Research article

Institute of Brewing & Distilling

Received: 23 July 2015 Revised: 3 November 2015 Accepted: 3 November 2015 Published online in Wiley Online Library: 6 January 2016

(wileyonlinelibrary.com) DOI 10.1002/jib.294

PLSR modelling of quality changes of lager and malt beer during storage

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The aim of this research was to create mathematical models for describing the changes in beer properties by using two chemometric methods applied on the experimental data. The models are intended to be useful and trustworthy for calculating four beer properties based on three easily measured ones. For that purpose, lager and malt beer were packaged in glass bottles, while lager beer was also packaged in polyethylene terephthalate (PET). Samples were placed at room temperature in the dark for 6 months. Fifteen physical and chemical properties of the beer were measured before bottling, immediately after bottling and once per month for the next 6 months. Standard MEBAK and Analytica-EBC methods of analysis were applied. During the 6 month period, seven properties changed >1%. Two partial least squares regression methods [polynomial regression, partial least squares regression with polynomial regression (PLSR-PR) and response surface method (PLSR-RSM)] were used for modelling the relationships amongst multivariate measurements. Models with high statistical significance were determined and two PLSR methods were compared. Both chemometric methods were found to be suitable for modelling physical and chemical changes in the beers during their commercial shelf-life. The PLS-RSM method was found to be the more precise and confident method in describing property changes for lager and malt beer in glass bottles, while the polynomial regression model was found to be better for the lager beer packaged in PET. The R^2 values determined for polynomial regression model were up to 0.939, while for the random surface method model the values were up to 1.000.

Keywords: beer; storage; PLSR; glass; PET

Introduction

Some degradation changes in beer occur during its shelf-life *(1–7)*. Previous research has shown that the intensity and impact of these changes differ in different beer types and packages *(4,8–10)*.

Analytical methods are both expensive and time consuming. Therefore, some mathematical models used in beer and malt technology have been investigated in the last few decades *(11–15)*. Often the result of modelling is a reduced number of necessary analyses and sources of variability. Consequently, mathematical and statistical methods have became important and useful tools in the field of science and engineering, especially the partial least square method.

The partial least squares regression (PLSR) method is in general simpler multiple linear regression *(16–20)*. It is adequate for use, especially in experiments with a large number of measured variables on a small number of highly correlated samples *(18)*. This method has become a standard tool in chemometrics for modelling linear relations between multivariate measurements *(20)*. It originated around 1975 with Herman Wold and was used in scientific research a few years later *(15,21,22)*. Since then, partial least squares methods have been used for predicting variables consisting of many different measurements in experiments in which relationships among these variables were not clear *(23)*.

The method is now routinely used as an exploratory analysis tool for selecting suitable predictor variables in a many different tasks *(24)*. Research has been conducted in the detection and quantification of the adulteration of sesame and vegetable oils *(25)*, for selecting optimal wavelength intervals for an optical sensor for milk fat and total protein analysis *(26)*, for the prediction of raspberry puree quality *(27)*, for correlating physical and chemical properties of pork ham *(28)* and in other areas of the food industry. In general, the precision of model parameters improves with the increasing number of relevant variables and observations *(21)*.

In this research, PLSR methods were used to create mathematical models that can be used instead of the more expensive, slow and complex analysis methods used during measurement of the shelf life of beer. Statistica version 12 was used for the statistical analysis and for modelling *(29)*. The null hypothesis in this research was that it is possible to calculate values of chosen beer properties using mathematical models applied on measured data of other analysed properties. Models are intended to be useful and trustworthy in calculating four beer properties based on the three easily measured properties.

The partial least squares regression methods with polynomial regression (PLSR-PR) and with response surface method (PLSR-RSM) was used. PLSR coefficients between measured matrices of data were calculated and used in creating mathematical models for calculating the values of four beer properties during a 6 month period of storage. The correlation coefficients between the measured and calculated values were also determined.

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In this research, the sensory testing of beer samples and the chemical analysis of easily volatilized compounds were also conducted and these results will be published in a future paper.

Materials and methods

Lager and malt beer from the an industrial brewery were used. The lager beer was produced with bottom-fermenting yeast and mashing with 20% maize. The malt beer was brewed with a bottom-fermenting yeast and mashing with 100% malt (no maize). Because the polyphenol content in these beers should be significantly different, it was assumed that the intensity of changes in the lager and malt beer properties during the storage period would be different. Lager beer was filled into glass bottles (LB-GB) and into one-layer PET (LB-PET), while the malt beer was filled only into glass bottles (MB-GB). Typical storage conditions for beer were chosen in this research *(30)*. Samples were kept in a room with an average temperature of $20 \pm 0.5\,°C$, and in the absence of sunlight and UV radiation. Fifteen physical and chemical properties were analysed over the 6 months. The average time interval between two series of physical-chemical analyses was 29.28 ± 0.77 days. The small deviation was caused by the non-working days in a month.

Original and apparent extract, specific gravity, alcohol by volume, the pH value, colour, bitterness, polyphenols, haze, dissolved oxygen, carbon dioxide and foam stability were measured in all of the samples. Samples were taken from a regular industrial production. The mixing of water, detergents and cleaning agents with beer during packaging could cause a change in the original and apparent extract, specific gravity, alcohol by volume and pH value. This could jeopardize the credibility of the other properties. The authors therefore considered that all physical–chemical properties should be measured in each sample during the 6 months of storage. Analysed physical–chemical properties had a small standard deviation (besides dissolved oxygen). Based on experience, two replications were chosen to be adequate for satisfactory and statistically acceptable results.

