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## **Smelling the past: a case study for identification, analysis and archival of historic potpourri as a heritage smell**

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### **Abstract**

Our interaction with heritage objects and spaces is very often limited to a visual experience. However, our perception is multisensory, whether deliberate or not; olfactory stimuli can significantly affect our experience of the world, including cultural heritage. Little is known about the smells of the past, and the olfactory properties of heritage objects and places are not systematically preserved and protected. This work presents scientific analysis of a potpourri identified as historic, by sampling and identification of volatile organic compounds using thermal desorption – gas chromatography with time-of-flight mass spectrometric detection (TD-GC-TOF-MS). The odour of the potpourri was also characterised using GC with olfactometric detection and evaluated by a sensory panel. The chemical and sensory information was used to create a historic potpourri odour wheel, as a conservation tool for archival and public engagement purposes.

### **Keywords**

olfaction, GC-MS, GC-sniffing, VOCs, heritage, sensory, headspace, aroma wheel

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## Introduction

Our interaction with heritage objects and spaces is very often limited to a visual experience. However, our perception is multisensory, whether deliberate or not; stimuli to senses other than vision, including olfaction, can significantly affect our experience of the world (Classen et al., 1994; Levant and Pascual-Leone, 2014), including cultural heritage.

Olfactory perception can be linked to memory, including that of a museum visit (Aggletton et al., 1999); traditions and intangible heritage (Jung, 2015) and generational identity (Hirsch, 1992). In addition, many heritage guidelines consider odours an important part of the identity of a space (The Burra Charter, 1999; Jones, 2012). The olfactory properties of heritage objects and places are not, however, systematically researched or documented, let alone conserved and protected.

As a result, little is known about the smells of the past. Scientific research of historic smells recognises the significant information they carry and the value they add to our cultural heritage, as evidenced by findings on the relation between volatile organic compounds (VOC) emissions and material change (Strlič et al., 2009; Fenech et al., 2010; Lattuati-Derieux et al., 2006). Recently, a framework to research and document olfactory properties of heritage objects and spaces has been proposed (Bembibre and Strlič, 2017), enabling the identification, analysis and archival of smells. This builds on the value of chemical analysis and adds an exploration of the sensory experience provided by smell in a heritage setting. Odour characterisation is shaped by many factors, including culture (Majid, 2015) and historic period (Smith 2007), so documenting a smell at a certain time contributes to its interpretation and future accessibility.

Following the above mentioned framework, this article presents scientific analysis and characterisation of the odour of a potpourri identified as historic (as discussed later) at National Trust's Knole House, both from a chemical and a sensory point of view.

Potpourri is a mixture of petals, spices and chemical compounds designed to aromatise the home, bringing the garden inside (Duggan, 2011). It was popular in Britain in the 17<sup>th</sup> and 18<sup>th</sup> centuries and there were many recipes for preparing it

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(Eaton, 1822; Dods, 1829). Knole, a 15<sup>th</sup>-century property in Kent, England, had its own. Today, the team at Knole use a recreation of the historic potpourri in public engagement activities.

The chemical analysis of odours involve techniques used to obtain and identify the VOCs emitted by a sample: sampling and chemical analysis using Thermal Desorption–Gas Chromatography (TD–GC) enables complete and solvent-free transfer of all analytes into the GC system, achieving high sensitivity (Dettmer, 2002). The technique of Time-of-Flight-Mass Spectrometry (ToF-MS) has significantly advanced in the last decades to offer high speed and efficiency for identification of chemical compounds (Standing et al., 2015).

In addition to the instrumental analysis, sensory evaluation helps understand perception and interpretation of an odour, offering information on quality, intensity and hedonic tone. The human nose is an important tool to characterise odours, because it is highly sensitive and accurate (Gardner et al., 1994), especially with the techniques of GC-Olfactometry and sensory panels. Following analysis, odour wheels are widely used to characterise and document odours in the perfume, food and flavour industries, and have also successfully been created to describe urban odours (Suffet et al., 2007).

## **Methodology**

### Cultural significance assessment

In order to establish the cultural and historic value of the potpourri, its historic value and associative aspects were examined using guidelines to determine cultural significance in monuments by Historic England (Heritage Collections Council, 2001). Existing documentation on the preparation, provenance and olfactory properties of the aromatic mix was reviewed to reveal its significance.

