Analysis of Inorganic Antimicrobial Agents in Antimicrobial Products: Evaluation of a Screening Method by X-ray Fluorescence Spectrometry and the Measurement of Metals by Inductively Coupled Plasma Atomic Emission Spectroscopy

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Antimicrobial agents used in antimicrobial products are classified into inorganic, organic, and natural organic compounds. Inorganic agents, such as Cu, Zn, and Ag compounds, are known to be relatively safe, and these agents are used in many kinds of products. Patients with metal allergy and infants should avoid coming in contact with products in which inorganic agents are used at high concentrations. However, areas treated with metal compound agents and their concentrations are not indicated in most commercially available products. In this study, to establish a simple method of measuring the concentrations of metals in product areas, we evaluated screening methods using non-destructive X-ray fluorescence spectrometry (XRF). Qualitative analysis by XRF and quantitative analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES) were performed in the same areas, and the results were compared. Furthermore, concentrations of metals used in 40 commercially available antimicrobial products (86 areas) were analyzed. As the result, XRF was useful for the screening of Cu and Zn, but not for the screening of Ag. The use of inorganic antimicrobial treatment was indicated on 11 products, but 25 products were treated with inorganic antimicrobial agents. Cu was detected in 11 products. Ag was detected in 5 products, in which Cu or Zn were contained at higher concentrations. In 18 products, Zn was used for the antimicrobial treatment.

Key words —— antimicrobial products, inorganic agents, fluorescence X-ray analysis, inductively coupled plasma atomic emission spectroscopy, screening method, measuring the metal concentrations

INTRODUCTION

Due to a greater orientation toward cleanliness in Japanese, commercially available antimicrobial products have been increasing.[1–4] Antimicrobial agents used in antimicrobial products are classified into inorganic, organic, and natural organic compounds.[4–6] Inorganic antimicrobial agents containing Cu, Ag, or Zn are regarded as relatively safe agents in various products. However, patients with metal allergy due to Cu or Zn have been reported.[7–12] Such patients and infants should avoid contact with products finished with a high concentration of inorganic agents, particularly the areas treated with that concentration. The OEKOTEX Standard, an independent standard for the safety of textile products in Europe, defines the limit values of heavy metal elution by artificial sweat and saliva,[13, 14] and establishes particularly strict values for products for infants. At present, there is no such restriction standard in Japan. Therefore, this study was performed as a part of a study for the "Establishment of guidelines to evaluate exposure to antimicrobial products."[15] The safety of products should be evaluated in terms of the treatment concentration in each area of the product, however, in most commercially available products, the areas and concentrations of treatment are not indicated. Therefore, we evaluated the possible applicability of

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X-ray fluorescence spectrometry (XRF) as a screening method. The same areas were evaluated by both qualitative analysis using non-destructive XRF and quantitative analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and obtained values were compared. In addition, metals other than Cu, Ag, and Zn were analyzed, and the metal concentration in commercially available antimicrobial products was surveyed.[16, 17)]

MATERIALS AND METHODS

Samples —— Forty commercially available antimicrobial products with labels stating that antimicrobial/deodorant finishes had been used were purchased, and 86 areas were analyzed.

Qualitative Analysis by XRF —— An SEA-2001 (Seikosha Co., Ltd., Tokyo, Japan) was used as the XRF system. For qualitative analysis, the sample area for measurement was directly placed on the collimator of this system, and measurement was performed under the following conditions: measurement time, 300 sec; diameter of collimator, 10 mm; tube voltage, 50 kV; tube current, 2–10 μA; sample chamber atmosphere, air; measured elements, Cu, Ag, Zn, Ti, Fe, Cr, Ca, S, and Ni.

Quantitative Analysis by ICP-AES —— As the ICP-AES system, an IRIS 1000 (Thermo Electron Corporation, kanagawa, Japan) was used. Analysis was performed under the following conditions: radio frequency power, 1150 W; auxiliary flow rate, 0.5 l/min; nebulizer pressure, 26.06 psi; pump rate, 130 rpm. The main analysis wavelengths were: Cu, 324.757 nm; Ag, 328.068 nm; Zn, 213.856 nm; Cr, 267.716 nm; Al, 309.271 nm; Ni, 231.604 nm; Co, 238.892 nm; Mg, 279.553 nm. Depending on samples, wavelengths with less interference were used. A test solution was prepared as follows. A 100 mg portion of chopped sample was put into a 50 ml Teflon vessel, mixed with 5 ml concentrated nitric acid, degraded in a microwave sample digestion system (ETHOS model 900: Milestone General Co., Ltd., Kanagawa, Japan) continuously at a power of 300 W for 4 min, at 400 W for 6 min, and at 800 W for 15 min. Samples after acid degradation were cooled, placed with wash solution in a beaker and dried on a hotplate. After the addition of 5 ml of 0.1 mol/l nitric acid, the samples were heated for 10 min, placed in test tubes, and mixed with 0.1 mol/m^3 nitric acid to obtain a volume of 20 ml as test solution. When there were insoluble substances, the sample solution was passed through a membrane filter (pore diameter, 0.45 μm).

