Detection of Adulteration in Orange Juices by a New Screening Method Using Proton NMR Spectroscopy in Combination with Pattern Recognition Techniques

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This paper describes the application of proton NMR spectroscopy as a screening tool for the determination of the authenticity of orange juices. Principal component and discriminant analyses were used to discriminate between authentic and nonauthentic (suspect) samples. In one set of profiles, additions of sucrose, beet medium invert sugar, sodium benzoate could easily be detected. In another set of data, *K*-nearest neighbor classification based on the principal component scores was used to correctly classify at least 94% of samples known to deviate from authentic samples when measured with analytical techniques such as high pressure liquid chromatography and atomic absorption spectroscopy. Principal component loading plots and factor spectra were an effective tool in the interpretation of the differences between the profiles.

Keywords: *Authenticity; orange juice; pattern recognition; proton NMR*

INTRODUCTION

Authentic orange juices are only those juices that are produced exclusively from the fleshy part of the orange, with no pulp wash, sugar, preservatives, or other ingredients added. However, orange juices are a valuable commodity so much profit can be made if the available stock can be made to last a little bit longer. In daily practice, many different techniques to authenticate orange juices are available. The methods range from relatively simply to measure parameters such as the Brix number (density of the juices) and the formol number (total amino acids) (Park *et al.*, 1983; VanderCook *et al.*, 1983) to more elaborate methods such as measuring the $^{18}O/^{16}O$, $^{13}C/^{12}C$, or $^{2}H/^{1}H$ isotope ratios to determine whether (beet medium invert) sugar has been added (Bricout and Koziet, 1987). Another popular method is HPLC profiling of flavonoid (Perfetti *et al.*, 1988) and carotenoids (Phillip *et al.*, 1989) compounds to detect the addition of pulpwash or other adulterants such as tangarine, mandarin, and grapefruit juices.

The main problem with all these methods is that they measure only compounds from one specific chemical class (i.e., only sugars, flavonoids, amino acids, etc.). As it is impossible to use all possible methods in day-to-day practice, a choice about which method to use has to be made based on an educated guess about which adulteration to expect. A solution to this problem is to use a very general analytical chemical screening tool that could detect a much wider range of different compounds in one sample run. Suspect samples could then be detected and evaluated by more rigorous methods as just described.

A possible screening tool is proton nuclear magnetic resonance spectroscopy (HNMR). In principle, and depending on the concentration, this technique can quantitatively and simultaneously detect all proton-bearing compounds in the samples such as sugars, flavonoids, amino acids, organic acids, esters, and ethers. The HNMR method is relatively simple, needing only a basic sample preparation (freeze-drying).

The application of HNMR will, however, generate spectra that are too complicated to be analyzed visually. A solution to this problem is to analyze the data by principal component analysis (PCA; Kowalski and Bender, 1972a,b). With this technique, the dimensionality of the data is reduced by combining correlated variables (peaks in the spectrum) to form a new smaller set of independent (orthogonal) variables called principal component axes or PCs. These PCs are ordered according to their ability to explain the variance contained in the original data. A projection of the samples into a space spanned by the first PCs provides insight into the similarity or dissimilarity of the samples. Unknown or test samples can also be projected onto this space and can thus (often visually) be compared with the reference samples. An additional advantage of this technique is that by including samples with several known adulterations in the reference set, suspect samples can also be classified as to the type of adulteration. This classification can assist the researcher in the choice of a subsequent classical chemical analysis technique, thereby saving time and money.

A problem in using HNMR to authenticate orange juices is the small shifts in the position of the NMR signals due to minor differences in concentration of the samples and apparatus instabilities. These variations were fully eliminated by a recently developed NMR spectroscopy data preprocessing tool called partial linear fit (PLF; Vogels *et al.*, 1993). This program corrects for small variations in the position of lines by selecting small regions from each spectrum, shifting within a

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Table 1. Description of Orange Juices in Set 1

description[a]	category
authentic juice I	1
juice I + 1% sugar	2
juice I + 5% sugar	3
juice I + 10% sugar	4
authentic juice II	5
juice II + 1% beet medium invert sugar	6
juice II + 5% beet medium invert sugar	7
juice II + 1% beet medium invert sugar (duplo)	8
juice II + 5% beet medium invert sugar (duplo)	9
juice II + 1% sodium benzoate	10

[a] All concentrations are expressed as percentage by weight.