The haze forcing test, total packaged oxygen and air in the headspace were measured in the first packaging only, while the haze forcing test was not conducted on the lager beer in PET. Standard MEBAK and Analytica-EBC methods were applied *(31,32)*. Analysed properties, the abbreviations used, units and methods of analysis are presented in Table 1.

Two beer bottles were opened for analysis on each particular day of analysis. Ninety samples in each step (30 samples of lager beer in a glass bottle, 30 samples in a PET and 30 samples of malt beer in a glass bottle) were used. Measurements with two replications for each sample and property were performed. Other samples were analysed in this research project as well but only the results for lager beer in glass bottles and PET, and the malt beer in glass bottles were chosen to be presented in this paper.

Measured values show that the original and apparent extract, specific gravity, alcohol by volume, pH value, haze forcing test, total packaged oxygen and air in headspace had not changed significantly (Table 2). Seven properties with significant changes during shelf life of beer (>1%) were chosen for model development.

PLSR-PR and PLSR-RSM have the ability to model and analyse several input and output variables together *(21,28,33–35)*. Therefore, they were used for modelling the relationship between two matrices, **X** and **Y**. The PLSR models were developed from a training set of N observations with K number of variables. Beer properties were measured for N number of times and produced a data matrix $\mathbf{X}(N \times K)$, where $K = 15$ (properties shown in Table 1) and $N = 8$ (series shown in Table 2.).

The colour of the beer, bitterness and haze values were chosen as the three x-variables used for PLSR coefficients calculation. Calculated coefficients were used as predictors for calculating values of other four (y-variables) properties (polyphenol content, dissolved oxygen, carbon dioxide and foam value). Models were over-specified by using three measured values for calculating the remaining four in all of the samples. The concept was to use an identical approach for both of the PLSR methods and for all three samples (LB-GB, LB-PET and MB-GB). Regression coefficients for both beer samples and both packagings were calculated. Models were created, evaluated and mutually compared. The results are presented in the tables and line plots of multiple variables.

Table 1. Physical and chemical properties of beer measured in samples

	Properties	Abbreviations	Units	Methods
1	Original extract	OE	°Plato	MEBAK 2.13.16.1
2	Apparent extract	AE	°Plato	MEBAK 2.13.16.1
3	Specific gravity	SG	g/mL	MEBAK 2.13.16.1
4	Alcohol by volume	AB	ml 100/mL	MEBAK 2.13.16.1
5	pH value	pH		MEBAK 2.17
6	Colour	CL	EBC	MEBAK 2.16.2
7	Bitterness	BI	BU	MEBAK 2.22.1
8	Polyphenols	PY	mg/L	MEBAK 2.21.1
9	Haze	HZ	EBC	MEBAK 2.19.1.2
10	Haze forcing test	HF	EBC	Analytica-EBC 9.30
11	Dissolved oxygen	DO	ppb	Analytica-EBC 9.37
12	Total packaged oxygen	TPO	ppb	Analytica-EBC 11.5
13	Carbon dioxide	CO	g/L	MEBAK, 2.35.1.1
14	Foam	FO	min	MEBAK, 2.23.1
15	Air in headspace	AI	mL	MEBAK, 2.37.2.4

Table 2. Measured values of physical and chemical properties and basic statistics (*N* = 2)

	Measured values (series)								Changes (0–1)				Changes (1–7)			
	0	1	2	3	4	5	6	7	Average	Standard deviation	CV	(%)	Average	Standard deviation	CV	(%)
OE_1	10.98	10.98	11.02	11.02	10.94	10.98	10.96	10.98	10.98	0.00	0.00	0.00	10.98	0.03	0.27	0.00
AE_1	2.14	2.14	2.16	2.18	2.14	2.15	2.14	2.15	2.14	0.00	0.00	0.00	2.15	0.01	0.68	0.47
SG_1	1.01								1.01	0.00	0.00	0.00	1.01	0.00	0.00	0.00
AB_1	4.69	4.68	4.69	4.69	4.68	4.69	4.67	4.68	4.69	0.01	0.15	−0.21	4.68	0.01	0.16	0.00
pH_1	4.4								4.40	0.00	0.00	0.00	4.40	0.00	0.00	0.00
CL_1	6.6	6.6	6.8	7.8	7.5	7.5	7.5	7.5	6.60				7.31	0.44	5.98	**13.64**
BI_1	19	19	18	19	19	18	19	18	19.00				18.57	0.53	2.88	**−5.26**
PY_1	97	97	95	104	104	105	104	102	97.00				101.57	3.95	3.89	**5.15**
HZ_1	0.37	0.27	0.28	0.29	0.29	0.31	0.35	0.4	0.32	0.07	22.10	**−27.03**	0.31	0.05	14.85	**48.15**
DO_1	74	35	30	29	29	29	29	29	54.50	27.58	50.60	**−52.70**	30.00	2.24	7.45	**−17.14**
CO_1	5.13	5.32	5.1	5.36	5.24	5.34	5.37	5.24	5.23	0.13	2.57	**3.70**	5.28	0.10	1.82	**−1.50**
FO_1	0	9	8	9	9	9	8	9					8.71	0.49	5.60	
OE_2	10.98	10.98	10.98	11.05	11.02	11.05	10.96	10.99	10.98				11.00	0.04	0.33	0.09
AE_2	2.14	2.14	2.16	2.17	2.16	2.15	2.14	2.15	2.14				2.15	0.01	0.52	0.47
SG_2	1.01								1.01				1.01			
AB_2	4.69	4.69	4.68	4.69	4.69	4.68	4.67	4.68	4.69				4.68	0.01	0.16	−0.21
pH_2	4.4								4.40				4.40			
CL_2	6.6	6.6	7.8	8.8	9.5	10	10.1	10.6	6.60				9.06	1.43	15.77	**60.61**
BI_2	19	19	19	18	18	18	18	17	19.00				18.14	0.69	3.80	**−10.53**
PY_2	97	97	91	103	104	105	105	103	97.00				101.14	5.24	5.18	**6.19**
HZ_2	0.37	0.33	0.29	0.32	0.44	0.52	1.6	3.07	0.35	0.03	8.08	**−10.81**	0.94	1.05	111.56	**830.30**
DO_2	74	40	50	53	78	90	100	118	57.00	24.04	42.18	**−45.95**	75.57	28.98	38.35	**195.00**
CO_2	5.13	5.36	4.64	4.45	4.18	4.09	3.96	3.7	5.25	0.16	3.10	**4.48**	4.34	0.55	12.57	**−30.97**
FO_2	0	9	6	6	6	6	5	4					6.00	1.53	25.46	**−55.56**
OE_3	11.47	11.47	11.43	11.45	11.47	11.48	11.46	11.42	11.47				11.45	0.02	0.19	−0.44
AE_3	2.6	2.59	2.58	2.59	2.6	2.6	2.6	2.59	2.60	0.01	0.27	−0.38	2.59	0.01	0.29	
SG_3	1.01								1.01				1.01			
AB_3	4.72	4.72	4.71	4.72	4.72	4.73	4.71	4.7	4.72				4.72	0.01	0.21	−0.42
pH_3	4.5								4.50				4.50			
CL_3	6.6	6.6	6.6	7.15	7.7	7.8	8.2	9	6.60				7.58	0.87	11.51	**36.36**
BI_3	17	17	17	16.5	16	16	17	17	17.00				16.64	0.48	2.86	
PY_3	157	157	157	157.5	158	150	159	157	157.00				156.50	2.96	1.89	
HZ_3	0.4	0.3	0.31	0.34	0.36	0.38	0.43	0.55	0.35	0.07	20.20	**−25.00**	0.38	0.09	22.63	**83.33**
DO_3	90	50	50	50	47	40	40	40	70	28.28	40.41	**−44.44**	45,29	5,06	11,17	**−20**
CO_3	5	5.34	5.1	5	5.1	5.2	5.04	5.16	5.17	0.24	4.65	**6.80**	5.13	0.11	2.20	**−3.37**
FO_3	0	9	9	9	9	8	8	8					8.57	0.53	6.24	**−11.11**

