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Determination of primary aromatic amines in cold water extract of coloured paper napkin samples by liquid chromatography-tandem mass spectrometry

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ABSTRACT

The aim of this study was the optimisation of a multi-analyte method for the analysis of primary aromatic amines (PAAs) from napkins in order to support official controls and food safety. We developed a UHPLC-MS/MS method for the simultaneous determination of 36 toxicologically relevant PAAs for paper and board. Good regression coefficients of the calibration curves in a range of 0.992–0.999 and reproducibilities in a range of 2.3–15% were obtained. Limits of detections (LODs) were in the range of 0.03–1.4 μg l^{-1} and recoveries were in a range of 21–110% for all the amines. A total of 93 coloured paper napkin samples from different European countries were bought and extracted with water to determine the PAAs. The results showed that 42 of 93 samples contained at least one PAA. More than half of the detected PAAs are considered as toxic, carcinogenic or probably carcinogenic to humans by the International Agency for Research on Cancer (IARC), or are classified as such in the European Union legislation on chemicals. Summed concentrations of PAAs in seven samples were higher than 10 μg l^{-1}, the limit of summed PAA in the European Union plastic food contact material regulation. Also, eight PAAs, classified as Category 1A and 1B carcinogen in the European Union legislation of chemicals, were detected at concentrations higher than 2 μg l^{-1}, exceeding the limit proposed by the Federal Institute for Risk Assessment in Germany. Aniline (n = 14) was most frequently present in higher concentrations followed by *o*-toluidine, *o*-anisidine, 2,4-dimethylaniline and 4-aminoazobenzene. Red, orange, yellow and multicoloured paper napkins contained the highest concentrations of total PAAs (> 10 μg l^{-1}). Although the European Union has not harmonised the legislation of paper and board materials and, thus, there is no specific migration limit for PAAs from paper napkins, the present study showed that coloured paper napkins can contain toxic and carcinogenic PAAs at concentrations that are relevant for monitoring.

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KEYWORDS
Primary aromatic amines (PAAs); paper napkins; cold water extract; UHPLC-MS/MS

Introduction

Primary aromatic amines (PAAs) are widely used chemicals in industry. Contamination of foodstuffs with PAAs can originate from printing azo-dyes, azo-pigments, isocyanate-based adhesives and monomers present in plastics, paper napkins and printed or recycled paper used for food packaging. Toxicological *in vitro* and *in vivo* studies have highlighted the genotoxic, carcinogenic and allergenic effects of a number of PAAs (EC 2008; Zhang et al. 2009; Trier et al. 2010; WHO/IARC 2010). Also, recent epidemiological studies showed that occupational exposure to carcinogens including PAAs (benzidine, 4-aminobiphenyl, 2-naphthylamine, 4-chloro-*o*-toluidine) is the second most important risk factor for urothelial bladder cancer, following smoking (Burger et al. 2013). Considering their toxicity, determination of these compounds in suspected foods and determination of migration of PAAs from food-contact materials (FCMs) is important for food and consumer safety (Aznar et al. 2009; Trier et al. 2010; Naegele & Helling 2012).

Legislation of paper and board materials used in contact with foods is not yet harmonised at the European Union (EU) level; however, restrictions for PAAs have been established in Regulation (EU) No 10/2011 on plastic FCMs (EU 2011). According to this regulation, plastic materials and articles shall not release PAAs in a detectable quantity into food or food simulant, excluding those appearing in table 1 of Annex I: the LOD of 0.01 mg of substance per kg of food or food simulant is applied to the sum of PAAs released. In table 1 of Annex I, 4,4′-diaminodiphenyl sulphone, 2-aminobenzamide and 1,3-phenylenediamine have a specific migration limit of 5 mg kg^{-1}, 0.05 mg kg^{-1} and not detectable, respectively.

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Table 1. Specific parameters for the investigated 36 PAAs.

