DETECTION AND ESTIMATION OF ESSENTIAL TRACE ELEMENTS IN TEA (THEA SINENSIS) BY ICPAES AND FAAS METHODS

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(Received July 15, 1992; revised July 7, 1993)

Seven essential trace elements have been detected and estimated, including cobalt and chromium in six samples of tea. The use of inductively coupled plasma atomic emission spectroscopy (ICPAES) and flame atomic absorption spectrophotometry (FAAS) has been made. Hot water extraction limits for these elements have also been estimated. The standardization of the methods was carried out by using Orchard Leaves NBS-1571.

Key words: Essential, Trace elements, Tea.

Introduction

ment with the certified values (Table 4), except for Fe, which

Tea is a very popular caffeine-containing beverage obtained from *Thea sinensis*. Trace elements occur naturally, but may also be due to contamination from dust, fumes, pesticides and contact metals during production. Some contaminations are produced deliberately arising due to food additives during processing. The study of trace elements in tea has been taken up as trace elements play an important role in the complex metabolic pathways in human system and their deficiency or excess may cause diseases.

More than 60 elements in various parts of human body have been detected. It has been reported by Schwarz [1] and Manser [2] that at least 25 elements are essential and out of which 14 are termed as trace elements (their concentration being less than 50 mg/kg body weight).

Aziz-Al-Rehman [3] estimated copper in tea by using two different methods of solution preparation for FAAS methods. Tarafdar *et al.* [4] analysed copper, nickel, zinc and manganese in Bangladesh tea by FAAS. Takeo [5] determined a number of inorganic components, including copper, iron, zinc and manganese by ICPAES in Japanese green and black tea. Imtiaz *et al.* [6] have reported the analysis of major and minor trace elements in tea, coffee and cocoa samples using ICPAES.

In the present study seven essential trace elements have been detected and estimated in tea by using flame atomic absorption spectrophotometry (FAAS) and inductively coupled plasma atomic emission spectroscopy (ICPAES). A very close comparison for the estimation of these elements by the two methods has been achieved. The presence of chromium in tea samples, not reported elsewhere, has also been determined.

Experimental

Instruments. The Atomic Absorption Spectrophotometer used was GBC Model SB900 with air-acetylene flame. The Inductively Coupled Plasma Atomic Emission Spectrophotometer, LABTAM - Model V-25, equipped with 100-2000 source and CRT - 1000-A computer, was used.

Preparation of solution of FAAS. The method of wet oxidation with HNO₃ and a mixture of HNO₃ and H_2SO_4 was adopted, in order to remove organic matter. Solutions were prepared by two methods, i.e. (a) a routine method for direct FAAS measurements and (b) solvent extraction (used for elements having very low concentrations such as zinc, nickel, cobalt and chromium).

For direct FAAS measurements, 1 g powdered tea was digested in 10ml conc. HNO_3 in a Kjeldahl flask for 16 hrs. The volume was reduced to 1ml and transferred into a 10ml volumetric flask and diluted up to the mark with distilled water. A blank was prepared similarly.

For solvent extraction method, 2.5 g of powdered tea was digested with 10 ml conc. HNO₃ and 10 ml conc. H₂SO₄. A further 20 ml conc. HNO, were added in aliquots of 5 ml at intervals. When the solution was clear, it was heated gently to remove excess of acid till the volume was reduced to 1 ml. This was dissolved in 50 ml distilled water and transferred to a 250 ml beaker. The pH of the solution was adjusted to 4 with NaOH solution, 5 ml 1% APDC (Ammonium pyrrolidine dithiocarbamate), aqueous solution was added and the pH was raised to 12 by further addition of NaOH. The solution was left for 5 min, when the pH was readjusted to 5 with dilute acetic acid. The solution was transferred to 250 ml separating funnel and extracted with 10 ml portions of chloroform till the solvent layer was colourless (40 ml in total required). 2 ml of 1% APDC were added followed by extraction with another portion of 10 ml chloroform. The extracts were mixed and evaporated to dryness. The residue was heated with 5 ml conc. HCl to remove organic matter till, evaporation reducing it to 1 ml, which was transferred to a 10 ml volumetric flask and made up to the mark with distilled water. A blank was prepared similarly.

