Semi-quantitative determination of potential migrants in food packaging materials - Part 1: Volatile compounds

Alexandra Mauer, Frank Welle

Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany,
email: welle@ivv.fraunhofer.de, phone: ++49 8161 491 724

Introduction

Migration of compounds from food packaging materials into the packed food is regulated by National and European Directives. For many compounds specific migration values (SML) and corresponding analysis methods exist and thus enable compliance testing. But also unknown compounds are detectable during extraction or migration tests. These compounds cannot always be identified, which poses a quantification problem because of the lack of reference substances. As a consequence approaches are necessary how to deal with unknown and non-intentionally added substances (NIAS) regarding compliance testing.
This study describes a screening method for volatile compounds like residual solvents, monomers or low molecular weight oligomers. Due to the fact, that the detectable mass is depending on the vapor pressure of the analyte as well as on the partition coefficient between the analyte and the polymer matrix, quantification is not possible on basis of static headspace gas chromatography without a reference standard of the analyte. Using the multiple headspace extraction (MHE) technique as well as the flame ionization detector (FID) as a mass selective detection system, the results of the quantification become independent on the polymer matrix and on the vapor pressure of the substance. Therefore, the method is able to semi-quantify also non-identified compounds in polymers on basis of multi-analyte standards.

Method

1.0 g of polymer samples or 1.0 dm^2 of film are sealed in a 22 ml headspace vial and analyzed by headspace gas chromatography (HS GC) without further sample preparation. Gas chromatograph: Perkin Elmer AutoSystem XL, column: ZB 1, length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm. Temperature program: 50 °C (4 min), rate 20 °C min^{-1}, 320 °C (15 min), pressure: 50 kPa helium, split: 10 ml min^{-1}. Headspace autosampler: Perkin Elmer HS 40 XL, oven temperature: 200 °C, needle temperature: 210 °C, transfer line: 210 °C, equilibration time: 1 h, pressurizing time: 3 min, injection time: 0.02 min, withdrawal time: 3 min. Multiple headspace extraction mode with six injections. The FID signals in the gas chromatograms were integrated.

Results

The MHE approach is using several injections of the headspace vapour over the same polymer sample after equilibration. Between the injections, the equilibrium between sample and headspace has to be established again. The area of the analyte decrease with increasing number of injections, because the concentration of the analyte is decreasing in the sample and therefore also in the headspace. According to theory [1], the logarithm of the peak area versus the number of injections results in a linear correlation. From this regression, the total amount of the analyte in the headspace vial can be calculated independent from the polymer type and the vapour pressure of the analyte. Using a multi-analyte standard (e.g. *n*-hexane) in combination with the total evaporation technique, the total area of the analyte and of the standard can be compared. Two examples for the MHE quantification of NIAS are given in Figure 1. The correlation of the molecular weight of standard substances versus the retention time under the above mentioned GC conditions is shown in Figure 2.

Conclusions

The described methodology is a tool for the determination of volatiles in packaging materials. Matrix effects and partition coefficients are negligible as long as a linear regression of the logarithm of the peak area and the number of injections is established. A major disadvantage of quantitative headspace gas chromatography, the dependency of the peak area from the vapor pressure, is therefore bypassed. Especially for non-identified volatile compounds, the MHE procedure is in most cases the only approach for getting semi-quantitative information of the concentration of an analyte in the polymer sample.
On the other hand, the migration of a compound from the packaging polymer into the foodstuff is the important information. The migration depends on the storage condition, but also from the molecular weight of the compound. The molecular weight of the volatile potential migrant are available from mass spectrometry or from the retention time (Figure 2). Both, molecular weight and concentration are the crucial parameters for an evaluation of the migration potential of NIAS in packaging polymers using migration modeling.

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

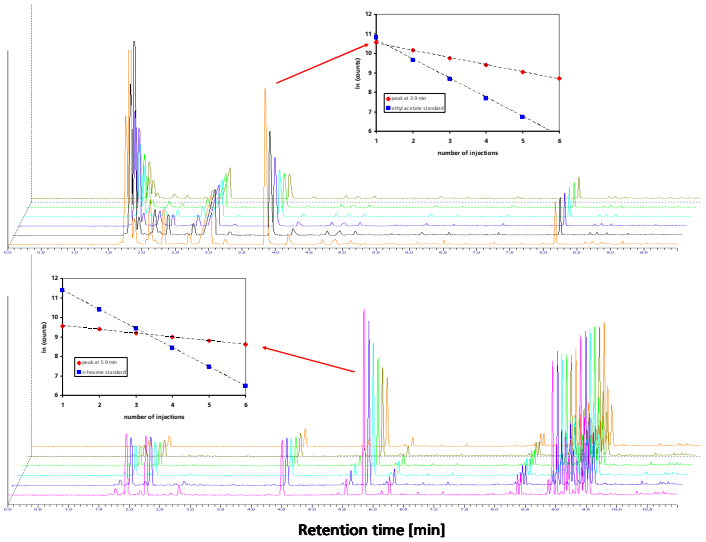

Figure 1: Headspace gas chromatograms of residual solvents in printed films (1 dm^2, top) and polypropylene pellets (1.0 g, below)

However, there are some limitations of the MHE method. Due to the huge time consumption per sample (approx. 6 h), the MHE method is not suitable for the routine control of large amounts of samples. In addition, due to the fact, that the quantification of the analyte needs a linear correlation of the logarithm of the peak area with the number of injections, analytes which are not stable within the headspace sampling procedure (faster decrease) or which are generated during the equilibration procedure in the headspace vial (slower decrease) cannot be quantified using the MHE approach. On the other hand, the evaluation of the linear correlation of the area versus injections gave useful hints on the stability or reactivity of the analyte, especially for unknown NIAS.
In conclusion, the described method is a pragmatic approach for the semi-quantification and evaluation of NIAS in packaging materials.

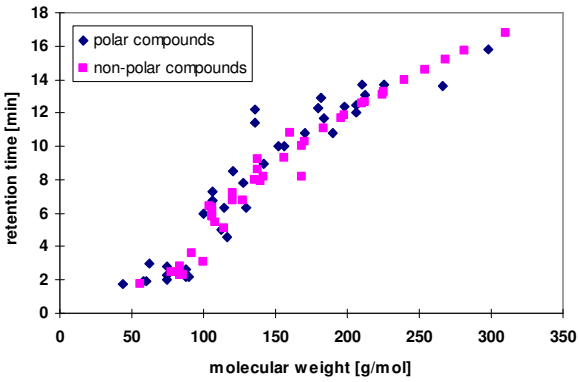

Figure 2: Correlation between the molecular weight of standard substances and the retention time

Reference

[1] B. Kolb, L. S. Ettre, Theory and practice of multiple headspace extraction, *Chromatographia*, **1991**, *32*, 505-514h.

Fraunhofer Institut Verfahrenstechnik und Verpackung