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Development of Solid Phase Microextraction Methods for Contraband Drugs

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DEVELOPMENT OF SOLID PHASE MICROEXTRACTION METHODS FOR CONTRABAND DRUGS

by

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ABSTRACT

DEVELOPMENT OF SOLID PHASE MICROEXTRACTION METHODS FOR CONTRABAND DRUGS

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Old Dominion University, 1997
Director: Dr. Edward J. Poziomek

The objective of this study is to develop analytical methods for studying contraband drugs at nanogram levels and to demonstrate the utility of the methods. A method which combines solid phase microextraction with ion mobility spectrometry (SPME-IMS) was developed. The SPME-IMS method was used as a rapid screening tool in studying the chemistry of cocaine•HCl, heroin•HCl, and heroin freebase on surfaces. The total time for sample preparation, reaction, and analysis is approximately seven minutes. Another method that was developed is one that combines solid phase microextraction with gas chromatography (SPME-GC) for the quantitative analysis of cocaine freebase and cocaine•HCl. The SPME-GC headspace method was used to examine the conversion reactions of the drugs on candidate reactive surfaces.

To my son Jonah.

ACKNOWLEDGMENTS

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CHAPTER I

INTRODUCTION

There is a major need to minimize/eliminate the movement of contraband drugs into the United States. Research is underway on new concepts of drug sensors that can be used by law enforcement agents to detect contraband drugs at border crossings and at ports of entry.[1,2,3] The emergence of new concepts for such sensors may be facilitated with new knowledge on the surface chemistry of contraband drugs at nanogram levels.[4] The surface chemistry of contraband drugs is very important in many detection techniques. It is also important choosing materials for sampling and sample handling. The chemical nature of surfaces may facilitate drug decomposition or serve to stabilize drugs. One detection concept being pursued at Old Dominion University is to convert cocaine, heroin, and their hydrochlorides to volatile materials which can be more easily detected than the drugs themselves.

The thesis research focuses on developing analytical methods for studying drug conversion chemistry on surfaces in addition to optimizing the conversion process. Use of solid phase microextraction (SPME) in the headspace above a candidate reaction system is the core of the analytical methods development.

Cocaine, heroin, and their hydrochlorides may decompose to a variety of products depending on many factors. Decomposition products of most interest to the present work are shown in Figure 1.

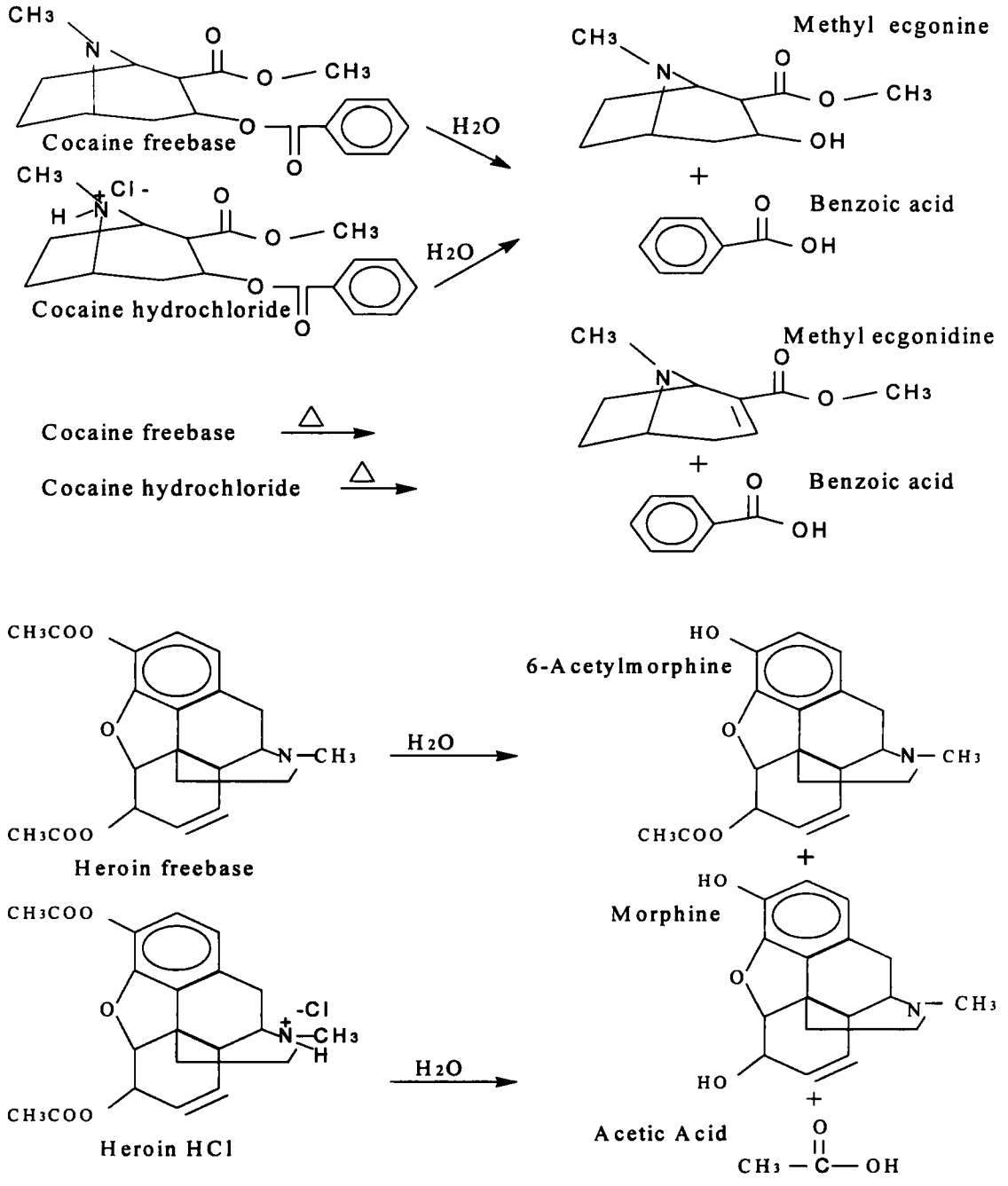


Figure 1: Structures of contraband drugs and their decomposition products of most interest.[5]

The analytical methods development described in this work focus on following both the loss of the target drugs and the formation of the decomposition products shown.

CHAPTER II

OBJECTIVES

The overall objective of this investigation is to develop analytical methods for cocaine, heroin, and their hydrochlorides, and specific decomposition products, which are useful in studying the chemistry of the target drugs on surfaces at nanogram levels. It is sought to develop methods which can be used for rapid screening, and for qualitative and quantitative analyses. Another objective is to demonstrate the use of these methods. The research focuses on developing SPME methods involving ion mobility spectrometry (IMS) and gas chromatography (GC) for headspace analyses of conversion reactions of cocaine, heroin, and their hydrochlorides. The purpose of combining solid phase microextraction with ion mobility spectrometry (SPME-IMS) is to develop a rapid screening tool to follow reactions in which reactants/products are readily detectable. The development of solid phase microextraction - gas chromatography (SPME-GC) methods is for both qualitative and quantitative analysis of cocaine freebase and cocaine•HCl conversion on candidate reactive surfaces.

CHAPTER III

DESCRIPTION OF SOLID PHASE MICROEXTRACTION

Definition

Solid phase microextraction is a relatively new technique[6] (developed in 1992) for the rapid, solventless extraction and/or pre-concentration of volatile and semi-volatile organic compounds.[7] Organic components are partitioned from a bulk aqueous or vapor phase onto a polymeric thin film coated onto a fused silica fiber. An equilibrium is established between analytes in the headspace above the sample and the stationary phase coating. Analytes are absorbed by the coated fiber and can be thermally desorbed in a GC[7,8,9] or desorbed in the mobile phase of a high performance liquid chromatograph[10] (HPLC). The SPME technique can be readily utilized in gas, liquid, and solid sample matrices. Unlike conventional extraction methods, it is inexpensive and requires little sample preparation time.

SPME Devices

An SPME device can be operated manually or automated for use with Varian® 8100 and 8200 CX series GC autosamplers (Varian® Chromatography Systems, Walnut Creek, CA).[6] Figure 2 demonstrates an apparatus introduced by Supelco® (Bellefonte, PA) for manual operation. The manual device is essentially a modified syringe having a spring-loaded plunger to be held in an extended position during the extraction phase and during the injection/desorption period.[7] A fused silica fiber is attached to a stainless steel tubing and enclosed in a stainless steel needle. The depth of the needle (not fiber coating) can

be adjusted from one to five cm to adapt to the sampling or desorption conditions. The bottom centimeter of the fiber is coated with a thin film of polymeric material to serve as a stationary phase. The fiber is exposed to the analytical matrix and volatile and semi-volatile compounds are absorbed to the coating. In direct immersion, other compounds are also absorbed such as water and organic solvents.

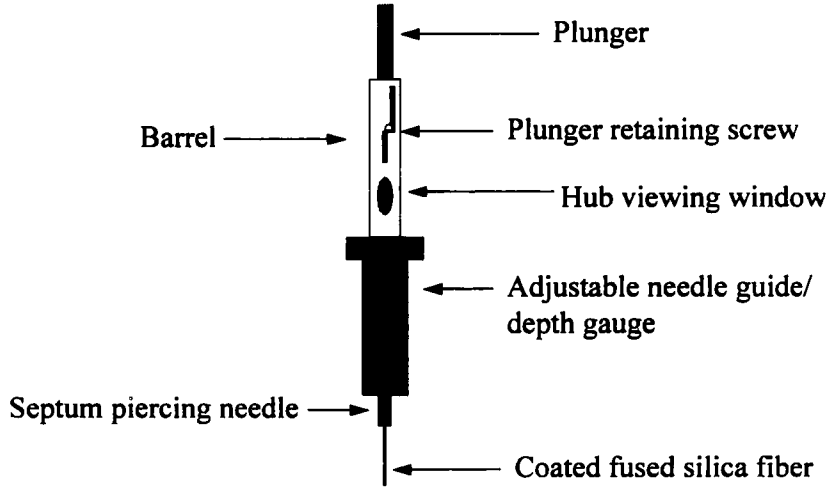


Figure 2: SPME device.[7]

SPME Process

The solid phase microextraction sampling process is relatively simple and is illustrated in Figure 3. A sample is deposited into a vial or an appropriate vessel which is then sealed with a septum-type cap. The SPME needle is used to pierce the septum and the fiber is extended through the needle and into the solution (in direct immersion extraction) or in the headspace above the solution or solid matrix. After a predetermined period of sampling, the fiber is withdrawn into the needle. The needle is immediately

inserted into the injection port of a GC or HPLC and the analytes are allowed to desorb from the fiber.

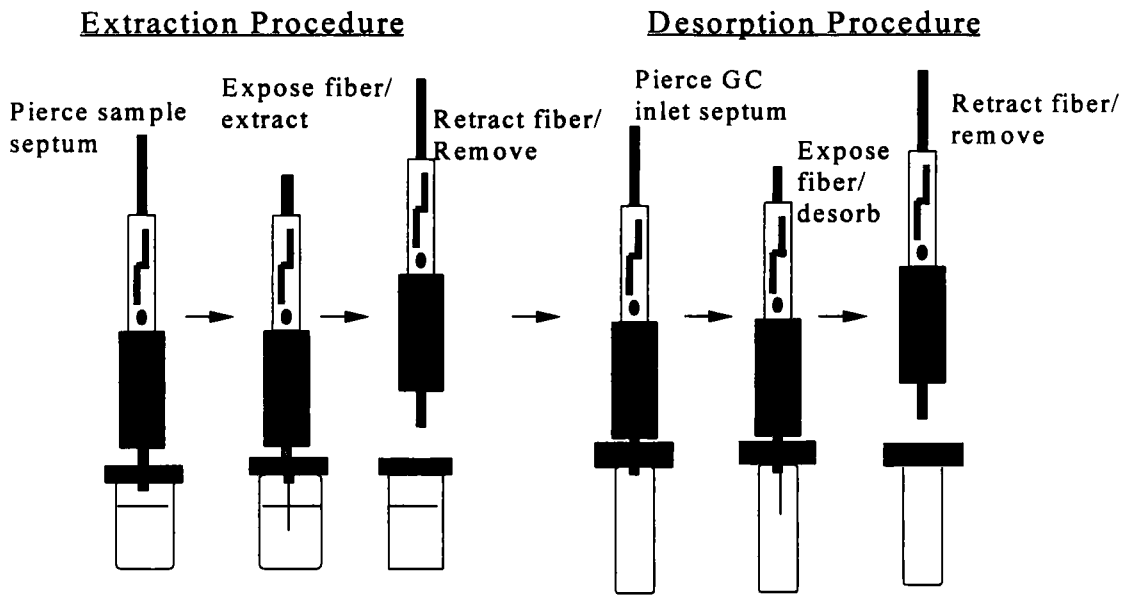


Figure 3: SPME process.[7]

Theory

In the partitioning process for direct immersion SPME, analytes establish equilibrium between the fiber stationary phase and the solution phase. The equilibrium is as follows[7]:

$$[X_l] \Leftrightarrow [X_f] \quad (1)$$

$$\text{hence } K_{lf} = [X_f] / [X_l] \quad (2)$$

where [X] is the analyte concentration in solution (l) and in the organic phase of the fiber (f). K_{lf} is the distribution coefficient for X between the liquid and fiber phases. The amount of analyte sorbed by the fiber at equilibrium and at infinite volume is linearly

dependent on the analyte's concentration in solution according to the following equation[11]:

$$n_f = KV_fC_o \quad (3)$$

where n_f is the number of moles of analyte absorbed by the stationary phase, V_f is the volume of the stationary phase, and C_o is the initial analyte concentration in solution.[7,11] In a finite volume of sample, such as 2mL, the sample can be significantly depleted, and the amount absorbed becomes:

$$n_f = \frac{KV_fV_lC_o}{KV_f + V_l} \quad (4)$$

where V_l is the volume of sample.[11]

The equilibrium partitioning for headspace extraction occurs between the fiber phase and the vapor phase above a liquid or solid sample.[7] The diffusion of analytes to the fiber in the vapor phase is about four orders of magnitude greater than in solution.[8] Headspace SPME can be much more efficient than liquid SPME and the extraction time can be significantly reduced maintaining high sensitivities and precision for many analytes.[7,8]

CHAPTER IV

DESCRIPTION OF ION MOBILITY SPECTROMETRY

Definition

Ion mobility spectrometry (IMS) is a technique normally used for the detection and characterization of organic compounds with high proton and electron affinities.[12,13,14] The principles of IMS involve the gentle ionization of molecules and the analysis of subsequent ions using gas ionic mobilities. This technique has diverse applications in both laboratory and field studies in forensic, environmental, and medical technologies.[15,16,17,18]

Ion mobility spectrometry was first introduced as an analytical device for the detection of organic compounds in air in the late 1960's.[19] The initial development of IMS was motivated by (a) drawing connections between particular gaseous ionic species and the chemical composition of airborne vapors, and (b) recognizing that ion separations based on mobilities were achievable at atmospheric pressure.[19] In the 1980s a renewed interest in IMS began and small rugged IMS units became commercially available.

