Determination and Assessment of Heavy Metals in Tobacco Sold and Smoked In Palestinian Market

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Abstract

Throughsmoking, important flux of heavy metals and many other toxins reaches smokers ' lungs. This project reports the heavy metal concentrations in tobacco from samples of 25 cigarette products, sold in Palestine. Cadmium (Cd), lead (Pb), cobalt (Co), nickel (Ni), copper (Cu) and zinc (Zn) contents were determined in 25 brands of tobacco cigarette commonly available in Palestine by flam atomic absorption spectrophotometer. The concentration of trace metals in the cigarettes ranged, Cd: from 0.85 to 2.11 µg/g with mean 1.20±0.15 µg/g, Pb: 2.21 to 5.06 µg/g with mean 3.12±1.33 µg/g, Co: 0.18 to 2.61 µg/g with mean 1.09±0.28 µg/g, Ni: 3.42 to 6.23 µg/g with mean 4.92±0.53 µg/g, Cu: 11.86 to 20.35 µg/g with mean 15.21±0.34 µg/g, and Zn: 30.55 to 114.43 µg/g with mean 51.15±0.14 µg/g.

Comparable results of trace metals are obtained in both imported and Palestinian cigarettes. The average trace metal contents of cigarettes available and sold in Palestine are Cd:0.82 µg/cigarette with range (0.60– 1.70) µg/cigarette, Pb: 2.13 µg/cigarette with range (1.41 – 3.54) µg/cigarette, Co: 0.74 µg/cigarette with range (0.12– 2.02) µg/cigarette, Ni: 3.37µg/cigarette with range (2.57– 5.66) µg/cigarette Cu: 10.42 µg/cigarette with range (7.80– 20.11) µg/cigarette, Zn: 35.02µg/cigarette with range (20.10- 88.80)µg/cigarette. The results indicate that smoking and exposure to cigarette

smoke is a serious problem to be taken into account when carrying out epidemiological studies on human exposure to trace metals.

Introduction

Tobacco manufacture consuming increases all over the world, although tobacco smoking is one of the main problems that cause morbidity and mortality[1].
While the harmful effects onhealth of carbon monoxide, nicotine, tar, irritants and other noxious gases that are presented in tobacco smoke are well known, those due to heavy metals and other toxic mineral elements in tobacco smoke are not sufficiently emphasized. Tobacco smoking influences the concentrations of many elements in some organs[2].

Cigarette smoking may be a substantial source of intake of these hazardous elements not only to the smoker but also through passive smoking, to those who don't smoke.The adverse health effects of these toxic elements on the fetus through maternal smoking, and on infants through parents` smoking, are with special concern[3].

Tobacco is a plant which grows fast and, like all the natural plants, it consumes heavy metals from the soil. Some of these metals can be naturally found in soils where tobacco plants are grown others were brought in soils through fertilizer and various pesticides during the cultivation of tobacco crops[4-5]. Tobacco plant is able to absorb and accumulate heavy metal species from the soil into its leaves[6].

Smoking of tobacco leaves is one of the main routes of exposure to heavy metals. Metals contain in tobacco leaves originate from root uptake and transfer to the shoots and also from deposition of aerosol particles on the leaves[7].

The exposure of plants to high concentrations of metals generally causes a stress, whose visible symptoms include an inhibition of root elongation, a decrease in shoot growth, leaf chlorosis, and necrosis of the tissues. This stress is generated by the perturbation of cell metabolism by metals, mostly because of the inactivation of proteins by adventitious binding. Plants have developed various mechanisms to tolerate heavy metals in their tissues[8].

Cigarette smoke contains particles and gases generated by the combustion of its various components at high temperature. The smoke can be inhaled directly by the smoker and non-smokers in cigarette-contaminated environment through passive smoking. In addition, smoking is connectedwith rising in heavy metals in human tissues[9-10].

Human population is exposed heavy metals from many sources (air, water, soils, foodstuffs, and anthropogenic sources). Smoking is not the main reason of heavy metals exposure for humans, but cigarette smoking also influences heavy metals toxicity[11].

Tobacco is one of the most widely used commodities in the world. It has been studied extensively because of its scientific rareness, its important economically in society, the health results of tobacco use, the economic and political importance of the industry it produced, because of it is able to generate massive revenues and because of governmental regulation[1].

A cigarette's shape features influence smoke particulate mass transport through the tobacco rod and filter, so cigarettes are characterized according to machine-smoked tar delivery categories which described as full flavor, light, and ultra-light[12].

In addition to occupational exposure tobacco smoke is a potential source of some toxic trace elements including inorganic carcinogens. Just the tobacco companies know exactly what each cigarette contains, and only some of this information can be known[13].

Nicotine is the major material in cigarettes. However, that cigarette smoke contains an addendum to this article on the 4000 article in the form of tar, carbon monoxide, ammonia, acetone, methanol, lead cadmium, mercury[2].

Since 1950, the cigarette industry began in changing gradually, as rates have dropped from 38 mg tar to 12 mg, and the percentage of nicotine from 2.7 mg to 1.0 mg per cigarette by improving the filter type[1].

Usually, cigarette is made up of tobacco, paper and additives. As much as 600 – 1400 additives are used in cigarette manufacture, with many of these additives containing environmental contamination and exposure to heavy metals such as mercury, cadmium and lead is a serious growing problem all over the world[14].

Cigarette production is a complicated process. The tobacco undergoes a conditioning process where high temperatures and humidity restore moisture to suitable levels for cutting and blending. Then tobaccos are precisely cut and mixed according to time-honored formulas, or recipes, to produce tobaccos for different brands of cigarettes. This brand recipe contains ingredients and favors which are added to the tobacco to give each brand its rare characteristics[15].

Cigarette production begins with manufacturing the filters. They are made as long filter rods that measure 120 mm and consist of fine gauze-like acetate fiber. Each filter rod is cut into four or six filters depending on how long the filter is on the individual cigarette. Cigarette and packing machines are usually combined together in one machine unit. The cigarette machine is supplied with tobacco and filters through pipes by means of a pneumatic conveying system. Three other materials are used: cigarette paper - which comes in six km long rolls wound on large bobbins - tipping paper and glue (for gluing the cigarette rod and filter together).

The cigarette is assembled in a three-step process. First, a tobacco rod is made of tobacco supplied from the feed table.Next,the tobacco rod is wrapped in cigarette paper. After that, the rod is glued in transit and a rotating knife cuts the cigarette to the right length. The filter and cigarette rod are then glued together by attaching tipping paper, and the finished cigarettes are conveyed to the packing machine. In the packing machine the cigarettes are packed in aluminum foil or metalized paper. Then they are packed in a cigarette pack[16-17].

Several heavy metals found in tobacco smoke such as Cd, Pb, Co, Ni, Cu and Zn also accumulate in tissues and fluids through smoking[18].
This research work reports the levels of heavy metals (Cd, Pb, Ni, Co, Cu, and Zn) in cigarette tobaccos sold in Palestine. Determination of these heavy metals in cigarette material is very important because of biological significance.

Objectives:

The main objective of this project was to determine the levels of heavy metals andthe percentage of organic matter in cigarettes sold in Palestine (locally and imported).

Materials and experiment

Apparatus

Flame Atomic Absorption Spectrophotometer model icE-3000 SERIES, Serial number c113500021deigned in UK AA Spectrometer, with a hollow cathode lamp for cadmium, lead, cobalt, nickel, copper and zinc.

Sample collection

Twenty five (25) brands of cigarettes commonly available in Palestine were purchased given in Table 1.

Table 1: Tobacco Sold In Palestinian Market.

NO.	Brand Name	Country of origin (manufacturer)	Information recorded on a pack of cigarettes	Source
1	Jamal/ red	Palestine	-	Local
2	Jamal	Palestine	-	
3	Imperial	Palestine	-	
4	Infinity	Palestine	-	
5	Victory	Palestine	-	
6	Lando	Palestine	-	
7	Arabic tobacco*	Palestine	-	
8	Rothmans	Britain	0.8 mg Nicotine 10 mg Tar	imported
9	Craven "A"	Turkey	1.1 mg Nicotine 12 mg Tar	
10	Viceroy	Turkey	-	
11	Next/ blue	Turkey	-	
12	Next/ light blue	Turkey	-	
13	Gold coast	Japan	0.8 mg Nicotine	

NO.	Brand Name	Country of origin (manufacturer)	Information recorded on a pack of cigarettes	Source
			12 mg Tar	
14	Winston/ red (Classic)	Japan	0.9 mg Nicotine 12 mg Tar	
15	Winston / blue	Japan	0.6 mg Nicotine 8 mg Tar	
16	Parliament	Switzerland		
17	Marlboro/ red	Switzerland	0.6 mg Nicotine 12 mg Tar	
18	Marlboro/white (gold original)	Switzerland	0.6 mg Nicotine 8 mg Tar	
19	LM/ red	Switzerland	0.8 mg Nicotine 12 mg carbon monoxide	
20	LM/ blue	Switzerland	0.6 mg Nicotine 8 mg carbon monoxide	
21	Davidoff classic	Germany	0.9 mg Nicotine 10 mg Tar	
22	Davidoff gold	Germany	0.6 mg Nicotine 7 mg Tar	
23	Gauloises/ blue	France	0.8 mg Nicotine 10 mg Tar	
24	Gauloises / red	France	0.6 mg Nicotine 8 mg Tar	
25	Gauloises/ orange	France	0.4 mg Nicotine 4 mg Tar	

*Not manufactured, but cigarettes are wrapped manually.

Sample preparation

Physical properties of samples

The average weigh of each cigarette brand was measured by weighing 5 sticks of each brand before and after removing the filters and papers. The samples were dried in an oven at a temperature of 90 °C for 1 h and then cooled in desiccators. The mean weight of each cigarette tobacco was calculated.

Grinding of Samples

The dried tobacco was grounded by a mortar and with a pestle until be powder finely as much as possible for homogenization, to simplify weighing and to facilitate organic matter digestion. After macerating the tobacco, the remaining tobacco particles were wiped off from the mortar and pestle before proceeding to the next sample to avoid contamination.

Sample Digestion

Digestion was carried out using two methods. One by using dry ashing method[19-20] and the wet aching method, in order to select the most suitable of them.

Wet Ashing Method

1- One gram of dry tobacco Arabic sample was treated with a mixture of concentrated HNO_3 and HCl acid in a ratio of 3:1 and heated to near dryness.
2- The digest was filtered through Whitman filter paper into volumetric flask and made up volume 100 ml with deionized water.
3- The solution was Analyzed for heavy metals (Cd, Pb, Co, Ni, Cu and Zn) using an atomic absorption spectrophotometer.

Dry Ashing Method

1- One gram of dry tobacco Arabic sample was ashed in muffle furnace at 500^{o}C.
2- The ash was treated with a mixture of concentrated HNO_3 and HCl acid in a ratio of 3:1 and heated to near dryness.
3- The digest was filtered through Whitman filter paper into 100 ml volumetric flask and the volume was completed withdeionized water.

The solution was analyzed for heavy metals (Cd, Pb, Co, Ni, Cu and Zn) using an atomic absorption spectrophotometer.

Results and discussion

The results of this work are represented in tabular and graphical form. Results were devoted to determine the heavy metals (Cadmium, Lead, Cobalt, Nickel, Copper and Zinc) in tobacco sold and smoked in Palestinian market.

