# Identification of Odor Signature Chemicals in Cocaine Using Solid-Phase Microextraction–Gas Chromatography and Detector-Dog Response to Isolated Compounds Spiked on U.S. Paper Currency

**Kenneth G. Furton*, Yi-cheng Hong, Ya-Li Hsu, Tianying Luo, Stefan Rose,** and **John Walton**

Department of Chemistry and the International Forensic Research Institute (IFRI), Florida International University, University Park, Miami, FL 33199

## Abstract

**Solid-phase microextraction (SPME) combined with gas chromatography (GC) is optimized and applied to the analysis of street-cocaine samples followed by the field-testing of isolated chemicals using certified detector dogs. SPME proves to be a very sensitive and rapid method for isolating odor chemicals from street-cocaine samples. SPME–GC and activated charcoal strip (ACS)–SPME–GC signature profile methods are developed for the detection and quantitation of cocaine-odor chemicals, including the optimization of controllable variables such as fiber chemistry, extraction time, and desorption time. The volatile odor chemicals in representative illicit cocaine samples are identified and quantitated by the ACS–SPME–GC signature profile method and direct injection. Field tests with drug detector dogs show methyl benzoate to be the dominant signature odor chemical along with cocaine on U.S. currency at a threshold level of approximately 1–10 µg when spiked or when 10 ng/s methyl benzoate is diffused from polymer bottles, which is required in order to initiate an alert. No other substance studied initiated consistent responses by the drug dogs. The results indicate that the microgram levels of cocaine that have been reported on circulated U.S. currency are insufficient to signal an alert from law-enforcement trained drug detector dogs.**

## Introduction

The use of detector dogs in forensic science is widely accepted in the forensic science field and legal community, but until recently there have been few scientific studies to support their capabilities under real-world scenarios. The ability and reliability of detector dogs in the area of narcotics detection has recently been in question. The use of drug detector dogs alerting to currency associated with drug trafficking has become a point of contention because of reports that most money in circulation is tainted with trace levels of cocaine (1–6). A study of the cocaine contamination of circulated U.S. currency demonstrated that cocaine is present on money in general circulation, but not in a sufficient enough quantity that it cannot be easily removed by any method other than solvent washing (1). Paper currency contaminated by counting the money with micrograms of cocaine on the fingertips did yield detectable quantities of cocaine by a shaking method (1). No drugs other than cocaine have been reported to be widely found innocently contaminated on circulated U.S. currency. In one study, a trace of diacetylmorphine and tetrahydrocannabinol was reported on two bills out of 21, but no quantitation was performed (2). Unfortunately, the limited studies to date have relied on tiny sample sizes chaotically sampled from specific sites, which cannot be reliably extrapolated to represent the more than $500 billion in U.S. paper currency (20 billion bank notes) in circulation at any given time. The published studies on the total solvent extractable amount of cocaine from circulated U.S. currency have shown an average amount of 14.5 µg cocaine per bill from a total of 286 notes tested in four different studies (3–6). Also, because the average lifetime of U.S. paper currency is less than four years, these studies are currently out of date. Studies would have to be carried out on a regular basis taking into account the constant turnover of paper bills and thus the variability of any contamination levels as a function of time.

Nonetheless, these reports have resulted in contaminated money theories purporting that because of this widespread contamination any person carrying currency could potentially initiate a drug-dog alert. The legal significance of this theory ranges from reducing the probative value of drug-dog alerts to the complete elimination of a drug-dog alert if indeed drug dogs can alert to any amount of circulated paper currency. This contaminated money theory was relied upon by the 9th U.S. Circuit Court of Appeals in 1994, which upheld the dismissal of a forfeiture case stating that "… evidence that greater than 75% of all circulated money … is contaminated with drug residue distin-

* Author to whom correspondence should be addressed: email furtonk@fiu.edu.

Reproduction (photocopying) of editorial content of this journal is prohibited without publisher's permission.

guishes this case from our previous cases" (7). In the case of the United States *v.* $506,231 U.S. Currency (1997), the Seventh Circuit Court held that a trained-drug-dog alert to narcotics odor on currency was insufficient to establish probable cause for forfeiture based on the assertion that at least one-third of the currency in the United States is contaminated with cocaine (8). The questions raised are the same for any forensic specimen ranging from drugs to explosives, including exactly what chemicals are certified detector dogs being trained to alert to and what is their sensitivity and specificity. The present results are part of a long-term project including laboratory experiments and optimized field-testing techniques to identify and quantitate the active odor signature chemicals in illicit forensic specimens, which certified detector dogs use for detection (9–11).

The major goals of this work were to confirm the identity and quantity of the unique volatile odor chemical (or chemicals) of illicit cocaine that dogs use to detect cocaine employing solid-phase microextraction (SPME) combined with gas chromatography (GC), including the optimization of controllable variables such as fiber chemistry, extraction time, and desorption time. Additionally, field tests of the identified volatile odor chemicals were performed using spiked samples and polymer-based controlled delivery devices with certified law-enforcement narcotics detector dogs under different field conditions. In this work, we apply SPME to the recovery of street-cocaine odor signature chemicals confirmed by alerts to individual isolated chemicals using detector dogs. SPME has been shown to be a valuable technique for the analysis of a variety of forensic specimens because of its ability of multiple sampling, preserving the sample, minimizing the risk of sample contamination, fast analysis time, and the fact that it is readily automated (12–15). Also, the lower detection limits generally afforded by SPME allow for the confirmation of positive samples that previously went undetected. An additional benefit of SPME is the elimination of solvents that can save forensic science laboratories money and the reduction or elimination of the risk of analysts being exposed to toxic substances.

The purities of cocaine base and cocaine hydrochloride from the production of illicit cocaine are typically 80–95% and 80–97%, respectively. Pharmaceutical-grade cocaine may contain more than 99.5% cocaine, but it also has some coca-related impurities (16). The quantity and quality of the impurities in illicit cocaine (i.e., benzoic acid, anhydroecgonine methyl ester, anhydroecgonine, *trans*-cinnamic acid, ecgonine methyl ester, ecgonine, pseudoecgonine, tropacocaine, benzoylecgonine, norcocaine, beta-truxinic acid, alpha-truxillic acid, *cis*-cinnamoyl ecgonine methyl ester, *trans*-cinnamoyl ecogonine methyl ester, and *N*-formylcocaine) are different from sample to sample and batch to batch (17). We have also found methyl benzoate to be commonly present, which was not analyzed for in previous studies (10). Solvent residues are also commonly found in illicit cocaine hydrochloride samples during the precipitation process (the crystalline cocaine traps solvent molecules into its crystal lattice). Some of the common solvents that are found in illicit cocaine include methyl ethyl ketone, hexane, toluene, benzene, acetone, methylene chloride, xylenes, ethyl ether, cyclohexane,

