A NOVEL APPROACH TO INCREASING COCAINE DETECTION CONFIDENCE UTILIZING ION MOBILITY SPECTROMETRY

J. Richard Jadamec and Chih-Wu Su
U.S. Coast Guard Research and Development Center
1082 Shennecossett Road
Groton, CT 06340

Stephen Rigdon
Analysis & Technology, Inc.
258 Bank Street
New London, CT 06320

LaVan Norwood
Tectonic Technologies, Inc.
468 Wells Road
Wethersfield, CT 06109

ABSTRACT

When a positive detection of a narcotic occurs during the search of a vessel, a decision has to be made whether further intensive search is warranted. In terms of unwarranted delays of vessels and possible property damage, the accuracy of the analytical determination is very important. Analytical accuracy becomes critical when the data may be used in court actions as evidence. For this purpose, the U.S. Coast Guard has been investigating several confirmatory ion mobility spectrometry (IMS) field methods for the detection and identification of cocaine. This paper presents the findings of our investigations on the use of catalytic pyrolysis and base hydrolysis as confirmatory methods. The catalytic effects of various metals on the pyrolysis reaction are reported. In addition, the effects of several different ion mobility spectrometer sample transfer mediums and varying laboratory conditions on the base hydrolysis of the cocaine molecule are also be reported.

BACKGROUND

The U.S. Coast Guard (USCG) R&D Center has conducted extensive tests and evaluations (T&E) of commercially available contraband detection systems in both laboratory and field environments since 1991. The objective of these T&E studies was to determine if commercially available illicit drug detection systems could be effectively used in the search of maritime vessels for the presence of smuggled narcotics. Criteria used in selecting appropriate systems for test and study included: minimal sample preparation and pretreatment; speed of sample analysis; low nanogram narcotic detection levels; portability; ease of operation; and affordability. As the amount of laboratory and field T&E data increased, with respect to system performance under actual field situations and the effects of natural environmental backgrounds on analytical results, the accuracy of a positive contraband detection became increasingly important. If a positive detection occurs a decision as to whether or not an in-depth search of a vessel should be undertaken has to be made. Therefore, with respect to unwarranted delays of vessels and possible property damage, the accuracy of a determination is very important. Furthermore, accuracy is critical when the analytical data may be used in court actions as evidence.

Acceptance of an analytical determination is based on the proven reliability of a given method or in the use of multiple technologies to confirm the results obtained by each system. Gas Chromatography/Mass Spectrometer (GC/MS) is an accepted analytical method employed by the EPA for organic pollutant and hazardous material analyses. In the urine drug testing program, NIDA, DOD and USCG require the use GC/MS to confirm and quantitate the level of narcotic or narcotic metabolite detected in the sample. DEA and FBI use GC/MS for both the identification of a seized narcotic and possible matching of the seized narcotic with a source of origin. However, present day GC/MS instrumentation and methodologies lack most of our selection criteria as mentioned above for use in the search of vessels for the detection of illicit drugs.

Other accepted means of verifying analytical results exist. These alternative methods require that a given sample be analyzed by different analytical methods, e.g., on different GC columns, and/or by different analytical technologies. This approach has been used by and recommended for use by the EPA in organic pollutant and hazardous chemical analysis; by the U.S. Coast Guard in oil identification analysis; by the DEA in the laboratory analysis of narcotics; and is recommended for cocaine and heroin analysis by the United Nations, Division of Narcotic Drugs.

IONSCAN (an ion mobility spectrometer), and SENTOR (a gas chromatographic system equipped with dual GC Columns and a chemiluminescence detector) are two of the contraband detection systems which have been extensively tested by the U.S. Coast Guard R&D Center under both laboratory and field conditions. Based on the knowledge acquired from these field T&E studies, two distinct modes of operation evolved for the use of these two systems in the detection of contraband aboard maritime vessels, a search mode and a forensic mode[1]. The forensic mode pertains to situations where the analytical results may be used as evidence in court or other legal actions. In order to generate reliable and scientifically acceptable results, these two systems are used in parallel which, in essence, is equal to a multimethod approach. To date, the analytical results obtained in the use of these two systems in actual searches of maritime vessels have been accepted in the Federal Courts as evidence, and have successfully withstood the challenges in court as to their reliability and accuracy.

INTRODUCTION

To improve the confidence of contraband detection results, specifically when only one detection system is used due to some uncontrollable and unavoidable situation, the use of additional confirmatory methods for the detection and identification of cocaine have been investigated.

Pyrolysis and hydrolysis reactions are two methods which have frequently been used by the analytical chemist to identify a compound, to verify the chemical structure of the compound, and to confirm the analytical result. Methylecgonidine has been reported to be the major pyrolysis product of both cocaine hydrochloride and crack (cocaine base)[2,3].