Explanations: '_1' in the first column stands for a lager beer in a glass bottle (LB-GB); '_2' for a lager beer in a PET (LB-PET); and '_3' for a malt beer in a glass bottle (MB-GB); CV, coefficient of variability; (%), change in percentage between values in series 1 and 7; zero values and changes <1% are omitted from the table.

Results and discussion

Analyses of fresh beer before transfer into packaging (series 0), immediately after (series 1) and once per month during 6 months storage period (series 2–7) were conducted. The results are presented in Table 2.

Measured values for series 1–7, presented in Table 2, were used for generating the PLSR polynomial and response surface method

Table 3. Eigenvalues of correlation matrix, and related statistics calculated by principal component analysis (PCA) method for series 1

Property	Eigenvalue	Total variance (%)	Cumulative eigenvalue	Cumulative (%)
CL_1	1.519870	50.66235	1.519870	50.66235
BI_1	1.098185	36.60615	2.618055	87.2685
HZ_1	0.381945	12.73150	3.000000	100.0000

Table 4. Eigenvalues of covariance matrix, and related statistics calculated by PCA method for Series 1

Property	Eigenvalue	Total variance (%)	Cumulative eigenvalue	Cumulative (%)
CL_1	0.291520	60.82205	0.291520	60.82205
BI_1	0.186396	38.88915	0.477916	99.7112
HZ_1	0.001384	0.28879	0.479300	100.0000

Table 5. Partial least squares regression with polynomial regression (PLSR-PR) predictors and correlation coefficients for LB-GB

Property	*x*-Intercept	CL_1	CL_1^2	BI_1	BI_1^2	HZ_1	HZ_1^2
PY_1	−198.139	57.164	−3.50687	0.655503	0.017716	310.361	−457.250
DO_1	395.433	−102.198	6.80597	0.531779	0.014372	3.086	10.437
CO_1	30.050	−8.619	0.59767	0.024744	0.000669	32.334	−46.151
FO_1	26.837	1.819	−0.05792	−0.005268	−0.000142	−167.558	243.132

Table 6. PLSR-PR predictors and correlation coefficients for LB-PET

Property	*x*-Intercept	CL_2	CL_2^2	BI_2	BI_2^2	HZ_2	HZ_2^2
PY_2	391.139	−22.894	1.258	−7.035	−0.185	9.150	−4.449
DO_2	64.693	−62.211	4.927	2.504	0.341	1.099	1.567
CO_2	17.033	−1.585	0.068	−0.191	−0.002	0.072	−0.076
FO_2	80.014	−11.030	0.592	−1.233	−0.001	−0.310	−0.355

Table 7. PLSR-PR predictors and correlation coefficients for MB-GB

Property	*x*-Intercept	CL_3	CL_3^2	BI_3	BI_3^2	HZ_3	HZ_3^2
PY_3	−1425.83	90.7150	−4.43842	154.5143	−4.33907	−878.235	780.481
DO_3	−1982.85	117.3593	−7.27353	210.8140	−6.26181	−970.444	1042.200
CO_3	96.69	−5.3537	0.39404	−8.6086	0.25902	−4.805	−3.724
FO_3	−166.57	10.2559	−0.55856	18.6885	−0.55268	−120.657	118.601

