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Analytical Methods

Characterization of trace metals in vegetables by graphite furnace atomic absorption spectrometry after closed vessel microwave digestion

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ABSTRACT

A simple and expeditious method for the determination of trace metals (cadmium, chromium, copper, manganese and lead) is proposed. The metals are extracted from their matrix by using nitric acid and hydrogen peroxide in a closed-vessel microwave digestion system for their subsequent detection by graphite furnace atomic absorption spectrometry (GFAAS). The sample preparation procedure facilitates the overall analytical process and enables the construction of calibration curves from inorganic standards. The ensuing method provides good linearity and sensitivity for the five metals, with limits of detection and quantization spanning the ranges 0.05–2.20 and 0.15–7.34 μg/kg, respectively. This sensitivity level is quite appropriate for the intended application. Accuracy was assessed by using a certified reference material (NCS ZC85006 Tomato), for which the proposed method provided amounts of metals consistent with their certified values. The proposed method was applied to tomato, pepper and onion, which are widely consumed in Mediterranean countries.

1. Introduction

Humans have traditionally been exposed to low concentrations of metals mainly via water and foods; some, however, are exposed to toxic concentrations via professional activities such as mining or, anecdotally, through suicidal attempts. With time, the range of potentially toxic metal sources has expanded substantially by effect of the increasing agricultural and industrial activities (Fraga, 2005). Heavy metal contamination in agricultural environments can come from atmospheric fall-out, pesticide formulations, contamination by chemical fertilizers and irrigation with water of poor quality (Marcovecchio, Botté, & Freije, 2007). A risk of contamination of the food chain may arise when heavy metals accumulate in plant tissues at concentrations above the threshold levels believed to threaten the health of humans or animals feeding on the same crops (Mantovi, Bonazzi, Maestri, & Marmiroli, 2003).

Lead, cadmium, arsenic and mercury are the metals and metalloids with the highest toxic potential among those present in foods. As such, they have elicited a response in most countries in the form of legal restrictions on their presence in foods (EEC, 2006; Järup, 2003; Reilly, 2002). Other metals including copper, iron, tin, zinc, antimony, aluminium, magnesium, manganese, molybdenum and chromium, which are present in trace amounts in the human diet, may also be the source of toxic hazards to humans under specific conditions (Ahmed, 1999).

Evidence of severe poisoning caused by some metal compounds and the proven carcinogenicity of some metal ions has fostered intensive research not only into the role of metals in food, but also into means of improving their determination (Vélez, Devesa, Súñer, & Montoro, 2004). For example, some plant species are currently widely used as bioindicators of pollution with metallic elements for environmental monitoring purposes (Marques, Queralt, Carvalho, & Bordalo, 2003). The large numbers of samples to be analysed in most cases requires simple, fast analytical procedures with adequate accuracy and precision (Wieteska, Zioek, & Drzewinska, 1996).

Many alternatives to improving the quality assurance of analytical methods for the determination of metals in food samples have been reported most of which involved digestion of sample. Wet and dry ashing are two most widely used methodologies for digesting the studied types of samples (Buckley & Ihnat, 1993; Liu, Montaser, Dolan, & Schwartz, 1996; Subramanian, 1996); however, these procedures have several drawbacks such as long sample-processing times, high costs and considerable hazards. In recent years, microwave ovens have been used for the acid digestion of many types of food samples as an effective alternative to classical digestion procedures. Thus, microwave ovens are less easily contaminated, minimise losses of volatile analytes, use small amounts of acids and shorten digestion times substantially relative to

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traditional methods (Ikem, Nwankwoala, Odueyungbo, Nyavor, & Egiebor, 2002; Smith & Arsenault, 1996; Vélez et al., 2004). Their digestion efficiency depends largely on factors such as the heating method, working pressure, and nature and volume of the acids used to dissolve the sample matrices (Anzano & Ruíz-Gil, 2005; Marguí, Queralt, Carvalho, & Hidalgo, 2005; Sapkota, Krachler, Scholz, Cheburkin, & Shotyk, 2005; Wu, Feng, & Wittmeier, 1997).

