



Analysis of primary aromatic amines (PAA) in black nylon kitchenware 2014 Selected samples from the Norwegian Market

Trier, Xenia; Granby, Kit

Publication date:
2015

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
Trier, X., & Granby, K. (2015). *Analysis of primary aromatic amines (PAA) in black nylon kitchenware 2014: Selected samples from the Norwegian Market*. National Food Institute, Technical University of Denmark.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Analysis of primary aromatic amines (PAA) in black nylon kitchenware 2014

Selected samples from the Norwegian Market



**Analysis of primary aromatic amines
(PAA) in black nylon kitchenware
2014
Selected samples from the Norwegian Market**

Xenia Trier and Kit Granby

March 2015

**Analysis of primary aromatic amines (PAA) in black nylon kitchenware 2014
Selected samples from the Norwegian market**

Report 2015

By Xenia Trier and Kit Granby

Copyright: Reproduction of this publication in whole or in part must include the customary bibliographic citation, including author attribution, report title, etc.

Cover photo: Black nylon kitchenware

Published by: National Food Institute, Mørkhøj Bygade 19, Technical University of Denmark

Request report

from: www.food.dtu.dk

ISBN: 978-87-93109-48-3 (electronic version)

Preface

This investigation was planned in cooperation with Julie Tesdal Håland, Norwegian Food Safety Authority (Mattilsynet), Chemical Safety and EEA Section.

Signe Sem and Sidsel Sæbøe were responsible for the sampling and follow up on results in the Region Øst.

The laboratory work and chemical analyses were performed by laboratory technicians Anni Helleskov, Vibeke Balswell and Annie Foverskov in cooperation with scientist, PhD Xenia Trier.

The DTU DOC-number was 14/10708 NA and Mattilsynets ePhortenummer: 2014/197728

Søborg, Denmark, March 18th 2015

Kit Granby
Senior scientist, Ph.d.

Content

Summary	6
1. Background	7
2. Regulation of primary aromatic amines (PAA) in polyamide kitchenware	7
3. Procedure for taking out samples for compliance testing of primary aromatic amines (PAA)	8
4. Results and discussion	10
5. Assessment and Conclusion.....	13
References	14
Appendix A Samples of black plastic kitchen utensils	15
Appendix B Name, CAS No., structure and molecular weight of the primary aromatic amines (PAA) studied.....	16
Appendix C. Analytical detection conditions	18
Appendix D. Samples containing PAA.....	19

Summary

Primary aromatic amines (PAA) are chemical compounds, of which some are carcinogenic and allergenic, while others of these compounds are suspected carcinogens. PAA may arise in materials intended for food contact as a result of the occurrence of impurities or degradation products of e.g. aromatic isocyanates used in lacquers and adhesives in azocolourants.

According to the regulation on plastics EC 10/2011:

'Plastic materials and articles shall not release primary aromatic amines, excluding those appearing in Table 1 of Annex I, in a detectable quantity into food or food simulant. The detection limit is 0,01 mg of substance per kg of food or food simulant. The detection limit applies to the sum of primary aromatic amines released'

Since July 1st 2011, an additional EU regulation has come into place, which states that each consignment of polyamide (nylon) kitchen utensils from China and Hong Kong shall be accompanied by appropriate documentation, including analytical results showing that it meets the requirements concerning the release of primary aromatic amines.

25 samples of black nylon kitchenware each of three articles were tested for migration of primary aromatic amines (PAA), using 3% acetic acid as food simulant at an exposure temperature of 100°C and time from ½-4 hours, depending on the foreseeable use of the utensil. The samples were collected by the Norwegian Food Safety Authority at importers and retail shops.

Of the 20 PAAs analysed. four PAAs were detected, being aniline (ANL) in 11 samples (0.6-2.3 µg/kg), 4,4'-Methylenedianiline (4,4'-MDA) in 11 samples (0.6-14µg/kg), 2,4-Toluenediamine (2,4-TDA) in one sample (2.3 µg/kg) and 2,4-Dimethylaniline (2,4-DMA) in one sample (0.45 µg/kg).

