

## Field demonstration of portable vapor sampling in a simulated cargo container



Megan E. Harries<sup>a,\*</sup>, Thomas J. Bruno<sup>b</sup>

<sup>a</sup> Department of Physics, University of Colorado Boulder, 2000 Colorado Avenue, Boulder, CO, USA

<sup>b</sup> National Institute of Standards and Technology, 325 Broadway, Boulder, CO, USA

### HIGHLIGHTS

- Portable vapor sampling unit rapidly collected analytes in first field deployment.
- Analytes of forensic interest were added to a simulated cargo container.
- Explosives-related and decomposition-related compounds were successfully detected.
- High humidity and low temperature conditions required longer sampling times.

### ARTICLE INFO

#### Keywords:

Trace detection  
Vapor analysis  
Portable instrumentation  
GC-MS

### ABSTRACT

Screening technologies are necessary to counteract illegal trafficking through ports of entry in the United States and internationally. Here we present results from initial field testing of a recently-developed portable vapor sensing unit, portable PLOT (porous layer open tubular)-cryoadsorption. A surplus US Army bunker was used as a simulated cargo container, and four sets of experiments demonstrated the unit's functionality in a field environment. Three chemical mixtures acted as surrogates for materials relevant to screening operations: explosives-related compounds, protein decomposition compounds, and gasoline. In this feasibility study, portable PLOT-cryoadsorption successfully collected components of each mixture in a variety of weather conditions and with short vapor collection times well suited to a field environment. Gas chromatography with mass spectrometry (GC-MS) was used for sample analysis.

### 1. Introduction

Current practice for cargo screening at ports of entry by customs agencies consists of random sampling and physical searches, inspection of provenance documents, x-ray or gamma-ray radiography, and sniffer dogs. Radiation detectors are used to locate nuclear materials [1]. These tools used together can be effective in detecting illicit materials, but they also have some disadvantages. Physical searches could be dangerous to the inspector and are time consuming, as is radiography. Dogs are incredibly sensitive to the compounds they are trained to identify and have been very successful when deployed for explosive and drug screening; however, they require expensive training and expert human partners, can only detect the compounds used in training, and are limited by a low duty cycle [2].

Ideally, a method should objectify the result by removing the human and canine component of chemical screening of cargo. Vapor

sampling could supplement, and offer a safer alternative to, the law enforcement tools currently in practice. Vapor-based methods can be non-destructive, minimally intrusive, rapid, and safer for the inspector than physical inspection of container interiors. Vapor sampling consists of collecting a quantity of air from inside a container and analyzing its chemical composition. The sample can be introduced directly to an analytical instrument or first concentrated on an adsorbent trap. Vapor sampling directly into an instrument without the use of a trap is advantageous for real-time measurements; however, preconcentration on a sorbent trap is often necessary to obtain enough analyte for a signal to be detected, especially for low-volatility compounds present in some explosives and drugs. Chemical analysis of the concentrated vapor can provide the analyst with a more complete chemical characterization of the container. Both vapor sampling devices and the corresponding analytical equipment can be made portable for use at a port of entry.

The portable vapor sampling device demonstrated in this work is

Abbreviations: PLOT, porous layer open tubular; RH, relative humidity

\* Corresponding author.

E-mail address: [megan.harries@colorado.edu](mailto:megan.harries@colorado.edu) (M.E. Harries).

<https://doi.org/10.1016/j.forc.2019.100182>

Received 27 June 2019; Received in revised form 29 August 2019; Accepted 31 August 2019

Available online 05 September 2019

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based on a new technology, developed at NIST, called porous layer open tubular cryoadsorption (PLOT-cryo), which uses a capillary column coated with an adsorbent phase (alumina in this case) and chilled to subzero temperatures as a trap to preconcentrate analytes present in the collected vapor. [3] PLOT-cryo sampling can be coupled with any analytical method, such as gas chromatography (GC), mass spectrometry (MS), and nuclear magnetic resonance (NMR). Over the last 10 years, this approach has been applied to explosives, arson fire debris, cannabis, and natural gas, among others [3–9]. In order to further expand the use of PLOT-cryo and address field applications of the method, the portable PLOT-cryo instrument was recently developed and tested under lab conditions [10,11]. This current work deployed portable PLOT-cryo into the field as a tool for cargo screening with a series of four experiments. The set of experiments investigated the detection of naphthalene, explosive-related compounds, protein decomposition compounds, and gasoline, using a test bed designed to simulate a shipping container. In these experiments, PLOT-cryo samples were analyzed using GC–MS.