As stated above, atomic spectrometric techniques are the preferred choices for determining metals in food samples (Bacon, Linge, Parrish, & van Vaeck, 2008). Flame atomic absorption spectrometry is specially favoured on account of its selectivity, expeditiousness and fairly low operational cost. However, it is inadequately sensitive for the extremely low concentrations of heavy metal residues present in some matrices such as foods (Anzano & Ruíz-Gil, 2005). Graphite furnace atomic absorption spectroscopy (GFAAS)-method more important of electrothermal atomization in absorption spectroscopy – is an effective choice for the determination of metals in food samples (Vélez et al., 2004). In these methods, researchers use a matrix modifier such as ammonium nitrate or ammonium phosphate to facilitate volatilisation of matrix salts and removal of potential interferents such as chloride; stabilize volatile analytes such as cadmium, lead and zinc; and enable the use of increased char temperatures (Acar, 2001; Pedro, Stripekis, Bonivardi, & Tudino, 2006; Viñas, López-García, Lanzón, & Hernández-Córdoba, 1997).

In this work, we have performed an exhaustive study of the variables that affect the determination of cadmium, copper, manganese, chromium and lead in tomato, pepper and onion and certified reference material by graphite furnace atomic absorption spectroscopy. Also, the operating conditions for the microwave digestion of samples (*viz.* acid mixture, reagent volume, temperature, processing time and pressure) were optimised with a view to obtaining the best possible results in the determination of the metals at the lowest possible levels with good precision and accuracy, all in the shortest possible time and with the smallest possible reagent consumption in order to facilitate implementation of the proposed method at any food quality control laboratory.

2. Experimental

2.1. Instrumentation

A Perkin–Elmer Analyst 800 atomic absorption spectrometer (AAS) equipped with two fully integrated atomizers (*viz.* a burner system for flame atomization and a graphite furnace for electrothermal atomization), a model AS-800 autosampler and a cooling system were used. The assembly was operated from an interfaced computer running AA WinLab software. A transversely-heated graphite furnace featuring full stabilized temperature platform was used in all tests. The AAS instrument was equipped with a deuterium and longitudinal Zeeman background corrector for flame atomization and electrothermal atomization, respectively. Perkin–Elmer hollow cathode lamps were used as line sources for all analytes.

A high performance O-I-Analytical model 7295 microwave digestion apparatus was used under the operating conditions to digest samples, and a Mettler AJ100 microbalance (0.1 μg sensitivity) was employed to weigh samples.

2.2. Reagents and chemical standard

Experimental work was done with nitric acid (65 wt%), hydrogen peroxide (30 wt%, Merck, Darmstadt, Germany) and multi-element calibration standard-2A (10 μg/ml, Agilent, Palo Alto, CA). Aqueous standards were prepared by appropriate dilution of a 10 mg/l multi-element solution with ultrapure water and stored refrigerated.

Table 1
Selected lines, pretreatment and atomization temperatures for GFAAS.

Element	Wavelength (nm)	Temperature of ashing (°C)	Atomization temperature (°C)
Pb	283.3	400	1600
Cr	357.9	1500	2300
Mn	279.5	1300	1900
Cu	324.8	1200	2000
Cd	228.8	500	1600

The accuracy of the method was assessed by analysing the following certified reference material: NCS ZC85006 Tomato (China National Analysis Center for Iron & Steel 2000).

2.3. Sample treatment

The studied samples were fresh vegetables including tomatoes, onions and peppers, all of Spanish origin. An amount of *ca.* 0.5 g of previously homogenised fresh sample was accurately weighed on the microanalytical balance and processed with a mixture of 6 ml of nitric acid and 2 ml of hydrogen peroxide in the microwave digestion system. The vegetables were digested according the following program: step 1 (time: 2 min, power: 250 w), step 2 (time: 2 min, power: 0 w), step 3 (time: 6 min, power: 250 w), step 4 (time: 5 min, power: 400 w), and step 5 (time: 5 min, power: 600 w). The resulting extracts being redissolved in 10 ml of ultrapure water for subsequent analysis by GFAAS.

For the certified reference material (NCS ZC85006 Tomato), an amount of ca. 0.5 g of sample was digested in microwave as described above for vegetable samples.

