

表11. 革製品中で検出されたPAAの濃度 ($\mu\text{g/g}$)^a

	Aniline	o-Toluidine	4-Chloroaniline	p-Cresidine	1,4-Phenylenediamine	2-Naphthylamine	4-Aminobiphenyl	Benzidine	3,3'-Dimethylbenzidine	4,4'-Thiodianiline	3,3'-Dimethoxybenzidine	Munsell Color ^b
L-A1	587	— ^c	3.9	—	21	—	—	1.0	0.37	0.66	—	
L-A2	22	—	—	—	—	—	—	—	—	—	—	
L-A3	1.7	—	—	—	—	—	—	—	—	—	—	
L-A4	0.83	—	—	—	—	—	—	—	—	—	—	
L-A5	0.14	—	—	—	—	—	—	—	—	—	—	
L-A6	0.13	—	—	—	—	—	—	—	—	—	—	
L-B1	15	—	—	—	—	0.44	—	—	0.15	—	—	
L-B2	24	—	0.12	—	—	—	—	—	—	—	—	
L-B3	0.45	—	—	—	—	—	—	—	—	—	—	
L-B4	16	0.064	—	0.21	—	—	—	—	—	—	—	
L-C1	93	—	—	—	—	—	1.2	0.38	40	—	—	7.5R 3/10
L-C2	92	—	0.17	—	—	—	1.1	16	0.74	—	—	
L-C3	78	—	0.27	—	—	—	2.0	31	11	—	15	7.5PB 2/2
L-C4	27	430	0.11	—	—	—	—	—	1.7	—	—	10PB 2/8
L-C5	2.2	—	—	—	—	—	—	—	4.8	—	—	
L-C6	81	—	0.34	—	8.6	—	0.81	—	—	—	—	
L-C7	0.78	—	—	—	—	—	—	—	—	—	—	
L-C8	0.12	—	—	—	—	—	—	—	—	—	—	
L-C9	61	—	—	—	—	—	—	—	—	—	—	
L-C10	39	—	0.10	—	—	—	—	—	—	—	—	
L-C11	53	—	0.16	—	—	—	—	—	—	—	—	
L-C12	33	—	0.27	—	—	—	—	—	—	—	—	
L-C13	0.64	—	0.24	—	3.6	—	—	—	—	—	—	

^a 赤字はEU基準値(30 $\mu\text{g/g}$)を超えた検体 ^b Munsell color systemによる分類: 色相(Hue) 明度(Value)/彩度(Chroma) ^c —: 不検出

