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Analysis of synthetic canine training aids by comprehensive two-dimensional gas chromatography–time of flight mass spectrometry

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ABSTRACT

Cadaver dogs are trained on a variety of materials, including artificial or pseudo scents. The chemical components of commercially available pseudo scents are not known, so their accuracy as a decomposition odour mimic and their effectiveness as a canine training aid have not been evaluated. Two pseudo scents that are commercially available and used for training cadaver dogs were analysed using comprehensive two-dimensional gas chromatography–time of flight mass spectrometry (GC × GC–TOFMS). The two formulations were determined to be simplistic in their composition, compared to real cadaveric volatile organic compound (VOC) mixtures, with only a few major components. The enhanced GC × GC–TOFMS peak capacity was nevertheless useful to discriminate less intense peaks from large overloaded peaks. The availability of both dimension retention times combined with the peak finding and deconvolution algorithm, enabled the chemical characterization of the two formulations. Additionally, high resolution (HR) TOFMS was used to extract molecular formulae and confirm identities of analytes. The seven compounds identified by this work have not been reported previously as volatile products of decomposition, indicating that these pseudo scents are not to be considered as an accurate representation of cadaveric decomposition odour. Further research on the olfaction of scent detection canines and the chemical composition of their target odourants needs to be conducted to develop improved canine training aids.

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1. Introduction

Scent detection canines are an essential member of any police force as they can be trained to discover various items of contraband including explosives, drugs and currency, and can be utilized in searches for missing persons or human remains. Canine training is extensive and once a canine and their handler are certified, ongoing training and scent imprinting is required throughout the dog's career [1,2]. For the training regimes, canine handlers use a variety of training aids including both natural and artificial scent sources. For dogs that are trained to detect human remains, called cadaver dogs, natural scent sources include materials such as human tissue collected from an autopsy, decomposition fluid or soil collected from a crime scene [2,3]. These materials are difficult to acquire due to legislation and can be a biohazard risk to both the canine and the handler [1]. Consequently, some handlers opt for artificial scents. These synthetic products are said to contain the essential

odour causing molecules of an original scent source [2]. The odour profile of human decomposition has not been fully characterized and the key odourants identified by canines are not understood [4]. Nevertheless, synthetic or pseudo scents claim to be accurate mimics of decomposition odour. The composition of these products is not known publicly, but they are thought to be overly simplistic, containing only a few compounds [5]. The exact compositions of pseudo scents are of interest to evaluate their efficacy as accurate canine training aids.

Characterization of an unknown and potentially complex sample poses several challenges, including co-elution and accurate spectra deconvolution. Conventional gas chromatography may not always provide sufficient resolution of compounds from several chemical classes and differing concentrations [6]. The additional separation efficiency provided by comprehensive two-dimensional gas chromatography (GC × GC) allows for the resolution of various unknown compounds, and when coupled with time-of-flight mass spectrometry (TOFMS), provides cleaner, more accurate spectra for compound identification [6,7]. Some of our recent investigation in geotaphonomy [8], where we were analysing soil samples taken at close proximity of cadavers, demonstrated the value of GC × GC coupled to TOFMS for the study of complex volatile organic

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compound (VOC) mixtures present in difficult gravesoil matrices. Such an analytical approach was also successfully applied to better characterization of the 'Smell of death' for which dozens of compounds were identified as specific postmortem volatile compounds [9]. In the present study, comprehensive GC × GC–TOFMS analysis was used to chemically characterize the components found in two synthetic canine training aids.

2. Material and methods

2.1. Chemicals

The artificial scents were purchased from Sigma–Aldrich® (Oakville, Ontario, Canada) as a Sigma Pseudo™ Corpse scent kit and comprised of Sigma Pseudo™ Corpse Scent Formulation I – for early detection and Sigma Pseudo™ Corpse Scent Formulation II – for post-putrefactive decay. Gas chromatography grade alkane standards, as well as 4-aminobutanoic acid (GABA), 1,4-diaminobutane (putrescine), 1,5-diaminopentane (cadaverine), pyrimido[1,2-*a*]azepine, 2,3,4,6,7,8,9,10-octahydro- (DBU), butyrolactone and tridecylamine were purchased from Sigma–Aldrich® (Schneidldorf, Germany) for compound identification.

