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MICRO-CRYSTAL IDENTIFICATION TESTS FOR MORPHINE, HEROIN, DILAUDID, AND COCAINE

Charles C. Fulton† and John B. Dalton‡

In the identification of small amounts of suspected drugs the most valuable tests are of two kinds: color tests on the spot-plate, and crystal tests under the microscope. The former are especially useful for compounds of phenolic character, such as adrenalin, arbutin, aspirin, and the opium alkaloids. The micro-crystal tests are particularly useful for amines, such as all alkaloids, and amides, such as phenacetin and acetanilid. This method of identification by recognition of characteristic crystals under the microscope was begun by Wormley (1), Lyons (2), Behrens (3), and others, and developed in more recent years for the alkaloids especially by Grutterink (4), Stephenson (5), and Amelink (6).

A number of the more recently developed tests, including some which were previously unpublished, will be described in the course of this paper. The photomicrographs¹ which accompany the text show the crystals of the four alkaloids, morphine, heroin, dilaudid, and cocaine, resulting from several of these tests. Some of the micro-crystals have been previously described (11, 12, 13, 14, 15), but until now no photographs of them have appeared in any of the literature.

The crystal tests for a particular alkaloid require selected reagents which

will most readily give highly characteristic crystals with the alkaloid in question (7, 8, 9, 10), for the usual result with a reagent and an alkaloid taken at random is an amorphous precipitate that does not crystallize at all. Generally the chosen tests are such that the crystals can be definitely recognized by mere inspection under a low power microscope (50 to 100 X). However, since many of the crystals are highly pleochroic with polarized light, or highly birefringent and beautifully illuminated with crossed nicols, it is best to use a polarizing microscope whenever available.

Either of two methods for making a crystalline test are generally employed. Method *A* involves dissolving the alkaloidal salt in water and adding the reagent, while with Method *B* the reagent is added directly to the solid alkaloid. A more detailed discussion of both procedures follows.

With Method *A* about 0.2 mg. or less of the alkaloidal salt is dissolved in one drop (about 0.04 cc.) of water on the microscope slide. (If the free alkaloid has been obtained by extraction or otherwise it is dissolved in dilute acid and a drop put on the slide.) One drop of a selected reagent is then added by letting it fall from a 1 cc. pipette. The precipitating compound may be in

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¹ The photomicrographs which accompany this article were prepared by John B. Dalton.

aqueous solution or in concentrated or very strong acid.

With Method *B* a drop of the precipitating reagent (ordinarily in strong acid) is added directly to about 0.1 mg. or less of the solid, powdered alkaloid or its salt and a cover-glass is placed over the material immediately. The alkaloid dissolves and is precipitated at varying concentrations. In this method the test-drop can be a concentrated acid (hydrochloric or phosphoric), or acid of a concentration at which the crystals form best and which might be difficult to obtain by mixing two solutions as in Method *A*. Formulas are given in this paper for making up directly the reagents used for Method *B*, but in practice they are usually obtained by suitable dilutions (to three times the volume) of the more concentrated reagents kept for Method *A*.

With both methods in a successful test a precipitate appears, either at once or after a few minutes' standing. Usually this precipitate is amorphous at first but crystallizes in a short time, although in some cases it is crystalline from the start. If the test is unsuccessful because of amine impurities the crystals may be distorted so as to be unrecognizable, but the more common unsuccessful result is an amorphous precipitate which fails to crystallize.

In the case of a mixture of alkaloids or amines some kind of separation—by extraction methods, for instance—is often necessary before micro-crystal tests can be applied. However, inert adulterants or dilutents, such as powdered sugar or lactose, usually do not interfere at all, except of course that

more of the material must be used to make the test.

A number of the reagents mentioned below can be used for many other alkaloids besides morphine, heroin, dilaudid, and cocaine. Thus, Stephenson's work on 51 alkaloids (5) shows that gold chloride gives especially good tests for 10 of them, platinum chloride for 6, and Wagner's reagent for 6. The newer reagents presented herein have not been so thoroughly studied. Gold bromide in half-concentrated hydrobromic acid is certainly quite useful, yet perhaps is not as satisfactory for general use as gold bromide in concentrated hydrochloric acid, which may be the best of all identifying reagents for alkaloids.

Tests for Morphine

The best-known tests for morphine are those made by Method *A* with Marme's reagent (5, 14) and Wagner's reagent (16, 5, 14). The latter test can be varied, using Method *B*, to identify less than a gamma (a millionth of a gram) of morphine (15). In addition to these better known tests are several which are quite valuable.

