CHEMICAL ANALYSIS OF THE CONSTITUENTS OF HOOKAH SMOKE

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ABSTRACT

Hookah smoking is a very common practice in the Middle East. This study presents a method for hookah smoke sampling, extraction and analysis. For comparison purposes, the developed techniques were also applied on the raw flavoured tobacco (mou'assal) using during Hookah smoking. Apple and grape flavoured tobacco by Al Fakher, a popular local tobacco company, were used in this study. Activated carbon and a molecular sieve (Tenax) were used as adsorbents in the sampling procedure. To determine the thermal profile of the sampled compounds, each adsorbent was analysed using thermal analysis (TA) where thermogravimetric (TG) and differential thermogravimetric (DTG) curves were obtained. Microwave assisted solvent extraction was used on the adsorbent tubes prior to gas chromatography- mass spectrometry (GC-MS) analysis. The extracted chemical components were analysed using GC-MS and the health impacts were identified for several of the emitted components. Moreover, microwave-assisted acid digestion extraction method was applied on the raw tobacco flavouring for inductively coupled plasma–optical emission spectroscopy (ICP–OES) analysis. Results reveal the presence of many heavy and trace metals that pose human health risks for hookah smokers.

Keywords: Hookah, smoke, chemical analysis, health risks, environment

1. Introduction

Hookah (also known as waterpipe, shisha or hubble bubble) is an old form of non-cigarette tobacco smoking that has been commonly practiced in the Middle-Eastern region for centuries [1]. Hookah smoking is becoming increasingly popular in Europe and the Western nations such as the United States and United Kingdom [2]. Nowadays, young college students are engaged in hookah smoking as a routine social practice. To meet the demands of an era of increased health consciousness by the public and more stringent health protocols, there has been growing interest by various health organizations to relocate resources to order to study the chemistry of hookah smoke, and develop clearer ideas on its health effects [3]. Research has taken to establish a scientific comparison with cigarette smoking and to study second-hand smoke. However, an even greater concern falls on the hookah users themselves who inhale first-hand smoke, which has been shown to contain high concentrations of chemical compounds per unit volume. These compounds include carcinogenic polycyclic aromatic hydrocarbons, ultrafine particles, volatile aldehydes, carbon monoxide, and other toxic components that make up hookah smoke [4-5]. Several researchers have even concluded that hookah smoke is more dangerous than cigarette smoke and called for bans for smoking it in public [6]. In light of the scientific research in this field, there is an urgent need to redefine hookah smoking and to state whether or not it should be included in clean air legislation and smoking bans in places where they are in effect.

Several studies have been dedicated to the development of an effective analytical method to selectively, accurately, and sensitively analyse hookah smoke chemical composition [7-9]. Nevertheless, due to the complexity of the smoke composition, there seems to be a lack in a single method that can generally screen hookah smoke. The aim of this study is to support research efforts by developing novel sampling and analytical techniques for hookah smoke that would then enrich the scientific database with new data necessary to inform future public health policies with regards to hookah smoking.

2. Materials and methods

2.1. Smoke sampling and analysis

Two types of flavoured tobacco (mou'assal) were used in this study: Grape and apple. Mou'assal was drained from extra fluids, weighed (around 14.0-15.0 g) and placed in the head piece of the hookah. A sheet of aluminium foil was tightly wrapped around the head piece. Two discs of quick lighting charcoal briquettes were used to heat the tobacco and generate the smoke. The smoke was collected on two types of adsorbents: activated carbon and a molecular sieve (Tenax). Fixed amounts of adsorbents were packed inside the sampling tubes and connected to each other in series along with a glycerine trap placed ahead. The adsorbent tubes were conditioned prior to sampling. The puff durations were chosen to be 5 seconds per puff and 10 seconds for inter-puff duration. A small amount (20 mg) of the adsorbents was immediately analysed using a Thermogravimetric (TG) Analyser (PerkinElmer, Netherlands). The rest of activated carbon and Tenax adsorbents were transferred to extraction vials for further preparation for GC-MS analysis. The TG method parameters were set to have an initial temperature of 35°C ramped to 500ºC at a heating rate of 10°C/min. The temperature was held constant at 500°C for 1 minute. The desorption took place in an inert atmosphere in presence of nitrogen gas flow at 20.0 ml/min. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were generated for the carbon adsorbent before and after sampling. A microwave extraction method for the activated carbon adsorbent was achieved using a mixture of toluene, acetone, and methanol (known as TAM) in 1:1:1 ratio by volume. Multiwave 3000 Solv (Anton Paar, Austria) was used where 0.25g of the activated carbon was extracted in 9ml of TAM. GC-MS (GCMS-QP-2010 Ultra with TD-20, Shimadzu, Japan) was used for analysis.

