Optimization and validation of GC-MS method for NIAS determination in food contact materials

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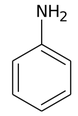
1. Introduction

Polymeric articles contact food → EU Regulation 10/2011 → Migration test → Food simulant

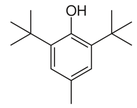
Aim of this study

Optimization of an analytical method that allows the identification and quantification of the specific migration of the analytes under investigation, that may occur following contact of the polyurethane product with dry foodstuffs

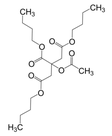
The polyurethane gasket



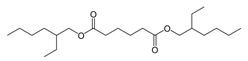
Aniline



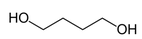
2,6-tertbutylhydroxytoluene (BHT)



Acetyltributyl citrate



Bis(2-ethylhexyl)adipate



1,4-butanediol

Figure 1. The polymer sample and the analytes under investigation

2. Experiments

Contact test with food simulant Tenax® and food matrices procedure

1. Cut a 4 cm x 4 cm sample polymer sheet
2. Contact with Tenax® or food matrices
3. Heat in the oven at 70 °C for 3 days
4. Two cold extractions with EtOH
5. Dry at room temperature
6. Recovery in CH_2Cl_2 and GC-MS analysis

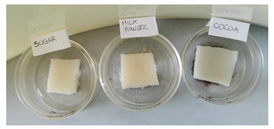


Figure 2. Contact tests with food matrices

Contact test with acetic acid procedure

1. Cut a 7.5 cm x 7.5 cm sample polymer sheet
2. Contact with 112.5 ml of CH_3COOH 3 % w/w
3. Heat in the oven at 70 °C for 3 days
4. ICP-MS analysis

Figure 3. Contact tests with CH_3COOH

Moisture content determination by oven and TGA analysis

1. The residual mass of the samples is determined in an oven
2. TGA analysis: heating with a gradient of 10 °C per minute, in an inert atmosphere, up to 200 °C .

Fat content

Extraction with petroleum ether in Soxhlet for 6 hours and the result is obtained by weighing. The fat content of milk powder is also determined by the Rose-Gottlieb method.

3. Moisture and fat content

Table 1. Moisture results

Food matrices	T oven [°C]	Oven		TGA	Fat	
		M %	SD	M %	%	SD
Milk powder	102	3.60	0.05	4.5	0.6 (1.0)*	0.2
Sugar	103	0.016	0.003	-	-	-
Rice	130	9.0	0.3	8.8	0.5	0.1
Flour	130	12.5	0.1	9.0	0.8	0.1
Corn starch	102	11.79	0.01	9.9	0	0
Cocoa	102	6.4	1.8	5.6	21.8	0.4

* Rose-Gottlieb method result

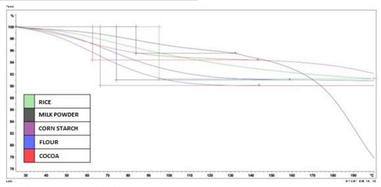


Figure 4. TGA analysis of food matrices

TGA advantages

- small sample quantity ~ 30 mg vs 2-30 g
- speed of analysis ~ 20 min per sample vs 3 ÷ 5 hours per sample

Sugar

Milk powder

Rice

Flour

Corn starch

Cocoa

Figure 5. The food matrices tested

4. ICP-MS results

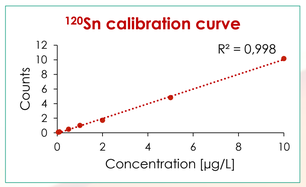


Figure 6. ICP-MS calibration curve

Table 2. ^{120}Sn ICP-MS

Repl.	µg Sn/g polymer sheet
1	0.25
2	0.23
3	0.21
4	0.22
Average	**0.23**
SD	**0.02**

5. GC-MS results

The characteristic ionic fragments:

- Aniline [m/z]: 64.5-65.5-66.5-92.5-93,5
- 1,4-butanediol [m/z]: 43.5-44.5-70.5-71.5
- BHT [m/z]: 204.5-205.5-219.5-220.5
- Bis(2-ethylhexyl)adipate [m/z]: 128.5-129.5
- Acetyltributyl citrate [m/z]: 185.05-185.10

Table 3. Contact tests between manufactured product and dry foodstuffs and Tenax as reported according to the regulations

POLYURETHANE SAMPLE	Unit of measure	1,4-Butanediol	Aniline	BHT	Acetyltributyl citrate	Bis-(2-ethylhexyl) adipate	Styrene (I. S.)
RICE	mg/kg	< LOD	< LOD	< LOD	< LOD	< LOD	1.9 ± 0.3
	mg/dm²x6	-	-	-	-	-	-
COCOA	mg/kg	< LOD	< LOD	< LOD	< LOD	3.0 ± 0.3	1.6 ± 0.9
	mg/dm²x6	-	-	-	-	0.48 ± 0.06	-
FLOUR	mg/kg	< LOD	< LOD	< LOD	< LOD	< LOD	2.2± 0.4
	mg/dm²x6	-	-	-	-	-	-
CORN STARCH	mg/kg	< LOD	< LOD	< LOD	< LOD	5 ± 1	1.5± 0.2
	mg/dm²x6	-	-	-	-	0.66 ± 0.03	-
SUGAR	mg/kg	< LOD	< LOD	< LOD	< LOD	< LOD	2.1± 0.2
	mg/dm²x6	-	-	-	-	-	-
MILK POWDER	mg/kg	< LOD	< LOD	< LOD	< LOD	< LOD	2.3± 0.1
	mg/dm²x6	-	-	-	-	-	-
TENAX	mg/kg	< LOD	< LOD	< LOD	< LOD	3.0 ± 0.3	1.8± 0.2
	mg/dm²x6	-	-	-	-	0.42 ± 0.01	-
LAW LIMIT	mg/dm²	5.0	0.01	3.0	60.0	18.0	-

6. Conclusions

TGA technique can be successfully applied and saves a lot of time in the determination.
The fat content values found are in line with those in the literature.

GC-MS quantification analysis show that:

- 1,4-butanediol, aniline, BHT and acetyltributyl citrate are never detected;
- Bis(2-ethylhexyl)adipate is only detected in cocoa, corn starch and Tenax®;
- The concentration of the analytes is always below the legal limits, so it can be said that the polyurethane seal complies with the Regulation.

The maximum limits for inorganic tin in dry foods are not stated in the legislation. According to the (EC) No 1881/2006, inorganic tin levels must not exceed 150 mg/kg in canned drinks and 250 mg/kg in other canned foods.
The results obtained from the ICP-MS analysis show that the tin values are lower than the currently regulated limits.

References

Urbelis, J. H.; Cooper, J. R. Food Additives & Contaminants: Part A
Reinas, I.; Oliveira, J.; Pereira, J.; Machado, F.; Poças, M. F. Food Control