Test Method

The purpose of this task is to select the appropriate method of digestion of tobacco. Results for the Flame Atomic Absorption spectrophotometric showed that the second method (dry ashing) is more accurate, as shown in Table 2, so it was used in this study.

Table 2: Results from the flame atomic absorption spectrophotometric analysis determination of heavy metal contents in Arabic tobacco (mg/L)

Method	Cd		Pb		Co		Ni		Cu		Zn	
	Conc (mg/L)	Rsd %	Conc (mg/L)	Rsd %	Conc (mg/L)	Rsd %	Conc (mg/L)	Rsd %	Conc (mg/L)	Rsd %	Conc (mg/L)	Rsd %
Wet ashing	0.065	4.3	0.173	32	0.075	23	0.303	47	0.769	2	0.541	0.3
	0.078	19	0.132	56	0.061	11	0.306	6.7	0.731	2.5	0.556	0.3
	0.067	6.4	0.120	43	0.050	38	0.319	8.1	0.771	4.2	0.562	0.4
dry	0.083	15	0.121	5.6	0.068	15	0.313	9	0.824	2.4	0.544	0.3

ashing	0.077	7.5	0.169	7.1	0.077	2.9	0.306	7.9	0.798	2.4	0.536	0.3
	0.079	6	0.157	1.4	0.075	4	0.309	4.8	0.808	0.9	0.544	0.5

The percentage of organic matter in cigarettes

The weight of the tobacco in a cigarette varies depending on the length of the cigarette and other factors. From the Table 3 it was noticed that the average weight of the cigarettes with paper and filter is 0.899 g with range (0.788-1.188) g the max for Arabic tobacco. The average weight of the cigarettes without the filter and paper is 0.658 g range (0.545-0.988) g. The average weight of dry tobacco in one cigarette is 0.596 g range (0.478-0.852) g. The average proportion of organic matter is 73% range (69%-74%). It is noticed that Arabic tobacco has the largest dry weight and the lowest proportion of organic matter, this is because of the absence of any additions where Arabic tobacco is not manufactured, but cigarettes are wrapped manually. Thus it has high proportion of ash (minerals).

Table 3: The weight of the cigarette tobacco (g) and the proportion of organic matter (%).Mean values of 5 cigarettes are given.

No.	Brand Name	Weight of cigarette (g)			Proportion of Organic matter (%)
		With paper and filter	After removing the paper and filter	Dry (After removing the paper and filter)	
1	Jamal/ red	0.986	0.769	0.664	73
2	Jamal	0.98	0.831	0.726	74
3	Imperial	0.935	0.776	0.676	74
4	Infinity	0.911	0.705	0.615	73
5	Victory	0.908	0.707	0.617	73
6	Lando	0.995	0.802	0.704	70
7	Arabic tobacco	1.188	0.988	0.852	69
8	Rothmans	0.832	0.611	0.53	73

9	Craven "A"	0.857	0.658	0.572	74
10	Viceroy	0.871	0.639	0.558	73
11	Next/ blue	0.849	0.651	0.562	73
12	Next/ light blue	0.834	0.573	0.498	74
13	Gold coast	0.887	0.676	0.588	73
14	Winston/ red (Classic)	0.828	0.631	0.55	74
15	Winston / blue	0.788	0.554	0.478	73
16	Parliament	1.057	0.812	0.702	74
17	Marlboro/ red	0.927	0.72	0.632	74
18	Marlboro/ white (gold original)	0.881	0.636	0.557	74
19	LM/ red	0.851	0.645	0.564	74
20	LM/ blue	0.864	0.614	0.535	73
21	Davidoff classic	0.895	0.67	0.578	73
22	Davidoff gold	0.867	0.644	0.558	73
23	Gauloises/ blue	0.848	0.645	0.563	74
24	Gauloises / red	0.842	0.617	0.54	74
25	Gauloises/ orange	0.791	0.545	0.48	74
	Mean	0.899	0.685	0.596	73
	Min	0.788	0.545	0.478	69
	Max	1.188	0.988	0.852	74

Determination the contents for some heavy metals

The determined concentrations of 6 heavy metals (Cd, Pb, Co, Ni, Cu and Zn) in 25 cigarette brands are presented in Table 4. The combined data are displayed as histograms Fig. 1,where the overall trends are immediately obvious.

The concentration of heavy metals in the cigarettes ranged, Cd: from 0.85 to 2.11 µg/g with mean 1.20±0.15 µg/g, Pb: 2.21 to 5.06 µg/g with mean 3.12±1.33 µg/g, Co: 0.18 to 2.61 µg/g with mean 1.09±0.28 µg/g, Ni: 3.42 to 6.23 µg/g with mean 4.92±0.53 µg/g, Cu: 11.86 to 20.35 µg/g with mean 15.21±0.34 µg/g, and Zn: 30.55 to 114.43 µg/g with mean 51.15±0.14 µg/g.

Such inner brand variations in trace element concentration of tobacco products have been observed by others as well[21]. However, these variations could possibly be related to agriculture soil contents of trace metals on which tobacco leaves were cultivated[23-24], farming fields close to roads and residential areas[22], the chemistry of tobacco leaves and finally to its processing[23].

Table 4: Results for the flame atomic absorption spectrophotometric determination of heavy metals contents (mean ± SD)(µg/g, dry weight) of 25 brands of cigarette tobacco sold in Palestine. Mean values of triplicate analyses (n = 3) are given.

Brands	Cd	Pb	Co	Ni	Cu	Zn
Jamal/ red	0.85±0.20	2.91±0.67	2.41±0.84	3.64±0.84	15.25±0.41	69.17±0.28
Jamal	0.96±0.44	4.10±0.94	1.79±0.30	3.42±0.79	17.34±0.16	53.21±0.05
Imperial	0.99±0.18	3.44±0.79	2.60±0.49	3.55±0.82	12.58±0.42	114.43±0.23
Infinity	1.13±0.42	3.35±0.77	2.61±0.48	4.67±0.63	18.07±0.07	46.14±0.05
Victory	1.04±0.26	4.06±3.97	2.41±0.08	4.50±0.75	16.52±0.31	45.34±0.14
Lando	2.11±0.09	4.41±1.01	1.92±0.71	5.15±2.43	14.55±0.29	47.03±0.14

Arabic tobacco	0.98±0.22	3.24±1.87	1.00±0.47	5.73±0.38	20.35±0.51	67.18±0.20
Rothmans	1.21±0.08	2.31±1.00	0.91±0.34	6.06±0.49	14.91±0.63	41.36±0.17
Craven "A"	1.01±0.15	5.06±2.85	1.29±0.19	5.30±0.48	11.86±0.64	30.55±0.09
Viceroy	1.21±0.09	3.32±0.76	1.56±0.46	6.23±0.49	18.57±0.45	41.98±0.13
Next/ blue	0.93±0.16	2.21±1.79	0.58±0.20	5.11±0.25	15.27±0.14	44.27±0.22
Next/ light blue	1.21±0.04	2.74±2.70	0.65±0.22	5.49±0.56	15.49±0.36	80.99±0.24
Gold coast	1.17±0.15	2.79±1.43	1.21±0.19	5.07±0.70	15.50±0.54	39.09±0.04
Winston/ red	1.10±0.21	2.93±0.67	1.42±0.09	4.74±0.08	15.35±0.40	44.89±0.04
Winston / blue	1.30±0.08	3.32±0.76	0.90±0.11	4.83±0.26	14.96±0.13	47.68±0.29
Parliament	1.09±0.10	2.92±0.67	0.77±0.31	4.71±0.37	12.83±0.17	41.20±0.16
Marlboro/ red	1.10±0.07	2.24±0.71	0.30±0.12	5.44±0.13	12.66±0.41	44.76±0.09
Marlboro/ white	1.31±0.08	2.58±2.34	0.30±0.11	5.79±0.14	13.68±0.67	45.95±0.05
LM/ red	1.25±0.15	2.58±1.38	0.22±0.05	5.31±0.22	15.87±0.05	71.80±0.14
LM/ blue	1.19±0.11	2.34±1.61	0.37±0.24	5.08±0.70	16.09±0.03	45.08±0.23
Davidoff classic	1.32±0.10	2.40±1.64	0.69±0.52	4.76±0.37	13.65±0.40	40.76±0.04
Davidoff gold	1.48±0.02	3.26±0.75	0.18±0.04	3.98±0.18	14.81±0.61	45.11±0.05
Gauloises/ blue	1.26±0.04	3.14±0.72	0.19±0.04	4.91±0.28	14.26±0.40	44.55±0.27
Gauloises / red	1.24±0.15	2.93±0.67	0.41±0.17	4.50±0.57	13.92±0.14	45.55±0.09
Gauloises/ orange	1.51±0.16	3.30±0.76	0.47±0.29	4.95±0.30	15.96±0.10	40.63±0.04
Mean	1.20±0.15	3.12±1.33	1.09±0.28	4.92±0.53	15.21±0.34	51.15±0.14
Min	0.85	2.21	0.18	3.42	11.86	30.55
Max	2.11	5.06	2.61	6.23	20.35	114.43