Principles of IMS

In IMS, vapors are drawn into a reaction region (or ion source region) where ionization occurs through collisional charge transfer between a reservoir of charge, i.e., the reactant ions and neutral analytes, M.[20] The most abundant reactant ions generated using a beta-emitting ionization source (typically ^{63}Ni) are $(H_2O)_n{*}H^+$ (in positive ion mode) and $(H_2O)_n{*}O^{2-}$ (in negative ion mode) in air at atmospheric pressure.[20,21,22] If

other molecules are added such as nicotinamide, which has a much higher affinity than water, the reactant ion becomes protonated nicotinamide. Little molecular fragmentation of an analyte occurs and the product ions exist commonly as M^+ and MH^+ or M^- and M^*O^{2-} depending on the proton or electron affinities of the neutral target analytes.[20] For positive ionization, the mechanism can involve proton transfer, attachment of the ion to the target molecule, hydride or hydroxide abstraction, or oxidation.[20,21,22] In negative ionization, the pathways include charge transfer, dissociative capture, proton abstraction, and attachment.[19,21,22]

Once the ions are formed in the reactant region, the ions are introduced into the drift region by means of an ion shutter. A voltage gradient is applied to this region and the ions move at a particular drift time (t_d) through the electric field, E.[20,21] The relationship between drift time, velocity (v_d, cm/s), and ion mobility (K, cm^2/V^*sec) is described by the following equations:

$$v_d = L/t_d \tag{5}$$

$$K = v_d/E \tag{6}$$

The ions strike a flat plate detector and a mobility spectrum or plot of detector current (in pA or nA) vs. t_d (usually in ms) is produced. The basis of selectivity in IMS is the difference in drift times for ions as governed by ion mobilities. Drift times are dependent upon temperature and are normalized to reduced mobility constants, K_o, that are related to molecular properties through the Mason-Shamp equation. [20,22] The reduced mobility constant can be defined by the following relationship:

$$K_o = \frac{v_d}{E} \bullet \frac{273}{T} \bullet \frac{P}{760} \qquad (cm^2/V{\cdot}sec) \tag{7}$$

where P is the pressure (mm Hg) and T is temperature (°K).

CHAPTER V

SPME - IMS METHOD DEVELOPMENT

Apparatus

A Supelco® solid phase microextraction manual holder and Supelco® 85μm polyacrylate coating fiber was used for all vapor extractions. A partially crosslinked polyacrylate polymer is coated on a fused silica fiber. It is recommended for extracting polar semivolatiles, and it is resistant to high temperatures. This fiber appears most appropriate for sampling compounds like cocaine, heroin, their hydrochlorides and their conversion products such as methyl ecgonidine, morphine, and 6-acetylmorphine. The conditioning treatment required for this fiber is 2 hours in a gas chromatograph injection port at a temperature of 300°C prior to regular use.

A modified Barringer® IONSCAN 400 ion mobility spectrometer was utilized to desorb and analyze species collected on the SPME fiber. The carrier flow gas was ambient air passed through charcoal and a dessicant to remove impurities and excess water. The IONSCAN 400 IMS uses protonated nicotinamide as the reactant ion and the calibrant ion in the positive mode. The positive ion mode was used in all analyses except as mentioned.

SPME-IMS Configuration

A Barringer® IMS sample holder was modified to accommodate the use of SPME fibers. A hole was drilled in the O-ring of the sample holder to fit the needle of the fiber as shown in Figure 4. The O-ring secures the Barringer® 50μm Teflon® membrane to the

sample ticket. It is not necessary to perform SPME-IMS analyses with the membrane however it minimizes contamination of the desorber heater plate and maintains fiber integrity. The sample holder is placed on the sample holder platform. The fiber protective case (needle) is inserted into the hole in the sample holder and the whole fiber is exposed just above the Teflon® membrane to insure sufficient heat transfer for analyte desorption. The sample holder platform is then moved to the right, into the desorption chamber as illustrated in Figure 5. The heater raises, pressing the membrane/sample holder upward against the drift tube inlet. The analytes are thermally desorbed from the fiber and the vapors flow into the ionization region.

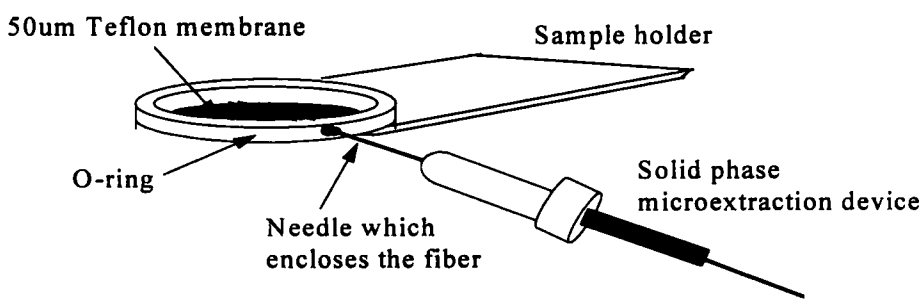


Figure 4. Configuration of SPME device and IMS sample holder.

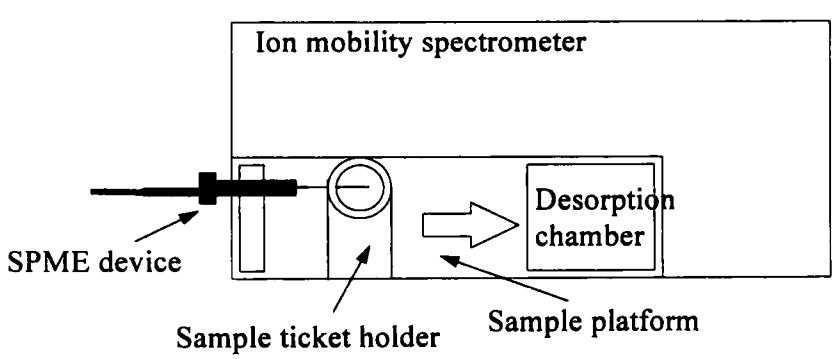


Figure 5. Illustration of SPME-IMS system as viewed from above it.

Standards and Reagents

Cocaine•HCl (1 mg/mL) and heroin•HCl (100μg/mL) 1mL volume standards in methanol (98+% purity) were obtained from Sigma® Chemicals. Further dilutions of these standards were made using HPLC grade methanol. Cocaine freebase and heroin freebase 1mL volume standards in acetonitrile (1 mg/mL, 99% purity) were purchased from Radian®. Dilutions of these standards were made using 99+% pure acetonitrile. All standards and diluted samples were stored in the freezer at -17° C to minimize drug decomposition and solvent evaporation.

SPME-IMS Procedure

Since the upper limit of the dynamic range of cocaine and cocaine•HCl is approximately 50ng using the IONSCAN 400 IMS, this concentration was used for all analyses. Fifty nanograms, 10μL of 5μg/mL concentration, was pipetted into a 0.1mL Ekonical® vial. For heroin and heroin•HCl experiments, 500ng was used (5μL of 100μg/mL concentration) since their IMS sensitivity is significantly lower than that of cocaine and cocaine•HCl. The Ekonical® vial was selected for its small volume, 0.1 mL, which allows efficient headspace extraction. The vial was immediately sealed with a black viton septum aluminum crimp cap.

The SPME needle depth was set to 1 cm which positions the fiber in the headspace just above the reactants in the vial. The SPME needle was allowed to pierce the center of the septum and the fiber was extended into the vial. The vial-SPME device was immediately transferred to an aluminum heat block in an Multi-Blok® heater which was set to 140°C. After the vapors were sampled for 5 minutes, the fiber was retracted into the

needle and removed from the vial. It was judged that a 5 minute sampling period was sufficient to absorb analyte vapors based on preliminary experiments.

The SPME needle depth was then adjusted to 4 cm which was optimal to position the fiber in the center of the IMS holder. The SPME needle was inserted through the hole of the modified sample holder and the fiber was exposed. The sample holder-SPME device was moved above the desorber heater plate which was set to 285°C and the analytes were allowed to thermally desorb for an analysis time of 20 seconds. During this time the SPME fiber reached a temperature of ca. 200°C as measured by a thermocouple. Blank runs were performed prior to each analysis to insure clean backgrounds. When necessary, the fiber was reheated in the IMS until all compounds were desorbed and a clean background was obtained.

In summary, the screening reactions involved the absorption of products and unreacted starting materials by the SPME fibers at 140°C for five minutes. The IMS desorption conditions involved heating the SPME fibers at 200°C for 20 seconds. The total time per run including sample preparation, reaction, desorption, and IMS analysis was no more than seven minutes on the average.

CHAPTER VI

SPME-IMS APPLICATIONS

Rapid Screening of Cocaine HCl Reactivity on Various Surfaces

Solid phase microextraction was examined with IMS for rapid screening of the reactivity of cocaine•HCl with various molecular sieves and zeolites. The following molecular sieves and zeolites were studied: 3Å molecular sieve, 4Å molecular sieve, 5Å molecular sieve, 13X molecular sieve, organophilic zeolite, silver exchanged zeolite, sodium Y zeolite, ammonium Y zeolite, and Sigma® zeolite. All molecular sieves and zeolites were obtained from Aldrich® Chemicals unless indicated otherwise.

The procedure followed the SPME-IMS technique described in Chapter 5 except for the presence of sieves/zeolites. These materials were dried in the oven at 210°C to drive off physically bound water, and stored in a dessicator. Approximately 1 – 2 mg of the sieves/zeolites were deposited in the conical insert/vial prior to cocaine•HCl addition.

Methyl ecgonidine appeared to be the most common conversion product indicating an elimination mechanism (Figure 6). Cocaine•HCl showed decomposition to methyl ecgonidine for all materials except organophilic zeolite and 3Å molecular sieve (Table 1). The latter materials facilitated hydrolysis and the formation of methyl ecgonine (Figure 6). Benzoic acid is formed in both pathways however it is not detected in the positive mode of the IMS. Several attempts to detect benzoic acid in the negative mode using ambient air as the source of reactant ions were not successful. Additional work is required to establish the optimum IMS conditions to detect benzoic acid. (The same

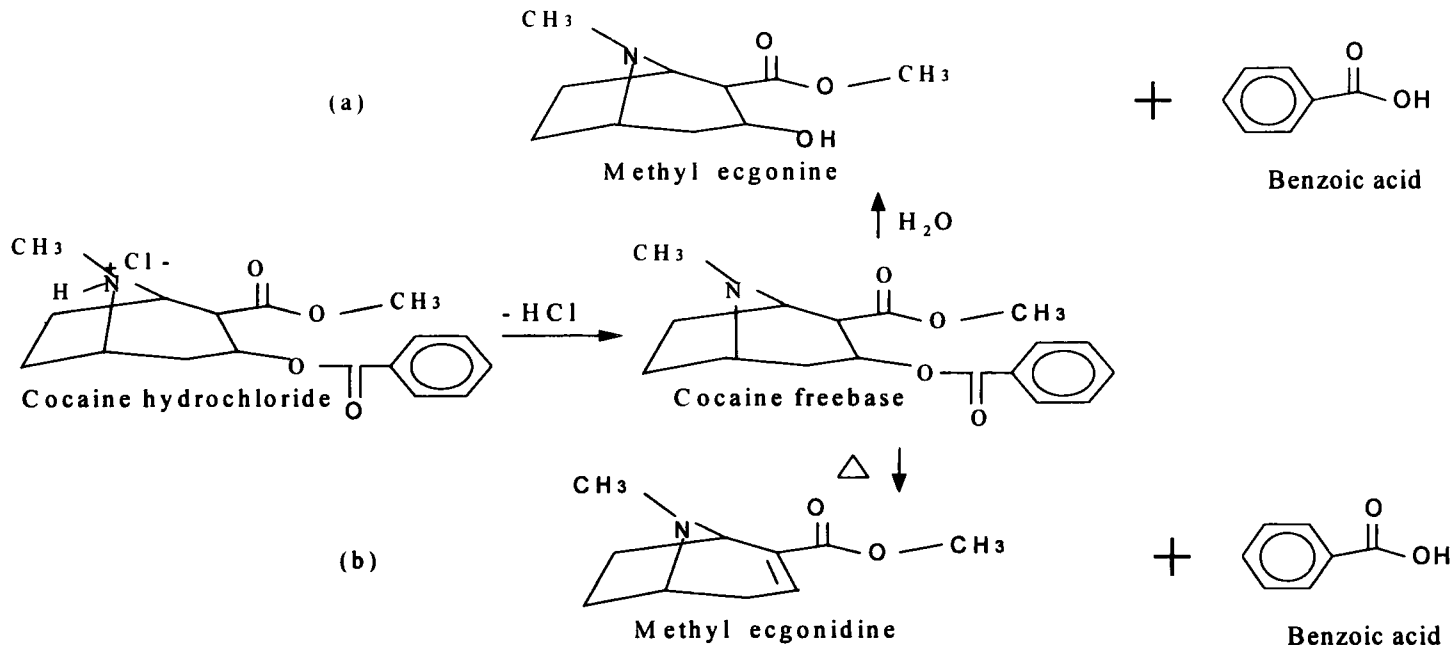


Figure 6 . Cocaine•HCl conversion pathways: (a) hydrolysis and (b) elimination.

applies to methyl benzoate). It is possible that both methyl ecgonine and methyl ecgonidine are present since their peaks can not be resolved. Recent IMS studies in our laboratory have shown that both compounds can be present to give a single peak having a K_o value which is characteristic of the predominant compound. However, one can at least use the K_o values to draw conclusions as to the major reaction mechanism.

Table 1. Products from the Reaction of Cocaine•HCl with Various Molecular Sieves and Zeolites.

