

Cooking Utensils: Determination of Primary Aromatic Amines by LC/MS/MS

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Abstract

A fast, simple, and sensitive LC/MS/MS method for the determination of 22 primary aromatic amines (PAAs) in cooking utensils has been developed using an Agilent 1290 Infinity II LC coupled to an Agilent 6470A triple quadrupole LC/MS. For this determination, migration tests of the amines were performed using 3% (w/v) aqueous acetic acid solution as food simulant, according to European Commission guideline EUR 24815 EN 2011. The 22 PAAs were detected in less than nine minutes using an Agilent InfinityLab Poroshell 120 PFP column. The limit of detection (LOD) in the European Commission Regulation (UE) N° 10/2011 for PAAs in food or food simulant is 10 µg/kg. The LOD obtained with the proposed method was at least 83 times lower than required by the legislation, and the limit of quantification (LOQ) was 24 times lower. Analytical curves with determination coefficients (R^2) greater than 0.995 for all analytes in a range of 1 to 500 µg/kg were achieved in food simulant. The method was validated in terms of precision (repeatability), intermediate precision, and trueness. It was then applied to determine the 22 PAAs in cooking utensil samples of different materials (polyamide, polypropylene, and silicone) and from different origins (Brazil and China).

Introduction

One of the biggest food safety concerns is the migration of undesired chemical substances from food contact materials (FCM), such as containers, packaging, cutlery, and dishes. Kitchen utensils made from plastic materials such as skimmers, ladles, and spoons are quite popular for cooking and frying due to their low cost, temperature resistance, and nonscratch properties. However, chemical substances can migrate from these articles to the food, contributing to food contamination. The migration of primary aromatic amines (PAAs) from cooking utensils into food can occur due to remaining residues present from the coloring process using azo-dyes and comonomer addition.¹

PAAs are a group of chemical substances that have a primary amine (-NH₂) attached to an aromatic hydrocarbon. Amino benzene (also called aniline) is the simplest PAA. The International Agency for Research on Cancer (IARC) have classified several PAAs as possible human carcinogens (group 2B). Other PAAs such as benzidine, *o*-toluidine, and 2-naphthylamine are classified as carcinogenic to humans (group 1), and should not be present in food.² Due to the potential risk to human health and consumer protection, European Union legislation has established a specific

migration limit for materials and articles of plastic material for food contact. These materials should not release PAAs in a detectable quantity above 0.01 mg of PAAs per kg of food or food simulant. The LOD applies to the sum of primary aromatic amines that are released.^{3,4}

Different analytical methods are used to determine PAAs in different matrices, but the most common is the spectrophotometric method that reports the result as aniline equivalents.⁵ Although the spectrophotometric method achieves the required sensitivity, it has a critical disadvantage, which is the absence of selectivity that does not allow individual quantification of the PAAs.⁵ More sophisticated, selective, and increasingly sensitive methods have been developed to determine low PAA concentrations in migration assays. These methods include gas chromatography with flame ionization (GC-FID) or mass spectrometry detection (GC/MS)^{6,7,8}, in both cases after derivatization, capillary electrophoresis with ultraviolet detection (CE-UV) or laser induced fluorescence detection (CE-LIF),^{9,10} and liquid chromatography with ultraviolet detection (LC-UV) or sequential mass spectrometry detection (LC/MS/MS).^{11,12,13} Among all of these techniques, LC/MS/MS is the most explored for the determination of PAAs. However, PAAs are basic compounds that are ionized in low pH medium,

and it is difficult to find a suitable stationary phase capable of retaining small and charged polar molecules in reversed-phase liquid chromatography, resulting in poor peak shape or total loss of retention. To improve the retention of PAAs on C18 conventional chromatography columns, approaches, such as decreasing the pH of the mobile phase or the use of ion-pairing chromatography, have been used.^{14,15} Even though these approaches can improve retention and separation of the PAAs in the column, they impair the ionization in the mass spectrometer, thereby decreasing the sensitivity of the method.

