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Food Chemistry

Food Chemistry 102 (2007) 1089-1095

www.elsevier.com/locate/foodchem

Evaluation of trace element contents in canned foods marketed from Turkey

Mustafa Tuzen^{a,*}, Mustafa Soylak^b

^a Gaziosmanpasa University, Faculty of Science and Arts, Department of Chemistry, 60250 Tokat, Turkey
^b Erciyes University, Faculty of Science and Arts, Department of Chemistry, 38039 Kayseri, Turkey

Received 12 March 2006; received in revised form 27 April 2006; accepted 23 June 2006

Abstract

Trace element contents of 10 canned foods (mushroom, corn, pea, mixed vegetable, tomato, red mullet, stuffed grape leaves, pickle, bean, delicatessen) from Turkish markets were determined by flame and graphite furnace atomic absorption spectrometry after microwave digestion. The accuracy of the method was determined by use of a standard reference material (NIST SRM 1573a Tomato Leaves). The contents of investigated trace elements in canned foods were found to be in the range of $2.85-7.77 \ \mu g/g$ for copper, $8.46-21.9 \ \mu g/g$ for zinc, $6.46-18.6 \ \mu g/g$ for manganese, $27.5-79.6 \ \mu g/g$ for iron, $0.05-0.35 \ \mu g/g$ for selenium, $0.93-3.17 \ \mu g/g$ for aluminium, $0.19-0.52 \ \mu g/g$ for chromium, $0.18-0.75 \ \mu g/g$ for nickel, and $0.20-1.10 \ \mu g/g$ for cobalt. The results found were compared with those reported by scientists from various countries.

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Keywords: Trace metals; Canned food; Atomic absorption spectrometry; Turkey

1. Introduction

Due to the importance of trace elements on human metabolism, their analysis is an important part of public health studies (Arslan & Gizir, 2006; Colak, Soylak, & Turkoglu, 2005; Pourreza & Ghanemi, 2006; Tuzen, 2003). Some transition metals at trace level in our metabolism play effective roles for healthy life. Heavy metals normally occurring in nature are not harmful, because they are only present in very small amounts. However, if the levels of these metals are elevated, then they can show negative effects. The main sources of heavy metal ions are directly foods, water and indirectly industrial activities and traffic in the investigated area, etc. (Bahemuka & Mubofu, 1999; Narin, Tuzen, Sari, & Soylak, 2005; Onabanjo & Oguntona, 2003; Saracoglu et al., 2004). Metals like selenium, iron, nickel, copper, zinc and manganese are essential metals since they play an important role in biological systems, whereas aluminium, lead and cadmium are non-essential metals as they are toxic even in trace amounts (Gogoasa, Marutoiu, Gergen, Rada, & Tigae, 2005; Schroeder, 1973; Somer, 1974). The essential metals can also produce toxic effects when the metal intake is excessively elevated.

Genetic factors, soil and weather conditions, the use of fertilizers, and the state of the plant's maturity at harvest all affect the final level of trace metal components in a plant (Sanchez-Castillo et al., 1998). The ingestion of food is an obvious means of exposure to metals, not only because many metals are natural components of foodstuffs, but also because of environmental contamination and contamination during processing. Trace metal levels of various vegetable samples have been widely reported in the literature (Bahemuka & Mubofu, 1999; Ferreira, Gomes, & Chaves, 2005; Onianwa, Adeyemo, Idowu, & Ogabiela, 2001; Onianwa, Lawal, Ogunkeye, & Orejimi, 2000; Sanchez-Castillo et al., 1998; Smrkolj, Pograjc, Hlastan-Ribic, & Stibilj, 2005). However, trace metal contents in canned foods

^{*} Corresponding author. Tel.: + 90 356 252 16 16; fax: + 90 356 252 15 85.

E-mail addresses: mtuzen@gop.edu.tr, m.tuzen@gmail.com (M. Tu-zen).

^{0308-8146/\$ -} see front matter @ 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.foodchem.2006.06.048

produced in Turkey is very limited. Canned foods are a popular food source in Turkey, like other countries around world. The aim of this study was to determine the levels of trace metals in canned foods widely.

