Objective

Competitive benchmarking, which consists of comparing one's products or processes to the leaders' ones, is a technique commonly employed by companies. This type of studies allows to position one's products in the market versus competitors and to give indications in order to improve, re-engineer or re-formulate products.
In this study, an Electronic Nose, an Electronic Tongue and an Electronic Eye were used to analyze and compare several brands of cat kibbles. The objective was to get detailed sensory information about target competitive products with an aim to re-formulate an existing recipe by retro-engineering technique.

Materials & Methods

Samples

Three brands of pet food (cat kibbles) are compared, Lycat which is the lowest budget brand and two higher priced competitive brands of pet food, Purina and Ultima. Kibbles made with same kind of raw ingredients were selected for the comparison.

Brand	Type of product	Cost per 100g
Lycat	Based on Chicken and Wheat	0.26 €
Purina	Based on Chicken and Wholegrain Cereals	0.55 €
Ultima	Based on Turkey, Rice and Wholegrain Cereals	0.56 €

Table 1. Pet food samples analyzed

HERACLES NEO Smell analyzer

HERACLES NEO Electronic Nose (Figure 1) is based on ultra-fast chromatography. It features 2 metal columns of different polarities (non-polar MXT-5 and slightly polar MXT-1701, 10 meters length, 0.18mm internal diameter, *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 (0-280°C) achieves an efficient pre-concentration of light volatiles and shows a great sensitivity.
With fast column heating rates (up to 480°C/min), results are delivered within seconds and the usual analysis cycle time is 8 minutes.

Figure 1: Ultra-Fast GC based HERACLES NEO 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 AlphaSoft software. In addition to classical chromatography functionalities, it provides chemometric 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 NEO 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 (Figure 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.
Samples were analyzed with the ASTREE electronic tongue system equipped with an Alpha MOS sensor set #6.

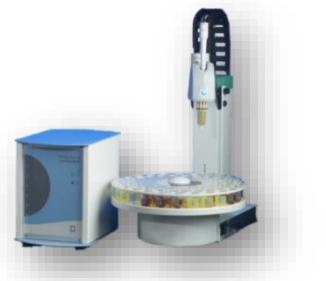


Figure 2: ASTREE Electronic Tongue (Alpha MOS, France)

IRIS visual analyzer

Through a CMOS camera, the IRIS analyzer achieves a detailed visual assessment of both color and shape parameters of the overall products or selected portions of these products. The analysis with IRIS instrument consists of taking a picture of the different samples. The pictures are then processed as a 4096-color spectrum, with the surface of each significant color calculated in percentage. A shape analysis of the samples is also integrated in the software. A visual characterization was performed with IRIS electronic eye with a 16mm lens with lightning from top and bottom after calibrating the instrument with a certified color scale.

Figure 3: IRIS Electronic Eye (Alpha MOS, France)

Data acquisition and data processing were achieved with AlphaSoft software (Alpha MOS, France) for the three instruments.

Methods

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

HERACLES NEO electronic nose parameters	
Sample mass	2.0 ± 0.1g of kibbles in a 20 mL vial 3 replicates
Headspace generation	20 min at 40°C
Injected volume	5 mL
Trap temperature	40°C / 240°C (desorption)
Columns program	50°C (2s) – to 80°C by 1°C/s – to 250°C by 3°C/s – 250 °C (21s)
FID temperature	260°C
ASTREE electronic tongue parameters	
Sample preparation	3 extractions prepared for each brand. 10.0 ± 0.1g of kibbles place in 100mL of deionized water heated at 80°C. Agitation of the mixture for 3min at 500rpm. Filtering of the clear phase for analysis.
Sample volume	25 mL
Acquisition time	120 s
IRIS electronic eye parameters	
Sample of kibbles (4.0 ± 0.1g) spread on the tray	

Table 2: Analytical parameters of the instruments

Odor analysis

The comparison of the chromatograms obtained with HERACLES NEO e-nose shows some significant differences between the volatile profiles of the three brands of pet food (Figure 4). some volatile compounds are common to the three brands, with more or less variation of intensities whereas some are characteristic of pet food brand. These volatile profiles variations are mostly linked to differences in flavors and raw materials used for the different recipes of pet food, which explains the significant differences noticed.