Material	Major Product(s)	Average K_o[a] (cm^2/V·sec)
Silver exchanged zeolite	Methyl ecgonidine	1.501
4Å Molecular sieve	Methyl ecgonidine	1.493
3Å Molecular sieve	Methyl ecgonine	1.487
13X Molecular sieve	Methyl ecgonidine	1.495
Organophilic zeolite	Methyl ecgonine	1.482
Sodium Y zeolite	Methyl ecgonidine	1.502
5Å Molecular sieve	Methyl ecgonidine	1.502
Ammonium Y zeolite	Methyl ecgonidine	1.496
Sigma® Zeolite	Methyl ecgonidine	1.497

[a] K_o values for methyl ecgonidine and methyl ecgonine standards were found to be 1.5046 ± 0.0006 and 1.485 ± 0.003 cm^2/V·sec, respectively.

Organophilic zeolite appeared most active for decomposing cocaine•HCl showing the highest conversion product signal relative to residual cocaine (Figure 7). It was necessary to reheat the fibers in the IMS to completely desorb the compounds; the product signal average amplitude from each subsequent rerun was totaled and is shown in Figure 7. The signal from the residual cocaine was also totaled to demonstrate the disappearance of cocaine as a function of conversion. Example IMS plasmagrams are

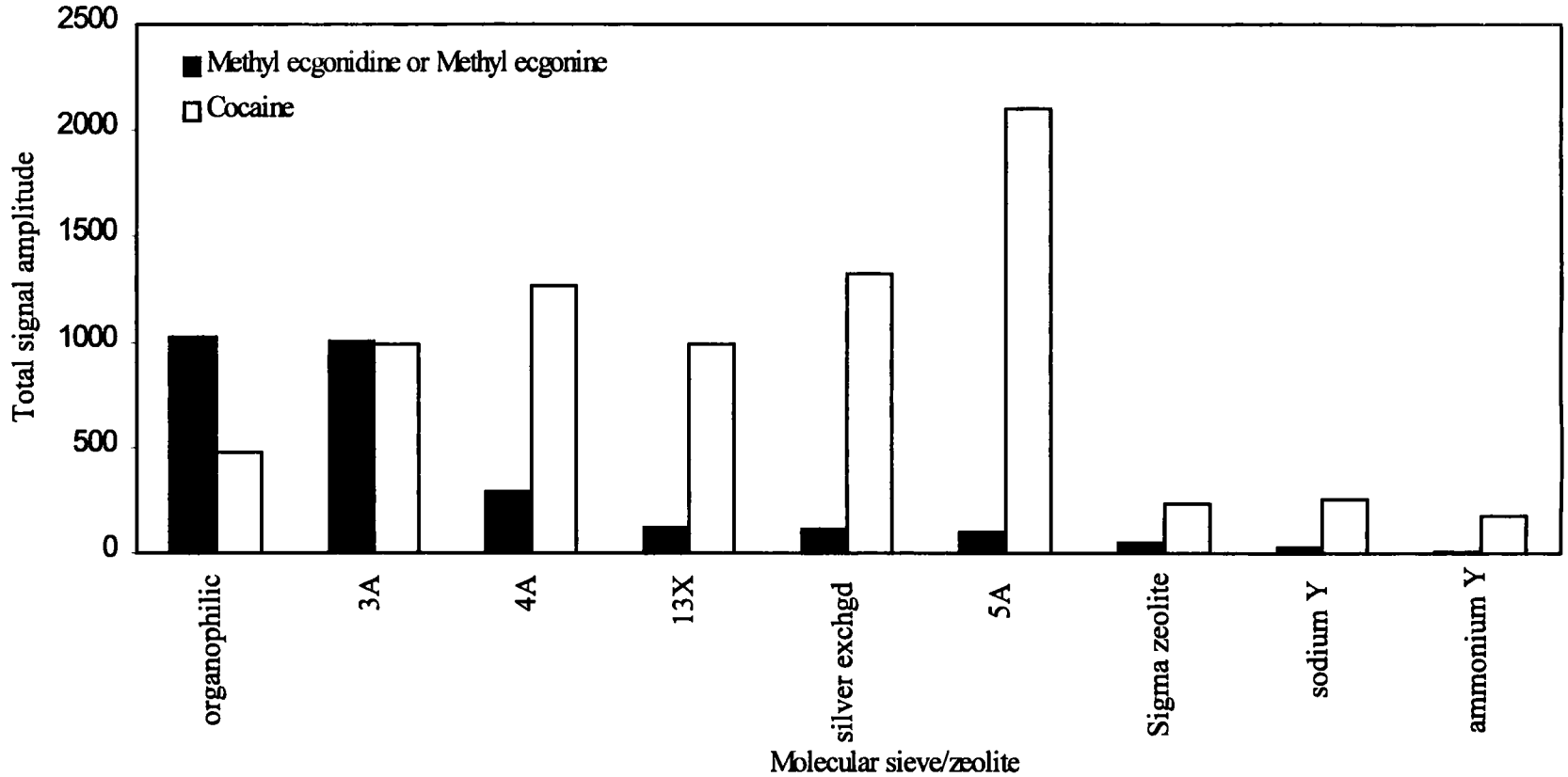


Figure 7: Methyl ecgonidine and/or methyl ecgonine and residual cocaine signal intensity from the reaction of cocaine•HCl with various molecular sieves and zeolites.

shown in Figures 8 and 9.

Sigma® zeolite, sodium Y zeolite, and ammonium Y zeolite seem to be least reactive since the intensities of the product peaks were very small. One would have expected these materials to show very high cocaine signals but the intensities were also small. It is possible that these materials strongly retain cocaine and the conversion products. Whatever the reason, these materials are not useful from a practical point of view under these SPME-IMS conditions. These materials were not further investigated

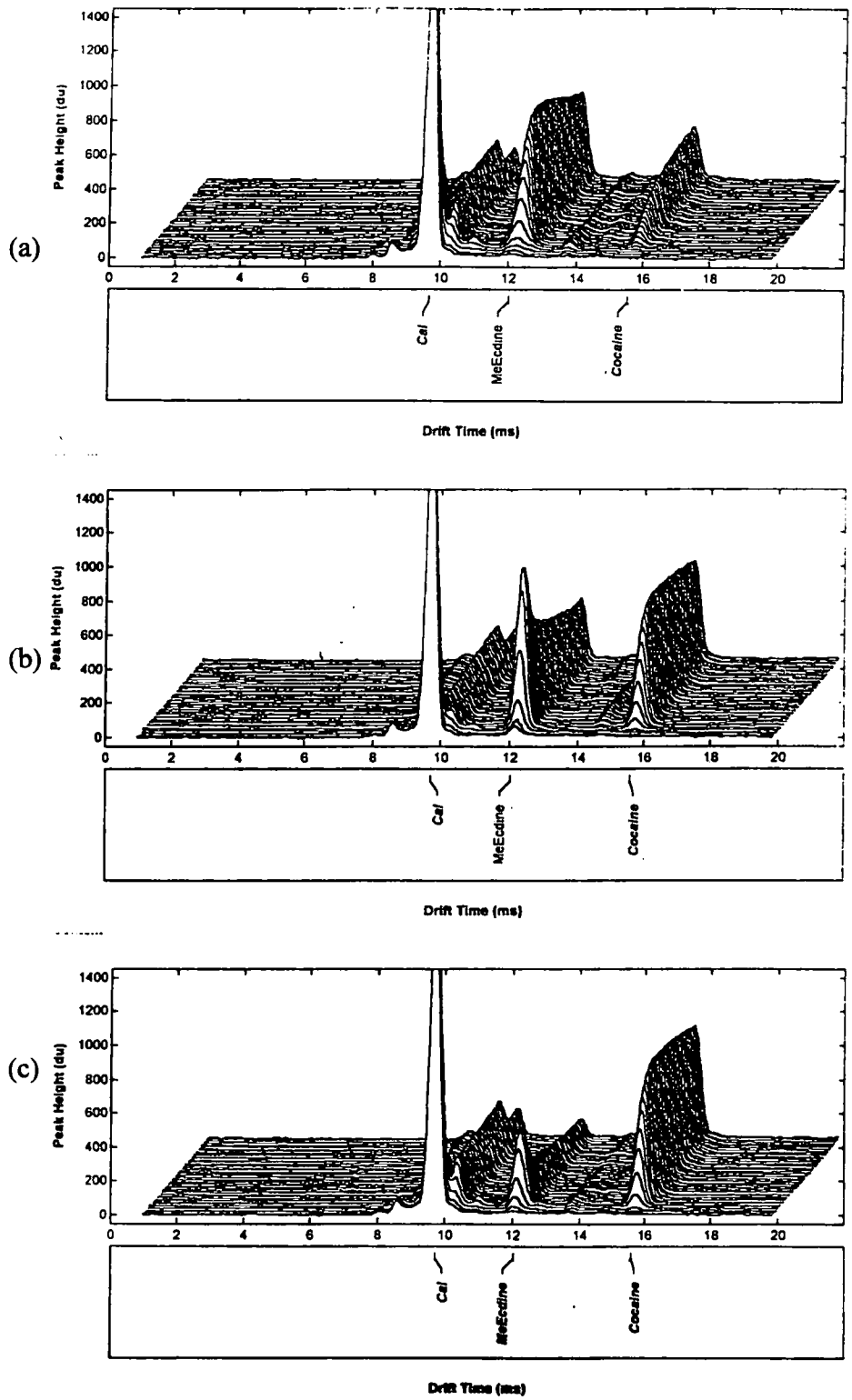


Figure 8. IMS plasmagrams from the reaction of cocaine•HCl with (a) organophilic zeolite, (b) 3Å molecular sieve, and (c) 4Å molecular sieve. Reaction conditions are 5 minutes at 140°C. The z-axis shows individual scans as a function of time during the 20 second analysis.

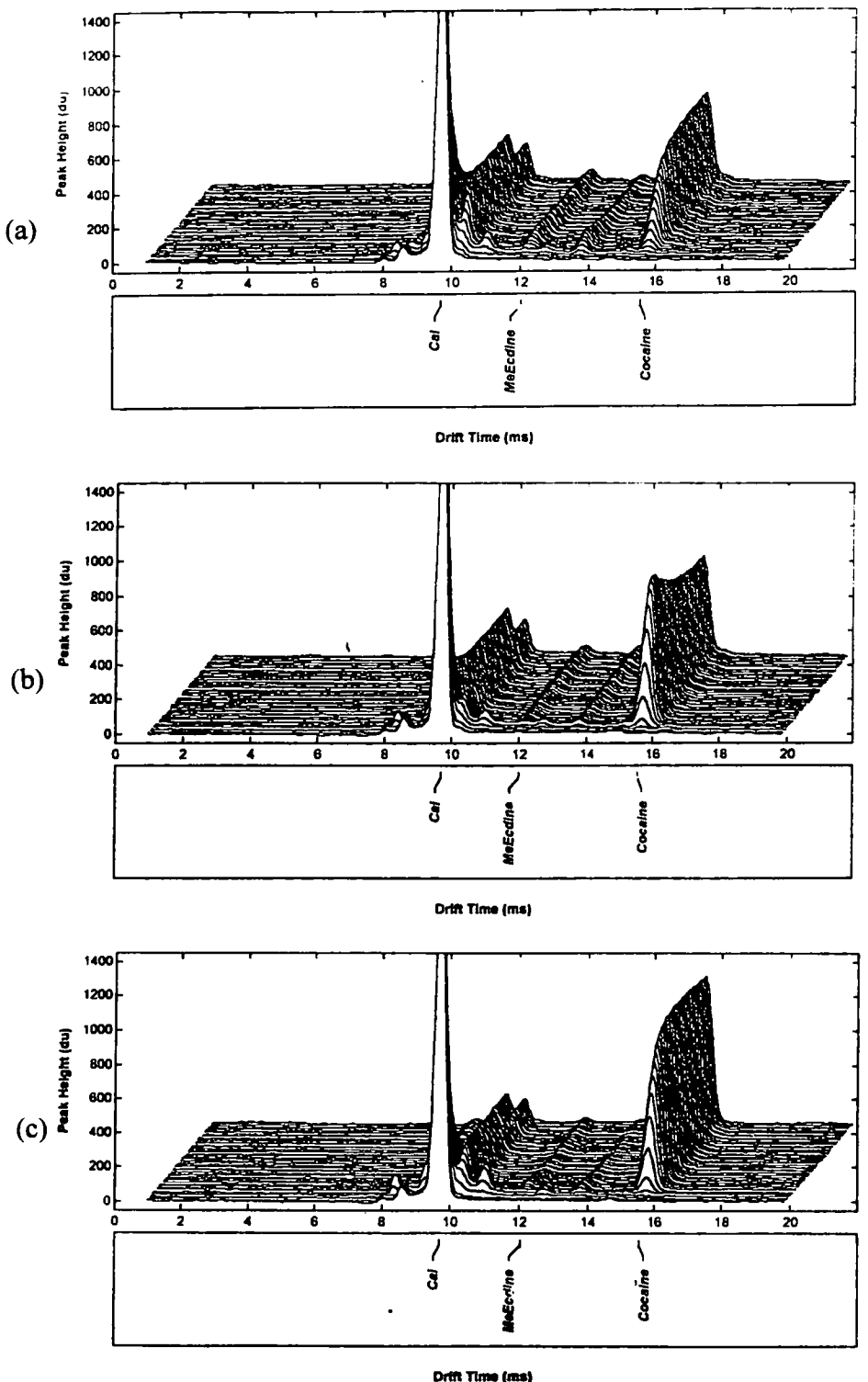


Figure 9. IMS plasmagrams from reaction of cocaine•HCl with (a) 13X molecular sieve, (b) silver exchanged zeolite, and (c) 5Å molecular sieve. Reaction conditions are 5 minutes at 140°C. The z-axis shows individual scans as a function of time during the 20 second analysis.

these materials to show very high cocaine signals but the intensities were also small. It is possible that these materials strongly retain cocaine and the conversion products. Whatever the reason, these materials are not useful from a practical point of view under these SPME-IMS conditions. These materials were not further investigated

Rapid Screening of Heroin and Heroin•HCl Reactivity on Various Surfaces

Solid phase microextraction - ion mobility spectrometry was used as a fast screening tool for evaluating the reactivity of heroin and heroin•HCl with various reagents, molecular sieves, and zeolites. Expected reaction products are 6-acetylmorphine, morphine, and acetic acid.

