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Extraction of capsaicins in aerosol defense sprays from fabrics

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Abstract

The use of aerosol defense sprays has increased as a means of self-defense and as a weapon in the commission of a crime. The residue of these sprays is often left behind as physical evidence on a victim's clothing or personal belongings. As the popularity of self-defense weaponry increases, so does the likelihood that it will be encountered in forensic casework. The extraction, recovery from fabrics, and identification of residue from defense sprays is described. The commonly used extraction method of liquid–liquid extraction is compared to solid phase microextraction (SPME) to recover capsaicin and dihydrocapsaicin from cotton swabs. The use of SPME resulted in lower limits of detection and greater recovery efficiency when compared to solvent extraction. SPME also provided more consistent recovery and less variability when compared to solvent extraction. The effect of use of various types of evidence packages on the preservation of this type of evidence is also reported. The collection and analysis of hand swabs after normal discharge of pepper spray canisters was studied indicating the low persistence of these compounds on the hands of the person conducting the spraying. Finally, the results of a real case whereby solvent–solvent extraction did not provide the necessary sensitivity for extracting the capsaicin compounds on the garments of a victim of an alleged spraying and the SPME extraction provided the recovery and identification of the compounds is also presented.

Keywords: Capsaicin; Dihydrocapsaicin; Pepper sprays; Aerosol defense sprays; SPME

1. Introduction

Aerosol defense sprays are compounds that cause temporary incapacitation by producing sensory irritation. As a result, extreme discomfort or pain is associated with the areas affected. The nose, eyes, and respiratory tract are the primary organs affected. The three basic components, which make up aerosol defense sprays, are: the active ingredient (irritant), carrier, and propellant. The carrier acts as a vehicle in which the irritant is suspended or dissolved. Alcohol, organic hydrocarbons, and methylene chloride are examples of carriers used in sprays [1,2]. Propellants are used to expel the irritant from the canister. Commonly used propellants, include butane, propane, and compressed gases (e.g. carbon dioxide or nitrogen) [2].

Aerosol defense sprays have garnered significant media attention recently. Their use has ranged from accidental discharge at airports, causing the closure of entire concourses, to claims of abuse by law enforcement used in dispersing large groups of protesters. Nationally televised and reported cases of excessive use of defense sprays have led to greater attention by the public. The World Trade Organization protests in Seattle, the apprehension of immigrants at sea in Miami, discharge of pepper spray in a Chicago nightclub, and protesting the destruction of Northern California's old growth forests has increased the public's awareness concerning the use of defense sprays. Pepper spray cases have also found their way into criminal and civil courtrooms.

1.1. Oleoresin capsicum (OC)

The latest addition to the list of active agents in defense sprays is oleoresin capsicum, classified as an inflammatory agent and the primary analyte of interest in this paper. Exposure to oleoresin capsicum (OC) produces inflammation and swelling of the mucous membranes associated with the eyes, nose, and throat. OC's inflammatory properties reportedly

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render the agent more effective than chloroacetophenone (CN) and *o*-chlorobenzylidene malononitrile (CS) on violent, impaired, and mentally ill individuals. OC is a reddish-brown oily liquid derived from the plants of the genus capsicum, commonly referred to as hot peppers or chilies [3]. OC contains a group of compounds called capsaicinoids, which are responsible for the pungency associated with cayenne and other varieties of peppers. Capsaicinoids are the pharmacologically active and pain producing components of the hot pepper [4]. The active ingredient believed to be responsible for the irritative properties of OC is capsaicin. The second most common capsaicinoid is dihydrocapsaicin. Five naturally occurring analogues of capsaicin have been reportedly isolated from pepper plants [4] (see Fig. 1 for structures). OC contains over 100 distinct volatile components in addition to capsaicin [5]. The exact chemical composition of OC varies with the type of pepper, its age, and parts of the plant from which the extract is obtained.

