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# Determination of Trace Metals in Soil, Bean and Tomato Samples Collected from Agricultural Areas Near the Motorway in Tokat, Turkey

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The concentrations of trace metals in the soil, bean and tomato samples collected from Tokat, Turkey have been determined by flame atomic absorption spectrometry after microwave digestion. Good accuracy was assured by the analysis of standard reference materials. The relative standard deviations for all measured metal concentrations were lower than 10%. Recovery values were nearly quantitative (≥ 95%). Metal accumulation factors were calculated for bean and tomato samples. The metal concentrations in samples were found to be 3.7–57.7, 1–15.3, 5.6–68.8, 4.2–517, 9.3–1020, 2.8–2890, 3356–9147, 818–4611 and 238–13956 μg/g for copper, lead, zinc, manganese, iron, sodium, potassium, calcium and magnesium, respectively.

**Key Words: Trace metal, Digestion, Soil, Bean, Tomato, Atomic absorption spectrometry.**

## INTRODUCTION

Trace metals are considered to be one of the main sources of pollution in the environment, since they have a significant effect on its ecological quality[1]. Lead, iron, copper, manganese, zinc, etc. were chosen as representative trace metals whose levels in the environment represent a reliable index of environmental pollution. Metals like iron, copper, zinc and manganese are essential metals since they play an important role in biological systems, whereas lead and cadmium are non-essential metals as they are toxic even in traces[2]. The essential metals can also produce toxic effects when the metal intake is excessively elevated.

Traffic is one of the sources of emission of trace metals such as Pb, Zn, Mn, Cu and Fe. Lead is a well known tracer of leaded gasoline and added to petrol as organic tetra-alkyl lead and ethyl-trimethyl lead. Lead is a well documented metal toxicant, exposure of which leads to many fatal diseases, including the dysfunction of renal blood and neurological systems[3]. The determination of heavy

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metal in soil samples is very important in monitoring environmental pollution[4]. Recently, both international and Turkish studies have drawn attention to the metal pollution of soil[5–7] and plant samples[8–11].

In this study, the levels of trace metals in soil, bean and tomato samples collected from Tokat, Turkey were determined by flame atomic absorption spectrometer after microwave digestion methods.

## EXPERIMENTAL

**Sampling:** Samples were collected from agricultural areas near the motorway (4 and 1200 m away) in Tokat, Turkey in 2003. The samples were dried at 105°C for 24 h. Dried samples were homogenized and stored in polyethylene bottles until analysis.

**Reagents:** All reagents were of analytical reagent grade unless otherwise stated. Double deionised water (Milli-Q Millipore 18.2 MΩ $cm^{-1}$ resistivity) was used for all dilutions. $HNO_3$, $H_2O_2$, and HCl were of supra-pure quality (E. Merck). All the plastic and glassware was cleaned by soaking in dilute $HNO_3$ (1 + 9) and rinsed with distilled water prior to use. The element standard solutions used for calibration were produced by diluting a stock solution of 1000 mg/L of the given element supplied by Sigma and Aldrich.

**Apparatus:** A Perkin-Elmer Analyst 700 atomic absorption spectrometer with deuterium background corrector was used in this study. All measurements were carried out in an air/acetylene flame. The operating parameters for working elements were set as recommended by the manufacturer. Milestone Ethos D microwave closed system (maximum pressure 1450 psi, maximum temperature 300°C was used in this study.

**Microwave Digestion:** Plant samples (1.0 g) were digested with 6 mL of $HNO_3$ (65%) and 2 mL of $H_2O_2$ (30%) in microwave digestion system and diluted to 10 mL with deionized water. A blank digest was carried out in the same way. Soil samples (0.5 g) were digested with 6 mL of $HNO_3$ (65%) and 2 mL of concentrated HCl in microwave and diluted to 10 mL. 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 method for accuracy and precision, certified reference materials (SRM 1515 Apple Leaves and SRM 2711 Montano Soil) were analyzed for corresponding elements.

