermometer scale, namely −1·23°C.

The statistical analysis of the 150 data pairs in Table 1 revealed a highly significant correlation between the *fp* of the cheese extracts and the measured water activities.

The initial freezing points of a variety of foods have been used by many authors for the calculation of water activities. Ferro Fontán & Chirife (1981) reported that A_w values calculated from *fp* measurements did not differ significantly from values measured at 25°C, and that, in most cases, differences in the upper A_w range were not likely to be larger than about 0·01 A_w units, an acceptable level of accuracy for most food-related applications. Our procedure obviously allows for no effects due to temperature differences.

The linear-regression equation obtained ($A_w = 1{\cdot}0198 + 0{\cdot}1188 \, . \, fp$) was used to calculate the water activity of the cheeses from the freezing points of

TABLE 1

Water Activity (A_w) of the cheeses and Freezing Point (*fp*) of their Extracts

Sample	A_w (20°C)	*fp* (°C)	*Sample*	A_w (20°C)	*fp* (°C)	*Sample*	A_w (20°C)	*fp* (°C)
1	0·956	−0·66	51	0·971	−0·73	101	0·961	−0·62
2	0·960	−0·58	52	0·975	−0·58	102	0·891	−1·04
3	0·972	−0·38	53	0·975	−0·59	103	0·987	−0·25
4	0·984	−0·28	54	0·917	−1·03	104	0·924	−0·73
5	0·953	−0·60	55	0·822	−0·94	105	0·896	−0·79
6	0·948	−0·61	56	0·989	−0·24	106	0·947	−0·70
7	0·953	−0·59	57	0·983	−0·34	107	0·955	−0·48
8	0·952	−0·54	58	0·985	−0·42	108	0·920	−0·83
9	0·986	−0·32	59	0·989	−0·25	109	0·977	−0·30
10	0·976	−0·25	60	0·987	−0·27	110	0·907	−0·85
11	0·976	−0·27	61	0·988	−0·25	111	0·964	−0·48
12	0·950	−0·67	62	0·984	−0·33	112	0·940	−0·74
13	0·955	−0·62	63	0·991	−0·36	113	0·919	−0·79
14	0·935	−0·56	64	0·989	−0·23	114	0·928	−0·69
15	0·929	−0·70	65	0·984	−0·35	115	0·934	−0·69
16	0·926	−0·79	66	0·990	−0·21	116	0·951	−0·54
17	0·919	−0·75	67	0·989	−0·30	117	0·959	−0·68
18	0·926	−0·66	68	0·981	−0·42	118	0·958	−0·66
19	0·949	−0·57	69	0·979	−0·53	119	0·849	−0·90
20	0·953	−0·63	70	0·990	−0·24	120	0·984	−0·25
21	0·940	−0·56	71	0·990	−0·28	121	0·970	−0·48
22	0·926	−1·00	72	0·974	−0·51	122	0·955	−0·61
23	0·894	−0·90	73	0·983	−0·39	123	0·960	−0·56
24	0·898	−0·96	74	0·990	−0·26	124	0·930	−0·56
25	0·958	−0·63	75	0·990	−0·24	125	0·870	−1·23
26	0·962	−0·59	76	0·989	−0·27	126	0·946	−0·51
27	0·961	−0·53	77	0·981	−0·36	127	0·875	−0·72
28	0·974	−0·61	78	0·908	−1·16	128	0·861	−0·98
29	0·964	−0·64	79	0·934	−0·72	129	0·947	−0·69
30	0·957	−0·66	80	0·958	−0·58	130	0·944	−0·64
31	0·914	−0·84	81	0·918	−0·64	131	0·967	−0·47
32	0·958	−0·70	82	0·955	−0·50	132	0·923	−0·82
33	0·955	−0·62	83	0·941	−0·64	133	0·951	−0·62
34	0·971	−0·51	84	0·923	−0·70	134	0·948	−0·64
35	0·948	−0·64	85	0·906	−1·23	135	0·913	−0·79
36	0·954	−0·60	86	0·990	−0·18	136	0·914	−0·75
37	0·972	−0·54	87	0·983	−0·34	137	0·918	−0·76
38	0·945	−0·60	88	0·978	−0·46	138	0·969	−0·46
39	0·883	−1·13	89	0·982	−0·37	139	0·980	−0·31
40	0·964	−0·40	90	0·994	−0·19	140	0·861	−0·80
41	0·964	−0·42	91	0·968	−0·34	141	0·927	−0·80
42	0·952	−0·57	92	0·982	−0·32	142	0·959	−0·56
43	0·962	−0·42	93	0·988	−0·19	143	0·938	−0·67
44	0·961	−0·50	94	0·989	−0·29	144	0·958	−0·40
45	0·957	−0·49	95	0·974	−0·52	145	0·946	−0·59
46	0·956	−0·60	96	0·986	−0·34	146	0·937	−0·67
47	0·949	−0·75	97	0·942	−0·68	147	0·947	−0·71
48	0·900	−0·76	98	0·920	−0·75	148	0·988	−0·24
49	0·931	−0·71	99	0·978	−0·39	149	0·980	−0·52
50	0·911	−0·97	100	0·943	−0·75	150	0·957	−0·62