RESULTS AND DISCUSSION

Qualitative Value Standard by XRF

Since the textile products examined in this study have uneven surfaces for irradiation and vary in the X-ray transmission state and coexisting elements, there is no standard for the evaluation of their measurement results. Therefore, we ranked detected element concentrations according to the measurement intensity, *i.e.*, the count per second (CPS) value. CPS values of 9 metals (Ti, Fe, Cr, Ca, S, and Ni in addition to Cu, Ag, and Zn) were ranked. The ranking is shown in Table 1.

Table 1. Ranking Table of Metal Concentrations According to the CPS Value (Fluorescent X-ray Analysis)

	±	+	++	+++	++++
Cu	Under 9	10–19	20– 39	40– 99	Over 100
Ag	Under 19	20–39	40–100		
Zn	Under 9	10–19	20– 29	30– 79	Over 80
Ti	Under 4	5– 9	10– 19	20– 49	Over 50
Fe	Under 9	10–19	20– 39	40– 99	Over 100
Cr	Under 4	5– 9	10– 19	20– 49	Over 50
Ca	Under 2	3– 9	10– 19	20– 39	Over 40
S	Under 3	4– 9	10– 19	20– 40	
Ni	Under 9	10–19	20– 39	40–100	

Quantification by ICP-AES

Eight types of metal (Al as a component of antimicrobial zeolites and Ni and Co, and Mg causing contact dermatitis in addition to Cu, Ag, Zn, and Cr with antimicrobial effects) were measured. The calibration curve of each metal showed good linearity (correlation coefficient, 0.991–1.000) in the range of 0–1.0 μg/ml. Recovery experiments by microwave ashing were performed, and all metals showed good recovery rates (94–100%).

Comparison between Qualitative Values by XRF and Quantitative Values by ICP-AES

The qualitative values of Cu, Ag, and Zn obtained by XRF were compared with the quantitative values obtained by ICP-AES (Table 2). Table 2 also shows the analysis values of Cr (qualitative, quantitative), Ti (qualitative), and Al and Mg (quantitative). The results showed that XRF is an effective screening method for Cu and Zn; however, this

Table 2. Comparison of Analytical Values between Qualitative Analysis (XFS) and Quantitative Analysis (ICP-AES) (1)