### Chemical analysis

A sample of the historic potpourri, prepared by contemporary perfumer Stephen Nelson following the published recipe from 1750 (Nelson, 2012) was obtained and stored at room temperature for one week. A sample of 0.074 g was introduced into a microchamber (M-CTE250, Markes International Limited, Llantrisant, UK), kept at

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room temperature and under a constant flow of dry nitrogen (65 ml/min). To collect a sample, a thermal desorption tube (Tenax/Carbograph5TD) was inserted in the output of each microchamber to collect a total volume of 500 ml of headspace. Two replicate analyses were carried out.

Analysis was performed using gas chromatography olfactometry-time of-flight mass spectrometry (GC-O TOF-MS; Agilent 7890 GC, Agilent, USA and BenchTOF-dx model, Almsco, Germany). Identification was carried out using TargetView V3 (Almsco).

Separation and detection were performed using a 7890N gas chromatograph and time-of-flight mass spectrometer, using a semi-polar DB-624 capillary column (60 m, 250  $\mu\text{m}$ , 1.4  $\mu\text{m}$ ) and He gas as the carrier at a flow rate of 1.6 ml/min. The oven temperature of the GC was initially held at 40 °C for 5 min, then raised to 45 °C at a rate of 2 °C/min and then raised again to 230 °C at a rate of 5 °C/min and held at that temperature for 4 min.

The GC-MS interface was set at 230 °C. The mass spectrometer acquired data in scan mode with an  $m/z$  interval from 28 to 330, operating at an electron impact energy of 70 eV.

#### Quantification

To calculate the concentration of analytes, 50  $\mu\text{g}$  of deuterated toluene (toluene-d8 solution, Sigma Aldrich) were injected into a thermal desorption tube and analysed using the same analytical methodology used for the samples. The chromatographic signal for toluene-d8 is used for quantification by direct comparison with the chromatographic signals obtained from the samples.

#### Sensory analysis

GC-sniffing analysis was performed using an olfactory detector port OP275 (GL Sciences Inc., Japan). The odour-active VOCs were measured by additional runs using the human nose of trained assessors as detector (GC-Sniffing). The chromatographic column was removed from the input of MS transfer line and connected to a shorter capillary column covered by a transfer line at 230 °C. Panellists performed sensory evaluation of the VOCs separated by chromatography.

As soon as an assessor detected an odour, its attribute, appearance time and intensity

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values (from 1=very faint odour to 5=very strong odour) were assigned.

The smelling task was performed by 2 panellists, at room temperature and isolated of distractions. During the analysis, they took turns, each performing the GC-sniffing task for 15 min. Each panellist analysed a sample twice, so to cover the entire chromatogram. Only odours detected at least twice were considered, and descriptors were combined for each smell. Odour intensity values were averaged for each odour.

In addition to GC characterization, sensory evaluation was also conducted following the European standard VDI 3882 (Beuth Verlag, 1997) for evaluation of odour intensity and hedonic tone. A panel of 9 untrained assessors were briefed to avoid using scented products on the day, avoid eating 30 min before the experiment, and to reveal any circumstances that might affect their sense of smell. The protocol also advised rating the perceived strength of the potpourri smell soon after commencing, to prevent olfactory adaptation (a decrease in sensitivity after a period of exposure). On the day, individual samples of the potpourri were decanted into clean ceramic bowls. The assessors were advised to sample the smell from a distance of 5 to 10 cm, and fill in a form with 23 pre-given descriptors of odour quality (referenced from the findings of the chemical analysis and odour-compound databases). Since descriptors were given, the effect of verbal cues on odour classification (Herz, 2003) was considered in the design of the experiment, but the need for the panellists to use easily understood odour descriptors (as opposed to personal associations), in which they had no training, was prioritized. The sample was also visible to assessors, so the potential influence of a related visual cue on odour classification (Gottfried and Dolan, 2003) was also considered. As part of the evaluation, the assessors were asked to also rate odour intensity and hedonic tone against standardised scales.

