Determination of different photoinitiators in sausage samples – Comparision of two sampling procedures

Karsten Müller, Elba Pajares Alva, Ruth Wildgruber

Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany, email: karsten.mueller@ivv.fraunhofer.de, phone: ++49 8161 491 727

Introduction

UV-curing technology is prevalent nowadays for printing of food packaging. Typical applications are sausage casings made of polyamide films. The hardening process is induced by using photoinitiators (PI) as polymerisation starters. To assess the food safety of UV-printed sausage casings, photoinitiators were considered as main migration compounds. However, many of these substances are not fully toxicologically evaluated. Hence, migration into the sausage meat may not occur. That means no photoinitiator should be measureable at a detection limit (LOD) of 10 µg kg^{-1} food. To quantify trace amounts sensitive analytical methods as well as advanced sample treatment are required. The conventional sampling technique underestimates the migration potential of photoinitiators because of dilution during homogenisation of the whole sausage. Within the present study a new method of sample treatment was developed and confirmed in comparison with conventional sample processing.

Material and Methods

Several sausages filled in UV printed casings, were investigated. After manufacturing the sausages were stored 10 days at 5 °C. All samples were treated applying two different procedures. On one hand three layers below the maximum printing were cut out (Figure 1) and analysed separately. Each layer was of about 3 mm thick. The filling related concentrations were calculated according to the dimensions of the entire sausage, applying the surface equation of a cylinder. Though the pinch-off area at the sausage ends was disregarded. The concentration of all three layers were added together and compared with the results of the replicate sausage which was homogenised in all.

As an analytical device a HPLC-MS/MS system equipped with triple quadrupol mass analyser and atmospheric pressure chemical ionisation interface was used. The substances were separated on a RP column with ether-linked phenyl groups and polar endcapping. Methanol and formic acid were used as mobile phase. For quantification a matrix calibration was performed with spiked sausage samples.
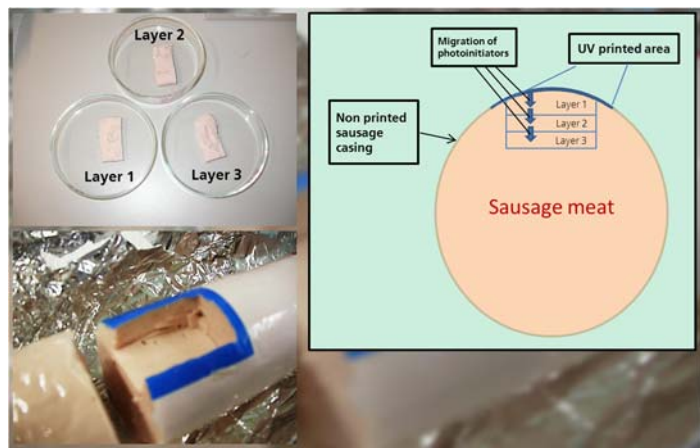

Figure 1: Novel sample preparation approach

Results and Discussion

As shown in table 1 exemplary for 2-Benzyl-2-(dimethylamino)-4'-morpholino-butyrophenone (PI 1) and an amine synergist (Col) similar results were obtained for both preparation techniques. The divergent concentrations which are determined by conventional sampling are semi-quantitative values (> LOD but < limit of quantification (LOQ)) or within the standard deviation of the new procedure. As expected the highest PI concentrations were determined in the 1st layer directly below the casing. The concentrations of the 2nd and 3rd layers are up to 100 times lower or beneath the detection limits. The concentrations of each layer are not shown in this poster. Because of performing the sampling in layers below the maximum printing a dilution of PI concentrations was prevented. Applicable to all substances under study the LOD of the new approach was < 2 µg per kg food, that means in average about 10 times lower than performing the conventional sample drawing (Figure 2). Therefore a reliable quantification of toxicological non evaluated PI at a range much lower than the commonly accepted migration threshold of 10 µg kg^{-1} is possible.

Table 1: Comparison of concentrations performing the new and conventional sample treatment exemplary for 2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone and an amine synergist.

Substance	Concentration [µg per kg food]	
	New sampling procedure	**Conventional sampling**
2-Benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone	11.1 ± 0.4	16.5 ± 1.6
	1.95 ± 0.14[2]	< LOD
	4.24 ± 0.51	< LOD
	8.98 ± 0.98	11.1 ± 2.2[2]
	0.75 ± 1.29	< LOD
	3.26 ± 3.76	< LOD
	2.34 ± 0.52	< LOD
amine synergist[1]	61.7 ± 4,0	61.5 ± 5.9
	20.6 ± 4.1	14.0 ± 3.3
	4.68 ± 1.0	7.44 ± 0.89[2]
	65.3 ± 3,4	60.4 ± 3.9
	27.0 ± 4.0	14.1 ± 9.9[2]
	28.0 ± 9.4	15.0 ± 10.0[2]
	129 ± 42	111 ± 3
	25.9 ± 10.0	28.2 ± 15.5
	120 ± 36	73.7 ± 43.9
	197 ± 44	147 ± 51.7

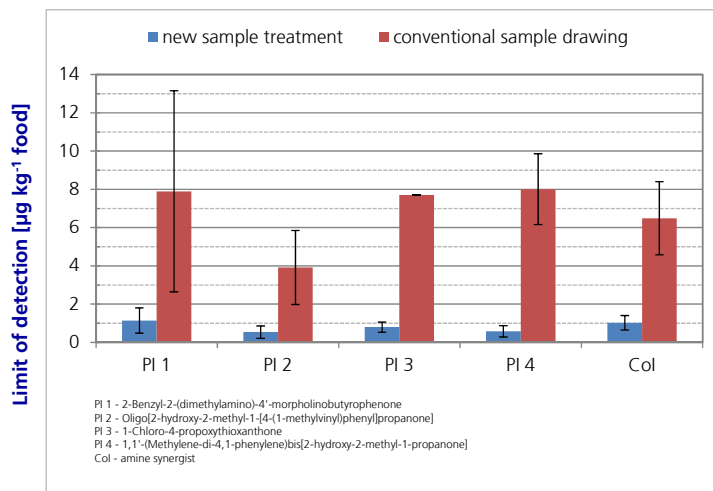[1] confidential structure
[2] results > LOD but < LOQ

Figure 2: Comparison of the detection limits of new and conventional sample treatment.

The LOD as well as the filling related concentration are directly proportional to the sausage diameter and decreases with increasing calibre. Hence, compared to the concentrations calculated according to the EU cube model the filling related concentrations are higher if the sausage calibre is < 0.66 dm.

The new sampling method enables a more sensitive evaluation of the migration potential of various photoinitiators. To carry out the measurements only a small printed casing area is used. Therefore multiple migration experiments can be performed with the same sample material which reduces the cost of development of new casings, as well as new UV printing inks. Moreover, the analysis of different layers permits a determination of concentration profiles. During further investigations, profile data could be used to exam the migration processes in solid foodstuff.