

Elemental Analysis of Coffee: a Comparison of ICP-MS and AAS Methods

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Abstract

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We determined the mineral nutrients and toxic elements (Ca, Cu, Fe, Mg, Zn, Cd, Cr, Mn, Ni, and Pb) in five types of coffee by atomic absorption spectrometry and inductively coupled plasma mass spectrometry. The decomposition of the samples took place in a microwave digestion system with HNO₃ and H₂O₂ reagents. Partial validation of the method was performed by using the certified reference material (NCS ZC 73014). Univariate and multivariate statistical methods were used to compare both the coffee samples and the techniques used. No significant differences were found between two used methods. Significant differences occurred between the coffee samples but only the application of multivariate statistics helps to distinguish among samples from different locations.

Keywords: coffea Arabica; atomic absorption spectrometry; inductively coupled plasma mass spectrometry metals; univariate statistics; multivariate statistics

Coffee is one of the most important agricultural products in the international business. Coffee, in terms of international trade, is the second product in value which, putting into motion approximately US\$ 35 billion per year and is comparable only to petroleum. The determination of mineral nutrients and toxic elements that are contained in it is of great interest due to its large consumption by millions of people around the world (DOS SANTOS & DE OLIVEIRA 2001).

Nowadays, many people are interested in healthy food. The analysis of individual components of raw and processed products is necessary in the food industry mainly to control the food safety (SÁDECKÁ & POLONSKÝ 1999). At present, essential and toxic metals in food and beverages are qualitatively and quantitatively studied by using mainly atomic absorption spectrometry (AAS) (DOS SANTOS *et al.* 2009; JALBANI *et al.* 2010; KAZI *et al.* 2010), inductively coupled plasma mass spectrometry (ICP-MS) (ROY-CHOWDHURY *et al.* 2003; NARDI *et al.* 2009; KAŇA

2010) and inductively coupled plasma optical emission spectrometry (LARA *et al.* 2005; OLESZCZUK *et al.* 2007; SANTOS *et al.* 2008). Other techniques include X-ray fluorescence spectrometry (JASTRZEBSKA *et al.* 2003), electromigration techniques (SADECKA & POLONSKY 1999; SZLYK *et al.* 2004), and some electrochemical techniques (KARADJOVA *et al.* 2000; ABBASI *et al.* 2010; ALGHAMDI 2010).

The objective of the articles mentioned was mainly the analysis of mineral nutrients and toxic elements in order to verify the quality of coffee and to determine its origin (DOS SANTOS *et al.* 2001; OLESZCZUK *et al.* 2007). The aim of this work was to compare ICP-MS and AAS for the determination of mineral nutrients and toxic elements (Ca, Cu, Fe, Mg, Zn, Cd, Cr, Mn, Ni, and Pb) in five types of coffee. Both methods were compared not only by the method performance criteria but also by the economic criteria and time-consumption of analysis. This article also presents the possibilities of applying univariate and multivariate statistics.

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MATERIAL AND METHODS

Apparatus. The material under study was digested in diffused microwave system (MLS 1200 Mega; Milestone S.r.L., Sorisole, Italy) using polytetrafluoroethylene digestion vessels.

An ICP-MS spectrometer (Agilent 7700x; Agilent Technologies, Tokyo, Japan) based on quadrupole mass analyser and octapole reaction system (ORS 3) equipped with concentric nebuliser and Ni cones served for quantitative analysis of all elements. The operating conditions of ICP-MS are shown in Table 1.

Table 1. ICP-MS conditions

Parameter	Value
RF power (W)	1550
Sampling depth (mm)	8
Cool gas flow rate (l/min)	14.95
Auxiliary gas flow rate (l/min)	0.9
Nebulizer gas flow rate (l/min)	1.09
He flow rate (ml/min)	4.3
Energy discrimination voltage (V)	5
Nebulizer pump speed (rps)	0.1
Chamber temperature	2°C

Two measuring modes were used for the determination. The isotopes ^{24}Mg , ^{44}Ca , ^{52}Cr , ^{55}Mn , ^{66}Zn , ^{111}Cd , and ^{208}Pb were selected as analytical masses in ICP-MS standard mode (no-gas) and ^{56}Fe , ^{60}Ni , ^{63}Cu were analysed by using ORS 3 through which helium was flowing as collision gas (purity 5.5; SIAD, Prague, Czech Republic). The torch position, lens settings, and voltage on the electron multiplier were optimised to reach the maximum signal intensity and stability while aspirating the tuning solution that contained 1 µg/l of Li, Y, and Tl (Agilent Technologies, Santa Clara, USA), the typical signal intensities achieving approximately 62 200, 183 000, and 156 000 counts per second, respectively.

