

Proc. Fla. State Hort. Soc. 117:407-410. 2004.

A REFEREED PAPER

**DIFFERENTIATING ORANGE JUICES USING ROUTINE ANALYSES
AS COMPARED TO INSTRUMENTAL METHODS**

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Additional index words. multivariate, statistics, PCA, DFA, ANOVA, MS, GC

Abstract. **Standard citrus laboratory procedures such as °Brix, acid, °Brix/acid ratio, color, pH, Scott oil, vitamin C and pulp, are compared to various instrumental methods for differentiating commercial orange juice products. Statistical models were generated using the data from an electronic nose (e-nose), a head space gas chromatograph (GC), and a mass spectrometer (MS) based chemical sensor. The separation using data from the standard procedures was similar to that obtained from the instrumental methods (e-nose, GC, MS), but has the**

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advantage that these tests are already being performed by industry and there is likely available data for modeling. Additionally, there would be no extra costs involved unlike with the other instrumental methods. Seven not-from-concentrate and 3 from-concentrate orange juice products were analyzed with excellent separation using the data from standard procedures. This compares favorably with the other methods examined in previous years.

The electronic nose is an important QA/QC tool used in many industries. Typically these instruments utilize advanced multivariate statistics coupled with a non-specific chemical sensor array in order to differentiate samples. Any type of sensor that responds to chemicals can be used for an electronic nose. For example, a flame ionization detector (FID) for a gas chromatograph (GC) can be used for a chemical sensor. As each compound elutes from the GC, the FID produces a response. The individual peaks of the chromatogram become the 'sensors'. This has some advantages in that the peaks are likely to be single compounds and thus the model can be related to specific chemicals, providing additional information. This method, however, is different from a traditional electronic nose since there is chemical separation of the individual constituents. There are currently no commercially available GC-FID electronic nose instruments.

In the case of a mass spectrometer (MS) based electronic nose, each mass to charge (m/z) is used as a 'sensor'. There is no chemical separation of the sample prior to analysis meaning that the mass spectra collected are that of the entire product. This lack of chemical separation is similar to the typical electronic nose method of introducing the sample to the non-specific sensor array which does not give individual chemical separation. Some of the advantages of the MS are apparent: sensitivity, selectivity, number of sensors, and speed, plus some basic information on mass range can be determined.

Traditional citrus processing utilizes many standard tests, some of which are decades old. Citrus processors have a tremendous amount of data available to them from the many analyses they have ran over the years. The most common tests are of °Brix (soluble solids), titratable acidity, °Brix/acid ratio, pH, color, pulp content, Scott oil, and vitamin C. Using these standard tests, a multivariate model can be built to differentiate orange juices.

Electronic nose instruments have been applied to citrus problems in the recent past (Bazemore et al., 1997; Goodner and Rouseff, 2001; Goodner et al., 2000; Goodner et al., 2001a; Shaw et al., 2000). This report is a continuation of research reported previously describing the various abilities of electronic nose types to differentiate orange juice samples. In this study, a multivariate model, based on standard tests of orange juice is compared to a traditional sensor based electronic nose, a GC-based electronic nose, and a MS-based electronic nose/chemical sensor.

Material and Methods

Seven 'premium' orange juice samples were obtained from a local grocer during the processing season. Six were 'not-from-concentrate' and one was a 'from-concentrate' juice. One sample was in a clear plastic container with the rest in gable top cartons. All samples were stored at -20 °C until time of analysis using a commercial metal oxide electronic nose and headspace (HS)-GC experiments. The samples analyzed by the MS-based chemical sensor were not the same as for the first two systems

(commercial e-nose and HS-GC) but were of the same type. They were purchased at a grocer in Baltimore, Md. and were stored at 4 °C until time of analysis (2 d). Ten orange juice samples, 7 'not-from-concentrate' and 3 'from-concentrate', were obtained from a local grocer in Winter Haven, Fla. for analysis using the standard citrus tests.

An Alpha Mos Fox 4000 e-nose was used for all metal oxide sensor data collection. The specifics for the data collection and analysis have previously been reported (Goodner et al., 2000).

