Evaluation using energy-dispersive X-ray fluorescence spectrometry of metal elements in consumer products

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Purpose: Dental metal allergies usually originate in iatrogenic circumstances, or occupational and household environments. Thus, knowing which metallic elements were contained in known and unknown metal objects is necessary to accurately diagnose and to provide daily life guide for patients with metal allergies. The aim of this study was to identify the metal elements in cosmetic and household products.

Materials and Methods: By energy-dispersive X-ray fluorescence spectrometry (EDXRF), 81 cosmetic products and 50 household products were analyzed. Solid samples were analyzed intact. Cream samples and liquid samples were dried to powder or paste before testing with a freeze-dryer. The examination was carried out in vacuum.

Results: Metal elements were detected in 60 out of 81 cosmetic products and in 39 out of 50 household products. The elements above 1,000 cps X-ray intensity in the cosmetic products were K, Ca, Ti, Fe, Zn, and Bi; in the household products, the elements found were K, Ca, Fe, Cu, and Zn. In the 23 make-up cosmetic products, Fe was detected in all, and Ti and Zn were detected in 20 and 19 products, respectively.

Conclusion: The results of this study suggest that when seeking a metal allergen, dermatologists and dentists must pay particular attention to both known and unknown metal objects.

(Int Chin J Dent 2002; 2: 134-142.)

Clinical Significance: In the differential diagnosis and daily life guide to patients with dental metal allergies, those results should be available.

Key words: consumer products, daily life guide, dental metal allergy, differential diagnosis, EDXRF.

INTRODUCTION

Allergies to metal are common, affecting about 10% to 15% of the population.[1-4] Dental metal allergies are usually caused by iatrogenic circumstances, and are aggravated by factors in occupational and household environments.[5] Dermal and mucosal contact with and ingestion of metals have been reported to cause immune reactions, which most typically manifest as hives, eczema, redness, and itching.[2,6,7] All metals in contact with biological systems undergo corrosion.[8,9] This electrochemical process leads to the formation of metal ions; while not sensitizers on their own, they can activate the immune system by

forming complexes with endogenous proteins.[4,10,11] These metal-protein complexes are considered to be candidate antigens (or, more loosely termed, "allergens") for eliciting hypersensitivity responses.

Included in the elements known as sensitizers are: nickel (Ni), cobalt (Co), chromium (Cr), mercury (Hg), gold (Au), palladium (Pd), rhodium (Rh), platinum (Pt), aluminum (Al), manganese (Mn), iron (Fe), zinc (Zn), cadmium (Cd), tin (Sn), copper (Cu), antimony (Sb), iridium (Ir), lead (Pb), zirconium (Zr), molybdenum (Mo), silver (Ag), indium (In) and beryllium (Be). In addition, occasional responses to tantalum (Ta), titanium (Ti), and vanadium (V) have been reported.[3,6,7,12-19] A Danish population-based study showed that 19% of females and 12% of males had at least one positive reaction to patch testing.[20] At least 10% of women in the Nordic countries were allergic to nickel, but only 1-2% of men.[21] Metals are used everywhere and are present in our daily environment at home, at work and at play. In the household environment, the metal elements contained in known and some unknown metal objects. Understanding which metal elements are contained in these objects is necessary for making the differential diagnosis and providing guidelines for daily life to patients with metal allergies.

Because cosmetic and household products are widely used by many people, mainly women, the question arose whether such cosmetic and household products might contain metallic elements that could provoke allergic responses. The aim of this study was to identify the metal elements in some cosmetic and household products.

MATERIALS AND METHODS

Samples of 81 cosmetic products and 50 household products were obtained from different suppliers in Japan (Table 1). Whenever available, data were recorded concerning material, country of origin, maker, and product number.

Table 1. Number of materials tested.

