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QUALITY ASSESSMENT OF FRUIT JUICES BY NIR SPECTROSCOPY

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Abstract

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In the article there is described the detection of substances used for adulteration of fruit juices. They were investigated in juice products distributed within the network of retail markets. This detection was performed using the method of near-infrared spectroscopy (NIR). There were analysed samples of orange juices, apple juices, and grapefruit juices. At the beginning, there were assessed quality parameters (soluble dry matter, total acids, formol number, malic acid, citric acid, ascorbic acid, lactic acid, specific density, and ethanol content) and their compatibility with the limit values specified by the Association of the Industries of Juices and Nectars. The research covered 45 kinds of fruit juices and there was found 10 cases when at least one parameter was out of the approved limits. After that there was used the discrimination analysis and it enabled to separate pure juices from those containing at least 1 % of admixtures. This method also helped to distinguish between the group of fresh squeezed juices and the juices made of fruit concentrates. Using the diagnostics "Principal Component Scores 3D Display", there were arranged various numbers of similar groups of juice samples with similar compound profiles.

fruit juice, NIR spectroscopy, discrimination analysis, squeezed juice, concentrate

Fruit juices are beverages made by a mechanic procedure of different fruit raw materials. Freshly squeezed juices may be processed to concentrates that can thereafter be diluted again in such a way that the content of dry matter corresponds with its level in the original fruit juice (ŠUHAJ, KOVÁČ, 1999). A regular consumption of fruit juices increases the supply of fibre, vitamins C, B6, B9 and minerals K and Mg (O'NEIL *et al.*, 2011). The first cases of food adulteration date back to times when food products began to be sold to consumers. The food falsification is motivated above all by economic factors (i.e. profit) and for that reason either expensive and luxury products (e.g. distillates, wine, and spices) or cheap foodstuffs sold in great volumes (e.g. meat and dairy products, fats and oils and fruit) are very often falsified (ČÍŽKOVÁ *et al.*, 2012). The adulteration of food products means the replacement of high-quality components with their cheaper substitutes (GURDENIZ, OZEN, 2009).

Consumers except that food products offered in the market will be safe and healthy. Many countries responded to these requirements in such a way that they developed efficient programmes and policies focused on food safety (ZHANG *et al.*, 2011). Initially, the adulteration of foodstuffs was motivated economically; manufacturers and distributors wanted to save money and deceive the customers. Nevertheless, as indicated for example by the melamine scandal, the adulteration can cause also serious health problems to consumers (SANTOS *et al.*, 2012). Production of fruit juices is one of the most quickly developing industries in the world. At present, many kinds of fruit are processed to juices but oranges are the most frequently used raw material (WASS – GARCIA *et al.*, 2000).

The adulteration of fruit juices and concentrates represents a permanent problem. Methods of falsification involve dilution with water, addition of pulp wash (wesos – water extracted soluble solids, i.e. low-quality concentrate obtained by repeated squeezing), admixtures of cheaper juices, colour substances and other compounds that can mimic the profile of an undiluted juice.

Because of the fact that there are many adulteration methods and technologies it is usually necessary to analyse and detect several components. Each fruit juice has its specific "acid profile" (i.e. the content of malic acid, citric acid, and total acids) and for that reason the determination of levels of these acids belongs to methods of evaluation of fruit juice purity (SAAVEDRA *et al*., 2000). In Europe, general mandatory rules and limit values of quality parameters of fruit juices are published by the Association of the Industries of Juices and Nectars from Fruits and Vegetables of the European Economic Community – AIJN). These regulations are based on models of multicomponent analysis. In Germany these standards are called Standard values and ranges of specific reference numbers for fruit juices (in German Richtwerte und Schwankungsbreiten bestimmter Kennzahlen – RSK) while in France they are administered by the Association Francaise de Normalisation (AFNOR). The quality control of fruit juices is a part of the European Quality Control System (EQCS) (HAMMOND, 1996). These regulations specify reference values of fruit juices quality and have the following two parts.