The SPME-IMS method described in Chapter 5 was used. Prior to drug deposition, 1 - 2 mg of reagent/sieve/zeolite was placed in the vial. The following were screened: 3Å molecular sieve, 4Å molecular sieve, 5Å molecular sieve, 13X molecular sieve, organophilic zeolite, silver exchanged zeolite, sodium Y zeolite, ammonium Y zeolite, acidic aluminum oxide, sodium methoxide on basic alumina, silicic acid, basic aluminum oxide, and montmorillonite K10. All of these materials were obtained from Aldrich® Chemicals.

The most common product with heroin•HCl was 6-acetylmorphine which was found with all of the materials except sodium methoxide on silica gel, silicic acid, and montmorillonite K10 which exhibited no IMS peaks. Morphine was seen when sodium methoxide on basic alumina, 13X molecular sieve, and organophilic zeolite were used. The heroin•HCl products are listed in Table 2.

The greatest 6-acetylmorphine signal was found with neutral aluminum oxide (Figure 10). Based on this observation, neutral aluminum oxide appears to be most reactive, although it shows the greatest heroin signal. If one considers the peak intensity ratios (product/heroin), then sodium methoxide on basic alumina and organophilic zeolite appear most active. Unfortunately, acetic acid could not be detected in either the positive

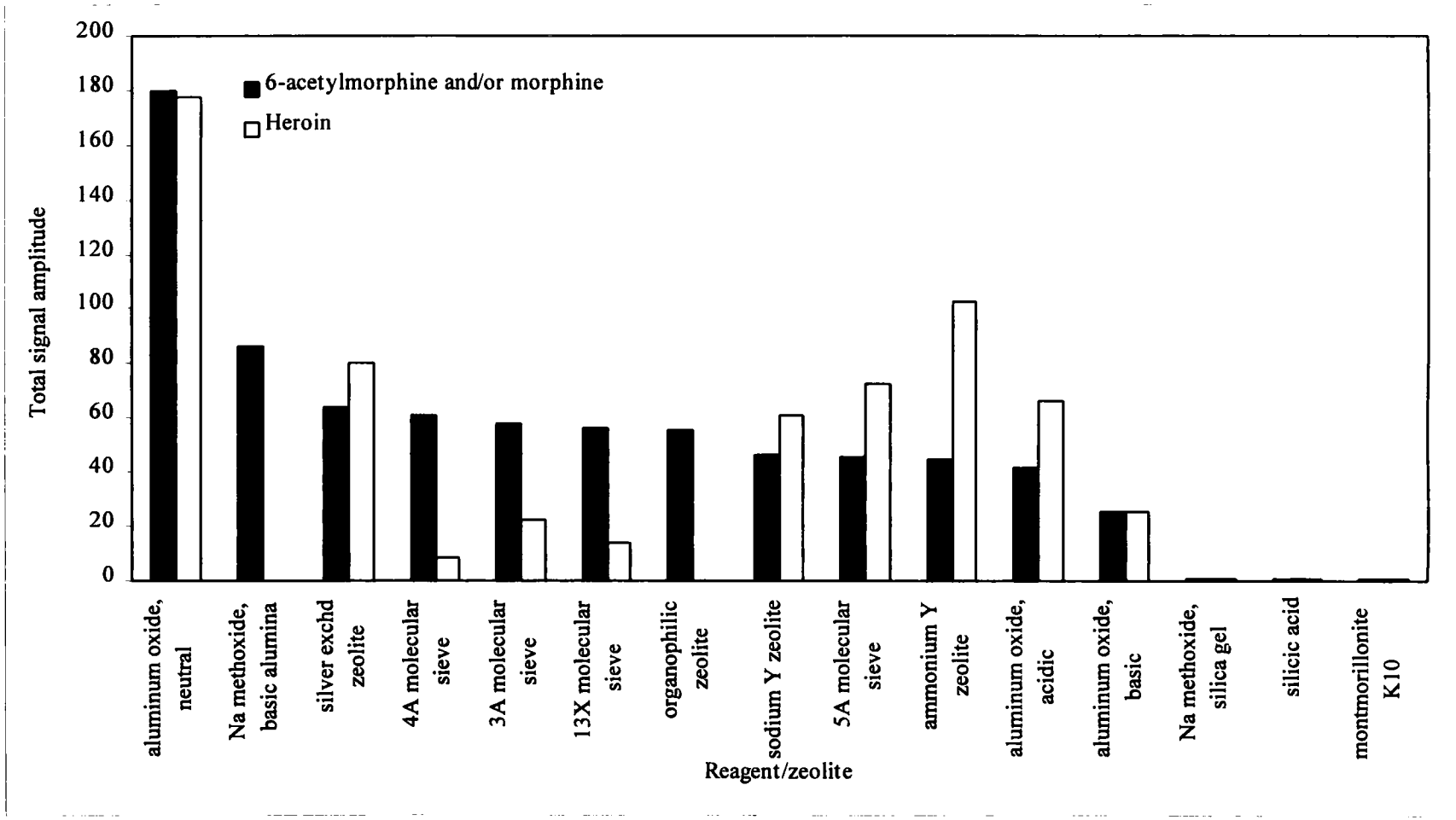
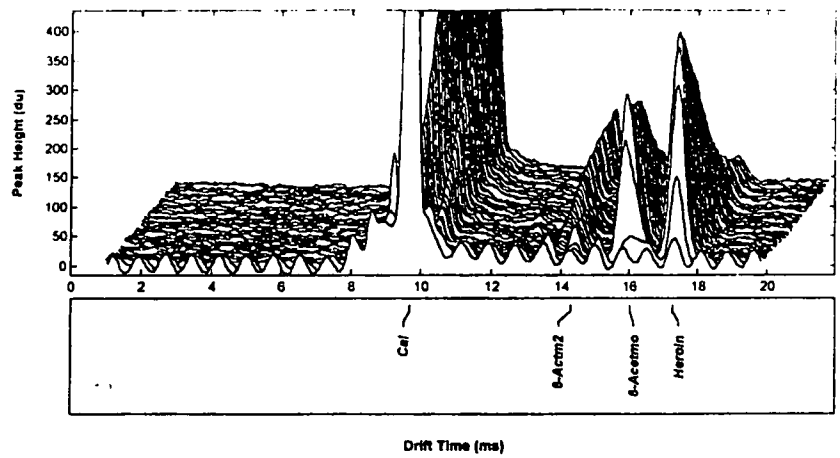


Figure 10. 6-Acetylmorphine and/or morphine with residual heroin signal intensity from the reaction of heroin•HCl with various reagents, molecular sieves, and zeolites.

(a)



(b)

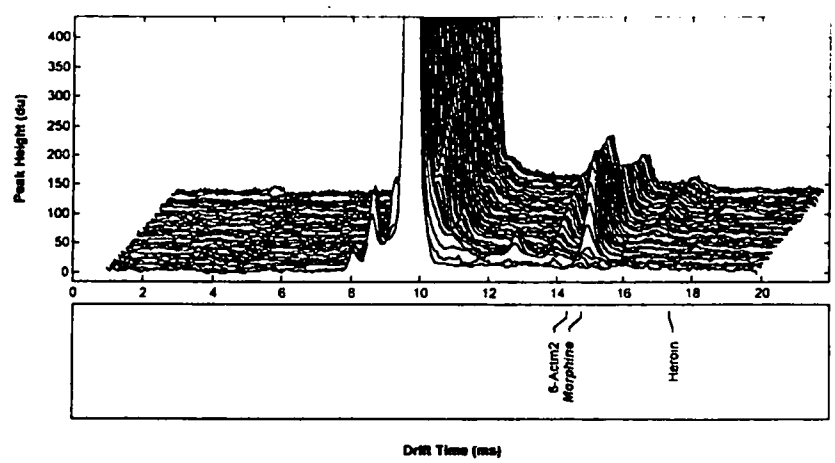


Figure 11. IMS plasmagrams from reaction of heroin•HCl with (a) neutral aluminum oxide and (b) sodium methoxide on basic alumina. Reaction conditions are 5 minutes at 140°C. The z-axis shows individual scans as a function of time during the 20 second analysis. (Note: Figure (b) shows one scan with high frequency noise probably due to slight changes in the initial pressure of the desorption chamber.)

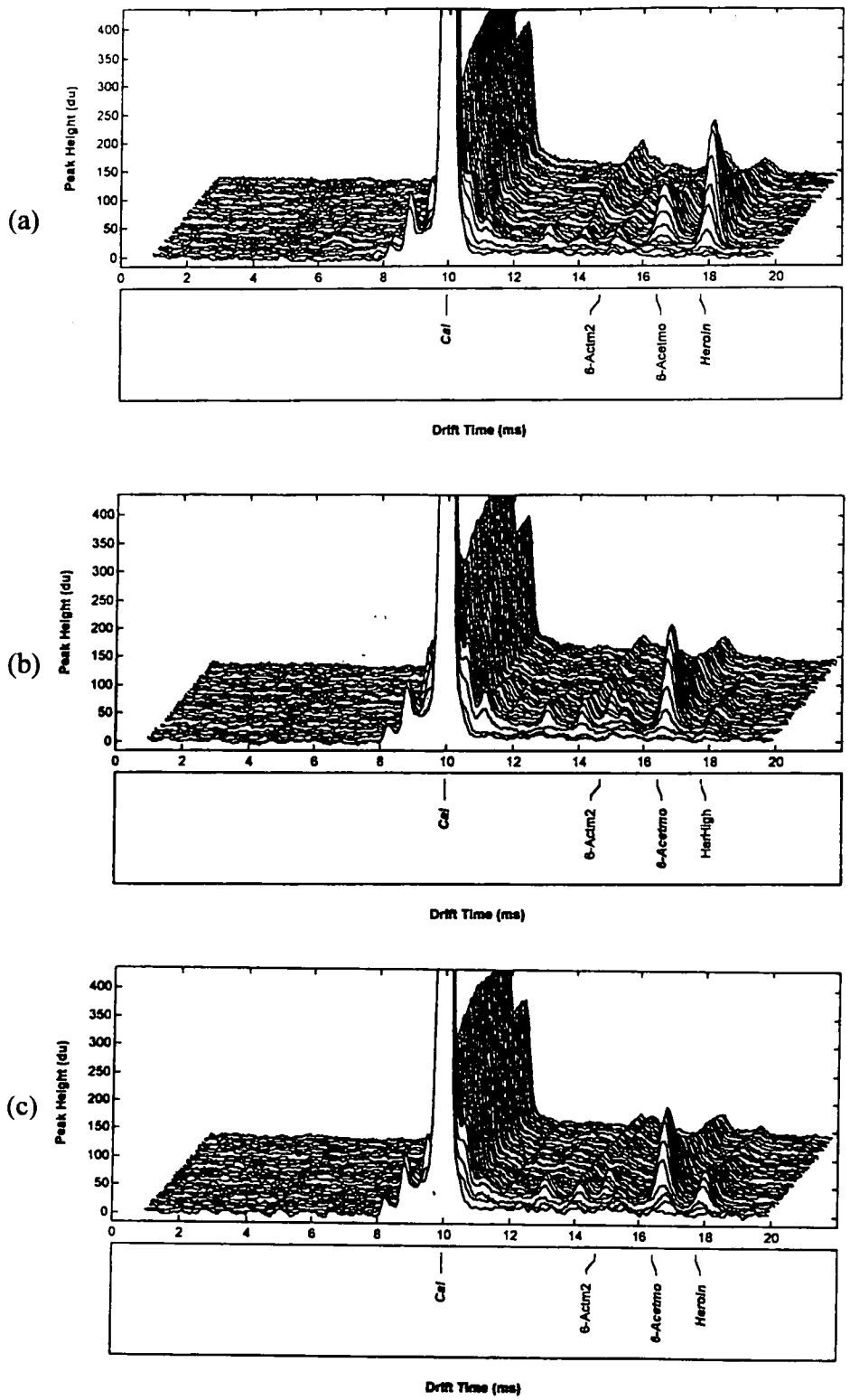


Figure 12. IMS plasmagrams from reaction of heroin HCl with (a) silver exchanged zeolite, (b) 4Å molecular sieve, and (c) 3Å molecular sieve. Reaction conditions are 5 minutes at 140°C. The z-axis are individual scans as a function of time during the 20 second analysis.

The most common conversion product for heroin on these materials was the 6-acetylmorphine (See Table 3). All of the reagents/zeolites showed reactions to form 6-acetylmorphine except basic aluminum oxide, 13X molecular sieve, and montmorillonite K10. Morphine was found with organophilic zeolite and was the single reaction product with neutral aluminum oxide.

Table 3. Products from the Reaction of Heroin Freebase with Various Reagents, Molecular Sieves, and Zeolites.

Material	Major Product(s)	K_o[a] (cm^2/V·sec)
Aluminum oxide, neutral	morphine	1.229
Sodium methoxide on basic alumina	6-acetylmorphine	1.122
Silver exchanged zeolite	6-acetylmorphine	1.120
4Å Molecular sieve	6-acetylmorphine	1.123
3Å Molecular sieve	6-acetylmorphine	1.126
13X Molecular sieve	none detected	N/A
Organophilic zeolite	6-acetylmorphine	1.129
	morphine	1.229
Sodium Y zeolite	6-acetylmorphine	1.121
5Å Molecular sieve	6-acetylmorphine	1.124
Ammonium Y zeolite	6-acetylmorphine	1.121
Aluminum oxide, acidic	6-acetylmorphine	1.123
Aluminum oxide, basic	none detected	N/A

[a] K_o value of 6-acetylmorphine and morphine standard were found to be 1.222 and 1.261 cm^2/V·sec., respectively.[23]

The highest conversion product signal with heroin freebase was found with organophilic zeolite. This zeolite showed a corresponding disappearance in heroin and appears to be the most reactive material. Neutral aluminum oxide also appears to be very active as it showed no residual heroin and reasonable conversion to morphine. A

comparison of the product and unreacted heroin signals for the various reagents/sieves/zeolites are shown in Figure 13 and some of the corresponding plasmagrams are shown in Figures 14-15.

Summary

A fast screening method using SPME-IMS has been developed which is useful in ranking the reactivity of cocaine•HCl, heroin freebase, and heroin•HCl on various surfaces. The same method is applicable to cocaine freebase but these experiments were not performed. The total time for sample preparation, reaction, and analysis is approximately seven minutes. The use of this methodology was demonstrated with various reagents/sieve/zeolites. Of the materials screened, organophilic zeolite appears the most promising candidate for conversion reactions. Neutral aluminum oxide is also a promising candidate for conversion of heroin•HCl.

The surface chemistry with the materials examined seems to follow a mechanism favoring loss of benzoic acid and formation of methyl ecgonidine. Both heroin and heroin•HCl tend to form 6-acetylmorphine as the predominant conversion product, although decomposition to morphine was also observed.