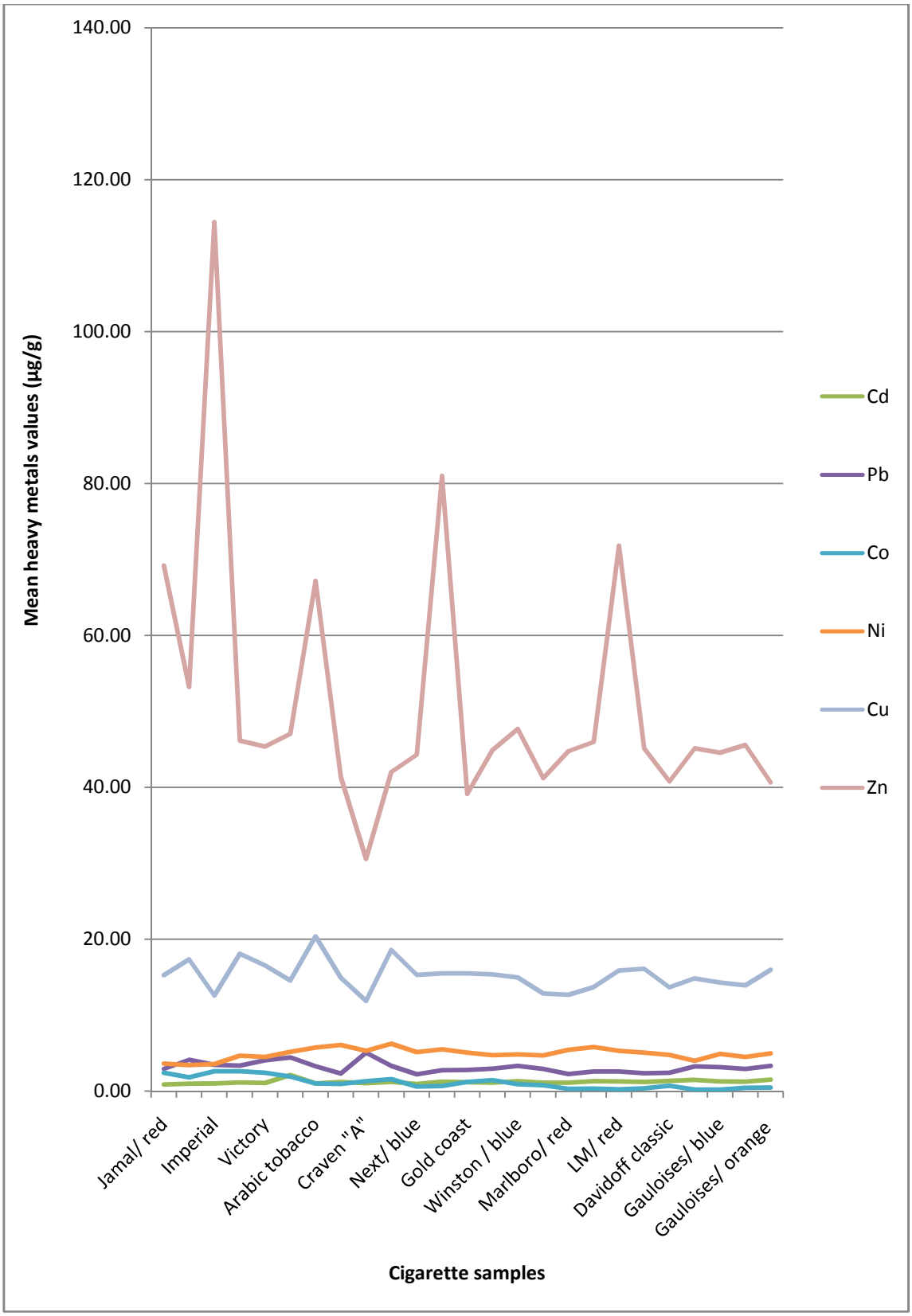

Fig.1 Histograms of comparison of the heavy metal contents of different brands of cigarette samples for the elements Cd, Pb, Co, Ni, Cu, and Zn.

Comparison of the levels of heavy metals in the Palestinian cigarettes with that imported cigarettes sold in Palestine

The mean Pb, Co, Cu and Zn contents of Palestinian cigarettes, as shown in Figure 4.4.1, are bit higher than imported brands. Imported cigarettes show a bit higher Cd and Ni contents than Palestinian cigarettes, as shown in Fig.2 and Tables 5 and 6.

On other hand, among cigarette brands, the highest concentration of cadmium element were found in Lando with 2.11±0.09µg/g (local brand), Gauloises/ orange with 1.51±0.16µg/g and Davidoff gold with 1.48±0.02 µg/g (imported brand), whereas lowest cadmium content was in Jamal/ red (local brand) and Next/ blue (imported brand) with 0.85±0.20 and 0.93±0.16 µg/g, respectively. It is likely that the major source cadmium in tobacco probably occurs from the widespread use of chemical fertilizers[14, 25]. the concentration of other elements including: Lead, Cobalt, Nickel, Copper and Zinc element is also indicated in Tables 5 and 6.

Table 5: Heavy metal contents (mean ± SD) (µg/g, dry weight) of Palestinian brands of cigarette tobacco

Brands	Cd	Pb	Co	Ni	Cu	Zn
Jamal/ red	0.85±0.20	2.91±0.67	2.41±0.84	3.64±0.84	15.25±0.41	69.17±0.28
Jamal	0.96±0.44	4.10±0.94	1.79±0.30	3.42±0.79	17.34±0.16	53.21±0.05
Imperial	0.99±0.18	3.44±0.79	2.60±0.49	3.55±0.82	12.58±0.42	114.43±0.23
Infinity	1.13±0.42	3.35±0.77	2.61±0.48	4.67±0.63	18.07±0.07	46.14±0.05
Victory	1.04±0.26	4.06±3.97	2.41±0.08	4.50±0.75	16.52±0.31	45.34±0.14
Lando	2.11±0.09	4.41±1.01	1.92±0.71	5.15±2.43	14.55±0.29	47.03±0.14
Arabic tobacco	0.98±0.22	3.24±1.87	1.00±0.47	5.73±0.38	20.35±0.51	67.18±0.20
Mean	1.15±0.26	3.65±1.43	2.10±0.48	4.38±0.95	16.38±0.31	63.21±0.15
Min	0.85	2.91	1.00	3.42	12.58	45.34
Max	2.11	4.41	2.61	5.73	20.35	114.43

Table 6: Heavy metal contents (mean ± SD) (µg/g, dry weight) of imported brands of cigarette tobacco

Brands	Cd	Pb	Co	Ni	Cu	Zn
Rothmans	1.21±0.08	2.31±1.00	0.91±0.34	6.06±0.49	14.91±0.63	41.36±0.17

Craven "A"	1.01±0.15	5.06±2.85	1.29±0.19	5.30±0.48	11.86±0.64	30.55±0.09
Viceroy	1.21±0.09	3.32±0.76	1.56±0.46	6.23±0.49	18.57±0.45	41.98±0.13
Next/ blue	0.93±0.16	2.21±1.79	0.58±0.20	5.11±0.25	15.27±0.14	44.27±0.22
Next/ light blue	1.21±0.04	2.74±2.70	0.65±0.22	5.49±0.56	15.49±0.36	80.99±0.24
Gold coast	1.17±0.15	2.79±1.43	1.21±0.19	5.07±0.70	15.50±0.54	39.09±0.04
Winston/ red	1.10±0.21	2.93±0.67	1.42±0.09	4.74±0.08	15.35±0.40	44.89±0.04
Winston / blue	1.30±0.08	3.32±0.76	0.90±0.11	4.83±0.26	14.96±0.13	47.68±0.29
Parliament	1.09±0.10	2.92±0.67	0.77±0.31	4.71±0.37	12.83±0.17	41.20±0.16
Marlboro/ red	1.10±0.07	2.24±0.71	0.30±0.12	5.44±0.13	12.66±0.41	44.76±0.09
Marlboro/ white	1.31±0.08	2.58±2.34	0.30±0.11	5.79±0.14	13.68±0.67	45.95±0.05
LM/ red	1.25±0.15	2.58±1.38	0.22±0.05	5.31±0.22	15.87±0.05	71.80±0.14
LM/ blue	1.19±0.11	2.34±1.61	0.37±0.24	5.08±0.70	16.09±0.03	45.08±0.23
Davidoff classic	1.32±0.10	2.40±1.64	0.69±0.52	4.76±0.37	13.65±0.40	40.76±0.04
Davidoff gold	1.48±0.02	3.26±0.75	0.18±0.04	3.98±0.18	14.81±0.61	45.11±0.05
Gauloises/ blue	1.26±0.04	3.14±0.72	0.19±0.04	4.91±0.28	14.26±0.40	44.55±0.27
Gauloises / red	1.24±0.15	2.93±0.67	0.41±0.17	4.50±0.57	13.92±0.14	45.55±0.09
Gauloises/ orange	1.51±0.16	3.30±0.76	0.47±0.29	4.95±0.30	15.96±0.10	40.63±0.04
Mean	1.22±0.11	2.91±1.29	0.69±0.21	5.13±0.36	14.76±0.35	46.46±0.13
Min	0.93	2.21	0.18	3.98	11.86	30.55
Max	1.51	5.06	1.56	6.23	18.57	80.99

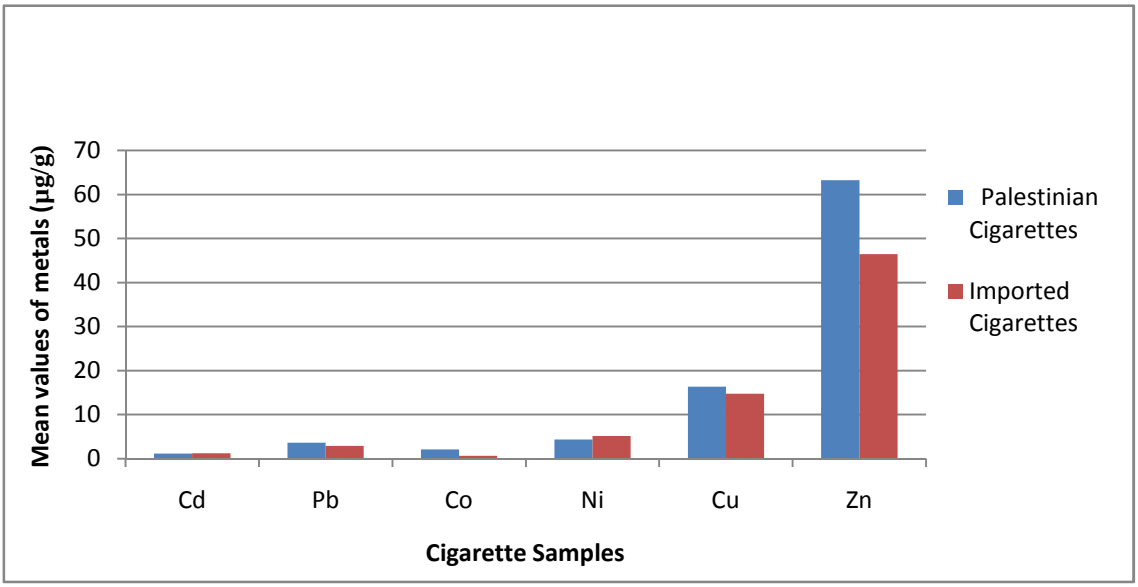

Fig. 2 Histogram of comparison of the heavy metal contents of imported and local cigarettes for the elements:Cd, Pb, Co, Ni, Cu and Zn.

Comparison of the levels of heavy metals by according to country of origin

In Table 7 and fig. 3, 4, 5, 6, 7, and 8, the results showed that the Cd content in Germany tobacco is much higher than another countries. Palestinian tobacco has the highest concentration of the heavy metals Pb, Co, Cu and Zn.

The British tobacco hasthe highest mean content of Ni and the lowest mean content of Pb and Zn. Swiss and Germany tobacco has the lowest mean content of Cu. The lowest Co tobacco content is from Swiss, Germany and France.

According to Nnorom*et al*[14], the mean metal contents of cigarettes varied clearly depending on the geographical area of production. However, it is not possible to obtain any evidence to suggest that the differences are related to the area of production or the extent of industrial development of the area. It was also reported that it is has been observed that some species of plant accumulate high concentrations of some metals, most especially Cd, in the leaf tissue rather than in the roots[14]. The processing, packaging and other technological processes (including the use of additives) used to bring raw food items to the consumer can significantly increase heavy metal contents in cigarette tobacco[25].For this reason, there are large variations in the content of metals in tobacco between countries.

Table 7: Comparison of heavy metals contents (mean ± SD) (µg/g, dry weight) of cigarettes sold in Palestine according to country of origin (manufacturer).