11 samples did not contain PAAs, 14 samples contained PAAs, where the sum (Σ PAA), however did not exceed the specific migration limit of 10 µg/kg food simulant after the expanded uncertainty is subtracted from the sum of PAA. The highest content of Σ PAA migrants was from a frying spatula originating from China containing Σ PAA of 16.0 µg/kg before correction for expanded uncertainty, however after correction the content of 9.7 µg/kg was compliant.

1. Background

Primary aromatic amines (PAA) are chemical compounds, of which some are carcinogenic and allergenic, while others of these compounds are suspected carcinogens. PAA may arise in materials intended for food contact as a result of the occurrence of impurities or degradation products of e.g. aromatic isocyanates used in lacquers and adhesives and in azo-colourants (Mortensen et al. 2005, Trier et al. 2010). Several notifications and alerts have been received by the Rapid Alert System for Food and Feed concerning food contact materials imported into the Union from China and Hong Kong, releasing into food or food simulant amounts of PAA that are not in compliance with the Union legislation. Hence, since July 1st 2011 The European Commission has implemented a regulation specifically on the import of polyamide kitchenware from China and Hong Kong.

In the present enforcement campaign 25 samples of polyamide (nylon) kitchenware from China and Europe were sampled in Norway in 2014, and were analysed for 20 PAA compounds by DTU, the National Food Institute according to the plastic regulation EC 10/2011. The structures and CAS numbers of the 20 PAAs are given in Appendix B.

1.1 Project period: 01-09-2014 - 01-04-2015

2. Regulation of primary aromatic amines (PAA) in polyamide kitchenware

2.1 Regulation:

The regulation on plastics EC 10/2011 states that:

'Plastic materials and articles shall not release primary aromatic amines, excluding those appearing in Table 1 of Annex I, in a detectable quantity into food or food simulant. The detection limit is 0,01 mg of substance per kg of food or food simulant. The detection limit applies to the sum of primary aromatic amines released'

This regulation also provides guidance for choice of migration testing such as temperatures, times, food simulants, conversion of units and reporting of results, which have been used in the campaign.

In addition, since July 1st 2011, import of polyamide (nylon) kitchen utensils from China and Hong Kong are regulated by:

COMMISSION REGULATION (EU) No 284/2011 of 22 March 2011 laying down specific conditions and detailed procedures for the import of polyamide and melamine plastic kitchenware originating in or consigned from the People's Republic of China and Hong Kong Special Administrative Region, China

The regulation states that each consignment shall be accompanied by appropriate documentation, including analytical results showing that it meets the requirements concerning

the release of primary aromatic amines. In addition, 10% of the consignments shall undergo identity and physical checks in such a way that it is not possible for the importers or their representatives to predict whether any particular consignment will be subjected to such checks. These samples are analysed for migration of PAA. According to the legislation EU 284/2011 plastic materials and articles shall not release primary aromatic amines in a detectable quantity into food or food simulant. The detection limit is 0,01 mg of substance per kg of food or food simulant. The detection limit applies to the sum of primary aromatic amines released. It means that an analytical result minus the analytical uncertainty must be above 0.01 mg/kg before the sample can be deemed non-compliant (Hoekstra et al. 2011).

3. Procedure for taking out samples for compliance testing of primary aromatic amines (PAA)

Overview: During the Norwegian Food Safety Authority's inspection of the importers and retail shops, samples were taken for analytical control of compliance with legislation. The food inspectors sent the samples of polyamide kitchenware by mail to the Norwegian Food Safety Authority, which forwarded the samples and their accompanying documentation to DTU, the National Food Institute for analysis.

At the Technical University of Denmark (DTU):

- 1) The samples were identified and photographed
- 2) The food contact surface areas were measured
- 3) Determination of migration after one migration test from the FCM to the acidic simulant (3% acetic acid) during realistic exposure conditions EC 10/2011 was performed
PAA contents were measured using an accredited method (FA 099.1) and results in ng mL^{-1} in the simulant converted into results of migration from the article (mg kg^{-1} food simulant)
- 4) Certificates with result and assessment of result were sent to the Norwegian Food Safety Authority.