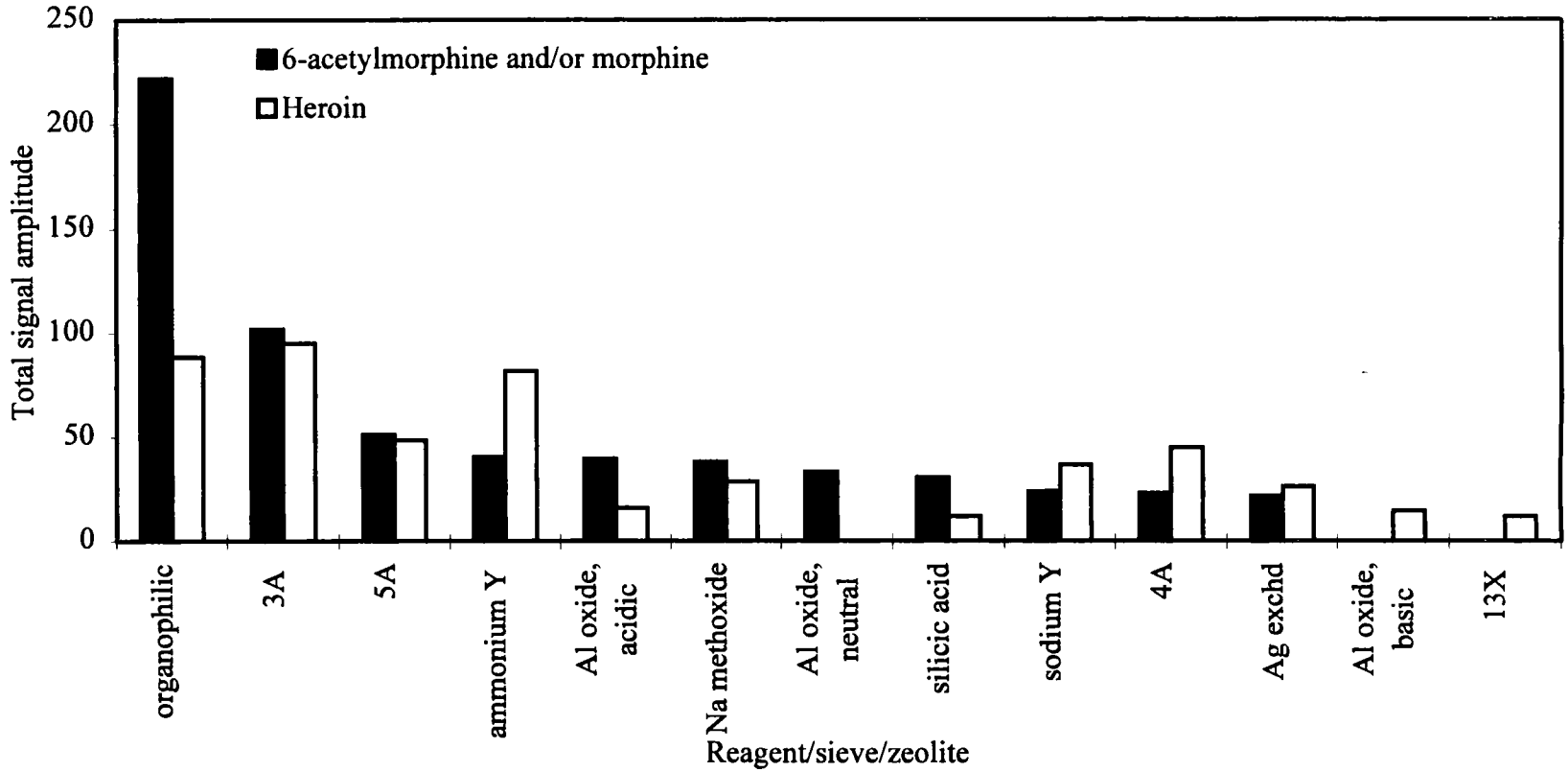


Figure 13: 6-Acetylmorphine/morphine and residual heroin signal intensity from the conversion of heroin freebase with various reagents, molecular sieves, and zeolites.

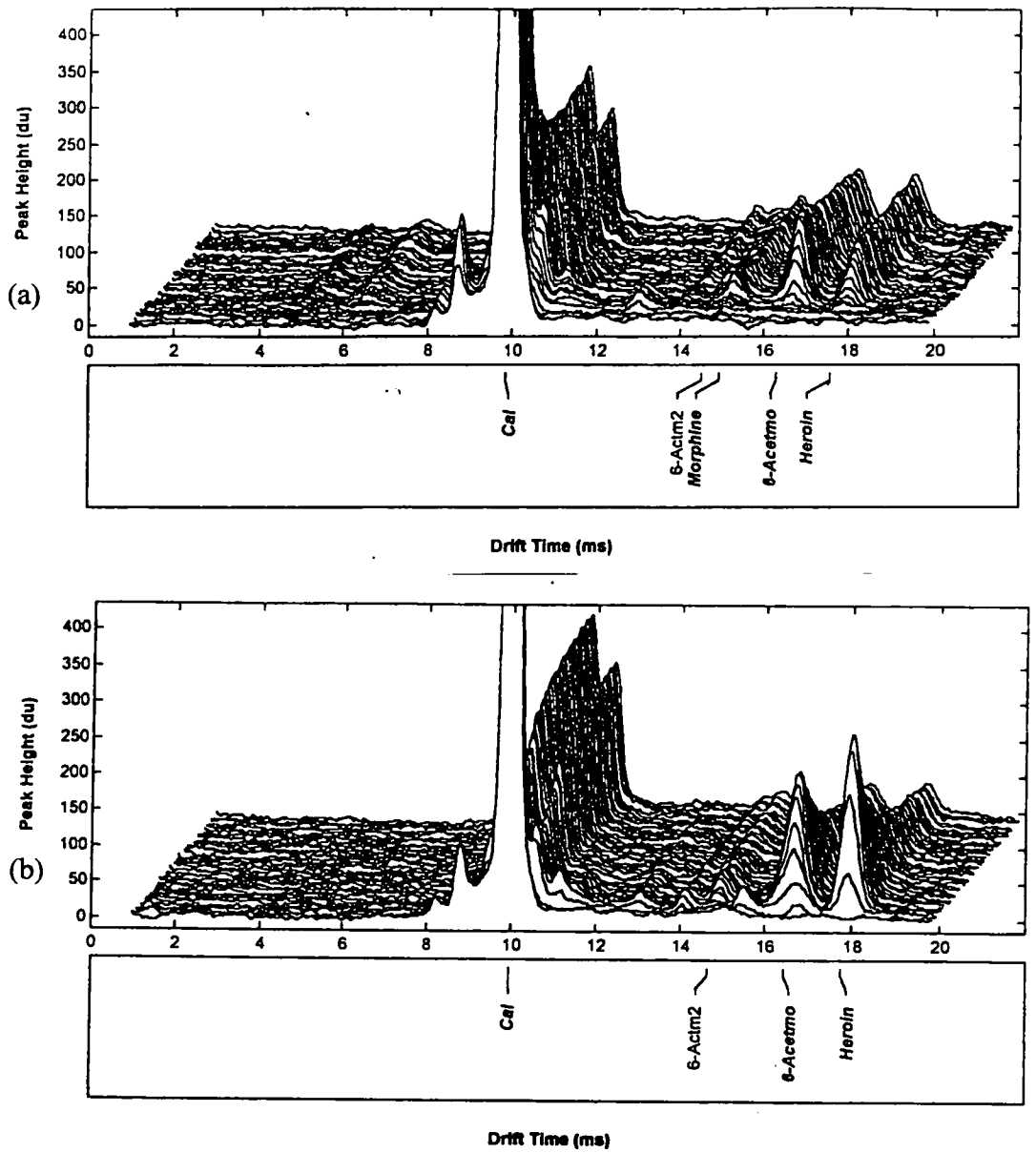


Figure 14. IMS plasmagrams from reaction of heroin freebase with (a) organophilic zeolite and (b) 3Å molecular sieve. Reaction conditions are 5 minute at 140°C. The z-axis are individual scans as a function of time during the 20 second analysis.

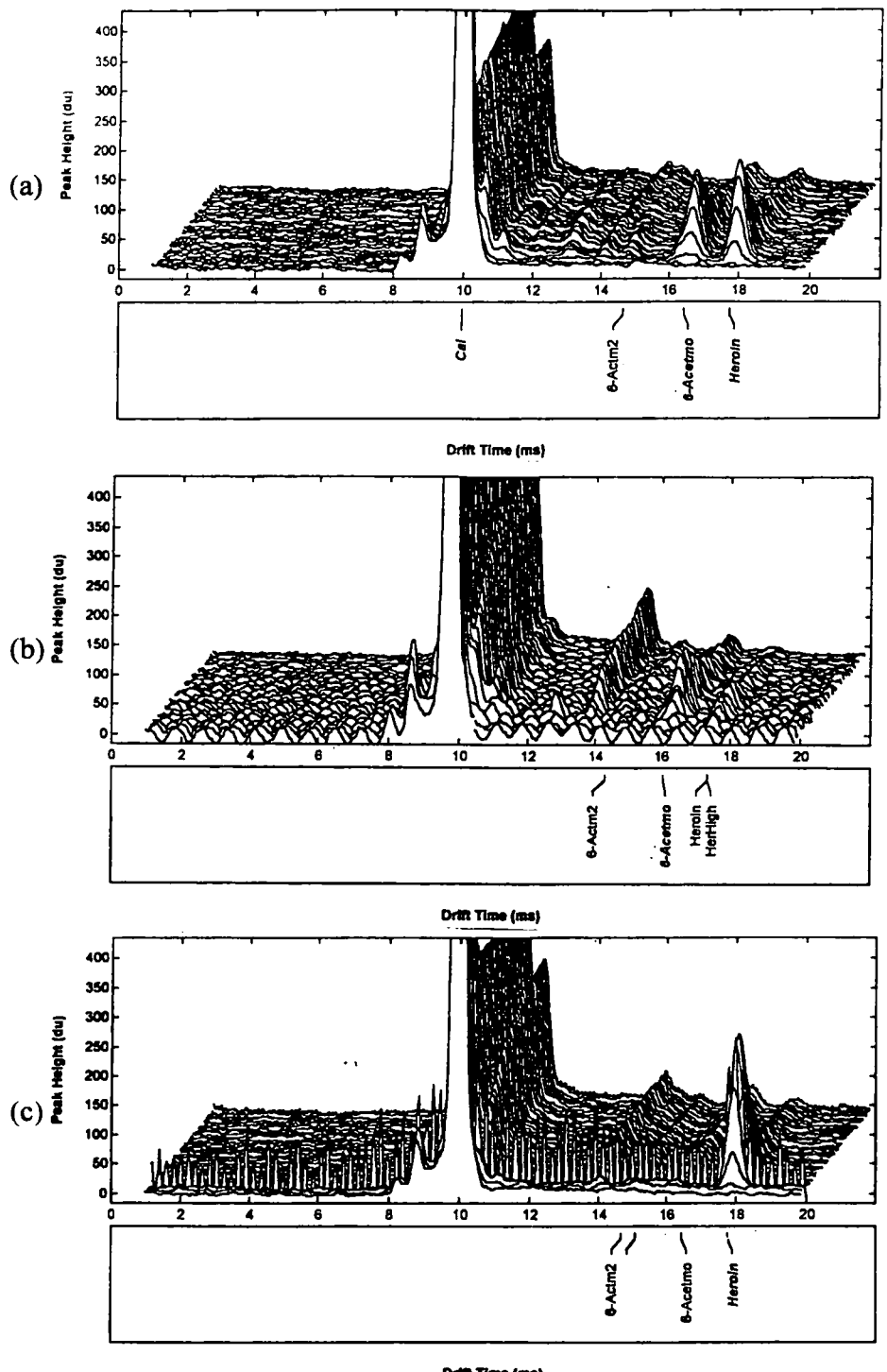


Figure 15. IMS plasmagrams from reaction of heroin freebase with (a) 5Å molecular sieve, (b) ammonium Y zeolite, and (c) acidic aluminum oxide. Reaction conditions are 5 minutes at 140°C. The z-axis are individual scans as a function of time during the 20 second analysis. (Note: Figure (b) and (c) show one scan with high frequency noise probably due to slight changes in the pressure of the desorption chamber.)

CHAPTER VII

SPME - GC METHOD DEVELOPMENT

Standards and Reagents

Cocaine•HCl (1 mg/mL) 1mL volume standards in methanol (98+% purity) were obtained from Sigma® Chemicals. Further dilutions of these standards were made in HPLC grade methanol. Cocaine freebase 1mL volume standards in acetonitrile (1 mg/mL, 99% purity) were purchased from Radian®. Dilutions of these standards were made in 99+% pure acetonitrile. All standards and diluted solutions were stored in the freezer at -17° C. A 10μL volume of a specific concentration was used for each analysis.

Gas Chromatograph Parameters

A Hewlett Packard® 6890 gas chromatograph system was used to perform conversion chemistry studies described below. A silanized Supelco® glass liner with a 0.75mm internal diameter was used for all SPME-GC analysis. Its narrow internal diameter minimizes dead volume and provides more efficient heat transfer for thermal desorption of analytes from the fiber than standard GC liners. The inlet temperature was maintained at 250°C, and a splitless mode was used. The developed GC parameters included a "pulsed" pressure (30.0 psi) for the initial 30 seconds after injection then maintained a constant pressure of 14.5 psi for the rest of the chromatographic process. The initial high pressure provides additional thrust for the desorption of analytes from the fiber and minimized solvent tailing. Helium was used as the carrier gas. After 4 minutes of desorption, a purge to vent is activated with a flow rate of 8.1 mL/min. The column

that was chosen for cocaine/cocaine HCl is the HP-INNOWax® which is an INNOphase™ bondable PEG semipolar capillary column.[24] The nominal length and diameter of the column is 15 m and 250 μm, with a film thickness of 0.25 μm. The temperature program of the oven was: 50°C held for the initial minute; then ramped from 50°C/min to 200°C, held for 2 minutes; 20°/min to 230°C, held for 2 minutes; and 20°C/min to 250°C, held for 2 minutes. The flame ionization detector was maintained at a temperature of 300°C with a hydrogen flow of 35.0 mL/min and an air flow of 375.0 mL/min. A constant column and make-up flow with nitrogen gas was maintained at 30.0 mL/min. All gases were purchased from BOC® Gases in ultrapure quality.

