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Uranium Concentration and Elemental Characterization of Moassel Smoking Mixtures

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Abstract: Smoking is a documented cause of a very serious health hazardous due to inhalation of various toxic agents. However, data about tobacco-derived products such as moassel/tabamel and jurak, used in the growingly popular shisha (narghile, hookah), have been scarce and scattered. In these conditions, the objective of this study, was to investigate the elemental contents of moassel mixture and compare it with that of other tobacco products. Representative samples from 3 different brands were collected. Concentration of U and other 33 elements was measured using the ICP-MS (Inductively Coupled Plasma Mass Spectrometer). Concentrations of U in tobacco products were 0.008, 0.089, 0.02 and 0.766 mg kg^{-1} in moassel, cigarette, tobacco leaves and chewing, respectively. Results show that U and other trace elements are much more abundant in cigarette tobacco than in shisha moassel. A wide range of variations was observed. For instance, the levels of As; Cd and Ni (mg kg^{-1}) were: 1.59, 1.0 and 0.146; 1.45, 0.5 and 0.075; 3.5, 5 and 0.63; for, respectively: cigarette, moassel and jurak. Since shisha smoking is continuously targeted by antismoking groups as a "global epidemic", a public health priority should be the design of culturally tailored products (for instance resins prepared from local plants to be mixed with the water of the pipes) based on well-established harm reduction techniques.

Keywords: Tobacco; Molasses; Smoking; Uranium; Elements.

1 Introduction

While cigarette smoking, as a method of tobacco use, has been intensively studied by biomedical researchers, this has not always been the case of shisha (narghile, hookah) in spite of its widespread historic use, particularly in Africa and Asia. Furthermore, research on this "exotic" form of smoking has suffered, over the past decade, from serious misconceptions and a global confusion regarding both of its health and anthropological aspects [1, 2, 3].

Then, and unlike cigarette smoking, tobacco-derived products used for the diverse types of water pipes can be grouped under three main forms: moassel/tabamel ("mu'assel" as a proper transliteration from Arabic which means "honeyed"), jurak and tumbak. Their composition is variable and not standardized. Moassel, these days, contains about 30% tobacco and up to 70% honey or molasses/sugar cane, in addition to glycerol and flavoring essences. Jurak contains about 30% tobacco, 50% juice of sugarcane, 20–25% various spices and dried fruits [2]. Tumbak (named 'ajamy in some parts) is made of shredded tobacco leaves left for some hours in water to wash them off nicotine excess [4]. The level of this alkaloid through the diverse products varies a lot [5] (Hadidi and Mohammed, 2004).

In Africa and Asia, all smoking products are used: from flavoured or un-flavoured moassel to jurak and tumbak whereas outside these two continents, flavoured moassel remains the almost only available and popular product. This peculiarity has many reasons: its mild taste to start with [4]. Mixing tobacco with molasses is a very ancient habit contrary to what a WHO report states, dating back "the addition of molasses to burley tobacco in the nineteenth century to create "American" blended tobacco" [6]. Health-oriented anthropological research on hookah smoking actually showed that this cultural invention is much older and can be traced back in the relation by an Arab traveller to India as early as the 17th century [3].

Data about the elemental characterization of tobacco leaves and tobacco products such as cigarette, cigar, bidi and snuff, and the related smoke is available for such countries as India, Pakistan, Mexico, Poland, Ghana, Jordan and others 2[7, 8, 9, 10, 11, 12].

The objective of the present study is to shed more light on elemental characterization of moassel since no previous study has been led so far on this issue.

1.1 Health Aspects of Shisha Smoking

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In response to the sudden emergence and unexpected global spread of shisha (narghile, hookah) smoking across the world, numerous papers of varying quality have been published by antismoking organizations since year 2002. Most of them contended that shisha smoking was much more hazardous than cigarette use and generally tended to hype health-related findings. However, the cited studies (of the past decades in many cases) were often misinterpreted. For instance, many of them did not distinguish between exclusive ever shisha smokers (i.e. non-dual cigarette and shisha users) and mixed smokers; between the diverse pipes and smoking preparations, etc. Inter-extrapolation of results has represented the main methodological flaw of these papers [2]. As an example of this confusion, a German team has recently found benzo-a-pyrene levels 20 times lower than in another one, widely advertised, at the US-American Lebanese University. Yet, both made use of a shisha smoking machine based on the same parameters (inter-puff time, notably) [13]. Not only these devices had been officially (including by the WHO) deemed confusing for poorly reflecting the reality of human smoking in the case of cigarettes (in spite of the rather short puffing sessions: about 5 minutes) but they have been used for shisha smoking "simulation" (in which the puffing sessions last for about one hour) [14].