CAS No.	PAA	Abbreviation	MRM traces (*m/z*)		RT (min)	Retention window (min)	Collision energy (eV)
			Precursor ion	Daughter ion			
101-80-4	4,4-Diaminodiphenylether	4,4′-DPE	201.04	108.00	1.94	1.25–2.75	22
101-77-9	4,4-Methylenedianiline	4,4′-MDA	199.08	76.41	2.20	1.5–3.0	36
108-45-2	*m*-Phenylenediamine	*m*-PDA	109.00	92.0	1.11	0.5–2.0	20
119-93-7	3,3-Dimethylbenzidine	3,3-DMB	213.00	196.0	2.26	1.5–3.0	24
2243-62-1	1,5-Diaminonaphtalene	1,5-DAN	159.04	115.0	1.30	0.75–2.25	30
62-53-3	Aniline	ANL	94.00	77.0	1.52	1.0–2.5	20
536-90-3	3-Anisidine (*m*-anisidine)	*m*-ANS	107.99	90.97	2.12	1.25–3.0	16
108-42-9	3-Chloroaniline	3-CA	123.99	92.193	1.99	1.25–3.0	20
92-87-5	Benzidine	BEN	127.90	92.99	2.75	2.0–3.5	16
90-04-0	*o*-Anisidine	*o*-ANS	184.02	156.034	1.48	1.0–2.25	32
95-53-4	*o*-Toluidine	*o*-T	123.99	108.989	1.86	1.25–3.0	16
97-52-9	2-Methoxy-4-nitroaniline	2,4-MONA	168.99	122.01	3.09	2.25–4.0	20
6358-64-1	4-Chloro-2,5-dimethoxyaniline	4,2,5-CDMA	187.95	172.99	3.19	2.5–4.0	28
823-40-5	2,6-Toluenediamine	2,6-TDA	123.00	106.0	1.12	0.5–2.0	16
95-68-1	2,4-Dimethylaniline	2,4-DMA	122.02	106.96	2.87	2.0–3.5	16
90-41-5	2-Aminobiphenyl	2-ABP	170.06	92.31	3.82	3.4–4.4	22
87-62-7	2,6-Dimethylaniline	2,6-DMA	122.02	104.05	2.72	2.2–3.2	14
120-71-8	2-Methoxy-5-methylaniline	2-MO-5-MA	138.02	105.99	2.66	2.2–3.2	20
99-55-8	2-Methyl-5-nitroaniline	2-M-5-NA	152.99	89.80	3.31	3.0–3.8	24
60-09-3	4-Aminoazobenzene	4-AAB	198.02	76.9	4.47	4.2–7.0	18
615-05-4	2,4-Diaminoanisole	2,4-DAS	139.01	107.70	1.37	0.8–2.0	14
92-67-1	4-Aminobiphenyl	4-ABP	170.06	92.18	3.82	3.4–4.4	20
156-43-4	4-Ethoxyaniline	4-EA	138.02	64.93	2.60	2.2–3.2	22
95-80-7	2,4-Toluenediamine	2,4-TDA	123.01	105.49	1.41	1.0–2.0	14
99-52-5	2-Methyl-4-nitroaniline	2-M-4-NA	152.99	106.00	3.11	2.8–3.6	20
95-69-2	4-Chloro-2-metylenaniline	4-C-2-MA	141.93	106.98	3.25	2.8–3.8	16
106-47-8	4-Chloroaniline	4-CA	127.96	92.99	2.64	2.2–3.2	14
91-59-8	b-Naphthylamine	B-NpA	144.03	116.95	3.12	2.8–3.8	16
120-35-4	3-Amino-4-methoxybenzanilidine	3A-4MOB	243.12	124.00	3.24	2.5–4.0	16
838-88-0	4,4′-Methylene-*bis*-(2-methyl-aniline)	4,4Mb-2MA	227.16	119.98	2.81	2.0–3.5	24
67014-36-2	5-Amino-6-methyl-benzimidazolone	5A-6MB	164.02	149.00	1.10	0.5–2.0	18
19406-86-1	3-Amino-4-methylbenzamide	3A-4MB	151.02	92.97	1.26	0.5–2.0	22
95-79-4	5-Chloro-2-methylaniline HCl	5C-2MA	142.00	106.98	3.52	3.0–4.0	16
94-70-2	*o*-Phenitidine (2-Ethoxyaniline)	*o*-PHE	138.08	64.93	2.48	2.0–3.0	24
2835-68-9	4-Aminobenzamide	4-AB	137.05	64.93	1.05	0.5–2.0	24
95-51-2	2-Chloraniline	2-CA	127.96	64.93	3.32	2.5–4.0	20

Furthermore, PAAs that are of toxicological concern are listed specifically in the REACH Regulation (EC) No 1907/2006 (EC 2006).