3.1 Sample material

In principle the samples are as taken at the importers of nylon kitchen utensils. However since few importers are registered by the Norwegian Food Safety Authority, samples may also be taken in the retail shops. This is to secure that the samples collected are representative for the samples on the Market. In case the products were sampled at retail shops the food inspector collected information details regarding the supplier company.

The sampling followed the procedure by the Norwegian Food Safety Authority (<http://kvalitet/Procedures/Prøvetaking%20i%20Mattilsynet.pdf>). In particular the inspectors had to inform the company about their rights to have a verification sample (extra sample for the company, so they can verify in case of a positive result).

One sample consisted of 3 articles (individual items) from one batch. The verification sample consisted of 3 articles (individual items) from the same batch as the sample.

3.2 Sampling period: 08-09-2014 - 24-10-2014

The samples were sent to DTU, where they were received December 1st 2014.

3.3 Chemicals, laboratory equipment and procedures used

A summary is presented here but details on materials and methods are available in in Mortensen *et al.* 2005. In addition Appendix B lists the chemical names, abbreviations, structures and molecular weights and Appendix C lists some of the analytical detection conditions.

The accredited method FA099.1 was used to determine the specific PAA in aqueous food simulants resulting from migration tests conducted in accordance with the current version of the CEN standard, which was developed by DTU. The PAAs ionpair with pentafluoropropionic acid (PFPA), are separated by liquid chromatography (UHPLC) on a reverse-phase C₁₈ column and analyzed by electrospray ionisation (ESI⁺) on a triple quadrupole mass spectrometer (LC-MS/MS).

HPLC separation was performed on an Acquity U-HPLC from Waters (Milford, MA, USA) equipped with a high-pressure gradient pump and a column heater. The amines were separated on a Acquity HSS-C18 column (2.1 mm × 50 mm, 1.8 μm) (Agilent Palo Alto, CA, USA) at 40 °C. The eluent was a gradient of 4.7 mM Perfluoro propionic acid in methanol and water respectively. A Quattro Ultima triple quadrupole instrument with Masslynx v. 4.1 software (Micromass) was used for data acquisition and processing. Ionisation of the analytes was achieved using an electrospray interface in the positive ion mode (ESI⁺), and ionisation source parameters were as follows: capillary voltage 1.0 kV; cone voltage 20 V; Hex 1 voltage 20 V; desolvation temperature, 400 °C; source temperature, 130 °C. Nitrogen was used as nebulizing gas (maximum flow), desolvation gas (flow-rate of 780 L/hr), and cone gas (flow-rate of 40 L/hr). Argon was used as collision gas at a pressure of 2.3×10^{-3} mbar. Calibration curves were constructed with standards containing all 20 PAA in 3% acetic acid at concentrations of 0, 2, 4, 7, 15, 25, and 50 μg/L, and the response of each calibration standard was determined at least twice. Linear regression of calibration data was calculated using a weighted least squares method (weight 1/x).

3.4 Test conditions

For each sample, three articles (utensils) were tested (triplicate testing). From each utensil one or two pieces of the food contact area of utensil was cut in the same way for all three articles, and the area was measured for one of the sub samples. Depending on the shape the area was determined by geometric calculation, or weighing of a paper or aluminium foil area, following the EURL guideline for determination of areas. In case PAAs were present the area was measured for all three sub samples-

Time and temperature conditions were chosen in accordance with the relevant legislation (Regulation (EU) No 10/2011), on the basis of the specific function of the kitchenware article(s).

The test was conducted with simulant B 3% (w/v) acetic acid, as it has been demonstrated that this simulant represents the worst case for the migration of PAAs from polyamide kitchenware. All samples were tested at the boiling point of the simulant (tolerance is +/- 3°C at 100°C), in a Büchi under reflux.

Articles that could be used or foreseeably used during cooking, (e.g. ladles, spatulas) were tested for 2 hours (- 0, + 5 minutes) However, samples which were foreseen to be in shorter contact times (5 min < t < 30 min) were exposed for ½ hr, and spoons which could be left cooking food for up to 1 hr and intended for use > 175 °C were tested for 4 hours (4 times 1 hr to compensate for the lower temperature), as shown in Table 1.