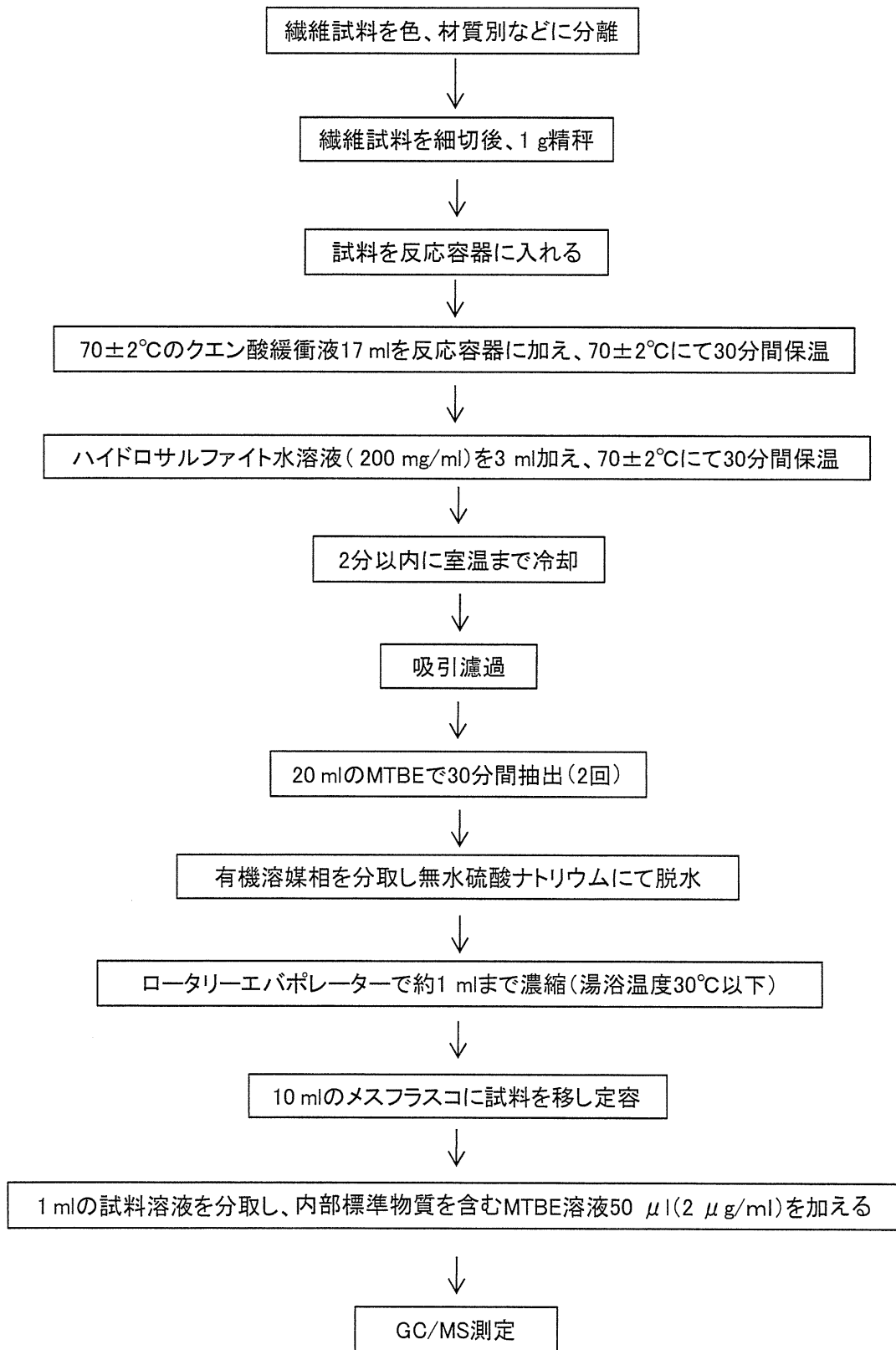


図 1. 繊維製品中の PAAs 分析法

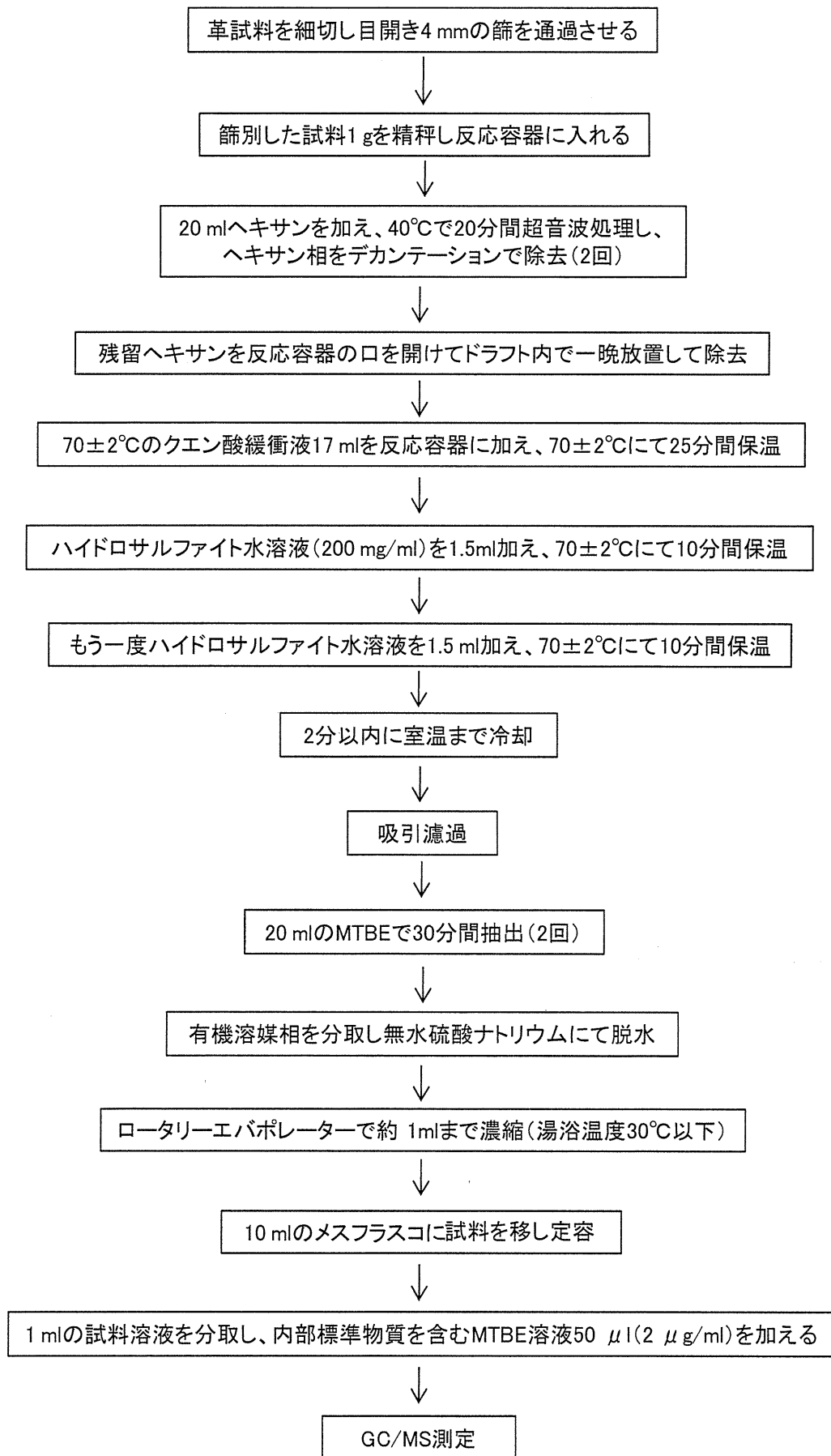


図 2. 革製品中の PAAs 分析法 (4-aminoazobenzene は除く)

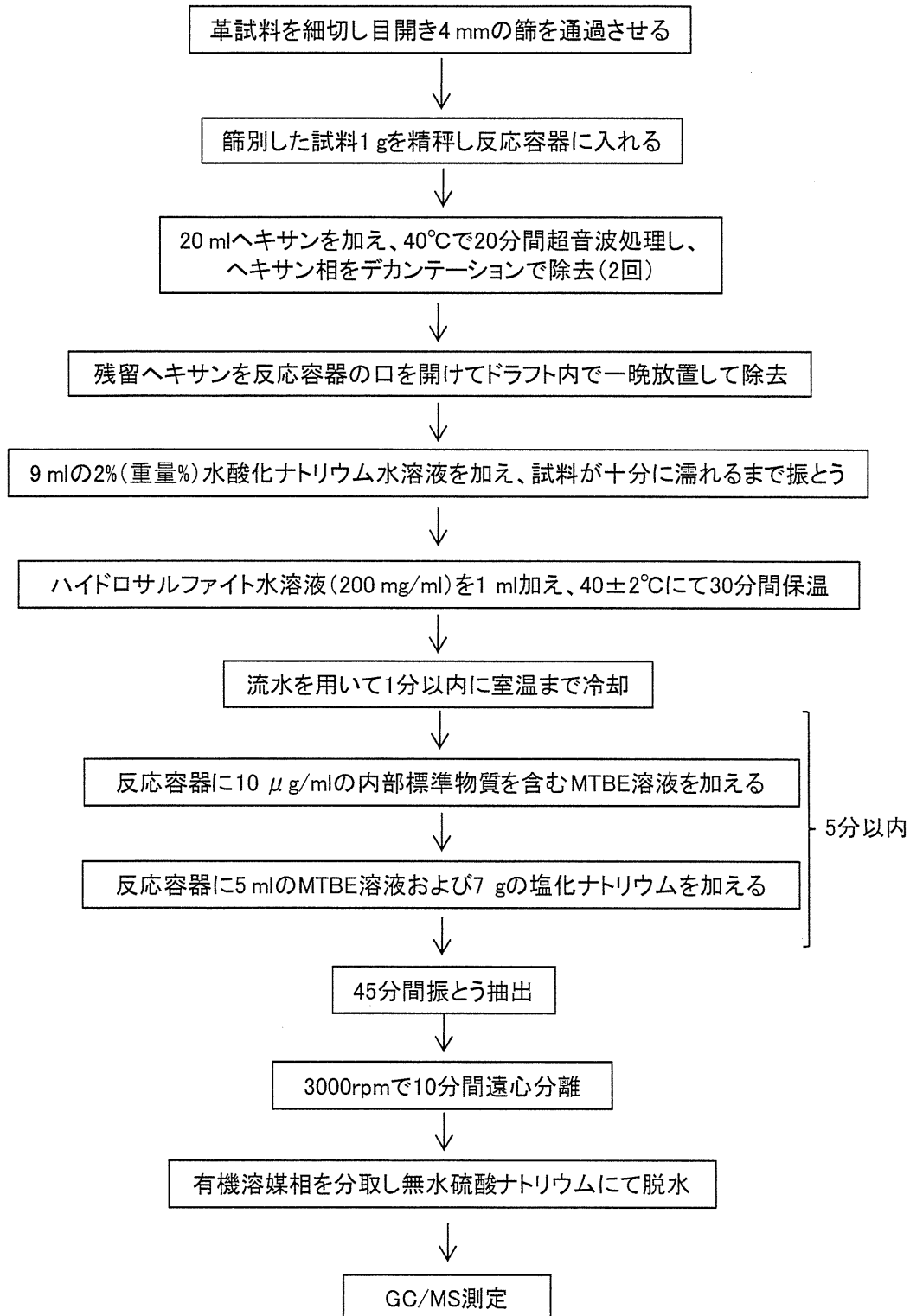


図 3. 革製品中の 4-aminoazobenzene 分析法

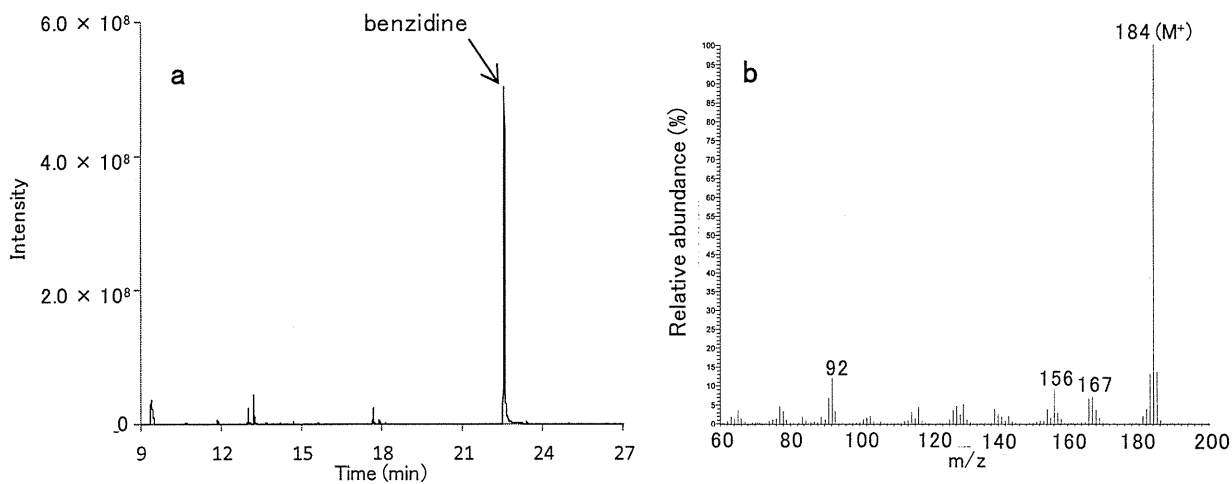


図 4. Benzidine が高濃度で検出された試料 (T-B3_O) の (a) トータルイオンクロマトグラム (SIM モード) および (b) Scan 分析 ($m/z=60\sim 300$) で得られた benzidine のマススペクトル

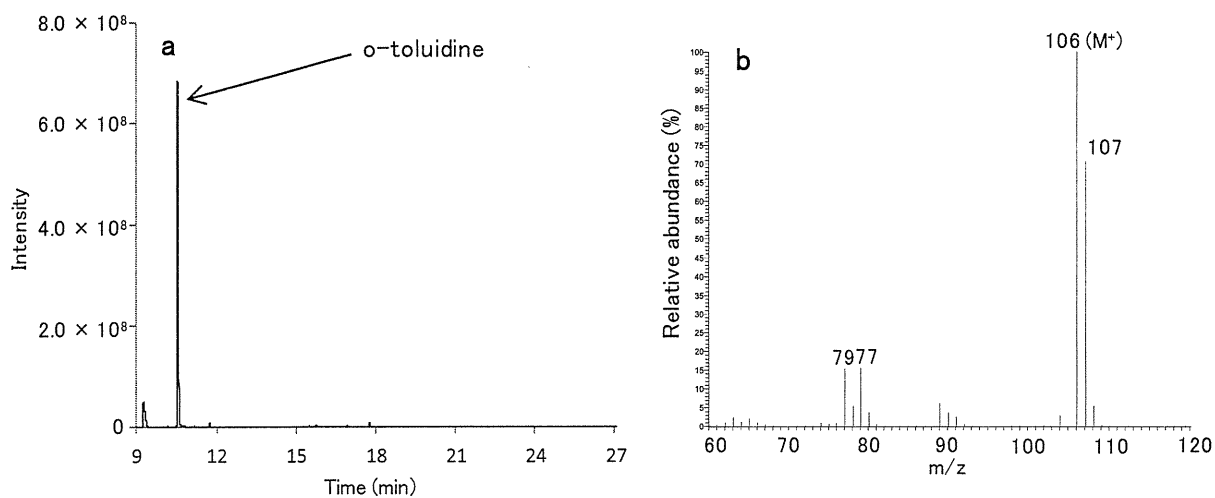


図 5. o-toluidine が高濃度で検出された試料 (L-C4) の (a) トータルイオンクロマトグラム (SIM モード) および (b) Scan 分析 ($m/z=60\sim 300$) で得られた o-toluidine のマススペクトル