Methylecgonidine has also been reported in the analysis of cocaine samples by GC methods and is attributed to thermal degradation occurring in the GC injection port[4]. Carbomethoxycycloheptatrienes have also been identified as the main pyrolysis product of cocaine hydrochloride[3].

The cocaine molecule contains two ester groups which can be hydrolyzed to form acid(s) and alcohol(s) under certain conditions. Hydrolysis of cocaine in samples at a pH of 5.5 and higher has been observed to produce benzoylecgonine[5]. In human blood or plasma, the esterase metabolizing of cocaine to methylecgonine has been reported[6].

Both IONSCAN and SENTOR systems utilize heat to desorb collected samples containing cocaine into its vapor form at approximately 280° C. The desorbed cocaine vapor is then carried into the analytical system in a heated gas stream. Occasionally, small amounts of cocaine degradation products have been observed during the routine operation of these two system by the USCG. This suggests that pyrolysis reactions may have occurred during sample analysis by both systems since heat is present, and that hydrolysis reactions may also have occurred as a result of cocaine being smuggled in the maritime environment.

Based on the above observations, a study to determine whether pyrolysis and hydrolysis reactions could be utilized to confirm the Ionscan detection of cocaine was undertaken. Pyrolysis reactions can be enhanced by applying a catalyst and hydrolysis reactions can be controlled by pH and reactants. This paper will present the results of our study and their application as a field confirmation.

EXPERIMENTAL METHOD

Methanol solutions (1mg/mL) of cocaine hydrochloride, benzoylecgonine, ecgonine and methylecgonine were purchased from Alltech Associates Inc. Methylecgonidine was synthesized in our laboratory and identified by comparing its mass spectra with the published mass spectra of methylecgonidine. Material used as sample holders were: filter paper, obtained from Schleicher & Schuell (S&S), having a nominal pore size of 20 to 30 um ; glass fiber filters having a nominal pore size less than 50 um obtained from both SKC Inc. and Omega Specialty Instrument Co.; and quartz glass filters having a nominal pore size less than 50 um obtained from Pallflex Products Corp., Putnam CT.

1) Catalytic pyrolysis: Copper, iron, steel and aluminum were selected as candidate catalysts. Fresh, fine powders of each metal were prepared by filing. Each metal powder was spread on an S&S filter paper and analyzed to ensure that no interferent responses were present in the cocaine and cocaine degradation regions of the ion mobility spectrum. Standard cocaine hydrochloride solutions (1 uL of a 5ug/mL standard) prepared in methanol, were deposited on top of each powder. The methanol was evaporated at room temperature. Normal routine IONSCAN analytical procedures were then followed in the analysis of these samples. The same amount of cocaine hydrochloride was also deposited on gold coated nickel screen obtained from Barringer Instruments Inc. (BII) and analyzed by the same procedures.

2) Base hydrolysis: Filter paper was selected for this study as a result of the water repellant properties of Teflon material. Three different sets of standard test conditions were employed as follows:

a) 1 uL of 5 ug/mL or 20 ng/mL standard cocaine hydrochloride in methanol was deposited on S&S filter paper. Methanol was evaporated at room temperature.
b) 1 uL of 5 ug/mL or 20 ng/mL standard cocaine hydroxide in methanol was deposited on S&S filter paper. After the methanol evaporated, 3 uL of 2% sodium hydrochloride in water solution was spotted on top of the cocaine hydrochloride.
c) 1 uL of 5 ug/mL or 20 ng/mL standard cocaine hydrochloride in methanol was deposited on S&S filter paper. After the methanol evaporated, 3 uL of 2% sodium hydroxide in methanol solution was spotted on top of the cocaine hydrochloride.

Standards prepared from (b) and (c) were then air dried at room temperature. All standard samples were analyzed by the same IONSCAN procedures. Black burned spots were observed to be present on the filter paper after IONSCAN analysis where the sodium hydroxide had been added . In order to determine whether the burning phenomenon affected the formation of the degradation products observed, quartz and glass fiber (brands A and B) filters were used for comparison purposes.

RESULTS AND DISCUSSION:

Figure 1 shows the IONSCAN ion mobility spectra (IIMS) of cocaine, benzoylecgonine, methylecgonine, methylecgonidine and ecgonine standards deposited on filter paper. As can be seen in this figure, each compound is readily identified by its reduced ion mobility spectrum. The results obtained in our pyrolysis and hydrolysis studies are summarized below:

1) Catalytic pyrolysis: Figure 2 shows the IIMS of 5 ng of cocaine hydrochloride on copper and iron powder. Table 1 lists the IONSCAN analytical results of 5 ng of cocaine hydrochloride deposited on the different metal powders used in this study. No cocaine degradation products were detected when copper and gold coated nickel screen were used as a catalytic surface. The ratio of the methylecgonidine amplitude to that of cocaine ranged from 20% to 26% when iron, steel and aluminum were present. The thermal conductivities (watt/cmC at 25° C) of copper, aluminum and iron are 3.98, 2.37 and 0.803, respectively. This suggests that the observed decrease in the cocaine amplitude may be related to the thermal conductivity of these metals. Unfortunately, the lack of enough standard methylecgonidine material prevented us from performing further semiquantitative calculations on the production of methylecgonidine under these experimental conditions.

