Introduction

Plastics such as Polyethylene (PE), polypropylene (PP), High Density Polyethylene (HDPE) and polyethylene terephthalate (PET) are increasingly recycled. However, the contamination of plastic can be a threat to the quality and security of recycled products. In order to minimize this risk, recycling factories count on dilution of possible contaminated sources and also on an intense cleaning process to eliminate most contaminants.

This sustainable business should respond to strict rules, such as FDA regulations, when pellets are intended for food grade packaging. The presence of residual off-odors can also be very problematic for products in which any foreign odor can be easily detected. The products should be odor-free like virgin polymer. The FDA1 recommends monitoring the presence of volatile compounds such as chloroform, toluene, benzophenone and methyl salicylate in recycled plastic.

Some other contaminants such as limonene can affect the organoleptic features - in particular the taste - of food due to their extensive use in soft drink bottles such as cola, orange and citrus beverages. This contaminant can be easily sensed by a consumer when the recycled plastic is used as a food packaging.

In this study, it is proposed to use HERACLES fast gas chromatography Electronic Nose to detect the main contaminants of recycled plastics.

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

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

Then, recycled HDPE resins without contamination and with addition of contaminants were analyzed with HERACLES instrument (Table 1).

Samples headspace is generated in septum capped 20-mL vials containing 2g of plastic pellets.

Calibrations were achieved using a mixture of chloroform, benzene, toluene, 4-vinyl-1-cyclohexene, trichloroethylene, limonene, methyl salicylate and benzophenone in methanol.

Table 1: Heracles e-nose parameters for plastic analysis

Parameters	Values
Sample mass	2 g
Headspace vial	20 ml
Heating temperature	100°C
Injection volume	5 ml
Trap concentrating temp.	40°C
Trap desorption temperature	240°C
Column pressure	80 kPa (0s) 1 kPa/s to 140 kPa
Initial isothermal temp.	40 (2 s) 3°C/s to 280°C (8 s)
Acquisition time	90 s
Time between two injections	7 min

Chromatograms

The potential contaminant molecules of plastics can be separated on a chromatogram in less than 2 minutes (Figure 2).

Concentration Quantification

Each volatile compound can be calibrated in a clean plastic matrix and calibration curves show a good linearity (Fig. 1, Fig. 2).
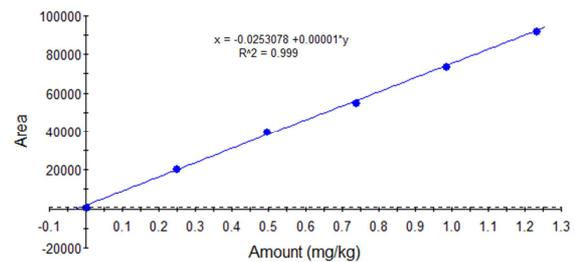

$x = -0.0253078 + 0.00001 * y$
$R^2 = 0.999$

Fig. 1: Calibration curve of benzene in plastic (MXT-5 column)

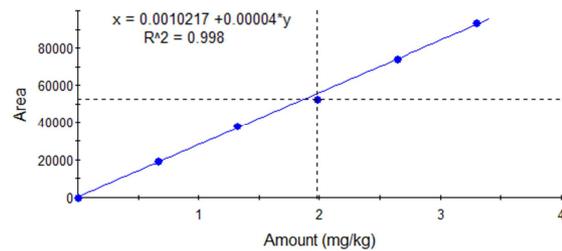$x = 0.0010217 + 0.00004 * y$
$R^2 = 0.998$

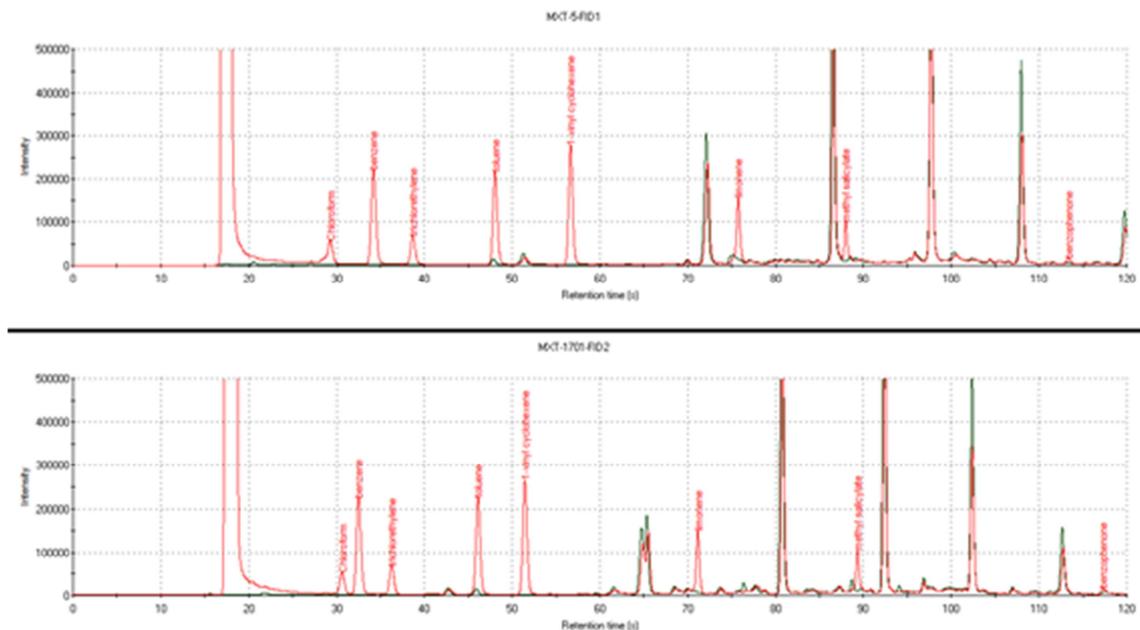Fig. 2: Calibration curve of 1-vinyl cyclohexene in plastic (MXT-5 column)

