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### ESTABLISHING MOISTURE SORPTION ISOTHERMS OF WILD MUSHROOM VARIETIES USING A DYNAMIC VAPOR SORPTION METHOD

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**ABSTRACT** *Boletus edulis* (Porcini), *Cantharellus cibarius* (chanterelle), *Lentinula edodes* (Shiitake), *Morchella deliciosa* (Morel), and *Tuber melanosporum* (truffle) are mushrooms of considerable economic, commercial and gastronomic importance in international markets. The objective of this research was to investigate the moisture sorption behavior of various highly favored mushrooms at a temperature of 30 °C. Also, it was intended to produce equilibrium moisture content data of wild mushroom species, which has limited coverage in the literature. The samples were subjected to hot-air drying in an experimental laboratory dryer and were equilibrated in the range of 0.05-0.95 water activity using the dynamic vapor sorption method. The GAB equation was selected to fit the experimental data by non-linear regression analysis. The accuracy of fit was based on standard error, mean relative error, and coefficient of determination. The model predicted successfully the equilibrium moisture content of mushrooms. Sigmoid characteristic curves of sorption isotherms were obtained. This means that the equilibrium moisture content of mushrooms increases with an increase in water activity at constant temperature. Reliable equilibrium moisture content data on moisture sorption isotherms were provided which is essential for the optimization of different processes in food industry.

**Keywords:** Wild mushrooms, Dynamic vapor sorption, Equilibrium moisture content

**INTRODUCTION** Mushrooms are highly regarded in human diet due to their organoleptic and nutritional characteristics. *Boletus edulis* (Porcini), *Cantharellus cibarius* (Chanterelle), *Lentinula edodes* (Shiitake), *Morchella deliciosa* (Morel), and *Tuber melanosporum* (Black Truffle) are commodities of considerable economic, commercial and gastronomic importance in international markets. Owing to their perishable nature with short shelf life under ambient conditions of temperature and humidity, drying is a common method for guaranteeing long term storage and distribution of mushrooms on a global scale. For the optimization of drying, packaging and storage, knowledge of the equilibrium relationship between the moisture content in the product and the relative humidity of the atmospheric surroundings at a given temperature is

fundamental. This relationship, known as sorption isotherm, predicts the physical, chemical and microbiological changes occurring during processing. Since theoretical prediction of the sorption behavior of foodstuffs is not possible, several methods for the determination of sorption isotherms have been developed and classified into three major categories namely, gravimetric, manometric and hygrometric (Gal, 1981). Furthermore, the methods involve either continuous or discontinuous measurements in dynamic and static systems. The static gravimetric technique using thermally stabilized desiccators filled with saturated salt solutions (Spiess & Wolf, 1987) is still frequently employed for mushrooms due to its simplicity. However, this method shows an inability to produce and maintain high values of relative humidity. Also, it is time-consuming with prolonged equilibrium periods. Sorption isotherms of various mushroom varieties using the static gravimetric method have been published for *L. trivialis* (Kurkela & Paakkonen, 1983; Paakkonen & Kurkela, 1986), for *A. bisporus* (Sahbaz et al., 1999), for freeze dried *L. edodes*, *F. velutipes* and *M. esculenta* (Khallufi et al., 2000), for *A. bisporus* and *P. florida* (Shivhare et al., 2004), for *I. obliquus* (Lee & Lee, 2008). Work by Janjai et al., (2007) studied the sorption isotherms of *G. Lucidum* mushroom using the gravimetric method but in a dynamic system. Alternatives based on hygrometric methods have been published for freeze dried *B. edulis* (Garcia-Pascual et al., 2002) and for *M. esculenta* (Mulet et al., 2002). No information is available on automated measurements of sorption isotherms of mushroom using a dynamic, gravimetric and fully controlled system. Dynamic vapor sorption (DVS) is a relatively new technique designed to measure the weight change caused by adsorption or desorption of the water vapor at any desired relative humidity between 0 and 98% in a short period of time. This method has been applied to test the moisture sorption kinetics of pharmaceutical products as well as packaging and building materials. A study close to the present one has been published by Desmorieux & Decaen (2006) on convective drying of blue algae using the DVS method to establish sorption isotherms of *Spirulina*. Several equations have been reported in the literature to describe the sorption characteristics of foodstuffs (Chirife & Iglesias, 1978; Van den Berg & Bruin, 1981; Schar & Rugg, 1985). Among them the GAB (Van den Berg, 1984) equation is one of the most widely used isotherm models for foods. It is a simple mathematical form with three parameters of physical significance and is applicable up to a water activity of 0.90. The GAB equation is recommended by the European Project Cost 90 on Physical Properties on Foods (Wolf et al., 1985) and is being established in US laboratories (Labuza, 1984). The objective of the present study was to investigate the moisture sorption behavior of several mushroom species at 30 °C by the dynamic vapor sorption method and to describe the experimental data using the GAB model.