## RESULTS AND DISCUSSION

The accuracy of the method was evaluated by means of trace metals determination in standard reference material (SRM). The results are shown in Table-1. The achieved results were in good agreement with certified values. The results from the analysis of SRM were all within the 95% confidence limit. The results are shown in Table-2. Metal bio-accumulation factors have been defined as metal concentration in plant/metal concentration in soils. Metal accumulation factors in bean samples were calculated as 0.15, 0.09, 0.28, 0.21, 0.05, 0.06, 0.47, 0.38 and 0.22 for Cu, Pb, Zn, Mn, Fe, Na, K, Ca and Mg, respectively. These were calculated in tomato samples as 0.27, 0.15, 0.24, 0.25, 0.05, 0.64, 0.79, 0.54 and 0.18 for Cu, Pb, Zn, Mn, Fe, Na, K, Ca and Mg, respectively (Table-3). The lowest and highest metal accumulation factors were observed in iron and potassium in all samples. Sodium accumulation was low (0.06) in bean samples, but it was high (0.64) in tomato samples.

TABLE-1
OBSERVED AND CERTIFIED VALUES (μg/g)[a] OF ELEMENTAL CONCENTRATIONS IN SRMs

| Element | SRM 2711 Montano Soi | | | SRM 1515 Apple Leaves | | |
|---|---|---|---|---|---|---|
| | Certified value | Observed value | Recovery (%) | Certified value | Observed value | Recovery (%) |
| Fe | 1.7[a] | 1.65 ± 0.12[a] | 97 | 83 | 80 ± 5 | 96 |
| Cu | 91 | 92.9 ± 4.2 | 102 | 5.64 | 5.50 ± 0.35 | 98 |
| Mn | 400 | 415 ± 16 | 104 | 54 | 52.4 ± 2.1 | 97 |
| Zn | 290 | 281 ± 12 | 97 | 12.5 | 11.9 ± 1.1 | 95 |
| Pb | 930 | 936 ± 36 | 101 | 0.470 | BDL | — |

Each value is the average of five separate digestions.
[a]Fe (%). BDL: Below detection limit.

The fact that toxic metals are present in high concentrations in plant samples is of particular importance in relation to the FAO/WHO[12] standards for Pb and Cd as toxic metals. The maximum permissible doses for an adult are 3 mg Pb and 0.5 mg Cd per week, but the recommended doses are only one-fifth of these quantities.

Lead concentrations in bean and tomato samples were found to be lower than 1 μg/g. The lowest and highest lead levels in the soil samples were in the range of 8.8–15.3 μg/g. Lead levels in roadside soils and plant samples have been reported as 89.6–272.2 and 1.1-7.3 μg/g, respectively in the literature[11]. Lead levels in green vegetables are reported in the range of 1.6–10.9 μg/g[8]. Copper levels in plant and soil samples were 3.7–16.2 and 36.2–57.7 μg/g. Zinc concentrations in plant and soil samples were 5.6–23.5 and 51.7–68.8 μg/g, respectively. In the present studies, the copper and zinc values were lower than the reported values in the literature[11]. Manganese concentrations were found 4.2–22.3 μg/g in plant samples and 389–517 μg/g in plant samples. Iron levels were found 9.3–76.0 μg/g in plant samples and 945–1027 μg/g in soil samples. Sodium levels in all samples were found to be lower than potassium, calcium and magnesium levels. Na, K, Ca and Mg levels are in agreement with those reported in the literature[10].

