Forensic Chemistry 26 (2021) 100380

Contents lists available at ScienceDirect

Forensic Chemistry

journal homepage: www.sciencedirect.com/journal/forensic-chemistry

Continuous vapor sampling of volatile organic compounds associated with explosives using capillary microextraction of volatiles (CMV) coupled to a portable GC–MS

Jacqueline L. Rodriguez, José R. Almirall *

Department of Chemistry and Biochemistry and Center for Advanced Research in Forensic Science (CARFS), Florida International University, Miami, FL, USA

ARTICLE INFO

Keywords:
Capillary microextraction of volatiles (CMV)
Gas chromatography-mass spectrometry (GC–MS)
Volatile organic compounds (VOCs) Associated with Explosives

ABSTRACT

The dynamic sampling and preconcentration device, capillary microextraction of volatiles (CMV), is coupled to a portable GC–MS for the rapid field detection of volatile organic compounds (VOCs) associated with explosives. The results of the portable GC–MS were compared to a benchtop GC–MS throughout this study. Sub-nanogram (ng) instrumental detection limits were achieved for each of the following analytes of interest (3-NT, 2,4-DNT, DPA, EC, DBP and 2-NDPA). Three different dynamic sampling methods were used with the CMV to sample and preconcentrate the volatiles prior to analysis. The headspace of a closed system was sampled over 10 min resulting in recoveries between 0.3 and 12%. Simulated open-air vapor sampling using a previously described vapor source resulted in an improvement of analyte recovery (ranging from 1.6 to 25%), for the same 10-minute sampling. A novel, continuous vapor delivery and sampling system was used, for the first time, to facilitate the delivery of sub-nanogram quantities of explosive analytes. The new continuous delivery system achieved significantly higher recoveries (3.0–89%) for all the analytes while requiring less sampling time (~5 min) and sampling volumes than the other sampling techniques. The rapid sampling and preconcentration of sub-ng levels of VOCs in field scenarios was coupled to a ~10-minute portable GC–MS method that compares favorably to the analytical figures of merit achieved by laboratory benchtop instruments and approximates the detection limits reported for canines.

Introduction

The unambiguous identification of low (ng) quantities of volatile organic compounds (VOCs) associated with explosives in the field provides an additional tool for the detection of hidden explosives. Smokeless powders are accessible to the general public as they are commonly found within ammunition, fireworks, and may be used illicitly as propellants within pipe bombs. Smokeless powders can be classified as either single-based (nitrocellulose only), double-based (nitrocellulose and nitroglycerin), or triple-based (nitrocellulose, nitroglycerin, and nitroguanidine) based on the composition. Manufacturers of smokeless powders also include various additives to control the burn rate and flash properties, such as stabilizers, plasticizers, flash suppressors, deterrents, and opacifiers [1]. Common characteristic stabilizers include ethyl centralite (EC) and diphenylamine (DPA). Derivatives of DPA are also known to be produced as a biproduct of the degradation of the present energetic material [2]. These derivatives include N-nitrosodiphenylamine (N-NODPA), 2-nitrodiphenylamine (2-NDPA), and 4-nitrodiphenylamine (4-NDPA) [2]. Other additives, such as 2,4-dinitrotoluene (2,4-DNT) and 3-nitrotoluene (3-NT) are commonly used as flash suppressors, while phthalates, such as dibutyl phthalate (DBP), are commonly included as plasticizers [1].

Canine teams are often used for the rapid detection of hidden explosives in the field such as in airports and ports of entry. The effectiveness of canines to detect VOCs associated with the presence of explosives can be attributed to their agility and to their highly sensitive olfactory systems [3–5]. Active sniffing canines can rapidly inspire and expire repeatedly with a frequency of 5 times per second [6–8] and inhale at a rate of 30 mL/sec/nostril, approximating an air flow of ~3.6 L min^{-1} [8]. Canines are reported as capable of rapidly detecting illicit substances such as a land mine within a 1–10 s sampling interval (with equivalent air sampling volumes between 60 mL and 600 mL) [9]. Harper, et al. have reported significant differences between the odor profiles of various types and brands of smokeless powders, identifying

* Corresponding author.
E-mail addresses: jrodr047@fiu.edu (J.L. Rodriguez), almirall@fiu.edu (J.R. Almirall).

https://doi.org/10.1016/j.forc.2021.100380
Received 29 July 2021; Received in revised form 3 November 2021; Accepted 9 November 2021
Available online 14 November 2021

several key odor chemicals that canines alert to for detecting these types of explosives [10,11]. The detection limits (equivalent to ~ 50% alert response rate) for trained canines for the odor compounds 2,4-DNT and 2,3-dimethyl-2,3-dinitrobenzene (DMNB, a VOC added and used as a detection taggant for explosives) were reported in the range of 500 ppt [4]. Detection limits of 10 ppb were also reported for the detection of nitroglycerine and for methyl benzoate (the dominant odor of Cocaine) [4]. Assuming a sampling time interval of 1–10 s for the detection, the mass loading equivalents range from approximately 30–300 ng of 2,4-DNT and DMNB. Other researchers determined that the detection limit for canines to detect piperonal (the dominant odor of the drug 3,4-methylenedioxymethamphetamine or MDMA) to be as low as ~ 1 ng [12]. However, there are reliability and safety concerns while identifying these target materials that are detrimental to the functionality of canine detection [5,13,14]. Occurrences of toxicity exposure have been reported as detrimental to the canine's health while training and detecting certain analytes [5,13]. There are also limitations and uncertainties of the quality control within the training and performance of canine detection [5,11,13,14].

