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ERRORS IN SORPTION ISOTHERMS APPROXIMATION WITH SELECTED EQUATIONS AND APPLICATION OF DIFFERENT COMPUTATIONAL PROGRAMS

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Summary. Results of comparative analysis of four sets of experimental data, cited in the literature equations, are presented. Two packages of statistic software - SAS and STATISTICA were used for this purpose. It was stated that the differences in computed equation coefficients and errors in the approximation occurred. With the application of GAB, Halsey and Oswin equations, the differences were insignificant, whereas Chung-Pfost and especially Henderson equations gave quite essential differences, amounting to 8% of absolute error and 36% of relative error, for equilibrium humidities of the wet material. The differences were increasing with the decreasing temperature. The application of the iterration step, smaller than nominal, in STATISTICA software resulted in better coincidence of approximation results for the both programs. The differences found in this work suggest the necessity of development of unified methodology for calculation of measurement results.

Keywords: equlibrium moisture content, equilibrium relative humidity, STATISTICA, SAS.

INTRODUCTION

Equilibrium moisture content *(M)* - equilibrium relative humidity *(φ)* relationships are necessary to optimize storage, handling and processing of foods. Moisture sorption isotherms show the dependence of water content on water activity of food at constant temperature and pressures. Five equations commonly used to describe the moisture sorption isotherm of biological materials are:

Henderson, modified Chung-Pfost, modified Halsey, modified Oswin, and modified GAB equations. These ones and all other 40 equations, with or without temperature as a variable, where φ or M can be calculated, were colected in [4]. The statistical description of experimental data is neglected in numerous papers. In the latest contributions [1,2], the authors present the set of results for experimental data. They included the tables with experimental results and fitted empirical formulas, including the fitting errors and collective plots with measurement points and description lines.

Up to now, the fact that the same experimental results, subjected to statistical evaluation with the use of different statistical programs, give similar mathematical description, has not been analysed. It was stated [3], only for one example, that is for one type of sorption isotherm, that there are some differences in the mathematical description of experimental results with the use of two statistical softwares - SAS and STATISTICA.

The aim of the work was the comparison of approximation results of exemplary 4 sets of experimental data, with the use of the most frequently applied equations, described in the literature. As the examples, the experimental results of materials having highly different sorption isotherms were selected. Two statistical softwares - SAS and STATISTICA were used. The work did not aim at the selection of equations, the most suitable for the description of experimental results.

METHODS

All equations, describing φ *vs.* M dependencies require the application of non-linear regression and the program must possess the ability of defining so called User Function. Since in the equations temperature is also variable, the software should take into account multi-component functions. In STATISTICA software, the procedure Non-linear Estimation should be applied and in SAS software, the procedure Non-linear Regression should be used.

For the comparative analysis, the results of equilibrium humidity of freeze-dried cherries (example 1), osmo-air dried cherries (example 2) (from [1]) and sunflower seeds (example 3), sunflower hulls (example 4) (from [2]) were selected. The course of sorption isotherms at temperatures $10^{o}C$ and $40^{o}C$ is shown in Fig. 1. Significant differences in the course of the curves, especially for cherries and sunflower seeds can be seen.

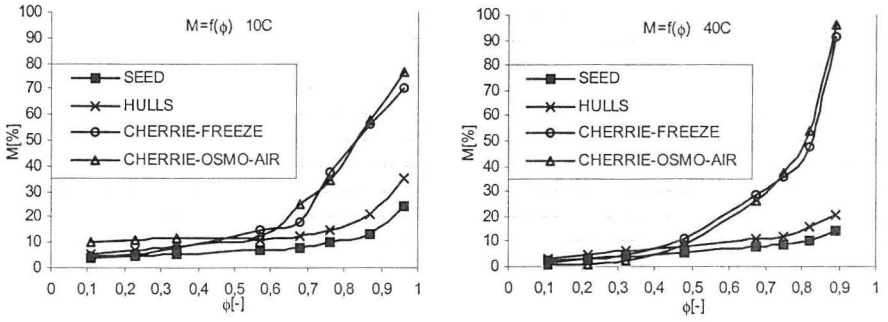

Fig. 1. Sorption isotherms for cherries and sunflower – taken to the analysis from the literature [1,2].

