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Article

Mathematical modelling of moisture sorption isotherms of some fruits

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The moisture sorption isotherms of some fruits namely pear and quince were determined at 15, 30, 45 and 60ºC over a range of water activity from 0.110 to 0.920 using the standard, static-gravimetric method. The experimental sorption data were fitted with generated three-parameter sorption isotherm models on Mitrevski et al., and the referent Anderson model known in the scientific and engineering literature as Guggenheim-Anderson-de Boer (GAB) model. In order to find which models give the best results, large number of numerical experiments was performed. After that, several statistical criteria for estimation and selection of the best sorption isotherm model was used. The performed statistical analysis shows that the generated three-parameter model from Mitrevski et al. gave the best fit to the sorption data of pear and quince than the referent three-parameter Anderson model.

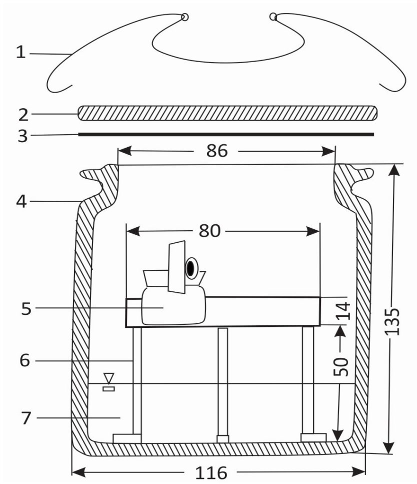
1. Introduction

The sorption isotherms of food materials are important practical tool in modelling the drying process, design and optimization of drying equipment, predicting shelf-life stability, calculating moisture changes which may occur during storage and selecting appropriate packaging material [1]. The published data for moisture sorption isotherms of pear and quince are scarce and for that reasons, its determination is interesting for the researchers. Several researches have reported sorption isotherm data for pear and quince at different temperatures and water activities [2-9]. In In scientific and engineering literature numerous mathematical models for approximation of the experimental data of sorption isotherm on food materials are available, [10-22]. For the goodness of fit of experimental moisture sorption data and selection of the best isotherm model, the most commonly used statistical criteria are: coefficient of determination, R^2, root mean squared error, *RMSE*, and the mean relative deviation, *MRD*. The selection of a sorption isotherm model with graphical evaluation of the residual randomness is also popular [23, 24]. The objectives of the presented study were: experimentally determination of adsorption isotherms of representative fruits, pear and quince at temperatures 15, 30, 45 and 60 ºC for a range of water activity from 0.110 to 0.920 and evaluation of three-parameter sorption isotherm models for approximation of equilibrium moisture data of pear and quince and to make comparison on their goodness of fit based on several statistical criteria.

2. Materials and methods

The materials used in the experimental part of the research were fresh pear cultivar "William" and quince, cultivar "Champion". Until the processing time, the pear and quince were stored in cold chamber at temperature of 4ºC and relative air humidity of 75%. To prepare samples, the pears and quinces were washed, peeled and from the mesocarp on the materials were sliced samples with thickness of 2 ± 10^{-1} mm, before being reduced to a cylinder form with diameter of 29 ± 10^{-1} mm. Several measurements were made using a caliper and only samples with a tolerance of ±5 % were used. The representative samples taken for determination of sorption isotherms were pre-dried to final moisture content in a convective dryer at air drying temperature of 60ºC, and air drying velocity of 1 ms^{-1} for a period of **7** hours. The equilibrium moisture content of pear and quince were determined at temperatures of 15, 30, 45 and 60 ºC using static gravimetric method [8, 9]. Ten saturated salt solutions L_iCl, CH_3COOK, MgCl, K_2CO_3, $Mg(NO_3)_2$, NaBr, $SrCl_2$, NaCl, KCl and $BaCl_2$ prepared according to the recommendation of Greenspan [25], were used to give defined constant equilibrium relative humidity in the glass jars from 0.110 to 0.920. Two dry representative samples of pear or quince separately were placed on holder into each of the ten glass jars and exposed to atmospheres of various relative humidity. At water activities, a_w >0.60, small quantity of crystalline thymol was placed in the glass jar in order to prevent microbial spoilage of the samples. The glass sorption jars were placed and kept in the temperature controlled cabinet type SANYO MCO-15AC (SANYO Electric Co., Ltd. Refrigeration Products Division 1-1-1, Sakata Oizumi - Machi, Ora-Gun, Gunma 370-0596 Japan), maintained at temperatures 15, 30, 45 and 60 ºC with an accuracy of ±0.1ºC (figure 1).


a).



b).

