

TECHNICAL NOTE

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The Effects of Microwave Irradiation on Occluded Solvents in Illicitly Produced Cocaine Hydrochloride

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ABSTRACT: The current clandestine methodology for the manufacture of illicit cocaine hydrochloride utilizes microwave heating in order to dry the finished product. This study addresses the effects this step has on the occluded solvents present in newly prepared cocaine hydrochloride. Nine 1-kilogram-sized batches of cocaine hydrochloride were prepared from cocaine base using a variety of solvents or solvent mixtures commonly utilized in clandestine laboratories, pressed into bricks, and submitted to microwave heating. Residual solvents were qualitatively and quantitatively monitored before, during, and following the microwaving step by static headspace-gas chromatography-mass spectrometry. All solvents used in the conversion process were easily detected in the bricks even after extensive irradiation, confirming that occluded solvents are extremely resistant to removal by microwave heating. Qualitative and quantitative data corresponding to the residual solvents in the prepared cocaine hydrochloride bricks are presented.

KEYWORDS: forensic science, cocaine hydrochloride, gas chromatography, static headspace, mass spectrometry, microwave irradiation, occluded solvents

Illicit cocaine hydrochloride is typically prepared by the addition of a solution of concentrated hydrochloric acid in a moderately polar organic solvent to a second solution of cocaine base dissolved in a relatively nonpolar organic solvent or solvents (1). This procedure usually results in rapid precipitation of cocaine hydrochloride, which in turn causes small quantities of the solvents used in the base-to-hydrochloride conversion to be trapped (i.e., “occluded”) within the crystal matrix. The analysis of illicit cocaine hydrochloride for these residual solvents has been performed by various methodologies (2–7), the most rigorous being a qualitative and quantitative procedure utilizing static headspace-gas chromatography-mass spectrometry (SHS-GC-MS) (8). The results are useful both for comparative analyses and intelligence-gathering purposes (9,10), such as monitoring the use and diver-

sion of solvents utilized in the manufacture of illicit cocaine hydrochloride.

Beginning in the mid-1980s, clandestine laboratory operators in South America began using microwave ovens to dry compressed bricks of cocaine hydrochloride prior to packaging and shipping. The use of microwave ovens expanded rapidly and is currently the predominant drying method. Prior to this point, drying was accomplished using a slower, less effective combination of conventional ovens, heat lamps, electric or gas-fired grills, and fans. All of these conventional methods transfer heat from the brick’s surface inward, whereas microwave heating transfers heat from inside the brick outward. Because of the inherent differences between microwave and conventional heating, it was unclear what effect(s), if any, microwaving would have on the resulting occluded solvent impurity profiles of the cocaine hydrochloride. This knowledge is critical in order to maintain the efficacy and validity of the monitoring and intelligence-gathering aspects of residual solvent analyses. Specifically, it was important to determine whether: (a) the sum total of occluded solvents would be significantly decreased; (b) whether certain solvents, particularly low-boiling solvents, would be selectively reduced or eliminated; and (c) whether new “artifactual” solvents would be produced by microwave-enhanced reactions occurring within the occluded solvent reservoirs in the crystal matrix.

To our knowledge, the effects of microwave irradiation upon occluded solvents have not been addressed for any illicit drug. Herein, we present the results of a study of both the qualitative and quantitative effects of microwaving on occluded solvents in compressed bricks of cocaine hydrochloride.

Experimental

Solvents, Chemicals, Standards and Materials

All solvents used for cocaine base to hydrochloride conversion were “distilled-in-glass products” of Burdick and Jackson Labs (Muskegon, MI). Hydrochloric acid (36.5 to 38%) was obtained from J. T. Baker (Phillipsburg, NJ), and was of reagent grade quality. All other chemicals and solvents were reagent grade or better. Illicit cocaine hydrochloride was obtained from confiscated stocks at the Drug Enforcement Administration’s Southeast Laboratory (Miami, FL). Internal standards used in the SHS-GC-MS analysis

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(acetone- d_6 , isopropanol- d_8 , toluene- d_8 , 2-chloro-2-methylpropane- d_9 , and n -hexane- d_{14}) were obtained from Cambridge Isotope Laboratories (Andover, MA). Deionized water, filtered through a Millipore Milli-Q™ System (Bedford, MA) to remove trace organic impurities, was used for all sample and standard solutions. The reaction vials and corresponding Mininert™ valve caps used to store standard solutions were supplied by Pierce (Rockford, IL) and Supelco (Bellefonte, PA), respectively. Headspace vials, 20 mL, were clear 20 mm × 75 mm glass with corresponding silicone/Teflon™ septa crimp caps (Phase Separations, Inc., Norwalk, CT.)

