Zinc, Copper, Lead and Cadmium Contents in Japanese Green Tea

By TOJIRO TSUSHIDA

Tea Technology Division, National Research Institute of Tea

There has been a remarkable increase in the interest shown to trace metal contents in various foodstuffs, since various heavy metals have been shown to be invariably present in environment and in the foodstuffs with the development of analytical methods and techniques.

Lead and cadmium have been recognized as important environmental pollutants with toxic effects on human at relatively low levels. On the other hand zinc and copper have been shown to be essential to plants and animals.

There has been a few reports on the trace metal contents in green tea and tea plants. Takeo showed the seasonal changes in manganese and copper in tea roots and also showed the contents of manganese and copper in both green and black teas by the method of neutron activation analysis[1]. As this method is not easy to use generally, the author has used the atomic absorption spectrophotometry combined with the method of extraction by means of iodide-methyl isobutyl ketone (MIBK)[2].

This paper reports the results of analyses for zinc, copper, lead and cadmium contents in 139 samples of green teas presented at the National Tea Contest in 1974 at Kagoshima. In addition, changes in the content of these four metals in tea leaves during the growth and development are shown. The cause of lead contamination in some samples is also discussed briefly.

Iodide-MIBK extraction method combined with atomic absorption spectrophotometry

In recent years the determination of metals by the combination of MIBK extraction of iodide with atomic absorption spectrophotometry has been investigated[3-5] and it was revealed that copper, lead and cadmium are almost completely extracted together by this method without an interference by the presence of significant amounts of calcium, manganese, magnesium, iron, and zinc contained in various foodstuffs. Since ammonium pyrrolidine dithiocarbamate-MIBK and Diethyl-dithiocarbamate-MIBK extraction methods which are now most widely used cannot extract these metals together and moreover these methods are affected by many other metals, it is reasonable to say that the iodide-MIBK extraction method is very useful. Therefore, the author adopted the iodide-MIBK method developed by Tsutsumi et al.[6] at the National Food Research Institute of Japan. The method used was as follows: 5 ml of saturated potassium iodide solution and 16 ml of 85% phosphoric acid were added to a 35 ml aliquot of the sample solution and metal iodides were extracted with 5 ml of MIBK. The lead, cadmium and copper contents of the organic extracts were then determined by atomic absorption spectrophotometry. On the other hand zinc content of the digested solution was directly determined by atomic absorption spectrophotometry.

Table 1. Accuracy of analysis for Zn, Cu, Pb and Cd in green tea

Six replicates of a sample	Content μg/g			
	Zn	Cu	Pb	Cd
Average value	30.2	12.0	0.81	0.043
Standard deviation	0.65	0.16	0.036	0.0019
Coefficient of variation (%)	2.2	1.3	4.4	4.4

The reproducibility of the method was investigated by analysing six replicates of a sample. Coefficient of variations of zinc, copper, lead, and cadmium were 2.2, 1.3, 4.4, and 4.4% respectively, as shown in Table 1. And when green tea (10–20 g) was ashed at 500°C in a muffle furnace, the recoveries of these four metals were between 98 and 106%.

Metal contents in Japanese green tea

Zinc, copper, lead and cadmium contents in samples of 139 green teas presented at the National Tea Contest at Kagoshima in 1974 were determined by the methods mentioned above. The range and mean of zinc, copper, lead, and cadmium were as follows: Zinc, 24.3 to 100.5, and 54.4μg/g; copper, 4.7 to 36.5, and 11.4μg/g; lead, 0.11 to 1.93, and 0.49μg/g; cadmium, 0.013 to 0.098, and 0.036μg/g (Table 2).

To make a comparison with other foodstuffs, the contents in green tea were converted into those in fresh tea leaf. The calculated mean contents of these metals in fresh tea leaf were as follows: zinc, 13.6μg/g; copper, 2.9μg/g; lead, 0.12μg/g; cadmium, 0.009μg/g. In Japan, zinc contents range from 0.2 to 2μg/g in cucumber, radish and tomato, and from 8 to 20μg/g in beans, cereals and sea weeds. Copper contents range from 0.5 to 2μg/g in cucumber, spinach and pear, and from 2 to 10μg/g in beans, cereals and sea weeds. That is to say, zinc and copper contents in tea leaf are nearly equal to those in beans, cereals and sea weeds. Lead and cadmium contents in tea leaf were also same as those in other normal, non-polluted, foodstuffs. Generally it is said that the made tea contains slightly high concentration of trace metals. But as shown in the above result, this is simply due to the concentration effect during the drying process involved in the tea manufacturing.

