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Waterpipe smoking: Analysis of the aroma profile of flavored waterpipe tobaccos



Jens Schubert*, Andreas Luch, Thomas G. Schulz¹

German Federal Institute for Risk Assessment (BfR), Department of Product Safety, Max-Dohrn-Strasse 8-10, 10589 Berlin, Germany

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ABSTRACT

In the last years the habit of smoking waterpipes has spread worldwide, especially among young people and emerged as global health issue. Although research is now under way for no less than 40 years in the field of waterpipe smoking, in comparison to cigarette smoking there is still insufficient knowledge on the real composition and the toxicity of the smoke inhaled and the resulting levels of exposure against particular hazardous ingredients. In most cases for waterpipe smoking a highly flavored tobacco called “moassel” is used. However, the number, quantity and toxicity of the added flavorings are widely unknown. In this study the static headspace gas chromatography–mass spectrometry (SHS–GC–MS) was used to identify 79 volatile flavor compounds present in waterpipe tobacco. Among these eleven compounds were analyzed quantitatively. The results show that waterpipe tobacco contains high amounts of the fragrance benzyl alcohol as well as considerable levels of limonene, linalool and eugenol, all of which are known as being allergenic in human skin. The proposed SHS–GC–MS method has been validated and found to be accurate, simple and characterized by low limits of detection (LOD) in the range of 0.016 to 4.3 µg/g tobacco for benzaldehyde and benzyl alcohol, respectively. The identification and characterization of waterpipe tobacco ingredients indeed reveals crucial for the assessment of potential health risks that may be posed by these additives in smokers.

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1. Introduction

Regardless of its form and function, waterpipes (shisha, hookah or narghile) represent a traditional aid for the consumption of tobacco. Formerly smoked mainly in Asia and Northern Africa [1], the waterpipe has spread worldwide especially among young people and emerged as global health issue [2,3]. A recent study conducted among U.S. university students revealed that waterpipe use was second after cigarettes in terms of tobacco use [4]. In the last years several studies focused on the toxicological effects of waterpipe smoke [5–9]. These studies clearly demonstrate that waterpipe smokers inhale high levels of hazardous compounds, such as carbon monoxide [5], polycyclic aromatic hydrocarbons [5,6], carbonyls [7,8] or primary aromatic amines [9], thereby pointing to considerable health risks.

For waterpipe smoking the following three kinds of tobacco are commonly used: “moassel”, “jurak” and “tumbak” [10,11]. The introduction of highly flavored “moassel” in the 1990s is considered as one of the main factors for the rapid spread of this form of smoking [12]. Many waterpipe smokers explain that one of

the reasons they started waterpipe smoking is the pleasant smell and the good taste of the smoke [13,14]. In addition, some smokers reported that the availability of a great variety of flavored tobaccos prompts people to start smoking [15]. An internet survey showed that today more than 250 different waterpipe tobacco flavors are commercially available. Among these “two apples” represents one of the most popular flavors. Correspondingly, in the Western hemisphere (i.e. North America and Europe) “moassel” is used almost exclusively. On the other side, the pleasant smell of the smoke may override the risk perception of smokers and therefore waterpipe smoking might be perceived less harmful.

For cigarettes it is well known that during the production process several additives are put into the tobacco. Many of these additives are used to improve taste and to decrease harshness [16]. In contrast, little is known on the composition of waterpipe tobacco. It can be assumed, however, that also to these matrix large quantities of flavoring substances are added although the toxicological effects of these flavors are largely unknown. Recently Sepetdjian et al. reported that waterpipe smoke, compared to cigarette smoke, contains 1000 times higher quantities of the artificial flavoring substance ethyl vanillin [17]. In light of this large knowledge gap it seems essential to gain much more analytical and toxicological information on the waterpipe tobacco additives used.

For the analysis of tobacco additives and volatiles mainly gas chromatography coupled to a mass selective detector (GC–MS)

* Corresponding author. Tel.: +49 30 18412 3963; fax: +49 30 18412 4928.

E-mail address: Jens.Schubert@bfr.bund.de (J. Schubert).

