AN035NT – Orange juice adulteration

Introduction

Due to its high concentration of Vitamin C, orange juice is a very common product on breakfast table that ensure to fill up your energy for the morning. It comes in several orange varieties that allow having a complete panel of tastes.
Orange juice producers are highly regulated, specifically on geographical origins traceability and authenticity.
In this study, it is proposed to use HERACLES fast gas chromatography, aroma analyzer and ASTREE taste analyzer to evaluate orange juice adulteration depending on the olfactory profile.

Materials & Methods

Samples

Five lots of commercial low pulp orange juices from concentrated (*Minute maid*) were used for analysis. The adulteration of orange juice was conducted by adding 0 to 20% of commercial grapefruit juice (*Florida Natural 100% Ruby Red*) in the orange juice samples as described in Table 1. Each level of adulteration was analyzed in five replicates.

Level of adulteration	Code
0% of grapefruit juice	0% GF
5% of grapefruit juice	5% GF
10% of grapefruit juice	10% GF
20% of grapefruit juice	20% GF
100% of grapefruit juice	100% GF

Table 1. Samples set

HERACLES Smell analyzer

HERACLES Electronic Nose (Fig. 1) is based on ultra fast chromatography. It features 2 metal columns of different polarities (non polar RXT-5 and slightly polar RXT-1701, length = 10m, diameter = 180µm, *Restek*) in parallel and coupled to 2 Flame Ionization Detectors (FID). Two chromatograms are obtained simultaneously, allowing a sharper identification of the chemical compounds. It allows headspace or liquid injection modes.
The integrated solid adsorbent trap thermo-regulated by Peltier cooler (0-260°C) achieves an efficient pre-concentration of light volatiles and shows a great sensitivity.
With fast column heating rates (up to 600°C/min), results are delivered within seconds and the analysis cycle time is around 5 to 9 minutes.

Fig. 1: Ultra Fast GC based HERACLES Electronic Nose (Alpha MOS, France)

The electronic nose is coupled to an autosampler (PAL3 RSI, CTC Analytics) to automate sampling and injection.
The instrument is operated through Alpha Soft software. In addition to classical chromatography functionalities, it provides chemometrics data processing tools such as sample fingerprint analysis and comparison, qualitative and quantitative models, quality control charts.

AroChemBase: Kovats Index library for chemical & sensory characterization

HERACLES e-nose was additionally equipped with AroChemBase module (Alpha MOS, France) that can be used within AlphaSoft E-Nose software. It consists of a library of chemical compounds with name, formula, CAS number, molecular weight, Kovats retention Index, sensory attributes and related bibliography. It allows pre-screening the chemical compounds and giving sensory features by directly clicking on the chromatograms' peaks.

ASTREE Taste analyzer

The ASTREE Electronic Tongue (Fig. 2) is based on liquid sensor array allowing a measurement of potential difference between each sensor and a reference electrode. Each sensor has a specific organic membrane, which interacts with chemicals present in the liquid sample. Recorded data are processed by the software as a global taste fingerprint.
Taste ranking module allows to have a direct measurement ranking of saltiness, umami and sourness. To evaluate taste attributes like sweetness, bitterness and astringency, it is strongly recommended to conduct the analysis with standard addition of the specific molecule related to the taste.

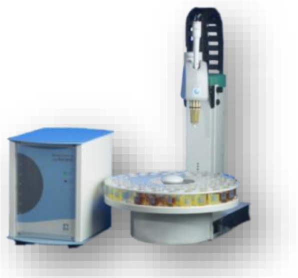

Fig.2: ASTREE Electronic Tongue (Alpha MOS, France)

Smell analysis

Analytical conditions

The analytical parameters optimized for this analysis are described in Table 2.

Parameters	
Sample mass	1 g
Vial	20 mL
Acquisition duration	110 s
Incubation temperature	40°C
Incubation time	10 min
Injection volume	1mL

Table 2: HERACLES e-nose analytical parameters

First, a standard mixture of n-alkanes (n-pentane to n-hexadecane) was analyzed, to allow retention time conversion into Kovats indices.

Volatile profiles

The odor profiles comparison of orange juice and grapefruit juice samples are displayed on Fig 3. The chromatograms showed quantitative and qualitative differences.