their extracts. The mean differences between the calculated and experimentally measured water activities (Δx = calc. A_w − exper. A_w) for various A_w ranges were as follows:

A_w range	Number of samples	$\Delta\bar{x}$
1·000–0·950	91	−0·005
0·949–0·900	48	+0·002
0·899–0·850	9	+0·025
0·849–0·800	2	+0·075

As the mean differences between the 11 samples with A_w values below 0·90 were too large, a new regression equation was obtained for the 139 samples with A_w values in the range 1·000 to 0·900, a more critical range from both the technological and the microbiological points of view, covering the A_w spectrum of most cheese varieties.

The correlation coefficient ($r = 0{\cdot}88$) of the new regression equation:

$$A_w = 1{\cdot}0155 + 0{\cdot}1068 \,.\, fp$$

was found to be highly significant ($p < 0{\cdot}001$). This equation is similar to that found by Esteban *et al.* (1987) from only nine data pairs (see the Introduction and Fig. 1)

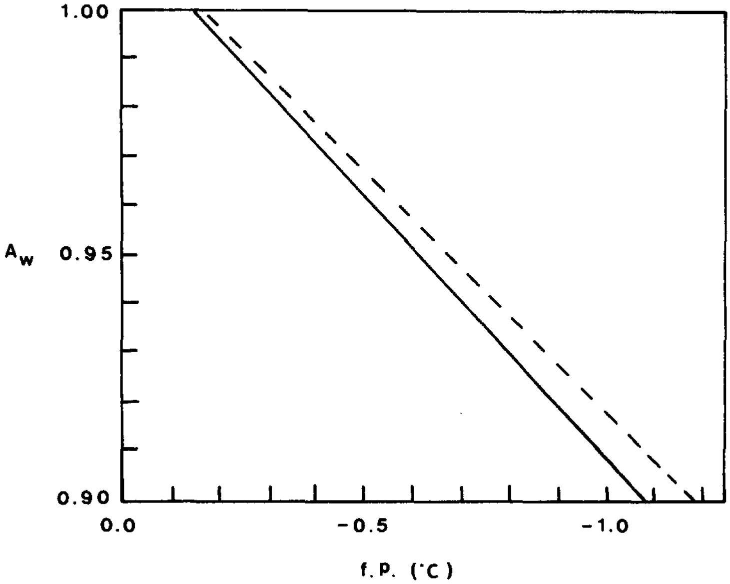

Fig. 1. Freezing point (*fp*) of aqueous cheese extracts versus water activity (A_w) of cheese. Best fit lines found by Esteban *et al.* (1987) with nine data pairs (– – – – – –) and in the present study with 139 data pairs (———).

The mean differences ($\Delta\bar{x}$) between measured A_w values and those calculated from the new, improved equation for various A_w ranges were as follows:

A_w range	Number of samples	$\Delta\bar{x}$
1·000–0·980	36	−0·002
0·979–0·960	30	−0·006
0·959–0·940	43	−0·002
0·939–0·920	18	+0·010
0·919–0·900	12	+0·013

Again, larger mean differences were observed for the lower A_w values. The relative (per cent) differences were:

$(A_w)_{calc} - (A_w)_{exp}$	Number of samples (%)
0·000–0·005	39·13
0·006–0·010	28·26
0·011–0·015	15·94
0·016–0·020	10·14
>0·020	6·52

The results show that the differences between the experimental and calculated A_w values were not larger than 0·02 A_w units in most cases (93%)

TABLE 2

Water Activity (A_w) of Imported Cheese Varieties Determined by the Cryoscopic and Psychrometric Methods

