

THE DETERMINATION OF MAJOR, MINOR AND TRACE ELEMENTS IN TEA, TEA LIQUOR, INSTANT COFFEE AND COCOA SAMPLES

IMTIAZ AHMED, S.S.H. ZAIDI AND Z.A. KHAN
National Physical and Standards Laboratory, Islamabad

(Received September 15, 1988; revised March 22, 1989)

Tea, coffee and cocoa samples used as common beverages were analysed for major and micro elemental constituents using inductively coupled plasma emission spectrometer. The possible uptake of certain elements by the human body from tea infusion has also been determined. The reliability of the analytical results was ascertained by comparing the analytical results for the NBS Standard Reference Material Orchard leaves (SRM No. 1571) with the values given by the NBS.

Key words: Tea, Trace elements, Spectrometry.

Introduction

Many elements present in food at major, minor and trace levels are reported to be essential to man's well being. However, their ingestion in excessive amount can cause severe health problems. Tea, coffee and cocoa drinks have become popular beverages among the masses replacing traditional local drinks. Major elements like K, Mg and Ca, minor elements Al, Fe, Mn, Zn and trace elements Cu, Ni, Co and Pb were determined in the samples by inductively coupled plasma (ICP) spectrometry. The ICP was preferred due to its certain advantages over traditional methods for plant and other materials [1-6]. In order to estimate the possible uptake of these elements in the human body, from tea liquor, these elements were determined in hot water extracts.

Wet acid digestion method was used and the dangerous perchloric acid was avoided for preparation of solution of the samples for analysis. To determine the accuracy of results and recovery of the elements in the acid digestion method, National Bureau of Standards Orchard leave, Standard Reference Material No. 1571 was also analysed.

Experimental

Instrumentation. Inductively coupled argon plasma emission, direct reading vacuum spectrometer, "Plasma Scan" Labtam Limited (Victoria) Australia, was used in the study.

Operating parameter

Polychromator. Grating 2160 groves/mm. Dispersion 0.46 nm/mm (first order). Wave length range 160-820 nm.

Monochromator. Grating 1800 groves/mm. Dispersion 0.74 nm/mm (first order). Wave length range 160-820 nm.

Computer. Labtam 3600 Series CPL 280A-8B17.

Generator. 2 KW, maximum 27.12 MHz (crystal controlled).

Forward power. 1.6 KW

Reflected power. 5 W

Nebulizer. GMK designed to operate on stop flow principle [7].

Instant coffee and cocoa samples were used as such, because they were already in powder form.

One gram of each sample in duplicate was taken in pyrex glass test tubes 25 cm long and 2.5 cm diameter. 10 ml of A.R. distilled concentrated nitric acid was added. The test tubes

Gas. Liquid argon.

Coolent. 14L/min (argon gas)

Observation height. 15 mm above load coil.

Sample uptake. 1.5 ml/min.

Sample material. (1) The orchard leaves were NBS, SRM No. 1571. (2) Six samples of tea, three of coffee and two sample of cocoa of different brands were collected from the market for analysis.

Calibration and standards. The instrument was calibrated with appropriate sets of calibration standards. Two point calibration was made according to the type of sample to be analysed.

Standard(I). Zero calibration solution (600 ml HCl + 214 ml HNO₃ in 10 L of distilled water).

Standard(II). High point calibration solution. Set (i) 100 ppm K, As, P, S and Se. Set (ii) 10 ppm Al, B, Ca, Cu, Fe, Mg, Mo, Na, Sn, Ti, Si, V, Zr. Set (iii) 10 ppm Zn, Cd, Sr, Pb, Co, Ni, Mn, V.

Standard(III). For K determination another set of calibration solution was also used containing 250 ppm of K standard, since the samples contained K to more than 100 ppm.

Sample preparation. Sample preparation of plant tissue and biological materials for ICP, AES is reported [8]. It has also been observed [9] that during high temperature ashing some trace elements are lost and some contamination occurs from the walls of the ashing vessel. In order to avoid ashing

and use of perchloric acid, concentrated nitric acid and hydrogen peroxide method was adopted [10].

