Determination of Iron and Manganese in Tea Samples by Flame Atomic Absorption Spectroscopy

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Summary: Tea samples, marketed by different companies through out the country, have been collected and analyzed for iron and manganese by flame atomic absorption spectroscopy. Dry ashing as well as wet procedures were employed for decomposing the tea samples and results obtained from both the procedures were compared. The average amount of iron, estimated in thirty samples, was 9.38 ppm while that of manganese was found 175 ppm. For both metals relatively higher results were obtained when samples were decomposed with sulphuric acid and hydrogen peroxide.

Introduction

Iron and manganese are two of the essential micronutrients for most of the organisms, animals and plants. Iron functions as a catalyst and is present in amounts greater than that of any other trace element. According to Jacobs and Worwood [1], 57.6 % of the body iron in man is contained in hemoglobin and 8.9 % in myoglobin. Approximately 33 % is contained in non- heme iron complexes including ferritin and hemosiderin. The cytochrome and catalase enzymes contain about 0.5 % of iron. The heme pigments, hemoglobin in erythrocytes and myoglobin in muscles, function as oxygen carriers [2]. Heme containing enzymes such as the cytochrome in mitochondria [3] and catalase in red blood cells[4] are concerned with electron transport and peroxidase breakdown. Iron can be satisfactorily determined by flame atomic absorption spectroscopy in various matrices [5,6] including natural herbs[7].

Manganese is also essential for normal growth, skeletal formation and for normal reproductive function in mammals and poultry [8]. An estimated 3-7 mg of manganese are ingested daily with a well balanced diet. Nuts and cereals are richest in manganese, followed in order by dried fruits, roots, fresh fruits, non-leafy vegetables, animal tissue, poultry and poultry products, fish and sea foods. Diets consisting primarily of milk, sugar refined cereals and little fruits and vegetables could contain insufficient manganese [9]. According to Schroeder and coworkers manganese deficiency may cause diabetes, nervous instability, disorders of bony and cartilaginous growth in infants and children, and rheumatoid arthritis in adults [10]. Flame atomic absorption spectroscopy has been frequently used for the determination of manganese in all types of samples including natural products[11] and medicines [12].

Tea is taken in almost every country of the world in various forms. Being cheaper and easy to prepare and serve, it is the most popular drink of east and west. It is a stimulant with minimum adverse effects. It adds a sense of well being and freshness.

According to an estimate, tea leaves amounting to Rs. 2 billion, are consumed annually in Pakistan. Mostly multinational companies are involved in tea business. A number of brands from these companies are marketed as well as un-branded tea leaves are also available everywhere in the country.

In this work tea samples, marketed by different companies under different brand names as well as a few unbranded samples available in the market, have been collected and analyzed for iron and manganese content by flame atomic absorption spectroscopy. Dry ashing as well as wet procedures were employed for decomposing the tea samples. The results obtained from both procedures are compared. Comparatively higher values were obtained when samples were decomposed with concentrated sulphuric acid and hydrogen peroxide.

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Results and Discussion:

Instrumental Parameters:

Iron and manganese could be satisfactorily determined in normal air-acetylene flame. However the absorption of both the elements was significantly found dependent on the fuel/oxidant ratio and zone of the absorption measurement in the flame. Absorption of iron was also affected by increasing the slit width. Relative lean flame (bluish in appearance) gave the most stable and reliable absorption values for iron and manganese. A slightly fuel rich flame simply enhanced the noise level without increasing the absorption of any of the element to a significant level. The optimum region for measuring the iron absorption was found a little lower (3-5 mm above the burner top) than that observed for manganese (5-8 mm above the burner top). Similarly the slit width of 0.2 mm gave better signal / noise ratio for iron, whereas 0.5 mm slit width gave satisfactorily results for manganese. 1000 ppm solution of magnesium nitrate was added as matrix modifier both in standards as well as samples in the case of manganese analysis[13,14].

Tea Samples Available in Pakistan:

The samples of tea leaves available in Pakistan and collected for this study can be roughly classified into four categories. The first category "A", shown in Table 1, composed of those brands of tea leaves which are relatively expensive, imported, processed and marketed under brand names in tins and packets by multinational companies. These brands are usually consumed by high and upper middle class and are available in cities throughout the country. The examples of these tea leaves are Lipton Yellow label; Supreme and Rich brue brands. The Second category "B", mostly used by lower middle class, is relatively cheaper. This type of tea is imported in bulk and then packed by local companies. The quality of this category usually varies from brand to brand. Golden tea, Prime tea and Choora Tea are the examples of this category. The third category "C" is of the tea leaves imported directly from other countries in large sacks and sold by weight in open market. This type of tea is always the cheapest and usually does not bear any brand name. It is mostly consumed in rural areas of the country and road-side hotels. There is also a class of

