A non-destructive method for the identification of VOCs in ancient Cypriot pottery: A preliminary case study

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Introduction:

- In this work, a non-destructive method was developed and applied to identify volatile organic compounds (VOCs) emitted from ancient pottery.
- The purpose of the work was to identify compounds that can be used as indicators to comprehend the use of ancient ceramics. For this purpose, 4 prehistoric vessels (3 juglets and a small amphora), which were recently (2020) excavated by the Department of Antiquities from tombs at the archaeological site of Alambra-Kato Lakkos (Nicosia) were measured at the premises of the Cyprus Museum, in Nicosia.
- Special custom made glass containers were prepared to place the objects and to properly sample emitted VOCs after they had previously been equilibrated for a certain period of time (24 and 72 hours). The objects were then processed according to established archaeological protocols, and then both the "clean" vessels and their contents (soil) were measured again.
- A total of 94 volatile organic compounds (VOCs) were detected; 78 VOCs before their cleaning treatment, 43 after the cleaning treatment, and 31 VOCs in the contained soil.
- Benzoic acid was probably the most important compound detected. Considering the shape, size, and recovery context of the analysed vessels, a substance such as aromatic resin could be contained in these vessels.
- More experiments should be carried out to draw safer results.

Figure 1. Prehistoric vessels from Early–Middle Bronze Age (ca. 2000-1700 BC) tombs at Alambra-Kato Lakkos, in central Cyprus.

Materials and methods:

A. Sample preparation and sampling procedure

- 4 ancient vessels were selected for their closed shape, archaeological context, fresh recovery, and possible content
- The vessels were analysed for VOCs before and after treatment (standard cleaning procedure)
- Soils removed from vessels were also analysed for their VOCs content

(Step 1). 4 Sampling jars were thoroughly washed and left closed for 24 hours in the laboratory.

(Step 2). Air samples were taken from the 4 closed jars and analyzed.

(Step 3). The jars were left open in the museum room for about 1 hour and then after being sealed they were left for 24 hours at room temperature.

(Step 4). Air samples were taken from the 4 closed containers and analyzed.

(Step 5). The 4 **vessels** were placed inside the jars and after being hermetically closed they were left for 24 hours at room temperature.

(Step 6). Samples were taken from the 4 closed containers and analyzed.

(Step 7). After spending another 48 hours again air samples were taken and analyzed.

(Step 8). The **vessels** were processed in the museum, soil was removed, washed and the same process followed as before.

(Step 9). The jars were washed, soil from the corresponding vessel was placed inside and sealed again. After 24 hours air samples were taken and analyzed.

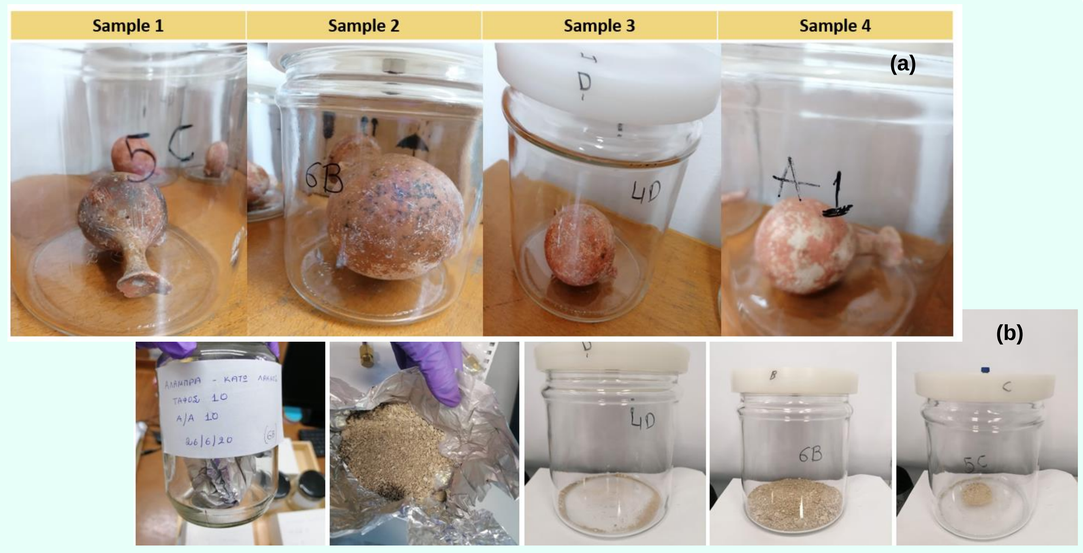


Figure 2. Experimental setup for air sampling (a) of vessels and (b) soil

B. Air sampling

- The sampling of emitted VOCs was performed inside the museum.
- The VOCs were collected on Tenax TA hydrophobic sorbent tubes (1/4 inches × 3 1/2 inches inert - coated porous material stainless steel tubes, 35/60®, 100 g, Markes International Ltd, UK), at a flow rate of 0.1 L min^{-1} for 10 min with the use of ACTI-VOC low-flow pump (Markes International Ltd, UK).
- Tenax sorbent is widely known and used due to its affinity for compounds with a wide range of boiling points (between 60 and 300 °C).
- After sampling, the sorbent tubes were sealed with long-term brass storage caps (1/4 inches, Markes International Ltd, UK) fitted with PTFE ferrules, and immediately transported to the laboratory, where samples were stored in a clean, cool (<4 °C) and organic solvent-free fridge until their chemical (US EPA TO-17, 1999).