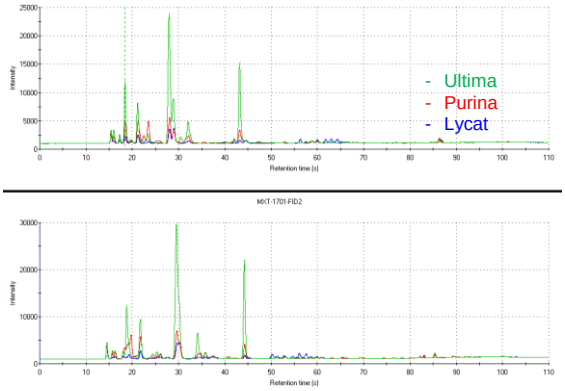


Figure 4: Superimposed chromatograms of the 3 brands of Pet food, obtained with HERACLES NEO e-nose

An odor map based on Principal Components Analysis (PCA) was generated using on all the volatile compounds detected in the headspace of the pet food samples (Figure 5).

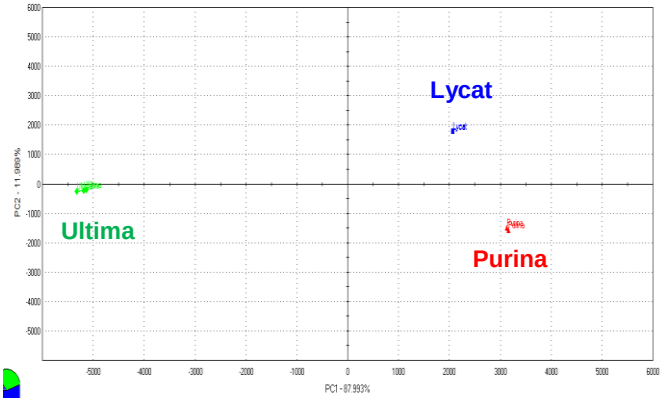


Figure 5: Odor map of pet food based on Principal Components Analysis (PCA)

The 3 brands are well discriminated on the PCA map and good reproducibility is observed between replicates. The odor of Lycat batches is closer to Purina. Ultima odor profile is the most different and presents highest volatile compounds intensity (figure 4).

The nature of volatile compounds involved in pet food flavor was investigated with the AroChemBase database using their Kovats indexes.

The possible identifications of these compounds are presented in table 3. The most discriminant compounds responsible of the main difference between the brands are in bold. The visualization of the area difference of these discriminant peaks is presented in the Figure 6.

KI MXT-5	KI MXT-1701	Possible matches	Odor Descriptor
435	458	Trimethylamine	Fishy, Pungent
447	**488**	**Methanthiol**	Fishy, Meaty
502	**577**	**Propanal**	Ethereal, Pungent
557	**635**	**Carbon disulfide**	Burnt
601	**600**	**Hexane**	Ethereal
654	738	Isopropyl acetate	Ethereal
665	**744**	**Thiophene**	Garlic, Sulfurous
698	784	Pentanal	Herbaceous, Green
804	890	Hexanal	Fishy, Herbaceous
951	**963**	**alpha-pinene**	Herbaceous
1049	**1046**	**5 -ethyl nonane**	-
1069	**1069**	**3-methyl decane**	-

Table 3. Possible volatile compounds responsible for pet food flavor

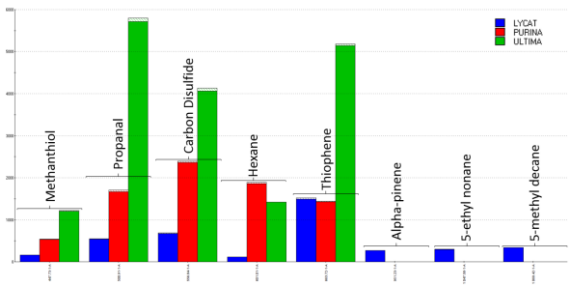


Figure 6: Concentration of various volatile compounds in the 3 brands of pet food

A Quality Control Card can be built up from a Statistical Quality Control (SQC) model (Figure 7). The Ultima batches were taken as reference because of it better food qualities. The Purina and the Lycat batches are plotted outside the area of acceptable quality (green area).

