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Electronic cigarette solutions and resultant aerosol profiles

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ABSTRACT

Electronic cigarettes (e-cigarettes) are growing in popularity exponentially. Despite their ever-growing acceptance, their aerosol has not been fully characterized. The current study focused on evaluating e-cigarette solutions and their resultant aerosol for potential differences. A simple sampling device was developed to draw e-cigarette aerosol into a multi-sorbent thermal desorption (TD) tube, which was then thermally extracted and analyzed via a gas chromatography (GC) mass spectrometry (GC–MS) method. This novel application provided detectable levels of over one hundred fifteen volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) from a single 40 mL puff. The aerosol profiles from four commercially available e-cigarettes were compared to their respective solution profiles with the same GC–MS method. Solution profiles produced upwards of sixty four unidentified and identified (some only tentatively) constituents and aerosol profiles produced upwards of eighty two compounds. Results demonstrated distinct analyte profiles between liquid and aerosol samples. Most notably, formaldehyde, acetaldehyde, acrolein, and siloxanes were found in the aerosol profiles; however, these compounds were never present in the solutions. These results implicate the aerosolization process in the formation of compounds not found in solutions; have potential implications for human health; and stress the need for an emphasis on electronic cigarette aerosol testing.

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1. Introduction

Electronic cigarettes (e-cigarettes) do not burn tobacco, rather they produce an aerosol (without flame or smoke) from a battery-powered, metal, heating element and liquid-containing cartridge [1]. The liquid typically consists of humectants (propylene glycol (1,2-propanediol) and/or glycerin), flavorings, and nicotine [2]. When an e-cigarette's power source is activated, the heating element aerosolizes the liquid to form a mist, which the end user then may inhale (often referred to as "vape") [3]. The smoke-like aerosol imitates tobacco smoke visually and replicates the burning sensation in the throat and lungs (often referred to as "throat hit"). These similarities with conventional tobacco smoke, combined with the same hand-to-mouth behaviors, have contributed to the rapid adaptation of electronic cigarettes [4–6]. Despite their increasing use on a global scale [3], relatively little is known about the e-cigarette chemical components. The majority of studies have focused on nicotine content and specific target compounds (e.g., nitrosamines) that are anticipated to be in e-cigarette liquid (e-juice) [7]. More importantly, relatively little is known about the

chemical composition of the aerosol, which is ultimately what end users are exposed to [7,8].

Only a few researchers (e.g., Goniewicz et al. [7], Kosmider [9], McAuley et al. [10], Schober et al. [8], and Uchiyama et al. [11]) have attempted to characterize electronic cigarette (EC) aerosol. Goniewicz et al. [7], Kosmider et al. [9], McAuley et al. [10], and Uchiyama et al. [11] all utilized smoking machines to generate and directly collect EC aerosol. Goniewicz et al. utilized solid adsorbent tubes for fifteen carbonyl compounds (aldehydes and ketones) and twelve volatile organic compounds (VOCs); and methanol impingers for two nitrosamines and sixteen heavy metals [7]. Kosmider et al. [9] and Uchiyama et al. [11] utilized 2,4-dinitrophenylhydrazine (DNPH) coated silica cartridges to capture and analyze twelve and six carbonyls, respectively. McAuley et al. [10] utilized thermal desorption (TD) tubes for five VOCs; DNPH coated cartridges for three carbonyls; quartz fiber filters treated with ground XAD-4 resin for seventeen polycyclic aromatic hydrocarbons (PAHs); and Teflon coated fiber filters for four nitrosamines. Schober et al. attempted to characterize the particulate matter (PM), particle number concentrations (PNC), VOCs, PAHs, carbonyls, and metals with the use of a "café-like" scenario [8]. The "café-like" scenario may have represented both primary EC aerosol constituents (i.e., directly emitted from the ECs) and secondary EC components, which resulted from atmospheric reactions

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of the primary EC compounds and/or reactions with café surfaces (e.g., study participants, chairs, tables, etc.).

The aforementioned studies were not without their limitations/shortcomings. Most notably, all of the aforementioned studies utilized very target analyte specific (e.g., DNPH-coated solid sorbents for a few carbonyls) methods and/or relatively small target lists; and therefore may have overlooked other important aerosol constituents. Furthermore, with the exception of the Schober et al. study, it appeared that none of these studies evaluated the raw e-juice in conjunction with the aerosol to verify that the aerosolization process was responsible for the generation of the observed aerosol compounds, as opposed to the compounds simply being present in the liquid. Although this may have relatively little impact from a human health perspective, this is a significant data gap. The following study was executed to evaluate for difference between electronic cigarette solutions and their respective aerosols with an open-ended analytical approach (i.e., not target analyte specific). The analytical techniques, obstacles, solutions, results, and implications are discussed.