Table 2. Description of Orange Juices in Set 2

description (analytical method)[a]	category	no. of samples
authentic juices	1	13
pulp wash	2	3
low amino acid content (IEC)	1	2
presence of D-malic acid (HPLC)	4	5
low proline content (IEC)	5	1
addition of grapefruit (HPLC)	6	1
low potassium content (AAS)	7	1

[a] IEC, ion-exchange chromatography; HPLC, high-performance liquid chromatography; AAS, atomic absorption spectroscopy.

certain range and comparing them with comparable regions in the average spectrum. This new screening method was tested on two sets of orange juice samples. To demonstrate and study the behavior of this technique, a set of orange juice samples was prepared from two authentic samples that we adulterated ourselves with large amounts of adulterating compounds. To test the performance of the system in a realistic environment we analyzed a second set of samples that contained 26 genuine, production grade orange juices (with known authenticities) from several varieties and regions in Brazil, South Africa, and Venezuela.

MATERIALS AND METHODS

Materials. The samples were obtained from several reliable sources. Set 1 (Table 1) consisted of 10 samples that we prepared by adulterating two authentic juices; one juice was adulterated with 1, 5, and 10% beet sucrose, and another with additions of 1 and 5% beet medium invert sugar (in duplicate) and 1% sodium benzoate. All additions are expressed as percentage by weight of the original juice. The second set (Table 2) was a collection of 26 real orange juice samples that were tested for their authenticity by the suppliers by established authentification methods. From this last set, 13 samples were authentic juices, 3 were pulp washes, and 10 samples deviated from authentic juices when measured by other analytical techniques such as atomic absorption spectroscopy (AAS), ion-exchange chromatography (IEC), or HPLC.

Proton NMR Spectroscopy. From each sample, 5 mL was freeze-dried overnight. Of each freeze-dried sample, 0.20 g was shaken with 1.0 mL of deuterium oxide and then the mixture was spun in a table centrifuge for 10 min at 12 000 rpm. The supernatant was then transferred to a 5-mm o.d. NMR tube and some TSP (sodium salt of trimethylsilylpropionic-*2,2,3,3-d*$_4$ sulfonic acid) was added as an internal NMR reference. All spectra were recorded on a Varian UNITY 400 NMR spectrometer operating at a proton NMR frequency of 400 MHz. A typical proton NMR spectrum consists of 512 transients using 64K data points over a 8000 Hz band width with a 8.4 μs (45°) radio frequency pulse.

The residual water in the spectra was suppressed by presaturating the water signal for 3 s with a low-power, continuous-frequency radio wave, which was just powerful enough to make the intensity of the water signal equal to the other signals in the spectrum. Total acquisition time was 1 h. The signal-to-noise ratio of the spectra was improved by multiplying each free induction decay with an additional exponential factor corresponding to 0.3 Hz in the Fourier transformed spectrum. The intensity and position (rounded to the nearest Hz) of the spectral lines was recorded by a macro with the standard Varian peak-picking software. To correct for differences in the signal-to-noise ratio between different spectra, each spectrum was normalized to unit intensity (sum of the squared intensities in each spectrum is equal to 1.0) after eliminating the water peak.

Data Preprocessing. The small variations between the resonance positions of comparable lines in different spectra were corrected for by fitting clusters of these lines to the average spectrum by the PLF preprocessing tool for HNMR data using a range of 1 Hz (a new cluster is started if the distance between two lines is larger than 1 Hz) and a maximum shift of 1 Hz left or right of the original position of the lines. Measuring each sample in triplicate and reducing the spectral resolution to 4 Hz resulted in a data set containing 30 objects (samples) with 480 features (different frequencies) for the samples from set 1 and a second data set containing 78 objects with 542 features for the samples from set 2.

Data Analysis. The data were analyzed by an unsupervised PCA on the variance/covariance data matrix as described by Kowalski *et al.* (1972). All calculations were performed on a SUN Sparcstation 1+ computer, using the EAGLES pattern recognition program (TNO Nutrition and Food Research, Zeist, The Netherlands). A typical data preprocessing/PCA analysis took ~3 min.

RESULTS AND DISCUSSION

Visual Analysis. A typical HNMR spectrum of an authentic orange juice sample is shown in Figure 1. Close examination of the spectrum reveals the presence of several readily identifiable compounds, such as residual water (4.70 ppm), sucrose (5.41 ppm Suc-H1, 4.20 ppm Suc-H3), glucose (5.35 ppm α-Glu-H1, 4.62 ppm β-Glu-H1), fructose (4.10 ppm β-Frc-H6), and malic acid (4.42 ppm). Comparing the spectra from all juices, in both sets, many similarities and dissimilarities can be seen. However, the sheer amount of combined data, with no obvious relation between the intensities of certain lines and the authenticity of the juices, makes a visual analysis of these sets virtually impossible. The need for multivariate analysis tools such as PCA is obvious.