Country of origin	Cd	Pb	Co	Ni	Cu	Zn
Palestine	1.15±0.26	3.65±1.43	2.10±0.48	4.38±0.95	16.38±0.31	63.21±0.15
Britain	1.21±0.08	2.31±1.00	0.91±0.34	6.06±0.49	14.91±0.63	41.36±0.17
Turkey	1.09±0.11	3.33±2.02	1.02±0.27	5.54±0.44	15.30±0.39	49.45±0.17
Japan	1.19±0.14	3.01±0.96	1.18±0.13	4.88±0.35	15.27±0.36	43.89±0.12
Switzerland	1.19±0.10	2.53±1.34	0.39±0.17	5.26±0.31	14.23±0.26	49.76±0.13
Germany	1.40±0.06	2.83±1.19	0.44±0.28	4.37±0.27	14.23±0.50	42.93±0.04
France	1.34±0.12	3.12±0.72	0.36±0.17	4.79±0.38	14.71±0.21	43.58±0.13

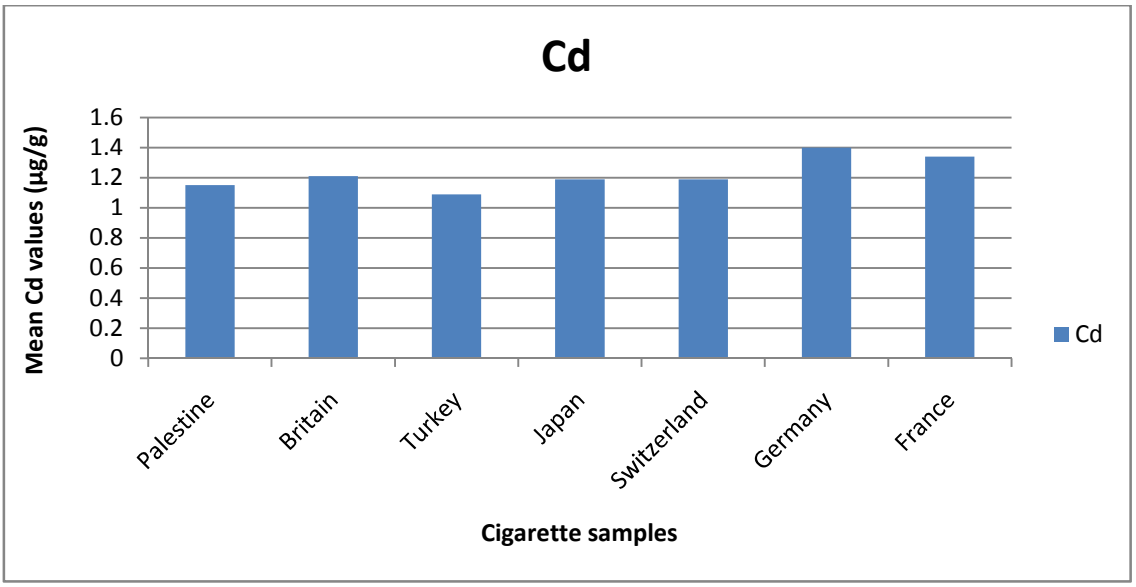

Fig. 3 Cadmium content in different brands of cigarette samples.

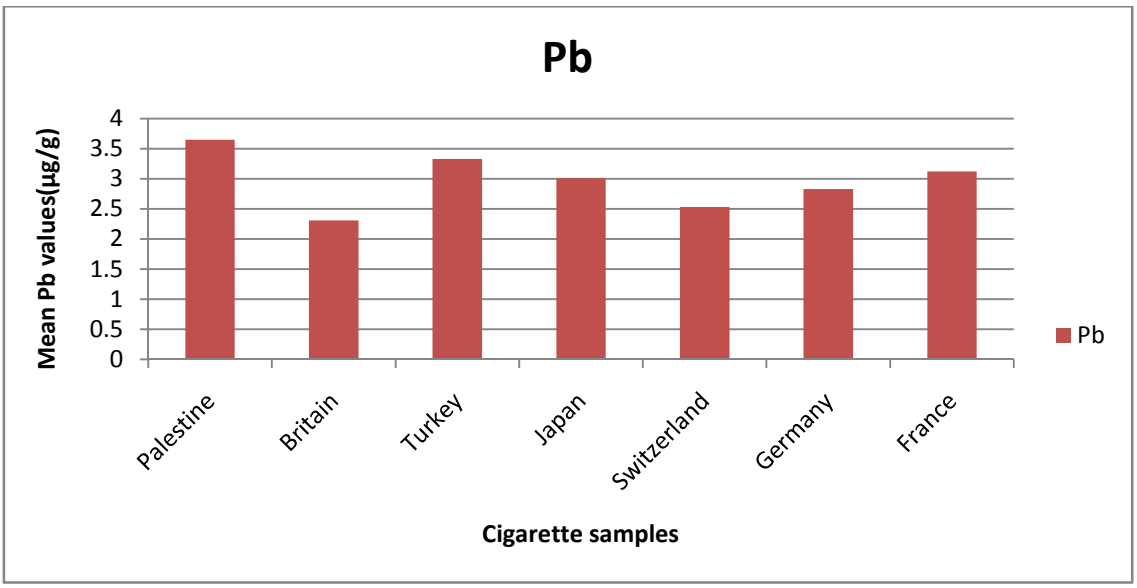

Fig. 4 Lead content in different brands of cigarette samples.

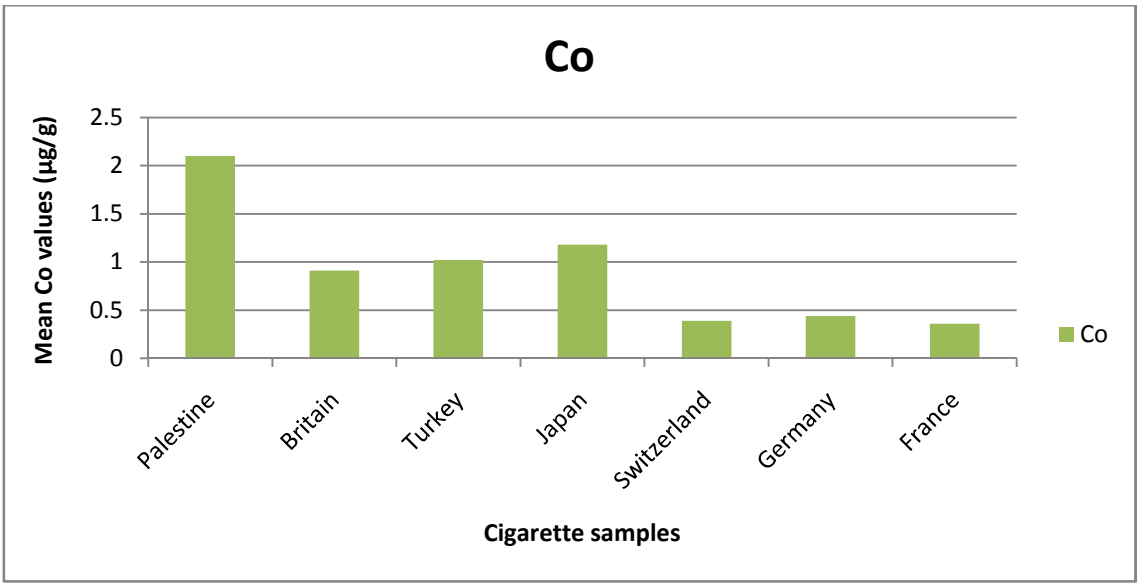

Fig. 5 Cobalt content in different brands of cigarette samples.

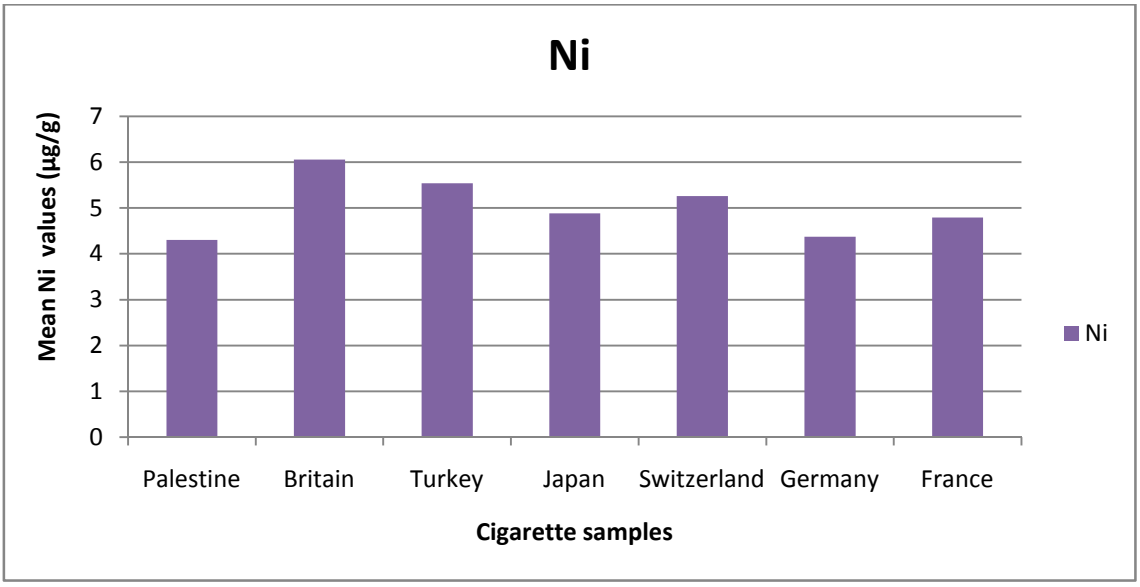

Fig. 6 Nickel content in different brands of cigarette samples.

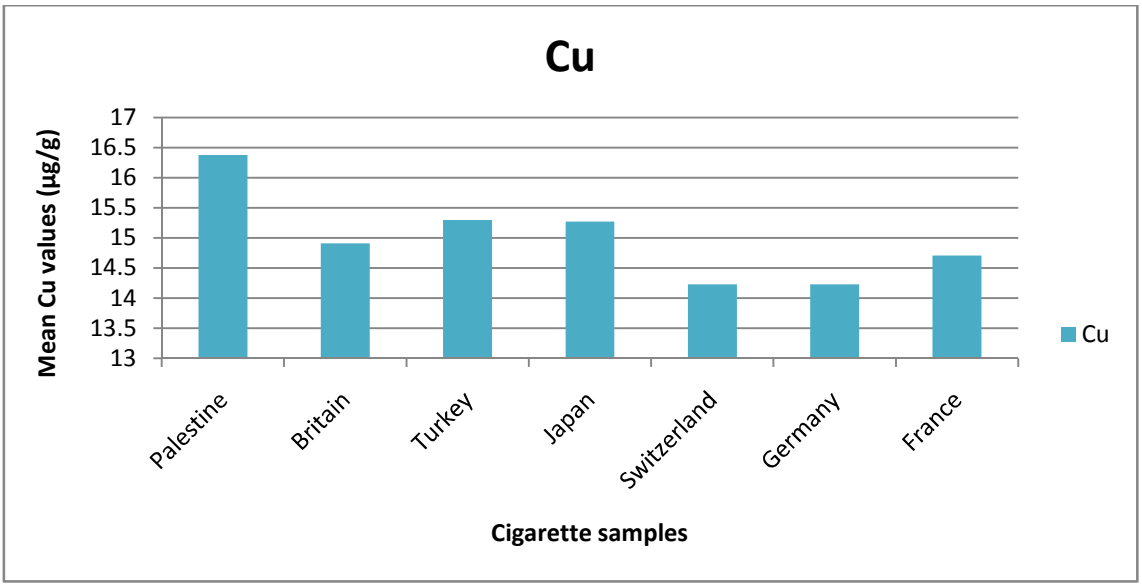

Fig. 7 Copper content in different brands of cigarette samples.