Another unfortunately frequent methodological bias is to compare the amounts of given chemicals produced during a one hour shisha smoking session with those delivered by a 5 minute cigarette one; as if the average shisha user sat for 10 to 20 pipes a day and the average cigarette user smoked only one fag a day. While biological levels of nicotine in the blood and cotinine (its metabolite) in urine of shisha users are generally similar to those found in smokers of 1 (two, at the most) cigarette(s), it is not uncommon to read alarming statements in the open antismoking literature. For instance, shisha use would induce "substantial increase[s] in plasma nicotine concentrations" that would be "comparable to cigarette smoking" [15]. There is definitively no need to hype the risk for "nicotine addiction" because all studies show that such a risk is almost null; particularly in view of the average frequency of use. Anthropological and epidemiological studies alike show that the fashionable shisha prepared with flavoured moassel is smoked on average 2 to 3 times a week. Consequently, systematic "addiction", in the light of the above levels of biological nicotine, is an absurd hypothesis. Such a conclusion is reflected in the interviewees' responses themselves who, in all surveys across the world, frankly state that they are not addicted and that they have stopped smoking shisha for one or several weeks without feeling any "craving" for it [3]. Further to running thorough tests themselves, some scientists were honest to "reveal" the rather simple explanation: "It is likely that cigarette smokers consume several cigarettes per day, thus resulting in a higher nicotine uptake" [13]. Furthermore, the example cited about nicotine also applies to many chemicals such as nitrosamines (the most hazardous substances in "tar") and polycyclic aromatic hydrocarbons whereby even biological markers of these products are generally found in very much lower quantities in shisha users than among cigarette smokers [13]; even when it is apparently difficult for some researchers to always admit the reality reflected in their own experiments [15]. In these conditions, and after one full decade of alarmist claims in the mainstream media (citing in particular the WHO flawed report [1] that one shisha session would be equivalent to inhaling 100 cigarettes, it is surprising to see the same researchers who prepared that report now declare that "there is a continuum of harm, with tobacco cigarettes and NR [nicotine "replacement"] products on opposite ends of both continua and other products (waterpipe i.e. shisha and ECIGs electronic cigarettes) somewhere in between" [16] (Fagerström and Eissenberg, 2012). Yet, Saudi research, dismissed in the same report, early and clearly established the key (chemical) differences between shisha smoke and cigarette smoke [17, 18].

Many other publications of the past decades had also clarified these issues. For instance, researchers in Pakistan had studied hookah CO levels as early as 1993 and clearly distinguished between types of smoking products, charcoal and even the size of the different pipes [19]. More recently in the same country, a two-fold aetiological study on hookah smoking and cancer was published [3, 19].Thanks to an original selection of volunteers; a clear questionnaire; biological measurements; a clear distinction between the types of smokers (cigarette-only, mixed cigarette/hookah, hookah-only); a further sub-distinction (light, medium or heavy use); and the quantity of consumed tobacco, the findings actually confirmed a dose-response relationship and an agreement with partial results scattered over several decades. All the data have been pointing to a weaker cancer risk (when compared with cigarette use). In the same vein, an Indian cancer specialist early performed a smoke chemical analysis for tar and nicotine delivered by a hookah and concluded that "the results were comparable to those for some of the mildest cigarettes on the world market. He added that "these results showed the efficiency of water as a filter for tobacco smoke" [20].

When studying such a complex (anthropological and tobaccological) system as a hookah, it is very important to keep paying attention to the apparently most insignificant details before publishing findings and advertising them. For instance, in the same region where the above mentioned study on hookah and cancer was carried out, another team from the Indian part of the international frontier, found, although based only on hospital statistics, a high lung cancer risk in relation to hookah smoking. In fact, not only water changing was not observed but other details of utmost importance led to the need for publishing a clarification regarding the very specificity of that region and its practices so that no extrapolation be made without extreme caution. Indeed, hookah heavy smoking of great quantities of tobacco-based products in Eastern Asia (or even the smoking of a tiny quantity of pure tobacco in the small "mobile" Chine water pipes) is completely different from today' shisha smoking of flavoured light smoking mixtures [21].

Indeed, for one decade, the greatest obstacle to sound research has been the widely advertised evidence-less equivalence made between cigarette and shisha smokes. In fact, both are qualitatively (therefore chemically) completely different from each other (Chaouachi, 2006). Fortunately, a comprehensive review showed that while around 5000 chemical have been identified so far in cigarette smoke, less than 150 ones were found in an early study by Saudi researchers [4, 17, 22]. Today' shisha smoke is mainly made up of water and glycerol. As a consequence of these revelations, WHO experts only recently but finally acknowledged that shisha smoking is so different from cigarette smoking that data on smoke composition and toxicity cannot be extrapolated from one to the other [23]. Furthermore, the same dismissed Saudi study shows that most of the remaining toxic chemicals (including heavy metals as the present study shows) come from the charcoal used to heat moassel, not the latter itself as the WHO report suggested [4,17]. Finally, to close this necessary introduction about health aspects and the need for clearing up the related global confusion, it is noteworthy that the authors of the present study have also analysed such rare aspects of tobacco use as radioactivity in the smoking mixtures used for shisha smoking [2].

Cigarette smoke contains notorious organ-specific carcinogenic substances such as polycyclic aromatic hydrocarbons and heavy metals. Some of them can cause serious diseases, including lung cancer [24]. Heavy metals prove to be highly toxic even at low levels as they get easily incorporated into the smoker's body [8, 25]. Recent studies have shown that metals carcinogenicity is the result of production of reactive species. Inhaled metals are not biodegradable and, as a result, tend to deposit and remain for long periods in various areas of the pulmonary tissue [24].

2 Experimental Techniques

2.1 Sampling and Sample Preparation

Forty moassel packs, 50 g each, of three different brands were randomly collected from the local markets of Cairo (Egypt) and Riyadh (Saudi Arabia). In total, 10 moassel composite samples of about 200 g each were prepared from the collected packs. Each sample resulted from the mixing of 4 moassel packs. Samples were dried in an oven at a temperature of about 80°C, then pulverized and homogenized. Samples aliquots were digested in a microwave digestion system using a mixture of HNO_3 and H_2O_2. After digestion, samples were cooled in a water bath and diluted for elemental analysis.