A variety of portable detection instrumentation has been developed in recent years to detect and analyze explosives in order to complement the use of canines in explosives detection. Laboratory analytical instrumentation such as gas chromatograph mass spectrometers (GC–MS), Raman, and ion mobility spectrometers (IMS), have been miniaturized and made portable to accommodate for use in the field [15–17]. As an example, the Griffin G510 (FLIR System) portable GC–MS instrument operates similarly to a benchtop quadrupole GC–MS with liquid and Solid Phase Microextraction (SPME) sample introduction, as well as with the ability to sample with desorption tubes.

In this study, a dynamic sampling extraction device, known as capillary microextraction of volatiles (CMV) [18,19] is coupled to a portable GC–MS (Griffin G510) for the detection of vapor trace explosive analytes via different sampling methods, and the results are reported here for the first time. The CMV is used to sample and preconcentrate VOCs in both open-air and in enclosed containers prior to analysis by the portable detection system. The CMV device is an open-ended glass capillary (2 cm long × 2 mm diameter) filled with multiple strips of glass microfibers that are coated with a thin layer of sol–gel PDMS, providing a hydrophobic, absorptive coating over the microfibers. The strips within the CMV provide 5000 times greater total surface area in comparison to SPME, a non-exhaustive, equilibrium technique commonly used to also sample volatile compounds [20]. This allows the CMV to perform rapid dynamic sampling, which has shown to provide greater sensitivity than the static sampling from SPME [20]. The small size of the capillary permits the CMV to be inserted directly into the inlet of a GC–MS for subsequent thermal desorption using a commercially available thermal separation probe (TSP) or, in the case of the portable Griffin GC–MS, by utilizing a "prepless sample introduction" (PSI) probe. A recent modification to the PDMS-based absorption phase was developed to improve the absorption of aromatic VOCs that resulted in improved sensitivity for the overall detection of aromatics, in comparison to the previously reported PDMS sol-gel CMV [21]. The versatility of the CMV device also extends its application to the analysis of a variety of analytes and matrices within forensic chemistry applications, including fire debris and drug analysis [19–26].

We also report the first application of a continuous vapor delivery and sampling device to facilitate the delivery of nanogram (ng) quantities of analytes in the vapor phase, the primary focus of this manuscript. The analytical figures of merit obtained from this novel delivery device is compared against previously reported sampling methodologies, including closed-system headspace sampling [20,21] and single-injection vapor sampling [21,27]. Closed-system headspace sampling occurs within an enclosed vessel to allow the volatiles to accumulate within the headspace prior to sampling, whereas single-injection vapor sampling vaporizes the analytes of interest to simulate open-air sampling of volatiles. A modification was made to the single-injection vapor source to construct the continuous vapor delivery and sampling device, to allow the gradual introduction and sampling of small (~ng) mass loadings of volatiles. This method of analyte delivery and sampling closely mimics on-field sampling within a laboratory setting, where a low concentration of the target vapors is consistently sampled over a brief amount of time. In this study, selected VOCs associated with explosives are sampled and preconcentrated with the CMV through these various sampling techniques, and was coupled to both a laboratory-based benchtop GC–MS (Agilent Technologies) and the portable Griffin G510 GC–MS (FLIR) for simulated field analysis.

Materials and methods

Materials

Methanol (A454-4, HPLC grade, 99.9%) was purchased from Fisher Scientific. Ethyl centralite (EC) (372889, 99%) and 3-nitrotoluene (3-NT) (N27314, 99%) was obtained from Sigma-Aldrich. 2,4-Dinitrotoluene (2,4-DNT) (A17452, 97%) and 2-nitrodiphenylamine (2-NDPA) (A18357, 97%) was purchased from Alfa Aesar. Dibutyl phthalate (DBP) (AC166602500, 99%) and diphenylamine (DPA) (AC150741000, 99%) was purchased from Acros Organics.

Direct inlet injections performed throughout this study were conducted with a 5 μL gas tight syringe (0.63 mm OD, SGE Model, 5BR-7) purchased from Trajan Scientific. Continuous analyte delivery was performed with a programmable single syringe automatic pump (NE-1000) from New Era Pump Systems, Inc. (Farmingdale, NY). 5 mL transfer pipettes (13–711-5AM) were obtained from Fisher Scientific. Unlined 1 L round paint cans (02991233) were purchased from Qorpak. A Nurture III portable vacuum pump was obtained from Bailey Medical Engineering (Los Osos, CA).

Instrumentation

The field-portable instrumentation used throughout the study was a Griffin G510 (FLIR Systems Inc., Wilsonville, OR) gas chromatograph-mass spectrometer. The unit was equipped with a "prepless sample introduction" (PSI) probe which allows capillaries, like the CMV device, to be inserted directed into the inlet. The system was also equipped with a DB-5MS (15 m × 0.18 mm × 0.18 μm) analytical column and possessed an on-board 13 L Helium gas cartridge as the carrier gas for on-site applications and analysis. The system was configured with an external helium connector which allowed the unit to utilize the primary gas tank for laboratory experiments. The inlet port was set to a temperature of 240 °C, and the initial oven temperature was set to 40 °C, with a hold of 1 min, and 0% split. The temperature of the oven was then increased to 250 °C at a rate of 25 °C/min with a 20% split, with no hold time, for a total run time of ~ 9 min. The electron impact (EI) source was maintained at 200 °C, while the quadrupole MS was set to full scan with an acquisition mass range set to m/z 45 – 400 for data collection. Analyte identification was automatically performed after each run by utilizing the system's on-board GriffinLib and NIST mass spectral libraries. The major fragment ions and retention times obtained from the portable unit are presented in Table 1.

Table 1
Major ion fragments and retention times for VOC analytes coupling CMV to both GC–MS systems (FLIR and Agilent).

