MICROCRYSTAL ANALYSIS OF COCAINE HYDROCHLORIDE AND ADDED ADULTERANTS: TRENDS IN THE CHANGES OF CRYSTAL MORPHOLOGY

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ABSTRACT

The objective of this project was to investigate the trends for the changes in the crystal morphology of cocaine in the presence of the common adulterants, caffeine, lidocaine HCl, procaine HCl, levamisole HCl, sugar, and baking soda. 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 appeared. The trends for cocaine/lidocaine mixtures include elongation of one axis with an X-shaped middle axis. The axes continued to grow and branching decreased until 50% concentration where spherical clusters of needles and X-shaped crystals appeared.

For cocaine/procaine mixtures, the trend is branching of both axes, sphere-shaped crystals with wavy branches, and tiny, colorful beads with a cross shape in the middle (like the procaine standard). For cocaine/levamisole mixtures, the trend is appearance of a third axis, asterisk-shaped crystals, and tiny, colorful beads with a cross shape in the middle that resembled the standard.

For cocaine/sugar mixtures, many samples produced crystals unchanged from the pure cocaine crystal shape. In the crystals that were transformed, the trend is elongation
of one axis, and X or U-shaped short axis, sphere-shaped crystals, and appearance of a third branch. For cocaine/baking soda mixtures, most were unchanged, but some crystals had an elongated axis with an X-shaped short axis, larger sphere-shaped crystals, and gray/white clumps that resembled the baking soda standard.

The methodology was tested on powder cocaine/adulterant mixtures and produced similar trends in crystal morphology. Some notable differences were the inhomogeneity of the powder samples and crystal formation time. These results indicate microcrystal analysis can be used as a novel method for presumptive identification of not only cocaine, but also the identity and concentration of the adulterant.

Keywords: Forensic science, microcrystal test, cocaine hydrochloride, adulterant
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CHAPTER 1

INTRODUCTION

The 2009 National Drug Threat Assessment (NDTA) reported that cocaine is the drug that causes the greatest threat to society, as evidenced by the variety of societal costs that accompany its illicit sale and usage (1). A 2005 study estimated $36 billion dollars was spent on cocaine in the U.S. that year. This accounts for half of the total spent on all illicit drugs, making it the illegal drug of choice for many users (2). Moreover, the introduction of crack cocaine in the 1980s made the drug cheaper and brought it into the hands of many more people. Crack cocaine is the smokable base form used by people ranging from white collar professionals to hard core drug addicts (3, 4). It comes as no surprise that 36.5% of law enforcement agencies nationwide feel that cocaine is the greatest threat in their respective communities (2).

Of all the illicit drugs in use, cocaine is one of the most addictive. Its powerful stimulant properties give the user a heightened sense of pleasure and leave them craving more of this intense euphoria. According to 2006 survey of drug abuse, 35 million Americans have used cocaine at least once in their lifetime, with almost one million of those experimenting with it for the first time that year. Although it is difficult to put an overall cost on American’s cocaine habit, the amount of money spent on hospital visits and drug rehabilitation centers each year indicates that abuse of the drug extends nationwide. In 2006, the estimated cost for almost 500,000 hospital visits and the 250,000 peo-
ple in drug rehabilitation was $60 billion dollars (2). Unfortunately, most of those in rehabilitation do not remain for the full length of the treatment program, and revert back to their old ways, resulting in more time and money lost (2).

The primary entry points of cocaine into the United States are along the southern border, stretching from California to Florida (2). A derivative of the coca plant, cocaine, is largely grown and distributed from South America, for legal and illegal import to the United States. Recently, the NDTA reported that the availability of cocaine in the United States decreased slightly in 2007 (1). Officials believe this decrease was due to increased police operations targeting prominent traffickers, more distribution in European countries, increased U.S. border security, and large seizures made by federal government agencies, such as the Drug Enforcement Administration (5). However, their belief is that this decrease won’t last long (1).

A Brief History of Cocaine: From Natural Stimulant to Street Drug

Cocaine has been produced from the Erythroxylum coca plant for over 2,000 years (2). Early records indicate that South American inhabitants constantly chewed the leaves of the plant while working to eliminate fatigue, and many indigenous people in the Americas still do. In 1860, cocaine was first extracted and isolated from the leaves of the coca plant for medicinal use in Europe by a German graduate student, Albert Niemann. Once its stimulating and anesthetic properties were realized, small amounts were used in Coca-Cola™, tea, wine, cigarettes, chewing gum, medicines, and was marketed to eliminate fatigue and pain (2). In fact, the original Coca-Cola™ recipe used a syrup made by extracting coca leaves and adding caffeine from the kola nut. It is unknown how much
cocaine was in this recipe, but over time, less was used and the beverage now contains no cocaine although other extracts from the coca plant are still used (6).