2.2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

The instrument used for trace elements measurements was a Perkin Elmer SCIEX ELAN6100 quadruple based ICP-mass spectrometer. A multi-channel peristaltic pump (Minipuls-3), a Gem Tip cross-flow nebulizer and a Perkin Elmer Type II spray chamber made of Ryton, drained by the peristaltic pump, were used for sample introduction. This instrument was further equipped with a Perkin Elmer corrosion-resistant torch with standard alumina injector and a Channel torn. Continuous dynode electron multiplier was operated in the pulse counting mode. Experimental conditions used in the measurements are summarized in Table1.

3 Results and Discussion

3.1 Elemental Characterization

Among the 10 representative moassel samples of three different brands collected from the local markets of Cairo and Riyadh that were analyzed using ICP-MS after dissolution, concentration mean, standard error, standard deviation, minimum, and maximum (mg kg^{-1}) of 34 elements, number of samples with concentration higher than lower limit of detection, and variation percentage, are given in Table 2. The average elemental concentrations of different tobacco products are based on the available literature and given in Table 3. Particular attention should be paid to the elemental characterization of the different tobacco and tobacco-derived products, their quality and treatment, chemical composition, the corresponding smoking behavior, and, finally, the quality of the available analytical data.

Elemental concentration percentages in different tobacco or tobacco-derived products are given in Table 4. In Moassel samples, the predominant elemental concentration percentages were 67% for K, 27% for Ca and 4.6% for Mg. Their summation was about 99%, in average, of elemental composition. The sum of the average concentrations was about 1% for Na, Fe, Al, Sr and Zn and about 0.24% for the remaining 34 elements. The results indicate the existence of a wide range of variations for some elements. Variation coefficient percentages range from 6% for Ca to 106% for La, Table 2. The likely reason is that moassel composition is variable and not as well standardized as that of tobacco. In the tobacco plant, the element concentration varies along the stalk, being higher in the older leaves than in the younger, top leaves. For example, in cigarette, element concentrations vary among brands and even within the same brand [26]. Shi-Xiang et al., 2010, studied the effect of cultivar, crop year and crowing area on Mn, Fe, Cu, Zn, Ca and Mg content in flue cured tobacco. The content of the 6 elements in leaves were obviously different between different crop years and dependent on their cultivar and growing area as well [27]. Therefore, it would be very

Table 1: Experimental conditions used in the ICP-MS measurements.

Instrument	ELAN6100 (Perkin Elmer-Sciex)
Filter type:	Quadruple rod
Nebulizer :	cross-flow type
Spray chamber:	Scott-type
Sample uptake/ $mL.min^{-1}$:	1.8
Wash solution:	1% HNO_3
RF frequency/ MHz:	40
RF power/ W:	1250
Plasma gas flow rate:	15
Auxiliary gas flow rate:	1.0
Carrier gas flow rate:	0.95
Lens voltage:	adjusted daily
Detector:	26-segment dynode operating in both pulse and analogue modes
Data acquisition mode:	peak hopping
Instrument tuning:	Performed using a 10 μgL^{-1} solution of Be, Mg, Cu, Pb, and U
Number of point per peak:	1
Number of scan weeps:	100
Dwell time per point:	50 ms
Integration:	100 times

Table 2: Elemental concentration, in [μg/g] mg kg^{-1}, in moassel samples.

Ser.	Element	Mean	SE#	SD+	Min.	Max.	No. &	Variation% *	VC %^
1	Ag	0.550	0.062	0.138	0.379	0.719	5	90	25
2	Al	65	3.8	10.8	55	86	8	56	16
3	As	0.15	0.005	0.012	0.13	0.17	6	25	8
5	B	0.94	0.14	0.32	0.57	1.3	5	130	34
4	Ba	3.4	0.14	0.36	2.8	4.0	7	41	11
6	Ca	6412	162	397	6034	7110	6	18	6
7	Cd	0.075	0.003	0.006	0.070	0.081	3	16	8
8	Ce	0.084	0.003	0.007	0.075	0.090	4	20	8
9	Co	0.077	0.008	0.022	0.046	0.11	8	147	29
10	Cr	0.75	0.055	0.14	0.53	0.91	6	70	18
11	Cs	0.024	0.009	0.020	0.003	0.046	5	1543	86
12	Cu	8.3	0.38	1.01	6.7	9.5	7	41	12
13	Eu	0.003	0.0003	0.001	0.002	0.003	3	45	20
14	Fe	67	4.0	11	53	88	8	67	17
15	Hf	0.012	0.001	0.001	0.010	0.014	4	33	12
16	K	15574	479	1070	14495	17172	5	18	7
20	La	0.37	0.16	0.39	0.050	0.89	6	1684	106

Table 3: Mean elemental concentration in mg kg^{-1} of different tobacco products