Table 2. Temperature program parameters

Stages of temperature program	Temperature (°C)	Ramp time (s)	Hold time (s)	Gas
Drying	90	5	5	Ar
Sample injection				
Drying	120	5	15	Ar
Ashing	700 ^c /800 ^a /900 ^{b,d} /1100 ^e	10	15	Ar
Ashing	700 ^c /800 ^a /900 ^{b,d} /1100 ^e	0	1	-
Atomization	1600 ^a /2000 ^b /2200 ^c /2400 ^d /2500 ^e	0.8 ^{a,b} /1 ^{c,d,e}	1 ^{a,b} /1.2 ^{c,d,e}	-
Cleaning	2650	1	3	Ar

^acadmium; ^blead; ^cmanganese; ^dnickel; ^echromium

A double beam AAS spectrometer (Avanta Σ; GBC, Braeside, Australia) equipped with flame and electrothermal atomisation (graphite furnace atomiser GF 3000 with auto sampler PAL 3000) was used for the determination of all metals studied. Hollow cathode lamps (Photron, Narre Warren, Australia) were used as sources of radiation and the background correction was provided by a deuterium lamp. Ca, Cu, Fe, Mg, and Zn were determined by the flame atomisation technique with an acetylene-air flame. The addition of the releasing agent LaCl_3 (25 g/l; Analytika Ltd., Prague, Czech Republic) diluted to 2.5 g/l was used to remove the non-spectral interferences of Ca. The determination of Cd, Cr, Mn, Ni, and Pb was carried out by electrothermal atomisation in a graphite furnace (Z-tek, Roodkaje, Netherlands). The matrix modifier, mixture in the ration 2 : 1 of $\text{Mg}(\text{NO}_3)_2$ (1 g/l) and $\text{Pd}(\text{NO}_3)_2$ (2 g/l) (both Analytika Ltd., Prague, Czech Republic) was used for Cd and Pb determination. A volume of 5 µl of the matrix modifier was injected into the graphite furnace together with 20 µl of sample. The temperature programs for electrothermal atomisation are described in Table 2.

The statistical software QC-Expert 3.2 (Trilobyte Ltd., Staré Hradiště u Pardubic, Czech Republic) was used for the univariate analysis (descriptive statistics, hypothesis testing, and analysis of variance) and principal component analysis, and NCSS 2007 (NCSS LLC, East Kaysville, USA) was used for the cluster analysis.

Reagents. The calibration solutions were prepared by diluting the single element certified reference materials with 1.000 ± 0.002 g/l for each element (Analytika Ltd., Prague, Czech Republic) with deionised water (18.2 MW·cm, Direct-Q; Millipore, Molsheim, France). The internal standard for ICP-MS was prepared by diluting the commercially available ICP-INT-MIX1 (Analytika Ltd., Prague,

Table 3. Values of limit of detection (LOD), precision and uncertainty

	LOD (mg/kg)		Precision (%)		Relative uncertainty (%)	
	ICP-MS	AAS	ICP-MS	AAS	ICP-MS	AAS
Ca	0.055	1.75	3.01	3.38	6.22	7.20
Cu	0.018	2.25	2.29	3.93	6.87	11.37
Fe	0.082	13.75	3.39	4.99	7.91	24.78
Mg	0.063	2.75	2.97	4.87	5.51	8.73
Zn	0.058	1.38	2.85	4.14	6.11	10.03
Cd	0.003	0.01	7.68	12.06	17.01	25.67
Cr	0.010	0.16	3.49	11.90	13.82	33.70
Mn	0.004	0.04	2.61	5.83	6.28	13.15
Ni	0.013	0.17	5.70	12.44	15.64	28.50
Pb	0.003	1.03	5.41	10.87	16.53	34.07

Czech Republic) which contains Bi, In, Sc, Tb, and Y, to the concentration of 100 µg/l.

Samples and reference material. Five coffee samples (*Coffea Arabica* L.) coming from India, Kenya, Honduras, Colombia, and Ethiopia were obtained from local coffee shops and from each sample 6 sub-samples were taken for analysis. The certified reference material NCS ZC 73014 Tea (China National Analysis Centre for Iron & Steel, Beijing, China) was used for method validation.