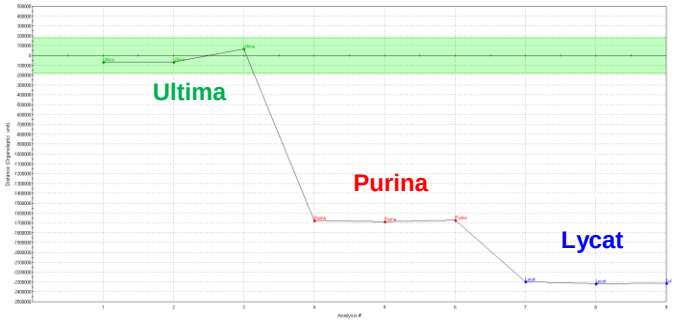


Figure 7: Odor Quality Control Card of Pet food

Taste analysis

Based on ASTREE measurements, it can be observed that the 3 brands of pet food show different taste profiles. The analyses of the 3 different extractions of the same brand are reproducible. According to the PCA map, Lycat batches have closer taste from the Ultima batches and Purina batches are more different (Figure 8).

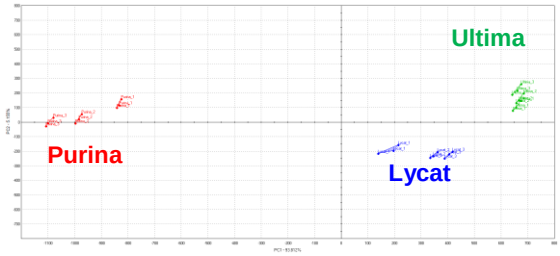


Figure 8: Taste map (Principal Components Analysis) of the 3 brands of kibbles obtained with ASTREE e-tongue

The sensor set#6 used for this study on ASTREE electronic tongue, combined with integrated software functionality allows to rank the samples according to taste attributes (Sourness, Saltiness and Umami). Samples are scored on a 0 to 12 intensity scale (Figure 10).
Purina is precepted more salted and less sour than the other brands. Ultima is the most acidic brand. Lycat is ranked intermediate regarding the 3 main sensory features measured by the e-tongue.

A Quality Control Card can be build up from a Statistical Quality Control (SQC) model (Figure 9). The Ultima batches were taken as reference because of their higher price. The Purina batches are plotted outside the area of acceptable quality (green area). The Lycat batches are also outside this area but closer to the limit.

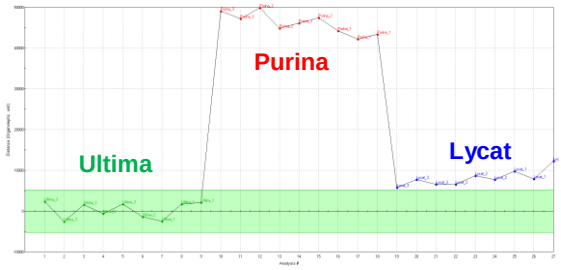
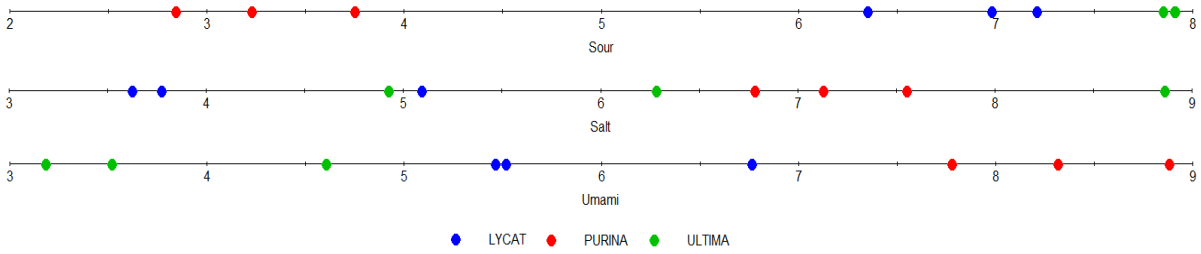