Flame atomic absorption spectrometry (FAAS) is the most widely used technique because most of the concentrations of trace metals in food samples are readily determined using this technique (Lemos, Gama, & Lima, 2006; Soylak, 1998). Lower concentrations of metal ions could be determined using graphite furnace atomic absorption spectrometry (GFAAS) (Tuzen & Soylak, 2005).

In this study, the contents of trace elements (copper, zinc, manganese, iron, selenium, aluminium, chromium, nickel and cobalt) in canned foods produced and marketed in Turkey were determined by flame and graphite furnace atomic absorption spectrometry after microwave digestion.

2. Materials and methods

2.1. Apparatus

A Perkin–Elmer Analyst 700 atomic absorption spectrometer with deuterium background corrector was used in this study. The operating parameters for working elements were set as recommended by the manufacturer. Selenium, aluminium, chromium, nickel and cobalt in canned foods were determined by HGA graphite furnace using argon as inert gas. The other elements were determined by using air-acetylene flame. Milestone Ethos D microwave closed system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

2.2. Reagents

All reagents used in the presented work were of analytical reagent grade unless otherwise stated. Double deionised water (Milli-Q Millipore 18.2 M Ω /cm conductivity) was used for all dilutions. Acids like HNO₃, H₂O₂, and HCl were of suprapur quality (E. Merck). All the plastic and glassware were cleaned by soaking in dilute HNO₃ (1 + 9) and were rinsed with distilled water prior to use. The standard solutions of analytes used for calibration were produced by diluting a stock solution of 1000 mg/l of the given element supplied by Sigma–Aldrich (St Louis, MO, USA).

2.3. Sampling

Canned foods including mushroom, corn, pea, mixed vegetable, tomato, red mullet, stuffed grape leaves, pickle, bean, delicatessen were purchased from supermarkets from Kayseri and Tokat-Turkey during 2005.

2.4. Microwave digestion

One gram of sample was digested with 6 ml of concentrated HNO_3 (65%) (Suprapure, Merck) and 2 ml of

concentrated H₂O₂ (30%) (Suprapure, Merck) in microwave digestion system and diluted to 10 ml with double deionized water (Milli-Q Millipore 18.2 MΩ/cm resistivity). A blank digest was carried out in the same way (digestion conditions for microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min, respectively).

In order to validate the microwave digestion method for accuracy and precision, NIST SRM 1573a Tomato Leaves certified reference material were analyzed for corresponding elements.

3. Results and discussion

The recovery values were nearly quantitative ($\geq 95\%$) for the microwave digestion method. The relative standard deviations were less than 10% for all investigated elements. *T*-test was used in this study (p < 0.05). The accuracy of the method was evaluated by means of trace metals determination in standard reference material (SRM). The achieved results were in good agreement with certified values. The results for this study are given in Table 1. Detection limit is defined as the concentration corresponding to three times the standard deviation of ten blanks. Detection limit values of elements as milligram per liter in flame AAS were found to be 0.013 for Cu, 0.019 for Zn, 0.011 for Fe, 0.010 for Mn. Selenium, aluminium, chromium, nickel and cobalt were below detection limit of flame AAS. These elements were determined by graphite furnace AAS using different matrix modifiers.

According to the results (Table 2), the metal contents in the samples studied depend on the analyzed species. All metal concentrations were determined on a dry weight basis. The contents of investigated trace metals in canned foods were found to be in the range of $2.85-7.77 \ \mu g/g$ for copper, $8.46-21.9 \ \mu g/g$ for zinc, $6.46-18.6 \ \mu g/g$ for manganese, $27.5-79.6 \ \mu g/g$ for iron, $0.05-0.35 \ \mu g/g$ for selenium, $0.93-3.17 \ \mu g/g$ for aluminium, $0.19-0.52 \ \mu g/g$ for chromium, $0.18-0.75 \ \mu g/g$ for nickel, and $0.20-1.10 \ \mu g/g$ for cobalt. According to these data, iron has the highest concentration and followed by zinc, manganese and copper. The lowest metal in canned foods was selenium. Generally,