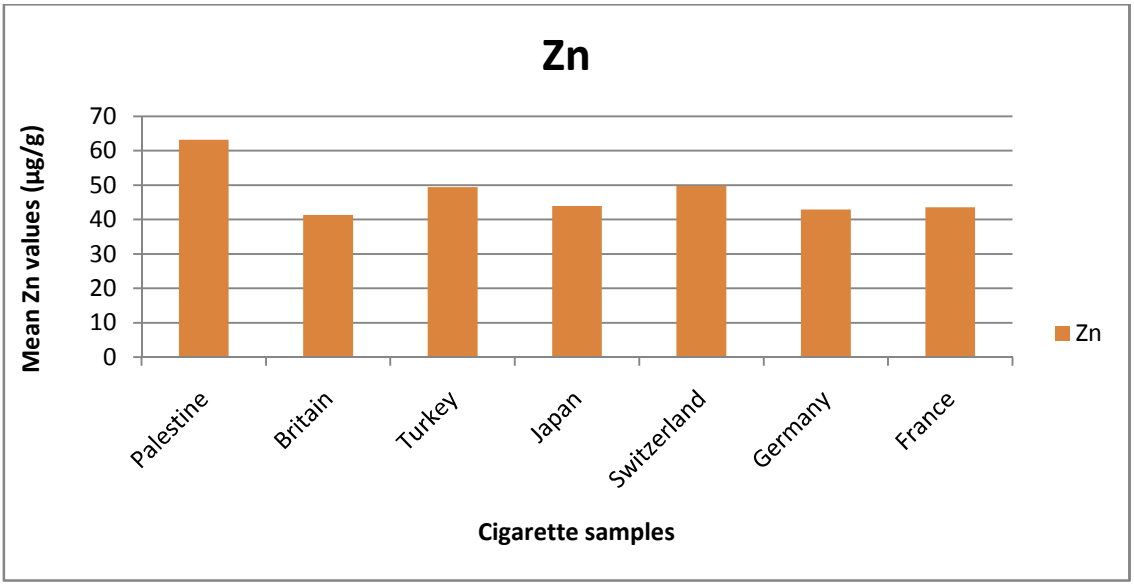

Fig. 8 Zinc content in different brands of cigarette samples.

Comparison ofheavy metals contents in the Palestinian cigarettes with literature reports in cigarettes sold or smoked around the world

The mean concentration Cd in the tobacco in this study 1.20 µg/g. This metal content was higher than its degree in China 0.18 µg/g India 0.4 µg/g, Pakistan 0.5 µg/g, and some reported investigation on Table 8, but comparable with cigarette tobaccos of

Nigeria and Turkey. Mussalo - Rauhama*etal*[10]investigated in different cigarettes and found the cadmium content ranging between 0.8 to 3.4 µg/g (DW).

The mean Pb concentration in tobacco samples 3.12 µg/g, have significantly lower concentration than Pakistan cigarette 14.4 µg/g , Nigeria cigarette 10.8 µg/g[26-27]and Ethiopia 6.07 µg/g[28] but almost agree with Andrade *et al*[29], Watanabe *et al*[30], Massadeh*et al*[31], and more published data on Table 8.

Table 8: Comparison of the results from studies of heavy metals contents in cigarettes (µg/g, dry weight) in various countries and results of the present study

Cd	Pb	Co	Ni	Cu	Zn	References
1.20	3.12	1.09	4.92	15.21	51.15	This study
2.71	2.07	4.42	17.93	9.7	27.02	Iran [75]
0.4	1.6	0.91	3.6	18	29	India [79]
0.9	4.3		3	39	39.5	India [80]
0.45	1.94		8.79	14	27	India [38]
2.49	6.24			13.7	36.22	Ethiopia [75]
0.5	14.53			7.89	8.57	Pakistan [73]
2.64	2.67			12.6	55.62	Jordan [77]
1.95	1.2		2.4	9.4	49.8	Germany [81]
1.7	1.02		0.22	2.45		Turkey [82]
0.18	0.64		2.23	4.13		China [83]
1.02	1.35			7.73	38.5	Korea [83]
0.9	0.74			13	31.9	Uk [83]
					51.4	Ohaio [84]
1.27	10.8					Nigeria [14]
2.3						France [14]
1.9						Switzerland [14]

The amount of heavy metals arising from smoking a pack of cigarettes

Due to differences in the rate of weight packaged tobacco per cigarette from one type to another, the concentration of heavy metals was calculated in each each pack (20 cigarettes) as shown in the Table 9 and fig.9, 10, 11, 12, 13, and 14.

The mean of heavy metal contents of cigarettes available and sold in Palestine are Cd:16.31µg/packet with range (12.09– 33.92) µg/packet, Pb: 42.67 µg/packet with range (28.29 – 70.74) µg/packet, Co:14.87 µg/packet with range (2.36– 40.38)

µg/packet, Ni: 67.34 µg/packet with range (51.31– 113.24) µg/packet Cu: 208.34 µg/packet with range (156.08–402.13) µg/packet, Zn: 700.47 µg/packet with range (402.02– 1775.93) µg/packet.

It has been observed that Lando cigarette brand has high mean Cd and Pb values with 1.70 and 3.54µg/cigarette, respectively. Imperial cigarette brand has high mean Co and Zn values with 2.02 and 88.80µg/cigarette, respectively. Arabic tobacco brand has high mean Ni and Cu values with 5.66 and 20.11 µg/cigarette, respectively. It is very important to point out that heavy metals Cd and Pb content in local cigarettes was high concentration than in imported brands.

In the report of an International (WHO/UNEP) program for assessment of human exposure to heavy metals has reported higher levels of Cd in kidney cortex samples of smokers compared to non-smokers[27, 12]. According to this project work the recommended cigarette with low mean trace metal contents are Jamal/ red and Next/ blue.

Table 9: Heavy metal contents in one packet (20 cigarettes) (µg/packet) of brands of cigarette tobacco sold in Palestinian market

Brands	Cd	Pb	Co	Ni	Cu	Zn
Jamal/ red	13.14	44.78	37.10	55.92	234.51	1063.79
Jamal	16.03	68.21	29.69	56.83	288.17	884.27
Imperial	15.34	53.34	40.38	55.07	195.22	1775.93
Infinity	15.87	47.27	36.74	65.80	254.84	650.55
Victory	14.74	57.47	34.05	63.62	233.66	641.06
Lando	33.92	70.74	30.72	82.56	233.44	754.36
Arabic tobacco	19.27	64.00	19.75	113.24	402.13	1327.42
Rothmans	14.77	28.29	11.08	74.07	182.26	505.39
Craven "A"	13.34	66.55	17.04	69.78	156.08	402.02
Viceroy	15.45	42.41	19.96	79.67	237.34	536.50
Next/ blue	12.09	28.75	7.53	66.58	198.82	576.37
Next/ light blue	13.90	31.35	7.48	62.96	177.51	928.13
Gold coast	15.84	37.65	16.34	68.59	209.55	528.53
Winston/ red	13.88	36.98	17.90	59.77	193.75	566.47
Winston / blue	14.39	36.83	10.02	53.55	165.72	528.31
Parliament	17.63	47.48	12.48	76.46	208.32	669.12

Marlboro/ red	15.91	32.24	4.30	78.35	182.26	644.47
Marlboro/ white	16.69	32.86	3.85	73.66	174.02	584.46
LM/ red	16.08	33.22	2.85	68.45	204.72	926.27
LM/ blue	14.61	28.77	4.52	62.35	197.64	553.63
Davidoff classic	17.62	32.18	9.23	63.78	182.92	546.15
Davidoff gold	19.06	42.01	2.36	51.31	190.79	581.01
Gauloises/ blue	16.30	40.49	2.49	63.32	183.97	574.76
Gauloises / red	15.34	36.11	5.02	55.55	171.76	562.07
Gauloises/ orange	16.46	35.96	5.09	53.97	173.93	442.83
Mean	16.31	42.67	14.87	67.34	208.34	700.47
Min	12.09	28.29	2.36	51.31	156.08	402.02
Max	33.92	70.74	40.38	113.24	402.13	1775.93

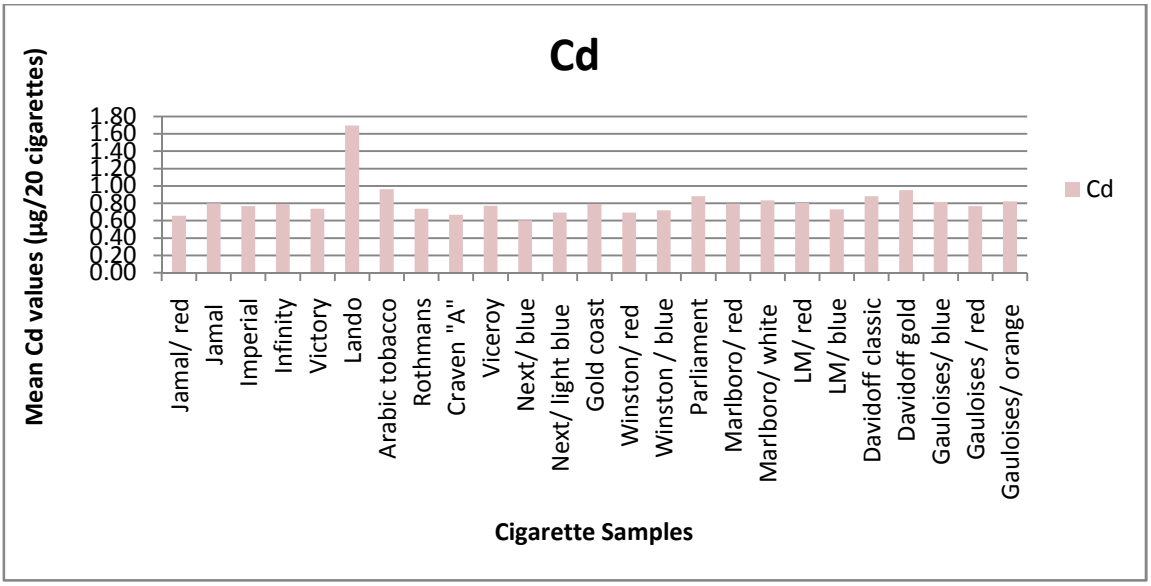

Fig. 9 Cadmium content in one packet of brands of cigarette tobacco sold in Palestinian market.

