

# Analytical Determination of Heavy Metals in Various Dokha and Shisha Products, and Related Health Implications

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## ABSTRACT

**Objective:** In this present study twelve metals were analyzed in various Dokha and Shisha products. The analysis was carried out using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). All the metals were found in each sample and at various concentrations. Furthermore, the concentration of various heavy metals with e-cigarette is compared in the discussion.

**Results:** Dokha tobacco contained very high metal concentrations compared to Shisha and Marlboro brand cigarette tobaccos. The highest level of aluminum(Al) (421.235 µg/g), boron(B) (219.815 µg/g), Cobalt(Co) (25.050 µg/g), copper(Cu) (24.000 µg/g), lead(Pb) (468.620 µg/g), and zinc(Zn) (342.740 µg/g), were found in Alward Alahmar Green Dokha tobacco. Due to the significant toxicity of these metals, it is very important to control and quantify their concentrations in the tobaccos.

**Abbreviations:** ICP-OES: Inductively Coupled Plasma Optical Emission Spectrometry; Fe: Iron; Mn: Manganese; Zn: Zinc; Cu: Copper; Cd: Cadmium; Cr: Chromium; As: Arsenic; Be: Beryllium; Ni: Nickel; Al: Aluminum; B: Boron; Co: Cobalt; Pb: Lead; A.R.: Analytical Reagent; HNO<sub>3</sub>: Nitric Acid; HCl: Hydrochloric Acid; EC: E-Cigarette; PDE: Permissible Daily Exposure

## Introduction

Tobacco is available in the market legally although it is harmful to humans [1]. During smoking, a complex mixture of compounds is inhaled into the respiratory system affecting different organs. In 1959, some 400 compounds were known to be present in tobacco leaves and tobacco smoke; today, the figure has risen to more than 4000 [2]. Harmful metals enter the body via food, drinking water, and the air we breathe, or by skin contact. They could accumulate in the liver, kidneys, bones, pancreas, and the central nervous system where they effect the health without being noticed and diagnosed. Heavy metals can cause cancer without ever being implicated in the diagnosis. Heavy metals cause sodium retention leading to high blood pressure. They can also cause heart disease and mental

retardation. Everyone is con-taminated with heavy metals, some seriously, without ever knowing it. Nonessential heavy metal ions cause aging in addition to serious diseases and death. People who are otherwise very healthy will have increased aging caused by heavy metal ions cross-linking between normal molecules in the body.

These ions are sometimes referred to as free radicals. The cross-linking has been identified in diseases such as hardening of the arteries, skin ailments, carpal tunnel syndrome, degeneration of organs, and nerve damage. When heavy metal poisoning is suspected, it is important to begin the treatment as soon as possible to minimize long-term damage to the patient's nervous system and

digestive tract. Heavy metal poisoning is considered a medical emergency, and the patient should be taken to a hospital emergency room. Heavy metals concentrations in Dokha and Shisha tobacco products have not been extensively studied in the Middle East. Tobacco leaves are rich sources of toxic heavy metals as metals get preferentially enriched in the tobacco leaves during plant growth [3,4]. The use of tobacco products always puts an impact/influence on the health of smokers directly as well as non-smokers via passive smoking and adds heavy metal content to the environment [5,6]. Dokha is commonly smoked out of an elongated wooden pipe called a Midwakh (alternatively spelled 'Medwakh').

Hookah is a water pipe used to smoke Shisha tobacco mixture in which charcoal heated air passes through a water-filled chamber [7-10]. According to a World Health Organization advisory, a typical one-hour session of hookah smoking exposes the user to 100 to 200 times the volume of smoke inhaled from a single cigarette. Even after passing through water, tobacco smoke still contains high levels of toxic compounds including carbon monoxide, heavy metals, and cancer-causing chemicals (carcinogens) [11]. The traditional Midwakh pipes have no filters so large amount of toxic heavy metals can easily enter the lungs [12]. The content of metals in tobacco varies a lot and it depends on several factors such as soil type and pH genotype, use of some metal-containing pesticides, fertilizers, etc. Some of the metals such as iron (Fe), manganese (Mn), zinc (Zn), and copper (Cu) are important micronutrients and they are also very important for plant growth and yield [13,14]. While soil factors have a large impact on the bioavailability of metals to plants, different species or varieties grown on the same soil can have different metal uptake [15].