Instrumentation and Equipment

Two similar automated SHS-GC-MS configurations were utilized, differing only in their associated mass spectrometers. All quantitative analyses were performed on the first instrument configuration, which utilized a more sensitive Ion-Trap MS detector (detailed below). Instrument settings are as follows for both configurations: solvent concentration was performed by a Tekmar SHS 7000/7050 Headspace-Autosampler Combination, fitted with a 2.0 mL stainless steel sample loop and a heated nickel transfer line. The headspace settings were: platen temperature, 80°C; transfer line temperature, 180°C; valve/line temperature, 180°C; vial size, 20 mL; mixer time, 15 min; mixer power, 1; vial pressurize time, 0.3 min; pressure/loop equilibration time, 0.05 min; loop fill, 0.2 min; and inject time, 1.5 min.

Separation of the liberated residual solvents was performed in both configurations by Hewlett-Packard Model 5890 Series II Gas Chromatographs fitted with 60 × 0.25 mm inside diameter fused silica capillary columns coated with 1 μm DB-1 (J&W Scientific, Folsom, CA). Helium (UHP) was used as the carrier gas, at an average linear velocity of 23 cm/s. The GCs were temperature programmed as follows: initial temperature, 40°C; initial hold, 14 min; temperature program rate, 7°C/min; final temperature, 210°C; final hold, 3 min. The injector temperatures were maintained at 180°C with a split ratio of 8:1.

Detection and identification were performed by a Finnigan-Mat Model 800 Ion Trap Detector (ITD) and a Hewlett-Packard Model 5972 Mass Selective Detector for the first and second configurations, respectively. Instrument settings were: scan range, 20 to 230 amu; scan/s, 2; acquire time, 42 min; transfer line temperature, 200°C; scan mode, full; filament/multiplier delay, 4 min.

Microwave irradiation of the cocaine hydrochloride bricks was performed with a Magic Chef Model DM5H-3 1200 watt microwave oven (Anniston, AL). The oven was set at 5 on a scale of

0 to 10, resulting in the magneto being energized 50% of the selected time frame, in one-second increments.

Preparation of Cocaine Hydrochloride Bricks

Cocaine base was prepared from confiscated illicit cocaine hydrochloride by dissolving the latter in water, precipitating the free base by the addition of dilute ammonium hydroxide, filtering, and drying to constant weight using heat lamps at 60°C. Solvent analysis of the dried base by SHS-GC-MS indicated no carry-over of any residual solvents present in the starting materials.

Nine solvent mixtures were used in the base-to-hydrochloride conversions (Table 1). In each case, approximately 1 kg of the dried base was dissolved in 10 L of solvent mix A, which then was filtered and set aside. Approximately 230 mL of concentrated hydrochloric acid was dissolved in 10 L of solvent B, and the resulting solution then was rapidly added to solvent mix A (cocaine base solution) with stirring; resulting in rapid precipitation of cocaine hydrochloride. The combined mixture was allowed to stand for 1 to 2 h to complete the crystallization process, after which the product was collected by suction filtration and dried under high-intensity heat lamps until its appearance was no longer wet. The resulting damp, crystalline powder was then compressed into 8 in. × 5.5 in. × 1 in. (~20 × 14 × 2.5 cm) bricks using a wooden mold and a hydraulic press applying a maximum pressure of 16 tons/in.² Each compressed brick, still moist with solvent and varying from off-white to white in color, was removed from the mold and stored in a plastic bag prior to microwave irradiation. The conversion procedures and selected solvents were in accordance with current methodologies in use by illicit laboratory operators in South America.

Microwave Irradiation, Sampling, and Occluded Solvent Analyses of Cocaine Hydrochloride Bricks

Each brick was handled independently and essentially identically; each was removed from its plastic bag, placed on a previously tared microwave tray, accurately weighed, sampled, and immediately subjected to microwave irradiation. Each brick was irradiated for 3 min, removed for a 15 min cooling period (during which time it was again weighed and sampled), then returned to the oven for additional irradiation. Total irradiation times varied from 15 to 24 min, i.e., five to eight 3-min sessions, intentionally longer than the 8 to 12 min typically used in the clandestine process (based on clandestine laboratory operator interviews, 1993–1996), in order to monitor the maximum effects on the occluded solvents. As the brick temperatures increased, it was common to observe hot solvents leach from the brick onto the microwave tray and rapidly

TABLE 1—Conversion solvent compositions.*

Brick No.	Solvent(s) A	Solvent(s) B	Ratio
1	Ethyl ether	acetone	1.6:1
2	Acetone	acetone	N/A
3	Methyl ethyl ketone (MEK)	MEK	N/A
4	Ethyl acetate/toluene	MEK	6:1:6
5	Ethyl acetate/toluene	MEK	1:1:1
6	Hexane/toluene	MEK	2:1:2
7	Hexane/methylene chloride	MEK	10:1:10
8	Hexane/ethyl acetate/methylene chloride	MEK	9:3:1:7
9	Ethyl ether	acetone/spike components†	100:100:1

* All solvent ratios are volume/volume.