Gold Bromide in Half-Concentrated Hydrobromic Acid. A form of this test in which gold bromide is used in concentrated HCl has been previously described (14). If the reagent is applied to the aqueous solution of morphine (Method *A*), threads in rosettes form gradually from the amorphous precipitate. When added to an HCl solution of morphine, or applied directly to the solid alkaloid or its salt (Method *B*) the reagent gives, upon standing, salmon-colored or brownish-yellow-orange

plates. These are often feathered, or form rosettes of blades or irregular plates, while with polarized light they show dichroism of pale yellow to dark red.

Now it has been found that in using Method B half-concentrated acid gives the most rapid and best crystallization. Half-concentrated HCl may be used, but HBr is better except for the deeper color of the solution. Two types of crystals are formed, needles and dichroic plates (Figure 1). As the test is quite sensitive, only a very little morphine should be used.

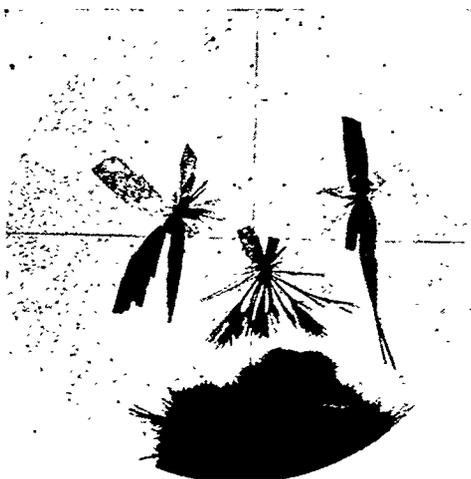


FIGURE 1

Morphine with HAuBr_4 in half-concentrated HBr. Method B. (Polarized light.)

The reagent is prepared according to the following formula: Gold chloride crystals ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$)—1 gram; HBr (40%)—30 cc; Water—30 cc.

This reagent also gives an exceptionally fine test for novocaine and may likewise be used for the identification of cocaine, nupercaine, heroin, cotarnine, creatinine, hyoscyamine, scopolamine, theophylline, and other alkaloids.

In general, these different crystals can be distinguished at a glance from those of morphine and from each other although dichroic plates with scopolamine show some resemblance to those with morphine.

Platinum Bromide in Hydrobromic Acid, and Bromo-Chlorides in Hydrobromic - Hydrochloric Acid. Using Method B, with various ratios of HBr to HCl, morphine forms a series of different platinum crystals, but these platinum reagents give no morphine crystals in plain water, requiring instead about 60% to 100% of concentrated acid. The different types of crystals were first studied with empirical mixtures, and some of them were found to correspond quite definitely to simple molecular ratios of HBr and HCl. There are some distinctions between the crystals for each of the six possible compounds from $\text{H}_2\text{PtBrCl}_5$ to H_2PtBr_6 . $\text{H}_2\text{PtBrCl}_5$ gives the most rapid crystallization, H_2PtBr_6 the slowest.

The reagents, their formulas, and a description of the crystals are given below which, to the writers' knowledge, have never previously been described. In all instances these reagents should stand for a few days after being mixed in order to bring them to final equilibrium. The first three (1a, 1b, 2, and 3) are much more satisfactory than the last three.

1a. $\text{H}_2\text{PtBrCl}_5$ in HCl. Platinum chloride crystals ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$)—1 gram, HBr (40%)—2 cc., HCl (conc.)—46 cc., Water—12 cc. The resulting crystals are light yellow, rectangular plates, which are very highly birefrin-

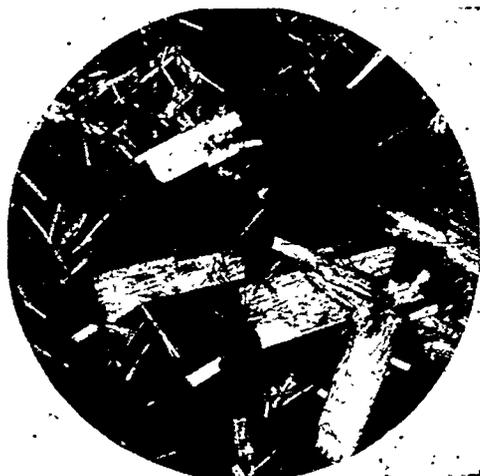


FIGURE 2

Morphine with $H_2PtBrCl_5$ in HCl. Method B.
(Crossed nicols.)

gent and form gradually on standing with little or no amorphous precipitation. Figure 2 shows these crystals photographed with crossed nicols.