This Application Note describes a sensitive LC/MS/MS method for simultaneously analyzing 22 PAAs in nine minutes using an InfinityLab Poroshell 120 PFP column with neither ion pairing reagents nor derivatization steps. Table 1 shows the molecular structure, CAS number, as well the IARC classification group of the PAAs analyzed in this work. The developed method was validated according to guideline EUR 24105 outlined by the EURL for food contact materials¹⁶, and applied in the determination of 22 PAAs in cooking utensils of different materials (polyamides, polypropylene, and silicone) and origins (Brazil and China).

Table 1. Primary aromatic amines selected for this study, CAS number, and IARC classification.

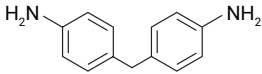
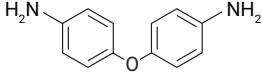
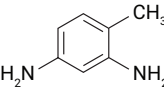
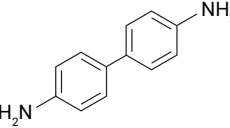
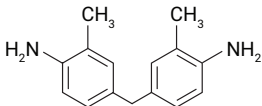
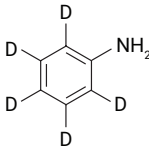
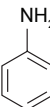
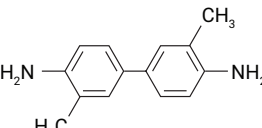
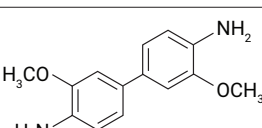
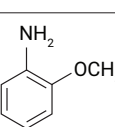
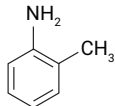
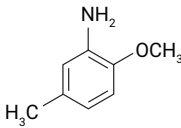
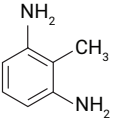
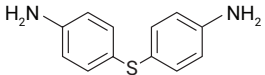
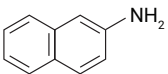
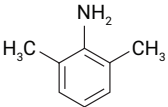
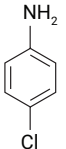
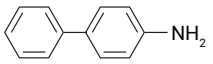
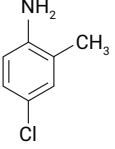
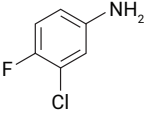
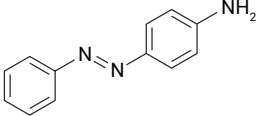
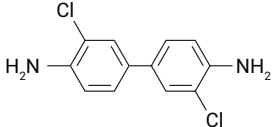
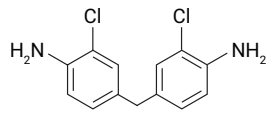
Compound	Structure	CAS	IARC Group
4,4'-Diaminodiphenylmethane		101-77-9	2B
4,4'-Oxydianiline		101-80-4	2B
2,4-Diaminotoluene		95-80-7	2B
Benzidine		92-87-5	1
4,4'-Methylene-bis-(2-Methylaniline)		838-88-0	2B
Aniline-d ₅ (Internal Standard)		4165-61-1	NF
Aniline		62-53-3	3
3,3'-Dimethylbenzidine		119-93-7	2B
o-Dianisidine		119-90-4	2B
o-Anisidine		90-04-0	2B
o-Toluidine		95-53-4	1
2-Methoxy-5-Methylaniline		120-71-8	2B

Table 1. Primary aromatic amines selected for this study, CAS number, and IARC classification (continued).

Compound	Structure	CAS	IARC Group
2,6-Diaminotoluene		823-40-5	NF
4,4'-Diaminodiphenyl Sulfide		139-65-1	2B
2-Naphthylamine		91-59-8	1
2,6-Dimethylaniline		87-62-7	2B
4-Chloroaniline		106-47-8	2B
4-Aminobiphenyl		92-67-1	1
4-Chloro-2-Methylaniline		95-69-2	2A
3-Chloro-4-Fluoroaniline		367-21-5	NF
4-Aminoazobenzene		60-09-3	2B
3,3'-Dichlorobenzidine		91-94-1	2B
4,4'-Methylene-bis-(2-Chloroaniline)		101-14-4	1

IARC groups: 1: carcinogenic to human; 2A: probably carcinogenic to humans; 2B: possibly carcinogenic to humans; 3: not classifiable as to its carcinogenicity to humans; NF: not found.

