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Determination of Toxic Metals in Tobacco from Selected Imported Cigarette Brands and Local Tobacco in Iraqi Markets

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ABSTRACT: Metals are essential in many physiological processes in the human body, but can also be detrimental to our health when the concentration is not within recommended permissible limits. Various types of cigarettes were selected from the local markets in Iraq in addition to the Iraqi tobacco from Sulaymaniyah governorate to conduct tests of the elements in these species. The selected samples were tested using EDX instrument. Results proved the presence of dangerous elements such as Cr, Ni, Zn, As, Al, P, S, Pb, Cd, Sn and Sb in quantities which could greatly affect the health of the smoker and have negative effects to the environment. The real danger is the result of the accumulation of these elements in the smoker's body, in the lungs, liver, blood or brain, the effects of which are chronic and dangerous, and can threaten the life of the person in the future. An acid digestion method was used to break down the organic matter in tobacco to release these elements, and solutions to measure their concentrations were prepared using an atomic absorption device.

Keywords: Heavy metals; Cigarette; Toxic elements; Carcinogenic elements; Tobacco.

تحديد العناصر السامة للتبغ لنماذج من السجائرالمستوردة والتبغ المحلي في الأسواق العراقية

وداد حمد الدهان ، عماد يوسف و حسن هاشم

الملخص: المعادن ضرورية لعدد من العمليات الفسيولوجية في جسم الإنسان، لكن يمكن أيضا أن تكون ضارة لصحتنا عندما يكون التركيز ليس ضمن الحدود المسموح بها. تم اختيار أنواع مختلفة من السجائر من الأسواق المحلية في العراق بالإضافة إلى التبغ العراقي من محافظة السليمانية لإجراء اختبارات العناصر في هذه الأنواع. تم اختبار العينات المختارة باستخدام جهاز (EDX). أثبتت النتائج وجود نسب من العناصر الخطيرة مثل (الكروم، النيكل، الزنك، الزرنيخ، الالمنيوم ،الفسفور، الكبريت، الرصاص، الكادميوم، الخارصين والانتمون) والتي تؤثر بشكل كبير على صحة المدخن وآثاره السلبية على البيئة. يكمن الخطر الحقيقي نتيجة تراكم هذه العناصر في الرئتين ، الكبد ،الدم او الدماغ للشخص المدخن مع الزمن.استخدمت طريقة الهضم للتبغ باستخدام الحامض لكسر المواد العضوية وتحرير العناصر لغرض الفحص بجهاز الامتصاص الذري.

الكلمات المفتاحية: المعادن الثقيلة، السجائر، العناصر السامة، العناصر المسرطنة، التبغ .

1. Introduction

As discussed in our papers on safety measures which affect human health [1-6], metals are essential for a number of physiological processes in the human body, but can also be detrimental to our health when the concentration is not within the World Health Organization/Food and Agricultural Organization of the United Nations/Joint Expert Committee on Food Additives (WHO/FAO/JECFA) recommended permissible limits [7]. Although there is no clear definition of what a heavy metal is, density is in most cases taken to be the defining factor. Heavy metals are thus commonly defined as those having a density of more than 5 g/cm^3 [8].

The heavy metals are widely dispersed in the environment, and at excessive levels are very toxic to humans [9]. Chronic exposure to these substances may also be hazardous. Although these metals occur naturally, exposure may be increased by human activities that release them into the air, soil, water and food, and from by-products containing them. Certain plants also can accumulate heavy metals that have no known biological function [10].

Plants, among them the tobacco plant [11-13] are amenable to absorbing and accumulating heavy metals from the soil into their leaves. The factors governing heavy metals speciation, adsorption and distribution in soil are pH, soluble organic matter content and soil type, and the presence of organic and other metal ions. Trace amounts of heavy metals accumulate in tobacco leaves, and they are known to transfer in trace quantities from the cured and processed tobacco to mainstream cigarette smoke. These metals include cadmium, lead, arsenic, iron, copper, chromium, nickel, and selenium [14-17]. The most abundant redox inactive metals in cigarette smoke generally are cadmium, lead and arsenic. The cigarette smoke contains both organic and inorganic human carcinogenic compounds. Containing 4000 identified chemical compounds, cigarette smoke is very harmful and toxic for human health [18]. Some of these toxic materials are heavy metals, particularly cadmium and lead.