Country of manufacturer	Cosmetics	Household products
Japan	66	45
People's Republic of China	9	1
Malaysia	0	3
Germany	2	0
France	2	0
Thailand	1	0
Indonesia	0	1
U.S.A.	1	0
Total	81	50

All samples were analyzed by energy-dispersive X-ray fluorescence spectrometry (EDXRF, SEA2110L, Element Monitor, Seiko Instruments Inc., Chiba, Japan). All elements can be analyzed by EDXRF from Na to U (except for Rh) in the periodic table. The accelerating voltage can be set at 5, 15 and 50 kV in this apparatus. The diameter of the analysis area was set at 10 mm. Solid samples such as lipstick, were analyzed intact. With a freeze-dryer (VD-250, Taitec Inc., Saitama, Japan), cream samples and liquid samples were dried to powder or paste before testing. Powder, or paste sample was placed in a sample container (XRF Sample Cup, Chemplex, Stuart, FL, USA). The examination was carried out in vacuum. Under these conditions, elements at levels higher than 200-300 ppm are detectable.[22]

RESULTS

An example of EDXRF analysis is shown in Fig. 1. The results of the present study are summarized in Tables 2-4. Metal elements were detected in 60 out of 81 cosmetic products and in 39 out of 50 household products. In the largest group of products tested, i.e., make-up products, Fe was detected in all 23 samples (100%), and Ti and Zn were detected in 20 (87%) and 19 (83%) products, respectively. The metal elements above 1,000 cps X-ray intensity in the cosmetic products were K, Ca, Ti, Fe, Zn, and Bi, and in household products were K, Ca, Fe, Cu, and Zn.

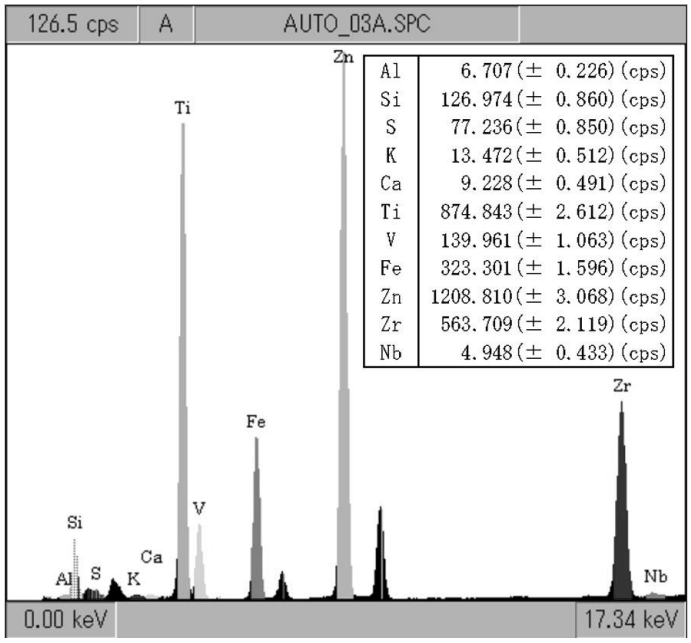

Fig. 1. An example of EDXRF analysis of a foundation make-up cosmetic. In the current analysis system, if an element was detected above 1,000 cps, this element was considered to be one of main components of the product quantitatively; and below 100cps, an amount of the element was a slight and close to the detection level.[23]

Ni and Cr were detected in one eyebrow pencil out of 81 cosmetic products (although the X-ray intensity for the elements was below 100 cps) and in one metal scourer out of 50 household products (within a range from 100 cps to 1,000 cps X-ray intensity). Hg was detected in one cleaner at less than 100 cps X-ray intensity. Co was not detected in any products. V was detected in 12 cosmetic products and one household product.

Table 2. Summary of EDXRF analysis of cosmetic and household products.