Recently, the Federal Institute for Risk Assessment (BfR) in Germany released an opinion and suggested that the limit value of not detectable with an LOD of 0.01 mg kg^{-1} food for PAAs indicated in Annex II of Regulation (EU) No 10/2011 should be applied to PAAs in printed FCMs such as paper napkins and bakery bags (BfR 2014). The BfR also recommended that in addition to the limit for total PAAs, the migration of genotoxic carcinogenic PAAs, i.e. categories 1A and 1B of the EU regulation on classification, labelling and packaging of substances and mixtures (EC 2008) into food or food simulants as individual substances, should not be detectable with an LOD of 0.002 mg kg^{-1} food. An inter-laboratory comparison study showed that such an LOD is feasible (Merkel et al. 2015).

Different analytical methods are used for the determination of PAAs in different matrices. A common method is a spectrophotometric technique that reports the result as aniline equivalents. This method is only used for screening purposes due to its lack of selectivity and risk of false-positive results. More sophisticated methods, such as GC-MS after derivatisation of the PAAs, LC-UV, and capillary electrophoresis with UV detection (CE-UV) are more sensitive and selective. LC-MS or LC-MS/MS, which have high sensitivity, reliability and selectivity, is also a popular technique for the analysis of PAAs (Pezo et al. 2012; Mattarozzi et al. 2013). These methods are used for the analysis of PAAs in migration extracts of plastic kitchen utensils and articles used as FCMs (Aznar et al. 2009; Sendon et al. 2010; Trier et al. 2010; McCall et al. 2012; Pezo et al. 2012; Mattarozzi et al. 2013). Problems have been reported within industry and by enforcement authorities regarding the release of carcinogenic PAAs from paper napkins (BfR 2014). However, there are a very limited number of studies on the migration of PAAs from paper and board FCMs.

The aim of this study was the optimisation of a multi-analyte method for the analysis of 36 toxicologically relevant PAAs from paper napkins in order

to support official controls and food safety. A survey study was the carried out for the determination of those PAAs in cold water extracts of coloured paper napkins obtained from different countries of the EU.

Materials and methods

Chemicals and solvents

All the analytical PAA standards (Table 1), pentafluoropropionic acid (PFPA, LC-MS grade), acetone (HPLC grade), ethanol (HPLC grade) and methanol (UHPLC-MS grade) were obtained from Sigma-Aldrich (St. Louis, MO, USA). A Milli-Q Advantage 10 system (Millipore, Bedford, MA, USA) produced the deionised water.

Samples

A total of 93 coloured paper napkin samples were obtained mainly from the Italian, Swiss and Dutch markets, although most were produced in Germany, Italy and Slovakia (Figure 1).

Sample preparation

CEN standard EN 645 was used for the extraction of PAAs from coloured paper napkins into cold water (CEN 1994). Briefly, colour napkins were cut into pieces approximately 1–2 cm^2 in size. A total of 10 g of napkin samples were weighed into a 500 ml conical flask and 200 ml deionised water were added. Prepared samples were stored for 24 h at 23 ± 2°C, and shaken every 2 h, except during the night. After 24 h the solution was decanted and the samples were washed twice with deionised water. The combined extract and washings were filtrated into a 250 ml conical flask, using nylon filters (0.45 µm), and added with deionised water up to the mark. Each sample was extracted and analysed in duplicate.

For the determination of the recovery, paper napkins of different colours, which on the basis of previous tests did not contain any PAAs, were spiked with three levels of a solution containing a mix of PAAs (5, 10 and 50 µg l^{-1}) in duplicate and the spiked samples were extracted and analysed as described above. Similarly, deionised water was spiked with same solution of mix PAAs and analysed. The recovery was calculated for each PAA from the difference of results for the spiked paper napkins and the spiked deionised water.

