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Potential of SPME-GC and Chemometrics To Detect Adulteration of Soft Fruit Purées

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The potential of combining solid-phase microextraction (SPME) with gas chromatography and chemometric data analysis to differentiate between pure strawberry samples (*Fragraria ananassa*) and strawberry samples adulterated with 10, 40, and 70% (v/v) apple purée was investigated. The method involved the extraction of aroma volatiles from the headspace of the purée samples using a SPME fiber followed by GC analysis with flame ionization detection. The principal component analysis (PCA) data matrix consisted of the relative percent peak areas of 37 compounds deemed to be significant in the differentiation of the samples on the basis of adulteration. The PCA results clearly showed that differentiation of the adulterated and unadulterated samples was possible, particularly at the higher levels of adulteration. Partial least-squares regression (PLSR) using a dummy set of *Y* variables (set to 0 for unadulterated and 1 for adulterated samples) resulted in clear discrimination between unadulterated purées and those containing 40 and 70% (v/v) apple. PLSR using a second set of *Y* variables, consisting of the actual level of adulteration, enabled quantification of apple purée with a standard error of prediction of 11.6%, implying a minimum detectable level of 25% (v/v) apple. GC-MS analysis enabled identification of the compounds with the greatest influence on sample differentiation. These compounds were identified as hexanoic acid, 2-hexenal, and α-farnesene, all of which are key aroma compounds in apples.

KEYWORDS: SPME-GC; strawberry; PCA; adulteration

INTRODUCTION

Purées from soft fruits, such as strawberries, are used in the food industry as a source of natural flavoring in the confectionery industry and as a base for jams and syrups. Although whole strawberries are difficult to adulterate, it is substantially easier to adulterate them in purée form. The principal reason for such adulteration is economic gain, as the most commonly used adulterants are extending substances, especially cheaper fruits such as apples, pears, and plums (*1*). The need for a reliable analytical technique to detect adulteration of fruit purées is clear, both to protect the economic interests of reputable food processors and to protect the consumers' right to know exactly what a food product contains (*2*).

Various analytical techniques have been tested to date in order to detect adulteration of soft fruit products, such as purées, with cheaper fruits. Visible and near-infrared spectroscopy methods have been used to detect and quantify adulteration of strawberry purée with apple purée (*3*), whereas high-performance liquid chromatography (HPLC) analysis of phenolic compounds in quince jam has been used to detect adulteration with pear purée (*4*). However, spectroscopic fingerprinting techniques are best suited to act as screening tools and are not generally capable of definitively identifying all of the individual constituents in a food product. Therefore, it is normally not possible to identify an adulterant in any given food product or raw material simply from any spectrum obtained. HPLC analysis of phenolic compounds is more specific but requires lengthy extraction and sample preparation steps, which significantly increase the analysis time.

Another option for the authentication of fruit purées is gas chromatography (GC). This is one of the most frequently used techniques for analyzing volatiles, including aroma compounds, in foods. It has been shown that different types of fruit possess very characteristic aroma profiles (*5*). Thus, the variations in aroma composition between strawberries and adulterant fruits may potentially serve as a basis for detecting adulteration of strawberry purée.

However, GC cannot handle the sample matrices directly, and some form of extraction and preconcentration is necessary prior to analysis of any given food sample. Solid-phase microextraction (SPME) was developed in the early 1990s as a means of extracting and preconcentrating pollutants in water samples (*6*). SPME involves the absorption/adsorption of volatiles and semivolatiles in a sample matrix onto a fused silica fiber. Direct desorption of the extracted compounds onto the GC column then occurs in the injection port of the GC system.

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SPME has many advantages over other extraction and preconcentration techniques used with GC (*7*). Solvent extraction techniques have the disadvantage of producing large amounts of chemical waste as well as possible contamination of the sample. Dynamic headspace sampling methods, such as purge-and-trap, are an alternative but tend to be costly in terms of both time and the required inert purge gas. Cross-contamination between samples is also a problem. SPME, on the other hand, does not require solvents or purge gas and can extract volatiles from the sample matrix in a relatively short space of time, usually <30 min.