2.2. Raw mou'assal analysis

In addition to hookah smoke analysis, microwave extraction was used to dissect the chemical composition of the raw mou'assal (apply and grape) using TAM method. Prior to solvent extraction, the raw mou'assal samples were drained from excess fluid as described above. GC-MS was used for further analysis. The raw apple and grape mou'assal samples of tobacco were also analyzed using ICP by the Liberty AX Sequential ICP-OES (Varian, Australia) for seven metals: lead (Pb), chromium (Cr), cadmium (Cd), nickel (Ni), zinc (Zn), copper (Cu) and manganese (Mn). Three raw apple and three raw grape samples were weighed and analyzed. For each metal, a calibration curve was generated in order to determine the concentration of metals in the mou'ssal samples. Prior to ICP analysis, a microwave-assisted acid digestion of 0.5g of the raw mou'assal (apple and grape) was done using 8ml of 15 M HNO_3 and 2 ml of H_2O_2 (34.5-36.5%). The microwave conditions were set at 1000 Watts and ramped at a rate of 10W/min and held for 10 minutes.

3. Results and discussions

Thermogravimetric (TG) curves were collected on activated carbon adsorbent which were used to trap the chemical compounds from the hookah smoke of both apple and grape mou'assal. Tenax showed lower thermal stability where Tenax started to decompose at temperatures higher than 300ºC as observed from the charred remains of the Tenax in the crucible. For comparison purposes, the TG curve for blank activated carbon was also measured. The importance of the TG curve is in providing the amount and the thermal profiles for the various compounds generated in the smoke and collected on the adsorbent traps. On the other hand, differential thermogravimetric (DTG) curves show the distribution of the trapped compounds in the form of peaks. The results from TA were also used to validate the sampling method and support the development of the GC-MS method later on. The shape of the DTG curves (Figure 1) of grape and apple tobacco smoke indicate the presence of different types of compounds collected on the carbon adsorbent. Weight loss observed at about 80°C refers to the desorption of volatile organic compounds (VOCs) of low boiling points and most likely of low molecular weight. The weight loss at higher temperatures indicates the desorption of semi-volatile and high boiling point compounds. Most of the compounds from the grape mou'assal have boiling points lower than 180°C which are present in higher amounts relative to those shown from the apple. There is relatively no weight loss in the blank reference carbon. This implies that volatile compounds were successfully adsorbed onto the surface of the activated carbon and that the sampling method was successful in producing such results.

The GC-MS chromatogram results obtained from the solvent extraction were searched using NIST library.

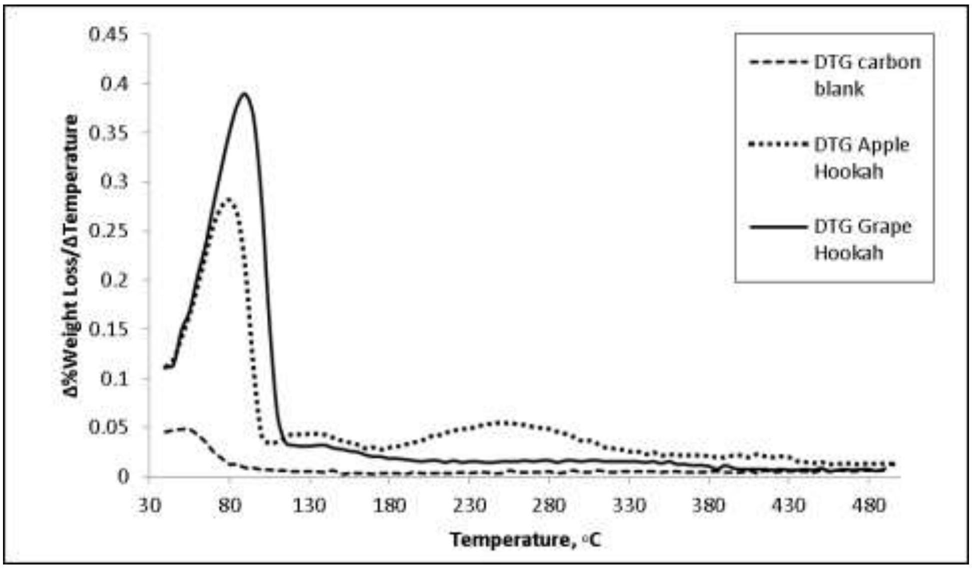

Figure 1: DTG curves from carbon blank, apple mou'assal and grape mou'assal.