No.	Products	Measurement area	No.	Detected elements											Antimicrobial agents indicated on the product label
				Cu		Ag		Zn		Cr		Ti	Al	Mg	
				XFS	AES (μg/g)	XFS	AES (μg/g)	XFS	AES (μg/g)	XFS	AES (μg/g)	XFS	AES (μg/g)	AES (μg/g)	
1	Underpants	Front: overlapping area	01–1	+	N.D.	+	N.D.	++	43.3	±	N.D.	±	630.0	92.6	Natural organic: Chitosan
		Front: Side area	01–2	+	N.D.	+	N.D.	+++	43.0	±	N.D.	±	524.5	81.3	Inorganics: Metal oxides
		Back: Buttocks area	01–3	+	N.D.	+	N.D.	++	44.6	±	N.D.	±	382.2	75.4	
		Back: Back of 01–1	01–4	+	N.D.	+	N.D.	+++	71.9	±	N.D.	±	469.8	94.1	
2	Socks	Sole area	02–1	+	N.D.	±	N.D.	++++	2495.0	±	N.D.	±	649.1	82.0	Inorganics: Antibiotic zeolite
		Ankle area	02–2	+	N.D.	+	N.D.	++++	2536.6	+	N.D.	+	668.5	82.7	
3	Socks	Sole area	03–1	+	N.D.	+	N.D.	++	6.7	+	N.D.	+	69.8	22.0	Natural sulfur
		Ankle area	03–2	+	N.D.	+	N.D.	++++	510.0	+	N.D.	+++	317.2	292.0	
4	Socks	Sole area	04–1	++	75.5	+	N.D.	++	14.2	+	30.4	++	327.6	25.6	Natural organics
		Ankle area	04–2	++	80.6	±	N.D.	+	13.0	±	30.0	+	297.2	29.9	
5	Socks	Sole area	05–1	+	N.D.	+	6.7	+++	194.2	++	316.0	++	156.8	94.3	Inorganics: Silver compound
		Ankle area	05–2	+	N.D.	+	2.4	+++	143.2	+	N.D.	±	129.2	44.9	
6	Lavatory seat cover	Frontal: middle area	06–1	+	N.D.	±	N.D.	++++	2221.4	+	N.D.	+++	611.3	8.5	Inorganics: Antibiotic zeolite
		Rear: right side	06–2	++	N.D.	+	N.D.	++++	2174.5	+	N.D.	+++	649.6	11.8	
7	Lavatory seat cover	Frontal: middle area	07–1	++	26.5	+	N.D.	+++	148.7	+	N.D.	+	36.6	31.5	Quarternary ammonium salt
		Rear: right side	07–2	++	39.7	+	N.D.	+++	152.4	+	N.D.	+	215.9	32.7	
8	Panty hose	Toe area	08–1	++	16.5	±	N.D.	++	4.5	+	N.D.	+++	54.6	4.3	Quarternary ammonium salt
		Thigh area	08–2	++	N.D.	±	N.D.	++	5.6	+	N.D.	++++	226.6	5.0	
		Around the crotch	08–3	++	N.D.	±	N.D.	++	3.0	++	N.D.	++++	154.8	3.1	
9	Antiperspirant pad	Front	09–1	++	N.D.	+	10.7	++	31.8	+	N.D.	++	179.0	19.7	Silver-zinc zeolite
		Back	09–2	++	N.D.	+	4.1	++	30.7	+	N.D.	++	57.0	18.2	
		Dried	09–3	++	N.D.	+	7.7	+++	42.0	+	N.D.	++++	137.8	41.1	
10	Undershirt	Back: area under the arm	10–1	+	N.D.	+	46.2	+++	195.1	+	N.D.	++	389.6	18.8	Silver zeolite
		Back: middle area	10–2	+	N.D.	+	52.3	+++	214.9	±	N.D.	++	420.2	23.0	
11	Undershirt	Back: area under the arm	11–1	+	N.D.	+	50.0	+++	195.3	±	N.D.	+	735.8	20.1	Silver zeolite
		Back: abdominal area	11–2	+	N.D.	+	55.5	+++	204.6	±	N.D.	++	468.0	19.3	
12	Socks	Sole area	12–1	++	N.D.	+	N.D.	++++	1114.8	+	N.D.	+	255.2	73.9	Natural organics: Flavonoid series
		Ankle area	12–2	++	N.D.	+	N.D.	++++	1131.7	+	N.D.	++	267.2	76.4	Inorganics: Metal oxides
13	Insole	Front: middle area	13–1	++	21.4	±	N.D.	++++	5075.7	±	N.D.	+	15295.0	179.4	Zeolite
		Back: middle area	13–2	++	5.4	±	N.D.	++++	18146.0	±	N.D.	++	92760.0	66.6	Aliphatic amine
14	Insole	Front: middle area	14–1	++	246.2	±	N.D.	++++	20180.0	±	N.D.	±	41800.0	58.1	Zeolite
		Back: middle area	14–2	++	76.5	±	N.D.	++++	18300.0	±	N.D.	++++	66039.0	61.3	
15	Socks	Sole area	15–1	+	N.D.	±	N.D.	++++	3354.0	++	380.4	+	429.6	31.4	Inorganics
		Ankle area	15–2	+	N.D.	±	N.D.	++++	3200.0	++	369.6	+	64.1	32.2	
16	Panty hose	Toe area	16–1	++	3.3	+	N.D.	++	19.2	+	N.D.	+++	63.8	5.2	Quarternary ammonium salt
		Thigh area	16–2	++	4.7	+	N.D.	++	8.3	+	N.D.	+	178.0	4.7	
		Around the crotch	16–3	++	3.1	+	N.D.	++	9.5	+	N.D.	++	170.0	59.1	
17	Socks	Sole area	17–1	+	N.D.	+	N.D.	++	9.8	+	N.D.	+	157.4	70.5	
		Ankle area	17–2	+	N.D.	+	N.D.	++	7.4	+	N.D.	+	346.0	73.0	
18	Socks	Sole area	18–1	++	N.D.	+	N.D.	++	5.0	++	378.3	++	221.2	57.0	
		Ankle area	18–2	++	N.D.	+	N.D.	++	3.6	++	375.5	++	85.0	53.5	
19	Socks	Sole area	19–1	+++	342.6	+	N.D.	++	2.1	+	N.D.	±	30.1	33.5	
		Ankle area	19–2	+++	290.4	+	N.D.	++	9.8	+	N.D.	+	34.2	29.2	