## MATERIALS AND METHODS

**Raw material** Four wild-growing edible species and one commercial cultivated species were used. Fresh *M. deliciosa* (Morel) mushrooms were collected from the forest of the Penteli Mountain (Greece). Raw *B. edulis* and *C. cibarius* samples were picked up from the region of Black forest (Germany). Samples of *L. edodes* and *T. melanosporum* were purchased from the local market in Stuttgart (Germany). Mushrooms were cleaned thoroughly, sliced and dried in a through-flow laboratory dryer at a temperature of 60 °C with 10 g/kg absolute humidity and constant air velocity of 0.9 m/s. The dried material

was kept vacuum packed in aluminum coated polyethylene bags and stored at ambient conditions.

**Sorption device** The sorption behavior of various mushrooms has been measured by dynamic vapor sorption at the institute of Applied Chemistry, Reutlingen University using a gravimetric DVS-1000 analyzer (Surface Measurement Systems Ltd., London, U.K.). The instrument essentially consists of a Cahn microbalance with two sample crucibles made of quartz and the humidifier in a temperature controlled chamber. One of the crucibles is used for reference and the other contains the sample to be analyzed. A stream of dry and wet inert gas flows along the crucibles. The relative humidity of the mixture is regulated by two electronic mass flow controllers. Temperature, humidity and mass are automatically recorded at regular intervals.

**Experimental procedure** Sample with a mass varied from 10 to 40 mg was used for each experiment. The sorption isotherms were determined at a temperature of 30 °C by exposing the sample at different values of relative humidity (0 to 95%). The sample was first dried by exposure to dry nitrogen until a constant weight of the sample was reached. Then, the relative humidity was subsequently increased stepwise and the sample weight was equilibrated at each step. Equilibrium was considered to have been reached when the mass variation became lower than 0.001 mg/min or the equilibration time had exceeded 360 min. To obtain the sorption isotherm the moisture content of the sample in g water per g dry solids (g/g d.b.) was directly provided by the equilibrium values of each relative humidity step.

**Mathematical description of isotherm** The Guggenheim-Anderson-de Boer model can be written as follows:

$$X = \frac{X_m CKa_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)} \quad (1)$$

The GAB equation could be rearranged according to Bizot (1983) into a second degree polynomial equation:

$$\frac{a_w}{X} = \alpha a_w^2 + \beta a_w + \gamma \quad (2)$$

where

$$\alpha = \frac{K}{X_m} \left[ \frac{1}{C} - 1 \right], \beta = \frac{1}{X_m} \left[ 1 - \frac{2}{C} \right], \gamma = \frac{1}{X_m CK} \quad (3)$$

where,  $a_w$  is the water activity (dimensionless),  $X$  is the moisture content (g/g d.b.),  $X_m$  is the monolayer moisture content (g/g d.b.),  $K$  and  $C$  are the GAB constants,  $\alpha$ ,  $\beta$ ,  $\gamma$  are coefficients.

