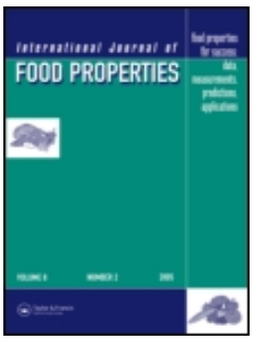

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Determination of Antioxidant Properties of Fruit Juice by Partial Least Squares and Principal Component Regression

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The multivariate calibration methods—principal component regression and partial least squares—were employed for the prediction of antioxidant capacities of fruit juices. High-performance liquid chromatography and spectrophotometric approaches were used to determine the antioxidant capacities of fruit juices. The importance of calibration design was investigated by calculating the prediction and validation errors. The influences of using independent validation sets were emphasized. Calibration design is shown to have major effect on principal component regression and partial least squares errors. The models developed on the basis of the mean-centered data were able to predict the total antioxidant activity with a precision comparable to that of the reference [2,2-azino-di-(3-ethylbenzothialozine-sulfonic acid)] method. The partial least squares model seems preferable because of its predictive and describing abilities and good interpretability of the contribution of compounds to the antioxidant capacity. The contribution of individual phenolic compounds to the antioxidant capacity was identified by high-performance liquid chromatography.

Keywords: Fruit juice, PLS, PCR, UV-VIS spectroscopy, HPLC, Antioxidant compounds.

INTRODUCTION

Fruit and fruit juice are important sources of phenolic compounds such as phenolic acids, flavonoids, and anthocyanins,[1–3] which have demonstrated considerable antioxidant properties *in vivo* and *in vitro*,[4,5] which are known to reduce lipid peroxidation mediated deterioration of foods during processing and storage[6] and which can also reduce the rate of mutagenicity resulting from oxidative stress in humans.[7] The measurement of the antioxidant capacity of food products, such as fruit and fruit juice, has become very important for researchers because it may provide information about resistance to oxidation, quantitative contribution of natural antioxidant substances.[8,9] Natural antioxidants are substances that may protect human cells against the effects of free radicals produced. Free radicals can damage cells, and may play a role in heart disease, cancer, and other diseases.[10,11] Therefore, the antioxidant compounds may play an important role in the prevention of certain diseases.[12]

Antioxidant activity has been determined by several assays such as chromium reducing antioxidant capacity (CHROMAC),[13] 2,2-azino-di-(3-ethylbenzothialozine-sulphonic acid; ABTS),

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2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging potential, cupric ion reducing antioxidant capacity (CUPRAC), ferric reducing antioxidant power (FRAP), oxygen radical absorbance capacity (ORAC), and total radical absorption potentials (TRAP) in food products.[14] These methods differ in terms of their assay principle and experimental conditions. Each method provides an estimate of antioxidant activity that is dependent on the type of assay selected and experimental conditions. Therefore, there is a need of a simple, convenient method for the fast quantization of antioxidant capacity, suitable for screening in the food and nutraceutical industry.

Multivariate chemometric methods such as partial least squares (PLS) and principal component regression (PCR) allow to extract analytical information from the full spectra/chromatograms, providing so to use simultaneously an elevated number of signals. Moreover, these techniques allow a rapid analytical response with minimum sample preparation, reasonable accuracy and precision, and without a preliminary separation step in complex matrices.[15] The multivariate chemometric methods have been involved in a wide range of studies for measurement of antioxidant capacity of plants and fruit,[16,17] identification, and quality control of herbal medicines.[18]

The aim of this work was to verify the potential use of chromatograms in the construction of multivariate calibration models relating the chromatographic profile with the antioxidant capacity of fruit juice. PCR and PLS multivariate calibration methods were successfully applied to the determination of antioxidant capacities of fruit juices. Also the potential compounds associated with the antioxidant capacity of fruit juice were identified by PLS calibration model.

MATERIALS AND METHODS

Chemicals

Trolox [(±)-6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid] and ABTS [2,2'-azinobis(3 ethylbenzothiazoline-6-sulphonic acid) diammonium salt] were purchased from Fluka (Buchs, Switzerland). HPLC grade of acetonitrile and formic acid were purchased from Merck (Merck, Darmstadt, Germany).

Fruit Juice Samples

Fruit juices were obtained from local market in Bursa, Turkey. Blueberry, cranberry, vitis vinifera, pomegranate, and cherry juices were used to achieve calibration and validation designs. The samples were stored at 4°C for analysis. The samples were analyzed by high performance liquid chromatography-diode array detection (HPLC-DAD) at 280 nm.

