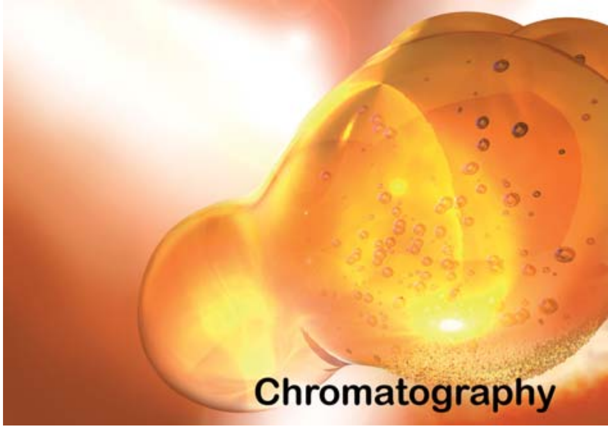


Application Note

Analysis of food wrappings with Double-Shot Pyrolyis-GCMS

Introduction

An important task for food hygiene is the analysis of the thermal properties of food wrappings as they are in close contact to the food. Compounds of high volatility can evaporate from the polymer (e.g. under sun light) and diffuse into the food material. Especially for longer intakes this can lead to health risks fort he consumer depending on the chemical and physical properties of the compound evaporated. It can thus be expected that in the near future more strict regulations for the maximum concentration of additives in food will be commanded.

Conventional analysis methods

Methods normally used for the analysis of food wrappings i.e.gas chromatography (GC) or gas-chromatographie coupled to mass spectrometry (GCMS) require a high effort in sample preparation using Soxhlet-, SF (Supercritical Fluid) or micro wave extraction.

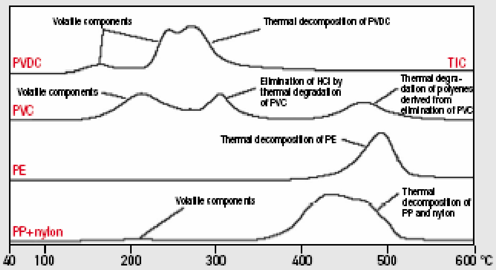
These expensive methods have the disadvantage, that for every analysis problem the method has to be adjusted due to the different solubilities of the polymers in different solvents.
Pyrolysis GCMS is here a very good alternative.

Pyrolysis GCMS analyzes smallest amounts and unknown mixtures

In pyrolysis GCMS the sample is fragmented in the hot pyrolysis oven without any sample preparation. The pyrolysis fragments built are then separated by GC and identified by MS. So it is possible to to analyse qualitatively and quantitatively not only very small amounts of sample but also mixtures of unknown composition.

For every analysis problem the right temperature

A special method is the so called Double-Shot Pyrolysis GCMS. In a first step an EGA (Evolved Gas analysis) is performed. With EGA the temperatures when volatile compounds (e.g. additives) evaporate from the polymer as well as the temperature when the polymer itself is decomposed are determined. So the right temperature for every analysis problem can be found easily.
In EGA the sample is heated using a linear temperature program and the compounds are directly detected in the mass spectrometer. No chromatographic separation takes place. The curves obtained show the intensity as a function of temperature (thermogram). Fig. 1 shows the thermograms of food wrappings based on different materials.



EGA Curves of Various Food Wrap Films
Pyrolysis furnace temp.: 40 - 600 °C (20 °C/min), Carrier gas: He 50 kPa,
Split ratio: ca. 1/50
EGA capillary tube: id 0.15 mm, Length 2.5 m (UADTM-25N), GC oven temp.: 300 °C
Injection port temp.: 320 °C; Sample size: 0.25 cm^2, MS scan range: m/z = 29-400,
Scan rate: 0.1 scan/sec

Fig. 1: thermograms of different food wrappings

With the so-called EGA-Heart-Cut techniques fractions can be analysied by GCMS.
The fractions are frozen at the column head, separated by GC and detected by mass spectrometry.

Fig. 2 shows as an example the analysis of poly vinylidene chloride (PVDC) with EGA-Heart-Cut. In zone A butanol, tributyl aconitate as well as tributyl acetylcitrate (CITROFLEX A-4, softener) could be identified. In zone B tributyl aconitate (small amounts) and as major compound tributyl acetylcitrate were detected. Furthermore HCL, a degradation product of PVCD, was found. In zone C the major component was HCL, but also benzene and chlorinated aromatic compounds originating form the polyen structure of the PVDC were detected.