Figure 1. Experimental apparatus for determination of sorption isotherms
a) temperature controlled cabinet b) preserving jar: 1-locking ring, 2-glass lid; 3-rubber ring, 4-glass container, 5-measuring container, 6-Petri-dish on tripod, 7-saturated salt solution

Three replications were made at each temperature and equilibrium relative humidity in the glass jars, using two samples per replication and the average values of equilibrium moisture content of samples were calculated. The change of samples mass was determined by electrical balance type KERN PLJ360-3M (Kern&Sohn GmbH, Ziegelei 1, 72336 Balingen, Germany), with precision of 0.001 g every 7 days. The equilibrium between samples and their environment was reached after 21 days as evidenced by the constant weight after two successive weighing of samples. The equilibrium moisture content of the samples was determined gravimetrically by drying in an oven at temperature of 105 ºC and atmospheric pressure for 24 h.

3. Results and discussions

The experimental values for the equilibrium moisture content, X_{eq} of pear and quince at each water activity, a_w for the four different temperatures given in table 1 and table 2.

Table 1. Equilibrium moisture content of pear*

15 °C		30 °C		45 °C		60 °C	
a_w [-]	X_{eq} [kg/kg d.b.]	a_w [-]	X_{eq} [kg/kg d.b.]	a_w [-]	X_{eq} [kg/kg d.b.]	a_w [-]	X_{eq} [kg/kg d.b.]
0.113	0.011±0.000	0.113	0.007±0.000	0.112	0.008±0.000	0.110	0.009±0.001
0.234	0.018±0.000	0.216	0.016±0.001	0.195	0.018±0.000	0.160	0.014±0.002
0.333	0.040±0.001	0.324	0.040±0.000	0.311	0.040±0.000	0.293	0.031±0.003
0.432	0.083±0.001	0.432	0.080±0.001	0.432	0.074±0.001	0.432	0.070±0.002
0.559	0.159±0.000	0.514	0.119±0.000	0.469	0.091±0.002	0.440	0.074±0.002
0.607	0.197±0.002	0.560	0.145±0.002	0.520	0.107±0.000	0.497	0.090±0.003
0.741	0.325±0.001	0.691	0.250±0.000	0.640	0.172±0.001	0.580	0.130±0.002
0.756	0.350±0.002	0.751	0.320±0.003	0.745	0.265±0.000	0.745	0.235±0.001
0.859	0.600±0.001	0.836	0.495±0.001	0.817	0.395±0.002	0.803	0.335±0.001
0.920	0.904±0.003	0.900	0.813±0.002	0.880	0.653±0.002	0.840	0.597±0.001

*mean and standard deviation based on N = 3 replications

Table 2. Equilibrium moisture content of quince*

15 °C		30 °C		45 °C		60 °C	
a_w [-]	X_{eq} [kg/kg d.b.]	a_w [-]	X_{eq} [kg/kg d.b.]	a_w [-]	X_{eq} [kg/kg d.b.]	a_w [-]	X_{eq} [kg/kg d.b.]
0.113	0.008±0.000	0.113	0.013±0.001	0.112	0.009±0.002	0.110	0.010±0.003
0.234	0.023±0.000	0.216	0.038±0.001	0.195	0.030±0.002	0.160	0.021±0.001
0.333	0.050±0.001	0.324	0.057±0.003	0.311	0.041±0.003	0.293	0.037±0.001
0.432	0.093±0.001	0.432	0.087±0.002	0.432	0.076±0.002	0.432	0.063±0.003
0.559	0.149±0.000	0.514	0.113±0.002	0.469	0.090±0.002	0.440	0.071±0.002
0.607	0.180±0.002	0.560	0.130±0.000	0.520	0.102±0.002	0.497	0.081±0.001
0.741	0.295±0.001	0.691	0.224±0.002	0.640	0.158±0.002	0.580	0.110±0.001
0.756	0.320±0.002	0.751	0.293±0.003	0.745	0.242±0.003	0.745	0.220±0.001
0.859	0.492±0.001	0.836	0.450±0.001	0.817	0.354±0.001	0.803	0.306±0.001
0.920	0.799±0.003	0.900	0.715±0.002	0.880	0.599±0.002	0.840	0.565±0.003

*mean and standard deviation based on N = 3 replications

The equilibrium moisture content of pear or quince were fitted with three parameters model generated from Miterevski *et al*., [21], and referent Anderson model [26] (table 3).