The first one involves absolute criteria of quality, i.e.

- Industrial requirements specifying minimum tolerable values of specific density and of refractometric dry matter;
- Hygienic requirements specifying maximum tolerable values of contents of volatile acids (acetic acid, ethanol, and lactic acid);
- Environmental requirements specifying maximum tolerable values of contents of arsenic and heavy metals;
- Composition requirements specifying minimum tolerable levels of ascorbic acid in orange and grapefruit juices and maximum tolerable contents of volatile oils and hydroxymethylfurfural.

The second one involves other criteria used for the assessment of purity of fruit juices, i.e.

- Requirements concerning contents of total titratable acids, malic acid, citric acid, minerals, saccharides and individual amino acids;
- Requirements concerning isotope values;
- Total amino acid profile expressed as the formol number (ANOMYN, 2012).

Recently, the method of NIR spectroscopy was frequently used when assessing the quality of solid and liquid products (BOBELYN *et al*., 2009). The method of NIR spectroscopy is a widely used alternative of the so-called wet chemistry. NIR spectroscopy is used for both quantitative and qualitative analyses in many different branches – e.g. in agriculture, pharmaceutic industry, food industry, cosmetic industry, and polymer industry. The NIR spectroscopy can be used also for the measuring of textural properties, e.g. of hardness (LAMMERTYN *et al*., 1998). Main advantages of NIR spectroscopy consist in its rapidness, accuracy and simplicity (LIU *et al*., 2011). Near-infrared radiation (NIR) has wavelengths between 780 and 2.500 nm (NICOLAI *et al*., 2007). However, in the case of assessment of sample components, it is necessary to perform an accurate calibration of the NIR spectrometer using a set of calibration standards with a known composition (reference methods). Its main disadvantages are: dependence on reference methods, low sensitivity to minority components, and complicated explanation of spectral data limited (BÜNING, 2003). Using the method of discrimination analysis, (YANG *et al*., 2005) performed a NIR spectroscopic differentiation of edible fats and oils. Analysed were the following products: soybean, peanut, rape, maize, olive and coconut oils, lard, coconut butter (solidified coconut oil) and cod liver oil. The discrimination analysis enabled to separate all groups of fats and oils from each other as well as coconut butter from coconut oil.

MATERIAL AND METHODS

Samples

Assessed was the quality of 100-percent fruit juices (both freshly squeezed and made of concentrates). Analysed samples were purchased in retail shops. Experiments involved altogether 45 samples of orange, apple and grapefruit juices.

● Freshly squeezed apple juice	8 samples
● Concentrated apple juice	13 samples
● Freshly squeezed orange juice	4 samples
● Concentrated orange juice	15 samples
● Freshly squeezed grapefruit juice	1 sample
● Concentrated grapefruit juice	4 samples

At first, all juices were measured using a NIR spectrophotometer; thereafter the samples were analysed and the obtained results were compared with the AIJN standard, which specified general, physical, chemical and microbiological criteria of fruit and vegetable juices and nectars consumed in EU.

As far as the juices were concerned, the following 11 parameters were evaluated: contents of citric, malic, and ascorbic acid, refractometric dry matter, formol number, contents of ethanol, lactic acid, and volatile acids, specific density, and content of total titratable acids. In addition to the AIJN specification, the content of polyphenols was also estimated. Obtained results were compared with AIJN data and evaluated.

