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Levels of Trace Elements in Black Teas Commercialized in Saudi Arabia Using Inductively Coupled Plasma Mass Spectrometry

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Abstract The present work has been demonstrated a developed method for the determination of Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, As, Cr, Pb, and V in different types of black teas collected from Saudi Arabia market using inductively coupled plasma mass spectrometry (ICP-MS). Each sample represents a well-mixed combination of ten packets from the same type collected from the market. Detection limits in ng g^{-1} were 76.06, 166.03, 5.94, 2.94, 18.29, 18.29, 9.00, 0.48, 0.48, 7.67, 3.07, and 4.21 for Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, As, Cr, Pb, and V, respectively. In order to validate the developed method, a certified reference material of green tea was analyzed. Further comparison with the results obtained from high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS) was demonstrated. The obtained good agreement confirms the validity of the investigated method. Fortunately, the concentrations of the heavy metals locate on the range of the international values. The highest metal content was found in Al-Rabee tea, and this type results should be confirmed by using a large number of samples in order to have satisfied and confirmed statistical analysis results.

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Introduction

Black tea has an economic and social interest and it represents one of the most widely popular beverages in the Arabic countries. It is prepared by different methods from the leaves, leaf buds, and internodes of the *Camellia sinensis* after a fermentation process [1, 2]. Although there are different types of tea, the black tea represents the most widely used tea in the Middle East. Some types of the teas were considered as a natural medicine whereas it has recognized therapeutic value for the prevention and treatment of some diseases such as cancer, Parkinson, myocardial infarction, coronary artery and the removal of cadmium in administered rates [3, 4]. In addition, black tea represents a source of several elements such as zinc, manganese, iron, magnesium, copper, titanium, aluminum, bromine, sodium, potassium, nickel, chromium, and phosphorus [5, 6]. Some of the metallic and non-metallic elements are essentially required within a certain permissible limits for the human body for healthy growth, development and the proper functioning of the body. Hence, the determination of trace elements in tea samples is essential in order to evaluate their nutritional value. The concentrations of these elements in tea are different according to the type of tea and geological sources [5]. However, their ingestion in excessive amount can accumulate trace and toxic metals to the human organisms, which consequently cause severe health problems [5, 6]. Therefore, the evaluation of these elements could be helpful against any expected ill effect. In addition, some undesirable substances also exist due to exposure to the environment. Therefore, the determination of the metallic and non-metallic elements in tea has a great of interest. Several attempts have been made to assess tea quality by chemical analysis usually with reference to pigmentation and the flavoring characteristics. Furthermore, various spectrometric analytical techniques have been used for the quantitative analysis of black teas such as atomic absorption spectrometry (AAS) [7], inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) [8, 9] and X-ray fluorescence spectrometry (XRF) [10]. A polarized X-ray fluorescence spectrometer (PXRF) is used for the quantitative analysis of essential and non-essential elements including Mn, Fe, Co, Cu, Zn, Ni, Cr, Cl, Br, I, K, Mg, Ca, P, S, Al, Rb, Sr, As, Cd, Sn, Pb, and Hg in different types of tea marked in Italy [11]. The accuracy of their results was confirmed by calibrating the instrument with certified reference materials. They found that, the evaluated elements in the different kinds of teas have different proportions according to the soil composition and the climate in which the plant grows. However, it should be mentioned that, it is impossible to present all published work about black tea. Recently, an effective and easy sample preparation method was developed for quantitative elemental analysis of sixteen elements in green and black teas infusions using inductively coupled plasma atomic emission spectrometry (ICP-AES) and flame atomic absorption spectrometry (FAAS) [12]. Twenty types of green and black teas commercialized in Poland were used in this study. The acidification of the sample under investigation with nitric acid seems to be essential before the quantitative analysis measurements. For quality control purposes, the developed method was verified. For quality assurance and food safety purposes, a survey from the last fifteen years about the quantitative elemental analysis using atomic and mass spectrometers of medicinal plants and herbal teas as well as their tisanes was recently presented [13]. The survey presented the different sample preparation method, the matrix effect, quality control, and quality assurance used for these types of samples. An important discussion about the origin and the sources of the different elements has been outlined. Similar study was investigated to determine the heavy metals in ten different brand black teas (bagged and non-bagged) collected from Poland [14]. Based on the quantitative analysis results of the dry material and its infusion, they estimated the percentages of the heavy metals that transferred to teas infusion. Surprising results showed that, the bagged teas contained higher concentrations of some heavy metals namely; Pb, Mn, Fe, Ni, Al, and Cr, however both bagged and non-bagged black teas are still safe for humans.