In the late 19th century, cocaine was widely used in medicines for eliminating headaches, toothaches, and even as a cure for morphine addiction. However, the negative effects of cocaine soon became apparent, and the first effort to regulate cocaine came with the passage of the Pure Food and Drug Act of 1906 (7). This law required that products be labeled with all their ingredients so consumers were aware of what they were buying. Later, the Harrison Narcotic Act of 1914 would label cocaine as a narcotic, stop over-the-counter sales, and enforce criminal penalties on users (8). Cocaine use became so widespread as a white-collar drug in the 1960s that stricter penalties were established, and all controlled substances were classified into schedules based on their medicinal use and power of addiction with the Controlled Substances Act of 1970. Cocaine is classified as a schedule II drug because it has accepted medical use as a local anesthetic and a high risk of addiction. For example, a low concentration solution of cocaine HCl is commonly used today in ear, nose, and throat surgeries (2).

The Use and Purpose of Adulterants

One factor that can affect the results of drug analysis techniques is the presence of an adulterant, which drug dealers commonly add to extend their product – and profits. By “cutting” the pure drug with a less expensive adulterant, it can increases the weight of the product (2). Since serious drug users typically want as much of the pure drug as possible to get the most from its effects, dealers must be able to convince their customers that their product is real. They achieve this by using adulterants with similar physical and chemi-
cal properties of the drug, i.e. a fine, white powder able to mimic the euphoric effects. Common adulterants for cocaine include caffeine, lidocaine, procaine, benzocaine, and tetracaine. Yet, these types of adulterants are more difficult to purchase and are slightly more expensive; so dealers may use other adulterants, such as table sugar, baking soda, cornstarch, or flour, instead. However, some of these adulterants, such as benzocaine, are harmful to the body because they are insoluble and if they reach the bloodstream can cause serious illness (2). Furthermore, the presence of an unknown adulterant in seized evidence can make analysis of the drug difficult, slowing down and potentially compromising the investigation and prosecution unless fast, accurate analysis is available.

The Role of Drug Analysis: Presumptive and Confirmatory Tests

From a drug enforcement standpoint, the goal of drug analysis is to correctly identify suspected controlled substances, which can be pure or a mixture of several components. In an effort to prosecute both dealers and users, and control the cocaine problem, law enforcement officials depend heavily on the analysis of controlled substances in forensic labs. However, those analysts must keep up with innovative dealers who are constantly developing new ways to mix and use drugs of abuse. In 1997, the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) recommended minimum standards for identifying drugs (9). Based on these standards, correct identification of a drug requires a competent analyst and an analytical scheme. Specifically, SWGDRUG has classified common techniques into three categories, based on their decreasing discriminating power (Table 1)(9).
Table 1

*Examples of Drug Analysis Techniques for Each Category*

<table>
<thead>
<tr>
<th>Category A</th>
<th>Category B</th>
<th>Category C</th>
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<tr>
<td>Infrared spectroscopy</td>
<td>Gas chromatography</td>
<td>Color tests</td>
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<tr>
<td>Mass spectrometry</td>
<td>Microcrystal test</td>
<td>Melting point</td>
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<tr>
<td><em>most discriminating</em></td>
<td><em>least discriminating</em></td>
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If a category A technique is used, at least one other technique from any category must also be used in conjunction. In the absence of a category A technique, two category B tests and one category C test must be done. Category A techniques are considered confirmatory tests because they produce results unique to a particular substance every time analysis is performed. Therefore, these types of analyses tend to hold up extremely well in court (10). Category B and C analyses are less discriminating, and a number of factors can affect the results. These techniques are often considered subjective and many are only used as presumptive tests, which determine the possible presence of a controlled substance. Presumptive tests have less discriminating power than confirmatory tests and can give false positive results, but they lead the analyst in the right direction toward identifying the substance. They do not hold up well in court by themselves, but when combined with a category A technique, they positively contribute to the results (9). By combining both types of tests, an analyst can more confidently support his or her work and defend a report.

*Advances in Forensic Science: Instrumental Analysis*

In the past 30 years, forensic science has progressed with advances in technology. Sophisticated instrumentation, such as infrared spectroscopy, gas chromatography, and
mass spectrometry, has made the identification of drug compounds almost effortless when used by professionals with the proper training. Not only are these types of instruments validated and widely accepted by the scientific community, they yield results that are so unique that the identity of the compound is established after comparison to a known standard (10). However, their benefits come at a cost. These instruments are expensive and require careful maintenance. Often, funding for a smaller forensic lab limits the types and number of instruments that can be purchased, causing a delay in evidence processing. Although these instruments should always be used as part of analysis, most experts agree that they should not be the only analysis performed.