参考

別表1 各国の繊維製品におけるPAAへの対応及び各自主基準(Oeko-Tex® Standard 100)について^a

国名等	規制区分	基準値	PAA	分析法	検出下限値	備考
日本	法規制無し					
米国	法規制無し ^b					
EU	REACH ^c	30 mg/kg 以下	22種類 ^d	EN14362-1:2003 EN14362-2:2003	5 mg/kg	分析法は2012年3月改訂予定、ISOに国際標準化提案されている
中国	GB18401:2003「繊維製品に関する国家一般安全技術規範」 ^e	20 mg/kg	24種類 (EU22種類+2,4-xylylidineおよび2,6-xylylidine)	GB/T 17592-2006	5 mg/kg	分析法は2006年に改訂、規制PAAを23種類と表記する報告書もあり確認が必要
韓国	品質経営及び工産品安全管理法	30 mg/kg 以下	KS K0147およびKS K0734に基づく			染色製品について実施、規制PAAは中国と同等
ベトナム	法規制あり(法令名は不明)		22種類 ^d	TCVN7619-1:2007 TCVN7619-2:2007		2009年11月より施行、分析法はEUと同じ
タイ	法規制無し(任意規定:タイ国基準 No.2231-2548「衣類(Fabrics):有害染料と化学物質からの安全」)	30 mg/kg 以下	24種類 (EU22種類+2,4-xylylidineおよび2,6-xylylidine)			
Oeko-Tex® Standard 100	自主基準	20 mg/kg 以下	24種類 (EU22種類+2,4-xylylidineおよび2,6-xylylidine)	非開示	定量下限値 20 mg/kg	欧州を中心に世界中で用いられている
エコマーク	自主基準	30 mg/kg 以下	24種類 (EU22種類+2,4-xylylidineおよび2,6-xylylidine)			日本

^a 大部分は引用文献10) 独立行政法人中小企業基盤整備機構・平成21年度情報調査業務「繊維製品中の有害物質に関する調査事業」を基にして作成した

^b ベンジジンを含む染料が1970年代より製造・使用禁止されているが、染色品の輸入は規制されていない

^c REACH Annex XVII (REACH発効前はEU Directive 2002/61/EC)

^d 表4参照

^e 法律ではないが法と同等の強制力を持つ

(資料 1)

Analysis of primary aromatic amines originated from azo dyes in
commercial textile products in Japan

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Analysis of primary aromatic amines originated from azo dyes in commercial textile products in Japan

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The purpose of this study was to clarify the actual condition of 26 types of carcinogenic primary aromatic amines (PAAs) originated from azo dyes in commercial textile products in Japan. In the case of textiles made of various fibers of various colors, the fibers were separated by color and analyzed. A total of 86 textile products (117 samples) were analyzed. Twenty-one kinds of PAAs were detected in the samples and almost all the PAAs were detected at low concentrations. However, the concentrations of benzidine, 3,3'-dimethoxybenzidine, and 2,4-diaminotoluene ($56\text{--}440\ \mu\text{g g}^{-1}$) in placemats made of cotton were found to exceed EU regulation limits of $30\ \mu\text{g g}^{-1}$. Although such placemats do not always come into contact with the user's skin, it is thought that they should be handled more carefully. Finally, 7 products (8 samples) contained PAAs at concentrations that exceeded the regulation limits. Two sample preparation methods (with and without solvent extraction) were performed on the same sample in order to compare the PAAs in samples in which it is difficult to separate the component materials, such as a cotton fabric that contained polyester fibers. In a comparison of the results obtained from the two methods, it was observed that the concentrations and/or kinds of PAAs detected in the samples were different. It was therefore thought that textile products that present this particular challenge should be analyzed by both methods.

Keywords: Aromatic amine, azo dye, textile products, solvent extraction, reduction.

Introduction

Azo dyes have been widely used in many industrial products since the second half of the 19th century on account of their wide variety of available colors and low cost. At present, three thousand azo dyes are used worldwide and they constitute more than 65% of the global commercial dye market.^[1] As one of the most popular dye groups in the world, azo dyes are used as colorants for a variety of consumable products such as papers, textiles, toys, leather goods, food items, and cosmetics, among others.^[1]

However, certain types of azo dyes are degraded by the liver, microorganisms on the skin and intestinal bacteria under reductive conditions. On account of these reductive reactions, carcinogenic primary aromatic amines (PAAs) are generated.^[2–4] For these reasons, in 1994, the German Government enacted a second amendment to the German

Consumer Goods Ordinance that banned the use of certain azo dyes in consumer goods that can potentially come into direct, long-term contact with human skin. According to this amendment, the azo dyes that are degraded by reduction and that generate the 20 kinds of PAAs listed in the Ordinance were banned for the first time (regulation limit: below $30\ \mu\text{g g}^{-1}$).^[5] Since 1999, the European Union (EU) has explored the restriction of azo dye usage, and in 2002, it published the 19th amendment to the Council Directive 76/69/EEC (related to restrictions on the marketing and use of certain dangerous substances and preparations).^[6]

This EU Directive banned the 20 kinds of PAAs listed in the German Ordinance that are found in textile products that can potentially come into direct contact with human skin. Two specific kinds of PAAs (o-anisidine and 4-aminoazobenzene) were also banned at the same time (thus, 22 kinds of PAAs were ultimately banned), and the regulation limit of these amines was established below at $30\ \mu\text{g g}^{-1}$.^[6] In addition to the 22 kinds of PAAs listed by the EU, 2 kinds of PAAs (2,4- and 2,6-xylylidine) were prohibited in China by the National Standard for the People's Republic of China (GB/T 17592-2006: below $20\ \mu\text{g g}^{-1}$).^[7]

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The Oeko-Tex[®] Standard 100 and Eco Mark schemes have voluntary regulations for textile products, and they have also limited the use of these 24 kinds of amines.^[8,9] However, few investigations into the amounts of PAAs in actual commercial products have been carried out^[10–12] although the amounts of PAAs in migration solution from paper products,^[10] plastic laminates, and cooking utensils^[11,12] have been investigated. An investigation into the use of these PAAs in commercial textile products is therefore necessary.

The purpose of this study is to clarify the amount of PAAs generated from the reduction of azo dyes in commercial textile products in Japan. In this study, the above-mentioned 24 kinds of PAAs that are used in commercial textile products were investigated. In addition, 2 kinds of PAAs (aniline and 1,4-phenylenediamine) were analyzed because their analysis is recommended in the EU. Thus, a total of 26 kinds of PAAs were investigated (Table 1).

Materials and methods

Samples

Commercial textile products were purchased from several retail stores in Japan between January and March 2009. They were divided into classes on the basis of usage, color, material, and country of manufacture (Table 2). In the case of textiles made of fibers of various colors, these fibers were separated as much as possible. However, these fibers could not be separated in the case of textiles composed of different materials of the same color, e.g., a densely woven textile composed of cotton and polyester. Therefore, such samples were analyzed by two sample preparation methods (the details of these extraction methods are provided below). Thus, a total of 86 textile products (117 samples) were analyzed.

Materials

The details of the 26 kinds of PAAs investigated in this study are listed in Table 1. Naphthalene-d₈ and anthracene-d₁₀, which were obtained from Kanto Chemical Co., Inc., and 2,4,5-trichloroaniline, which was obtained from Wako Pure Chemical Industries Ltd., were used as internal standards for gas-chromatography/mass-spectrometry (GC/MS) analysis. The pesticide residue-grade methyl *tert*-butyl ether (MTBE) and methanol were obtained from Wako Pure Chemical Industries Ltd. Chlorobenzene, citrate acid, and sodium dithionite were obtained from Sigma-Aldrich. The diatomaceous column (Chemelute, 20 mL) were obtained from Varian. The citrate buffer solution used for sample processing was adjusted to pH 6.0 (0.06 mol L⁻¹ as citrate acid). A sodium dithionite solution (200 mg mL⁻¹) was prepared immediately before use.