† Spike components: benzene, butyl cellosolve, chloroform, cyclohexanone, dimethoxymethane, ethyl acetate, n -hexane, 2-butanol, mesityl oxide, methyl acetate, methylene chloride, methyl ethyl ketone, methyl isobutyl ketone, tetrachloroethylene, toluene, m -xylene.

evaporate. The actual temperatures of the bricks were not monitored, but they quickly reached the point where they could not be manipulated by hand without protective (thermal) gloves. By the final irradiation session, the bricks had achieved the characteristically dry, hardened appearance of clandestinely manufactured bricks. Following the final irradiation session, each brick was again weighed and sampled.

All samples were taken using a standard 0.8 cm outside diameter cork borer. The removed material was punched out of the borer into a glass vial, weighed and held for future SHS-GC-MS analysis. All samples were left open to air to allow final evaporation of any remaining nonoccluded solvent(s). The average amount of material removed by the cork borer during each sampling was about 500 mg. The respective weights of the removed samples were taken into account when determining brick weights.

For each sample, a single 30 mg equivalent of cocaine hydrochloride was removed for SHS-GC-MS analysis. The workup and analysis of each sample were identical to the previously described protocol (8), except that only single (not triplicate) analyses were performed, and 30 (not 15) mg equivalents of cocaine hydrochloride were used. In addition, method blanks containing the five deuterated internal standards were analyzed by SHS-GC-MS to identify any isotopic impurities; no detectable impurities were observed.

Results and Discussion

In general, there are two types of solvents associated with the precipitation of cocaine hydrochloride from organic solutions:

“wetting” solvents, i.e., those adhering to the outside surfaces of the crystals, and “occluded” solvents, i.e., those trapped in interstitial cavities created throughout the crystal matrix during crystal growth. The crude production techniques utilized in clandestine laboratories (i.e., rapid precipitation) are especially conducive to occlusion of the precipitating media. Prior studies have indicated significant quantities of occluded solvents in illicit cocaine hydrochloride, typically varying from 0.1 to 1.5% (2–8). Most of these studies were completed before the advent of microwaving in clandestine laboratories, and therefore offer valid baseline data for comparison. Analysis of pharmaceutical grade cocaine hydrochloride, which is produced slowly and under cold conditions, indicated occluded solvents at only the 0.005 % level.

It was previously suspected that occluded solvents would be dramatically impacted by microwave heating—a suspicion lent additional credence by the high brick temperatures observed during the irradiation sessions (well above the boiling points of the more volatile solvents utilized to precipitate the cocaine hydrochloride.) Surprisingly, however, the sample analyses indicate only moderate effects (Fig. 1). Total occluded solvent levels in the nine bricks ranged from 0.13 to 2.1% before and 0.10 to 1.7% after irradiation, respectively. These values compare favorably with those derived in the prior (i.e., pre-microwave) studies. Furthermore, each individual solvent, including highly volatile solvents such as diethyl ether and methylene chloride, appear equally unaffected (Table 2, Fig. 2). The collective results confirm that microwave irradiation of illicit cocaine hydrochloride bricks does not significantly diminish individual or total occluded solvent levels.

