Acrylonitrile in Food Contact Materials – Two Different Legislative Approaches: Comparison of Direct Determination with Indirect Evaluation Using Migration into Food Simulants

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Abstract

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In this study, the comparison was carried out of two different legislative approaches for acrylonitrile content assessment in food contact materials based on the former analysis using gas chromatography with nitrogen-phosphorous detection, and the recent evaluation using acrylonitrile migration into food simulants – distilled water, 3% acetic acid, 10% ethanol, and 95% ethanol, based on liquid chromatography with ultraviolet detection. Different samples were tested: 7 kitchen device parts and 16 acrylonitrile-butadiene-styrene and styrene-acrylonitrile granulates. The level of acrylonitrile content in founded polymer mass was in the range from 0.4 to 25.1 mg/kg in the case of kitchen device parts, and from 6.2 to 283.9 mg/kg in the case of granulates. The highest migration of acrylonitrile in food simulants for kitchen device parts and granulates was found to be 5.2 µg/dm^2 (3% acetic acid) and 9.6 µg/dm^2 (95% ethanol), respectively. A correlation of the results obtained by two different methodologies was tested, but no evident relation was found between acrylonitrile content in the polymer mass and its migrations into food simulants. Based on the realised experiments, no equivalence of the approaches compared was proved.

Keywords: acrylonitrile monomer; migration; food simulants; chromatography; food

Polymers with acrylonitrile monomer (ANM) as a component – for example acrylonitrile butadiene styrene (ABS) and styrene-acrylonitrile (SAN) – are used for packages and household articles designed for foodstuffs. During the production of acrylonitrile copolymers, a small fraction of unreacted acrylonitrile monomer becomes physically entrapped in the polymer and can migrate slowly during storage or the contact with food or other materials (Gawell 1979). As regards toxicity, acrylonitrile is a carcinogen and mutagen, the breathing of high concentrations of acrylonitrile can cause nose and throat irritation, tightness in the chest, breathing difficulty, nausea, weakness, or headache. Decreased fertility and birth defects have been observed in some laboratory animals exposed to high concentrations of acrylonitrile in air or drinking water (ATSDR 2004).

The former legislation set the maximal hygienic limit allowed for acrylonitrile content in the polymer mass at 5 mg/kg (Decree No. 73, 1992). In the recent legislation, specific migration limit for acrylonitrile in food or in food simulants is established at the level of 0.02 mg/dm^2 of food package surface (Decree No. 38/2001). This directive is fully harmonised with European legislation (90/128/EEC, 1990). Migration tests for food packaging are usually realised by means of food simulants. The simulants are chosen as models of the basic food categories (i.e. aqueous, acidic, alcoholic, and fatty). Some articles were published that concern the migration of acrylonitrile monomer into food-simulating liquids (Lickly *et al.* 1991, 1993; Markelov *et al.* 1992) – the data showed that a linear relationship exists between the logarithm of the ANM diffusion coefficients as calculated from the experimental data using a simple Fickian diffusion model, and the inverse of the absolute temperature of exposure.

In the presented study, the new method for the acrylonitrile content determination in polymer mass was optimised, based on the formerly published method (Di Pasquale *et al.* 1978), while for acrylonitrile migration into food simulants (distilled water, 3% acetic acid, 10% ethanol and 95% ethanol) the modified EPA Method 8316 was used. The aim of this study was to compare the results achieved by using the former legislative recommended method (ANM content in polymer mass) with the recent legislative recommended method (ANM migrations). Accordingly, a comparison is presented here of two different legislative approaches based on a correlation testing to estimate the relation between two ways of ANM content evaluation originating from two different directives.

MATERIALS AND METHODS

Acrylonitrile (> 99.5%, ANM) and *N,N*-dimethylacetamide (> 99.5%, DMA) were obtained from Fluka (Switzerland), acetonitrile (> 99.9%, ACN) was obtained from Riedel de Haën (Germany). 99% acetic acid was obtained from Penta (Czech Republic) and 95% ethanol was obtained from Lachema (Czech Republic).

For *acrylonitrile content in the polymer mass,* the stock solution of ANM in DMA was prepared at the concentration 0.4 mg/ml and was used for the preparation of calibration solutions in the range from 2 to 16 µg/ml in 10 ml vials (0, 2, 4, 8 and 16 µg/ml). After the introduction of the solution, each respective vial was immediately sealed with the PTFE faced septum. The spiked solution was heated at the temperature of 90°C in the water bath for 2 h, then the headspace sampling was carried out using a gastight syringe (heated at 90°C) with the volume of 1 ml followed by analysis using GC/NPD. In the case of real samples, 0.5 g of acrylonitrile material tested was put into the vial, then the appropriate amount of the stock ANM solution was added to reach the levels of ANM standard addition 2–20 µg/kg (0, 2.5, 5, 10 and 20 µg/kg). The next procedure of the sample handling was the same as in the case of calibration solutions. With each sample two parallel determinations were carried out.