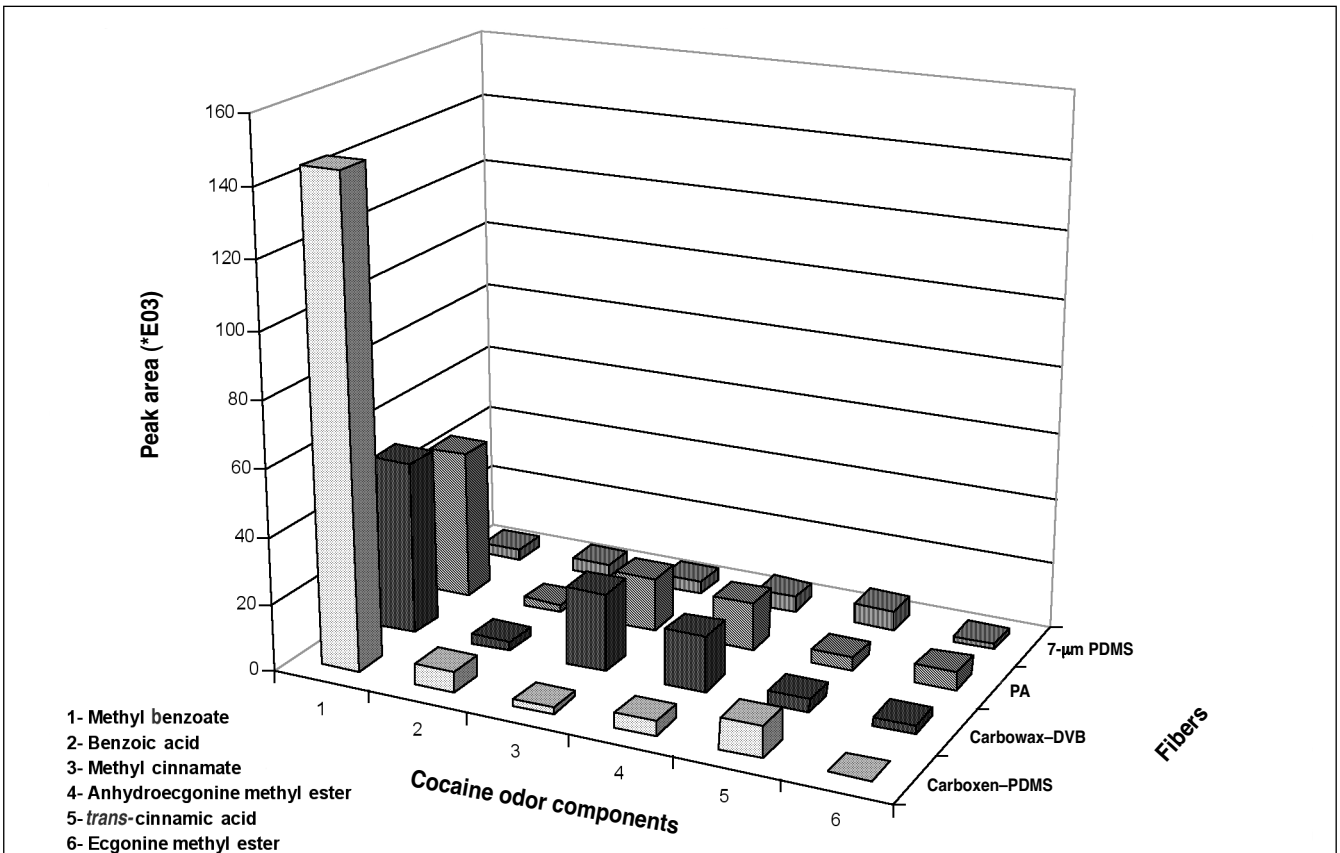


**Figure 1.** Comparison of the GC–FID response of cocaine odors extracted by various fibers for 12 h.

and ethyl acetate (18). The chromatographic impurity signature profile analysis of cocaine (including relatively high-molecular-weight components) has proven to be useful in matching cocaine exhibits assumed to originate from the same source or batch (15). Only the volatile odor signature chemicals were the focus of this study. The limited olfactory psychophysical studies to date have involved either laboratory tests with olfactometers in which dogs were trained and then tested using sniffer ports or "search-and-find" procedures with dogs trained for police work (19). This latter type of test was used in this study.