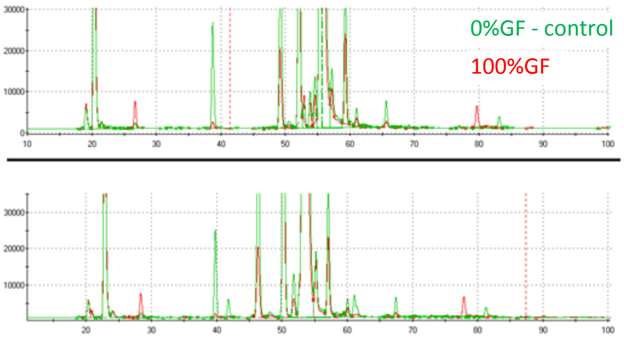

Figure 3. Heracles e-nose volatile profiles of orange and grapefruit juice samples

An odor map based on Principal Component Analysis can be generated using discriminating volatile compounds (Figure 4). There is discrimination between the reference orange juices and the adulterated samples.

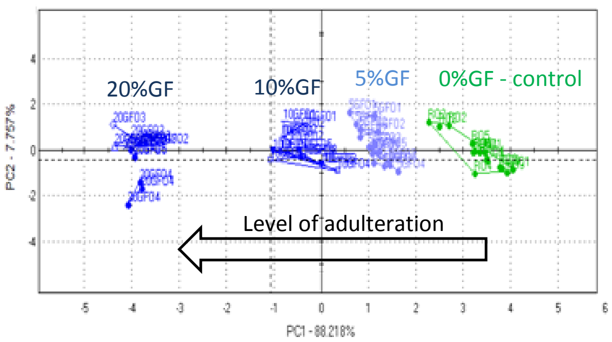

Fig.4: Odor map of orange juice samples based on principal component analysis (PCA) using selected volatile compounds of Heracles e-nose

Sensory ID: ensure your quality

AlphaSoft has a patent pending model to control sensory features of products and ensure quality of juice is conform to standard one.

Sensory ID algorithm is built using the entire signal of each orange juice sample in order to compare them and check deviation from standard quality. Results are displayed on a chart with a pass/fail representation for an easy interpretation. This typical model can be used online for quality control. The control orange juices were used as reference (Fig 5). The adulterated samples were clearly differentiated to the adulterated ones.

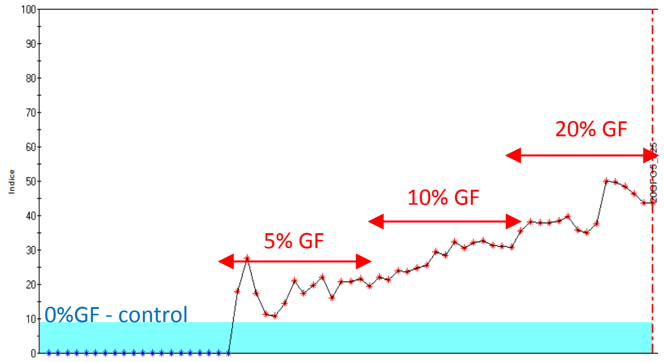

Fig.5: Sensory ID results for orange juice samples odor

AroChemBase: volatile compounds identification

The nature of most discriminative volatile compounds in the juice samples was investigated by using their Kovats index and the AroChemBase database.

Ester and aldehydes are the main discriminative compounds. The relative intensities of compounds are presented in Figure 6. The control orange juices samples are less concentrated in compounds like ethyl acetate, αselinene and dodecanal. These compounds gave added fruity and citrus notes to the adulterated samples.

Predictable model of adulteration

A PLS (Partial Least Square) model can be used to predict the adulteration of orange juice. On Figure 7, unknown samples (samples corresponding to 10% of adulteration of orange juice and 5% of adulteration of orange juice) were projected.

