

CHROM. 18 198

## WATER SORPTION ISOTHERMS ON SUCROSE AND STARCH BY MODIFIED INVERSE FRONTAL GAS CHROMATOGRAPHY

S. W. PAIK\* and S. G. GILBERT

*Department of Food Science, Cook College, New Jersey Agricultural Experiment Station, Rutgers University, New Brunswick, NJ 08903 (U.S.A.)*

(Received August 26th, 1985)

---

### SUMMARY

A modification of the inverse frontal gas chromatography method was made to allow for obtaining equilibrium water sorption isotherms at around room temperature. Modification consists of allowing sufficient wet-gas contact time for samples to reach equilibrium then measuring the water uptake by increasing the column temperature to 70°C at the later phase of water desorption. Good agreement was observed between the water sorption isotherms of starch and crystalline sucrose obtained with the modified inverse gas chromatography method and the static method.

---

### INTRODUCTION

Conventional gas chromatography (GC) which separates components based on partition or adsorption equilibrium can be used to determine the sorption isotherm equilibria. The principles of inverse frontal GC were developed by Wilson<sup>1</sup>, De Vault<sup>2</sup> and Glueckauf<sup>3</sup>. Basically, inverse frontal GC uses a step shaped concentration profile as a probe. The concentration of the probe is increased suddenly from zero to some finite value to be returned to zero after steady state is obtained. From an analysis of the chromatogram, which is a concentration profile of the effluent stream as a function of time, the adsorption isotherm can be calculated provided that diffusion and non-equilibrium phenomena are kept to a minimum.

The calculation of sorption isotherm from inverse frontal GC is performed by using the following equation<sup>4</sup>.

$$a = \frac{nc + u}{g}$$

where  $a$  = equilibrium amount adsorbed corresponding to the outgoing concentration of adsorbate (moles of adsorbate/g adsorbent);  $c$  = outgoing concentration of adsorbate (moles of adsorbate/moles of carrier gas);  $n$  = number of moles of carrier gas fed to the column after the feeding of adsorbate had been stopped (moles of carrier gas for desorption);  $u$  = The number of moles of adsorbate retained in the

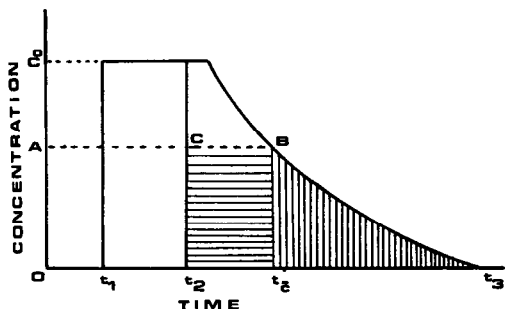


Fig. 1. Desorption phase of the inverse frontal GC concentration profile.

column when its outgoing desorption concentration is  $c$  (moles of adsorbate);  $g$  = weight of adsorbant in the column (gram adsorbant)

Fig. 1 illustrates the method of calculating sorption isotherm from a chromatogram using the above equation. The product  $nc$  in the above equation is proportional to the product of area  $BCt_2t_2'$  in Fig. 1 and volumetric flow-rate.  $u$  is proportional to the product of the  $Bt_2t_3$  and the volumetric flow-rate. In this way, uptake corresponding to  $c$  can be obtained. By repeating the procedure for different values of  $c$  a whole sorption isotherm can be constructed.

To verify the theoretical principles of frontal analysis, Everly<sup>4</sup> compared sorption isotherms of *n*-butane on silica gel at 48°C obtained from frontal analysis and equilibrium method. Good agreement was observed at lower adsorbate concentrations, however at higher concentrations data from frontal analysis deviated from the equilibrium isotherm. The purpose of the present work was to determine the feasibility of using inverse frontal GC to obtain water sorption isotherms of food components around room temperature, since most of the useful sorption isotherms of foods are obtained around room temperature.