Table 8. PLSR-RSM predictors and correlation coefficients for LB-GB

Property	*x*-Intercept	BI_1	BI_1^2	HZ_1	HZ_1^2	CL_1	CL_1^2	BI_1*HZ_1	BI_1*CL_1	HZ_1*CL_1
PY_1	−891.758	24.468	0.661	623.807	−959.364	172.465	−6.466	−33.822	−5.158	84.374
DO_1	−28.480	14.465	0.391	1.763	−112.423	−21.692	5.234	−7.870	−3.520	29.295
CO_1	3.007	0.944	0.026	1.046	−40.446	−2.255	0.466	0.447	−0.273	2.470
FO_1	−167.695	6.353	0.172	87.602	49.150	28.043	−0.638	−13.226	−1.197	15.410

Table 9. PLSR-RSM predictors and correlation coefficients for LB-PET

Property	*x*-Intercept	CL_2	CL_2^2	BI_2	BI_2^2	HZ_2	HZ_2^2	CL_2*BI_2	CL_2*HZ_2	BI_2*HZ_2
PY_2	280.845	−4.565	1.055	−3.268	−0.107	3.751	−4.755	−0.811	0.079	0.294
DO_2	−267.791	−8.773	4.334	14.400	0.551	3.899	0.037	−2.367	0.190	−0.078
CO_2	9.410	−0.350	0.054	0.078	0.003	0.082	−0.106	−0.054	0.000	0.003
FO_2	24.793	−2.153	0.490	0.733	0.033	0.369	−0.585	−0.389	−0.014	−0.002

Table 10. PLSR-RSM predictors and correlation coefficients for MB-GB

Property	*x*-Intercept	CL_3	CL_3^2	BI_3	BI_3^2	HZ_3	HZ_3^2	CL_3*BI_3	CL_3*HZ_3	BI_3*HZ_3
PY_3	−20.207	−14.428	−2.478	33.926	−1.935	−834.349	794.740	4.876	−23.164	8.273
DO_3	−6.027	−24.979	−3.814	39.642	−2.663	−966.726	1012.667	5.900	−30.549	15.966
CO_3	9.688	0.514	0.210	−1.195	0.105	8.097	−3.283	−0.216	1.849	−1.690
FO_3	3.773	−2.549	−0.328	4.070	−0.261	−113.816	119.572	0.597	−2.637	0.865

models of changes. As expected, differences between samples during storage were found to be statistically significant. It was also noted that six properties changed by >1% of their initial values in the LB-GB, seven properties in the LB-PET and four in the MB-GB. Seven properties changed significantly in all samples that were chosen for model development.

The principal components analysis (PCA) method was used for checking the predictive potential of three easily measured properties, in calculating values of the four other properties. Eigenvalues of correlation and covariance matrix and related statistics for series 1, presented in Table 3 and 4, confirmed values of beer colour, bitterness and haze as confident and sufficient predictors of polyphenol content, dissolved oxygen, carbon dioxide and foam values. These three predictors explained 100% variance in all three of the analysed samples. Model overfitting was noticed. Repeated PCA analysis showed for all samples that even two of three predictors were enough to explain 100% of the variance.

Regression coefficients (predictors) and calculated values of four beer properties were calculated using Statistica version 12 (data analysis software system). Results for PLSR-PR models are presented in Tables 5–7 and for PLSR-RSM models in Tables 8–10.

For lager beer in glass bottles, PY, DO, CO and FO values can be calculated using predictors from the Table 5, as follows in this example:

$$PY = -198.139 + 57.164*CL - 3.50687*CL^2 + 0.655503*BI + 0.017716*BI^2 + 310.361*HZ - 457.250*HZ^2$$

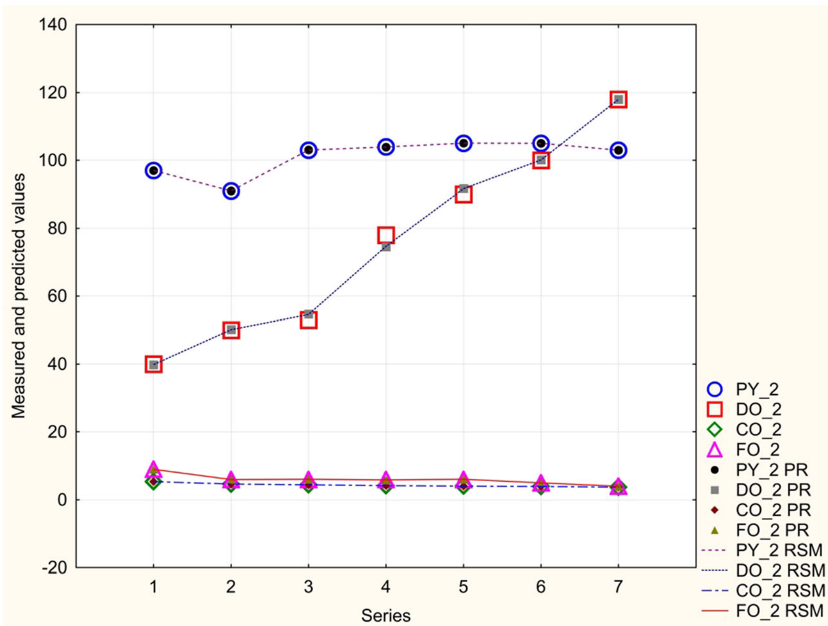

Figure 1. Lager beer in a PET – measured property values and values calculated by partial least squares regression (PLSR) models.