2.2. Instrumentation and parameters

An Agilent® 7890 GC chromatograph (Palo Alto, CA, USA) equipped with a secondary oven and a quad-jet dual stage modulator was coupled with a Pegasus® 4D GC × GC–TOFMS from LECO Corporation (St Joseph, MI, USA). The first dimension column was a Rxi®-5Sil MS (Restek, Bellefonte, PA, USA) low polarity Crossbond® silarylene phase equivalent to a 5% phenyl/95% dimethyl polysiloxane (29.5 m × 0.25 mm id × 0.25 μm df) and the second dimension was a BPX-50 (SGE Analytical Science, Austin, TX, USA) 50% phenyl polysilphenylene-siloxane (1.0 m × 0.1 mm id × 0.10 μm df). The liquid injection port was maintained at 300 °C. The GC oven temperature ramp was as follows: the initial temperature of 60 °C was held for 3 min, ramped to 205 °C at a rate of 5 °C/min; the final temperature of 250 °C was achieved at a rate of 30 °C/min and held for 5 min. The temperature offset for the secondary oven was 5 °C. The modulation period was 4 and 6 s for formulation I and II respectively, with a hot pulse time of 0.70 s and a temperature offset of 15 °C. The transfer line was held at 250 °C. The low resolution (LR, unit mass resolution) TOFMS was operated in electron ionization mode at 70 eV. Experimentally, microchannel plate (MCP), with a mass range of 29–550 amu, an acquisition rate of 100 Hz, and a detector voltage of 1500 V. More details on the experimental procedure can be found in previous reports [8,9]. For headspace analyses, a GERS-TEL multipurpose sampler (MPS) equipped with GERSTEL dynamic headspace (DHS), thermal desorption unit (TDU) and cooled injection system (CIS-4) was used. Samples were incubated at 30 °C and 40 °C for 1 min as well as 50 °C for 5 min 25 mL of headspace was trapped on a thermal desorption tube containing a bed of Tenax® TA. The tube was desorbed at 300 °C and refocused with cryogenic cooling at –20 °C. Direct thermal desorption of samples was also performed; desorption and injection was carried out at both 300 °C and 120 °C. Compounds that were identified in the two formulations using the LRTOFMS instrument were confirmed with exact mass measurements on a JEOL AccuTOF GC system (Tokyo, Japan) (HRTOFMS), equipped with an Agilent 6890 GC, and a ZX1 – LN₂ Cooled Loop Modulator (Zoex Corp., Houston, USA). The HRTOFMS was tuned to 6500 mass resolution. Most of the GC × GC–MS experimental conditions were held constant between the two methods, with the exception of the TOFMS acquisition rate of 25 Hz, and the detector voltage of 2300 V. No secondary oven was used on the HRTOFMS instrument.

2.3. Sample analysis and method validation

One microlitre of formulation I and II was injected manually in split mode (10:1 and 20:1, respectively) on the GC × GC–TOFMS instruments. The injections of each formulation were performed at least in triplicate. A mixed standard of the compounds identified by spectral match was prepared and analysed in several replicates for both split and modulation conditions using the same parameters as described above. The 4-aminobutanoic acid (GABA) standard was also analysed by headspace and direct thermal desorption. For headspace analysis, crystalline GABA was placed in a 20 mL headspace vial and 25 mL of headspace was sampled onto a Tenax® tube and desorbed using the above parameters. Additionally, direct thermal desorption of GABA was carried out without the trapping step; GABA crystals were placed in a sample cup inside an empty thermal desorption tube, which was then desorbed in the thermal desorption unit as per above. An alkane standard (C₈–C₂₀) was run with both liquid and headspace injections for retention index calculations. Both formulations were also analysed in replicates by GC × GC–HRTOFMS to obtain exact mass measurements and further confirm the identity of compounds.