For repeated use articles, such as polyamide kitchenware three successive migration tests should be performed on triplicate samples. As of 01/01/2013 the rules under Regulation (EU) No 10/2011 will apply. These provisions include that: - **For primary aromatic amine migration from polyamide kitchenware only one migration test will be carried out (for non-detectable substances, its compliance will be checked on the basis of the level of the migration found in the first test).** The Norwegian Food Safety Authority decided to follow this rule.

3.5 Quality assurance

The Danish accreditation body (DANAK) supervises the methods applied in DTU the National Food Institute, Division of Food Chemistry, including those applied for the determination of primary aromatic amines in food simulants. Routines are established for daily quality control of the methods taking into consideration a suitable composition of the analytical assays with respect to the number of samples that are analysed in multiplicity, laboratory/solvent blanks and known samples for the control chart. The identity of PAAs are verified by use of a verification ion and ion ratios that match those of standards, according to SANCO /12571/2013.

In addition a quality control sample (FAPAS) was run, and gave the correct result for both aniline and 4,4'-MDA.

4. Results and discussion

The food inspector was asked to take samples of nylon kitchen utensils. In total 25 samples of kitchenware were samples of which 15 originated from China, 4 from Lithuania, 4 from Sweden and 2 from Germany. All were repeated use articles. Sample information appears from Appendix A.

The results of the migration of the specific PAAs and the sum of PAAs (Σ PAAs) appear from Table 1. Results are given above the detection limit (LOD), since the restriction does not relate to substances which are supposed to be 'non-detectable'.

The measured concentrations in the food simulants in µg/L, were converted to units of µg/kg by 1) calculation of the total mass of PAA migrated into the food simulant 2) conversion into

migration per area of exposed utensil and 3) final conversion into µg/kg food using the conventional surface area-to-volume factor of 6 dm²/kg:

Result (µg/kg) =

$$[\text{Conc. (}\mu\text{g/L)} * \text{food simulant in contact with sample (L)} / \text{surface area of sample in contact (dm}^2\text{)}] * 6 \text{ dm}^2/\text{kg}$$

The results were calculated for each utensil by addition of the mean of the triplicates, for each specific PAA. : The uncertainty was calculated as the expanded uncertainty (S) on the triplicates for each PAA, and summed.

$$\Sigma\text{PAAs} = \Sigma (\text{mean PAA}_1) + (\text{mean PAA}_2) + \dots + (\text{mean PAA}_n)$$

$$\text{Uncertainty} = (\text{S}_{\text{PAA1}}^2 + \text{S}_{\text{PAA2}}^2 + \dots + \text{S}_{\text{PAA}_n}^2)^{1/2}$$

A result was compliant if :

$$\Sigma\text{PAAs} - \text{Uncertainty} < 10 \mu\text{g/kg food or food simulant}$$

The results show that no samples were non-compliant, though several samples contained PAAs but at varying concentrations within the three articles. This sample in-homogeneity is common for black nylon kitchen utensils which are made from nylon pellets and sometimes from recycled nylon (Trier et al 2010). It is possible that the PAA levels at this low level can be due to carry-over in the manufacturing machines.

The level of non-compliance (none) is lower than what has been found in the import control from China and Hong Kong sampled in Denmark in recent years, but in the present Norwegian survey samples also originated from other countries than China and Hong Kong.

The PAA detection frequency of 56% (14 of 25 samples) is somewhat higher than usual. It could be explained by that we in this study tested the PAA levels in the first migrate, whereas it until recently was typical to test the PAA levels in the third migrate. However, since migration decreases with repeated exposure it can be expected that at least half, and possibly 10 of the 14 samples would fall below the detection limit in a third migration test (Trier et al. 2010).