## 2. Material and methods

### 2.1. Materials

Diffusers were made from clean, commercially obtained 8 oz nominal steel paint cans or 4 mL borosilicate glass vials. Pure test compounds, solvents used in GC analyses, and gasoline were purchased from commercial sources, analyzed by GC–MS, and used as received. All test compounds and solvents were obtained from Sigma Aldrich (St. Louis, MO) except for isophorone (Fluka, Morris Plains, NJ) and gasoline.

### 2.2. Experimental setup

A shipping container was simulated by adapting a surplus United States Army communications bunker (“bunker” hereafter) for this field demonstration of portable PLOT-cryo. It was repurposed from another location at the NIST laboratory site and moved to a parking space outside the laboratory building, where it became a test bed for these experiments. Fig. 1 shows photographs of the bunker setup. The bunker interior dimensions were 1.91 m wide by 1.86 m high by 3.85 m deep. After adjusting for the other elements inside the bunker (e.g., HVAC duct) which occupied some of its volume, the total volume was determined to be  $13.6 \text{ m}^3 \pm 0.31 \text{ m}^3$ . Holes in the walls of the bunker, including vents and incidental holes and gaps incurred due to age, were sealed using gaffer’s tape, epoxy, and pop rivets. While the unit was not airtight, it was rendered weather resistant and fit for the purpose. Shipping containers undergoing screening in a real scenario would also not be perfectly sealed.

Although shipping containers are often equipped with air vents, none were built into the bunker through which to sample the vapor. Five (0.125” diameter nominal) ports in each side of the bunker were therefore drilled to enable introduction of the sampling probe to the inside of the container. Two rows of ports located at the bottom, middle, and top of the bunker wall were made at 1/3 and 1/2 the full length of the bunker. A heavy steel rail prevented drilling the bottom port at the halfway point, resulting in five total ports on either side. These multiple sampling locations were used to preliminarily explore whether the location of vapor collection affects the results. Some research has shown that sampling vapor from different locations on a shipping container affects the aerodynamics within, suggesting that the composition of the sample would be dependent on sampling point [12]. The volume was not intentionally mixed. These experiments did not test the effect of cargo on mixing or sampling, although this is potential future work.

Because the bunker was outside and exposed to the elements and variable weather, many experimental variables which can be controlled

in a laboratory setting were left up to nature: the temperatures inside and outside the bunker, atmospheric pressure, relative humidity, contamination inside the bunker, and diffusion of analyte vapor through the volume. These values, when known, were always recorded.

### 2.3. Sampling protocol

Operation of the portable PLOT-cryo unit has been described in detail in previous work [10,11]. The device, powered by compressed air, is housed in an aluminum briefcase containing three major components: the unit’s operating platform, which controls temperature and sample collection, the insulated standoff module containing an adsorbent multicapillary PLOT trap, and the probe used to access vapor inside the volume of interest. The multicapillary PLOT traps were composed of six individual PLOT capillaries cast into an epoxy monolith with connections to inlet and outlet fittings. The multicapillary trap has also been referred to as the wafer, and these terms are interchangeable. To prepare the portable unit for use, a compressed air line is connected to the operating platform through a quick connect fitting. Compressed air operates the entire unit, providing (1) suction to pull vapor from the bunker and through the multicapillary trap, and (2) hot and cold air, using vortex tubes, for temperature control of the standoff module.

In preparation for a vapor sample collection, cold air from the operating platform is applied to chill the module and multicapillary trap to temperatures below  $0 \text{ }^\circ\text{C}$  (to promote adsorption of volatile analytes and stabilize reactive species). The probe is attached to the standoff module opposite the suction and inserted into the space to be sampled. When suction is switched on, sample collection begins, and vapor from the bunker passes over the cold multicapillary trap, where analytes are captured. The sample must then be released from the trap for analysis. To desorb the sample from the multicapillary trap, it is heated to about  $60 \text{ }^\circ\text{C}$  and eluted with 1 mL of solvent for analysis. The sample in liquid form can be analyzed by any analytical method(s), in this case, GC–MS. Once the sample is desorbed, the multicapillary trap is reactivated for reuse by evaporating the solvent using gentle heat and a flow of air. Desorption and reactivation of the multicapillary traps can be done in the field, but in these experiments, they were primarily done in the lab.