Hot water extraction method. Dried tea leaves (5 g) were boiled with distilled water (10 ml) for about 5 min. The liquor was filtered and evaporated to dryness in a platinum dish. The residue was made into a solution in a similar way as the powdered tea samples.

Preparation of solution for ICPAES. Powdered tea (1 g) was digested with 10 ml conc. HNO_3 and when clear was reduced to 2 ml by evaporation. These were transferred to a 10 ml volumetric flask and made up to the mark with distilled water. A blank was prepared similarly.

Standard solutions. The standard solutions from Fixanal (R.D.H.), Germany were used for all elements.

Results and Discussion

Tea samples consisting of low, mdeium and high quality were procured from the market. Seven essential trace elements have been determined by FAAS and ICPAES (Table 1). In Table 2, the range of concentrations of these elements in tea samples and of their percent extraction by hot water are given.

The ratio of detection limits for FAAS and ICPAES [7] are given in Table 3. It should be noted that, except for zinc, the detection limit by ICPAES is lower than by FAAS. The standardization of the methods has been accomplished using trace elements in Orchard leaves NBS-1571, as shown in Table 4. The concentration of cobalt and chromium have not been certified for NBS-1571; we consider our measurements

by ICPAES as the more reliable. Other elements are in agreement with the certified values (Table 4), except for Fe, which lies just outside the standard deviation.

Chromium. Tea contains $1.4 - 3.5 \mu g/g$ of chromium and upto 55% is extractable by hot water. Chromium has an essential role in carbohydrate and liquid metabolism [9]. It activates several enzymes and stimulates fatty acid and cholesterol synthesis. It has important relationship with diabetes and its role in glucose utilization [10].

Cobalt. The concentration of cobalt ranges from 0.32 to $1.2 \,\mu$ g/g in tea and upto 32% is extractable by hot water. Cobalt is an essential trace element, being a component of vitamin B12.

Manganese. Tea is a rich source of manganese, having 400 - 1160 μ g/g of which upto 51% is hot water extractable. Manganese is a cofactor of enzymes is protein synthesis and energy metabolism [11]. A cup of tea contains about 0.3 - 1.3 mg of manganese and therefore its safe upper level of intake comes into consideration. The Food and Nutrition Board lists 2.5 - 5 mg/day as a safe and adequate intake for adults [12].

Copper. Copper occurs in a range of $23 - 38 \mu g/g$ in tea and upto 19% to extracted in hot water. Copper is involved in a wide variety of enzymes and its role in haemoglobin synthesis, bone and elastic tissue development is well known. The maximum daily intake of copper for humans that can be safely maintained is 0.5 mg/kg body weight [8].