Analytes	Ion Fragments (m/z)	Griffin G510 R_t (min)	Agilent GC–MS R_t (min)
3-NT	91, 137, 65	4.96	7.63
2,4-DNT	165, 89, 63	6.86	10.64
DPA	169, 168,167	7.27	11.41
EC	120, 148, 77	8.52	13.35
DBP	149, 150, 41	8.78	13.73
2-NDPA	167, 214, 169	8.88	13.90

For laboratory-based experiments, an Agilent Technologies 7890A gas chromatograph system coupled to a 5975C inert XL mass spectrometer with a triple-axis detector was utilized (Agilent Technologies, Santa Clara, CA). This gas chromatograph is equipped with an Agilent Technologies Thermal Separation Probe (TSP), which permits the CMVs to be inserted directly into the inlet to be thermally desorbed. The temperature of the injection port was set to 180 °C, and the gas chromatograph was programmed for a split injection with a 5:1 ratio. The analytical column that was utilized was a DB-5MS Ultra Inert (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas and was set with a flow rate of 1.2 L/min. The temperature of the oven began at 40 °C and was maintained for 0.5 min. From there, the temperature of the oven increased to 240 °C at a rate of 15 °C/min, with a hold of 1.2 min, for a total run time of 15.03 min. The EI source was maintained at 230 °C, the analyzer was kept at 150 °C, and the transfer line to the mass spectrometer was set to 280 °C. Data collection was performed with a mass-to-charge range from *m/z* 40 – 300. Confirmation of the target analytes were determined by the mass spectra and expected retention times, shown in Table 1, obtained from the injection of standard solutions. Peak areas of the target analytes within the chromatograph were integrated for quantification.

Method development

Sampling preparation

A stock solution of the analytes was prepared in methanol at 10,000 μg mL^{-1} (w/v), which contained the following compounds: 3-nitrotoluene, 2,4-dinitrotoluene, diphenylamine, ethyl centralite, dibutyl phthalate, and 2-nitrodiphenylamine. Serial dilutions were then performed to generate solutions at lesser concentrations: 1,000, 500, 100, 50, 25, 15, and 5 μg mL^{-1}. These solutions were used to construct calibration curves and for the optimization of the sampling methodology that was conducted throughout the study to produce the analyte vapors. The calibration curves were developed by spiking 1 μL of the analyte mixture, at the varying concentrations, directly onto the CMV to be thermally desorbed into the GC inlet. Prior to sampling, the CMVs were conditioned in an oven at 250 °C for 30 min. To ensure that all prior analytes were completely removed, a blank sample of the CMV was analyzed by the GC–MS. The sampling was performed with four replicates and the results are reported as average values.

Closed-System headspace sampling

Closed-system headspace extractions were conducted with the analytes of interest utilizing the portable vacuum pump for dynamic sampling. Based on previously reported sampling parameters, 1 L unlined metal paint cans were conditioned at 250 °C in an oven overnight prior to usage to remove any residual contaminants [20,21]. Two holes were created on the cans' lids and fitted with rubber septa (Capitol Scientific Inc., Austin, TX) to ensure a tight seal and to avoid leakage during sampling. One hole was created in the center of the lid for CMV sampling and the other was made off-center for ambient air flow. A 10 μL aliquot of 100 ng μL^{-1} of the analyte mixture was spiked directly into the can before immediately being sealed to equilibrate for 10 min. Following headspace equilibrium, the septa were then pierced with individual 16-gauge hypodermic needles, which were both connected to perfluoroalkoxy (PFA) tubing and to the CMV for sampling. The other end of the CMV was inserted with separate tubing connected directly to a vacuum pump and flow meter. The needle and tubing of the off-center septa remained open to the surrounding air. The vacuum pump was retained at a constant flow rate of 0.2 L min^{-1}, and varying extraction times (5 min, 10 min, 15 min) were observed at room temperature (20 °C). Following optimization, recovery experiments were performed with the same sampling parameters at various can temperatures (60 °C, 70 °C, 80 °C, 90 °C, 100 °C) by placing the cans into a heating mantle immediately after sample introduction. Once sampling was complete, the CMV was removed from the tubing and inserted to either the PSI-Probe for analysis by the portable GC–MS or the TSP for analysis by the benchtop GC–MS.

Single injection vapor delivery and sampling

As previously reported in our laboratory, the injector port of a Varian (Palo Alto, CA) CP 3800 gas chromatograph was utilized to produce analyte vapors from 1 μL injections of the stock solution at a concentration of 100 ng μL^{-1} [21,27]. The inlet of the GC was set to splitless mode and was equipped with a splitless liner (4 mm ID, Single Taper, Ultra Inert Inlet Liner, Agilent). The injection port was installed with an 8 cm intermediate narrow-bore column (DB-5MS, 30 m × 0.25 mm × 0.25 μm, Agilent), and was pre-heated to ensure complete vaporization of the analytes. Optimization experiments were carried out at various inlet temperatures (160 °C, 170 °C, 180 °C, 190 °C, 200 °C). For this sampling setup, illustrated in Fig. 1, two small holes were punctured atop of a 5 mL volume disposable plastic pipette (13–711-5AM Fisher). With this, 2 cm of the intermediate column was inserted into one of the holes of the pipette, while the other punctured hole was used to allow ambient air into the system. The tip of the pipette was cut to securely fit one end of the CMV.

The other end of the CMV was attached to the portable vacuum pump, via PFA tubing, with a flowmeter to complete the dynamic sampling system. To begin sampling, the vacuum pump was turned on and maintained a constant flow rate of 0.2 L min^{-1}. After the sample was introduced and injected into the inlet, a nitrogen carrier gas flow, which was maintained at a rate of 50 mL min^{-1}, was utilized to move the analytes through the column and into the pipette. After sampling, which occurred at different extraction times (5 min, 10 min, 15 min), the CMV device was removed from the tubing and inserted to either the PSI-Probe for analysis by the portable GC–MS or the TSP for analysis by the benchtop GC–MS.