In Saudi Arabia, drinking tea is a traditional habit among Saudi people and plays an important role for the families and social occasions. Although, Saudi Arabia considers as a one of the largest tea markets in the Middle East, a few numbers of studies were carried out to assess tea quality by chemical analysis [15, 16]. It was reported that, manganese was the most abundant elements in all tea samples and concentration reaches to 1071.7 μg g^{-1}. Furthermore, they did not able to detected Pb and Cd in all tea samples due to the low detection limits of these elements. However, they concluded that, the amounts of heavy metals in tea match the acceptable daily intake. Indeed, more investigation should be carried out in order to confirm this fact. Therefore, there is an urgent need to find out an adopted analytical method to measure the elements at low detection. Recently, our group has been developed a method for quantitative analysis of Cd, Cu, Ni, and Pb in the same black tea samples using High-resolution continuum source Graphite Furnace Atomic Absorption Spectrometry (HR-CS-GF-AAS) without chemical modifiers [17]. For this purpose, the pyrolysis and atomization temperatures were investigated. The obtained results were confirmed by analyzing Certified Reference Materials (CRM) of green tea.

Therefore, more investigation should be provided on the different types of black tea samples in locally available in Saudi Arabia market. The aim of the present work has been the quantitative determination of the different metallic elements in black tea available in Saudi Arabia. Inductively coupled plasma mass spectrometry (ICP-MS) has been chosen because this technique makes possible to visualize potential spectral interferences that might occur when conventional analytical techniques are used. Microwave-assisted acid digestion was optimized for the tea samples prior to the injection of the sample solutions to the ICP-MS. The precision and accuracy of the present method was demonstrated with the analysis of a green tea certified reference material (CRM). Further comparison with our previous published data was also carried out using high-resolution continuum source graphite furnace atomic absorption spectrometry.

Experimental

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

An inductively coupled plasma mass spectrometer (ELAN 6000, Perkin Elmer) was used for quantitative analysis of black tea samples. Argon gas with high purity was used for plasma generation and gas nebulization. A microconcentric nebulizer MCN-100 acquired from CETAC Technologies (Omaha, USA) was coupled to a cyclonic spray chamber. For the sample flow control, a specific peristaltic pump was used (Ismatec-Glattbrugg, Switzerland). The flow rate of the sample solution was 30 μL min^{-1}. Nebulizer gas flow rate was fixed at 0.7 L min^{-1}. The radio frequency (RF) power was operated at 1400 W. A Tygon orange/red 0.19-mm i.d. and 40-cm long peristaltic pump tubing was used. The other operating conditions for the ICP-MS were described in our previous work [18]. Prior to using the microconcentric nebulizer, a performance check for sensitivity, oxide and doubly charged ions formation was implemented using a conventional cross flow nebulizer.

Reagents

Purified and deionized high purity water was used (Millipore, Bedford, MA, USA). The standard solutions for Fe, Co, Ni, Cu, Zn, Mo, Cd, As, Cr, Pb, and V, containing 1000 mg L^{-1}, were prepared from a Titrisol® concentrate (Merck, Darmstadt, Germany). Nitric acid (HNO_3, 69 %, Fluka, France) was used for sample digestion. Fresh standard solutions for ICP-MS measurements were prepared daily. Other analytical reagent grades were used.