Analysis

An ACQUITY Ultra Performance LC System and a Xevo TQ MS Tandem Quadruple Mass Spectrometer with electrospray interface (Waters, Milford, MA, USA) equipped with a ACQUITY UPLC BEH C18

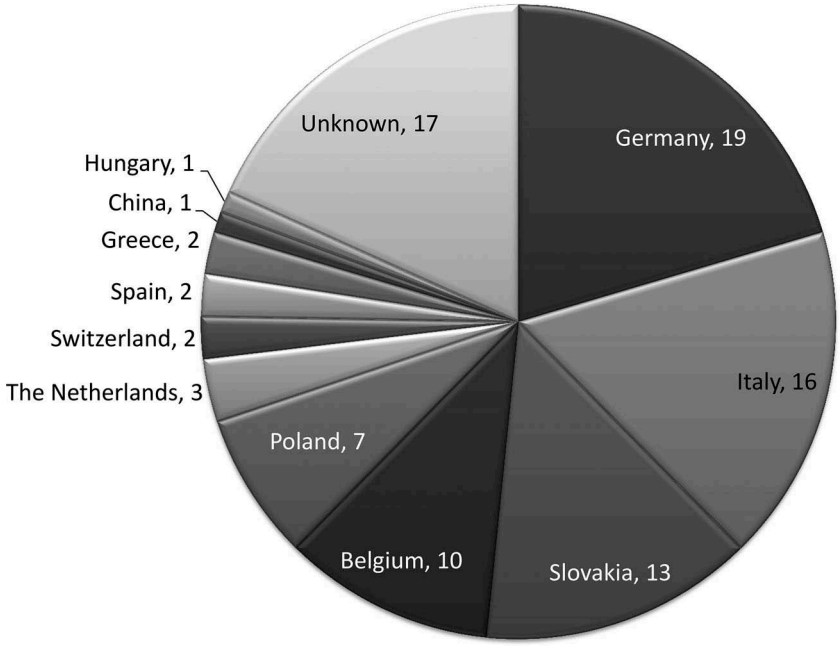

Figure 1. Countries of production of the samples.

analytical column (1.7 µm × 2.1 mm × 50 mm) and a 0.5 µm stainless pre-column filter (Waters) were used.

Mobile phases A and B consisted of 4.7 nM perfluoropentanoic acid (PFPA) in water and 4.7 nM PFPA in methanol, respectively. The gradient programme was as follows: 0–0.5 min: 80% A and 20% B, 0.5–3.0 min: 40% A and 60% B, 3.0–3.5 min: 10% A and 90% B and 3.5–6 min: 80% A and 20% B. The injection volume was 7.5 µl, the column temperature was 45 °C and flow rate was 0.2 ml min^{-1}.

The analytes ionised in an electrospray interface in the positive ion mode (ESI+). The nebulising gas was nitrogen (desolvation gas maximum 1000 l h^{-1} and cone gas maximum 40 l h^{-1}) and the collision gas was argon (0.24 ml min^{-1}). Source conditions of ESI+ were as follows: capillary voltage 0.50 kV; cone voltage 34.00 V; desolvation temperature 500°C; source temperature 150°C. Data acquisition mode was MRM mode using MH+ as the precursor ion. Table 1 shows specific MS parameters for each PAA.

Stock solutions of each PAA (about 1000 mg l^{-1}) were prepared in ethanol except for 4,4-diaminodipheniylether which was prepared in acetone. Working standard solutions of 10 mg l^{-1} and 100 µg l^{-1} were prepared by combining the stock solutions and diluting with deionised water. External calibration standards were made with concentrations of 1, 2.5, 5, 10, 25 and 50 µg l^{-1} of PAAs in water, with each calibration level injected twice. We calculated the concentrations of the PAAs from the calibration curve without a correction for the recovery.

Results and discussion

Analytical performances

The mobile phases, solvent solutions, and LC and MS parameters of multi-analyte existing methods (Mortensen et al. 2005; Simoneau 2011) were optimised for the determination of 36 PAAs from cold water extracts of coloured paper napkins. Table 2 shows the main analytical performances.

Repeatability of the analysis was calculated on 10 injections of a water solution spiked with 10 µg l^{-1} of

Table 2. Main analytical parameters[a].