GC/NPD system consisted of Carlo Erba HRGC 5300 Megaseries gas chromatograph (Carlo Erba, Italy) equipped with nitrogen-phosphorous detector. Fused silica capillary column DB-23 (30 m × 0.32 mm i.d. with 0.25 µm film thickness, J & W Scientific, USA) was used for chromatographic separation. GC conditions were as follows: initial oven temperature 45°C, initial time 1 min, oven temperature from 45°C to 150°C at 10°C/min, then from 150°C to 240°C at 30°C/min. The carrier gas (helium) flow rate was held constant at 0.6 ml/min. The injector temperature was 160°C and the detector temperature was 270°C.

For *acrylonitrile migrations into the food simulants* (distilled water, 3% acetic acid, 10% ethanol, and 95% ethanol), the stock solution in acetonitrile at the concentration of 2 mg/ml was used for the preparation of calibration solutions in the range from 0.02 to 0.10 µg/ml in 2 ml vials (0.02, 0.04, 0.06, 0.08 and 0.10 µg/ml). The migration conditions in the case of real samples were as follows: 1 dm^2 of polymer mass surface in 100 ml of food simulant, 24 h at the temperature 40°C (short-time contact in accordance with the Czech legislation). After the end of migration, the simulants were separated from the samples and analysed using liquid chromatography. With each sample two parallel determinations were carried out.

The HPLC system consisted of high pressure gradient pump P580 ALPG (Gynkotek, Germany), autosampler GINA 50T (Gynkotek, Germany),

Table 1. Tested samples

Sample	Material	Specification	Sample	Material	Specification
Kitchen device parts			**Granulates**		
KDP1	ABS*	top of the juicer	G5	SAN	B2
KDP2	ABS	part of the onion grater	G6	SAN	B3
KDP3	SAN*	top of the juicer	G7	SAN	C1
KDP4	ABS	part of the beater	G8	SAN	C2
KDP5	SAN	top of the beater	G9	SAN	D1
KDP6	ABS	part of the juicer	G10	SAN	D2
KDP7	ABS	part of the beater	G11	ABS	E1
Granulates			G12	ABS	E2
G1	ABS	A1**	G13	ABS	E3
G2	ABS	A2	G14	ABS	F1
G3	ABS	A3	G15	ABS	F2
G4	SAN	B1	G16	ABS	F3

*ABS = acrylonitrilebutadienestyrene, SAN = styreneacrylonitrilebutadiene

**The description in accordance with the polymers producing company Kaučuk, a. s. (Kralupy nad Vltavou, Czech Republic)

analytical column Purospher Star RP-18e (250 × 4 mm, guard column Purospher Star RP-18e, 4 × 4 mm, both by Merck, Germany) heated at the temperature of 25°C using column thermostat LCO 101 (ECOM, Czech Republic), and ultraviolet detector UVD 170S (Gynkotek, Germany). The mobile phase consisted of acetonitrile and distilled water (15/85, v/v). The flow rate was set to 1 ml/min and isocratic elution was used. The injection volume was 20 µl, for the UV detection the wavelength of 200 nm was used. Isocratic elution was carried out using the mixture acetonitrile: distilled water (15:85, v/v) at the flow rate 1 ml/min.

During the experiments, various kinds of polymer samples containing acrylonitrile (Table 1) were analysed: kitchen device parts (parts of juicer, grater, beater) and raw ABS and SAN granulates obtained from the polymers producing company Kaučuk, a. s. (Kralupy nad Vltavou, Czech Republic). The granulates tested are commonly used in food industry or are intended for the contact with food; all the samples were investigated because of the legislation requirements.

