Introduction

Coconut oil is used in many personal care, homecare or food products. That is why its organoleptic properties must be strictly controlled to guarantee a consistent quality in the final product.
In this study, several samples of coconut oils previously assessed by a sensory panel were tested with a Fast Gas Chromatography based electronic nose, with an aim to further control the quality of the ingredient.

Equipment

HERACLES Flash GC Electronic Nose

HERACLES Electronic Nose (Alpha MOS, France – 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 (in the pg range).
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

The electronic nose is coupled to an autosampler (HS 100, 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.

Samples & Analytical Conditions

A total of 13 samples (table 1) were analyzed, among which 7 samples were used to build up the models and 6 were blind samples for which quality determination is needed. The samples were first evaluated by a sensory panel according to rancidity, sweetness and caramel notes intensities, from 0 (low intensity) to 3 (high intensity).

Table 1: coconut oil samples list

Sample Label	Rancidity	Sweetness	Caramel
R1 (reference)	0	1	1
R2	0	2	1
R3	0	2	2
R4	0	3	3
R5	0	0	0
R6	3	0	0
R7	1	1	1
A1 to A7	Blind samples		

Then, the samples were analyzed with HERACLES E-Nose (table 2). The analytical method was calibrated using an alkane mix (n-pentane to n-hexadecane) in order to convert

retention times in Kovats indices for further characterization of the molecules with AroChemBase module.

Table 2. HERACLES analytical parameters

Parameter	Value
Sample mass	2 ± 0.02 g
Vial volume	20 mL
Injected volume	5 mL
Incubation temperature	80°C
Incubation time	20 min
Columns temperature program	50 to 80°C by 1°C/s, then 80 to 250°C by 3°C/s and isothermal 250°C for 21s
Acquisition duration	110 s

Chromatograms

The comparison of chromatograms showed clear differences of volatile profiles between coconut oil samples (Figure 2). Rancid sample R6 contains higher concentration of multiple molecules compared to sample R4 or to blind sample A2.

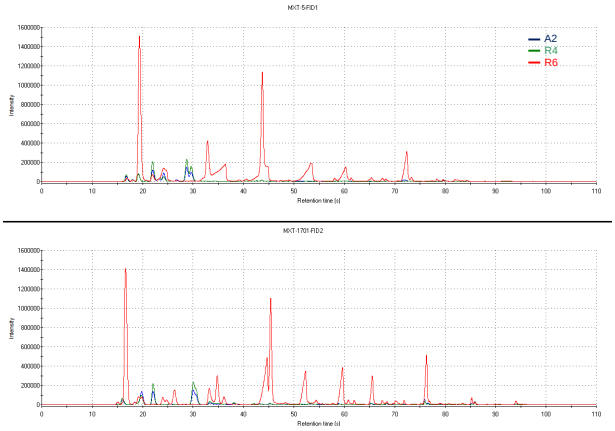

Fig.2: Volatile profile of three coconut oil samples obtained on HERACLES e-nose

Odor map

An odor map based on Principal Component Analysis (Figure 3) applied to HERACLES measurements, was generated by taking into account all chromatography data (retention times and peak areas for all compounds) for the set of known samples (R1 to R7).

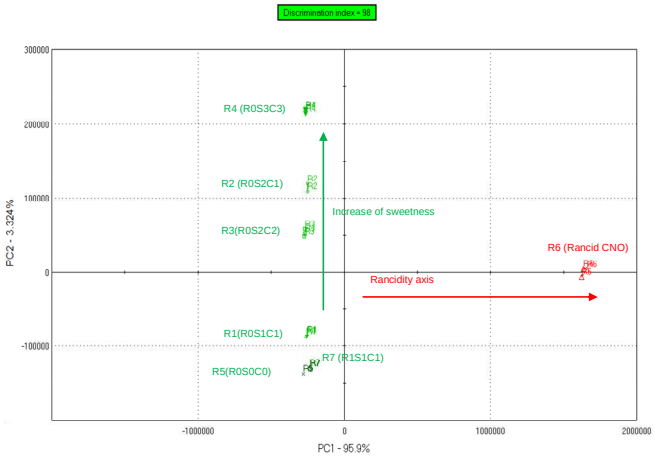

Fig. 3: Odor map of coconut oils R1 to R7 based on Principal Components Analysis (PCA) on all detected molecules