#### Odour wheel

Sensory descriptors obtained by GC-sniffing and panel evaluation were collected and classified according to established aroma families taken from two published odour wheels, as follows: ‘fragrant/vegetable/fruity/flowery’, ‘medicinal/phenolic’, earthy/musty/mouldy’ and ‘grassy/woody’ characteristics were modelled after Suffet and Rosenfeld’s (2007) and ‘citrus’, ‘pungent’ and ‘spicy’ after Ann C. Noble’s

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(Robinson, 2006). Two further categories were created in order to represent those odours detected in analysis that did not belong to any of the previous categories, following the concept of odour wheel evolution (Suffet and Rosenfeld, 2007). These were ‘leather’ and ‘oily’. Descriptors produced with GC-O were combined with published descriptors (Heinrich Arn (2004); Mosciano (1997); Luebke (1995); CAMEO Chemicals (2016); Nijssen et al. (2016); Czerny et al. (2011) to validate and contextualize the findings.

## **Results and discussion**

### Cultural significance

Several members of the Sackville-West family, who built Knole and whose descendants still live there, have been writers or acquainted with writers. Many mentions for the potpourri were found in published texts, including in the novel *Orlando*, by Virginia Woolf, set at Knole, whose protagonist ‘buried her face in the potpourri, which was made as the Conqueror had taught them many hundred years ago and from the same roses.’ (Woolf, 2012). Vita Sackville-West wrote about the potpourri: ‘bowls of lavender and dried rose-leaves stand on the window-sills; and if you stir them up you get the quintessence of the smell, a sort of dusty fragrance, sweeter in the under layers where it has held the damp of the spices. The pot pourri at Knole is always made from the recipe of a prim-looking little old lady who lived there for many years as a guest in the reigns of George I and George II’ (Sackville-West, 1923). And then, the recipe created in 1750 by Lady Betty Germaine, a courtier of Queen Anne who lived at Knole, had been published: ‘Gather dry, double violets, rose leaves, lavender, myrtle flowers, verbena, bay leaves, rosemary, balm, musk, geranium. Pick these from the stalks and dry on paper in the sun for a day or two before putting them in a jar (...) mix all well together and spread bay salt on top to exclude air until the January or February following’ (Jekyll, 2011).

### Chemical analysis

A total of 122 compounds were identified in the sample, during 48 min of analysis time, with the highest concentration of peaks found between 27 and 42 min.

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The ten compounds listed in Table 1 were in a much higher concentration than the rest of the compounds (an average of 43  $\mu\text{g}/\text{M}^3$ , in comparison with 13.7  $\mu\text{g}/\text{M}^3$  for the next most concentrated compound). A higher concentration of a compound does not, however, make it detectable by the human nose, as it is shown by the results of the GC-O analysis below.

Compound	CAS Number	Chemical Group	Concentration ( $\mu\text{g}/\text{m}^3$ )
Decane	124-18-5	Aliphatic Hydrocarbons	94.9
Furfural	98-01-1	Oxygen-containing compounds	78.1
Acetone	67-64-1	Ketones	44.0
Undecane	1120-21-4	Aliphatic Hydrocarbons	41.6
Acetic acid	64-19-7	Organic acids	32.7
Phenylethyl Alcohol	60-12-8	Alcohols	31.9
Benzaldehyde	100-52-7	Aldehydes	27.6
t-Terpinene	99-85-4	Terpenes	27.0
Isopropyl Alcohol	67-63-0	Alcohols	24.3
(-)- $\beta$ -pinene	18172-67-3	Terpenes	21.2

**Table 1.** Compounds with highest concentration in the sample, expressed in  $\mu\text{g}/\text{m}^3$ .

#### Sensory analysis

A total of 24 smells were identified by GC-O. Around 40% of those smells were correlated to chemical compounds present in the sample, as can be seen in Table 2 (accuracy in the identification of odour-active compounds using GC-O may be affected by the high number of co-elutions that can occur during analysis (d'Acampora Zellner et al., 2008) and the fact that the human nose is more sensitive than most GC detectors for certain odour compounds (Acree, 1994). Green, floral, herbal and spicy odours predominated, as expected, with the highest frequency occurring between 28 and 44 min.

In terms of hedonic tone, most of the odours were perceived as pleasant or neutral, with a few exceptions characterised as unpleasant (at 26.3, 36, 39.1 min).