## Experimental

Methyl benzoate, propyl benzoate, and methyl *trans*-cinna-

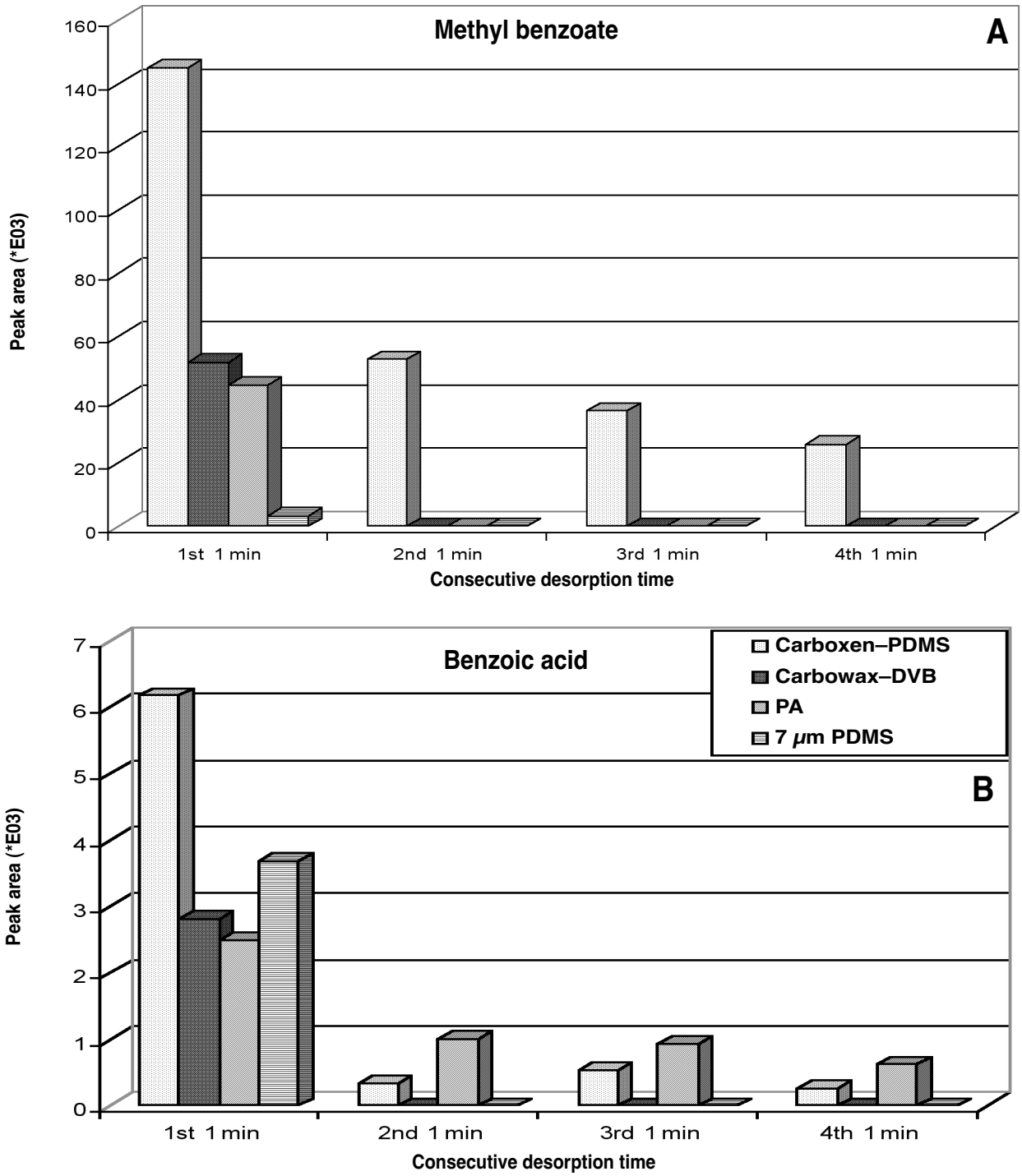


**Figure 2.** GC–FID response for consecutive 1-min desorptions of (A) methyl benzoate and (B) benzoic acid from Carbon–PDMS, Carbowax–DVB, PA, and PDMS–7-µm SPME fibers.