One example of how advanced instrument analysis can be used in combination with subjective tests is a study done by Wielbo and Tebbett, who combined the microcrystal test and FTIR (11). Their aim was to find a microcrystal test reagent that could be used with FTIR without causing interference. In fact, 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. For example, the crystal structure of the gold (III) tetrachloride salt of L-cocaine was solved in 2007 and determined to be orthorhombic (12). As shown by Wielbo and Tebbett, this structure does not change in the presence of adulterants indicating 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 (13). These changes could occur as the presence of the adulterant interferes preferentially with the growth one axis over another, or causes defects during crystal growth, resulting in a change in the direction of the growth or twinning.
Re-examining the Microcrystal Test

In a high technology society, older methods, like microcrystal tests, have been scrutinized for their accuracy in the identification of compounds. These tests are often deemed outdated and criticized because of their difficulty to present in court. However, it could be argued that these “old-fashioned” tests still have a place in the modern crime lab (14). One such test is the microcrystal test that was originally used by organic chemists, and has been in use since about the 1870s (15). 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, such as cocaine the tetrachloroauroate (III), \((C_{17}H_{22}NO_4)[AuCl_4]\) (15,16,17). 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 (15).

In a historical survey of microcrystal tests, Hiram Evans attributes their advancement in the 20th century to lawyers, largely because of the numerous regulations imposed on users. It became necessary to identify these substances to continue prosecution (18). During the drug epidemic of the 1960s, researchers produced a substantial increase in the literature on microcrystal tests. One of the most prominent figures in the history of microcrystal tests, Charles Fulton, published several articles and contributed to books like *Modern Microcrystal Tests for Drugs* and *Handbook of Analytical Toxicology* (18). As Fulton observed, one disadvantage of microcrystal tests, when used for drug analysis, is that the results are complicated by the alteration of the crystal morphology due to the reaction of adulterants with the drug (15,19). Today microcrystal tests, once the gold stan-
A Closer Look at Presumptive Color Testing

The most common presumptive test used in forensic labs is the color test. Color tests detect certain functional groups on the molecule. The presence of these groups is indicated by a color change once the reagents are added to a small amount of sample. Therefore, a positive reaction (a color change) indicates the possible presence of the drug in question. However, since most molecules contain one or more functional groups, it is likely that another substance can give the same reaction as a drug. For example, methaqualone and phencyclidine produce a blue color when cobalt thiocyanate reagent is used, giving a false positive result for cocaine (3). Like microcrystal tests, color tests can also be complicated by the presence of an adulterant. The color change may be faint or not appear at all (20).

Color tests are often preferred over microcrystal tests because they are easier to perform when compared with the extensive training and experience required to properly conduct the microcrystal test (20). The results of the microcrystal test depend on the reagent used and the type of drug being identified. The analyst is required to recognize many different types of crystals and understand the shape of the crystal changes based on the reagent type and concentration. Nevertheless, traditional microcrystal tests are still more specific than color tests. A study done by Swaitko et al. used three color tests (Wagner’s, marquis, and cobalt thiocyanate) and two microcrystal tests (gold chloride and platinic chloride) to determine specificity for cocaine. Specifically, they tested 17
drugs using the color tests and positive samples were then subjected to two microcrystal tests using gold chloride and platinic chloride as crystallizing reagents. The goal was to compare the discriminating power of color and microcrystal tests. Their results showed the color tests could not differentiate between cocaine and nine other compounds, brom-pheniramine, phendimetrazine, pheniramine, scopolamine HCl, scopolamine methylbromide, sparteine, carbinxamine, methadone, and scopolamine methylnitrate. There were no false positives with the microcrystal test for any of the compounds examined in this study. The cocaine produced crystals that were fine needles with perpendicular branches with the gold chloride reagent and V-shaped, long, needle like crystals with branching with platinic chloride. Six of the compounds tested produced other types of crystals and three produced no crystals using the gold chloride reagent. With platinic chloride as the precipitating reagent, cocaine was the only compound that produced crystals. This study also noted several variables such as presence of adulterant, level of experience of the analyst, concentration of the reagent, humidity, and temperature that could affect the results of the microcrystal test (10). The study demonstrates the advantages microcrystal tests have over color tests by their specificity to cocaine and the elimination of false positives.

Microcrystalline tests are also non-destructive and sensitive enough to detect even microgram quantities of the drug. A recent study by Bell and Hanes developed a microfluidic device to perform color and a microcrystal tests simultaneously, reducing the amount of sample and reagents needed to achieve the same results (21). In this study, three color tests and one microcrystal test were performed from the same one milligram sample simultaneously in four different channels. They determined each test channel contained about 5 mg of the drug mixture. 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 even if the color test did not produce results. The authors made no
attempt to identify the adulterant or its effects on crystal habit. The study demonstrates
that in the absence of a positive color test, the microcrystal test still produced positive
results that allowed the analyst to make the identification as cocaine.

Research Using Microcrystal Tests and Cocaine

Research has been conducted with cocaine and adulterants, but it primarily fo-
cuses on using instrumentation to identify the adulterant. In a study by Fucci and Gio-
vanni, GC/MS was used to analyze street samples of cocaine and identify the adulterant.
This data identified the most common adulterants mixed with cocaine and to establish
trends found in the illicit cocaine market in Rome, Italy (22). Another study by Lopez-
Artiguez et al. used IR spectroscopy to identify several adulterants mixed with cocaine by
examining two areas of the spectrum and looking for shifts in infrared transmission.
They were able to identify nine out of ten adulterants using IR (23).

