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TECHNICAL NOTE

CRIMINALISTICS

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Microcrystal Analysis of Cocaine Hydrochloride and Added Adulterants*,†

ABSTRACT: The objective of this project was to investigate the trends of changes in the crystal morphology of cocaine in the presence of the common adulterants, caffeine and lidocaine HCl. By performing gold chloride microcrystal tests on samples of cocaine with adulterants at 10, 20, and 50% concentrations, trends in the changes of the crystal morphology can be linked to specific adulterants and concentrations. For cocaine/caffeine mixtures, the trend is elongation of one axis, additional branching, and brown discoloration of the crystals. At 50:50 cocaine/caffeine mixtures, branched spherical crystals and long needles appear. The trends for cocaine/lidocaine mixtures include elongation of one axis with an X-shaped middle axis. The axes continue to grow and branching decreases until at 50%, spherical clusters of needles appear. These results indicate microcrystal analysis can be used as a novel method for presumptively identifying not only cocaine but also the identity and concentration of the adulterant.

KEYWORDS: forensic science, microcrystal test, cocaine hydrochloride, caffeine, lidocaine hydrochloride, adulterant

Forensic science has progressed in pace with the advances in technology. Sophisticated instrumentation such as infrared spectroscopy, gas chromatography (GC), and mass spectrometry (MS) have made the identification of drug compounds almost effortless with the proper training. Many older methods, such as microcrystalline analysis, have been discarded as outdated and criticized because of their difficulty to present in court. However, these "old-fashioned" tests still have a place in the crime laboratory and should not be lost in the midst of twenty-first century technology.

Microcrystal tests are highly developed chemical precipitation tests that use specific reagents and a polarizing light microscope to form and document the characteristic crystal formation of a substance, in this study, cocaine tetrachloroaurate (III), $(C_{17}H_{22}NO_4)[AuCl_4]$ (1,2,3,4). These tests rely on the chemical properties of cocaine to form crystals of a distinct shape and color, eliminating false positive results that may result with color tests (5). Microcrystalline tests are also nondestructive and sensitive enough to detect even microgram quantities of the drug. One disadvantage to microcrystal tests is that the results are complicated by alteration of the crystal morphology because of the reaction of adulterants with the drug (6,7).

Currently, microcrystal tests are accepted by the Scientific Working Group for the Analysis of Seized Drugs as a Category B technique. Category B analyses can be used in conjunction with one Category A technique such as mass spectroscopy or Fourier transform infrared spectroscopy (FTIR). In the absence of a Category A technique, two Category B and C tests must be carried out in addition to the microcrystal test. In addition to microcrystal tests, Category B includes GC, liquid chromatography, and thin layer chromatography. Category C techniques include color tests, melting point, and immunoassay (8).

The crystal structure of the gold (III) tetrachloride salt of L-cocaine was solved in 2007 and determined to be orthorhombic (9). This structure does not change in the presence of adulterants, as shown by Wielbo and Tebbett. Their study combined the microcrystal test and FTIR (10). The aim was to find a microcrystal test reagent that could be used with FTIR without causing interference. They found that the FTIR spectra of cocaine tetrachloroaurate did not change in the presence of adulterants, such as sugars, starch, and other drugs, even when only 1–2% of the sample was cocaine. This study indicates that the adulterant does not become incorporated into the crystal lattice of the cocaine salt, but rather only affects the crystal habit, as seen in the changes in the external crystal morphology (11). These changes could occur as the presence of the adulterant interferes preferentially with the growth of one axis over another, or causes defects during crystal growth, resulting in a change in the direction of the growth or twinning.

A recent study by Bell and Hanes (12) developed a microfluidic device to perform color and a microcrystal test simultaneously, reducing the amount of sample and reagents needed to achieve the same results. As decreasing amounts of cocaine were mixed with an adulterant, the number of positive color test results also decreased. In the case of the concurrent microcrystal tests, there were still enough crystals to positively identify the drug as cocaine, although they made no attempt to identify the adulterant or its effects on crystal habit. In this study, cocaine mixtures with two adulterants were also tested.

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The objective of this research is to exploit the trends for the changes in crystal morphology in the presence of a common cocaine adulterant and to develop an analytical method that will link these changes to both the identity and concentration of the adulterant. The advantages of the microcrystal test are the low cost of performing the tests, the small sample volume required, and that the only instrumentation required is an optical microscope.