Table 11. Descriptive statistics for LB – GB model parameters

Variable	Mean	Confidence −95.000%	Confidence 95.000%	Minimum	Maximum	Standard deviation	Confidence SD, −95.000%	Confidence SD, +95.000%	Standard error
PY_1	101.5714	99.37908	103.7638	95.00000	105.0000	3.797049	2.752686	6.117207	1.014804
DO_1	30.0000	28.75958	31.2404	29.00000	35.0000	2.148345	1.557451	3.461074	0.574169
CO_1	5.2814	5.22818	5.3347	5.10000	5.3700	0.092225	0.066859	0.148579	0.024648
FO_1	8.7143	8.44360	8.9850	8.00000	9.0000	0.468807	0.339864	0.755268	0.125294
PY_1 PR	101.5714	99.50598	103.6369	95.69749	104.7921	3.577257	2.593346	5.763113	0.956062
DO_1 PR	30.0000	28.82758	31.1724	27.97399	34.2822	2.030569	1.472069	3.271333	0.542692
CO_1 PR	5.2814	5.23505	5.3278	5.17153	5.3982	0.080326	0.058232	0.129408	0.021468
FO_1 PR	8.7143	8.52706	8.9015	8.21066	9.2078	0.324271	0.235081	0.522414	0.086665
PY_1 RSM	101.5714	97.91635	105.2265	95.00000	105.0000	3.952094	2.546703	8.702772	1.493751
DO_1 RSM	30.0000	27.93198	32.0680	29.00000	35.0000	2.236068	1.440907	4.923970	0.845154
CO_1 RSM	5.2814	5.19265	5.3702	5.10000	5.3700	0.095991	0.061856	0.211379	0.036281
FO_1 RSM	8.7143	8.26301	9.1656	8.00000	9.0000	0.487950	0.314432	1.074498	0.184428

* Abbreviations: DO_1, Dissolved oxygen; CO_1, carbon dioxide; FO_1, foam stability; PY_1, measured value; PY_1 PR, value calculated by applying PLSR-PR model; PY_1 RSM, value calculated by applying PLSR-RSM model. Rest of the variables are named in the same way.

Table 12. Descriptive statistics for LB-PET model parameters

Variable	Mean	Confidence, −95.000%	Confidence, 95.000%	Minimum	Maximum	Standard deviation	Confidence SDm −95.000%	Confidence SD, +95.000%	Standard error
PY_2	101.5714	99.37908	103.7638	95.00000	105.0000	3.79705	2.75269	6.11721	1.01480
DO_2	30.0000	28.75958	31.2404	29.00000	35.0000	2.14834	1.55745	3.46107	0.57417
CO_2	5.2814	5.22818	5.3347	5.10000	5.3700	0.09223	0.06686	0.14858	0.02465
FO_2	8.7143	8.44360	8.9850	8.00000	9.0000	0.46881	0.33986	0.75527	0.12529
PY_2 PR	101.3571	98.83192	103.8824	91.00403	105.0478	4.37357	3.17064	7.04601	1.16889
DO_2 PR	52.7857	35.01198	70.5594	27.97399	117.9751	30.78327	22.31645	49.59316	8.22718
CO_2 PR	4.8107	4.45525	5.1662	3.70021	5.3982	0.61565	0.44632	0.99184	0.16454
FO_2 PR	7.3571	6.33866	8.3756	3.99916	9.2078	1.76397	1.27880	2.84183	0.47144
PY_2 RSM	101.1429	96.29522	105.9905	91.00403	105.0478	5.24156	3.37763	11.54226	1.98112
DO_2 RSM	75.5714	48.81081	102.3321	39.83573	117.9751	28.93523	18.64567	63.71728	10.93649
CO_2 RSM	4.3400	3.83578	4.8442	3.70021	5.3614	0.54519	0.35132	1.20055	0.20606
FO_2 RSM	6.0000	4.58820	7.4118	3.99916	8.9945	1.52652	0.98368	3.36150	0.57697

Table 13. Descriptive statistics for MB-GB model parameters

Variable	Mean	Confidence, −95.000%	Confidence, 95.000%	Minimum	Maximum	Standard deviation	Confidence SD, −95.000%	Confidence SD, +95.000%	Standard error
PY_3	129.0357	112.4662	145.6053	95.0000	159.0000	28.69767	20.80449	46.23317	7.669775
DO_3	37.6429	32.5758	42.7099	29.0000	50.0000	8.77590	6.36213	14.13835	2.345459
CO_3	5.2079	5.1349	5.2808	5.0000	5.3700	0.12638	0.09162	0.20360	0.033777
FO_3	8.6429	8.3558	8.9300	8.0000	9.0000	0.49725	0.36048	0.80108	0.132894
PY_3 PR	129.0357	112.4874	145.5841	95.6975	159.0706	28.66096	20.77788	46.17403	7.659964
DO_3 PR	37.6429	32.6136	42.6722	27.9740	51.7234	8.71052	6.31473	14.03302	2.327985
CO_3 PR	5.2079	5.1429	5.2728	5.0030	5.3982	0.11248	0.08154	0.18121	0.030061
FO_3 PR	8.6429	8.4039	8.8818	7.9887	9.2488	0.41382	0.30000	0.66668	0.110598
PY_3 RSM	156.5000	154.1598	158.8402	151.7630	159.0114	2.53037	1.63055	5.57204	0.956389
DO_3 RSM	45.2857	40.7386	49.8329	39.9395	51.3203	4.91667	3.16827	10.82683	1.858326
CO_3 RSM	5.1343	5.0443	5.2242	4.9801	5.2758	0.09725	0.06267	0.21415	0.036756
FO_3 RSM	8.5714	8.1075	9.0354	7.9906	9.2060	0.50167	0.32327	1.10472	0.189614