Selection of Reaction Vessel

The first priority was to select a vessel that would allow cocaine freebase and cocaine•HCl reactions to be studied at nanogram levels and higher. The criteria involved were: (a) size; (b) compatibility with a SPME device; (c) heat transfer ability; (d) headspace collection efficiency; and (d) convenience and availability.

Microreaction vessels with a 0.1mL capacity that are commercially available should be very suitable for reactions at nanogram levels. In addition, the small volume should provide high sampling efficiency of headspace. The two vessels that were considered were Supelco® Ekonical® 0.1mL vials and standard 2mL GC vials with 0.1mL capacity conical inserts and self-centering supports as illustrated in Figure 16. The two vials can be sealed with septum caps which will permit insertion of the SPME fiber and fit perfectly into commercially available heating blocks.

The headspace sampling efficiency for Ekonical® vials and standard vials/conical

inserts was compared. Using an 85μm polyacrylate fiber, the headspace of 1μg cocaine•HCl was sampled for 2.5 min and 5 min at 140°C in a heating block. The results are shown in Figure 17. A comparison of the two vials is summarized in Table 4.

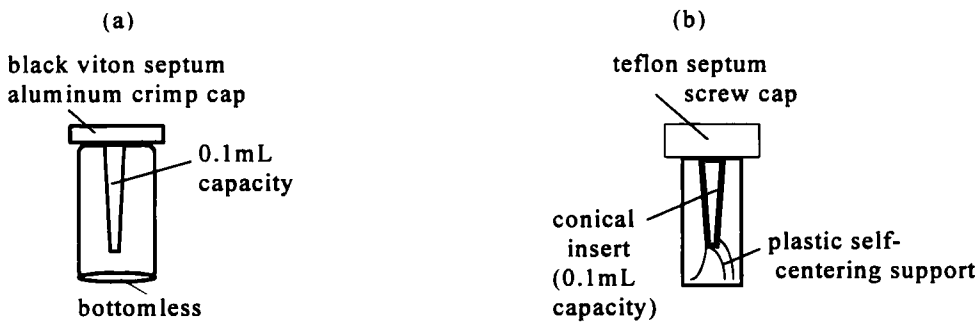


Figure 16. Candidate microreaction vessels: (a) Ekonical® vial and (b) standard GC vial with conical insert and self-centering support.

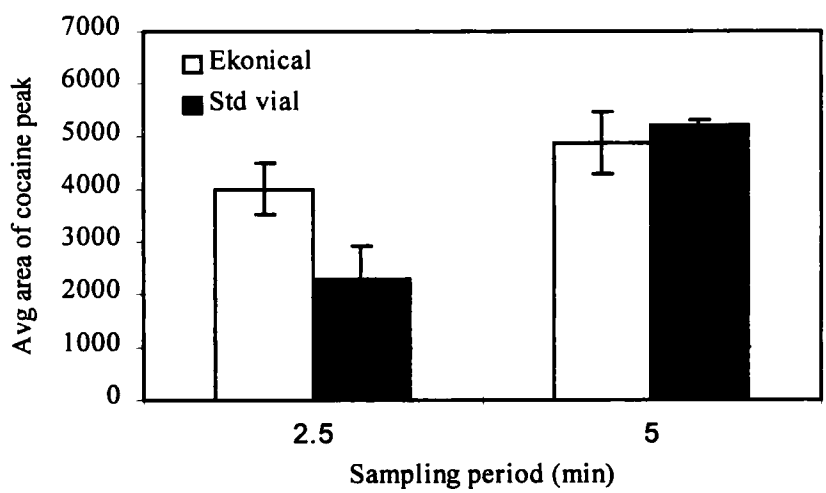


Figure 17. Comparison of sampling efficiency using Ekonical® and standard GC vials with conical inserts.

Table 4. Comparison of Microreaction Vessels.

Criteria	Standard GC vial w/ insert	Ekonical® vial
size	good	good
compatibility with SPME device	good	good
heat transfer ability	reasonable	good
headspace collection efficiency	reasonable	good
diffusion control	reasonable	good
convenience	poor	good

The Ekonical® vial was selected as the candidate reaction vessel. This vial can be described as having a 0.1mL glass vessel held within a bottomless 2mL clear glass vial. An SPME needle can be readily inserted into this microreaction vessel and its bottomless characteristic provides good heat transfer. The vial requires a crimp cap seal which should minimize vapor diffusion. A black viton septum was chosen for its high temperature resistivity and thickness. Both Ekonical® vials and black viton septum crimp caps are commercially available.

Higher cocaine signal intensities and better reproducibility were seen with Ekonical® vials using a 2.5 minute sampling period. A 5 minute sampling period showed comparable cocaine extraction efficiencies for both vials.

Although the standard vial/conical insert is easily adaptable to SPME and is commercially available, it was not chosen for several reasons. Unlike the Ekonical® vials, the vessel configuration needs to be set up for each vial which is less convenient. The set-up procedure involves insertion of the plastic self-centering support into a 2mL

vial, followed by the placement of the glass 0.1mL conical insert above the support. The PTFE/silicone septum is then fit into a high temperature resistant screw cap and is carefully screwed to the vial as to not shift the conical insert off center. An off-centered placement of the conical insert could potentially create a leak in the system. In addition, the plastic self-centering support melts at a reaction temperature of 140°C.

Temperature Control

Temperature control was provided using an aluminum heating block in an Multi-Blok® heater, which fits the Ekonical® vials. The temperature variation in the vials contained in the heating block was measured using a temperature probe, (HANNA® Instruments Thermohygrometer (HI 9161C) and penetration probe (HI 762PW)). The probe was inserted in an Ekonical vial which was placed in the heating block and allowed to equilibrate at ca. 140°C (maximum dial setting: high 9). The temperature was measured at 30 second intervals for a 20 minute period (Figure 18). The average temperature was 139.5°C ± 0.2 showing excellent control.

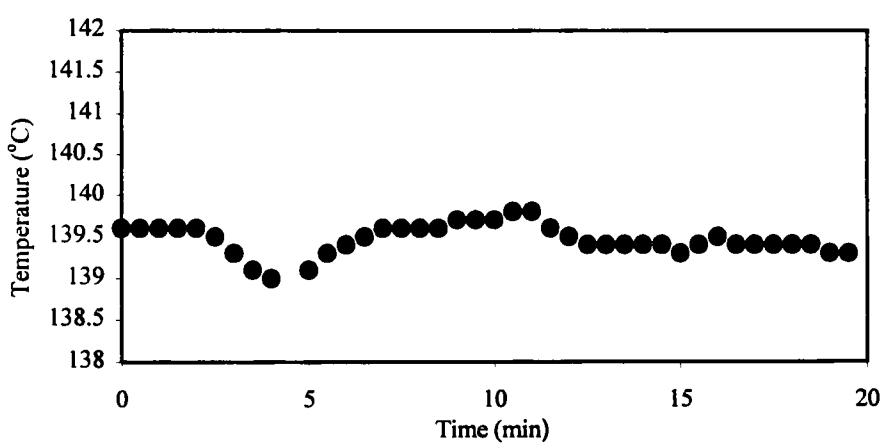


Figure 18. Temperature control of an Ekonical® vial in the heating block.

Selection of a Solid Phase Microextraction Fiber Coating

The two coatings that were considered for headspace extraction of contraband drugs and their volatile/semi-volatile conversion products were a polyacrylate coating (85μm) and a Carbowax®/divinylbenzene coating (65μm) which are designed for polar semi-volatiles and polar analytes, respectively.[6] Both polymer coatings are partially crosslinked. These fibers appeared most suitable for extracting the drugs, as well as their decomposition products such as methyl benzoate, benzoic acid, methyl ecgonine, acetic acid, and 6-acetylmorphine.

The headspace extraction efficiency of the polyacrylate and Carbowax® coatings was compared. The headspace was sampled for 2.5 and 5 min at 140°C Ekonical® vials (black viton crimp cap seals) containing cocaine•HCl using both fibers. The polyacrylate fiber demonstrated slightly higher GC signals than the Carbowax® (Figure 19).

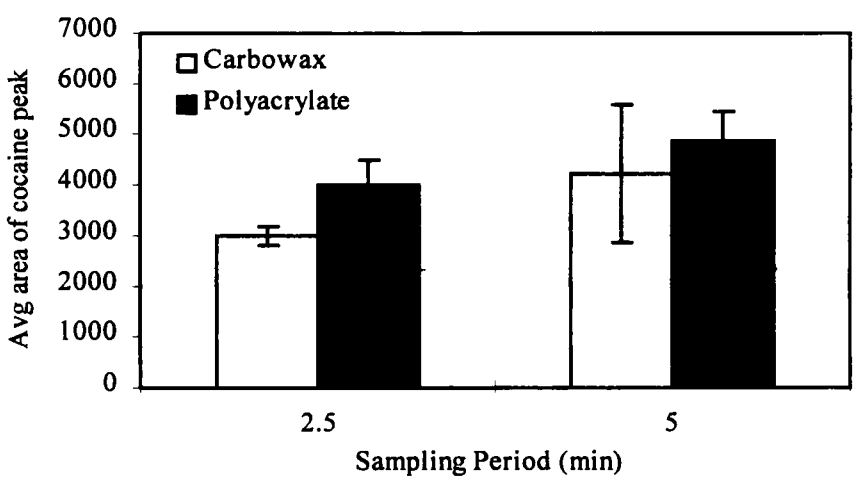


Figure 19. Comparison of cocaine sampling efficiency using 65μm Carbowax® and 85μm polyacrylate SPME fiber coatings.

The 85μm polyacrylate coating fiber was selected as the candidate SPME fiber because of the higher signals and lower standard deviations. In addition, the polyacrylate fiber has higher temperature stability. The recommended operating range for the polyacrylate fiber is 220-310°C compared to 200-260°C for the Carbowax® fiber.[25]

Selection of Solvent Evaporation Technique

The cocaine freebase and cocaine•HCl used in studying the conversion chemistry are contained in acetonitrile and methanol, respectively. Higher cocaine signals were seen when the amount of solvent was reduced. The methods that were considered for solvent evaporation were: (a) evaporation under ambient laboratory conditions in a fume hood at room temperature, (b) vacuum suction, and (c) nitrogen purge.

Preliminary studies indicated that purging with ultrapure nitrogen was the best option for evaporation of cocaine•HCl solutions. One μg of cocaine•HCl (10μL of 100μg/mL in methanol) was deposited in Ekonical® vials and allowed to evaporate using the three techniques mentioned above. In the nitrogen purge technique, ultrapure nitrogen is swept across the vial opening. This method is rapid, has minimal exposure to water or impurities in the air, and demonstrated the highest cocaine signal. Allowing the solution to evaporate under ambient laboratory conditions in a fume hood was found to be the most time consuming. Solvent evaporation by vacuum suction using a Marvac® mechanical high vacuum pump for various periods appeared to draw off some of the cocaine. The technique led to variable cocaine signals.

The next task was to determine the optimal nitrogen purge time and pressure sufficient to remove all or most of the solvent. Two purge conditions were studied, a low

and high purge: (a) 1 minute at 10 psi, and (b) 5 minutes at 20 psi. One μg cocaine•HCl (10μL of 100μg/mL in methanol) was deposited in an Ekonical® vial. The solvent was allowed to evaporate by sweeping the atmosphere ca. 1 cm above the vial mouth with ultrapure nitrogen using the conditions described above. The vial was immediately sealed with a black viton septum crimp cap and placed in the heating block set at 140°C for 2.5 minutes. An 85μm polyacrylate fiber was inserted after the 2.5 minute sample incubation and was exposed to the headspace for 5 minutes for subsequent analysis using GC. A significantly higher cocaine signal (peak area = 2088) was seen with a 1 minute purge at 10 psi technique compared to a 5 minute purge (peak area = 654). The 1 minute nitrogen purge at 10 psi was selected as the solvent evaporation technique. In this set-up, the nitrogen flows through an Imperial Eastman® Poly-Flo Tubing 44-P-1/4 (external diameter is 0.25 inches, and internal diameter is approximately 4mm) which is connected to a 1000μL capacity Eppendorf® pipette tip. This technique reduces the solvent to an approximate volume and is reproducible.

Optimum Incubation Period

The next challenge in method development was to determine an optimal incubation period for cocaine headspace analyses. In many solid phase microextraction applications which require heat, utilization of an incubation period or equilibration period prior to sampling with an SPME fiber leads to a more efficient extraction than without an incubation period[26,27,28,29] Several incubation periods were examined.

One μg of cocaine•HCl (10μL of 100μg/mL in methanol) was deposited in an Ekonical® vial and purged with ultrapure nitrogen (1 minute, 10 psi) for partial solvent

evaporation. The vial was immediately sealed with a black viton septum crimp cap and placed in the heating block set at 140°C. The cocaine HCl solution was allowed to incubate for 2.5, 5, and 10 minutes. Following the incubation period, a 85μm polyacrylate fiber was inserted into the sample headspace, and extraction was allowed to proceed for 5 minutes at the same temperature. GC analyses showed that the 2.5 minute incubation period analyses gave significantly higher signals than the longer periods (Figure 20).

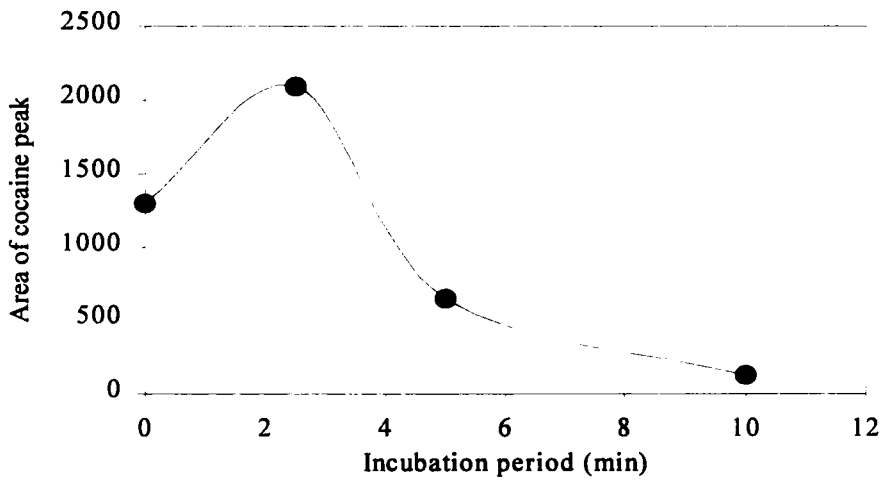


Figure 20. Cocaine GC signal as a function of incubation period at 140°C.