Figure 9: Taste Quality Control Card of Pet food

Figure 10: Taste raking of the 3 brands of kibbles obtained with ASTREE e-tongue (Sour, Umami and Salt)



Visual analysis

The visual aspect, which is linked to the composition and manufacturing process is an important parameter for the sensory benchmarking since it influences the visual perception.

Various shades of brown colors were observed, in different proportions according to the brand (Figure 11, 12 & 13).

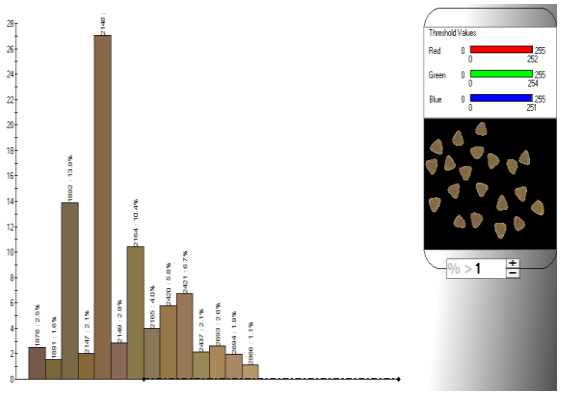


Figure 11: Color spectrum of the Lycat pet food obtained with IRIS system

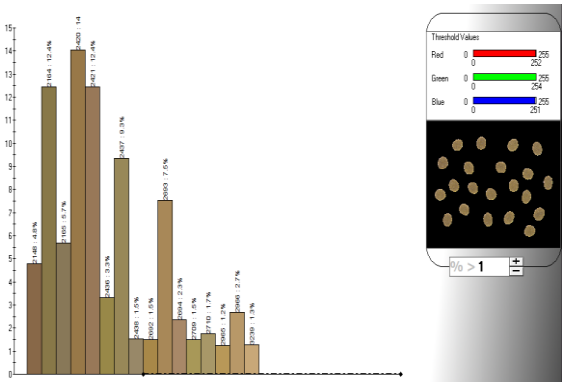


Figure 12: Color spectrum of the Ultima pet food obtained with IRIS system

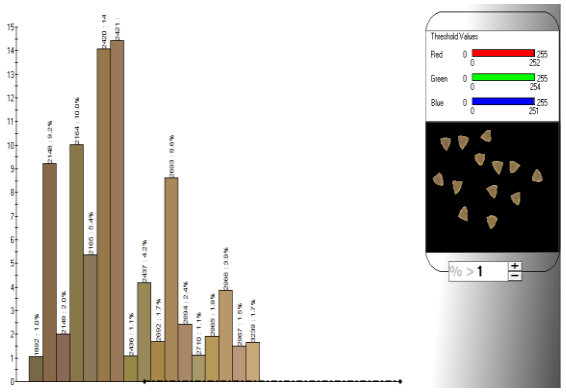


Figure 13: Color spectrum of the Purina pet food obtained with IRIS system

To rapidly and easily compare the global visual aspect of the different pet foods, the color and shape parameters measured with IRIS instrument were computed on Principal Components Analysis models (Figure 14 & 15).