Experimental

Instrumentation

An Agilent 1290 Infinity II LC, configured with an Agilent 1290 Infinity II high speed pump (G7120A), multisampler (G7167B), and multicolumn thermostat (G7116B), coupled to an Agilent 6470A triple quadrupole LC/MS (G6470AA), was used to determine PAAs using an Agilent Jet Stream (AJS) ion source in positive mode. Table 2 shows the LC/MS/MS optimized conditions.

The mass spectrometer was operated in dynamic multiple reaction monitoring (dMRM) mode using two specific transitions for each target compound, which was obtained using the Agilent MassHunter Optimizer software tool and infusing individual 1,000 µg/kg standards into the mass spectrometer. The most intense transition was used for quantification and the second for qualification of PAAs. Table 3 lists the retention time (RT) and the optimized multiple reaction monitoring (MRM) parameters for the 6470A triple quadrupole LC/MS.

Sample preparation

Briefly, kitchen utensils were submerged in 3% acetic acid, used as food simulant, following the technical guide for PAA migration³ and standard number EN 13130-1. After two hours at 100 °C, the samples were removed from the simulant, and the extract was transferred to a 10 mL volumetric flask in which aniline-d₅ was added as internal standard (IS) to a final concentration of 20 µg/kg. The extract was filtered using a 0.2 µm membrane filter then transferred to a 2 mL A-Line vial (part number 5190-9589) for LC/MS/MS analysis.

Table 2. Liquid chromatography and triple quadrupole MS-optimized run parameters.

Liquid Chromatography			
Column	Agilent InfinityLab Poroshell 120 PFP, 2.1 × 150 mm, 2.7 µm (p/n 693775-408)		
Column Temperature	40 °C		
Injection Volume	2 µL		
Mobile Phase	A) Water with 0.1% formic acid B) Acetonitrile		
Gradient	Time (min)	A (%)	B (%)
	0.0	70	30
	0.2	70	30
	6.0	10	90
	7.0	10	90
7.01	70	30	
Stop Time	9 minutes		
Flow Rate	0.250 mL/min		
Triple Quadrupole MS			
Sheath Gas Heater	300 °C		
Sheath Gas Flow	10 L/min		
Drying Gas Flow (N ₂)	10 L/min		
Drying Gas Temperature	350 °C		
Nebulizer Pressure	30 psi		
Capillary Voltage	2,500 V		
V Charging	0 V		

Kitchen utensils are objects that come into repeated contact with food, and for this reason, the procedure described was repeated twice more with the same specimen, using fresh food simulants, totaling three repetitions (first migration, second migration, and third migration). Table 4 lists the material, origin, and number of specimens of the samples analyzed in this work.

Table 3. Retention time and optimized MRM acquisition parameters used for the identification and quantification of PAAs in cooking utensils.

Number	Compound	RT (min)	Q1 ^a (m/z)	Q3 ^b (m/z)	CE ^c (V)	FE ^d (V)
1	4,4'-Diaminodiphenylmethane	1.05	199.1	106.1 77.1	24 60	116
2	4,4'-Oxydianiline	1.06	201.1	184.0 108.0	20 20	96
3	2,4-Diaminotoluene	1.14	123.1	106.0 79.1	20 20	96
4	Benzidine	1.15	185.1	167.0 93.0	40 20	100
5	4,4'-Methylene-bis-(2-methylaniline)	1.16	227.2	120.1 77.1	40 60	150
6	Aniline-d ₅ (IS)	1.22	99.1	82.1 54.2	20 40	100
7	Aniline	1.24	94.0	77.0 51.0	20 40	100
8	3,3'-Dimethylbenzidine	1.30	213.1	198.0 181.0	20 40	150
9	o-Dianisidine	1.30	245.1	230.0 187.0	20 40	150
10	o-Anisidine	1.34	124.1	109.0 92.1	20 20	100
11	o-Toluidine	1.40	108.0	91.0 65.0	20 40	100
12	2-Methoxy-5-methylaniline	1.53	138.1	123.0 106.0	20 20	100
13	2,6-Diaminotoluene	1.54	123.1	77.1 51.2	36 56	146
14	4,4'-Diaminodiphenyl sulfide	1.68	217.1	124.0 80.1	20 40	100
15	2-Naphthylamine	2.19	144.1	127.1 77.0	20 40	100
16	2,6-Dimethylaniline	2.32	122.1	105.0 77.0	20 40	96
17	4-Chloroaniline	2.39	128.0	93.1 75.1	20 40	96
18	4-Aminobiphenyl	2.82	170.1	152.0 128.0	40 40	100
19	4-Chloro-2-methylaniline	3.57	142.0	125.0 107.1	20 20	96
20	3-Chloro-4-fluoroaniline	3.57	146.0	111.0 74.1	20 40	100
21	4-Aminoazobenzene	5.18	198.1	93.1 77.1	20 20	101
22	3,3'-Dichlorobenzidine	5.31	253.0	216.9 182.0	20 40	100
23	4,4'-Methylene-bis-(2-chloroaniline)	5.39	267.0	230.9 195.0	40 40	100