Principal Component Analysis of Set 1. One of the advantages of using PCA to analyse complex multivariate chemical analysis problems is that allmost all results can be presented graphically. The position of the samples can be plotted in a two-dimensional "score" plot in which similar samples will tend to form clusters and dissimilar samples will be found at larger distances. The reliability of these observations will increase if the two principal component axes that span the space in the displayed score plot explain a larger proportion of the variance contained in the original variables.

The location of the 30 objects after the PCA on the samples from set 1 in Figure 2 (spanned by first two PCs explaining 34% of the original variance) clearly demonstrates the power of using this HNMR technique in orange juice analysis. Despite the relative low total explained variance of these first two PCs, the score plot displays (with the exception of the addition of the sample containing 1% sodium benzoate) well-separated groups for all the different adulterations examined in this study. This result suggests that set 1 contains a relatively simple underlying structure describable by a few PCs, with a large amount of spurious noise superimposed on this base. In this example, where we only want to give a demonstration of this technique, we limit

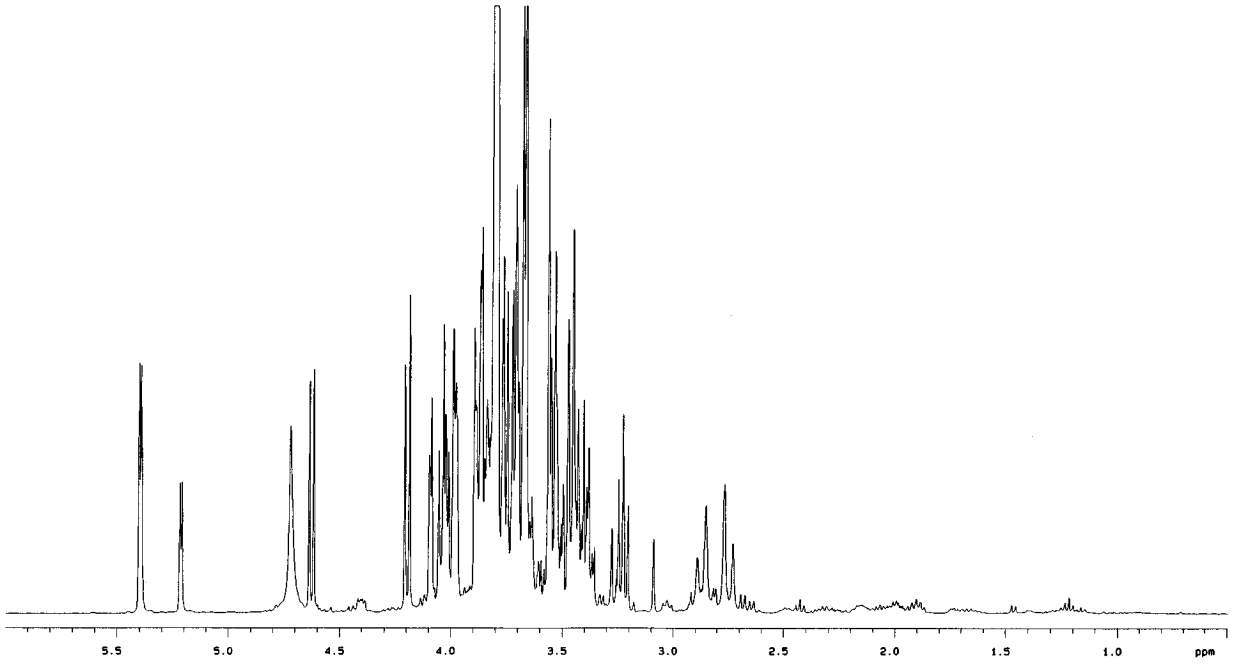

Figure 1. Example of a typical orange juice HNMR spectrum obtained with water peak suppression.

