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The relationship between chemical concentration and odor activity value explains the inconsistency in making a comprehensive surrogate scent training tool representative of illicit drugs

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ABSTRACT

This report highlights the importance of an individual chemical's odor impact in the olfactory identification of marijuana, cocaine, and heroin. There are small amounts of highly odorous compounds present in headspace of these drugs, with very low odor detection thresholds, that are more likely responsible for contributing to the overall odor of these drugs. Previous reports of the most abundant compounds in headspace can mislead researchers when dealing with whole odor of these drugs. Surrogate scent formulations, therefore, must match the odor impact of key compounds and not just the chemical abundance of compounds. The objective of this study was to compare odorous volatile organic compounds (VOCs) emitted from illicit drug samples of marijuana, cocaine, and heroin to surrogate smell formulations using simultaneous sensory (via human olfaction) and chemical analyses. Use of solid phase microextraction (SPME) allowed VOCs in drug headspace to be extracted and pre-concentrated on site, and analyzed by multidimensional gas chromatography–mass spectrometry–olfactometry (MDGC–MS-O). Use of MDGC–MS-O allowed for further separation of odorous compounds and simultaneous detection by the human nose of the separate odor parts that make up the total aroma of these drugs. The compounds most abundant in headspace were not the most odor impactful when ranked by odor activity values (OAVs) (defined as ratio of concentration to odor detection threshold, ODT). There were no apparent correlations between concentrations and OAVs. A 1 g marijuana surrogate lacked in odor active acids, aldehydes, ethers, hydrocarbons, N-containing, and S-containing VOCs and was overabundant in odor active alcohols and aromatics compared with real marijuana. A 1 g cocaine surrogate was overabundant in odor active alcohols, aldehydes, aromatics, esters, ethers, halogenates, hydrocarbons, ketones and N-containing compounds compared with real. A 1 g heroin surrogate should contain less odor active acids, alcohols, aromatics, esters, ketones, and N-containing compounds. Drug quantity, age and adulterants can affect VOC emissions and their odor impact. The concept of odor activity value, then, is useful to researchers without access to more sophisticated instrumentation. Odor activity values can be calculated from published odor detection thresholds. More research is warranted to expand the database, and determine odor detection thresholds for compounds of interest. Additional information could be obtained from establishing ODTs of key odorants for canines.

1. Introduction

Identification of odors has been widely explored with differing theories as to the mechanism of action. Odor character of 281 compounds in water was characterized as early as 1988 [1]. Yoshii, Yamada, et al. investigated 62 structurally rigid compounds and characterized the corresponding odor strengths [2]. Steric and electrostatic properties of compounds have been used to determine the odor characteristic as perceived by human olfaction [3]. It has been suggested that structure–activity can be used to predict odor detection thresholds (ODT) [4], which is the lowest concentration at which 50% of the population can detect an odorant [5]. Odor activity value (OAV) is calculated as the ratio of the concentration to the ODT, in dimensionless units [6]. Despite studies spanning over 30 years on odor, odor character, and

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mechanisms of detection, there is still no consensus on perception of odor.

ODT and OAV have been used to identify the characteristic odors of many sample matrices. For example, highly odorous compounds have been identified in essential oils [7] young Riesling and non-Riesling wines [8], and emissions from animal buildings [9]. It has been shown that ODTs decrease with increase in carbon chain length from propanal to octanal, but ODT sharply increased with nonanal [10]. Although odor intensity and odorant concentration has been directly correlated under intense sources [11], highly impactful odor compounds are found in smaller concentration and can easily be overlooked [12].

There has been long standing interest in research investigating odor, chemical odor signatures, and its application to forensics. Pig carcasses have been evaluated for volatile organic compounds (VOCs) generated by decomposition; pig carcasses are the current surrogates for human decomposition studies [13]. It has been shown that cadaver detector dogs were able to detect human remains 667 days post removal of a body, although the chemical composition of the emitted VOCs was not investigated [14]. Seasoned bloodhounds can track and discriminate between two individuals [15], and human scent remains in the environment even when an object is not touched [16]. An electronic nose was used to differentiate cannabis and tobacco smoking subjects by human body odor [17]. Research has focused on the VOCs emitted, not on the odor character, ODTs, or OAVs of key odorous compounds.