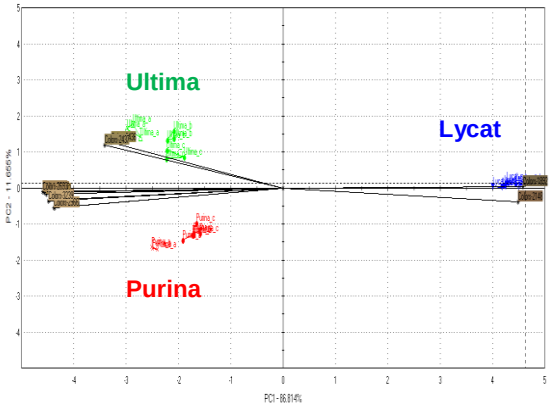


Figure 14: Principal Components Analysis model applied to color parameter measured with IRIS on the pet food

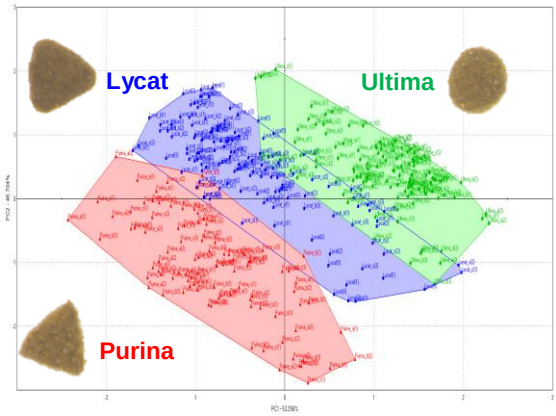


Figure15: Principal Components Analysis model applied to shape parameter measured with IRIS on the pet food

The comparison of the visual profiles based on color and shape criteria shows a clear discrimination between the brands:

- The differentiation of the 3 brands is mostly correlated with brown colors intensity
- The Ultima brand is closer to Purina based on the color parameters, whereas Lycat is quite different (darker).
- About the shape, variations are less important compared to color. The dispersion of kibbles within each brand is equivalent for each group and more important compared to discrimination between brands. Ultima and Purina are different and Lycat is in between these two brands. This can be explained by the overall shape of the products: Purina

kibbles are sharp triangles, Lycat kibbles are round edge triangles and Ultima kibbles are ovals (figure 15).

A Quality Control Card can be built up from a Statistical Quality Control (SQC) model (Figure 16). as previously, Ultima batches were taken as reference for this study. The Purina batches are in majority plotted inside the area of acceptable quality (green band) whereas the Lycat batches are outside this area. The quality control card allows to rapidly decide whether the visual aspect of pet foods is compliant or not.

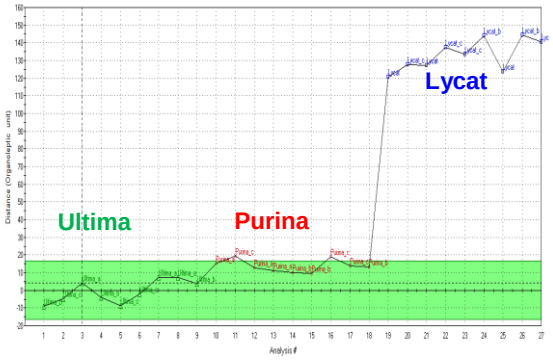


Figure 16. Visual Quality Control Card of pet food

Conclusion

Benchmarking study on various brands of cat kibbles was conducted using the HERACLES NEO e-nose, ASTREE e-tongue and IRIS e-eye. The e-nose was able to highlight differences of volatile profile between the brands. The odor of the Lycat kibbles is closer from the Purina kibbles and Ultima is further. Thanks to the AroChemBase, the compounds responsible of these differences were identified such as Propanal, Methanthiol or Carbon Disulfide.

The e-tongue allows to compare the product tastes and to rank them according to different attribute such as Umami or Sourness. Investigation on tastes shows different repartition of brands with Purina brand far apart of other competitors.

Finally, the evaluation of the overall visual aspect with the e-eye allows to show that Lycat product is darker and then more distant from the other products in term of color.

With each system, it is possible to explore the sensory profile of cat kibble and extract various information related to aroma , taste or visual aspect. A quality control model was created in order to visualize the differences between the brands and the acceptance area.

These instrumental results can be correlated with sensory value to develop more palatable product and be closer to target quality.