The goal of the analysis was to find out if the discrimination analysis could enable that the NIR spectroscopy would help to identify individual substances (water, sugar solution) added to juices and if it could be possible to discriminate between the same kinds of fruit juice supplied by different manufacturers. At first, the tested juices were measured in their initial (i.e. unchanged) condition and thereafter they were used to make new samples

I: *Ratios of individual substances used from preparation of new samples*

Final concentration %	Amount of added substances (water, juice, sugar solution) ml	Juice volume ml
1	0.1	9.9
2	0.2	9.8
3	0.3	9.7
4	0.4	9.6
5	0.5	9.5
6	0.6	9.4
7	0.7	9.3
8	0.8	9.2
9	0.9	9.1
10	1.0	9.0
20	2.0	8.0
30	3.0	7.0
40	4.0	6.0
50	5.0	5.0

containing different amounts of a given admixture. New samples (Tab. I) were made in such a way that, using a micropipette, and exact volume of the original juice sample was mixed with different pre-calculated volumes of water, fruit juice and/or sugar solution containing the same amount of refractometric dry matter as the original juice sample.

New samples were thoroughly stirred and measured. Analyses were performed using the chemometric package TQ Analyst. This program enables to identify and verify various samples and to perform their qualitative and quantitative analysis by means of molecular spectroscopy.

The algorithms developed in this research enabled to calculate and/or classify samples of unknown substances using a set of calibration standards.

Analytical methods

HPLC assessment of ascorbic acid (vitamin C)

Juice sample (2 ml) was diluted with oxalic acid to the final volume of 10 ml. Using a nylon filter, the diluted sample was filtered (Ø 22 µm) into a brown vial. Assessment conditions: Column: Prevail 5µm Organic Acid 110A HPLC Column 250 × 4.6 mm, flow rate of mobile phase 25 mM KH_2PO_4 1ml/min, wavelength 210 nm, temperature +30 °C.

HPLC assessment of malic acid, citric acid, and lactic acid

Juice sample (2 ml) was diluted with distilled water to the final volume of 10 ml. Using a nylon filter, he diluted sample was filtered (Ø 22 µm) into a brown vial. Assessment conditions:

Column: Prevail 5µm Organic Acid 110A HPLC Column 250 × 4.6 mm, flow rate of mobile phase 25 mM KH_2PO_4 1ml/min, wavelength 210 nm, temperature +30 °C.

Determination of total titratable acids

A juice sample (10 ml) was used in this case. Total acids were assessed by a pH meter with a combined electrode by alcalimetric titration using the 0.1 M NaOH (up to pH 8.1). Contents of acids were expressed as content of either citric (in orange and grapefruit juice) or malic acid (in apple juice).

Determination of soluble dry matter

Dry matter content was assessed by an Abbe refractometer. As first the calibration with distilled water was performed and thereafter a sample of fruit juice was placed between two prisms and the content of soluble dry matter was read on the scale at the temperature of 20 °C.

Determination of density

The pycnometric determination of sample density was performed according to Commission Regulation EEC n° 2676/90, Community methods for the analysis of wines (BALÍK, 1998).

Determination of the formol number

The formol number expresses the total content of free amino acids. A juice sample (25 ml) was adjusted with NaOH (c = 0.25 mol/l) exactly to pH 8.1. Thereafter, 10 ml of formaldehyde (35%) adjusted also with the same NaOH solution pH 8.1 was added.

After 1 minute, the sample was titrated with NaOH back to the pH value of 8.1.

The formol number was expressed as ml of 0.1M NaOH.100ml^{-1} of the sample.

Determination of volatile acids

Volatile acids were determined by water steam distillation and titration with the NaOH according to the Commission Regulation EEC n° 2676/90, Community methods for the analysis of wines (BALÍK, 1998).

Determination of alcohol

Alcohol was determined according to the Commission Regulation EEC n° 2676/90, Community methods for the analysis of wines (BALÍK, 1998).

Determination of total polyphenols (Folin – Ciocalteau)

This method is based on spectrophotometric measuring of colour products occurring during the reaction of hydroxyl groups of phenolic compounds with Folin-Ciocalteau reagent.

Sample preparation: The juice sample (0.1 ml) was pipetted into a 50 ml volumetric flask and mixed with 20 ml of distilled water and 1 ml of Folin-Ciocalteau reagent.