SPME has found many applications in the area of food analysis. In a recent survey of publications dealing with SPME, it was found that 20% were concerned with food or botanical analysis (*8*). The various applications of SPME in food analysis have been extensively reviewed (*9*) and have shown that it can be used to detect characteristic aromas, off-flavors, pesticides, and antibiotics in various foods.

Fruit aromas, including those of soft fruits such as strawberry and raspberry, have been successfully analyzed using SPME-GC. Differences in the aroma composition between different fruits are clearly seen using this technique (*5*, *10*). A rapid spectroscopic technique known as time-of-flight mass spectrometry (TOFMS) has been coupled to SPME-GC and enabled analysis of aroma compounds in tomatoes, strawberries, and apples in <5 min (*11*, *12*). Subtle differences between soft fruit samples of the same species, such as aroma changes during storage, ripening, and processing, have also been detected using SPME-GC (*13*−*17*). The presence of insecticides in strawberry juice has been detected using this technique (*18*). However, despite the interest in SPME-GC as a technique for the analysis of fruits, it has not been applied to the detection of adulteration in fruit products, such as purées and jams.

The application of chemometric techniques to SPME-GC data has been investigated as a means of differentiating food samples. Different strawberry varieties were analyzed by SPME-GC and the chromatographic data subjected to statistical analysis (*19*). This enabled classification and discrimination of the different varieties on the basis of aroma differences. Chemometrics in conjunction with SPME-GC has also been applied to differentiation studies on whiskey (*20*), coffee (*21*), vegetable oil (*22*), and honey (*23*).

The aim of this research was to study the potential of SPME-GC in conjunction with chemometrics for the detection of adulteration in strawberry purée. The adulterant investigated was apple purée, which was added to strawberry purée samples at different levels. Headspace SPME (HS-SPME) was the particular extraction technique used. This involved extraction of the aroma volatiles present in the headspace above the samples. Principal component analysis (PCA) was employed to identify any differences present between samples that were exhibited by the GC data.

MATERIALS AND METHODS

Sample Preparation. Authentic Irish strawberry samples were obtained directly from producer farms at various times between May and September 2002. Purées were produced after removal of the green sepals; seeds were not removed from the purées. The purée samples for GC analysis were chosen randomly so that a range of strawberry varieties would be included in the sample set. The varieties used were Cambridge Favourite (two samples), Elsanta (two samples), and Symphony (three samples). There was also one sample each of Bolero, Florence, and Everest. Prior to analysis, the samples were frozen at −20 °C for 6 months. Each 100 mL sample of strawberry purée was thawed in a refrigerator set at 5 °C overnight prior to analysis. Apples (cv. Granny Smith) were purchased from a local food retailer and puréed after being cored and peeled. It was not deemed necessary to carry out any measure to minimize nonenzymic browning of the apple purée as fresh apple purée was made each day. The apple purée was used to adulterate the strawberry purées at levels of 10, 40, and 70% (v/v). A 100% apple purée was also included in the sample set.

HS-SPME Analysis. A manual SPME holder (Supelco, Bellefonte, PA) was used in the experiments. A 100 μm polydimethylsiloxane (PDMS) fiber (Supelco), 1 cm in length, was used for volatile sequestration. Prior to extraction, the fiber was conditioned for 30 min in the injection port of the GC at 250 °C. Aliquots (4 mL) of the purée preparations were transferred to 10 mL headspace vials. The sample vials also contained 1 mL of distilled water to aid agitation of the purée sample and a 60 μL aliquot of 1,2,3-trichloropropane (90 mg/l in H_2O/CH_3OH; Aldrich Chemical Co., Milwaukee, WI) as an internal standard to enable assessment of the retention time precision for the volatile component peaks. To promote the release of aroma volatiles into the sample headspace, 25% (w/v) of NaCl was also added to the sample vials. The vials were crimp-closed with a Teflon-lined silica cap and equilibrated at 50 °C for 20 min with constant stirring. The SPME fiber was exposed to the sample headspace at a constant depth for 30 min. The equilibration conditions for temperature and agitation were maintained during extraction of the aroma volatiles.