Sample processing

The samples were processed using the following two standard European methods with minor modifications: EN 14362-1 (without solvent extraction, particularly for textiles made of cellulose and protein fibers)^[14] and EN 14362-2 (with solvent extraction, particularly for textiles made of synthetic fibers such as polyester).^[15] Fifteen samples were analyzed by these two methods to compare the different effects of sample preparation. During the processing of these samples, *o*-aminoazotoluene and 5-nitro-*o*-toluidine were further reduced to *o*-toluidine and 2,4-diaminotoluene, respectively.^[14,15] In addition, 4-aminoazobenzene generated aniline and 1,4-phenylenediamine under the reaction conditions used in these methods.^[14,15]

In accordance with EN 14362-1, each textile sample was cut in an appropriate manner and 1.00 g of the sample was weighed and placed in a reaction tube. To this tube, 17 mL of citrate buffer solution preheated to 70 ± 2°C was added. After being shaken by hand, the reaction tube was kept for 30 min at 70 ± 2°C. Subsequently, 3 mL of aqueous sodium dithionite solution was added to bring about the reductive cleavage of the azo group. The reaction tube was shaken vigorously by hand and immediately kept again for 30 min at 70 ± 2°C. After 30 min, the reaction tube was cooled to room temperature within 2 min. After cooling, this sample solution was filtered and transferred to a separating funnel.

Then, 20 mL of MTBE was added to the sample solution, the mixture was shaken by hand for 5 min, and the MTBE layer was separated from the aqueous phase. This extraction procedure was performed twice and the MTBE layer was combined and filtered through anhydrous sodium sulfate. The filtrate was concentrated to approximately 1 mL with a rotary evaporator keeping the temperature of the water bath below 30°C. Next, the volume of the sample solution was adjusted to 5 mL with MTBE. Then, 50 μL of MTBE solution containing 2 μg mL⁻¹ of internal standard was added to 1 mL of the sample solution, and this solution was then analyzed by GC/MS.

In accordance with EN 14362-2, the textile sample was cut in an appropriate manner. Then, 1.00 g of the sample was weighed and hung by inert material in the extractor to soak the condensed extraction solvent, which was not in direct contact with the boiling solvent. For reflux extraction, 70 mL of chlorobenzene was used, and the extraction procedure was performed for 25 min. In the case of insufficient decolorization, the extraction time was increased. After this extraction procedure, the extracted solution was cooled to room temperature and concentrated to approximately 1 mL with a rotary evaporator, with the temperature of the water bath kept below 45°C.


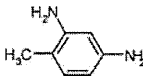
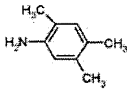

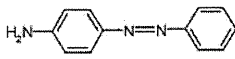
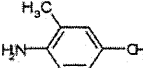
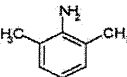
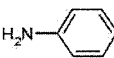
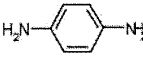
The sample was transferred to a reaction tube with methanol using an ultrasonic bath to disperse the sample as required. The solvent in the reaction tube was removed by a gentle stream of N₂, with the temperature of the water bath kept below 65°C. The residue was dissolved in 2 mL

Table 1. Physical and chemical properties and some characteristics of the investigated PAAs.

No.	Name	CAS No.	Chemical structure	Properties	EU Directive ^{a)}	IARC Group ^{b)}	Supplier ^{c)}
1	4-Aminobiphenyl	92-67-1		M.W. 169.22 m.p.: 53°C, b.p.: 302°C pKa 4.3	+	1	A
2	Benzidine	92-87-5		M.W. 184.24 m.p.: 128°C, b.p.: 401°C pKa 4.7	+	1	A
3	4-Chloro- <i>o</i> -toluidine	95-69-2		M.W. 141.60 m.p.: 240–270°C, b.p.: 241°C pKa 3.8	+	2A	B
4	2-Naphthylamine	91-59-8		M.W. 143.20 pKa 4.2	+	1	A
5	<i>o</i> -Aminoazotoluene (Solvent Yellow 3)	97-56-3		M.W. 225.29 m.p.: 101–102°C pKa 3.0	+	2B	B
6	5-Nitro- <i>o</i> -toluidine	99-55-8		M.W. 152.15 m.p.: 107.5°C pKa 2.3	+	3	B
7	4-Chloroaniline	106-47-8		M.W. 127.57 m.p.: 72.5°C, b.p.: 232°C pKa 4.0	+	2B	C
8	2,4-Diaminoanisole	615-05-4		M.W. 138.19 m.p.: 67°C pKa 5.3	+	2B	D
9	4,4'-methylenedianiline	101-77-9		M.W. 198.26 m.p.: 93°C, b.p.: 398–399°C pKa 5.3	+	2B	D
10	3,3'-Dichlorobenzidine	91-94-1		M.W. 253.13 m.p.: 133°C, b.p.: 368°C pKa 2.7	+	2B	C
11	3,3'-Dimethoxybenzidine	119-90-4		M.W. 244.29 m.p.: 171.5–174.5°C pKa 4.7	+	2B	D
12	3,3'-Dimethylbenzidine	119-93-7		M.W. 212.29 m.p.: 129°C, b.p.: 200°C pKa 4.6	+	2B	C
13	4,4'-Methylenedi- <i>o</i> -toluidine	838-88-0		M.W. 226.32 m.p.: 149°C pKa 5.2	+	2B	B
14	<i>p</i> -Cresidine	120-71-8		M.W. 137.18 m.p.: 53°C, b.p.: 235°C pKa 4.7	+	2B	D
15	4,4'-Methylene-bis-(2-chloro-aniline)	101-14-4		M.W. 267.16 m.p.: 110°C pKa 3.3	+	1	B
16	4,4'-Oxydianiline	101-80-4		M.W. 200.24 m.p.: 188–190°C, b.p.: 190°C pKa 5.5	+	2B	B
17	4,4'-Thiodianiline	139-65-1		M.W. 216.30 m.p.: 108°C pKa 4.6	+	2B	D

(Continued on next page)

Table 1. Physical and chemical properties and some characteristics of the investigated PAAs. (Continued)

No.	Name	CAS No.	Chemical structure	Properties	EU Directive ^{a)}	IARC Group ^{b)}	Supplier ^{c)}
18	<i>o</i> -Toluidine	95-53-4		M.W. 107.15 m.p.: -14.7°C, b.p.: 200.2°C pKa4.5	+	2A	D
19	2,4-Diaminotoluene	95-80-7		M.W. 122.17 m.p.: 99°C, b.p.: 292°C pKa5.1	+	2B	C
20	2,4,5-Trimethylaniline	137-17-7		M.W. 135.21 m.p.: 68°C, b.p.: 234°C pKa5.0	+	3	C
21	<i>o</i> -Anisidine	90-04-0		M.W. 123.15 m.p.: 6.2°C, b.p.: 225°C pKa4.5	+	2B	D
22	4-Aminoazobenzene (Solvent Yellow 1)	60-09-3		M.W. 197.24 m.p.: 12.4°C pKa3.1	+	2B	E
23	2,4-Xylidine	95-68-1		M.W. 121.18 m.p.: -26°C, b.p.: 226°C	—	3	F
24	2,6-Xylidine	87-62-7		M.W. 121.18 m.p.: 10°C, b.p.: 216°C	—	2B	F
25	Aniline	62-53-3		M.W. 93.13	—	3	D
26	1,4-Phenylenediamine	106-50-3		M.W. 108.14 m.p.: 145°C, b.p.: 267°C	—	3	F

^{a)}List of primary aromatic amines in the Directive 2002/61/EC.

^{b)}IARC classification groups: 1 = Carcinogenic to humans, 2A = Probably carcinogenic to humans, 2B = Possibly carcinogenic to humans, 3 = Not classifiable as to carcinogenic to humans.

^{c)}A: SUPELCO, B: Sigma-Aldrich, C: AccuStandard Inc., D: Wako Pure Chemical Industries, Ltd., E: Fulka, F: Tokyo Kasei Kogyo Co., Ltd.

of methanol using an ultrasonic bath as required. Next, 15 mL of citrate buffer preheated to 70°C was added to this tube. The reaction tube was ultrasonicated for 30 min at 70°C. Subsequently, 3 mL of aqueous sodium dithionite solution was added to the reaction tube, which was then vigorously shaken by hand and immediately kept again for 30 min at 70 ± 2°C without ultrasonication. After 30 min, the reaction tube was cooled to room temperature within 2 min. Then, the sample solution was extracted by MTBE in the same manner as in the case of EN14362-1.

GC/MS analysis

All samples in this study were analyzed by a Focus GC equipped with a DSQII MS (Thermo Fisher Scientific). A DB-35MS fused silica capillary column (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm, Agilent) was used for analysis in this study. A DB-5MS fused silica (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm, Agilent) was also used in a preliminary test. The carrier gas used was He gas, with the gas flow rate being set to a constant value of 1.0 mL min⁻¹. The tempera-

tures of the injector, transfer line and ion source were 230, 250, and 230°C, respectively. The sample was injected in the splitless mode and the injected volume was 1 μL. The GC oven temperature was initially maintained at 55°C for 5 min and programmed to undergo temperature increases in three steps. In the first step, the temperature increased to 230°C at a rate of 15°C min⁻¹; in the second step, to 290°C at 5°C min⁻¹; and in the final step, to 310°C at 20°C min⁻¹. The oven temperature was then maintained at 310°C for 5 min. The MS was operated in the electron ionization mode at 70 eV and the analysis was performed using the selected ion monitoring (SIM) mode. The retention times and the quantifying and qualifying ions are listed in Table 3.

