

Research Article

Determination of Major, Minor and Trace Elements in Cigarette Tobacco Samples from Karbala, Iraq

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Article Info

Article history:

Received 12-01-2022

Received in revised form
16-01-2022

Accepted 17-01-2022

Available online 07-06-
2022

Keywords:

Trace elements; Tobacco; ICP-AES; Smoking activity.

Abstract

In recent years, cigarette smoking has become a major health issue, especially in terms of active and passive smoking exposure to chemicals released from the combustion of tobacco. The determination of trace elements in biological and environmental samples is very important since they play an important role in the physiological processes of humans and other living organisms. In this study, sixteen commercial cigarette brands were collected from Karbala, Iraq. The levels of Na, P, K, Fe, Cu, Zn, Sr, Cd, Sn, and Ba were determined in digested tobacco samples by using inductively coupled plasma atomic emission spectrometry (ICP-AES). The range of elemental levels for the 16 tobacco samples were Na (84 – 384 mg/L d.w.), P (1262 – 1687 mg/L d.w.), K (16878 - 30492 mg/L d.w.), Fe (166 - 349 mg/L d.w.), Cu (3 - 10 mg/L d.w.), Zn (18 - 35 mg/L d.w.), Sr (53 - 102 mg/L d.w.), Cd (0.24 – 2.03 mg/L d.w.), Sn (25 – 35 mg/L d.w.), Ba (7 – 16 mg/L d.w.). The levels of precision and accuracy for the ICP-MS instrument were confirmed by calculation of the relative standard deviation (%RSD) and percentage recoveries (%R) using ten replicate measurements of a "pooled" tobacco sample, and certified reference materials (CRMs). The results show a good range of precision (0.8 – 2.77 %RSD) and accuracy (90 -107 %R) was obtained.

1. Introduction

Tobacco contains a complex mixture of more than 7000 chemicals [1]. They include the stimulant nicotine, along with benzo-pyrene, benzene, lead, chlorinated dioxins, and furans [2]. In addition, cigarettes also contain hydrogen cyanide, arsenic, acrolein, acetaldehyde, 1,3-butadiene, toluene, and phenol which can cause adverse effects on vital human processes, such as the cardiovascular, respiratory, reproductive, and nervous systems [3,4]. Furthermore, high levels of heavy toxic elements have also been reported in tobacco [5, 6]. A previous study has reported that smoking is mainly a source of heavy metals, while the use of electronic cigarettes is a potential source of rare earth elements [7]. Therefore, cigarette tobacco becomes a high-risk source for various diseases, such as mouth cancer [8]. Cigarette smoking provides a significant risk in terms of several eye diseases, for example, macular degeneration, glaucoma, and cataract formation. It was found that toxic and oxidative effects of tobacco lead to damage of the eye tissue, including the onset of dry eye disease [9]. In recent years cigarette smoking has become a major health issue, especially in terms of active and passive smoking linked to exposure to chemicals released from the combustion of tobacco [10, 11]. The World Health Organisation reported the smoking rates for males, females, and total population in different regions in the world: Africa (36.2, 9.4 and 22.9%); Americas (34.7, 23 and 28.7%); Eastern Mediterranean (34.2, 8.7 and 21.8%); Europe (43.5, 23.4 and 33%); Southeast Asia (48.2, 8.2 and 28.6%); and the Western Pacific (62.3, 5.8 and 34.4%) [12]. Amongst pregnant women in USA between 13 - 20% smoke during pregnancy [13]. Previous studies have shown that exposure to

tobacco can lead to health disorders for children, such as childhood cancer [14]. The World Health Organization reported that many diseases can be caused by smoking, such as cancers (namely; larynx, oropharynx, lung, leukemia, stomach, pancreas, kidney, colon, cervix, and bladder) and chronic diseases, for example, stroke, periodontitis, coronary heart disease, asthma, and reproductive effects in women (including reduced fertility) [11]. In addition, there are some diseases caused by second-hand smoke, especially in children, for example, brain tumors, asthma, lymphoma, leukemia, and lower respiratory disease [14]. Adults can also suffer from diseases caused by second-hand smoke, such as stroke, breast cancer, lung cancer, asthma, and reproductive effects in women (including reduced fertility) [11]. Smoking has been recognized to be an important risk factor in diabetes [2,15], with one study in the USA reporting a link between cigarette tobacco and the onset of this disease [15,16].

Smoking is considered to be a major environmental risk factor associated with many serious systemic diseases, including respiratory diseases, heart diseases, and cancers [17-20]. One study in the USA reported that there is a link between smoking tobacco and the onset of type 2 diabetes [15]. Many toxic trace elements are found in cigarette tobacco which can cause more health problems and disorders [21, 22]. This study aimed to develop an analytical method for the determination of trace elements in cigarette tobacco.

2. Materials and Methods

Study area

Karbala is a city in Iraq located about 60 miles southwest of Baghdad with approximately one million inhabitants. Although there is no data for smokers in Karbala, Iraq, the majority of smokers are

men, with more than 50% of them being heavy smokers (smoked >1 pack/day) []. This finding is based on the questionnaire that was used during the collection of biological samples from Karbala [23,27].