Fytche et al., reported that the IONSCAN detection level for cocaine was substantially reduced when cocaine was deposited on silica[7]. The reduction in the detection level of cocaine was considered to be the result of the slow heat conduction property of silica. Whether the decreasing amount of cocaine observed in our studies is the result of the slow heat transfer of the metal powders, similar to that reported by Fytche et. al.[7], or if it is due to the conversion reaction of cocaine to methylecgonidine needs further investigation.

2) Base hydrolysis: The results of Ionscan analysis of cocaine on paper, quartz and glass fiber (brands A and B) filters are listed in Table 2. Except for filter paper, methylecgonidine was observed to be the major compound detected when 5 ng of cocaine was spotted on all types of sample holding material used in this study . When 20 ng of cocaine was spotted on quartz and glass fiber filters, only methylecgonine was observed for brand A glass fiber filters. However, when brand B Quartz and glass fiber filters were used

both methylecgonidine and cocaine were detected. Table 3 shows that the addition of 3 uL of 2% sodium hydroxide on cocaine produced subtle changes in the relative response of these compounds as seen in comparing the data contained in Tables 2 and 3. However, when 20 ng of cocaine was spotted on quartz the cocaine response diminished but the amount of methylecgonidine did not increase. Table 4 shows that the addition of 3 uL of 2% sodium hydroxide in methanol did not hydrolyze cocaine when filter paper was used as the sample holder. However, methylecgonine was the dominant product detected for all other test conditions except for the test in which 20 ng cocaine was deposited on brand B glass fiber filters. The contradiction between the results obtained when 5 ng and 20 ng of cocaine were spotted on brand B glass fiber filters requires further investigation.

Methylpseudoecgonine is produced when cocaine is hydrolyzed by sodium hydroxide and subsequent esterification occurs in the presence of methanol[8]. Methylecgonine and methylpsuedoecgonine differ only in structure, i.e., whether the 2-carboxylic methyl ester is located in the exo or endo position. Therefore their reduced mobilities should be approximately the same. Whether the methylecgonine detected in our study is actually methylpsuedoecgonine requires further investigation.

The structure of cocaine is a 8-methyl-8-azabicyclo[3.2.1]octane with both the 2-carboxylic methyl ester and 3-benzoyloxy groups located at exo positions. The elimination of benzoic acid from the cocaine molecule produces a double bond between the 2- and 3-carbon positions of the ring structure and forms the molecular structure of methylecgonidine. The double bond between the 2 and 3 carbons reduces the free rotation of the ring structure. However, the ring structure has less steric hindrance due to the elimination of exo-locatedfunctional groups located at the 2- and 3- carbon positions. These two chemicals, cocaine and methylecgonidine, are likely to have approximately the same ground state energies based on their ring structures. Although a six membered ring structure (a favorable transition state for a concerted reaction) can be formed by the connection of the exo benzoyloxy group and the endo hydrogen at the 2 carbon position (Figure 3) in the cocaine molecule coupled with the elimination of the benzoic acid, this study showed that at temperatures up to 280° C the cocaine molecule is very stable. This indicates that the activation energy required to convert cocaine to methylecgonidine is high.

Glass, with the main component being silica, is a common material for containers used to store organic chemicals due to its inertness toward most organic compounds. Quartz is a pure form of silica. It is well known that the surface of both quartz and glass contain many surface active sites, such as silanols (Si-OH) and siloxanes (Si-O-Si)[9]. These surface active sites frequently affect the quality of analytical separations of gas chromatographic glass columns, especially when capillary columns are used to separate polar compounds. The catalysis reaction leading to the conversion of cocaine to methylecgonidine on or in the presence of quartz and glass fiber filters suggests that the transition state might involve a cyclic ring structure larger than a six membered ring as shown in Figure 4.

When 1 uL of a liquid solution is deposited on quartz or glass fiber filter, the liquid does not disperse horizontally to the same degree as on filter paper, but penetrates downward. This is related to the different capillary properties of paper and glass filters. After the methanol has been removed by evaporation, the cocaine coats the surface of individual quartz or glass fibers that have been wetted by the methanol solution containing cocaine. As the concentration of cocaine in the solution increases, the residual coating thickness increases. Therefore, some of cocaine molecules are not in direct contact with a quartz or a glass fiber surface. As soon as sufficient heat is supplied, the cocaine molecule evaporates (vaporizes) and migrates through the filter without a decomposition reaction occurring since the active sites of the glass fibers are already coated with cocaine or involved in a reaction with cocaine vapor.