1b. $H_2PtBrCl_5$ in 1 HBr:5 HCl. $H_2PtCl_6 \cdot 6H_2O$ —1 gram, HBr (40%)—12.5 cc., HCl (conc.)—35.5 cc., Water—12 cc. The crystals are similar to the preceding but deeper yellow and not so perfectly formed, and there is an amorphous precipitate before crystallization. The test, however, is a little more sensitive than with 1a.

2. $H_2PtBr_2Cl_4$ in 1 HBr:2HCl. $H_2PtCl_6 \cdot 6H_2O$ —1 gram, HBr (40%)—27.5 cc., HCl (conc.)—29.5 cc., Water—3 cc. The crystals are orange-yellow and have pointed rather than square-cut ends—that is, they have become hexagons which are more or less elongated.

3. $H_2PtBr_3Cl_3$ in 1 HBr:1 HCl. $H_2PtCl_6 \cdot 6H_2O$ —1 gram, HBr (40%)—35.5 cc., HCl (conc.)—18.5 cc., Water—6 cc. The crystals are orange plates,

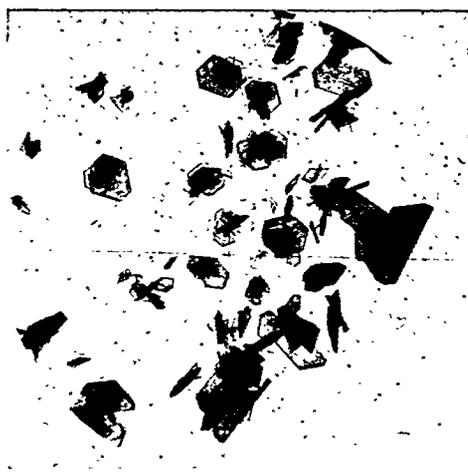


FIGURE 3

Morphine with $H_2PtBr_3Cl_3$ in 1 HBr : 1 HCl.
Method B.

usually hexagonal but sometimes diamond or coffin-shaped. (Figure 3.)

4. $H_2PtBr_4Cl_2$ in 2 HBr:1 HCl. $H_2PtCl_6 \cdot 6H_2O$ —1 gram, HBr (40%)—42.5 cc., HCl (conc.)—11.5 cc., Water—6 cc. This gives crystals which are orange-red, thick, and hexagonal, coffin-shaped, or diamond-shaped plates, smaller than with the preceding reagent. A few rosettes or sheaves of needles (morphine with H_2PtBr_6) may also form.

5. H_2PtBr_5Cl in 5 HBr:1 HCl. $H_2PtCl_6 \cdot 6H_2O$ —1 gram, HBr (40%)—52 cc., HCl (conc.)—5 cc., Water—3 cc. The characteristic crystals are quite small diamond-shaped plates varying in color from orange to red. Usually a considerable part of the precipitate crystallizes in the morphine- H_2PtBr_6 needles instead.

6. H_2PtBr_6 in HBr. $H_2PtCl_6 \cdot 6H_2O$ —1 gram, HBr (40%)—48 cc., Water—12 cc. The crystals are small rosettes of dark red needles, nearly opaque to

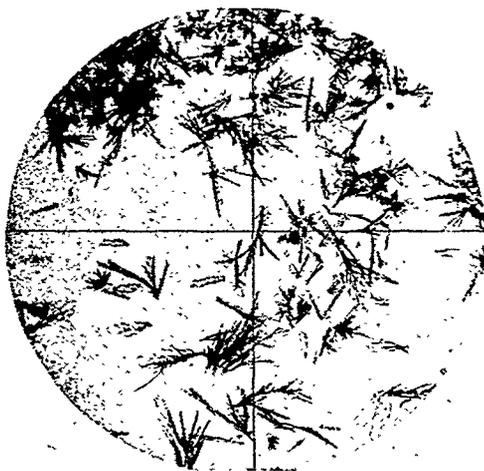


FIGURE 4
Heroin with HgI_2 in 10% HCl . Method B.

transmitted light, but highly reflecting when illuminated with light coming obliquely from above.

TESTS FOR HEROIN

In the past the favorite test for heroin has been the one made with platinum chloride (16, 5). However, heroin in the illegal traffic is nowadays so grossly adulterated that this test often fails. The adulteration is chiefly with milk sugar, powdered sugar, mannitol, or other inert material, but novocaine, morphine, or other alkaloids, are sometimes present in small proportion, hence the need for more sensitive heroin tests and, if possible, some less affected by impurities.