PAA	Equation	R^2	LOD (µg l^{-1})	LOQ (µg l^{-1})	RSD (%)	Rec (%)
4,4′-DPE	$y = 379.54x - 171.61$	0.999	0.40	1.32	10.81	66.6
4,4′-MDA	$y = 471.55x - 241.7$	0.999	0.14	0.47	11.6	70.8
m-PDA	$y = 859.83x + 19.145$	0.999	0.55	1.84	11.38	21.3
3,3-DMB	$y = 293.98x - 412.27$	0.998	0.57	1.90	9.76	62.3
1,5-DAN	$y = 126.65x - 55.271$	0.999	1.38	4.60	14.91	32.8
ANL	$y = 1776.5x + 98.177$	0.999	0.27	0.89	3.69	75.3
m-ANS	$y = 899.01x - 81.33$	0.999	0.42	1.41	3.56	79.0
3-CA	$y = 576.25x - 668.72$	0.998	0.14	0.47	4.05	80.2
BEN	$y = 179.69x - 62.485$	0.999	0.41	1.35	14.98	41.7
o-ANS	$y = 4319.6x + 517.13$	0.999	0.19	0.62	3.21	80.0
o-T	$y = 1533.4x + 357.61$	0.999	0.27	0.89	3.58	78.7
2,4-MONA	$y = 216.14x - 361.84$	0.999	0.18	0.60	3.80	79.5
4,2,5-CDMA	$y = 716.5x - 107.38$	0.998	0.03	0.08	3.23	84.1
2,6-TDA	$y = 1256.1x + 669.8$	0.999	1.33	4.43	12.35	36.4
2,4-DMA	$y = 2739.1x + 324.65$	0.999	0.21	0.69	3.48	89.4
2-ABP	$y = 2810.1x + 4910.8$	0.994	0.24	0.79	6.66	110.9
2,6-DMA	$y = 4471.5x + 641$	0.999	0.54	1.81	4.01	80.4
2-MO-5-MA	$y = 13432x + 3104.8$	0.999	0.17	0.56	4.52	77.4
2-M-5-NA	$y = 23.608x - 14.581$	0.998	0.45	1.51	6.85	85.1
4-AAB	$y = 4136.9x - 8931.4$	0.992	0.15	0.50	10.01	25.9
2,4-DAS	$y = 1007.8x - 89.65$	0.999	0.52	1.72	7.52	52.3
4-ABP	$y = 23.608x - 14.581$	0.998	0.21	0.69	5.87	94.4
4-EA	$y = 3905x + 2958.6$	0.999	0.30	0.99	2.29	67.1
2,4-TDA	$y = 90.201x + 1804.1$	0.994	0.39	1.30	9.4	60.5
2-M-4-NA	$y = 3204.3x - 4092.7$	0.998	0.53	1.75	4.30	78.1
4-C-2-MA	$y = 1337.7x - 1154.5$	0.998	0.21	0.70	3.36	81.8
4-CA	$y = 1203.3x - 183.38$	0.999	0.28	0.92	4.43	76.7
B-NpA	$y = 3204.3x - 4092.7$	0.998	0.15	0.49	5.40	60.0
3A-4MOB	$y = 395.11x - 399.24$	0.997	0.14	0.46	4.92	102.1
4,4Mb-2MA	$y = 344.28x - 243.4$	0.992	0.45	1.50	7.59	104.3
5A-6MB	$y = 185.96x + 23.675$	0.999	0.64	2.13	8.86	30.9
3A-4MB	$y = 194.89x + 26.806$	0.999	0.66	2.20	6.89	45.0
5C-2MA	$y = 770.2x - 820.73$	0.998	0.37	1.23	4.52	79.3
o-PHE	$y = 4727.6x - 306.33$	0.999	0.39	1.30	8.18	65.9
4-AB	$y = 334.08x + 93.538$	0.999	1.10	3.66	7.76	28.4
2-CA	$y = 556.33x - 233.55$	0.999	0.37	1.25	6.40	81.9

Note: [a]Calibration curve equations, regression coefficients (R^2), limit of detection (LOD), limit of quantification (LOQ), repeatability of three different analysis at 10 µl (RSD%) and mean recovery of 3 (5, 10 and 50 µg l^{-1}) spike levels.