**Parameters calculation** The parameters of the equation were estimated using a non-linear least squares procedure since this method has been proposed as the most reliable at just one temperature (Schar & Ruegg, 1985). The accuracy of fit of the GAB equation to

the experimental sorption data was evaluated by three statistical criteria, the coefficient of determination ( $R^2$ ), the mean relative percentage error (E) and the standard error (S.E.).

$$E\% = \frac{100}{n} \sum_{i=1}^n \left( \frac{X_{i\text{exp}} - X_{i\text{pre}}}{X_{i\text{exp}}} \right) \quad (4)$$

$$S.E. = \sqrt{\frac{\sum_{i=1}^n (X_{i\text{exp}} - X_{i\text{pre}})^2}{n}} \quad (5)$$

where  $n$  is the number of experimental data,  $X_{i\text{exp}}$  are experimental values, and  $X_{i\text{pre}}$  are predicted values from the model. In general, a good fit is obtained when  $E < 10\%$  (McLaughlin & Magee, 1998), with low values of S.E. and high values of  $R^2$ .

## RESULTS AND DISCUSSION

**Sorption isotherms** The experimental procedure performed to construct the sorption isotherms of each mushroom species by the dynamic vapor sorption method at 30 °C is shown in figure 1. The dry reference mass was established in approximately 16 hours. The effect of relative humidity on adsorption and desorption can be observed as an increase and decrease in mass respectively. The time required for all samples to reach equilibrium was 6 hours except those ones equilibrated at values of relative humidity higher than 90% which exhibited longer periods. The data from the sorption profile were further used to estimate the equilibrium moisture contents at the different target values of relative humidity.

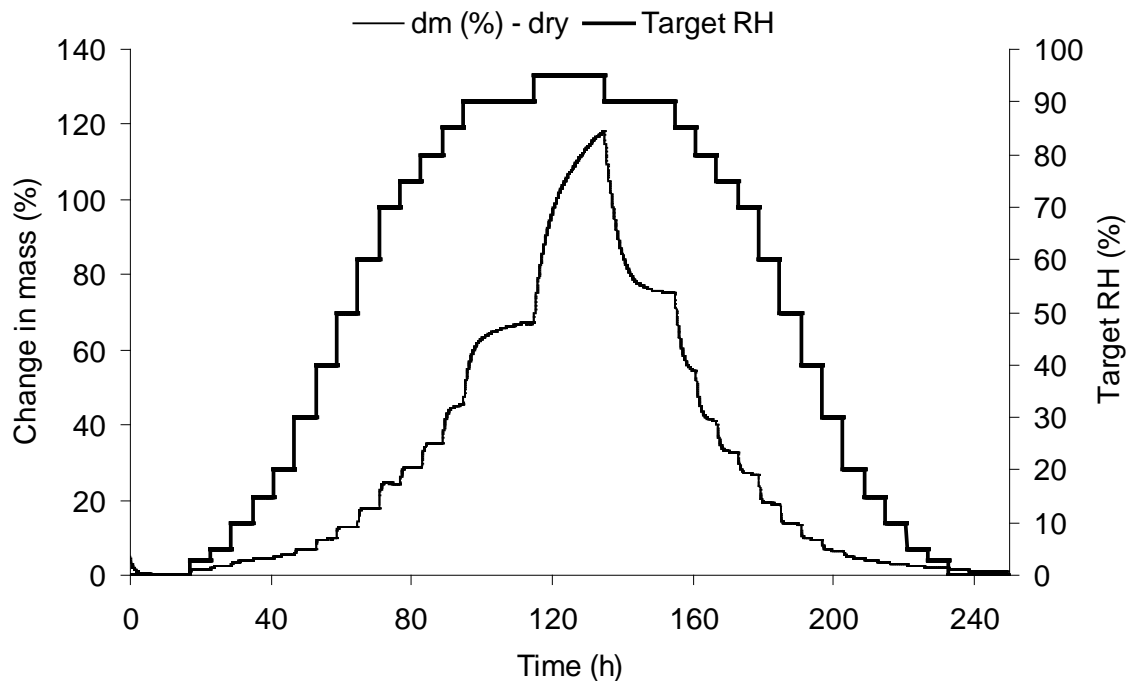


Figure 1. Equilibrium moisture adsorption-desorption profile of *B. edulis* mushroom exposed to different values of relative humidity at 30°C

