Research Note

Comparison of Methods for Determination of High Water Activities. Application to Dairy Products and Juices

ABSTRACT

Water activity was determined in various dairy products (ice creams, yoghourts and flavoured milks) and several juices by three different methods: psychrometric, cryoscopic and gravimetric. The differences between the A_w values provided by the three methods were also calculated. Such differences were always smaller than 0.005 A_w units, which allows the use of a straightforward method (gravimetric) together with two instrumental methods (psychrometric and cryoscopic) for the determination of high A_w values (in the range 0.999–0.900) in the aforesaid types of products.

INTRODUCTION

Water activity can be determined by various measurement methods reported in the literature (Labuza *et al.*, 1976; Troller & Christian, 1978; Prior, 1979; Uboldi, 1981).

The cryoscopic method, based on the relationship between the freezing point depression of a solution and its vapour pressure decrease, is of great use in determining high A_w values (0.999–0.900), particularly of liquid foods with $A_w > 0.98$. Instrumental methods based on the HRE are also widely used for this purpose. There are other simpler, non-instrumental methods of comparable efficiency. In this respect, Marcos *et al.* (1985) refined and simplified the method proposed by McCune *et al.* (1981), which is based on the linear relationship between the water content of the filter paper exposed over the sample $\log(1 - A_w)$, and was later improved by Esteban *et al.* (1989).

Food Chemistry 0308-8146/89/\$03.50 © 1989 Elsevier Science Publishers Ltd, England. Printed in Great Britain The aim of this work was to determine A_w in various dairy products and juices by three different methods; namely, psychrometric, cryoscopic and gravimetric, and check for the consistency of the results obtained with a view to determining their applicability to the measurement of high-end A_w values.

MATERIAL AND METHODS

Samples

The experimental batch consisted of 26 samples of which 18 were dairy products (five ice creams, seven yoghourts and six flavoured milks) and eight were juices. All the samples were purchased at commercial establishments.

The samples were duly homogenized prior to use.

Determination of A_w

Water activity was determined by three experimental procedures; namely:

Psychrometric method

This was implemented with the aid of an SC-10 thermoelectrical psychrometer (Nanovoltmeter Thermometer System MT-3 from Decagon Devices, Inc., Pullman, WA, USA) under conditions established in previous work (Esteban *et al.*, 1987; Cabezas *et al.*, 1987).

Cryoscopic method

Water activities were calculated from the cryoscopic points determined on water extracts of the samples in ratios of 1:3 (w/v), according to the procedure described by Esteban *et al.* (1987). The equations used were:

$$A_{\rm w} = 1.0162 + 0.0981 \times \text{f.p.}$$
(1)

for the ice creams and yoghourts, and

$$A_{\rm w} = \exp({\rm f.p.}/103)$$
 (2)

for the flavoured milks and juices.

Equation (1), obtained for the calculation of A_w from various cheese samples by least-squares linear regression, was later refined on the basis of a larger number of data pairs (A_w and f.p.) (Cabezas *et al.*, 1988).

Gravimetric method

Determinations were carried out as described by Esteban et al. (1989).

RESULTS AND DISCUSSION

Tables 1–4 list the experimental A_w values obtained for the different groups of samples, as well as the differences between the values provided by the cryoscopic and gravimetric methods and those found by the psychrometric method (taken as reference), and the corresponding means and standard deviations.

As can be seen, the mean A_w of the ice creams was slightly above 0.970 for all three methods (Table 1), with a coefficient of variation less than 1%. The yoghourt group (Table 2) provided a mean A_w between 0.985 and 0.990, with

Flavour (brand)		Meth	hod	Gravi- metric ^b	Difference from psychrometric	
		Psychrometric	Cryoscopic ^a		Cryoscopic- psychrometric	Gravimetric- psychrometric
Vanilla	(A)	0.9732	0.9770	0.9679	+0.0038	-0.0053
Vanilla	(B)	0.9752	0.9760	0.9782	+0.0008	+0.0030
Vanilla	(C)	0.9788	0.9838	0.9807	+0.0050	+0.0019
Vanilla	(D)	0-974 5	0.9721	0.9767	-0.0024	+0.0025
Cream	(D)	0.9745	0.9721	0.9657	-0.0024	-0.0088
Mean		0.9752	0.978 9	0.9738	+0.0038	-0.0013
SD		0.0021	0.0057	0.0066	0.004 2	0.0054

TABLE 1Water Activity (A_w) of Some Ice Creams Determined by Three Methods

^{*a*} $A_w = 1.0162 + 0.0981 \times \text{f.p.; dilution, 1:3 (w/v).}$

^b In duplicate.

TABLE 2Water Activity (A_w) of Some Yoghourt Beverages Determined by Three Methods

Flavour (brand)		Method		Gravi- metric ^b	Difference from psychrometric	
(012000)		P sychrometric	Cryoscopic ^a		Cryoscopic- psychrometric	Gravimetric- psychrometric
Plain	(A)	0.9890	0.990 2	0.9890	+0.001 2	0.000 0
Plain	(B)	0.9868	0.9868	0.9888	0.000 0	+0.0020
Strawberry	(A)	0.9872	0.9878	0.9908	+0.0006	+0.0036
Strawberry	(B)	0.9881	0.9878	0.9888	-0.000 3	+0.0007
Orange	(A)	0.9866	0.9868	0.9893	+0.0005	+0.0027
Lemon	(A)	0.9874	0.9887	0.9910	+0.0013	+0.0036
Pineapple	(B)	0.9879	0-991 2	0-991 3	+0.0033	+0.0034
Mean		0.9876	0.988 5	0.9899	+0.0009	+0.0023
SD		0.0008	0.001 7	0.0011	0.001 2	0.001 5

^a $A_w = 1.0162 + 0.0981 \times \text{f.p.}$; dilution, 1:3 (w/v).