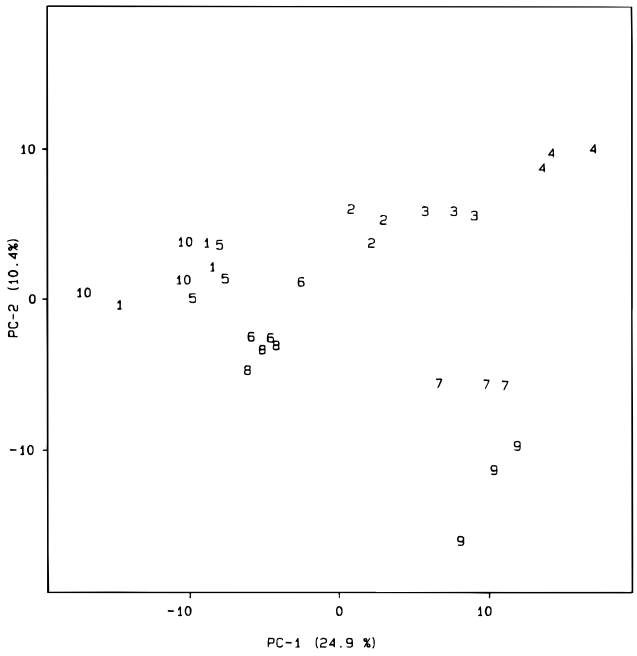

Figure 2. PCA plot of triplicate ^{1}HNMR measurements from samples in set 1 containing two authentic and eight adulterated orange juice samples. Juice I (1) was adulterated with 1% (2), 5% (3) or 10% (4) sucrose. Juice II (5) was adulterated with 1% (6) or 5% (7) BMIS, 1% (8) or 5% (9) BMIS (duplo measurement), or 1% (10) sodium benzoate. Concentrations are by weight. Numbers in parentheses correspond to the category assigned to the samples.

ourselves to an examination of the first two PCs. If we wanted to classify these samples, selecting only the first two PCs would be not sufficient. In such a case, we would first have to establish the number of singificant PCs by some type of cross-validation and then analyze all the significant PCs.

In Figure 2 the two authentic juices are seen close together, but the addition of the three different concentrations of beet sugar (1, 5, and 10%) causes a gradual shift of the position of the related objects toward the positive end of both PC-1 and PC-2. Addition of 1 and 5% beet medium invert sugar induces a shift of the objects toward the positive end of PC-1 and the negative end of PC-2. Obviously, PC-1 is correlated to excess sugars (sucrose/glucose/fructose) whereas PC-2 is correlated to the relative amounts of either glucose, fructose, or sucrose in the samples. These observations were confirmed by examining the factor spectra extracted from the "loading" plot in the direction of both PC-1 and PC-2 (Figures 3 and 4).

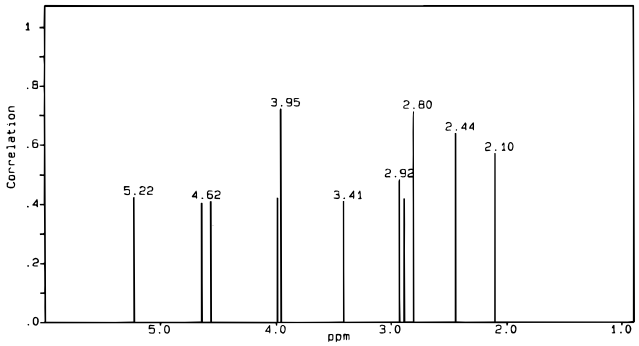

Figure 3. Factor spectrum (NMR/PCA function correlations) in the direction of 0° corresponding to the direction of PC-1.

In general multivariate analysis theory, a representation like Figure 2, in which the samples are projected onto one or more principal component axes, is generally referred to as a score plot; Loading plots are the variable or factor projections onto the principal component axes in which the position of a variable directly corresponds to the correlation of that variable with the principle component it is projected on. A factor spectrum can be prepared from these loading plots by projecting the variable vectors in the loading plot onto a counterclockwise rotating vector, as proposed by Windig *et al.* (1983). A high positive value (long projection length) for a certain variable on this rotating vector will then correspond to a relative higher concentration of the compound(s) represented by that variable in the selected direction. Similarly, a negative value for a certain variable will correspond to a decrease in the relative concentration for the compound(s) containing that variable in the selected direction.

