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Sniffing VOCs emitted by books

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Abstract. Headspace solid-phase micro extraction-gas chromatography/mass spectrometry (HS-SPME-GC/MS) was performed for the analysis of volatile organic compounds (VOCs) emitted from books. Towards this, books of different ages were examined (old = 50-300 years and new = 2-25 years) using a CAR/PDMS fiber. The examined books were placed into an in-house made glass sampling chamber, where they remained enclosed for 24 h prior to SPME sampling and subsequent analysis. SPME is a green and non-destructive preconcentration technique based on the absorption of analytes on a fiber coating placed inside the sample's headspace volume. The results were in line with previous reports; the most prominent VOCs released from old books were furfural, acetic acid, and acetone, whereas new books emitted toluene, acetone, and heptanal. This natural process takes place over time due to the decay of paper and degradation of ink and its mitigation is important for the preservation of texts that are considered cultural heritage. The method can be leveraged for monitoring the decay process, as well as the effect of external pollution on the books.

Keywords: VOCs; HS-SPME-GC/MS; books; indoor air; degradation.

1. Introduction

Over the last decade, the global effects of climate change as a result of industrialization have permeated all aspects of our lives. The global rise of CO_2 due to the continued demand and supply of crude oil impacts negatively even indoor air quality. All aspects of the oil industry named the 'extraction-to-refinery pathway', contribute to the release of various volatile organic compounds (VOCs), mainly toluene, benzene, hexane, and heptane (Rajabi et al., 2020).

VOCs are defined as organic chemicals with high vapor pressure at ordinary room temperature, and lately they are under the scrutiny of researchers for their global effects, including: (a) their contribution to the production of photochemical ozone and secondary organic aerosols, (b) their interaction with NOx to form ground-level ozone, known as tropospheric ozone, and (c) their effect on air quality and human health. Since humans spend most of their time indoors, in enclosed environments (*e.g.* houses, offices, cars, *etc.*), they are often exposed to various natural and artificial VOCs, also known as xenobiotic VOCs. The latter category are subject to regulation despite their low concentrations.

Cultural heritage buildings are usually located in urban areas, and in addition to their inherent prestige, they often contain unique historical artifacts. However, both the location as well as the building constructing materials, the assets, and the visitors, all contribute to the release of various air pollutants. These may include (in addition to the VOCs) particulate matter (PM), SO_2, O_3, NO_2, H_2S, ozone, *etc*. The work of Cincinelli et al. (2016) performed to libraries and archives in Florence revealed the presence of BTEX (Benzene, Toluene, Ethylbenzene, Xylenes), acetic acid, and furfural. Furthermore, other chemical deterioration markers reported in the literature were formic acid, 4-hydroxy benzoic acid, and 4-hydroxy acetophenone related to lignin or cellulose degradation. A step ahead is the indoor air quality monitoring in other important cultural heritage institutions such as at Florentine museum in Italy (Martellini et al., 2020).

Headspace solid-phase micro extraction-gas chromatography/mass spectrometry (HS-SPME-GC/MS) method is considered a non-destructive and green analytical technique, as no solvent is used. Therefore, it was applied to study the VOCs degradation profile of historical books (Gaspar et al., 2010), and researchers were also focused on the importance of two key-players book degradation VOCs, that of furfural and acetic acid.

The aim of the present work was to analyze the VOCs emitted by various books, dating from different centuries and different countries.

2. Materials and Methods

The samples consisted of old and new books enclosed in glass jars (Figure 1). Two fibers were examined for their VOCs performance: the DVB/CAR/PDMS fiber and CAR/PDMS fiber. The GC-MS analytical parameters for the subsequent analysis are presented in Table 1.

Table 1. GC-MS experimental parameters

Instrument	5977B MSD coupled to Agilent GC 7890B (Agilent)
Column	SPB-624 (60 m x 0.25 mm x 1.4 μm film thickness, Supelco)
Temperature program	5 min at 35 °C, followed by heating to 180 °C at the rate of 4 °C/min^{-1} (remain for 20 min)
Temperatures (interface, quadrupole)	250°C, 150 °C
Split/splitless mode	Spitless
Mass range	35-350 *m/z*
Carrier gas (flow rate)	He (1.7 mL/min^{-1})
Library	NIST 17

Figure 1. Old books enclosed in glass jars

3. Results

The best fiber for the respective application was the CAR/PDMS fiber.

The analysis of gas-phase emissions from old and new books revealed numerous VOCs in the low ppb_v to ppt_v levels. The respective results agreed with that of Cincinelli et al. (2016), highlighted the presence of BTEX, cyclic volatile methylsiloxanes, aldehydes, terpenes, and organic acids.

In a similar study focused in historical books, potential volatile markers of cellulose degradation were mentioned that of linear hydrocarbons, linear aldehydes, and 2-furfural, as well as the isopropylic esters (Gaspar et al., 2010).

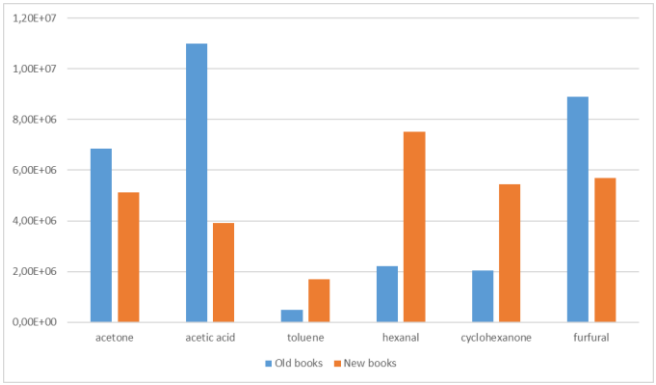

Figure 2. VOCs emitted by old and new books

As shown in Figure 2, exemplary VOCs released from old books were furfural, acetic acid, and acetone, whereas new books emitted toluene, acetone, and heptanal. Acetic acid and furfural were detected in almost all old books; the first can oxidise books, whereas furfural is considered a marker of paper degradation. Its emissions were strongly correlated with the pH of the cellulosic environment (Strlič et al, 2007).

3. Conclusions

Books emit an array of VOCs originated from cellulose and the respective internal material (cotton, linen, wood pulp, ink) due to natural aging and degradation. A great number of samples are needed to fully decode the aroma profile of old and new books, either for exposure or for conservation purposes.

4. Acknowledgments

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References

Cincinelli A., Martellini T., Amore A., L. Dei, Marrazza G., Carretti E., Belosi F., Ravegnani F., Leva P. (2016) Measurement of volatile organic compounds (VOCs) in libraries and archives in Florence (Italy), Science of the Total Environment (572) 333-339.

Martellini T., Berlangieri C., Dei L. et al. (2020) Indoor levels of volatile organic compounds at Florentine museum environments in Italy, Indoor Air (30) 900-913.

Rajabi H., Hadi M.M., Mandal P., Lea-Langton A., Sedighi M. (2020) Emissions of volatile organic compounds from

crude oil processing - Global emission inventory and environmental release. Sci Total Environ (727) 138654.

Gaspar E.M., Santana J.C., Lopes J.F. et al. (2010) Volatile organic compounds in paper-an approach for identification of markers in aged books. Anal Bioanal Chem (397) 369-380.

Strlič M., Cigić I.K., Kolar J., De Bruin G., Pihlar B. (2007) Non-destructive evaluation of historical paper based on pH estimation from VOC emissions. Sensors 7(12) 3136-3145.