Significant differences in the contents of metals among tea producing districts

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Table 2. Zn, Cu, Pb and Cd contents in green tea obtained from various producing districts

Producing District	Number of samples*	Zn μg/g		Cu μg/g		Pb μg/g		Cd μg/g	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
Kagoshima	53	31.0–80.0	57.0	4.7–36.5	14.2***	0.13–0.93	0.38	0.014–0.098	0.032
Shizuoka	34	30.0–90.0	52.2	5.5–18.8	11.6	0.11–1.93	0.41	0.013–0.075	0.032
Miyazaki	9	47.3–62.8	52.4	8.6–13.5	11.8	0.22–0.58	0.43	0.015–0.076	0.031
Nara	9	35.7–100.5	57.4	4.8– 9.5	6.8***	0.27–0.54	0.41	0.020–0.089	0.035
Saitama	7	31.5–72.6	54.8	8.0–13.5	10.4	0.25–1.33	0.84***	0.027–0.044	0.032
Kyoto	7	23.8–85.5	46.7	7.5–11.6	9.6	0.25–0.86	0.63**	0.023–0.060	0.033
Fukuoka	6	38.6–74.1	54.6	11.1–19.2	13.5	0.38–0.67	0.49	0.020–0.078	0.042
Oita	5	30.7–59.5	46.0	6.6–11.7	9.7	0.12–0.49	0.30	0.033–0.053	0.041
Other places	9	33.2–81.0	55.1	9.7–15.9	12.1	0.21–0.94	0.62**	0.027–0.055	0.034
TOTAL	139	23.4–100.5	54.4	4.7–36.5	11.4	0.11–1.93	0.49	0.013–0.098	0.036

* This number is in proportion to the number presented at national tea contest in 1974 at Kagoshima.
Level of significance: **, 1%; ***, 0.1%.

copper and lead among the tea producing districts were found out. As shown in Table 2, the content of copper in green tea from Nara was of low level, whereas that from Kagoshima was of high level compared with that in the other producing districts. And also lead contents in green tea from Saitama, Kyoto and other places were relatively high. However, the level of lead content in green tea was not over the allowance value of lead (2.5 ppm) defined by the Law Concerning Control of Export Commodities (Ministries of Health and Welfare, Agriculture and Forestry, and International Trade and Industry Ordinance Notification No. 2 of 1950).

It is difficult to ascertain the reason for the inter-district differences of copper content, because copper contents of the soil in each producing districts are not reflected to that of the green tea. For example, copper contents of the soil and of the green tea of Kagoshima were about 38.5μg/g and 14.2μg/g, those in Nara were about 29.6μg/g and 6.8μg/g, and those in Saitama were about 118.4μg/g and 10.4μg/g, respectively. Since it is said that the elements-uptake from organic forms is higher than that from inorganic forms[7], the forms of copper in soil may dominantly affect the concentration of copper in tea leaf. On the other hand, the differences in lead contents may be due to atmospheric contamination by automobile exhaust gas, because lead contents in the tea producing districts near megalopolises were about two times those in other places. More detailed discussion is given in the next section.