After 3 minutes, 5 ml of 20-percent Na_2CO_3 solution was added, the volumetric flask was filled with distilled water to the mark and stirred. Thirty minutes later, the absorbancy was measured in a spectrophotometer at the wavelength of 700 nm using a 10-mm cuvette. The result was compared with absorbancy of a blind sample (1 ml of Folin-Ciocalteau reagent, 5 ml of 20% Na_2CO_3 solution, and distilled water up to 50 ml). The content of total polyphenols was thereafter converted to the fresh plant matter and expressed as milligrams of gallic acid per 1 litre of juice.

Near-infrared spectrometry

NIR spectra were measured using the OMNIC software. This program enables not only to setup suitable parameters of the spectrometer and to control the course of the measuring but also to adjust and analyse measured spectra. Each sample was measured twice, in two batches and the resulting spectra were pooled to obtain an average spectrum. NIR spectra were measured as an attenuation of light after passing through the sample (transmisional measuring) placed in a quartz cell Suprasil, Type 110-QS.

Measurings were performed under the following conditions:

No. of scans:	50
Resolution:	16 cm^{-1}
Spectral range:	4 000–10 000 cm^{-1}
Gain:	1x
Detector:	PbS
Beamsplitter:	CaF_2

The analysis of measured spectra was performed using the chemometric package TQ Analyst, algorithm Discriminant Analysis. This spectral technique enables to determine the class (or classes) that is (are) at most similar to the unknown material. There are several classes in the calibration model and each of them is described by means of a deliberate number of standards (at least two).

RESULTS AND DISCUSSION

Analyses of contents of total acids, ethanol, volatile acids, malic acid, citric acid, ascorbic acid, and lactic acid were performed in 45 samples of fruit juices. Determined were also values of refractometric dry matter, total polyphenols, formol number and density. Obtained results were compared with data published in the AIJN regulation to find out in how many samples individual measured parameters were the same or different.

In one and two samples of apple juice and orange juice made of concentrates, respectively, values of formol number were lower than data published in the AIJN regulation. In orange juice, this could be caused by processing of either unripe or frost-damaged raw material while in apple juice the cause could be too sweet apples. Contents of citric acid were beyond limits in altogether 5 samples. Increased levels were detected in 2 samples of directly squeezed apple juice and in 2 samples made of concentrate. These samples contained more than 0.150 g.l^{-1}of citric acid. This could signalise either the addition of citric acid or an admixture of other fruit juice. One sample of apple juice did not contain any citric acid.

In the case of malic acid, 3 samples showed contents lower than the tolerable minimum. One sample and two samples of grapefruit and orange juice, respectively, were made of concentrates. Provided that these juices would be adulterated with apple juice, the detected value should be higher. A lower content could signalise microbial contamination. In all samples, the other parameters were within AIJN limits.

Values of refractometric dry matter were below the minimum limit only in one sample. This was orange juice made of concentrate and the actual content was only 10.2 instead of 11.2 percent.

Juice samples were analysed using a NIR spectrometer and the presence of admixtures was detected by the discrimination analysis method. Juice samples were mixed with various concentrations of admixtures (water or sugar solution); orange juice was also mixed with apple juice. At first, individual spectra of original juices were measured and thereafter the samples were mixed with calculated volumes of admixtures. Sample spectrum was measured after each addition of a foreign substance.

Orange juice was mixed with apple juice; added volumes were 1; 3; 4; 6; 7; 8; 10; 20; 30; 40 and 50 percent. A discrimination cross was the result of a comparison of juice spectra; this means that the NIR spectrometry was able to detect admixtures of apple juice into the orange juice. (LEÓN *et al*., 2005) used the method of discrimination analysis when detecting admixtures of foreign substances into apple juices. Juice samples were mixed with different concentrations of sugars (10; 20; 30 and 40 percent). In the first case a fruit syrup containing 45 and 55 percent of fructose and glucose, respectively, was used. In other cases, a sugar solution containing 60; 25 and 15 percent of fructose, glucose and sucrose, respectively, was used.