High-Performance Liquid Chromatography (HPLC)

An Agilent 1200 HPLC system (Waldbronn, Germany), consisting of a vacuum degasser, binary pump, autosampler, and a diode array detector, was used. Chromatographic separations were carried out using an XBridge C18 (4.6 × 250 mm, 3.5 μm) column from Waters (USA). Mobile phase consists of 1% formic acid in water (solvent A) and acetonitrile (solvent B). Gradient conditions are as follows: 0–10 min 13% B, 10–20 min 41.5% B, 20–25 min 70% B, 25–35 min 10% B, total run time is 35 min. The column was equilibrated for 10 min prior to each analysis. Flow rate was 0.5 mL/min, and injection volume was 10 mL. Data acquisition and preprocessing were carried out with Chemstation for LC (Agilent). The monitoring wavelength was 280 nm for gallic acid, chlorogenic acid, caffeic acid, rutin, ellagic acid, kaempherol glycoside, and

ferulic acid. Peaks were identified on the basis of comparison of retention times and UV-Vis spectra with standards of phenolic compounds.

ABTS Method

The antioxidant capacity of fruit juice was determined with ABTS [2,2-azino-di-(3-ethylbenzothialozine-sulfonic acid)] method as described in our previous work.[3] Spectrophotometric measurements were performed on a UV/vis spectrometer (Varian Cary 50 Conc, Australia) equipped with 10 mm quartz cuvettes. The absorbance was recorded at 734 nm against blank after 6 min. The results were expressed as mg of trolox equivalent (TE) per liter of fruit juice.

Multivariate Calibration

Two multivariate calibration methods were employed for the prediction of antioxidant capacity of fruit juices. Principal component analysis based methods do not require details about the spectra or concentrations of all the compounds in a mixture, although it is important to make a sensible estimate of how many significant components characterize a mixture. The aim is to convert these components to concentrations in multivariate calibration. PCR uses regression to convert principal component scores to concentration.[19] PLS is often presented as the major regression technique for multivariate data to express the relation between x and y. PLS uses the non-linear iterative PLS algorithm (NIPALS).[20–23]

Calibration Design

A calibration design was used for 25 samples to model the multivariate calibrations. The calibration design is based on five levels, which is coded between –2 and +2 for each compound in the mixture. Calibration and validation sets were prepared by adding x mL of blueberry, cranberry, vitis vinifera, pomegranate, cherry juices into 5-mL calibrated flasks and (5-x) mL water was added to the initial mixture so as to make the final volume 5 mL. The levels –2, –1, 0, 1 and 2 relate to 0.2, 0.4, 0.6, 0.8, and 1 mL of fruit juices. The antioxidant capacities of fruit juices at the five coded levels are shown in Table 1. The design has a value of $r_{12} = 0$, so the two vectors are orthogonal to one another.[24] The difference vector [0231] and cyclical generator –2, –1, 2, 1 were used in the calibration design. The construction of multilevel calibration designs is described in literature.[25] To see how well the calibration set predicts the antioxidant capacities of the five fruit juices, two independent validation sets were generated. The validation set 1 (Table 2) has a value of $r_{12} = 0$ and the validation set 2 (Table 3) has a value of $r_{12} = 1$. The difference vector [1320] and cyclical generator –2, –1, 2, 1 were used in the validation set 1. The two validation sets consist of 25 chromatograms. The prediction of antioxidant capacities of calibration/validation sets by PCR and PLS models was executed using MATLAB version 8.1.0.604 (R2013a; MathWorks, Inc., Natick, MA, USA).

RESULTS AND DISCUSSION

Antioxidant Capacities of Fruit Juices

After generation of calibration and validation sets, antioxidant capacities of calibration and validation sets were determined by ABTS method (Tables 1–3). The antioxidant capacity of blueberry was ranged from 0.386 to 1.930, cranberry from 0.488 to 2.442, vitis vinifera from 0.287 to 1.435, pomegranate from 0.449 to 2.243, and cherry juices from 0.301 to 1.504 mg of TE per liter of fruit juice.