The equations (from [4]) applied in the comparative analysis, are:

Henderson $\varphi = 1-exp[-a*(T+c)*M^b]$ (1)

Chung-Pfost: $\varphi = exp[-a/(T+c)*exp(-b*M/100)]$ (2)

Halsey: $\varphi = exp[-exp(a+b*T)*M^{-c}]$ (3)

Oswin: $\varphi = 1/[((a+b*T)/M)^c+1]$ (4)

GAB: $M = [a*(c/T)*b*\varphi]/[(1-b*\varphi)*(1-b*\varphi+(c/T)*b*\varphi)]$ (5)

where: M - equilibrium moisture content, in dry mass [kg H_2O/kg *100],
T - temperature [°C], φ - relative humidity [-], A,B,C - constants.

The comparative analysis consisted in estimation of *A, B* and *C* constants with the computer software, as well as the relative percentage error P and standard error of moisture content *SEM*.

$$P = 100/N * \sum [(|M - M'|) / M] \quad (6)$$

$$SEM = \sqrt{\frac{\sum \frac{(M - M')^2}{M}}{df}} \quad (7)$$

where: M - measured equilibrium moisture content value,
M' - eqiulibrium moisture content value predicted by equation,
N - number of data points,
df - degree of freedom of the regression model (N minus number of constants in the model).

STATISTICA software does not give the fitting errors, thus separate calculations were required. The comparative analysis of approximation results obtained with the use of SAS and STATISTICA software, was done by estimation of absolute error *AE(M)* and relative error *RE(M)* in the calculation of moisture content *M*, where:

$$AE(M) = Predicted\ M_{SAS} - Predicted\ M_{STAT} \quad [\text{kg } H_2O/\text{kg dry mass}] \quad (8)$$

$$RE(M) = (Predicted\ M_{SAS} - Predicted\ M_{STAT})/\ Predicted\ M_{SAS} * 100\% \quad (9)$$

These errors, were also calculated, for relative humidity $AE(\varphi)$ and $RE(\varphi)$ and, for the better ilustration of differences between both statistical programs for moisture content expressed on wet mass $AE(W)$ and $RE(W)$, where

$$W = M/(M+100) * 100\ \% \quad [\ \%\ ] \quad (10)$$

RESULTS AND DISCUSSION

The comparative analysis was carried out separately for the examples 1 and 2 (cherries) and the examples 3 and 4 (sunflower seeds and hulls), as the difference in the course of isotherms.

Table 1. Constants and calculation errors, calculated by programs SAS and STATISTICA - for examples 1 and 2

Const.	equation/calculation program									
	Henderson		Chung-Pfost		Halsey		Oswin		GAB	
	SAS	Statistica	SAS	Statistica	SAS	Statistica	SAS	Statistica	SAS	Statistica
	Example 1 (Cherries-Freeze dried)									
A	**0.0001**	**0.0005**	**81109**	**5483291**	1.9	1.92	13	13.48	13	13.0
B	0.8	0.8	5.5	5.6	-0.005	-0.005	-0.02	-0.02	0.9	0.9
C	**950**	**140.92**	**46034**	**3083482**	0.88	0.88	1.22	1.22	118	117.7
R^2	-	0.95	-	0.92	-	0.97	-	0.97	-	0.87
SEM	**13.89**	**12.83**	12.76	13.03	56.33	53.22	24.53	23.77	10.48	9.57
P	**27.44**	**23.86**	**52.16**	**51.24**	35.63	35.83	25.09	25.34	47.20	47.05
	Example 2 (Cherries-Osmo-air dried)									
A	**0.0007**	**0.0008**	**221**	**208.7**	2.5	2.56	20	20.1	13	13.2
B	0.78	0.78	5.4	5.4	-0.017	-0.018	-0.23	-0.245	0.9	0.9
C	**101**	**81.15**	**100**	**92.2**	0.96	0.96	1.2	1.2	114	114.9
R^2	-	0.87	-	0.88	-	0.85	-	0.87	-	0.87
SEM	**14.61**	**16.07**	14.42	14.36	55.89	54.8	**42.3**	**37.63**	**10.82**	**9.85**
P	50.88	51.27	**76.53**	**80.69**	74.54	74.4	**70.09**	**61.15**	**89.18**	**84.68**