The basic chemical structure of capsaicin and its analogues is a 4-hydroxy-3-methoxybenzylamide, connected to an acyl chain containing 10–11 carbon atoms. Pure capsaicin is insoluble in water, but soluble in oils and some solvents. Capsaicin forms crystals, has a melting point of 65 °C and a boiling point at 210–220 °C. Capsaicin has been used in neurological research to stimulate sensory nerves and also to treat bladder inflammation. It is also found in topical ointments used for arthritis and neuralgia. Capsaicin exerts its effect on the sensory nerves by interacting with the vanilloid receptor, promoting the release of substance P, as well as other cytokines [6]. The release of these cytokines from the peripheral sensory neurons causes a sensation of intense burning and pain.

The extraction and identification of these compounds has become increasingly important in forensic casework. Inadequate extraction procedures may lead to a conclusion of a false negative determination. A procedure that is capable of extracting and detecting very small quantities of these compounds from fabrics is required in order to identify capsaicin compounds in a pepper spray case. Previous efforts to extract capsaicin compounds from cotton, wool, nylon, and other fabrics have all involved liquid–liquid solvent extraction to recover capsaicin. Lewis et al. compared four solvents for the recovery of 2-chlorobenzylidenemalononitrile (CS) and capsaicin from cotton fabric followed by GC–MS analysis. [7]. These authors concluded that ethylacetate was the most efficient solvent, although all solvents investigated resulted in very low recovery rates when analyzed. A similar study performed by Pepler, used a solution of ethylacetate/heneicosane to extract spiked samples from cotton, denim, fake leather, chenille, wool and courduroy [8]. Capsaicin was successfully separated and identified by GC–MS analysis following extraction. This study noted that the fake leather material interfered with detecting trace levels. The study also included results on the persistence of capsaicin residue on fabric when samples were properly stored, although no recovery efficiencies were reported to assess the effectiveness of the solvent solution. Finally, Reilly et al. spiked cotton, wool, blended, and nylon fabric samples with pepper spray (containing ~0.5 mg capsaicinoids) and extracted each with *n*-butyl chloride followed by liquid chromatography–mass spectrometry (LC–MS) analysis [6]. This study demonstrated that 85% of the original concentrations of capsaicin was detectable by LC/MS for up to 6 months after storage. The main purpose of this study is to develop a sensitive method for the extraction of capsaicin compounds from fabrics and compare the utility and sensitivity of the method to previously methods of recovery.

Solid phase microextraction (SPME) has proven to be an important sample preparation technique for the analysis of forensic specimens due to the many advantages that the technique offers when it is applied to these types of samples [9]. SPME allows for multiple sampling, preservation of the sample, minimizes the risk of sample contamination due to the simplicity of the technique, is often faster than

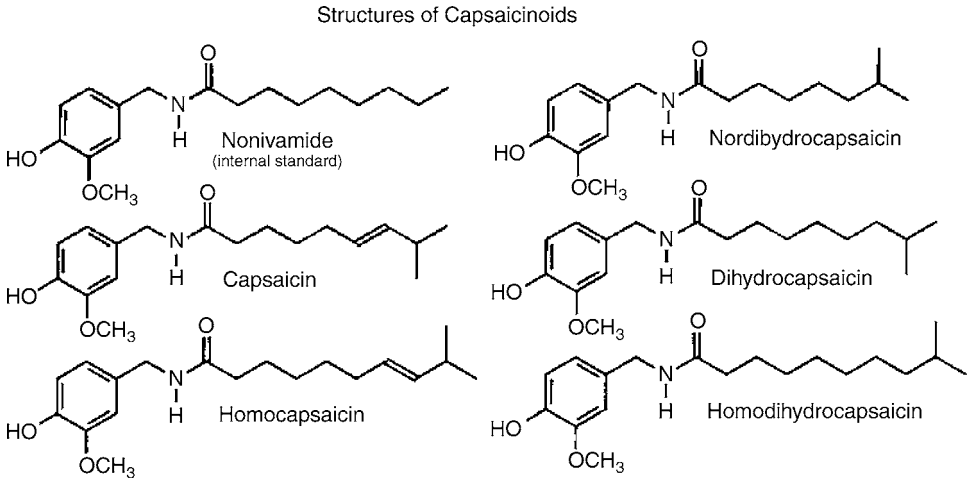

Fig. 1. Chemical structures of the capsaicinoids and nonivamide (IS).