Table 3. Mathematical models for fitting the equilibrium moisture data

Model	Equation	References
M1	$X_{eq} = \exp[P_1+P_2\, a_w/\arctan a_w)+P_3(a_w/\text{argtan } a_w)^2]$	[21]
M2	$X_{eq} = P_1 a_w/[(1-P_2 a_w)\,(1-P_3 a_w)]$	[26]

For selection of the most appropriate sorption isotherm model several statistical criteria proposed by Ruiz-López, and Herman-Lara, [24] were used. The value of performance index, ϕ, is the first statistical criterion for selection of isotherm sorption model [24]:

$$\phi = \frac{R^2}{RMSE \cdot MRD} \tag{1}$$

Higher values of performance index, ϕ, indicate that the sorption model better approximates the experimental sorption data.

The D'Agostino-Pearson's test of normality is the most effective procedure for assessing a goodness of fit for a normal distribution. This test is based on the individual statistics for testing of the residual population of skewness, z_1, and kurtosis, z_2, and is the second statistical criterion as adequate of sorption model [27]

$$\chi^2 = z_1^2 + z_2^2 \tag{2}$$

The χ^2 statistics has a chi-squared distribution with 2 degrees of freedom (*df*). The tabled critical 0.05 chi-square value for $df = 2$ is $\chi^2_{0.05} = 5.99$. Therefore, if the computed value of chi-square is equal to, or greater than, either of the aforementioned values, the null hypothesis can be rejected at the appropriate level of significance ($p > 0.95$), i.e. the sorption model should be rejected [27].

The single-sample run test is one of numerous statistical procedures that have been developed for evaluating whether or not the distribution of series is random. This test is the third statistical criterion for effectiveness of sorption model. In this test, the number of positive and negative residuals, n_1 and n_2, and the number of times the sequence of residuals changes sign, g, are used to calculate the following test statistic [27]:

$$z_r = \frac{|g - g_1| - 0.5}{\sigma_r}, g_1 = \frac{2n_1 n_2}{n_1 + n_2} + 1, \sigma_r = \sqrt{\frac{2n_1 n_2 (2n_1 n_2 - n_1 - n_2)}{(n_1 + n_2)^2 (n_1 + n_2 - 1)}} \tag{3}$$

If the computed value of, z_r, is greater than the tabled critical two-tailed value $z_{0.05} = 1.96$, the null hypothesis should be rejected ($p > 0.95$), i.e. the sorption model should be rejected [27].

A fourth statistical criterion for selection of sorption isotherm model is the evaluation of significance and precision of the model constant. That can be done by constructing individual confidence intervals, CI, and with calculated two-tailed p-value of estimated parameters. If the estimated value of parameters is out of the 95% confidence interval or estimated two-tailed *p*-value according to, t test of statistic is ($p < 0.05$) the model contains non-significant parameters for approximation of experimental sorption data i.e. sorption isotherm model should be rejected.

Because the regression methods (indirect nonlinear or direct nonlinear), estimation method, the initial step size, the start values of parameters, convergence criterion and form of the function have significant influence on accuracy of estimated parameters [8], a large number of numerical experiments were performed. The method of indirect non-linear regression and estimation methods of Quasi-Newton, Simplex, Simplex and quasi-Newton, Hooke-Jeeves pattern moves, Hooke-Jeeves pattern moves and quasi-Newton, Rosenbrock pattern search, Rosenbrock pattern search and quasi-Newton, Gauss-Newton and Levenberg-Marquardt from computer program Statistica [28], were used to approximate the experimental equilibrium moisture content data of pear or quince. On the basis of experimental data, and each mathematical model from table 3, the values of: coefficient of determination, R^2, root mean squared error, *RMSE*, the mean relative deviation, *MRD*, and performance index, ϕ, were calculated. After that, the models were ranked on the basis of values of the performance index, ϕ, (table 4).