The results of A,B,C coefficients for particular equations, together with the fitting errors are collected in Table 2. It can be seen that for Halsey, Oswin and GAB equations, the SAS and STATISTICA software calculated very similar coefficients, in spite of the fact that *SEM* errors indicated some differences (for example 2 - Oswin, $P = 70$ and 61). Significant differences in the coefficients were observed for example 1 (freeze-dried cherries), but for Henderson equation the discrepancies were essential ($A = 0.01$ and 0.05 and $C = 950$ and 140). For example 2 (cherries-osmo air dried), the differences in coefficients and errors are much lower ($C = 101$ and 81). In Chung-Pfost equation, significant differences only for example 1 occurred, in the values of coefficient A (81109 and 5483291), and C (46034 and 3083482), however *SEM* and P errors are very similar. The differences in equations fitting to experimental results, with the use of SAS and STATISTICA software are shown on the plots in Figs. 2, 3 and 4. From Fig. 2, it can be seen that the differences in calculation of relative humidity increase with temperature decrease. Absolute error in calculation of moisture on wet mass for relative air humidity $\varphi = 0.9$ approaches even $AE(W) = 8\%$, whereas when $\varphi = 0.3$, the relative calculation error of moisture content on wet mass amounts to $RE(W) = 36\%$ - both for the temperature of $10^{o}C$.

Table 2. Constants and calculation errors, calculated by both programs (examples 3 and 4)

Constants	equation / calculation program					
	Henderson		Chung-Pfost		Halsey	
	SAS	Statistica	SAS	Statistica	SAS	Statistica
	Example 3 (Seeds from sunflower)					
A	**0.0003**	**0.0004**	399.47	399.22	3.29	3.29
B	1.75	1.73	32.14	32.11	-0.01	-0.01
C	**66.60**	**39.07**	53.49	53.55	1.86	1.86
R^2	-	0.96	-	0.98	-	0.98
SEM	1.89	1.71	1.99	2.01	1.30	1.37
P	10.70	11.01	8.44	8.75	7.39	7.85
	Example 4 (Hulls from sunflower)					
A	**0.0004**	**0.0005**	208.59	208.55	3.91	3.90
B	1.59	1.54	21.39	21.39	-0.03	-0.03
C	**24.43**	**21.89**	19.69	19.66	1.69	1.69
R^2	-	0.93	-	0.95	-	0.95
SEM	2.21	2.01	2.83	2.81	4.64	4.73
P	15.46	15.98	13.56	14.03	13.29	13.87