Continuous vapor delivery and sampling

A new continuous vapor delivery system was configured for the sampling and extraction of volatile explosive analytes with the CMV device. Similar to the sampling methodology previously discussed (Method Development-Single Injection Vapor Delivery and Sampling section), the inlet of a GC was used to heat the analytes after introduction of the stock solution with a gas-tight syringe, while the system maintained a constant carrier gas flow of nitrogen at a rate of 50 mL

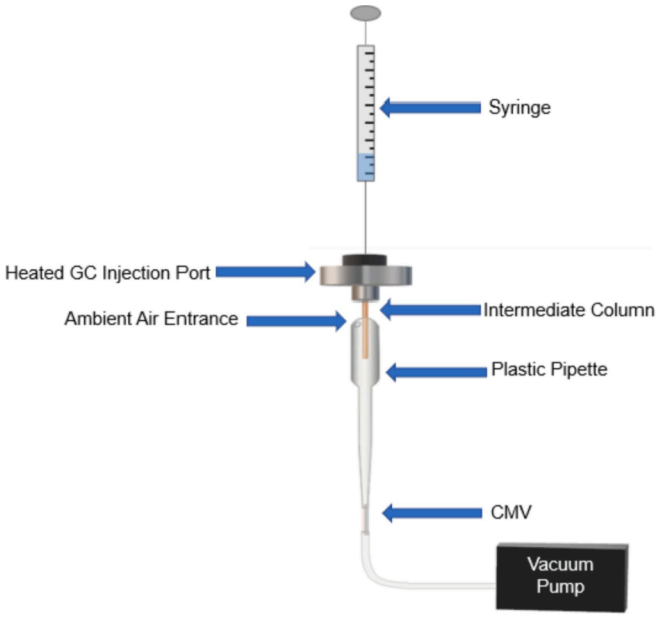

Fig. 1. Schematic drawing of the vapor sampling set-up used to deliver ng mass loadings of analytes.

min^{-1}. For this delivery set-up, an auto-syringe pump was configured onto the inlet of the GC inlet to slowly introduce the sample at a controlled rate. The continuous delivery and sampling parameters are shown in Table 2. Every experiment was conducted to sample a total of 100 ng of the target analytes. Utilizing a 5 μL syringe (Trajan Scientific), the analyte mixture was prepared at an ultra-low sample concentration of 20 ng μL^{-1}. The auto-syringe pump was configured to introduce the sample into the system at fixed sampling rates of 1 μL min^{-1}, 0.5 μL min^{-1}, and 0.2 μL min^{-1} throughout various extraction times (5 min, 10 min, 25 min). Different vacuum flow rates of 0.4 L min^{-1}, 0.2 L min^{-1}, and 0.08 L min^{-1} were also investigated to determine how the flow rate of the vacuum affects the recovery of the targets. This analyte delivery and sampling system closely mimics on-field sampling within a laboratory setting, where a low concentration of the target is consistently sampled over a set amount of time.

Results and discussion

Method validation

The Griffin system software, known as GSS Touch™, provides a Level 1 use designed for ease of use by the operators in the field and does not allow for any method or setting configurations. The Griffin also allows for Level 2 use, permitting users to control the instrument's configurations, as well as develop methods and analyze data. All of the experiments, runs, and data analysis for this study was conducted on the Level 2 Griffin System Software.

Rapid analysis (total run time of ~ 9 min) was used on the portable GC–MS for the detection of common volatile smokeless powders utilizing the CMV sampling device. The retention times for each compound were determined from the portable unit by spiking 1 μL of the stock solution at a concentration of 100 ng μL^{-1} directly into the CMV to be thermally desorbed, shown in Table 1. The unit was capable of accurately identifying each of the compounds immediately after each run by comparing the obtained mass spectrums to its on-board libraries. Two of the analytes, however, EC and 2-NDPA, were not a part of any of the standard Griffin mass spectral libraries, so these compounds were added.

Calibration curves of the analytes were constructed from the portable GC–MS by spiking 1 μL of the standard mixture directly onto the CMV at varying concentrations between 5 and 100 ng μL^{-1}, illustrated in Fig. 2a. To construct the curves, each concentration of the mixture was performed in quadruplicate, utilizing four different CMV devices. These calibration curves derived from the portable unit demonstrate linearity performance between 0.95 and 1.0. The error bars presented on each curve (Fig. 2a) was constructed as plus or minus one standard error at each concentration. The limit of detection (LOD) and limit of quantitation (LOQ) for each analyte was determined by multiplying 3 and 10 times the standard deviation of the lowest concentration (5 ng μL^{-1}) divided by the slope of the calibration curves, respectively (Table 3). With the target analytes, the portable GC–MS was capable of achieving a detection limit between 0.3 and 1.0 ng, and a quantitation limit between 0.9 and 3.0 ng off of the CMV device.

The same methodology was employed on the benchtop GC–MS to compare with the performance of the portable GC–MS. The calibration curves from the benchtop, illustrated in Fig. 2b, were also achieved by spiking 1 μL of the standard mixture directly onto the CMV at the same varying concentrations (5, 15, 25, 50, and 100 μg mL^{-1}). This was also performed in quadruplicate, utilizing four different CMV devices. The R^2 values from these calibration curves derived from the benchtop GC–MS range between 0.98 and 1.0. The error bars shown within Fig. 2b were also constructed as plus or minus one standard error at each concentration. The detection and quantitation limits for each analyte was determined, as shown in Table 3, with instrumental LODs ranging between 0.1 and 1.9 ng depending on the analyte of interest. An internal standard of 1,3-DNB (1,3-dinitrobenzene) was applied to account for potential temporal and instrumental variation; however, it was found that the use of the internal standard did not significantly impact the results. The experiments presented throughout this study were conducted within the same day, providing similar results for same day analysis both with or without the use of the internal standard. Thus, the results from using 1,3-DNB as the internal standard will not be discussed within this manuscript.