2.4. Determination procedure

The solutions provided by the sample treatment and those used to construct the calibration curves, which were made in water containing 0.5% (v/v) HNO_3, were injected into the graphite furnace atomic absorption spectrometer; the temperature program and resonance lines used for measurement are shown in Table 1. A volume of sample or standard solution of 15–30 μl depending on the particular metal, which was supplied with 1 μl of 10 g/l magnesium nitrate as modifier, was used in each run.

3. Results and discussion

3.1. Effect of experimental variables

This section describes the tests conducted with a view to optimizing the variables potentially influencing the outcome of the sample treatment (microwave digestion) and the determination of the metals by GFAAS (*viz.* pyrolysis and atomization temperatures, and sample volume).

An amount of *ca.* 0.5 g of vegetable sample was subjected to the digestion treatment in the microwave oven as described in Section 2.3. The digestion reagents included various inorganic acids (hydrogen chloride acid, perchloric acid, sulphuric acid and nitric acid) and hydrogen peroxide, which were tested at variable volumes (2, 4, 6, 8 and 10 ml the acids, and 0.5, 1, 1.5, 2 and 3 ml the peroxide). Nitric acid was that providing the best digestion results for all types of samples (tomato, pepper and onion). Fig. 1A shows the variation of the concentration of each heavy metal by effect of the microwave digestion treatment of pepper sample with a variable volume of nitric acid in the presence of a fixed volume of hydrogen peroxide (2 ml) – the results for tomato and onion were

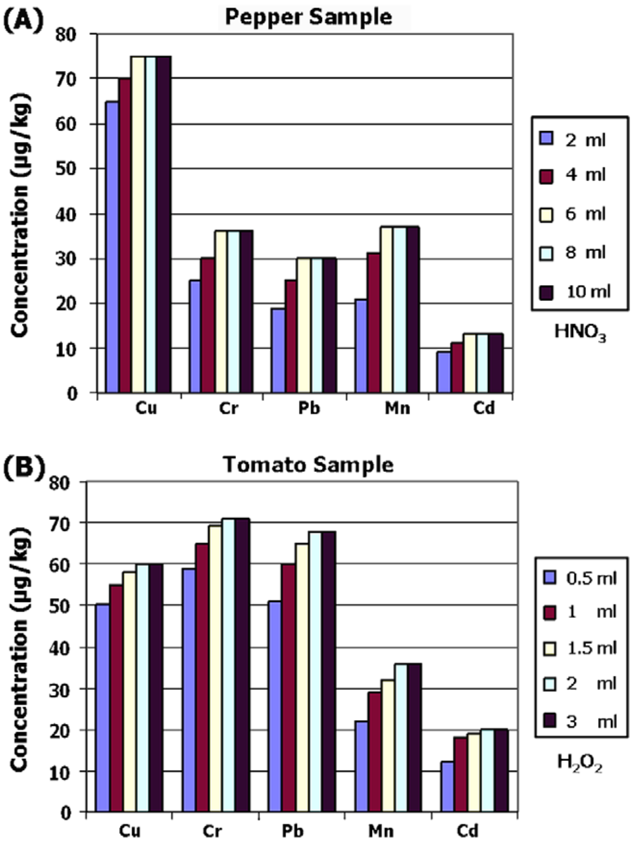

Fig. 1. Influence of the volume of nitric acid (A) and hydrogen peroxide (B) on the microwave digestion of pepper and tomato samples, respectively.

similar. Fig. 1B shows the influence of the volume of hydrogen peroxide at a constant volume of 6 ml of nitric acid on the digestion of a tomato sample – the results for pepper and onion were similar. Based on the results, the volumes of nitric acid and hydrogen peroxide should be at least 6 and 2 ml, respectively. This led us to use a mixture consisting of 6 ml HNO_3 and 2 ml H_2O_2 to digest the three types of samples.

The pyrolysis and atomization temperatures were further optimised by using curves obtained from samples that were processed as described above. Table 1 summarises the optimised temperature programs, which were also used for calibration.

The amount of sample was optimised by using volumes of 5, 10, 20, 30 and 40 µl of a 10 µg/l multi-element standard solution. The optimum volume was found to be 20 µl for Cr, Cu and Pb, 15 µl for Mn and 30 µl for Cd.