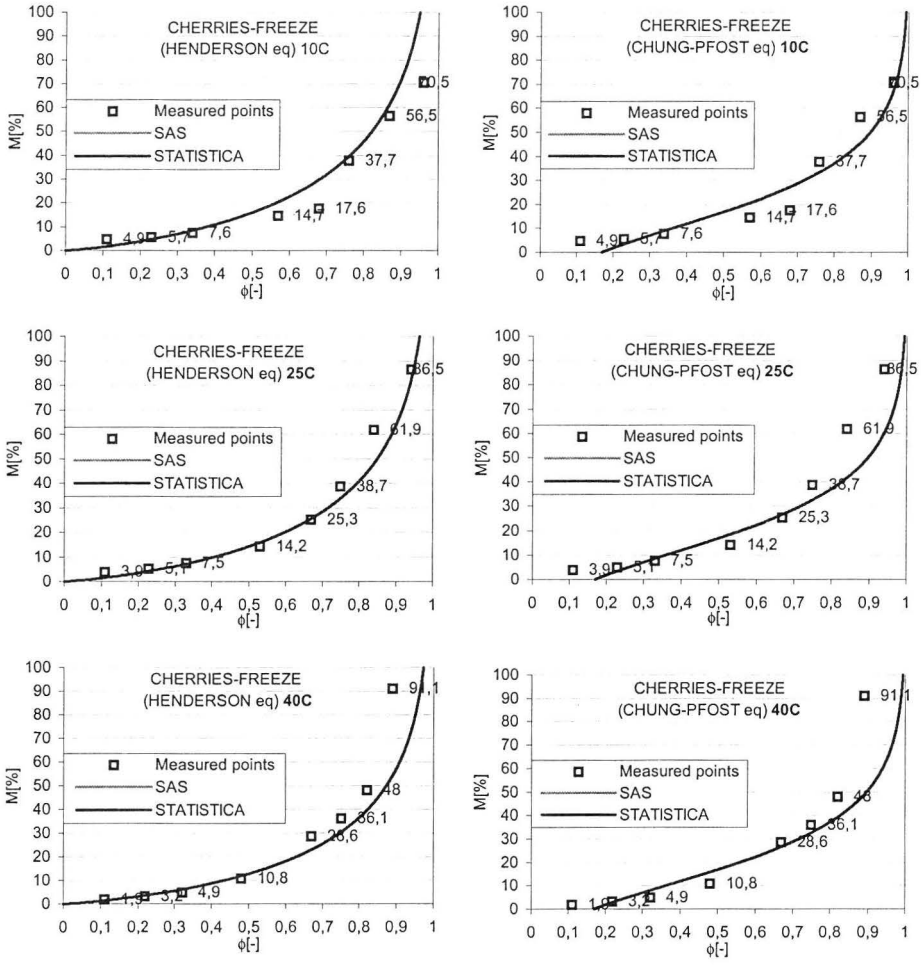

Fig. 2. Moisture content on dry mass M [%] versus relative humidity φ [-], predicted by programs SAS and STATISTICA, with the use of Henderson and Chung-Pfost equations (for example 1).

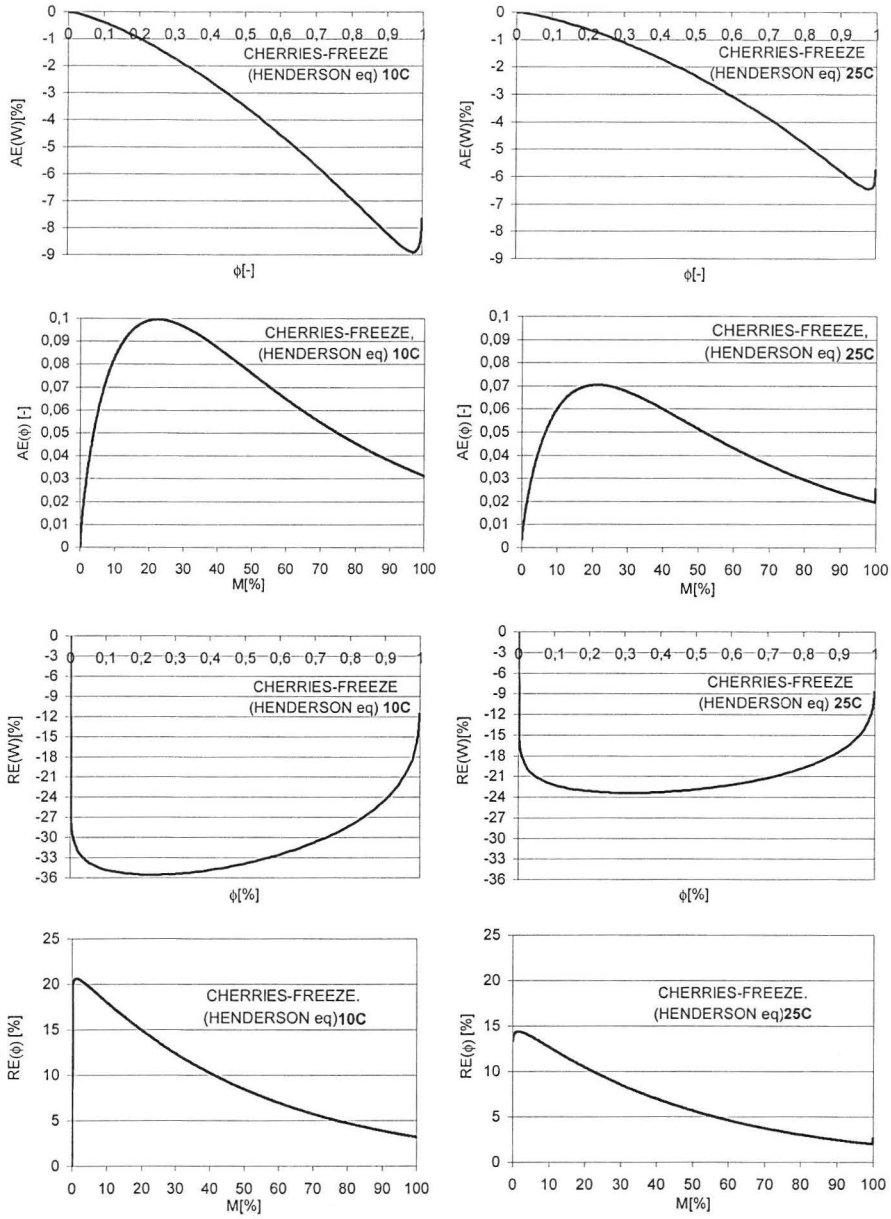

Fig. 3. Absolute errors *AE* and relative errors *RE* in the calculation of moisture content *W* and relative humidity φ in relation to relative humidity φ [-] or moisture content *M* [%], when programs SAS and STATISTICA and Henderson equation were used (example 1).