Several heavy metals found in tobacco smoke, such as Cd, Cr, Pb, and Ni, can also accumulate in tissues and fluids through smoking [19- 25]. Tobacco smoking is the most important single source of Cd exposure in the general population. According to Al-Bader et al. [21], the most important sources of Cd in humans are smoking and food. Cadmium can enter the body through tobacco smoking, diet, drinking water, and inhaling it from the air. Small amounts of Cd taken over many years may cause kidney damage and fragile bones, since Cd is mainly stored in bone, liver, and kidneys [26]. The scientific literature is filled with evidence of the harmful health effects of carbon monoxide, nicotine, tar, irritants and other noxious gases emitted in tobacco smoke. Not enough attention, however, has been paid to the presence of heavy metals and other toxic and trace elements in tobacco smoke and their possible effects on biochemical processes in the human body. Once inhaled through smoking, heavy metals have a long biological half-life. Chronic adverse effects on human health may, therefore, result in later years from prolonged intake of such toxic elements, some of which are powerful carcinogens. Several of them accumulate in bone and may trigger disorders of mineral metabolism, e.g. osteoporosis. The body burden of heavy metals increases as a result of occupational exposure, and tobacco smoking enhances the adverse effects of such exposure. Table 1 illustrates some of the main trace and heavy elements in some American brands of cigarette tobacco [27].

Table 1. Concentration range for main trace and heavy elements in cigarette tobacco of American brands.

Element	Concentration range (µg/g)
Al	699-1200
As	< 1
Ba	40.7-56.6
Ca	1.39-1.96 (mg/100g)
Co	< 0.01-.94
Cr	< 0.1-0.345
Fe	325-520
Mg	0.13-.54(mg/100g)
Mn	155-400
Ni	<2-200
Se	<0.007-0.091
Sr	29.7-49.5
Zn	16.8-30.5

Tobacco smoking not only affects human health, but it is also associated with environmental pollution. Most of the environmental problems associated with tobacco smoking have been attributed to the tobacco smoke itself, commonly regarded as Environmental Tobacco Smoke (ETS). However, several researchers have reported environmental contamination by smoked cigarette butts. Several other smoking devices also need the attention of environmental monitoring studies. These devices include kretek, bidi and shisha which are not just a human health problem, but also contaminate the air by releasing smoke which is classified as ETS and is a source of soil and water pollution by the water which is discarded after every smoking session. [28]. This research spans a series of research specialized in safety aspects to lay the groundwork for improvements in human health and that of environment [29-33]. The work aims to determine the toxic metals in tobacco from selected imported cigarette brands and local tobacco in Iraq using an acid digestion method to break organic matter in tobacco down to release elements to determine their concentrations using Energy-dispersive X-ray spectroscopy and atomic absorption devices.

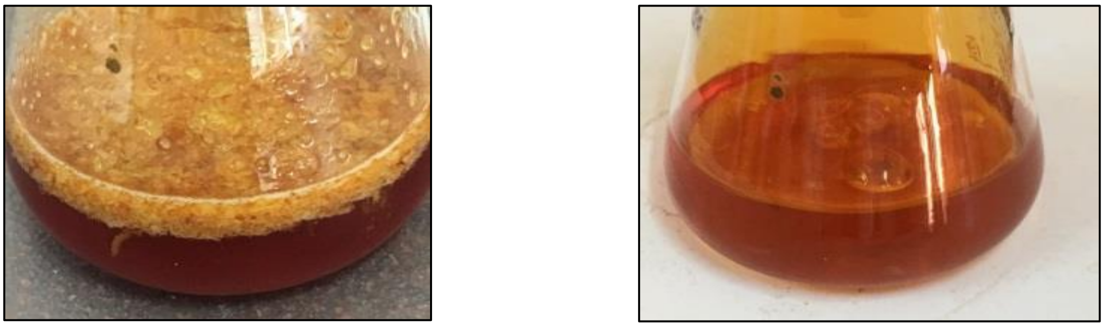
2. Experimental

2.1 Sampling

Samples of three common brands of cigarettes (1-3) were purchased, along with one of molasses tobacco and one raw local tobacco sample. The raw Sulaimaniyah tobacco sample was selected from the market as the major origin of tobacco in Iraq.