Type and number of products		Metal containing products		Type and number of products		Metal containing products	
		Number	%			Number	%
Cosmetics				Household products			
Wash (body, hair, and face)	12	5	42	Detergent	12	6	50
Hair dye	2	2	100	Bleach	3	2	67
Hair conditioner	2	2	100	Deodorant	5	2	40
Care (base)	15	2	13	Metal scourer	4	4	100
Make-up	23	23	100	Scrub and nylon scourer	4	3	75
Nail cosmetic	5	5	100	Cleaner (sponge)	10	10	100
Lipstick	8	8	100	Brush	2	2	100
Lipliner	3	3	100	Wiper	4	4	100
Toothpaste	4	3	75	Cleaning pad	1	1	100
Bath cosmetic	5	5	100	Cleaning sheet	2	2	100
Body-hair remover	1	1	100	Rubber glove	3	3	100
Nose clear pack	1	1	100				
Total	81	60	74	Total	50	39	78

In 23 make-up items, there are seven foundations, six eye colors, eight eyebrow pencils, one eyeliner, and one mascara. There are four body washes, five shampoos, and three face cleansers in 12 washes.

DISCUSSION

There is a significant number of metal elements, either in free atomic form or as inorganic or organic compounds, that may be absorbed through the skin or via oral, parenteral, respiratory, conjunctival, and mucosal routes. Dermal and mucosal reactions may take the form of eczema, dermatitis, systemic contact dermatitis, urticaria or *lichen planus*, and oral reactions may occur as dental metal eruptions.[15,24] It is conceivable that metal ions released from the dental alloys and metal subjects in people's daily environments could penetrate the oral and/or intestinal mucosa and the skin, and activate these sensitized T-cells *in vivo*. The immune system has many regulatory peptides and receptors that are known to be expressed in the brain. An activated T-cell might thus cause distant effects.[25] The ability of allergenic metal ions to elicit a reaction in a particular person is dependent upon their concentration, the area of skin or mucosa exposed, and the duration of exposure.[26] In some cases, the source of metal contact is known (earrings, jewelry, metal objects), but in others, it is difficult to identify the particular source of contact. The latter forces the physician to search for less obvious sources of metal contact.

Of the top ten contact allergens found in large prevalence studies conducted among European populations, four were metal compounds: nickel, chromium, cobalt and mercury. Among these, nickel consistently ranked as the most common cause of allergic contact dermatitis overall. A random survey of

the Danish population showed 11.1% and 2.2% Ni sensitivity for females and males, respectively.[27] However, the figure was only 0.67% in a group of male soldiers.[28]

Table 3. Number and type of cosmetic products containing each element.

Element	Intensity (cps)		
	Below 100	100-1,000	Over 1,000
Na	3 bat		
Mg	3 fod, 5 eyc, 2 eyb, 1 nco, 1 lis, 2 bat		
Al	5 fod, 6 eyc, 6 eyb, 1 eyl, 1 mac, 1 nco, 7 lis, 2 lil, 3 bac	1 eyb	
Si	2 bwa, 1 hdy, 1 hco, 3 fod, 3 eyb, 1 mac, 4 nco, 8 lis, 3 lil, 5 bat	2 bco, 4 fod, 6 eyc, 4 eyb, 1 eyl, 1 nco, 3 top, 1 hrc	
K	1 bwa, 1 hwa, 2 hdy, 4 fod, 2 eyc, 1 eyb, 1 eyl, 2 nco, 4 lis, 1 bat	1 bwa, 4 eyc, 5 eyb, 3 lis, 3 lil, 1 bat	2 bwa, 2 bat
Ca	1 bwa, 1 hwa, 2 hdy, 2 hco, 2 bac, 1 ncp, 5 fod, 3 eyc, 3 eyb, 1 eyl, 1 mac, 4 nco, 3 lis, 1 top	1 eyb, 1 eyl, 1 lis	2 top, 1 hrc
Ti	2 bwa, 2 fod, 1 eyc, 1 mac, 1 nco, 1 top, 2 bat	1 hdy, 2 fod, 4 eyc, 6 eyb, 2 nco, 8 lis, 2 lil, 1 hrc	2 fod, 1 eyc, 1 eyb, 1 lil,
V	3 eyb, 1 mac, 2 lil	2 fod, 2 eyc, 2 eyb	
Cr	1 eyb		
Mn	1 eyc, 1 eyb, 1 nco, 2 lil		
Fe	3 fod, 1 eyc, 1 eyb, 2 nco, 4 lis, 2 top, 1 ncp	4 fod, 3 eyc, 1 eyb, 3 nco, 4 lis, 2 lil, 2 bac	2 eyc, 6 eyb, 1 eyl, 1 mac, 2 lil
Ni	1 eyb		
Cu		1 ncp	
Zn	1 fod, 2 eyc, 6 eyb, 1 eyl, 1 mac, 1 nco, 2 lis, 1 lil	1 hwa, 4 eyc	4 fod
Ga	1 eyb		
Rb	2 fod, 4 eyc, 5 eyb, 1 eyl, 4 lis, 3 lil		
Sr	3 fod, 2 eyb, 1 eyl, 3 lis, 2 top, 1 hrc		
Zr	2 fod, 1 eyc, 4 eyb, 1 eyl	3 fod	
Nb	3 fod, 1 eyc, 3 eyb, 2 lis, 1 lil		
Ba	2 fod, 3 lis	1 fod	
Bi	1 eyb	2 eyc	1 eyb