Methods

Stock solutions of cocaine HCl (Sigma Aldrich, St Louis, MO), caffeine (Alfa Aesar, Ward Hill, MA), and lidocaine HCl (MP Biomedical, Solon, OH) were prepared by dissolving 250 mg of powder into 1-mL distilled water. The stock solution was further diluted to 2.50 mg/mL for the controls and experiments.

Microcrystalline Tests of Pure Cocaine and Adulterant Solutions

The samples included purchased standards of cocaine HCl, caffeine, or lidocaine HCl. A 10-μL drop of stock solution was placed on a glass microscope slide followed by 10 μL of 5% gold chloride ($HAuCl_4$) (MP Biomedical) and finally 10 μL of 20% acetic acid. The crystals that formed were observed with an Olympus BX51 polarizing light microscope (Olympus America Inc., Center Valley, PA) under crossed polars at 100× and 200× magnification. As the crystals formed, the crystal morphology and physical properties were observed and recorded.

Negative Control

A negative control was run with the gold chloride and acetic acid reagents in the absence of cocaine and adulterants. Ten microliters each of 5% gold chloride and 20% acetic acid was placed on a slide and observed over a period of an hour.

Microcrystalline Tests of Cocaine and Adulterant Solutions

A minimum of 10 samples of cocaine with added adulterant (caffeine or lidocaine) were analyzed at 10%, 20%, or 50% adulterant. For a 10% sample, 1-μL adulterant stock was mixed with 9-μL cocaine stock. For a 20% sample, 2-μL adulterant was mixed with 8-μL cocaine, and for a 50% sample, 5-μL adulterant was mixed with 5-μL cocaine. The solutions were mixed with a spatula, and the spatula was cleaned between each sample to avoid contamination. Each sample was observed and notes and photographs recorded using a Kodak M863 camera (Kodak, Rochester, NY) and Olympus Q Color 5 camera (Olympus America Inc.).

Concentration Effects

In order to determine whether the cocaine concentration was a factor in the changes in crystal morphology observed, the analysis was repeated by mixing the cocaine stock solution and pure water in substitution for the adulterant stock solution. For a 10% sample, 1 μL of water was mixed with 9 μL of cocaine stock solution. For a 20% sample, 2 μL of water was mixed with 8 μL of cocaine. For a 50% sample, 5 μL of cocaine was mixed with 5 μL of water. These are actually 90, 80, and 50% cocaine. Fewer crystals formed, but they matched the crystal observed in the cocaine standard. The same procedure was performed with caffeine and lidocaine.

Each sample was observed and notes and photographs recorded using a Kodak M863 camera and Olympus Q Color 5 camera.

Microcrystal Tests of Cocaine and Adulterant Powders

The analysis was repeated with solid samples of cocaine mixed with solid adulterant. In order to minimize waste, the mixtures were made through a series of additions of the adulterant. A 10% sample was prepared by mixing 45-mg cocaine HCl with 5.0-mg adulterant. A 20% sample was prepared by taking 40 mg of the 10% mixture and adding 5.0-mg adulterant. A 50% sample was prepared by taking 20 mg of the 20% mixture and adding 12-mg adulterant. The drugs were ground with a mortar and pestle to ensure homogeneity. A minimum of five solid samples were analyzed for each concentration. The same volume of reagents was added to 2–4 mg of the solid mixture and observed under crossed polars of the microscope. Notes and photographs were recorded for each.

Results

The first step was to document the crystals produced by solutions of pure cocaine and each of the common adulterants. The cocaine crystal is white in color and forms two long rods (axes) that cross at a 90° angle. Each axis has shorter branches perpendicular to the main axis. Caffeine crystals are long, thin, and needle-shaped with a white or pale yellow color. Lidocaine crystals are birefringent square and rectangular-shaped (Fig. 1). Finally, the reagents in the absence of cocaine and adulterants were examined under the experimental conditions. It was found that over the span of an hour, 10 μL of 5% gold chloride and 10 μL of 20% acetic acid will form brownish clumps.

Each test of the samples in solution was performed in multiples of 10 and was repeated by another researcher. The powder samples were performed in multiples of five samples for each concentration of the adulterant.