Closed-system headspace sampling

The evaluation of the CMV as a closed-system headspace sampling device was previously reported for several VOCs and it was found that a sampling flow rate of 0.2 L min^{-1} over a 10 min sampling time (total sampling volume of 2.0 L) was the optimal for recovery of VOCs spiked into a 1 L can [20,21]. The same sample preparation steps were employed, with both instruments as detectors. A constant sampling flow rate of 0.2 L min^{-1} was used at room temperature (20 ℃) with sampling times of 5 min, 10 min, and 15 min, to evaluate the recovery of the analytes (total sampling volumes of 1 L, 2 L, and 3 L) of a 1 L can. As shown in Appendix A (Supplementary data), it was found that the optimal extraction time for the explosives analytes of interest was 10 min (2 L sample) which is double the volume present within the 1 L paint cans. At 15 min, when 3 L of total air was sampled, some loss of analytes was detected suggesting sample breakthrough. The results were consistent between both the benchtop GC–MS and the portable GC–MS. It should be noted that throughout the various extraction times the less volatile compounds, DBP and 2-NDPA, were not recovered at room temperature (20 °C), while analyzing on both instruments.

The cans were spiked with a known amount of a standard mixture (1,000 ng of each analyte) and heated to 60 °C, 70 °C, 80 °C, 90 °C and 100 °C using a heating mantle. The response curves are shown in Fig. 3 as the relative abundance for each analyte. As expected, heating the cans provided greater responses amongst all of the analytes, including with DBP and 2-NDPA, demonstrating greater relative recovery over sampling at room temperature. While the potential for degradation products can appear throughout sampling at higher can temperatures, none were noted. As illustrated in Fig. 3, it was discovered between both instruments that the abundances increased as the temperature of the cans is increased, until the can was heated to 100 °C, possibly due to sample loss or breakthrough. Sampling with the cans at 90 °C provided the greatest relative abundance for all the analytes on both instruments.

By using the CMV as the sampling device, the mass recoveries for each of the analytes within the mixture are shown in Table 4 and reported in nanograms (ng) after converting the integrated peak areas by using the calibration curves from the direct spikes onto the CMV (Fig. 2). The reported uncertainties were determined by standard error of each analyte (n = 4). With this sampling configuration, the overall analytical precision achieved on the portable unit was within 13% RSD for all the volatile compounds in the mixture, while the analytical precision

Table 2
Continuous vapor delivery and sampling parameters.

Concentration	Syringe	Sampling Rate	Sampling Time	Vacuum Flow Rate	Total Mass	Total Air
20 ng μL^{-1}	5 μL	1 μL min^{-1}	5 min	0.2 L min^{-1}	100 ng	1 L
				0.4 L min^{-1}		2 L
		0.5 μL min^{-1}	10 min	0.2 L min^{-1}		
		0.2 μL min^{-1}	25 min	0.08 L min^{-1}		