However, other metals such as lead, cadmium, and nickel are not important for the plant growth but they can cause serious health and ecological problems, and several toxic metals as carcinogens. Cadmium (Cd), chromium (Cr), arsenic (As), beryllium (Be) and nickel (Ni) are classified as group 1 human carcinogens [16]. In shisha, the concentration of toxic elements per portion smoked is diluted by the molasses and glycerin. It is noted that the most important measure regarding the toxic metals is the amount reaching the smoker's respiratory system from the smoke. The aim of the present study is to determine the concentrations of twelve metals (Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in 11 various tobaccos found in different Dokha, Shisha, and cigarette brands for sale in the UAE. The samples were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

## Methodology

### Sample Collection and Storage

Dokha and Shisha samples analyzed during this study such as "TURBO" Dhoka, "Alward Alahmar" Dhoka, "Yusuf Redha" Dokha, Shisha "Arguilla Premium Natural", "MAZAYA" and "Al Fakher" Shisha samples were purchased from different stores. All samples were assigned an identification number and logged into a database.

They were sealed in plastic bags and stored at 27 °C in their original packaging until tested.

### Chemical Reagents and Preparation

Analytical Reagent (A.R.) grade chemicals and reagents used for the preparation of concentrated Hydrochloric acid (HCl) A.R (37%), concentrated Nitric acid (HNO<sub>3</sub>) A.R (65%) were purchased from Sigma-Aldrich. ICP multi-element standard solution IV, (23 elements in diluted nitric acid) 1000 mg was used to prepare the calibration standards used in determining the heavy metal concentration in the samples. To dilute the standard solution deionized water was used.

### Instrument and Apparatus

Inductively Coupled Plasma ICP-OES (Varian-VISTA MPX) was used to determine the concentration of heavy metals. Ceramic pestle and mortar used for grinding and homogenizing the tobacco samples. Digital analytical balance (Scientech with model no SA210), and Whatman No. 42 filters (ash less-Germany) were used for weighing, and filtering the samples, respectively. All Glassware were soaked in 5% nitric acid for 24 h, washed with deionized water, and dried to ensure that any contamination from glassware does not occur.

### Preparation of Tobacco Samples

The samples were air dried on clean watch glass and care was taken to avoid influence by dust during air drying. The dried leaves were ground using mortar and pestle and sieved with mesh sieve.

### Acid Digestion of Tobacco Samples

In this present work, the solid samples were digested using acid digestion method. Digestion with acid or acid mixtures has long been the traditional method for the determination of metals in plants. It is very strong acid digestion that will dissolve all elements that could become environmentally available. About 0.2 g of ground tobacco leaves was weighed into a clean 125 mL Erlenmeyer flask. A 10 mL mixture of HNO<sub>3</sub> (65%) and HCl (37%) with a ratio of 4:1 (v/v) were added and allowed to digest by heating the vessel in a water bath-shaker for 12 h at 100 °C. The mixture was finally heated strongly to a medium heat for 3 minutes and allowed to cool.

The solution was filtered using 9 cm diameter Whatman (No. 42) filter papers and transferred into 100 mL volumetric flask and made up to the mark with deionized water. The filtrate solution was stored in the refrigerator waiting for heavy metal analysis by ICP-OES. Quantification was achieved by interpolating the relevant calibration curves prepared from aqueous solutions of multi-element (Merk CertiPUR-1.11355.0100, Germany) metal standards in the same acid concentration, to minimize matrix effects.

### Analysis of Standard Reference Materials

All samples were analyzed for Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn concentrations. Moreover, the precision, accuracy, and reproducibility of results for every run was started with a control, blank and testing several quality controls (QC) solutions.

## Results

Our research provided information related to possible toxic heavy metals present in Dokha and Shisha products locally sold in UAE market. The metal concentrations in various tobacco samples are presented in Table 1 in  $\mu\text{g/g}$  units and plotted in Figure 1. The concentrations of each element along with range of minimum and maximum values in all samples are shown in Table 2. The range

of Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in various Dokha and Shisha products are shown as follows:

Al (8.170 to 421.235  $\mu\text{g/g}$ ), B (3.2155 to 219.815  $\mu\text{g/g}$ ), Cd (0.964 to 58.460  $\mu\text{g/g}$ ), Co (0.113 to 25.050  $\mu\text{g/g}$ ), Cr (0.185 to 58.165  $\mu\text{g/g}$ ), Cu (8.689-24.000  $\mu\text{g/g}$ ), Fe (20.730-654.700  $\mu\text{g/g}$ ), Mn (10.526-159.240  $\mu\text{g/g}$ ), Ni (2.047-59.000  $\mu\text{g/g}$ ), Pb (5.560-468.620  $\mu\text{g/g}$ ), and Zn (0.375-342.740  $\mu\text{g/g}$ ).