Several compounds were identified in both grape and apple smoke (Table 1). However, a few compounds were only identified in the apple tobacco smoke (Table 2). Several of these compounds are known to be carcinogens or may impose various toxicities and health hazards. For instance, naphthalene found in the apple flavored tobacco is classified as a group 2B possible human and animal carcinogen by the International Agency for Research on Cancer (IARC). It also causes hemolytic anemia, which is the breakdown of red blood cells during inhalation. Ethyl Benzene, a component of coal, paints, and pesticides was also found in hookah smoke and it is also a possible human carcinogen categorized by the IARC. Health effects include kidney damage as a result of prolonged exposure at low concentrations and irreversible damage to the inner ear. Benzene and many benzene derivatives were present in both types of flavored tobacco. Indene, another compound found in hookah smoke, is a polycyclic aromatic hydrocarbon present naturally in coal tar. Other substances are added to tobacco as flavoring agents like anethole and benzaldehyde. A major concern with these flavoring agents is their ability to conceal the bitterness of tobacco smoke compared to cigarettes making it seem more appealing to use, especially amongst the young.

ICP analysis revealed 8 metal concentrations in apple and grape mou'assal and are summarized in table 3. These are compared to similar data from two other studies [10-11]. Sadaawi (2012) analyzed 12 types of mou'assal, 8 of which were formulated in the United States, and four were from the Middle East. The ranges of the metal concentrations for these types of mou'assal are given in table 3. Musharraf *et al*. (2012) also analyzed tobacco leaves that are used for hookah smoking which are commercially available in Pakistan [10]. Table 3 shows that the data from this study for both apple and grape mou'assal metal concentrations exceed the concentration ranges in mou'assal brands analyzed by Sadaawi [10] for all 8 metals. However, when compared to Musharraf *et al*. [11] the concentrations for apple and grape mou'assal are below the levels with respect to zinc, nickel, manganese, and copper. For chromium it was approximately the same, while for lead and cadmium metal concentrations were higher. The differences in the results of these studies are possibly attributed to the fact that the tobacco plants accumulate metals in their leaves differently depending on the conditions that they are grown and cultivated in.

Table 1: Compounds found in both grape and apple flavoured mou’assal smoke

Compound Name	
1-Methylcycloheptene	Diisooctyl phthalate
Cyclohexane, 1,2-dimethyl-, cis-	N-(Trifluoroacetyl)-N,O,O',O''-tetrakis(trimethylsilyl)norepinephrine
2-Furancarboxylic acid, undec-10-enyl ester	.alpha.-Hydroxyisobutyric acid, acetate
Cyclohexane, 1,1,3-trimethyl-	3-Hexen-1-ol, acetate, (Z)-
2-Pentanone, 4-hydroxy-4-methyl-	Acetic acid, hexyl ester
Butanoic acid, 2-methyl-, ethyl ester	D-Limonene
3-Hexen-1-ol	4,4-Dimethyl-1-hexene
Ethylbenzene	Benzyl sulfone
p-Xylene	2-Methyl-2-propyl methylphosphonofluoridate
Phenylethyne	Ethanone, 1-(2-furanyl)-
4-Cyclopentene-1,3-dione	2-Furancarboxaldehyde, 5-methyl-
Styrene	Butanoic acid, 3-hexenyl ester, (Z)-
Oxirane, 2-[2-(benzyloxy)-1-(1-methoxy-1-methylethoxy)ethyl]	

Table 2: Additional compounds collected from apple flavoured mou’assal smoke

Compound Name	
3-Bromooctane	Propane, 1-bromo-
2-Furanone, 2,5-dihydro-3,5-dimethyl	Benzylephedrine
Cyclohexanol, 1-methyl-4-(1-methylethyl)-	Anethole
Naphthalene	Benzaldehyde
(4-Methoxy-benzyl)-phenethyl-amine	Benzyl alcohol
Oxalic acid, isobutyl hexyl ester	Indene

Table 3: ICP analysis for apple and grape flavored mou’assal from this study compared to two other studies; references 10 and 11.

Metal	**Mean Apple Mou'assal** ± Standard Error (mg/Kg)	**Mean Grape Mou'assal±** Standard Error (mg/kg)	**Mean Tobacco Leaves** ±Standard Deviation (mg/kg) [10]	**Range of 12 mou'assal types** (mg/kg) [11]
Zinc	25.6±0.76	29.1±0.97	45.7 ± 0.72	3.51-5.62
Lead	9.6±1.63	8.3±1.05	2.0 ± 0.01	<0.001-0.07
Nickel	2.4±0.56	1.6±1.11	4.47 ± 0.10	0.14-0.64
Manganese	46.0±3.54	35.0±0.55	140 ± 0.34	8.82-17.2
Copper	9.5±0.50	8.7±0.057	13.7 ± 0.14	0.93-5.67
Chromium	4.2±0.46	6.1±1.47	5.37 ± 0.10	0.15-0.37
Cadmium	1.6±0.08	1.4±0.21	0.50 ± 0.08	0.10-0.27

4. Conclusions

In conclusion, this study developed an efficient method for the sampling, extraction, and analysis of hookah smoke. The findings of this study emphasize the need for further research into hookah smoke, which is a prevalent custom in this region, and the importance of developing methods capable of providing valid scientific evidence about the health risks associated with this practice.

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