Table 1. Results of migration of PAAs and ΣPAAs into 3% acetic acid as food simulant (µg/kg food simulant) of migration of PAAs and ΣPAAs into 3% acetic acid as food simulant (µg/kg food simulant)

Sample identity (DTU)	Sample identity (N)	Article name	Exposure time (h) at 100°C	Aniline (ANL)				4,4'-Methylenedianiline				2,4-Toluediamine (2,4-TDA)				2,4-Dimethylaniline(DMA)				ΣPAA µg/kg food	Expanded uncertainty of PAA µg/kg food
				Item No.				Item No.				Item No.				Item No.					
				1	2	3	mean	1	2	3	mean	1	2	3	mean	1	2	3	mean		
K14-1007	31014053689	Spagettislev	½ h																<LOD		
K14-1008	31014053690	Suppeøse	4t																<LOD		
K14-1009	31014053693	Stekespade	2 h																<LOD		
K14-1010	71014054415	Suppeøse	4h	0.62	0.84	0.73	0.73												0.7	0.5	
K14-1011	81014055271	Palettkniv	2 h	0.77	0.78	0.88	0.81	1.9	<LOD	<LOD	0.63								1.4	0.6	
K14-1012	81014055272	Øse	4h																<LOD		
K14-1013	81014055273	Stekespade	2 h																<LOD		
K14-1014	61014054325	Stekespade	2 h					1.3	1.6	<LOD	0.94								0.9	0.8	
K14-1015	61014054326	Potetstapper	½ h	1.7	<LOD	<LOD	0.56	8.5	5.7	13	9.1								9.6	3.8	
K14-1016	81014055301	Plastskje	4h	0.95	0.93	<LOD	0.63	3.8	5.8	5.5	5.0	2.5	2.2	2.2	2.3				8.0	5.0	
K14-1017	81014055302	Stekepinsett	2 h	0.90	1.6	1.1	1.2	2.4	2.3	2.0	2.2								3.4	1.2	
K14-1018	31014053682	Suppeøse	4h	2.5	1.9	2.4	2.3								0.84	<LOD	<LOD	0.45	2.7	1.5	
K14-1019	31014053683	Stekespade	2 h	0.96	2.3	1.9	1.7	7.3	10	25	14								16.0	9.7	
K14-1020	31014053684	Pastaøse	2 h	1.8	1.8	1.7	1.8	2.1	2.4	2.4	2.3								4.0	1.4	
K14-1021	31014053685	Whisk	2 h					6.3	5.2	7.0	6.2								6.2	2.4	
K14-1022	31014053686	Spatula	2 h					1.9	<LOD	<LOD	0.64								0.6	1.1	
K14-1023	81014055163	Opøser	4h	0.55	0.49	3.9	1.7	0.99	0.52	0.60	0.70								2.4	2.0	
K14-1024	81014055164	Stekespade	2 h																<LOD		
K14-1025	81014055274	Suppeøse	4h																<LOD		
K14-1026	81014055276	Stekespade	2 h	0.67	0.58	0.57	0.61												0.6	0.4	
K14-1027	81014055260	Suppeøse	4h																<LOD		
K14-1028	81014055262	Suppeøse	4h																<LOD		
K14-1029	Varenr 34-8030-2	Øse	4h	0.96	1.0	<LOD	0.68	23	1.7	2.1	9.1								9.8	12.4	
K14-1030	101014055682	Øse	4h																<LOD		
K14-1031	988824844	stekespade	2 h																<LOD		

LOD: Limit of detection, h: hour

5. Assessment and Conclusion

Of the 25 samples of black nylon kitchenware 11 samples did not show migration of primary aromatic amines (PAA) to the 3 % acetic acid simulant; 14 samples (56%) showed migration to the food simulant at concentrations below the limits of migration of PAA from plastic materials and articles intended to come into contact with food of 10 µg/kg after subtraction of the expanded uncertainty of the measurements. The sample with the highest content of ΣPAA of 16.0 µg/kg, was a frying spatula (Menuett stekespade) from China, which was compliant after subtraction of the expanded uncertainty resulting in a concentration of ΣPAA of 9.7 µg/kg, just below the specific migration limit of 10 µg/kg food simulant.

The PAA found in the black nylon kitchenware were aniline (ANL) in 11 samples (0.5-2.3 µg/kg), 4,4'-Methylenedianilin (4,4'-MDA) in 11 samples (0.6-14 µg/kg), 2,4-Toluenediamine (2,4-TDA) in one sample (2.3 µg/kg) and 2,4-Dimethylaniline (2,4-DMA) in one sample (0.45 µg/kg).