Table.1. Iron and Manganese found in different brands of tea

Sr.No	Category	Brand Name	Fe by dry ashing (ppm)	Fe by wet digestion (ppm)	Mn by dry ashing (ppm)	Mn by wet digestion (ppm)
1.	A	Lipton Yellow label	13.5	12.0	176	170
2.		Supreme Tea	8.0	7.5	178	174
3.		Lipton Danedar	8.0	7.0	184	182
4.		Tapal Danedar	10.5	10.0	162	164
5.		Richbrue Tea	8.0	8.0	182	175
6.	B	Prime Tea	15.0	13.0	165	160
7.		Maizban Tea	17.0	15.0	178	174
8.		Golden Kenya Tea	10.0	8.0	156	142
9.		Red Label Tea	3.5	3.0	142	135
10.		Family Mix. Tea	12.5	12.0	136	132
11.		Habib tea	10.5	9.0	210	188
12.		Gold label Super leaf	7.0	7.0	142	132
13.		Lipton Top Star	6.0	5.0	152	138
14.	C	Bangla Desh Tea	10.0	9.0	135	132
15.		China Green Tea	3.5	3.0	208	205
16.		Anjak Kenya Tea	13.0	12.0	176	170
17.		Golden Cup Tea	11.0	10.5	145	144
18.		Golden Green label	7.0	5.0	140	136
19.		Ansari Tea	12.0	10.0	176	170
20.		Choora Tea	6.5	6.0	216	212
21.		Kenya Hotel Tea	12.0	10.0	150	146
22.		Kenya Super Tea	12.0	10.5	185	180
23.	D	Peshawri Qehwa	6.5	6.0	200	192
24.		Lemon Grass Tea	6.5	6.0	18	16
25.		Jasmine Tea	6.5	4.0	120	115
26.		Safari PF1 Tea	9.0	8.5	220	215
27.		Brazil Qehwa	8.5	7.0	296	290
28.		Kashmir Sabaz Tea	5.5	4.0	100	92
29.		Kebriso Tea	12.5	11.0	245	240
30.		Chocolate Tea	10.0	10.0	172	170

consumers in the society which uses some special types of tea leaves just as Jasmine Tea or Lemon Grass etc. This type of tea leaves are grouped as fourth Category "D". Similarly in certain areas of the country special tea leaves are used. For example different brands of Qhewa are mostly used without milk in the northern parts of Pakistan.

Decomposition Procedures:

Identical tea samples were analyzed after decomposing by wet digestion as well as by dry ashing. Although a number of reagents have been recommended for the wet digestion of plant material such as perchloric acid, nitric acid and liquid bromine but in this work concentrated sulphuric acid followed by 35 % hydrogen peroxide was used. The digestion was carried out in specially designed hard glass tubes. First 1 g tea sample was charred with sulphuric acid for 10 min. and then the hot carboneous material was slowly oxidized by dropwise addition of hydrogen peroxide with constant heating till the contents turned into a clear colorless solution. Using this process the digestion of one tea sample was completed in 30 min.

Second procedure used for decomposition was the dry ashing process in which the sample was first charred by slow heating at 250 ^{0}C and then ignited at 600 ^{0}C in a furnace. As revealed by the Table showing the results of both the metals, relatively higher results, found in the case of wet digestion, indicate some losses occur during dry ashing as the reagent blank, containing identical quantities of sulphuric acid and hydrogen peroxide, was used for the analysis of the samples decomposed by wet digestion.

Calibration Standards and Precision:

Calibration standards of both the metals were prepared by dissolving their AnalaR grade powders in minimum quantity of sulphuric acid and diluting the solutions to appropriate volume. Linear calibration of iron was obtained in the range 0.2-1 ppm at 248.3 nm. As in the case of manganese at 279.5 nm a sensitivity for 1 % absorption of 0.03 ppm was attainable therefore a linear calibration was plotted in the range 0.05-0.5 ppm.

Precision of both the procedures used for decomposition of samples was checked by decomposing and analyzing eight identical samples of the same brand of tea leaves for manganese and calculating the relative standard deviation in both cases. Although the results of metal contents obtained in case of dry ashing were slightly lower than those obtained by wet ashing, the standard deviation found in the case of dry ashing was significantly better than that found for wet digestion. The values of relative standard deviation found for wet digestion and dry ashing were 3.5 % and 2.5 % respectively. This reveals that the dry ashing procedure for the sample decomposition is more precise than the wet digestion by sulphuric acid and hydrogen peroxide as the manganese determination by atomic absorption spectroscopy was involved in both cases.

Iron and Manganese Found in Tea Samples:

The results obtained for iron and manganese in different brands of tea are given in Table.1. The quantity of manganese found in various tea samples ranges from 100 to 290 μg/g. Exceptionally low value of manganese i. e. 18 μg/g is found in lemon grass tea which is a very special brand of tea family. Similarly another brand of tea, marketed as Brazil Qehwa, contained the maximum quantity of manganese i.e. 296 μg/g. Most of the common brands of tea leaves which are used by the 80% of the population in Pakistan have an average value of 175 μg/g of manganese. As shown in the Table, the quantities of iron found in the collected tea samples are far less than those of manganese. The average value of manganese found in the samples is almost twenty times greater than that of iron. This is in agreement what already has been reported in the literature[15]. The maximum amount of iron i.e. 13.5 μg/g has been found in Lipton Yellow label which is a very popular brand of tea leaves in the country. On the other hand Red Label Tea, which is a brand of "B" category, contained iron content only one third of the average value. From the results obtained in this work two conclusions can be drawn: first that tea leaves available in the country contain a wide range of iron and manganese in them and second that brands of "A" category are moderately rich in iron and manganese.