TABLE 1
Antioxidant capacity of calibration set (difference vector: [0 2 3 1], repeater: –2, –1, 2, 1)

	(mg TE/L fruit juice)				
Experiment	*Blueberry*	*Cranberry*	*Vitis vinifera*	*Pomegranate*	*Cherry*
1	1.158	1.465	0.861	1.346	0.903
2	1.158	0.488	0.287	2.243	0.602
3	0.386	0.488	1.435	0.897	1.504
4	0.386	2.442	0.574	2.243	0.903
5	1.930	0.977	1.435	1.346	0.602
6	0.772	2.442	0.861	0.897	0.602
7	1.930	1.465	0.574	0.897	1.203
8	1.158	0.977	0.574	1.794	1.504
9	0.772	0.977	1.148	2.243	1.203
10	0.772	1.954	1.435	1.794	0.903
11	1.544	2.442	1.148	1.346	1.504
12	1.930	1.954	0.861	2.243	1.504
13	1.544	1.465	1.435	2.243	0.301
14	1.158	2.442	1.435	0.449	1.203
15	1.930	2.442	0.287	1.794	0.301
16	1.930	0.488	1.148	0.449	0.903
17	0.386	1.954	0.287	1.346	1.203
18	1.544	0.488	0.861	1.794	1.203
19	0.386	1.465	1.148	1.794	0.602
20	1.158	1.954	1.148	0.897	0.301
21	1.544	1.954	0.574	0.449	0.602
22	1.544	0.977	0.287	0.897	0.903
23	0.772	0.488	0.574	1.346	0.301
24	0.386	0.977	0.861	0.449	0.301
25	0.772	1.465	0.287	0.449	1.504

Selection of the Optimum Number of Components

To select the number of factors to be used in the PLS and PCR calibration models a cross-validation procedure was used. In this procedure, calibration is carried out with all calibration samples less one. The process was repeated 25 times for each number of factors until each sample has been left out once. The predicted and known antioxidant capacities of the fruit juices were compared for each giving number of factors. Then the root mean square error of cross-validation (RMSECV) was computed for PCR and PLS models with different number of components.[22]

$$\mathrm{RMSECV} = \sqrt{\frac{\sum_{i.=1}^{M} (y_i - \hat{y}_i)^2}{M}} \tag{1}$$

where, y_i is the measured antioxidant capacity of the ith sample and $\hat{y}_i$ is the predicted antioxidant capacity from a calibration equation obtained for the data without the ith sample, M is the number of the calibration samples. The optimum number of factors of the PCR and PLS model corresponds to the number of factors resulting in the lowest RMSECV.

The performance of the calibration model and its prediction ability is measured by the root mean square error (RMSE) obtained on the calibration set and root mean square error of prediction (RMSEP) obtained on the validation set, respectively.

TABLE 2
Antioxidant capacity of validation set 1 (difference vector: [1 3 2 0], repeater: –2, –1, 2)

	(mg TE/L fruit juice)				
Experiment	*Blueberry*	*Cranberry*	*Vitis vinifera*	*Pomegranate*	*Cherry*
1	1.158	1.465	0.861	1.346	0.903
2	1.158	0.488	0.574	0.449	1.504
3	0.386	0.977	0.287	2.243	1.504
4	0.772	0.488	1.435	2.243	0.903
5	0.386	2.442	1.435	1.346	0.602
6	1.930	2.442	0.861	0.897	1.504
7	1.930	1.465	0.574	2.243	0.602
8	1.158	0.977	1.435	0.897	1.203
9	0.772	2.442	0.574	1.794	1.203
10	1.930	0.977	1.148	1.794	0.903
11	0.772	1.954	1.148	1.346	1.504
12	1.544	1.954	0.861	2.243	1.203
13	1.544	1.465	1.435	1.794	1.504
14	1.158	2.442	1.148	2.243	0.301
15	1.930	1.954	1.435	0.449	0.301
16	1.544	2.442	0.287	0.449	0.903
17	1.930	0.488	0.287	1.346	1.203
18	0.386	0.488	0.861	1.794	0.301
19	0.386	1.465	1.148	0.449	1.203
20	1.158	1.954	0.287	1.794	0.602
21	1.544	0.488	1.148	0.897	0.602
22	0.386	1.954	0.574	0.897	0.903
23	1.544	0.977	0.574	1.346	0.301
24	0.772	0.977	0.861	0.449	0.602
25	0.772	1.465	0.287	0.897	0.301

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i.=1}^{M} (y_i - \hat{y}_i)^2}{M}} \tag{2}$$

$$\mathrm{RMSEP} = \sqrt{\frac{\sum_{i.=1}^{Mt} (y^t{}_i - \hat{y}^t{}_i)^2}{Mt}} \tag{3}$$

where, M and Mt are the number of samples in the calibration and validation sets, y_i^t and $\hat{y}_i^t$ denote the experimental value and the predicted value from the model for the ith sample from validation set.