Table 2. Comparison of Analytical Values between Qualitative Analysis (XFS) and Quantitative Analysis (ICP-AES) (2)

No.	Products	Measurement area	No.	Detected elements										Antimicrobial agents indicated on the product label
				Cu		Ag		Zn		Cr		Ti	Al	Mg	
				XFS	AES (μg/g)	XFS	AES (μg/g)	XFS	AES (μg/g)	XFS	AES (μg/g)	XFS	AES (μg/g)	AES (μg/g)	
20	Socks	Sole area	20–1	+	N.D.	+	N.D.	++++	1017.8	+	N.D.	+	47.0	232.5	
		Ankle area	20–2	+	N.D.	+	N.D.	++++	1083.2	+	N.D.	++	63.4	247.3	
21	Socks	Sole area	21–1	+	N.D.	+	N.D.	++	9.4	+	N.D.	+	46.0	45.0	
		Ankle area	21–2	+	N.D.	+	N.D.	++	8.3	±	N.D.	+	46.4	38.4	
22	Socks	Sole area	22–1	+	N.D.	±	N.D.	+	11.1	±	N.D.	++	268.6	21.0	
		Ankle area	22–2	+	N.D.	+	N.D.	++	12.2	+	N.D.	+++	240.8	17.4	
23	Pillowcases	Front: middle area (Area in contact with the head)	23–1	++	N.D.	±	N.D.	++	5.1	++	10.7	±	528.8	74.5	
		Front: Bottom	23–2	++	N.D.	+	N.D.	++	2.5	++	4.7	±	74.3	51.1	
24	Panty hose	Toe area	24–1	++	3.2	+	N.D.	++	15.2	+	N.D.	++++	53.0	15.3	Organics: Quarternary ammonium Salt
		Thigh area	24–2	++	2.6	+	N.D.	++	12.4	+	N.D.	+++	27.1	7.3	
		Around the crotch	24–3	++	2.9	+	N.D.	++	10.5	+	N.D.	+++	44.3	7.5	
25	Sleeping pad	Front: Side	25–1	+	N.D.	+	N.D.	++	23.7	±	N.D.	±	19.9	261.2	
		Front: The other side	25–2	++	N.D.	+	N.D.	++	21.2	+	N.D.	±	18.7	276.2	
26	Bed pad	Texture	26–1	++	24.2	+	N.D.	+	8.2	+	N.D.	±	539.2	809.7	Inorganics: Silver
		Cotton in 26–1	26–2	+++	233.4	+	149.1	++	20.6	+	N.D.	+++	1164.9	28.4	
		Texture in an area other than 26–1	26–3	++	21.7	+	N.D.	+	7.9	+	N.D.	±	159.6	770.4	
		Cotton in 26–3	26–4	+++	231.0	+	151.4	++	19.6	+	N.D.	+++	1157.0	24.6	
27	Undershirt	Back: area under the arm	27–1	++	6.0	+	N.D.	++	5.6	+	N.D.	±	561.2	25.4	Natural organics
		Back: abdominal area	27–2	++	6.2	+	N.D.	++	5.2	+	N.D.	±	36.5	23.5	
28	Baby's gloves	Front	28–1	++	N.D.	+	N.D.	++	2.2	+	N.D.	±	18.6	56.0	Cedar leaf oil
29	Baby's gloves	Front: Palm area	29–1	+	N.D.	+	N.D.	++	125.9	±	N.D.	±	154.5	33.5	Chitosan