To set up each experiment, known quantities of the analytes were placed in individual diffusers made from either steel cans (8 oz nominal) with perforated lids or 4 mL borosilicate glass vials without caps, depending on the quantity of analyte and the number of compounds being simultaneously tested. The diffusers were placed in the center of the bunker floor. Individual vapor samplings occurred between 24 h and several weeks after the sample introduction. After each experiment, the diffusers were removed and weighed to estimate the fraction that vaporized during the experiment, although the infiltration of moisture or other contaminants that added mass to the diffuser during the experiment precluded any quantitation using this information. Before starting a new experiment, removal of any residual analyte was attempted by airing out the bunker with the door open and a fan to circulate fresh outdoor air. Bunker “blank” samples were then collected in between sets of experiments; analytes from previous experiments were sometimes observed, but this was easily detected and disregarded.

Each experiment tested a range of sample collection times to determine the approximate time needed to detect the test compounds. For each individual vapor collection, the following parameters were recorded: port used, ambient outdoor temperature, temperature inside the bunker, temperature inside the module containing the multicapillary trap, ambient relative humidity, and ambient pressure. Temperatures were measured using thermocouples with an uncertainty of  $1 \text{ }^\circ\text{C}$ . Relative humidity data from a monitoring station at the National Center for Atmospheric Research (NCAR, 1.1 miles away) were used. Ambient pressure was measured with an electronic barometer with an uncertainty of 0.03 kPa. Samples were desorbed with acetone and characterized by gas chromatography-mass spectrometry (GC–MS).



**Fig. 1.** Photographs of the bunker are presented. (a) Exterior front and side of the bunker. (b) Bunker interior. (c) Open hatch on the front wall. (d) Side view of the bunker; one of the walls into which sampling ports were drilled. Port locations are indicated with ★.

#### 2.4. GC–MS analysis

All analyses were conducted using an Agilent 7890A gas chromatograph with an Agilent 5975C mass spectrometer (Agilent Technologies, Santa Clara, CA). The GC column stationary phase was 5% phenyl polydimethylsiloxane (Agilent HP-5MS UI, 30 m × 0.25 mm inner diameter × 0.25 μm film thickness, Agilent Technologies). The acquisition methods are summarized in [Table 1](#).

#### 2.5. Background signal

Before embarking on this series of experiments, the vapor contents of the bunker itself, in the absence of any test compounds, were analyzed to establish a baseline. The bunker had its own musty, slightly sweet smell, and analysis revealed a mixture of compounds, dominated

by C6–C12 unsaturated ketones with and without rings. We suspect that these are the byproducts of degradation of polyurethane foam insulation exposed to years of weathering. This type of insulation was found sandwiched between the aluminum walls of the bunker. It was a light yellow color consistent with the discoloration of polyurethane foam exposed to heat over time.

The background compounds were at times detected more strongly than the analytes used in the experiments. This may have interfered with the collection of target analyte or led to chemical reactions, changing the composition of the vapor in the bunker, but these potential complications are beyond the scope of the current experiments and may be investigated in the future.

**Table 1**

Summary of GC–MS acquisition methods.

Experiment	
Naphthalene	Injection volume 1 μL, splitless mode, inlet temperature 275 °C, head pressure of 12 psi, oven held at 50 °C for 0 min, then 20 °C/min to 200 °C for 0 min. MS transfer line temperature 300 °C, EI source 230 °C, quadrupole 150 °C. MS solvent delay 3 min, scan range 33–300 <i>m/z</i> , SIM ion 128.
Explosives-related suite	Injection volume 1 μL, split mode (50:1), inlet temperature 275 °C, head pressure of 12 psi, oven held at 40 °C for 0 min, then 10 °C/min to 230 °C for 0 min. MS transfer line temperature 300 °C, EI source 230 °C, quadrupole 150 °C. MS solvent delay 2.5 min, scan range 33–300 <i>m/z</i> , SIM ions 86, 118, 128, 138, 146, 149, 177, 222.
Protein decomposition suite	Injection volume 1 μL, splitless mode, inlet temperature 325 °C, head pressure of 8 psi, oven held at 30 °C for 4 min, then 15 °C/min to 120 °C, then 30 °C/min to 260 °C for 2 min. MS transfer line temperature 300 °C, EI source 230 °C, quadrupole 150 °C. MS solvent delay 2.5 min, scan range 33–300 <i>m/z</i> , SIM ions 43, 45, 56, 59, 61, 73, 77, 79, 85, 88, 90, 94, 121, 126, 152, 185, 186.
Gasoline	Injection volume 1 μL, splitless mode, inlet temperature 300 °C, head pressure of 9.5 psi, oven held at 40 °C for 0 min, then 20 °C/min to 200 °C for 2 min. MS transfer line temperature 280 °C, EI source 230 °C, quadrupole 150 °C. MS solvent delay 1.5 min, scan range 33–205 <i>m/z</i> , SIM ions 57, 71, 91, 105, 106.