Figure 2 shows the experimental adsorption and desorption isotherms of *B. edulis* mushroom at 30 °C. The obtained curves closely resemble the characteristic sigmoid shape of the type II pattern isotherm indicating relatively small amounts of water at low values of relative humidity and exhibiting an asymptotic trend as relative humidity approaches 95%. Moreover, the DVS method determined the hysteresis effect from the same sample of which the equilibrium moisture content was higher at a constant relative humidity for desorption than for adsorption. The hysteresis was significant at values of relative humidity above 60%. Similar sorption behavior was observed for all mushroom varieties examined.

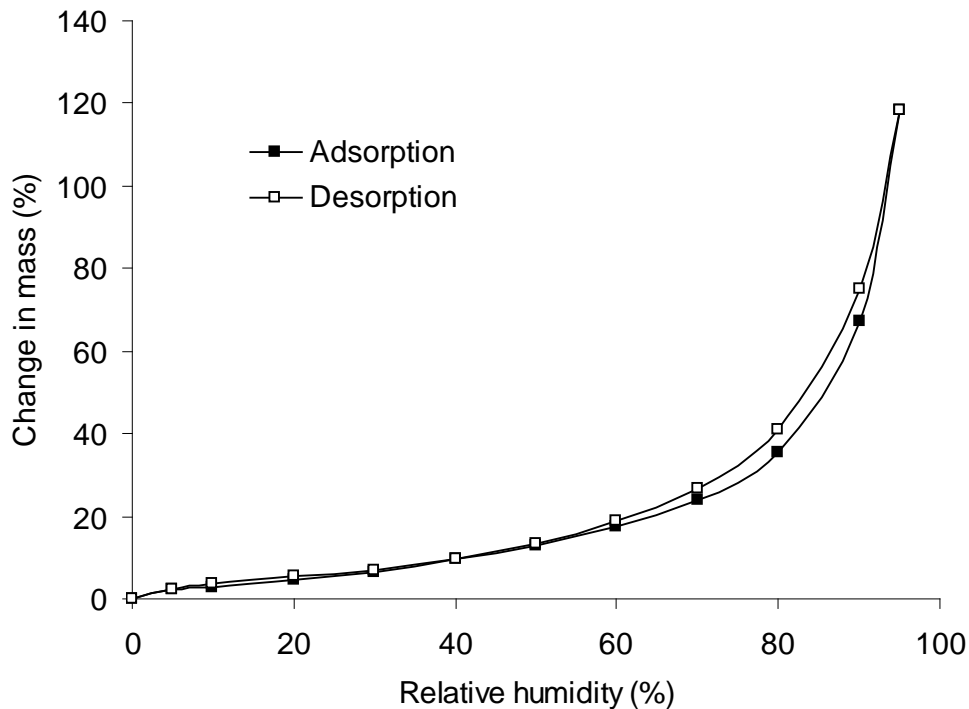


Figure 2. Adsorption-desorption hysteresis of *B. edulis* mushroom at 30 °C

The experimental results of the equilibrium moisture content (EMC) for several mushroom varieties at each water activity for 30 °C are presented in table 1. The DVS method provided equilibrium moisture content data in the entire range of relative humidity under controlled conditions with high accuracy. This is an advantage of the technique since the static gravimetric method provides a limited coverage of target relative humidity especially at higher temperatures and the hygrometric method a slightly improved range, nevertheless, both procedures indicate inconsistent accuracy. As expected, the equilibrium moisture content of all mushroom species increased with water activity at constant temperature. Black truffle, followed by morel is apparently the least hygroscopic mushroom species in the whole range of water activity. The other mushrooms exhibited higher values with almost the same trends of hygroscopicity. More specifically, at the hygienically safe water activity of 0.6, *T. melanosporum*, *M. deliciosa*, *L. edodes*, *C. cibarius* and *B. edulis* mushrooms contained 0.098, 0.10, 0.16, 0.175, and 0.176 g water per g dry solids respectively. Khalloufi et al. (2000) studied the sorption isotherms of freeze dried mushrooms (*M. esculenta*, *L. edodes* and *F. velutipes*) at three temperatures. A variation was found in sorption behavior among the different species of