3.2. Analytical performance

As noted in the Introduction, volatilisation of the sample matrix in the graphite tube of the instrument can be facilitated by the use of a matrix modifier. The main purpose of using a modifier or modifier mixture is to stabilize volatile elements in order to use higher pyrolysis temperatures and reduce interferences with the analyte in the atomization step (Acar, 2001; Acar, Kiliç, & Türker, 1999).

We examined the effect of four different modifiers (*viz.* magnesium nitrate, ammonium nitrate, nitric acid and ammonium dihydrogen phosphate) on tomato, onion and pepper samples, and certified reference material that were previously spiked with a 10 µg/l concentration of each metal. Each modifier was used at variable concentrations from 1 to 50 g/l and in variable volumes from 0.5 to 3 µl. Magnesium nitrate was found to be the more effective modifier in order to diminish the matrix effect of the types of vegetables; 1 µl of 10 g/l magnesium nitrate was thus selected as modifier.

We also studied the effect of various species commonly accompanying the target analytes in the samples on the determination of 5 µg/kg Cd and Mn, and 10 µg/kg Cr, Cu and Pb, by adding a known amount of each potential interferent to the analyte solution. The tolerated level was taken to be the foreign species concentration causing an error not exceeding ±5% the analyte concentration. As can be seen from Table 2, the proposed method is quite tolerant of other species present in the samples. The least tolerated species were phosphate and sulphate in the determinations of Cd and Mn, and potassium in that of Mn. On the other hand, the determinations of Pb and Cr tolerated the presence of all studied interferents at concentrations more than one hundred times those of the analytes.

We used the previously optimised operating conditions to assess the performance of the proposed method (see Table 3). The method was calibrated with seven aqueous standards of the metals including a blank. The regression coefficients obtained were all greater than 0.992. In order to evaluate the precision of the method, ten independent analyses of a solution containing a 2.0 µg/l concentration for Cd and Mn, and one of 5 µg/l for Cu, Cr, and Pb, were performed. As can be seen in Table 3, the reproducibility, expressed as relative standard deviation, ranged from 2.6% to 4.2%. The limits of detection (LOD) and quantification (LOQ) were calculated as the blank signal plus three or ten times, respectively, its standard deviation (Currie, 1999). All LOQs were below the maximum residue limits (MRLs) for metals (Pb and Cd) in vegetables set by the European Community (EEC, 2006).

Accuracy of the developed method for determination of metals was verified by analysis of the certified reference material (NCS ZC85006 Tomato). This material was previously used to validate a method for the determination of heavy metals by inductively coupled plasma optical emission spectrometry and flame atomic absorption spectrometry following co-preconcentration of the metals (Feist, Mikula, Pytlakowska, Puzio, & Buhl, 2008). As can be seen in Table 4, the amounts of metals found in the reference material were consistent with the certified values.

Due to the unavailability of reference materials on the market for onion and pepper, the robustness of the method was also checked by performing a recovery test on these types of vegetables. For this purpose, each type of sample was spiked at two different concentrations (*viz.* 7 and 10 µg/kg for Cu, Cr and Pb, and 3 and 7 µg/kg for Mn and Cd) prior to processing as described above. All samples were analysed in triplicate ($n = 3$) and their standard deviations calculated. The recoveries ranged from 96% to 105%, which testifies to the applicability of the proposed method to vegetable samples.

3.3. Analysis of vegetable samples

The proposed method was applied to the determination of metals in vegetable samples (tomato, pepper and onion). Each type of

Table 2
Tolerance of interferents.

Species	Tolerated ratio [µg/l (species)/µg/l (analyte)]				
	Cd	Cr	Cu	Mn	Pb
Ca	1000	2000	500	500	2000
K	2000	2000	2000	10	1000
Na	10	1000	1000	500	1000
PO_4^{3-}	5	2000	100	5	2000
SO_4^{2-}	5	2000	10	5	2000
Fe	2000	100	500	100	2000

Table 3
Analytical figures of merit of the proposed method for the determination of metals in vegetable samples*.