In our case, it was found that the optimum number of factors for each fruit juice was five by the PCR and PLS methods (Figs. 1a and 1b). It is possible to verify that the lowest value for the RMSECV was obtained using five factors. The number of factors found and the compounds present in the mixture are the same for PCR and PLS calibration methods. In generally, it is expected to get as many factors as compounds are present in the mixture in the case of non-highly overlapped system when standards are used during the calibration step. The results confirm that the system is well modeled by the number of factors selected. The calibration design is seen to be of major importance when assessing the quality of the model.

TABLE 3
Antioxidant capacity of validation set 2

	(mg TE/L fruit juice)				
Experiment	*Blueberry*	*Cranberry*	*Vitis vinifera*	*Pomegranate*	*Cherry*
1	1.1578	1.4651	0.8611	1.3458	0.9025
2	1.1578	1.4651	0.8611	1.3458	0.9025
3	0.3859	0.4884	0.2870	0.4486	0.3008
4	0.3859	0.4884	0.2870	0.4486	0.3008
5	1.9296	2.4419	1.4351	2.2429	1.5042
6	0.7718	0.9768	0.5740	0.8972	0.6017
7	1.9296	2.4419	1.4351	2.2429	1.5042
8	1.1578	1.4651	0.8611	1.3458	0.9025
9	0.7718	0.9768	0.5740	0.8972	0.6017
10	0.7718	0.9768	0.5740	0.8972	0.6017
11	1.5437	1.9535	1.1481	1.7944	1.2033
12	1.9296	2.4419	1.4351	2.2429	1.5042
13	1.5437	1.9535	1.1481	1.7944	1.2033
14	1.1578	1.4651	0.8611	1.3458	0.9025
15	1.9296	2.4419	1.4351	2.2429	1.5042
16	1.9296	2.4419	1.4351	2.2429	1.5042
17	0.3859	0.4884	0.2870	0.4486	0.3008
18	1.5437	1.9535	1.1481	1.7944	1.2033
19	0.3859	0.4884	0.2870	0.4486	0.3008
20	1.1578	1.4651	0.8611	1.3458	0.9025
21	1.5437	1.9535	1.1481	1.7944	1.2033
22	1.5437	1.9535	1.1481	1.7944	1.2033
23	0.7718	0.9768	0.5740	0.8972	0.6017
24	0.3859	0.4884	0.2870	0.4486	0.3008
25	0.7718	0.9768	0.5740	0.8972	0.6017

PCR and PLS Analysis

Multivariate calibration models were built with data matrix x consisting of the 25 chromatograms and a response vector y representing the antioxidant capacity results. The HPLC chromatogram of calibration set was shown in Fig. 1c. PCR and PLS calibration models were obtained from calibration set described in experimental design. The aim of PCR calibration model is to convert components to concentrations in multivariate calibration. PLS calibration model was applied for simultaneous determination and removal of the interference effects of one component in the presence of the others. The predictions of antioxidant capacity by ABTS method were calculated based on the RMSE (Table 4). It can be seen that the RMSEs of the PLS based calibration model show significant improvement over PCR. The results indicate that the predicted antioxidant capacities by PLS model is close to the real antioxidant capacities for each fruit juice that reveal the validity of the proposed method. The two independent validation sets were generated with values of r_{12} at 0.0 and 1.0 to see how well the calibration set predicts the antioxidant capacities of five fruit juices. The RMSEs of the predictions by the PCR and PLS calibration models for calibration set and two validation sets are shown in Table 4. Both validation sets of results show different trend, in that RMSE values increase as the value of the correlation coefficient of the validation set increases. This indicates that a well-constructed design with r_{12} at 0.0 would give the lowest error when predicting the validation set with r_{12} at 0.0 and badly designed validation set with r_{12} at 1.0 has considerably higher error. This is because a well-constructed validation set