Orchard leaves (SRM No. 1571) sample was dried at 85° over night according to the instructions laid down in the certificate. Dried tea leaves samples were ground into a fine powder, were placed on an aluminium heating block overnight at about 25°. So that the excessive frothing ceased. The temperature of the aluminium block was then gradually raised to 80°, and heating was continued for about two hours. This allowed the initial digestion of the samples. The test tubes were then cooled down to room temperature. After attaining room temperature, 6 ml of 27% A.R. grade hydrogen peroxide was slowly added to each sample. The block temperature was then raised to 170° and heating continued until about 1.5 ml of the solution was left behind. This treatment was also followed for the preparation of the blank solution. This allowed complete digestion of the sample and destroyed nearly all the organic material [10].

The procedure described above for the digestion of instant tea, coffee and NBS orchard leaves samples failed for digestion of cocoa samples because it contains a lot of fatty matter. One gram of the cocoa samples in duplicate were taken in 100 ml pyrex glass beakers, 5 ml of A.R. grade concentrated sulphuric acid was added and heated to 160° on a hot plate for one and a half hour to char the samples. The contents were then cooled down to room temperature. Then 10 ml of concentrated nitric acid was added slowly and the temperature of the hot plate was raised to 180° gradually. The heating was continued to strong fumes of sulfuric acid till almost complete removal of H₂SO₄. Then 2 ml of concentrated nitric acid was again added to the solution, heated to 100° to dissolve all the residue and about 1.5 ml of solution was left behind. Finally the volume of each solution and the blanks was made to 10 ml with zero calibration solution. For the determination of the major elements, the dilutions were made to 100 ml.

Hot water extraction of tea samples. Tea samples (5 g) of all brands were boiled with 50 ml of distilled water for two minutes and filtered. The boiled tea samples were transferred to 50 ml of fresh distilled water and boiled again for two minutes. In this way the samples were boiled five times to get maximum hot water extraction of the elements in the tea samples. The final filtrate which was about 250 ml was evaporate to near dryness. The residue was digested with concentrated nitric acid and hydrogen peroxide methods as described previously. The final volume of the solutions were made up to 25 ml with zero calibration solution. These solutions were then analysed on ICP under the parameters described previously.

Results and Discussion

The wavelengths at which elements were analysed and the detection limits are given in Table 1. The inter-element interferences in determination of multielements in actual solutions by inductively coupled plasma atomic emission spectrometry has been discussed by Larson *et.al* [11] Particularly K, Na, Ca and Mg showed high interference on the spectrum of 10 trace elements in tea [12]. By selection of appropriate wavelengths the interferences due to Na, Ca, Mg, Mn and P on minor elements, like Al, Fe, Zn, Cu, Ni and Co were minimized and any residual interferences encountered were corrected by "On-Peak" spectral interferences software sub-routines.

The certified values of elements in the orchard leaves SRM, and the values determined by ICP, spectrometer are given in Table 2. The concentration of elements in the coffee and cocoa samples are summarized in Table 3. Concentration of elements in the six brands of tea samples are given in Table 4. The concentration of elements transferred to hot water from the tea brands are summarized in Table 5.

TABLE 1.

Element	Wavelength (nm)	Detection limit (ug/ml)
K	766.400	1.0
Ca	317.933	0.010
Mg	279.553	0.00015
Al	396.152	0.028
Fe	259.940	0.0063
Mn	257.610	0.0014
Zn	213.856	0.0018
Cu	224.700	0.0077
Co	228.616	0.0070
Ni	231.604	0.0150
Pb	261.418	0.13

TABLE 2. COMPARISON OF THE VALUES GIVEN BY N.B.S. AND THE VALUES DETERMINED BY ICP FOR ORCHARD LEAVES SRM.

Element	NBS value	Determined value
K %	1.47 ± 0.03	1.45
Ca %	2.09 ± 0.03	1.94
Mg %	0.62 ± 0.02	0.65
Mn ug/g	91.00 ± 4.00	88.99
Fe "	300.00 ± 20.00	264.00
Zn "	25.00 ± 3.00	24.00
Cu "	12.00 ± 1.00	12.35
Ni "	1.30 ± 0.20	1.39
Co "	0.2	0.20
Pb "	45.0 ± 3.00	42.00

TABLE 3. ANALYSIS RESULTS OF COFFEE AND COCOA SAMPLES.