**Table 1:** Concentrations of metals ( $\mu\text{g/g}$  tobacco) in various Dokha and Shisha brands.

$\mu\text{g/g}$ Tobacco												
No.	Brands	Al	B	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
D1	Alward Alahmar Green Dokha	421.235	219.815	1.707	25.050	2.926	24.000	420.050	58.240	8.453	468.620	342.740
D2	Alward Alahmar Red Dokha	110.660	162.005	1.309	2.849	2.794	11.737	460.515	52.850	11.108	384.975	43.590
D3	Alward Alahmar Gold Dokha	142.125	101.530	1.627	1.311	4.361	15.818	293.570	10.526	33.053	449.890	32.647
D4	Yusuf Redha Dokha-Gold 50	114.865	3.216	1.887	2.411	3.416	20.651	340.170	58.135	28.727	315.595	6.341
D5	Yusuf Redha Dokha-White	196.400	64.320	1.283	0.113	47.004	18.618	374.430	57.105	8.619	265.780	6.124
D6	TURBO Dokha Premium-3	124.030	40.718	1.487	3.368	3.365	8.689	334.125	66.575	7.063	363.870	6.402
D7	TURBO Dokha Premium-1	231.575	162.455	58.460	2.818	7.932	19.248	654.700	51.345	6.893	438.170	7.262
D8	Yusuf Redha Dokha-Blue 50	8.170	124.595	5.865	0.652	7.713	10.293	20.730	159.240	2.237	81.630	8.024
D9	TURBO Dokha Black-2	172.150	81.465	0.964	2.940	1.372	11.555	345.150	54.645	18.594	403.515	5.241
D10	TURBO Dokha Premium-2	219.220	98.275	1.771	1.945	2.870	17.694	301.905	52.475	2.047	345.450	4.191
S1	Shisha Arguilla (Iranian)	167.180	58.160	1.126	3.019	0.185	15.751	312.125	71.520	2.191	197.485	3.359
S2	MAZAYA Watermelon Mint Shisha	22.165	29.570	1.318	1.831	58.165	14.566	96.235	22.095	59.000	5.560	0.375
S3	Al Fakher Double Apple Shisha	14.905	15.075	4.960	5.977	1.380	13.795	62.480	11.095	73.730	24.155	1.530
S4	Marlboro Cigarette Tobacco	41.829	12.110	3.775	2.634	1.010	17.245	249.435	136.870	31.495	78.965	3.910

**Table 2:** Minimum and maximum concentrations of heavy metals ( $\mu\text{g/g}$  tobacco) in various Dokha and Shisha brands.

Metal	Minimum Level ( $\mu\text{g/g}$ Tobacco)	Brand	Maximum Level ( $\mu\text{g/g}$ Tobacco)	Brand
Al	8.170	(D8) Yusuf Redha Dokha - Blue 50	421.235	(D1) Alward Alahmar - Green Dokha
B	3.2155	(D4) Yusuf Redha Dokha - Gold 50	219.815	(D1) Alward Alahmar - Green Dokha
Cd	0.964	(D9) TURBO Dokha Black-2	58.460	(D7) TURBO Dokha - Premium-1
Co	0.113	(D5) Yusuf Redha Dokha - White	25.050	(D1) Alward Alahmar - Green Dokha
Cr	0.185	(S1) Shisha Arguilla (Iranian)	58.165	(S2) MAZAYA Watermelon Mint Shisha
Cu	8.689	(D6) TURBO Dokha - Premium-3	24.000	(D1) Alward Alahmar - Green Dokha
Fe	20.730	(D8) Yusuf Redha Dokha-Blue 50	654.700	(D7) TURBO Dokha - Premium-1
Mn	10.526	(D3) Alward Alahmar - Gold Dokha	159.240	(D8) Yusuf Redha Dokha-Blue 50
Ni	2.047	(D10) TURBO Dokha Premium-2	59.000	(S2) MAZAYA Watermelon Mint Shisha
Pb	5.560	(S2) MAZAYA Watermelon Mint Shisha	468.620	(D1) Alward Alahmar - Green Dokha