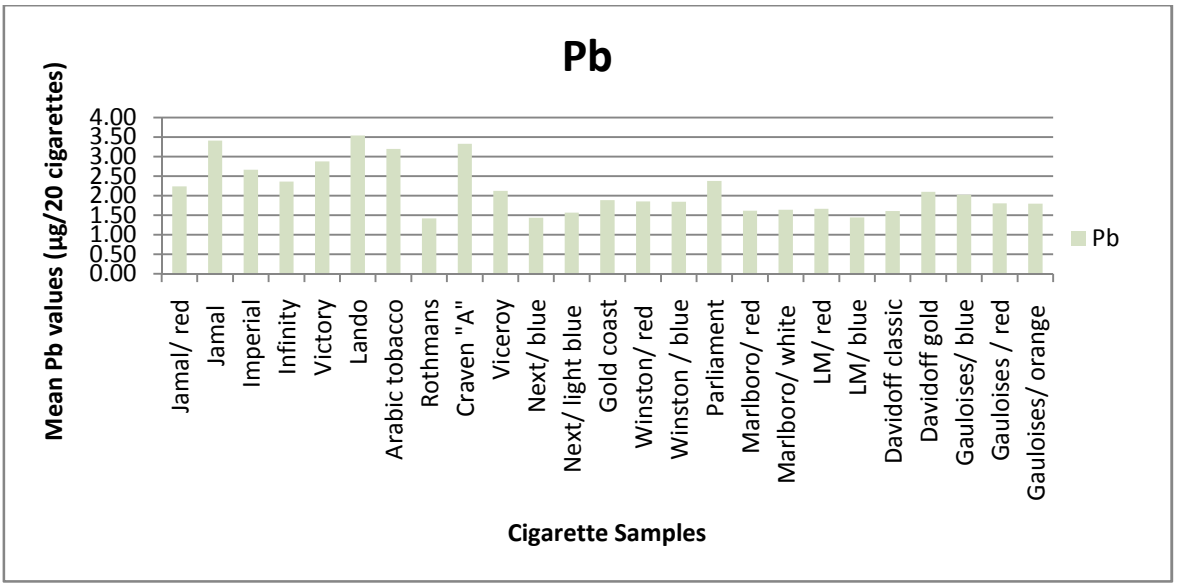

Fig.10 Lead content in one packet of brands of cigarette tobacco sold in Palestinian market.

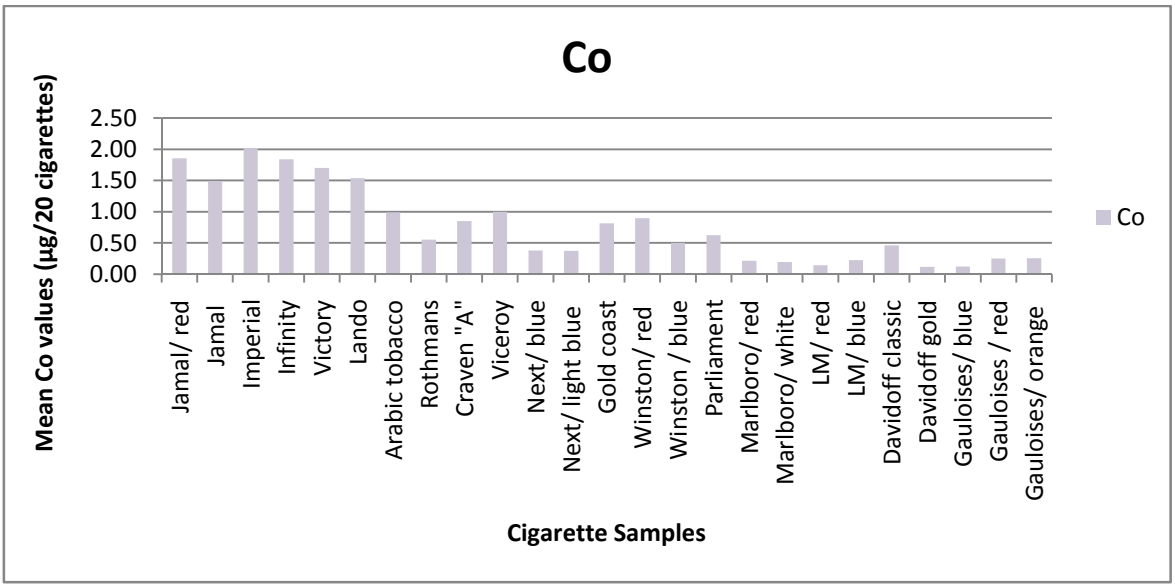

Fig. 11 Cobalt content in one packet of brands of cigarette tobacco sold in Palestinian market.

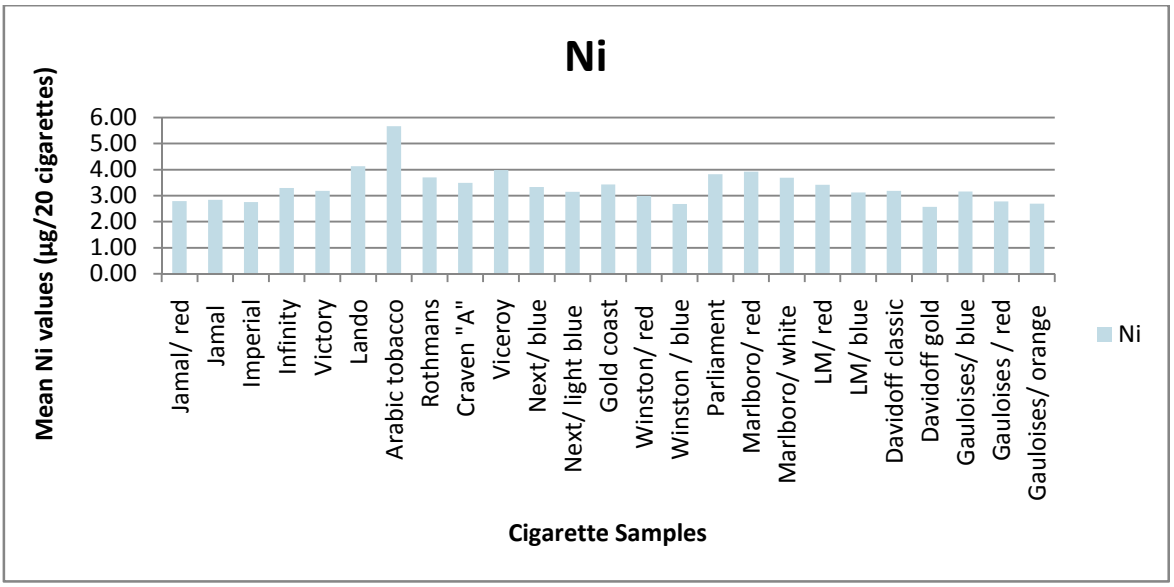

Fig.12 Nickel content in one packet of brands of cigarette tobacco sold in Palestinian market.

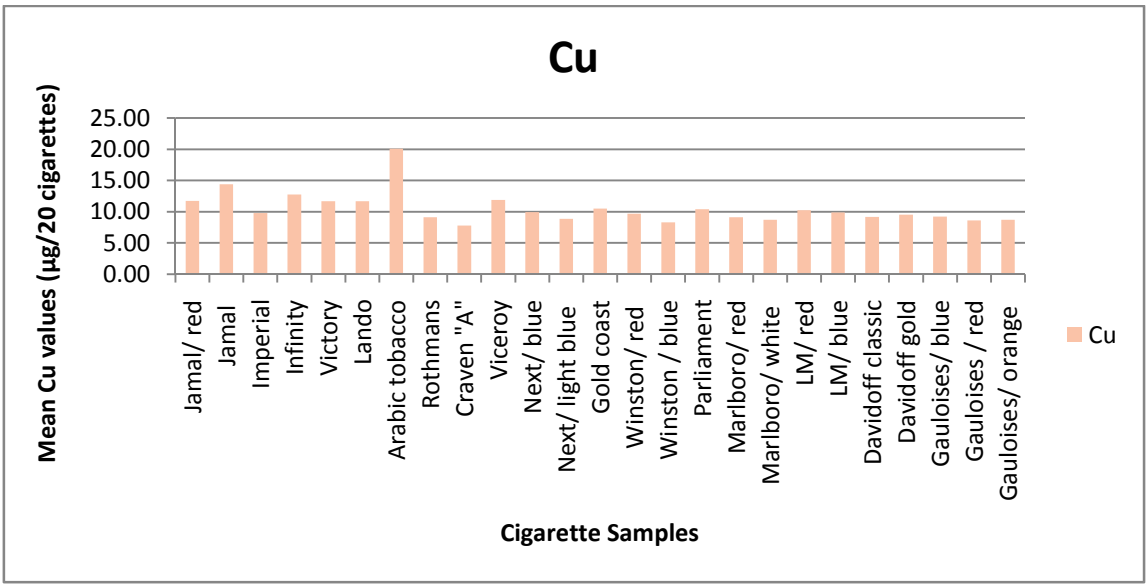

Fig.13 Nickel content in one packet of brands of cigarette tobacco sold in Palestinian market.

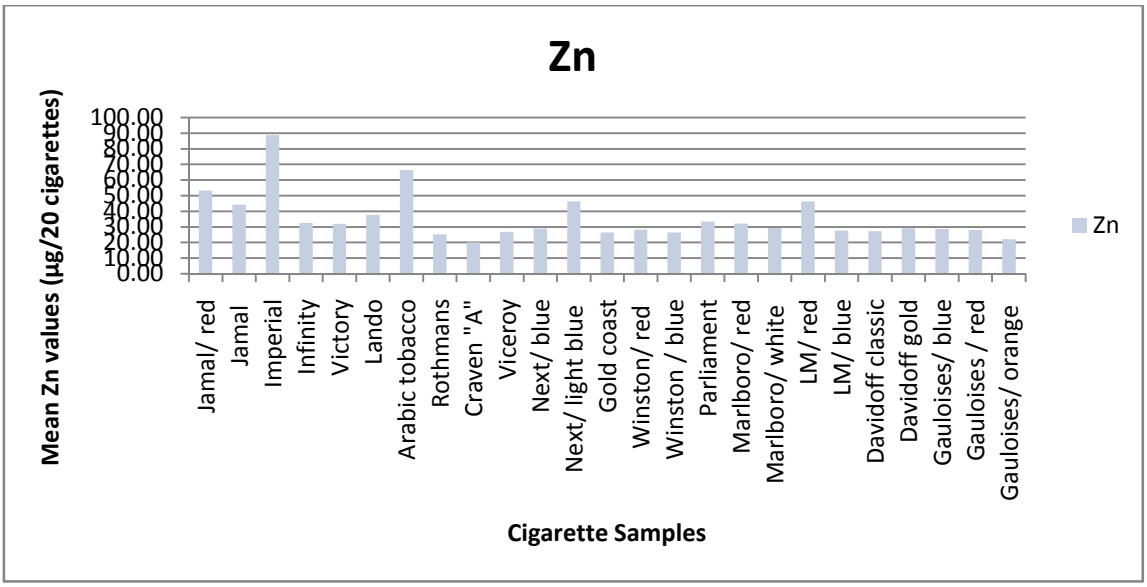

Fig.14 Zinc content in one packet of brands of cigarette tobacco sold in Palestinian market.

Comparison ofheavy metals contents between heavy and light brands of cigarettes

The results in Tables 10 and 11 and fig. 15, indicate that the mean Cd content of heavy brands of cigarette are near to the light brands of cigarette, showed a lowerPb, Co, Ni, Cu, and Zn content than heavy cigarettes. As the light cigarettes have a low weight average than heavy cigarettes.