The HS-GC system consisted of a Chrompak purge and trap headspace analyzer connected to an HP 5890 GC with an FID detector. The specifics for the data collection and analysis have previously been reported (Goodner et al., 2001a).

The MS-based chemsensor used was a Gerstel ChemSensor 4440A that includes a headspace sampling unit (7694, Agilent Technologies) with a mass selective detector (5973, Agilent Technologies). The juice samples used with the chemsensor were not the same as with the electronic nose and HS-GC. The specifics of the data collection and analysis have previously been reported (Goodner et al., 2002).

For the physical data experiments, 10 orange juice samples were obtained from a local grocer. Seven were "not-from-concentrate" and three were a "from-concentrate" juice. Six samples were in gable top cartons and four in plastic containers (either polyethylene terephthalate [PET] or polyethylene). °Brix and optical density were obtained using an AR200 digital refractometer (Reichert, Depew, N.Y.). Titratable acidity (pH 8.2 endpoint) and pH were obtained using a 614 Impulsomat, 605 pH-meter, and a 665 Dosimat (Metrohm, Herisau, Switzerland). Color was measured using a CR-300 Choma Meter (Minolta, Japan) (Anonymous, 1981). Vitamin C using 2,6-dichloroindophenol, Scott oil (Scott, 1968), and suspended pulp were analyzed using standard methods (Anonymous, 1981). Data was analyzed using Statistica versions 5 and 6 with discriminant function analysis, principal components analysis, and step-wise discriminant analysis.

Results and Discussion

The metal oxide based electronic nose provided adequate separation of the components as can be seen in Fig. 1. This

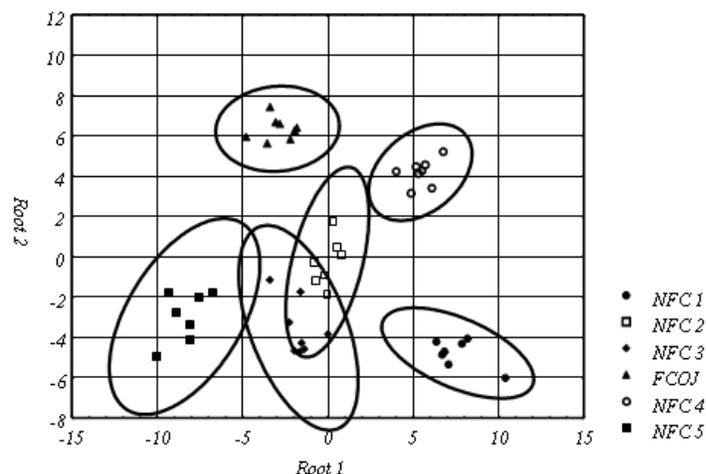


Fig. 1. Discriminant function analysis (DFA) of the electronic nose showing the best results.

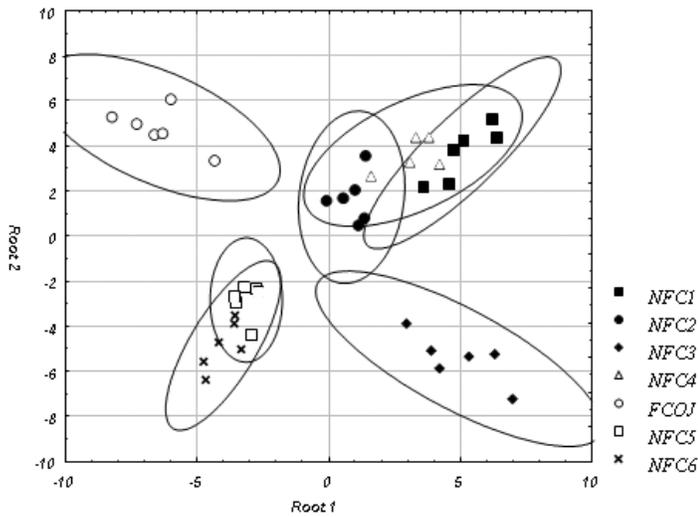


Fig. 2. Discriminant function analysis (DFA) of the HSGC showing the best results.

graph was produced by using a discriminant function analysis (DFA) with 15 variables which gave a data point to variable ratio of 3:1. There were 3 samples completely isolated from the others as the 90% confidence ellipses show with the FCOJ group being most differentiated. This was the best result obtained by Goodner et al. (2000) for the electronic nose.