Glass structures also contain various trace metal impurities. Low level concentrations of trace metals impurities still exist even after the glass filter has been acid leached. However, the catalysis reaction of cocaine resulting in the decomposition of cocaine to methylecgonidine is unlikely due to the presence of these trace metals, since our results of intentionally using large amounts of metal, as discussed previously, did not indicate that this decomposition reaction occurred (Table 1).

In order to determine whether this elimination reaction of benzoyl acid from cocaine can occur only through contact of cocaine vapors with the surfaces of glass fibers, rather than through the direct contact of solid cocaine with the glass fiber during the sample desorption stage, the following study was performed. 1 uL of 5ug/nL standard cocaine hydrochloride in methanol was deposited on filter paper positioned in the Barringer sample holder and a glass fiber filter was placed above the sample holder. In this configuration a 2 mm space exists between the filter paper and the glass fiber filter. Figure 5 clearly shows that under this condition methylecgonidine is generated by the contact of cocaine vapor with the glass fiber filter at a desorption temperature of 280° C .

APPLICATION AND PRECAUTIONS

This reaction and formation of methylecgonidine under these conditions has been observed to be repeatable and therefore has the potential of being used as a method for the confirmation of the presence of cocaine in a collected sample.

Filler materials are commonly added to paper and glass fiber filters. Manufacturers of paper and glass fiber use binders and fillers to obtain specific performance characteristics of these materials for their intended use as filtering mediums. The kinds of material added depend on the desired performance characteristics of the filter membrane and are dependent on the manufacturing process. Some of these fillers may dramatically alter the pyrolysis reaction product(s) observed in this study. The source of material used to perform this confirmation reaction should be screened and tested prior to its use.

REFERENCES

[1] Jadamec, J.R., Su, C., Rigdon, S., Norwood, L., and Kaplain, C., "Confidence in the Detection of Cocaine Particulates," Presented at the Society of PhotoOptical Instrumentation Engineers 1994 International Symposium, San Diego, CA, July 1994.

[2] Martin, B.R., Lue, L.P., and Boni, J.P., "Pyrolysis and Volatization of Cocaine," Journal of Analytical Toxicology, Vol. 13, 1989, pp. 158162.

[3] LeBelle, M.J., Dawson, B., Lauriault, G., and Savard, C., "Identification of Nformylnorcocaine and NBenzoylnormethylecgonine in Illicit Cocaine," Analyst, Vol. 116, 1991, pp. 10631065.

[4] Lukaszewski, T., and Jeffery, W.K., "Impurities and Artifacts of Illicit Cocaine," Journal of Forensic Sciences, Vol. 25, 1980, pp. 499507.

[5] Gupta, Das V., "Stability of Cocaine Hydrochloride Solutions at Various pH Values as Determined by Highpressure Liquid Chromatography," International Journal of Pharmaceutics, Vol. 10, 1982, pp. 249257.

[6] Baselt, R.C., "Stability of Cocaine in Biological Fluids," Journal of Chromatography, Vol. 268, 1983, pp. 502505.

[7] Fytche, L.M., Hupe, M., Kovar, J.B., and Pilon, P., "Ion Mobility Spectrometry of Drugs of Abuse in Customs Scenarios: Concentration and Temperature Study," Journal of Forensic Sciences, JFSCA, Vol. 37, No. 6, November 1992, pp.1550-1566.

[8] Sinnema, A., Matt, L., Van Der Gugten, A.J., and Beyerman, H.C., "Configuration and Conformation of All Four Cocaines from NMR Spectra," Recueil des Travaux Chimiques des PaysBas, Vol. 87, 1968, pp. 10271041.

[9] Dorsey, J. G., and Cooper, W. T. "Retention Mechanisms of BondedPhase Liquid Chromatograohy" Analytical Chemistry, Vol. 66, 1994, pp.857A.