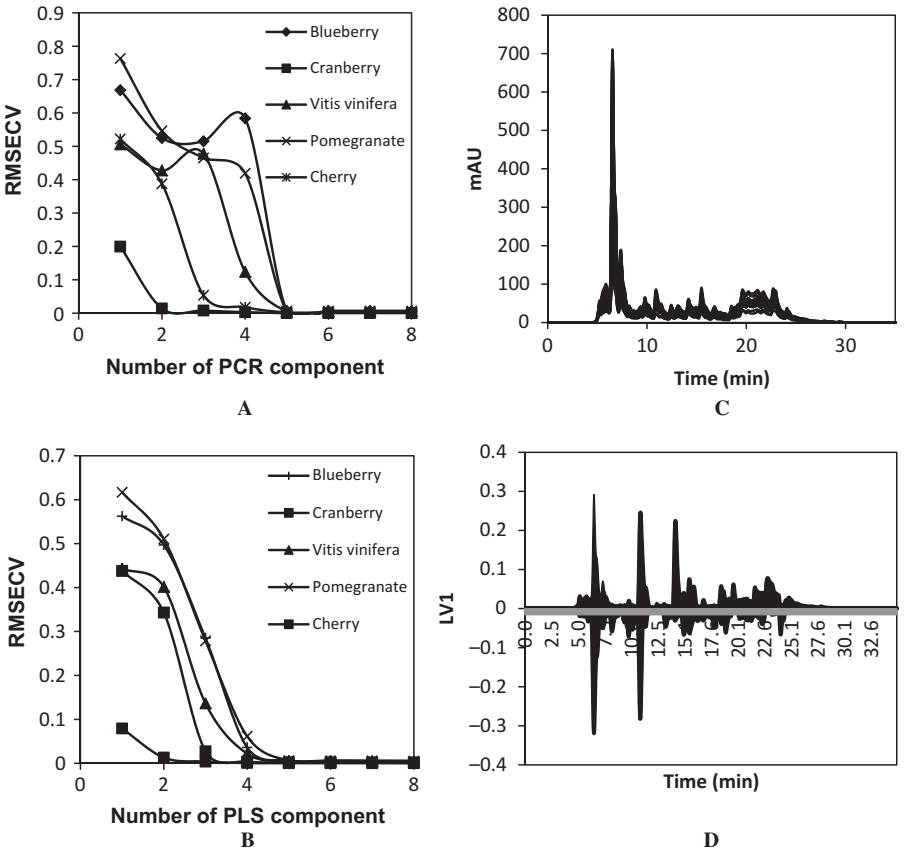

FIGURE 1 A: RMSECV as a function of number of PCR component; B: RMSECV as a function of number of PLS component; C: HPLC chromatogram of calibration set at 280 nm; D: Loadings plot for LV1 obtained by PLS calibration for antioxidant capacity.

TABLE 4
Root mean square errors for the prediction of antioxidant capacity (mg TE/L fruit juice)

		Blueberry	*Cranberry*	*V. vinifera*	*Pomegranate*	*Cherry*
PCR	Calibration set	1.1600	1.470	0.8600	1.3500	0.9000
	Validation set 1	1.2500	1.5600	0.9100	1.4300	0.9700
	Validation set 2	1.1600	1.7500	1.0300	1.6100	1.0800
PLS	Calibration set	0.5457	0.6907	0.4052	0.6254	0.4267
	Validation set 1	0.5457	0.8551	0.4056	0.6327	0.4255
	Validation set 2	0.6237	1.1301	0.6265	0.7577	0.9006

is easier to predict by a well-constructed calibration set, whereas less well-constructed validation set will be hard to predict.

One of the major aspects of this study is to identify the compounds in the fruit juices potentially responsible for the antioxidant capacity of the samples. A great deal of information can come from loadings plots. For this purpose, the loading plot for PLS model was evaluated