Despite their forensic potential, little research exists about the use of microcrystal
tests to identify cocaine and the adulterant, especially as it relates to the use of aqueous
samples. In the research presented here, aqueous samples were used first to establish a
baseline of crystal characteristics and to exert more control over sample mixtures. Once
the adulterant characteristics were established, the same methodology was applied to
powder mixtures of cocaine and adulterants as this is the type of evidence that enters a
forensic lab for analysis.
Our primary objective 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, minimal amount of sample required, and the need for limited instrumentation, such as an optical microscope. The adulterants examined were: caffeine, lidocaine, procaine, levamisole, sugar, and baking soda. All of these adulterants, except levamisole, are commonly seen in cocaine samples (2). Levamisole is a relatively new cocaine adulterant. Although it has been used as an adulterant for about five years, the Alabama Department of Forensic Sciences, other state labs, and the Drug Enforcement Administration have reported a notable increase in cocaine samples adulterated with levamisole in the last year; therefore, it was included in this research (24). Its legitimate uses have been cancer treatments and as an anti-parasitic drug employed by veterinarians to treat animals for worms (24). It is unknown why this drug is being used as an adulterant and what, if any, stimulating effects it produces. However, it does create a serious health threat. Levamisole suppresses the immune system and can lead to agranulocytosis, which decreases the number of white blood cells, lowering the body’s defense system (25). As previously discussed, the microcrystal test is complicated by the alteration of the crystal formation due to the presence of an adulterant. We pose that those changes in crystal shape can be used to identify cocaine, the adulterant, and potentially the concentration.
CHAPTER 2
MATERIALS AND METHODS

Standards and Controls

The microcrystal test itself is simple, but there are four main phases to this research: preparation and testing of standards, controls, testing of cocaine/adulterant aqueous samples, and testing of powder samples. First, in order to establish crystal habit, it was necessary to prepare pure standards and test cocaine, each adulterant, and the reagents. A stock solution of cocaine was prepared from 250 mg cocaine HCl (Sigma Aldrich, St. Louis, MO) dissolved in 1 mL distilled water. The stock solution was further diluted to 2.50 mg/ml for the control and experiments. Caffeine (Alfa Aesar, Ward Hill, MA), lidocaine HCl (MP Biomedical, Solon, OH), procaine HCl (Acros, Fair Lawn, NJ), levamisole HCl (MP Biomedical, Solon, OH), sugar (Domino, Yonkers, NY), and baking soda (Arm & Hammer, Princeton, NJ) stock were prepared in the same manner and concentration as cocaine. The reagents were a 5% by mass solution of gold chloride in water (MP Biomedical, Solon, OH) and 20% by mass solution of acetic acid (Acros, Fair Lawn, NJ).

The microcrystal test was performed on 100% standards of cocaine and each adulterant. To do this, a 10 µL drop of sample was placed on a glass microscope slide followed by 10 µL of 5% gold chloride and finally, 10 µL 20% acetic acid. The crystals that formed were observed using an Olympus BX51 polarizing light microscope (Center Valley, PA) under crossed polars at 100X and 200X magnification. As the crystal formed,
the crystal structure and physical properties were observed and recorded. Each sample was photographed using a Kodak M863 camera (Rochester, NY) or Olympus Q Color 5 camera (Center Valley, PA).

The second phase included preparing control samples of cocaine, caffeine and lidocaine in water in concentrations of 10, 20, and 50% to show that the crystal shape of a pure sample does not change with increasing concentration and to determine solubility of the adulterants. For a 10% sample, 1µL of adulterant solution was mixed with 9 µL of water. For a 20% sample, 2 µL of adulterant was mixed with 8 µL of water. For a 50% sample, 5 µL of adulterant was mixed with 5 µL of water. Then, 10 µL of gold chloride and acetic acid reagents were added. Only two adulterants were tested in this manner. Finally, both the gold chloride and acetic acid reagents were mixed and allowed to sit for one hour to observe any crystal formation.

Microcrystal Tests of Cocaine/Adulterant Aqueous Solutions

The third phase of testing involved performing microcrystal tests on mixtures of cocaine and each adulterant in aqueous form. A minimum of ten samples were prepared in a 10, 20, or 50% adulterant to cocaine ratio. For a 10% cocaine sample, 1µL of cocaine was mixed with 9 µL of adulterant. For a 20% sample, 2 µL of cocaine was mixed with 8 µL of adulterant. For a 50% sample, 5 µL of cocaine was mixed with 5 µL of adulterant. The solutions were mixed with a spatula and the spatula cleaned between each sample to avoid contamination. Again, notes and photographs were recorded.
Microcrystal Tests of Cocaine/Adulterant Powders

In the fourth phase, the analysis was repeated with powder samples of cocaine mixed with an 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 were added to 2-4 mg of the solid mixture and observed under crossed polars of the microscope. Notes and photographs were recorded for each.