Samples Collection and Digestions

For the validation of the present work, a certified reference material (CRM) was used (NCSZC73014 green tea, Institute of Geophysical and Geochemical Exploration, Langfang, China). Six marked brands of black tea were collected for local markets of Saudi Arabia. The collected black tea represents the most commonly consumed in Saudi Arabia. The collected black tea samples are Al-Lord (T01), Red Marked (T02), Al-Rabee (T03), Bentalize (T04), Lipton (T05), and Al-Khair (T06). The collected black tea samples were dissolved using microwave digestion system (TOPwave, PM60, Analytik Jena AG, Germany). The present microwave system allows digesting eight samples simultaneously with the same digestion program. Before each digestion program, the Teflon digestion vessels were soaked for 24 h at room temperature in diluted nitric acid (10 % *m*/*v* HNO_3), followed by a microwave cleaning program which is recommended by the manufacturer. For the digestion of black tea samples, 5 mL of concentrated nitric acid (69 % *m*/*v*, Fluka, France) were added to 0.5 g of the black tea samples in the Teflon digestion vessel of the microwave. The Teflon vessels were shaken and introduced to the microwave oven. The optimized digestion program was used. To avoid foaming and splashing, the vessels were allowed to cool at room temperature after the digestion process and opened carefully. The prepared solutions were transferred to polypropylene bottles and completed to 14 mL with water. The digested samples were further diluted in order to be fitted with the calibration curve and to overcome with the maximum tolerable level of digested samples in ICP-MS. More details about the collected black teas and the digestion program were described in our previous work [17].

Results and Discussion

Small amounts of the heavy metals are common in black tea and are actually necessary for health, but large amounts of any of them may cause acute or chronic toxicity. The toxicity of the heavy metals can result severe different health problems such as reduced mental, central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. For these reasons, quantitative analysis of different black tea in Saudi Arabia was demonstrated.

Quantitative Analysis of Black Tea

Calibration curves of Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, As, Cr, Pb, and V were prepared from individual standard solutions at different concentrations ranging from to 5 to 250 ng g^{-1}. Excellent regression coefficients for the linear equation were obtained. The optimum isotopes for the elements of interest were used. The expected interferences were automatically corrected by the software of the manufacturer. In order to overcome with the maximum acceptable level of the elements, the dissolved black tea samples were more diluted before the quantitative analysis. Table 1 depicts the quantitative analysis

Table 1 Concentrations of trace elements (μg g^{-1}) in black tea in the Saudi Arabian market

El	T01	T02	T03	T04	T05	T06
Mn	444.53 ± 4.84	507.67 ± 0.63	1136.66 ± 2.15	602.80 ± 2.55	802.79 ± 0.13	211.14 ± 0.60
Fe	73.31 ± 0.91	153.32 ± 0.33	220.53 ± 0.63	142.60 ± 0.54	131.21 ± 1.02	170.42 ± 0.61
Co	0.10 ± 0.00	0.20 ± 0.00	0.43 ± 0.00	0.25 ± 0.00	0.19 ± 0.00	0.13 ± 0.00
Ni	2.62 ± 0.05	6.96 ± 0.05	10.76 ± 0.03	6.00 ± 0.02	5.69 ± 0.03	4.77 ± 0.01
Cu	6.92 ± 0.06	14.41 ± 0.04	28.10 ± 0.09	18.01 ± 0.02	13.23 ± 0.02	14.40 ± 0.06
Zn	10.70 ± 0.07	22.66 ± 0.17	46.18 ± 0.09	23.41 ± 0.05	20.32 ± 0.07	18.48 ± 0.05
Mo	0.04 ± 0.00	0.14 ± 0.00	0.18 ± 0.00	0.04 ± 0.00	0.08 ± 0.00	0.11 ± 0.00
Cd	0.01 ± 0.00	0.02 ± 0.00	0.05 ± 0.01	0.02 ± 0.00	0.03 ± 0.00	0.01 ± 0.00
As	0.07 ± 0.01	0.12 ± 0.02	0.19 ± 0.01	0.11 ± 0.01	0.12 ± 0.01	0.11 ± 0.02
Cr	9.99 ± 0.06	38.05 ± 0.38	45.03 ± 0.18	15.77 ± 0.09	25.59 ± 0.34	30.94 ± 0.13
Pb	0.23 ± 0.00	0.23 ± 0.00	0.53 ± 0.00	0.55 ± 0.01	0.30 ± 0.00	0.26 ± 0.00
V	0.36 ± 0.00	0.72 ± 0.01	0.82 ± 0.01	0.79 ± 0.01	0.69 ± 0.01	0.74 ± 0.01