		Front: Arm area	29–2	++	N.D.	+	N.D.	+++	133.8	+	N.D.	±	177.2	36.7	
30	Socks	Sole area	30–1	+	N.D.	+	N.D.	+++	193.7	±	N.D.	±	501.0	40.2	Chitosan
		Ankle area	30–2	+	N.D.	±	N.D.	+++	1080.0	±	N.D.	+	42.9	252.7	
31	Baby's mask	Gauze (area in direct contact with the mouth)	31–1	++	N.D.	+	N.D.	++	2.7	++	N.D.	+	177.7	18.2	Chitosan
		Special filter inside	31–2	++	N.D.	+	N.D.	++	2.2	++	N.D.	++++	173.0	6.5	
32	Sheet/cover	Front: Side	32–1	++	N.D.	+	N.D.	++	9.5	+	N.D.	±	521.4	41.4	4-Isopropyl-2-hydroxy-cyclohepta-2,4,6-triene-1-one
		Front: Middle area	32–2	++	N.D.	+	N.D.	++	14.8	++	N.D.	±	187.5	42.0	
33	Fabric diaper	Front: Area with a pattern	33–1	++	N.D.	+	N.D.	++	1.1	+	N.D.	±	363.4	3.8	Hinoki oil
		Back: Plain area	33–2	++	N.D.	+	N.D.	++	1.9	+	N.D.	±	509.2	4.2	
34	Sheet/cover	Front	34–1	+	N.D.	±	N.D.	++++	2328.0	+	N.D.	++++	628.4	29.8	
35	Sheet/cover	Front: Plain area	35–1	++	N.D.	+	N.D.	+++	333.9	+	N.D.	++++	841.6	51.4	
		Front: Area with a pattern	35–2	++	36.5	+	N.D.	+++	294.2	±	N.D.	++++	678.0	49.2	
36	Gauze handkerchief for baby	Front	36–1	++	N.D.	+	N.D.	++	2.6	+	N.D.	±	390.6	43.7	4-Isopropyl-2-hydroxy-cyclohepta-2,4,6-triene-1-one
		Back	36–2	++	N.D.	+	N.D.	++	1.9	+	N.D.	±	26.7	42.8	
37	Towel for baby	Front	37–1	++	N.D.	+	N.D.	++	1.9	+	N.D.	±	163.9	17.2	4–Isopropyl-2-hydroxy-cyclohepta-2,4,6-triene-1-one
		Back	37–2	++	N.D.	+	N.D.	++	8.3	+	N.D.	±	452.8	33.2	
38	Baby's underwear	Front: Collar area	38–1	+	N.D.	+	N.D.	++	3.4	+	N.D.	±	329.8	44.2	4-Isopropyl-2-hydroxy-cyclohepta-2,4,6-triene-1-one
		Back: Dorsal area	38–2	+	N.D.	+	N.D.	+	2.9	+	N.D.	±	164.7	44.5	
39	Baby's underwear	Front: Chest area	39–1	+	N.D.	+	N.D.	+	2.2	+	N.D.	±	14.5	37.2	4-Isopropyl-2-hydroxy-cyclohepta-2,4,6-triene-1-one
		Back: Dorsal area	39–2	+	N.D.	+	N.D.	+	5.1	+	N.D.	±	25.5	39.9	
40	Baby's underwear	Front: Chest area	40–1	+	N.D.	+	N.D.	+	4.2	+++	N.D.	±	164.4	110.2	4-Isopropyl-2-hydroxy-cyclohepta-2,4,6-triene-1-one
		Back: Dorsal area	40–2	+	N.D.	+	N.D.	+	4.0	±	N.D.	±	14.2	121.4	