Considerations for Analysis

The techniques used in this research differ slightly from published ASTM International guides. Those guides call for the acid reagent to be added first, then the gold chloride. It is believed that the purpose for this order of reagents is to dissolve the powder samples first. The guides do not address aqueous samples. In this research, the order of reagents was reversed. After comparing the two methods, no difference in crystal formation or crystal shape was observed.

Another important consideration for performing the microcrystal test is timing. As soon as the reagents and sample are mixed, crystals begin forming and continue growing and forming new crystals. Therefore, it is critical to observe the crystals immediately after adding the reagents and continue observation for 3-4 minutes. Concentration of the
sample is directly related to the number of crystals that form, but after this short time period, generally there are too many crystals and they become too large to make an accurate assessment. It would be best to use a new sample if the 3-4 minute window has passed.

Unknown Analysis

Once data collection was complete, several unknowns were distributed to a group of undergraduate students to have them attempt to link an unknown to a specific adulterant and concentration. The students were inexperienced in microcrystal analysis and were only shown a short presentation outlining crystal characteristics of each adulterant. Instead of having the group actually perform the microcrystal test, they were given pictures of crystals and asked to identify each based on the characteristics discussed in the presentation.
The shape of the cocaine crystal after the microcrystal test can be distorted if another substance is present, but the challenge is learning to utilize those distortions to link them to cocaine and an adulterant. These observations can glean more information about the sample without further presumptive testing. The first step was to document the crystals produced by a solution of pure cocaine, those of the reagents, and then each of the adulterants. The crystals from each sample were always compared to the pure cocaine crystal (Figure 1a). It was important to observe the shape, length, and color of each axis, as these areas are where the most significant changes occurred. In the mixture of gold chloride and acetic acid reagents brown clumps formed, which were originally thought to be a characteristic procaine crystal, but after further observation, were seen with each adulterant. Therefore, they were attributed to the reaction of the reagents (Figure 1b).

(a) Cocaine
- white color
- two axes that cross at 90°
- one may be longer
- shorter branches perpendicular to each axis

(b) 5% Gold Chloride and 20% Acetic Acid
- brown clumps
- seen in most samples

Figure 1. Crystal habit of cocaine and mixture of reagents.
Caffeine crystals are long, thin, and needle-shaped with a white or pale yellow color (Figure 2a). Lidocaine crystals are birefringent square and rectangular shaped (Figure 2b). No crystals formed for procaine and levamisole, only tiny, colorful beads with a black cross shape in the center (Figure 2c and 2d). These beads seem to be a non-crystalline precipitate. The levamisole was light sensitive and began to degrade after a few minutes. Sugar and baking soda samples did not form any crystal structures, only gray/white clumps (Figure 2e and 2f). It will be discussed further in the results that follow, but typically as the concentration of the adulterant increased, more crystals or substances resembling the pure adulterant appeared. It is important to be able to distinguish between the standard and a cocaine crystal distorted by the adulterant.

Figure 2. Trends in crystal morphology of adulterant standard aqueous samples.
Aqueous Samples

Cocaine and Caffeine

A 10% caffeine in cocaine sample showed few changes to the cocaine 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 (Figure 3a). For the sample with 20% caffeine, crystal formation was delayed (about 30 seconds) and more distorted crystals were observed. The short axis curved out more at the ends, and the crystals’ brown discoloration intensified (Figure 3b). A 50% caffeine sample showed the most pronounced 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. Two new shapes not previously observed, a long, thin, needle-like crystal and a sphere shaped crystal presented (Figure 3c). It is possible that the needle-shaped crystals are caffeine crystals.

Figure 3. Trends in crystal morphology of cocaine and caffeine aqueous samples.
**Cocaine and Lidocaine**

Lidocaine had an immediate effect on the shape of the cocaine crystals. In 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, exhibited a u-shaped curve (Figure 4a) 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 (Figure 4b). Also the short branches on the main axes (previously perpendicular to the axis) were longer and with a sharper angle. A couple of samples had a few sphere-shaped crystals. Overall, it took 30-45 seconds longer for crystals to form and they were fewer in number. With the 50% lidocaine samples, the cross shape was lost almost entirely and converted to X-shaped crystals with some smaller branches still protruding along the axis. Also, in some samples, a few small clusters of crystals formed (Figure 4c). There was no color change observed for any lidocaine samples.

![Figure 4. Trends in crystal morphology of cocaine and lidocaine aqueous samples.](image-url)
Cocaine and Procaine

Procaine had an immediate effect on cocaine crystals. A 10% procaine sample formed three types of crystals. The first was a crystal with two rods that crossed in the middle at 90°, much like the pure cocaine crystal, but with both axes branched. The other crystals seen were X-shaped and sphere-shaped. The branches of the sphere-shaped crystals were wavy (Figure 5a). A 20% procaine sample produced only sphere-shaped crystals. These crystals looked exactly like the sphere-shaped crystals with wavy branches of the 10% procaine samples, but no other types of crystals were present (Figure 5b). Also, only a few crystals formed with each sample. A 50% procaine sample did not produce crystals at all, but resembled the procaine standard (Figure 5c).