results of the elements under investigation in the black tea samples. As we can see from Table 1, iron and manganese have the highest concentrations in all samples under investigation. The concentrations of Mn represent the highest concentrations all over the elements of interest and it range from 211.14 to 1136.66 μg g^{-1} with an average of 617.60 ± 319.80 μg g^{-1}. Al-Rabee tea (T03) originated from unknown sources, has the highest concentrations of manganese (1136.66 ± 2.15 μg g^{-1}).

On the other hand, iron concentrations varied from 73.31 to 220.53 μg g^{-1} with an average of 148.56 ± 48.30 μg g^{-1}. Similarly, Al-Rabee tea also has the highest concentration of iron. It is well known that Zn/Cu ratio is the most effective method in order to evaluate the influence of the individual concentration of Cu and Zn. In addition, Zn/Cu ratio is related to the development of coronary disease in diabetic patients [19]. Based on the obtained results, Zn/Cu ratio ranges from 1.28 to 1.64 with an average of 1.48 and this confirms the strong relation between Cu and Zn. On the other hand, the higher ratio was found also at Al-Rabee tea, which is equal 1.64. As the Zn/Cu ratio decreases, a severe health problem could be arises such as copper toxicity, excessive breakdown, emotional instability, impotence, slow healing, loss of appetite, and hair loss. Of course, drinking black tea is not the only source of Cu and Zn but there are also many other nutrition sources. Meanwhile, one could take in consideration Zn/Cu ratio originated from black tea especially if drinking tea is daily usual.

In the case of Cr, its concentration ranges from 9.99 to 45.03 μg g^{-1} with an average of 27.56 ± 13.25 μg g^{-1}. The highest concentration of Cr was also found in Al-Rabee tea. Cr toxicity is associated to the free radical processes generating from reactive oxygen species. Although trivalent chromium (III) is used as a nutritional supplement, hexavalent chromium (VI) is considered more toxic and carcinogenic. Therefore, the most dangerous concern is the existence of Cr(VI) in black tea samples. Although the quantitative analysis of Cr did not recognize between Cr(III) and Cr(VI), the high concentration of Cr in some tea samples gives more attention for more investigation of these kind free radicals. For Ni, the concentration is up to 10.76 μg g^{-1} with an average of 6.13 ± 2.70 μg g^{-1} and it is not essential for humans. However, it can cause adverse effects on kidney, spleen and lungs due to ingested nickel compounds. The average daily nickel intake from diet ranges from 0.00 to 0.02 μg g^{-1}. The obtained results seem to be higher than these values, which represents more effects on health. Al-Rabee tea still has the highest concentration of Ni. The quantitative analysis results of Pb in tea samples revealed that, the concentrations are ranging from 0.23 to 0.55 μg g^{-1} with an average of 0.35 ± 0.15 μg g^{-1}. The maximum Pb concentration was found in Al-Rabee tea (0.53 μg g^{-1}) and Bentalize tea (0.55 μg g^{-1}). The concentrations of Pb in the other tea samples are comparable and less than the average value. Although, the maximum daily intake of lead equals 1 μg g^{-1}, a prolonged intake can be hazardous to human beings. Lead poisoning originates from ingestion of food or water contaminated with lead whereas it is rapidly absorbed into the bloodstream. The long-term exposure of Pb compounds has an influence on the central nervous system, the cardiovascular system, kidneys, and the immune system.