method could not be applied to Ag.

Cu —— ICP-AES showed Cu in 11 products (Cu-finished products; 24 areas). Two products (4 areas) ranked +++ by XRF contained Cu at high concentrations (342–231 μg/g). Of 23 products (46 areas) ranked ++, 10 (20 areas) were Cu-finished products. In this rank, the Cu concentration varied from 246 μg/g to "not detected." In samples ranked + or lower, Cu was not detected. Therefore, screening may be possible by ICP analysis of samples ranked ++ or higher. Screening for high concentration areas can be performed by ICP analysis of areas ranked +++ or higher.

Ag —— XRF showed only ranks + and ± for Ag. At the Ag levels in the samples in this study, XRF may not be applicable for screening due to the marked influences of rhodium used in the XRF system and the background. ICP analysis showed Ag in 11 areas of 5 products (Ag-finished products). Ag was detected in all samples for which it was indicated on the label, but not on those in which it was not indicated. Therefore, screening may be possible by the analysis of products on which the use of Ag is indicated.

Zn —— Since Zn is always present in the environment, it was detected in all samples. XRF also showed a CPS value of + or higher in all samples. Therefore, the presence or absence of Zn finish was determined based on not only values of ICP analysis but also finishing agents indicated on products. The use of Zn was indicated on product No. 9. In the areas of this product, the lowest Zn concentration was 30.7 μg/g; areas showing 30.7 μg/g or more were thus regarded as Zn-finished areas. A total of 18 products (35 areas) were considered to be Zn-finished (product No. 1–7, 9–13, 15, 20, 29, 30, 34, 35). All 9 products (all 16 areas) ranked ++++ by XRF showed Zn at a high concentration (510–20180 μg/g). All 9 products (all 16 areas) ranked +++ showed Zn at a finishing concentration (highest, 1080 μg/g). In rank ++, 3 products (5 areas) showed Zn at a concentration regarded as a finishing concentration (30.7–126 μg/g), but the other samples showed a relatively low concentration. In rank +, all samples showed a low concentration ($\leq$ 23.7 μg/g) below the finishing concentration. Therefore, screening may be possible by ICP analysis of areas ranked ++ or higher. Screening for high concentration areas can be performed by quantitative analysis of areas ranked ++++ or +++.

In No. 3 socks, the Zn concentration was high (++++, 510 μg/g) in the ankle area (No. 03–2) and low (++, 6.7 μg/g) in the sole (No. 03–1).

Metal Concentrations in Commercially Available Products and Status of the Use of Inorganic Antimicrobial Agents

The results of analysis of commercially available products showed the following. Of the 40 products, 25 were finished with inorganic antimicrobial agents (Cu, Ag, Zn). However, the use of these agents was indicated on only 11 products.

In No. 19 socks, Cu at a high concentration (342 μg/g) was detected. The OEKOTEX Standard limits Cu elution by artificial sweat/saliva should to 25 (products for infants)–50 ppm,[13, 14] making a safety evaluation by experiments using sweat and saliva necessary.

All 5 Ag-finished products were also treated with Zn or Cu. Products on which the use of Ag finish is indicated may also use Zn and Cu to obtain increased antimicrobial effects. Product No. 26 may use Ag in combination mainly with Cu.

Zn is relatively safe and has relatively slight antimicrobial effects. Therefore, many Zn-finished products have a high Zn concentration.

An antimicrobial zeolite is a zeolite consisting of Al, Si, and Na that carries the metal ions Cu, Ag, or Zn. Therefore, in products using antimicrobial zeolites, Al at high concentrations is also detected (19 products). Antimicrobial zeolites were used in 5 of 11 Cu-finished products, 17 of 18 Zn-finished products, and 4 of 5 Ag-finished products.

The 13 products from No. 28 to No. 40 were those for infants. Antimicrobial finishes should not be applied to products for infants, and "No antimicrobial finish" is an agreed upon phrase to use among companies who are members of the Japan Textile Evaluation Technology Council (SEK mark). Products of companies who are members of this council should have labels with the SEK mark, so that none of the products for infants purchased in this study had this mark. On most of these products, the use of chitosan or Hiba oil (hinokitiol) as a safe natural antimicrobial agent was indicated (11 products). However, 4 products (No. 29, 30, 34, 35) used inorganic antimicrobial agents. In 2 products (No. 29, 30), Zn was detected although the use of chitosan was indicated, suggesting their combined use to increase the antimicrobial effect.

Cr was detected in 5 products (9 areas); in 3 sock products (5 areas), it was found at a high concentration. The 3 products were also ranked ++ by XRF. Many patients with metal allergy due to Cr

have been reported.[12] Cr has an antimicrobial effect but is generally used as a dye and not as an antimicrobial agent. The OEKOTEX standard limits the Cr elution limit by artificial sweat and saliva to 1 (products for infants)–2 ppm.[13, 14] Safety tests by elution experiments using sweat and saliva are necessary.

Ti showing a CPS value of +++ or higher was detected by XRF in 11 products (17 areas). The detected Ti may not have been used for an antimicrobial effect. Rather, it may have been titanium oxide commonly used in dull fibers of synthetic fibers. Since conversion of Ti to solution by ashing is difficult, Ti was not quantified by ICP-AES.

Ni and Co are known to cause metal allergy.[12] Neither metal was detected in the samples analyzed in this study.

Mg is always present in the environment and, therefore, was detected in all samples by ICP-AES. Mg derived from plant fibers and minerals in products may have been detected at a high concentration.

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