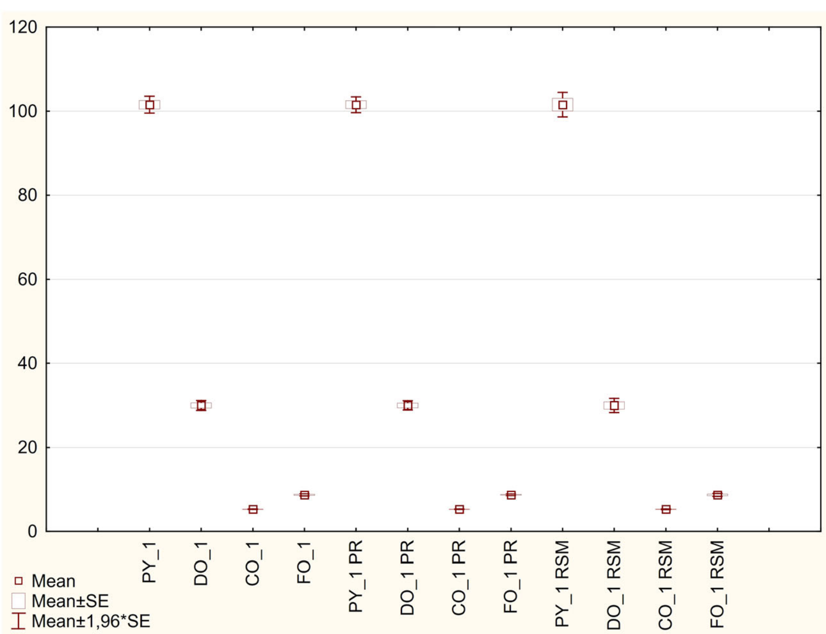

Figure 2. Box–whisker plot for lager beer in a glass bottle (LB-GB).

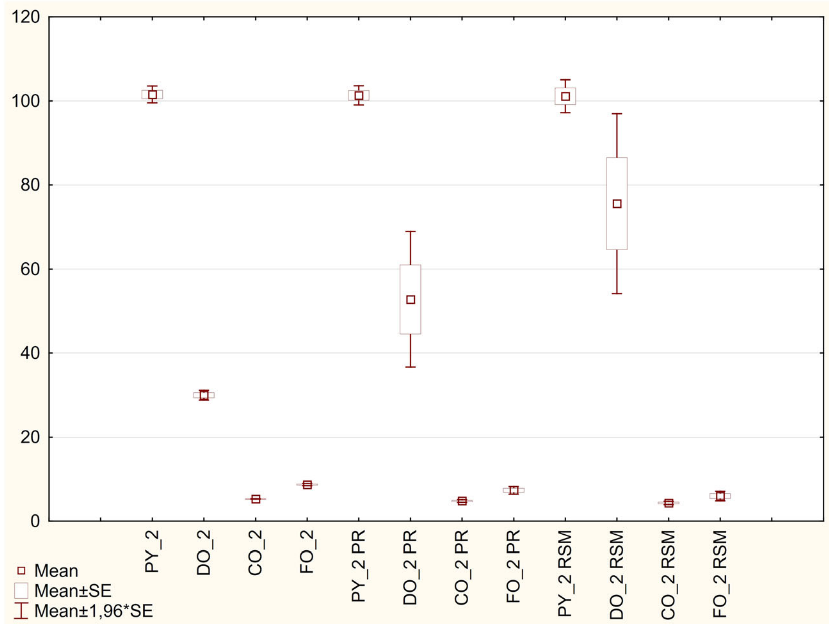

Figure 3. Box–whisker plot for lager beer in a PET (LB-PET).

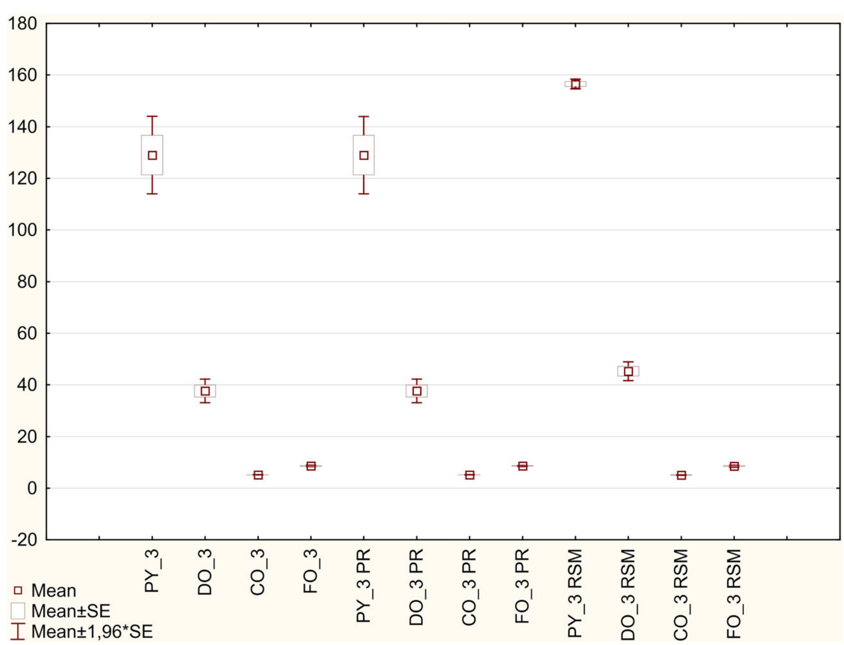

Figure 4. Box–whisker plot for malt beer filled into glass bottles (MB-GB).