Table 1. Detections of Cocaine and Methylecgonidine by Ionscan When Cocaine Deposited on Different Metal Powders

				Metal Powder on Filter Paper									
		Filter Paper		Copper		Iron		Steel		Aluminum		Gold Screen*	
		Max Amp	# of Hit	Max Amp	# of Hit	Max Amp	# of Hit	Max Amp	# of Hit	Max Amp	# of Hit	Max Amp	# of Hit
1	cocaine	904	14	871	13	476	13	227	12	516	13	464	14
2	methylecgonidine	63	5	0		104	9	58	5	94	10	0	
3	Me-Ecgd**/cocaine	0.07		0		0.22		0.26		0.18		0	
4	Relative amptitue	1.00		0.96		0.53		0.25		0.57		0.51	

* : Gold coated nickel screen

** : Methylecgonidine

Table 2. Compounds Dectected by Ionscan when Cocaine Deposited on Paper, Quartz or Glass Fiber Filter

Sample holding material	Amount of cocaine added (ng)	Treat with NaOH	Solvent for NaOH	Cocaine		Methyl ecgonine		Methyl ecgonidine	
				Max Amp	# of Hit	Max Amp	# of Hit	Max Amp	# of Hit
paper	5	no	-	807	14	-		74	7
quartz	5	no	-	trace		-		438	13
glass (a)	5	no	-	-		-		535	9
glass (b)	5	no	-	trace		-		300	13
quartz	20	no	-	582	14	-		623	14
glass (a)	20	no	-	-		-		761	14
glass (b)	20	no	-	444	6	-		562	14

Table 3. Compounds Detected by Ionscan When Cocaine Was Deposited on Paper, Quartz or Glass Fiber Filter And Then Treated With 2% NaOH (in Water)

Sample holding material	Amount of cocaine added (ng)	Treat with NaOH	Solvent for NaOH	Cocaine		Methyl ecgonine		Methyl ecgonidine	
				Max Amp	# of Hit	Max Amp	# of Hit	Max Amp	# of Hit
paper	5	yes	water	809	14	-		61	2
quartz	5	yes	water	-		-		348	8
glass (b)	5	yes	water	63	2	-		247	13
quartz	20	yes	water	98	2	-		582	14
glass (a)	20	yes	water	-		-		725	14
glass (b)	20	yes	water	342	5	-		504	14

Table 4. Compounds Detected by Ionscan When Cocaine Was Deposited on Paper, Quartz or Glass Fiber Filter And Then Treated With 2% NaOH (in Methanol)

Sample holding material	Amount of cocaine added (ng)	Treat with NaOH	Solvent for NaOH	Cocaine		Methyl ecgonine		Methyl ecgonidine	
				Max Amp	# of Hit	Max Amp	# of Hit	Max Amp	# of Hit
quartz	5	yes	methanol	-		647	6	-	
glass (b)	5	yes	methanol	141	3	472	2	122	2
paper	20	yes	methanol	1061	14	-		trace	
quartz	20	yes	methanol	144	4	1016	6	-	
glass (b)	20	yes	methanol	519	5	-		150	4