2.4. Data processing

LRTOFMS data were processed with LECO's proprietary software, ChromaTOF® 4.33. This software was used to generate two dimensional contour plots, calculate baselines, peak finding and deconvolution, library searching and peak integration. For library identifications the Wiley (2008) and NIST (2008) databases were used. Following manual review, peaks of interest were selected to confirm the preliminary library identification. The following thresholds were used to process the data: S/N > 100, baseline offset of one and library match factors >700. The forward and reverse match factors along with the probability value generated by the NIST search algorithm were used to evaluate the potential library identifications. A forward match factor is a number from 0 to 999 that describes how well the unknown spectra matches the library hit, with 999 being a perfect match. The reverse match factor (0–999) describes the opposite; i.e. how well the library hit matches the sample spectra. For both match factors, generally a score of 700+ is considered acceptable, 800+ is good and 900+ is excellent. The probability value has a maximum of 10 000 and indicates the likelihood that the library hit is the correct one. A probability of 9000+ indicates a strong match [10,11].

3. Results and discussion

Two major components were identified in the first formulation, 2-pyrrolidone and 4-aminobutanoic acid (GABA). In the second formulation, in addition to the above compounds, 1,4-diaminobutane (putrescine) and 1,5-diaminopentane (cadaverine) were identified as major components. Very few additional compounds were found within the two pseudo scents at lower concentrations. They were DBU, butyrolactone, and tridecylamine (Table 1). These compounds were selected for further identification with known standards due to their abundance, occurrence in replicate injections, and strong library matches. The retention times for the compounds showed good repeatability across multiple injections (Table 1). However, overloading of compounds can create broad peaks across several modulation periods. In such cases, peak finding algorithms are unsuccessful and retention times can vary [10]. For example, 2-pyrrolidone and GABA were present in high concentrations and had varied retention times. These large peaks also had an effect on the retention times of other compounds, e.g. tridecylamine (Fig. 1). If a compound is present in the solvent trace or in close

Table 1

Identification of compounds present within pseudo scent formulations I and II. Match factors are obtained from the library search engine of the LRTOFMS system. Retention time deviations were obtained from triplicate injections. First dimension retention indices were calculated from n-alkane retention times.

Compound name	Chemical formula	Cas #	Library match factors			Retention times						Retention index (¹ DRI) (n-alkanes)
			Forward	Reverse	Probability	Average (s)		SD (s)		RSD (%)		
						¹ t _R	² t _R	¹ t _R	² t _R	¹ t _R	² t _R	
Formulation I												
2-Pyrrolidone	C ₄ H ₇ NO	616-45-5	964	964	9537	1395	1.84	330	1.07	23.7	58.1	1401
4-Aminobutanoic acid	C ₄ H ₉ NO ₂	56-12-2	857	869	4700	1945	1.32	7	0.01	0.4	0.8	1807
Butyrolactone	C ₄ H ₆ O ₂	96-48-0	972	972	7993	555	2.52	2	0.07	0.3	2.8	913
DBU	C ₉ H ₁₆ N ₂	6674-22-2	722	722	4884	1475	2.46	2	0.02	0.1	0.6	1456
Tridecylamine	C ₁₃ H ₂₉ N	2869-34-3	893	975	2779	1662	1.43	286	0.11	17.2	7.3	1587
Formulation II												
2-Pyrrolidone	C ₄ H ₇ NO	616-45-5	952	952	9746	843	3.36	15	0.19	1.8	5.5	1072
4-Aminobutanoic acid	C ₄ H ₉ NO ₂	56-12-2	829	839	2809	1956	1.30	12	0.00	0.6	0.3	1821
1,4-Diaminobutane	C ₄ H ₁₂ N ₂	110-60-1	934	947	9391	508	1.70	3	0.01	0.5	0.4	882
1,5-Diaminopentane	C ₅ H ₁₄ N ₂	462-94-2	858	883	6998	688	1.75	3	0.01	0.4	0.6	986
Butyrolactone	C ₄ H ₆ O ₂	96-48-0	972	972	9024	554	2.49	3	0.02	0.5	0.8	911
DBU	C ₉ H ₁₆ N ₂	6674-22-2	714	714	5038	1476	2.47	0	0.00	0.0	0.2	1456
Tridecylamine	C ₁₃ H ₂₉ N	2869-34-3	907	968	3200	1980	1.08	0	0.00	0.0	0.0	1591

proximity to the peak itself, the retention time can shift along with the overloaded compound. Standards for 4-aminobutanoic acid, 1,4-diaminobutane, 1,5-diaminopentane, DBU, butyrolactone and tridecylamine were analysed. The first and second dimension retention times (¹t_R and ²t_R), first dimension retention indices (¹DRI) and mass spectra of the standards were compared to the pseudo scents and provided confirmatory identifications for the seven compounds. Retention indices were calculated using the following formula and are shown in Table 1.