| Sample | Iror | n (ppm) | Coppo | er (ppm) | Mangan | ese (ppm) | Zinc | (ppm) | Nick | el (ppm) | Coba | lt (ppm) | Chrom | ium (ppm) |
|--------|-------|---------|-------|----------|--------|-----------|-------|--------|------|----------|------|----------|-------|-----------|
| | FAAS | ICPAES | FAAS | ICPAES | FAAS | ICPAES | FAAS | ICPAES | FAAS | ICPAES | FAAS | ICPAES | FAAS | ICPAES |
| 1 | 185.0 | 195.0 | 26.40 | 26.60 | 774 | 750 | 35.60 | 36.90 | 3.10 | 3.50 | 1.20 | 1.10 | 1.40 | 2.30 |
| 2 | 126.0 | 125.0 | 25.60 | 26.90 | 574 | 586 | 35.60 | 35.70 | 3.70 | 3.60 | 0.44 | 0.50 | 1.60 | 3.00 |
| 3 | 227.0 | 199.0 | 38.40 | 36.50 | 1157 | 1160 | 29.60 | 30.00 | 3.80 | 3.60 | 1.14 | 1.20 | 2.80 | 3.50 |
| 4 | 302.0 | 284.0 | 25.60 | 26.00 | 1038 | 1103 | 40.00 | 38.95 | 7.10 | 6.50 | 1.10 | 1.00 | 3.00 | 2.90 |
| 5 | 130.0 | 88.0 | 23.20 | 23.40 | 400 | 400 | 44.40 | 44.20 | 4.80 | 4.70 | 0.46 | 0.32 | 1.80 | 2.30 |
| 6 | 200.0 | 203.0 | 28.80 | 31.00 | 748 | 752 | 30.00 | 30.50 | 3.50 | 3.60 | 0.48 | 0.40 | 3.00 | 3.00 |

TABLE 1, ESTIMATION OF TRACE ELEMENTS IN TEA SAMPLES BY FASS AND ICPAES.

TABLE 2. RANGE OF CONCENTRATION OF ELEMENTS AND PERCENTAGE OF HOT WATER EXTRACTS IN TEA SAMPLES ESTIMATIONS BY FAAS AND ICPAES METHODS.

| Elements | Range of occ in tea sample | currence s (μg/g) | Range of hot water extracts in % | | | |
|-----------|-------------------------------|----------------------|-------------------------------------|---------|--|--|
| Chromium | 1.40 - | 3.50 | 28.57 | - 55.5 | | |
| Cobalt | 0.32 - | 1.20 | 9.16 | - 31.8 | | |
| Manganese | 400.00 - 1 | 160.00 | 43.72 | - 51.20 | | |
| Copper | 23.20 - | 38.40 | 4.40 | - 19.00 | | |
| Zinc | 29.60 - | 44.40 | 67.40 | - 85.00 | | |
| Nickel | 3.10 - | 7.10 | 2.60 | - 7.02 | | |
| Iron | 88.00 - | 302.00 | 3.24 | - 8.26 | | |

TABLE 3. RATIO OF DETECTION LIMITS FOR FAAS AND ICPAES*.

| No. E | lement | Detection | limits ng/ml | Ratio of detection limits |
|-------|--------|-----------|--------------|---------------------------|
| | | FAAS | ICPAES | FAAS/ICPAES |
| 1 | Co | 5 | 4 | 1 |
| 2 | Cr | 10 | 5 | 2 |
| 3 | Cu | 5 | 3 | 2 |
| 4 | Fe | 5 | 3 | 2 |
| 5 | Mn | 3 | 1 | 3 |
| 6 | Zn | 2 | 3 | 0.6 |
| 7 | Ni | 5 | 10 | 0.5 |

*(Ref. No. 7)

| Elements | Standard concentration (ppm) | Concentration found in the present work (ppm) |
|----------|------------------------------|---|
| Ni | 1.3 ± 0.2 | 1.40 |
| Cr | (2.3)* | 3.15 |
| Co | (0.2)* | 0.3 |
| Mn | 91.0 ± 4.0 | 94.6 |
| Cu | 12.0 ± 1.0 | 11.0 |
| Fe | 300.0 ± 2.0 | 294.0 |
| Zn | 25.0 ± 3.0 | 24.0 |

TABLE 4. CONCENTRATION OF TRACE ELEMENTS IN ORCHARD

LEAVES NBS-1571 BY FAAS METHOD

Zinc. Zinc is widely distributed is food; its presence in tea lies between 30 - 44 μ g/g. It is highly extractable by hot water (upto than 85%). It occurs in a wide variety of enzymes and its role in protein and carbohydrate metabolism is well established. Nutritional problems from zinc arise from it deficiency rather than its excess.

Nickel. Nickel is present from $3.1 - 7.1 \mu g/g$ in tea and upto 7% is extractable by hot water.