GC Analysis. A Varian 3800 GC system (Varian Chromatography Systems, Walnut Creek, CA), equipped with a flame ionization detector (FID) was used to perform the analysis. The system was coupled to a Star chromatography software system (v. 5.0; Varian Chromatography Systems). A fused silica capillary column (30 m × 0.25 mm i.d.; Alltech Associates Inc., Deerfield, IL) coated with a 0.25 μm layer of 5% phenyl and 95% PDMS (AT-5) was used. Helium was used as the carrier gas. Thermal desorption of the compounds took place in the GC injection port, equipped with a 0.75 mm i.d. splitless glass liner, at 250 °C for 5 min in splitless mode. The split valve was then opened (1:50), and the fiber remained in the injection port for the entire GC run to ensure complete desorption of the aroma compounds. The detector was operated at 250 °C. The oven temperature was programmed to range from 50 °C (maintained for 3 min) to 250 °C at a rate of 5 °C/min. The final temperature was maintained for 15 min.

Statistical Analysis. Relative peak areas (percent total) were calculated for all resolved GC peaks of interest. It was discovered that there were major compound peaks present in some samples that were heavily influencing the derived PCA model. These peaks were causing clustering of some samples based on strawberry variety and masking the discrimination of the samples due to the level of adulteration. It was therefore decided to exclude these peaks from the final PCA model. Also, to avoid the influence of solvent peaks and evaporation at the start of each chromatographic run, components having retention times of <5.5 min were omitted from the percent peak area calculations. The internal standard peak, with a retention time of 9.66 min, was also omitted from the calculations, as its influence on the PCA model was not related to the level of adulterant present. Thus, 37 chromatographic components were selected as significant in discriminations based on the level of adulteration. The majority of these peaks were chosen as their levels in strawberries were seen to decrease markedly according to the level of adulteration with apple purée. There were also a few peaks that were chosen for inclusion in the analysis due to their presence in samples adulterated with apple purée and their apparent absence in the pure strawberry purées.

PCA was carried out on the chosen components using The Unscrambler v. 7.6 (Camo ASA, Oslo, Norway). Using the same software, partial least-squares regression (PLSR) was employed against a dummy variable (set to 0 or 1) to test the ability of the method to discriminate between pure and adulterated purées on the basis of chromatographic data. Full-cross validation of the samples was carried out during PLSR due to the small number of samples and to increase the relevance and power of the PLSR model. An additional PLS1 model was developed to predict the percent apple content. Evaluation of this model involved determination of the correlation coefficient, root-mean-square error of prediction (RMSEP), slope of the regression line, and bias value (difference between the mean actual and predicted apple contents). The small number of samples used obviously prevented the development