Table	1								
Metal	levels	in	certified	reference	material	(NIST	SRM	1573a	tomato
leaves)	N =	4							

Element	Certified value (µg/g)	Our value $(\mu g/g)^a$	Recovery (%)
Cu	4.7	4.65 ± 0.32	99
Zn	30.9	30.3 ± 1.5	98
Mn	246	233.7 ± 10.5	95
Fe	368	353.3 ± 24.6	96
Se	0.054	0.052 ± 0.005	96
Al	598	568.1 ± 35.7	95
Cr	1.99	1.95 ± 0.17	98
Ni	1.59	1.53 ± 0.10	96
Co	0.57	0.54 ± 0.05	95

^a $P = 0.05, \pm ts/\sqrt{N}.$

Table 2 Trace metal contents of canned foods marketed from Turkey $(\mu g/g)^a$, N = 4

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Sample	Cu	Zn	Mn	Fe	Se	Al	Cr	Ni	Со
Mushroom	4.80 ± 0.21	21.9 ± 1.7	18.6 ± 1.5	79.6 ± 4.4	0.35 ± 0.02	2.86 ± 0.21	0.40 ± 0.04	0.75 ± 0.06	1.10 ± 0.10
Corn	3.52 ± 0.19	8.50 ± 0.5	7.89 ± 0.6	51.2 ± 3.6	0.15 ± 0.01	1.73 ± 0.12	0.25 ± 0.03	0.66 ± 0.05	0.32 ± 0.03
Pea	2.94 ± 0.24	11.6 ± 1.1	9.47 ± 0.7	65.1 ± 5.2	0.10 ± 0.01	1.27 ± 0.10	0.19 ± 0.02	0.55 ± 0.04	0.58 ± 0.05
Mixed vegetable	5.10 ± 0.45	15.2 ± 0.8	12.5 ± 0.9	27.9 ± 2.1	0.16 ± 0.02	3.17 ± 0.25	0.33 ± 0.03	0.38 ± 0.03	0.45 ± 0.05
Tomato	4.24 ± 0.36	10.5 ± 0.6	6.46 ± 0.5	47.7 ± 3.7	0.09 ± 0.01	1.55 ± 0.11	0.52 ± 0.04	0.18 ± 0.02	0.72 ± 0.06
Red mullet	7.62 ± 0.62	14.3 ± 1.2	11.3 ± 1.2	33.3 ± 2.7	0.14 ± 0.01	0.93 ± 0.08	0.25 ± 0.02	0.62 ± 0.05	0.62 ± 0.05
Stuffed grape leaves	5.33 ± 0.31	9.22 ± 0.6	15.6 ± 1.3	74.9 ± 6.3	0.09 ± 0.01	1.48 ± 0.12	0.32 ± 0.03	0.58 ± 0.05	0.68 ± 0.05
Pickle	2.85 ± 0.17	8.46 ± 0.7	7.52 ± 0.5	40.1 ± 3.1	0.08 ± 0.01	1.93 ± 0.15	0.50 ± 0.05	0.38 ± 0.03	0.45 ± 0.04
Bean	7.77 ± 0.57	12.8 ± 1.1	15.5 ± 1.2	31.3 ± 2.5	0.05 ± 0.01	1.42 ± 0.10	0.37 ± 0.04	0.55 ± 0.04	0.20 ± 0.02
Delicatessen	4.72 ± 0.35	16.2 ± 1.5	10.9 ± 0.9	27.5 ± 1.7	0.06 ± 0.01	1.11 ± 0.09	0.29 ± 0.02	0.41 ± 0.03	0.38 ± 0.03

^a $P = 0.05, \pm ts/\sqrt{N}.$

canned mushroom samples contained higher metal levels. Trace metal contents of canned foods and vegetables in the literature are given in Table 3.