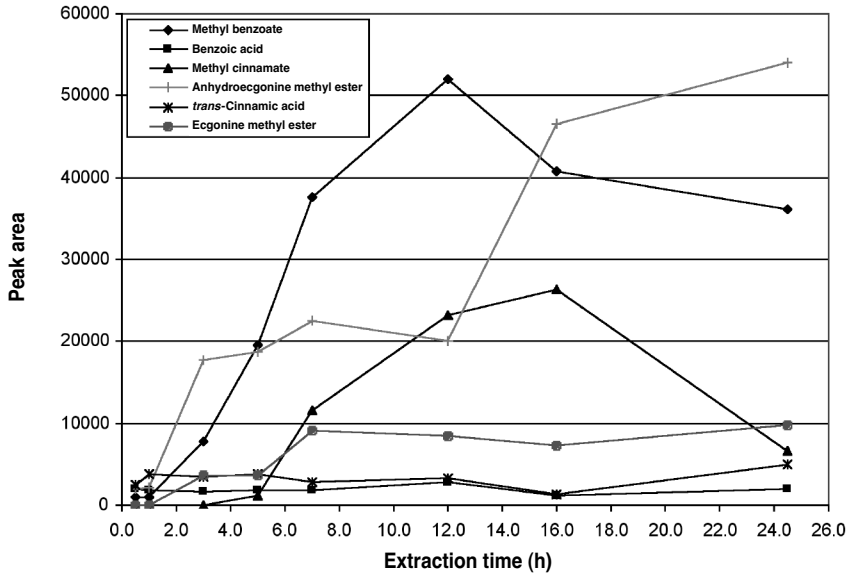


**Figure 3.** GC–FID response of cocaine odors extracted by Carbowax–DVB as a function of time.

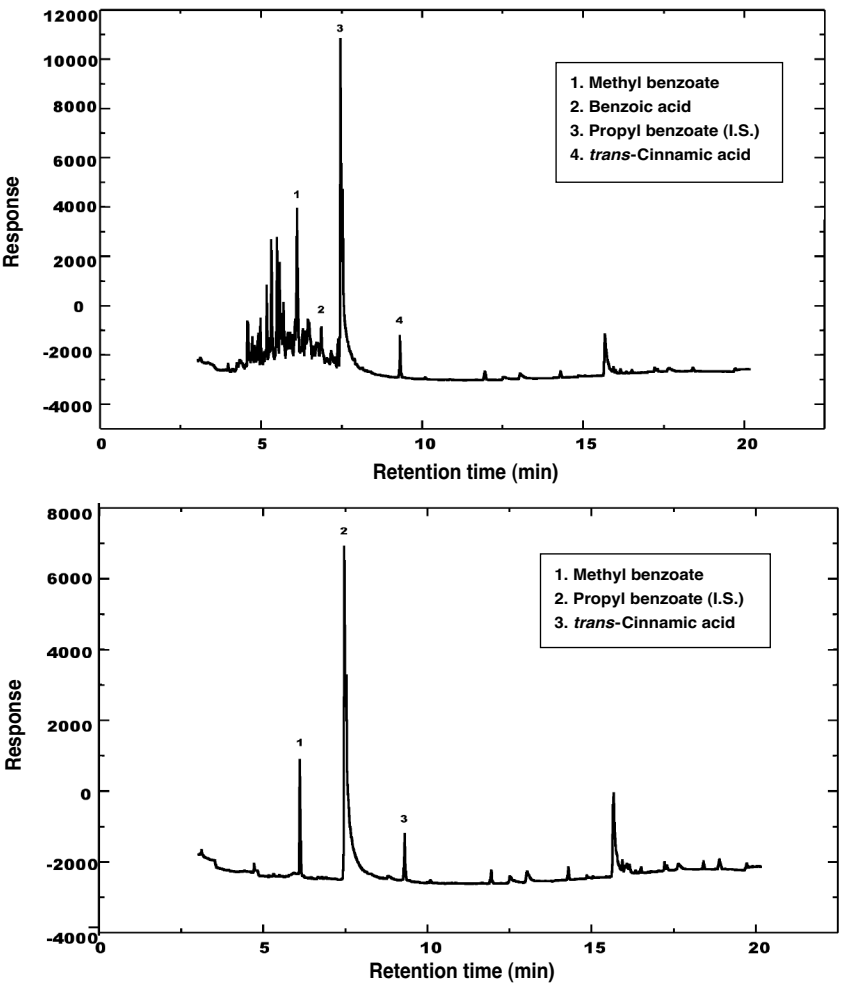


**Figure 4.** Headspace SPME–GC–FID chromatograms of cocaine odor chemicals from two different street cocaine samples.

mate were purchased from Aldrich Chemical Co. (Milwaukee, WI). *trans*-Cinnamic acid, tropacocaine, and cocaine base were purchased from Sigma Chemical Co. (St. Louis, MO). Ecgonine methyl ester (1000 µg/mL in acetonitrile) and anhydroecgonine methyl ester (1000 µg/mL in acetonitrile) were purchased from Radian. All other chemicals were purchased from Fisher Scientific. Street-cocaine samples were supplied by the Miami-Dade Police Department (Miami, FL). Paint cans were obtained from American International Containers (Miami, FL). DFLEX active charcoal strips (ACSs) were obtained from Albrayco Labs Inc. (Cromwell, CT). A Hewlett-Packard (HP) (Wilmington, DE) GC (HP 6890) coupled with a flame ionization detector (FID) or mass spectrometer (MS) (5973) and a J&W Scientific (Folsom, CA) DB-5MS capillary column (30-m × 0.25-mm i.d., 0.25-µm film thickness) were used in the SPME–GC detection. The fiber from the sampling process was introduced to the split/splitless injection port of the GC, in which the analytes from the fiber were thermally desorbed. The temperature of the injection port and the detection port were 250°C and 300°C, respectively. For the GC–MS experiments the transfer line was kept at 280°C. The temperature of the oven was programmed at 45°C and held for 1 min, then it was ramped at 20°C/min to 160°C and held for 0 min, 2°C/min to 170°C and held for 0 min, and 15°C/min to 250°C and held for 3 min. A purge delay time for venting was set for 2 min. The flow rate of the carrier gas (helium) was 1 mL/min.

SPME fibers with different polymeric coatings including Carboxen–poly(dimethylsiloxane) (PDMS) (75 µm), poly(ethylene glycol)–poly(divinylbenzene) (Carbowax–DVB) (65 µm), poly(acrylate) (PA) (85 µm), PDMS (7 µm), PA (85 µm) fibers, and an SPME holder were purchased from Supelco Inc. (Bellefonte, PA). Each fiber was preconditioned in the GC injection port prior to use according to the manufacturer's recommendations (250–320°C for 0.5–2 h). For the cocaine-odor sampling, each SPME fiber was set up to extract the headspace of mixtures of cocaine odors prepared from working solutions at room temperature for 12 h. They were then transferred to the GC injection port for thermal desorption for successive 1-min desorptions. The Car-

bowax–DVB fiber was used to extract the headspace above the cocaine-odor standard mixture (i.e., the working solution) at different extraction times: 0.5, 1, 3, 5, 7, 12, 16, and 24.5 h. GC–FID analysis was carried out immediately after each extraction.

For the street cocaine sampling, a 200-ppm propyl benzoate solution was used as the internal standard. A charcoal strip together with its metal support and protective Teflon membrane was placed into a quart paint can followed by 1 g of street cocaine contained in a 4-mL glass vial uncapped into the same can. The can was then sealed tightly with a hammer. After 24 h, the can was opened and the charcoal taken out. The ACS was transferred into a 15-mL sample glass vial after the outer protective Teflon membrane was cut off. Four milliliters of the internal standard solution in acetonitrile was added in order to extract the analytes absorbed on the charcoal strip out into the solvent. Five-hundred microliters of this extract was pipetted into a 2-mL GC autosampler vial. The Carbowax–DVB was set up to extract the headspace of the acetonitrile extract for 1.5 h. The fiber was then thermally desorbed in the GC injection port for 1 min. Perfume analysis was performed by headspace SPME–GC–MS sampling for 5 min followed by a 1-min desorption into the injection port at 250°C.

For the detector-dog tests, precleaned and oven-dried 9-inch round galvanized steel boxes with six small holes on the top containing one-dollar denominations of U.S. currency were placed in test areas with carefully monitored humidity and temperature. Solutions containing different amounts of cocaine and byproducts were prepared in chloroform solutions and delivered to the currency at least 20 min before testing. This time allowed the chloroform to completely evaporate without significantly reducing the amount of odor chemicals present. The U.S. paper currency was spiked with successively increasing amounts of pharmaceutical-grade cocaine, street cocaine, and volatile cocaine byproducts, including methyl benzoate, benzoic acid, ecgonine, ecgonine methyl ester, *trans*-cinnamic acid, methyl *trans*-cinnamate, benzaldehyde, and ethylbenzoate. What we refer to as pharmaceutical-grade cocaine was actually highly purified cocaine from Sigma. In addition, ten different 400- to 650-µL capacity microcentrifuge tubes were tested as controlled delivery devices for the odor chemical methyl benzoate. Two tubes with delivery rates (studied over a 5-mo period) of 21 ng/s (Fisher snap-cap polyethylene tubes, 0.4 mL) and 1.5 ng/s (Corning polypropylene tubes, 0.5 mL) were chosen for testing. In order to eliminate possible cross-contamination, the negative control boxes were delivered to the test field by different scientists than those who handled the spiked containers. The boxes were handled with precleaned metal tongs. The dog handlers did not know the contents of the containers and were simply instructed to have their dogs sweep the test field for controlled substances and identify which containers contained the odor of controlled substances as indicated by their detector dog's response. Each different detector dog team was given an

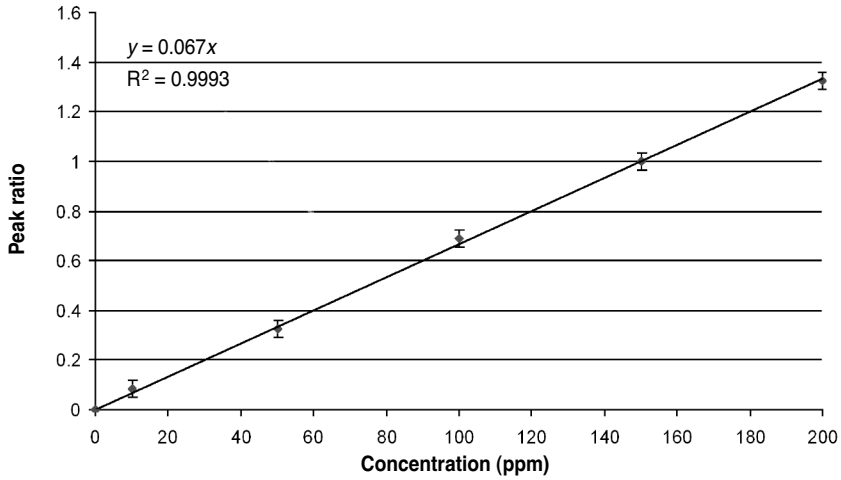


**Figure 5.** Calibration curve for methyl benzoate extracted with the Carbowax–DVB fiber sampling for 90 min at room temperature (20°C).