Sample preparation. The samples (about 0.2 g) were weighed using an analytical balance into polytetrafluoroethylene vessels and 3 ml of HNO₃ (67%, analpure) and 1 ml of H₂O₂ (30%, analytical grade) (both Analytika Ltd., Prague, Czech Republic) were added. The time program used was as follows: 2 min at 250 W, 2 min at 0 W, 5 min using 400 W, 2 min at 0 W, 2 min at 400 W and finally 7 min using 600 W. After the digestion, each solution was diluted to 25 ml in a volumetric flask with deionised water and then the analytes were determined by AAS and ICP-MS.

RESULTS AND DISCUSSION

Method validation. Both methods were partially validated by the following parameters:

– The limit of detection (LOD) was calculated by Kaiser's approach (PRICE 1979). LODs (Table 3) are about two orders of magnitude better for ICP-MS than for AAS. The higher value of LOD for Pb determined by AAS is ascribed to a low stability of radiation coming from the hollow cathode lamp at the wavelength used.

– Linearity was tested by the observation of the calibration curves and statistical testing of the correlation coefficients for linear and polynomial dependence (MELOUN & MILITKY 2011). The linearity for AAS was above two orders of magnitude and for ICP-MS five orders of magnitude.

– The intermediate precision was evaluated as the relative standard deviation from 34 (the number obtained by CRM analysis during the development and measuring) repeated measurements of CRM

Table 4. Analysis of CRM for elements determination (mg/kg), expressed as mean value ± standard deviation

Element	Found values by ICP-MS	Found values by AAS	Certified values
Ca	$(3.26 \pm 0.10) \times 10^3$	$(3.27 \pm 0.11) \times 10^3$	$(3.26 \pm 0.04) \times 10^3$
Mg	$(1.86 \pm 0.06) \times 10^3$	$(1.85 \pm 0.09) \times 10^3$	$(1.86 \pm 0.06) \times 10^3$
Fe	241 ± 8	241 ± 12	242 ± 9
Cu	18.4 ± 0.4	18.7 ± 0.7	18.6 ± 0.4
Zn	51.1 ± 1.5	49.8 ± 2.1	51 ± 1
Cd	0.064 ± 0.005	0.062 ± 0.002	0.062 ± 0.002
Cr	0.44 ± 0.02	0.47 ± 0.06	0.45 ± 0.05
Mn	507 ± 13	502 ± 29	500 ± 10
Ni	3.3 ± 0.2	3.6 ± 0.5	3.4 ± 0.2
Pb	1.6 ± 0.1	1.6 ± 0.2	1.5 ± 0.1

Table 5. Mineral and toxic elements (mg/kg) present in coffee

Elements		India	Kenya	Colombia	Honduras	Ethiopia
Ca ($\times 10^3$)	ICP-MS	0.79 \pm 0.09	0.77 \pm 0.05	1.08 \pm 0.02	0.53 \pm 0.04	0.80 \pm 0.04
	AAS	0.73 \pm 0.09	0.76 \pm 0.06	1.06 \pm 0.25	0.53 \pm 0.10	0.80 \pm 0.06
Mg ($\times 10^3$)	ICP-MS	2.09 \pm 0.09	2.18 \pm 0.09	1.78 \pm 0.09	1.93 \pm 0.05	2.05 \pm 0.08
	AAS	2.19 \pm 0.13	2.29 \pm 0.20	1.75 \pm 0.40	1.96 \pm 0.09	2.07 \pm 0.13
Fe	ICP-MS	47.75 \pm 3.39	35.19 \pm 1.11	23.91 \pm 2.87	45.93 \pm 3.27	34.44 \pm 2.25
	AAS	46.78 \pm 4.86	35.98 \pm 5.94	23.38 \pm 7.24	45.70 \pm 0.97	34.06 \pm 4.88
Cu	ICP-MS	17.59 \pm 0.95	19.25 \pm 0.77	17.47 \pm 0.87	16.61 \pm 0.52	17.64 \pm 1.25
	AAS	17.66 \pm 1.42	19.37 \pm 1.38	17.63 \pm 1.41	16.51 \pm 1.74	17.99 \pm 2.15
Zn	ICP-MS	7.12 \pm 0.64	1.71 \pm 0.09	6.07 \pm 0.85	4.54 \pm 0.27	4.63 \pm 0.13
	AAS	7.04 \pm 1.62	1.72 \pm 1.27	6.12 \pm 1.02	4.44 \pm 0.61	4.66 \pm 1.00
Cd	ICP-MS	0.04 \pm 0.01	0.01 \pm 0.001	0.05 \pm 0.01	0.05 \pm 0.004	0.04 \pm 0.01
	AAS	0.04 \pm 0.02	0.01 \pm 0.002	<LOD	0.05 \pm 0.01	0.04 \pm 0.01
Cr	ICP-MS	0.85 \pm 0.03	0.72 \pm 0.07	0.02 \pm 0.002	0.29 \pm 0.03	0.28 \pm 0.01
	AAS	0.89 \pm 0.14	0.70 \pm 0.12	< LOD	0.29 \pm 0.07	0.29 \pm 0.09
Mn	ICP-MS	108.52 \pm 11.89	123.38 \pm 9.16	52.19 \pm 1.75	114.59 \pm 7.52	27.32 \pm 1.80
	AAS	109.19 \pm 10.06	124.17 \pm 14.43	52.40 \pm 1.70	111.29 \pm 17.75	27.94 \pm 4.59
Ni	ICP-MS	3.69 \pm 0.56	1.63 \pm 0.11	0.07 \pm 0.02	0.58 \pm 0.02	0.46 \pm 0.02
	AAS	3.64 \pm 0.86	1.66 \pm 0.69	< LOD	0.59 \pm 0.14	0.47 \pm 0.15
Pb	ICP-MS	0.03 \pm 0.01	0.02 \pm 0.01	0.005 \pm 0.002	0.03 \pm 0.004	< LOD
	AAS	< LOD	< LOD	< LOD	< LOD	< LOD