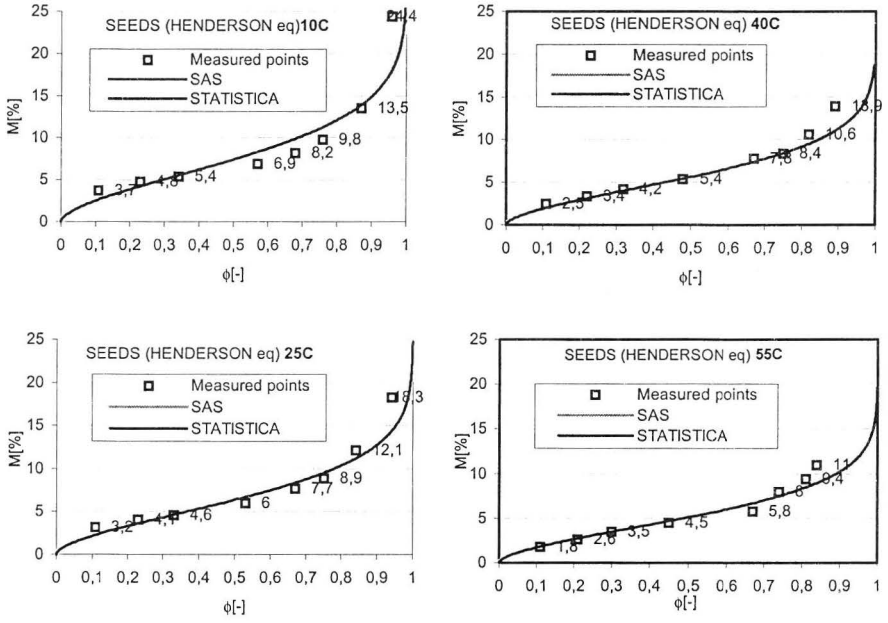

Fig. 4. Moisture content M [%] versus relative humidity φ [-], predicted by programs SAS and STATISTICA, with the use of Henderson equation (for example 3 – seeds from sunflower).

Results of calculation of the coefficients and errors for some other literature data, example 3 and 4, are shown in Table 3. For seeds Chung-Pfost and Henderson equations, give both A, B, C coefficients and *SEM* and *P* fitting errors very similar and even identical. The higher discrepancies occur only in the coefficients of Henderson equation (A = 0.00031 and 0.00044, C = 66 and 39), but *SEM* and P errors are not different. For the illustration of the differences values, the plots of particular errors are shown in Figs 4 and 5. Higher discrepancies occur only for the lowest temperature of 10°C. The run of errors in calculation of moisture content on wet mass W for seeds resemble essentially the one for cherries, but the error value is lower, $ER(W) = 7\%$ and the absolute error for $\varphi = 0.9$, is only $AE(\varphi) = 1\%$. For the example 4, for hulls, the differences in coefficients and errors are very low and the curves of sorption isotherms almost coincide.

Table 3. Calculation of constants, in program STATISTICA, for different calculation steps and estimations, when Henderson equation was used (example 1).

Calculation program	Calc. step	Constants in Henderson equation			
		A	B	C	R^2
SAS	Not given	**0,0001**	**0,81**	**950**	-
STATISTICA Estimation QuasiNewton	0.5	0.000501	0.79576	140.9182	95.28
	0.1	0.000204	0.80309	372.816	95.84
	0.05	0.000133	0.80309	582.99	95.92
	0.03	0.000100	0.8053	783.5548	95.95
	0.02	**0.000080**	**0.8039**	**984.9406**	**95.96**
	0.01	0.000054	0.8059	1453.458	95.98
	0.001	0.000014	0.8076	5846.74	96.01
STATISTICA Calc. step 0.001	Estimation:				
	Sympleks	No result			
	Hooke`a-Jeevs	0.000947	0.75874	76.2804	94.03
	Rosenbrok	No result			