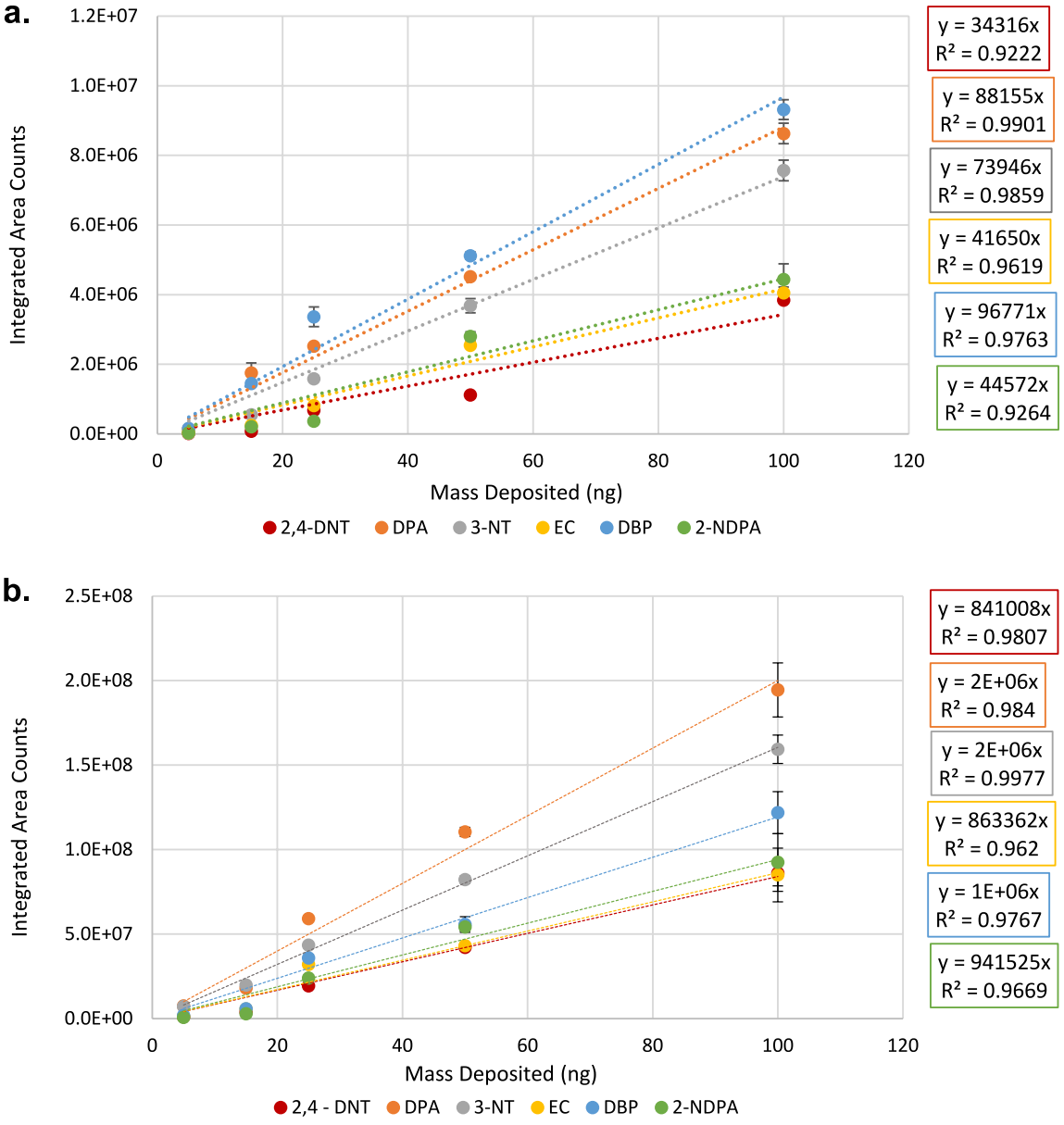

Fig. 2. Calibration curves for each of the VOC analytes of interest for the portable Griffin G510 GC–MS (a. above) and for the Agilent GC–MS (b. below) developed from 1 μL spikes, at different concentrations, directly onto the CMV.

Table 3
Limits of detection (LODs) and limits of quantitation (LOQs) for VOC analytes coupling CMV to both GC–MS systems.

	Griffin G510		Agilent GC–MS	
Analytes	LOD (ng)	LOQ (ng)	LOD (ng)	LOQ (ng)
3-NT	0.8	2.5	1.9	5.7
2,4-DNT	0.3	0.9	0.7	2.2
DPA	1.0	3.0	1.4	4.2
EC	0.4	1.1	1.1	3.3
DBP	0.6	1.9	0.7	2.2
2-NDPA	0.5	1.4	0.1	0.2

measured on the benchtop GC–MS was within 12% RSD. Both instruments demonstrated the highest recovery for the most volatile compound in the mixture, 3-NT, with recoveries between 12 and 16%.

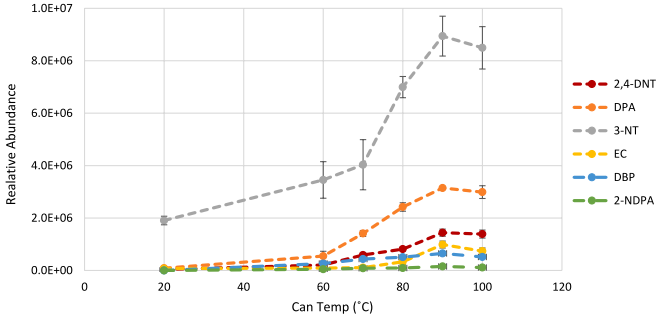

Fig. 3. Response curves of the relative abundance/peak area from the can temperatures for closed-system headspace sampling *(results from the portable GC–MS are shown)*.

Table 4
Average analyte recoveries from closed-system headspace sampling of 10 μL spiked standard solution at a concentration of 100 μg mL^{-1} (mass loading of 1,000 ng) obtained from both GC–MS systems (10 min extraction) (n = 4).

	Griffin G510			Agilent GC–MS		
Analytes	Mass Recovered (ng)	% Recovered	% RSD	Mass Recovered (ng)	% Recovered	% RSD
3-NT	121 ± 10	12	8.5	164 ± 14	16	8.6
2,4-DNT	42 ± 4.0	4.2	9.5	69 ± 8.4	6.9	12
DPA	36 ± 0.4	3.6	1.2	59 ± 5.4	5.9	9.1
EC	24 ± 3.2	2.4	13	17 ± 1.4	1.7	8.2
DBP	7 ± 0.7	0.7	11	20 ± 1.2	2.0	5.9
2-NDPA	3 ± 0.2	0.3	6.8	10 ± 0.4	1.0	4.2

Single injection vapor delivery and sampling

To further evaluate the CMV sampling capabilities when coupled to the portable GC–MS, vapor delivery and sampling of the analytes was performed using the methodology discussed above, whereby a single injection of the analytes into the heated inlet delivered the 100 ng of analytes at the same time. Similar to the closed-system headspace sampling experiments, a constant sampling flow rate of 0.2 L min^{-1} was maintained at extraction times of 5 min, 10 min, and 15 min, to evaluate the recovery of the analytes after sampling a total of 1 L, 2 L, and 3 L. Based on the previous optimization study in Fig. 4, the inlet temperature was kept at 180 °C. This experiment was performed in quadruplicate and on both GC–MS instruments. The optimal sampling time for the analytes was 10 min, when a total of 2 L of air was sampled, as shown in Fig. 5. Similar to the closed-system headspace sampling experiments, sampling for 15 min resulted in ~ 50% lower recoveries for most analytes relative to 10 min sampling times. The results were consistent between both the benchtop GC–MS and the portable GC–MS. Unlike the initial closed-system headspace sampling experiments that occurred at room temperature, DBP and 2-NDPA were consistently recovered throughout all the vapor sampling experiments, as the heated inlet assists in immediate vaporization of the spiked solution.

Once the parameters were optimized for vapor sampling, the percent recoveries of the analytes and associated precision (reported as % RSD) from both instruments were calculated in the same manner as described in the "Closed-System Headspace Sampling" section and presented in Table 5. The benchtop GC–MS resulted in better precision (ranging from 3 to 10% RSD) in comparison to the portable GC–MS (8–14% RSD). Both instruments displayed approximately a two-fold increase in recoveries relative to closed-headspace sampling.

Continuous vapor delivery and sampling

An automatic syringe pump was configured to deliver a fixed rate of volume into the heated inlet for a gradual and continuous delivery of vapor analytes for subsequent sampling by CMV. Similar to the single injection delivery and sampling configuration described in the previous section, a total of 100 ng of each analyte was introduced into the heated inlet over the course of the experiment. The inlet was maintained at 180 °C throughout sampling based on the optimization from the previous section. A 5 μL syringe was used to introduce 20 ng $μL^{-1}$ of the stock solution into the system (total delivery of 100 ng) for all the experiments. Sampling times of 5 min, 10 min, and 25 min were used requiring syringe delivery rates of 1 μL min^{-1}, 0.5 μL min^{-1}, and 0.2 μL min^{-1}, respectively. The CMV sampling that resulted in the greatest relative abundance of the analytes was determined to be with a vacuum flow rate set to 0.4 L min^{-1} over 5 min (total sampling volume of 2 L) as in other experiments.