Researchers know that these forensic samples emit chemical odor signatures. When surrogate formulations are made to mimic real field samples, and tested using odor detection dogs, they often fail to illicit the same response as the actual sample. Canine response to cadaver surrogate scent was evaluated [18], composition C-4 volatiles investigated [19], and narcotic scents have been studied [20,21]. A comparison of published ODTs and calculated OAVs between canines and humans is given in Rice and Koziel [22] Tables 1 and 2. There is high variability of reported ODTs between studies, and even studies performed by the same researchers. The odorant delivery method can affect actual test concentrations. Therefore, only canine ODTs in the study by Neuhaus [23] reporting delivered gas concentrations can be useful for comparisons. See Table 1 in Rice and Koziel [22]. Canine odor detection thresholds are up to 10 orders of magnitude lower than that of humans for common odorants such as volatile fatty acids based on Neuhaus [23] and Devos [24]. Passe and Walker [25] summarized previous research and reported wide ranges of canine ODTs. However, results from Ashton, Eayrs and Moulton [26] were interpreted by Passe and Walker [25] as vapor phase concentrations but were originally reported as (much greater) liquid phase concentrations. This interpretation is likely the reason for higher canine ODTs reported [25]. Reported ODTs were further confounded by assumptions about the experimental design [26,27]. The crucibles containing odorous solution were not held in a closed system and had an undefined air flow across the surface. Therefore the system was not at equilibrium between the liquid and vapor phases and actual vapor concentrations available to canines were likely diluted [26,27]. In a following study by Moulton, Ashton, and Eayrs [27] there was an attempt to correct odor detection thresholds for gas phase concentration, but the same experimental design assumptions existed. Clearly, there is a need for standardizing methods for canine ODT, reliable training aids for detection of drugs, cadavers, and explosives by smell. The previously

Table 1
Key of all samples analyzed in this study.

In text reference	Matrix condition	Code
Marijuana		
Duffel bag sample	~50 kg of marijuana in duffel bag	A1
Duffel bag sample	~50 kg of marijuana in duffel bag	A2
Duffel bag sample	~50 kg of marijuana in duffel bag + lab air	A3
1 g sample	~1 g of marijuana in plastic bag	A4
1 g sample	~1 g of marijuana in plastic bag	A5
1 g sample	~1 g of marijuana loose in jar	A6
1 g sample	~1 g of marijuana loose in jar	A7
Residual sample	Empty marijuana sample jar, ~1 g of marijuana removed	B1
Residual sample	Empty marijuana sample jar, ~1 g of marijuana removed	B2
Residual sample	Empty plastic Bag in jar, ~1 g of marijuana removed	B3
Residual sample	Empty plastic Bag in jar, ~1 g of marijuana removed	B4
Surrogate sample	~1 g of marijuana surrogate scent	C1
Surrogate sample	~1 g of marijuana surrogate scent	C2
Surrogate sample	~1 g of marijuana surrogate scent	C3
Cocaine		
1 g sample	~1 g of cocaine-crack in teardrops	D1
1 g sample	~1 g of cocaine with levamisole	D2
Evidence pack	~1 kg cocaine-through evidence pack	D3
1 g sample	~1 g of cocaine, bag opened, in jar	D4
1 g sample	~1 g of cocaine, bag opened, in jar	D5
1 g sample	~1 g of cocaine surrogate scent	E1
Heroin		
1 g sample	~1 g of heroin (1997)	F1
1 g sample	~1 g of heroin	F2
Surrogate sample	~1 g of heroin surrogate scent	G1

Table 2
Olfactometry results of sensory analysis of Sigma Pseudo™ Narcotic Scent Marijuana formulation.

Event#	Descriptor	Hedonic tone	Intensity	RT (min)	Width	Event area
1	Solvent	Unpleasant −1	30	1.37	0.07	209
2	Buttery	Pleasant +1	17	3.28	0.07	118
3	Solvent	Unpleasant −1	20	9.15	0.08	159
4	Mushroom, Moldy	Neutral 0	11	10.77	0.1	109
5	Mint, Fruity, Sweet, Characteristic	Pleasant +2	70	11.30	0.4	2795
6	Solvent, Gasoline, Mint	Unpleasant −1	50	11.76	0.26	1297
7	Mint, Fruity	Pleasant +1	40	12.39	0.11	439
8	Foul	Unpleasant −1	30	12.99	0.05	149
9	Burnt, Burnt food	Unpleasant −2	40	13.90	0.08	319
10	Potato, Resiny	Neutral 0	41	14.12	0.13	532
11	Resiny	Unpleasant −1	30	15.58	0.11	329
12	Burnt food, Burnt	Unpleasant −1	30	20.02	0.1	299
13	Burnt, Burnt food	Unpleasant −1	39	20.20	0.17	661

Event# corresponds to numbered peaks in Fig. 6. "Characteristic" descriptor is used to tag an odor component that represent the overall aroma of the sample (i.e., smell of marijuana). Hedonic tone is the overall pleasant or unpleasantness of the descriptor (range is Unpleasant −4, through 0, to Pleasant +4). Intensity is on a scale of 0–100, with 100 being most intense; intensity sets the peak height. RT = Retention Time. Width is defined as width at half-height of the Aromagram peak. Event area is a dimensionless value = Intensity × Width × 100, and is comparable to peak area counts generated with a mass selective detector.