The unexpected resistance of occluded solvents to removal via

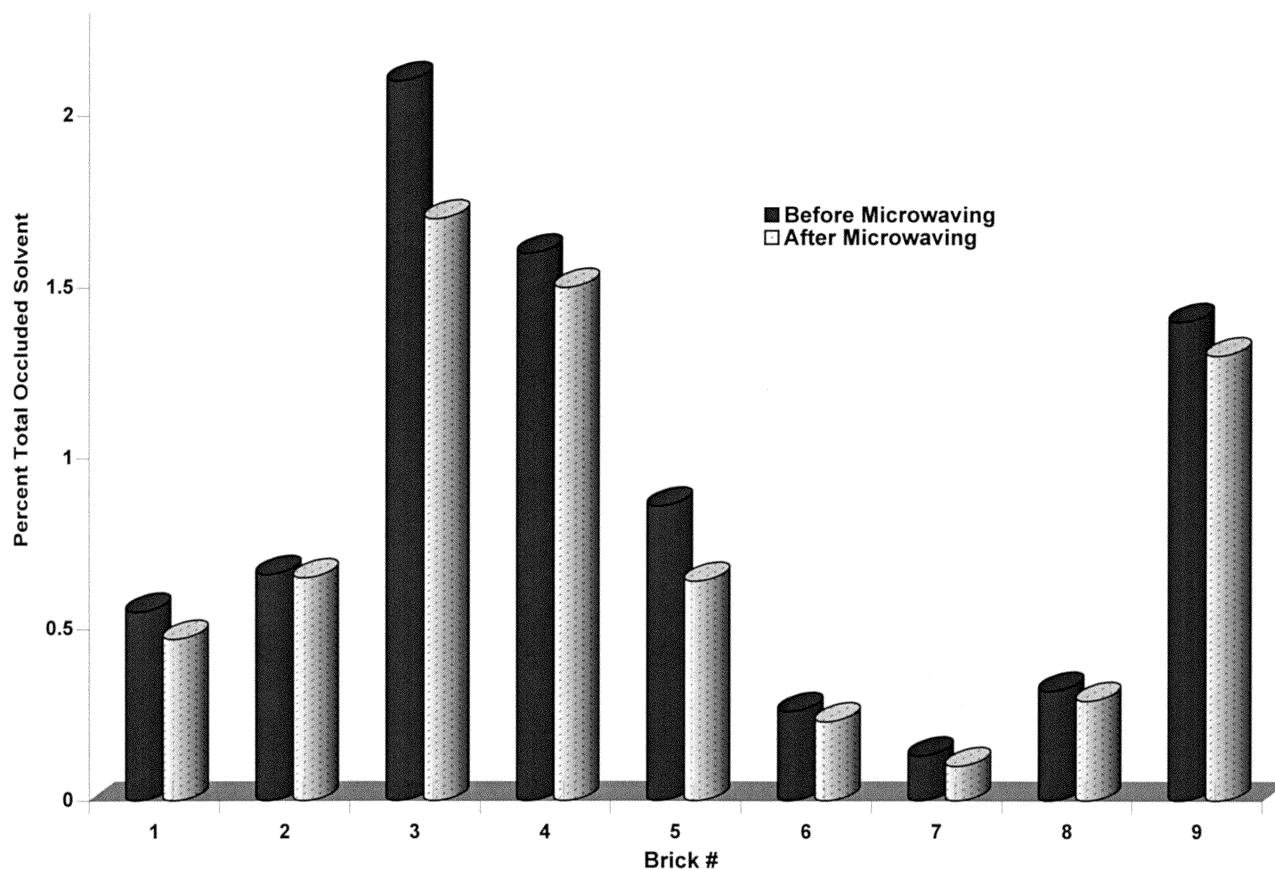


FIG. 1—Total percent occluded solvents before and after microwaving (see Table 2 for brick identifications).

TABLE 2—Cocaine hydrochloride brick weights before and after microwaving.

Brick No.	Solvent(s)*	Weight Before (g)	Weight After (g)	Loss (g/(%))
1	1.6:1 Ethyl ether/acetone	806.4	785.2	21.2 (-3)
2	Acetone only	820.3	710.3	110.0 (-13)
3	Methyl ethyl ketone (MEK) only	793.1	741.9	51.2 (-7)
4	6:6:1 Ethyl acetate/MEK/toluene	1101.1	809.8	291.3 (-27)
5	1:1:1 Ethyl acetate/MEK/toluene	813.5	761.1	52.4 (-6)
6	2:2:1 Hexane/MEK/toluene	824.3	770.6	53.7 (-7)
7	10:10:1 Hexane/MEK/methylene chloride	810.2	769.7	40.5 (-5)
8	9:7:3:1 Hexane/MEK/Ethyl acetate/methylene chloride	710.3	667.3	43.0 (-6)
9	100:100:1 Ethyl ether/acetone/spike components†	831.9	748.3	83.6 (-10)

* All solvent ratios are volume/volume.

† Spike components: benzene, butyl cellosolve, chloroform, cyclohexanone, dimethoxymethane, ethyl acetate, *n*-hexane, 2-butanol, mesityl oxide, methyl acetate, methylene chloride, methyl ethyl ketone, methyl isobutyl ketone, tetrachloroethylene, toluene, *m*-xylene.