**Table 2**

Available vapor pressures of test compounds, in order of decreasing volatility, calculated using Antoine coefficients from Yaws [14]. NA = not available.

Compound	VP (kPa) 20 °C
Dimethyl disulfide	2.87
Putrescine	$1.39 \times 10^{-1}$
2,4,6-trimethyl pyridine	$1.31 \times 10^{-1}$
Butyrolactone	$1.13 \times 10^{-1}$
Cadaverine	$4.28 \times 10^{-2}$
Isophorone	$3.95 \times 10^{-2}$
Naphthalene	$6.13 \times 10^{-3}$
Diphenyl sulfide	$1.00 \times 10^{-3}$
Diethyl phthalate	$2.37 \times 10^{-5}$
Allyl methyl sulfide	NA
Dimethyl trisulfide	NA
Methyl thioacetate	NA

### 3. Results

We present results from four experiments, which tested the following compounds: naphthalene, explosive-related compounds, protein decomposition compounds, and gasoline. Vapor pressures of the test compounds ranged widely from 2.87 kPa (dimethyl disulfide) to  $2.37 \times 10^{-5}$  kPa (diethyl phthalate), calculated at 20 °C. Table 2 summarizes the vapor pressures of all test compounds. All vapor pressures and concentrations provided here and in the following subsections were determined using the Antoine equation and the ideal gas law [13,14]. Because the bunker was not well sealed or well mixed, any calculated concentrations provided represent an upper limit only.

#### 3.1. Naphthalene

The first analyte tested in the bunker was naphthalene, because it was used in the development of PLOT-cryo and subsequently as a test compound to indicate that the instrumentation is working correctly. During the development and initial testing of portable PLOT-cryo, a diffuser containing 50 mg of naphthalene was placed inside a valise with a volume of  $1.68 \times 10^{-2} \text{ m}^3$  (resulting in a saturated vapor concentration of approximately 1234 mg/m<sup>3</sup>). The analyte was detected in a 3 s sample using the portable unit [11].

For the bunker experiment, a diffuser containing 0.53 g of naphthalene was placed on the floor in the center of the bunker, and vapor was allowed to develop for 24 h before the first vapor collection. To provide a point of comparison to the previous work, the calculated vapor concentration was 39 mg/m<sup>3</sup>, assuming full vaporization of the analyte; however, most of the naphthalene remained in the diffuser when the experiment concluded. The diffuser's mass after removal from the bunker was greater than its initial mass, likely due to the intrusion of moisture; naphthalene is hygroscopic. This prevented us from determining the precise mass lost or a better estimate of the vapor concentration.

Two samples were taken on each of two separate days, two days apart, for a total of four samples. The bunker temperatures at times of collection on the first day were 33 and 42 °C. The relative humidity was 26%. Naphthalene was detected in a 30-second sample under these conditions. An example result is shown in Fig. 2. On the second day, the weather was rainy with 91% RH. The bunker temperature was 17 °C for both samples. A sample with a 30 s collection time did not collect naphthalene under these conditions. An extended two-minute collection time successfully collected naphthalene.

#### 3.2. Explosive-related compound suite

The second experiment in the bunker involved three analytes related to the manufacture of explosive materials: diethyl phthalate (a

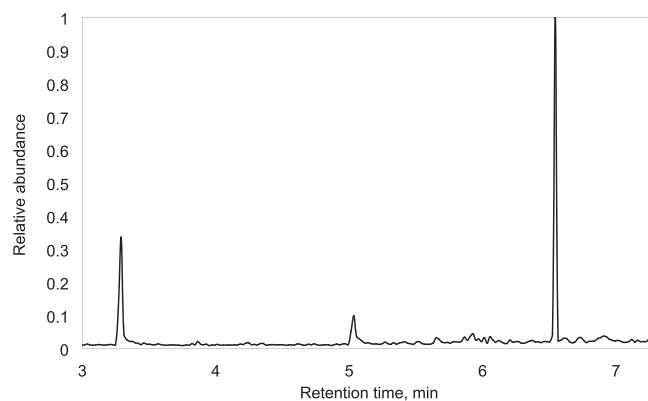


Fig. 2. This background-subtracted, representative chromatogram is the result of a 30 s collection with portable PLOT-cryo. Naphthalene is the peak around 5 min. The two other peaks are constituents of the bunker background signal.

plasticizer), butyrolactone, and isophorone (both solvents). These were detected as components of explosive materials previously analyzed using laboratory PLOT-cryo [4]. The compounds were introduced to the bunker in three diffusers. A fourth diffuser with a small amount of naphthalene was also included to confirm proper functioning of the unit.