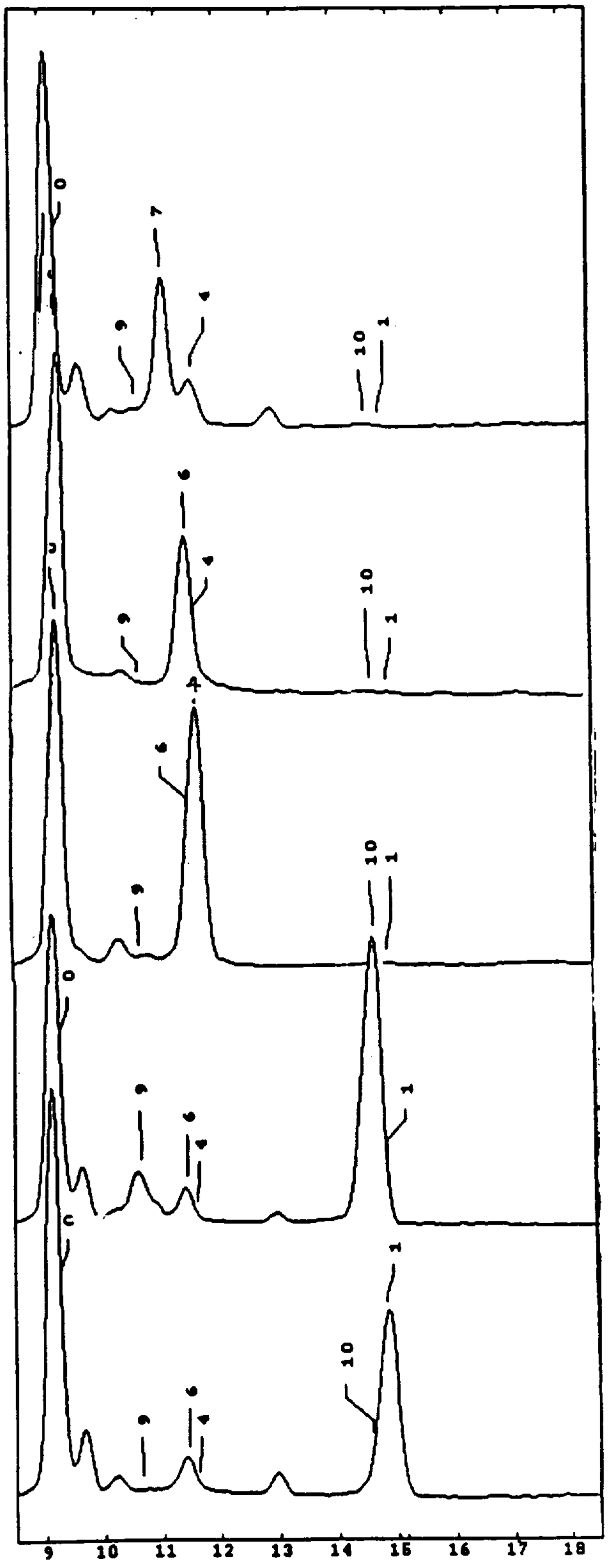


Figure 1. Ion Mobility Spectra of

a) Ecgonine

b) Methylecgonidine

c) Methylecgonine