LOD – limit of detection

for all elements. The results are summarised in Table 3 and they are satisfactory both as for flame and electrothermal atomisation in AAS and for ICP-MS.

– Uncertainty was calculated from the analysis of CRM according to NORDTEST Technical Report 537 (MAGNUSON *et al.* 2004) and expressed as expanded uncertainty U with coverage factor $k = 2$. The higher uncertainty for the elements determined by electrothermal atomisation in AAS was caused by the poorer repeatability of this technique.

– Trueness was tested by the evaluation of the results from the repeated analysis ($n = 34$) of CRM. The measured concentrations of all elements were inside the expanded uncertainties of the certified values of CRM as can be seen in Table 4.

Comparison of samples and methods. The results obtained for mineral nutrients and toxic elements expressed as the mean and standard deviations of six replicates are presented in Table 5. The concentrations of all studied elements from ICP-MS and AAS determinations were compared using Student's t -test ($P = 0.05$), no significant differences between the methods having been found.

Considering the time consumption when analysing 10 elements in 25 samples, we can come to the

conclusion that ICP-MS analysis is five times faster than AAS method. The time for the sample preparation is the same for both methods but the analysis on AAS (both flame and electrothermal atomisation) takes approximately 15 h while that on ICP-MS takes approximately 3 hours.

The economic aspects are nowadays of great importance. In this work, we compared the running costs of the analysis of 10 elements in 25 samples. The price of the calibration solutions and reagents (matrix modifiers + releasing agents for AAS; and internal standards and tuning solutions for ICP-MS) is the same. The consumption of Ar is similar, in both methods. AAS needs graphite tubes and acetylene (for flame atomisation), on the other hand high purity helium is needed for ICP-MS. In conclusion, the running costs for AAS are slightly higher than those for ICP-MS.

Statistical analysis. The application of univariate and multivariate statistical methods to the results obtained is shown. Using the descriptive statistics was the first step. We obtained and compared different mean values (arithmetic mean, median, pivot half sum from the order statistics procedure introduced by Horn (MELOUN & MILITKY 2011)). The assump-