In addition, this can cause increasing in blood pressure as well as anemia. Naturally, organic and inorganic arsenic can be found in the different plants with low levels whereas it is widely found in the earth's crust through natural and anthropogenic sources. In the present work, the total arsenic including organic and inorganic arsenic was quantified. Its concentration ranges from 0.08 to 0.19 μg g^{-1} with an average of 0.12 ± 0.04 μg g^{-1}. The maximum As concentration was found also in Al-Rabee tea (0.19 ± 0.01 μg g^{-1}). Arsenic level seems to be safe without any remarkable risk assessment.

Cadmium content of the present black tea sample ranges from 8.41 to 52.16 ng g^{-1} with an average of 24.67 ± 15.9 ng g^{-1}. The existed cadmium in black tea sample can be originated from soils because insecticides, fungicides, sludge, and commercial fertilizers. In the case of cobalt, its concentration ranges 98.29 ± 1.50 ng g^{-1} to 430.30 ± 1.90 ng g^{-1} and its average value equals 215.30 ± 118 ng g^{-1}. It is used in minute amounts as a component of Vitamin B_{12}. The excessive levels of cobalt may case intoxication leading to pernicious anemia but this is rarely recognized in the literature. The concentration of molybdenum ranges from 36.14 ± 1.40 ng g^{-1} to 175.70 ± 4.30 ng g^{-1} with an average of 96.31 ± 54.90 ng g^{-1}. Meanwhile, the acute molybdenum poisoning in human beings is very unlikely. Finally, vanadium concentrations ranges from 364.10 ± 3 ng g^{-1} to 824 ± 10 ng g^{-1} with an average of 688.60 ± 166 ng g^{-1} and it is used extensively in various heavy industries. Disposition of vanadium in specific tissues may be involved in the pathogenesis of certain neurological disorders and cardiovascular diseases [20]. It seems that all black tea samples have high vanadium concentration above 100 ng g^{-1}, which is toxic. As illustrated earlier, Al-Rabee black tea samples have the highest concentration for Co, Mo, and V. In general, we could confirm that, the trace and heavy metals in Al-Rabee black tea represents the highest concentration and this type of black tea is not recommended for daily use in Saudi Arabia.

For comparison with the international levels of the elements of interest, Table 2 compares the elemental composition of the present study to those reported in the previous studies from Japan [8], Turkey [9], Saudi Arabia [16], Nigeria [21], India [22], and recent international values [23]. The average concentration of Mn was lower than the published data but the average concentration Fe is comparable with the published work. In the case of Co, Cd, and As, the average

Table 2 Comparison between the element concentrations (μg g^{-1}) in black tea found in this work and published data

Element	Concentration, μg g^{-1}						
	This work	Nigeria [21]	Turkey [9]	Japan [8]	KSA [16]	India [19]	International [20]
Mn	617.60 ± 320		806.00 ± 34.20	5030 ± 7	750.90 ± 185		N.D-15,000
Fe	148.56 ± 48.3	1.65 ± 0.16		134 ± 48	250.50 ± 199		0.7–11,700
Co	0.22 ± 0.12		21.80 ± 1.10	0.51 ± 0.04	11.00 ± 3.40		N.D-17.4
Ni	6.13 ± 2.70		20.90 ± 1.50	8.06 ± 0.19	16.80 ± 4.50	2.53 ± 1.01	N.D-1960
Cu	15.84 ± 7.01	0.22 ± 0.03	24.80 ± 1.40	27.70 ± 0.70	18.10 ± 6.90	24.07 ± 2.25	0.05–602
Zn	23.63 ± 11.95	0.02 ± 0.01	140.90 ± 9.10	36.60 ± 0.70	65.70 ± 31.30		N.D-1120
Mo	0.10 ± 0.06			0.04 ± 0.00			N.D-571
Cd	0.03 ± 0.02	0.12 ± 0.01	2.00 ± 0.80	0.71 ± 0.02	1.10 ± 0.50	0.14 ± 0.06	N.D-8.60
As	0.12 ± 0.04	2.22 ± 0.01					N.D-10.20
Cr	27.56 ± 13.25		11.70 ± 0.10		9.80 ± 4.50	4.76 ± 1.27	N.D-129
Pb	0.35 ± 0.15	0.19 ± 0.02	8.30 ± 0.10		1.70 ± 0.80	0.81 ± 0.32	0–240
V	0.69 ± 0.17						0.02–29