MATERIALS AND METHODS

*Inverse frontal GC*

A flow diagram of the apparatus is illustrated in Fig. 2. Helium gas from the tank was humidified by bubbling the gas through distilled water at 70°C. The hu-

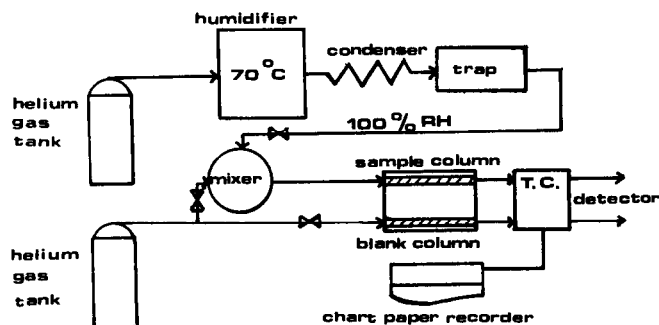


Fig. 2. Block flow diagram of the inverse frontal GC apparatus.

midified gas was passed through the condenser kept at column temperature to remove excess water in the vapor phase. Excess water removed was trapped and water vapor saturated helium gas was mixed with dry helium gas to obtain desired percentage relative humidity. The helium gas was also passed through the blank column at the same flow-rate. The concentration profile of the water vapor coming out of the sample column was measured with a thermal conductivity detector.

The carbohydrate sample packed inside the column was prepared by mixing 1–50% (w/w) of 65–75 mesh samples with 60–80 mesh acid washed, DMCS-treated diatomaceous support (Supelco Chromatography Supplies) in aluminum columns (3 ft.  $\times$  1/4 in.). The weight percent of the sample was varied depending on the water uptake of the sample. After installing a sample column inside the oven of the inverse frontal GC apparatus, the column was conditioned for 4 h to remove moisture by passing dry helium gas at 70°C. Crystalline sucrose was obtained from Fisher Scientific and the corn starch was supplied by National Starch and Chemical Co.

### Static method

The particle size of the samples were reduced to 65–70 mesh to increase the mass transfer rate of water. About 2 g of samples were placed inside the desiccators containing saturated salt solutions on an aluminum tray at 25°C. The percent relative humidity values for the salts were obtained from Lang *et al.*<sup>5</sup>, Rockland<sup>6</sup> and Hodgman<sup>7</sup>. Water uptake of the samples was determined by vacuum oven method using 70°C for 36 h. Determinations were made in duplicate.

## RESULTS AND DISCUSSION

The inverse frontal GC method was compared with the static method for obtaining water sorption isotherms of corn starch and crystalline sucrose at 25°C. As shown in Fig. 3, water sorption isotherm of corn starch determined by the static method has a sigmoid shape curve and the water sorption isotherm obtained by inverse frontal GC has a convex shaped curve having substantially less uptake at given partial pressures. With crystalline sucrose, the difference between water sorption isotherms determined by inverse frontal GC and the static method is substantial

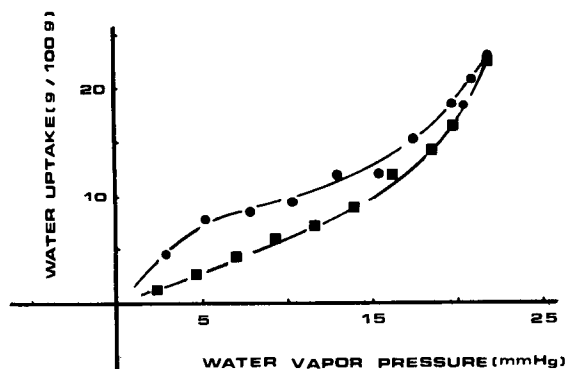


Fig. 3. Sorption isotherms of corn starch determined at 25°C by frontal analysis (■) and static method (●).

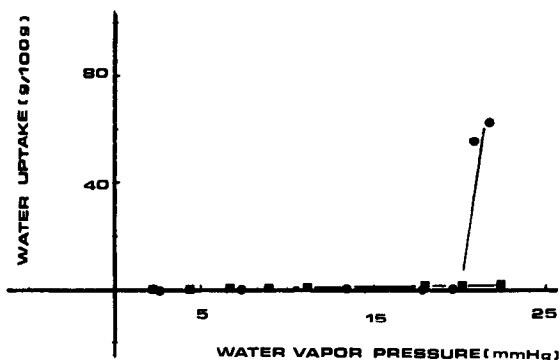


Fig. 4. Sorption isotherms of crystalline sucrose determined at 25°C by frontal analysis (■) and static method (●).