Ser.	Element	Moassel	Jurak	Cigarette	Leaves	Cigars	Bidi	Chewing	Snuff
1	Ag	0.550		0.126	1.83	-	-	-	1.6
2	Al	65	640	728	860	-	-	-	4075
3	As	0.146	1	1.59	0.190	-	-	-	0.210
4	Au	-	-	0.023	-	-		-	-
5	B	0.936	-	-	-	-	-	-	-
6	Ba	3.4		49	550	-	-	-	166
7	Br	-	-	108	33	-	-	155	103
8	Ca*	0.641	1.13	2.54	0.851	-	-	-	1.33
9	Cd	0.075	0.5	1.45	0.425	0.710	0.490	0.590	0.780
10	Ce	0.084	-	1.37	1.26	-	-	-	6.58
11	Co	0.077	1.6	0.548	1.16		-	0.6115	0.291
12	Cr	0.75	1.6	4.20	0.517	6.23	5.75	6.99	5.89
13	Cs	0.024	-	0.155	0.011	-	-	-	0.081
14	Cu	8.3	23	20	194	23	17	26	22
15	Eu	0.003		0.0286	0.029		-		0.172
16	Fe	67	1175	710	2192	927	963	1279	2636
17	Hf	0.012	-	0.135		-	-	0.965	0.07
18	Hg	-	-	0.726	0.011	-	-	-	0.009
19	I	-	-	-	0.182	-	-	-	0.515
20	K*	1.56	180	1.86	1.80	-	-	1.60	2.515
21	La	0.366		0.943	1.96	-	-	0.7	7.9
22	LI	1.14				-	-		
23	Mg*	0.107		0.171	0.460	-	-		3.93
24	Mn	12	29	95	554	-	-	170	140
25	Mo	0.452	-	-	0.965	-	-	-	
26	Na	76	-	457	103	-	-	-	4468
27	Ni	0.63	5	3.5	-	9	7	1.66	4.74
28	Pb	0.29	8	3.2		2.23	3.31	7.5	6.3
29	Rb	4.0	-	23	10.5	-	-	18	13
30	Sb	0.010	-	0.161	0.020	-	-	0.1	-
31	Sc	0.018	-	0.2372	1.17	-	-	0.365	0.476
32	Se	0.42	-	0.4435	31	-	-	-	
33	Sm	0.008	-	0.236	0.090	-	-	-	0.083
34	Sr	43	94	113	2060	-	-	-	3181

35	Ta	-	-	-	-	-	-	-	-
36	Tb	-	-	0.0385	-	-	-	-	-
37	Th	-	-	0.213	0.0286		-	0.442	.579
38	Ti	0.027	48	25	-	-	-	-	-
39	Ti	-	-	123	-	-	-	-	-
40	U	0.008	-	0.089	0.02	-	-	0.766	-
41	V	0.146	-	1.18	3.09	-	-	2.53	8
42	Yb	-	-	-	0.334	-	-	-	0.63
43	Zn	21	24	37	-	35	22	28	42
21	Li	1.1	0.65	1.1	0.018	2.3	3	12511	98
17	Mg	1067	61	151	949	1350	6	42	14
18	Mn	12	0.57	1.4	9.8	14	6	40	11
19	Mo	0.45	0.12	0.28	0.16	0.76	5	376	61
22	Na	76	3.0	6.7	69	87	5	25	9
23	Ni	0.63	0.11	0.27	0.31	0.98	6	217	43
24	Pb	0.29	0.05	0.09	0.18	0.36	3	100	33
25	Rb	4.0	0.26	0.64	3.5	5.2	6	48	16
26	Sb	0.010	0.002	0.005	0.005	0.016	5	220	47
27	Sc	0.018	0.002	0.005	0.011	0.024	8	122	28
28	Se	0.42	0.017	0.039	0.38	0.48	5	28	9
29	Sm	0.008	-	-	0.008	0.008	2	-	-
30	Sr	43	3.8	10	27	52	7	91	24
31	Ti	0.027	0.002	0.003	0.025	0.030	3	20	11
32	U	0.008	0.002	0.005	0.004	0.014	4	241	57
33	V	0.146	0.014	0.039	0.092	0.198	8	115	27
34	Zn	21	0.81	2.3	17	24	8	40	11

Standard Error, + Standard Deviation & number of samples with concentration higher than lower limit of detection

* (Max-Min) x100/Min + Variation coefficient % = Mean x 100/ standard deviation ^ Variation Coefficient (Mean/SD)

Table 4: Elemental concentration percentage* in different tobacco products.

Ser.	Element	Moassel	Jurak	Cigarette	Leaves	Cigars	Bidi	Chewing	Snuff
1	K	6.67E+01+	1.30E+00	8.15E+01	4.76E+01			9.04E+01	3.17E+01
2	Ca	2.74E+01	8.11E+01	1.11E-02	2.26E+01				1.68E-03
3	Mg	4.57E+00	0.00E+00	7.48E+00	1.22E+01				4.95E+01
4	Na	3.26E-01		2.00E+00	2.74E-01				5.63E+00
5	Fe	2.89E-01	8.45E+00	3.11E+00	5.83E+00	9.24E+01	9.45E+01	7.22E+00	3.32E+00
6	Al	2.80E-01	4.61E+00	3.19E+00	2.29E+00				5.14E+00
7	Sr	1.83E-01	6.77E-01	4.94E-01	5.48E+00				4.01E+00
8	Zn	8.88E-02	1.76E-01	1.63E-01		3.49E+00	2.16E+00	1.57E-01	5.29E-02
9	Mn	5.30E-02	2.09E-01	4.15E-01	1.47E+00			9.61E-01	1.76E-01
10	Cu	3.55E-02	1.64E-01	8.63E-02	5.16E-01	2.29E+00	1.67E+00	1.45E-01	2.75E-02
11	Rb	1.73E-02		1.01E-01	2.79E-02			1.02E-01	1.64E-02
12	Ba	1.47E-02		2.15E-01	1.46E+00				2.09E-01
13	LI	4.90E-03							
14	B	4.01E-03							
15	Cr	3.19E-03	1.15E-02	1.84E-02	1.37E-03	6.21E-01	5.64E-01	3.95E-02	7.42E-03
16	Ni	2.69E-03	3.60E-02	1.54E-02		8.83E-01	6.97E-01	9.36E-03	5.98E-03
17	Ag	2.35E-03		5.50E-04	4.87E-03				2.02E-03