Optimum Sampling Period

The next step was to determine the optimum sampling or extraction period using an 85μm polyacrylate fiber under the conditions established to this point in the SPME-GC method development. Too short a sampling time could result in incomplete headspace collection while a lengthy sampling period can lead to diffusion of analyte vapor out of the vial.

Various extraction periods were evaluated. One μg of cocaine•HCl (10μL of 100μg/mL in methanol) was deposited in an Ekonical® vial and the solvent was allowed to evaporate using a 1 minute nitrogen purge (10 psi). The vial was immediately sealed with a black viton septum crimp cap and was incubated in the heating block at 140°C for 2.5 minute. An 85μm polyacrylate fiber was inserted, exposed in the headspace for 1, 3.5, and 5 minutes, and then immediately placed in the GC for analyte desorption. Figure 21 demonstrates that the 1 minute extraction period is sufficient for cocaine vapor analyses under the above conditions.

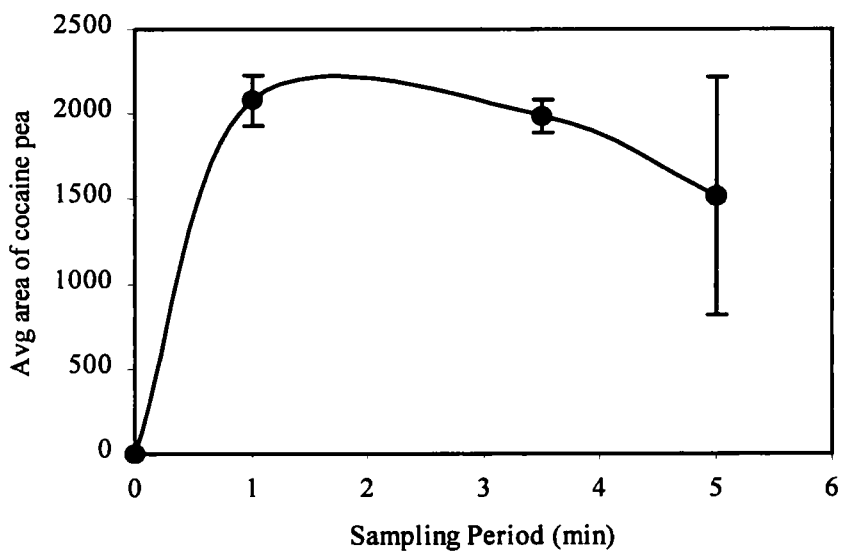


Figure 21. Cocaine GC signals as a function of sampling period at 140°C with an 85μm polyacrylate fiber.

Summary of SPME-GC Method

A 10μL volume of cocaine freebase or cocaine•HCl solution is deposited in an Ekonical® vial and purged for 1 minute with ultrapure nitrogen gas. The gas is swept approximately 1 cm above the mouth of the vial at a pressure of 10 psi. The vial is then immediately sealed with a black viton septum crimp cap with a hand crimper. The vial is placed in the heating block and is allowed to incubate at 140°C for a total of 2.5 minutes. An 85μm polyacrylate fiber which, set to needle depth of 1 cm, is inserted after the 2.5 minute equilibration and allowed to extract the vapors for 1 minute while heating at the same temperature. The fiber is then removed from the vial, set to needle depth of 3 cm, and is immediately exposed in the GC inlet. The fiber is allowed to desorb in the GC inlet for 4 minutes before the purge flow to vent is activated. The GC parameters are given at the beginning of the chapter.

CHAPTER VIII

SPME-GC APPLICATIONS

Quantitative Analysis of Contraband Drugs

Cocaine freebase and cocaine•HCl studies at nanogram to microgram level can be performed using the SPME-GC headspace method which has been developed. Calibration curves were produced for both the compounds. This method demonstrated a dynamic range between 25ng and 2000ng with a correlation coefficient of 0.999 for cocaine freebase headspace analyses as shown in Figure 22. For an initial concentration range of 0-200ng, the cocaine freebase curve showed a correlation coefficient of 0.946 with a slightly higher slope (Figure 23). Similarly, the calibration curve for cocaine•HCl exhibited a dynamic range between 25ng and 2000ng and a correlation coefficient of 0.994 as demonstrated in Figure 24. The sensitivity and precision of this technique is less for the hydrochloride than the freebase which is expected since cocaine•HCl undergoes dissociation of the HCl before the freebase is allowed to vaporize. The slope of its curve was 5.2 compared to 7.5 for the freebase. The calibration curve was also replotted for the initial concentration range of 0-500ng cocaine•HCl (Figure 25). This curve had a comparable slope to that of the full range curve, however its linearity was improved to 0.999.

Calibration curves were also obtained using direct injection of cocaine freebase and cocaine•HCl solutions (acetonitrile and methanol, respectively). As one would expect, the slopes obtained using the direct injection technique are higher (Figures 22 - 25).

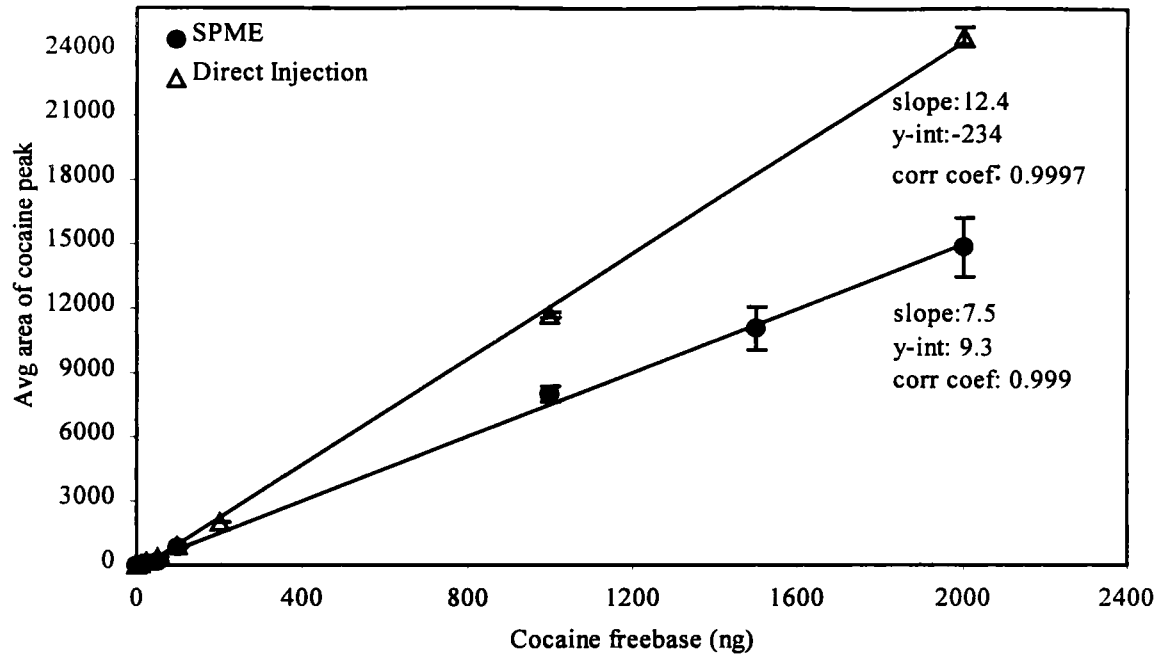


Figure 22. GC Calibration curve for cocaine freebase using direct injection and SPME techniques for an initial concentration range of 0 - 2000ng.

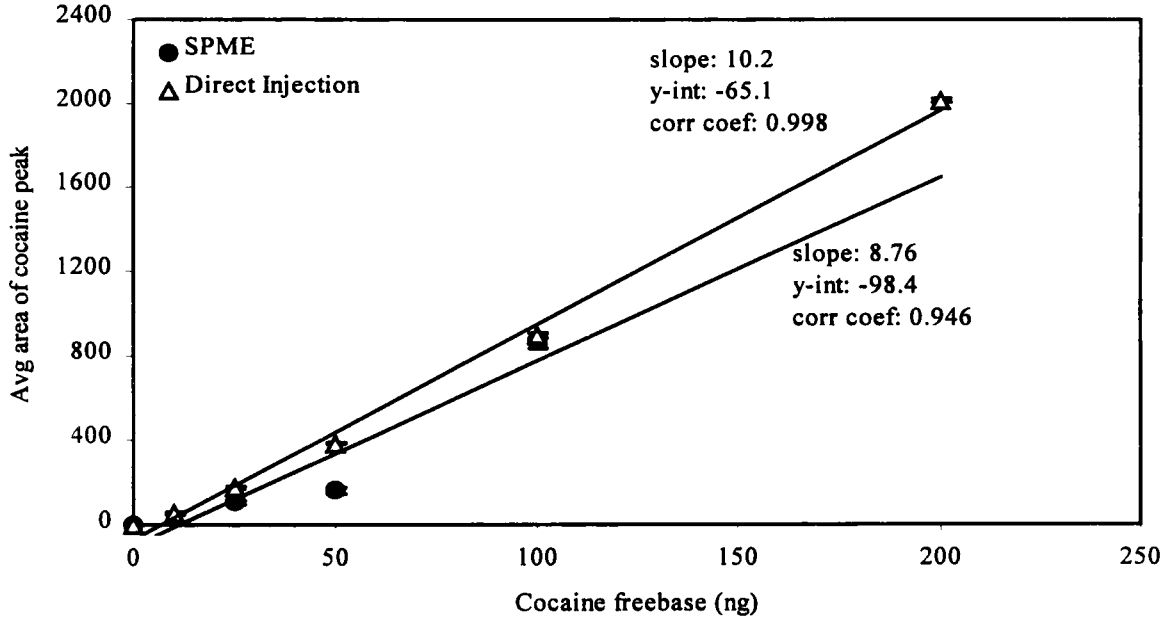


Figure 23. GC Calibration curve for cocaine freebase using direct injection and SPME techniques for an initial concentration range of 0 - 200ng.

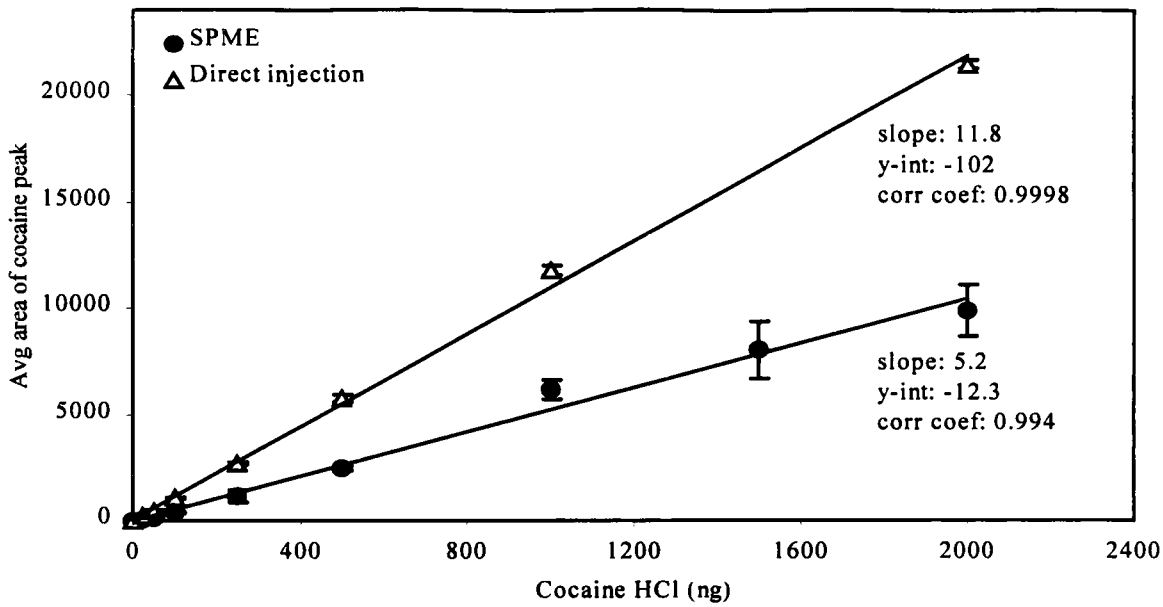


Figure 24. GC Calibration curve for cocaine•HCl using direct injection and SPME techniques for the initial concentration range of 0 - 2000ng.

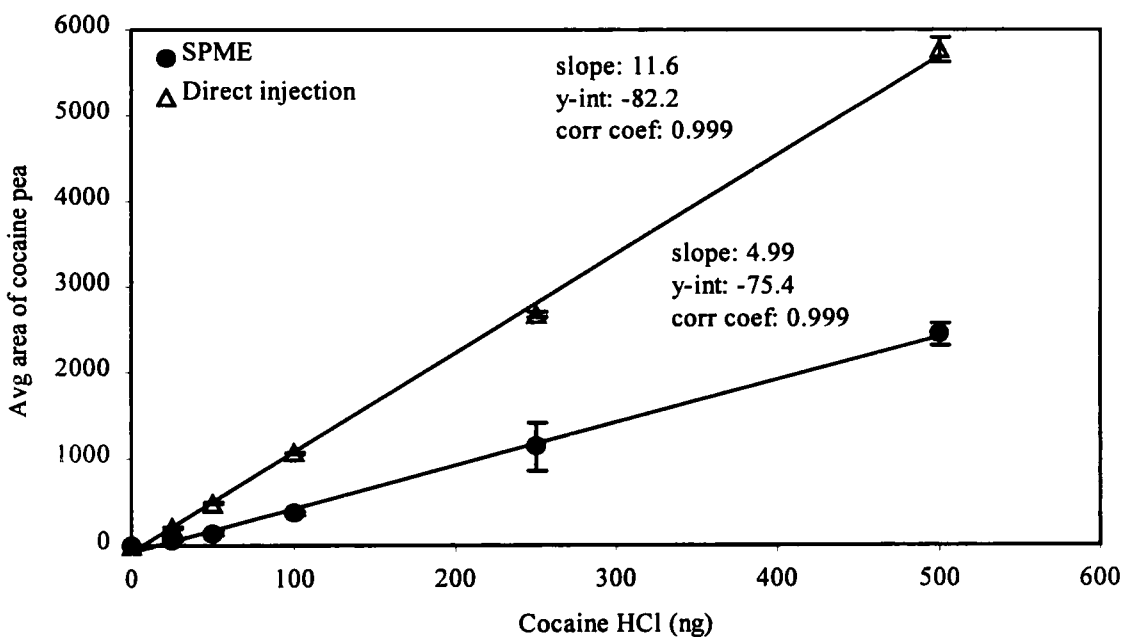


Figure 25. GC Calibration curve for cocaine•HCl using direct injection and SPME techniques for an initial concentration range of 0 - 500ng.