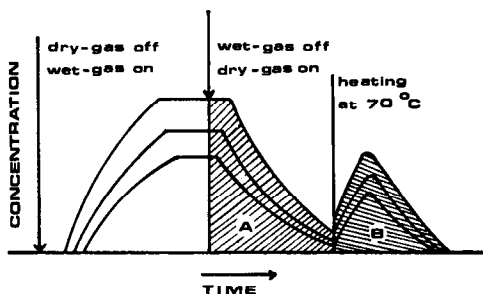


Fig. 5. Concentration profile formed during operation of modified frontal IGC.

at the higher vapor pressure region as shown in Fig. 4. This indicates that conditions used during sorption isotherm measurement of corn starch and crystalline sucrose by inverse frontal GC did not fulfill the assumption that equilibrium is established rapidly during operation.

The frontal analysis method was modified as follows to obtain equilibrium

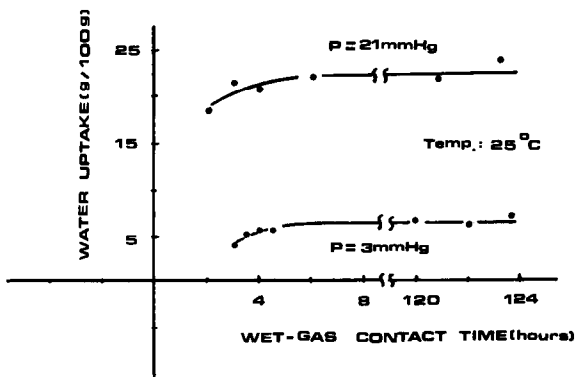


Fig. 6. Wet-gas contact time versus water uptake for starch.

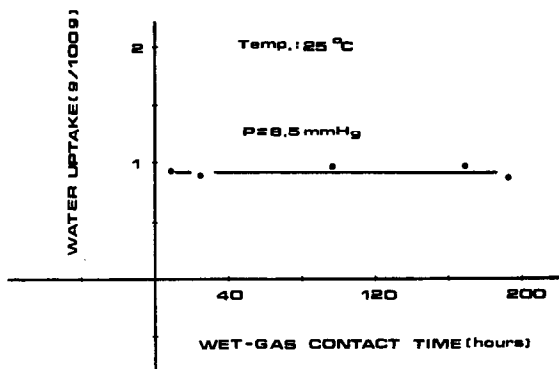


Fig. 7. Wet-gas contact time *versus* water uptake for crystalline sucrose at low water vapor pressure.

uptake at low temperature of 25°C. In the outlet vapor concentration profile formed during frontal analysis, as shown in Fig. 5, outlet vapor concentration increases, then it becomes constant and forms a plateau. At this plateau region of the concentration profile, the water adsorbed to the sample is the equilibrium uptake at the partial pressure of the vapor corresponding to the height of the plateau. The equilibrium water uptake by the sample was measured by flushing the column with dry carrier gas at 25°C, then increasing the oven temperature to 70°C to desorb the more tightly bound water of the sample. The sample column was replaced after each measurement to prevent hysteresis. To obtain a representative water sorption isotherm, this process was repeated at increments of water vapor pressure.

Equilibrium water uptake was calculated using the following equation

$$a = \frac{(A + B)S}{g} = \frac{A_T S}{g}$$

where  $a$  = equilibrium amount adsorbed corresponding to equilibrium adsorbate concentration. (moles of adsorbate/g adsorbent);  $A$  = shaded area in the chromatogram shown in Fig. 5 after turning off wet-gas and before heating ( $\text{cm}^2$ );  $B$  = shaded area in the chromatogram shown in Fig. 5 after heating ( $\text{cm}^2$ );  $A_T$  = sum of the

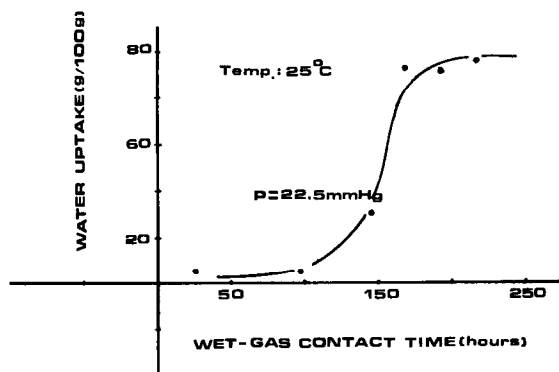


Fig. 8. Wet-gas contact time *versus* water uptake for crystalline sucrose at high water vapor pressure.