With the optimal parameters, the percent recoveries and correlating % RSD obtained from both instruments were determined to evaluate this continuous analyte delivery and sampling set-up, shown in Table 6. As exhibited from both instruments, consistently higher average recoveries (n = 4) were obtained from this set-up for extracting all the analytes, compared to the other two sampling methodologies previously discussed the "Closed-System Headspace Sampling" and the "Single Injection Vapor Delivery and Sampling" sections. This was achieved even with a rapid sampling time of only 5 min, whereas the other methodologies both had optimal recovery after extracting for 10 min. The average results indicated by the benchtop GC–MS demonstrated a percent recovery greater than 10% for all the targets, excluding 2-NDPA, which was the least volatile analyte in the mixture and had a recovery of 8.8%. This recovery was still an improvement from the other sampling

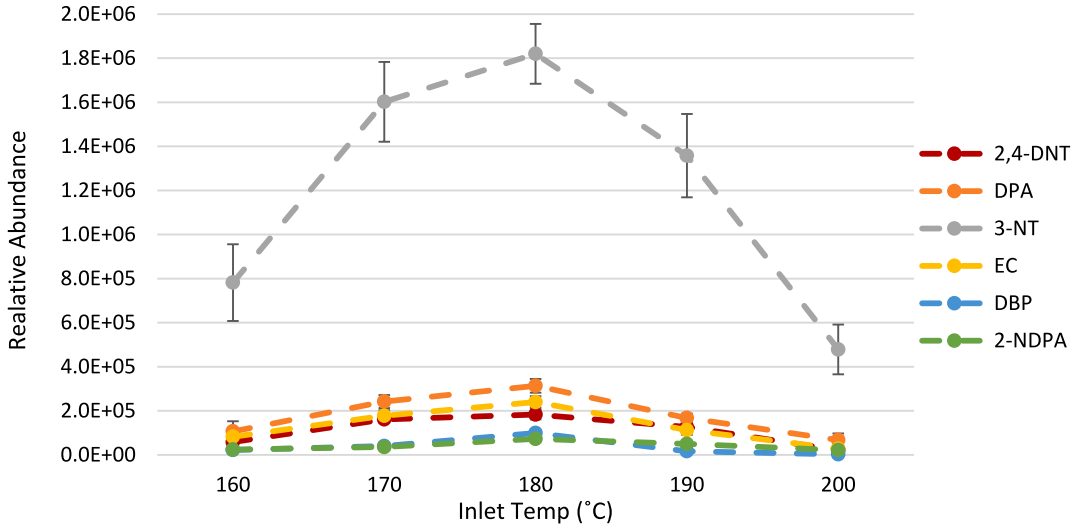

Fig. 4. Response curves of the relative abundance/peak area from different inlet temperatures for single injection vapor delivery and sampling *(results from the portable GC–MS are shown)*.

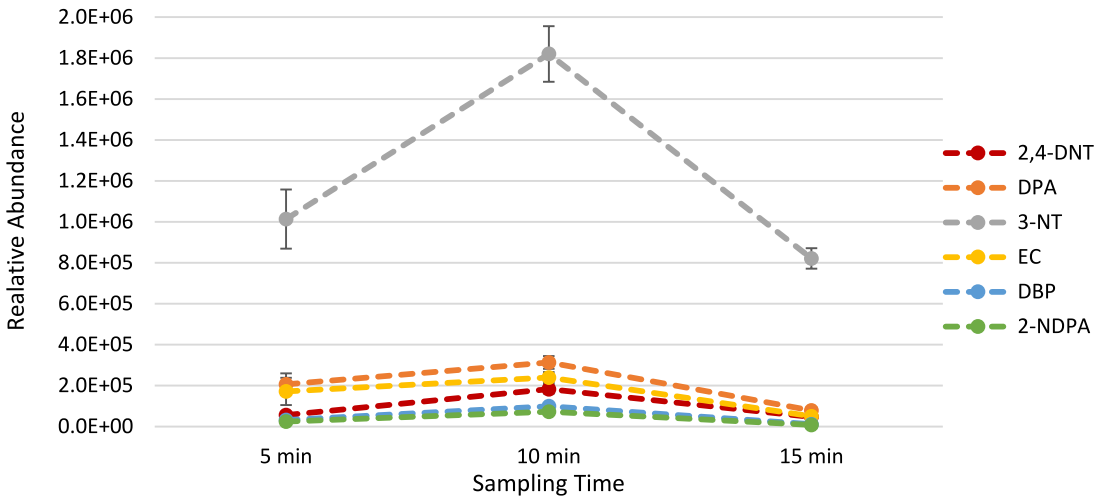

Fig. 5. Response curves of the relative abundance/peak area from different extraction times for single injection vapor delivery and sampling *(results from the portable GC–MS are shown)*.

Table 5
Average analyte recoveries from single injection vapor delivery and sampling of 1 μL spiked standard solution at a concentration of 100 μg mL^{-1} (mass loading of 100 ng) obtained from both GC–MS systems (10 min extraction) (n = 4).