to investigate the contribution of phenolic compounds to the antioxidant capacity (Fig. 1d). It can be stated that the larger the loading of a phenolic compound on LV1, the larger the influence on the predicted antioxidant capacity. The peaks with negative loadings correspond to the compounds with high antioxidant capacity. Peaks at 7.7, 8.9, 10.4, 12.1, 13.1, 15.4, 17.6, 20.1, 21.1, 22.4, 22.7, 23.4, 24.5, and 26.2 min with negative PLS loadings contribute to the antioxidant capacity in samples. It was observed that seven compounds are in small and high amount present in the fruit juices. Gallic acid (peak at 7.7 min), chlorogenic acid (peak at 15.4 min), caffeic acid (peak at 20.1 min), rutin (peak at 22.4 min), ellagic acid (peak at 22.7 min), kaempherol glycoside (peak at 23.4 min), and ferulic acid (peak at 24.5 min) have negative PLS loadings. Antioxidant capacity has positive correlation with the concentration of proanthocyanidins, flavonoids, and phenolic compounds.[26] Thus, phenolic compounds might be the major components responsible for antioxidant capacity of fruit juices. The phenolic compounds (gallic acid, chlorogenic acid, caffeic acid, rutin, ellagic acid, kaempherol glycoside, and ferulic acid) determined in fruit juices seem to be responsible for antioxidant capacity. Negative PLS loadings give information about the phenolic compounds that are responsible for antioxidant capacity in fruit juices. However, in the case of mixture of phenolic compounds in fruits/plants, antioxidant capacity may not have correlation with total phenolics because of the different type of phenolic compounds, number of OH groups and their positions in phenolic compound structure. Therefore, in the case of unknown individual phenolic compounds present in the sample, it is better to explain the antioxidant capacity with the presence/absence of certain phenolic compounds. This implies that all phenolic compounds represented by a peak in the chromatogram should give antioxidant capacity proportional to their concentration. Peaks at 8.7 and 13.1 min with negative PLS loadings have high influence on the antioxidant capacity, they show high contribution to the PLS model. However these peaks have not identified.

Determination of Antioxidant Capacity of Real Samples

In order to test the applicability of the proposed method to the analysis of real samples, the method was applied to a mixture containing 25 different fruit juices. The antioxidant capacities of fruit juices were investigated and the results were summarized in Table 5. The prediction of RMSEs of PCR and PLS were 1.1245 and 0.4101, respectively. It can be seen that the results obtained by PLS method is very similar with the measured results. The PLS method was rapid, easy, and of low cost for the determination of antioxidant capacity of fruit juices in mixture.

CONCLUSION

Calibration models of PCR and PLS were constructed to model the antioxidant capacity of fruit juices from the HPLC profile and relate the peaks responsible for the antioxidant capacity. The effectiveness of PLS model for predictions of antioxidant capacities was described in the chromatograms of the fruit juices. PLS calibration model has some advantages over PCR and performs slightly better prediction. Calibration design and construction of validation set are seem to be of major importance when assessing the quality of the model. It is shown that the low correlation coefficient ($r_{12} = 0$) between the concentrations in the validation set results much lower prediction error.

By comparing the peaks in the chromatograms with the loadings of the calibration models, peaks responsible for antioxidant capacity can be identified. The application of PLS resulted in better model to predict the antioxidant capacity of fruit juices from chromatograms, and the contribution of each compound to the antioxidant capacity is easy to interpret. Peaks with major negative PLS loadings are responsible for the antioxidant capacity determined by HPLC as gallic

TABLE 5
Measured/predicted antioxidant capacities (mg TE/L fruit juice) of real samples

		Antioxidant capacity		
Sample	*Percentage of fruit (%)*	*Measured*	*PCR (RMSE = 1.1245)*	*PLS (RMSE = 0.4101)*
Strawberry	10	0.9296	0.9296	0.9390
Orange	4	1.5107	1.4683	1.5125
Apple	80	0.5619	0.5395	0.5667
Mandarin	4	1.1089	1.1868	1.1144
Mandarin	5	1.2370	1.0511	1.2439
Pomegranate	4	1.3004	1.4365	1.3011
Pear	12	0.6277	0.6349	0.6313
Lemon	16	0.5658	0.5316	0.5720
Grapefruit	18	0.3874	0.2619	0.3883
Orange	50	0.9641	0.8907	0.9767
Apricot	40	1.3644	1.3160	1.3579
Apple	100	0.8657	0.7087	0.8544
Lemon	4	0.9337	0.7237	0.9325
Strawberry	45	1.7230	1.7654	1.7213
Apricot	35	0.7284	0.7508	0.7213
Peach	50	1.0308	0.9529	1.0199
Cherry	35	1.9791	2.1650	1.9670
Peach	55	1.3882	1.2521	1.3750
Orange	55	0.7897	0.7825	0.8036
Apricot	45	0.7604	0.7946	0.7538
Apple	90	0.4224	0.5479	0.4159
Orange	60	1.5882	1.6616	1.6087
Apricot	50	0.9993	1.0477	0.9992
Cherry	30	1.5302	1.6872	1.5177
Lemon	10	1.0412	1.2512	1.0441

acid, chlorogenic acid, caffeic acid, rutin, ellagic acid, kaempherol glycoside, and ferulic acid in fruit juices. The retention time of seven peaks indicated potentially interesting compounds with negative PLS loadings.

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