
Abstract (english)

The quantity of foodstuffs packed in coated cans and laminates increased in the last decades due to their advantages like long storage time and low costs. A mass transfer of metal ions is prevented by the plastic-based coating or the plastic film in the laminate but a mass transfer (migration) of plastic components exists instead. Two legal regulations focus on the amount of migrating substances from these types of packaging. Firstly, the Council of Europe imposes a limit of 10 mg/dm² packaging for the sum of migrating substances (overall or total migrate) which can be determined by the gravimetric reference method. Secondly, the Directive 2002/16/EC limits the migration of bisphenol A diglycidyl ether (BADGE) and bisphenol F diglycidyl ether as well as their hydrolysis and hydrochlorination derivatives to 1 mg/kg foodstuff.

Most previously published investigations based on methods for the surveillance of these legal regulations. However, another decisive point is the fact that the Scientific Committee on Food differentiates the migrants into the substances with a molecular weight < 1000 Da, potentially being absorbable by the gastro-intestinal tract, and the less toxicologically relevant species > 1000 Da. This thesis is the first approach to develop applicable methods for the elucidation of the total migrate < 1000 Da. Finally, a mass balance of migration was achieved by comparing the sum of the single results for these migrate components with the value determined for the total migrate < 1000 Da. This concept was tested for an epoxy and a polyester coating.

Therefore, an alternative method for the simultaneous determination of the global migrate and the migrants < 1000 Da based upon separation by size exclusion chromatography (SEC) followed by evaporative light scattering detection (ELSD) was developed. A statistical comparison of both methods (the gravimetric method is also extended in order to determine the part < 1000 Da) revealed that the SEC-ELSD method is not an equivalent substitute for the gravimetric reference method due to significantly lower results considering the overall migrate. However, the SEC-ELSD method is the tool of choice due to better reproducibility and lower limit of detection analysing the part < 1000 Da for which a reference method does not exist.

About 50 % of the total migrate < 1000 Da in 95 % ethanol (for both coating types about 1.3 mg/dm²) were elucidated as resin-related substances, mainly residual oligomers and reaction products with other constituents of the lacquer. A screening gradient was developed on a reverse phase in order to achieve highest resolution for all resin-related substances < 1000 Da. The migrants of epoxy resin were identified using electrospray ionisation-mass selective detection (ESI-MSD) and were confirmed by micro-syntheses of monomeric and dimeric BADGE with solvents and phenols. The sensitive fluorescence detection and the commercially available BADGE standard was used for the quantification of all migrants < 1000 Da including a bisphenol A (BPA)-backbone as BADGE-equivalents, since the fluorescence response relies on the amount of BPA-moiety in the respective molecule. The quantification could be extended by combining fluorescence response and structural information gained from the mass spectra, which provides more accurate results for each single migrant. The calculation is based on the calibration of the BPA-chromophore content of the molecule.

For the regulated BADGE-derivatives a specific method using a ternary gradient, reference standards for each substance and an internal standard was developed and fully validated for surveillance purposes.

The structural elucidation of polyester migrants required an identification of the monomeric polyvalent acids and polyols after hydrolysis by specific methods. With the knowledge of the polyester monomers it was possible to - at least tentatively - identify the main components in the migrate as cyclic oligoesters by ESI-MSD based on terephthalic acid (TPA) and isophthalic acid (IPA) as well as several polyols. The amount of the migrating oligoesters was determined using an UV_{232nm} calibration of a commercially available TPA/IPA-ester (bis-hydroxyethylene terephthalate, BHET) and the number of IPA/TPA moieties/molecule gained from the mass spectra.

The specific method used for the identification of polyester monomers also enabled the identification and quantification of residual trimellitic acid (about 0.08 mg/dm²) in the 95 % ethanol migrate used as anhydride hardener in the epoxy coating.

Migrating lubricants made up another part of about 20 % of the total migrate < 1000 Da in 95 % ethanol for the tested epoxy coating. A normal-phase liquid chromatography method was developed for the identification and quantitative estimation of mainly used lubricants which were separated on a diol phase by their polarity into twelve lipid classes (paraffins, wax esters, cholesterol esters, fatty acid methyl esters, triacyl glycerols, fatty alcohols, free fatty acids, cholesterol, 1,3-diacyl glycerols, 1,2-diacyl glycerols, monoacyl glycerols and fatty acid amide). Since the detector response of the used ELSD depends on the chain length and the degree of saturation, the quantification of a lipid class with unknown composition is only semi-quantitative.

In conclusion, about 75 % of the total migrate < 1000 Da in 95 % ethanol from the epoxy coating have been elucidated. The fact that nearly 60 % of the migrate < 1000 Da in 95 % ethanol of the polyester coating remained unknown is dissatisfying. A reasonable uncertainty of the determined values especially due to the substance depending response of the ELS-detector (determination of the total migrate < 1000 Da and of the lubricants) has to be considered when discussing the amount of unknowns. Moreover this analysis schema should be enlarged by the determination of hardener components (especially for coatings cured with phenol- or aminoplasts) and of other additives like pigments, catalysts, defoamers and flow aids in order to enhance the comprehensiveness. Nevertheless, this is one of the first approaches to identify the actual migrating substances from coatings < 1000 Da.