each PAA and it ranged from 2.3% to 15.0%, with an average of 6.7%. Within-laboratory reproducibility (intermediate precision) was also calculated by repeating the procedure described for repeatability at three different times and with different operators and it ranged from 2.9% to 18.5%, with an average of 8.2%. Average recoveries were > 70% for 21 PAAs and 50–70% for seven PAAs. However, recoveries of three PAAs were very low in the range of 20–30% (*m*-PDA: 21%, 4-AAB: 26% and 4-AB: 28%). Recoveries could be highly dependent on the paper type of the napkin, possibly due to signal suppression from other components of the extract. Therefore, further studies should be performed on the recoveries of PAAs in relation with characteristics of various types of paper napkins.

The linearity of instrumental response evaluated in a concentration range between 1 and 50 μg l^{-1} showed very good regression coefficients for all the PAAs (0.992–0.999). The International Union of Pure and Applied Chemistry (IUPAC) approach based on blank measurements (IUPAC 1987; Mortensen et al. 2005) was used for the calculation of LOD and LOQ. LODs were in the range of 0.03–1.38 μg l^{-1} for 36 PAAs (Table 2). LOD values are comparable with other methods on PAAs analysis in plastics (Mortensen et al. 2005; Mutsuga et al. 2009; Mattarozzi et al. 2013) and lower than the limit of total PAA of 10 μg l^{-1} in the EU plastic FCM Regulation (EU) No 10/2011 and the limit of carcinogenic PAAs of 2 μg l^{-1} mentioned in the BfR proposal for PAAs in paper napkins and bakery bags (BfR 2014).

Sample analysis

The survey on the coloured paper napkins from the European Market showed that 42 out of 93 samples contained a minimum one PAA higher than LOD. Two samples contained eight different PAAs and five samples contained five different PAAs, while the majority contained from one to three PAAs (Figure 2).

In those 42 samples, 21 out of 36 analysed PAAs were detected in the range of 0.19–17.6 μg l^{-1}. Aniline was detected most frequently (n = 14) followed by 2,4-DMA (n = 12), *o*-T (n = 11), 3A-4MOB (n = 9) and *o*-ANS (n = 8). The IARC and EU legislation on chemicals (EC 2006, 2008) consider more than half of the detected PAAs are as toxic, carcinogenic or probably carcinogenic to humans (Table 3).

The sum of PAAs was in the range of 0.19–43 μg l^{-1}. Almost half of PAAs detected in samples (n = 19) contained total PAAs in the range of 0.19–3.0 μg l^{-1}. Total concentrations of PAAs in seven samples were higher than 10 μg l^{-1}, exceeding the limit of total PAA in the EU plastic FCM Regulation (EU) No 10/2011, which is also proposed by the BfR for paper napkins (Figure 3). In addition, eight car-

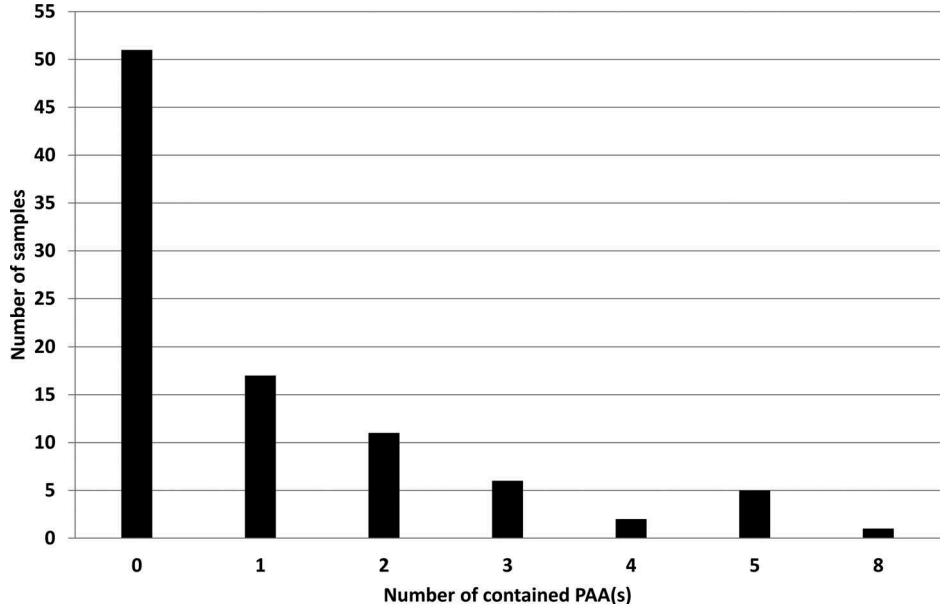

Figure 2. Number of PAAs detected in the samples.