	Griffin G510			Agilent GC–MS		
Analytes	Mass Recovered (ng)	% Recovered	% RSD	Mass Recovered (ng)	% Recovered	% RSD
3-NT	25 ± 1.8	25	7.5	45 ± 1.5	45	3.4
2,4-DNT	5.3 ± 0.6	5.3	12	12 ± 1.0	12	8.4
DPA	3.6 ± 0.4	3.6	9.9	7.6 ± 0.4	7.6	5.5
EC	5.8 ± 0.6	5.8	11	8.0 ± 0.8	8.0	9.6
DBP	3.2 ± 0.4	3.2	12	6.3 ± 0.2	6.3	3.9
2-NDPA	1.6 ± 0.2	1.6	14	4.6 ± 0.3	4.6	7.5

Table 6
Average analyte recoveries from continuous vapor delivery/sampling of 5 μL standard solution at a concentration of 20 μg mL^{-1} (mass loading of 100 ng) obtained from both GC–MS systems (5 min extraction) (n = 4).

	Griffin G510			Agilent GC–MS		
Analytes	Mass Recovered (ng)	% Recovered	% RSD	Mass Recovered (ng)	% Recovered	% RSD
3-NT	89 ± 2.6	89	3.0	90 ± 8.3	90	9.2
2,4-DNT	12 ± 1.6	12	14	31 ± 2.9	31	9.1
DPA	9.3 ± 0.6	9.3	6.8	28 ± 2.7	28	9.7
EC	8.1 ± 1.2	8.1	14	16 ± 0.9	16	5.4
DBP	4.1 ± 0.5	4.1	12	10 ± 0.7	10	7.1
2-NDPA	3.0 ± 0.3	3.0	11	8.8 ± 0.9	8.8	9.9

methodologies previously discussed, the 4.6% recovery from the immediate vapor sampling (Table 5) and the 1.0% recovery from the closed-system headspace sampling (Table 4). On the other hand, both instruments indicated the greatest recovery of 3-NT, the most volatile compound in the mixture, recovering about 90% of the analyte that was originally introduced into the system. The benchtop GC–MS reported that this methodology was capable of high precision with a bias of about 10% or better for all the analytes within the mixture. For the Griffin unit, the overall analytical precision achieved was within 14% between replications.

Table 7 summarizes the recoveries of the analytes for all three modes of sample delivery and sampling when coupled to the portable GC–MS. The continuous vapor delivery and sampling configuration results in the best recovery of the target analytes in comparison to the other two sampling methodologies. Throughout the experiments presented, the portable GC–MS was capable of rapidly (~9 min. GC–MS method) providing compound identification using a library search and confirmation by comparing the resulting mass spectrum to a standard. Sub-nanogram recoveries of the target volatiles associated with explosives were achieved from vapor sampling using the CMV device, demonstrating rapid sampling and detection for on-site investigations.

Table 7
Comparison of average analyte recoveries for three sampling modes (closed headspace, single injection heated inlet, and continuous vapor delivery) reported as % recovered for the portable GC–MS (n = 4).

Analytes	Closed Headspace Sampling	Open-Air Sampling (Immediate)	Continuous Vapor Delivery / Sampling
3-NT	12	25	89
2,4-DNT	4.2	5.3	12
DPA	3.6	3.6	9.3
EC	2.4	5.8	8.1
DBP	0.7	3.2	4.1
2-NDPA	0.3	1.6	3.0

Conclusion

The primary aim of this study was to evaluate the continuous vapor

delivery and sampling of VOCs associated with explosives using the CMV and determine the recoveries and other analytical figures of merit for the explosive analytes. By implementing dynamic sampling with the CMV, sub-nanogram recoveries were possible for 5 – 10 min sampling times throughout different sampling modes, including simulated open-air sampling. With an ultra-low mass loading of only 20 ng μL^{-1}, it was discovered that the optimal rate for continuous vapor delivery was at 1 $\mu L\ min^{-1}$, permitting for a rapid sampling time of only 5 min. It was observed that increasing the vacuum flow rate to 0.4 $L\ min^{-1}$, to sample a total volume of 2 L of air, obtained the greater recovery of the volatiles within the mixture. This novel analyte delivery and sampling system resembles on-field sampling yet performed within a laboratory setting, where a low concentration of the target is consistently sampled over a set amount of time. When implementing this methodology, the CMV device obtained significantly higher recoveries for all the compounds with a rapid sampling time (5 min), providing a faster recovery than the commonly utilized passive equilibrium technique of SPME. Some of the limitations observed with the continuous vapor delivery and sampling system include: a limited range of mass loadings available for sample introduction, which is based on the size of the syringe used, and the apparatus required to set up this sampling system. However, this sampling apparatus can be reconstructed in any lab that has access to an empty GC oven and an automatic syringe pump.

The versatility of the CMV device permitted simple coupling directly into the portable GC–MS using a commercially available PSI-Probe. Throughout this study, the portable GC–MS and the laboratory benchtop GC–MS displayed similar analytical figures of merit which can be accredited to similarities between both instruments. Both units were equipped with the same analytical column (DB-5MS), a linear quadrupole mass analyzer with a 70 eV EI ionization source, and an electron multiplier detector. To accommodate for field testing, the portable GC–MS possesses miniaturized adaptations of certain components, such as a shorter linear quadrupole and a shorter analytical column measuring at 15 m, while the benchtop GC–MS is equipped with a 30 m version. This benefits the portable system to provide a faster analysis time (~9 min. method) but hinders the overall sensitivity of the unit, as demonstrated throughout this study amongst the analyte recoveries between both instruments. Nonetheless, the recoveries and analytical figures of merit presented following the rapid sampling and analysis of the CMV coupled to a portable GC–MS, compete favorably with the previously reported detection by canines (~1 ng of VOC), providing a potential alternative to canine detection for these compounds in the field.

Future work includes the use of the CMV device coupled to a portable GC–MS for the detection of trace (ng quantities) of VOCs associated with illicit drugs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors would like to acknowledge the Center for Advanced Research in Forensic Science (CARFS), a National Science Foundation and National Institute of Justice funded Industry University Cooperative Research Center at Florida International University (award 1739805).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.forc.2021.100380.

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