Other old tests are with sodium carbonate, sodium phosphate, mercuric chloride, and picric acid (5). The crystals of free heroin, obtained with sodium carbonate or tri-sodium phosphate, are characteristic, but the test is even less sensitive than with platinum chloride. Mercuric chloride is more

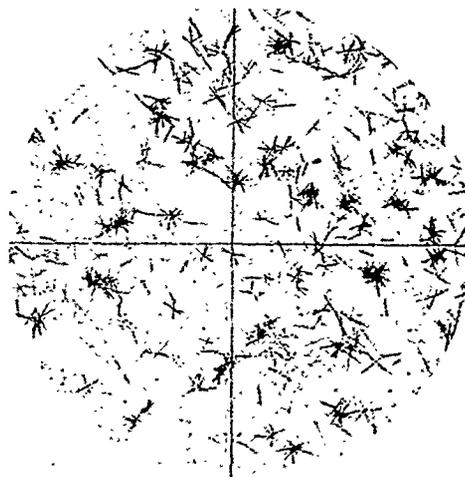


FIGURE 5
Heroin with HAuBr_4 in diluted H_2SO_4 . Method A. (Extremely dilute solution.)

sensitive but less characteristic while the picric acid test, modified to the extent of using sodium picrate (13), is very sensitive.

The best tests now known for heroin are made with mercuric iodide in hydrochloric acid (13), gold bromide in sulfuric acid (8), and gold chloride in sulfuric acid (8). Below are descriptions and the first published photographs of these crystals (Figures 4, 5, and 6). Gold bromide in concentrated hydrochloric acid, and gold chloride in concentrated hydrochloric acid, can also be used (13), but do not form crystals as readily as the sulfuric acid reagents, nor are they as sensitive.

Mercuric Iodide in 10% Hydrochloric Acid. HCl (conc.)—27 cc., Water—73 cc., HgI_2 —to saturation. This reagent was originally used by Method A, but it has been found to give a more sensitive test by Method B. As the crystals are colorless, care should be taken that

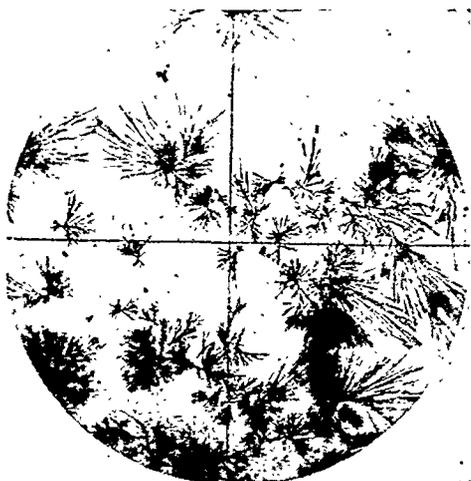


FIGURE 6

Heroin with HAuCl_4 in diluted H_2SO_4 , Method A.

they are not confused with crystals of undissolved material. They are slender blades and branching threads (Figure 4), and are only feebly illuminated when viewed with crossed nicols, thus appearing as pale gray "ghosts".

Gold Bromide in Diluted Sulfuric Acid. Gold chloride crystals ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$)—1 gram, HBr (40%)—1.5 cc., Diluted H_2SO_4 (H_2SO_4 —2 vol., Water—3 vol.)—to make 20 cc. By using Method A this reagent gives the most sensitive crystal test known for heroin, and the best results can be obtained with a minute amount of the sample. The crystals so formed are fine needles, mostly scattered. (Figure 5.)

Gold Chloride in Diluted Sulfuric Acid. Gold chloride crystals ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$)—1 gram, Diluted H_2SO_4 (H_2SO_4 —1 vol., Water—1 vol.)—20 cc. Again Method A is used. This reagent, however, is much less sensitive than the preceding, but still superior to older

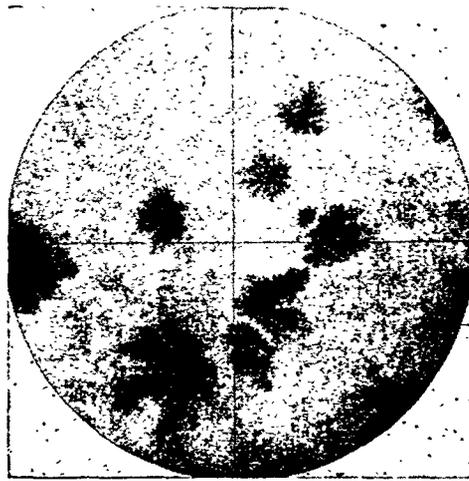


FIGURE 7

Dilaudid with H_2PtBr_6 in diluted H_2SO_4 , Method A.

tests. The resulting crystals are rosettes of needles and are illustrated in Figure 6.