Table 3. Detected samples in the napkin samples.

	PAA	Number of detected samples	Minimum-maximum (μg l^{-1})	Mean (μg l^{-1})	Average (μg kg^{-1}napkin)	IARC[a]	Restriction in the REACH legislation[b]	CLP regulation[c]
1	4,4′-DPE	1	2.1	2.1	51.3	2B	+	Category 1B carcinogen
2	4,4-MDA	2	0.19–0.19	0.19	4.8	2B	+	Category 1B carcinogen
3	*m*-PDA	2	0.7–2.7	1.7	41.9	3		
4	ANL	14	0.3–17.6	3.1	76.6	3		Category 2 carcinogen
5	*o*-T	11	0.23–10.9	2.3	56.8	1	+	Category 1B carcinogen
6	*m*-ANS	2	0.3–5.1	2.7	67.6	–	–	
7	3-CA	3	0.5–6.1	2.4	60.3	–	–	
8	BEN	3	0.2–2.7	1.6	39.4	1	+	Category 1A carcinogen
9	*o*-ANS	8	0.7–12.0	3.3	82.2	2B	+	Category 1B carcinogen
10	2,4-MONA	6	0.5–1.9	1.1	26.4	–	–	
11	4,2,5-CDMA	7	0.3–5.2	2.1	52.0	–	–	
12	2,4-DMA	12	0.2–10.6	4.5	80.7	3	–	
13	2-ABP	1	0.3	0.3	8.0	–		Category 2 carcinogen
14	4-AAB	6	0.7–10.3	4.2	105.9	2B	+	Category 1B carcinogen
15	4-ABP	1	0.3	0.3	8.3	1	+	Category 1A carcinogen
16	4-EA	1	0.3	0.3	6.8	–		
17	2,4-TDA	2	1.6–2.4	2.0	51.0	2B	+	Category 1B carcinogen
18	2-M-4-NA	1	3.3	3.3	83.2	–		
19	4-CA	3	0.3–5.9	2.3	56.9	2B	+	Category 1B carcinogen
20	3A-4MOB	9	0.7–1.2	0.88	21.9	–	–	
21	4,4Mb-2MA	3	1.6–2.3	1.8	45.8	2B	–	Category 1B carcinogen

Notes: [a]IARC classification groups: 1 = carcinogenic to humans; 2A = probably carcinogenic to humans; 2B = possibly carcinogenic to humans; 3 = not classifiable as carcinogenic to humans.

[b]List of PAA that restricts the use of azo-dyes in Regulation (EC) No 1907/2006 concerning the registration, evaluation, authorisation and restriction of chemicals (REACH).

[c]Hazard categories for carcinogens in the CLP regulation (EC 1272/2008): category 1: known and presumed human carcinogens; 1A: known to have carcinogenic potential for humans, classification largely based on human evidence; 1B: presumed to have carcinogenic potential for humans, classification largely based on animal evidence; and 2: suspected human carcinogens.