2. Experimental

2.1. Electronic cigarettes and solutions

Four commercially available electronic cigarettes (Table S1) were chosen from the “Best E-Cigarettes of 2014,” which is a top 10 list of e-cigarettes as viewed by “experts and users.” These four chosen e-cigarettes also routinely appeared on other web-based review sites as “top 10” performers.” In addition, these four brands were readily obtained from local stores. All four e-cigarettes were “1st generation” cigarettes (i.e., generally mimicking the size and look of regular cigarettes) and contained solutions of propylene glycol and glycerin.

2.2. Solution analysis

The following analytical system was used for the qualitative determination of compounds found in the electronic cigarette solutions: an Agilent 7890B GC coupled with an Agilent 5977A MS detector. The GC-MS parameters are presented in Table 1. In order to provide representative results, solutions were extracted from the same e-cigarette utilized for the aerosol experiment. Solutions were obtained post aerosol sampling, as the e-cigarettes were permanently destroyed while disassembling for solution extraction.

2.3. Aerosol compounds

Electronic cigarette aerosol was analyzed for nicotine and compounds by trapping the aerosol on thermal desorption tubes. It is important to note that e-cigarette emissions contain compounds both in gas and liquid droplet phase (i.e., the “vapor” is technically an aerosol). It was expected that the thermal TD tubes collected the total aerosol emitted from the e-cigarettes. Goniewicz et al. and other researchers used smoking machines (e.g., Teague TE-2, Borgwaldt RM20S) to generate and collect e-cigarette aerosols; however, access to such an apparatus was not available for this study. Therefore, in order to provide reproducible and quantitative results, a simple sampling device (Fig. 1) was adapted from

Table 1

Analytical system and parameters utilized for determination of electronic cigarette solutions and aerosol compounds. The “Injection” parameters were not utilized for aerosol analysis, as the thermal desorption system injected directly on column.

Agilent 7890B/5977A GC-MS parameters	
Column	Rtx-VMS, 30 m, 0.25 mm ID, 1.40 μ m (Restek Corporation, Bellefonte, PA, USA)
Injection	Diluted (2:1) electronic cigarette liquid
Inj. vol.	1.0 μ L split (10:1)
Liner	Sky 4 mm precision liner w/wool (Restek Corporation, Bellefonte, PA, USA)
Inj. temp.	250 °C
Purge flow	3 mL/min
Oven	35 °C (hold 1 min) to 250 °C at 11 °C/min (hold 4 min)
Carrier gas	He, constant flow
Flow rate	2.0 mL/min
Linear velocity	51.15 cm/s
Detector	MS
Mode	Scan
Transfer line temp.	250 °C
Analyzer type	Single quadrupole
Source temp.	230 °C
Quad temp.	150 °C
Electron energy	70 eV
Tune type	BFB
Ionization mode	EI
Acquisition range	15–550 amu
Rate	5.2 scans/s

a 50 mL gas-tight syringe. The syringe was used to draw 40 mL of aerosol in \sim 4 s from the e-cigarettes across a stainless steel thermal desorption tube packed with Tenax TA, Carbograph 1TD, and Carboxen 1003 (Restek Corporation, Bellefonte, PA, USA). This tube was chosen based on the optimized combination of three sorbents to screen for VOCs in the C_{2–3} range up to SVOCs in the C_{30–32} range. Although this method was manual, a \sim 4 s puff was utilized, as suggested based on Farsalinos et al.’s observations on e-cigarette topography [12]. In addition to the single puff sample, a 10-puff sample was also taken in order to mimic a smoking regime. This sample was taken by manually drawing ten 4 s puffs separated by 10 s intervals between puffs. The desorption tube was then transferred to the following analytical system for determining the VOCs and SVOCs directly emitted from an e-cigarette: a Markes UNITY™ paired with an Agilent 7890B GC coupled with an Agilent 5977A MS detector. The UNITY™ and GC-MS parameters are presented in Table S2 and Table 1, respectively.

The aerosol concentrations of selected VOCs were calculated from a five-point calibration curve generated by analyzing a series of volumes of a 10.0 ppb_v primary gas standard. The 10.0 ppb_v primary gas standard was generated by injecting 180 mL of a 1.00 ppm_v seventy five component TO-15 + NJ mix (Restek Corporation, Bellefonte, PA, USA) and 180 mL of a 1.00 ppm_v fifty seven ozone precursor mixture/PAMS (Restek Corporation, Bellefonte, PA, USA) into an evacuated 6-liter SilcoCan® air monitoring canister (Restek Corporation, Bellefonte, PA, USA) and pressurizing the canister to 30 psig with 50% RH nitrogen. Ochiai et al. [13] determined 50% RH to be optimal for stability. The standard was allowed to age for 7 days. The aforementioned standard afforded positive

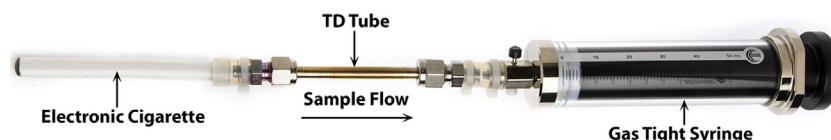


Fig. 1. Gas tight syringe sampling apparatus for quantitatively drawing electronic cigarette aerosol into a thermal desorption tube.

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