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A rapid method for the chromatographic analysis of volatile organic compounds in exhaled breath of tobacco cigarette and electronic cigarette smokers☆

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ABSTRACT

A method for the rapid analysis of volatile organic compounds (VOCs) in smoke from tobacco and electronic cigarettes and in exhaled breath of users of these smoking systems has been developed. Both disposable and rechargeable e-cigarettes were considered. Smoke or breath were collected in Bio-VOCs. VOCs were then desorbed in Tenax cartridges which were subsequently analyzed by thermal desorption coupled to gas chromatography–mass spectrometry. The method provides consistent results when comparing the VOC compositions from cigarette smoke and the equivalent exhaled breath of the smokers. The differences in composition of these two sample types are useful to ascertain which compounds are retained in the respiratory system after tobacco cigarette or e-cigarette smoking.

Strong differences were observed in the VOC composition of tobacco cigarette smoke and exhaled breath when comparing with those of e-cigarette smoking. The former involved transfers of a much larger burden of organic compounds into smokers, including benzene, toluene, naphthalene and other pollutants of general concern. e-Cigarettes led to strong absorptions of propylene glycol and glycerin in the users of these systems. Tobacco cigarettes were also those showing highest concentration differences between nicotine concentrations in smoke and exhaled breath. The results from disposable e-cigarettes were very similar to those from rechargeable e-cigarettes.

1. Introduction

Electronic cigarettes (e-cigarettes) are designed to transfer mixtures of air and vapors into the respiratory system [1–3]. They use plastic or metal cylinders that contain electronic vaporization systems, a battery, in some cases, a charger, electronic controls and, optionally, replaceable cartridges. Different humectants, e.g. propylene glycol or glycerin, flavorings and nicotine at various concentrations are generally contained in the cartridges. They can be disposable (Type 1 e-cigarette) or rechargeable (Type 2 e-cigarette). Concern has been raised for the compounds incorporated into smokers as consequence of e-cigarette vaping.

Exhaled breath, namely the alveolar breath [4], may provide significant clues on the compounds that are retained in humans as consequence of this activity. Studies on VOCs in exhaled breath from e-cigarette smokers have been developed using solid phase microextraction inside a breath collection device [5] or exposure chambers which are subsequently sampled by absorption into solid phase sorption tubes. These tubes are then analyzed by desorption into gas chromatography coupled to mass spectrometry (GC–MS) [6]. In other cases, the absorption cartridge has been installed at the outlet of a smoking machine and the retained compounds are eluted with CS_2 and methanol for subsequent analysis by GC–MS [7].

In the present study, we describe a simplified method using a Bio-VOCs exhaled air sampler developed by the UK Health and Safety Laboratory (Markes International Ltd, Llantrisant, UK) for the comparison of the smoke generated by Type 1 and Type 2 e-cigarettes, tobacco cigarettes and the exhaled breath after vaping or smoking. This device has been used in the analysis of both exhaled alveolar air and mouth air [8–15]. Now, we are using BIO-VOCs for a rapid method of characterization of the volatile organic constituents in tobacco cigarettes and e-cigarettes. Blend type American tobacco cigarettes with filters (length 83 mm, length of filter 23 mm, diameter 8 mm) were used as test examples. Cigarettes with low nicotine content (0.6 mg), low tar (8 mg) and

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low carbon monoxide (9 mg) were chosen. The compounds analyzed in the present study were mostly in the gas phase. The results add to the current knowledge of exposure of smokers to organic compounds that so far have been mostly characterized in particulate phase transfer processes [16–23].

2. Experimental

2.1. Sampling cartridges

Volatile organic compounds were concentrated by sorption into stainless steel sorbent cartridges (89 mm long 0.64 cm outer diameter) packed with 200 mg of Tenax TA 35/60 mesh (Markes International Ltd, Pontyclun, UK). The sorbent cartridges were preconditioned using helium (5N grade; 100 ml/min) at 320 °C for 2 h and then at 335 °C for 30 min. In later conditioning cycles these cartridges were reconditioned at 335 °C for 20 min with the same flow carrier gas. Once cleaned, the cartridges were sealed with brass Swagelock storage endcaps fitted with PTFE ferrules and stored in solvent-free clean environments.

2.2. Sampling

Exhaled breath was sampled with a Bio-VOC system 30 min after tobacco cigarette or e-cigarette smoking. To avoid metabolic differences all volunteers were asked to smoke with the tobacco cigarettes and Type 1 and 2 e-cigarettes considered in this study. People inspired and expired deeply three times, then retained the breath for 20 s and blew into the Bio-VOC body through a disposable cardboard mouthpiece at their highest capacity. The air remaining in the Bio-VOC was transferred into the sorbent cartridge by pushing a screw-in plunger through the Bio-VOC body. This procedure was repeated five times in each smoking test and all exhaled VOCs were accumulated in the same cartridge. Thus, a total volume of 750 mL of exhaled breath was collected.