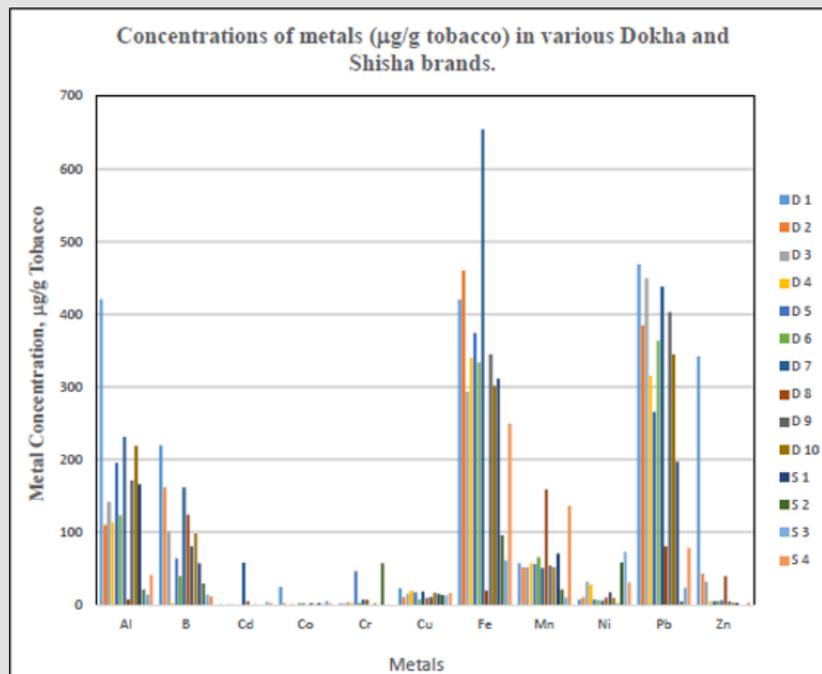


Figure 1: Concentrations of metals ( $\mu\text{g/g}$  tobacco) in various Dokha and Shisha brands.

## Discussion

### Dokha Discussion

**Aluminum:** The Al levels in the studied samples ranged from 8.170  $\mu\text{g/g}$  to 421.235  $\mu\text{g/g}$ . The highest concentration was found in the “Alward Alahmar Green Dokha” and the lowest in “Yusuf Redha Dokha-Blue 50”. In humans, Al replaces  $\text{Mg}^{2+}$  and  $\text{Fe}^{3+}$ , which causes many disturbances associated with intercellular communication, cellular growth and secretory functions. The greatest complications of aluminum toxicity are neurotoxicity effects such as neuronal atrophy in the locus ceruleus, substantia nigra and striatum.

**Boron:** The concentration of boron varied from sample to another; and its highest concentration was found in “Alward Alahmar Green Dokha” (219.815  $\mu\text{g/g}$ ); while the lowest boron concentration was found in “Yusuf Redha Dokha-Gold 50” (3.2155  $\mu\text{g/g}$ ).

**Cadmium:** Cadmium (Cd) is highly toxic, and is one of the most important heavy metals, when the adverse health effects of smoking are considered. It can cause bone mineralization either through renal dysfunction or bone damage. Inhaling higher levels of cadmium can cause severe damage to the lungs [17]. The analysis showed that “TURBO Dokha Premium-1” contained very high concentration of cadmium (58.460  $\mu\text{g/g}$ ) compared to the rest of the studied tobaccos which ranged from 1  $\mu\text{g/g}$  to 5  $\mu\text{g/g}$ . This high content of cadmium classifies the “TURBO Dokha Premium-1” tobacco among other poisoning products.

**Cobalt:** Cobalt is an essential element but at high concentrations, it becomes toxic and mainly effects the central nervous system. In

addition, cardiovascular and kidney diseases and lung fibrosis are potential effects of long-term chronic exposure to nickel [18].

**Chromium:** Moreover, exposure to chromium compounds can result in the formation of ulcers, which will persist for months and heal very slowly. Ulcers on the nasal septum are very common in case of chromate workers. Exposure to higher amounts of chromium compounds in humans can lead to the inhibition of erythrocyte glutathione reeductases, which in turn lowers the capacity to reduce methemoglobin to hemoglobin [19,20].

**Iron:** Furthermore, a very high level of iron enters the body crossing the rate-limiting absorption step hence becoming saturated. These free irons penetrate cells of the heart, liver, and brain. The free iron can also lead to lipid peroxidation, which results in severe damage to mitochondria, microsomes, and other cellular organelles [21]. In the analyzed samples the Fe concentrations ranged from 20.730  $\mu\text{g/g}$  (Yusuf Redha Dokha-Blue 50) to 654.700  $\mu\text{g/g}$  (TURBO Dokha Premium-1).