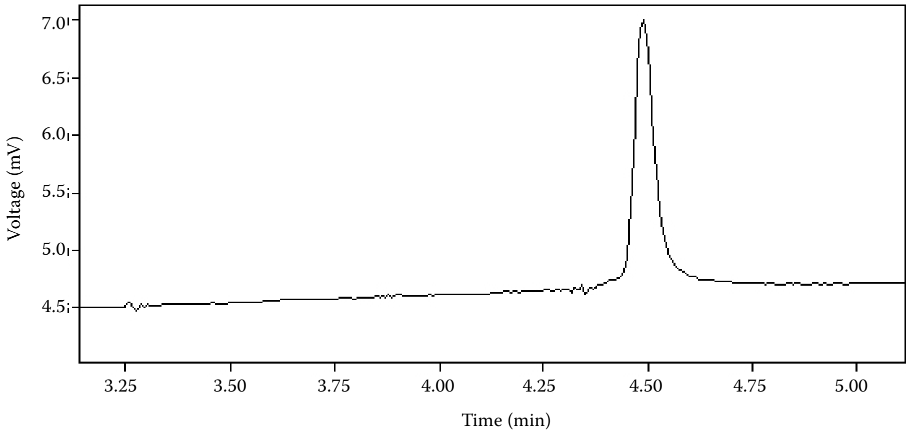

Figure 1. GC/NPD chromatogram of standard acrylonitrile solution (4 µg/ml)

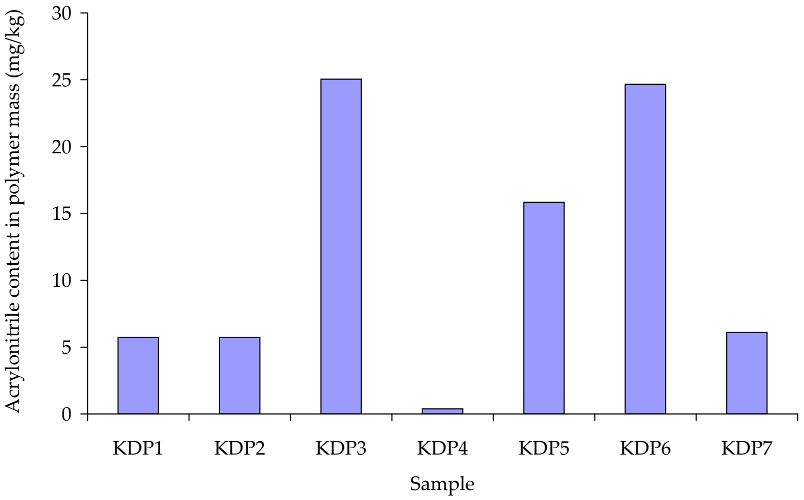

Figure 2. Acrylonitrile content in the polymer mass – kitchen device parts

RESULTS AND DISCUSSION

Determination of acrylonitrile content in the polymer mass (GC/NPD)

The limit of detection (LOD) and that of quantification (LOQ) were determined as 8.2 μg/kg and 37.3 μg/kg, respectively. The method repeatability expressed as the relative standard deviation (RSD) was measured with ten replicates at the concentration level of 1 mg/kg and its value was 4.2% which indicates a good repeatability. Figure 1 shows GC/NPD chromatogram, Figures 2 and 3 present the results found for the kitchen device parts and ABS and SAN granulates. The content of acrylonitrile found was in the range from 0.4 to 25.1 mg/kg in the case of the kitchen device parts, and in the range from 6.2 to 283.9 mg/kg in the case of granulates.

Determination of acrylonitrile migration into the food simulants (HPLC/UV)

The limit of detection (LOD) and the limit of quantification (LOQ) were determined as 0.4 ng/ml and 1.3 ng/ml, respectively. The relative standard deviation (RSD) was measured with ten replicates at the concentration level of 0.06 μg/ml and its value was 1.5% which indicates a very good repeatability. Figure 4 shows HPLC/UV chromatogram, Tables 2 and 3 summarise the results obtained with the kitchen device parts and ABS and SAN granulates. With some of the samples tested no acrylonitrile migration into some food simulant was observed. The highest migration of acrylonitrile found was 5.2 μg/dm^2 in 3% acetic acid (KDP1) and 9.6 μg/dm^2 in 95% ethanol (G9).