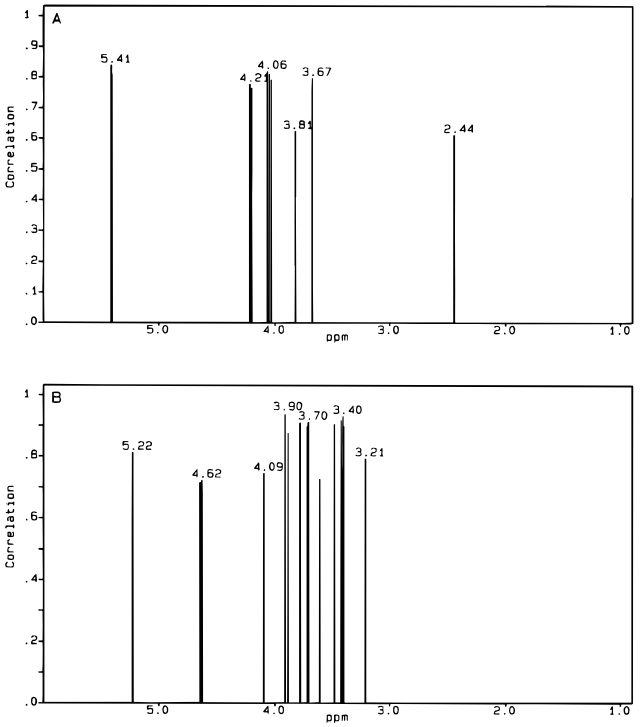

Figure 4. Factor spectrum (NMR/PCA function correlations) in the direction of (A) 90° and (B) 270° corresponding to the positive and negative the direction of PC-2, respectively.

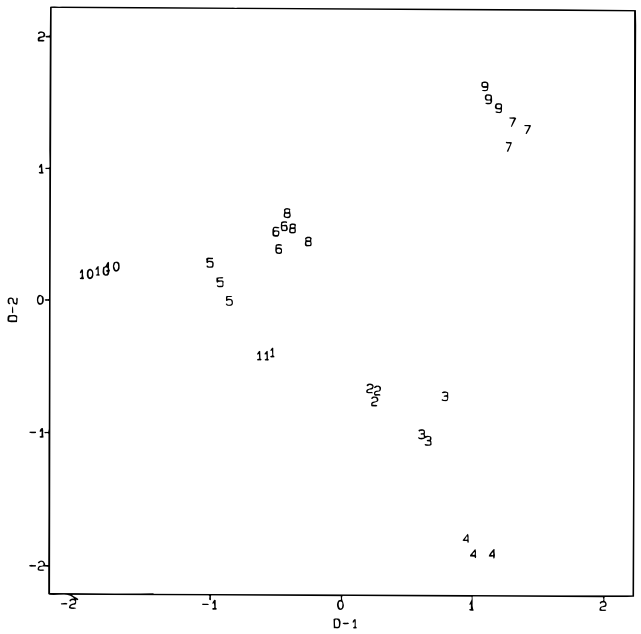

Figure 5. Unsupervised DA plot of triplicate HNMR measurements from samples in set 1 containing two authentic and eight adulterated orange juice samples. Juice I (1) was adulterated with 1% (2), 5% (3), or 10% (4) sucrose. Juice II (5) was adulterated with 1% (6) or 5% (7) BMIS, 1% (8) or 5% (9) BMIS (duplicate measurement), or 1% (10) sodium benzoate. Concentrations are by weight. Numbers in parentheses correspond to the category assigned to the samples.

Using these rotating vectors the factors (peaks) contributing to the two PC from Figure 2 can be analyzed. By selecting the angle parallel to the positive end of PC-1 (angle = 0 degrees), as represented in Figure 3, it can be shown that the positive end of PC-1 has a strong correlation ($r \geq 0.7$) with peaks corresponding to the concentration of several organic acids at 3.95 ppm (quinic acid), 2.92 ppm (malic acid), 2.80 ppm (citric acid), 2.44 ppm (succinic acid) and 2.10 ppm (acetic acid). The high correlation of PC-1 with these compounds demonstrates an often neglected, but still very useful, NMR effect that is comparable to the better known solvent-induced shifts in an NMR spectrum described by Jackman *et al.* (1969). The relative concentration of a certain compound can influence not only the height of related peaks, but also the resonance positions of lines from another compound. The relative higher concentrations of glucose, fructose, and sucrose can so shift the positions of the aforementioned organic acids to a new position that is readily detected by the PCA. These very small variations (on the order of a few Hz) can either be compensated for by a reduction in resolution of the peaks or, as we did, used in the analysis as a telltale sign of an adulteration. The choice whether to leave them in or to remove them depends mainly on the samples under consideration. The small variations can be useful for studying small sets. For larger sets, these variations will often add more noise than information and they should therefore be deleted.

This approach was applied in the analysis of the second set of samples where these small variations were eliminated by a simple reduction of the resolution of the position of the peaks. The peaks at the next level of correlation ($r \geq 0.5$) in Figure 3 correspond mainly to the signals for glucose at 5.22, 4.62, 3.41, and 2.92 ppm. The factor spectrum for the negative end of PC-1 is not included in this first global analysis because it is overloaded with the majority of peaks in this set and no obvious correlations between the signals and identifiable compounds can be made. The factor spectra parallel to PC-2 (from Figure 2) and as represented in Figure 4) reveals a strong correlation between sucrose (5.41, 4.21, 4.06, 3.81, and 3.67 ppm) and the positive end of PC-2 (Figure 4A) and an almost equally strong correlation between the signals of glucose (5.22, 4.62, 3.90, 3.70, 3.40 and 3.21 ppm; $r > 0.8$) and fructose (4.09, 3.90, 3.70, and 3.40 ppm; $r \geq 0.7$) and the negative end of PC-2 (Figure 4B).