TESTS FOR DILAUDID

Dilaudid (dihydromorphinone hydrochloride) is a synthetic derivative of morphine now used in medicine, and may also be used in drug addiction. The established test is with sodium nitroprusside, adding a small solid crystal of the reagent to a drop of aqueous dilaudid solution (6). In addition the following new tests are of value.

Platinum Bromide in Diluted Sulfuric Acid. Platinic chloride crystals ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$)—1 gram, HBr (40%)—1.7 cc., Diluted H_2SO_4 (H_2O —2 vol., H_2SO_4 —3 vol.)—to make 20 cc.

Using Method A one drop of the reagent is applied to a drop of aqueous dilaudid solution giving orange-yellow mossy rosettes of very vague structure. Whether definitely crystals or not,



FIGURE 8

Dilaudid with H_2PtBr_6 in $\text{HBr-H}_2\text{SO}_4$ solution. Method B. (Reflected light).

these are quite characteristic in appearance. (Figure 7.) Aqueous platinum bromide reagent gives a similar result, but with a heavier amorphous precipitate, which crystallizes more slowly.

A second technique following Method A consists of dissolving the dilaudid in a drop of diluted sulfuric acid (1 part H_2O and 1 part H_2SO_4) instead of in water and then adding a drop of the reagent. Crystals form as fine needles in sheaves and rosettes. They are nearly opaque to transmitted light, but with light falling on them obliquely from above they are seen to be highly reflecting, with a red-gold sheen.

Platinum Bromide in Hydrobromic-Sulphuric Acid Solution. Platinic chloride crystals ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$)—1 gram, HBr (40%)—10 cc., Diluted H_2SO_4 (H_2O —1 vol. to H_2SO_4 —1 vol.)—20 cc. Add a drop of this reagent to a little solid dilaudid powder and apply a cover glass. The crystals are the fine needles in sheaves and rosettes just described



FIGURE 9

Cocaine with HAuCl_4 in diluted Acetic acid. Method B. (Crossed nicols).

above, and are shown in Figure 8. This Method B test is much more sensitive than the preceding method.

TEST FOR COCAINE

The best Method A tests for cocaine, with platinum chloride (16, 5) and gold chloride (5, 6), have been known for a long time (2, 3). Gold chloride in concentrated hydrochloric acid will give better results than aqueous gold chloride—quicker and more complete crystallization with less interference from most impurities. To supplement these tests two new Method B tests are presented herewith.

Gold Chloride in Acetic Acid. Gold chloride crystals ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$)—1 gram, glacial acetic acid—40 cc., Water—20 cc. When a drop of this reagent is added to a little solid cocaine or its salt the characteristic crystals form immediately. These are pale yellow plates, very transparent and intensely birefringent, and Figure 9 shows them photographed with crossed nicols. Un-

fortunately the photograph can give no idea of the brilliance and beauty of the interference colors.

Gold Bromide in Acetic Acid. Gold chloride crystals—1 gram, HBr (40%)—1.5 cc., Diluted acetic acid (glacial acetic acid—2 vol. to H₂O—1 vol.)—to make 60 cc. If a drop of the reagent is added to a little solid cocaine or its salt the crystals form immediately. They are strongly birefringent and also very highly dichroic with polarized light, showing pale straw color or light yellow when oriented in one direction, and

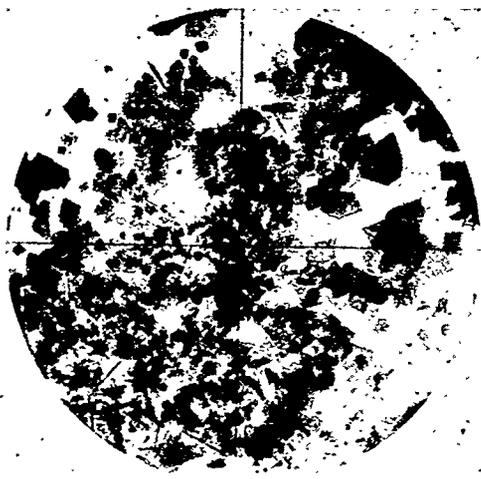


FIGURE 10

Cocaine with H₂AuBr₄ in diluted Acetic acid.
Method B. (Ordinary light).

deep orange or even red at right angles to this. By ordinary light they are light salmon where the light comes through a single crystal but orange to red where the crystals overlap with differing orientation. Figure 10, showing the crystals, was taken with ordinary light.

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