New understanding of ink components migrating from packaging material into foodstuffs

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Food packaging is important and for food producers the visual aspect of packaging material is a very powerful medium, so that consumers and competitors consider a brand name as an established value. In the process, the chosen varieties of ink play a crucial role. The choice may not only be based on marketing strategy, but the potential health risks as a result of the migration issues of the ink components have to be taken into account. Printing inks used in food packaging materials contain substances that are able to migrate, such as raw materials and by-products of hardeners and solvents. So far, the knowledge of migration of specific components from printing inks is limited, therefore public health risk cannot be well assessed.

The issue of migration of components from inks and glues originated in 2005 when 2-isopropylthioxanton (ITX) threw the packaging and food industry into commotion. ITX was found in undesirable high concentrations in milk powder for babies and chocolate milk powder. Later on it appeared that the commonly used photoinitiator originated from the used packaging. In 2009, the photoinitiators benzophenone and 4-methylbenzophenone were found in cereals and milk, increasingly alarming migration issues. Next to primary migrant substances, secondary products can also be formed due to a reaction in the foodstuff. These secondary products can also be harmful and they could possibly have an effect on food too, such as odor, taste, etc. Problems with bisphenol A diglycidyl ether (BADGE), used in epoxy coatings of tins, clarified this additional aspect. Moreover, it has recently been revealed that BADGE is not only unstable in acetic acid, but shows certain reactivity towards food components such as peptides and amino acids. This reveals that characterizing secondary migration products is at least as important as the migration issue of primary migrant substances.

In order to gain a larger understanding concerning the stability of migrating components from printing inks of packaging materials to food, an investigation of the FPS at ILVO-T&V is taking place together with the research group NutriFOODchem of the UGent. First of all, an inventory was made of components which can migrate from printing inks and of which could be derived, based on their chemical properties, that they are reactive/unstable in the official food simulants water, acetic acid and ethanol with or without the use of light. Harmful components shown in simulants indicate a potentially food safety risk in foodstuffs. A priorities list was composed in consultation with some industrial stakeholders. Components of the following 9 different classes have been put forward: nitrocellulose, acrylates, phthalates, isocyanates, phosphates, adipates, citrates, high boiling point solvents and photoinitiators. Because of the limited research time, acrylates, phthalates and nitrocellulose are the compounds of interest in this research.
Acylates are energy hardening monomers present as such during the printing process and they polymerize during ink drying. Sometimes photoinitiators are added to initiate polymerization. A considerable amount of these acrylates can still be present in the final print. Phthalates on the contrary are added to ink as an additive to affect the physical properties. These are plasticizers having an impact on rheological and elastic properties of inks. The stability of bis(2-ethylhexyl)phthalate and dodecyl acrylate has been investigated in the official food simulants 3% aqueous acetic acid (pH = 2.5), ethanol and modified polyphenylene oxide (MPPO). Both components are stable in 95% ethanol. They did not undergo any thermal degradation or oxidation at high temperatures on MPPO. On the contrary, phthalate as well as acrylate appear to hydrolyze in a 3% aqueous amino acid solution. Degradation curves showed pseudo first order kinetics. The activation energy of the phthalate was $96 \pm 24$ kJ mol$^{-1}$ ($k = 0.09 \pm 0.02$ and $8.1 \pm 0.3$ μs$^{-1}$, at 20 and 60°C respectively). The activation energy for the hydrolysis of acrylate took about half the energy ($41 \pm 4$ kJ mol$^{-1}$) with $k = 14.5 \pm 0.5$ and $162 \pm 2$ μs$^{-1}$, at 20 and 60°C respectively.

Sometimes nitrocellulose is used as a polymer in the binding agent of solvent-based inks. At increased temperature, it causes the formation of nitrogen oxides (NOx). Strictly speaking, these gases cannot be considered as migrants, but they can cause reactions in the foodstuff. It is possible that NOx react with amines in food and form carcinogenic nitrosamines. In a preliminary experiment, it has been revealed that NOx can be released significantly from nitrocellulose printing inks heated to 85°C and that the release increases exponentially at a temperature rise. This experiment also confirmed the hypothesis that the released NOx is capable to form the carcinogenic N-nitroso-di-n-butylamine out of the equivalent amine. Heating up ready-to-eat meals in printed packaging materials is a potential risk for nitrosamines to be formed in our food. In order to evaluate these findings quantitatively, an analytical procedure has been developed based on a solid phase extraction (SPE), followed by gas chromatography-mass spectrometry (GC-MS; Figure 1). Nitrosamines have been extracted from an aqueous solution using SPE and the extract has been evaporated using mild concentration techniques. Analysis by GC-MS is carried out by programmed temperature vaporization (PTV) and large volume injection (LVI). Figure 2 displays the result of a GC-MS analysis of a 20 µg/ml nitrosamine standard mixture. Combined with SPE and evaporation, the method is capable of detecting nitrosamine concentrations on sub-ppb level with a better precision than 5% and a recovery of about 70%, depending on the component.

Figure 1: Gas chromatography coupled to mass spectrometry (GC-MS) detection
In order to have an experimental approach of the above-mentioned hypothesis, packaging material and food or a food simulant have to be brought into contact as if it were a real packaged food product. A migration cell has been chosen to approach reality as good as possible. This cell is composed of two plates of stainless steel covered with a packaging material of choice. Both plates are clipped onto both sides of a metal ring (Figure 3). A liquid simulant fills the space between the plates and the ring, creating close contact with the packaging material. In order to follow up nitrosation during the heating of nitrocellulose ink, relevant amines are dissolved in water and buffered at an optimal pH. The migration cell is covered by a film homogeneously printed with nitrocellulose ink. This cell is filled with a buffered amino solution and heated during a few hours. After this process and a successive cooling down step, the quantity of nitrosamines in the cell solution is analyzed using the above-mentioned SPE-GC-MS determination method.
The purpose of this research project is to obtain a full picture of kinetics and of the circumstances during the formation of nitrosamines out of printed food packages. At present experiments are carried out. There is strong evidence that nitrosamines indeed can be formed during heating of ready-to-eat meals in packaging materials with nitrocellulose ink prints. In order to be able to evaluate the importance for public health, exposure by this process must be compared with other ways of exposure in our environment. However, more experimental data are needed to prove this. In any case, the packaging sector is looking for a solution to eliminate the current uncertainty of using nitrocellulose in food contact materials.

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