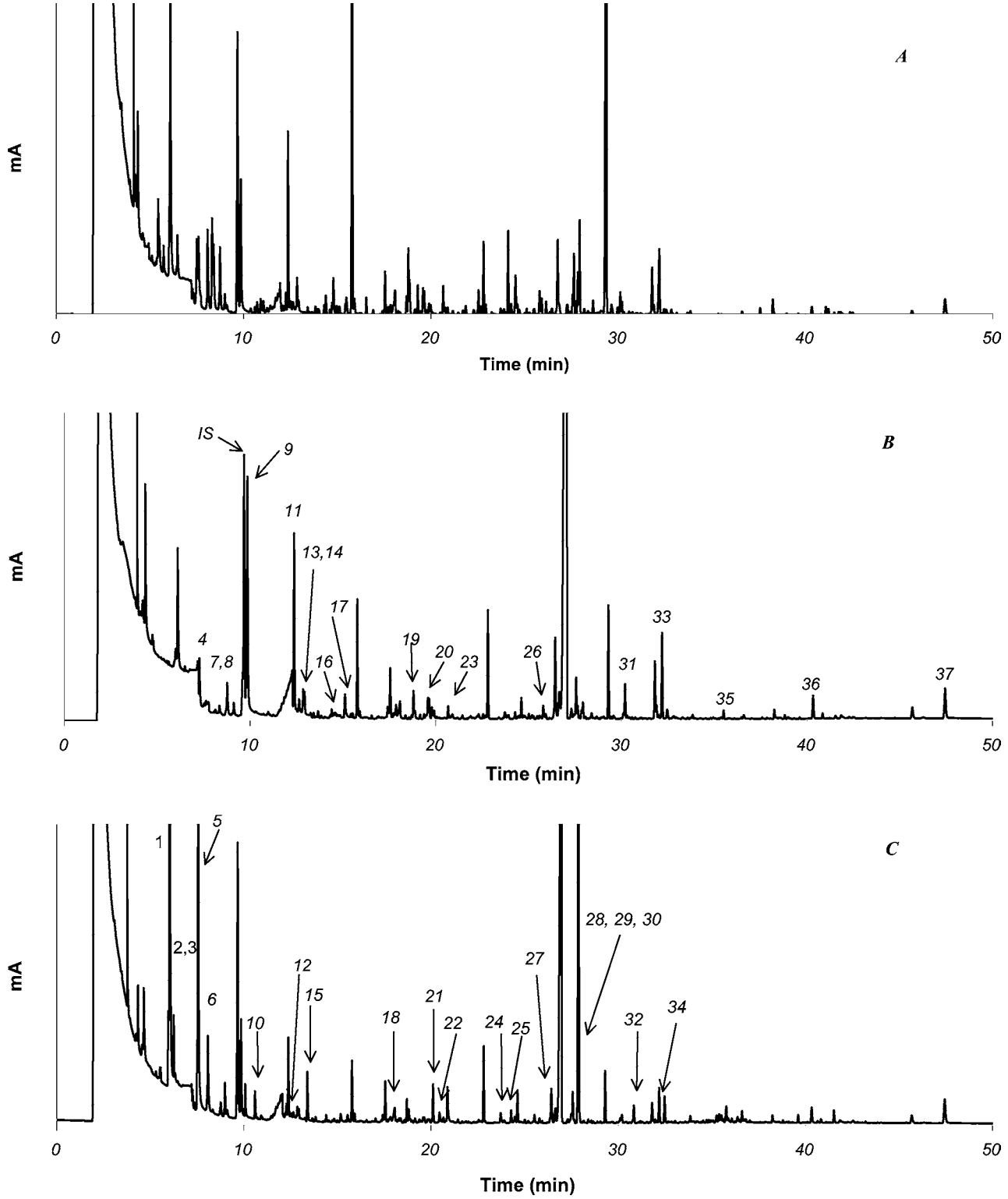

Figure 1. Chromatograms from a pure Cambridge Favourite sample (**A**), a pure Symphony sample (**B**), and a Symphony sample adulterated with 70% apple purée (**C**). Panels **B** and **C** show the 37 individual peaks that were selected for chemometric analysis. IS, internal standard.

of a definitive prediction model for PLSR but was deemed to be sufficient to enable a preliminary assessment of the potential of the technique to be carried out.

Identification of Headspace Volatiles. GC-MS was carried out to aid in the identification of the headspace volatiles responsible for the greatest amount of variation between samples. The system used was a Varian 3800 GC equipped with a Varian Saturn 2000 ion-trap mass spectrometer (Varian Chromatography Systems). The injection volume was 1 μL, and all other conditions were identical to those used for the GC-FID analysis. The mass range studied was m/z 40−650. Compounds were identified by matching their mass spectra with the data stored in the NIST library of standard compounds.