mushrooms and *F. velutipes* was denoted as the most hygroscopic species. A similar result was also published for *A. bisporus* in comparison with *P. florida* by Shivhare et al. (2004). The above mentioned values of moisture content for each mushroom variety can be recommended to guarantee adequate preservation. In other words, to avoid microbial growth or spore germination at 30 °C, truffle and morel should be stored at a maximum moisture content of 10% wet basis as well as shiitake, porcini and chanterelle at 15% wet basis.

Table 1. Experimental EMC (g/g d.b.) values of various mushroom species at 30 °C

Water activity (dimensionless)	<i>B.edulis</i> (Porcini)	<i>C.cibarius</i> (Chanterelle)	<i>L.edodes</i> (Shiitake)	<i>M.deliciosa</i> (Morel)	<i>T.melanosporum</i> (Truffle)
0.05	0.023	0.019	0.017	0.0018	0.0015
0.10	0.038	0.031	0.029	0.0064	0.0085
0.20	0.053	0.045	0.042	0.0145	0.0207
0.30	0.071	0.062	0.059	0.0240	0.0331
0.40	0.097	0.089	0.087	0.0397	0.0489
0.50	0.130	0.126	0.119	0.0642	0.0697
0.60	0.176	0.175	0.160	0.1007	0.0987
0.70	0.241	0.248	0.222	0.1523	0.1367
0.80	0.353	0.376	0.325	0.2508	0.1998
0.85	0.453	0.483	0.420	0.3329	0.2521
0.90	0.672	0.698	0.668	0.5196	0.3492
0.95	1.182	1.186	1.241	0.9204	0.6014

The GAB model was tested for its effectiveness to describe the experimental sorption data of mushrooms. The estimated parameters of the GAB equation and the statistical criteria are listed in table 2. For all mushroom varieties except *T. melanosporum* the sorption characteristics were predicted well by the model as can be observed from the low values of the standard error and the high values of the coefficient of determination. Additionally, the mean relative error was lower than 10%. Figure 3 shows the experimental sorption isotherms of four mushroom varieties at 30 °C along with the model estimations.

Table 2. GAB parameters for moisture sorption isotherm data of mushrooms at 30 °C

Mushroom species	C	K	X <sub>m</sub>	R <sup>2</sup>	E (%)	S.E.
<i>B. edulis</i>	7.3202	0.9847	0.0770	0.999	4.5915	0.00712
<i>C. cibarius</i>	5.3860	0.9798	0.0835	0.998	9.1425	0.01167
<i>L. edodes</i>	5.2902	0.9936	0.0705	0.999	5.2564	0.00993
<i>M. deliciosa</i>	0.6785	0.9734	0.0775	0.996	8.2183	0.00601
<i>T. melanosporum</i>	0.8653	0.9536	0.0621	0.994	23.643	0.01499

Apart from microbial damage, which typically occurs for water activity above 0.6, oxidation, enzymatic reactions and non enzymatic browning can even occur at very low water activity. It has been empirically observed that most of the dried food products display their greatest stability at moisture contents comparable to monolayer moisture content. Therefore, information about the monolayer moisture content is highly important for the overall product safety. The values of monolayer moisture content predicted by the GAB model for *B. edulis*, *C. cibarius*, *L. edodes*, *M. deliciosa* and *T. melanosporum* were

0.077, 0.0835, 0.0705, 0.0775 and 0.0621 g/g d.b. respectively. These values correspond to a limit of water activity near to 0.4. The value for *M. deliciosa* was slightly higher than the value calculated for adsorption on freeze dried morel (0.043 g/g d.b.) by Khalloufi et al. (2000) and similar to the value computed for desorption on hot air dried morel (0.098 g/g d.b.) by Mulet et al. (2002). Furthermore, the value for *L. edodes* was lower than the figure (0.12 g/g d.b.) obtained by Khalloufi et al. (2000).