Table 4. Statistic summary of the regression analysis

Model	Fruit	R^2	*RMSE*	*MRD*	ϕ	Rank
M1	Pear Quince	0.9820 0.9788	0.0321 0.0305	0.5378 0.4212	56.964 76.202	2
M2	Pear Quince	0.9860 0.9823	0.0282 0.0279	0.1526 0.1350	229.18 260.77	1

From table 4 it is evident that the Anderson model i.e. GAB model (M2), has the highest value of performance index, $\phi = 229.18$ for pear and $\phi = 260.77$ for quince (rank 1). In agreement with the first statistic criterion, this model correlates the experimental values of sorption data of pear and quince better than model of Mitrevski et al.

In table 5, the computed values for, χ^2, and, z_r, are given. From table 5 it can be see that Anderson model have value of, χ^2, and, z_r, greater than the tabled critical value. In accordance with the proposed statistical criteria, this model was rejected in further statistical evaluation. From the same table, it is obviously that Mitrevski *et al.*, model M1, have value of, χ^2 and z_r, smaller than the tabled critical value. In accordance with the proposed statistical criteria, this model is able to correlate the experimental values of sorption isotherms of pear with 3.21% root mean squared error and with 3.05% root mean squared error for quince.

Table 5. Rejection criteria for sorption models

Model	Fruit	χ^2	z_r	Rejection criteria
M1	Pear Quince	1.2945 5.1826	1.7155 1.6561	-
M2	Pear Quince	**7.1785*** **18.768***	**3.0708*** **2.0392***	χ^2, z_r

*Bold numbers indicate a significant lack of normality of the moisture residuals ($p > 0.05$)

The values of model parameters for models M1 were estimated by fitting the model to experimental equilibrium moisture content data of pear or quince using Gauss-Newton estimation method which minimizes the sum squares errors. The 95% confidence intervals of the estimated parameters were determined by using the **nlparci** (beta, resid,'jacobian', J) function of the Statistics Toolbox of Matlab®8.3, [29], while the significance of each of the estimated parameters, P_1, P_2, P_3 was evaluated through, t-test statistic. The estimated values of parameters, 95% confidence intervals and two-tailed p-value of estimated parameters are given in table 6. The calculated two-tailed p-values for all parameters for model M1 for each of estimated parameters has statistical significance (table 6).

Table 6. Estimated values of parameters, 95% confidence intervals and p value

Model-Fruit	Parameter	Value	95% CI	p
M1-Pear	P_1	-9.3113	(-28.446 , 9.8179)	3.30E-01
	P_2	-0.7462	(-33.509 , 32.031)	9.64E-01
	P_3	6.6193	(-7.4048 , 20.633)	3.45E-01
M1-Quince	P_1	-5.8999	(-24.687 , 12.868)	5.28E-01
	P_2	-6.1358	(-38.387 , 26.150)	7.03E-01
	P_3	8.6669	(-5.1900 , 22.504)	2.13E-01

In accordance to proposed statistical criterion the model of Mitrevski *et al.*, is able to approximate moisture equilibrium content data of pear and quince in the whole range of water activity.

The experimental and predicted values for equilibrium moisture content for pear at four temperatures are shown of figure 2, while for quince are shown on figure 3.