Table 10. Heavy metal contents in one packet (µg/ packet) of heavy brands of cigarette tobacco sold in Palestinian market

Brands	Cd	Pb	Co	Ni	Cu	Zn
Jamal/ red	13.14	44.78	37.10	55.92	234.51	1063.79
Imperial	15.34	53.34	40.38	55.07	195.22	1775.93
Infinity	15.87	47.27	36.74	65.80	254.84	650.55
Victory	14.74	57.47	34.05	63.62	233.66	641.06
Lando	33.92	70.74	30.72	82.56	233.44	754.36
Arabic tobacco	19.27	64.00	19.75	113.24	402.13	1327.42
Rothmans	14.77	28.29	11.08	74.07	182.26	505.39
Craven "A"	13.34	66.55	17.04	69.78	156.08	402.02
Viceroy	15.45	42.41	19.96	79.67	237.34	536.50
Next/ blue	12.09	28.75	7.53	66.58	198.82	576.37
Gold coast	15.84	37.65	16.34	68.59	209.55	528.53
Winston/ red	13.88	36.98	17.90	59.77	193.75	566.47

Parliament	17.63	47.48	12.48	76.46	208.32	669.12
Marlboro/ red	15.91	32.24	4.30	78.35	182.26	644.47
LM/ red	16.08	33.22	2.85	68.45	204.72	926.27
Davidoff classic	17.62	32.18	9.23	63.78	182.92	546.15
Gauloises/ blue	16.30	40.49	2.49	63.32	183.97	574.76
Mean	16.54	44.93	18.82	70.88	217.28	746.42
Min	12.09	28.29	2.49	55.07	156.08	402.02
Max	33.92	70.74	40.38	113.24	402.13	1775.93

Table 11. Heavy metal contents in one packet (µg/ packet) of Light brands of cigarette tobacco sold in Palestinian market

Brands	Cd	Pb	Co	Ni	Cu	Zn
Jamal	16.03	68.21	29.69	56.83	288.17	884.27
Next/ light blue	13.90	31.35	7.48	62.96	177.51	928.13
Winston / blue	14.39	36.83	10.02	53.55	165.72	528.31
Marlboro/ white	16.69	32.86	3.85	73.66	174.02	584.46
LM/ blue	14.61	28.77	4.52	62.35	197.64	553.63
Davidoff gold	19.06	42.01	2.36	51.31	190.79	581.01
Gauloises / red	15.34	36.11	5.02	55.55	171.76	562.07
Gauloises/ orange	16.46	35.96	5.09	53.97	173.93	442.83
Mean	15.81	39.01	8.50	58.77	192.44	633.09
Min	13.90	28.77	2.36	51.31	165.72	442.83
Max	19.06	68.21	29.69	73.66	288.17	928.13

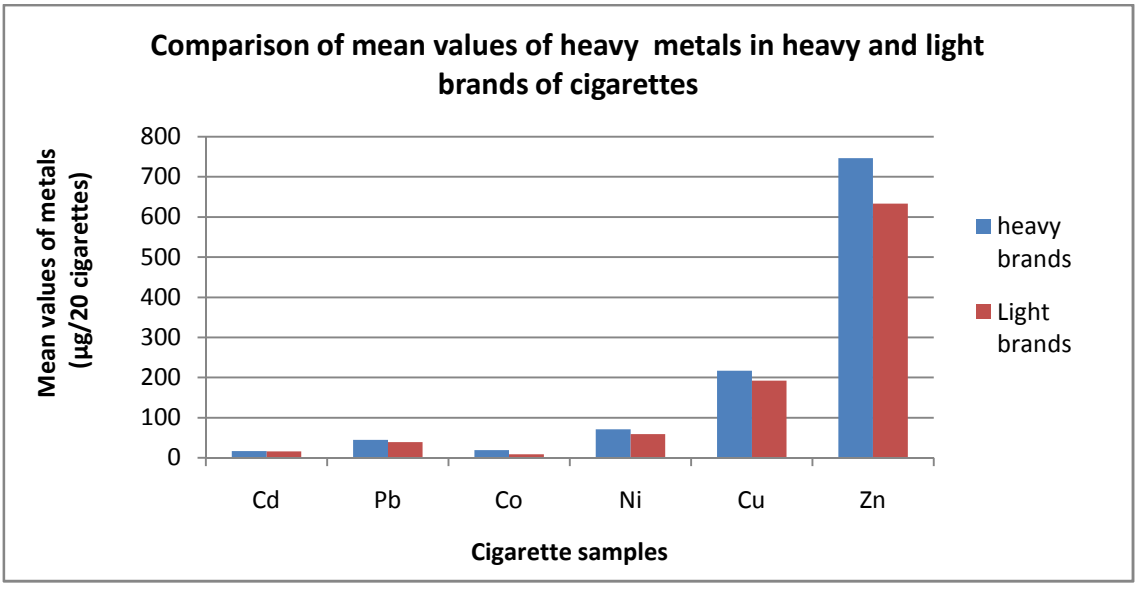

Fig.15 Histogram comparing the heavy metal contents of heavy and light brands of cigarettes for the elements:Cd, Pb, Co, Ni, Cu and Zn.

Estimation of heavy metals contents in mainstream smoke

The amount of heavy metals in mainstream smoke was estimated and shown in Table 12 and fig. 16, 17, 18, 19, and 20. It has been documented in the literature that the average of 2.0 % for Cd, 5.8% of Pb, 2.0% for Cu, 1.0 % for Zn contained in cigarettes are passed to mainstream smoke[10]. There was no studies for Co and Ni. The results show that the concentration of heavy metals in the mainstream smoke for one packet ranged Cd: 0.24 to 0.68 µg with mean 0.33 µg. Pb: 1.64 to 4.10 µg with mean 2.47 µg. Cu: 0.31 to 0.80 µg with mean 0.42 µg. Zn: 4.02 to 17.76 µg with mean 7.00 µg.

When smoking, about 6 % and 11 % of lead in tobacco moves to mainstream smoke[32, 18](WHO andGalażyn-Sidorczuk et al), it is thought that half of this quantity reaches to smokers' lungs. Most of the rest can be found in the ash. That causes increasing in the levels of lead in the house's dust, and this can cause the air pollution. So the use of cigarette products damage the smokers and also effects on health of nonsmokers especially children, pregnant women and adults that result in high metals content in blood stream.

An average of 40-60% of cadmium inhaled via smoking can directly affect the blood stream of the smoker easily. Smoking more than 20 cigarettes daily (one packet) can increase Cd contents in body by 10 folds and impair the body organs. On the other hand, the reports[24] proved that excess zinc can prevent cadmium toxicology .The ratio of zinc-cadmium is very important because cadmium toxicity causes greater activity in tissue function with zinc deficiency, so cadmium may displace zinc from binding sites like enzymatic and organ functions .Because of that, the competition between Cd and Zn is proved by the fact that extra Zn is able to prevent Cd toxicity.

Another point is that other heavy metals like Ni, Co and Cu may also enter the lungs and bloodstream, and the results may be additional or even synergistic with Cd, but experimental transfer coefficients between tobacco and smoke are not presently well determined for many heavy metals. If any of these low-dose effects proves to cause significant harm, then the role of enhanced levels of Cd and other heavy metals in cigarette smoke becomes rather more important than currently appreciated[24].

Table 12. Estimated amount of heavy metals contents in mainstream smoke (µg) for one packet (20 cigarettes) of brands of cigarette tobacco sold in Palestinian market

Brands	Cd	Pb	Cu	Zn
Jamal/ red	0.26	2.60	0.47	10.64
Jamal	0.32	3.96	0.58	8.84
Imperial	0.31	3.09	0.39	17.76
Infinity	0.32	2.74	0.51	6.51
Victory	0.29	3.33	0.47	6.41
Lando	0.68	4.10	0.47	7.54
Arabic tobacco	0.39	3.71	0.80	13.27
Rothmans	0.30	1.64	0.36	5.05
Craven "A"	0.27	3.86	0.31	4.02
Viceroy	0.31	2.46	0.47	5.36
Next/ blue	0.24	1.67	0.40	5.76
Next/ light blue	0.28	1.82	0.36	9.28
Gold coast	0.32	2.18	0.42	5.29
Winston/ red	0.28	2.14	0.39	5.66
Winston / blue	0.29	2.14	0.33	5.28
Parliament	0.35	2.75	0.42	6.69
Marlboro/ red	0.32	1.87	0.36	6.44
Marlboro/ white	0.33	1.91	0.35	5.84
LM/ red	0.32	1.93	0.41	9.26
LM/ blue	0.29	1.67	0.40	5.54
Davidoff classic	0.35	1.87	0.37	5.46
Davidoff gold	0.38	2.44	0.38	5.81
Gauloises/ blue	0.33	2.35	0.37	5.75
Gauloises / red	0.31	2.09	0.34	5.62
Gauloises/ orange	0.33	2.09	0.35	4.43
Mean	0.33	2.47	0.42	7.00
Min	0.24	1.64	0.31	4.02
Max	0.68	4.10	0.80	17.76

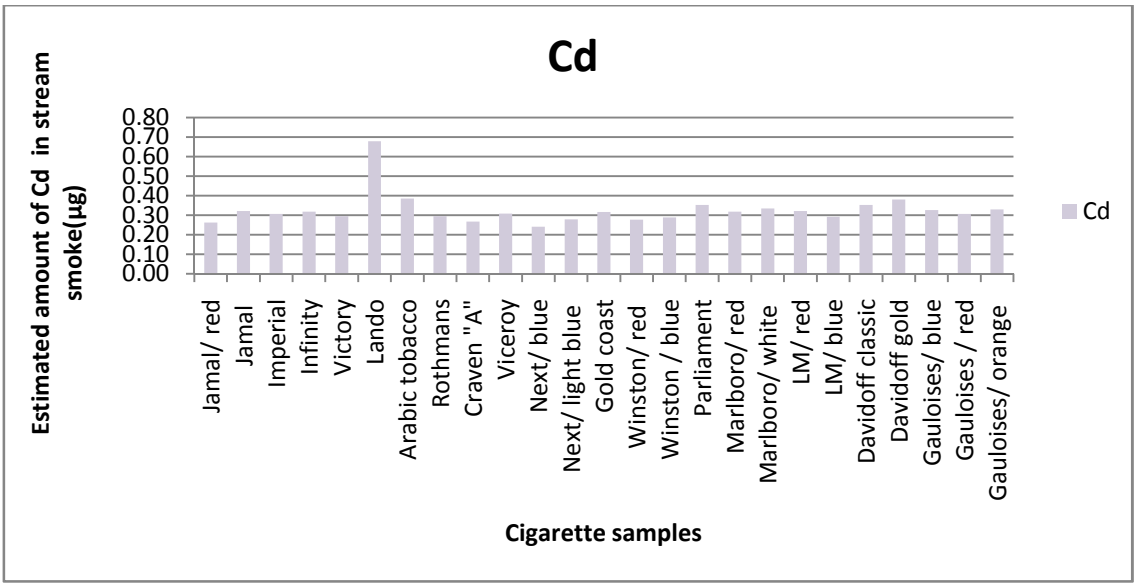

Fig.16 Estimated Cadmium content in one packet in mainstream smoke of different brands of cigarette samples.

