Objective

Water is used in many food preparation processes for washing and rinsing. As required volumes may be important in these processes, water recycling is often used.

However, if water is not changed with a sufficient rate it can concentrate off-odors that could be transferred to the product. Electronic nose can be used to monitor the water odor evolution in order to determine the water refreshing rate.

Equipment

HERACLES Flash GC Electronic Nose

The HERACLES Electronic Nose (Alpha MOS, France – Fig. 1) is based on the technology of ultra fast chromatography. It features two metal columns of different polarities (non polar RXT-5 and slightly polar RXT-1701, length = 10m, diameter = 180µm, Restek) mounted in parallel and coupled to 2 Flame Ionization Detectors (FID). Therefore, 2 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.
Headspace was generated in septum capped 50-ml vials (ref. 201-0190, Figure 2) on a heated tray (ref. 201-0020). This analysis could also be realized in 20-ml flasks using the HS100 oven.

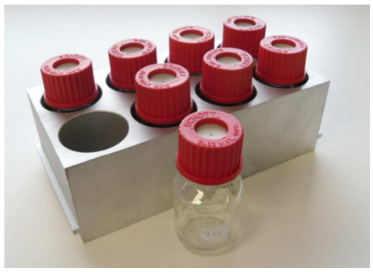

Figure 2. 50-ml vial aluminum tray for headspace generation (ref. 201-0190)

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.

Analytical conditions and samples

Chromatographic conditions were set to obtain high sensitivity in a short time range (Table 1).

Table 1. Heracles e-nose parameters

Parameters	Values
Sample volume	5 mL in a 50 mL vial
Heating temperature	heated tray at 50°C
Injection volume	5 mL
Trap concentrating temp.	40°C
Trap desorption temp.	240°C
Initial isothermal temp.	40 (2 s) 3°C/s to 280°C (88 s)
Acquisition time	90 s
Time between 2 injections	7 min

Water samples issued by a potato rinsing process were tested (Table 2).

Table 2. Process water sample

Process time	Odor level
Fresh water (0h)	Low odor
4 hours	Low odor
10 hours	Low odor
19 hours	Intermediate odor
48 hours	Strong off-odor
50 hours	Strong off-odor
54 hours	Strong off-odor

A standard mixture of n-alkanes (n-heptane to n-heptadecane) in ethanol was analyzed to allow retention time conversion.
Calibrations were conducted using butan-1-ol (Fluka, ref. 19417) and 3-methyl butan-1-ol (Sigma, ref. I9392) at concentrations of 0, 0.5, 1.0, 1.5 and 2.0 mg/L in deionized water.

Results & Discussions

The volatile compounds formed in the water during the rinsing process were detected with high sensitivity in 90s (Figure 1, Figure 2). Some compounds that were coleluted on column MXT-1701 were separated on column MXT-5, and *vice versa*.

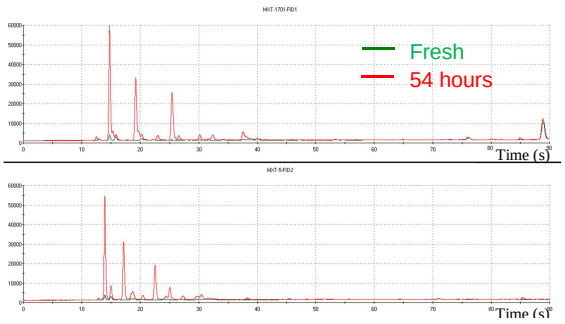

Figure 1. Volatile profile of fresh and odorous water on Heracles e-nose

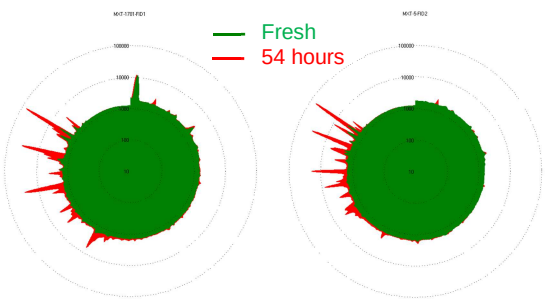

Figure 2. Radar plot representation of volatile compounds of fresh and odorous water on Heracles e-nose

A statistical data treatment was achieved on volatile profile of process water. The principal component analysis representation showed a clear evolution according to off-odor level in accordance with process time (Figure 3).

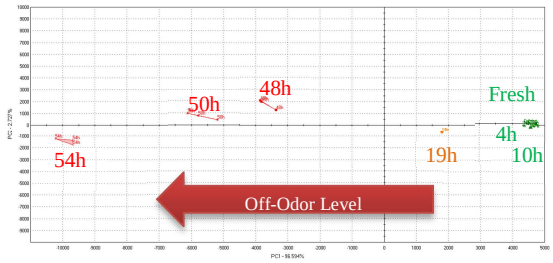

Figure 3. Principal Component Analysis (PCA) representation of volatile profile of process water

This evolution can be monitored in a statistical control chart that can be included in the analytical method in order to give on-line results (Figure 6).