¹ Present address: Department of Chemicals Safety, German Federal Institute for Risk Assessment (BfR), Berlin, Germany.

is employed. However, in most cases, prior to analysis, a pre-concentration step becomes necessary [18]. Generally the following techniques are used for this: enrichment on solid sorbents [19], liquid–liquid microextraction (LLME) [20], solid-phase microextraction (SPME) [21–23], stir bar sorptive extraction (SBSE) [24,25], and static (SHS) or dynamic headspace (DHS) [26–35]. The HS-SPME-GC-MS technique for example, was used by Merckel et al. to identify 89 individual tobacco additives [21]. On the other hand, the SHS-GC-MS technique was employed for the analysis of olives and olive oil [28], green propolis [30] and lubricant oil [32]. In this study we used the SHS-GC-MS technique for the analysis of waterpipe tobacco by focusing on ethyl 2-methylbutyrate, hexanal, limonene, 1-hexanol, *cis*-3-hexen-1-ol, benzaldehyde, linalool, menthol, benzyl acetate, *trans*-anethole and benzyl alcohol. To our knowledge, data on these eleven flavored compounds have not been reported for waterpipe tobacco before. Nonetheless such data are crucial for the assessment of potential health risks associated with these additives after being inhaled by the waterpipe smoker.

2. Materials and methods

2.1. Reagents and materials

All chemicals used in this study were of analytical grade. The authentic standards of the flavoring substances listed in Table 1 were obtained from Sigma-Aldrich (Munich, Germany). Hexanal-*d*₁₂, 1-hexan-*d*₁₃-ol and benzyl-2,3,4,5,6-*d*₅ alcohol were used as internal standards. Hexanal-*d*₁₂ was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), whereas 1-hexan-*d*₁₃-ol and benzyl-2,3,4,5,6-*d*₅ alcohol were purchased from Sigma-Aldrich. Ethyl acetate, sodium chloride, potassium chloride and sodium sulfate were obtained from Sigma-Aldrich. Waterpipe tobaccos were purchased from different manufacturers, namely Nakhla Tobacco (Cairo, Egypt), Middle East Tobacco (Zarqa, Jordan), Al Fakher Tobacco Trading Co. (Ajman, United Arab Emirates), Eastern Tombac & Tobacco EST. (Amman, Jordan) and Soex India Pvt. Ltd. (Mumbai, India). Some of the waterpipe tobaccos were imported to Germany and are therefore not in accordance with the German tobacco regulation. Glass beads (Ø 0.8 cm) were obtained from Omnilab (Bremen, Germany).

2.2. Gas chromatography–mass spectrometry (GC–MS)

GC–MS analysis was performed on an HP 6890 gas chromatograph equipped with an Agilent MSD 5975C mass spectrometer

(Agilent Technologies, Waldbronn, Germany) and a Gerstel Cold Injection System (CIS) (Gerstel, Mühlheim an der Ruhr, Germany). A Multi Purpose Sampler (MPS-2, Gerstel) was used for automated HS measurements. Chromatographic separation was achieved with a DB-WAX (30 m × 0.25 mm i.d. × 0.25 µm film) capillary column (Agilent Technologies). The GC–MS conditions were as follows: injection mode: split; split ratio: 12:1; CIS temperature program: initial temperature: 45 °C; 1. heating rate: 12 °C/s; 1. end temperature: 300 °C; 1. hold time: 2.0 min; 2. heating rate: 10 °C/s; 2. end temperature: 350 °C; 2. hold time: 3.0 min; helium was used as carrier gas at a constant flow of 1.0 ml/min; oven temperature program: initial temperature: 45 °C; 1. hold time: 2.0 min; 1. heating rate: 8 °C/min; 1. end temperature: 100 °C; 2. hold time: 0.0 min; 2. heating rate: 15 °C/min; 2. end temperature: 250 °C; 3. hold time: 5.0 min; total run time: 23.88 min; detector conditions: detector: MSD; MSD acquisition mode: SCAN (*m/z* 38–380); MSD transfer line: 280 °C; MSD ion source temperature: 230 °C; MSD quadrupole temperature: 150 °C; MSD solvent delay: 4.0 min; MSD data acquisition rate: 4.13 scans/min. Chromatograms were recorded and processed with GC MSD ChemStation (E.01.00.237, Agilent Technologies) software. Data on retention times as well as quantifier and qualifier ions are summarized in Table 1. Quantification was performed by using the ion chromatograms of quantifiers upon extraction from total ion chromatograms. Additional peaks were identified by using the NIST08 (National Institute of Standards and Technology, version 8.0) and W8N05ST (Wiley, version 8.0 and NIST, version 5.0) mass spectral libraries.