The masses of each compound added to the bunker were 2.33 g diethyl phthalate, 2.50 g isophorone, and 5.69 g butyrolactone. Table 2 lists vapor pressures, from which one could approximately determine theoretical vapor concentrations. Sampling times were 30 s and 3 min; both intervals were sufficient to detect diethyl phthalate and isophorone. In these two collections, five days apart, the bunker temperature was 38 °C and RH was 20% and 15%. Although it is the most volatile of the three compounds, butyrolactone was not detected in any sample, even after increasing collection time up to 15 min in hot, dry weather. The very light compound may have passed through the unit without adsorbing to the capillary. It may also have been lost to the bunker surfaces, or to reaction or decomposition inside the bunker.

#### 3.3. Protein decomposition suite

In the third experiment, a suite of eight compounds associated with protein decomposition were used to simulate a cargo container containing a shipment of meat or poultry that must be tested for spoilage. The compounds, some of which are also indicators of human decomposition, another potential target of cargo screening, were phenyl sulfide (2.87 g), trimethyl pyridine (2.48 g), dimethyl trisulfide (1.30 g), dimethyl disulfide (2.85 g), methyl thioacetate (1.47 g), allyl methyl sulfide (1.96 g), 1,5-pentanediamine (cadaverine, 1.75 g), and 1,4-butanediamine (putrescine, 1.79 g). These compounds were chosen because they were identified as decomposition markers during previous PLOT-cryo experiments [8].

The eight compounds were added to the bunker in the same experiment, each in its own diffuser. Allyl methyl sulfide and dimethyl disulfide, two of the more volatile analytes, were identified in a two-minute PLOT-cryo sample. After increasing collection time to 15 min, both previous analytes plus methyl thioacetate and dimethyl trisulfide were detected. The other four less volatile compounds were not detected in any sample. Bunker temperatures during these collections were relatively low (in October), ranging from 11 to 23 °C. Higher temperatures would increase the likelihood of detecting some of the lower volatility compounds. Other markers of decomposition, or real decomposing material, would be interesting targets of future work.

#### 3.4. Simulated gasoline spill

In the fourth and final experiment, approximately 250 mL of

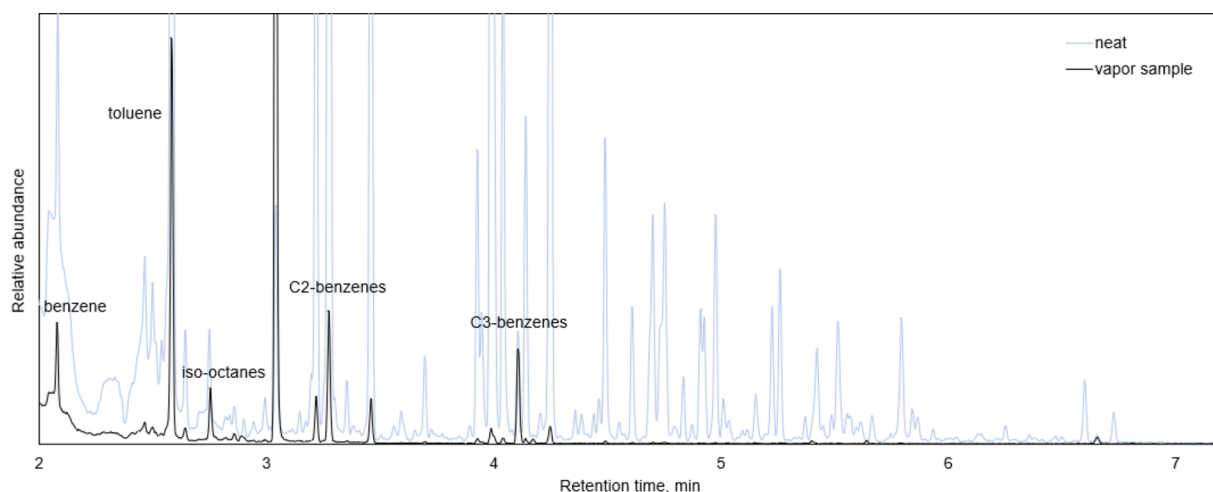


Fig. 3. More volatile, less retained gasoline components were enriched in the vapor sample (black) compared to the composition of neat gasoline (blue).

gasoline was placed in the bunker in a quarter-size (23 cm × 33 cm) baking sheet. This simulated the ruptured fuel tank of a car being transported by freight. Gasoline is also relevant as a possible fuel used in crude explosive devices. Portable PLOT-cryo detected gasoline components with a sample collection time of 10 s, even at low temperature (17 °C).