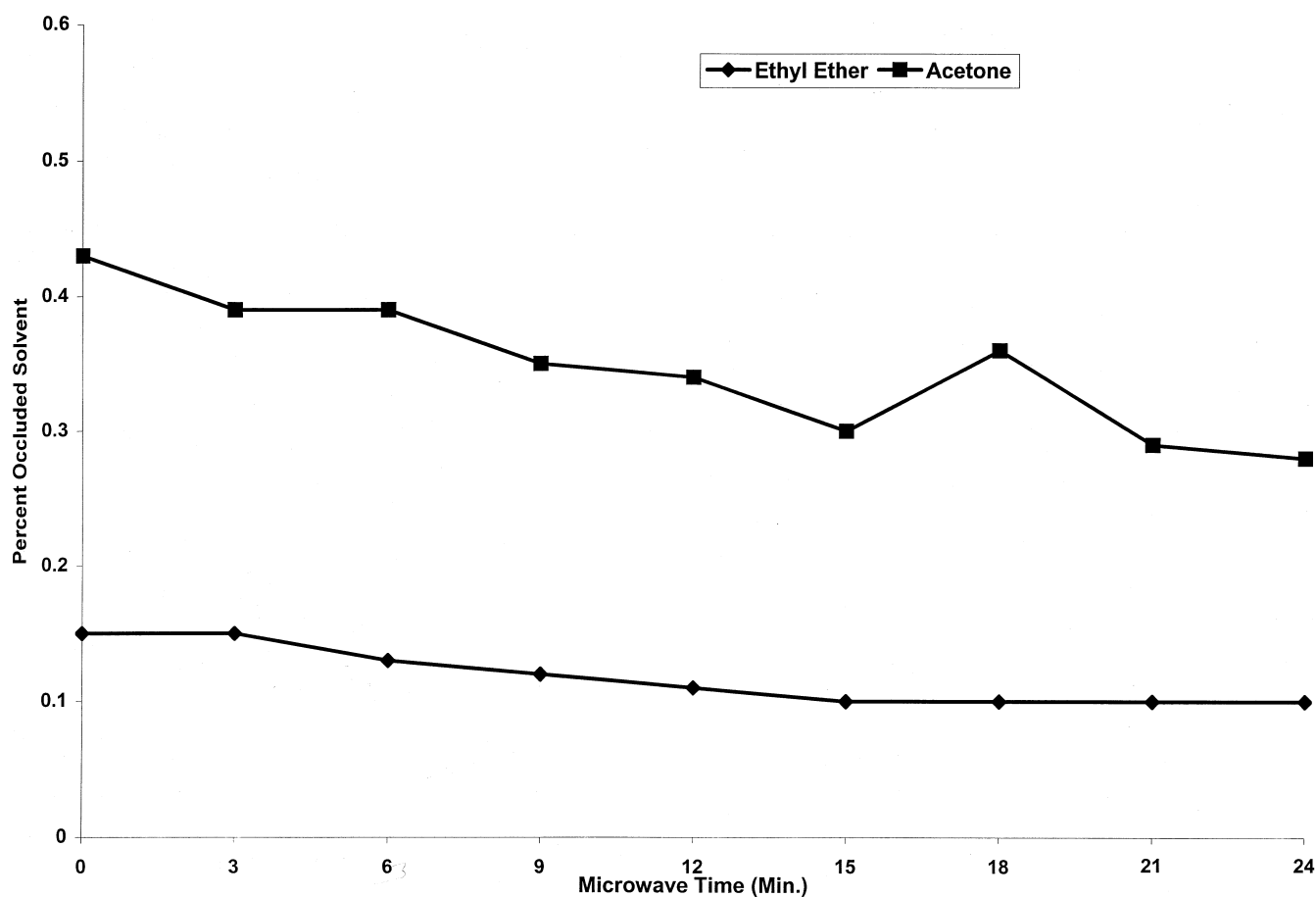


FIG. 2—Percent occluded solvent vs. microwave time for 1.6:1 ethyl ether/acetone brick.

microwave heating prompted additional studies into qualitative and quantitative analyses. Of particular interest was the relationship between the occluded solvent ratios and the makeup of the original precipitating media used in the base to hydrochloride conversions (Table 3). In general, the correlations are not very

good. The best agreement is noted for Brick #4 (6:6:1 ethyl acetate/methyl ethyl ketone/toluene), with an occluded solvent ratio of 5:4:1. However, poor correlations were noted in bricks where nonpolar solvents were utilized. This is best illustrated by Bricks #6 (2:2:1 hexane/methylene chloride/toluene) and 7 (10:10:1 hex-

TABLE 3—Conversion and occluded solvent ratios.