Figure 5. Trends in crystal morphology of cocaine and procaine aqueous samples.
**Cocaine and Levamisole**

A 10% levamisole sample typically displayed an extra branch that gave the crystal a Y-shape. Another type of crystal was present, an asterisk-shaped crystal with 5-6 arms. Also, some crystals resembled cocaine, but other tiny branches off the main axis were present (Figure 6a). A 20% sample consisted of two types of crystals. The first was asterisk-shaped and the second was Y-shaped. Both types were also seen with a 10% sample, but the 20% samples also revealed some tiny beads with a black cross shape in the center, like the pure levamisole samples (Figure 6b). A 50% levamisole sample consisted mostly of the tiny beads resembling the pure levamisole and a few asterisk-shaped crystals, but no Y-shaped crystals were observed (Figure 6c). Also, as the levamisole concentration rose, crystal formation time increased.

**Figure 6.** Trends in crystal morphology of cocaine and levamisole aqueous samples.
Cocaine and Sugar

Many of the crystals were unchanged from the pure cocaine shape, but some trends observed were similar to those seen with other adulterants. A 10% sugar sample produced crystals with one elongated axis and an X or U-shaped short axis. Also present were X-shaped crystals and sphere shaped crystals (Figure 7a). Many of the samples also had several crystals that resembled cocaine and did not have any noticeable transformation. A 20% sample had crystals with one elongated axis and an X-shaped short axis and some crystals that had a third branch giving the crystal a Y-shape. Also present were sphere-shaped crystals (Figure 7b). Fewer samples had crystals that resembled cocaine. A 50% sample had crystals with one elongated axis (some branching in a few samples) and an X-shaped short axis. Some X-shaped crystals and sphere-shaped crystals were observed, but were not as defined as in other concentrations (Figure 7c).

Figure 7. Trends in crystal morphology of cocaine and sugar aqueous samples.
**Cocaine and Baking Soda**

The majority of crystals in baking soda samples were shaped like pure cocaine with some branching at the ends of one axis. Also present in a 10% concentration were larger sphere shaped crystals with 5-6 branches and crystals with one very long axis with a small X-shaped short axis (Figure 8a). A 20% sample had the same types of crystals as a 10% sample, but the only difference was a lesser number of crystals shaped like cocaine, although they were still present (Figure 8b). A 50% baking soda sample showed the most differences. Some crystals shaped like cocaine were present, but the appearance of an X-shaped crystal made this concentration different from the others. Also, some gray/white clumps were present and were believed to be baking soda (Figure 8c).

![Figure 8. Trends in crystal morphology of cocaine and baking soda aqueous samples.](image)

(a) 10% Baking Soda
- Most shaped like cocaine
- Some with branched ends
- Larger sphere shape
- 5-6 branches
- Long, single axis with short branches

(b) 20% Baking Soda
- Very similar to 10% solutions
- Fewer shaped like cocaine
- Larger sphere shaped
- 5-6 branches
- Some with longer axis with X-shaped short axis

(c) 50% Baking Soda
- Some shaped like cocaine
- Some X-shaped with no branching
- Gray/white clumps
Powder Samples

Cocaine and Caffeine

For the 10% caffeine sample, the crystal shapes were comparable to the liquid samples and showed the same trends. 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%. Also seen were some X-shaped crystals resembling caffeine. 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 (Figure 9a).

<table>
<thead>
<tr>
<th>Powder</th>
<th>10%</th>
<th>20%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Caffeine</td>
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<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>(b) Lidocaine</td>
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<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 9. Trends in crystal morphology of cocaine and caffeine/lidocaine powder samples.
**Cocaine and Lidocaine**

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 crystals, however, the few X-shaped crystals did resemble those in the liquid samples (See figure 9b above).

**Cocaine and Procaine**

The powder samples were similar to the liquid samples, however the 20% and 50% samples produced more types of crystals. The 10% samples showed the same types of crystals as the liquids. The 20% samples produced the wavy-branched, sphere-shaped crystals in addition to X-shaped and cross-shaped with both axes branching. These crystals closely resemble the 10% liquid samples. Also, the 20% samples had the tiny beads (like procaine standard). The 50% samples exhibited many of the tiny beads as well as sphere shaped crystals. There was one 50% sample with a few X-shaped crystals and some crystals resembling pure cocaine (Figure 10a).
Cocaine and Levamisole

The cocaine and levamisole powder samples had similar crystal shapes as the liquid samples. At 10% there were Y-shaped and asterisk shaped crystals, although they were much smaller in size than the liquid samples. At 20%, there were mostly asterisk shaped crystals with 5-6 branches. Many of these crystals also had tiny branches protruding at different angles from the main axes. At 50%, there were a few asterisk shaped crystals, but mostly tiny beads resembling pure levamisole. The difference between liquid and powder samples was that every concentration of powder samples had some degree of the tiny beads with a black cross in the middle, like the pure levamisole. Again, as levamisole concentration increased, more tiny beads were observed (See figure 10b above).