**Table I. Relative Concentrations of Cocaine-Odor Compounds in Street Cocaine Samples (%, w/w)**

| Compound | Case 1 | Case 2 | Case 3 | Case 4 | Average | Range |
|---|---|---|---|---|---|---|
| Methyl benzoate | 0.010 | 0.018 | 0.036 | 0.013 | 0.020 | 0.010–0.036 |
| Benzoic acid | 3.7 | 0.51 | 1.7 | 0.20 | 1.53 | 0.20–3.7 |
| Methyl *trans*-cinnamate | 0.20 | 0.15 | 0.058 | 0.080 | 0.12 | 0.058–0.20 |
| Anhydroecgonine methyl ester | 8.5 | 10.8 | 2.6 | 3.2 | 6.28 | 2.6–10.8 |
| *trans*-Cinnamic acid | 0.30 | 0.093 | 0.29 | 0.17 | 0.21 | 0.093–0.30 |
| Ecgonine methyl ester | 1.9 | 2.3 | 1.50 | 1.50 | 1.80 | 1.5–2.3 |

**Table II. Percent Methyl Benzoate Formed in Cocaine Specimens in the Presence and Absence of Solvents**

| Cocaine sample | Initial | 1 week | 2 weeks |
|---|---|---|---|
| Solid pharmaceutical-grade cocaine base | 0.00013% | 0.00015% | 0.00010% |
| Solid pharmaceutical-grade cocaine HCl | 0.00069% | 0.00068% | 0.00061% |
| 10,000-ppm cocaine base in chloroform | 0.00070% | 0.00013% | 0.00015% |
| 10.000-ppm cocaine HCl in chloroform | 0.00049% | 0.00045% | 0.00059% |
| 10,000-ppm cocaine HCl in methanol | 0.0048% | 0.0019% | 0.019% |
| 10,000-ppm cocaine base in methanol | 0.034% | 3.6% | 6.2% |

identifying number, which is included in the tables summarizing the results. Temperature, humidity, and time were monitored over the whole test period.

## Results and Discussion

A comparison of GC–FID responses of the cocaine-odors mixture extracted by Carboxen–PDMS, Carbowax–DVB, PA, and PDMS at room temperature for 12 h is shown in Figure 1. Higher molecular-weight standards including tropacocaine and cocaine were not extracted by headspace SPME with the fibers tested. As a general guideline, the chemical nature of a target analyte determines the type of coatings used. As expected, the PDMS fiber showed the lowest response because it is a nonpolar phase and thus has a lower retention of polar compounds such as the cocaine-odor chemicals mentioned. The PA phase however is suitable for more-polar compounds. As can be seen, its responses dramatically increased compared with that for the PDMS fiber. The Carboxen–PDMS proved to be an optimal adsorption fiber chemistry for methyl benzoate; however, it took significantly longer time for methyl benzoate to be released from Carboxen–PDMS than all the other three fibers (as seen in Figure 2). Although methyl benzoate was released completely from the other three fibers within 1 min at 250°C, approximately 15% was still trapped on the Carboxen–PDMS even after a fourth 1-min desorption. Similarly, it took multiple 1-min desorptions for the other analytes and fibers, including PA and Carboxen–PDMS requiring more than 4 min to completely desorbed benzoic acid (as shown in Figure 2). Overall, of all the fibers tested, Carbowax–DVB was chosen for further study because it extracted all of the cocaine odors efficiently (with high sensitivity) and released them quickly (within 1 min), minimizing possible carryover problems. Subsequently, newer blended fibers (including Carboxen–DVB) have great potential as long as sufficient desorption and fiber-conditioning times are employed.

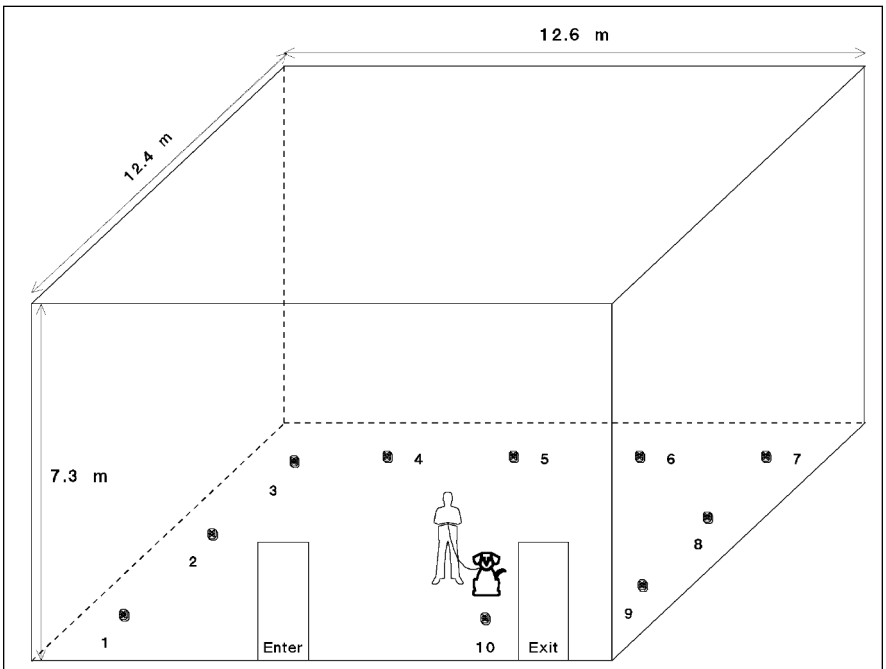


**Figure 6.** Layout of a typical test room with metal boxes containing an unknown chemical (or chemicals).

The headspace SPME extraction of the cocaine-odor chemicals as a function of time at room temperature using the Carbowax–DVB fiber is shown in Figure 3. The acidic components benzoic acid and *trans*-cinnamic acid