Brick No.	Solvents*	Conversion Solvent Ratios	Occluded Solvent Ratios
1	Ethyl ether/acetone	1.6:1	1:5
2	Acetone only	N/A	N/A
3	Methyl ethyl ketone (MEK) only	N/A	N/A
4	Ethyl acetate/MEK/toluene	6:6:1	5:4:1
5	Ethyl acetate/MEK/toluene	1:1:1	3:5:2
6	Hexane/MEK/toluene	2:2:1	1:250:20
7	Hexane/MEK/methylene chloride	10:10:1	2:5:1
8	Hexane/MEK/ethyl acetate/methylene chloride	9:7:3:1	2:5:1:1
9	Spiked ethyl ether/acetone†	1:1	1:2

* All solvent ratios are volume/volume.

† Acetone and ethyl ether being primary solvents in the 100:100:1 spike brick.

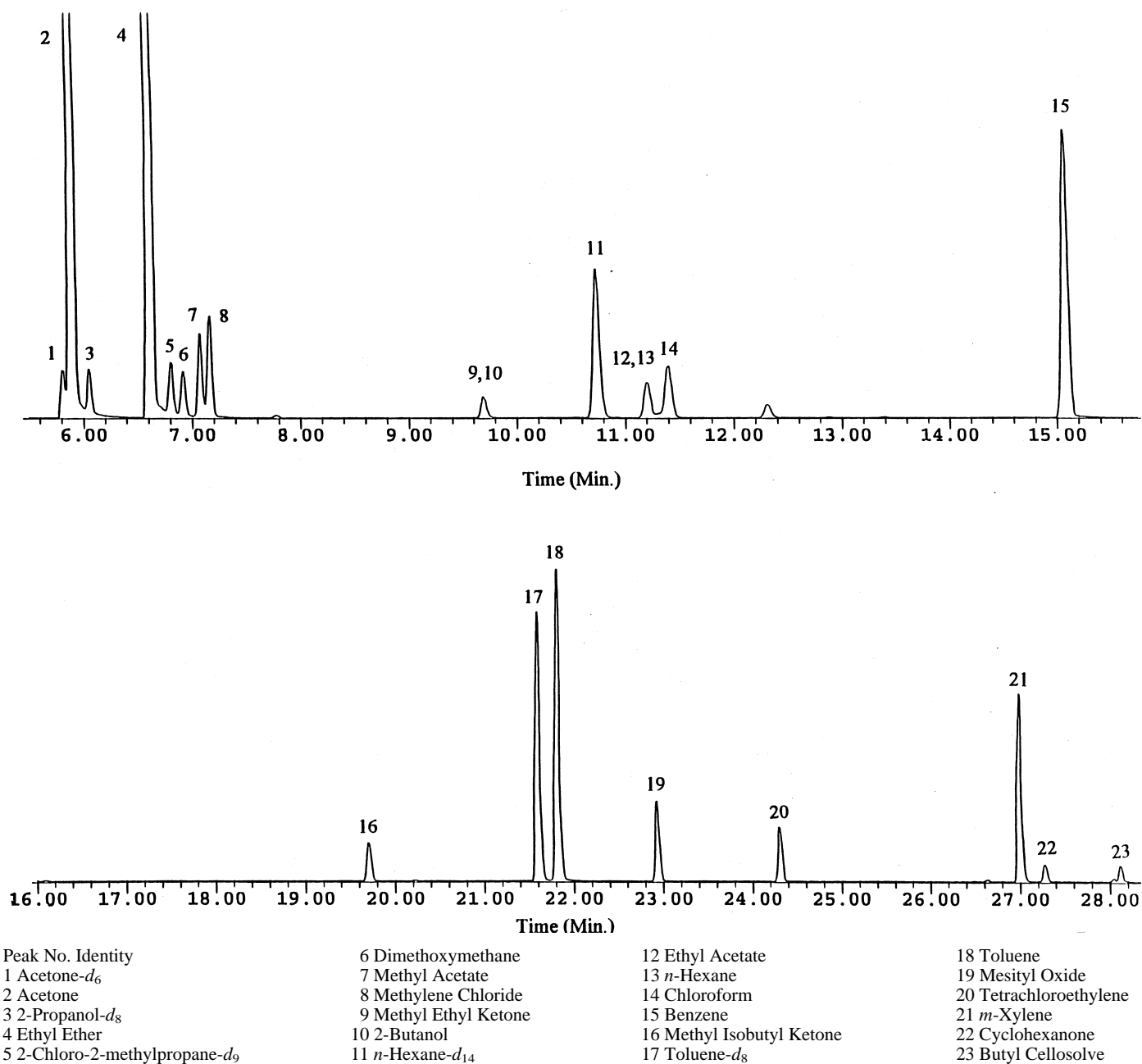


FIG. 3—Reconstructed total ion chromatogram of the fully irradiated 100:100:(1 × 16) ethyl ether/acetone/16 component spike brick.