<table>
<thead>
<tr>
<th>Powders</th>
<th>10%</th>
<th>20%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Procaine</td>
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<tr>
<td>(b) Levamisole</td>
<td><img src="image4.png" alt="image" /></td>
<td><img src="image5.png" alt="image" /></td>
<td><img src="image6.png" alt="image" /></td>
</tr>
</tbody>
</table>

*all had some small beads with cross in the middle*
Cocaine and Sugar

Powder samples of a cocaine and sugar mixture were comparable to liquid samples with one difference; the crystals seen in the powder samples were much smaller in size than those in the liquid samples. Numerous X-shaped crystals were present. Again, a 20% sample had crystals like cocaine, but also some gray clumps like the sugar standard. A 50% sample had crystals like cocaine and gray clumps like the sugar standard, but some X-shaped crystals were present (Figure 11a). The main difference between liquid and powder sugar samples was the presence of sphere-shaped crystals in all concentrations. One possible explanation for this could be that the liquid samples were more homogenous than the powder samples.

<table>
<thead>
<tr>
<th>Powders</th>
<th>10%</th>
<th>20%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Sugar</td>
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<tr>
<td>(b) Baking Soda</td>
<td><img src="image4" alt="Baking Soda" /></td>
<td><img src="image5" alt="Baking Soda" /></td>
<td><img src="image6" alt="Baking Soda" /></td>
</tr>
</tbody>
</table>

Figure 11. Trends in crystal morphology of cocaine and sugar/baking soda powder samples.
**Cocaine and Baking Soda**

The majority of crystals in a 10% baking soda powder sample were unchanged from the cocaine shape, except they were much smaller in size. A few samples had some X-shaped crystals, previously only seen in the 50% concentration of the liquid samples. A 20% sample again had mostly crystals shaped like cocaine with some gray/white clumps resembling pure baking soda. The 50% baking soda samples showed the greatest variety in crystal shape. Unchanged crystals resembling cocaine, X-shaped, and sphere shaped crystals were all present. All of these crystals were smaller in size than the liquid samples (See figure 11b above).

**Unknown Analysis**

A group of sixteen undergraduate students was asked to identify a set of unknown samples based on cocaine/adulterant trends presented in this research. The results are shown in Table 2. The two students that identified the adulterant, but incorrectly identified the concentration both identified the samples as 50% sugar when they were actually 20% sugar. The two students that did not correctly identify the adulterant or concentration both misidentified the 10% levamisole sample as sugar. One student identified the sample as 10% sugar, and the other 20% sugar. The results of this unknown analysis showed that the differences in each adulterant and concentration are discernable by a limited amount of training, as 75% of the samples were identified correctly. It appears the difficulty in analysis was when sugar was the adulterant. This could be because there are not many differences in the crystal shape when sugar is used as an adulterant. The results also show that it can be difficult to determine the concentration of the sample once the
adulterant has been identified, but that the crystal characteristics are different enough that inexperienced analysts can distinguish between them.

Table 2

Results of Unknown Analysis

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Correct adulterant, concentration</td>
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</tr>
<tr>
<td>Correct adulterant, incorrect concentration</td>
<td>2</td>
</tr>
<tr>
<td>Incorrect adulterant, concentration</td>
<td>2</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>16</strong></td>
</tr>
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</table>
CHAPTER 4

DISCUSSION

Overall, this study documents a change in crystal habit for a range of six common cocaine adulterants when tested using the gold chloride/acetic acid microcrystal test, a presumptive test that was previously considered the gold standard until replaced by modern techniques. These adulterants are caffeine, lidocaine HCl, procaine HCl, levamisole HCl, sugar, and baking soda. This is the first research that documents the trends in crystal morphology for these common adulterants.

Color tests are often preferred over microcrystal tests because they are relatively simple to understand and use. However, color tests can often give false positive results (3). Microcrystal tests offer an advantage because they are contingent upon the chemical properties of the drug, therefore, the resulting crystals are unique to a particular substance (15). As shown by Swaitko et al., microcrystal tests could distinguish between cocaine and several compounds that produced false positive results with a color test. The microcrystal test offers the benefits of specificity, quickness, and lower cost (10). The disadvantage is that the presence of an adulterant can alter the crystal morphology, however, this research has shown those changes can be beneficial and can offer more information to the analyst without further testing.

Currently, confirmatory tests offer similar information, as it relates to the identity and concentration of an adulterant, but they require more time for analysis, are more ex-
pensive, and require careful maintenance (10). Instrumentation that gives confirmatory results is generally accepted in court because of its validated methods and specificity of analysis (9). These types of tests should never be overlooked, but should be corroborated with other techniques, such as the microcrystal test.