The minimum and maximum copper values were found as 2.85 μ g/g in canned pickle and 7.77 μ g/g in canned bean samples (Fig. 1). Copper levels in vegetables have been reported in the range of 0.07–7.30 μ g/g (Onianwa et al., 2001), 4.9–9.4 μ g/g (Bahemuka & Mubofu, 1999), 0.3– 1.4 μ g/g (Sanchez-Castillo et al., 1998), 3.7–16.2 μ g/g (Gebeloglu et al., 2004), 7.6–9.6 μ g/g (Tuzen, 2003), 0.2–8.5 μ g/ g (Ferreira et al., 2005), and 0.8–5.3 μ g/g (Divrikli, Saracoglu, Soylak, & Elci, 2003). Copper is known to both vital and toxic for many biological systems and may enter the food materials from soil through mineralization by crops, food processing or environmental contamination, as in the application of agricultural inputs, such as copper-based pesticides which are in common use in farms in some countries (Onianwa et al., 2001).

The lowest and highest zinc contents were found as 8.46 μ g/g in canned pickle and 21.9 μ g/g in canned mushroom samples (Fig. 2). Zinc levels in vegetables have been reported in the range of 1.0–8.9 μ g/g (Sanchez-Castillo et al., 1998), 1.0–17.3 μ g/g (Onianwa et al., 2001), 15.9– 49.3 μ g/g (Bahemuka & Mubofu, 1999), 3.6–7.7 μ g/g (Tuzen, 2003), 5.6–23.5 μ g/g (Gebeloglu et al., 2004), and 0.3–3.4 μ g/g (Divrikli et al., 2003). Zinc is one of the most important trace metals for normal growth and development of humans. Deficiency of zinc can result from inadequate dietary intake, impaired absorption, excessive



Fig. 1. Distribution of copper in canned samples: (1) mushroom, (2) corn, (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean, and (10) delicatessen.

excretion or inherited defects in zinc metabolism (Colak et al., 2005). The FAO/WHO has set a limit for heavy metal intakes based on body weight. For an average adult (60 kg body weight), the provisional tolerable daily intake (PTDI) for iron, copper and zinc are 48, 3 and 60 mg, respectively (Joint FAO/WHO Expert Committee on Food Additives, 1999).

The level of manganese in foods may vary due to soil deficiencies. High-tech farming and lime added to soil can lower the manganese levels of certain foods. Manganese levels may also be affected by food processing. Manganese content ranged from $6.46 \,\mu\text{g/g}$ in canned tomato

Table 3 Trace metal contents of canned foods and vegetables in the literature

Element	Literature values
Cu	0.07-7.30 μg/g (Onianwa et al., 2001), 4.9-9.4 μg/g (Bahemuka & Mubofu, 1999), 0.3-1.4 μg/g (Sanchez-Castillo et al., 1998),
	3.7-16.2 µg/g (Gebeloglu et al., 2004), 7.6-9.6 µg/g (Tuzen, 2003), 0.2-8.5 µg/g (Ferreira et al., 2005), 0.8-5.3 µg/g (Divrikli et al., 2003)
Zn	1.0-8.9 μg/g (Sanchez-Castillo et al., 1998), 1.0-17.3 μg/g (Onianwa et al., 2001), 15.9-49.3 μg/g (Bahemuka & Mubofu, 1999),
	3.6-7.7 µg/g (Tuzen, 2003), 5.6-23.5 µg/g (Gebeloglu et al., 2004), 0.3-3.4 µg/g (Divrikli et al., 2003)
Mn	0.5-7.0 µg/g (Sanchez-Castillo et al., 1998), 4.2-22.3 µg/g (Gebeloglu et al., 2004), 2.5-39.4 µg/g (Divrikli et al., 2003)
Fe	9.3-76.0 μg/g (Gebeloglu et al., 2004), 4.5-9.7 μg/g (Tuzen, 2003), 40.1-261.6 μg/g (Divrikli et al., 2003)
Se	1.1-81.4 ng/g (Smrkolj et al., 2005), 1.0-3.8 µg/100 g (Murphy & Cashman, 2001), 0.1-12.7 µg/100 g (Sirichakwal et al., 2005)
Cr	0.037–0.089 μg/g (Tuzen, 2003), 0.02–0.28 μg/g (Bratakos et al., 2002), 0.011–0.456 μg/g (Lendinez et al., 2001)
Ni	0.53-3.63 μg/g (Onianwa et al., 2000), 0.028-0.80 μg/g (Dabeka & Mckenzie, 1995), 0.043-0.089 μg/g (Tuzen, 2003)
Со	0.01-0.13 µg/100 g (Sanchez-Castillo et al., 1998), 0.019-0.024 µg/g (Tuzen, 2003), 0.1-4.0 µg/g (Divrikli et al., 2003)