Abbreviations: bwa: body wash; hwa: hair wash; fwa: face wash; hdy: hair dye; hco: hair conditioner; bac: base cosmetic; ncp: nose clear pack; fod: foundation; eyc: eye color; eyb: eyebrow pencil; eyl: eyeliner; mac: mascara; nco: nail cosmetic; lis: lipstick; lil: lipliner; top: toothpaste; bat: bath cosmetic; hrc: hair removal cream.

Schubert *et al.*[29] stated that costume jewelry, wristwatches and metal clothing buckles are not only the most important sources of primary nickel sensitization but also of relapses and persistence of the allergy.

Nickel is found in medicines, fungicides, nickel-plated objects, taps, coins, scissor, zippers, garter clasps, hairpins, eyelash curlers, metal frames for eyeglasses and costume jewelry. Because of its special properties, nickel is still found in dental alloys or in implants such as joint prostheses, plates and screws for fractured bones, and surgical clips.

Table 4. Number and type of household products containing each element.

Element	Intensity (cps)		
	Below 100	100-1,000	Over 1,000
Na	2 dtg, 1 blc, 1 ddr, 3 cln		
Mg	1 ddr, 1 cln, 3 wip		
Al	2 dtg, 1 blc, 2 cln		
Si	2 dtg, 1 blc, 1 mts, 1 scs, 4 cln, 1 wip, 1 clp, 1 cls	1 dtg, 1 scs, 2 cln, 1 cls	
K	2 dtg, 2 blc, 1 cln, 1 cls, 2 rug	1 scs, 1 cln, 1 brs	1 ddr
Ca	4 dtg, 1 blc, 2 ddr, 3 mts, 2 scs, 9 cln, 1 brs, 4 wip, 2 cls, 1 rug	1 rug	1 ddr, 1 blc, 1 brs, 1 clp, 1 rug
Ti	1 blc, 1 ddr, 2 scs, 1 cls, 4 cln, 1 brs, 1 wip, 1 rug	1 dtg, 1 wip, 1 cls, 2 rug	
V	1 rug		
Cr	1 mts		
Mn	2 dtg, 2 mts, 1 cln	1 mts	
Fe	2 dtg, 2 blc, 2 ddr, 1 scs, 4 cln, 4 wip, 1 brs, 1 clp, 1 rug		3 mts
Ni	1 mts		
Cu	1 dtg, 1 ddr, 1 mts, 1 cln, 1 clp, 1 wip		1 mts
Zn	1 dtg, 1 ddr, 1 wip, 1 rug,	1 clp, 2 rug	1 ddr, 1 mts
Rb	1 mts		
Sr	1 ddr, 1 blc, 1 brs, 1 clp		
Zr	2 rug		
Nb	1 mts		
Mo	1 mts		
Sn	1 cln		
Hg	1 cln		

Abbreviations: dtg: detergent; blc: bleach; ddr: deodorant; mts: metal scourer; scs: scrub scourer; cln: cleaner; brs: brush; wip: wiper; clp: cleaning pad; cls: cleaning sheet; rug: rubber glove.