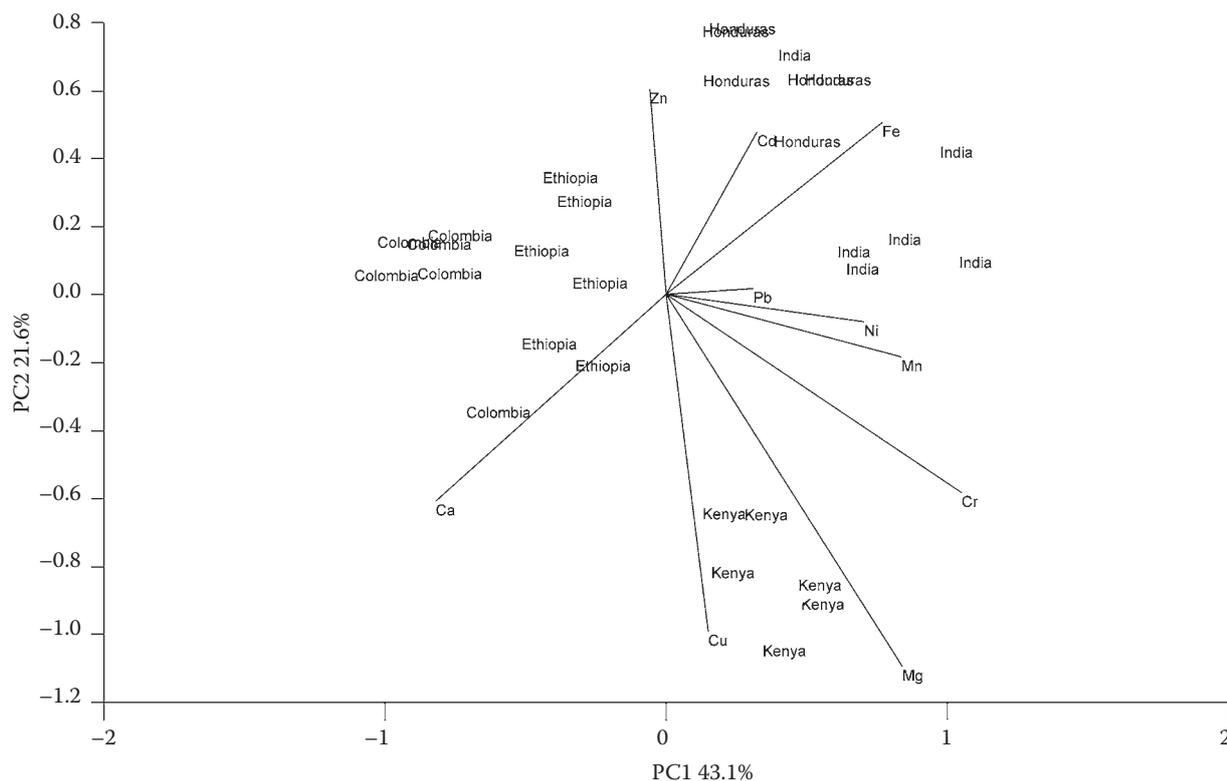


Figure 1. Biplot from PCA

tion of normality of the data was also tested and confirmed for all data sets. No significant differences were found between arithmetic means, median and pivot half sums, even though we have a small number of repeated measurements ($n = 6$) for each coffee sample taken into statistical evaluation. To compare the concentrations of the analysed metals between locations, one way analysis of variance was utilised. Statistically significant differences ($P = 0.05$) were found for all metals. Scheffé procedure for multiple comparison revealed that the greatest differences in the metal levels were for Cr, Mn, and Fe while the smallest differences were for Mg, Pb, and Cu.

Principal component analysis (PCA) as one of the widely used techniques of multivariate statistics was applied on our data. The coffee samples were analysed by PCA using ten element concentrations as variables. Kaiser criterion (eigenvalues of PC should be above 1) was used to choose the appropriate number of the extracted PCs. Thus, no more than three principal components should be extracted (eigenvalues PC1: 4.73; PC2: 1.95; PC3: 1.13) that explain 79.3% of variability hidden in the original data. The results from PCA can be graphically shown on biplot (Figure 1), where PC1 and PC2 are depicted. Almost perfect separation into clusters according to the country of origin is

seen. One result of the repeated analysis of coffee from India was classified into the cluster of Honduras samples. Also, the separation between Colombia and Ethiopia samples into clusters is not ideal either. The length of the radius vectors shows the influence of individual elements when creating the principal components. It can be seen that the least significant elements are Pb and Ni, while the most significant ones are Mg, Cu, and Cr.

CONCLUSIONS

Both methods described in this article were successfully validated and are applicable to the analysis of plant samples like coffee. ICP-MS is, of course, less time consuming than AAS, because ICP-MS allows simultaneous analysis. When the laboratory is equipped with both instruments, it is cheaper (capital costs are not compared) to use ICP-MS for the analysis if the determination of more than five or six elements is required. The use of suitable statistical procedures can help to reveal relations in the data sets that are not obvious. Detailed evaluation of the analysis of variance showed between which elements exist the greatest and the smallest differences. When several analytes are measured in each sample, it is useful to apply the multivariate statistical method.

The utilisation of PCA confirmed the potential of the localisation of the coffee samples origin.

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