2.2 Digestion of Tobacco Samples

A 2 g sample of each type of tobacco was weighed and placed separately into a 500 ml and 20 ml mixture of HNO_3 and $HClO_4$ of ratio 9: 4, and the contents were well mixed by swirling thoroughly [34]. Each with its contents was then placed on a hot plate in a fume chamber and heated to boiling; heating continued until the production of red nitrous oxide fumes ceased. The contents were further heated until the volume was reduced to 8-10 ml and the mixture became colorless or yellowish, but not dry. This was done to reduce interference by organic matter and to convert metal associated particulates to a form (the free metal) that could be determined by the Atomic Absorption Spectrophotometer (AAS). Contents were cooled and filtered through Whatman. No.1 filter paper and the volume made up with deionized water to 100 ml. The resulting solution was used for spectrophotometric determination of various metals (see Figure 1).



A Semi-digested tobacco   B Fully digested tobacco

Figure 1. Tobacco acid digestion.

2.3 Atomic Absorption Spectrophotometry (AAS) analysis

Atomic Absorption Spectrophotometer (Agilent) model FS240 was used in determining the content of heavy metals and their concentrations in the previously acid digested tobacco samples. Standard solutions were prepared in different concentrations for each element to establish the calibration curve, according to the detection limit concentration defined in the instrument. An air-acetylene burner was used for spectrophotometric determination of the various metal concentrations in the range of (ppm). Fe, Mg, Cr, Cd, Zn, K, As and Pb metals were tested in the AAS spectrophotometer.

2.4 Energy-dispersive X-ray spectroscopy (EDX) analysis

Energy-dispersive X-ray spectroscopy (EDX) Bruker model XFlash6I10, sometimes called energy dispersive X-ray analysis (EDXA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. Tobaccos from the selected types of cigarettes were tested in this instrument.

3. Results and Discussion

3.1 EDX Results

Samples of three common brands of cigarettes (1-3) were tested, along with one of molasses tobacco and one of raw local tobacco in an EDX instrument for elemental analysis. Results obtained from these tests are illustrated in Figures (2, 3,4,5,6 and 7) respectively.

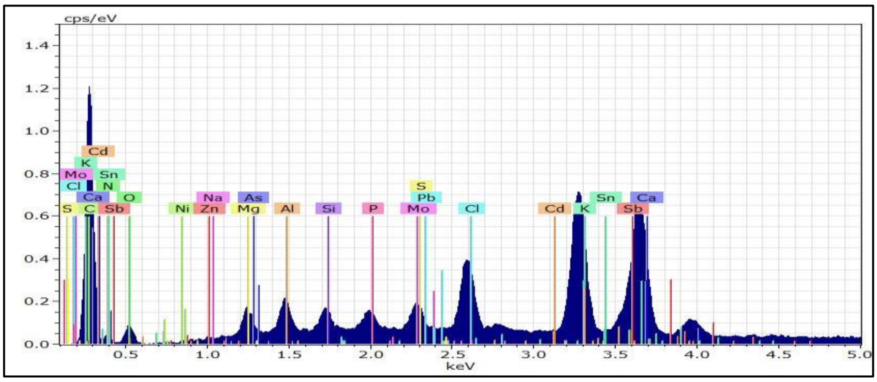


Figure 2. EDX spectrum of sample -1 cigarette tobacco.

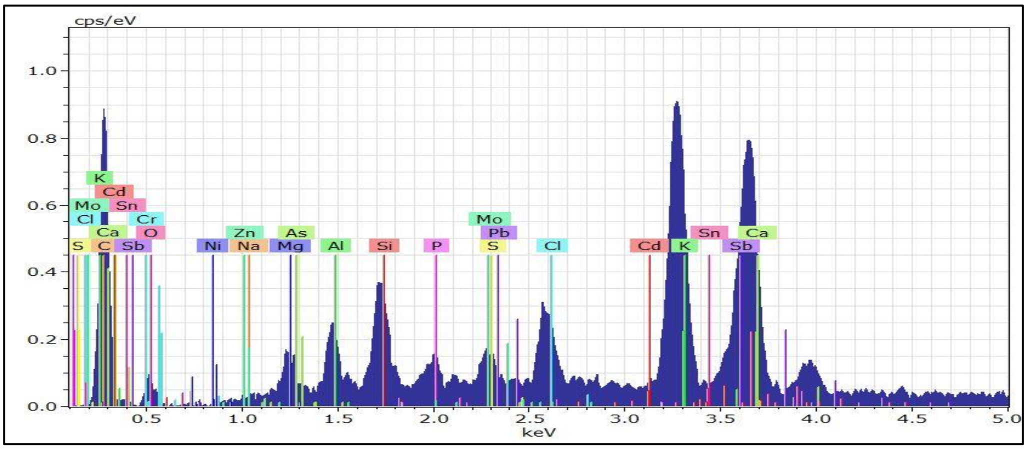


Figure 3. EDX spectrum of sample - 2 cigarette tobacco.