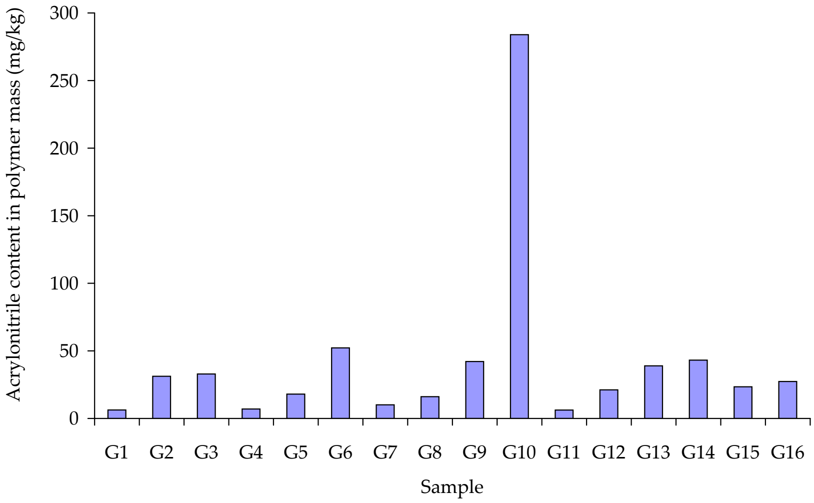

Figure 3. Acrylonitrile content in the polymer mass – ABS and SAN granulates

Table 2. Acrylonitrile migration into food simulants – kitchen device parts (μg/dm^2)

Sample	Distilled water	3% acetic acid	10% ethanol	95% ethanol
KDP1	≤ LOD	5.23	≤ LOD	≤ LOD
KDP2	≤ LOD	2.58	≤ LOD	≤ LOD
KDP3	0.92	≤ LOD	≤ LOD	≤ LOD
KDP4	0.75	≤ LOD	≤ LOD	≤ LOD
KDP5	1.58	0.80	4.12	0.57
KDP6	0.76	≤ LOD	≤ LOD	≤ LOD
KDP7	1.26	0.42	2.81	1.11

Testing relation of results from two different methodologies – acrylonitrile content in polymer mass and acrylonitrile migrated into food simulants

The main objective of this study was to compare the results obtained by testing the correlation between acrylonitrile migration and its content in the polymer mass based on the two different approaches – the former legislative requirement (ANM total content determination in polymer mass) and the recent legislative recommendation (ANM migration into food simulants). A few studies were published concerning the migration of acrylonitrile monomer into food-simulating liquids (Lickly *et al.* 1991, 1993; Markelov *et al.* 1992) in relation to the acrylonitrile content in polymer mass based on the principle of diffusion coefficients using the simple Fickian diffusion model. Unfortunately, the lack of studies analogous to the investigations presented in this work did not allow a relevant comparison of the results achieved with the published data. As regards the samples, first the kitchen device parts, second the ABS granulates, and third the SAN granulates were tested. The respective correlation

Table 3. Acrylonitrile migration into food simulants – ABS and SAN granulates (μg/dm^2)

Sample	Distilled water	3% acetic acid	10% ethanol	95% ethanol
G1	≤ LOD	≤ LOD	0.55	0.57
G2	≤ LOD	≤ LOD	0.44	0.50
G3	0.44	0.74	0.45	0.69
G4	≤ LOD	≤ LOD	1.87	2.36
G5	1.15	0.34	2.32	9.57
G6	0.68	0.32	1.18	3.07
G7	0.97	0.36	1.17	0.46
G8	1.34	0.41	1.35	0.62
G9	0.66	0.52	≤ LOD	0.09
G10	0.55	0.67	0.08	0.45
G11	≤ LOD	≤ LOD	≤ LOD	0.62
G12	≤ LOD	0.45	≤ LOD	≤ LOD
G13	0.27	0.46	≤ LOD	≤ LOD
G14	1.14	≤ LOD	≤ LOD	5.09
G15	0.14	0.50	≤ LOD	2.68
G16	0.02	0.01	1.53	≤ LOD

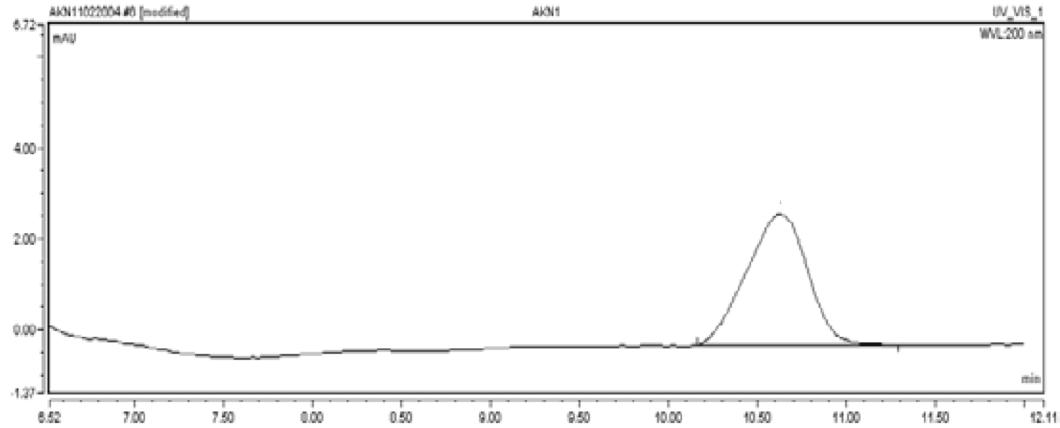

Figure 4. HPLC/UV chromatogram of standard acrylonitrile solution (25 µg/l)