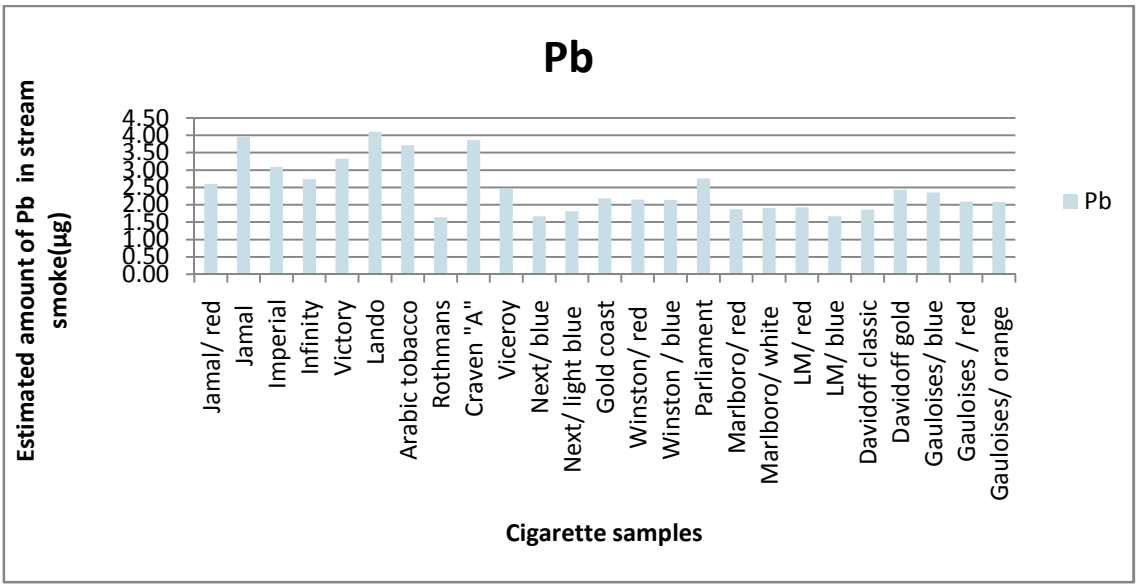

Fig.17 Estimated Lead content in one packet in mainstream smoke of different brands of cigarette samples.

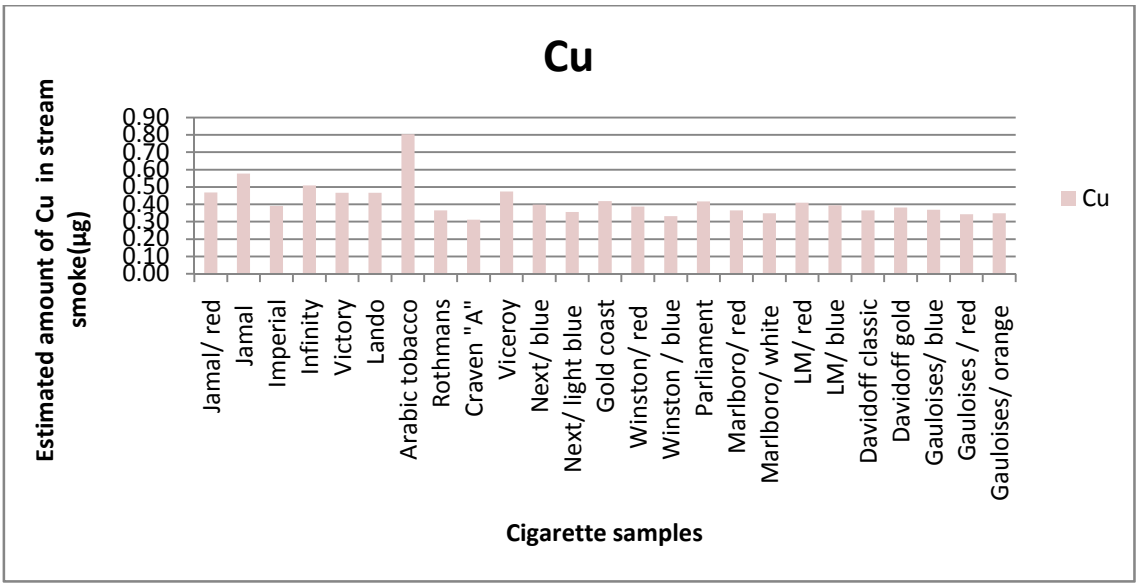

Fig.18 Estimated Copper content in one packet in mainstream smoke of different brands of cigarette samples.

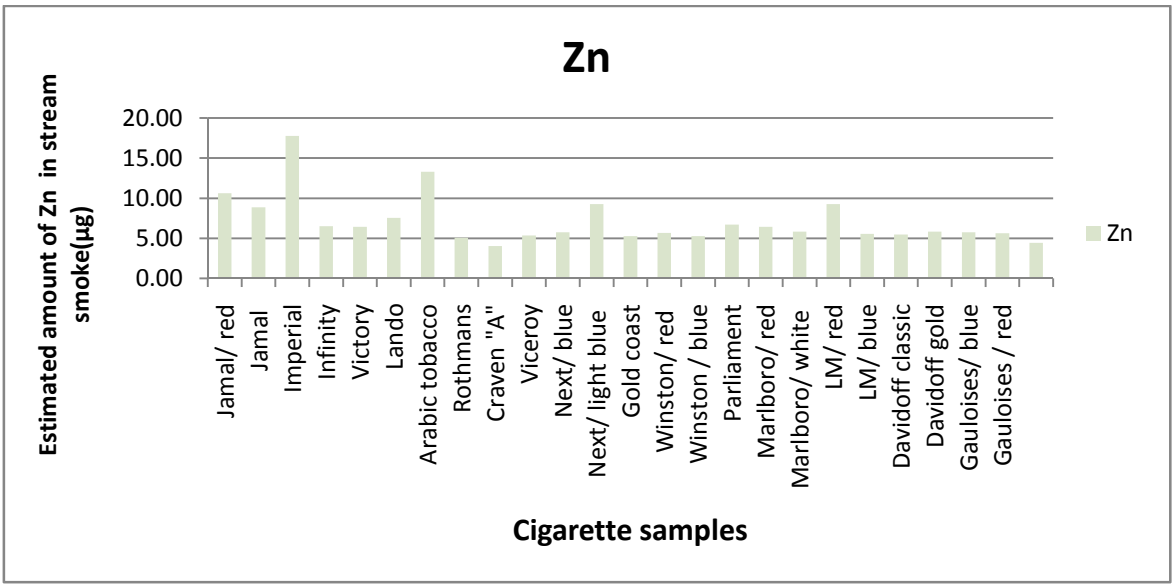

Fig.19 Estimated Zinc content in one packet in mainstream smoke of different brands of cigarette samples.

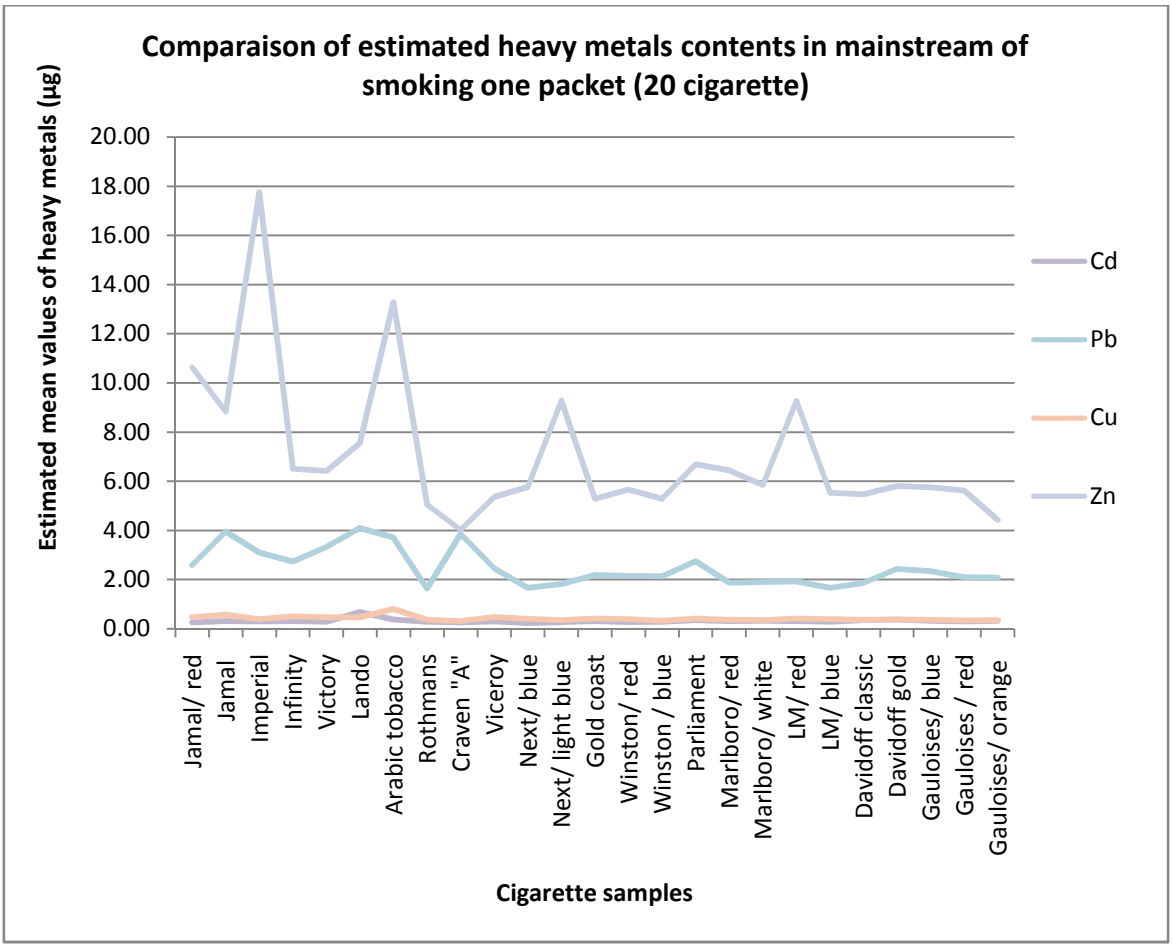

Fig.20 Histograms comparing the estimated heavy metal contents in mainstream smoke of different brands of cigarette samples for the elements: Cd, Pb, Cu and Zn.

Conclusion:

The conclusion obtained from this study are:

1. The levels of Cd, Pb, Co, Ni, Cu and Zn in cigarettes sold in Palestine are nearly similar to levels in cigarettes from other parts of the world.
2. The level of Pb,Co, Cu and Zn are slightly higher in local cigarettes than in imported cigarettes.
3. The level of Cd and Ni are slightly lower in local cigarettes than in imported cigarettes.

4. The British tobacco has the highest level of Ni and the lowest levels of Pb and Zn. While Swiss and Germany tobacco has the lowest level of Cu.
5. The lowest Co level is in Swiss, Germany and France cigarettes.
6. Arabic tobacco has the heaviest dry weight and the lowest proportion of organic matter, this is due to the absence of any additions where Arabic tobacco is not manufactured, but cigarettes are wrapped manually. Thus it has high proportion of ash (minerals).
7. Lando cigarette brand has high Cd and Pb levels.
8. Imperial cigarette brand has high Co and Zn levels.
9. Arabic tobacco brand has high mean Ni and Cu values.
10. The concentration of heavy metals Cd and Pb in local cigarettes are high than imported brands.
11. Light cigarettes show a low Pb, Co, Ni, Cu, and Zn content than heavy cigarettes.
12. Presence of significant amounts of two toxic heavy metals Cd and Pb in the cigarette sold in Palestine. Thus the smokers in Palestine have higher intake of Cd and Pb than the non-smokers.

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