**Table III. Results of Indoor Detector-Dog Tests with Cocaine Added to U.S. Currency and Added Amounts of Various Identified Cocaine Byproducts***

| Spiked cocaine | Spiked byproducts | Nonalert by K-9 No. | Alert by K-9 No. |
|---|---|---|---|
| 0 | 0 | 1,4,6,8,9,10,11,12 | |
| 0.1 mg cocaine HCl | 10 µg ecgonine | 1,4,6,8,9,10,11,12 | |
| 0.1 mg cocaine HCl | 10 µg ecgonine methyl ester | 1,4,6,8,9,10,11,12 | |
| 0.1 mg cocaine HCl | 10 µg benzoic acid | 1,4,6,8,9,10,11,12 | |
| 0.1 mg cocaine HCl | 0 | 1,3,4,6,7,8,10,11,12,14,15 | |
| 0.1 mg cocaine HCl | 1 µg methyl benzoate | 1,3,4,7,8,11,15 | 6,10,12,14 |
| 0.1 mg cocaine HCl | 10 µg methyl benzoate | 4,15 | 1,3,6,7,8,10,11,12,14 |
| 1 g cocaine HCl | 0 | 1,3,4,7,10,11,12,14,15 | 6 |
| 0 | 0 | 1,4,6,9,10,11,12 | |
| 0.1 mg cocaine base | 10 µg *trans*-cinnamic acid | 1,4,6,9,10,11,12 | |
| 0.1 mg cocaine base | 10 µg methyl trans-cinnamate | 1,4,6,9,10,11,12 | |
| 0.1 mg cocaine base | 10 µg ethyl benzoate | 1,4,6,9,10,11,12 | |
| 0.1 mg cocaine base | 1 µg methyl benzoate | 1,3,4,7,11,14,15 | 6,10,12 |
| 0.1 mg cocaine base | 10 µg methyl benzoate | 7 | 1,3,4,6,10,11,12,14 |
| 1 g cocaine base | 0 | 1,3,4,6,7,8,10,11,14,15 | 12 |

* Average temperature was 20°C. Average relative humidity was 59.4%. K-9 number was that assigned to the next individual certified drug detector dog participating in the research study.

reached maximum recovery within an hour, while others including anhydroecgonine methyl ester continued to increase up to the maximum time studied (24 h) and yet others (including methyl benzoate and methyl *trans*-cinnamate) reached a maximum in 12–14 h and then decreased presumably because of the displacement effect reported previously (15). Street-cocaine samples were analyzed by the two-step extraction method using passive headspace concentration with ACSs followed by acetonitrile elution and headspace SPME–GC analysis extracted by Carbowax–DVB. This method allows for the sensitive, inexpensive, and convenient analysis of drug odor chemicals from case samples and detector-dog training aids. The GC–FID chromatograms of two representative street-cocaine extractions are demonstrated in Figure 4 with the propyl benzoate internal standard peak seen at 7.5 min. Methyl benzoate and *trans*-cinnamic acid were extracted from all of the samples tested, and benzoic acid was detected in one of four tested samples.

For studying the linearity of the method, the extraction time was controlled at 1.5 h because this was the shortest time available to extract all the compounds from the mixture. An equal amount of propyl benzoate was spiked in each solution as the internal standard, and the calibration curves were drawn by plotting the average peak ratio of each individual compound over the internal standard against the concentration of that compound. The method was linear for most analytes studied within the concentration range of 10 to 200 ppm. The acidic components benzoic acid and *trans*-cinnamic acid demonstrated the poorest linearity. Triplicate extractions carried out for each concentration level for methyl benzoate using the Carbowax–DVB fiber is shown in Figure 5 with excellent linearity over the entire range studied. The precision of replicate samplings was generally within 5% of the relative standard deviation (RSD). The relative concentrations of cocaine-odor chemicals for the samples studied are shown in Table I using the direct injection of acetonitrile extracts. In general, the cocaine-odor concentrations varied widely with methyl benzoate from 0.010% to 0.036% (w/w) or 31 to 59 ppm using 90-min headspace SPME extractions. These values are approximately two orders of magnitude higher than that observed for pharmaceutical-grade cocaine with methyl benzoate ranging from 0.00010% to 0.000069% as seen in Table II. We have also found that methyl

**Table IV. Results of Outdoor Detector-Dog Tests of Cocaine Samples (Pharmaceutical-Grade and Street Samples) or Various Identified Cocaine Byproducts***

| Cocaine HCl | Methyl benzoate | Added byproduct | Nonalert by K-9 No. | Alert by K-9 No. |
|---|---|---|---|---|
| 0 mg | 0 µg | 0 ng ($CHCl_3$ alone) | 23,24,3,12,23,24,25,26,27,28,3,6, 12,16,18,23,24,25,28,29 | |
| 1 g† | 0 µg | 0 ng | 23,3,12,23,24,25,26,27,28, 16,18,23,24,25,28,29 | 24,3,6,12 |
| 0 mg | 0 µg | 1 mg *trans*-cinnamic acid | 23,24,3,12,23,24,25,26,27,28, 3,6,12,16,18,23,24,25,28,29 | |
| 0 mg | 0 µg | 1 mg benzoic acid | 23,24,3,12,23,24,25,26,27,28,3, 6,12,16,18,23,24,25,28,29 | |
| 0 mg | 1 µg | 0 µg | 23,24,12,23,24,25,26,27,28,3,6, 12,16,18,23,24,25,28,29 | 3 |
| 0 mg | 1 µg | 1 mg *trans*-cinnamic acid | 23,24,3,12,23,24,25,26,27,28,3, 6,12,16,18,23,24,25,28,29 | |
| 0 mg | 1 µg | 1 mg benzoic acid | 23,24,3,23,24,25,26,27,28,3, 6,12,16,18,23,24,25,28,29 | 12 |
| 0 mg | 10 µg | 0 µg | 23,25,26,27,28,3,12,16, 23,24,25,28 | 23,24,3,12,24,6,18,29 |
| 0 mg | 0 µg | 10 µg benzaldehyde | 3,12,23,24,25,26,27,28 | |
| 0 mg | 1 µg | 1 µg benzaldehyde | 3,6,12,16,18,23,24,25,28,29 | |
| 0 mg | 0 µg | 3 g Sigma Pseudo cocaine | 27 | 23,24,3,12,23,24,25,26,28,3, 6,12,16,18,23,24,25,28,29 |
| 0 mg | 250 µg | Polymer 1 (1.5 ng/s) | 3,6,12,16,18,23,24,25,28,29 | |
| 0 mg | 250 µg | Polymer 2 (21 ng/s) | 12,28,3,6,16,18,24,28,29 | 3,23,24,25,26,27,12,23,25 |
| 1 g‡ | 0 µg | 0 ng | 6,25,28,29 | 3,12,16,18,23,24 |
| 0 mg | 0 µg | perfume with methyl benzoate | 23,24 | |

* Average temperature was 30°C. Average relative humidity was 82%.
† Sigma pharmaceutical-grade cocaine with 0.0007% methyl benzoate quanitated.
‡ 15-year-old street-cocaine sample with purity of 85.9% cocaine quantitated.

benzoate readily forms in cocaine formulations over a period of time when exposed to methylating solvents such as methanol, but does not form to any appreciable extent in pharmaceutical-grade cocaine or chloroform (the solvent used to prepare solutions in this study) (as seen in Table II).

