Scientific Letters

Poster Communication 67

Volatile chemical fingerprinting of alternative tobacco products: insights into electronic cigarette and heated tobacco aerosol composition

Vânia Monteiro [1,2,3,4,5*], **Diana Dias da Silva** [1,2,3,4,5], **Sara Ricardo** [4,6], **Paula Guedes de Pinho** [1,2,ǂ] **and Joana Pinto** [1,2,ǂ,*]

[1] Associate Laboratory i4HB – Institute for Health and Bioeconomy, University of Porto, Porto, Portugal
[2] UCIBIO – Applied Molecular Biosciences Unit, Laboratory of Toxicology, Faculty of Pharmacy, University of Porto, Porto, Portugal
[3] UCIBIO - Applied Molecular Biosciences Unit, Forensics and Biomedical Sciences Research Laboratory, University Institute of Health Sciences (1H-TOXRUN, IUCS-CESPU), Gandra, Portugal
[4] Associate Laboratory i4HB - Institute for Health and Bioeconomy, University Institute of Health Sciences - CESPU, Gandra, Portugal
[5] REQUIMTE/LAQV, ESS, Polytechnic of Porto, Rua Dr. António Bernardino de Almeida, Porto
[6] UCIBIO—Applied Molecular Biosciences Unit, Toxicologic Pathology Research Laboratory**,** University Institute of Health Sciences (UCIBIO-IUCS-CESPU), 4585-116 Gandra, Portugal
ǂ These authors contributed equally to this work

* Correspondence: a26323@alunos.cespu.pt; jipinto@ff.up.pt

Abstract

Background: Next-generation nicotine delivery systems, including electronic cigarettes (E-cig) and heated tobacco products (HTP), are often promoted as reduced-risk alternatives to conventional tobacco (CT). However, the extent to which they limit user exposure to harmful chemicals remains insufficiently characterized [1]. **Objective:** In this study, we compared the volatile organic compounds (VOCs) present in native materials (pre-heating) with those emitted during the heating or combustion of E-cigs, HTPs, and CTs. **Methods:** For each product category, the three most commercially popular brands in Portugal were selected. Native matrices (138 ± 3.84 mg of tobacco or e-liquid) were sealed in glass vials for analysis, while aerosols/smoke were produced under controlled puffing or smoking conditions using standardized machine-smoking protocols [2,3] and collected in dedicated flasks. VOCs from native materials and aerosol/smoke were extracted via headspace solid-phase microextraction (HS-SPME) and dichloromethane solvent extraction, followed by gas chromatography–mass spectrometry (GC–MS). **Results:** More than 100 compounds were identified across all products. The volatile profiles of unheated HTP sticks and CT shared notable similarities, with ketones, alcohols, terpenoids, and pyridine derivatives dominating. In contrast, e-liquids displayed more chemically diverse signatures enriched in alcohols, esters, pyranones, and lactones. Thermal processing substantially reshaped these profiles, generating VOCs which were absent from the native materials. HTP aerosols showed additional aldehydes and ketones, E-cig aerosols contained newly esters, and CT combustion produced benzenoid compounds and polycyclic aromatic hydrocarbons, which were not detected in E-cig or HTP aerosols. **Conclusion:** Importantly, many VOCs detected in E-cig and HTP aerosols currently lack hazard classification under the Globally Harmonized System (GHS), underscoring major gaps in toxicological knowledge. Overall, these findings demonstrate that thermal processes induce extensive chemical transformations across all product types, highlighting the need for comprehensive toxicological evaluation of both known and uncharacterized constituents to support evidence-based regulatory policies.

Keywords: Electronic cigarettes; heated tobacco products; volatile chemical composition; temperature-induced compound formation

Acknowledgements/Funding

This work was funded by national funds from FCT-Fundação para a Ciência e a Tecnologia, I.P., in the scope of the project UID/04378/2025 (DOI identifier 10.54499/UID/04378/2025), and UID/PRR/04378/2025 (DOI identifier 10.54499/UID/PRR/04378/2025), of the Research Unit on Applied Molecular Biosciences – UCIBIO, the project LA/P/0140/2020 (DOI identifier 10.54499/LA/P/0140/2020) of the Associate Laboratory Institute for Health and Bioeconomy - i4HB, the project UID/50006/2025 DOI 10.54499/UID/50006/2025 - *Laboratório Associado para a Química Verde* -

Tecnologias e Processos Limpos, and the project 2024.13406.PEX (DOI identifier 10.54499/2024.13406.PEX). The Cooperativa de Ensino Superior Politécnico e Universitário (CESPU) is gratefully acknowledged for the PhD grant no. *BD/DCB/CESPU/02/2023* to Vânia Monteiro.

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