$${}^1\text{DRI}(\text{target}) = 100 \times \left[\left(\frac{{}^1t_{\text{R}}(s) - {}^1t_{\text{R}}(n)}{{}^1t_{\text{R}}(n+1) - {}^1t_{\text{R}}(n)} \right) + n \right]$$

where ¹t_R(s) = retention time of target, ¹t_R(n) = retention time of alkane preceding target, ¹t_R(n+1) = retention time of alkane after target, n = number of carbon atoms of preceding alkane. Despite an early report on the use of specifically designed reference solution for column set characterisation [12], ²D retention indices were not calculated. The solubility of GABA posed problems during the preparation of the standards, so the headspace of GABA was sampled to attain ¹t_R(s) for comparison. Even with headspace sampling, large amounts of 2-pyrrolidone appeared in the chromatogram. The

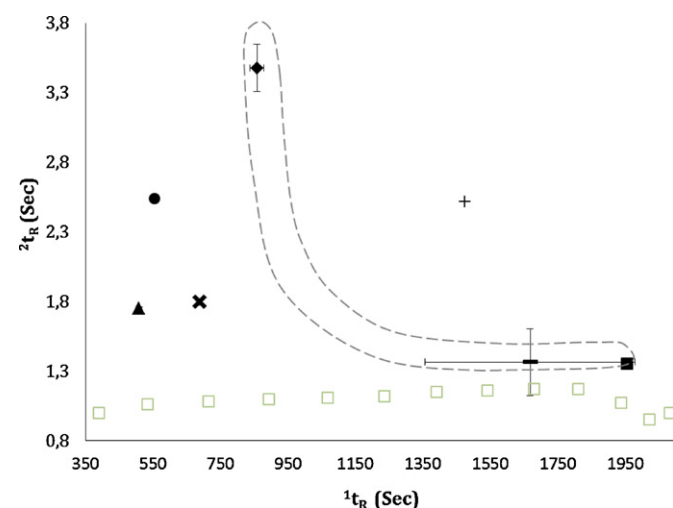


Fig. 1. Apex plot of Corpse Scent Formulation II. (◆) 2-Pyrrolidone, (▲) putrescine, (×) cadaverine, (+) DBU, (●) butyrolactone, (○) tridecylamine, (□) alkanes C₈–C₂₀, (■) GABA. Error bars indicate the calculated standard deviation. The area outlined by the dashed-line represents the tailing of 2-pyrrolidone.

cyclization of GABA to produce 2-pyrrolidone was hypothesized to take place under the high temperatures used for desorption and injection. At temperatures above 250 °C, GABA undergoes cyclization without a catalyst to produce high yields of 2-pyrrolidone [13]. However, Lammens et al. [13] did not test the cyclization of GABA at temperatures below 250 °C. To investigate this, direct thermal desorption of pure GABA was carried out at a temperature of 120 °C; the injector inlet was also kept at 120 °C. At these lower temperatures, GABA was more evident in the chromatogram, indicating the thermal lability of GABA and its possible conversion to 2-pyrrolidone.

Despite the simplicity of the mixture, GC × GC-TOFMS was originally used because of the expected complexity of the training solutions as cadaveric VOC signature is known to be complex [14]. Fig. 2A illustrates the case of the GC × GC VOC profile obtained from a sample of air trapped above a pig carcass at the advanced decay stage from one of our current forensic study. More than 400 compounds are identified, compared to the seven compounds identified in the training solution (Fig. 2B). Even for such simple case of separation, GC × GC however offered two retention time values (¹t_R and ²t_R) for each compounds, helping in further identification of the pseudo scent composition. The identification of compounds based on retention indices (¹DRI), library matches, and both dimension retention times (¹t_R and ²t_R) was further completed by repeated exact mass measurement carried out on a HRTOFMS instrument (Table 2). For each compound, good mass accuracies were reported (6–25 ppm differences) with very good reproducibility (RSDs below 0.001%). Despite the fact that they were still acceptable, mass accuracies for pyrimido[1,2-a]azepine, 2,3,4,6,7,8,9,10-octahydro-(DBU) were lower for both formulations (235 and 239 ppm differences). Repeated injections of the DBU standard solution also conducted to similar mass accuracies. We were not able to trace the origin of these discrepancies. No HRTOFMS data were reported for tridecylamine because this long hydrocarbon chain was readily fragmented inside the ion source of the HRTOFMS instrument, compared to the ion source of the LRTOFMS instrument.