Iron. Iron occurs in a range of $88 - 302 \mu g/g$ in tea and upto 8% is hot water extractable. Iron deficiency may cause anaemia.

It may be concluded that as regards the presence of essential trace elements, tea may be considered as a useful

Ownotic pressure (m osin kg²¹). Fresh and targid third nodal leaves were collected in the carly morning hears in small polythene bags. Leaf samples were then stored in a deep freezer for three days till cell wall breakage. Tissue sap was extracted and contrifuged at 6500 RPM for 10 minutes. Ton micro liters of this sap sample were used to determine osmotic pressure by asing automatic micro-osmoneter.

Stonated frequency and stomated size (ng¹). Loaf strips of about 3 cm longth were taken from the midle part of finird nodal leave, dipped into Carnoy's scintion to arrest stomated structure and remove ethorophyR. After washing with alcohol samples were examined under the microscope at 10x magnificafications to count number of stomata and at 40x magnifications to measure size of stomatal opening, by using a stage micromoter (scaled at 0.01 mm increments) and an ocular micrometer (scaled at 0.1 mm increments). beverage, supplying some of the nutritional trace elements. Only the richness of manganese in tea is alarming and that may be checked if, the habit of excess of tea drinking is a avoided.

References

- K. Schwarz, *Clinical Chemistry and Clinical Toxicology* of Metals, S.S. Brown (ed.) (Elsevier, Amsterdam, 1977), pp. 3-22.
- 2. W.W.T. Manser, J. Pak. Med. Assoc., 12, 325 (1989).
- A.M. Aziz-Al-Rahman, Intern. J. Environ. Anal. Chem., 22, 25 (1985).
- 4. S.A. Tarafdar, A.H. Khan and M. Rahman, Agric. Biol. Chem., **49**, 201 (1985).
 - 5. Tadakazu Takeo, Jap. Agric. Res. Quart, 19, 32 (1985).
 - Imtiaz Ahmad, S.S.H. Zaidi and Z.A. Khan, Pak. j. sci. ind. res., 32, 513 (1989).
 - K.K. Stewart and J.R. Whitaker, *Modern Methods of* Food Analysis (Avi. Pub. Company, Inc. Westport, Connecticut, U.S.A., 1984).
 - Joint Expert Committee on Food Additives, WHO/FAO (1970).
 - 9. K.M. Hambidge, Am. J. Clin. Nutr., 27, 505 (1974).
 - 10. W. Mertz, Physiol. Rev., 49, 163 (1969).
 - 11. E.J. Underwood, Trace Elements in Human and Animal Nutrition (Academic Press, New York, 1977), 4th ed.
 - Food and Nutrition Board, Recommended Dietry Allowances (National Academy of Sciences, Washington D.C., 1980), 9th ed.

water stress plant [1]. In many plants there is a good correlation between the build up of ABA and the closure of stomata atimulated by water stress. In some cases, however, stomata begin to close before the level of ABA in the plant has risen appreciably [2]. Further ABA also enhances the growth rate thats enabling the plant to complete its life-cycle before a serious moisture defielt develops. The number of stomata on than in irrigated conditions [3]. High osmoule pressure is detain in irrigated conditions [3]. High osmoule pressure is detaget us this enables the plants to develop a high suction detaget in this enables the plants to develop a high suction detaget in this enables the plants to develop a high suction detaget in this enables the plants to develop a high suction detaget in the enables the plants to develop a high suction detaget in the enables the plants to develop a high suction detaget. This is due to inadequate supply of water at the time of verses. This is due to inadequate supply of water at the time of grain filling period, seed is invariably shrivelied and low weightage due to reduced carbohydrates.

In a line x tester analysis of combining ability, non additive gene action occurred for grain yield per plant, number of ear bouring tillers and synchrony of ulicring, while additive gene action controlled early growth vigour, days.