Tobacco cigarette and e-cigarette smoke were sampled by connecting the mouth outlets to the Bio-VOC outlet. The screw-in plunger was used to pull smoke into the Bio-VOC cylinder. Then, the tobacco cigarette or e-cigarettes were removed and the cartridge was connected to the Bio-VOC outlet and the screw-in pluger was used to push the smoke present in the Bio-VOC into the cartridge which sorbed the VOCs from the sample. The sampled volume with this procedure was 150 mL.

Indoor ambient air was also sampled for comparison using this device. The procedure was the same as that used for tobacco cigarette and e-cigarette smoke but without connecting any of those devices to the sorbent cartridge. In this case the procedure was repeated four times and a total volume of 600 mL was collected.

2.3. Transfer of the VOC into the GC–MS

VOCs trapped in the sorbent cartridges were transferred with helium (5N grade; no inlet split flow) to a thermal desorption (TD) instrument equipped with a Unity Series 2 Thermal Desorber and an Ultra 50:50 Multi-tube Auto-sampler (Markes International Ltd). The compounds were desorbed from the cartridges at 300 °C for 5 min (desorption flow 40 mL/min) and re-concentrated in a graphitized carbon sorbent cold trap (U-T11GPC-2S for General Purpose; Markes International Ltd) cooled at −20 °C. This cold trap was heated to 300 °C over 5 min while passing a helium flow of 7.5 ml/min (split flow 6 ml/min) for VOC transfer to an uncoated and deactivated fused-silica capillary transfer line of 1 m length (internal and outer diameters 0.25 and 0.35 mm, respectively) heated at 200 °C. Total split ratio was 5:1.

For the Type 2 e-cigarette analyses, inlet split flow during cartridge desorption was 50 mL/min and desorption trap conditions operated at a carrier helium flow of 28.5 mL/min and an outlet split flow of 27 mL/min. Total split ratio was 95:1.

2.4. GC–MS operational conditions

The transfer line introduced the compounds into a Gas Chromatograph 7890 (GC; Agilent Technologies Inc., Santa Clara, CA) coupled to a Mass Spectrometer 5975C Inert XL MSD. The GC was equipped with a DB-5MS UI capillary column (length 60 m; internal diameter 0.32 mm; film thickness 1 μm; Agilent J&W GC Columns). Helium (5N grade) was the carrier gas at a flow of 1.5 ml/min (constant flow mode). The GC oven temperature program started at 40 °C (holding time 10 min) then it increased to 150 °C at 5 °C/min and to 210 °C at 15 °C/min (final holding time 10 min).

A transfer line heated to 280 °C carried the compounds from the GC to the MS. The MS source and quadrupol temperatures were 230 °C and 150 °C, respectively. The MS operated in electron impact mode. The detector was full scanned between 30 and 380 amu.

2.5. Compound identification and quantification

VOCs were identified based on retention times and library identification of the mass spectrum from each chromatographic peak (NIST2009, Mass Spectral Search Program, version 2.0f). Quantification was performed by the external standard method.

Calibration curves encompassed nine calibration solutions in methanol (Merck KGaA, Darmstadt, Germany) at different concentration in the range between 0.5 and 200 μg/ml. They were prepared from commercial solutions: UST Modified Gasoline Range Organics (1000 μg/ml in methanol; Supelco, Inc. Bellefonte, PA, USA), FIA Paraffin Standard (Accustandard Inc., New Haven, CT), and the individual standards: 2-methylbutane, 1-pentene, cis-2-pentene, trans-2-pentene and 4-methyl-1-pentene, all grade GC Standard (Sigma-Aldrich Co., St. Louis, Mo).

A Calibration Solution Loading Ring (CSLR™, Markes International Ltd., Llantrisant, UK) was used to introduce the calibration solution into clean sorbent cartridges which allowed controlled vaporization and purging of the solvent (carrier gas flow at 50 ml/min during 3 min). The different standard solutions were directly introduced into the cartridges which were subsequently analyzed in the TD-GC–MS. This allowed the determination of linear concentration ranges and limits of detection. Recoveries were determined by introduction of standard solutions into the Bio-VOCs heated at 50 °C. Repetitivity was also determined by sequential analysis of standards introduced into the Bio-VOCs.

3. Results and discussion

3.1. Exhaled breath and air concentrations

The gas chromatograms corresponding to indoor air from a building of Barcelona and exhaled breath of volunteers present in this indoor environment without smoking are compared in Fig. 1. Compound identification is reported in Table 1. Acetone and isoprene were the main compounds in exhaled breath. These are two endogenous compounds usually present in this type of sample. Both chromatograms also had some common peaks such as benzene, toluene, styrene, benzaldehyde, δ-limonene, decanal, nonanoic acid, and a siloxane series. Benzene and toluene may constitute trace amounts of vehicular exhaust in the area. The siloxane series may represent some background input of the analytical system. The other compounds may reflect a relationship between in-door atmospheric VOCs and exhaled breath of residents in this environment.