The limits of detection and quantification (LOD and LOQ, respectively) were calculated using the computer software named Total Optimization of Chemical Operations (TOCO), version 2.0, the operation of which is based on the function of mutual information (FUMI) theory.^[16] The concentrations obtained from relative standard deviation of 33% and 10% on the basis of mass chromatograms of standard and blank solutions were used to define the instrumental LOD and LOQ, respectively (Table 3).^[17] No

Table 2. List of textile products investigated.

<i>Usage</i>	<i>Sample Name^{a)}</i>	<i>Country</i>	<i>Materials^{b)}</i>	<i>Colors</i>	<i>Remarks</i>
Handkerchief	AJ1	Japan	Cotton (100%)	Light blue	
	AJ2	Japan	Cotton (100%)	Light pink	
	AC1	China	Cotton (100%)	Orange	
	AC2	China	Cotton (100%)	Yellow	
	AC3	China	Cotton (100%)	Red	
	AC4	China	Cotton (100%)	Black	
	AC5	China	Cotton (100%)	Black	
	AK1	Korea	Polyester (100%)	Sky blue	
	BJ1	Japan	Cotton (100%)	Light pink	Japanese type facecloth
	BJ2	Japan	Cotton (100%)	Deep red	
BJ3 (Y,R,G)	Japan	Cotton (100%)	Yellow(Y), red (R), green(G)		
Towel	BC1	China	Cotton (100%)	Light pink	
	BC2	China	Cotton (100%)	Orange	
	BC3	China	Cotton (100%)	Light blue	
	BC4	China	Cotton (100%)	Light pink	
	BC5	China	Cotton (100%)	Light pink	
	BC6	China	Cotton (100%)	Black	
	BC7	China	Cotton (100%)	Violet	
	BC8	China	Cotton (100%)	Blue	
Socks	CC1	China	Cotton, polyester, polyurethane	Light yellow	
	CC2	China	Cotton, nylon, polyurethane	Black	
	CC3	China	Cotton, polyester, polyurethane	Black	
	CL1	Laos	Cotton, acryl, others	Beige	
	CL2	Laos	Cotton, acryl, others	Light pink	
Placemat	DI1	India	Cotton (100%)	Yellow	
	DI2(R,V)	India	Cotton (100%)	Red (R), Violet (V)	
	DI3	India	Cotton (100%)	Orange	
	DI4	India	Cotton (100%)	Deep red	
	DI5	India	Cotton (100%)	Red	
	DI6	India	Cotton (100%)	Brown	
	DI7(SK,V)	India	Cotton (100%)	Sky blue (SK), Violet (V)	
	DI8(G,Y)	India	Cotton (100%)	Green (G), Yellow (Y)	
	DI(R,O)	India	Cotton (100%)	Red (R), Orange (O)	
	DI10(B,Be)	India	Cotton (100%)	Blue (B), Beige (Be)	
	DI11(BLA,V)	India	Cotton (100%)	Black (BLA), Violet (V)	
	DI12	India	Cotton (100%)	Black	
	DI13	India	Cotton (100%)	Blue	
	DI14	India	Cotton (100%)	Deep red	
	DI15	India	Cotton (100%)	Black	
Handicraft felt	DB1(B)	Bolivia	Cotton (100%)	Blue (B), Brown	
	DB2(G,BR)	Bolivia	Cotton (100%)	Green (G), Brown (BR)	
	DB3(B)	Bolivia	Cotton (100%)	Blue (B), Red, Violet, Pink	
	EJ2	Japan	Polyester	Red	
	EJ3	Japan	Polyester	Blue	
	FC2(B,O)	China	Polyester	Blue(B), Orange(O)	
	FC3	China	Polyester	Black	

(Continued on next page)

Table 2. List of textile products investigated. (*Continued*)

<i>Usage</i>	<i>Sample Name^{a)}</i>	<i>Country</i>	<i>Materials^{b)}</i>	<i>Colors</i>	<i>Remarks</i>
Undershorts	FC4	China	Polyester (65%), cotton (35%)	Black	
	FC5(B,P,V)	China	Cotton (100%)	Black(B), Pink(P), Violet(V)	
	FC6	China	Nylon (93%), Polyurethane (7%)	Black	
Tie	GC1	China	Polyester	Black	
	GC2	China	Polyester	Black	
	GC3	China	Polyester	Black	
T-shirts	HC1	China	Cotton	Black	
	HC2	China	Cotton	Greenish brown	
	HC3	China	Cotton	Black	
	HC4	China	Cotton	Black	
	HH1	Honduras	Cotton	Black	
Glove	IC1	China	Polyester	Black	Long-type, suntan prevention
	IC2	China	Polyester	Black	Work gloves
	IC3	China	Acryl, nylon, polyurethane	Black	
Muffler and stole	JC1 (BLA,GR)	China	Acryl	Black (BLA), Grey (GR)	Muffler
	JC2	China	Polyester	Black	Stole
	JC3	China	Polyester	Brown	Stole
	JC4	China	Polyester	Black	Stole
Wrist band and supporter	KC1	China	Cotton, nylon	Navy blue	Arm cover
	KC2	China	Unknown	Black	Wrist band
	KC3	China	Acryl, polyester, polyurethane	Black	Leg warmer
	KC4	China	Polyester	Black	Wrist supporter
	KC5	China	Polyester (86%), polypropylene (14%)	Black	Athletic knee supporter
Thread, string, belt	LC1	China	Polyester	Black	Shoestring
	LC2	China	Wool	Navy blue	Woolen yarn
	LC3	China	Wool	Brown	Woolen yarn
	LC4(BLA,GR)	China	Polyester	Black (BLA), Grey (GR)	Belt
	LC5	China	Polyester	Black	Sewing thread
	LC6	China	Unknown	Blue	Hair band
	LA1	U.S.A.	Cotton (32%), polyester (68%)	Navy blue	Quilting thread
	NJ1(DG,G,N,B)	Japan	Cotton	Dark green (DG), Green (G), Navy blue (N), Blue (B)	
Cushion cover	NC1	China	Cotton	Brown	
	NC2	China	Cotton	Navy blue	
Pants	OC1	China	Cotton (52%), polyester (45%), polyurethane (3%)	Black	
Toy	PC1(BLA,B)	China	Unknown	Black (BLA), Blue(B)	Stuffed dog (with ST mark)
	PC2 (R)	China	Unknown	Red (R), Black	Stuffed toy
Others	ZC1(BLA)	China	Polyester	Black (BLA), Yellow green	Knapsack
	ZC3	China	Acryl, polyester, polyurethane	Black	Toilet seat cover
	ZC4	China	Cotton (90%), rayon (5%), polyester (5%)	Reddish brown	Coaster
	ZC5 (BLA,R,BRIR)	China	Polyester	Black (BLA), Bright red (BRIR), Red(R)	Accessory case

Table 3. Retention times, quantifying and qualifying ions, limits of quantification (LOQ) and detection (LOD), recoveries^{a)}, and coefficient of variation.