The first part of the study was done with aqueous solutions in order to ensure accurate measurement of the components, a homogeneous mixture, and minimize waste. By examining aqueous mixtures, a baseline of trends in crystal shape was established. The use of aqueous samples may not be practical for use in a forensic lab, but it was necessary to document the power of this methodology. Some might argue that this represents an extra step in the research, however, it may offer other information about the sample. For example, some adulterants such as benzocaine have low water solubility, so by dissolving the sample in water, cocaine HCl can be separated. Nevertheless, for research purposes, aqueous samples gave beneficial information for further studies with powders.

There were some notable differences between aqueous and powder samples. Overall, the aqueous samples were more homogenous than powder samples. An example of this was observed with caffeine samples. Needle-like X-shaped crystals previously seen only at 50% caffeine liquid concentration were observed at all concentrations in the powder samples. Since these crystals closely resemble caffeine, it is likely that inhomogeneity of the powder resulted in localized high concentrations of caffeine. Further evidence of this inhomogeneity is seen in the procaine powder samples. The 20% samples produced some crystals like those of the 10% liquid samples (branching of both axes) and the tiny beads (resembling the procaine standard) like those of the 50% samples.
Second, the time required for crystal formation was less for powder samples and produced so many crystals that they clumped in one area and it was often difficult to find individual crystals to observe and photograph. However, crystals in aqueous 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 aqueous samples, possibly causing their effectiveness to be diminished. Finally, another difference observed with powder samples was the size of the crystals. Crystals produced from powder cocaine/adulterant mixtures were generally smaller than those of the aqueous samples. Since the powder samples were more concentrated, faster crystallization could result in numerous, smaller crystals.

The microcrystal test is not limited to cocaine and to use it properly, the analyst must possess knowledge of crystal structures for many drugs. Some have used this rationale as the basis for an argument against the use of the microcrystal test. Yet, the most effective forensic analyst should have multiple tools at their disposal as this only substantiates their results. One quality of an effective analyst in forensic science is their attention to detail and this research demonstrates that quality is critical as crystal characteristics are often subtle. An example of this is the types of crystals observed at the 50% caffeine and 50% lidocaine concentrations. Both produced X-shaped and sphere-shaped crystals, but the adulterant determination was made by carefully looking at the X-shaped crystals for the presence of branches protruding from the axis. With pure cocaine, these branches are perpendicular to the axis, but with lidocaine they are not. However, these branches were not seen at all in the caffeine X-shaped crystals. The presence of these branches made enough difference to distinguish between caffeine and lidocaine. Another
difference between the two was the frequency of branching in the spheres. The caffeine spheres were denser while the lidocaine had fewer branches. These subtle differences are critical to distinguishing between some adulterants.

Another example of small details that are essential to observe to distinguish between adulterants is the types of crystals observed at the 50% procaine and levamisole samples. The 50% levamisole samples consisted mostly of the tiny beads with a black cross in the middle. These beads were also present in procaine samples. There is no way to distinguish between procaine and levamisole at the 50% concentration if the tiny beads are all that is observed. However, some asterisk shaped crystals were seen in the levamisole samples, so their presence can be used to differentiate between procaine and levamisole since no other crystals were observed with procaine.

Conclusions

This study sheds new light on an old technique and can help analysts identify adulterants more quickly. The trends for the changes in crystal morphology for aqueous solutions of cocaine in the presence of caffeine, lidocaine HCl, procaine HCl, levamisole HCl, sugar, and baking soda were documented and are summarized in Table 3. The changes were unique to both the specific adulterant and the concentration of that adulterant. Similar trends were seen for powder samples with some general differences noted between the two types of samples.

This research shows that with higher adulterant concentrations, the crystal shape can change so much that it could lead to a misidentification because the shape looks nothing like pure cocaine. The results demonstrate that the microcrystal test can minimize the
margin for error because the exploitations of crystal morphology were used to correlate crystal shape to a specific adulterant and concentration. Using changes in crystal morphology in the presence of common adulterants is a novel approach to presumptively testing street samples of cocaine. Specifically, this method shows the potential for adding another tool to drug analysis that remains highly useful for labs in search of a quick, inexpensive, and accurate method of testing.

Future Studies

This study has been primarily concerned with six common cocaine adulterants. As indicated by the results, each adulterant affected the shape of the cocaine crystal in some way. Presumably, there are other substances that will do the same so it may become necessary to document how they affect crystal shape. Others that might be considered are benzocaine, tetracaine, and flour (2). Also, this study focused on cocaine mixed with one other adulterant. Dealers often cut the pure drug multiple times with multiple adulterants. The presence of two or more adulterants could have a significant effect on the crystal shape and should be considered in analysis. Finally, all samples used in this study were prepared in the laboratory. It would be beneficial to conduct analysis on real street samples to test the methodology.
LIST OF REFERENCES