^a Precursor ion (Q1)

^b Fragment ion (Q3)

^c Collision energy

^d Fragmentor energy

Table 4. Samples analyzed, material, origin, and number of specimens analyzed.

Sample No.	Sample	Material	Origin	Specimens No.
1		Silicone	China	5
2		Silicone	China	5
3		Silicone	China	5
4		Silicone	China	4
5		Silicone	China	4
6		Silicone	China	4

Sample No.	Sample	Material	Origin	Specimens No.
7		Silicone	China	5
8		Silicone	China	5
9		Silicone	China	5
10		Polyamide	China	5
11		Polyamide	Brazil	5
12		Polyamide	Brazil	5
13		Polypropylene	China	1

Results and discussion

During the method development, the main goal was to achieve appropriate resolution and low retention times for all the analytes. Mobile phase composition, gradient, and pH of the mobile phase had significant effects on these chromatographic parameters, so fresh mobile phases should be prepared daily. The proposed method for PAA analysis takes only nine minutes, and the separation was reached using the InfinityLab Poroshell 120 PFP column, even for position isomers such as 2,4-diaminotoluene (No. 3) and 2,6-diaminotoluene (No. 13). Figure 1 shows a typical dynamic MRM chromatogram of all PAAs analyzed.

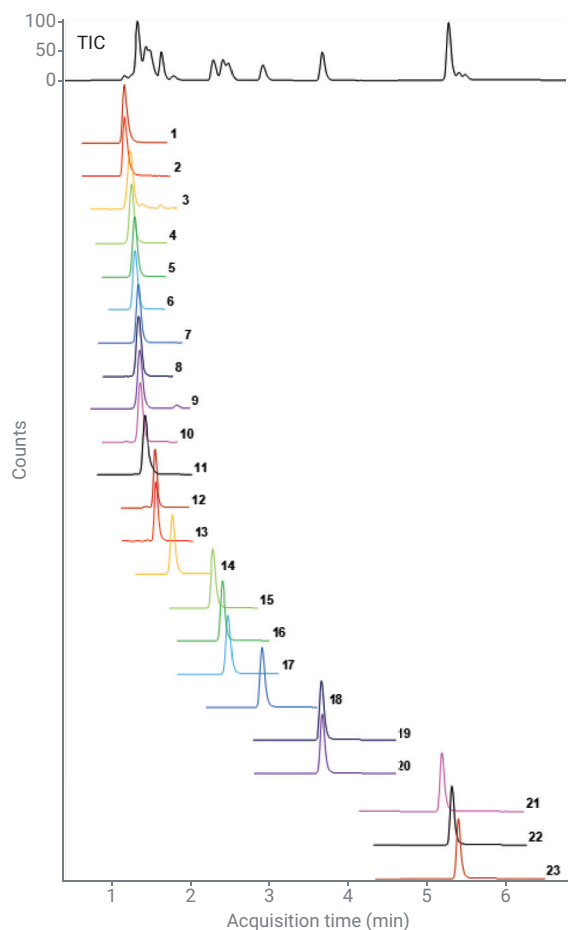


Figure 1. Dynamic MRM chromatogram of PAAs all at 20 $\mu\text{g}/\text{kg}$. Identification of the peaks is the same as shown in Table 3.

Analytical curves, at 16 different levels, were created with standard solutions in a concentration ranging from 1 to 500 µg/kg using aniline-d₅ as internal standard. Each concentration level was analyzed in triplicate. A linear fitting with no weighting was used for all analytical curves, and the values of the coefficient of determination (R²) were higher than 0.995 for all compounds. Figure 2 shows an example of the response for 4,4'-oxydianiline using Agilent MassHunter Quantitative software (version 10.0).