2.3. Quantification of flavoring substance contents in waterpipe tobaccos

For the analysis of waterpipe tobacco 3.00 g (± 0.05 g) of a well homogenized sample was added to a 20 ml headspace vial. Subsequently 4.0 g (± 0.1 g) sodium chloride, 10 ml water and 35 µl of the internal standard solution (hexanal-*d*₁₂; 1-hexan-*d*₁₃-ol; benzyl-2,3,4,5,6-*d*₅ alcohol) were added. The headspace vials were tightly closed (18 mm magnetic screw caps; septum: butyl red/PTFE gray) and shaken vigorously for 1 min on a Vortex Genie 2 (Scientific Industries, Inc., New York, USA). The headspace vials were transferred to the autosampler tray and incubated for 15.0 min at a temperature of 90 °C (agitator speed: 250 rpm). Then 1 ml of the vial headspace (syringe temperature: 105 °C; vial penetration: 22.0 mm) was injected into the GC–MS. Each headspace vial was punctured only once and then discarded. For each waterpipe tobacco, five headspace vials were prepared and measured

Table 1
Purities, corresponding internal standards, retention times, quantifier and qualifier ions of eleven volatile flavor substances. These compounds are listed in the order of their retention times.

Substance	Purity (%)	Substance number	CAS number	Internal standard	Retention time (min)	Quantifier (<i>m/z</i>)	Qualifier (<i>m/z</i>)
Ethyl 2-methylbutyrate	99.0	4	7452–79–1	Hexanal- <i>d</i> ₁₂	4.74	57	41
Hexanal	98.0	8	66–25–1	Hexanal- <i>d</i> ₁₂	5.17	56	44
Limonene	97.0	16	5989–27–5	Hexanal- <i>d</i> ₁₂	7.19	68	93
1-Hexanol	99.5	32	111–27–3	1-Hexan- <i>d</i> ₁₃ -ol	9.95	56	43
<i>cis</i> -3-Hexen-1-ol	98.0	34	928–96–1	1-Hexan- <i>d</i> ₁₃ -ol	10.38	67	41
Benzaldehyde	99.0	46	100–52–7	1-Hexan- <i>d</i> ₁₃ -ol	12.06	106	77
Linalool	97.0	47	78–70–6	Benzyl-2,3,4,5,6- <i>d</i> ₅ alcohol	12.25	71	93
L-Menthol	99.0	52	2216–51–5	Benzyl-2,3,4,5,6- <i>d</i> ₅ alcohol	13.21	71	81
Benzyl acetate	99.0	60	140–11–4	1-Hexan- <i>d</i> ₁₃ -ol	13.98	108	91
<i>trans</i> -Anethole	99.0	62	4180–23–8	Benzyl-2,3,4,5,6- <i>d</i> ₅ alcohol	14.78	148	117
Benzyl alcohol	99.0	65	100–51–6	Benzyl-2,3,4,5,6- <i>d</i> ₅ alcohol	15.13	108	79
Hexanal- <i>d</i> ₁₂	98.8 ^a	–	1219803–74–3	–	5.07	48	64
1-Hexan- <i>d</i> ₁₃ -ol	98.0 ^a	–	204244–84–8	–	9.76	64	78
Benzyl-2,3,4,5,6- <i>d</i> ₅ alcohol	98.0 ^a	–	68661–10–9	–	15.12	113	84

^a Atom % D.

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