Table 14. Skewness for measured and calculated values

Variable	LB-GB			LB-PET			MB-GB		
	Measured	PLSR-PR	PLSR-RSM	Measured	PLSR-PR	PLSR-RSM	Measured	PLSR-PR	PLSR-RSM
CL_	−0.67860			−0.60969			0.36546		
BI_	−0.33050			−0.18135			−0.64816		
HZ_	1.07705			1.47936			1.14157		
PY_	−0.75893	−0.85164	−1.11873	−1.11797	−1.32147	−1.55898	−1.82702	−0.01596	−1.13661
DO_	1.71072	1.46681	2.50440	0.20296	1.12439	0.22970	−0.23498	0.37426	0.05526
CO_	−0.98506	0.42691	−1.23354	0.75920	−0.65482	1.08758	0.65525	−0.06328	−0.38898
FO_	−0.98173	0.01036	−1.22963	0.84155	−0.59336	1.17088	−0.35052	−0.23362	−0.07103

Table 15. Evaluated adjusted correlation coefficients for LB-GB model

Variable *x* and variable y	Mean	Standard deviation	*r*(*x*, *y*)	r^2	*t*	*p*	*N*	Constant dep: *y*	Slope dep: *y*	Constant dep: *x*	Slope dep: *x*
PY_1	101.5714	3.952094									
PY_1 PR	101.5714	3.723327	0.942115	0.887581	6.28302	0.001501	7	11.4186	0.88758	−0.0000	1.00000
PY_1	101.5714	3.952094									
PY_1 RSM	101.5714	3.952094	1.000000	1.000000			7	0.0000	1.00000	−0.0000	1.00000
DO_1	30.0000	2.236068									
DO_1 PR	30.0000	2.113484	0.945179	0.893363	6.47208	0.001312	7	3.1991	0.89336	−0.0000	1.00000
DO_1	30.0000	2.236068									
DO_1 RSM	30.0000	2.236068	1.000000	1.000000			7	−0.0000	1.00000	0.0000	1.00000
CO_1	5.2814	0.095991									
CO_1 PR	5.2814	0.083606	0.870973	0.758594	3.96384	0.010702	7	1.2750	0.75859	−0.0000	1.00000
CO_1	5.2814	0.095991									
CO_1 RSM	5.2814	0.095991	1.000000	1.000000			7	0.0000	1.00000	−0.0000	1.00000
FO_1	8.7143	0.487950									
FO_1 PR	8.7143	0.337512	0.691693	0.478439	2.14164	0.085141	7	4.5450	0.47844	−0.0000	1.00000
FO_1	8.7143	0.487950									
FO_1 RSM	8.7143	0.487950	1.000000	1.000000			7	−0.0000	1.00000	0.0000	1.00000
PY_1 PR	101.5714	3.723327									
PY_1 RSM	101.5714	3.952094	0.942115	0.887581	6.28302	0.001501	7	0.0000	1.00000	11.4186	0.88758
DO_1 PR	30.0000	2.113484									
DO_1 RSM	30.0000	2.236068	0.945179	0.893363	6.47208	0.001312	7	−0.0000	1.00000	3.1991	0.89336
CO_1 PR	5.2814	0.083606									
CO_1 RSM	5.2814	0.095991	0.870973	0.758594	3.96384	0.010702	7	−0.0000	1.00000	1.2750	0.75859
FO_1 PR	8.7143	0.337512									
FO_1 RSM	8.7143	0.487950	0.691693	0.478439	2.14164	0.085141	7	−0.0000	1.00000	4.5450	0.47844

Table 16. Evaluated adjusted correlation coefficients for LB-PET model

Variable *x* and variable y	Mean	Standard deviation	*r*(*x*, *y*)	r^2	*t*	*p*	*N*	Constant dep: *y*	Slope dep: *y*	Constant dep: *x*	Slope dep: *x*
PY_2	101.5714	3.95209									
PY_2 PR	101.1429	5.24129	0.969506	0.939943	8.8461	0.000307	7	−29.454	1.2858	27.632	0.7310
PY_2	101.5714	3.95209									
PY_2 RSM	101.1429	5.24156	0.969298	0.939538	8.8145	0.000312	7	−29.433	1.2856	27.652	0.7308
DO_2	30.0000	2.23607									
DO_2 PR	75.5714	28.93075	−0.618568	0.382626	−1.7603	0.138661	7	315.667	−8.0032	33.613	−0.0478
DO_2	30.0000	2.23607									
DO_2 RSM	75.5714	28.93523	−0.617831	0.381715	−1.7570	0.139269	7	315.417	−7.9949	33.608	−0.0477
CO_2	5.2814	0.09599									
CO_2 PR	4.3400	0.54524	−0.076712	0.005885	−0.1720	0.870153	7	6.641	−0.4357	5.340	−0.0135
CO_2	5.2814	0.09599									
CO_2 RSM	4.3400	0.54519	−0.078024	0.006088	−0.1750	0.867945	7	6.680	−0.4431	5.341	−0.0137
FO_2	8.7143	0.48795									
FO_2 PR	6.0000	1.52597	0.220989	0.048836	0.5067	0.633930	7	−0.022	0.6911	8.290	0.0707
FO_2	8.7143	0.48795									
FO_2 RSM	6.0000	1.52652	0.221920	0.049249	0.5089	0.632464	7	−0.050	0.6943	8.289	0.0709
PY_2 PR	101.1429	5.24129									
PY_2 RSM	101.1429	5.24156	0.999990	0.999979	492.2255	0.000000	7	−0.004	1.0000	0.006	0.9999
DO_2 PR	75.5714	28.93075									
DO_2 RSM	75.5714	28.93523	0.999996	0.999991	758.6917	0.000000	7	−0.011	1.0002	0.012	0.9998
CO_2 PR	4.3400	0.54524									
CO_2 RSM	4.3400	0.54519	0.999994	0.999989	664.0256	0.000000	7	0.000	0.9999	−0.000	1.0001
FO_2 PR	6.0000	1.52597									
FO_2 RSM	6.0000	1.52652	0.999961	0.999922	252.7646	0.000000	7	−0.002	1.0003	0.002	0.9996

