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Migration of Copper and Some Other Metals from Copper Tableware

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Intake of heavy metals is an important problem in human health. Certain heavy metals are avoided with regard to their use for utensils or tableware coming into contact with food, although copper is widely used in food processing factories or at home. The use of copper products for the processing, cooking or serving of foods and beverages is considered to be a cause of a copper contamination. Although copper is essential element, its excess ingestion is undesirable (WHO 1973, Ochiai et al. 1985). In this study, the migration of copper from tin-plated or non-plated copperware under several experimental conditions was investigated using food-simulating solvents.

MATERIALS AND METHODS

Copper-made mugs plated on the inside with tin and coasters with unplated interiors were used for the migration test. Volume, height and diameter of the mugs were 275 ml, 82 mm and 68 mm, and those of the coaster were 210 ml, 48 mm and 81 mm, respectively. A plastic film coating the inside surface of each coaster was removed with acetone. The items of tableware, except those used for the boiling test, were filled with food-simulating solvents, water or 4(v/v)% acetic acid, up to 5 mm below the rim and each was covered with a watch-glass. In the case of the boiling test, solvent 2/3 the volume of the capacity of each item of tableware was added. Migration conditions were (a) 60°C for 30 min, (b) room temperature for 24 hr and (c) boiling for 2 hr. The amount of solvent which evaporated during boiling was replaced with the same kind of solvent after cooling. Room temperature was between 19°C and 24°C. Copper, lead and cadmium in the migration solution were determined by flameless atomic absorption spectrometry (Pharmaceutical Society of Japan 1980) using a Perkin-Elmer 403. Determination wavelength and charring and atomizing temperature and time were as follows: 324.8 nm, 1000°C for 30 sec and

Table 1. Migration of heavy metals from tableware made of tin-plated copper.

Solvent	Condition	Copper (ppb)	Lead (ppb)	Cadmium (ppb)	Tin (ppm)
Water	60°C,30min	nd	nd	nd	nd
	r.t., 24hr	nd	nd	nd	nd
	100°C, 2hr	nd	nd	nd	nd
4%acetic acid	60°C,30min	17± 3	53±15	nd	3.4±0.8
	r.t., 24hr	23±14	68± 7	nd	7.3±1.5
	100°C, 2hr	27±20	136±24	nd	9.9±1.7

nd; not detected, less than 15 ppb for copper, 20 ppb for lead, 2 ppb for cadmium and 0.1 ppm for tin: r.t.; room temperature, 19-24°C. Results are shown as mean ± S.D. (n=3).

2500°C for 5 sec for copper; 283.8 nm, 550°C for 30 sec and 2000°C for 5 sec for lead; and 228.8 nm, 400°C for 30 sec and 1500°C for 5 sec for cadmium. For the determination of tin, 20 ml of the migration solution was evaporated on a porcelain dish. The residue was dissolved with 2 ml of 6N HCl and the solution was evaporated. The residue was then dissolved in 10 ml of 1N HCl. Tin in the solution was determined by colorimetry using salicylideneamino-2-thiophenol (Pharmaceutical Society of Japan 1980). Recovery of tin by this method was 97.5% (average of two trials).

RESULTS AND DISCUSSION

There are two kinds of copperware which come into contact with food. One is plated copperware of which the inside surface is plated with a metal such as tin, silver or nickel and the other is ground copperware of which the inside surface is not plated. In the present paper, tin-plated mugs and non-plated coasters were used. No copperware of laboratory scale without plating could be found on the market. Coasters were therefore used in place of non-plated copperware coming into contact with food. Both mugs and coasters were also substituted for boiling tableware for the same reason, although their original purpose was not for boiling. The conditions applied in the migration test were typical or almost the same as those described in the Japanese Food Sanitation Law (1982) or by the International Organization for Standardization (1982a, b).

The migration of heavy metals from tin-plated ware is shown in Table 1. No detectable heavy metals migrated into water under any conditions. Copper, tin and lead were detected in the migration solution with 4% acetic

Table 2. Migration of heavy metals from tableware made of non-plated copper.