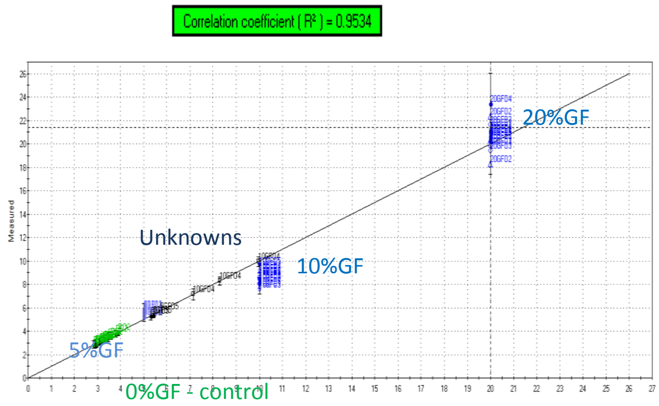

Fig.7: PLS predictable model of adulteration

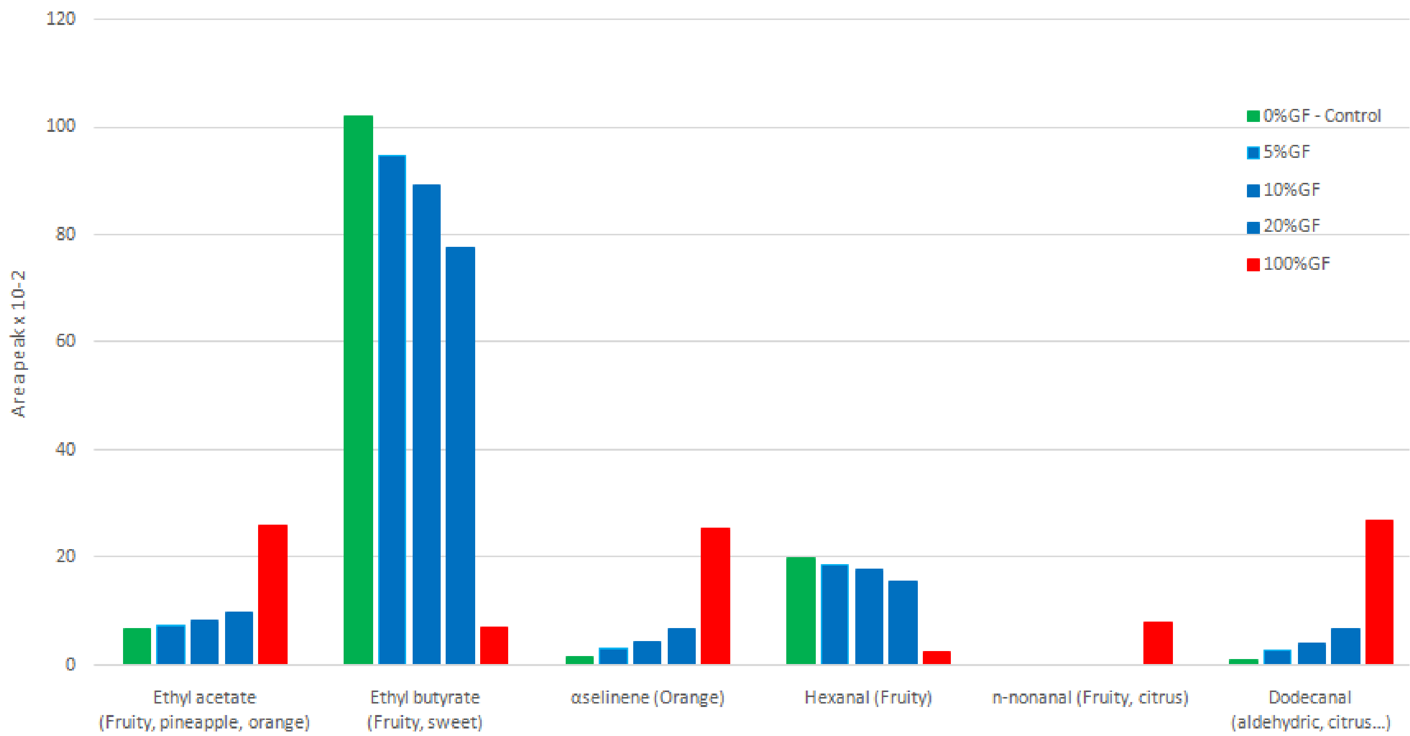

Fig.6: Most discriminated volatile compounds

Analytical conditions

Samples were analyzed with the ASTREE electronic tongue system equipped with an Alpha MOS sensor set #6 and the analytical conditions are described in the following table.