^b In duplicate.

a coefficient of variation less than 0.5%. As regards flavoured milks and juices (Tables 3 and 4, respectively), the mean A_w was virtually the same (0.990) whatever the method used, and their coefficients of variation were both less than 0.5%.

The A_w values obtained by the three methods were compared subsequently in order to check their potential applicability. The results showed

Flavour (brand)		Met	hod	Gravi- metric ^b	Difference from psychrometric	
		Psychrometric	Cryoscopic ^a		Cryoscopic- psychrometric	Gravimetric- psychrometric
Strawberry	(A)	0.9896	0.9896	0.9896	0.000 0	0.000 0
Strawberry	(B)	0.9894	0.9901	0.9904	+0.0002	+0.0010
Vanilla	(A)	0.989 3	0.9896	0.9898	+0.0003	+0.0002
Vanilla	(B)	0.9913	0.9914	0.9904	+0.0001	-0.000 9
Cocoa	(A)	0.9901	0.9901	0.9899	0.0000	-0.0005
Cocoa	(A)	0.9897	0.9898	0.9894	+0.0001	-0.0003
Mean		0.9899	0-990 1	0.9899	+0.0005	0.0000
SD		0.000 2	0.0007	0.0004	0.0003	0.000 2

TABLE 3Water Activity (A_w) of Some Flavoured Milks Determined by Three Methods

^{*a*} $A_{w} = \exp(f.p./103).$

^b In duplicate.

Flavour (brand)		Method		Gravi- metric ^b	Difference from psychrometric	
(,		Psychrometric	Cryoscopic ^a		Cryoscopic- psychrometric	Gravimetric- psychrometric
Orange	(A)	0.9922	0.9929	0.994 5	+0.0007	+0.0023
Orange	(B)	0.9893	0.9897	0.991 5	+0.0004	+0.0022
Apple	(A)	0.9914	0.9917	0.9936	+0.0003	+0.0022
Apple	(B)	0.9867	0·984 8°	0.9876	-0.001 9	+0.0009
Lemon	(A)	0.9896	0.9886	0.9872	-0.0010	-0.0024
Pineapple	(B)	0.990 2	0.989 5	0.9878	-0.0002	-0.0024
Strawberry	(B)	0.9901	0.9901	0.9934	0.000.0	+0.0023
Orgeat	(C)	0.991 3	0.9922	0.9940	+0.000 9	+0.0027
Mean		0.9901	0.9899	0.9912	-0.0005	+0.0010
SD		0.001 7	0.002 5	0.0032	0.0010	0.0021

TABLE 4Water Activity (A_w) of Some Juices Determined by Three Methods

^{*a*} $A_{w} = \exp(f.p./103).$

^b In duplicate.

^c $A_w = 1.0162 + 0.0981 \times \text{f.p.}$; dilution, 1:3 (w/v).

that the differences in the A_w values determined by the cryoscopic and psychrometric method were smaller than 0.005 units; the similarity was even greater between the results provided by the gravimetric and the psychrometric method (the differences were only 0.002 units for yoghourts and even less for the other three groups of samples).

The above results confirm those previously obtained for other dairy products (Cabezas *et al.*, 1987): out of 150 samples, 93% had differences less than $0.005A_w$ units in the range 0.999-0.990. They are also consistent with those found by Fernández-Salguero *et al.* (1989) for canned fish, and with those reported by Esteban *et al.* (1989), who obtained differences smaller than 0.005 units in the A_w values determined in different dairy products with intermediate, high and very high water activities by the improved gravimetric method and the psychrometric method. The results obtained (differences smaller than 0.005 units in every case) therefore allow one to state that the three experimental methods used are valid (for the determination of high-end A_w values) on the types of products dealt with here.

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REFERENCES

- Cabezas, L., Marcos, A., Alcalá, M., Esteban, M. A. & Fernández-Salguero, J. (1987). Comparación de dos métodos para determinar la actividad del agua. *Alimentación: Equipos y tecnología*, VI(3), 167–71.
- Cabezas, L., Marcos, A., Esteban, M. A., Fernández-Salguero, J. & Alcalá, M. (1988). Improved equation for cryoscopic estimation of water activity in cheese. *Food. Chem.*, **30**, 59–66.
- 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**, 31–9.
- Esteban, M. A., Marcos, A., Fernández-Salguero, J. & Alcalá, M. (1989). An improved simple gravimetric method for measurement of high water activities. *Intern. J. Food Sci. Technol.*, 24, 139–46.
- Fernández-Salguero, J., Alcalá, M., Marcos, A., Esteban, M. A., Cabezas, L. & Gomez, R. (1989). Determination of water activity of canned fish using gravimetric, hydrometric and psychrometric methods. *Intern. J. Food Sci. Technol.*, 24, 233-6.

- 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. & Alcalá, M. (1985). Water activity measurement near to 1.00. J. Food Technol., 20, 523-6.
- McCune, T. D., Lang, K. W. & Steinberg, M. P. (1981). Water activity determination with the proximity equilibration cell. J. Food Sci., 46, 1978-9.
- Prior, B. A. (1979). Measurement of water activity in foods: A review. J. Food Protec., 42, 668-74.
- Troller, J. A. & Christian, J. H. B. (1978). Water Activity and Foods. Academic Press, New York, pp. 15–29.
- Uboldi, M. (1981). Water activity: Its influence on the growth of microorganisms and methods for its determination in foods. *Boletin ITAL*, *Campinas*, 18, 353-83.

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