concentrations of the present work are lower than the published work. The Cd and Co concentrations found in Turkey are the highest and the As concentration found in Nigeria is the highest. In addition, the average concentration of Cu of this study are comparable with other studies except the found values of Nigeria [21], whereas the Cu content is much lower than in the other studies. On the other hand, the average concentration of Zn in the present study seems to be lower than the previous study of Saudi Arabia and the average concentration found in Turkey is the highest. In the case of Pb, the average concentrations found in this work is comparable with other values found in the literature with the expectation of Turkey whereas Pb concentration seems to be the highest values. For Ni, the average concentration of the present work is located in the middle with other values and it is lower than the concentration found in Saudi Arabia before. Although the average concentrations of Cr and Mo in the present work represents the highest values but both of them is located in the range of the international values. Finally, the average concentration V was not found in compared results but it is also in the range of the international data. Therefore, the collected black tea samples from Saudi Arabia do not seem to be seriously contaminated with heavy metals.

Sensitivity of the Method

Table 3 illustrates the linear regression equations, the correlation coefficients and the limits of detection in ng g^{-1} for the elements under study. A good linearity for the calibration curves was obtained for all the elements under study in the concentration ranging from 5 to 250 ng g^{-1}. The obtained correlation coefficients are $R^2 = 0.99$. The limits of detections (LODs) were calculated as three times standard deviation of the 20 measurements of the blanks multiplied by the dilution factor of the samples under study. It was found that, the LODs range from 0.48 ng g^{-1} for Cd to 166 ng g^{-1} for Fe. The values of the LODs show the ability of the present technique for the determination of the concentration at low levels of elements under investigation in the black teas samples.

Accuracy

Based on the quantitative analysis of the black tea samples using ICP-MS, accuracy and precision of the quantitative analysis of the black tea samples using ICP-MS were assured. For this purpose, average values of ten replicates were taken for each determination. A comparison with our previous work using high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS)

Table 3 Linear regression, the correlation coefficients, and the limit of detection of elements found in the black tea collected from Saudi Arabia market

	Equation	R^2	LOD (ng g^{-1})
Mn	$Y = 12237X + 28703$	0.99	76.06
Fe	$Y = 241.5X + 7365$	0.99	166.03
Co	$Y = 44152X - 21846$	0.99	5.94
Ni	$Y = 1733X + 5055$	0.99	2.94
Cu	$Y = 10747X + 12518$	0.99	18.29
Zn	$Y = 1161X + 4254$	0.99	18.29
Mo	$Y = 4673X + 6737$	0.99	9.00
Cd	$Y = 2026X + 2099$	0.99	0.48
As	$Y = 27650X + 43185$	0.99	0.48
Cr	$Y = 6698X + 27832$	0.99	7.67
Pb	$Y = 21019X - 127.6$	0.99	3.07
V	$Y = 8688X + 14856$	0.99	4.21

Table 4 The concentration levels of Cd, Cu, Ni, and Pb by ICP-MS and HR-CS-AAS in the present black tea samples