Fig. 2. Distribution of zinc in canned samples: (1) mushroom, (2) corn, (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean, and (10) delicatessen.

samples and $18.6 \,\mu\text{g/g}$ in canned mushroom samples (Fig. 3). Manganese levels in vegetables have been reported in the range of 0.5–7.0 $\mu\text{g/g}$ (Sanchez-Castillo et al., 1998), 4.2–22.3 $\mu\text{g/g}$ (Gebeloglu et al., 2004), and 2.5–39.4 $\mu\text{g/g}$ (Divrikli et al., 2003). The US National Academy of Sciences (1980) recommend 2.5–5 mg per day manganese and, the WHO (World Health Organization, 1994) recommend 2–9 mg per day for an adult.

It is known that adequate iron in a diet is very important for decreasing the incidence of anemia. Iron deficiency occurs when the demand for iron is high, e.g., in growth, high menstrual loss, and pregnancy, and the intake is quantitatively inadequate or contains elements that render the iron unavailable for absorption (Lynch & Baynes, 1996). Poor bioavailability is considered to be an important factor leading to iron deficiency in many countries. Iron content ranged from 27.5 μ g/g in canned delicatessen to 79.6 μ g/g in canned mushroom samples (Fig. 4). Iron levels in vegetables have been reported in the range of $9.3-76.0 \,\mu g/g$ (Gebeloglu et al., 2004), 4.5–9.7 µg/g (Tuzen, 2003), and 40.1–261.6 µg/g (Divrikli et al., 2003). The maximum iron level permitted for canned food is $15 \,\mu g/g$ according to Turkish Food Codex (Anonymous, 2002). Iron levels in analyzed canned samples were found to be higher than



Fig. 4. Distribution of iron in canned samples: (1) mushroom, (2) corn, (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean, and (10) delicatessen.

legal limits. It is predicted that high iron level is sourced from processing of raw materials.

The minimum and maximum selenium values were found as 0.05 μ g/g in canned bean samples and 0.35 μ g/g in canned mushroom samples (Fig. 5). Selenium levels in vegetables have been reported in the range of 1.1-81.4 ng/g (Smrkolj et al., 2005), 1.0–3.8 µg/100 g (Murphy & Cashman, 2001), and $0.1-12.7 \,\mu\text{g}/100 \,\text{g}$ (Sirichakwal, Puwastien, Polngam, & Kongkachuichai, 2005). Selenium content in analyzed samples was higher than the reported values from other countries. Selenium plays a protective role in preventing carcinogenesis and other chronic diseases (Dashti, Al-Awadi, AlKandari, Ali, & Al-Otaibi, 2004). There is evidence that selenium has an antioxidant role in man (Stadtman, 1990). Low concentrations of selenium can cause anomalies in organisms and high concentrations are toxic. Daily intake of selenium in Turkey has been reported as 30 µg/day (Foster & Sumar, 1997). However, selenium requirement of adults is calculated to be 70 and $55 \,\mu g/day$ for males and females, respectively (RDA, 1989). Bioavailability of selenium in food samples is affected by its chemical form and also other dietary factors such as total protein, fat and heavy metal contents.



Fig. 3. Distribution of manganese in canned samples: (1) mushroom, (2) corn, (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean and (10) delicatessen.



Fig. 5. Distribution of selenium in canned samples: (1) mushroom, (2) corn, (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean, and (10) delicatessen.