Sample Collection and Preparation

Samples of the sixteenth of the most consumed cigarette brands in the Karbala market were randomly purchased from local grocery stores as well as all cigarette brands have a filter. The tobacco samples were randomly extracted from one cigarette of each brand after the wrapping paper was carefully separated. All samples were dried at 104 °C for 4 hours and accurately weighted to 0.5 g. Samples were digested using dry ashing and Kjeldhal™ tube with 1 ml of concentrated Aristar® nitric acid. The digested solutions were then diluted to 50 ml in a polyethylene volumetric flask with deionised distilled water before the analysis by ICP-AES [28]. Ten replicates for tobacco were prepared to evaluate measurement repeatability. Reagent blank also was prepared for detection limits determinations. In addition, three subsamples of each one of the standard reference materials (SRM, NIST 1573 "Tomato Leaves" and NIST 1572 "Citrus Leaves") were subjected to acidic digestion and ICP-AES analysis to verify accuracy [28].

Instrumentation

A Perkin Elmer Optima™ 5300 DV ICP-AES (Perkin Elmer Life and Analytical Sciences, Shelton, CT, USA) with WinLab32™ software and a PerkinElmer S10 autosampler (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) was used in this study. An echelle grating and the charge-coupled device (CCD) were used in the ICP-AES instrument.

3. Result and Discussion

Limit of Detection (LOD)

The instrumental LOD may be defined as that quantity of the element which gives rise to a reading equal to three times the SD of a series of at least ten determinations ($n = 10$) at near the blank level [29,30]. The LODs for Perkin Elmer Optima™ 5300 DV ICP-AES instruments were determined for a range of elements in this study. The LODs were calculated for a total of 15 blank solutions (1% HNO₃). The resulting LOD data, based on a mean blank ($n = 15$) signal + 3SD is shown in Table 1.

Element	Wavelength (nm)	LOD
Na	589.59	0.006
P	177.43	0.010
K	404.49	0.587
Fe	224.71	0.002
Cu	196.03	0.001
Zn	213.86	0.001
Sr	206.84	0.011
Cd	228.62	0.001
Sn	228.80	0.003
Ba	232.235	0.001

Accuracy and Precision

In this study, precision levels were evaluated for any matrix effects by replicate analysis ($n = 10$) of a "pooled" sample that was prepared from at least 6 samples of tobacco. Mean, standard deviation (SD), and relative standard deviation (%RSD) values are summarized in Table 2. In general, good levels of precision were obtained for most elements with an acceptable range of 0.80 – 2.77% RSD. Measured CRM values obtained for the analysis of trace elements by ICP-AES were highly comparative to certified levels

(Table 2). Analytical recoveries ranged from 90 to 107% for all elements determined.

Table 2: Accuracy and precision levels for tobacco (n=10), NIST SRM@ 1573a Tomato Leaves (n=3), presented as mean \pm SD, %RSD and R% for measured values and mean for certified values.					
Element	Elemental level (mg/kg)				
	Accuracy			Precision	
	Measured value mean \pm SD	Certified value mean	Percentage recovery (%R)	mean \pm SD	%R SD
Na	141 \pm 2.46	136	104	371 \pm 8.7	2.4
P	2090 \pm 11	2160	97	1318 \pm 28.4	2.2
K	29082 \pm 380	27000	107	26262 \pm 55.4	2.1
Fe	348 \pm 0.6	368	95	258.3 \pm 2.8	1.1
Cu	5 \pm 0.02	4.7	106	3 \pm 0.04	1.2
Zn	28 \pm 0.25	29	97	24 \pm 0.2	0.8
Sr	94 \pm 2.7	100	94	69 \pm 0.78	1.1
Cd	1.6 \pm 0.03	1.52	105	0.89 \pm 0.02	2.8
Sn	29 \pm 0.5	29	100	28.95 \pm 0.66	2.3
Ba	19 \pm 0.34	21	90	13 \pm 0.35	2.7

SD is standard deviation; RSD is the relative standard deviation (quoted as a % in brackets).

Elemental Levels of Cigarette Tobacco

Soil is the main source of trace elements in plants. The mobility of trace elements from the soil solution into the plant as free ionic or complex forms occurs either by ion exchange or adsorption between the root and soil. The processes of mobility and availability of trace elements in plants are based on several factors, namely pH, redox reactions, geochemical, biological, external weathering and condition, and the internal bond to various compounds [31]. Tobacco leaves are widely used in manufacturing smoking materials [32]. Because of the possible transfer of certain elements from the tobacco-to-tobacco smoke during the com-