ane/methyl ethyl ketone/methylene chloride), with occluded solvent ratios of 1:250:20 and 2:5:1, respectively. These results suggest that nonpolar solvents are less susceptible to occlusion in cocaine hydrochloride than polar solvents. However, additional factors other than solvent polarity may influence occlusion of solvents, including rate of precipitation, conversion solution temperature, degree of mixing, and percent water in the precipitating media.

Another point of interest was the fate of trace level solvents present as contaminants in the primary conversion solvents. First, it was determined that the method blanks run with the five deuterated internal standards contained no detectable impurities that might contribute to the solvent profiles (e.g., toluene in toluene- d_8 .) Preliminary SHS-GC-MS analyses of each of the primary solvents utilized in this study indicated 0.05% toluene in methyl ethyl ketone and 1.0% mesityl oxide in acetone. It has long been suspected that these contaminants could be carried through the conversion process and therefore persist as occluded solvents. In fact, analyses of those bricks produced with either methyl ethyl ketone or acetone confirmed trace amounts of toluene and mesityl oxide, respectively, in the occluded solvent mixtures. However, care must be taken in interpreting the latter result, since mesityl oxide is a condensation product of acetone, and may legitimately be expected to arise as a result of the reaction of acetone within the occluded solvent reservoirs during irradiation.

In order to test this hypothesis even more rigorously, one brick (Brick #9) was manufactured with a 100:100:(1 × 16) diethyl ether/acetone/"spiked components" conversion mixture (i.e., the 16 spiked components were each added to the conversion mixture

at 1/100th the concentration of diethyl ether and acetone). Notably, all 16 were easily detected in the subsequent occluded solvent analysis; Fig. 3 illustrates the reconstructed total ion chromatogram for Brick #9 after 15 min of collective irradiation, while Fig. 4 displays the relative concentrations of all 18 solvent components. These results confirm that trace level contaminant solvents present in the precipitating media are retained in the occluded solvent reservoirs (and also demonstrates the viability of "tagging" bulk solvents for enforcement purposes).

A related issue involved the question of "artifactual" solvents, i.e., new solvents arising from intra- and/or intermolecular reactions of occluded solvents during microwave irradiation. The best known example of this phenomenon is methanol, which arises from hydrolysis of cocaine itself, and is ubiquitous in all occluded solvent analyses of cocaine hydrochloride. Similar artifacts were anticipated from condensation, hydrolysis or solvolysis of (especially) ester- and/or ketone-based occluded solvents. Somewhat surprisingly, however, very few such solvents were observed in this study. Most notably, mesitylene (another acetone condensation product, similar to mesityl oxide, which was not detected in the acetone originally utilized as a primary solvent) was detected in all bricks precipitated from conversion solvents containing acetone. Furthermore, the relative concentrations of both mesityl oxide and mesitylene increased during the irradiation steps, confirming that they were being created during microwave heating.

Finally, although the primary goal of this study was to monitor the effects of microwave irradiation on occluded solvents, it also offered a unique opportunity to monitor the effectiveness of microwave drying of cocaine hydrochloride bricks in clandestine set-