TABLE-2
CONCENTRATIONS OF TRACE METALS IN SOIL, BEAN AND TOMATO SAMPLES COLLECTED FROM TOKAT, TURKEY

| Sample | No | Cu | Pb | Zn | Mn | Fe | Na | K | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|---|
| Bean | 1 | 7.7 ± 0.6 | > 1 | 13.1 ± 0.6 | 22.3 ± 2.1 | 29.9 ± 2.9 | 16.5 ± 1.4 | 4109 ± 256 | 1474 ± 121 | 639 ± 12 |
| | 2 | 7.4 ± 0.5 | > 1 | 13.8 ± 0.8 | 10.2 ± 1.1 | 36.7 ± 3.3 | 2.8 ± 0.3 | 4469 ± 278 | 1691 ± 132 | 1059 ± 45 |
| | 3 | 4.8 ± 0.2 | > 1 | 11.3 ± 0.5 | 9.6 ± 0.7 | 76.0 ± 5.2 | 20.9 ± 1.7 | 4275 ± 350 | 1703 ± 97 | 550 ± 17 |
| | 4 | 8.9 ± 0.4 | > 1 | 22.1 ± 2.8 | 12.9 ± 0.8 | 41.3 ± 5.6 | 18.3 ± 1.6 | 3786 ± 187 | 1679 ± 190 | 1666 ± 76 |
| | 5 | 4.6 ± 0.1 | > 1 | 12.8 ± 1.1 | 11.2 ± 1.1 | 35.7 ± 3.9 | 13.5 ± 0.8 | 3718 ± 123 | 1166 ± 87 | 711 ± 21 |
| | 6 | 5.6 ± 0.3 | > 1 | 23.5 ± 2.2 | 9.9 ± 0.6 | 58.6 ± 4.4 | 28.8 ± 2.8 | 4180 ± 370 | 1592 ± 134 | 881 ± 59 |
| | 7 | 7.6 ± 0.8 | > 1 | 18.6 ± 1.7 | 9.7 ± 0.9 | 54.6 ± 3.7 | 16.7 ± 1.1 | 3994 ± 259 | 1234 ± 111 | 1210 ± 32 |
| Tomato | 1 | 3.7 ± 0.2 | > 1 | 5.6 ± 0.3 | 6.2 ± 0.5 | 9.3 ± 1.1 | 126 ± 7 | 4277 ± 430 | 1343 ± 145 | 245 ± 32 |
| | 2 | 7.1 ± 0.5 | > 1 | 6.8 ± 0.4 | 8.3 ± 0.7 | 31.6 ± 1.2 | 62.8 ± 5.3 | 4078 ± 223 | 818 ± 32 | 252 ± 17 |
| | 3 | 3.7 ± 0.4 | > 1 | 6.1 ± 0.8 | 4.2 ± 0.3 | 22.6 ± 1.5 | 110 ± 5 | 3540 ± 158 | 993 ± 63 | 238 ± 13 |
| | 4 | 16.2 ± 1.2 | > 1 | 9.1 ± 1.0 | 7.1 ± 0.4 | 18.9 ± 0.9 | 125 ± 6 | 3939 ± 242 | 1500 ± 104 | 432 ± 24 |
| | 5 | 5.7 ± 0.6 | > 1 | 9.9 ± 0.9 | 8.5 ± 2.9 | 25.7 ± 2.2 | 107 ± 4 | 3356 ± 121 | 1266 ± 47 | 453 ± 37 |
| | 6 | 8.7 ± 0.4 | > 1 | 11.7 ± 0.7 | 6.5 ± 0.4 | 27.3 ± 3.1 | 128 ± 9 | 4051 ± 176 | 992 ± 35 | 331 ± 36 |
| | 7 | 6.8 ± 0.6 | > 1 | 7.1 ± 0.5 | 15.8 ± 1.2 | 39.6 ± 2.8 | 127 ± 13 | 4017 ± 416 | 1218 ± 122 | 734 ± 57 |
| Soil | 1 | 36.2 ± 2.9 | 11.9 ± 0.9 | 53.8 ± 2.7 | 389 ± 27 | 969 ± 67 | 274 ± 18 | 8524 ± 765 | 4076 ± 250 | 11247 ± 380 |
| | 2 | 41.7 ± 13.6 | 12.6 ± 1.6 | 51.7 ± 4.2 | 487 ± 39 | 1020 ± 97 | 292 ± 12 | 9147 ± 876 | 4364 ± 429 | 13956 ± 835 |
| | 3 | 36.6 ± 2.4 | 8.9 ± 3.7 | 64.5 ± 5.2 | 516 ± 42 | 1010 ± 56 | 291 ± 14 | 9032 ± 756 | 4611 ± 87 | 9301 ± 245 |
| | 4 | 57.7 ± 4.7 | 12.5 ± 0.7 | 68.8 ± 5.7 | 517 ± 61 | 1027 ± 63 | 281 ± 17 | 8990 ± 344 | 4474 ± 156 | 4537 ± 211 |
| | 5 | 48.2 ± 3.4 | 12.5 ± 1.3 | 65.1 ± 4.3 | 499 ± 21 | 993 ± 86 | 2890 ± 156 | 8955 ± 689 | 2887 ± 204 | 2270 ± 193 |
| | 6 | 47.4 ± 5.8 | 15.3 ± 1.7 | 58.6 ± 3.6 | 470 ± 15 | 945 ± 25 | 275 ± 32 | 8515 ± 359 | 3799 ± 259 | 4066 ± 158 |
| | 7 | 47.6 ± 7.2 | 8.8 ± 0.9 | 53.7 ± 3.9 | 508 ± 49 | 1020 ± 104 | 232 ± 19 | 7871 ± 699 | 3602 ± 67 | 2608 ± 115 |