18	Mo	1.93E-03			2.57E-03				
19	Se	1.79E-03		1.94E-03	8.24E-02				
20	La	1.57E-03		4.13E-03	5.21E-03			3.96E-03	9.96E-03
21	Pb	1.22E-03	6.05E-02	1.41E-02		2.22E-01	3.25E-01	4.22E-02	7.94E-03
22	As	6.25E-04		6.98E-03	5.05E-04				2.65E-04
23	V	6.23E-04		5.16E-03	8.21E-03			1.43E-02	1.06E-02
24	Ce	3.58E-04		5.99E-03	3.35E-03				8.29E-03
25	Co	3.31E-04	1.15E-02	2.40E-03	3.08E-03			3.46E-03	3.67E-04
26	Cd	3.19E-04		6.37E-03	1.13E-03	7.08E-02	4.81E-02	3.33E-03	9.83E-04
27	Ti	1.14E-04	3.46E-01	5.39E-01					
28	Cs	1.01E-04		6.81E-04	2.92E-05				1.02E-04
29	Sc	7.70E-05		1.04E-03	3.11E-03			2.06E-03	6.00E-04
30	Hf	4.96E-05		5.90E-04	0.00E+00			5.45E-03	8.82E-05
31	Sb	4.44E-05		7.03E-04	5.32E-05			5.65E-04	
32	U	3.43E-05		3.90E-04	5.32E-05			4.33E-03	
33	Sm	3.42E-05		1.03E-03	2.39E-04				1.05E-04
34	Eu	1.11E-05		1.25E-04	7.71E-05				2.17E-04
35	Br			4.72E-01	8.77E-02			8.76E-01	1.30E-01
36	Hg			3.18E-03	2.92E-05				1.13E-05
37	I				4.84E-04				6.49E-04
38	Tb			1.69E-04					
39	Th			9.34E-04	7.60E-05			2.49E-03	7.29E-04
40	Yb				8.88E-04				7.94E-04
41	Au			9.86E-05					
42	Ti			1.10E-01					

*Element concentration x 100/ total elemental concentration +maximum percentages are bold

Table 5: Lead content (μg g^{-1}) in cigarette versus an Egyptian water pipe.

	Pre-smoking	Post-smoking/ 1st korsi (the bowl)	Post-smoking/ 2nd korsi (the bowl)	P
Cigarette tobacco	7.39 ± 0.6	2.82 ± 0.28		<0.001
Water pipe tobacco (unspecified)	2.125 ± 0.142	1.48 ± 0.09		<0.001
Cigarette filter	0.52 ± 0.032	1.0 ± 0.19		<0.001
Water in the water pipe (likely a goza)	2.13 ± 0.14	3.48 ± 0.11	3.93 ± 0.12	<0.001

Source:(WHO-EMRO, 2007)

useful to know the source of variation. Unfortunately, the elemental characterization of moassel mixtures has not been studied in detail.

For jurak, the other tobacco derived smoking mixture for shisha, the highest elements concentration percentages were 77 % for Ca, 8% for Si, 8 % for Fe and 4% for Al. The sum of the other elements concentration was about 3%. As mentioned before, there are several studies on the elemental characterization of cigarette tobacco, few studies on other tobacco products such as cigar, snuff, tobacco leaves and chewing tobacco, and even much less on jurak and moassel. The total elemental concentrations, (see Table 3) , were 23, 15, 23, 79, 1, 18 and 38 mg g^{-1} in moassel, jurak, cigarette, tobacco leaves, cigar, chewing and snuff. The concentrations of most prominent metal ions such as Ca, Mg, K and Na are not available in the literature about cigar. There is an obvious variation in their elemental constituent whose explanation could be their different tobacco type and quality, treatment of the tobacco plant and gradients.

The metals found in tobacco have many sources. Elemental level in tobacco is a function of many factors such as soil characteristics, climatic condition, soil and leaf residues resulting from application of metal-containing pesticides, insecticides and soil amendments including fertilizers and municipal sludge, and plant variety. For example, the tobacco plant preferentially absorbs Cd than Pb as the former is more mobile and migrates upward to accumulate in the plant according to the following order: leaves> roots> stems. In general, tobacco plants stocks heavy metals: e.g., Pb, Cd and Zn preferentially [12, 28, 29] (Dhaware et al., 2009; Pappas et al., 2006; Verma et al., 2010).

3.2 Biochemical Effects

During tobacco combustion inside a cigarette, the bulk of metallic constituents remains in the ashes, but some compounds are transferred into the smoke stream. Among 76 metals detected in cigarette, 30 have been identified in the smoke including Pb, Ni, Al, Cd, As, Bi, Si and Se. With respect to tobacco carcinogenesis, focus has been on As, Ni and Cd [18, 24]. Elemental concentration percentage in different tobacco products are given in Table 4.

Aluminium: Concentrations (%) of Al in tobacco or tobacco-derived products were relatively high: 65 (0.28), 640 (4.4), 728 (3.2), 860 (2.3) and 4075 (4.1) mg kg^{-1} in moassel, jurak, cigarette, tobacco leaves and snuff, respectively. In occupationally non-exposed males subject, Al concentration in urine, plasma and erythrocytes were not influenced by smoking or by age. Aluminum is interesting because of its alleged association with Alzheimer's diseases [26].