The use of synthetic trainings aids is highly debated. Canines trained with pseudo scent products have found human remains; however, canines trained on original scent sources do not mark on pseudo scents. As a result, some agencies and certification programs will not use synthetic odourants [15]. This has also been the case with other Sigma Pseudo odour products [16], indicating a disconnect between the two types of training aids. The marketing of this product as a synthetic mimic of decomposition odour suitable for the training of cadaver dogs is questionable as it does not appear to be representative of decomposition odour (Fig. 2). The current

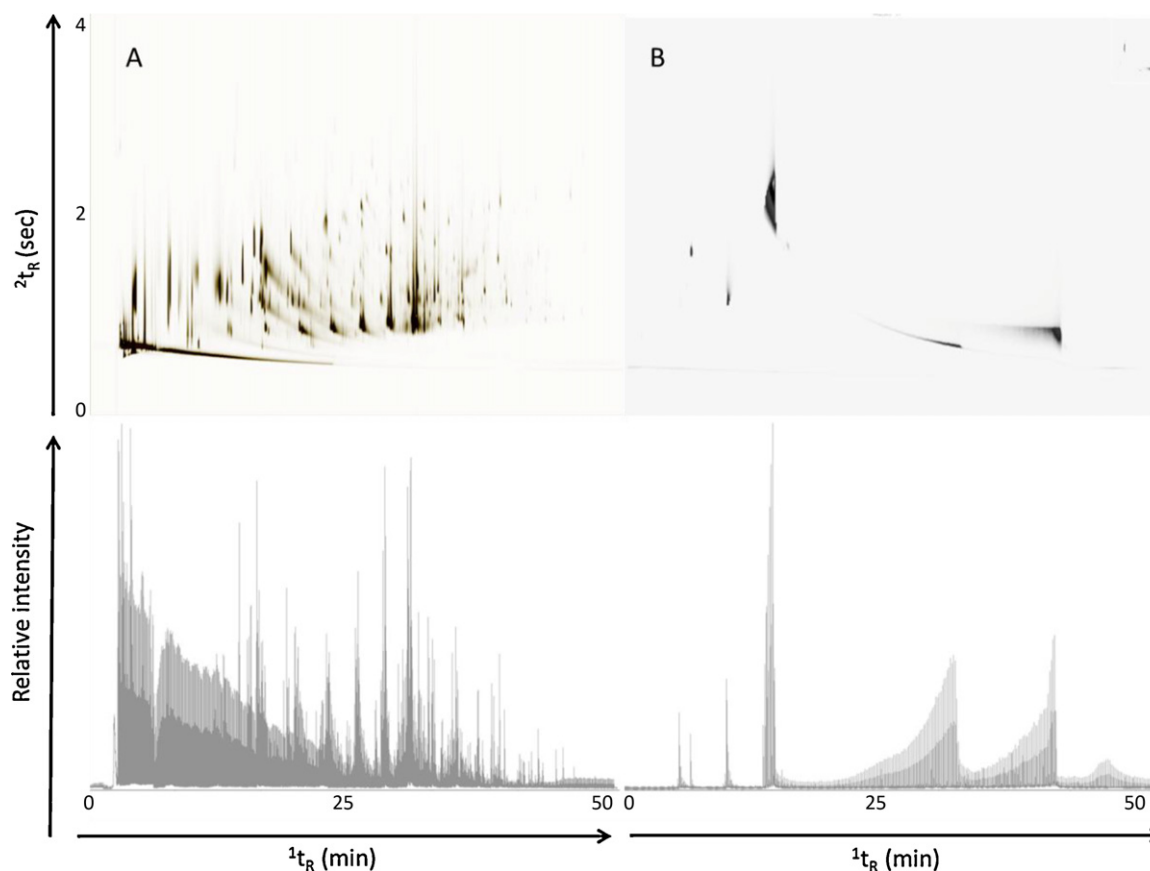
Table 2
HRTOFMS exact masses from replicate ($n=5$) injections of formulation I and II.