On this odor map, the most rancid sample (R6) is clearly discriminated from all others. This suggests that a horizontal rancidity axis can be defined on this map. All other samples are also clearly differentiated one from another.

Blind samples were then projected on the odor map in order to evaluate their odor profile (Figure 4).

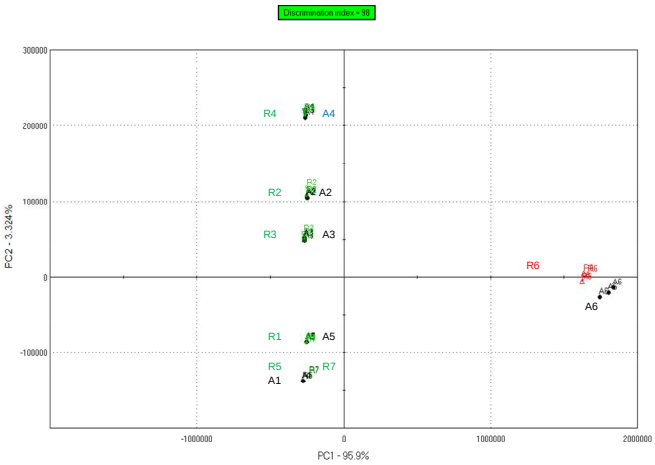

Fig. 4: Principal Components Analysis (PCA) of coconut oil samples with projection of blind samples (in black)

On the odor map, each blind sample is projected close to a sample from the training set:

- A1 to R5
- A2 to R2
- A3 to R3
- A4 to R4
- A5 to R1
- A6 to R6.

Characterization of volatile compounds

The nature of the most discriminant volatile compounds involved in coconut oil differences was investigated using Kovats indices and the AroChemBase database (Table 3).

Table 3. Volatile compounds identified in coconut oil

RT MXT-5 (± 0.1s)	RT MXT-1701 (±0. 1s)	KI MXT-5 (± 20)	KI MXT-1701 (± 20)	Possible identification	Descriptor
19.3	16.6	505	**505**	pentane	alkane
19.2	19.8	**501**	**600**	2-propanol	ethereal
22.0	22.1	**560**	**637**	2-methylpropanal	fruity, malty, spicy
24.2	19.8	**601**	602	hexane	alkane, kerosene
24.2	26.2	**601**	**701**	2-butanol	alcoholic
28.8	30.1	**655**	**742**	2-methyl butanal	almond, cocoa, green
29.6	30.1	**666**	745	3-methyl butanal	almond,malty, toasted
32.8	26.2	701	**701**	heptane	alkane, fruity, sweet
32.8	34.7	701	**789**	pentanal	almond, malty, pungent
36.4	-	**736**	-	3-methylbutanol	alcoholic, burnt, fermented
43.7	36.0	**804**	802	octane	alkane, fruity, sweet
43.7	45.3	**804**	895	hexanal	fatty, fishy, fruity
53.3	59.6	**906**	**1070**	pentanoic acid	cheese, pungent, sour
60.3	65.7	**994**	**1161**	(E,E)-2,4-heptadienal	fatty, nutty, oily, rancid
72.6	76.5	1185	**1354**	p-methylacetophenone	bitter almond, sweet
78.5	85.3	**1294**	1547	(Z) whiskey lactone	coconut