Table 17. Evaluated adjusted correlation coefficients for MB-GB model

Variable *x* and variable y	Mean	Standard deviation	*r*(*x*, *y*)	r^2	*t*	*p*	*N*	Constant dep: *y*	Slope dep: *y*	Constant dep: *x*	Slope dep: *x*
PY_3	156.5000	2.958040									
PY_3 PR	156.5000	2.437991	0.824191	0.679291	3.25430	0.022588	7	50.1909	0.67929	0.0000	1.00000
PY_3	156.5000	2.958040									
PY_3 RSM	156.5000	2.530367	0.855420	0.731744	3.69309	0.014100	7	41.9821	0.73174	0.0000	1.00000
DO_3	45.2857	5.056820									
DO_3 PR	45.2857	4.860814	0.961239	0.923981	7.79571	0.000556	7	3.4426	0.92398	0.0000	1.00000
DO_3	45.2857	5.056820									
DO_3 RSM	45.2857	4.916668	0.972285	0.945337	9.29893	0.000242	7	2.4754	0.94534	0.0000	1.00000
CO_3	5.1343	0.112969									
CO_3 PR	5.1343	0.088274	0.781402	0.610590	2.79999	0.037994	7	1.9993	0.61059	0.0000	1.00000
CO_3	5.1343	0.112969									
CO_3 RSM	5.1343	0.097248	0.860838	0.741043	3.78262	0.012855	7	1.3296	0.74104	0.0000	1.00000
FO_3	8.5714	0.534522									
FO_3 PR	8.5714	0.495192	0.926419	0.858252	5.50217	0.002710	7	1.2150	0.85825	0.0000	1.00000
FO_3	8.5714	0.534522									
FO_3 RSM	8.5714	0.501672	0.938543	0.880863	6.08017	0.001740	7	1.0212	0.88086	0.0000	1.00000
PY_3 PR	156.5000	2.437991									
PY_3 RSM	156.5000	2.530367	0.992394	0.984846	18.02604	0.000010	7	−4.6944	1.03000	6.8603	0.95616
DO_3 PR	45.2857	4.860814									
DO_3 RSM	45.2857	4.916668	0.998025	0.996054	35.52438	0.000000	7	−0.4299	1.00949	0.6029	0.98669
CO_3 PR	5.1343	0.088274									
CO_3 RSM	5.1343	0.097248	0.987302	0.974765	13.89750	0.000035	7	−0.4501	1.08767	0.5330	0.89620
FO_3 PR	8.5714	0.495192									
FO_3 RSM	8.5714	0.501672	0.997135	0.994279	29.47777	0.000001	7	−0.0873	1.01018	0.1350	0.98425

where PY is the polyphenol content, value −198.139 is the *x*-intercept, and CL, BI and HZ are measured data presented in Table 2. The *x*-intercept is the point where the graph of the line crosses the *x*-axis.

The values of PY, DO, CO and FO in series 1 can be calculated applying the proposed model on the measured data of CL, BI and HZ. The correlation coefficient (*r*) between measured and data determined by model for polyphenols content (PY_1) was found to be 0.942115. The same procedure can be used for all samples (LB-GB, LB-PET and MB-GB) in each particular series of analysis.

Measured and calculated values of beer properties are illustrated in Fig. 1. Figures for the rest of the samples and the PLSR models are very similar to this one. Confidence intervals and standard error for the model parameters are presented in Tables 11–13. Box–whisker plots for measured and calculated values are presented in Figs. 2–4.

The Kolmogorow–Smirnow and Liliefors test for normality were performed. Data distribution of measured and calculated values is shown in Table 14. Normal distribution has a skewness of zero. Results in Table 14 show that the data distribution was not normal but highly skewed to the left and right (in minus and plus). This would be expected for a small sample size. Because of high skewness, the analysed data set became an ideal candidate for a nonparametric approach. Therefore nonparametric statistics was used in this paper.

The evaluated adjusted correlation coefficients for the three models are presented in Tables 15–17. The variance of measured and calculated data was found to be zero or almost zero. Therefore, the reliability of the determined PLSR models (degree of model overfitting) could not be estimated by performing cross-validation.

Conclusions

Fifteen beer properties were measured during the commercial shelf-life of a lager and a malt beer. By comparing the lager and malt beer in glass bottles, it was noticed that larger changes occurred in the lager beer immediately after filling into the bottle. In contrast, the malt beer showed the largest changes during the 6 months of storage time in the bottles.

Lager beer in PET showed larger changes than lager beer in glass bottles during the storage period. The changes for eight physical–chemical properties of the beer were <1% and were accepted as less significant, while seven properties changed >1% and thus were the ones chosen for model development. Three of the seven properties (bitterness, haze and colour) were found to be accurate predictors of the other four properties (polyphenol content, dissolved oxygen, carbon dioxide and foam). The PCA method showed model overfitting and that even two predictors could explain 100% of the variance.

The partial least squares regression methods with polynomial regression (PLSR-PR) and with response surface method (PLSR-RSM) were used to create the models of property changes. Models were used to calculate the property values immediately after filling from the bright beer tank to the bottle and then once per month during the 6 months of storage in the bottle.

Data distribution was skewed, as it would have been expected for a small set of data, and non-parametric statistics were applied. The evaluated adjusted correlation coefficients for the three models were determined. The R^2 values ranged from 0.006 to 0.939 for the polynomial regression model, while for the random surface method model they ranged from 0.006 to 1.000.

The results calculated, using PLSR-PR and PLSR-RSM models, were compared. The PLSR-RSM models were found to be more accurate in describing property changes for the lager and malt beer in glass bottles, while the polynomial regression models were found to be better for the lager beer in PET.

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