Chemical	Retention time (min)	Quantifying ion (m/z)	Qualifying ion (m/z)	LOQ ^{b)} (ng mL ⁻¹)	LOD ^{b)} (ng mL ⁻¹)	Extraction by diatomaceous earth column (n=3)		Liquid-liquid extraction (n=3)		Required recovery ^{c)}
						Recovery (%)	CV (%)	Recovery (%)	CV (%)	
Aniline	9.33	93	66	1.7	0.50	74	6.1	81	6.4	–
<i>o</i> -Toluidine	10.63	106	107	4.0	1.2	84	6.2	84	8.2	50%
2,4-Xylidine	11.68	121	120	0.30	0.10	100	2.1	100	3.4	–
2,6-Xylidine	11.73	121	120	0.40	0.10	79	3.5	87	4.6	–
<i>o</i> -Anisidine	11.97	123	108	0.90	0.30	83	3.1	93	5.3	70%
4-Chloroaniline	12.35	127	129	2.8	0.90	96	3.7	100	4.6	70%
<i>p</i> -Cresidine	12.93	137	122	3.0	0.90	100	1.2	110	2.2	70%
2,4,5-Trimethylaniline	12.99	120	135	4.1	1.2	86	3.1	92	1.5	70%
1,4-Phenylenediamine	13.31	108	80	1.9	0.60	5.0	0.20	15	0.80	–
4-Chloro- <i>o</i> -toluidine	13.34	141	143	2.2	0.70	97	1.8	100	1.7	70%
2,4-Diaminotoluene	14.52	121	122	11	3.3	22	14	42	3.5	50%
2,4-Diaminoanisole	15.38	123	138	8.8	2.6	7.5	1.4	21	8.2	20%
2-Naphthylamine	16.03	115	143	8.1	2.4	79	1.8	92	4.8	70%
5-Nitro- <i>o</i> -toluidine	16.52	152	106	7.7	2.3	85	0.66	99	3.6	–
4-Aminobiphenyl	17.66	169	152	0.90	0.30	88	5.0	110	3.6	70%
4-Aminoazobenzene	21.41	197	120	20	6.0	99	0.87	110	0.66	–
4,4'-oxydianiline	22.22	200	171	1.8	0.60	110	1.9	130	2.3	70%
4,4'-Methylenedianiline	22.36	198	197	4.6	1.4	140	1.4	170	1.0	70%
Benzidine	22.48	184	167	1.2	0.30	120	0.57	160	0.47	70%
<i>o</i> -Aminoazotoluene	23.49	225	106	16	4.9	79	1.0	110	0.82	–
4,4'-Methylenedi- <i>o</i> -toluidine	24.49	226	211	3.1	0.90	160	1.0	180	2.2	70%
3,3'-Dimethylbenzidine	24.91	212	196	2.5	0.80	110	0.81	140	2.3	70%
4,4'-Thiodianiline	26.40	216	184	1.9	0.60	72	3.3	82	3.8	70%
4,4'-Methylene-bis-(2-chloro-aniline)	26.99	266	268	6.6	2.0	64	1.8	90	3.9	70%
3,3'-Dichlorobenzidine	27.00	252	254	2.9	0.90	62	1.9	88	5.6	70%
3,3'-Dimethoxybenzidine	27.17	244	201	3.5	1.1	63	5.1	100	3.6	70%
Naphthalene-d ₈ ^{d)}	11.84	136								
2,4,5-Trichloroaniline ^{d)}	15.61	195								
Anthracene-d ₁₀ ^{d)}	17.89	188								

^{a)}The method described in EN14362.^{b)}Calculated by TOCO version 2.0 (FUMI theory). The values correspond to the concentration in the injected solution.^{c)}Minimum requirement described in EN14362.^{d)}Internal standard (naphthalene-d₈ aniline to 2,4-diaminotoluene, 2,4,5-trichloroaniline; 2-naphthylamine, anthracene-d₁₀; 5-nitro-*o*-toluidine to 3,3'-dimethoxybenzidine).

interfering peaks were observed in the sample mass chromatogram obtained from the SIM scan. Thus, in this study, it was considered that the experimental LOD value could be used to calculate the volume of the final sample solution and the instrumental LOD. The LODs calculated for this study were lower than the values mandated by EN14362-1 and -2 (below $5 \mu\text{g g}^{-1}$).^[14,15]

Results and discussion

Examination of GC/MS determination

First, a preliminary experiment was carried out to investigate the condition of target PAAs that were separated by the DB-5MS fused silica capillary column because this column was used in GB/T 17592-2006^[7] and Mutsuga et al. (2009).^[10] The polarity of this column was different to DB-35MS used in EN14362.^[14,15] DB-35MS and DB-5MS correspond to the mid-polarity stationary phase and non-polar stationary phase, respectively. On the mass chromatograms

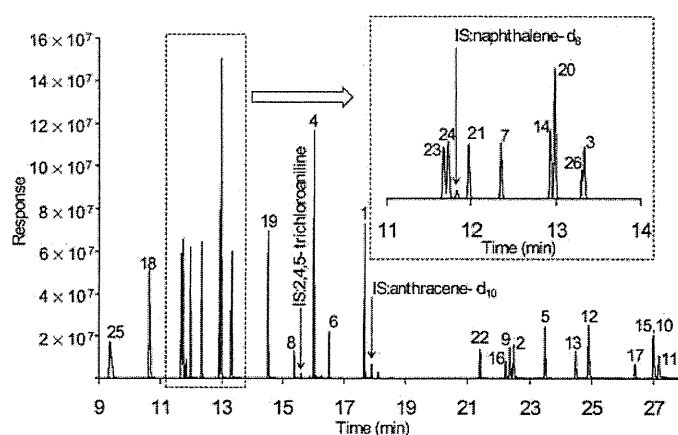


Fig. 1. Total ion chromatogram (SIM) of standard solution ($1.0 \mu\text{g mL}^{-1}$, IS: $0.1 \mu\text{g mL}^{-1}$). The peak numbers correspond to Table 1.

Table 4. Detection frequencies and concentration ranges of investigated PAAs.^{a)}

Chemical	Sample (n=117)											
	Products (n=86)				Without solvent extraction (n=77)				With solvent extraction (n=40)			
	Above LOQ	Above LOD ^{b)}	above LOQ	Range ($\mu\text{g g}^{-1}$)	Above LOD ^{b)}	Above LOQ	Range ($\mu\text{g g}^{-1}$)	Above LOD ^{b)}				
4-Aminobiphenyl	21	3	20	0.031–29	3	5	0.051–2.9	0				
Benzidine	19(6)	0	16(7)	0.12–440	0	7	0.25–6.7	0				
4-Chloro- <i>o</i> -toluidine	0	0	0	– ^{c)}	0	0	–	0				
2-Naphthylamine	2	0	2	0.071–0.19	0	0	–	0				
<i>o</i> -Aminoazotoluene	0	0	0	–	0	0	–	0				
5-Nitro- <i>o</i> -toluidine	1	0	1	0.83	0	0	–	0				
4-Chloroaniline	35	0	25	0.041–2.7	0	15	0.037–0.73	1				
2,4-Diaminoanisole	1	0	1	17	0	0	–	0				
4,4'-Methylenedianiline	7	0	2	0.26–0.92	0	7	0.23–2.2	0				
3,3'-Dichlorobenzidine	2	0	2	0.28–0.40	0	1	0.29	0				
3,3'-Dimethoxybenzidine	12(3)	2	16(3)	0.045–390	2	0	–	0				
3,3'-Dimethylbenzidine	4	0	4	0.072–2.4	1	0	–	0				
4,4'-Methylenedi- <i>o</i> -toluidine	2	0	1	0.52	0	1	2.8	0				
<i>p</i> -Cresidine	8	0	9	0.013–14	0	0	–	0				
4,4'-Methylene-bis-(2-chloro-aniline)	0	0	0	–	0	0	–	0				
4,4'-Oxydianiline	2	0	1	2.5	0	1	4.7	0				
4,4'-Thiodianiline	2	0	2	0.045–0.10	0	0	–	0				
<i>o</i> -Toluidine	7	1	11	0.019–6.8	3	0	–	0				
2,4-Diaminotoluene	1(1)	0	1(1)	92	0	0	–	0				
2,4,5-Trimethylaniline	0	0	0	–	0	0	–	0				
<i>o</i> -Anisidine	15	4	10	0.017–0.60	4	7	0.022–0.73	2				
4-Aminoazobenzene	0	0	0	–	0	0	–	0				
2,4-Xylidine	6	1	6	0.019–0.93	1	0	–	0				
2,6-Xylidine	5	0	5	0.016–0.022	0	0	–	0				
Aniline	62	21	46	0.018–210	25	29	0.025–880	9				
1,4-Phenylenediamine	19	1	3	0.13–1.5	0	18	0.17–22	1				

^{a)}The numbers in parentheses denote the number of samples in which the PAAs concentrations exceeded the regulation limit of $30 \mu\text{g g}^{-1}$.

^{b)}Between LOD and LOQ. ^{c)}Not detected.

thus obtained, the peaks of some PAAs separated by DB-35MS were observed to be sharper than those separated by DB-5MS, and the sensitivities of these compounds analyzed by DB-35MS were also higher than those analyzed by DB-5MS (data not shown). In general, adsorption and degradation of the compounds, which have the same polarity as the PAAs investigated in this study, occur in the GC column with a non-polar stationary phase; in addition, a tailing peak and a decrease in sensitivity are observed.^[18] However, both columns can be used to detect excess quantities of these amines with reference to the regulation limits.

Because 2,4- and 2,6-xylylidine are isomers and their mass fragment patterns are similar, it is necessary to separate them completely on the GC column. This necessary degree of separation could be obtained using DB-35MS for the GC/MS analysis (Fig. 1), although it was not obtained using DB-5MS. Although 3,3-dichlorobenzidine and 3,3-dimethoxybenzidine could not be separated and analyzed by GC/MS using DB-5MS,^[10] good separation of these compounds on the GC column using DB-35MS was observed (Fig. 1). Thus, DB-35MS was used for GC/MS determination in this study.