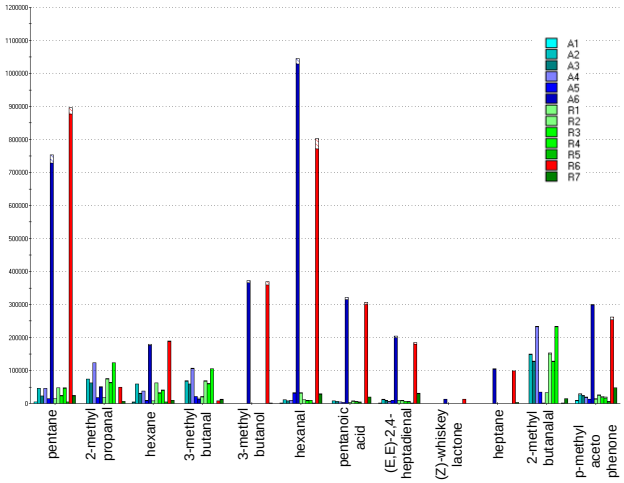

Fig. 5: Concentration (peak are) of the main volatile compounds from coconut oils

Figure 5 represents the proportion of the main volatile compounds in each coconut oil sample.

Correlation with sensory scores

AlphaSoft software allows to calculate the correlation coefficient between the sensory scores from the panel and the peaks detected with HERACLES instrument. This enables to define the molecules most correlated to each descriptor (Table 4).

Table 4. Correlation coefficients between molecules detected by e-nose and sensory attributes

RI*	Rancid	RI*	Sweet	RI*	Caramel
994.58(1)	0.96	666.15(1)	0928	666.15(1)	0.784
1354.47(2)	0.954	742.42(2)	0.919	742.42(2)	0.769
1161.11(2)	0.945	655.13(1)	0.908	637.92(2)	0.754
906.11(1)	0.922	637.92(2)	0.905		
701.84(2)	0.915				
884.33(2)	0.902				
804.77(1)	0.901				

*RI = Retention Index (number of the column on which the Retention Index is measured)

In addition, Partial Least Square (PLS) models correlating sensory scores to instrumental measurements (Figure 6) were set up in order to determine the sensory score of each blind sample on the three sensory attributes (Table 5).

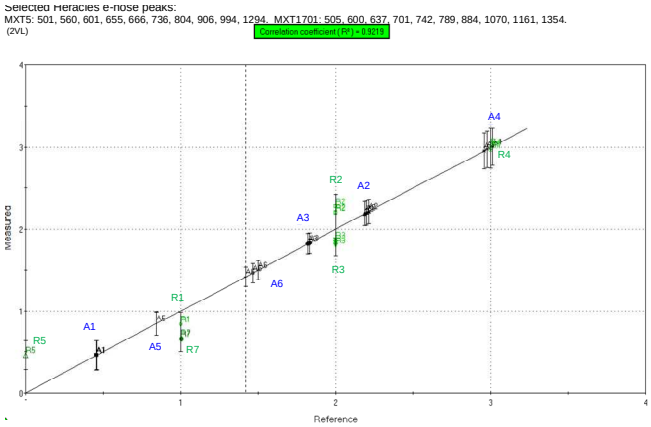

Fig.6: Sensory correlation model based on PLS algorithm for sweetness scoring of coconut oil (projection of unknown batches in black)

Table 5. Sensory scores of blind samples determined upon projecting on the PLS models

Sample Label	Rancidity	Sweetness	Caramel
A1	-0.07	0.46	0.36
A2	0.04	2.20	1.01
A3	0.10	1.83	1.84
A4	0.00	2.98	3.20
A5	0.17	0.84	0.93
A6	16.68	1.46	9.44

Conclusion

The analysis with HERACLES electronic nose proved to be very well correlated with sensory evaluation, since the scores obtained for the 3 attributes based on the instrumental models were confirmed by the panel.
In addition, the electronic nose allows a fast comparison of the overall odor profile of samples as well as a chemical characterization of the odorant compounds.