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T1	Intensity	Descriptors GC-O	Published descriptors	Compound	CAS
16.29	2	vinegar, sour, acid	n/a	n/a	n/a
17.33	1	mushroom, toasted, acid	sour (I)	acetic acid*	64-19-7
22.33	2/3	rubber, sythetic, fruity	n/a	n/a	n/a
26.32	2	unpleasant, rotten, fermented	n/a	n/a	n/a
27.40	1/2	tea, green, hay	pungent, ethereal, fusel oil, fruity and alcoholic, sweet with a green top note (II)	1-hexanol	111-27-3
30.57	2	lemon, metal, rain, green	n/a	n/a	n/a
31.30	2	green, lemon, flowers	dry woody resinous pine hay green (III)	$\beta$ -pinene	127-91-3
32.12	1	fresh, herbal, dry grass	fresh herbal lavender sweet mushroom (III) pungent (IV)	3-octanone	106-68-3
33.57	2	fresh, green, synthetic, floral, mothballs	citrus fresh floral oily sweet (III) citrus, green, oil, rose (V)	2-ethyl-1-hexanol	104-76-7
36.02	2/3	peroxide, pungent, unpleasant	n/a	n/a	n/a
36.35	2	petals, flowers, sour	fat, citrus, green (I)	nonanal*	124-19-6
37.12	2	plastic, hand cream, powder	n/a	n/a	n/a
37.30	2	licorice, dry straw, organic	n/a	n/a	n/a
38.54	1/2	flower, petal	n/a	n/a	n/a
39.16	2	organic, unpleasant, fried food	n/a	n/a	n/a
39.47	2/3	organic, roses	camphor, earth, green (V)	isobornyl formate	1200-67-5
42.14	2	broth, oily, gasoline	ink-like, leather-like, medicinal (IV)	3-isopropylphenol	618-45-1
43.33	2	cinnamon	cassia, cinnamon, cinnamon bark and red hots (II)	3-phenyl-2-propenal	104-55-2
47.53	2	cinnamon, pleasant, vegetable, fresh, pine	n/a	n/a	n/a

**Table 2.** Odours registered during GC-O analysis of the sample. T1 indicates the time the analyst first perceived the smell. The asterisk (\*) next to a compound name indicates that it was not possible to fully validate the identification. Published odour descriptors: (I) Heinrich Arn (2004), (II) Mosciano (1997), (III) Luebke (1995), (IV) CAMEO Chemicals (2016), (V) Nijssen et al. (2016), (VI) Czerny et al. (2011).

Regarding the chemical compounds identified as sources of perceived smells during the task, acetic acid has a sour, vinegar-like odour (Heinrich Arn, 2004) often a

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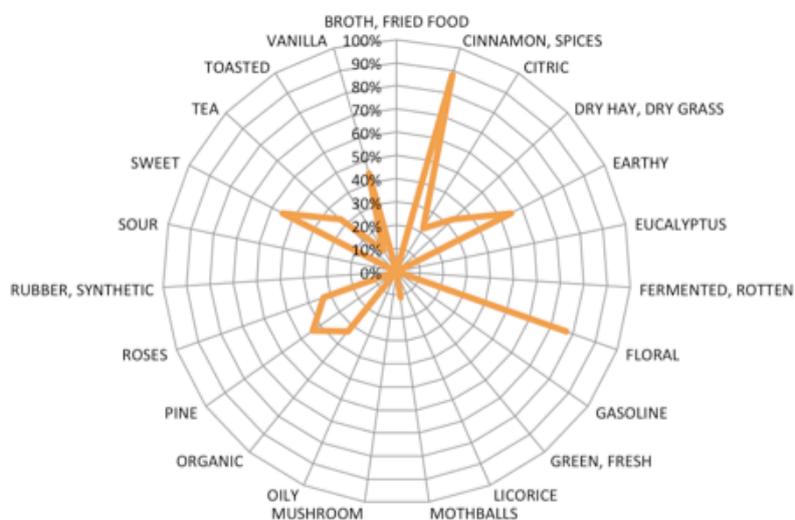
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product of cellulose degradation (Strlič et al., 2009). 1-Hexanol smells pungent, ethereal, fusel alcohol, fruity and alcoholic, sweet with a green top note (Mosciano, 1993). It is naturally occurring in rose otto, lavender and violet oil (Luebke, 1995), all present in the sample. Beta-pinene has a dry woody resinous pine hay green smell (Luebke, 1995) and it is present in calamus, cassia bark, cinnamon, lavender and laurel oil, lemon, myrtle, nutmeg, pepper and rosemary oil (Luebke, 1995), all in the sample. 3-Octanone is present in many plant, fruit and flower aromas; has a fresh herbal lavender sweet mushroom smell (Luebke, 1995), also described as pungent (Cameo Chemicals, 2016) and it is naturally present in bay leaf, lavender and rosemary (Luebke, 1995), all in the sample. 2-Ethylhexanol is a natural component of rose aroma, and could correspond with the presence of rose petals in the sample. It has been characterised as citrus, green, oil, rose (Nijssen et al., 2016). Nonanal occurs naturally in many essential oils, and it is present in cinnamon, rose and lemon (Luebke, 1995), all in the potpourri. It smells fatty, citrus, green (Heinrich Arn, 2004). Isobornyl formate has a camphor, earth, green smell (Nijssen et al., 2016). It is emitted naturally by the *Anthemis coelopoda* plant, pertaining to the chamomile family (Luebke, 1995). 3-Isopropylphenol has an odour described as ink-like, leather-like and medicinal (Czerny et al., 2004). It is naturally present in *Helichrysum italicum*, or curry plant (Luebke, 1995). 3-Phenyl-2-propenal, also known as cinnamaldehyde, is the main compound responsible for the smell of cinnamon.