Metal	*r**	LR* (μg/kg)	LOD* (μg/kg)	LOQ* (μg/kg)	RSD* (%)	MRL* (mg/kg)
Cu	0.923	7.5–100	2.20	7.34	3.7	–
Cr	0.958	5.0–80	1.33	4.43	4.2	–
Pb	0.995	3.0–80	0.81	2.69	3.4	0.10
Mn	0.989	0.5–40	0.13	0.44	3.4	–
Cd	0.952	0.2–25	0.05	0.15	2.6	0.050

* *r*, regression coefficient; LR, linear range; LOD, limit of detection; LOQ, limit of quantitation; RSD, relative standard deviation (*n* = 10); MRL, maximum residue limit (6).

Table 4
Determination of Cu, Cr, Pb, Mn and Cd (μg/g) dry mass in certified reference material NCS ZC85006 Tomato.

Metal	Certified value	Found*
Cu	21.1 ± 2.5	20.57 ± 1.8
Pb	4.97 ± 0.54	4.78 ± 0.35
Mn	87.1 ± 7.3	87.8 ± 6.6
Cd	0.82 ± 0.09	0.83 ± 0.07
Cr	Not certified	–

* (±SD, n = 3).

Table 5
Analytical application of proposed method to vegetable samples.

Metal	Tomato Found* (μg/kg)	Pepper Found* (μg/kg)	Onion Found* (μg/kg)
Cu	78.8 ± 5.1	75.9 ± 6.9	75.1 ± 2.7
	33.3 ± 1.4	40.9 ± 3.5	75.7 ± 3.0
	59.5 ± 3.2	81.7 ± 2.5	80.9 ± 4.0
Cr	52.9 ± 3.0	35.2 ± 0.9	23.9 ± 0.8
	19.4 ± 0.8	36.9 ± 2.4	25.1 ± 1.0
	71.6 ± 2.1	69.1 ± 4.1	27.7 ± 2.1
Pb	30.3 ± 1.4	29.1 ± 0.8	59.6 ± 0.6
	34.5 ± 0.5	18.1 ± 1.0	12.2 ± 0.9
	67.7 ± 3.6	70.6 ± 4.1	40.6 ± 1.5
Mn	31.9 ± 2.3	34.7 ± 0.8	27.3 ± 0.4
	22.3 ± 1.1	37.8 ± 1.4	26.8 ± 1.5
	35.8 ± 4.8	34.5 ± 0.9	22.9 ± 0.7
Cd	14.2 ± 0.8	11.8 ± 0.7	12.1 ± 0.7
	13.4 ± 0.4	12.7 ± 0.8	13.2 ± 0.6
	19.9 ± 0.6	15.0 ± 1.1	10.7 ± 0.4

* (*n* = 3, ±SD).

vegetable was analysed in triplicate in three different samples. As can be seen from Table 5, all samples contained the five analytes. Copper was present at higher concentrations (33.3–78.8 μg/kg) and Cd at lower concentrations (13.4–19.9 μg/kg) in the tomato samples. Also, the Mn and Cu concentrations in these samples were lower than those previously found in tomatoes of Spanish (0.24–0.53 mg Mn/kg and 0.27–1.39 mg Cu/kg) and Turkish origin (6.46 mg Mn/kg and 4.24 mg Cu/kg, respectively) (Paredes, Prats, Maestre, & Todolí, 2008; Tuzen & Soylak, 2007). Tuzen and Soylak (2007) found Cr concentrations in tomatoes 0.52 μg/g higher than those obtained with the proposed method (19.4–71.6 μg/kg). On the other hand, the Cd and Pb concentrations in onions provided by the proposed method exceeded those found by Oymak, Tokalioglu, Yilmaz, Kartal and Aydin (2009) (6–7 and 1.59–2.76 μg/kg, respectively) in Turkish onions. Finally, the Cu concentrations in pepper obtained with the proponed method, 40.9–81.7 μg/kg, were higher than those previously found by other authors (Karve & Rajgor, 2007) in black pepper: 22.7 μg/kg.