Parameters	
Sample volume	25 ml
Time per analysis	180 s
Acquisition time	120 s

Table 3: ASTREE taste analyzer parameters

Results: spider chart

The signal observed on each of the 7 e-tongue sensors presents difference between the orange juice and grapefruit juice samples (Figure 8).

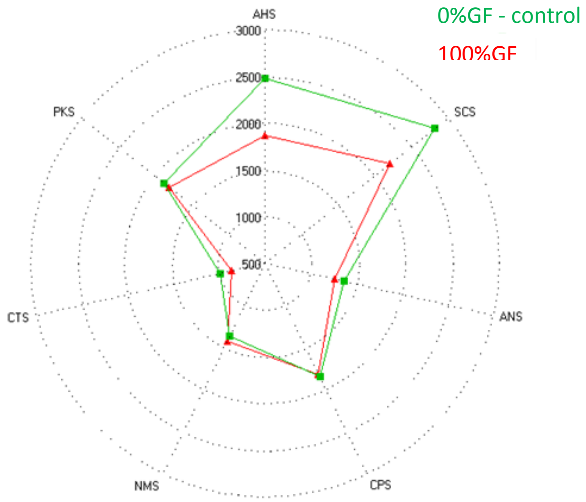

Fig.8: signal observed on the 7 ASTREE sensors

Taste comparison

Based on ASTREE measurements, a direct taste evaluation of sourness attribute of the orange juice is made using taste ranking scale from AlphaSoft (Figure 9). The 100% grapefruit juice sample is the sourest. Contamination of the control by the grapefruit juice increases the sourness level of the adulterated samples.

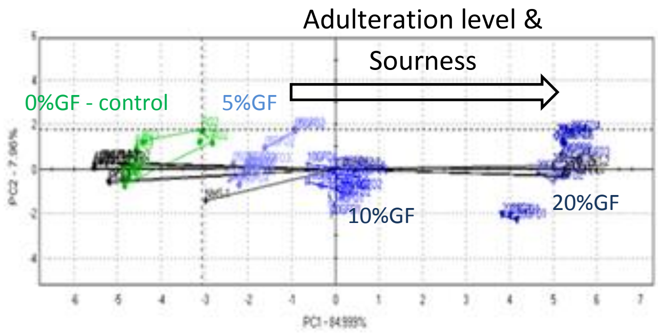

Fig.10: Organoleptic map of orange juice samples base on principal component analysis (PCA) with peaks of Heracles e-nose and Astree e-tongue

The data generated from HERACLES smell analyzer and from ASTREE taste analyzer can be combined in a single library on which multi-dimensional statistic can be operated (Figure 10). This analysis can give an organoleptic repartition of the samples. The control orange juice samples are least sour and less concentrated in compounds like ethyl acetate and dodecanal than the adulterated samples. These compounds add fruity and citrus notes to the adulterated samples.

Conclusion

Adulteration of commercial orange juice samples by grapefruit juice was investigated by using the HERACLES e-nose and ASTREE e-tongue.

The e-nose was able to clearly discriminate between the control orange juice and adulterated samples by grapefruit juice.

AroChemBase showed that contamination of orange juice by grapefruit increase the concentration in compounds like ethyl acetate and dodecanal with some added fruity and citrus notes.

The contamination of orange juice by grapefruit increases the sourness level of the samples.

This study demonstrates that HERACLES e-nose and ASTREE e-tongue can be valuable tools for quality control of fruit juices and suitable solutions to prevent cross contamination in the industrial production.

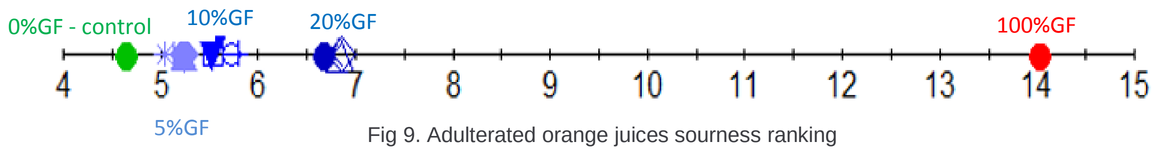

Fig 9. Adulterated orange juices sourness ranking