Element	Coffee			Cocoa	
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2
K %	3.88±0.01	3.57±0.02	4.03±0.02	3.98±0.02	3.80±0.02
Ca %	0.14±0.02	0.13±0.01	0.10±0.02	0.13±0.02	0.13±0.03
Mg %	0.72±0.01	0.80±0.03	0.86±0.03	0.01±0.01	0.12±0.01
Al ug/g	13.90±1.10	6.00±1.00	6.80±0.50	47.90±2.00	50.20±2.00
Mn ug/g	20.00±1.00	20.30±1.00	12.10±0.50	67.40±2.00	78.00±3.00
Fe ug/g	50.00±2.00	23.00±3.00	24.10±1.00	141.00±2.00	126.00±1.00
Zn ug/g	6.50±1.00	5.00±0.50	5.00±1.00	72.00±3.00	67.00±1.00
Cu ug/g	2.08±0.20	0.98±0.20	1.30±0.20	38.00±1.00	35.00±1.00
Ni ug/g	1.50±0.20	1.60±0.10	1.25±0.20	9.80±1.00	9.20±2.00
Co ug/g	0.47±0.02	0.50±0.02	0.38±0.01	1.70±0.02	2.10±0.02
Pb ug/g	3.10±0.10	2.40±0.30	2.20±0.30	4.50±0.30	3.80±0.20

TABLE 4. ANALYSIS RESULTS OF TEA SAMPLES.

Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
K%	1.70±0.01	1.86±0.01	1.79±0.01	1.77±0.01	1.81±0.02	1.79±0.02
Ca%	0.32±0.01	0.37±0.02	0.33±0.01	0.33±0.01	0.43±0.01	0.45±0.03
Mg%	0.29±0.01	0.32±0.02	0.33±0.01	0.33±0.01	0.31±0.01	0.32±0.01
Al ug/g	650.00±3.00	626.00±2.00	860.00±4.00	865.00±4.00	610.00±2.00	866.00±3.00
Mn ug/g	750.00±2.00	586.00±1.00	1160.00±2.00	1103.00±2.00	400.00±1.00	752.00±1.00
Fe ug/g	195.00±2.00	125.00±1.00	199.00±1.00	284.00±2.00	88.00±1.00	203.00±2.00
Zn ug/g	36.94±0.50	35.70±0.30	30.00±0.10	38.40±0.10	44.00±0.20	38.50±0.50
Cu ug/g	26.06±0.10	26.90±0.20	36.50±2.00	26.00±0.20	23.00±0.20	31.00±0.10
Ni ug/g	3.50±0.10	3.60±0.20	3.60±0.20	6.80±0.20	4.70±0.10	3.80±0.10
Co ug/g	1.10±0.02	0.50±0.01	1.20±0.02	1.00±0.03	0.34±0.03	0.80±0.02

TABLE 5. ANALYSIS RESULTS FROM HOT WATER EXTRACT OF TEA SAMPLES.

Element	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
K%	1.69±0.01	1.52±0.02	1.65±0.02	1.65±0.02	1.61±0.02	1.70±0.01
Ca%	0.03±0.01	0.03±0.02	0.04±0.02	0.03±0.01	0.09±0.02	0.04±0.01
Mg %	0.25±0.02	0.29±0.03	320.00±0.02	0.27±0.01	0.20±0.00	0.03±0.01
Al ug/g	246.00±3.00	181.00±2.00	0.22±3.00	215.00±2.00	146.00±2.00	355.00±2.00
Mn ug/g	412.00±2.00	293.00±3.00	654.00±2.00	564.00±3.00	199.00±1.00	425.00±2.00
Fe ug/g	20.00±1.00	86.00±1.00	15.10±2.00	15.10±1.00	6.56±1.00	15.00±2.00
Zn ug/g	25.30±1.00	20.60±1.00	22.50±1.00	29.50±2.00	30.00±2.00	25.00±2.00
Cu ug/g	4.00±1.00	2.00±0.10	3.60±0.20	2.50±0.10	1.80±0.02	3.40±0.20
Ni ug/g	3.50±0.01	3.30±0.02	3.50±0.30	6.80±0.01	4.60±0.01	3.60±0.10
Co ug/g	0.22	0.112	0.455	0.45	0.19	0.320