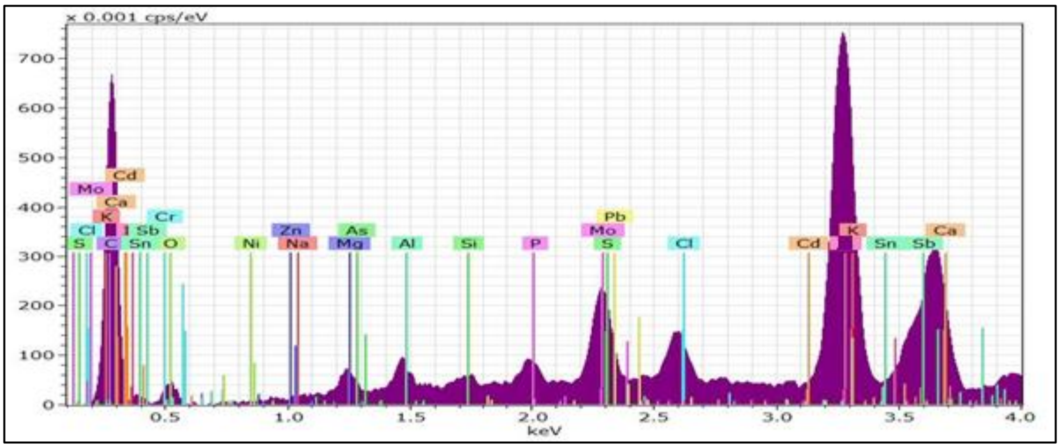


Figure 4. EDX spectrum of sample - 3 cigarette tobacco.

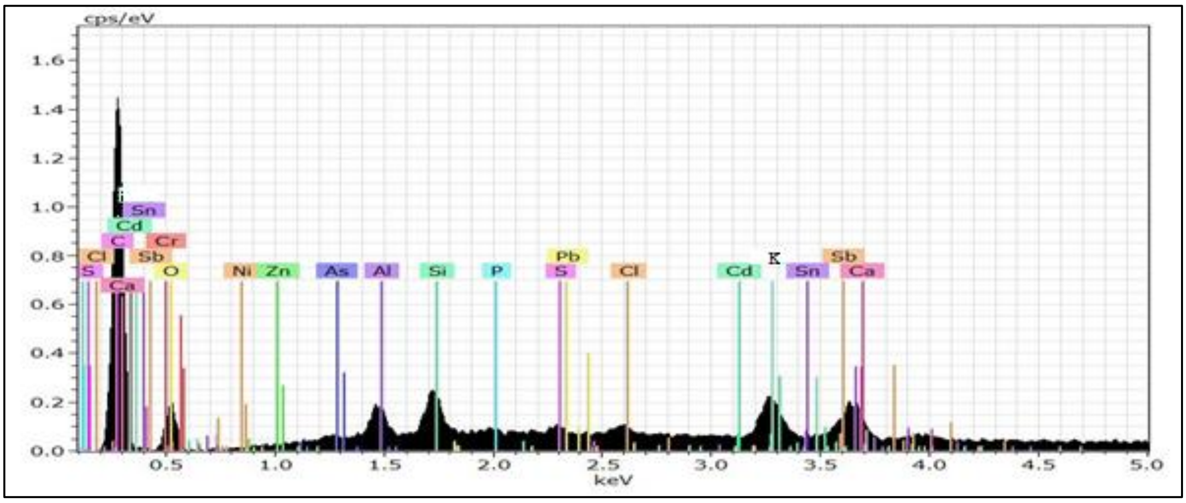


Figure 5. EDX spectrum of molasses tobacco.