Arsenic: Concentrations (%) of As in tobacco or tobacco-derived products were relatively low: 0.15 (0.00036), 1.0 (0.0068), 1.59 (0.007), 0.19 (0.00051) and 0.21 (0.00027) mg kg^{-1} in moassel, jurak, cigarette, tobacco leaves and snuff, respectively. During human hookah sessions in a laboratory, Breusova et al (2002) have not detected the presence of As [30]. Replacement of arsenical insecticides with non-arsenical ones reduced As content in American tobacco [18]. No significant differences were found in As levels in liver, kidney cortex, lung and hair among smokers and non-smokers. Arsenic in urine of adult was not influenced by smoking. On the other hand, a positive association was found between urinary As level in children and parental smoking habits [26].

Beryllium: Concentrations (%) of Br in tobacco products or tobacco-derived were 108 (0.47), 33 (0.088), 155 (0.88) and 103 (0.13) mg kg^{-1} in cigarette, tobacco leaves, chewing and snuff, respectively.

Cadmium: Concentrations (%) of Cd in tobacco products were 0.075 (0.00032), 0.5 (0.0034), 1.45 (0.0064), 0.425 (0.0011), 0.71 (0.071), 0.59 (0.0033) and 0.78 (0.00098) mg kg^{-1} in moassel, Jurak, cigarette, tobacco leaves, cigar, chewing and snuff, respectively. Cadmium is highly toxic and is one of the most important heavy metals, when adverse health effects of smoking are considered. Possible relationships between smoking, Cd tissue levels, hypertension, and cardiovascular diseases have been reported [26].

Galazyn-Sidorczuk et al have found 0.6801± 0.1765 µg per cigarette. On average, 33% of Cd present in the whole cigarette was released into the smoke. "For Cd, there was a high positive correlation between the metal content in cigarettes and tobacco and its release into the smoke. Moreover, the subjects smoking cigarettes containing the highest Cd amount had higher blood Cd concentration than smokers of other cigarette brands. The results give clear evidence that in the case of inhabitants of areas polluted with Cd habitual cigarette smoking through tobacco contamination, a serious source of chronic exposure to this metal is expected [8].

Chromium: Concentrations (%) of Cd in tobacco or tobacco-derived products were 0.75 (0.0032), 1.6 (0.011), 4.2 (0.0184), 0.517 (0.0014), 6.23 (0.062), 6.99 (0.00395) and 5.89 (0.0074) mg kg^{-1} in moassel, jurak, cigarette, tobacco leaves, cigar, chewing and snuff, respectively. It is noteworthy that the biological effects of Cr depend on its valence; in the trivalent form, Cr is an essential element. Under its hexavalent form, Cr is carcinogenic [26].

Cobalt: Concentrations (%) of Co in tobacco or tobacco-derived products were 0.077 (0.00033), 1.6 (0.011), 0.548 (0.0024), 1.16 (0.0031), 0.612 (0.00346) and 0.291 (0.00037) mg kg^{-1} in moassel, jurak, cigarette, tobacco leaves, chewing and snuff, respectively.

Lead: Concentrations (%) of Pb in tobacco or tobacco-derived products were 0.29 (0.0012), 8.0 (0.0572), 3.2 (0.014), 2.23 (0.222), 7.5 (0.042) and 6.3 (0.0079) mg kg^{-1} in moassel, jurak, cigarette, cigar, chewing and snuff, respectively. Lead is a major chemical pollutant in the environment and Mouchet et al suggest that "even if Pb is bio-available from soils to plants, complex mechanisms could occur in plants protecting them from the toxic impact of Pb" [31]. Smokers and former smokers have higher blood Pb levels than non-smokers. Passive smoking plays an important role in exposure of children to Pb [26]. Galazyn-Sidorczuk et al have found that the mean Pb content in cigarettes was 0.6853±0.0746 µg and that 11% of Pb present in the whole cigarette was released into the smoke [8].

During human hookah sessions in a laboratory, Breusova et al have found concentrations of 0.027 µg to 0.003 µg per litre in the smoke and 0.076 µg to 0.083 µg per gram in the moassel itself [30].

Salem et al, who measured mean lead content in the water (of 12 water-pipes) and 12 cigarette filters before and after smoking, revealed higher levels of lead in the water than in the cigarette filters. The authors of this work reported that water was a more powerful filter than the regular cigarette cellulose filter [32, 42]. Salem et al have found (see Table 5) concentrations of 2.125 µg/dl and 1.48 µg/dl in the moassel itself, before and after smoking; and 2.13 µg/dl and 3.48 µg/dl in the water itself (after the first "korsi"/bout) and 3.93 µg/dl after the second one [32]. The WHO report notes that Salem's findings show "an interesting phenomenon. The water retained about 1.36 µg of lead as mean concentration difference after the first korsi. The concentration difference drops to 0.45 µg after the second korsi. The authors of the previous study worked in a laboratory environment. In real life, smokers do not change the water with each korsi, especially in cafés. Further research is required on the filtering capacity of water [42].

Manganese: Concentrations (%) of Mn in tobacco or tobacco-derived products were 12 (0.053), 29 (0.197), 95 (0.415), 554 (1.47), 170 (0.961) and 140 (0.176) mg kg^{-1} in moassel, jurak, cigarette, tobacco leaves, chewing and snuff, respectively. In humans, no significant correlation was found between Mn levels in blood and smoking habits [26].