Solvent	Condition	Copper (ppm)	Lead (ppb)	Cadmium (ppb)	Tin (ppm)
Water	60°C,30min	0.6±0.1	nd	nd	nd
	r.t., 24hr	1.7±0.1	nd	nd	nd
	100°C, 2hr	1.7±0.6	nd	nd	nd
4%acetic acid	60°C,30min	18±9	nd	nd	
	r.t., 24hr	103±10	nd	nd	
	100°C, 2hr	79±17	20±0	nd	

footnote, see Table 1.

acid, but not cadmium. The highest concentration of migration in these determined metals was observed for tin, 9.9±1.7 ppm, when the plated items were treated with boiling 4% acetic acid. The migration solution with boiling 4% acetic acid became cloudy, and the surface of the plated tin lost its luster after the test. Migration of lead, 53 - 136 ppb, may have been caused by lead which was contained in tin as an impurity. The origin of copper, 17 - 27 ppb, in the migration solutions was considered to be as ground metal which migrated out through pin-holes or cracks made with 4% acetic acid.

Migration of heavy metals from non-plated copperware is shown in Table 2. When water was used as a food-simulating solvent, only copper among the 4 kinds of determined metals was detected. The migration of copper into water was 0.6 ± 0.1 ppm by standing at 60°C for 30 min, but was increased about 3 times by standing at room temperature for 24 hr or by boiling for 2 hr. These concentrations of copper in the migration solutions were almost the same levels as the copper contents of meat (Dalton 1969, Teraoka et al. 1981, Holak 1983), fish (Teraoka et al. 1981) or vegetables (Holak 1975, Teraoka et al. 1981). The maximum migration of copper with 4% acetic acid, 103 ± 10 ppm, was observed by standing at room temperature for 24 hr. In this case, the color of the rim changed to bluish green after 24 hr, but the inside surface, where contact with the solvent was maintained, kept its original copper color. When the item was treated at 100°C for 2 hr with 4% acetic acid, 20 ppb of lead was detected. Tin in the migration solution with 4% acetic acid could not be determined owing to the interference of co-existing copper in the solution. No cadmium was detected in any migration solutions obtained from tin-plated or non-plated copperware.

Odachi and Oshiba (1982) reported that the migration of copper from new pots made of tin-plated copper with water or various seasonings such as vinegar, soy sauce or soy bean paste, was less than 0.5 ppm, but that the migration of copper from old vessels was about two times higher than that from new ones. In the present results using water, no copper migrated from tin-plated ware, although about 1 ppm of copper migrated from non-plated ware. These results show that plating is effective for preventing the migration of copper. However, a vessel in which the plating is cracked may increase the migration of copper because of contact between the food and the ground metal. The conditions, 60°C for 30 min, mentioned in the Japanese Food Sanitation Law (1982) are more moderate than those, 22°C for 24 hr, specified by the International Organization for Standardization (1982a). The same tendency has been observed in the migration of heavy metals from ceramic ware, glassware or enamel ware (Inoue et al. 1984, Ishiwata et al. 1984).

REFERENCES

Dalton EF, Malanoski AJ (1969) Atomic absorption analysis of copper and lead in meat and meat products. J Assoc Off Anal Chem 52:1035-1038

Holak W (1975) Determination of heavy metals in foods by anodic stripping voltammetry after sample decomposition with sodium and potassium nitrate fusion. ibid 58:777-780

Holak W (1983) Determination of copper, nickel, and chromium in foods. ibid 66:620-624

Inoue T, Ishiwata H, Yamada T, Tanimura A (1984) Migration of lead, cadmium, arsenic and alkali from glasswares. Bull Natl Inst Hyg Sci 102:141-144

International Organization for Standardization (1982a) Glassware and glass ceramic ware in contact with food—Release of lead and cadmium. ISO 7086/1-1982

International Organization for Standardization (1982b) Ceramic cookware in contact with food—Release of lead and cadmium. ISO/TC 107/SC 6N

Ishiwata H, Inoue T, Yamada T, Tanimura A (1984) Comparative migration tests of lead and cadmium from tablewares. J Food Hyg Soc Japan 25:445-448

Japanese food sanitation law (1982) Equipment and package. Notice No 20 from the Ministry of Health and Welfare

Ochiai T, Usui A, Matsumoto K, Sekita K, Naito K, Kawasaki K, Furuya T, Tobe M (1985) Oral and chronic feeding toxicity tests on green patina: cupric carbonates, basic in rats. J Food Hyg Soc Japan 26: 605-616

Odachi J, Oshiba K (1982) Studies on copper elution after cooking with copper pots. Ann Rep Osaka City Inst Pub Health Environ Sci 45:110-114

Pharmaceutical Society of Japan (ed) (1980) Standard method of analytical hygienic chemists. Kanehara Shuppan, Tokyo, pp 2-41
Teraoka H, Morii F, Kobayashi J (1981) The concentrations of 24 elements in foodstuffs and the estimate of their daily intake. Food & Nutr. 34:221-239
WHO (1973) WHO Tec Rep Ser No 532 pp 15-19
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