Nickel is also found in kitchen utensils, e.g., cans and tins, pots and pans, electric kettles, and cutlery. Water taps, pipes, sinks and bathtubs can all contain and release nickel.[24,30] Modern formulations of consumer products, with the possible exception of mascara, contain only trace levels of nickel.[2] Current good manufacturing practice ensures that traces of nickel, cobalt and chromium concentrations in consumer

products are less than 5 ppm of each metal. It has been recommended that this amount be adopted as a standard for maximum concentrations and that the target should be to achieve concentrations as low as 1 ppm.[2,31]

A series of studies related to the safety of cosmetics for consumers were reported.[31-33] Eye shadow is a typical example of a group of cosmetic products in which the significance of pigments is great. Some toxic elements and their compounds are water-soluble, and moist skin can, therefore, promote the percutaneous absorption of elements occurring as impurities in pigments. The excipients used also affect the absorption through the skin.[2,27,31] For indeed, the frequency of administration of cosmetic formulations is generally scheduled on a daily basis, and in some instances, several cosmetic products, such as lipstick or hand cream, can be applied to the body two or more times a day. Because eyebrow pencil is a "leave-on" cosmetic product, i.e., it is applied to the body repeatedly and left on the skin for a relatively long period of time, the same problem may be expected as occurred with eye shadow and mascara. Foundation is a leave-on cosmetic product in contact with the skin up to approximately 10 hours every day. Make-up such as lip-liner and lipstick products are leave-on cosmetic products and are applied undiluted to the skin/mucosa. A low concentration of allergenic metal has the risk of eliciting a response for such long durations and large areas of exposure to skin/mucosa. Although the traces found in these consumer products will not be the primary cause of sensitization to these metals, they could be sufficient to maintain an allergy.[2] Products such as shampoo and nose cleaning packs are "wash-off" cosmetic products; since they are rapidly diluted and quickly rinsed off during use, the level of allergenic metal will be very low on the skin/mcosa. Nonetheless, in areas where the product can be trapped (ear canals, under rings), such wash-off products can cause allergies. Thus, it is important that the content labelling is shown for all cosmetic products, so that consumers can avoid the use of the products containing specific chemical(s) that they cannot tolerate. Furthermore, dermatologists and dentists can use the content labelling on cosmetic products as a guide to identify specific chemical(s) in cosmetic products that may be the cause of skin/mucosa reactions in certain people. All household products should also have this content labeling.

A large segment of the public is exposed to metal-containing compounds, potentially resulting in their unintentional absorption through the skin. Of course, both finished products and ingredients, including metal compounds, are designed to be biologically inactive and nontoxic, and are formulated to minimize their absorption. However, present knowledge of percutaneous absorption and pharmacokinetics teach that such criteria cannot be viewed in absolute terms.[27] The authors suggest when seeking a metal allergen, dermatologists and dentists must pay particular attention to both known and unknown metal objects.

CONCLUSION

In 81 cosmetic products tested in this study, 21 elements were detected. In 23 make-up cosmetic products, Fe was detected in all, and Ti and Zn were detected in 20 and 19 products, respectively. Twenty-one elements were detected in this study from 50 household products tested. These results are important for the differential diagnosis of allergic reactions as guidelines for patients being treated for

metal allergies.

ACKNOWLEDGMENT

This study was partly supported by Grant-in-Aid for Scientific Research (B)(2) No.11470419 from The Japanese Ministry of Education, Science, Sports and Culture.

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Received on October 8, 2002. Revised on November 11, 2002. Accepted on November 18, 2002.