Because gasoline is a complex mixture of hundreds of components, a comparison could be made between the composition of the collected vapor sample and the liquid gasoline itself. As expected, samples collected from the bunker were enriched in the more volatile components of gasoline, especially aromatic compounds, and did not contain lower-volatility species (Fig. 3).

Another ten-second vapor collection taken three weeks after the introduction of the gasoline sample (and in colder weather, 9 °C) did not collect any markers of gasoline, suggesting that compounds had leaked away or been lost to the inside walls of the bunker.

#### 4. Discussion

Bolstering the safety and security at ports of entry internationally is one important motivation for the development of field portable vapor sampling technology. These experiments were the first demonstrations of portable PLOT-cryo technology deployed in a field environment. Using an old U.S. Army communications bunker as a simulated shipping container, the portable PLOT-cryo unit successfully detected naphthalene, two explosives-related compounds (diethyl phthalate, isophorone), four protein decomposition markers (allyl methyl sulfide, methyl thioacetate, dimethyl disulfide, dimethyl trisulfide), and gasoline. The sampling intervals required for detection were on the order of minutes or less.

The background signal of the bunker—vapor chemistry present in the absence of any added analyte—was primarily attributable to ketone decomposition products of the polyurethane insulation used in its construction. Background compounds were often collected in greater abundance than the analytes, and the analytical challenge this presents must be considered. Background vapor signatures of shipping containers are likely to vary widely based on their construction and contents.

Some qualitative conclusions can be drawn from this preliminary series of experiments about the effects of field conditions on the environment inside the bunker as well as on the performance of the portable PLOT-cryo unit. During these experiments, temperatures inside the bunker ranged from 2.2 to 43 °C. Temperatures outside the bunker ranged from 3 to 37 °C. Relative humidity ranged from 9% to 92%. The primary factor influencing detection ability was the

temperature inside the bunker, as expected. Temperatures observed in real shipping containers are typically higher than those observed during these experiments. Internal temperatures around 70 °C have been considered typical, but temperatures likely vary widely [15]. High humidity (RH > 90%) required longer sampling times in the naphthalene experiment. Water content inside the bunker may have affected the vapor concentration of the analyte. There could also be an effect of water vapor outcompeting the analyte for adsorption to the capillary trap.

The minimal change in the mass of analyte observed during all experiments indicated that the true concentration in the vapor was consistently lower than the theoretical value. Wall losses and lack of airtightness also likely affected the vapor concentration present. Compound vapor pressure was a good predictor of detectability.

There was no observable effect of port location. Across all the experiments, the analyte-containing diffusers were located on the floor in the center of the bunker, which was sampled from a limited number of locations. In a real cargo container, however, crates or other contents could serve as diffusion barriers and make port location a crucial factor. Another study has shown that in real circumstances, port location may matter [12]. The current study, which utilized an empty container and a simple setup, is merely a necessary first step towards understanding the factors affecting compound detection.

#### 5. Conclusion

The results of this feasibility study indicate that portable PLOT-cryo is a good candidate for in-the-field chemical screening of cargo in transit. The current observations are qualitative, and the lack of controlled conditions inherent in a field study means extensive work will be required to fully characterize the capabilities and limits of the technology. Designing the unit for thermal desorption and testing it coupled to a field analysis method—such as micro GC or direct mass spectrometry—are modifications that would both support portability. This work has informed further development of portable PLOT-cryo for continually enhanced sensitivity and a broad array of applications in forensics and beyond.

#### Disclaimer

Certain commercial entities are identified in order to specify experimental procedures as completely as possible. In no case does such identification imply a recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that any of the entities identified are necessarily the best available for the purpose.

## Declaration of competing interest

The authors have no competing interests to declare.

## Acknowledgments

The authors gratefully acknowledge the NIST Boulder Maintenance and Support Services Division and funding from the NIST Special Programs Office.

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