RESULTS AND DISCUSSION

The principal volatile compound peaks present in the strawberry purée samples varied according to the variety of strawberry tested. Chromatograms of unadulterated strawberry samples of different varieties are shown in **Figure 1A** (Cambridge Favourite) and **Figure 1B** (Symphony). The differences

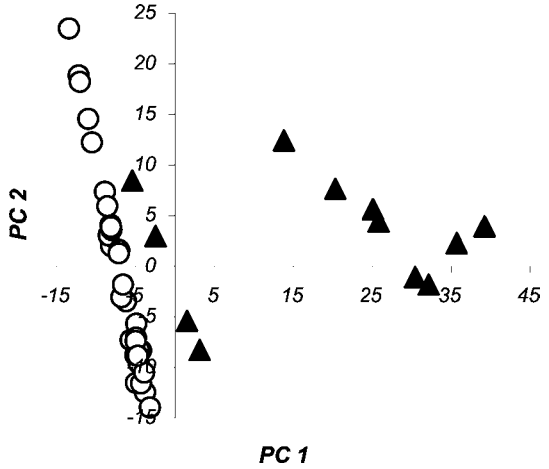

Figure 2. PCA scores plot showing the differentiation of strawberries of the variety Symphony from all other strawberry varieties tested: (solid triangle) Symphony; (open circle) all other varieties.

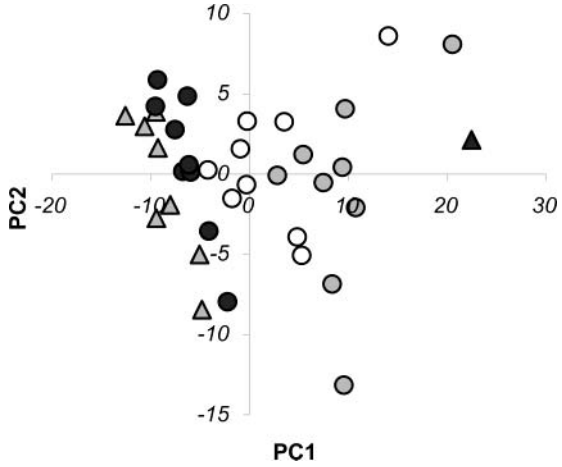

Figure 3. PC 1 versus PC 2 scores plot of the adulterated and unadulterated strawberry samples: (shaded triangle) 100% strawberry; (solid circle) 10% apple; (open circle) 40% apple; (shaded circle) 70% apple; (solid triangle) 100% apple.

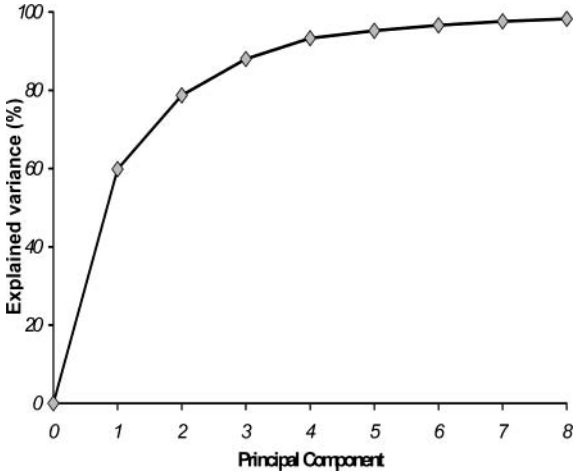

Figure 4. Cumulative explained variance plot for the PCA of selected GC peaks.

in composition between different varieties of strawberry are immediately evident from comparison of these two chromatograms. When initial PCA studies were carried out on the chromatographic data, it was discovered that there was some extent of clustering of strawberries based on variety. Specifically, the strawberries of the variety Symphony were separated from the other varieties used in the study. **Figure 2** shows the extent of this differentiation. From an examination of the loadings plot, the compound responsible for this differentiation was characterized by a retention time of 27.022 min. GC-MS results identified this compound as caryophyllene, an aroma compound that is present in a variety of fruits. It has been reported in black currant (*24*), raspberry (*13*), and mango (*10*). These obvious differences between strawberry varieties illustrate the need for analysis of the percent areas of individual compound peaks to enable the optimum number and choice of compound peaks to be included in the appropriate statistical analysis. In other words, compound peaks responsible for differences between varieties of strawberries were omitted from the statistical analysis, as they did not contribute to the differentiation of samples on the basis of adulteration. Also, by including such peaks in the PCA analysis, variability between samples on the basis of strawberry variety would be introduced, thus clouding the differentiation between samples on the basis of adulteration with apple purée.