Table III summarizes indoor tests for eight different detector dogs using a typical indoor test area shown in Figure 6. The only chemical tested, which elicited a consistent response, was methyl benzoate at a level of 1 to 10 µg. The presence of cocaine hydrochloride or cocaine base does not appear to influence the threshold seen. In fact, testing with 1 g of cocaine hydrochloride and 1 g of cocaine base (Sigma) did not elicit responses from most of the dogs tested presumably because of the very low levels of methyl benzoate (from Table II). Table IV summarizes outdoor field tests for 14 different detector dogs (some more than once) using a typical outdoor test (shown in Figure 7). Again, the only chemical tested that elicited a consistent response was methyl benzoate at a consistent level of 10 µg. In addition, Sigma Pseudo cocaine (which was confirmed to contain primarily methyl benzoate using SPME) and a polymer bottle delivering methyl benzoate at a rate of 21 ng/s elicited consistent responses from the detector dogs tested. Interestingly, 1 g of a 15-year-old street cocaine sample was confirmed to elicit responses from the majority of the detector dogs, and 1 g of the pharmaceutical-grade cocaine hydrochloride did not (as seen previously).

Figure 8 summarizes the averages of 245 measurements for indoor field tests spiking 0.01, 0.1, 1, 10, and 100 µg of methyl benzoate in the presence of 0.1 mg of cocaine HCl or cocaine base (10) and demonstrates the sigmoid curve characteristic of biological dose-response curves. Because the special sense of smell is a ligand-receptor mediated biologic process (20), the law of mass action should apply and a dose-response relationship should exist (21). One method used to quantitate a drug dose-response relationship is to plot the logarithm of the drug concentration against the biologic response (21). In this case the concentration of methyl benzoate is plotted against the behavioral response of a drug dog (i.e., the dog alerting). The data graphed demonstrate the results of experiments designed to determine the threshold of the detection of methyl benzoate. The results suggest that a dose-response relationship exists between methyl benzoate and drug dogs tested for alerting and that the effective dose for 50% of the animals tested is approximately 1 µg of methyl benzoate. These results have been corroborated with additional field tests using different numbers, types, and arrangements of delivery devices. Overall, more than 120 field tests have been performed in a similar manner testing more than 28 different detector dogs from 10 different local, state, and federal agencies. The conclusions from this study support the U.S. Patent "Available Odor of Cocaine", which is described as "a method and product for providing the aroma of cocaine to the olfactory senses by volatilizing methyl benzoate … whereby the aroma of street cocaine is perceived" (22).

The finding that methyl benzoate, rather than the cocaine itself, is responsible for alerting drug detector dogs is not surprising based on our current knowledge of how detection dogs alert to forensic specimens. When a dog is trained to alert to an item (such as a human body, explosives, munitions, accelerants, drugs, and currency), the dog is often being trained to alert to a scent associated with the item rather than the item itself. That scent is commonly composed of volatile compounds or classes of compounds, which are detected by the dog. If, indeed, drug detector dogs use one dominant chemical to find the controlled substance cocaine, one natural question is are there noncontrolled substances that have similar odor signatures. We have tested numerous potential interfering substances and to date have only found that some fragrances contain methyl benzoate (and only in relatively small amounts). Figure 9 shows the SPME–GC–MS analysis of one of 10 perfume samples found to

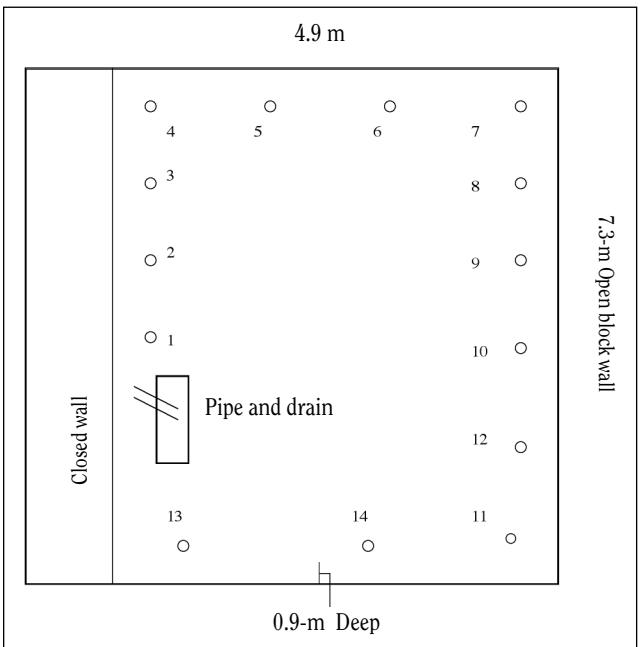


**Figure 7.** Layout of outdoor test area with metal boxes containing cocaine samples (pharmaceutical-grade and street samples) or various identified cocaine byproducts.

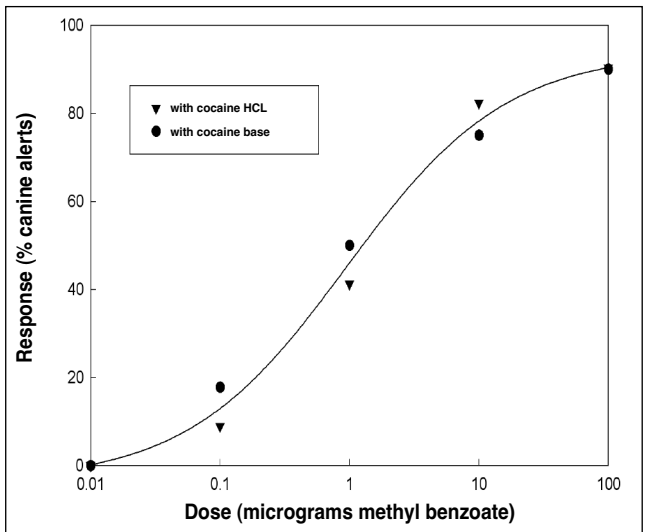


**Figure 8.** Percent of tested drug detector dogs alerting to various amounts of methyl benzoate spiked onto U.S. currency in the presence of 0.1 mg of cocaine or 0.1 mg of cocaine hydrochloride (averages of a 245-test total).

contain 3% methyl benzoate (relative to the other volatile components). Although such an item has a minority component in common with street cocaine in which it is a majority component; overall, the odors are quite different and the limited field tests included in Table IV show that certified detector dogs can readily distinguish these odors.