The lowest and highest aluminum contents were found as 0.93 μ g/g in canned red mullet and 3.17 μ g/g in canned mixed vegetable samples (Fig. 6). Aluminum is not considered to be an essential element in humans. Exposure of aluminum has been implicated in a number of human pathologies including encephalopathy/dialysis dementia, Parkinson disease and Alzheimer's disease (Narin, Tuzen, & Soylak, 2004). The permissible aluminum dose for an adult is quite high (60 mg per day) (World Health Organization, 1989). The main sources of aluminum for the human organism are foods and drinking water. Aluminum is present in food naturally, from its addition as food additives, and through contact with Al used in food preparation and storage (Saiyed & Yokel, 2005).

Chromium is an essential mineral to humans and has been related to carbohydrate, lipid, and protein metabolism. The recommended daily intake is 50–200 µg (RDA, 1989). Ducros (1992) considers that 0.5–2% of chromium from food is absorbed. The lowest and highest chromium contents were found as 0.19 µg/g in canned pea samples and 0.52 µg/g in canned tomato samples (Fig. 7). Chromium levels in canned foods in the literature are limited. Chromium levels in vegetable samples have been reported in the range of 0.037–0.089 µg/g (Tuzen, 2003), 0.02– 0.28 µg/g (Bratakos, Lazos, & Bratakos, 2002), and 0.011–0.456 µg/g (Lendinez, Lorenzo, Cabrera, & Lopez, 2001).

Trace amounts of nickel may be beneficial as an activator of some enzyme systems (Underwood, 1977), but its toxicity at higher levels is more prominent. It accumulates in the lungs and may cause bronchial haemorrhage or collapse. Apart from environmental contamination sources of nickel in foods, the metal may also be derived in foods from processing activities such as drying, cooking and canning in nickel-containing vessels (Onianwa et al., 2000; Underwood, 1977). The minimum and maximum nickel levels were found as $0.18 \ \mu g/g$ in canned tomato samples and $0.75 \ \mu g/g$ in canned mushroom samples (Fig. 8). Nickel levels in canned processed foods have reported in the range of $0.53-3.63 \ \mu g/g$ (Onianwa et al., 2000), 0.028-



Fig. 6. Distribution of aluminum in canned samples: (1) mushroom, (2) corn, (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean, and (10) delicatessen.



Fig. 7. Distribution of chromium in canned samples: (1) mushroom, (2) corn, (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean, and (10) delicatessen.



Fig. 8. Distribution of nickel in canned samples: (1) mushroom, (2) corn, (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean, and (10) delicatessen.

 $0.80 \ \mu g/g$ (Dabeka & Mckenzie, 1995), and $0.043-0.089 \ \mu g/g$ (Tuzen, 2003). The WHO (World Health Organization, 1994) recommends 100–300 μg nickel for daily intake. However, the amount of nickel ingested daily can reach 900 μg after consumption of foods rich in nickel (Biego, Joyeux, Hartemann, & Debry, 1998).



Fig. 9. Distribution of cobalt in canned samples: (1) mushroom, (2) corn (3) pea, (4) mixed vegetable, (5) tomato, (6) red mullet, (7) stuffed grape leaves, (8) pickle, (9) bean, and (10) delicatessen.

The lowest and highest cobalt levels were found as $0.20 \ \mu g/g$ in canned bean samples and $1.10 \ \mu g/g$ in canned mushroom samples (Fig. 9). Cobalt levels in vegetable samples have been reported in the range of $0.01-0.13 \ \mu g/100 \ g$ (Sanchez-Castillo et al., 1998), $0.019-0.024 \ \mu g/g$ (Tuzen, 2003), and $0.1-4.0 \ \mu g/g$ (Divrikli et al., 2003). Cobalt is an important trace element in nature and can be either essential or toxic for many biological systems depending on its concentration range (Underwood, 1977). Limited data exist for cobalt intake. It is reported that foods of vegetable origin represent 88% of the whole intake of dietary cobalt (Yamagata, Kurioka, & Shimizu, 1963).

The results obtained for trace metals in analyzed canned foods were acceptable for human consumption at nutritional and toxic levels. In general, the levels of trace metals in canned foods were higher than reported vegetable samples. The levels may be reduced by more careful handling practices and processing of raw materials.

Acknowledgments

The authors are grateful for the financial support of the Scientific and Technological Research Council of Turkey, TUBITAK (Project No. 104T 448).

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