LOD and LOQ were determined by analytical curve as showed in Equations 1 and 2, respectively:¹⁶

$$\text{Equation 1. } \text{LOD} = 3 \frac{\delta}{b}$$

$$\text{Equation 2. } \text{LOQ} = 10 \frac{\delta}{b}$$

Where:

δ = standard deviation

b = angular coefficient of analytical curve

The LOD ranged from 0.06 to 0.1 µg/kg,

and are at least two orders of magnitude lower than the values recommended by the EU plastic FCM Regulation (EU) No 10/2011.⁴ Intraday precision (repeatability) was determined through the triplicate analysis of 10 replicates at three different concentration levels (5, 10, and 30 µg/kg), conducted on the same day, while the same replicates were analyzed on three different days for the determination of within-laboratory reproducibility (intermediate precision).

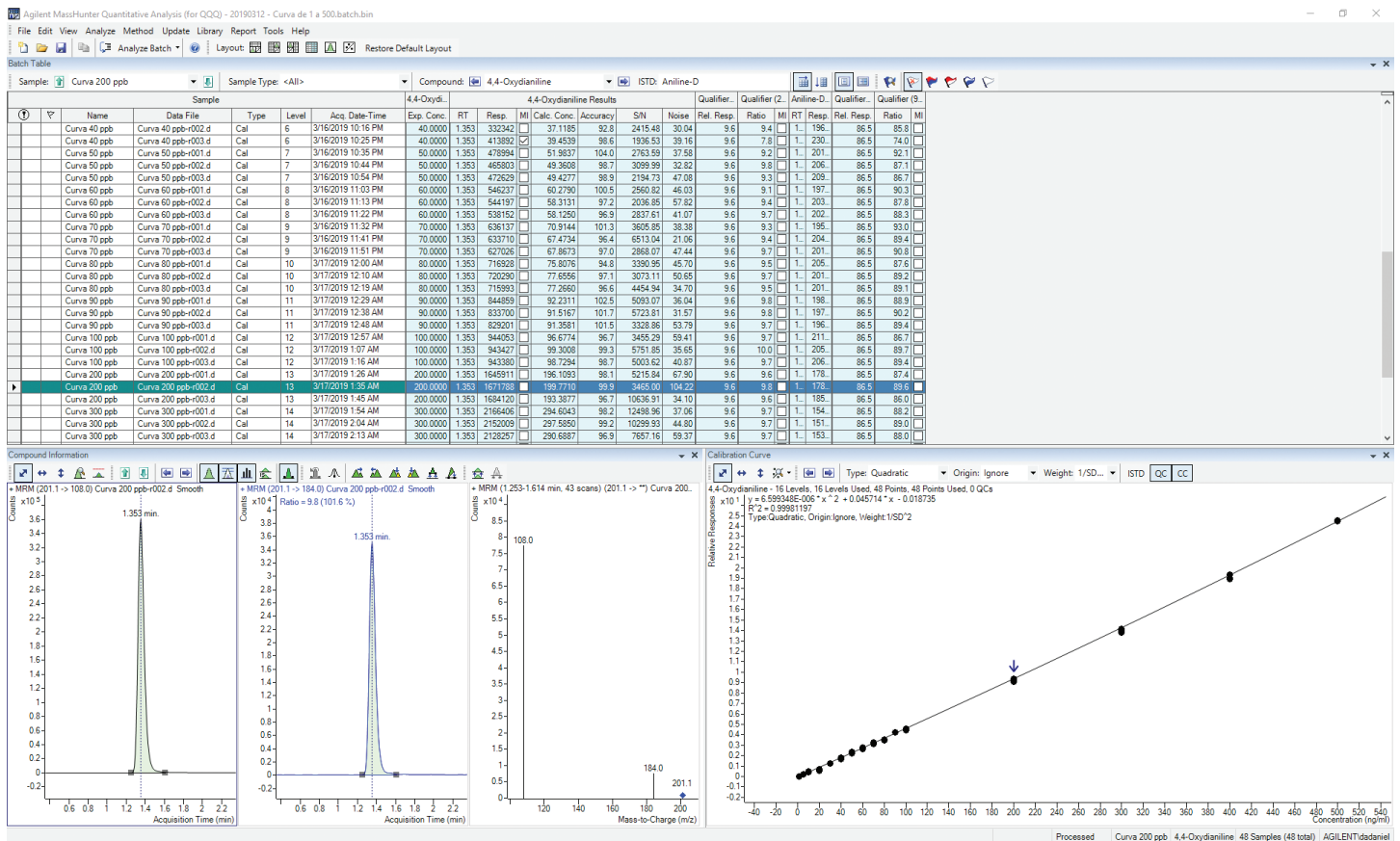


Figure 2. Analytical curve of 4,4'-oxydianiline using Agilent MassHunter Quantitative software (version 10.0).

In both cases, the precision expressed as relative standard deviation (RSD%) was $\leq 26\%$ for 5 $\mu\text{g}/\text{kg}$ and $\leq 18\%$ for 10 and 30 $\mu\text{g}/\text{kg}$ for all PAAs. The acceptable value of RSD within the laboratory, according to INMETRO (the Brazil National Metrology, Quality and Technology Institute), depending on the concentration of the analyte, so for concentrations up to 5 $\mu\text{g}/\text{kg}$ the value is 45%, while for concentrations of 10 $\mu\text{g}/\text{kg}$ and 30 $\mu\text{g}/\text{kg}$ the value of RSD is up to 32%.¹⁸ Table 5 shows the results for LOD, LOQ, repeatability, and intermediate precision for the developed method.

Table 5. LOD, LOQ, precision (repeatability), and intermediate precision by LC/MS/MS.