Compound name	Exact mass			
	Calculated (amu)	Measured (amu)	Difference (mamu)	RSD (%)
Formulation I				
2-Pyrrolidone	85.0528	85.0542	-1.4	5.6E-04
4-Aminobutanoic acid	103.0633	103.0652	-1.8	1.5E-03
Butyrolactone	86.0368	86.0377	-1.0	2.0E-03
DBU	152.1314	152.0956	35.8	5.3E-04
Tridecylamine	199.2300	-	-	-
Formulation II				
2-Pyrrolidone	85.0528	85.0536	-0.8	1.0E-03
4-Aminobutanoic acid	103.0633	103.0660	-2.6	9.4E-04
1,4-Diaminobutane	88.1001	88.0992	0.9	1.0E-03
1,5-Diaminopentane	86.0980	86.0969	1.1	6.1E-04
Butyrolactone	86.0368	86.0373	-0.5	1.6E-03
DBU	152.1314	152.0949	36.4	1.1E-03
Tridecylamine	199.2300	-	-	-

literature on decomposition VOCs has identified tens to hundreds of compounds [4,14,17–20], whereas this investigation has identified only seven compounds between two formulations. Although it is possible that cadaver dogs only rely on a few chemicals to identify remains, it is not known currently which chemicals elicit a response in cadaver dogs. Therefore, this oversimplification of decomposition odour could cause poor odour imprinting during training [2,4,16,21].

Ideally, a scent mimic should produce an odour profile that is comparable to the parent source [22], and Sigma Pseudo Corpse Scent is supposed to be representative of decomposition odour [15]. Interestingly, none of the major components of decomposition odour are included in the product, e.g. poly-sulphides. It may

be possible that canines respond to the minor compounds of an odourant and not the major ones present within the headspace [16]. However, the seven compounds found in these products have not been reported as key odourants of decomposition nor have they been identified within the headspace of decomposition [4,14,17–20]. The compounds 1,4-diaminobutane (putrescine) and 1,5-diaminopentane (cadaverine) are the result of the putrefactive degradation of the amino acids ornithine and lysine, respectively [23]. These compounds were thought to be representative of decomposition odour and the key odourant for the detection of remains by cadaver dogs [23], but these compounds have not been detected within the headspace of decomposition [4,14,17–20]. 4-Aminobutanoic acid (GABA) is a neurotransmitter that is

**Fig. 2.** GC \times GC chromatograms (top) and reconstructed one dimension chromatogram (bottom) for a sample of VOCs trapped above a decaying pig body at the advanced decay stage (A) and for the pseudo solution studied here (B). Traces are given in total ion current (TIC).

synthesized in the brain and is not generally known as a decomposition product. Vass et al. [24] used GABA as a potential biomarker for post-mortem interval estimation by extracting it from cadaveric tissues following derivatization [24]. The absence of these compounds within the vapour phase required for olfaction indicates that they may not be suitable target odourants [25].

4. Conclusion

Components constituting synthetic canine training aids have been identified by GC × GC coupled to both LR and HRTOFMS. The two pseudo scent products appear to be oversimplifications of decomposition odour and do not contain compounds that have been previously reported within the headspace of decomposition. A synthetic composition incorporating a larger variety of compounds that represent the variation seen during decomposition would be beneficial. Further research using sensitive instrumentation such as GC × GC-TOFMS will provide a more detailed analysis of both the major and minor components of decomposition odour. From such a profile, the compounds that elicit a response for trained cadaver dogs could be identified and would allow for the selection of compounds to produce a more effective canine training aid.