Cocaine and Caffeine Liquid Samples

A 10% caffeine sample showed few changes to the crystal. The majority of crystals that formed were unchanged from the cocaine cross shape. On some crystals, one axis (usually the shorter one) began to curve slightly at the ends and had a slightly darker brown tint to them (Fig. 2*a*). For the sample with 20% caffeine, crystal formation was delayed and there were more distorted crystals. The short axis curved out more at the ends, and the brown discoloration intensified. In some crystals, another second short axis appeared, forming an X where it intersected with the longer axis (Fig. 2*b*).

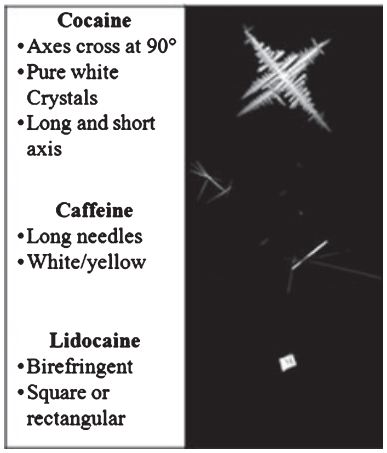

FIG. 1—*Crystal habit of cocaine, caffeine, and lidocaine.*

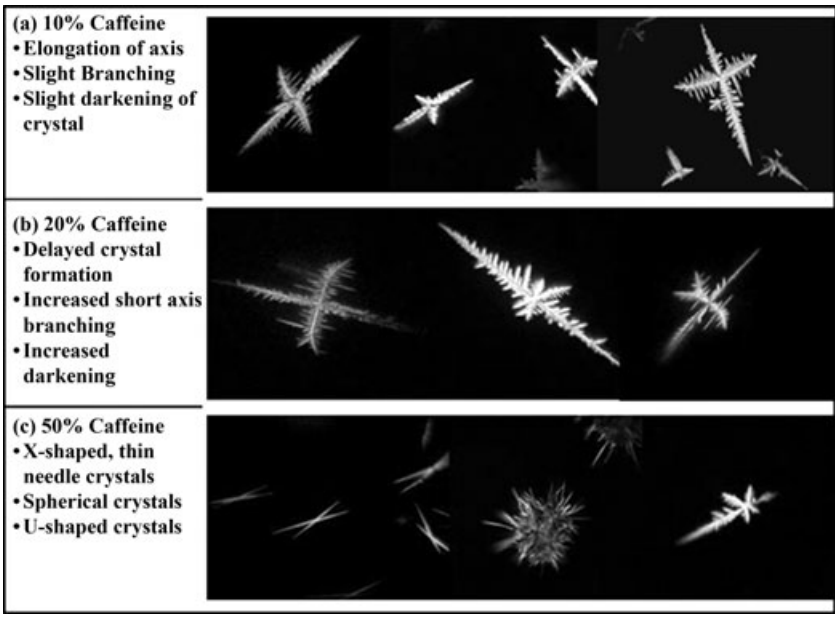

FIG. 2—*Crystal habit of cocaine with 10%, 20%, and 50% caffeine.*

A 50% caffeine sample showed the most dramatic changes, forming three different crystal morphologies. One was similar to the crystal seen in 10% and 20% samples, but with a U-shaped short axis. There were two new shapes not previously observed, a long, thin, needle-like crystal and a sphere-shaped crystal (Fig. 2*c*). It is possible that the needle-shaped crystals are caffeine crystals.

Cocaine and Lidocaine-Liquid Samples

Lidocaine had an immediate effect on the shape of the cocaine crystals. For the 10% lidocaine sample, the crystals were longer and one axis was markedly shorter. The shorter axis was no longer perpendicular to the long axis and in some samples had a U-shaped curve (Fig. 3*a*) and in others was X-shaped. A 20% lidocaine sample produced fewer crystals with a curved short axis and more with a straight, X-shaped short axis (Fig. 3*b*). Also the short branches on the main axes that were previously perpendicular to the axis were longer and with a sharper angle. Some of the samples had a few sphere-shaped crystals. Overall, it took longer for crystals to form and they were fewer in number. The cross shape was lost almost entirely with the 50% lidocaine samples and became X-shaped crystals with some smaller branches still protruding along the axis. Also, in some samples, a few small clusters of crystals formed (Fig. 3*c*). There was no color change observed for any samples with lidocaine as the impurity.