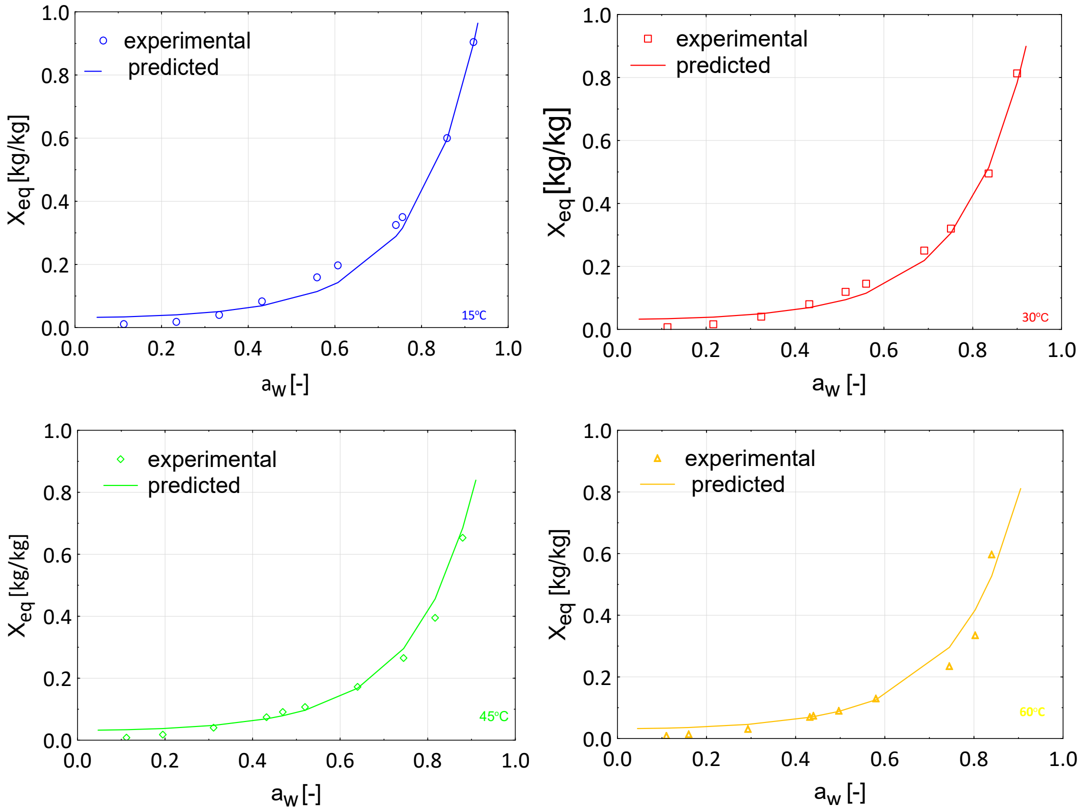


Figure 2. Experimental and predicted sorption isotherms for pear at 15, 30, 45 and 60 °C

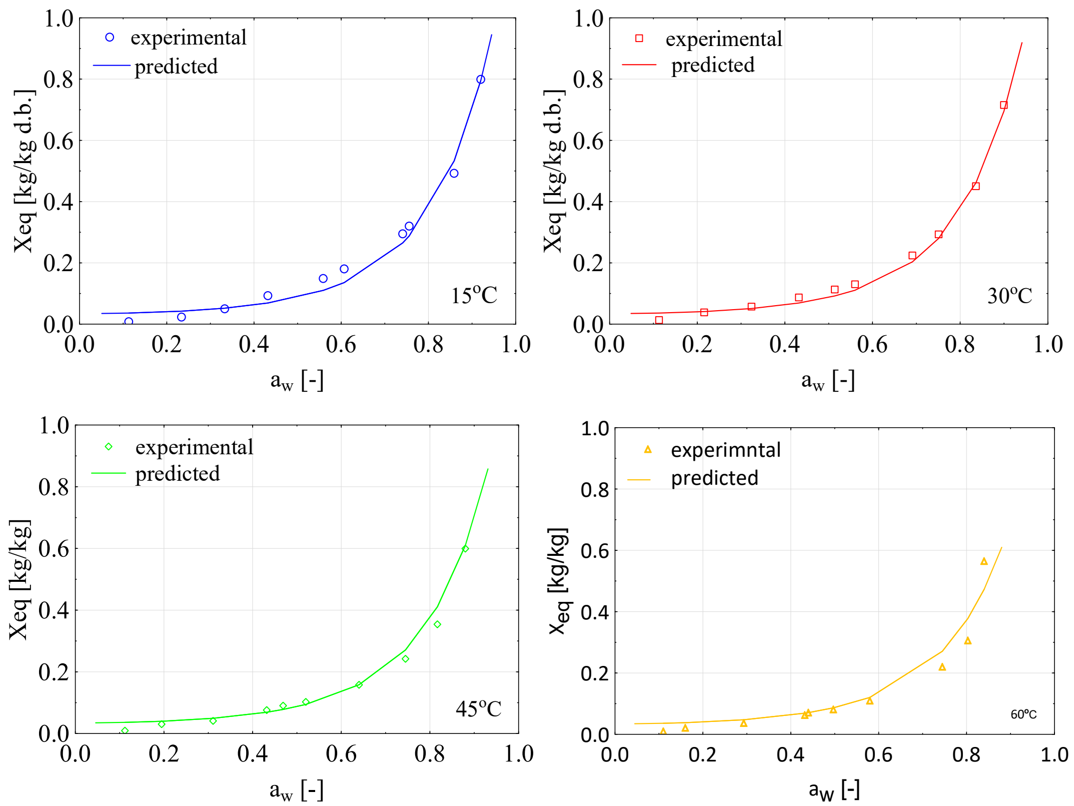


Figure 3. Experimental and predicted sorption isotherms for quince at 15, 30, 45 and 60 °C