The level of non-compliance (none) is lower than what has been found in the import control from China and Hong Kong from Denmark in recent years, but samples also originated from other countries than China and Hong Kong. The PAA detection frequency of 56% (14 of 25 samples) measured in the first migrate, is expected to decrease to at least half in third migrate (Trier et al. 2010), which compares well with other studies of black nylon kitchen utensils.

References

CEN, may 2004, EN 13130-1:2004: "Materials and articles in contact with foodstuffs – Plastics substances subject to limitation – Part 1: Guide to test methods for the specific migration of substances from plastics to foods and food simulants and the determination of substances in plastics and the selection of conditions of exposure to food simulants", European Committee for Standardization, Rue de Stassart 36, B-1050 Brussels

DTU Fødevarerinstitutionen 2005. Akkrediteret Analysemetode FA099.1; Bestemmelse af primære aromatiske aminer (PAA) i vandige fødevarer simulatorer ved LC-MS/MS.

European Commission 2011. Commission regulation (EU) No. 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food

European Commission 2011. Commission regulation (EU) No. 284/2011 of 22 March 2011 laying down specific conditions and detailed procedures for the import of polyamide and melamine plastic kitchenware originating in or consigned from the People's Republic of China and Hong Kong Special Administrative Region, China

Hoekstra E.J., Petersen J.H., Bustos J. (2011) Guidance document on fat reduction factor, functional barrier concept, phthalates and primary aromatic amines. Publication Office of the European Union, Luxembourg, JRC Scientific and Technical Report, EUR 25112 EN

Mortensen, SK; Trier, XT; Foverskov, A, Petersen JH. 2005. Specific determination of 20 primary aromatic amines in aqueous food simulants by liquid chromatography-electrospray ionization-tandem mass spectrometry , J. Chrom. A, 1091, 40-50

Simoneau C., Hoekstra E., Bradley E., Bustos J., Golja V., Kappenstein O., Kalsbeek D., Keegan J., Milana M.R., Cwiek-Ludwicka K., Petersen J.H., Polz M., Sauvegrain P., Vanhee F. 2011. Technical guidelines on testing the migration of primary aromatic amines from polyamide kitchenware and of formaldehyde from melamine kitchenware - in support of Commission Regulation 284/2011 laying down specific conditions and detailed procedures for the import of polyamide and melamine plastic kitchenware originating in or consigned from People's Republic of China and Hong Kong Special Administrative Region, China. 1st edition 2011. Office for Official Publications of the European Union, JRC Scientific and Technical Report, EUR 24815 EN

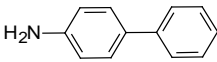

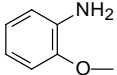
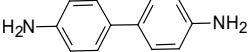
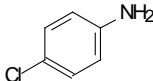
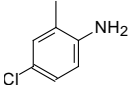
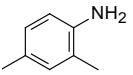
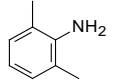
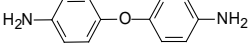
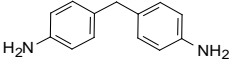
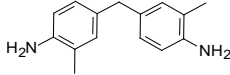
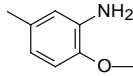
SANCO/12571/2013, 19 November 2013 Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed

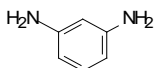
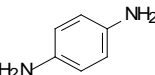
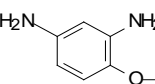
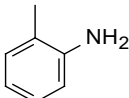
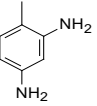
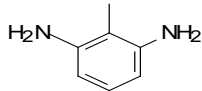
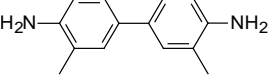
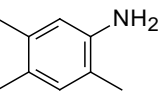
Trier, X.; Okholm, B.; Foverskov, A.; Binderup ML; Petersen JH. 2010 Primary aromatic amines (PAAs) in black nylon and other food-contact materials, 2004-2009 Food. Additives Contaminants A , 27, 1325-1335