Some coffee samples were analysed and reported for K, Mg, Fe, Zn and Cu by atomic absorption spectrometry [13]. Some important elements in some samples of coffee were reported for assessment of nutritional status and as a guide to the fertilizer programme [14]. Our results agree with the previous data except that our tea samples contain slight excess of K. Various authors have analysed tea samples for inorganic constituents by different analytical techniques and concentration of major and minor elements [15]. Atomic absorption spectrometry has been applied as an analytical tool for analysis of elements like Mn, Zn, Cu and Ni in Bangladesh tea samples and their transfer to hot water is also reported [16]. Simultaneous multi-elements determination of tea

samples, after dry ashing, by inductively coupled plasma spectrometry has been reported recently in Japan tea samples [12]. Our results revealed that the most abundant elements which were transferred to hot water from tea samples were Ni (ranging from 90 to 100%) and K (ranging from 88 to 94%). The other abundant element which was transferred to hot water was Mg (64 to 90%). This indicates that K, Ni and Mg complexes are more water soluble than the complexes of the other elements present in tea. The percentage transfer in hot water of the other elements was Mn (47-61%), Zn (65-73%), Al (23-36%). Fe and Cu were transferred to hot water in the range of 5-7% and 7-11% respectively, revealing that these are in the form of least water soluble complexes. The Co

transfer to hot water was between 20-50%. Tea drinking has been reported to be a possible source of Co present in humans [17].

It may be mentioned here that the various metallic elements found in beverages are present in the raw material, used to prepare the beverages, and are not the result of subsequent processing. In this connection four elements Pb, Cd, Cu and As were determined in raw, semi-finished and finished cocoa chocolate products by ICP, using dry ashing techniques [18] and it was shown that no contamination occurs during the manufacturing process of the finished products of the cocoa samples.

The analysis results show that tea, cocoa and coffee could serve as one of the sources of human intake of various metallic elements, which are essential for humans upto certain levels. Of course the effects of other compounds present in the beverages has also to be taken into account in order to determine the amount of these beverages that should be taken.

References

1. A.F. Ward, L.F. Marciello, L. Carrara and V.J. Luciano, *Spectroscopy letters*, **13** (11), 803 (1980).
2. R.H. Scott and A. Strasheim, *Anal. Chem. Acta*, **76**, 71 (1975).
3. R.C. Munter, R.A. Grande and P.C. Ahn, *ICP Info. Newsletter*, **5**, 368 (1979).
4. R.T. Good Pasture, R.J. McElhaney and R.W. Morrow, *Dev. At. Plasma Spectrochem, Anal. Proc. Winter Conf.*, ed. R.M. Barns (Heyden London, 1981) pp. 697-705.
5. J.B. Jones, *Dev. At. Plasma Spectrochem, Anal. Proc. Winter Conf.*, ed. R.M. Barns (Heyden London, 1981), pp. 644-652.
6. W.H. Evans and Dorothy Dellar, *Analyst*, **107**, 977 (1982).
7. P.J. Mckinon, K.C. Giess and T.V. Knight, *Dev. At. Plasma Spectrochem, Anal. Proc. Winter Conf.*, ed. R.M. Barns (Heyden, London, 1981), pp. 287-301.
8. Neil R. McQuaker, David F. Brown and Paul D. Klukner *Anal. Chem.*, **51** (7), 1082 (1979).
9. A.D. Hill, K.Y. Patterson, C. Veilon and E.R. Marris, *Anal. Chem.*, **58** (11), 2340 (1986).
10. Chao Yang Luh Huang and E.E. Schulte, *Commun. Soil. Sci. Plant Anal.*, **16** (9), 943 (1985).
11. G.F. Larson and Velmer A. Fassel, *Anal. Chem.*, **48** (8) 1161 (1976).
12. Tadakazu Takeo, *Jap. Agric. Re. Quart.*, **19** (1), 32 (1985).
13. R.J. Clarke and L.J. Walker, *J. Sci. Fd. Agric.*, **25**, 1389 (1974).
14. M.N. Clifford and K.C. Willon, *Coffee, Botany Biochemistry, Production of Beans and Beverages* (Croom Helm, London, 1985).
15. T. Eden, *Tea* (Longman, 1976).
16. S.A. Tarafdar, A.H. Khan and M. Rahman, *Agric. Biol. Chem.*, **49** (1), 201 (1985).
17. Chen Xiangyon, Ma Tansyen and Qui jiakui, *Huanjing Baoku*, Beijing, **11**, 15 (1984).
18. C.K. Lee and K.S. Low, *Pertanika*, **8** (2), 243 (1985).