traditional techniques and can be readily automated. Also, the lower detection limits generally afforded by SPME allow for confirmation of positive samples that previously went undetected. An additional benefit of SPME is the elimination of solvents which can save forensic science laboratories money and reduce or eliminate the risk of analysts being exposed to toxic substances. Forensic applications of SPME have included the analysis of ignitable liquid residues, often referred to as accelerants [10–18], trace residues of explosives [19–25], drugs and poisons from biological specimens [26–40], and other forensic applications.

2. Materials and methods

Capsaicin (8-methyl-*n*-vanillyl-6-nonenamide), dihydrocapsaicin (8-methyl-*n*-vanillylnonanamide), and nonivamide (*n*-vanillylnonamide) were purchased from Sigma–Aldrich Chemicals (St. Louis, Missouri). All solvents used were of analytical grade and purchased from Fisher Scientific (Fairlawn, NJ). Pepper spray canisters were purchased locally from various police supply vendors. Spices and topical products were purchased from local grocers and pharmacies.

The solid phase microextraction (SPME) holder and fibers (100 μm polydimethylsiloxane (PDMS), 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 85 μm carboxen™/polydi-methylsiloxane (CAR/PDMS), 70 μm carbowax®/divinylbenzene (CW/DVB), and 50/30 μm divinylbenzene/carboxen/PDMS (DVB/CAR/PDMS)) were purchased from Supelco (Bellefonte, PA). Autosampler vials, rubber septa, glass vials, and 13 mm × 100 mm disposable glass tubes were all purchased from Fisher Scientific (Pittsburgh, PA).

Analytical standards were prepared by weighing the appropriate quantity of capsaicin and dihydrocapsaicin using a Mettler AE 160 analytical balance to prepare a 1 mg/mL solution. Stock solutions of 1, 10, 100, 500, and 1000 ng/μL were prepared by serial dilution in methanol for each analytical technique used.

Analysis of capsaicin and dihydrocapsaicin was performed using an Agilent (Hewlett-Packard) 5890 equipped with a 5970 mass selective detector (Agilent Technologies, Palo Alto, CA). Separation of the analytes and internal standard was achieved using a J&W (Agilent Technologies, Palo Alto, CA) HP-5MS, 30 m × 0.25 mm i.d., 0.25 μm column. The gas chromatograph was equipped with an auto sampler with the injection volume set to 1 μL. The mass spectrometer was operated in the full scan mode from 40 to 400 amu. The chromatographic conditions included an initial oven temperature of 150 °C with no hold and a temperature ramp of 20 °C/min to 200°, followed by a temperature ramp of 10.0 °C/min, until the final temperature of 280 °C was reached and held for 5 min. The injection port and transfer line temperatures were set to 250 and 280 °C, respectively. The gas flow rate was set to 1 mL/min and a splitless injection was used.

2.1. Standards preparation

Capsaicin and dihydrocapsaicin standards were spiked onto cotton swabs by adding 100 μL of a methanol solution containing 0.1 μg of capsaicin and dihydrocapsaicin. For each method evaluated, cotton swabs spiked with standards were used. All samples were dried overnight in a fume hood at room temperature.

2.2. Liquid solvent extraction conditions

Methanol, ethylacetate, chloroform, and methylene chloride were each used as extraction solvents in order to determine the most effective solvent for the extraction of capsaicin and dihydrocapsaicin from cotton swabs. Twelve previously spiked cotton swabs that were prepared in triplicate for each solvent used contained 10 μg of capsaicin and dihydrocapsaicin. The swabs were placed individually into separate 13 mm × 100 mm test tubes. Two milliliter of each solvent were added to the test tube and sonicated for 20 min. The solvent was decanted and, with the aid of a pipette tip, the cotton swabs were pushed through the tip to express any remaining solvent from the swabs. To each test tube, 100 μL of 250 ng/μL of nonivamide was added as an internal standard (IS). The extracts were then reduced to dryness under a stream of nitrogen, and reconstituted with 100 μL of methanol. The reconstituted extract was then transferred to an autosample vial containing an insert for analysis. The final concentration of the internal standard in the reconstituted extract is 250 ng/μL.