Despite the very obvious presence of two very characteristic peaks at 7.98 and 7.53 ppm in the samples containing 1% sodium benzoate, the locations of the triplicates this sample are not clearly separated from those of the authentic samples. Apparently, these peaks do not contribute much to either PC-1 or PC-2 (correlations between the two major PCs and the peaks at 7.98 and 7.53 ppm are 0.46 and 0.05, respectively, for PC-1 and PC-2). Thus, authentic samples that have 1% sodium benzoate added are not clearly separated from the authentic samples in the space spanned by these two axes. This unwanted effect can be remedied by performing a discriminant analysis (DA) on the PCA result as described by Hoogerbrugge *et al.* (1983).

With this PC/DA technique a second PCA is performed on the centroids of the reconstructed triplicate measurements, resulting in an optimal separation of the samples. The result of such an unsupervised DA on the samples in this set is displayed in Figure 5. This figure excellently demonstrates the power of the DA technique; all similar samples (duplications and similar concentrations) remain close together, whereas all the different types of adulterations are well separated both as to the type and as to the concentration of the added compounds.

Principal Component Analysis of Set 2. The locations of the 26 samples (measured in triplicate) from set 2, projected into the plane spanned by the first two PCs explaining 29% of the variance contained in the

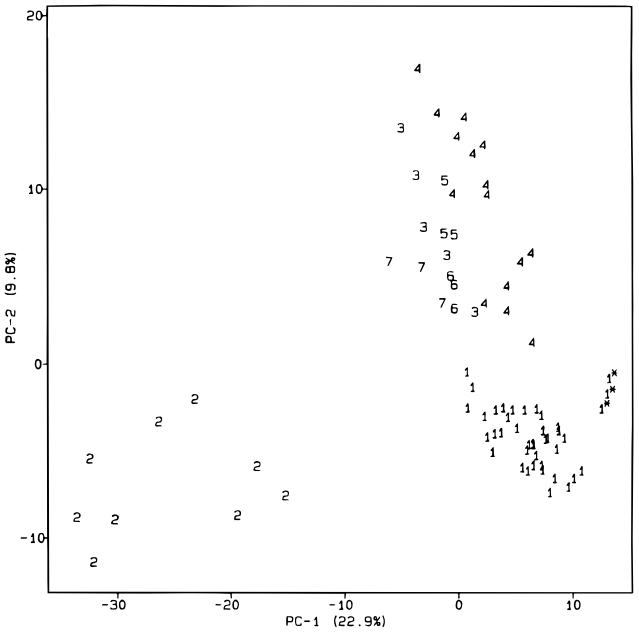

Figure 6. PCA plot of triplicate HNMR measurements in set 2 containing 26 samples of which 13 (1) are authentic and 13 are nonauthentic with known deviations of the presence of pulp wash (2), low amino acid content (3), presence of D-malic acid (4), low proline content (5), addition of grapefruit (6), and low potassium content (7). Numbers in parentheses correspond to the category assigned to the samples.

original variables, are shown in Figure 6. The objects in this plot can be divided into three clusters. The best separated cluster was, as expected because of the very different production method, the one containing the triplicates of the pulp wash samples (category 2 in Figure 6). A second cluster contains the authentic samples (category 1). In this cluster, only the triplicates from one sample (Valencia oranges from South Africa; marked in Figure 6 with an asterisk) are different from the other authentic samples. The remaining cluster (samples from categories 3−7) is more dispersed and contains the triplicate measurements of the samples with a wide variety of known deviations from a normal orange juice composition, as described in Table 2. The relative proximity of the object scores of these samples in the plot suggests that all the deviations found by the classical analysis techniques are just symptoms of the same problem that is, dilution of authentic juices with an unknown matrix.

The classification ability and the significant number of PCs of the NMR/PCA method were obtained by a cross-validation experiment in which each sample was removed from the set and the classified against the rest of the set. The excluded test objects were then classified using the K nearest neighbor (KNN) method, as described by Kowalski and Bender (1972a,b). In this method, the Euclidean distance between the samples (using the first P principal component axes) is used as a measure of their similarity. An unknown or test sample is classified by comparing and summing the categories of the *K* nearest neighbors and then assigning the category with the highest score to the object under investigation. The result of this KNN analysis using a three-category system (1 = authentic juices, 2 = pulp wash, and 3 = other nonauthentic juices) for 3, 4, 5, 6, 7, 8, 9, 10 nearest neighbors using the first 2, 3, 4, and 76 PCs, respectively, is shown in Table 3. The best classification ability (i.e., 98.8% of the samples replaced correctly) was achieved with the first 2 PCs and 3, 4, 9, or 10 nearest neighbors. So, despite a very low combined explained variance of 29%, this set has only two significant PCs.