d) Benzoylecgonine

e) Cocaine

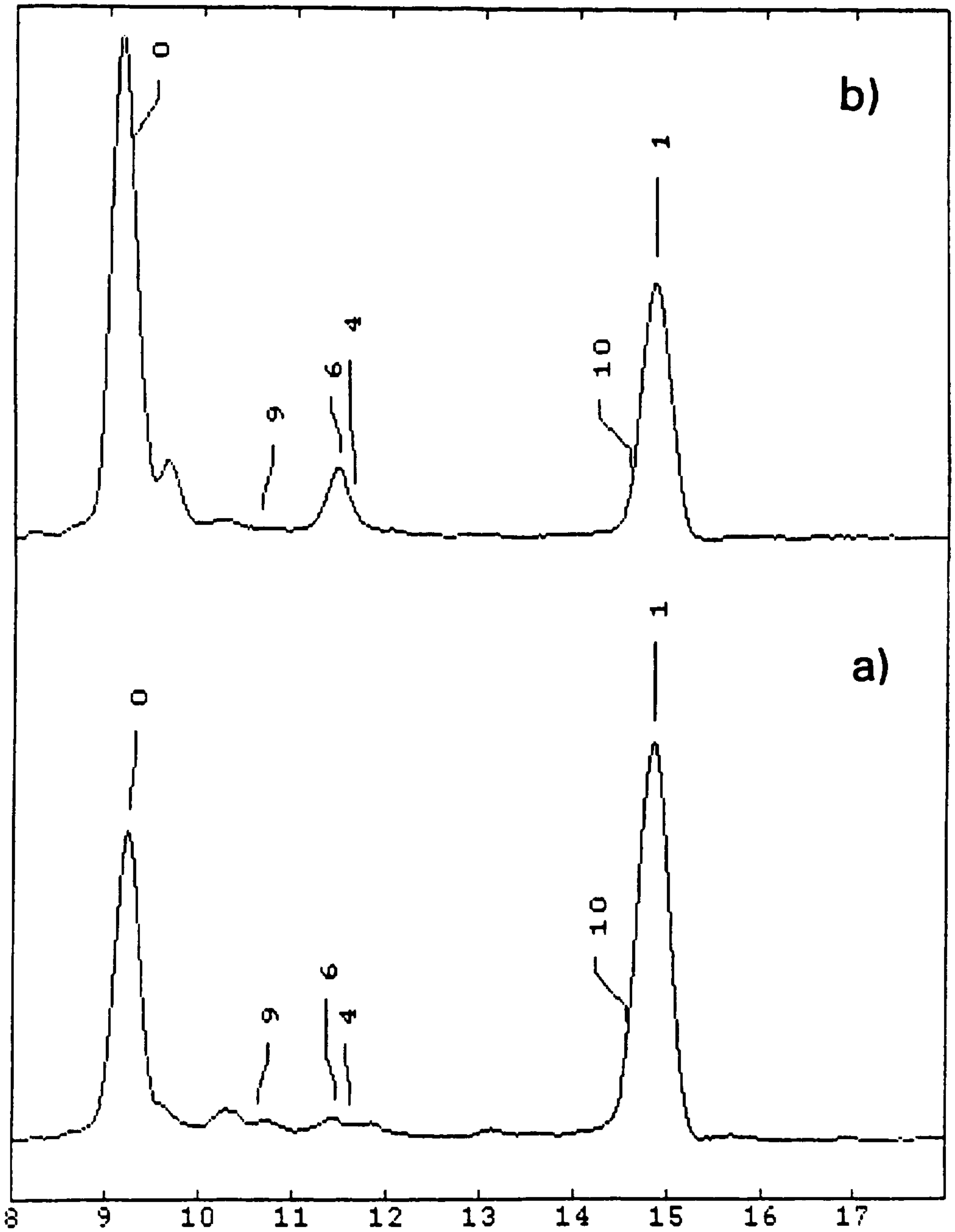
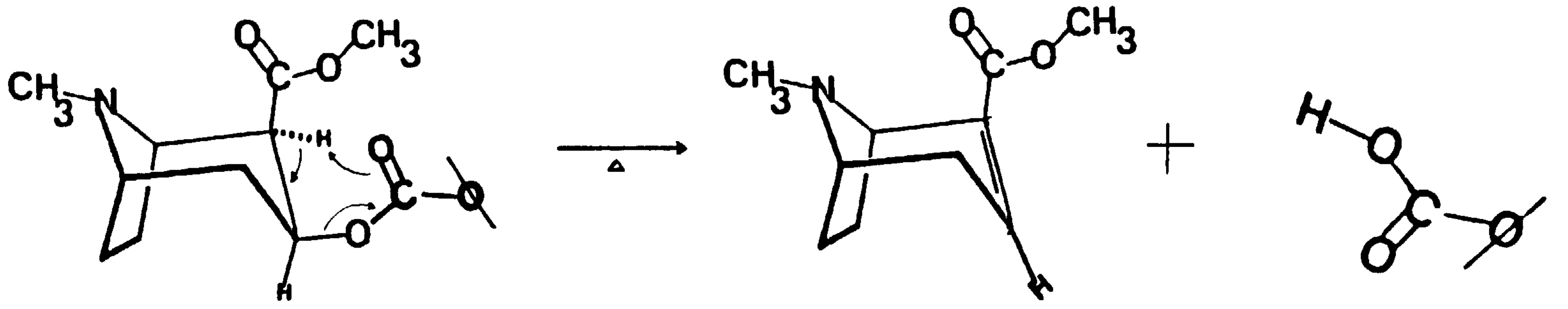