Cheese variety	*fp extract (°C)*[c]	*A_w cryoscopy*		*A_w psychrometry*[c]	*Differences*	
		Eqn (a)[c]	*Eqn (b)*		*(a)-Psy*[c]	*(b)-Psy*
Processed cheese	−0·45	0·972	0·967	0·973	−0·001	−0·006
Camembert	−0·42	0·975	0·971	0·972	+0·003	−0·001
Gruyère (processed)	−0·54	0·963	0·958	0·963	0·000	−0·005
Chaumes	−0·50	0·967	0·962	0·963	+0·004	−0·001
Brie	−0·49	0·968	0·963	0·962	+0·006	+0·001
Emmenthal	−0·32	0·985	0·981	0·959	+0·026	+0·022
Havarti	−0·47	0·970	0·965	0·956	+0·014	+0·009
Gouda	−0·62	0·955	0·949	0·939	+0·016	+0·010
Roquefort	−1·22	0·897	0·885	0·890	+0·007	−0·005

[a] $A_w = 1{\cdot}0162 + 0{\cdot}0981\,.fp$ aqueous cheese extract; equation from Esteban *et al.* (1987).
[b] $A_w = 1{\cdot}0155 + 0{\cdot}1068\,.fp$ aqueous cheese extract; new improved equation.
[c] Data from Esteban *et al.* (1987).

and that, allowing for a measurement error of 0·02 A_w units in values above 0·87 (Labuza *et al.*, 1976), this cryoscopic procedure can be used by the dairy industry as a straightforward quality control technique in cheese manufacture.

The application of the equation obtained from the freezing points of the 139 samples used in this study, for the calculation of A_w for the nine cheeses tested by Esteban *et al.* (1987), yielded the results listed in Table 2. As can be seen (rightmost column), the differences between the A_w values calculated from the above-mentioned equation and those measured by the psychrometric method were slightly lower than those found by using the equation proposed by Esteban *et al.* (1987).

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the Spanish 'Comisión Asesora de Investigación Científica y Técnica (CAICYT Research Project No. 1022/84) of the Ministry of Science and Education. One of us, L. Cabezas, holds a post-doctoral grant from the Junta de Andalucía.

REFERENCES

Choisy, M., Desmazeaud, M., Gripon, J. C., Lamberet, G., Lenoir, J. & Tourneur, C. (1984). Les phénomènes microbiologiques et enzimatiques et la biochimie de l'affinage. In *Le Fromage* Co-ordinator, A. Eck, Technique et Documentation (Lavoisier), Paris, 62–100.

Esteban, M. A., Marcos, A. & Fernández-Salguero, J. (1987). Cryoscopic approach to water activity measurement of non-liquid foods: Application to cheese. *Food Chem.*, **25**, 31–39.

Ferro Fontán, C. & Chirife, J. (1981). The evaluation of water activity in aqueous solutions from freezing point depression. *J. Food Technol.*, **16**, 21–30.

Hardy, J. (1984). L'activité de l'eau et le salage des fromages. In *Le Fromage*. (Co-ordinator, A. Eck, Technique et Documentation (Lavoisier), Paris, 37–61.

Labuza, T. P., Acott, K., Tatini, S. R., Lee, R. Y., Flink, J. & McCall, W. (1976). Water activity determination: A collaborative study of different methods. *J. Food Sci.*, **41**, 910–17.

Marcos, A., Fernández-Salguero, J., Esteban, M. A., León, F., Alcalá, M. & Beltrán, F. (1985). *Quesos Españoles: Tablas de Composición, Valor Nutritivo y Estabilidad.* Servicio de Publicaciones, Universidad de Córdoba.

Rüegg, M. (1985). Water in dairy products related to quality, with special reference to cheese. In *Properties of Water in Foods*, ed. D. Simatos & J. L. Multon, Martinus Nijhoff Publishers, Dordrecht, pp. 603–25.

Rüegg, M. & Blanc, B. (1981). Influence of water activity on the manufacture and aging of cheese. In *Water Activity: Influences on Food Quality*, ed. L. B. Rockland & G. F. Stewart. Academic Press, New York, pp. 791–811.

Veillet-Poncet, L. (1984). L'hygiène des fabrications. In *Le Fromage*. Co-ordinator, A. Eck. Technique et Documentation (Lavoisier), Paris, pp. 476–86.

Weber, F. & Ramet, J. P. (1984). Technologie comparée de l'affinage des différents types de fromage. In *Le Fromage*. Co-ordinator, A. Eck. Technique et Documentation (Lavoisier), Paris, pp. 291–307.