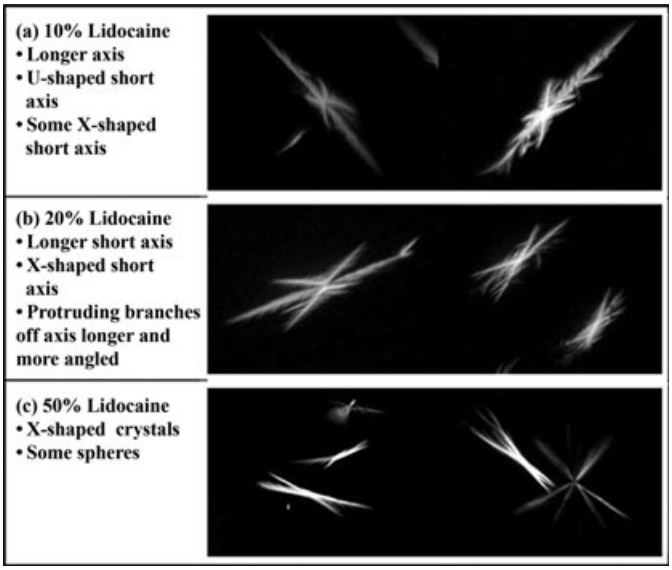

FIG. 3—*Crystal habit of cocaine with 10%, 20%, and 50% lidocaine.*

Concentration Effects

In order to eliminate cocaine concentration as a factor in the changes in crystal morphology, the experiments were run adding pure distilled water to the cocaine instead of the adulterant stock solution. For all concentrations, the cocaine crystals remained the same, merely decreasing in number as cocaine concentration decreased.

The concentration experiment was repeated with the two adulterants. Caffeine was similar to cocaine, crystals typical of caffeine formed at all concentrations. For lidocaine, crystals only formed at the 50% concentration and were identical to the 100% standard. This demonstrates that lidocaine is soluble in water at the 10% and 20% concentrations, thus no crystals formed.

Cocaine and Caffeine-Powder Samples

For the 10% caffeine sample, the crystal shapes were comparable to the liquid samples. The short axis of the transformed crystals was slightly curved at the ends of some, and on others, the curvature was more intense. Overall, the crystals were darker brown in color. For a 20% caffeine sample, the crystals were longer, thinner, and had a more curved short axis than the 10% sample. Also, some X-shaped crystals resembling caffeine were seen. For a 50% caffeine sample, sphere-shaped crystals and long, needle-like crystals were seen. Both of these types were seen with liquid samples, but the third type (U-shaped short axis) was absent from the powder samples (Fig. 4).

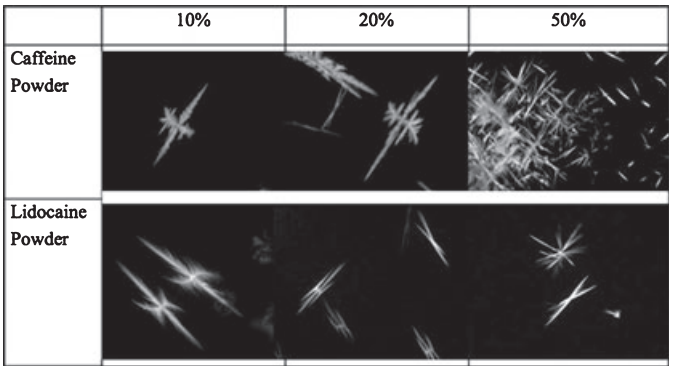

FIG. 4—*Crystal habit of cocaine with caffeine and lidocaine powders at 10%, 20%, and 50% concentration.*

Cocaine and Lidocaine Powder Samples

A 10% lidocaine powder sample produced crystals similar to the liquid samples. The short axis of the crystal was U-shaped, and the crystal was long and narrow. A 20% lidocaine sample had a longer, more curved short axis than the 10% samples and some sphere-shaped clusters as seen in the liquid samples. A 50% lidocaine powder sample did not closely correspond to the liquid samples. There were more sphere-shaped crystals and only a few X-shaped. The X-shaped crystals did resemble the liquid samples (Fig. 4).

Discussion

Controls

The microcrystal tests were performed on the stock solutions of cocaine, caffeine, and lidocaine to provide standards for comparison. The microcrystal test was also run with only the gold chloride and acetic acid reagents in order to eliminate the reagents as the source of the crystals in the concentration studies. The final control was a concentration study of the cocaine crystallization to determine whether the concentration of the cocaine was a factor in the changes in the crystal morphology. The results of these tests eliminated the crystallizing agents and cocaine concentration as a factor in crystal morphology under the conditions of these experiments.