Table 3. Percentage of Correctly Classified Patterns in KNN Result of Set 2

no. of PCs used	explained variance	K^a							
		3	4	5	6	7	8	9	10
2	29.3	98.7	98.7	96.4	97.4	97.4	97.4	98.7	98.7
3	34.4	96.4	96.4	96.4	96.4	96.4	96.4	96.4	96.4
4	39.1	96.4	96.4	94.9	96.4	94.4	94.4	94.4	94.4
76 (all)	100.0	87.4	84.9	86.1	87.4	86.1	84.9	79.8	78.5

[a] Number of nearest neighbors used.

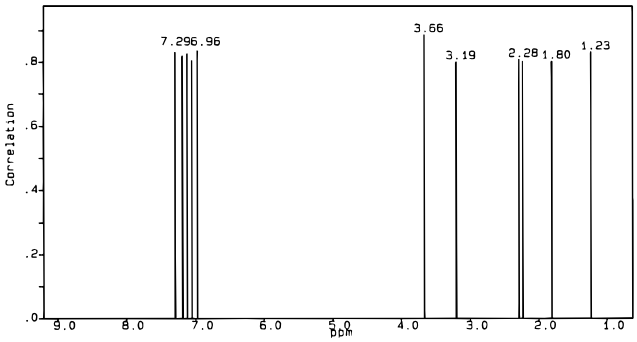

Figure 7. Factor spectrum (NMR/PCA function correlations) in the direction 200°, corresponding to the direction of the pulp wash samples.

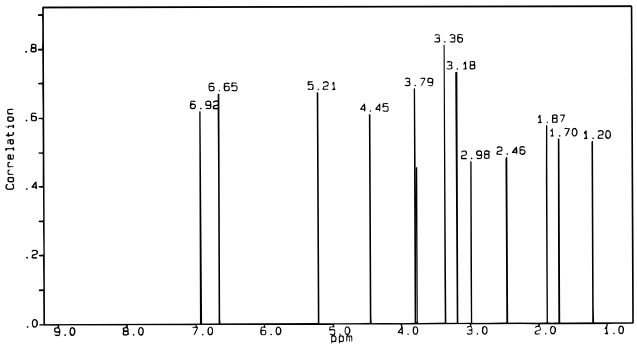

Figure 8. Factor spectrum (NMR/PCA function correlations) in the direction 90°, corresponding to the direction of the adulterated non-pulp-wash samples.

Because we were mainly interested in the potential of this NMR/PCA technique as a screening tool for determining the authenticity of orange juices, we performed only a preliminary investigation of the factor spectra in the direction of the three most distinct clusters. The factor spectrum in the direction of the pulp wash samples from Figure 6 is represented in Figure 7 (rotated over 200°). This plot reveals a high correlation ($r \geq 0.8$) with NMR resonances between 6.95 and 7.30 ppm, indicating a relatively high concentration of an aromatic compound like naringenine or hesperidine in these samples. The presence of naringenine could be confirmed by the peaks at 5.05, 3.66, 3.59, 3.10, and 1.23 ppm. A second group of high-loading features can be seen at 2.23, 2.28, and 2.29 ppm. These peaks, together with the cluster of peaks at 1.03 ppm, indicate an elevated concentration of a (possibly aromatic) ester of butyric acid in this direction of the plot. In the direction of the combined cluster of "adulterated" samples, the factor spectrum (Figure 8; rotated over 90°) is dominated by several groups of high-loading features ($r \geq 0.6$), almost all of which can be ascribed to either glucose or fructose. A second group of interest can be

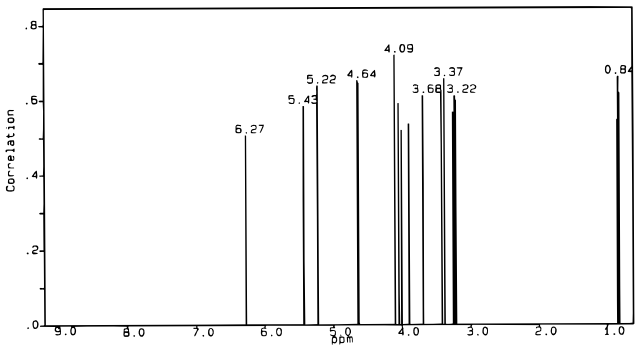

Figure 9. Factor spectrum (NMR/PCA function correlations) in the direction 315°, corresponding to the direction of the authentic samples.