Orange juice was diluted with water in amounts of 1; 2; 3; 4; 5; 6; 7; 8; 9 and 10 percent, respectively. When comparing spectra of individual juice samples, it was also possible to construct a discrimination cross so that the NIR spectrometer was able to detect admixtures of water into orange juice. (TWOMEY *et al*., 2006) used discrimination analysis when examining authenticity of orange juices originating from Brazil and Israel. Tested samples were adulterated with water, sugar, pulp wash, and grapefruit juice. The discrimination analysis was used to differentiate samples of pure and adulterated orange juice. Obtained results indicated that the discrimination analysis enabled to detect juice falsification with 90-percent accuracy. (VARDIN *et al*., 2008) used the NIR spectroscopy for the detection of grape juice made of a concentrate

II: *Comparison of measured values orange juice with those published in the AIJN standard*

Orange juice	Ascorbic acid mg.l^{-1}	Malic acid g.l^{-1}	Citric acid g.l^{-1}	Soluble dry matter %	Titration acids g.l^{-1}	Density g.cm^{-3}	Volatile acids g.l^{-1}	Formol nr. (ml 0,1 M NaOH)	Ethanol g.l^{-1}	Lactic acid g.l^{-1}
Orange squeezed) S1	374	0.8	8.8	10.9	7.4	1.0475	0.190	21.5	0.0	N.D.
S2	288	1.6	9.0	11.2	6.7	1.0458	0.150	22.0	0.0	N.D.
S3	289	1.1	10.0	11.5	7.2	1.0485	0.050	25.5	0.0	N.D.
S4	370	1.9	9.8	11.6	7.7	1.0494	0.170	25.5	0.2	N.D.
Standard value	**min. 200**	**0,8–3**	**6.3–17**	**min. 10**	**5.8–15.4**	**min.1,040**	**max. 0.4**	**15–26**	**max. 3.0**	**max. 0.2**
Orange (concentrate) C1	278	1.0	10.6	11.2	6.9	1.0469	0.085	20.3	0.0	N.D.
C2	366	0.9	12.0	11.3	8.0	1.0474	0.096	17.9	0.0	N.D.
C3	323	1.0	9.7	11.5	7.9	1.0477	0.056	19.4	0.0	N.D.
C4	360	1.3	10.0	11.2	6.9	1.0469	0.204	19.8	0.1	N.D.
C5	780	1.0	6.3	**10.2**	7.9	1.0469	0.084	**13.3**	0.0	N.D.
C6	340	**0.2**	10.5	11.7	8.1	1.0478	0.068	24.5	0.0	N.D.
C7	309	1.5	10.6	11.5	7.3	1.0479	0.097	24.5	0.0	N.D.
C8	377	1.0	8.8	12.8	8.4	1.0529	0.112	25.0	0.0	N.D.
C9	280	0.8	11.0	11.2	7.9	1.0488	0.074	17.9	0.0	N.D.
C10	458	0.7	10.5	11.4	8.2	1.0471	0.058	10.2	0	N.D.
C11	287	1.1	10.8	11.5	8.2	1.0483	0.062	23.5	0	N.D.
C12	325	0.9	10.7	11.2	7.9	1.0473	0.073	17.4	0	N.D.
C13	345	1.0	7.4	11.5	8.0	1.0471	0.067	24.5	0	N.D.
C14	318	1.2	8.4	11.2	8.0	1.0469	0.090	23.5	0	N.D.
C15	218	0.9	7.3	11,2	8.3	1.0469	0.090	22.0	0	N.D.
Standard value	**min. 200**	**0.8–3**	**6.3–17**	**min. 11.2**	**5.8–15.4**	**min. 1.045**	**max. 0.4**	**15–26**	**max. 3.0**	**max. 0.2**

III: *Comparison of measured values apple juice with those published in the AIJN standard*