Experimental:

Equipment and Chemical Reagents:

A Varian-1275 Atomic Absorption Spectrophotometer equipped with standard hallow cathode

lamps and air-acetylene flame was used for absorption measurements.

All the chemicals and reagents used were of AnalaR Grade. Doubly distilled water prepared in quartz still was used throughout this work.

Working Parameters:

The instrumental conditions used for the analysis of standards and samples were as follows:

Parameter	For Iron	For Manganese
Wavelength	248.3 nm	279.5 nm
Flame	Air-Acetylene, Oxidizing	Air-Acetylene, Oxidizing
Lamp Current	20 mA	15 mA
Range of Standards	0.2-2 μg/ mL	1-10 μg/ mL
Slit Width	0.2	0.5
Zone of Measurement	3-5 mm above top of burner	5-8 mm above top of burner

Preparation of Standards:

To prepare 1000 ppm solution, 0.25 g of anhydrous manganese powder was dissolved in 5 mL conc.H_2SO_4 by gentle heating and diluted to 250 mL with water. Calibration solutions, in the range 0.05-0.5 ppm, were prepared by appropriate dilution of this standard solution.

Iron standard solution, 1000 ppm, was prepared by dissolving 0.5 g iron powder in 5 mL conc.H_2SO_4 and diluting to 1000 mL with water. Working solutions of iron, in the range 0.2-1 ppm were prepared by further dilution of this solution.

Decomposition of Tea Sample:

Wet Digestion

1.0 g sample of tea leaves, after drying in an oven at 100 ^{0}C for 1 h and cooling in a dessicator, was taken in a specially designed hard glass digestion tube with a bulb at one end. 5 mL of conc. H_2SO_4 was added to it and the contents were gently heated over a burner in a fuming cupboard. When the black mass started to boil, a few drops of 35 % H_2O_2 were added . The addition of H_2O_2 was repeated occasionally with constant heating until a clear and colorless solution was obtained. This solution was transferred in a 25 mL standard flask. The digestion tube was washed with distilled water and the washings were also added into the flask. The volume of the standard flask was made up with water.

Dry Ashing:

2.0 gram dried and cooled sample of tea leaves (as described for wet digestion) was transferred in a platinum crucible and heated first at 250 ^{0}C for 30 min. and then at 600 ^{0}C for 2 h in a muffle furnace. The white ash obtained was leached with 3 mL conc. HCl and transferred in a 50 mL standard flask. The volume of the flask was made up with water.

References:

1. A. Jacobs and M. Worwood, "*Blood and its Disorders*" Eds. R. M. Hardesty and D. J. Weatherall, Oxford, Blackwell, (1974).
2. M. Worwood, *Seminars in Hematology*, **14**, 3, (1977).
3. R. Lembert and J. Barrett, "*Cytochromes*" Academic Press, New York, (1973).
4. A. S. Brill, *Comprhensive Biochemistry*, Eds. M. Florkin and E. H. Stotz, Elsevier, (1966).
5. Al-Howaidy, H. Ibraheem and M. M. Ahmed, *Int. J. Chem.* **8**(I),31-36, (1997).
6. J. Nevado, J. Berzas, L. Bermejo, F. Gracia, R. Martin-Doimeadios and C. Rodriguez, *Quim. Anal.* **17**(1), 3-8, (1998).
7. J. O. Ouma, C.C. Sumesh and N. Gather, *J. Ethnopharmacol.* **58**(2), 97-102, (1997).
8. R. M. Leach, Jr., A. M. Muenster and E. M. Wien, *Arch. Biochem. Biophys.* **133**, 22, (1969).
9. E. J. Underwood, *Trace Elements Human and Animal Nutrition*", academic Press, New York (1971).
10. H. A. Schroeder, J. J. Balassa and I. H. Tipton, *J. Chronic. Dis.* **19**, 545, (1966).
11. L. Peng, L. Shuying, H. Aidong, *Guangdong Weiliang Yuansu Kexue*, **4**(9) 65-68, (1997). *Chem. Abstract*, 254811g, **128**, No. 21, (1998).
12. D. Shunfu, Z. Zhigud, Z. Yi, C. Jinghua and Xu Zhian, Aidong, *Guangdong Weiliang Yuansu Kexue*, **4**(9) 48-50, (1997). Chem. Abstract, 299655a **128**, No. 24, (1998).
13. W. Slavin, G. R. Carnrick and D. C. Manning, *Anal. Chem.* **54**, 621, (1982).
14. W. Slavin, G. R. Carnrick and D. C. Manning, *Atomic Spectroscopy*, **2**, 137, (1981).
15. E. Berman, Toxic Metals and Their Analysis, Heyden and Son Ltd. London, p-141 (1980).