The unadulterated strawberry sample in **Figure 1B** can be compared with the chromatogram of the same sample adulterated with 70% apple purée shown in **Figure 1C**. Initial visual examination of these two chromatograms indicates that significant differences can be detected between the pure and adulterated samples. This points to the potential for SPME-GC as an efficient means of detecting adulteration of strawberry purées with high levels of apple purée. The presence of a major peak at 27.48 min in **Figure 1C** is the most obvious difference between the adulterated and unadulterated sample chromatograms. However, for differentiating samples on the basis of the level of adulteration present, it was necessary to employ multivariate statistical analysis. This was because minor differences present between the pure strawberry purée samples and those samples adulterated with 10 and 40% apple purée could not be easily detected simply by visual comparison of the chromatograms. The 37 individual peaks chosen for chemometric analysis are indicated in **Figure 1B**,**C**. Several very small compound peaks were chosen for chemometric analysis, and this underscores the fact that the compounds with the largest peak areas were not necessarily the ones with the most influence on detection of adulteration.

Figure 3 shows the sample scores plot for the first two principal components for discrimination of the strawberry samples on the basis of adulteration. The samples are separated along a diagonal running from the bottom left-hand quadrant to the top right-hand quadrant according to the level of adulterant they contain. This indicates that statistical analysis based on the chosen compound peaks enables differentiation of the samples according to level of adulteration. The fact that the samples are separated along this diagonal shows that the level of adulteration is a very large source of variation between samples when the chosen compound peaks are studied. The first component (PC1) accounted for 60% of the variation present between samples, compared to 19% for the second PC. The explained variance for each PC is shown in **Figure 4**. The use of eight principal components was sufficient to explain 98.28% of the variance between samples.

It can be seen from **Figure 3** that one sample adulterated with 40% apple purée was not well differentiated from the samples adulterated with 70% apple purée. In particular, a sample adulterated with 70% apple purée lies very close to this 40% apple purée sample in this two-dimensional plot. Both of these samples come from the same strawberry sample of the variety Bolero. This was the only sample of this variety of

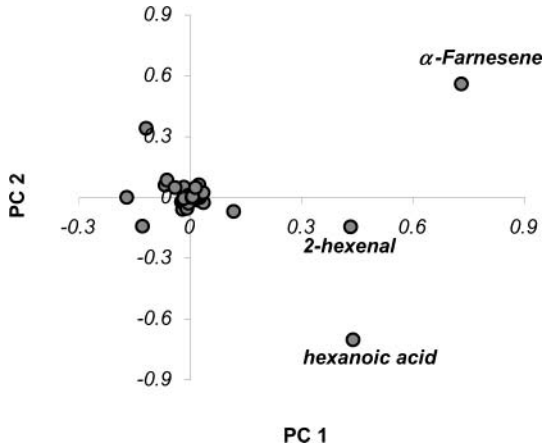

Figure 5. PC loadings plot for PC 1 versus PC 2 showing the influence of individual compounds on the differentiation of samples based on the level of adulteration.

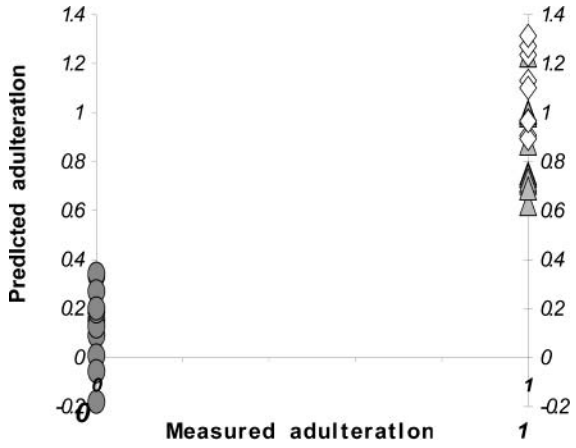

Figure 6. PLS1 results for pure strawberry purée samples and those adulterated with 40 and 70% apple purée, using eight PLS factors: (shaded circle) unadulterated strawberry purée; (shaded triangle) 40% apple purée; (open diamond) 70% apple purée.