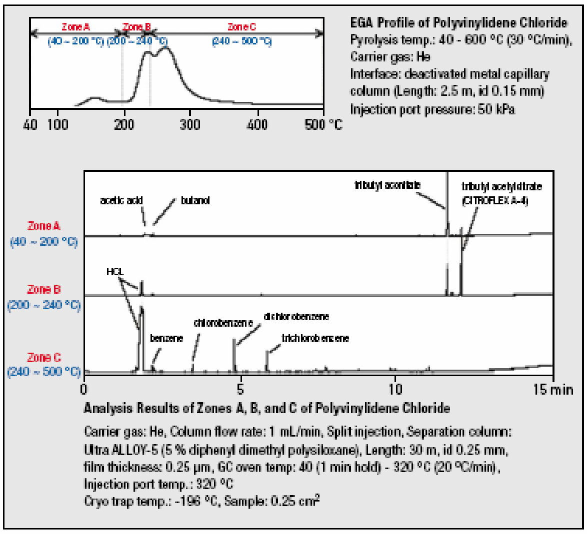


Fig. 2: Analysis of poly vinylidene chloride (PVDC) with EGA-Heart-Cut

In Fig. 3 the EGA-Heart-Cut analysis of a food wrapping based on poly propylen (PP) and Nylon is shown. The chromatogram in zone A showns acetic acid and as the major compounds fatty acids which were used as softeners. The chromatogram of zone B showns olefinic hydrocarbons (C_6, C_9, C_{12} and C_{15}), which are formed in the pyrolysis of PP, as the major compounds but also the ε-caprolactam, the monomer of Nylon-6.

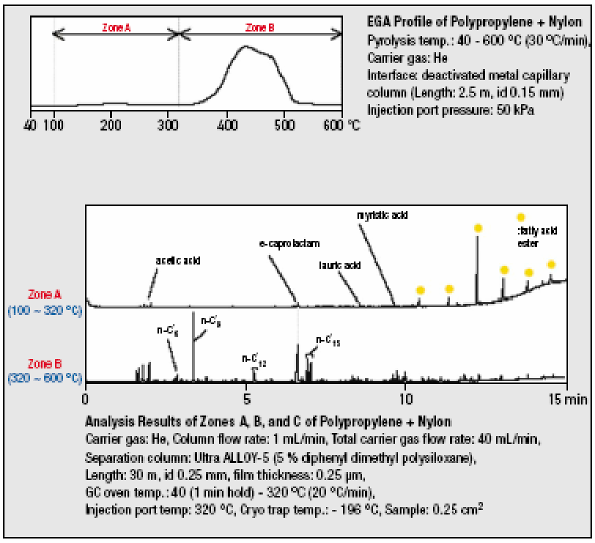


Fig. 3: EGA-Heart-Cut analysis of a food wrapping based on poly propylene (PP) and Nylon

To facilitate the identification of a polymer a comprehensive data base and search software (F-Search) can be used which is based on the mass spectra of the polymers and which contains also co-polymers. Fig. 4 shows the identification of PP by using the data base.

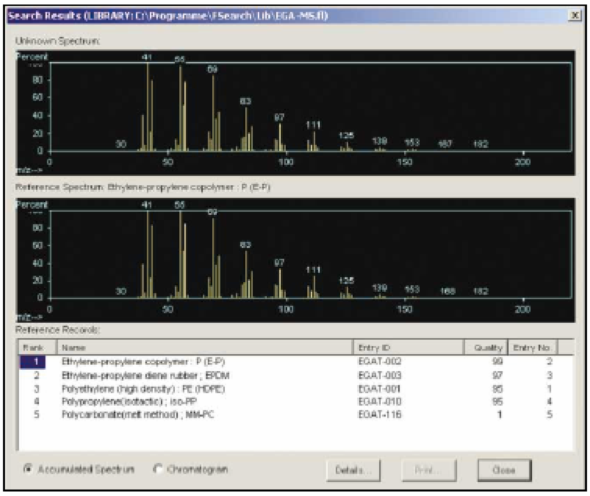


Fig. 4: Identification of PP using the F-Search software and data base