References

- [1] K. Furton, J. Greb, H. Holness, The Scientific Working Group on Dog and Orthogonal Detector Guidelines (SWGDOG), National Criminal Justice Reference Service, U.S. Dept of Justice, Rockville, MD, 2010, p. 155 <http://www.ncjrs.gov/app/publications/abstract.aspx?ID=254031>.
- [2] A. Rebmann, E. David, M.H. Sorg, *Cadaver Dog Handbook: Forensic Training and Tactics for the Recovery of Human Remains*, CRC Press, New York, 2000.
- [3] D. Komar, J. *Forensic Sci.* 44 (1999) 405.
- [4] E.M. Hoffman, A.M. Curran, N. Dulgerian, R.A. Stockham, B.A. Eckenrode, *Forensic Sci. Int.* 186 (2009) 6.
- [5] L.E. Degreeff, B. Weakley-Jones, K.G. Furton, *Forensic Sci. Int.* 217 (2012) 32.
- [6] J. Dalluge, J. Beens, U.A. Brinkman, *J. Chromatogr. A* 1000 (2003) 69.
- [7] G. Semard, A. Mohamed, J.-F. Focant, in: L. Ramos (Ed.), *Comprehensive Analytical Chemistry*, vol. 55, 2009, p. 15.
- [8] C. Brasseur, J. Dekeirsschieter, E.M.J. Schotsmans, S. de Koning, A.S. Wilson, E. Haubruge, J.-F. Focant, *J. Chromatogr. A* (2012), <http://dx.doi.org/10.1016/j.chroma.2012.03.048>.
- [9] J. Dekeirsschieter, P.-H. Stefanuto, C. Brasseur, E. Haubruge, J.-F. Focant, *PLoS One*, submitted for publication.
- [10] J. Dalluge, L.L. van Stee, X. Xu, J. Williams, J. Beens, R.J. Vreuls, U.A. Brinkman, *J. Chromatogr. A* 974 (2002) 169.
- [11] X. Lu, J. Cai, H. Kong, M. Wu, R. Hua, M. Zhao, J. Liu, G. Xu, *Anal. Chem.* 75 (2003) 4441.
- [12] J.M. Dimandja, G.C. Clouden, I. Colon, J.F. Focant, W.V. Cabey, R.C. Parry, *J. Chromatogr. A* 1019 (2003) 261.
- [13] T.M. Lammens, M.C.R. Franssen, E.L. Scott, J.P.M. Sanders, *Green Chem.* 12 (2010) 1430.
- [14] A.A. Vass, R.R. Smith, C.V. Thompson, M.N. Burnett, N. Dulgerian, B.A. Eckenrode, *J. Forensic Sci.* 53 (2008) 384.
- [15] M. Koenig, *Do Pseudo Scents Work?* 2001 (accessed on October 19, 2011) <http://www.cadaverdog.com/articles/pseudoscents.htm>.
- [16] M.S. Macias, R.J. Harper, K.G. Furton, *Am. Lab.* 40 (2008) 16.
- [17] J. Dekeirsschieter, F.J. Verheggen, M. Gohy, F. Hubrecht, L. Bourguignon, G. Lognag, E. Haubruge, *Forensic Sci. Int.* 189 (2009) 46.
- [18] M. Statheropoulos, A. Agapiou, C. Spiliopoulou, G.C. Pallis, E. Sianos, *Sci. Total Environ.* 385 (2007) 221.
- [19] M. Statheropoulos, C. Spiliopoulou, A. Agapiou, *Forensic Sci. Int.* 153 (2005) 147.
- [20] A.A. Vass, R.R. Smith, C.V. Thompson, M.N. Burnett, D.A. Wolf, J.A. Synsteliën, N. Dulgerian, B.A. Eckenrode, *J. Forensic Sci.* 49 (2004) 760.
- [21] L. Oesterhelweg, S. Krober, K. Rottmann, J. Willhoft, C. Braun, N. Thies, K. Puschel, J. Silkenath, A. Gehl, *Forensic Sci. Int.* 174 (2008) 35.
- [22] S. Moore, W. Maccreehan, M. Schantz, *Forensic Sci. Int.* 212 (2011) 90.
- [23] H. Gill-King, in: W.D. Haglund, M.H. Sorg (Eds.), *Forensic Taphonomy: The Postmortem Fate of Human Remains*, CRC Press, New York, 1997, p. 93.
- [24] A.A. Vass, S.A. Barshick, G. Sega, J. Caton, J.T. Skeen, J.C. Love, J.A. Synsteliën, *J. Forensic Sci.* 47 (2002) 542.
- [25] K.G. Furton, L.J. Myers, *Talanta* 54 (2001) 487.