TABLE 3
BIO-ACCUMULATION FACTORS OF TRACE METALS FROM SOIL TO BEAN AND TOMATO, n = 5

| Sample | No | Cu | Pb | Zn | Mn | Fe | Na | K | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 0.21 | 0.08 | 0.24 | 0.41 | 0.03 | 0.06 | 0.48 | 0.36 | 0.06 |
| | 2 | 0.18 | 0.08 | 0.27 | 0.20 | 0.04 | 0.01 | 0.49 | 0.39 | 0.08 |
| Bean | 3 | 0.13 | 0.11 | 0.18 | 0.15 | 0.08 | 0.07 | 0.47 | 0.37 | 0.06 |
| | 4 | 0.15 | 0.08 | 0.32 | 0.19 | 0.04 | 0.07 | 0.42 | 0.38 | 0.37 |
| | 5 | 0.10 | 0.08 | 0.20 | 0.17 | 0.04 | 0.01 | 0.42 | 0.40 | 0.31 |
| | 6 | 0.12 | 0.07 | 0.40 | 0.17 | 0.06 | 0.11 | 0.49 | 0.42 | 0.22 |
| | 7 | 0.16 | 0.11 | 0.35 | 0.18 | 0.05 | 0.07 | 0.51 | 0.34 | 0.46 |
| Mean | | 0.15 | 0.09 | 0.28 | 0.21 | 0.05 | 0.06 | 0.47 | 0.38 | 0.22 |
| | 1 | 0.10 | 0.08 | 0.10 | 0.12 | 0.01 | 0.46 | 0.50 | 0.33 | 0.02 |
| | 2 | 0.17 | 0.08 | 0.13 | 0.16 | 0.03 | 0.22 | 0.45 | 0.19 | 0.02 |
| | 3 | 0.10 | 0.11 | 0.10 | 0.07 | 0.02 | 0.38 | 0.39 | 0.22 | 0.03 |
| Tomato | 4 | 0.28 | 0.08 | 0.13 | 0.10 | 0.02 | 0.45 | 0.44 | 0.34 | 0.10 |
| | 5 | 0.12 | 0.08 | 0.15 | 0.13 | 0.03 | 0.04 | 0.38 | 0.44 | 0.20 |
| | 6 | 0.18 | 0.07 | 0.20 | 0.11 | 0.03 | 0.47 | 0.48 | 0.26 | 0.08 |
| | 7 | 0.14 | 0.11 | 0.13 | 0.29 | 0.04 | 0.55 | 0.51 | 0.39 | 0.28 |
| Mean | | 0.27 | 0.15 | 0.24 | 0.25 | 0.05 | 0.64 | 0.79 | 0.54 | 0.18 |

## Conclusion

It was observed that the proposed method was efficient for the simple, rapid and reliable determination of trace metals in the plant and soil samples. The relative standard deviation was found to be lower than 10%. Recovery studies show that the digestion methods used in this study are satisfactory and reproducible for analysis of soil, bean and tomato samples. The trace metal levels in analyzed samples were found below the mean world-wide contents.

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## REFERENCES

1. J. Sastre, A. Sahuquillo, M. Vidal and G. Rauret, *Anal. Chim. Acta*, **462**, 59 (2002).
2. H.A. Schroeder, The Trace Elements and Nutrition, London, Faber & Faber (1973).
3. S.K. Mittal and S. Goyal, *Indian J. Environ. Prot.*, **15**, 839 (1995).
4. C.Y. Zhou, M.K. Wong, L.L. Koh and Y.C. Wee, *Environ. Monitor. Assess.*, **44**, 605 (1997).
5. M. Soylak and O. Turkoglu, *J. Trace Microprobe Tech.*, **17**, 209 (1999).
6. M. Tüzen, *Microchem. J.*, **74**, 289 (2003).
7. I. Narin, M. Soylak and M. Dogan, *Fresen. Environ. Bull.*, **6**, 749 (1997).
8. U. Divrikli, S. Saracoglu, M. Soylak and L. Elci, *Fresen. Environ. Bull.*, **12**, 1123 (2003).
9. M. Yaman, Y. Dilgin and S. G|ger, *Anal. Chim. Acta*, **410**, 119 (2000).
10. S. Shallari, C. Schwartz, A. Hasko and J.L. Morel, *Sci. Total Environ.*, **209**, 133 (1998).
11. Q.M. Jaradat and K.A. Momani, *Turkish J. Chem.*, **23**, 209 (1999).
12. FAO/ WHO, List of Maximum Levels Recommended for Contaminants by the Joint FAO/ WHO Codex, Alimentarius Commission, Second Series, CAC/ FAL, Rome, 3, 1-8 (1976).

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