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Short communication

Development of a sampling method for carbonyl compounds released due to the use of electronic cigarettes and quantitation of their conversion from liquid to aerosol

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ABSTRACT

In this study, an experimental method for the collection and analysis of carbonyl compounds (CCs) released due to the use of electronic cigarettes (e-cigarettes or ECs) was developed and validated through a series of laboratory experiments. As part of this work, the conversion of CCs from a refill solution (e-solution) to aerosol also was investigated based on mass change tracking (MCT) approach. Aerosol samples generated from an e-cigarette were collected manually using 2,4-dinitrophenylhydrazine (DNPH) cartridges at a constant sampling (puffing) velocity of 1 L min^{-1} with the following puff conditions: puff duration (2 s), interpuff interval (10 s), and puff number (5, 10, and 15 times). The MCT approach allowed us to improve the sampling of CCs through critical evaluation of the puff conditions in relation to the consumed quantities of refill solution. The emission concentrations of CCs remained constant when e-cigarettes were sampled at or above 10 puff. Upon aerosolization, the concentrations of formaldehyde and acetaldehyde increased 6.23- and 58.4-fold, respectively, relative to their concentrations in e-solution. Furthermore, a number of CCs were found to be present in the aerosol samples which were not detected in the initial e-solution (e.g., acetone, butyraldehyde, and *o*-tolualdehyde).

1. Introduction

Electronic cigarettes (e-cigarettes or ECs) are battery-powered devices that vaporize refill solutions and their ingredients (nicotine and flavors) into aerosol [1]. In general, e-cigarette refill solutions (e-solutions) contain a mixture of solvents (propylene glycol (PG), vegetable glycerol (VG), and water) and ingredients [2]. Their popularity has increased gradually through the years, as each user can blend ingredients according to his/her preferences. However, their reliability has been questioned, as various pollutants (including tobacco-specific nitrosamines (TSNA), carbonyl compounds (aldehydes and ketones), and nicotine degradation products (*cis*-*N*-oxide and myosmine)) have been detected in e-solutions or their aerosols [3–6].

Among these pollutants, carbonyl compounds (CCs) like formaldehyde and acetaldehyde pose human health threats due to their carcinogenic properties [7]. CCs have been detected in both e-solutions and aerosols [8]. It has been demonstrated that the major medium of e-solution (PG/VG) can be converted into formaldehyde, acetaldehyde, and acrolein due to vaping (or heating of the e-solution) [9,10]. Considering that about 75–80% of e-solutions are composed of PG/VG, e-cigarette users are expected to inhale considerably large quantities of CCs, depending on their vaping habits [2].

Despite the significance of CCs from e-cigarettes, no standardized methods have been established for their collection and analysis unlike those of conventional cigarette by ISO/WHO [11,12] which allow to collect its smoke automatically (e.g., puffing velocity (25–30 mL s^{-1}), puff duration (2 s), interpuff interval (30 or 60 s), and puff number (~10)). It should be noted that the testing method for conventional cigarettes is not directly applicable to e-cigarettes, due to the unique vaping mechanisms of the latter. First, an automatic sampler (like smoking machine) has not been developed yet. Moreover, the phase of e-cigarette smoke changes to viscous aerosols immediately after vaporizing by an atomizer. Therefore, sorptive loss of e-cigarette aerosols should be considered during its sampling or analysis process. Hence, there is an urgent need to establish sampling approaches appropriate for the quantitation of CCs in e-cigarette samples with the proper knowledge on the conversion between different e-cigarette phases.

In this study, new approaches for the quantitation of CCs from e-cigarette samples were developed based on DNPH derivatization

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and HPLC/UV analysis through modification of the standardized method for conventional cigarette. In addition, the emission concentrations of CCs in liquid/aerosol samples were quantified and their production rate (or solution-to-smoke conversion) was assessed with a mass change tracking (MCT) approach [13,14]. Accordingly, the mechanisms of CC formation via vaping were evaluated in various respects.