Appendix A Samples of black plastic kitchen utensils

Sampling date	Country of origin	Trade name	Sample identity	Limit exposure conditions
30.09.2014	Sweden	Spagettislev (spaghetti ladle) art.85-5116 PA66	31014053689/ K14-1007	260°C
30.09.2014	Sweden	Suppeøse (soup ladle) art.85-5114 PA66	31014053690/ K14-1008	260°C
30.09.2014	Sweden	Liten stekespade (frying ladle) 85-5111PA66	31014053693/ K14-1009	
06.10.2014	Germany	Inox suppeløse(soup spoon) EAN4006501240576	71014054415/ K14-1010	160°C
07.10.2014	China	Palettkniv(spatula) nylon 34-8030-7	81014055271/ K14-1011	220°C
07.10.2014	Sweden	Øse (spoon) fra kokkensæt PA 34-1737	81014055272/ K14-1012	200°C
07.10.2014	China	Stekespade(frying ladle) fra kokkensæt PA 34-1737	81014055273/ K14-1013	200°C
06.10.2014	China	Cuisine stekespade(frying ladle) art.69306 EAN 70228101693060	61014054325/ K14-1014	210°C
06.10.2014	China	Cuisine potetstapper(potato art.69307 EAN 70228101693077	61014054326/ K14-1015	210°C
30.09.2014	Lithuania	Fiskars plastskje (plast ladle) EAN 5702268581516	81014055301/ K14-1016	
30.09.2014	Germany	Fiskars stekepinsett EAN 5702268581431	81014055302/ K14-1017	max 180°C 30min
30.09.2014		Menuett suppeøse(soup spoon)	31014053682/ K14-1018	
30.09.2014	China	Menuett stekespade(frying spatula)	31014053683/ K14-1019	210°C
30.09.2014	China	Menuett pastaøse(pasta spoon)	31014053684/ K14-1020	210°C
30.09.2014	Lithuania	Fiskars Easy care Whisk	31014053685/ K14-1021	
30.09.2014	Lithuania	Fiskars Spatula	31014053686/ K14-1022	
08.10.2014	China	Weber spoon, nylon, EAN 7792403026	81014055163/ K14-1023	
08.10.2014	China	Coop cocware stekespade (frying spatula) nylon, EAN 5700382487585	81014055164/ K14-1024	220°C
07.10.2014	China	Invite suppeøse(soup spoon) EAN 5722002454975	81014055274/ K14-1025	204°C
07.10.2014	China	Invite stekespade (frying ladle) EAN 5722001016983	81014055276/ K14-1026	
07.10.2014	Lithuania	Fiskars dryppfri suppeøse(soup spoon); PA; EAN 5702268581530	81014055260/ K14-1027	
07.10.2014	China	Unike suppeøse(soup spoon); EAN 7033250466008	81014055262/ K14-1028	204°C
	China	Ladle EAN 7393173209954	Varenr. 34-8030/ K14-1029	220°C
08.10.2014	China	Øse (spoon)PA; EAN 7070514412258	101014055682/ K14-1030	
08.10.2014	China	Stekespade (spatula)	988824844/ K14-1031	

Appendix B Name, CAS No., structure and molecular weight of the primary aromatic amines (PAA) studied

Name(abbreviation)	CAS No.	Structure	MW (Dalton)
4-Aminobiphenyl (4-ABP)	92-67-1		169,2
Aniline (ANL)	62-53-3		93,1
o-Anisidine (o-ASD)	90-04-0		123,2
Benzidine (BNZ)	92-87-5		184,2
4-Chloro-Aniline (4-CA)	106-47-8		127,6
4-Chloro-o-Toluidine (4-CoT)	95-69-2		141,6
2,4-Dimethylaniline (2,4-DMA)	95-68-1		121,2
2,6-Dimethylaniline (2,6-DMA)	87-62-7		121,2
4,4'-Diaminodiphenylether (4,4'-DPE)	101-80-4		200,2
4,4'-Methylenedianiline (4,4'-MDA)	101-77-9		198,3
4,4'-Methylenedi-o-toluidine (4,4'-MDoT)	838-88-0		226,3
2-Methoxy-5-Methylaniline (2-M-5-MA)	120-71-8		137,2

m-Phenylenediamine (m-PDA)	108-45-2		108,1
p-Phenylenediamine (p-PDA)	106-50-3		108,1
4-Methoxy-m-phenylenediamine (4-M-mPDA)	615-05-4		138,2
o-Toluidine (o-T)	95-53-4		107,2
2,4-Toluenediamine (2,4-TDA)	95-80-7		122,1
2,6-Toluenediamine (2,6-TDA)	823-40-5		122,1
3,3'-Dimethylbenzidine (3,3'-DMB)	119-93-7		212,3
2,4,5-Trimethylaniline (2,4,5-TMA)	137-17-7		135,2