Table 4. Correlation coefficients of acrylonitrile content in polymer mass (A) and acrylonitrile migration into food simulants (B – distilled water, C – 3% acetic acid, D – 10% ethanol, E – 95% ethanol)

	Correlation coefficient	Number of samples (*n*)	Critical values of correlation coefficients
Kitchen device parts			
A × B	–0.0716	5	0.8783
A × C	–0.4694	4	0.9500
A × D	1	2	–
A × D	–1	2	–
ABS granulates			
A × B	0.7978	5	0.8783
A × C	0.2167	5	0.8783
A × D	0.0649	4	0.9500
A × D	0.6144	6	0.8114
SAN granulates			
A × B	*–0.8126*	*6*	*0.8114*
A × C	0.1602	6	0.8114
A × D	–0.3597	6	0.8114
A × D	–0.0747	7	0.7545

coefficients are summarised in Table 4. As can be seen, in some cases the correlation coefficients closely approached the critical value for the correlation – but overall (except only one event) no correlation was found. Therefore, it is possible to state that, with the correlative statistic method employed for the testing of the relation between the acrylonitrile migration and its total content in the polymer mass, no significant degree of conformity was proved.

CONCLUSIONS

This study was realised for the comparison of two different legislative approaches used for the evaluation of acrylonitrile release from food contact materials. It was shown that the former methodology based on the total acrylonitrile content determination in polymer mass cannot be simply compared with the recent recommended methodology based on the acrylonitrile migration into food simulants. To evaluate the conformity of acrylonitrile releasing by two philosophically different approaches, the correlative statistic method was applied to find the relation between the data measured. Unfortunately, no significant degree of correlation or any other systematic relation was found. This may have been caused by significant differences in the methodologies mentioned and/or characteristics of the polymers tested. For example, polymerisation during the polymer production or acrylonitrile unit building in molecular chain, where for the same matrix polymers with different properties can be obtained. Furthermore, various additives such as stabilisers, plasticisers or dyes, can influence polymer properties. In compliance with the results obtained, it can be stated that, from the known total acrylonitrile content in polymer mass, acrylonitrile migration into food simulants cannot be predicted. Generally, regarding the recent legislative requirements, it is not possible to recommend the older methodology (determination of total acrylonitrile content in polymer mass) as an approach equivalent to the recent legislative requirement (based on acrylonitrile migration into food simulants) for the evaluation of acrylonitrile release from food contact materials.

References

ATSDR – Agency for Toxic Substances and Disease Registry (2004): Acrylonitrile CAS # 107-13-1.

Di Pasquale G., Di Iorio G., Capaccioli T., Gagliardi P., Verga G.R. (1978): Gas chromatographic head-space determination of residual acrylonitrile in acrylonitrile-butadiene-styrene resins and migration into a simulated fatty foodstuffs liquid. Journal of Chromatography, **160***:* 133–140.

Gawell G.B.M. (1979): Determination of acrylonitrile monomer in plastic packaging and beverages by Headspace Gas Chromatography. Analyst, **104***:* 106–110.

Commission of the European Communities (1990): Directive 90/128/EEC relating to plastics materials and articles intended to come into contact with foodstuffs.

Decree No. 38/2001 (2001): Directive for sanitary requirements for products that are intended for the contact with food. Ministry of Health of the Czech Republic, Prague.

Decree No. 73 (1992): Amendment of Decree No. 49/1978 for hygienic requirements for plastics and products that are intended for the contact with food. Ministry of Health of the Czech Republic, Prague.

Lickly T.D., Markham D.A., Rainey M.L. (1991): The migration of acrylonitrile from acrylonitrile/butadiene/styrene polymers into food-simulating liquids. Food Chemistry and Toxicology, **91***:* 25–29.

Lickly T.D., Markham D.A., McDonald M.E. (1993): Migration of acrylonitrile from styrene/acrylonitrile copolymers into food-simulating liquids. Journal of Agricultural and Food Chemistry, **41***:* 119–124.

Markelov M., Alger M.M., Lickly T.D., Rosen E.M. (1992): Migration studies of acrylonitrile from commercial copolymers. Industrial & Engineering Chemistry Research, **31***:* 2140–2146.

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