Apple juice	**Ascorbic acid mg.l^{-1}**	**Malic acid g.l^{-1}**	**Citric acid g.l^{-1}**	**Soluble dry matter %**	**Titration acids g.l^{-1}**	**Density g.cm^{-3}**	**Volatile acids g.l^{-1}**	**Formol nr. (ml 0,1 M NaOH)**	**Ethanol g.l^{-1}**	**Lactic acid g.l^{-1}**
Apple (squeezed) S1	269	5.9	0.15	11.7	4.7	1.0496	0.051	3.8	0.1	N.D.
S2	65	5.9	**0.18**	10.9	5.3	1.0454	0.162	3.0	0.0	N.D.
S3	36	3.8	0.05	11.2	3.5	1.0468	0.046	4.3	0.1	N.D.
S4	1 400	6.0	0.05	10.7	5.1	1.0437	0.142	3.8	0.3	N.D.
S5	76	8.2	0.14	12.2	6.5	1.0512	0.168	3.0	0.0	N.D.
S6	497	4.8	0.05	11.5	4.3	1.0497	0.079	5.7	0.2	N.D.
S7	634	5.8	0.14	11.5	5.5	1.0476	0.061	5.7	0.1	N.D.
S8	50	5.5	**0.17**	10.5	5.0	1,046	0,061	4.8	0,1	N.D.
Standard value		**min 3**	**0.05–0.150**	**min. 10**	**2.2–7.5**	**1.040**	**max. 0.4**	**3–10**	**max. 3.0**	**max. 0.5**
Apple (concentrate) C1	49	6.3	0.06	11,2	4.1	1.0468	0.180	3.3	0.1	N.D.
C2	100	6.0	**0.20**	11.2	4.3	1.0468	0.048	3.8	0.0	N.D.
C3	70	6.9	0.11	12.2	5.7	1.0473	0.041	5.2	0.1	N.D.
C4	54	7.2	**0.20**	11.2	5.0	1.0455	0.041	4.7	0.2	N.D.
C5	73	7.9	0.09	11.2	6.0	1.0473	0.051	4.3	0.1	N.D.
C6	518	5.5	0.10	11.2	5.0	1.0468	0.051	4.7	0.2	N.D.
C7	45	7.2	**0.0**	11.5	4.9	1.0489	0.056	3.8	0.0	N.D.
C8	79	6.4	0.06	11.2	5.0	1.0468	0.066	4.3	0.1	0.2
C9	54	7.6	0.12	12.3	4.9	1.0468	0.041	3.8	0.0	N.D.
C10	40	7.7	0.05	11.2	4.2	1.0468	0.068	4.2	0.3	N.D.
C11	29	6.7	0.06	11.5	5.8	1.0482	0.056	**2.8**	0.0	N.D.
C12	43	7.9	0.14	11.2	5.3	1.0468	0.036	4.7	0.0	N.D.
C13	60	6.3	0.15	11.2	4.8	1.0468	0.090	4.7	0.1	N.D.
Standard value		**min 3**	**0.05–0.150**	**min. 11.2**	**2.2–7.5**	**1.045**	**max. 0.4**	**3–10**	**max. 3.0**	**max. 0.5**

IV: *Comparison of measured values grapefruit juice with those published in the AIJN standard*