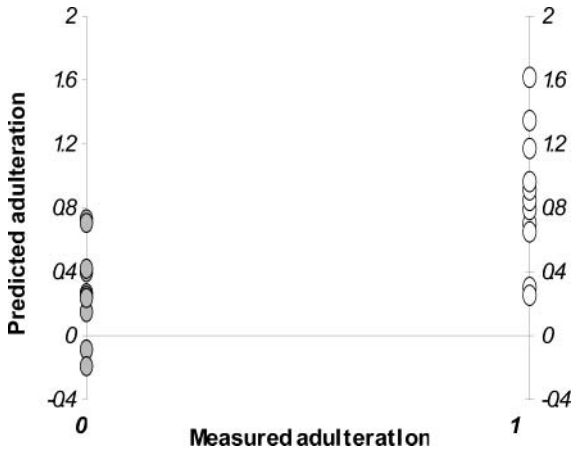

Figure 7. PLS1 results for pure strawberry samples and those adulterated with 10% apple purée, using eight PLS factors: (shaded circle) unadulterated strawberry purée; (open circle) 10% apple purée.

strawberry to be tested. Although it is not possible to determine if this is an indication of varietal differentiation similar to that shown in **Figure 1**, it again highlights the influence that strawberry variety may have on the chemometric results (*19*).

PCA analysis of the percent peak area for the selected compound peaks also enabled identification of the compounds that influenced the differentiation of the pure and adulterated samples to the greatest extent. The loadings plot in **Figure 5** pinpointed the compound peaks of greatest interest prior to their GC-MS identification. It was determined that the compound with a retention time of 27.85 min had the greatest influence on differentiating samples. This compound was identified by GC-MS as α-farnesene, one of the principal aroma marker compounds present in apples.

Other compounds that made significant contributions to the separation of samples according to adulteration level had retention times of 6 and 7.54 min. The relative percent area of both of these compounds was found to increase in direct proportion to the level of apple purée present in the sample (data not shown). The compound with the retention time of 6 min was identified by GC-MS as hexanoic acid. GC-MS analysis identified the compound with a retention time of 7.54 min as 2-hexenal. This compound has been reported as being an important flavor constituent of apples (*25*, *26*).

This research demonstrates that SPME-GC in conjunction with chemometric data analysis has considerable potential for the differentiation of unadulterated strawberry purée samples and those adulterated with different levels of apple purée. The principal substances responsible for differentiating the samples were characteristic aroma compounds for apple, as seen in **Figure 5**. This underscores the potential usefulness of the technique not only for detecting the presence of absence of adulteration but also for identifying the particular adulterant used by the presence of marker aroma compounds.

PLSR on a dummy variable was used to discriminate between unadulterated and adulterated strawberry purées. The PLSR results shown in **Figure 6** refer to the ability of the model to predict whether the purée samples are unadulterated or adulterated with 40 or 70% apple purée. It can be seen that the predicted values, along the ordinate axis, are well separated and clearly do not overlap. This is a sign that the model has potential for predicting whether an unknown sample is unadulterated or adulterated at apple purée levels of ≥40%. When the samples adulterated with 10% apple purée were included in the PLS1 model, its prediction capabilities were significantly reduced. Modeling of the unadulterated and 10% adulterated samples alone showed considerable overlapping (**Figure 7**). These results give an indication of the sensitivity of the prediction capabilities of the model.