Mercury: Concentrations (%) of Hg in tobacco or tobacco-derived–were 0.726 (0.0032), 0. 011 (0.000029) and 0.009 (0.000011) mg kg^{-1} in cigarette, tobacco leaves and snuff, respectively. Smoking does not affect the Hg levels in urine, hair, blood, kidney, cortex, liver, or lung [26]. Nickel: Concentrations (%) of Ni in tobacco or tobacco-derived products were 0.63 (0.0027), 5 (0.036), 3.5 (0.0154), 9 (0.883), 1.66 (0.0094) and 4.74 (0.006) mg kg^{-1} in moassel, jurak, cigarette, cigar, chewing and snuff, respectively. During human hookah sessions in a laboratory, Breusova et al have found concentrations of 0.008 µg to 0.009 µg per litre in the smoke and 0.24 µg to 0.25 µg per gram in the moassel itself [30]. Nickel forms a toxic carbonyl compound. Because of the high carbon monoxide level in tobacco smoke, the Ni carbonyl produced this way is considered as a potential carcinogen.

Selenium: Concentrations (%) of Se in tobacco or tobacco-derived products were 0.42 (0.089), 0.444 (0.0019), 31 (0.082) mg kg^{-1} in moassel, cigarette and tobacco leaves respectively.

Uranium: Concentrations (%) of U in tobacco or tobacco-derived products were 0.008 (0.000034), 0.089 (0.00039), 0.02 (0.00005) and 0.766 (0.00011) mg kg^{-1} in moassel, cigarette, tobacco leaves and chewing, respectively. The radioactive elements in tobacco, especially ^{210}Po and ^{210}Pb, were studied by the authors of the present work and published elsewhere [2]. ^{210}Po is the focus of a special interest as far as tobacco smoking is concerned [33]. There are few studies on the other radioactive element such as Ra and U isotopes. The hazardous effects of U mainly depend on its retention time in the human organism.

Zinc: Concentrations (%) of Zn in tobacco or tobacco-derived products were 12 (0.053), 21 (0.176), 37 (0.163), 35 (3.49), 28 (0.157) and 42 (0.0529) mg kg^{-1} in moassel, jurak, cigarette, cigar, chewing and snuff, respectively

3.3 Elemental Transfer to Smoke and Condensate

Tobacco smoking influences the concentrations of several elements in some organs. Cigarette smoking may be a substantial source of intake of these hazardous elements not only to the smoker but also, through passive smoking, to non-smokers [26]. So far, it is clear that there is a wide variation in elemental characterization of different tobacco products and even within anyone of these products. Not only is elemental characterization very significant but also elemental transfer from tobacco to the smoker (smoke, condensate) and, in some instances, to the non-smoker (environmental smoke). The available data about elemental transfer from tobacco to smoke and condensate are quite limited as well as the role of the cigarette and shisha water filters in helping reduce the harm caused by smoking.

Mussalo-Rauhamaa et al found that cigarette filters do significantly prevent the inhalation of cadmium, lead, magnesium, and iron and that the mean content of cadmium in the fat tissues of male smokers reaches four times that of non-smokers [34]. Salem et al have studied lead levels in the smoking mixture, the water in the vase and in the resulting smoke in Egyptian shisha/goza and cigarettes [32]. Breusova et al. also tested shisha moassel smoke (produced by a human) for arsenic and lead [30]. The results are discussed further down in the light of our findings.

The calculation method of the transfer percentage to smoke should be outlined. For instance, which amount of smoke (drawn at what frequency) is taken into consideration for a cigarette? For shisha, it is even more complex because the smoking behavior is completely different and varies a lot during the smoking session (about 1 hour vs.5 minutes for a single cigarette). Even jurak and moassel are not smoked the same way as early Saudi research showed [35]. Such data, usually, is not available.

The elemental transfer percentages from tobacco and jurak, as reflected in literature, are given in Table 6. Because elemental transfer from moassel to smoke and condensates was not included in the present work, comments on elemental transfer (see Table 6) will be limited to the following points:

Most metals are present as particulate matter (condensate) in cigarette smoke because of their relatively high melting

Table 6: Elemental transfer percentage from tobacco to smoke (S), smoke condensates (C), and their ratio.

Ser.	Element	Cigarette[&]				Jurak[+]			
		S	C	A+F*	S/C	S	C	A+F	S/C
1	Ag		0.92						
2	Al	2.9		97		0.000	0.0004	100	0.008
3	As	78		22		0.150	0.15	85	0.010
4	Ba	26	0.13	73	204				
5	Br	54	1.4	45	38				
6	Ca					0.019	0.019	98	0.010
7	Cd					1.200	0.12	87	0.100
8	Ce	11	0.3	89	37				
9	Co	58	0.68	42	85	0.100	0.10	90	0.010
10	Cr	17	2.2	81	8	0.113	0.11	89	0.010
11	Cs	20	1.4	78	14				
12	Cu					0.018	0.018	98	0.010
13	Eu	13	0.88	86	15				
14	Fe	10	0.21	90	45	0.005	0.0048	100	0.010
15	Hf	21	0.7	78	30				
16	Hg	89	5.9	5	15				
17	K	12	0.16	88	73	0.024	0.024	98	0.010
18	La	9	0.15	91	60				
19	Mn	5	0.03	95	167	0.003	0.0027	100	0.010
20	Na	10	0.42	90	24				
21	Ni	5		95		0.160	0.160	84	0.010
22	Pb					0.143	10	86	0.010
23	Rb	24	0.3	75	81				
24	Sb	45	3.4	52	13				
25	Sc	7	2.1	91	3				
26	Se	44	2.9	53	15				
27	Si					0.063	0.063	94	0.010
28	Sm		0.1						
29	Sr	10		91		0.002	0.0019	100	0.011
30	Tb		0.41						
31	Th	12	0.39	87	31				
32	Ti						0.0004		0.010
33	Zn	59	1.9	39	31	0.197	0.20	80	0.010