2.3. SPME extraction and fiber selection

All the SPME fibers were conditioned according to manufacture's conditioning recommendations prior to use. Fiber selection was experimentally determined by comparing the results of the extraction of a known concentration of samples in duplicate for each fiber type. The cotton swabs that were previously spiked with capsaicin and dihydrocapsaicin and dried over night were used to determine the initial recovery of the analytes. The ends of the applicator sticks were cut off and each swab was placed individually in a 10 mL vial. Three milliliter of a 10% aqueous solution of methanol containing 25 μg/mL (ppm) nonivamide as an internal standard was added to the vial and sealed with a crimp cap. A ring stand was used to hold a SPME needle vertically above a water bath under sonication. The rubber septum on the 10 mL vial was pre-pierced to prevent bending of the SPME needle. The vial containing the swab and internal standard mixture was then placed inside a beaker and immersed in the water bath. The SPME holder was positioned above the vial and the needle was inserted into the pre-pierced hole. The SPME fiber was then directly exposed to the aqueous liquid under sonication for 20 min. The fiber was then retracted and the SPME needle was inserted into the injection port of the GC.

2.4. Preservation studies

Long-term persistence and preservation studies were conducted using various types of evidence packaging in order to determine the best packaging for storing evidence with capsaicin compounds. Duplicate sets of swabs were spiked for each evidence package evaluated. Metal cans, heat-sealed plastic bags, and brown bags were used as preservation packaging. Analyses were conducted at the following intervals after spiking with the analyte compounds: 12 h, 2, 3, and 4 months. Spiked samples were dried overnight, labeled and stored at room temperature.

2.5. Hand swab studies

Volunteers were asked to discharge pepper spray canisters at paper silhouettes in an open field. Various types of pepper sprays were used. Each volunteer was instructed to discharge the canisters according to the manufacturers directions several times in 1 s bursts. Hand swabs were collected prior to discharge, within 15 min after discharge, and at 30 min intervals for up to 1.5 h. Sterile cotton applicator swabs saturated with methanol were used to swab the left and right palms and fingertips of each volunteer.

3. Results and discussion

3.1. Solvent extraction

The chromatogram corresponding to the separation using solvent extraction is shown in Fig. 2. The components capsaicin, dihydrocapsaicin, and the internal standard are clearly separated by GC/MS analysis. The detection limits for capsaicin and dihydrocapsaicin in the split-less mode using a 1 μL injection volume were 7.6 and 7.0 ng, respectively. The extraction efficiencies of the organic solvents methanol, ethylacetate, methylene chloride, and chloroform, were compared. Methanol provided the best recovery (50–60%) for capsaicin followed by ethylacetate (44%), chloroform (35%), and methylene chloride (30%). Recovery of dihydrocapsaicin was considerably less than capsaicin for all solvents with methanol providing the best recovery (36%), followed by ethyl acetate (35%), chloroform (32%), and methylene chloride (28%). These recoveries compare favorably with previous reports of solvent extractions where the authors reported "a very low recovery rate" for similar solvents [7]. Calibration curves for the solvent extractions of capsaicin and dihydrocapsaicin were linear from 10 to 500 μg/mL (ppm), with correlation coefficients of 0.998 and 0.996, respectively.