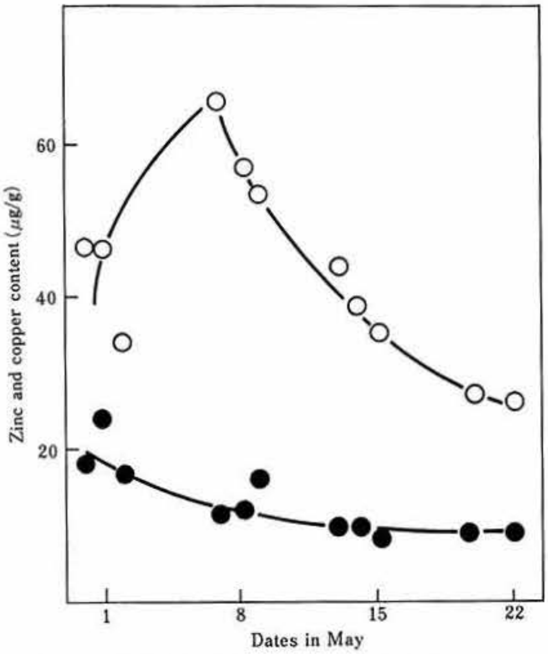

Fig. 1. Changes in contents of zinc and copper in tea shoots during growth and development (○) zinc; (●) copper.

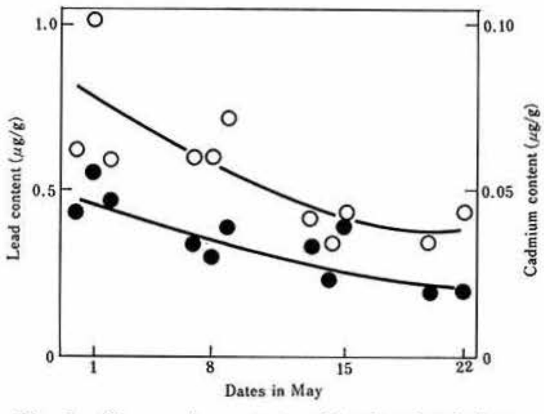

Fig. 2. Changes in contents of lead and cadmium in tea shoots during growth and development. (○) lead; (●) cadmium

Changes in metal contents with the growth and development of tea leaf

As shown in Figs. 1–2, concentrations of copper, lead, and cadmium in green tea leaves were decreased with the growth and development of leaf. Since the total content of those metals, except zinc, in a leaf was not increased during the growth of the leaf, it may be able to say that those metals were absorbed mainly during an earlier period of bud formation. On the other hand, zinc was absorbed in a longer period as compared with the other three metals. As the zinc deficiency is liable to occur in tea plants, tea plants may demand a significant amount of zinc.

The difference in concentration of zinc and

Table 3. Effect of washing on metal contents in green tea

Percentage of banjhi shoots* to the total	Lead (μg/g)			Cadmium(μg/g)	
	non-washed	washed	washed-out/non-washed	non-washed	washed
30.0	0.851	0.798	6.2 (%)	0.054	0.048
59.4	0.957	0.745	22.2	0.059	0.059
77.0	1.702	0.872	48.8	0.067	0.062
82.8	1.968	1.064	45.9	0.067	0.056

* A banjhi shoot is one with stunted bud, from which no further growth is to be expected.

copper among leaves at different position on the stem was shown by Takeo[1]. A bud and the first leaf on the stem showed the highest contents of zinc and copper, followed by the second leaf, and the oldest leaf showed the lowest contents of them. Namely, there is apparently a general trend that young leaf contains high concentration of metals.

Some samples obtained from tea producing districts near megalopolis showed high contents of lead, though not exceeding the allowance value, and the content was increased with the growth and development of tea leaf. It is said that plants do not generally absorb any substantial amounts of lead from soil. Takeo also showed that the content of lead in tea leaf was not increased, even when the lead was supplied to plant roots at about 50 ppm for ten days[8]. The increase of lead concentration with growth and development may be due to an atmospheric contamination, and the lead may be attached mainly to the surface of tea leaf.

Marletta et al. examined the relation between lead contents of grapes and the distance of grape fields from the center of road and clarified that the contamination caused by automobile exhaust gas reached 100 to 120 m away from the road, but it was virtually negligeable at 50 m from the road[9]. They showed that simple washing of grapes with water causes no significant changes in the lead contamination. On the other hand, Schuck and Locke suggested that automobile lead particulates were absorbed by strawberry but they existed as coatings, of which 50% could be removed by the simple washing. In case of tea leaf 6.3% to 48.8% of lead was washed out with water (Table 3). Although there is no green tea with the lead content exceeding the allowance value it may be desirable to wash the leaves before manufacturing to decrease the contamination when they show the lead content higher than the average value.

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