ANH17 – Odor Quality Control of Plastic Materials
Application to Polyethylene pellets

Objective

Polyethylene pellets are used as a raw material in a wide range of target markets for both domestic and industrial products (food packaging, plastic bottles, films, cosmetics…).
Controlling the olfactory quality of these products is very important: pellets should be free of off-odors as “plastic smell” or VOCs that can come from residual solvents or monomers due to an incomplete polymerization of ethylene or a degradation of molecules.
Very often, the quality of granules is checked through a long sensory panel testing procedure which involves pellets soaking in water for several hours, then evaluation after successive dilutions until no odor / taste is detected by the panelists.
This application describes the method and results obtained with an electronic nose for the analysis of polyethylene pellets.

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.
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

Six samples of polyethylene pellets obtained through 3 different processes, were analyzed with HERACLES II electronic nose:

- 2 good samples G1 & G2 obtained by a first process,
- 2 medium quality samples M1 & M2 obtained by a second process,
- 2 bad samples B1 & B2 obtained by a third process.

Main Analytical Conditions

Sample Preparation	
Vial	20mL
Sample mass	2 ± 0.01g
Headspace generation	
Incubation temperature	60°C
Incubation time	20min
Syringe volume	5mL
Injector	
Injected volume	5mL
Injection speed	500µL/s
Injector temperature	200°C
Injector carrier pressure	25kPa
Injector vent	30mL/min

Trap	
Initial temperature	40°C
Trap pressure	80kPa
Split	10mL/min
Trapping duration	20s
Heating duration	35s
Final temperature	240°C
Columns temperature program	
Program	40°C (2S) to 280°C (28s) by 3°C/s
Acquisition time	110s
Detectors	
Temperature	290°C
Gain FID	12

Chromatography profiles

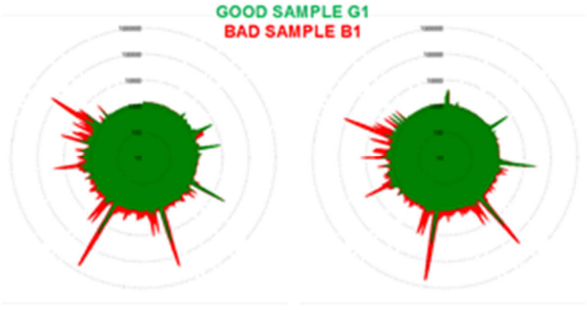

Fig. 1: Radar plots (odor fingerprints) of G1 (good) and B1 (bad) samples of polyethylene obtained with the chromatograms of HERACLES II on the 2 columns

The comparison of the chromatograms (fig. 1) run with HERACLES e-nose shows important differences in terms of VOCs concentration between samples produced through various processes. As an example, batches obtained with the first process and corresponding to good quality (sample G1 in green) contain a lower amount of volatile compounds than bad pellets obtained with the third process (sample B1 in red).

Odor Characterization

Chemical characterization

Using the AroChemBase and Kovats indices on MXT-5 & MXT-1701 columns (table 2) it could be observed that the major peaks correspond to alkanes and derivatives.
The presence of hexane at a higher concentration in bad samples is suspected to be responsible for the off-odor that can be detected in these samples.

RI* MXT5 (± 10)	RI* MXT1701 (± 10)	Possible matching compounds	Sensory attributes	Presence in samples
400	400	**Butane**	Alkane	Medium, Good, Bad
500	500	**Pentane**	Alkane	Bad
519	619	2-methylpropanal / acrylonitrile	Pungent	Bad
560	560	2-methyl-pentane	Alkane	Bad
578	578	3-methyl-pentane	Alkane	Bad
600	600	**Hexane**	Ethereal, kerosene-like	Good, Medium, Bad
629	635	*Methyl-cyclopentane*	Alkane	Medium, Bad
664	661	Cyclohexane	Alkane	Good, Medium, Bad
671	671	2-methylhexane / *hexamethyldisiloxane*	-	Good, Medium, Bad
700	700	**Heptane**	-	Good, Medium, Bad
730	735	2,2,3-trimethylpentane	Alkane	Good, Bad, Medium
800	800	**Octane**	Sweet, fusel-like	Good, Bad, Medium
960	960	Methyl-nonane	-	Bad, Medium
970	970	Methyl-nonene	-	Bad, Medium
1000	1000	**Decane**	Fusel-like	Good, Bad, Medium
1046	1052	*Alkene*	-	Bad, Medium
1056	1054	*3,8-dimethylundecane / 1-ethyl-3-methyl-cyclopentane*	-	Medium
1099	1098	**Undecane**	-	Medium, Bad
1155	1154	6-methyl-undecane	-	Bad, Medium
1171	1171	3-methyl-undecane	-	Bad, Medium
1200	1200	**Dodecane**	Alkane, fusel-like	Good, Bad, Medium
1400	1400	**Tetradecane**	Sweet, fusel-like	Medium
1600	1600	**Hexadecane**	Alkane	Bad, Good, Medium

Table 2: Possible volatile compounds identified by their Kovats indices in the headspace of polyethylene pellets
*Retention Index (Kovats Index)

Polyethylene pellets odor map

The odor map based on Principal Components Analysis (PCA) shows a clear discrimination of pellets according to their volatile compounds composition (fig. 3).

Good pellets on the right part of the PCA graph, have the lowest odor level.

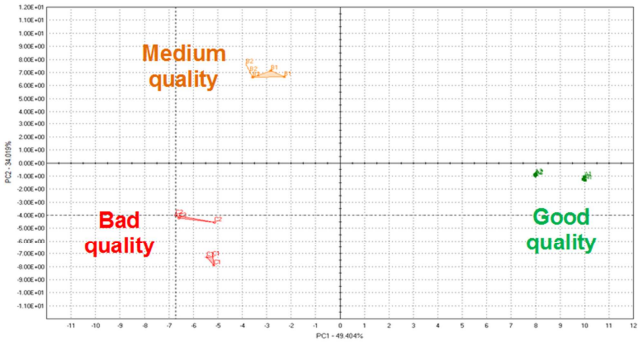

Fig. 3: Principal Components Analysis of polyethylene pellets obtained with HERACLES e-nose measurements

Polymer Pellets Quality Control Card

To achieve the quality control of pellet batches, a Statistical Quality Control model was set up with good samples G1 & G2 taken as the gold standards.
Figure 4 shows the area of good quality (in green) and out of specifications area (in white). Medium and bad samples clearly appear out of the area of acceptance.

Fig. 4: Statistical Quality Control model of polyethylene pellets obtained with the major peaks measured with HERACLES e-nose

Conclusion

The e-nose can be a very powerful tool to rapidly assess the character of plastic pellets and minimize the risk of contamination due to the presence of unintended components in the product. In addition it could be used to qualify suppliers and packaging components and select those that are less prone to give up any contaminants while better protecting the product.