Examination of sample preparation

In accordance with approved EU methods (EN14362-1 and -2), target PAAs were extracted by a diatomaceous earth column after the reductive cleavage of the azo dye had taken place.^[14,15] In these methods, the recovery test was performed for PAAs, except for 3 kinds whose chemical structures changed during the reduction process. In addition, the minimum requirements with regard to the recovery rates of these PAAs are described in EN14362 (Table 3).^[14,15] In the EN14362^[14,15] recovery test, the standard solution was spiked with the citrate buffer solution, and the PAAs were extracted by a diatomaceous column. On the other hand, liquid-liquid extraction using MTBE^[19] and dichloromethane^[10] was performed in previous studies. Therefore, in this study, the results of the recovery test involving extraction by a diatomaceous earth column were compared with the results of liquid-liquid extraction by MTBE. The results of the recovery test are described in Table 2.

In the results of the diatomaceous earth recovery test, the recovery values of 2,4-diaminotoluene, 2,4-

Table 5. Concentrations of the PAAs in placemat samples in which the PAAs concentrations exceeded the regulation limit (unit: $\mu\text{g g}^{-1}$).^{a)}

Chemical	Store A							Store C
	DI2-R (Red)	DI2-V (Violet)	DI7-V (Violet)	DI10-B (Blue)	DI11-V (Violet)	DI13 (Blue)	DI14 (Deep red)	DI5 (Red)
4-Aminobiphenyl	3.5	3.3	29	7.2	12	5.6	14	0.062
Benzidine	230	180	360	200	440	210	440	0.46
4-Chloro- <i>o</i> -toluidine	—	—	—	—	—	—	—	—
2-Naphthylamine	—	—	—	—	—	—	—	—
<i>o</i> -Aminoazotoluene	—	—	—	—	—	—	—	—
5-Nitro- <i>o</i> -toluidine	—	—	—	—	—	—	—	0.83
4-Chloroaniline	0.030	—	—	—	—	—	—	—
2,4-Diaminoanisole	—	—	—	—	—	—	—	17
4,4'-Methylenedianiline	—	—	—	—	—	—	—	—
3,3'-Dichlorobenzidine	—	—	—	—	—	—	—	—
3,3'-Dimethoxybenzidine	0.054	0.17	56	280	0.69	390	1.2	0.047
3,3'-Dimethylbenzidine	—	—	—	0.072	0.89	—	2.4	—
4,4'-Methylenedi- <i>o</i> -toluidine	—	—	—	—	—	—	—	—
<i>p</i> -Cresidine	—	14	3.9	0.041	1.1	4.2	0.44	—
4,4'-Methylene-bis-(2-chloro-aniline)	—	—	—	—	—	—	—	—
4,4'-Oxydianiline	—	2.5	—	—	—	—	—	—
4,4'-Thiodianiline	—	—	—	—	—	—	—	—
<i>o</i> -Toluidine	—	—	—	—	—	—	—	6.8
2,4-Diaminotoluene	—	—	—	—	—	—	—	92
2,4,5-Trimethylaniline	—	—	—	—	—	—	—	—
<i>o</i> -Anisidine	0.056	0.074	0.017	0.41	—	0.60	—	0.031
4-Aminoazobenzene	—	—	—	—	—	—	—	—
2,4-Xylylidine	—	0.93	0.41	—	<i>tr.</i>	0.060	—	—
2,6-Xylylidine	—	—	—	—	—	—	—	—
Aniline	210	140	19	31	50	3.6	34	5.2
1,4-Phenylenediamine	—	—	—	—	—	—	—	1.5

^{a)} Not detected, *tr.*: trace amount.

diaminoanisole, 4,4'-methylene-bis-(2-chloro-aniline), 3,3'-dichlorobenzidine, and 3,3'-dimethoxybenzidine were below the minimum requirement; in particular, the coefficient of variation (C.V.) of 2,4-diaminotoluene was over 10%. On the other hand, the recovery values of these compounds in the case of liquid-liquid extraction by MTBE exceeded the minimum requirement, except in the case of 2,4-diaminotoluene. In this case, the recovery of 2,4-diaminotoluene was also below the minimum requirement (50%), although the value increased from 21.5% to 41.6%, and the C.V. was sufficiently small. Mutsuga et al. performed extraction experiments using diatomaceous earth and dichloromethane and concluded that the recovery values obtained by diatomaceous earth were lower than those obtained by liquid-liquid extraction using dichloromethane.^[10] Thus, it was suitable to use liquid-liquid extraction by MTBE as the extraction method. However, both methods yielded relatively high recovery values for 4,4'-methylenedianiline, benzidine, 4,4'-methylenedio-toluidine, and 3,3'-dimethylbenzidine. These phenomena might be caused by the matrix effect (which prevents decomposition and adsorption of the compound in the GC injector) that is generally observed in polar compound analysis by GC, e.g., residual pesticide analysis;^[18] this is because these PAAs were polar compounds. However, there is still no detailed explanation for these high recovery rates. In the present study, because exceeding the value of the minimum requirement was considered to be greater importance, the method involving liquid-liquid extraction by MTBE was employed. The data obtained by this method were not corrected by the obtained recovery results.

Concentrations of PAAs in textile samples without solvent extraction

Seventy-seven textile samples made of cotton and protein fibers were analyzed without solvent extraction. The frequency of detection and the concentration ranges of each PAA in the samples are listed in Table 4. Twenty-one kinds of PAAs were detected at concentrations over the LOD in these samples. In particular, the following compounds were detected at a high frequency (expressed as the number of samples detected over the quantification limit vs. the number of samples analyzed): aniline (46/77), 4-chloroaniline (25/77), 4-aminobiphenyl (20/77), benzidine (16/77), and 3,3'-dimethoxybenzidine (16/77) (Table 4). The chemical structures of many kinds of dyes and compounds contain aniline, which can explain why the frequency of detection and the concentration of aniline might be higher than those observed in the other aromatic amines in this study. Although 4-chloroaniline was detected in various samples (for example, handkerchiefs, towels, socks, and under shorts), 4-aminobiphenyl, benzidine, and 3,3'-dimethoxybenzidine were mostly detected in placemat samples that were manufactured in India (Table 4).

Most of the samples contained target PAAs at very low concentrations that were below the regulation limit ($30 \mu\text{g g}^{-1}$). It has been reported that certain kinds of these PAAs are formed as impurities during the synthesis of a dye that has not been banned.^[20] Furthermore, 4,4'-methylenedianiline, 2,4-diaminotoluene, and 2,6-diaminotoluene were detected as migrates in aqueous food simulants obtained from multi-layered plastic laminates and food packaging materials; this is because the residues of the aromatic isocyanate monomers in polyurethane products reacted with water to form PAAs such as 2,4-diaminotoluene and 2,6-diaminotoluene.^[11,12] In this study, 4,4'-methylenedianiline was also detected in the samples that consisted of polyurethane and other fibers (CC3 and FC6). Thus, the PAAs at concentrations below the regulation limit that were detected in this study might have originated as impurities in the dye and other materials.

Benzidine, 3,3'-dimethoxybenzidine, and 2,4-diaminotoluene were observed at high concentrations in several placemat samples manufactured in India, with values exceeding the regulation limit ($30 \mu\text{g g}^{-1}$). The concentrations of these three PAAs in the samples were very high ($56\text{--}440 \mu\text{g g}^{-1}$) (Table 4). The textile products regulated in the EU are those could potentially come into direct contact with human skin.^[6] Although a placemat does not always come into contact with human skin,

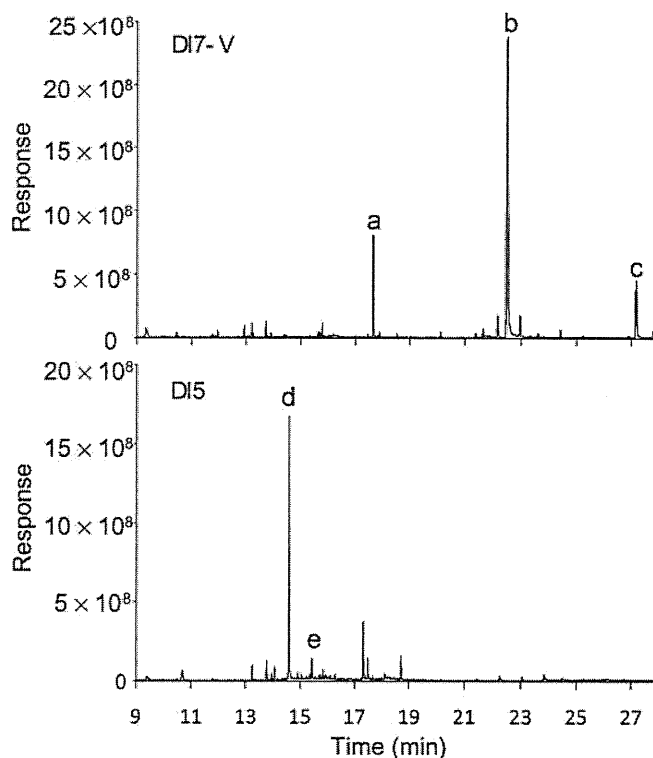


Fig. 2. Total ion chromatogram (full-scan mode: $m/z = 60\text{--}300$) of DI7-V and DI5 (a: 4-aminobiphenyl, b: benzidine, c: 3,3'-dimethoxybenzidine, d: 2,4-diaminotoluene, e: 2,4-diaminoanisole).