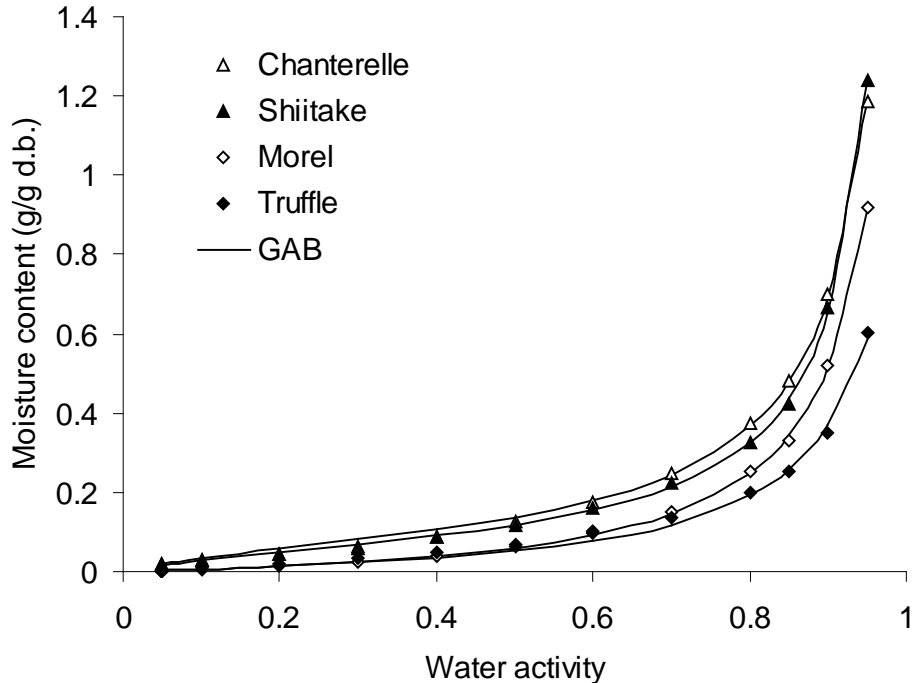


Figure 3. Experimental data and adsorption isotherms of various mushroom species at 30 °C

**CONCLUSION** The dynamic vapor sorption technique has been successfully employed for the determination of the sorption isotherms of various mushroom species. The relatively low sample mass used significantly reduced the entire process time. The experimental results obtained were comparable to the values reported in the literature for mushrooms, providing equilibrium moisture content data for the entire range of relative humidity examined. The GAB model adequately described the sorption characteristics of mushrooms. Values of the monolayer moisture content were also computed. Further experiments will be conducted using the DVS method to evaluate the effect of temperature on the sorption isotherms and to calculate the net isosteric heat of sorption.

## REFERENCES

- Bizot, H. 1983. Using the 'G.A.B.' model to construct sorption isotherms. In R. Jowitt, F. Escher, B. Hallstrom, H. Mefert, W. Spiess, & G. Vos (Eds.), *Physical properties of foods* (p. 43). London: Applied Science publishers.
- Chirife, J., & Iglesias, H. A. 1978. Equations for fitting water sorption isotherms of foods: Part 1 - A review. *Journal of Food Technology*, 13: 159-174.
- Desmorieux, H. & Decaen, N. 2006. Convective drying of *Spirulina* in thin layer. *Journal of Food Engineering*, 77: 64-70.

