New strategies in on-line screening analysis and compliance test procedures for plastic materials

Frank Welle[1], Gerhard Horner[2]

[1]Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany,
email: welle@ivv.fraunhofer.de, phone: ++49 8161 491 724
[2]five technologies GmbH, Frauenstraße 22, 80469 Munich, Germany

Introduction

Frequent attempts were made to perform true odor measurements with "electronic nose" type measurement systems. In doing so, either the basic methodological conditions were not complied with, or the constraints were not defined carefully. New strategies based on principal components analysis (PCA) allow a more reliable analysis of emissions from plastic materials using gas chromatographic screening data. These approaches, however, are not restricted to odorous compounds only. In contrast, all migration relevant substances determined in packaging materials can be evaluated. The PCA can therefore be used for the control of non-intentionally added substances (NIAS) e.g. polymer impurities and by-products of additives. These strategies can be applied to a wide range of detectors from chemical sensors, gas chromatographic (GC) systems or mass spectrometers (MS) .
Within this study, the PCA approach has been applied for the quality assurance of "super-clean" recycling of post-consumer PET softdrink bottles as well as HDPE milk bottles [1,2].

Method

The applied method uses the raw data from the headspace gas chromatograms as input for the PCA. For example, the quantitative information from headspace gas chromatograms is separated into retention time frames. The detector respond of the peaks within these time frames were integrated separately. The applied PCA software uses the Gaussian Decision Function for discrimination of the samples. The ellipses around the different clusters are 95% borders with equal distance to the centre of the cluster (Mahalanobis Distance). A (virtual) headspace gas chromatogram with no substance peaks was used as reference sample (marked as "0" in Figure 2).

Results

Figure 1 shows the evaluation of post-consumer PET flakes in comparison to super-clean recycled PET pellets and virgin PET pellets [1]. The post-consumer PET flakes show a broad cloud. In contrast, the super-clean recycled pellets were separated from the virgin PET pellets only by a higher concentration of acetaldehyde. Therefore the PCA discriminates these samples only in the direction of the acetaldehyde vector. No discrimination occurs in the direction of the vector for unknown compounds and limonene which indicates, that the investigated super-clean recycled PET pellets are successfully decontaminated during recycling.
In the case of HDPE milk bottle recycling, the applied PCA method is able to discriminate the recycle containing bottles due to their recycle content (Figure 2). In contrast to PET, the virgin HDPE materials contain some polymerisation by-products (e.g. decane, dodecane), which were also reduced in concentration during super-clean recycling. These differences in the oligomer concentrations are sufficient for a clear discrimination.

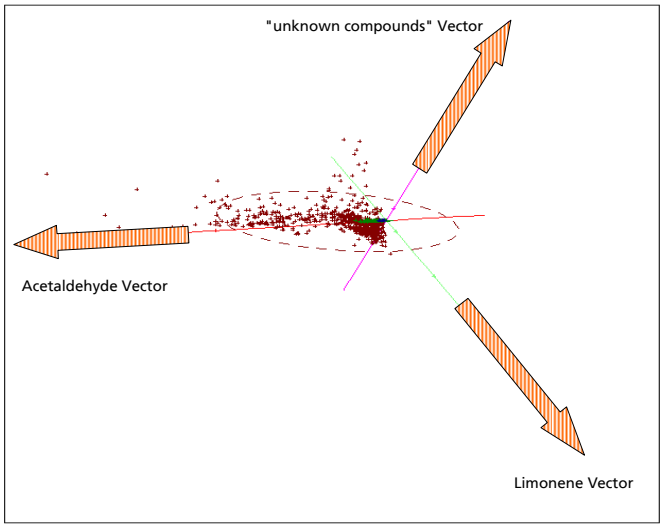

Figure 1: PCA analysis of post-consumer PET flakes (red), super-clean recycled PET pellets (green) and virgin PET pellets (blue) [1]

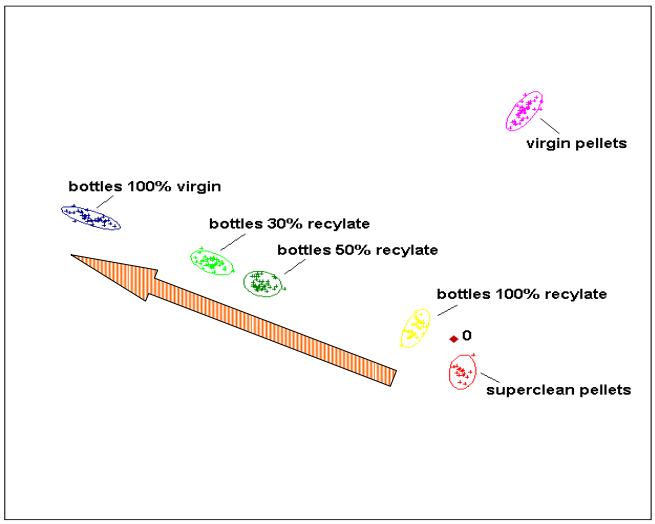

Figure 2: PCA analysis of virgin HDPE pellets, super-clean recycled pellets and recyclate containing HDPE milk bottles [2]

The distance of the clouds to the zero point can be also used for the evaluation. The higher the recyclate content of the HDPE milk bottles, the larger is the distance to the zero point. This indicates, that the overall migration potential of super-clean recycled HDPE pellets is lower than in virgin HDPE pellets.

Conclusions

The applied headspace GC method has a high sensitivity and selectivity towards low molecular weight migration relevant target compounds. Furthermore quantitative information is available without huge calibration efforts. The combination of gas chromatographic screening data with PCA is a powerful tool for the control of NIAS in packaging materials. If calibration standards are available with a certain amount of the analyte (e.g. limonene), the vectors can be calibrated and could be used to evaluate if a certain threshold limit is exceeded or not.
At the moment, the applied PCA method is using only retention time and concentration of the substance peak for the evaluation. A forthcoming development will be the introduction of mass spectrometry data into the evaluation [3]. This has the advantage, that differences in the retention time will be negligible. Using the additional information resulting from the mass spectrometry data, target compounds e.g. well known hazardous substances post-consumer typical compounds can be determined automatically. Such an approach can be used for the online production control of packaging materials.

References

[1] R. Franz, A. Mauer, F. Welle, European survey on post-consumer poly(ethylene terephthalate) materials to determine contamination levels and maximum consumer exposure from food packages made from recycled PET, *Food Additives and Contaminants*, **2004**, *21(3)*, 265-286.
[2] F. Welle, Post-consumer contamination in HDPE milk bottles and design of a bottle-to-bottle recycling process, *Food Additives and Contaminants*, **2005**, *22(10)*, 999-1011.
[3] Software program Target View, five technologies GmbH, in progress.

Poster presentation at the 4th international Symposium on Food Packaging, 19-21 November 2008, Prague

Fraunhofer Institut Verfahrenstechnik und Verpackung