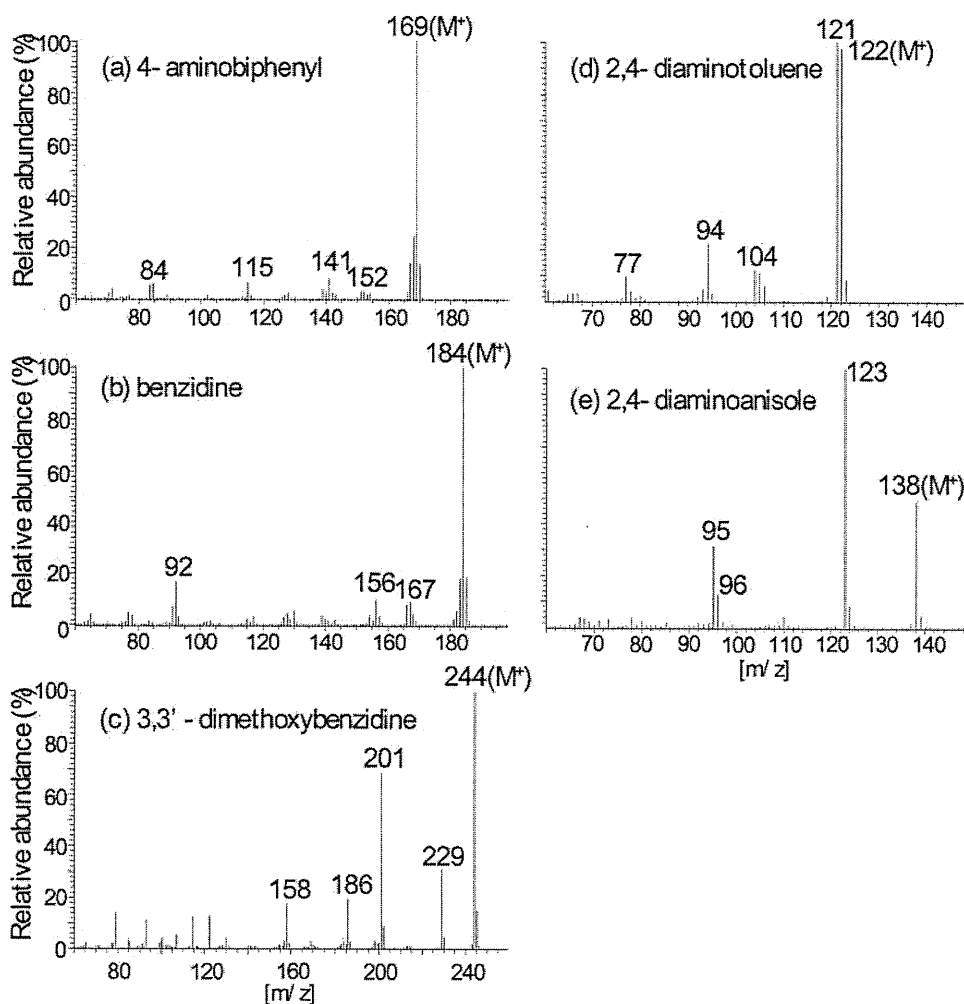


Fig. 3. Mass spectra of PAAs obtained by full-scan analysis ($m/z = 60\text{--}300$) of DI7-V and DI5 in Fig. 2 (a: 4-aminobiphenyl, b: benzidine, c: 3,3'-dimethoxybenzidine, d: 2,4-diaminotoluene, e: 2,4-diaminoanisole).

it is thought that these placemats should be used more carefully. In particular, benzidine is classified as group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC) (Table 1).^[13]

In this study, the placemats manufactured in India were purchased from three retail stores. DI1, DI2 and DI7 - DI15 were purchased from Store A; DI3 and DI4, from Store B; DI5 and DI6, from Store C. The placemats with PAAs at concentrations that exceeded the regulation limit were purchased from Store A and Store C (Table 5). Benzidine and 3,3'-dimethoxybenzidine were detected at concentrations of 180 to 440 and 56 to 390 $\mu\text{g g}^{-1}$ in the samples purchased from Store A, respectively (Table 5). Relatively high concentrations of 4-aminobiphenyl (3.3–29 $\mu\text{g g}^{-1}$) and p-cresidine (0.041–14 $\mu\text{g g}^{-1}$) were also detected in the same samples. The samples with PAAs at concentrations exceeding the regulation values were analyzed in the full scan mode, and mass spectra were obtained by GC/MS to definitively confirm the presence of these PAAs. The total ion chromatogram of DI7-V (full-scan mode; $m/z = 60\text{--}$

300) and mass spectra of these PAAs are shown in Figures 2, 3a, 3b, and 3c, as examples.

High concentrations of benzidine and 4-aminobiphenyl were observed in samples that were colored red, deep red, violet, and blue (Table 5). A high concentration of 3,3'-dimethoxybenzidine was also detected in the blue and violet samples, although a low concentration of the same compound was detected in the red samples (Table 5). Certain dyestuffs are often used to obtain not just a single color but also a mixture of various colors. Therefore, the azo dyes that generated benzidine and 4-aminobiphenyl might have been used for obtaining various colors, and the azo dyes that generated 3,3'-dimethoxybenzidine might have been used for obtaining blue. In the case of some blue samples such as DI10-B, the color of the buffer solution immediately changed from clear to blue when the sample was placed in a buffer solution. This finding can be attributed to the very low degree of color fastness of the dye used in these samples. Because the investigated samples were cotton products and had a low degree of color fastness, the azo

Table 6. Summary of the results analyzed by two sample processing methods (unit: $\mu\text{g g}^{-1}$)^a.

<i>Usage</i>	<i>Sample Name</i>	<i>4-aminobiphenyl</i>	<i>benzidine</i>	<i>4-chloroaniline</i>	<i>4,4'-Methylenedianiline</i>	<i>3,3'-dichlorobenzidine</i>	<i>3,3'-dimethoxybenzidine</i>	
Without solvent extraction	Socks	CC1	—	—	0.032	—	—	
		CC2	—	—	—	—	—	
		CC3	—	—	0.76	0.92	—	
	Under shorts	FC4	—	—	0.025	—	—	
		FC6	—	—	—	0.26	—	
	Glove	IC3	—	—	—	—	—	
	Wrist band and supporter	KC1	—	—	0.036	—	—	
		KC3	—	—	—	—	—	
	Thread, string, belt	LA1	—	—	—	—	—	
	Pants	OC1	—	0.12	0.54	—	—	
	Others	ZC3	—	—	—	—	—	
	With solvent extraction	Socks	CC1	—	—	—	—	—
			CC2	—	—	—	—	—
CC3			—	—	—	2.0	0.29	
Under short		FC4	0.22	—	0.058	—	—	
		FC6	—	—	—	0.97	—	
Glove		IC3	—	—	—	—	—	
Wrist band and supporter		KC1	2.9	6.7	0.73	—	—	
Thread, string, belt		LA1	—	—	—	—	—	
Pants		OC1	—	—	—	0.75	—	
Others		ZC3	—	—	—	—	—	

<i>Usage</i>	<i>Sample Name</i>	<i>4,4'-methylenedi-o-toludine</i>	<i>p-cresidine</i>	<i>4,4'-oxydianiline</i>	<i>o-anisidine</i>	<i>2,6-xylydine</i>	<i>aniline</i>	<i>1,4-phenylenediaminie</i>	
Without solvent extraction	Socks	CC1	—	—	—	—	tr.	—	
		CC2	—	—	—	—	tr.	—	
		CC3	—	—	—	—	0.018	0.60	
	Under shorts	FC4	—	—	—	—	—	0.18	0.13
		FC6	—	—	—	—	—	tr.	—
	Glove	IC3	0.52	—	—	—	—	tr.	—
	Wrist band and supporter	KC1	—	0.028	—	—	—	9.9	—
		KC3	—	—	—	—	—	—	—
	Thread, string, belt	LA1	—	—	—	—	—	—	—
	Paints	OC1	—	—	—	—	—	0.17	—
	Others	ZC3	—	—	—	—	—	tr.	—
	With solvent extraction	Socks	CC1	—	—	—	—	0.025	—
			CC2	—	—	—	—	0.51	—
CC3			—	—	—	—	0.90	0.68	
Under shorts		FC4	—	—	—	—	—	0.13	5.7
		FC6	—	—	—	—	—	0.059	—
Glove		IC3	2.8	—	—	0.026	—	0.063	—
Wrist band and supporter		KC1	—	—	4.7	—	—	880	16
		KC3	—	—	—	—	—	tr.	—
Thread, string, belt		LA1	—	—	—	—	—	tr.	—
Paints		OC1	—	—	—	—	—	0.059	0.76
Others	ZC3	—	—	—	—	—	tr.	—	

^{a)}Not detected, tr.: trace amount.