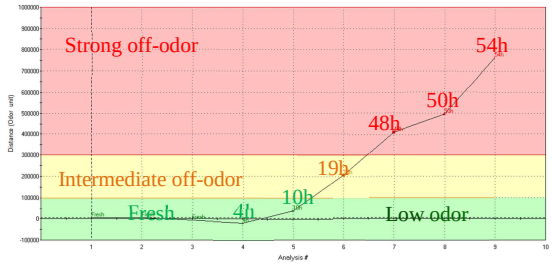

Figure 4. Statistical Quality control chart of process water odor based on Heracles e-nose results

AroChemBase was used to investigate the nature of volatile compounds of process water based on retention index of main peaks (Table 2). Most compounds were identified as alcohols. The identity of several identified compounds was verified by standard addition.

Table 2. Main volatile compounds identification using AroChemBase

RT MXT-5	RT MXT-1701	Compound Identification	Odor Descriptor
13.9	14.8	ethanol	alcoholic
15.0	15.8	acetone	glue
17.6	19.2	propan-1-ol	plastic
18.6	20.2	butan-2-ol	wine-like
22.5	25.4	butan-1-ol*	fermented
24.4	26.6	pentan-2-ol*	pungent
25.0	25.4	pentanal	herbaceous
27.3	30.2	3-methyl butan-1-ol*	cheese
29.7	37.6	2-methyl propionic acid*	cheese

* Off-odor related

Among these compounds, butan-1-ol and 3-methyl butan-1-ol were particularly associated with process water off-odors. The method was calibrated using standard solutions of these volatile compounds in water (**Erreur ! Source du renvoi introuvable.**, **Erreur ! Source du renvoi introuvable.**). These assays showed good linearity on the concentration range 0 to 2 mg/L.

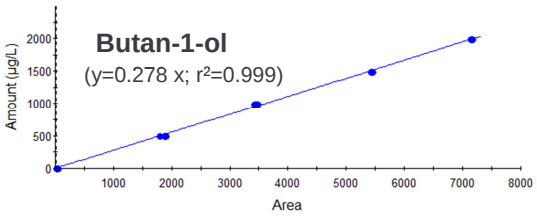

Figure 7. Calibration curve for butan-1-ol on column MXT-5

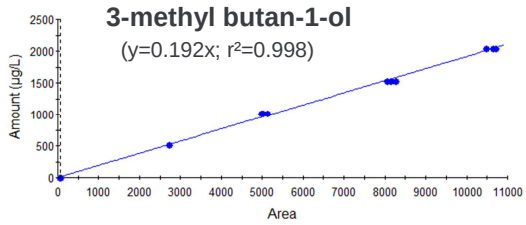

Figure 8. Calibration curve for 3-methyl butan-1-ol on column MXT-5

The repeatability was measured on one sample (Table 3). It showed a relative standard deviation (RSD) lower than 3% even at low concentration.

Table 3. Repeatability of quantification on Heracles e-nose on sample 54h

	1-Butanol	3-methyl butanol
Replicates	5	5
Mean (mg/L)	1.905	0.198
Standard deviation (mg/L)	0.009	0.005
RSD (%)	0.5	2.5

The quantification limit was estimated at 0.1 mg/L for each of these two compounds.

The amount of these 2 molecules was quantified in each water sample (
Figure 5). These compound showed increasing concentrations with process time, which is in good correlation with detected off-odor.

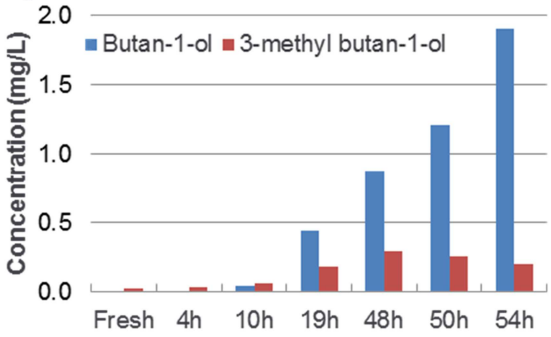

Figure 5. Concentration of butan-1-ol and 3-methyl butan-1-ol in process water samples

Conclusion

The HERACLES Electronic Nose allows analyzing water off-odors in few seconds, with a high sensitivity and repeatability.
Off-odor was associated with alcohols such as 1-butanol, 2-pentanol, 3-methyl butanol and 3-methyl propionic acid.
These molecules can be monitored in a statistical quality control chart or quantified after calibration. A good linearity and repeatability lower than 2.5% on the range 0 to 2 mg/L were obtained for butan-1-ol and 3-methyl butan-1-ol. This method showed high sensitivity with a quantification limit of 0.1 mg/L.
Globally, Heracles e-nose system is able to evaluate very rapidly the olfactory quality of process water to decide whether it could be kept or should be changed.