**Lead:** Toxicity of lead, also called lead poisoning, can be either acute or chronic. Acute exposure can cause loss of appetite, headache, hypertension, abdominal pain, renal dysfunction, fatigue, sleeplessness, arthritis, hallucinations, and vertigo. Chronic exposure of lead can result in mental retardation, birth defects, psychosis, autism, allergies, dyslexia, weight loss, hyperactivity, paralysis, muscular weakness, brain damage, kidney damage and may even cause death [22]. The Pb levels were high in most of the analyzed samples and the lowest levels were found in “MAZAYA Watermelon Mint Shisha” (5.560  $\mu\text{g/g}$ ), and “Al Fakher Double

Apple Shisha" (24.155 µg/g); whereas the highest level was found in "Alward Alahmar Green Dokha" (468.620 µg/g).

From the results shown in Table 1, "Alward Alahmar Green Dokha" had the highest content of Al, B, Co, Cu, Pb, and Zn. This dokha product was found to be the most hazardous compared to the other analyzed tobacco samples.

"TURBO Dokha Premium-1" was found to contain the highest level of cadmium (58.460 µg/g), whereas the cadmium level did not exceed 5 µg/g in all the other tobacco samples. Apart from its high level of cadmium, "TURBO Dokha Premium-1" also contained high levels of Al (231.575 µg/g), B (162.455 µg/g), Fe (654.700 µg/g), and Pb (438.170 µg/g). It is worth noting that "Al Fakher Double Apple Shisha" contained small concentrations of the heavy metals compared to the other studied tobaccos. This was also noticed with the Marlboro Cigarette Tobacco with the exception of its high contents of Fe, Mn, and Pb. "Dokha" tobacco has been very much spread among youngsters and a wide variety of this product is available in the market. Smoking "dokha" is very damaging since 100% of the smoke is directly inhaled to the lungs and no pauses exist between one inhale and the other as it is common with cigarettes, cigars, and shisha smoking.

### Heavy Metal and E-Cigarettes

E-cigarette (EC) has been widely considered safer than other forms of smoking [23]. However, recently the health hazards are becoming a widely questionable aspect. Propylene glycol and vegetable glycerin being toxic to cells [24] and acrolein, used to kill weeds, that causes acute lung injury, asthma, lung cancer and Chronic Obstructive Pulmonary Disease [25]. A number of published researches have studied the level of heavy metal in e-cigarettes. Farsalinos et al. published a review article and concluded that heavy metals produced from e-cigarette aerosol are considered "safe", do not produce a significant health adverse effect and produce metals at a lesser concentration than the Permissible Daily Exposure (PDE) defined by the U.S levels from inhalational medications. However, they recommend that companies should further reduce unnecessary exposure to metals [26]. Conversely, Olmedo et al. found that e-cigarette contain CR, Ni, PB, Mn and Zn in toxic concentration to humans [27].

### Conclusion

Smokers are exposed to a variety of hazardous toxic heavy metals which are present in tobaccos and damage their health as well as the environment. The sources of these heavy metals are closely related to the soil, fertilizers, irrigation, manufacturing processes, types of additives, and other factors. In this present work, twelve metals (Al, B, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) were analyzed in various Dokha and Shisha products. The metal concentrations varied from one tobacco product to another. High levels of Fe and Pb were found in almost all the Dokha tobacco brands. The trace metals in the Dokha and Shisha tobaccos, are important to assure a

good reference point for future studies, which will give formulations to the popular suppliers. Awareness on the heavy metals content in "Dokha" and other tobaccos and their related health implications must be publicized in order to reduce the number of smokers and to aim for a healthy society. In order to regulate the heavy metals content of tobacco and to protect smokers from heavy metals exposure international legislation should be passed.

In conclusion, awareness on the heavy metals content in "Dokha" and other tobaccos and their related health implications must be publicized in order to reduce the number of smokers and to aim for a healthy society. In order to regulate the heavy metals content of tobacco and to protect smokers from heavy metals exposure international legislation should be passed.

### Limitations

The main limitation of our study is the inability of measuring all the types of "Midwakh" in the market.

### Declaration

### Ethics Approval and Consent to Participate

No ethics approval needed since no human participants are involved.

### Consent for Publication

Not applicable.

### Availability of Data and Materials

The datasets used and/or analyzed during the current study are presented within the manuscript and available from the corresponding author on reasonable request.

### Competing Interests

The authors declare that they have no competing interests.

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### Authors' Contributions

- B.M.: Structured the idea of the research and helped in the literature review. In addition to going through the final article for publication.
- A.N.: Has written the result and discussion section. In addition to validating the methodology.
- A.B.: Has written the methodology section and underwent the chemical experiment.
- O.A.: Has provided the material for research and written the introduction section. In addition to helping in the literature review.

e) H.Z.: Has provided the material, written the abstract, helped in the introduction. In addition to helping in the literature review.

f) M.E.: Has edited the discussion and reviewed the final manuscript.

All authors have read and approved the manuscript.

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