Conversion Chemistry of Contraband Drugs

The SPME-GC method described above was utilized to study surface reactions of cocaine freebase and cocaine•HCl with selected material. Approximately 1 - 2 mg of the test materials were weighed in Ekonical® vials prior to cocaine/cocaine•HCl deposition. The materials included Whatman® QM-A quartz fiber filters (QMA), Aldrich® organophilic zeolite (OPZ), 1A organophilic zeolite - teflon membrane (OPZ 1A) fabricated by FluoroTechniques®, and Aldrich® 4Å molecular sieve.

Both methyl ecgonidine product and residual cocaine were found in all chromatograms (Figures 26 and 27). This indicates that elimination of benzoic acid is a major mechanism. In the case of QMA, a peak for benzoic acid and several other peaks were also observed. The other peaks are due to impurities in QMA. Benzoic acid peaks did not appear in the chromatograms for the other test materials. Our experience is that some materials such as a OPZ tend to strongly sorb benzoic acid.

The percent reaction of cocaine freebase and cocaine•HCl was estimated from the residual cocaine appearing in the chromatogram using the SPME calibration curves (concentration range from 0 - 2000ng) shown in Figures 23 and 25. The results are given in Tables 5 and 6.

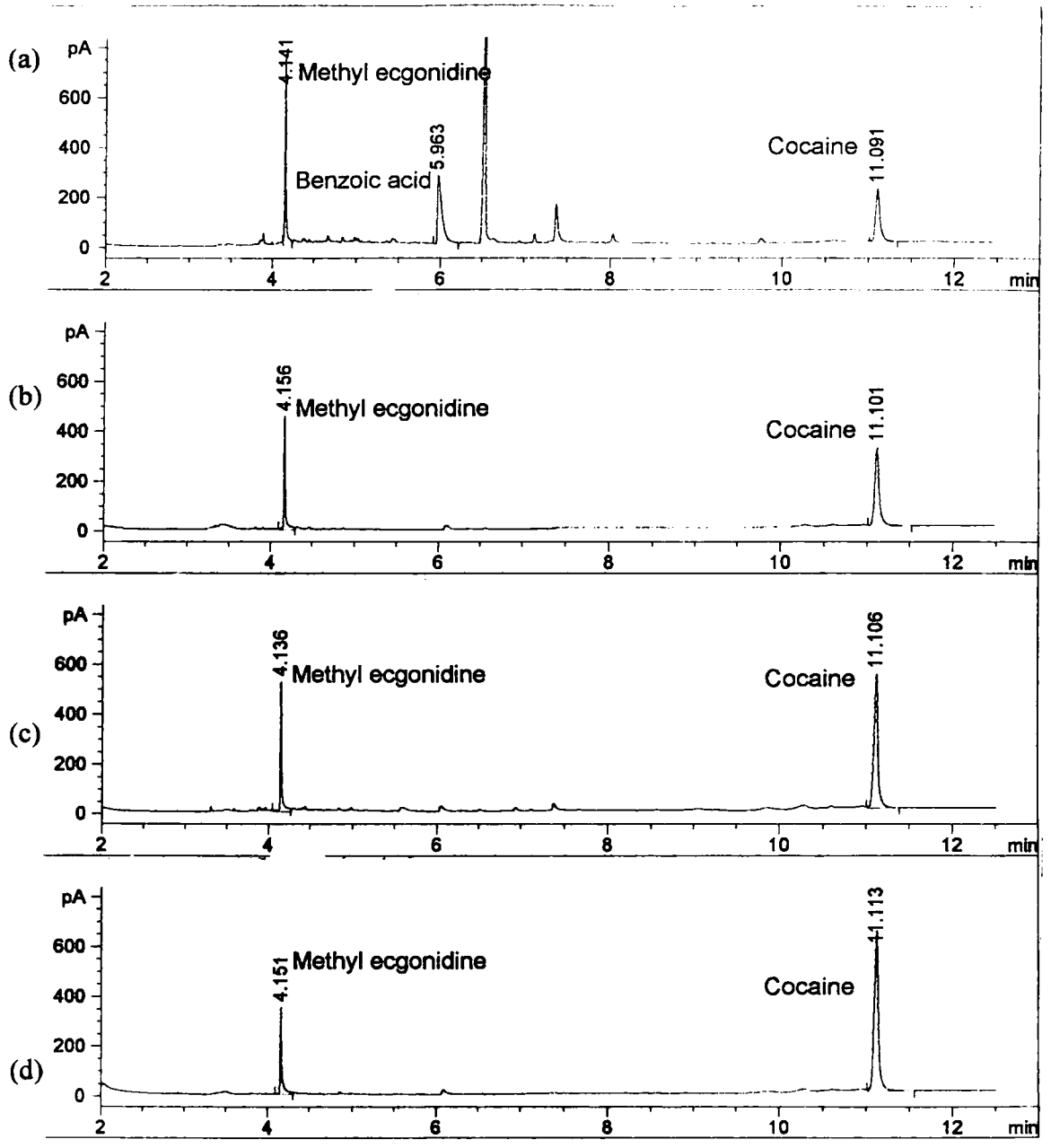


Figure 26. GC chromatograms from reaction of cocaine freebase with (a) QMA, (b) organophilic zeolite, (c) OPZ 1A, and (d) 4Å molecular sieve.

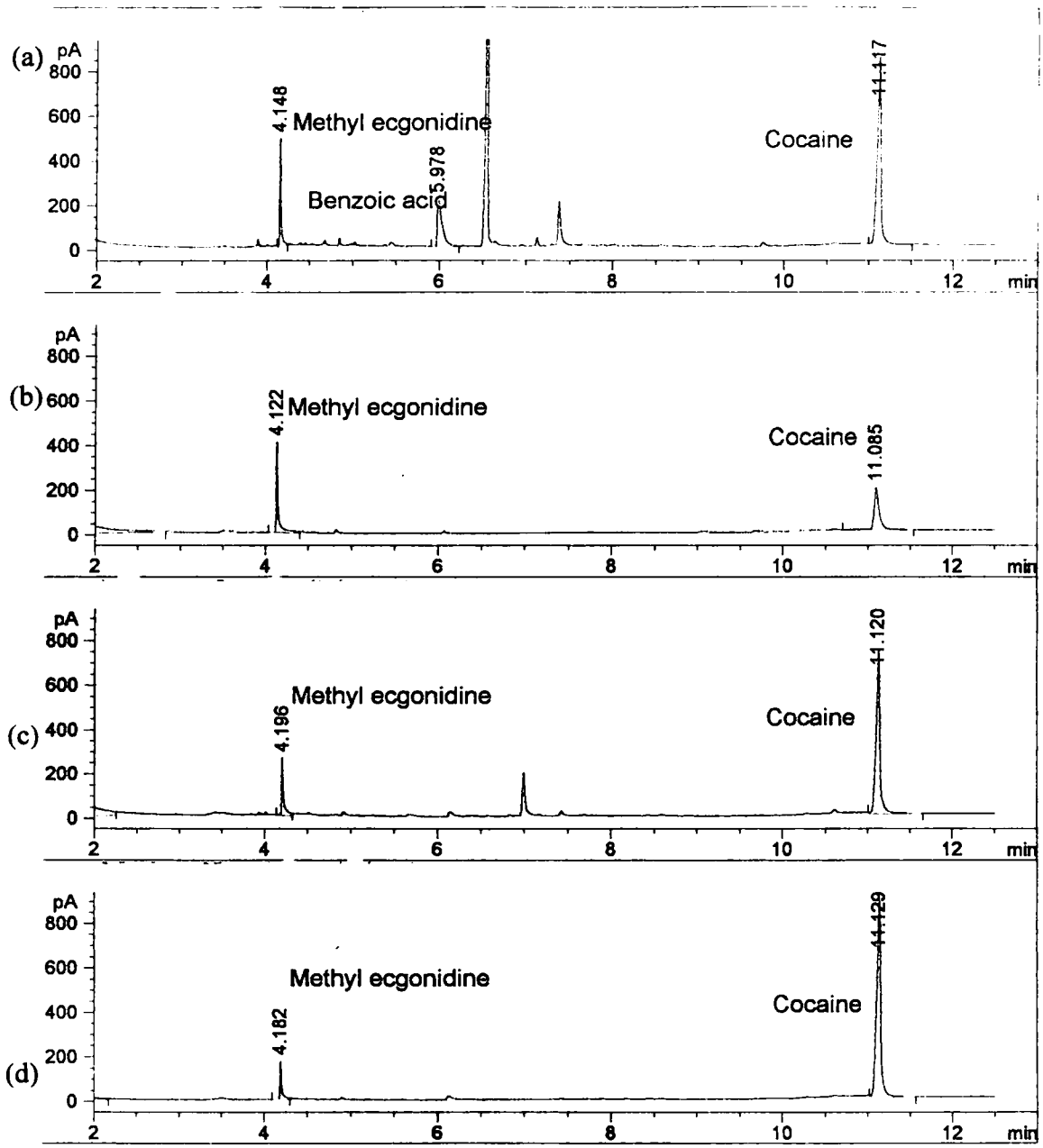


Figure 27. GC chromatograms from reaction of cocaine•HCl with (a) QMA, (b) organophilic zeolite, (c) OPZ 1A, and (d) 4Å molecular sieve.

Table 5. Cocaine Freebase Conversion Chemistry on Several Surfaces. Starting Cocaine Concentration is 1 μg. Percent Conversion based on Calibration Curve using SPME.

Catalytic Material	Conversion Product(s)	Residual Cocaine	Percent conversion
QMA	Methyl ecgonidine Benzoic acid	98ng	90%
OPZ	Methyl ecgonidine	145ng	86%
OPZ 1A	Methyl ecgonidine	227ng	77%
Sieve 4Å	Methyl ecgonidine	280ng	72%

Table 6. Cocaine•HCl Conversion Chemistry on Several Surfaces. Starting Cocaine•HCl Concentration is 1 μg. Percent Conversion based on Calibration Curve using SPME.

Catalytic Material	Conversion Product(s)	Residual Cocaine	Percent conversion
QMA	Methyl ecgonidine Benzoic acid	344ng	66%
OPZ	Methyl ecgonidine	96ng	90%
OPZ 1A	Methyl ecgonidine	305ng	70%
Sieve 4Å	Methyl ecgonidine	397ng	60%

Use of organophilic zeolite (OPZ) gave high conversion of cocaine freebase and cocaine•HCl. QMA quartz fibers were much more reactive with cocaine freebase than with cocaine•HCl. Molecular sieve 4Å appears to be the least reactive of the four materials examined.

Summary

A SPME-GC headspace method has been developed for quantitative analysis of cocaine freebase and cocaine•HCl. The use of the methodology was demonstrated in conversion reactions of cocaine freebase and cocaine•HCl on various surfaces. Of the materials examined organophilic zeolite and QMA quartz fibers appear to be excellent candidates for additional studies in the conversion chemistry of cocaine freebase and cocaine•HCl. As found using SPME-IMS, elimination of benzoic acid with formation of methyl ecgonidine is the major mechanism.

CHAPTER IX

CONCLUSIONS

The objective of this study was to develop analytical methods for cocaine, heroin, and their hydrochlorides which are useful in studying the chemistry of target drugs on surfaces at nanogram levels. Another objective was to demonstrate use of these methods.

A solid phase microextraction - ion mobility spectrometry (SPME-IMS) method has been developed which has been used as a rapid screening tool in studying the chemistry of cocaine hydrochloride, heroin hydrochloride, and heroin freebase on surfaces. The total time for sample preparation, reaction, and analysis is approximately seven minutes. We report the first use of SPME with IMS.[30,31,32,33] The SPME-IMS technique can be applied to other studies and is not limited to contraband drugs.

Under the SPME-IMS conditions, the major products formed from the reaction of cocaine•HCl and the studied solid surfaces appeared to be methyl ecgonidine and methyl ecgonine. The major products formed from the reaction of heroin and heroin•HCl with the solid surfaces appeared to be 6-acetylmorphine and morphine. Organophilic zeolite appears the most promising candidate for conversion reactions of the drugs.

A solid phase microextraction - gas chromatography (SPME-GC) headspace method has been developed for the quantitative analysis of cocaine freebase and cocaine•HCl at nanogram levels. The methodology was used to examine the conversion of the drugs on selected reactive surfaces. As we know it, this is the first report of an analytical method for the headspace analysis of cocaine freebase and cocaine•HCl.

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B.S. in Chemistry, *Cum Laude*, American Chemical Society Certified Degree, Old Dominion University, Norfolk, VA, December, 1995.

Academic Experience

Graduate Research Assistant, Interdisciplinary Research Laboratory, Department of Chemistry and Biochemistry, Old Dominion University, January 1996 - May 1997.
President of American Chemical Society Student Affiliates. Old Dominion University, June 1995 - December 1995.
Undergraduate Research Fellow, School of Ocean and Earth Science and Technology, University of Hawai'i in O'ahu, June 1995 - August 1995; Marine Science Institute, University of Texas at Austin, June 1994 - August 1994.
Undergraduate Research Intern, Department of Chemistry and Biochemistry, Old Dominion University, August 1994 - May 1995; Jones Institute of Reproduction, Eastern Virginia Medical School, January 1994 - May 1994.
Undergraduate Teaching Assistant, Department of Chemistry and Biochemistry, Old Dominion University, June 1994 - December 1994.

Honors and Awards

- ◊ Sigma Xi Graduate Research Award for Tidewater Virginia Chapter, April, 1997.
- ◊ Nominee for Anna Louise Hoffman Award by Department of Chemistry and Biochemistry, Old Dominion University, February, 1997.
- ◊ Outstanding Graduating Chemistry Student Award for 1995-1996.
- ◊ NSF Fellowships, only 10 students selected nationally, June, 1995; June 1994.
- ◊ Outstanding Physical Chemistry Student Award for 1994-1995, May, 1995.
- ◊ C.S. Sherwood Scholarship for the amount of $1200, May, 1995.
- ◊ Academic Honors Research Award for $1000 to fund research for one semester, August, 1994.

Professional Affiliations

Sigma Xi, The Scientific Research Society, Associate member, April, 1997.

Publications

One journal article and four papers in proceedings of scientific meetings.