Grapefruit juice	Ascorbic acid mg.l^{-1}	Malic acid g.l^{-1}	Citric acid g.l^{-1}	Soluble dry matter %	Titration acids g.l^{-1}	Density g.cm^{-3}	Volatile acids g.l^{-1}	Formol nr. (ml 0,1 M NaOH)	Ethanol g.l^{-1}	Lactic acid g.l^{-1}
Grapefruit (squeezed) S1	365	0.20	15.2	10.0	10.6	1.0422	0.090	17.0	0.0	N.D.
Standard value	**min. 200**	**0.2–1.2**	**8–20**	**min. 9.5**	**7.7–18.5**	**min.1.038**	**max. 0.4**	**14–30**	**max. 3.0**	**max. 0.2**
Grapefruit (concentrate) C1	200	**0.18**	13.4	10.0	12.9	1.0407	0.078	18.0	0.0	N.D.
C2	250	0.31	12.3	10.0	11.3	1.0419	0.048	17.0	0.0	N.D.
C3	304	0.30	15.5	10.2	23.0	1.0437	0.046	17.0	0.0	N.D.
C4	238	0.33	15.6	11.3	13.1	1.0423	0.040	17.9	0.0	N.D.
Standard value	**min. 200**	**0.2–1.2**	**8–20**	**min. 10**	**7.7–18.5**	**min.1,040**	**max. 0.4**	**14–30**	**max. 3.0**	**max. 0.2**

Notes: N.D. – not detected; S – squeezed juice; C – concentrate

into pomegranate juice made also of a concentrate. The apparatus could reliably detect admixtures of grape juice within the range of 2 to 14 percent.

Fruit juices were mixed with sugar solutions containing the same refractometric dry matter as these juices. Added were 1; 3; 4; 7; 8; 9; 10; 20; 30 and 50 percent.

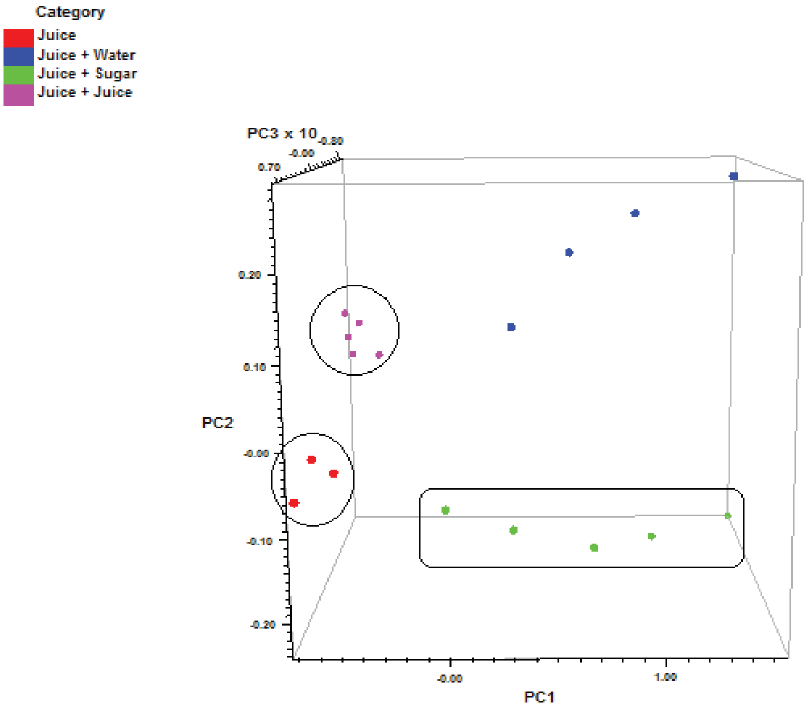
When comparing spectra of individual juices it was also possible to construct a discrimination cross; this indicated that the NIR spectrometer was able to detect admixtures of sugar solution into fruit juice.

This diagnostics enables a 3D (spatial) projection of calibration standards. Calibration standards of orange juice and of orange juice with admixtures of sugar, water and apple juice are presented in Fig. 1.

The NIR spectroscopy is a rapid and accurate method enabling to detect admixtures of substances used for adulteration of foodstuffs. It is obvious that it can be used for analyses of different groups of foodstuffs (e.g. beverages, fats and oils, dairy and meat products etc.). The NIR spectroscopy enables the detection of relatively low concentration of admixtures, and can be used also for the differentiation of individual samples from all others. The NIR spectroscopy enables to detect reliably admixtures of 1 percent of water and/or sugar solution in juices. This method can also differentiate between juice samples made by different methods of processing (i.e. between freshly squeeze juice and that made of concentrates). It can also play an important role when separating several groups of samples because it enables to obtain separate clusters indicating either similarity or dissimilarity of individual groups.