3.2. SPME extraction

The comparison of the results for the extraction efficiency for the different SPME fibers is shown in Fig. 3. PDMS/DVB and DVB/CAR/PDMS resulted in nearly identical recovery for both capsaicin and dihydrocapsaicin. PDMS/DVB was selected over DVB/CAR/PDMS due to the fact that the PDMS/DVB produces less background and the fiber can be conditioned faster than the DVB/CAR/PDMS fiber. The calibration curves for capsaicin and dihydrocapsaicin using the PDMS/DVB fiber were found to be linear for the concentration range of 10–50 μg/mL, with correlation coefficients of 0.999 and 0.996, respectively. The recovery efficiency repre-

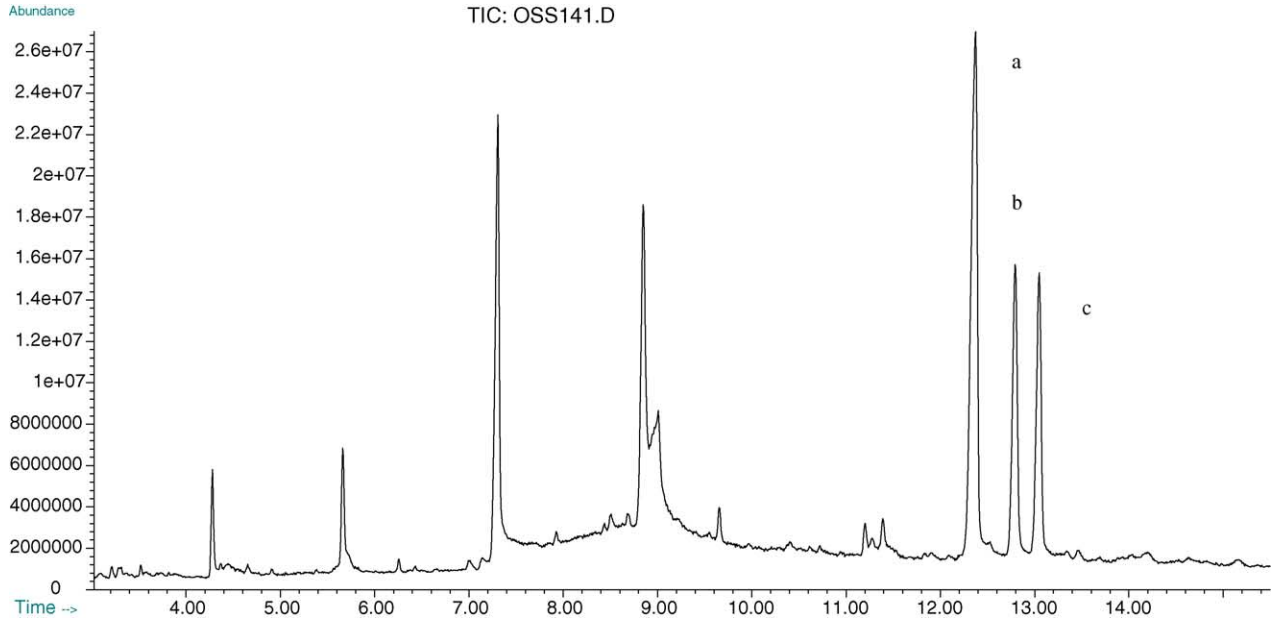

Fig. 2. Chromatogram of: (a) nonivamide, (b) capsaicin, and (c) dihydrocapsaicin from a spiked sample extracted with methanol.

Table 1
Persistence based on evidence packaging

Packaging	Compound	Month 2 (%)	Month 3 (%)	Month 4 (%)
Metal can	Capsaicin, dihydrocapsaicin	89.4, 100	71.0, 91.4	68.7, 71.4
Plastic bag	Capsaicin, dihydrocapsaicin	89.4, 97.4	90.6, 90.1	77.9, 54.5
Brown bag	Capsaicin, dihydrocapsaicin	53.5, 63.8	46.8, 63.8	33.6, 41.5

Amount recovered as percentage after time stored in packaging.

sents the initial recovery from swabs spiked with capsaicin and dried overnight in a fume hood and determined to be 77% for capsaicin, and 53% for dihydrocapsaicin using SPME. These recoveries are considerably better than previous reports using solvent extractions [7].