The normal quantile of the residuals is verified on figure 4 for pear and figure 5 for quince.

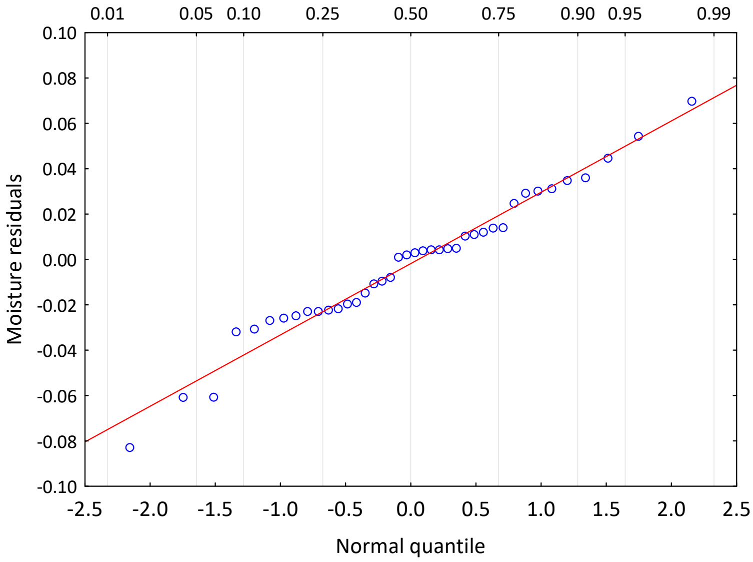


Figure 4. Normal quantile plot of the residuals for pear data

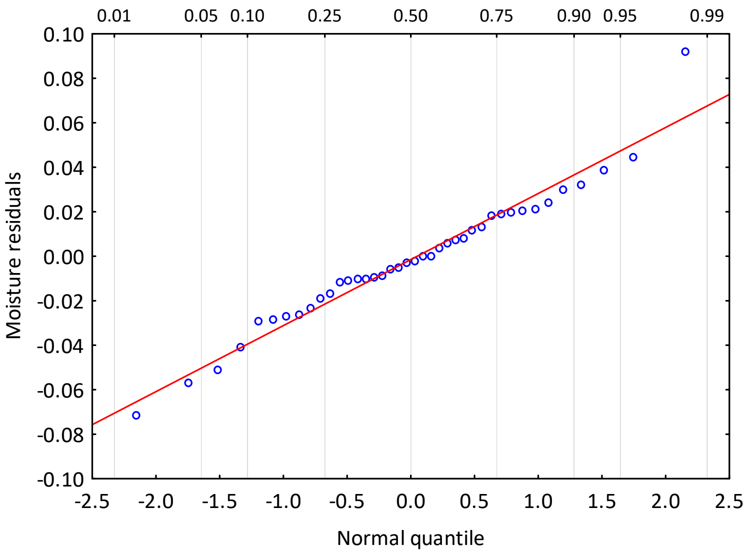


Figure 5. Normal quantile plot of the residuals for quince data

4. Conclusions

The moisture sorption isotherms of pear and quince at four temperatures 15, 30, 45 and 60ºC and ten different water activities were experimentally determined with the gravimetric static method. The experimental equilibrium moisture content data of pear and quince were fitted with the three-parameter sorption isotherm model on Mitrevski *et al.,* and the referent Anderson model. In accordance to proposed statistical criterion it was concluded that the model of Mitrevski *et al*., have a better statistical fit on experimental equilibrium moisture data of pear and quince in whole range of water activity than referent Anderson. So, this model can be successfully used in practical calculations of the equilibrium moisture content data, which is important parameter in storage conditions of dry food materials.

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