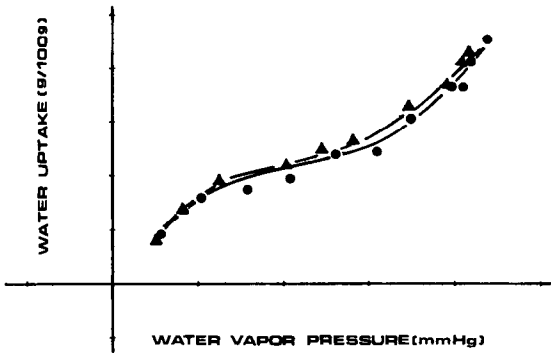


Fig. 9. Sorption isotherm of starch determined at 25°C by modified inverse frontal GC ( $\blacktriangle$ ) and static method ( $\bullet$ ).

areas A and B;  $S$  = calibration constant (moles of adsorbate/cm<sup>2</sup>);  $g$  = weight of adsorbent in the column (g adsorbant).

Corn starch and sucrose were exposed to the highest and lowest vapor pressure at 25°C to determine the wet-gas contact time required to achieve equilibrium. Results showed that corn starch required approximately 5 h of wet-gas contact to reach equilibrium uptake at both 3 and 21 mmHg water vapor pressure (Fig. 6). Equilibrium was achieved very rapidly with crystalline sucrose at the low water vapor pressure of 8.5 mmHg (Fig. 7). However, when water vapor pressure was increased to 22.5 mmHg, water uptake remained low up to about 100 h, then increased sharply and reached equilibrium after 200 h of wet-gas contact (Fig. 8).

The crystalline structure of sucrose seems to collapse after contact with wet-gas for a certain period of time at high water vapor pressure. Therefore, a longer wet-gas time is required to reach equilibrium uptake than at lower water vapor pressure where the crystalline structure is unchanged.

Water sorption isotherms of corn starch and sucrose were determined by modified inverse frontal GC using the minimum wet-gas contact time required to reach equilibrium water uptake for corn starch and sucrose. The results are shown in Figs. 9 and 10. Fig. 10 shows that water sorption isotherms for corn starch obtained by

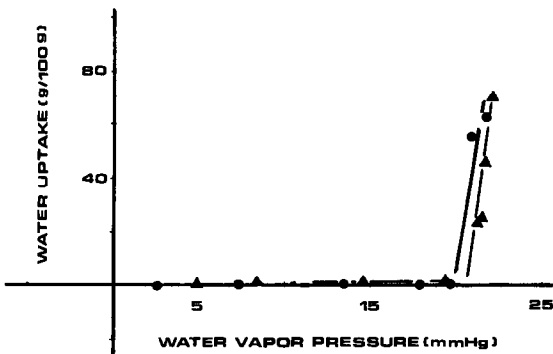


Fig. 10. Sorption isotherm of crystalline sucrose determined at 25°C by modified inverse frontal GC ( $\blacktriangle$ ) and static method ( $\bullet$ ).

modified inverse frontal GC are in good agreement with those of the static method at 25°C. Also with crystalline sucrose, good agreement was observed with water sorption isotherms obtained by modified inverse frontal GC and the static method at 25°C (Fig. 10).

#### CONCLUSIONS

Inverse frontal GC does not give equilibrium water sorption isotherms at low temperature of 25°C. However, with modification of the procedure, it was found to be a reliable method for determination of water sorption isotherms of corn starch and crystalline sucrose at 25°C. Water sorption isotherm data concur with values obtained by the static method here and in the literature.

#### ACKNOWLEDGEMENTS

A paper of the Journal Series, NJ Agricultural Experimental Station, Cook College, Rutgers, The State University, Department of Food Science, New Brunswick, NJ, U.S.A. This work was performed as a part of NJAES No. D 10535-1-85, supported by the N.J. Agricultural Experimental Station.

#### REFERENCES

- 1 J. N. Wilson, *J. Am. Chem. Soc.*, 62 (1940) 1583.
- 2 D. J. de Vault, *J. Am. Chem. Soc.*, 65 (1943) 532.
- 3 G. Glueckauf, *Nature (London)*, 156 (1945) 748.
- 4 P. E. Everly, *J. Phys. Chem.*, 65 (1961) 1261.
- 5 K. W. Lang and M. P. Steinberg, *J. Food Sci.*, 46 (1981) 1450.
- 6 L. B. Rockland, *Anal. Chem.*, 30 (1960) 1375.
- 7 C. D. Hodgmann, *Handbook of Chemistry and Physics*, Chemical Rubber Publ., Cleveland, OH, 1954.