CONCLUSIONS

The objective of this study was to evaluate quality of orange, apple and grapefruit juices. Altogether 45 juice samples were purchased in retail shops. In all samples the following parameters were estimated: contents of citric, malic, ascorbic and lactic acid, refractometric dry matter, formol number, ethanol content, content of volatile acids, density, content of total titratable acids, and content of total polyphenols. Obtained results were compared with reference values published by the Association of the Industries of Juices and Nectars from Fruits and Vegetables of the European Economic Community for 100-percent fruit juices. To detect adulterated fruit juices, it is necessary to evaluate a wide analytical spectrum of a given juice. The study evaluated 10 parameters contained in the AIJN regulation and assessed also contents of total polyphenols; this parameter is not contained in the AIJN regulation because the content of total polyphenols can be changed during the processing of fruit to juices. Of 45 samples, 10 showed wrong values of at least one parameter. The most frequent differences were found out in formol numbers and contents of soluble dry matter, citric acid and malic



1: *Discrimination of calibration standards by means of Principal Component Scores 3D Display diagnostics*

acid. The content of total polyphenols ranged from 0.248 to 1.657 g.l^{-1}.

Possibilities of detection of presence of various admixtures in fruit juices were studied by means of NIR spectroscopy. Juice samples were diluted with different amounts of water, sugar solution, and other fruit juices. The discrimination analysis enabled a reliable differentiation of pure and adulterated juices even at very low concentrations as well as to distinguish between fresh squeezed juices and those made of a concentrate. The diagnostics Principal Component Scores 3D Display separated 4 different groups of samples. It can be concluded that the discrimination analysis is a method that enables to detect various admixtures to fruit juices.

SUMMARY

In this study, the quality of pure (100-percent) fruit juices was evaluated. It was also tested that the NIR spectroscopy is a method enabling the detection of various admixtures to fruit juices. The authenticity of fruit juices was evaluated on the base of AIJN regulations. In the research 45 fruit juices (apple, orange, and grapefruit) were analysed, produced either by fresh squeezing or made from concentrates. Evaluated samples were contents of citric, malic, ascorbic and lactic acid. Individual acids were analysed by means of High Performance Liquid Chromatography (HPLC). Contents of total titratable acids and formol numbers were assessed by means of a pH meter Total acids were assessed by a pH meter with a combined electrode by alkalimetric titration and the content was expressed on the base of the predominating acid. Soluble dry matter was assessed by the Abbe refractometer and expressed in percent. Ethanol content was determined according to the Commission Regulation EEC n° 2676/90, Community methods for the analysis of wines.

Volatile acids were determined by water steam distillation and titration with the NaOH according to the Commission Regulation EEC n° 2676/90, Community methods for the analysis of wines.

The pycnometric determination of sample density was performed according to Commission Regulation EEC n° 2676/90, Community methods for the analysis of wines, and the content of total polyphenols by means of spectrophotometry at the wavelength of 700 nm. Of 45 samples, 10 showed wrong values of at least one parameter. The most frequent differences were found out in formol numbers and contents of soluble dry matter, citric acid, and malic acid. Juices were diluted with different amounts of other components (water, sugar solution, and other fruit juices). The discrimination analysis was performed to found out if the NIR spectroscopy could separate the genuine juice from adulterated ones. The analysis of measured spectra was performed using the chemometric package TQ Analyst, algorithm "Discriminant Analysis". This program enables to identify and verify various samples and to

perform their qualitative and quantitative analysis by means of molecular spectroscopy. This spectral technique enables to determine the class (or classes) that is (are) at most similar to the unknown material. In all cases is was possible to construct a discrimination cross so that the NIR spectroscopy was able to detect admixtures of various substance to fruit juices.

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