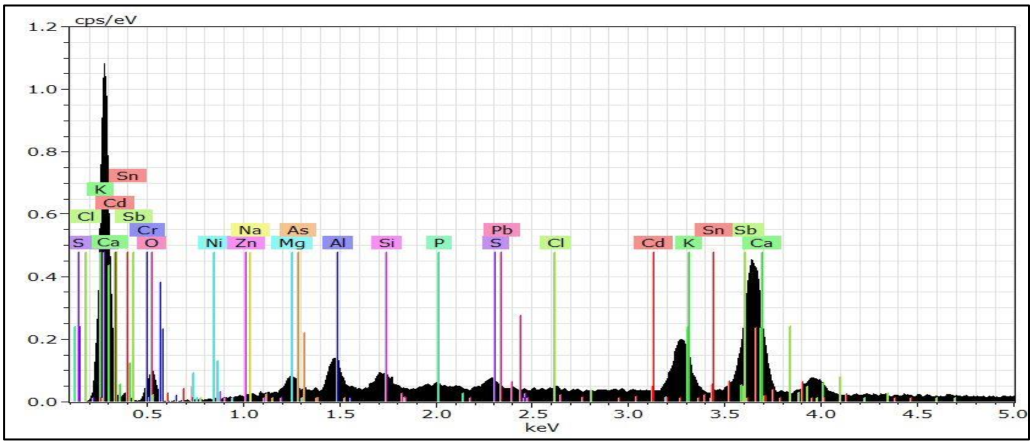


Figure 6. EDX spectrum of raw local tobacco.

3.2 Atomic Absorption test

Some selected elements were tested using atomic absorption apparatus (see Tables - 2, 3 and 4).

Table 2. Concentration of selected elements in (μg/g) for some prepared samples.

Sample	Cr	Mg	Fe	Cd	Zn	K	Pb
1	<1	29.7	<1	<1	0.12	50.00	<1
2	<1	3.38	<1	<1	0.06	25.00	<1
3	<1	15.3	<1	<1	0.82	55.00	<1
Molasses	<1	3.38	<1	<1	0.06	25.00	<1
Local tobacco	<1	13.2	<1	<1	0.03	18.00	<1

Table 3. Weight of selected elements in (mg) for some prepared samples in the total extracted solutions.

Sample	Mg	Zn	K	Total extracted solution(ml)
1	14.85	0.06	25.00	500
2	1.69	0.03	12.50	500
3	7.65	0.41	27.50	500
Molasses	1.69	0.03	12.50	500

Table 4. Weight % of selected elements for some prepared samples with respect to total sample weight.

Sample	Mg	Zn	K	Total sample weight(g)
1	7.40	0.03	12.50	2
2	0.85	0.015	6.25	2
3	3.82	0.20	13.75	2
Molasses	0.85	0.015	6.25	2
Local tobacco	3.30	0.0075	4.50	2

4. Discussion

Results of the Energy-dispersive X-ray spectroscopy tests for the samples (1,2) clearly showed the presence of Mg, Ca, Al, Si, P, Mo, Cl, Sb and K in high percentages compared with the elements Cd, Ni, Zn, Na, As, S, Sn, and Pb which were found at low concentration while the third sample (3) showed a large proportion of elements Mg, Ca, Al, Si, P, Mo and Sb. Except for K, these were found at a lower percentage than in samples (1,2). Low percentages were found for Ni, Zn, Na, As, Sn and Pb. As for the molasses used in Shisha (also known as narghile), the test results for the elements Al, K, Si and Ca were the highest for this sample, but much less than in samples (1 and 2). The results for local Iraqi tobacco from Sulaymaniyah governorate were very close to the results for molasses, which contained limited concentrations of the elements found in samples 1 and 2 except for Ca, which is the metal found in the highest percentage in this type of tobacco.

An atomic absorption device was used to determine the accurate concentrations of some trace elements that showed high and low ratios in the Energy-dispersive X-ray spectroscopy test used to find the approximate concentrations of the other elements. The results showed the low concentrations of Pb, Fe, Cd and Cr, in the level of (μg/g). This is clearly what we found in the percentages of these elements in the Energy-dispersive X-ray spectroscopy test. These results can be used to determine the approximate concentrations of Sn, S, As, Na, Zn and Ni by means of approximate comparison.

The results of the atomic absorption test of the molasses and local tobacco in Iraq coincided with the results from the Energy-dispersive X-ray spectroscopy in terms of the lowest percentage being found in the content of these samples.

5. Conclusion

Three selected varieties of cigarette tobacco and a type of molasses for Shisha, in addition to Iraqi tobacco were digested using nitric acid to break down the organic substances to release the elements in the tobacco components. The prepared samples were tested using Energy-dispersive X-ray spectroscopy. The results proved the presence of dangerous elements such as Cr, Ni, Zn, Na, As, Al, P, S, Pb, Cd, Sn and Sb, which greatly affect the health of the smoker and have negative effects on the environment. The real danger results from the accumulation of these elements in the smoker's body in the lungs, liver, blood or brain, and the effects of this are chronic and threaten the life of the person in the future.

Conflict of Interest

The authors declare no conflict of interest.

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