[+] (EL-Aasar and El-Merzabani, 1991) [&] (Abedinzadeh et al., 1977; Ahmad et al., 1979; Gulovali and Gunduz, 1983; Iskander, 1985) *Calculated ash and filter transfer percentage points (greater than 200 ºC with the exception of Hg). Indeed, researchers have found that the temperatures in the centre of the tip of a cigarette may approach 900 ºC [36, 37].

The predominant elements (transfer percentages %) in cigarette smoke, Table 4, were: Hg (89), As (78), Zn (59), Co (58), Br (54), Sb (45) and Se (44). Their transfer percentages in smoke condensate were: 6, not available, 1.9, 0.68, 1.4, 3.4 and 2.9, respectively. It is obvious that a considerably high percentage of some elements transfer from tobacco during cigarette smoking, e.g. 91 % for Hg. Filters are efficient in reducing the elemental contents of cigarette smoke, especially for the previous mentioned elements. For other elements (Ba, Rb, Hf, Cs, Cr, Eu, Th, K, Ce, Na, Fe, Sr, La, Sc, La, Sc, Mn, Ni and Al), their data are given in Table 6. One may assume that their relatively low transfer percentage to smoke means their accumulation in cigarette's ash and filter. This may be considered as source of environmental contamination [38].

The heating temperature of shisha tobacco derived products such as moassel is much lower than in a cigarette. Also, the charcoal is very likely the main source of toxicity in shisha smoking. Evidence for this assumption is that Saudi researchers early found extremely low levels of heavy metals in a laboratory shisha prepared with jurak heated by an electric appliance (resistance), not by pieces of charcoal. Out of 14.685 mg (heavy) metals present in 1 g of the jurak paste, only 3.075 µg were transferred to the smoker [18].

The tobacco smoking mixture temperature affects the elemental transfer to smoke and the water filter is more efficient for reducing the elemental transfer to smoke, Table 6. The same Saudi researchers found that most of jurak elemental contents was trapped in water and their percentage in water ranged from 80 (Zn) to about 100 (Al, Fe, Mn, Sr and Ti) using an experimental shisha [18].

Al-Arifi (2005) found that about 69% of ^{210}Po concentration in moassel was inhaled by the shisha smoker while 30% and only 1.7% were found in the ash and water filter, respectively [39]. It is obvious that more research is needed to understand the distribution pattern of different elements between the smoke, smoke condensate, ash and water filter in relation to different shisha tobacco derived products (moassel, jurak and tumbak).

3.4 Limitations of this Study

Because tumbak (also named ‘ajamy in some countries: particularly Lebanon, Syria, Jordan) was not easily available in Cairo and Riyadh’s markets, its elemental characterization was not analyzed in this study. However, since this widely used product is actually made of shredded tobacco leaves (left, for nicotine washing, in water for a few hours or even overnight) pressed in the hand then packed in the bowl of the narghile, one may assume that its trace elements are similar to those of tobacco leaves or cigars.

4 Conclusions

Differences in elemental concentration between samples of different tobacco or tobacco derived products (moassel, jurak, cigarette, cigar, bidi, chewing and snuff) are striking. This may be due to a number of factors: among others, the nature of the soil in which the tobacco plant is grown, its variety and the treatment of its leaves (Soylak and Turkoglu, 1999). In these conditions, further research is needed for elemental characterization of some tobacco (derived) products; especially shisha (hookah, narghile) smoking mixtures such as moassel/tabamel and jurak as well as the elemental transfer to smoke given the peculiarity and high complexity of shisha smoking behaviour. As in Salem’ study, levels in the water recipient could also be measured (Salem et al., 1990). The same goes for trace elements in the smoke actually inhaled by humans, as in Breusova's study [30].The results of the present study are in agreement with the findings of other Saudi researchers who, two decades ago, found low levels of trace elements in a shisha prepared with jurak [18]. As in the case of CO generation in hookah smoking, one may assume that the levels of elements depend on the type of charcoal used to heat the smoking mixture: natural vs. commercial (particularly quick-lighting commercial) charcoal [19]. Significant differences are expected in this field.

If it happens that the quick lighting charcoal is a major source of heavy metals, then public health recommendations should be immediately issued on the basis of the corresponding findings. Almost half a century ago, Wynder and Hoffmann, pioneers of research on smoking, concluded their tobacco harm reduction program with the wisest proposal ever: “In view of the fact that man may not always accomplish this objective [quitting (smoking)], research efforts towards reducing the experimentally established tumorigenicity of smoking products should be vigorously continued [19, 40].

Although the present study reveals that heavy metals are much more abundant in cigarette tobacco than in shisha moassel, the picture seems to differ a little when it comes to users of jurak pastes. In these conditions, the design of culturally tailored harm reduction products (for instance resins to be mixed with water in the shisha pipes, etc.) should be encouraged as a realistic public health response; that is one embracing all possible known harm reduction techniques in the world.

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