Compound	LOD	LOQ	Repeatability (1 day), RSD%			Intermediate Precision (3 days), RSD%		
	$\mu\text{g}/\text{kg}$	$\mu\text{g}/\text{kg}$	5 $\mu\text{g}/\text{kg}^a$	10 $\mu\text{g}/\text{kg}^a$	30 $\mu\text{g}/\text{kg}^a$	5 $\mu\text{g}/\text{kg}^a$	10 $\mu\text{g}/\text{kg}^a$	30 $\mu\text{g}/\text{kg}^a$
4,4'-Diaminodiphenylmethane	0.07	0.24	4	7	3	13	10	6
4,4'-Oxydianiline	0.08	0.26	7	7	3	18	10	5
2,4-Diaminotoluene	0.07	0.23	9	7	4	9	9	7
Benzidine	0.07	0.22	7	10	6	20	13	8
4,4'-Methylene-bis-(2-Methylaniline)	0.12	0.41	9	13	4	11	14	10
Aniline	0.06	0.21	6	7	3	12	11	12
3,3'-Dimethylbenzidine	0.10	0.32	8	9	5	15	11	5
o-Dianisidine	0.07	0.23	10	8	4	13	10	8
o-Anisidine	0.06	0.21	4	8	3	5	8	4
o-Toluidine	0.10	0.35	6	7	2	26	7	6
2-Methoxy-5-Methylaniline	0.06	0.21	9	9	3	17	18	10
2,6-Diaminotoluene	0.07	0.23	13	10	2	21	17	9
4,4'-Diaminodiphenyl Sulfide	0.09	0.31	8	7	14	12	7	10
2-Naphthylamine	0.08	0.25	6	8	3	9	15	3
2,6-Dimethylaniline	0.07	0.23	7	8	3	14	12	5
4-Chloroaniline	0.06	0.21	6	7	3	15	13	7
4-Aminobiphenyl	0.07	0.23	8	8	2	13	10	4
4-Chloro-2-Methylaniline	0.07	0.25	15	8	3	15	14	6
3-Chloro-4-Fluoroaniline	0.07	0.23	9	8	4	16	14	7
4-Aminoazobenzene	0.08	0.27	7	9	2	16	15	5
3,3'-Dichlorobenzidine	0.07	0.23	10	10	4	9	14	7
4,4'-Methylene-bis-(2-Chloroaniline)	0.07	0.22	7	13	4	17	11	5
All Compounds	-	-	4-15	7-13	2-14	5-26	7-18	3-12

^a Average of 10 determinations

Recovery experiments (trueness) were carried out, in triplicate, at three concentration levels (5, 20, and 40 µg/kg). The analyte percent recoveries were between 88 to 115 %, with RSD ≤13%. For the concentration 5 µg/kg, the mean recovery maximum acceptable values were 40 to 120% and for 20 and 40 µg/kg, they were 60 to 110%.¹⁶ Table 6 presents these results.