Figure 2 is a graph of the DFA of data from the HS-GC using a 3:1 data point to variable ratio (13 variables). There are 4 distinct groups: 2 that are composed of single samples and 2 that are composed of multiple samples. The ellipses drawn are for the 90% confidence interval. The FCOJ sample is well separated from the other samples and NFC 5 is well separated from NFC 2 and 4. The samples that have significant overlap have no obvious similarities (i.e. they are not multiple brands from the same producer, but it is possible that some are actually from the same source). The groupings are different than those produced by the metal oxide electronic nose and have more overlap (Goodner et al., 2001a).

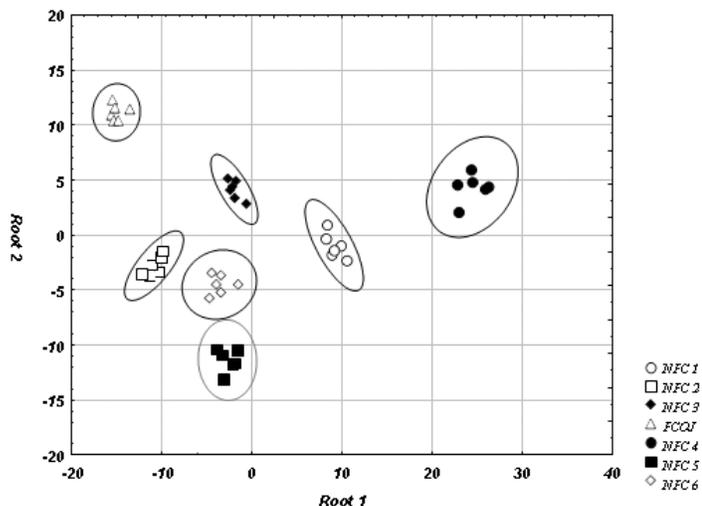


Fig. 3. Discriminant function analysis (DFA) of the MS-based electronic nose with 3:1 data point to variable ratio which is the same criteria as Figs. 1 and 2.

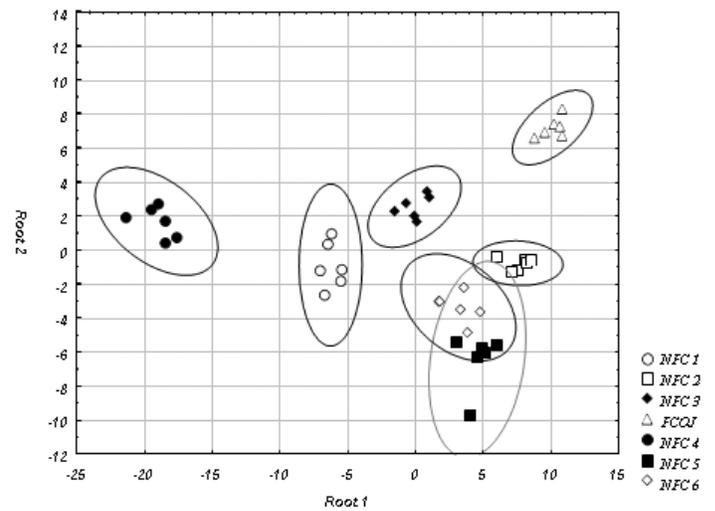


Fig. 4. Discriminant function analysis (DFA) of the MS-based electronic nose with 10:1 data point to variable ratio.