bustion process, it is desirable to study the concentration of various elements present in cigarette tobacco [33]. Multi-trace element analysis by ICP-AES was performed for cigarette tobacco samples. The concentration mean \pm SD and ranges (mg/kg) of 10 elements in 16 cigarette tobacco from Karbala, Iraq are shown in Table 3. It was found that the levels of K, P, Na, and Fe were higher than those reported for other elements in the whole sample. Potassium levels (25887 \pm 3658.38 mg/kg K dry wt) on average were similar to those found in Turkey cigarettes range (23000 – 31000 mg/kg) [34]. The lower concentration was reported for Cu (5.36 \pm 2.54 mg/kg Cu dry wt) which is slightly lower than those reported for American and Algerian cigarettes (9 – 17 mg/kg Cu dry wt) [33]. The average concentration of P was (1478.53 \pm 96.66 mg/kg P dry wt), but unfortunately, there is no published value for P that has been found to compare with this study. The iron average concentration was 257.13 \pm 16.25 mg/kg Fe dry wt which was lower than those reported for Turkey and Iranian cigarettes [35]. Zinc average concentration was 26.83 \pm 5.23 mg/kg Zn dry wt was in agreement with the reported ranges [34-37]. Sodium levels (203.19 \pm 81.24 mg/kg Na dry wt) were lower than reported ranges for other cigarette tobacco. The levels of Sr level (75.29 \pm 13.98) were higher than those reported for other cigarettes [22] but it was lower than those reported in the USA and Algerian [27]. The concentration of Cd (0.90 \pm 0.46 mg/kg Cd dry wt) agreed with those reported for the USA and Algerian cigarettes [27]. In contrast, the Sn level (29.98 \pm 2.73) was higher than those reported for Turkey and the USA cigarettes samples. Finally, Ba (12.73 \pm 2.73 mg/kg Ba dry wt) levels were found to be variable compared with other studies [23]. The findings are confirmed that the concentration of all elements has differed from one

country to another. This may be due to the older leaves having higher elemental levels than in the younger [22]. In addition, tobacco plants are absorbed many essential, non-essential, and toxic elements from the soils, fertilizers, pesticide treatments, storage, processing, packing, and other processes [33].

Many studies have investigated the elemental levels of cigarette tobacco and associated health/pollution implications. It has been known for a few decades that tobacco combustion has the potential to deliver dangerous quantities of heavy metals to the blood and various organs [22,36].

Cadmium in particular is regarded as one of the “strong carcinogens” in tobacco smoke [4]. Tobacco plants have a special ability to absorb Cd from soil and to accumulate it in unusually high concentrations in the leaves (ranging from 0.77 to 7.02 mg/kg) [38]. In cigarettes, Cd concentrations range in this study from 0.24 to 2.03 mg/kg, with a mean level of 0.90 ± 0.46 mg/kg (dry weight). These are very high levels compared with those in food which are normally below 0.05 mg/kg[36].

Table 3: Comparison of the elemental levels for commercial tobacco (n = 16) used in this study and those reported in the literature (mg/kg, dry weight).

Element	Elemental level (mg/kg, dry weight), mean \pm SD (range)	
	This study	Literature range
Na	203.19 \pm 81.24 (84 – 383.29)	(241-376 []), (394-425 []), (804-1028 [])
P	1478.53 \pm 96.66 (1262 – 1687)	nf
K	25887 \pm 3658.38 (16878 – 30492)	(2200-2800 []), (23000-31000 []), (36700-37500 [])
Fe	257.13 \pm 16.25 (166 – 349)	(621-1031, 900-1200 []), 325-520 [], 359-562 [])
Cu	5.36 \pm 2.54 (2.45 – 9.88)	(9-17 [])
Zn	26.83 \pm 5.23 (18.09 – 34.95)	(12.655.8 []), (15-45 []), (16.8-30.20 []), (41.1-62.9 [])
Sr	75.29 \pm 13.98 (53 – 101.9)	(29.7-49.5 []), 136.88-203.20 [])
Cd	0.90 \pm 0.46 (0.24 – 2.03)	(0.23-5.8 [])
Sn	29.98 \pm 2.73 (25 – 35)	(0.18 []), (0.29 [])
Ba	12.73 \pm 2.73 (7 – 16)	(1.15*5.78 []), 46-88 []), (40.7-56.6 [], (100.3-101.3 [])

A large proportion of the Cd contained in the cigarette passes into the smoke. Since Cd concentration in the ash is practically constant (about 16% of that present in the unsmoked cigarette and a further 15% is retained by the filter), the

greater part (nearly 70%) passes into the smoke [39-41]. Furthermore, the boiling point of trace elements can play a significant role in increasing or decreasing the levels of trace elements in cigarette smoke, and hence their effects on smoker

health [42]. For example, the boiling points of Cd and V are 767°C and 3000°C, respectively; the temperature of a cigarette could exceed 800°C at the end when ignited [42]. Therefore, the concentration of Cd in cigarette smoke could potentially be higher than V since the boiling point of Cd is lower than that of V. In contrast, the concentration of V in filter and ash is higher than Cd [36]. As a result, the impact of Cd on the smoker's health will increase.

4. Conclusions

The levels of trace elements in cigarette tobacco are reported in Table 3. It was found that all the elements are found in cigarette tobacco according to the following order: K > P > Fe > Na > Sr > Sn > Zn > Ba > Cu > Cd. The findings confirm that the levels of elements in cigarette tobacco are in general agreement with the reported data for other countries and in somewhat disagreement with other countries.

Acknowledgment

This research was supported by the department of chemistry, college of science at the University of Kerbala, Iraq. in Iraq.

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