In the panel sensory evaluation of the potpourri, within the given list, ‘cinnamon, spices’ was the descriptor of the list selected by the most assessors (88%), followed by ‘floral’ (77%), ‘earthy’ and ‘sweet’ (both 55%) and vanilla (44%), as shown in Figure 1. The smell was also described as ‘dry hay, dry grass’, ‘organic’, ‘roses’ and ‘tea’ by 33% of the panellists. Finally, 22% noted a ‘citric’ quality to the smell, and 11% attributed the ‘mothballs’ and ‘toasted’ descriptors to the sample. Odours perceived repeatedly in the GC-sniffing analysis such as ‘rubber, synthetic’, ‘eucalyptus’, ‘fermented, rotten’, ‘mushroom’, ‘oily’ and ‘sour’ were not identified by the sensory panel.

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**Figure 1.** Chart representing a sensory profile of the sample.

With regards to intensity, of the nine panellists, three evaluated the intensity as ‘4=strong’, five as ‘3=distinct’ and one as ‘2=faint’, with the average of 3.2 being between ‘distinct’ and ‘strong’.

Finally, the panellists rated their perceived pleasantness or unpleasantness (hedonic tone) of the library odour. On a scale that ranges from -4 (‘very unpleasant’) to +4 (‘very pleasant’), of the 9 panellists, 4 described the odour as ‘pleasant’, 3 as ‘mildly pleasant’ and 1 as ‘mildly unpleasant’.

In order to combine the chemical and sensory information, an odour wheel was developed (Figure 2). It is a documentation piece for public engagement and archiving purposes, enabling a potential reproduction of the smell, preserving a sensory experience and therefore contributing to the conservation of olfactory heritage.

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**Figure 2.** Odour wheel of historic potpourri containing general aroma categories, sensory descriptors and chemical information. Colours are arbitrary.

## Conclusions

The impact that smells can have on our perception of history, and heritage in general, makes understanding and conserving sensory experiences related to cultural heritage highly relevant.

This work has shown how a smell can be identified and defined for its significance, and how scientific techniques can help understand and document it. In addition to chemical data, research into human experience of smells provides context of vocabulary, perception of intensity and pleasantness. This information is essential to preserve not just the smell but the sensory experience, which depends on cultural

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values, historic period and many other factors. Therefore, the preservation of odours is in itself a potential new area of research of cultural and anthropological value.

The potpourri odour wheel is a new tool that enables understanding and documenting of the odour experience through articulating chemical and sensory information. Visitor experience and collection interpretation could use it to engage and educate visitors, offering new and inclusive information, promoting awareness about olfactory perception and contributing to a more personal experience of heritage.

Given the unique odour profile of each historic object or space, further research is needed to build expertise towards quicker, more efficient identification and more accurate description of compounds. This is essential for the odour wheel to be an archival piece, and for the documentation to lead to a potential future reproduction of the heritage smell and its future interpretation.

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