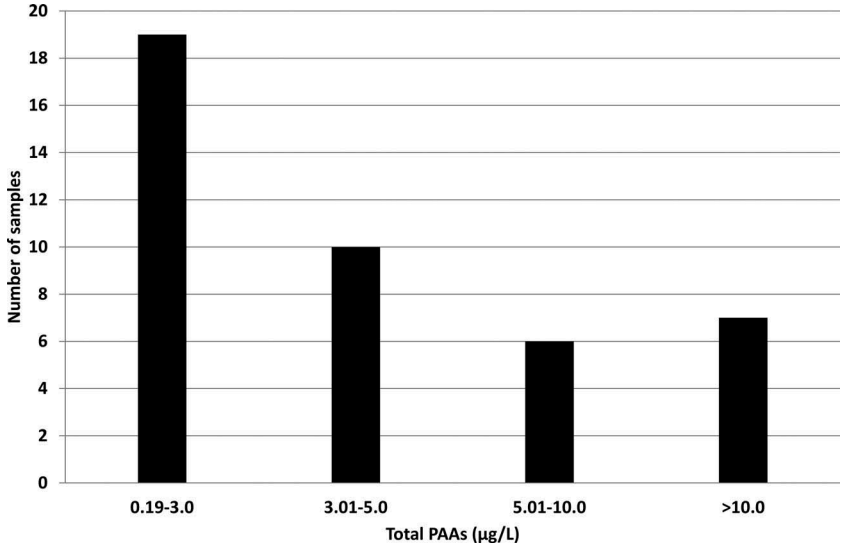

Figure 3. Total PAA values of the samples (n = 42).

cinogen PAAs (categories 1A and 1B) were detected higher than 2 μg l^{-1}, exceeding the limit of individual PAA proposed by BfR (Table 3). 4-AAB, a category 1B carcinogen and with very low recovery, was detected in six samples. In one sample the concentration of 4-AAB was above 10 μg l^{-1} without correction for recovery. In the case of recovery correction, all six samples may potentially exceed the proposed BfR limit of 2 μg l^{-1} for 4-AAB.

Red, orange, yellow and multicolour napkins contained higher levels of PAAs compared with other colours. Also, green, black and blue napkins contained certain level of PAAs (Figure 4). These results confirm data indicated in previous reports (BfR 2014) that

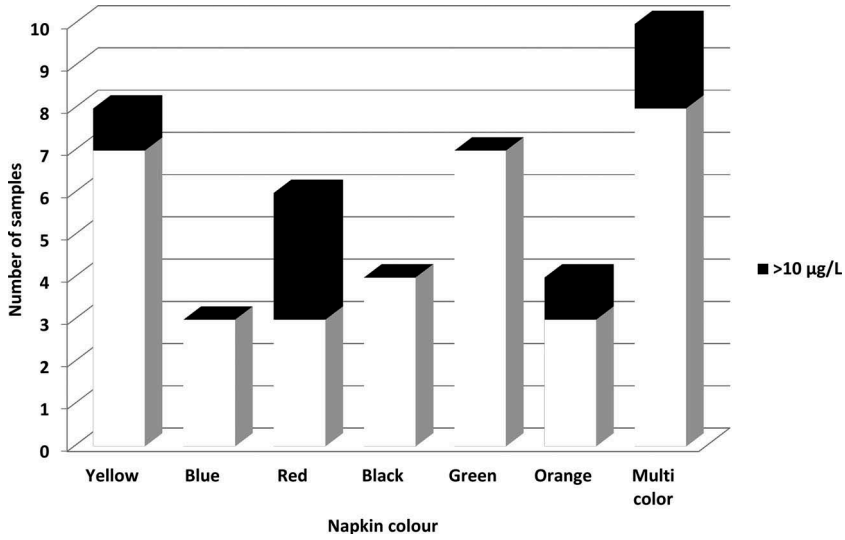

Figure 4. Colours of napkins in which PAAs were detected.

suggested that red, orange and yellow napkins contain PAAs that are readily extracted into cold water. However, there are very limited public data regarding the relationship between napkin colour and PAA presence and we could not compare the results with other studies.

Conclusions

This study developed a multi-analyte method based on cold water extraction and UHPLC-MS/MS quantification for the analysis of PAAs from coloured paper napkins. The survey on PAA content in coloured paper napkins from the European market showed the presence of ANL, *o*-T, *o*-ANS, 2,4-DMA and 4-AAB at concentrations that sometimes exceeded 10 µg l^{-1}, the EU limit for PAA in plastic FCMs. About 50% of the detected PAAs are considered toxic, carcinogenic or probably carcinogenic to humans and the concentrations of eight carcinogenic PAAs were higher than 2 µg l^{-1}, the proposed limit by the BfR. The highest concentrations of total PAAs (> 10 µg l^{-1}) were observed in red, orange, yellow and multi-coloured napkins. The present study shows that coloured paper napkins can release carcinogenic PAAs.

Disclosure statement

No potential conflict of interest was reported by the authors.

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