C. VOCs analysis

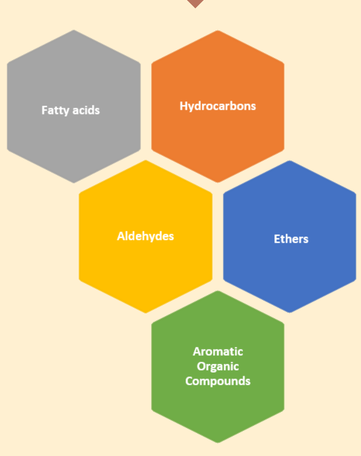
- Before sampling, the sorbent cartridges were preconditioned for 30 min in the TD unit (Unity-xr, Markes International Ltd, UK).
- Prior to sampling, the clean tubes were spiked with 1 μL of 300 ppb Chlorobenzene-d5 served as Internal Standard (I.S.), using the Calibration Solution Loading Rig (CSLR, Markes International Ltd, UK).
- The flow rate of CSLR system was set at 80 mL min^{-1} with Nitrogen as the carrier gas (99,999%, Linde).
- The chromatographic analysis was accomplished using a TD system coupled with gas chromatography (Agilent GC-7890 B, Agilent Technologies Inc, USA) and mass spectrometry (Agilent MS-5977 B, Agilent Technologies Inc, USA).
- All the chromatograms were processed using the area under the curve (ChemStation software, Agilent Technologies Inc, USA), and the NIST20 mass spectra library was used to identify the detected VOCs.

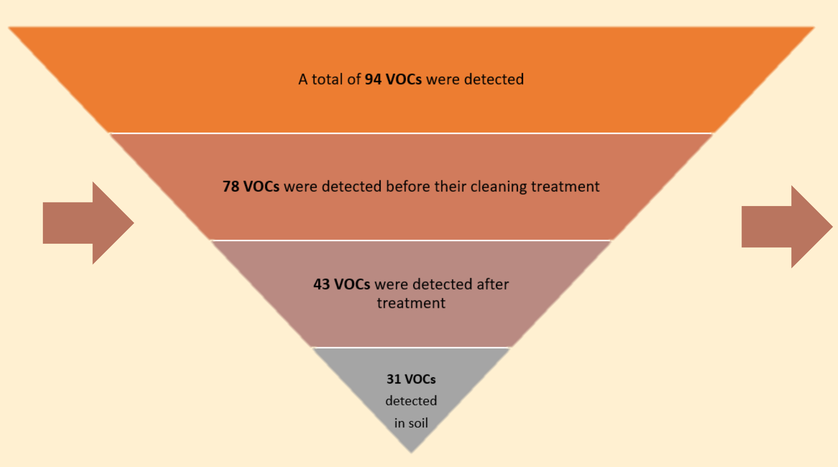
Figure 3.(a) Sampling empty container (blank sample)

Figure 3.(b) Vessel sampling

Results - Conclusions:

A total of 94 VOCs were detected.





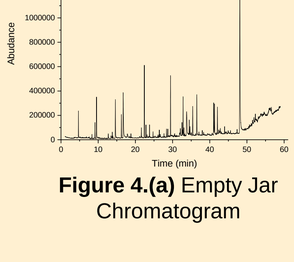


Figure 4.(a) Empty Jar Chromatogram

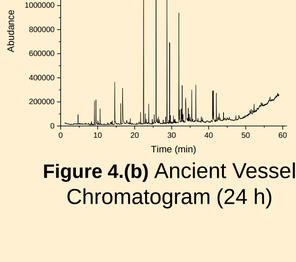


Figure 4.(b) Ancient Vessel Chromatogram (24 h)

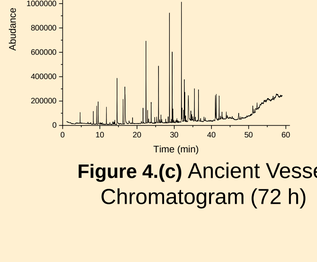


Figure 4.(c) Ancient Vessel Chromatogram (72 h)

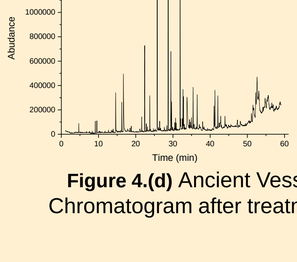


Figure 4.(d) Ancient Vessel Chromatogram after treatment

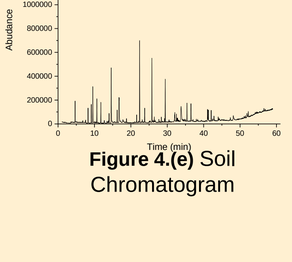


Figure 4.(e) Soil Chromatogram

VOCs	Probable Origin	Ref
Benzoic acid	Aromatic resin	[1]
	Biomass burning and/or charcoal combustion	[2]
.beta, Myrcene	-	-
o-cymene	Medicinal and/or funerary ritual use	[3]
Cyclohexene, 3-methyl-6-(1-methylethylidene)	-	-
p-(1-propenyl)-toluene	-	-
Cyclohexane, ethyl-	-	-
Squalene	Human skin (as a sample contaminant through sampling procedure)	[4,5]

Tenax sorbent tubes can be used for sampling VOCs from ancient pottery

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