	Cd (μg g^{-1})		Cu (μg g^{-1})		Ni (μg g^{-1})		Pb (μg g^{-1})	
Sample	ICP-MS	HRCSAAS	ICP-MS	HRCSAAS	ICP-MS	HRCSAAS	ICP-MS	HRCSAAS
T01	0.01 ± 0.00	0.01	6.92 ± 0.06	7.55	2.62 ± 0.05	6.94	0.23 ± 0.00	0.21
T02	0.02 ± 0.00	0.02	14.41 ± 0.04	15.60	6.96 ± 0.05	9.24	0.23 ± 0.00	0.09
T03	0.05 ± 0.01	0.05	28.10 ± 0.09	28.30	10.76 ± 0.03	11.90	0.53 ± 0.00	0.13
T04	0.02 ± 0.00	0.02	18.01 ± 0.02	19.20	6.00 ± 0.02	6.52	0.55 ± 0.01	0.20
T05	0.03 ± 0.00	0.03	13.23 ± 0.02	13.90	5.69 ± 0.03	5.63	0.30 ± 0.00	0.19
T06	0.01 ± 0.00	0.01	14.40 ± 0.06	17.20	4.77 ± 0.01	6.06	0.26 ± 0.00	0.23
Average	0.02 ± 0.02	0.02 ± 0.01	15.84 ± 7.01	17.00 ± 6.80	6.13 ± 2.70	7.70 ± 2.40	0.350 ± 0.15	0.18 ± 0.06

was demonstrated (Table 4). There are a good agreements for the results of Cd, Cu, and Ni, but a remarkable difference reaches to 51.43 % was appeared for the average value of lead. Furthermore, repeated analysis of a certified reference material (NCS ZC 73014 Green Tea CRM) subjected to the same protocol was also taken place. Table 5 illustrates a comparison of the certified values for the element of interests versus the present measured values using ICP-MS respectively. The obtained results were statistically analyzed by using the Student's *t* test. Based on Table 5, the significant difference between the measured and certified values at a 95 % level of confidence; $p = 0.05$, has been calculated. It was found that, there is no significant statistical differences at this level between certified and measured and the zero hypothesis is acceptable. Therefore, there is a good agreement between the measured and the certified values. Therefore, the accuracy and precision of the present method seems to be acceptable.

Table 5 Quality assurance of the present method in NCS ZC 73014 Green Tea CRM; all values in μg g^{-1}

Analyte	Certified value	Measured value
Mn	500.00 ± 20	409.72 ± 3.38
Fe	242.00 ± 18	198.56 ± 1.80
Co	0.22 ± 0.02	0.28 ± 0.00
Ni	3.40 ± 0.30	3.22 ± 0.04
Cu	18.60 ± 0.70	16.76 ± 0.17
Zn	51.00 ± 2.00	40.96 ± 0.38
Mo	0.04 ± 0.01	0.01 ± 0.00
Cd	0.06 ± 0.00	0.07 ± 0.00
As	0.09 ± 0.01	0.12 ± 0.01
Cr	0.45 ± 0.10	0.39 ± 0.01
Pb	1.50 ± 0.20	1.48 ± 0.02
V	0.17 ± 0.03	0.92 ± 0.00

Conclusion

The initiative of the present work comes from that, there is a remarkable lack of information about the levels of trace elements in black tea commercialized in Saudi Arabia. Therefore, the present method has been introduced for quantitative analysis of twelve elements in black teas collected from the market of Saudi Arabia using inductively coupled plasma mass spectrometry (ICP-MS). The sensitivity of the developed method was demonstrated. Furthermore, the accuracy of the method was confirmed by analyzing a certified reference material of green tea. In addition, the accuracy was also confirmed by comparing the present results with our previous data obtained from high-resolution continuum source atomic absorption spectrometry (HR-CS-AAS). A surprised result was found for Al-Rabee tea who is one of the most widely used in at Saudi Arabia. It has the highest concentration of all elements under study. For this reason, further study with a great number of samples should be carried out at Al-Rabee tea in order to confirm the present obtained results.

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