found around 1.55 and 0.90 ppm, indicating a relatively higher concentration of a compound containing an isopropyl group as such that present in isoleucine. The presence of this amino acid can, however, not be proved. The factor spectrum (Figure 9: rotated over 315°) in the direction of the cluster containing the authentic samples primarily contains peaks that can be ascribed to hesperidine. The rest of this factor spectrum is a wide variety of (still) uninterpretable peaks.

Conclusions. We are aware of the fact that the present limited access to modern high-resolution NMR spectrometers will severely limit a general adaptation of this technique to day-to-day testing of orange juices. The potential advantages of using the NMR/PCA system as proposed in this paper are, however, still manifold. For instance, this system reduce the costs of a simple orange juice screening by a factor of two to three. The versatility of this method (i.e., its ability to test a lot of compounds simultaneously) makes adulterations difficult and therefore unattractive. Furthermore, when the problem of the long sample preparation are solved and reduced to (possibly) no sample preparation at all, this method is a very fast analysis tool, potentially giving a result within an hour.

In this publication, we have limited ourselves to the results obtained from data prepared from standard NMR line listings. Although this approach already gives excellent results, for future studies with larger more complicated data sets, it seems prudent to further develop and investigate more stable NMR descriptors. A possible way to do this could be to preprocess the NMR spectra with lineshape enhancement routines, like Linear Prediction, as was proposed by Gesman *et al.* (1990). Considering all the results and taking into account all remarks, NMR/PCA seems to be a very promising tool for the authentication and quality control of fruit juices and other related products.

LITERATURE CITED

Bricout, J.; Koziet, Control of the authenticity of orange juice by isotopic analysis *J. Agric. Food Chem.* **1987**, *35*, 758−760.

Gesman, H.; Led, J. J.; Abilgaard, F. Improved methods for quantitative spectral analysis of NMR data. *Prog. Nucl. Magn. Reson, Spectrosc.* **1990**, *22* , 255−288.

Hoogerbrugge, R.; Willig, S. J.; Kistemaker, P. G. Discriminant analysis by double stage principal component analysis. *Anal. Chem.* **1983**, *55*, 1710−1712.

Jackman, L. M.; Sternhell S. Applications of nuclear magnetic resonance spectroscopy. In *Organic Chemistry,* 2nd ed., Pergamon: Oxford, U.K., 1969.

Kowalski, B. R.; Bender, C. F. Pattern recognition a powerful approach to interpreting chemical data. *J. Am. Chem. Soc.* **1972**, *94*, 5632−5639.

Kowalski, B. R.; Bender, C. F. The K-nearest neighbour classification rule (pattern recognition) applied to nuclear magnetic resonance spectral interpretation. *Anal. Chem.* **1972b**, *44*, 1405−1410.

Park, G. L.; Byers, J. L.; Pritz, C. M.; Nelson, B; Navarro, J. L.; Smolensky, D. C.; VanderCook, C. E. Characteristics of California naval orange juice and pulpwash. *J. Food Sci.* **1983**, *48*, 627−32.

Perfetti, G. A.; Joe, F. L.; Fazio, T.; Page, S. W. Liquid chromatographic methodology for the characterisation of orange juice. *J. Assoc. Off. Anal. Chem.* **1988**, *71*, 469−473.

Phillip, T.; Chen, T.; Nelson, D. B. Detection of adulteration of california orange juice concentrates with externally added carotenoids by liquid chromatography. *J. Agric. Food Chem.* **1989**, *37*, 90−95.

VanderCook, C. E.; Navarro, J. L.; Smolensky, D. C.; Nelson, D. B.; Park, G. L. Statistical evaluation of data for detecting adulteration of California naval orange juice. *J. Food Sci.* **1983**, *48*, 636−640.

Vogels, J. T. W. E.; Tas A. C.; Van den Berg, F.; Van der Greef, J. A new method for classification of wines based on proton and carbon-13 NMR spectroscopy in combination with pattern recognition techniques. *Chem. Intell. Lab. Syst.* **1993**, *21*, 149−258.

Windig, W.; Haverkamp, J.; Kistemaker P. G. Chemical interpretation of sets of pyrolyis mass spectra by discriminant analysis and graphical rotation. *Anal. Chem.* **1983**, *55*, 81−88.

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