This method was applied to determine the PAAs in cooking utensils samples collected from different areas in Campinas city, Brazil. Table 7 shows the results.

Comparing the results obtained for the cooking utensil samples (Table 7), it is possible to observe that the polyamide samples have more PAAs and in larger amounts compared to the silicone or the polypropylene samples. Just aniline and 4,4'-diaminodiphenylmethane were found in the samples of silicone. The aniline concentration in samples 1 and 8 were lower than that established by the EU plastic FCM Regulation (EU) No 10/2011⁴ (10 µg/kg), but the concentration of 4,4'-diaminodiphenylmethane in sample 8 was three times above the limit.

From three cooking utensil samples made of polyamide, two were out of compliance. Two PAAs, benzidine and o-toluidine, classified as group 1 by the IARC, were found in sample 10. In the same sample, 4,4'-diaminodiphenylmethane was found in a concentration almost 2,000 times above the set values for the first migration. In addition to 4,4'-diaminodiphenylmethane, the aniline was another PAA that presented a high concentration value in the first, second, and third migration tests. The 4,4'-oxydianiline, 2,4-diaminotoluene, 3,3'-dimethylbenzidine, and

4-chloroaniline were also found in sample 10. For sample 11, only 4,4'-diaminodiphenylmethane was above the limit established by EU legislation No. 10/2011. The high RSD values observed for the samples are due to the lack of traceability, batch identification, and homogeneity of the specimens of the same sample.

The information obtained in this work is compatible with a finding presented in current literature: aniline and 4,4'-diaminodiphenylmethane are the most commonly found PAAs in cooking utensils.¹⁹

Table 6. Recovery of the PAAs by LC/MS/MS.

Compound	Trueness (%)		
	5 µg/kg ^a	20 µg/kg ^a	40 µg/kg ^a
4,4'-Diaminodiphenylmethane	110 (10)	93 (9)	102 (6)
4,4'-Oxydianiline	96 (7)	103 (7)	99 (4)
2,4-Diaminotoluene	96 (4)	96 (10)	103 (10)
Benzidine	91(6)	100 (7)	102 (9)
4,4'-Methylene-bis-(2-Methylaniline)	97 (11)	109 (8)	108 (5)
Aniline	98 (8)	105 (12)	98 (3)
3,3'-Dimethylbenzidine	103 (10)	107 (13)	100 (9)
o-Dianisidine	100 (4)	115 (9)	104 (9)
o-Anisidine	97 (6)	100 (7)	105 (8)
o-Toluidine	90 (12)	111 (10)	109 (4)
2-Methoxy-5-Methylaniline	103 (11)	106 (13)	99 (11)
2,6-Diaminotoluene	105 (8)	97 (6)	100 (9)
4,4'-Diaminodiphenyl Sulfide	97 (12)	107 (8)	101 (7)
2-Naphthylamine	97 (10)	105 (9)	99 (7)
2,6-Dimethylaniline	96 (11)	105 (7)	97 (8)
4-Chloroaniline	101 (5)	102 (7)	99 (5)
4-Aminobiphenyl	88 (4)	103 (9)	106 (5)
4-Chloro-2-Methylaniline	96 (9)	107 (8)	102 (8)
3-Chloro-4-Fluoroaniline	98 (9)	99 (8)	93 (8)
4-Aminoazobenzene	106 (7)	95 (9)	97 (9)
3,3'-Dichlorobenzidine	107 (13)	101 (11)	98 (4)
4,4'-Methylene-bis-(2-Chloroaniline)	92 (8)	97 (10)	104 (4)
All Compounds	88-110 (4-13)	93-115 (6-13)	93-109 (3-10)

^a Average of 10 determinations. The values between () are RSD%.

Table 7. Concentration of PAAs in the cooking utensils by LC/MS/MS in µg/kg.