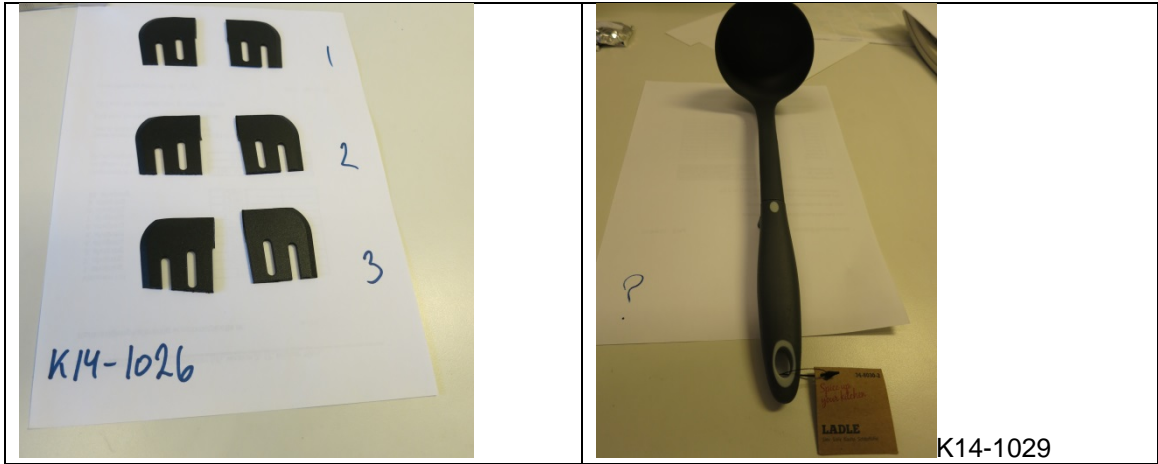
Appendix C. Analytical detection conditions

Substance	Mol. Weight	MRM	Collision Energy (eV)	Verifications mass	Collision Energy, verification	Retention time (min)
p-PDA	108,07	109,08 > 92,05	22	65,04	22	1,00
m-PDA	108,07	109,08 > 92,05	22	65,04	22	1,15
2.6-TDA	122,08	123,09 > 108,07	18	106,05	18	1,25
4-M-mPDA	138,08	139,09 > 124,06	14	107,07	14	1,66
2.4-TDA	122,08	123,09 > 108,07	18	106,05	18	1,73
BNZ	184,10	184,10 > 156,09	30	166,07	30	1,91
ANL	93,06	94,07 > 77,04	18	51,02	30	1,92
o-ASD	123,07	124,08 > 109,05	14	92,05	14	2,43
4.4'-DPE	200,09	201,10 > 108,04	18	184,10	18	2,63
o-T	107,07	108,08 > 91,05	18	93,06	18	2,71
4.4'-MDA	198,12	199,12 > 106,07	22	77,04	55	2,92
3.3'-DMB	212,13	212,13 > 196,11	25	180,09	25	2,97
4-CA	127,02	128,03 > 93,06	18	111,00	18	3,32
2-M-5-MA	137,08	138,09 > 123,07	14	106,05	14	3,54
2.6-DMA	121,09	122,10 > 105,07	18	107,07	14	3,61
2.4-DMA	121,09	122,10 > 107,07	18	105,07	18	3,92
4.4'-MDoT	226,15	227,15 > 120,08	22			4,02
4-CoT	141,03	142,04 > 107,07	18	125,02	18	4,48
4-ABP	169,09	170,10 > 153,1	18	152,06	30	4,80
2.4.5-TMA	135,10	136,11 > 121,09	18	119,09	18	

Appendix D. Samples containing PAA







National Food Institute
Technical University of Denmark
Mørkhøj Bygade 19
DK - 2860 Søborg

Tel. 35 88 70 00
Fax 35 88 70 01

www.food.dtu.dk

ISBN: 978-87-93109-48-3