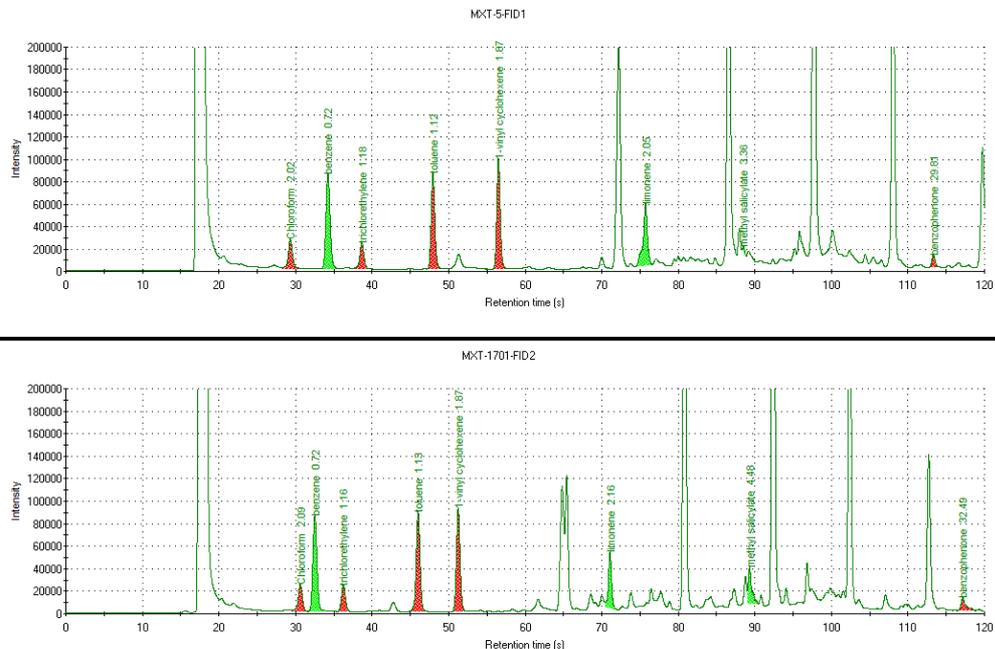Fig.2: Volatile profile of HDPE with chemical contamination on Heracles

Fig.5: Composition analysis (in mg/kg) of volatile contaminants of HDPE with limit interpretation (green for pass and red for fail)

The concentration of contaminants in unknown samples can be displayed directly on the volatile profile (chromatogram Figure 5). For each peak, the concentration conformity is directly displayed: peaks colored in green indicate that the concentration of this compound is in the conformity range, whereas peaks colored in red indicate that the concentration of this peak is not conforming.

With this analytical method, the detection limits in plastic ranges from 0.5 µg/kg to 2 mg/kg depending on the compound (Table 2).

Table 1. Detection limit of main contaminants of plastic using HERACLES

Compound	Detection limit (mg/kg)
chloroforme	0.1
benzene	0.0005
trichloroethylene	0.01
toluene	0.01
1-vinyl cyclohexene	0.001
limonene	0.01
methyl salicylate	1
benzophenone	2

Compounds characterization

AroChemBase can be used to investigate the nature of unknown volatile compounds in plastics based on the retention indices of the main peaks (Figure 6). Information on odor threshold of several volatile compounds is additionally available.
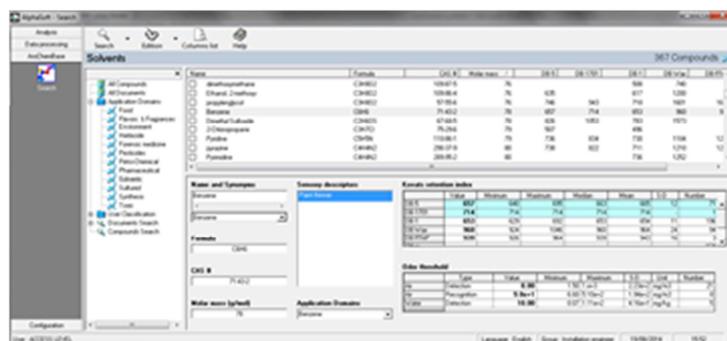

Fig. 6: Retention indices and odor threshold data of benzene in AroChemBase software

Conclusion

This application note shows that HERACLES instrument can be a very suitable analytical tool to evaluate the level of contamination in incoming plastic waste and to control residual volatile contamination in recycled plastic pellets. This quantification can be conducted in a few minutes upon receipt of the plastic waste or during the production process.
The AroChemBase software can also be used to investigate the nature of unexpected volatile compounds and have information about their related odor detection threshold.

[1] Guidance for Industry: Use of Recycled Plastics in Food Packaging: Chemistry Considerations. Food and Drug Administration (FDA).