Figure 2. Ion Mobility Spectra of

a) 5 ng of cocaine on copper powder
b) 5 ng of cocaine on iron powder



Cocaine

Methylecgonidine

Benzoic Acid

Figure 3. Elimination of Benzoic Acid From Cocaine Throught a Conserted Reaction Mechanism

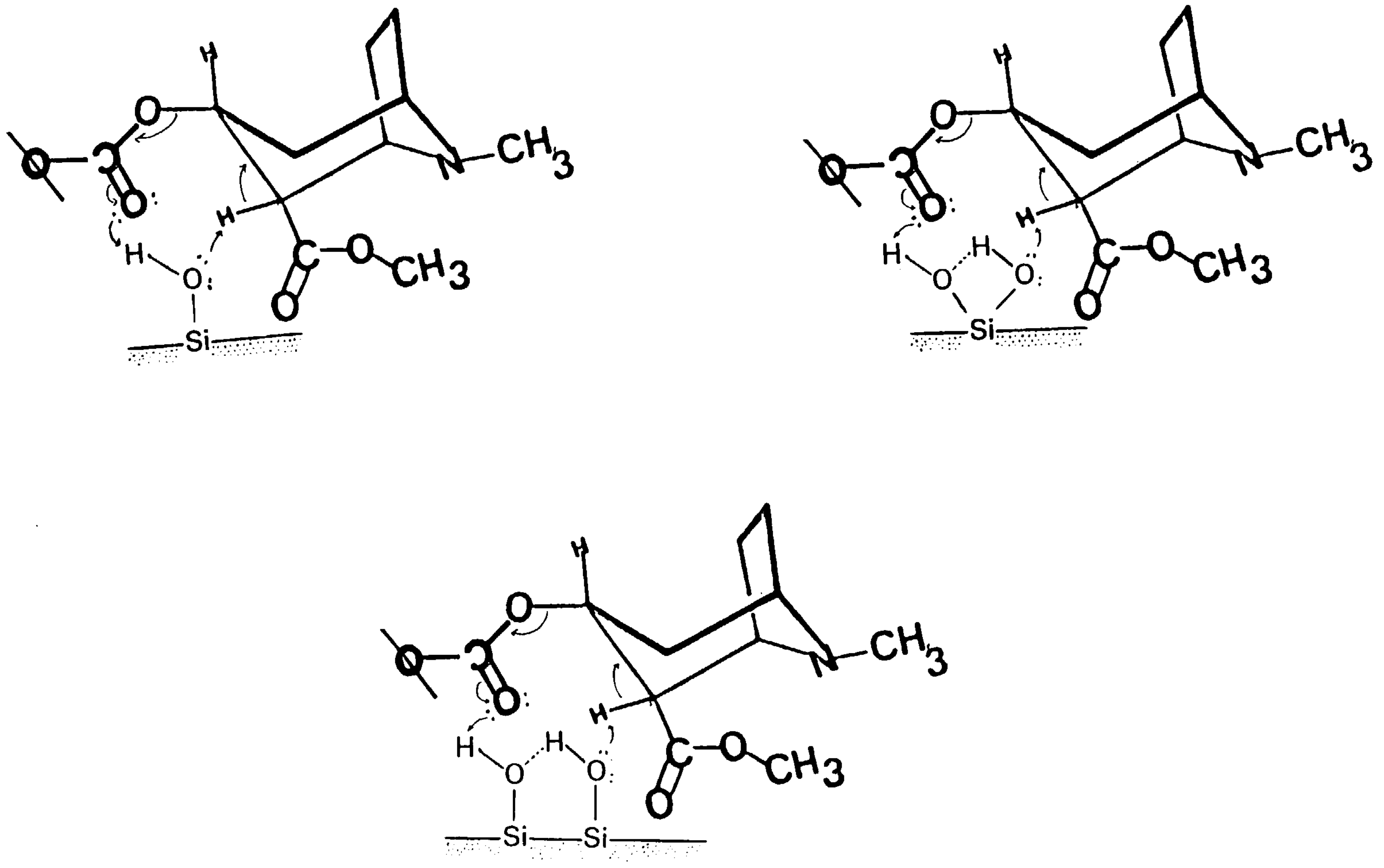


Figure 4. Catalytic Elimination of Benzoic Acid From Cocaine by Quartz or Glass Surface Active Sites

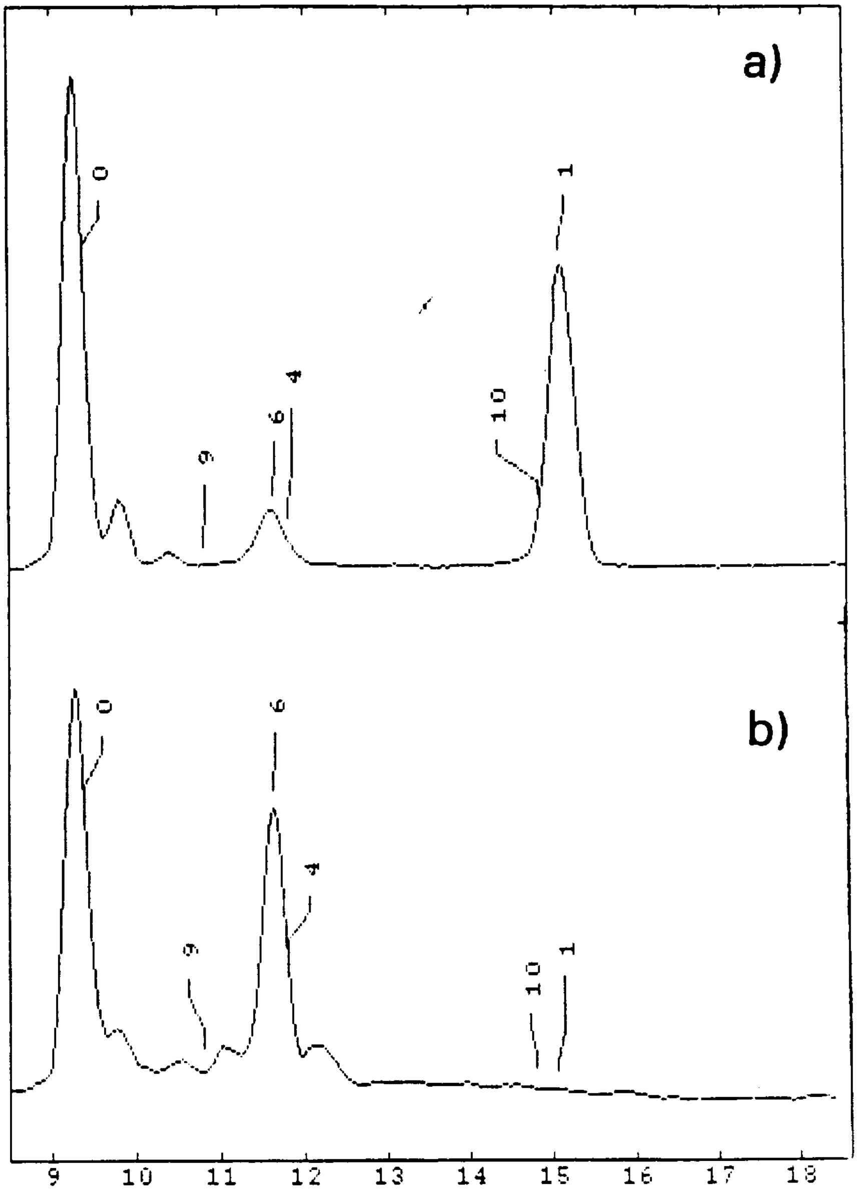


Figure 5. Ion Mobility Spectra of

a) 5 ng of cocaine on paper filter
b) 5 ng of cocaine on paper filter
then covered with glass fiber filter (brand a)