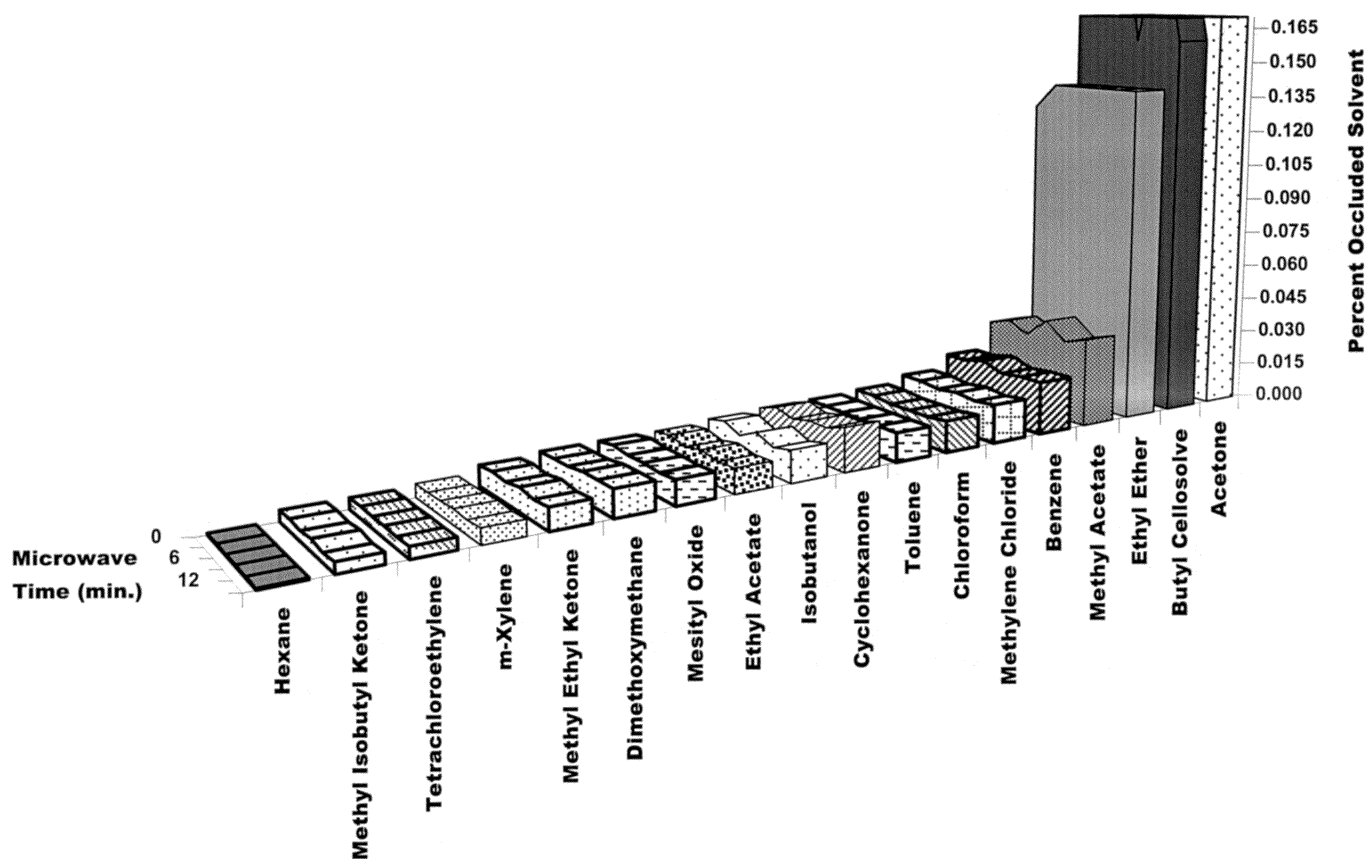


FIG. 4—Percent occluded solvent vs. microwave time for 100:100:(1 × 16) ethyl ether/acetone/spike components brick.

tings. Not surprisingly, all nine bricks studied exhibited significant decreases in weight as a result of microwave drying (Table 2). Collective losses ranged from 3 to 27%, with an average loss of 10%. The large variance of losses suggests that certain solvents or solvent mixtures are more effective "wetting" agents; however, there do not appear to be any correlations between the boiling points, mobilities, or polarities of the various solvents and their retention as wetting solvents on cocaine hydrochloride. As expected, the collective results confirm the efficacy of microwaves for drying cocaine hydrochloride bricks.

Conclusions

In summary, this study has established, first, that occluded solvents in cocaine hydrochloride are extremely resistant to removal by microwave heating; second, that even low-boiling occluded solvents (e.g., diethyl ether or methylene chloride) are equally unaffected by microwave heating versus higher boiling solvents, even when excessive overheating is employed; third, that trace-level solvents present in primary conversion solvents are carried through the conversion process and persist as occluded solvents; fourth, that although the occluded solvents accurately reflect the components of the original precipitating media, they are at best only roughly indicative of the original ratios of those components (however, differentiation between primary conversion solvents and trace-level contaminants is routinely accomplished via quantitation); and fifth, that certain artifactual solvents (e.g., mesitylene) are created within the occluded solvent reservoirs during microwave heating. The collective results confirm that analysis of residual solvents in illicit cocaine hydrochloride for diversion monitoring and intelligence gathering purposes remains valid despite the wholesale adoption of microwave over conventional drying in clandestine laboratories.

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