PAAs	Migration	Silicone Sample Number									Polyamide Sample Number			Polypropylene Sample Number
		1 ^a	2 ^a	3 ^a	4 ^b	5 ^b	6 ^b	7 ^a	8 ^a	9 ^a	10 ^a	11 ^a	12 ^a	13 ^c
4,4'-Diaminodiphenylmethane	1st	-	<LOQ	-	<LOQ	<LOQ	-	<LOQ	30.3 (62.1)	-	19353 (17150)	1019 (505)	<LOQ	<LOQ
	2nd	-	-	-	-	-	-	-	-	-	12855 (12219)	285 (203)	<LOQ	-
	3nd	-	-	-	-	-	-	-	-	-	10386 (9794)	176 (99)	<LOQ	<LOQ
Aniline	1st	2.9 (0.2)	-	-	-	-	-	-	1.6 (1.6)	<LOQ	615 (194)	3.0 (2.3)	-	-
	2nd	<LOQ	<LOQ	<LOQ	-	<LOQ	-	<LOQ	<LOQ	<LOQ	343 (130)	1.1 (1.0)	-	<LOQ
	3nd	<LOQ	<LOQ	-	-	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	268 (70)	1.0 (0.4)	-	<LOQ
4,4'-Oxydianiline	1st	-	-	-	-	-	-	<LOQ	<LOQ	<LOQ	14 (13)	1.4 (1.2)	-	-
	2nd	-	-	-	-	-	-	-	-	-	9 (8)	<LOQ	-	-
	3nd	-	-	-	-	-	-	-	-	-	8 (8)	<LOQ	-	<LOQ
2,4-Diaminotoluene	1st	<LOQ	-	-	-	<LOQ	-	-	-	-	31 (39)	<LOQ	-	<LOQ
	2nd	<LOQ	<LOQ	<LOQ	<LOQ	-	<LOQ	<LOQ	<LOQ	<LOQ	30 (43)	<LOQ	-	-
	3nd	<LOQ	<LOQ	<LOQ	<LOQ	-	<LOQ	-	-	<LOQ	31 (39)	<LOQ	<LOQ	-
Benzidine	1st	-	-	-	-	-	-	-	-	-	1.3 (1)	-	-	-
	2nd	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-
	3nd	-	-	-	-	-	-	-	-	-	-	-	-	-
3,3'-Dimethylbenzidine	1st	-	-	-	-	-	-	-	-	-	30 (37)	-	-	-
	2nd	-	-	-	-	-	-	-	-	-	19 (22)	-	-	-
	3nd	-	-	-	-	-	-	-	-	-	16 (20)	-	-	-
o-Toluidine	1st	-	-	-	-	-	-	-	<LOQ	-	20 (17)	-	-	<LOQ
	2nd	-	-	-	-	-	-	-	-	-	14 (14)	-	-	-
	3nd	-	-	-	-	-	-	-	-	-	14 (13)	-	-	-
2,6-Diaminotoluene	1st	-	-	-	-	-	-	-	-	-	1.7 (1.4)	<LOQ	-	-
	2nd	-	-	-	-	-	-	-	-	-	1.4 (1.2)	<LOQ	-	-
	3nd	-	<LOQ	-	-	-	-	-	-	-	1.3 (1.1)	<LOQ	-	-
4-Chloroaniline	1st	-	-	-	-	-	-	-	-	-	2.8 (0.6)	<LOQ	-	-
	2nd	-	-	-	-	-	-	-	-	-	2.0 (0.2)	<LOQ	-	-
	3nd	-	-	-	-	-	-	-	-	-	1.7 (0.2)	<LOQ	-	-

^a Mean of five replicate specimens

^b Mean of four replicate specimens

^c One specimen

- Not detected

Values between () are standard deviation.

Conclusion

The developed LC/MS/MS method is useful for the determination of PAAs in cooking utensils. The proposed method presented a linear response, and was validated in terms of precision (repeatability), intermediate precision, and trueness (recovery). In addition, the separation method is simple and fast, lasting only 9 minutes per sample. The study showed that the specific migration of PAAs from cooking utensils is not uncommon, with 23% of the analyzed samples being out of compliance. Aniline and 4,4'-diaminodiphenylmethane are also the most commonly abundant PAAs in these samples, representing a risk to public health.

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