To estimate the lowest possible detectable level of apple adulteration, a further PLSR model was created using the apple purée content of the unadulterated and adulterated strawberry samples as the *Y* variable. A visual examination of the residual variance plot for this model revealed four loadings to be optimum (first local minimum value), and the predicted versus actual line for this model is shown in **Figure 8**. The associated model statistics shown in **Table 1** describe a good model with a correlation coefficient of 0.91 and a RMSEP value of 11.5%. Given that the approximate detection limit, or reliability range, is ±2(RMSEP), one can conclude that the detection limit for the PLS1 model used is approximately ±25% (v/v). A plot of the regression coefficients for this model (**Figure 9**) reveals the role played by components eluting at 7.54 and 27.85 min in quantifying the apple content of purées. These have previously been identified as 2-hexenal and α-farnesene, respectively. On the contrary, troughs at 28.93, 26.86, and 9.24 min in **Figure 9** are key to the opposing feature of the purées, namely, strawberry content. The GC-MS data enabled identification of the compound eluting at 26.84 min as humulene. Unfortunately, the other two compounds could not be identified using the GC-MS data.

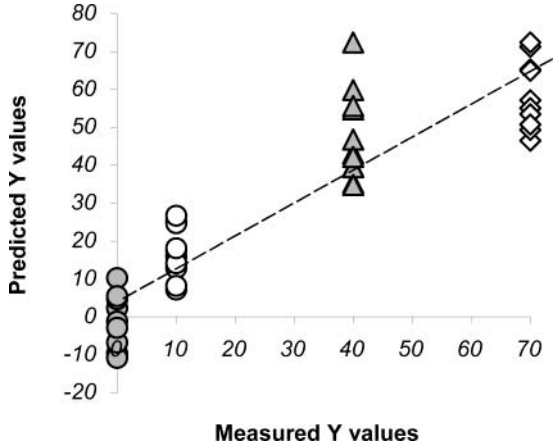

Figure 8. PLS results for predicted versus measured values of percent apple purée in the strawberry samples: (shaded circle) unadulterated purée samples; (open circle) 10% apple purée; (shaded triangle) 40% apple purée; (open diamond) 70% apple purée. The regression line (dashed line) is also included.

Table 1. Performance Statistics for the PLS1 Discrimination of the Strawberry Purée Samples Based on the Level of Adulteration Used and Using Eight PLS Factors

property	value
slope of regression line	0.864
intercept	4.27
correlation	0.91
RMSEP	11.5
bias	0.3

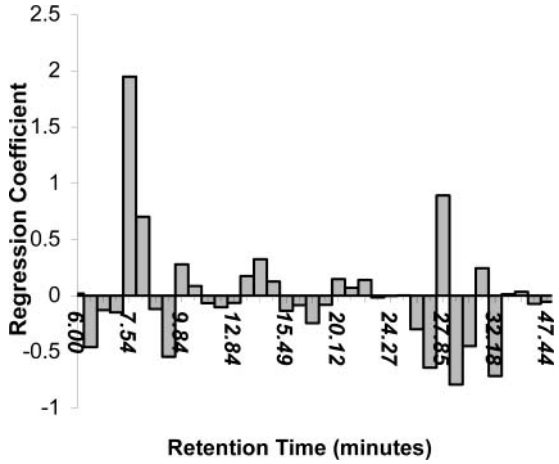

Figure 9. Regression coefficients showing the influence of individual *X* variables (compound retention times) used in the PLS1 model.

The advantages of the method include the minimal sample preparation that is involved prior to GC analysis and the fact that the main volatile compounds responsible for the differentiation of the samples can be identified. This would allow the data relating to these compounds to be easily isolated prior to statistical analysis while omitting the irrelevant data relating to unimportant compound chromatographic peaks.

It is clear from this feasibility study that, although preliminary results on the possibility of the applied technique appear to be promising, further research is required to extend the capabilities of the technique and analyze its potential for use in strawberry purée authentication in an industrial setting. This would involve the determination of the absolute minimum level of detection for adulteration of the strawberry purée with apple purée using a less ideal scenario of apple purées from different varieties of apple as opposed to just one variety as used in this study. Also, it would be interesting to carry out tests using strawberry purées at different stages of fermentation, as often occurs in bulk purée samples. However, the results do show that SPME-GC, as an analytical technique, has potential applications in food authentication that have not yet been fully addressed.

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