Liquid Samples

The first microcrystal study was carried out with aqueous solution in order to ensure accurate measurement of the components, a homogeneous mixture, and minimized waste. The results from the experiments indicate that the cocaine crystal morphology changes if an adulterant is present, and characteristic trends in the crystal can be correlated with the type and amount of adulterant present in the sample.

As increasing amounts of caffeine were added to the cocaine, the resulting crystals lost their cross shape, first changing to a cross shape with curved ends and finally to a sphere or needle shape. In a sample with 10% caffeine, the changes to the crystal structure were subtle and often difficult to see. Most of the crystals remained unchanged because of the small amount of caffeine in the sample. As more was added, the changes became more apparent and even began to resemble caffeine (Fig. 1*c*). By comparing photographs of the crystals at each stage, these characteristic trends became more visible and could be correlated with a certain percentage of caffeine adulterant.

Unlike caffeine, the changes in crystal morphology of lidocaine were seen immediately. A small amount of lidocaine changed the structure to a longer, thinner crystal with an X- or U-shaped short axis, and as the concentration was increased, the crystals were mostly X-shaped. At a concentration of 50% lidocaine, the X-shaped crystals strongly resemble crystals seen with 50% caffeine. However, the lidocaine samples still had branches protruding from the axis and the caffeine samples did not. The types of spheres seen in both samples were different. The caffeine spheres had more branching, while the lidocaine spheres were sparser. By looking at all the crystals in a sample, caffeine and lidocaine can be differentiated even though some crystals may be similar.

Powder Samples

It was important to repeat the study on powder samples of the cocaine/adulterant mixtures as this is the form most often encountered in seized drugs. The same methodology was applied to powder samples of cocaine and adulterants. The resulting crystals for caffeine from powder samples were comparable to liquid samples. Similar crystal characteristic trends at each concentration were observed. Overall, liquid samples were more homogenous than powder samples. This observation is based on 10% and 20% caffeine concentrations. Needle-like X-shaped crystals previously seen only at 50% caffeine liquid concentration were observed at all concentrations in the powder samples. As these crystals closely resemble caffeine, it is likely that inhomogeneity of the powder resulted in localized high concentrations of caffeine.

The primary difference between liquid and powder samples was evident in the 50% lidocaine concentration. The liquid sample was made up of mostly X-shaped crystals with branching off the axis and a few sphere clusters. The powder sample was made up of mostly sphere clusters and only a few X-shaped crystals. The adulterant determination was made by carefully looking at the X-shaped crystals for the presence of branches off the axis. These branches were not seen in the caffeine X-shaped crystals and made enough difference to distinguish the two. Another way to differentiate between caffeine and lidocaine when there are X-shaped crystals in the powder samples was the frequency of branching in the spheres. The caffeine spheres were denser, while the lidocaine had fewer branches. As powder samples will be encountered more in a laboratory, standards for comparison should be made using powders as there were some differences from liquid samples.

The time required for crystal formation was less for powder samples and produced so many crystals that clumped in one area that it was often difficult to find individual ones to observe and photograph. However, the liquid samples may take longer to develop as they were far less concentrated than the powder samples. In addition, the gold chloride reagents were slightly diluted when added to the liquid samples, possibly causing their effectiveness to be diminished.

Conclusions

The trends for the changes in crystal morphology for aqueous solutions of cocaine in the presence of caffeine and lidocaine were documented. The changes were unique to both the specific adulterant and the concentration of that adulterant. Similar trends were seen for powder samples.

Cocaine with caffeine as an adulterant can be identified by the appearance of curved short axes. The degree of curvature increases

with caffeine concentration until at 50% caffeine, sphere-shaped, branched crystals appear. Lidocaine adulterant can be identified by longer, thinner crystals with an X-shaped short axis. As the lidocaine concentration increases, the crystals become X-shaped and at 50% lidocaine, the crystals form an X with the presence of few nonbranched spherical crystals.

Correlating the trends of the changes in crystal morphology of cocaine tetrachloroaurate in the presence of common adulterants is a novel approach to presumptively testing street samples of cocaine. A disadvantage of this method is that street samples often contain more than one adulterant.

The next steps in this research include testing more cocaine and adulterant mixtures, looking at drug and adulterant mixtures of additional controlled substances, performing the test on authentic street samples, examining samples with two or more adulterants, and finally, developing blind studies to test the analysts with unknown concentrations of the cocaine and adulterant mixtures.

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