4. Conclusions

The proposed method, based on the closed-vessel microwave digestion of vegetable samples in a mixture of nitric acid and hydrogen peroxide, allows the determination of trace elements by graphite furnace atomic absorption spectrometry. The method affords the determination of the metals at the microgram-per-gram level in samples of tomato, pepper and onion, and certified reference material, with LODs ranging from 0.05 to 2.20 μg/kg; therefore, it surpasses existing alternatives for the determination of these metals in such complex matrices in sensitivity. For example, Wu et al. determined the metals in plants and grain by ICP–MS, using various mixtures of acids for microwave digestion, and obtained LODs of 0.01–0.05 mg/kg [Feng, Wu, Wharmby, & Wittmeier, 1999; Wu et al., 1997]. Also, the proposed method is quite selective and is only interfered with by the presence of phosphate or sulphate at concentrations at least five times higher than those of Cd and Mn in their determinations. Based on the results for the tomato, pepper and onion samples, all contained the five studied metals. Also, Cu and Cd were the individual metals present in the largest (33.3–81.7 μg/kg) and smallest (10.7–19.9 μg/kg) amounts, respectively. Finally, the concentrations of Cd and Pb were all below their legally established MRLs (EEC, 2006).

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References

Acar, O. (2001). Determination of cadmium and lead in biological samples by Zeeman ETAAS using various chemical modifiers. *Talanta, 55*(3), 613–622.

Acar, O., Kiliç, Z., & Türker, A. R. (1999). Determination of bismuth, indium and lead in geological and sea-water samples by electrothermal atomic absorption spectrometry with nickel-containing chemical modifiers. *Analytica Chimica Acta, 382*(3), 329–338.

Ahmed, F. E. (1999). Trace metal contaminants in food. In C. F. Moffat & K. J. Whittle (Eds.), *Environmental contaminants in food* (pp. 146–214). Sheffield: CRC Press.

Anzano, J. M., & Ruíz-Gil, M. (2005). Comparison of microwave acid digestion with the wet digestion and ashing methods for the determination of Fe, Mn, and Zn in food samples by flame AAS. *Atomic Spectroscopy, 26*(1), 28–33.

Bacon, J. R., Linge, K. L., Parrish, R. R., & van Vaeck, L. (2008). Atomic spectrometry update. Atomic mass spectrometry. *Journal of Analytical Atomic Spectrometry, 23*(8), 1130–1162.

Buckley, W. T., & Ihnat, M. (1993). Determination of copper, molybdenum and selenium in biological reference materials by inductively coupled plasma mass spectrometry. *Fresenius' Journal of Analytical Chemistry, 345*(2–4), 217–220.

Currie, L. A. (1999). Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC Recommendations 1995). *Analytica Chimica Acta, 391*(2), 105–126.

EEC, Economic European Communities. (2006). Setting maximum levels for certain contaminants in foodstuffs. *Official Journal European Communities*, L 364/5-L 364/24, Directive No. 1881/2006, Brussels.

Feist, B., Mikula, B., Pytlakowska, K., Puzio, B., & Buhl, F. (2008). Determination of heavy metals by ICP–OES and F-AAS after preconcentration with 2,2'-bipyridyl and erythrosine. *Journal of Hazardous Materials, 152*(3), 1122–1129.

Feng, X., Wu, S., Wharmby, A., & Wittmeier, A. (1999). Microwave digestion of plant and grain standard reference materials in nitric and hydrofluoric acids for multi-elemental determination by inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry, 14*(6), 939–946.

Fraga, C. G. (2005). Relevance, essentiality and toxicity of trace elements in human health. *Molecular Aspects of Medicine, 26*(4–5), 235–244.

Ikem, A., Nwankwoala, A., Odueyungbo, S., Nyavor, K., & Egiebor, N. (2002). Levels of 26 elements in infant formula from USA, UK, and Nigeria by microwave digestion and ICP–OES. *Food Chemistry, 77*(4), 439–447.

Järup, L. (2003). Hazards of heavy metal contamination. *British Medical Bulletin, 68*, 67–182.

Karve, M., & Rajgor, R. V. (2007). Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Cyanex302 and determination by flame atomic absorption spectrometry. *Journal of Hazardous Materials, 141*(3), 607–613.

Liu, H., Montaser, A., Dolan, S. P., & Schwartz, R. S. (1996). Evaluation of a low sample consumption, high-efficiency nebulizer for elemental analysis of biological samples using inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry, 11*(4), 307–311.