- Gal, S. 1981. Techniques for obtaining complete sorption isotherms. *Water Activity: Influences on Food Quality* (pp 89-154), Rockland, L. B. and Stewart, G. F. (Eds.) (Academic Press, New York, USA).
- García-Pascual, P., Sanjuán, N., Cárcel, J. A., García-Reverter, J. & Mulet, A. 2002. Adsorption isotherm of freeze dried *Boletus edulis* mushrooms. In *Proceedings of the 13th International Drying Symposium IDS, Beijing, China, vol. B.* (p. 1281).
- Janjai, S., Tohsing, K. & Bala, B. K. 2007. Moisture sorption isotherms of lincheu mushroom (*Ganoderma lucidum*). *Food Science and Technology Research*, 13 (4): 315-320.
- Khalloufi, S. 2000. Water activity of freeze dried mushrooms and berries. *Canadian Biosystems Engineering / Le Genie des biosystems au Canada*, 42 (1): 51-56.
- Kurkela, R., & Paakkonen, K. 1983. Water sorption of Northern milk cap mushroom (*Lactarius trivialis*). *Lebensmittel-Wissenschaft und-Technologie*, 17: 285-288.
- Labuza, T. P. 1984. Moisture sorption: practical aspects of isotherm measurement and use. Minnesota, USA: American Association of Cereal Chemists.
- Lee, J. H. & Lee, M. J. 2008. Effect of drying method on the moisture sorption isotherms for *Inonotus obliquus* mushroom. *LWT - Food Science and Technology*, 41 (8): 1478-1484.
- McLaughlin, C. P. & Magee, T. R. A. 1998. The determination of sorption isotherm and the isosteric heats of sorption for potatoes. *Journal of Food Engineering*, 35 (3): 267-280.
- Mulet, A., Garcia-Pascual, P., Sanjuan, N. & Garcia-Reverter, J. 2002. Equilibrium isotherms and isosteric heats of morel (*Morchella esculenta*). *Journal of Food Engineering*, 53 (1): 75-81.
- Paakkonen, K., & Kurkela, R. 1986. Temperature effect on the water sorption of Northern milk cap mushrooms (*Lactarius trivialis*) in processing and storage. *Lebensmittel-Wissenschaft und-Technologie*, 19 (3): 215-217.
- Sahbaz, F., Palazoglu, T. K. & Uzman, D. 1999. Moisture sorption and the applicability of the Brunauer-Emmet-Teller (BET) equation for blanched and unblanched mushrooms. *Nahrung - Food*, 43 (5): 325-329.
- Schar, W., & Ruegg, M. 1985. The evaluation of GAB constants from water vapour sorption data. *Lebensmittel-Wissenschaft und Technologie*, 18: 225-229.
- Shivhare, U. S., Arora, S., Ahmed, J. & Raghavan, G. S. V. 2004. Moisture adsorption isotherms for mushroom. *LWT - Food Science and Technology*, 37 (1): 133-137.
- Spiess, W. E. L., & Wolf, W. 1987. Critical evaluation of methods to determine moisture sorption isotherms. In L. B. Rockland, & L. R. Beuchat (Eds.), *Water activity: theory and applications to food*. New York: Marcel Dekker, Inc.
- Van den Berg, C. 1984. Description of water activity of foods for engineering purposes by means of the GAB model of sorption. In B. M. Mc Kenna (Eds.), *Engineering and food, Vol. 1.* (pp. 311-321). London: Elsevier Applied Science.
- Van den Berg, C., & Bruin, S. 1981. Water activity and its estimation in food systems: theoretical aspects. In L. B. Rockland, & G. E. Stewart (Eds.), *Water Activity; Influence on Food Quality* (p. 45). New York: Academic Press.
- Wolf, W., Spiess, W. E. L., & Jung, G. 1985. Standardization of isotherm measurements (COST-project 90 and 90 BIS). In D. Simatos, & J. L. Multon (Eds.), *Properties of water in foods* (pp. 661-677). Dordrecht, Netherlands: Martinus Nijhoff Publishers.