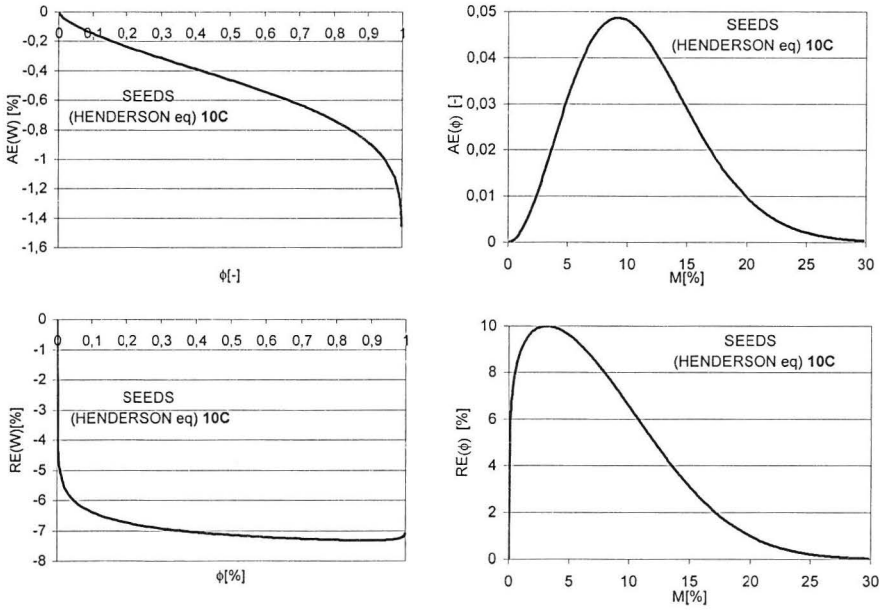

Fig. 5. Absolute errors AE and relative errors RE in the calculation of moisture content W and relative humidity φ in relation to relative humidity φ [-] or moisture content M [%], when programs SAS and STATISTICA and Henderson equation were used (for example 3).

In further studies of the comparison of both programs, an attempt of changing some procedures in STATISTICA program was undertaken. In the beginning, the change in the standard calculation step k = 0.5 to lower values was made. In Table 3, for cherries, it can be seen that with the reduction of the step, the values of A,B,C coefficients approach the values obtained with SAS software but the determined coefficient R^2 became higher. The application of estimation other than QuasiNewton does not result in the improvement of R^2 coefficient and even no solution can be achieved.

None of the equations described the equilibrium moisture content *M* data for the entire range of equilibrium relative humidity (φ), because mean relative percent error (P) is higher than 5% and standard error of moisture content *(SEM)* is higher than 10%. But it is another problem.

The differences in coefficient selection for the equations with the use of SAS and STATISTICA programs can result from the fact of different methods of application. In SAS software, Levenberg-Marquardt method is used, as standard to search fit for nonlinear models. However there is no possibility to change step.

CONCLUSIONS

1. For the same relative air humidity φ, equilibrium moisture content *M*, calculated in program SAS is always lower. Otherwise, for the same equilibrium moisture content M, relative air humidity φ, is always higher.
2. The discrepancies in calculation of material moisture in wet mass approach even 36% in relative error and 8% in absolute error.
3. The temperature is lower, the errors in calculation of M are higher, when software SAS was used. No kind of material seems to have the influence on the errors in calculations.
4. The application of the iterration step, smaller than nominal, in STATISTICA software resulted in better coincidence of approximation results for the both programs.
5. There is a necessity of elaboration of unified procedure for mathematical processing of experimental data of equilibrium humidity of plant material.

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BŁĘDY APROKSYMACJI IZOTERM SORPCJI WYBRANYMI RÓWNANIAMI PRZY UŻYCIU RÓŻNYCH PROGRAMÓW OBLICZENIOWYCH

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Streszczenie. W pracy przedstawiono wyniki analizy porównawczej aproksymacji czterech danych pomiarowych, znanymi w literaturze równaniami, przy użyciu dwóch pakietów statystycznych SAS i STATISTICA. Stwierdzono, że występowały różnice w obliczonych współczynnikach do równań i błędach aproksymacji. Przy zastosowaniu równań GAB, Halsey, Oswin, różnice te były jednak małe, natomiast dla równania Chung-Pfosta, a w szczególności Hendersona, różnice były już duże, wynoszące 8 % błędu bezwzględnego i 36 % błędu względnego obliczania wilgotności równowagowej materiału w masie wilgotnej, przy użyciu obu programów. Różnice się zwiększały wraz ze zmniejszaniem się temperatury. Zastosowanie w programie STATISTICA mniejszego kroku obliczeń, aniżeli nominalny, prowadzi do większej zgodności wyników aproksymacji dla obu programów. Stwierdzone różnice oznaczają konieczność opracowania jednolitej metodyki opracowywania danych pomiarowych.

Słowa kluczowe: równowagowa zawartość wody, równowagowa wilgotność względna, SAS, STATISTICA.