2. Materials and methods

To learn the emission characteristics of CCs in e-cigarette samples, an e-cigarette product (and refill solution) commonly available in Korean markets was purchased (Table S1). Target compounds investigated in this study are presented in Table S2. The purchased product consisted of a 900 mAh rechargeable battery, a 2 mL cartridge for the e-solution, and an atomizer at a fixed voltage of 4.2 V. A nicotine-free e-solution with no known flavor additives (Korean product) was also purchased without specific information (e.g., composition of the e-solution or flavor additives). In general, e-solution was heated by atomizer (heating coil) at above 350 °C with the switch on [15]. Details of the experimental procedures shown are described below in Supplementary information: 2.1 collection of carbonyl compounds from e-cigarette samples; 2.2 analysis of carbonyl compounds using an HPLC/UV system; and 2.3 QA information.

3. Results and discussion

The background concentrations of formaldehyde, acetaldehyde, and acrolein were quite large, accounting for 86.7, 63.2, and 100% (vapor) and 22.8, 7.52, and 72.8% (A/V), respectively. Note that vapor-phase concentrations of ACT can be almost ignored. The resulting concentration values of formaldehyde and acetaldehyde in vapor samples after corrections were 5.15 ± 2.33 and 6.86 ± 5.98 μg m^{-3}, respectively.

3.1. Validity of the sample collection approach using DNPH cartridges

For the analysis of CCs in e-solutions, headspace gas chromatography (GC)/mass spectrometry (MS) analysis with solid-phase micro extraction (SPME) or a gas-tight syringe generally has been employed [5,16]. However, headspace analysis can have a considerably lower recovery than direct analysis of the e-solution. In this study, we measured three types of e-cigarette samples (liquid, vapor, and A/V) to cover upto 11 target CCs. Some of e-solution remained at the top of the cartridge due to its high viscosity when undiluted e-solution was injected into the DNPH cartridge in a preliminary experiment (data not shown). As a possible solution to this problem, the analysis of the e-solutions was conducted after 5-fold dilution with acetonitrile to facilitate the CC–DNPH derivative formation.

The A/V samples were collected manually with the help of a mini vacuum pump. The weights of e-solution consumed for different puff numbers (5, 10, and 15) were measured in triplicate such as 13.0 ± 0.36, 27.2 ± 1.07, and 41.3 ± 1.00 mg, respectively. The average consumed weights of e-solution per puff were fairly constant at 2.60 ± 0.07 (5), 2.72 ± 0.11 (10), and 2.75 ± 0.07 mg (15) (Table 1). Although the consumed amount was not measured for each puff, the concentration of CCs in each puff could be determined by dividing the total emission amount of CCs (μg) by the consumed volume of e-solution (mL) (Tables 2A and 2B).

Table 1
Information of sample code and sampling information of 'vapor (interpuff)' and 'aerosol plus vapor (A/V) (puffing)' using e-cigarette product.

Order	Phase of sample	Sample code	Puff duration (s)	Interpuff interval (s)	Number of puffs	Puff velocity (mL s^{-1}) (L min^{-1})		Sampling time (min)	Total sampling volume of ambient air (L)	Puff volume (L)	Consumed quantity (mg) of refill solution	Consumed quantity (mg) solution per puff (mg puff^{-1})
1		V-1L						1	1.0	0	0	0
2	Vapor	V-2L	0	10	0	16.7	1.0	2	2.0	0	0	0
3		V-3L						3	3.0	0	0	0
4	Aerosol	A/V-5P			5			1	1.0	0.17	13.0 ± 0.36[a]	2.60 ± 0.07
5	Plus	A/V-10P	2	10	10 L	16.7	1.0	2	2.0	0.33	27.2 ± 1.07	2.72 ± 0.11
6	Vapor	A/V-15P			15			3	3.0	0.50	41.3 ± 1.00	2.75 ± 0.07

[a] Mean ± standard deviation.