The MS-based electronic nose performed well. Figure 3 shows the results of a DFA of the data with a 3:1 data point to variable ratio (14 variables). All the groups are totally separated from each other with the 90% confidence ellipses drawn. The author has shown that the general rule of thumb of 3:1 ratio of data points to variables is not generally enough to ensure adequate modeling (Goodner et al., 2001b). It is statistically better to have a higher data point to variable ratio, generally 6:1 or even higher. Given this more stringent requirement, the author re-analyzed that only the chemical sensor was able to produce data sufficient for analysis with a data point to variable ratio of 10:1 (4 variables). The results are shown in Figure 4. There is still a good separation with 4 of the products completely differentiated and some overlap of the remaining three (Goodner et al., 2002).

Using routine physical analysis data for multivariate analysis worked satisfactorily. Figure 5 shows the results of a DFA for a data set with a 10:1 data point to variable ratio: 10 vari-

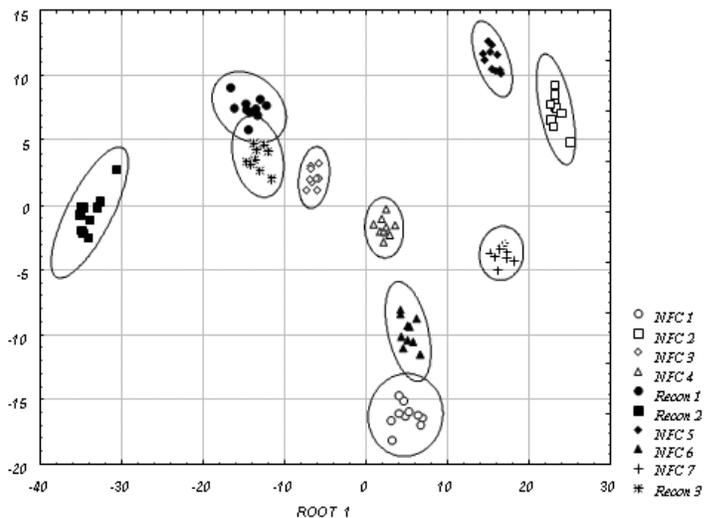


Fig. 5. Discriminant function analysis (DFA) of the physical data with 10:1 data point to variable ratio of ten juices.

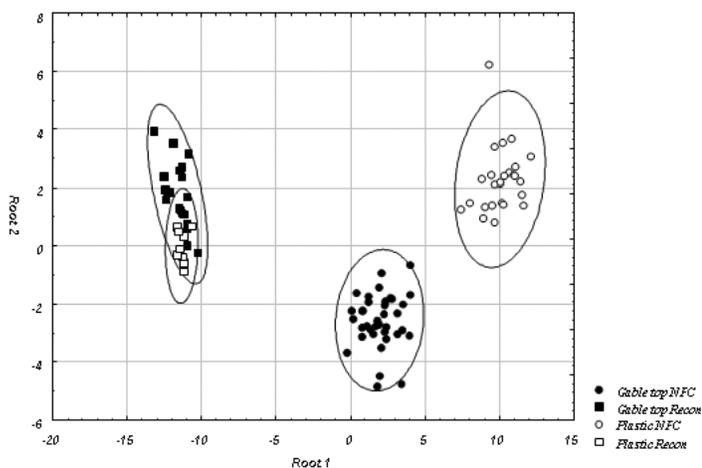


Fig. 6. Discriminant function analysis (DFA) of the physical data with 10:1 data point to variable ratio differentiating container type and processing method.

ables—color (HL, Ha, Hb), °Brix, titratable acidity, ratio, Scott oil, vitamin C, pulp, pH. The data are very well separated with only slight overlap of the 95% ellipses in two cases. In the first overlap, the two samples are both reconstituted orange juice. In the second overlap, the two samples are juice from the same company, packaged in different containers: paper-board gable-top carton versus PET bottle. The separation seen in Fig. 5 is equivalent or better than the other methods.

A DFA of the samples showing separation based on container and processing technique is shown in Fig. 6. The not-from-concentrate samples are both clearly separated from

each other (different containers) and from the reconstituted (recon) juice products indicating that there is a difference due to container and to processing. The reconstituted (recon) orange juice, however, shows no separation based on container indicating that there is little difference due to packaging for reconstituted orange juice.

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