Short Communication

Effect of column material on sorption isotherms obtained by inverse gas chromatography

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ABSTRACT

The dependence of sucrose sorption isotherm data obtained by inverse gas chromatography on column material was studied. Columns made of polyamide glass, copper and stainless steel were used. The results obtained indicate that the interaction between water vapour and the column wall cannot be ignored when products with very low equilibrium moisture content are considered.

INTRODUCTION

Most of the current methods for determination of water sorption isotherms rely upon the measurements of the changes in weight of samples equilibrated in atmospheres with different relative humidities, as described by Labuza [1]. A different procedure that is particularly suitable for the study of the lower region of water activity and for products with very low equilibrium moisture contents uses inverse gas chromatography (IGC), and has been extensively used by Smith *et al.* [2].

With IGC the sorbed solute is injected into the carrier gas stream and its linear transport is retarded owing to interaction with the product under study, which constitutes the stationary phase. Kiselev and Yashin [3] derived a method for calculating sorption isotherms, based on Glueckauf's [4] theory, using the chromatographic data obtained. The development of this theory results in the following equations, which relate chromatograph operating parameters and peak data to the sorption isotherm

$$a = \frac{m_a \, I_{ads}}{m \, I_{pic}} \qquad (1)$$

where a = uptake of sorbed water (g/g stationary phase), m_a = mass of water injected (g), m = mass of stationary phase (g) and I_{ads}/I_{pic} = ratio of the areas (A + B)/B calculated from the chromatogram (Fig. 1), and

$$p = \frac{m_a \, h \, R \, T}{I_{pic} \, W} \qquad (2)$$

where p = partial pressure (atm), h = peak height (detector units), R = gas constant (82.0567 cm^3
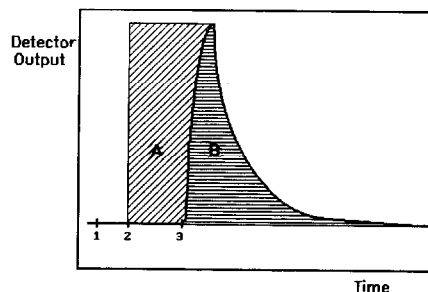

Fig. 1. Typical gas chromatogram obtained by IGC. 1 = Point of injection; 2 = point of emergence of unadsorbed peak (air); 3 = point of emergence of probe peak (water). I_{pic} = Area B; I_{ads} = area A + B.

atm mol^{-1} K^{-1}), T = absolute temperature (K), W = flow-rate of carrier gas (cm^3/min) and I_{pic} = area B in Fig. 1 (detector units min).

IGC provides a rapid and reliable method for the determination of sorption isotherms, but some attention is required to the choice of the material for the chromatographic column, particularly with very low equilibrium moisture contents.

EXPERIMENTAL

A Perkin Elmer SIGMA 3B dual-column gas chromatograph with a thermal conductivity detector was used. Helium (2 ppm water, 6 ppm maximum impurity) at a flow-rate of 60 cm^3/min was used as the carrier gas.

The study as conducted at 45°C with sucrose as the stationary phase. A 50–63 mesh fraction of sucrose (0.03% moisture content, 0.007% ash and 0.002% inverted sugars, dry weight basis) obtained from Refinarias de Açucar Reunidas (Porto, Portugal) was packed into 5 ft. × 0.25 in. I.D. columns. Columns made from polyamide, glass, copper and stainless steel were used. Distilled water was injected in amounts ranging from 0.2 to 2 µl. In order to remove most of the moisture contained in the sucrose, the columns were purged for 24 h with dry helium before use. Injector and detector temperatures were kept at 150°C.

Detector data were acquired by an XT-type microcomputer using a custom-built amplifier and a 12-bit dual-slope integrator analogue-to digital converter from Digital Design & Development (UK). Data collection and calculations were made by an existing computer program, CROMADATA, developed by Cardoso and Sereno [5].

RESULTS AND DISCUSSION

The operating conditions were similar to the ones described by Smith et al. [2]. Water sorption isotherms calculated using eqns. 1 and 2 are plotted in Fig. 2. Each data point represents the mean value of three determinations with the same amount of injected water.

The set of data obtained with each column was fitted to the GAB (Guggenheim [6], Anderson [7] and De Boer [8]) equation using a non-linear regression program written by Sereno and Medeiros [9].
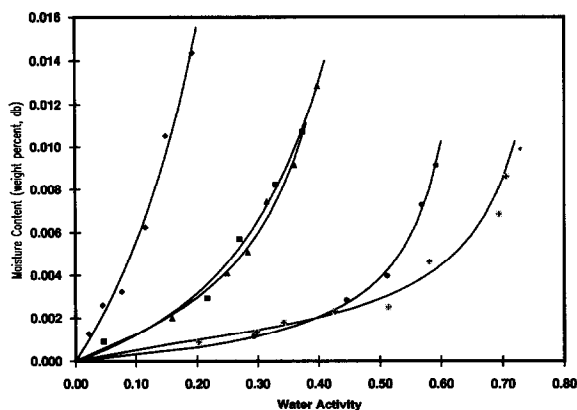

Fig. 2. Sorption isotherms for sucrose by IGC with different columns: polyamide (♦), glass (▲), copper (■), stainless steel (this work) (●) and stainless steel (Smith et al. [2]) (+). The solid lines represent the result obtained by fitting the data to the GAB equation.

The dependence of the results on column material is clear.

The results obtained by Smith et al. [2], using a stainless-steel column are also plotted in Fig. 2. The observed deviations are throught to be caused by different characteristics or ash contents of the sucrose crystals as implied in the works of Bienenstock and Powers [10], Rodgers and Lewis [11] and Bagster [12].

In conclusion, while IGC remains a fast and reliable technique for the experimental determination of water sorption isotherms of particulate or ground solids, the results of this research indicate that the interaction between water vapour and the column wall cannot be ignored when products with very low equilibrium moisture content are considered.

ACKNOWLEDGEMENTS

REFERENCES

1 T. P. Labuza, *Food Technol.*, 22 (1968) 15.
2 D. S. Smith, C. H. Mannheim and S. G. Gilbert, *J. Food Sci.*, 46 (1981) 1051.
3 A. V. Kiselev and Y. I. Yashin, *Gas Adsorption Chromatography*, Plenum Press, New York, 1969.
4 E. Glueckauf, *Proc. Faraday Soc.*, Part 6 (1949).
5 E. L. Cardoso and A. M. Sereno, *Digital Techniques for Laboratory Automation: Application to Gas Chromatography*, Department of Chemical Engineering, University of Porto, Porto, 1987.
6 E. A. Guggenheim, *Applications of Statistical Mechanics*, Clarendon Press, Oxford, 1966.
7 R. B. Anderson, *J. Am. Chem. Soc.*, 68 (1946) 686.
8 J. H. De Boer, *The Dynamical Character of Adsorption*, Clarendon Press, Oxford, 2nd ed., 1953.
9 A. M. Sereno and G. L. Medeiros, *SIF —Program for Sorption Isotherm Fitting— User's Manual*, Department of Chemical Engineering, University of Porto, Porto, 1989.
10 B. Bienenstock and H. E. Powers, *Int. Sugar J.*, 53 (1951) 254.
11 T. Rodgers and C. Lewis, *Int. Sugar J.*, 64 (1962) 359; 65 (1963) 12.
12 D. F. Bagster, *Int. Sugar J.*, 72 (1970) 263, 293.