Mantovi, P., Bonazzi, G., Maestri, E., & Marmiroli, N. (2003). Accumulation of copper and zinc from liquid manure in agricultural soils and crop plants. *Plant and Soil, 250*(2), 249–257.

Marcovecchio, J. E., Botté, S. E., & Freije, R. H. (2007). Heavy metals, major metals, trace elements. In L. M. L. Nollet (Ed.), *Handbook of water analysis* (2nd ed., pp. 275–311). Boca Raton: CRC Press.

Marguí, E., Queralt, I., Carvalho, M. L., & Hidalgo, M. (2005). Comparison of EDXRF and ICP–OES after microwave digestion for element determination in plant specimens from an abandoned mining area. *Analytica Chimica Acta, 549*(1–2), 197–204.

Marques, A. F., Queralt, I., Carvalho, M. L., & Bordalo, M. (2003). Total reflection X-ray fluorescence and energy-dispersive X-ray fluorescence analysis of runoff water and vegetation from abandoned mining of Pb–Zn ores. *Spectrochimica Acta Part B, 58*(12), 2191–2198.

Oymak, T., Tokalioglu, S., Yilmaz, V., Kartal, S., & Aydin, D. (2009). Determination of lead and cadmium in food samples by the coprecipitation method. *Food Chemistry, 113*(4), 1314–1317.

Paredes, E., Prats, M. S., Maestre, S. E., & Todolí, J. L. (2008). Rapid analytical method for the determination of organic and inorganic species in tomato samples through HPLC-IC-AES coupling. *Food Chemistry, 111*(2), 468–475.

Pedro, J., Stripekis, J., Bonivardi, A., & Tudino, M. (2006). Thermal stabilization of tellurium in mineral acid solutions: Use of permanent modifiers for its determination in sulfur by GFAAS. *Talanta, 69*(1), 199–203.

Reilly, C. (2002). Metals in food. In C. Reilly (Ed.), *Metal contamination of food: Its significance for food quality and human health* (3rd ed., pp. 12–22). Oxford: Blackwell.

Sapkota, A., Krachler, M., Scholz, C., Cheburkin, A. K., & Shotyk, W. (2005). Analytical procedures for the determination of selected major (Al, Ca, Fe, K, Mg, Na, and Ti) and trace (Li, Mn, Sr, and Zn) elements in peat and plant samples using inductively coupled plasma-optical emission spectrometry. *Analytica Chimica Acta, 540*(2), 247–256.

Smith, F. E., & Arsenault, E. A. (1996). Microwave-assisted sample preparation in analytical chemistry. *Talanta, 43*(8), 1207–1268.

Subramanian, K. (1996). Determination of metals in biofluids and tissues: Sample preparation methods for atomic spectroscopic techniques. *Spectrochimica Acta Part B, 51*(3), 291–319.

Tuzen, M., & Soylak, M. (2007). Evaluation of trace element contents in canned food marketed from Turkey. *Food Chemistry, 102*(4), 1089–1095.

Vélez, D., Devesa, V., Súñer, M. A., & Montoro, R. (2004). Metal contamination in food. In L. M. L. Nollet (Ed.), *Handbook of food analysis* (2nd ed., pp. 1485–1511). New York: Marcel Dekker.

Viñas, P., López-García, I., Lanzón, M., & Hernández-Córdoba, M. (1997). Direct determination of lead, cadmium, zinc, and copper in honey by electrothermal atomic absorption spectrometry using hydrogen peroxide as a matrix modifier. *Journal of Agricultural and Food Chemistry, 45*(10), 3952–3956.

Wieteska, E., Zioek, A., & Drzewinska, A. (1996). Extraction as a method for preparation of vegetable samples for the determination of trace metals by atomic absorption spectrometry. *Analytica Chimica Acta, 330*(2–3), 251–257.

Wu, S., Feng, X., & Wittmeier, A. (1997). Microwave digestion of plant and grain reference materials in nitric acid or a mixture of nitric acid and hydrogen peroxide for the determination of multi-elements by inductively coupled plasma mass spectrometry. *Journal of Analytical Atomic Spectrometry, 12*(8), 797–806.