Overall, this study demonstrates that SPME is a powerful method for studying drug odor chemicals, and the results confirm that drug detector dogs alert to the common volatile cocaine byproduct methyl benzoate rather than to the cocaine itself. None of the dogs tested alerted to byproducts other than methyl benzoate, and the majority did not alert to pharmaceutical-grade cocaine even at the highest levels tested of 1 g. Because this level is some 100,000 times greater than that reported on circulated currency, it is not plausible that innocently contaminated U.S. currency contains sufficient enough quantities of cocaine and associated volatile chemicals to signal an alert from a properly trained drug detector dog.

## Acknowledgments

The authors would like to thank Sgt. Wesley Dallas of the Metro-Dade Police Department Narcotics Bureau (Miami, FL) for coordinating the testing of the drug detector dogs. Partial financial support from Supelco is also gratefully acknowledged.

## References

1. R. Aaron and P. Lewis. Cocaine residues on money. *Crime Lab. Digest* **14(1):** 18 (1987).
2. R. Sleeman, F. Burton, J. Carter, D. Roberts, and P. Hulmston. Drugs on money. *Anal. Chem.* **72(11):** 397A–403A (2000).
3. "Crime and Chemical Analysis" in Research news. *Science.* **March:** 1555 (1989).
4. J. Oyler, W.D. Darwin, and E.J. Cone. Cocaine contamination of United States paper currency. *J. Anal. Toxicol.* **20(July/August):** 213–16 (1996).
5. D. Song, S. Zhang, and K. Kohlhof. Determination of a trace amount of cocaine on a bank note by gas chromatography—positive-ion chemical-ionization mass spectrometry. *J. Chromatogr.* **731:** 355–60 (1996).
6. A. Negrusz, J.L. Perry, and C.M. Moore. Detection of cocaine on various denominations of United States currency. *J. Forensic Sci.* **43(3):** 626–29 (1998).
7. United States *v.* U.S. Currency, $30,060.00. 9th Circuit Cal., WL 613703, 1994.
8. United States *v.* $506,231 U.S. Currency. 7th Circuit, 125 F. 3d 442, 1997.
9. K.G. Furton, Y.-L. Hsu, T. Luo, N. Alvarez, and P. Lagos. "Novel Sample Preparation Methods and Field Testing Procedures Used to Determine the Chemical Basis of Cocaine Detection by Canines". In *Forensic Evidence Analysis and Crime Scene Investigation.* J. Hicks, P. De Forest, and V.M. Baylor, Eds. The International Society of Optical Engineering, Washington, D.C., 1997, Vol. 2941, pp. 56–62.
10. K.G. Furton, Y.-L. Hsu, T. Luo, A. Norelus, and S. Rose. "Field and Laboratory Comparison of the Sensitivity and Reliability of Cocaine Detection on Currency Using Chemical Sensors, Humans, K-9s and SPME/GC/MS/MS Analysis". In *Investigation and Forensic Science Technologies* Kathleen Higgins, Ed. The International Society of Optical Engineering, Washington, D.C.,1999, Vol. 3576, pp. 41–46.
11. K.G. Furton and L.J. Myers. The scientific foundation and efficacy of the use of canines and chemical detectors for explosives. *Talanta* **43(3):** 487–500 (2001).
12. R.F. Mindrup. Solid phase microextraction simplifies preparation of forensic, pharmaceutical, and food and beverage samples. *Chem. New Zealand* **3:** 21–23 (1995).
13. J.R. Almirall and K.G. Furton. "Forensic and Toxicology Applications." In *Solid Phase Microextraction: A Practical Guide.* S.A. Scheppers Wercinski, Ed. Marcel Dekker, New York, NY, 1999, Chapter 7, pp. 203–16.
14. K.G. Furton, J. Wang, Y.-L. Hsu, J. Walton, and J.R. Almirall. The use of solid-phase microextraction–gas chromatography in forensic analysis. *J. Chromatogr. Sci.* **38(7):** 297–306 (2000).
15. K.G. Furton, J.R. Almirall, M. Bi, J. Wang, and L. Wu. Application of solid-phase microextraction to the recovery of explosives and ignitable liquid residues from forensic specimens. *J. Chromatogr.* **885:** 419–32 (2000).
16. J.F. Casale and R.F.X. Klein. Illicit production of cocaine. *Forensic Sci. Review* **5(2):** 96–107 (1993).
17. J.F. Casale and R.W. Waggoner. A chromatographic impurity signature profile analysis for cocaine using capillary gas chromatography. *J. Forensic Sci.* **36(5):** 1312–30 (1991).
18. D.R. Morello and R.P. Meyer. Qualitative and quantitative determination of residual solvents in illicit cocaine HCl and heroin HCl. *J. Forensic Sci.* **40(6):** 957–63 (1995).
19. D.H. Passe and J.C. Walker. Odor psychophysics in vertebrates. *Neurosci. Behavioral Reviews* **9:** 431–67 (1985).
20. A.C. Guyton. *Textbook of Medical Physiology*, 7th ed. W.B. Saunders Company, Philadelphia, PA, 1986, pp. 748–51.
21. A. Goodman Gilman, T.W. Rall, A.S. Nies, and P. Taylor. *The Pharmacologic Basis of Therapeutics*, 8th ed. Pergamon Press, 1990, pp. 66–69.
22. W.J. Woodford. U.S. Patent 4,260,517. "Available Odor of Cocaine". April 7, 1981.

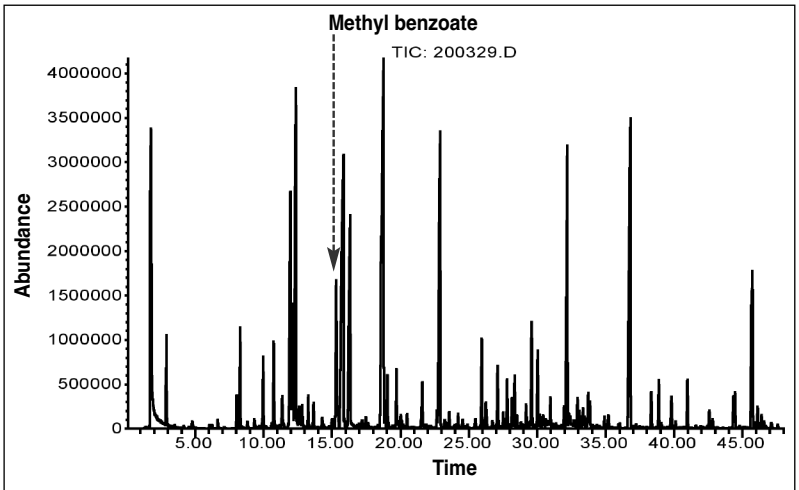


**Figure 9.** Headspace SPME–GC–MS analysis of a perfume sample (Jovan) with methyl benzoate identified as 3% of the total volatiles.

Manuscript accepted November 6, 2001.