3.3. Persistence study

Table 1 summarizes the results of the persistence study for capsaicin and dihydrocapsaicin when different packaging materials were used. The results show that the use of certain evidence packaging contributed to the persistence of capsaicin. Metal cans that are typically used in the collection of fire debris evidence from suspicious fires had nearly identical concentrations to heat sealed plastic bags after 2 months of storage. After 2 months of storage in a brown bag, the concentration of capsaicin was nearly reduced to half. The concentrations after 4 months of storage in metal cans and heat sealed plastic were still generally 70% of the original concentration and above for capsaicin. Samples stored in brown bags resulted in lower concentrations throughout the duration of storage.

3.4. Hand swabs

Swabs were taken from the hands of volunteers 10 min after discharge of pepper spray canisters. SPME/GC/MS analysis was performed on the swabs within 24 h after collection in brown bags. The results are summarized in Table 2. Capsaicin or dihydrocapsaicin was detected on two out of seven volunteers whose hands were swabbed after the initial discharge.

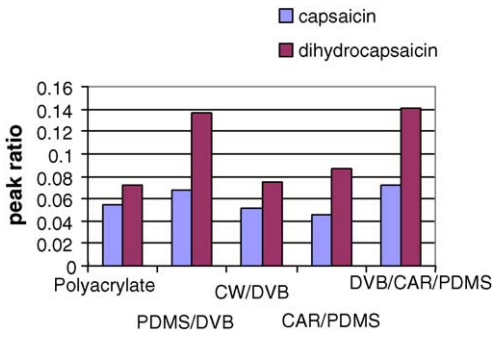

Fig. 3. Comparison of the results for the extraction efficiency for the different SPME fiber types for both capsaicin and dihydrocapsaicin.

Table 2
Results of hand swab extraction followed by SPME/GC/MS analysis of hands of volunteers that discharged aerosol products

Volunteer	Left hand	Right hand	Aerosol product
#1	–	–	Sabre red
#2	–	+	Sabre red/disabler
#3	–	+	911
#4	–	–	MK-4
#5	–	–	MK-4
#6	–	–	911
#7	–	–	Sabre red #2

All but two extractions resulted in negative results.

3.5. Case study

Clothing from a case involving the alleged use of pepper spray was submitted for analysis. Simultaneous extractions were performed using both the solvent and SPME techniques described above. Several sections of clothing measuring 1 cm × 1 cm were cut from the same area suspected of having residue and analyzed. The SPME/GC/MS procedure was sensitive enough to positively identify capsaicin and dihydrocapsaicin in these samples while solvent extraction failed to recover enough of either of these compounds.

4. Conclusions

Methanol was found to recover all three compounds of interest in this study from swabs with an efficiency of 50–60%. SPME extraction resulted in better recovery (>70%) and identification of lower quantities of the compounds of interest when compared to solvent extraction. The solvent extraction results in LODs of 7.6 and 7.0 ng for capsaicin and dihydrocapsaicin, respectively, but more sample preparation (multiple steps) is required than the SPME method and the extract contains more background substrate. The LODs found for the SPME are 1.08 and 0.73 ng for capsaicin and dihydrocapsaicin, respectively. Reduced sample preparation is required (extraction occurs in a sealed vial in a single step) and the extraction results in less background than with solvent while achieving good calibration and linearity.

Hand swabs can be of value in determining recent use of pepper sprays. Based on the results from this study, it appears that with normal use, residue from sprays is not likely to be deposited on the fingers of the person spraying. Further studies are needed to determine long-term persistence after use. One possible area of concern is being able

to distinguish between capsaicin found in aerosol sprays and capsaicin found in spices and medicinal ointments. While it is unlikely that the amount of capsaicin found in these products would elicit a positive response, the detection of solvents and propellants normally found in defense sprays would provide additional evidence that a defense spray has been used. Capsaicin can persist on clothing for a relatively long period of time if properly packaged and stored. Cans and heat sealed plastic bags provide the best packaging for the collection and preservation of this type of evidence. SPME/GC/MS was used to extract and analyze small sections of clothing containing residue from the spray of pepper spray formulations. In one case, containing very small amounts of residue, solvent extraction and SPME were both used as the extraction methods. The solvent extraction failed to recover capsaicin while the reported method using SPME recovered capsaicin.

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