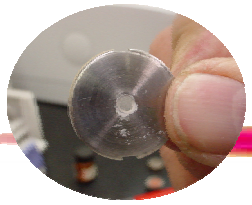


# Chemical Analysis

(Unit 9)



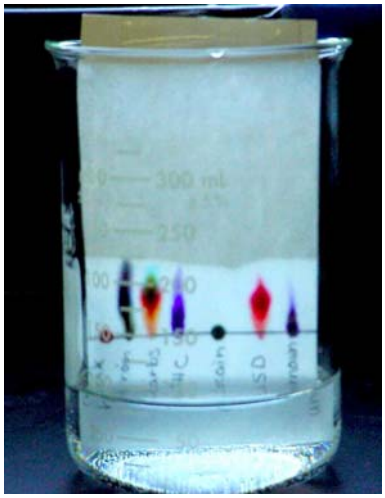
Chemical analysis is arguably one of the most important aspects of forensic science. Nearly every piece of evidence yields additional information when analyzed by a chemical procedure. Chemical procedures allow us to develop latent fingerprints, obtain DNA from a myriad of substances, and analyze nearly any unknown substance with ease. Chemists are consistently inventing ways to do such tests in the field with amazing speed and accuracy. Samples that once sat in a lab for weeks may now be analyzed at the crime scene in a matter of seconds.

Several chemical procedures, such as developing latent prints and DNA typing, are described in detail in other chapters of this book. It would be impossible to discuss each and every type of chemical analysis being used in forensics. Instead this chapter will provide an overview of some of the more common practices.

## Drug Identification

When a forensic chemist analyzes a drug specimen, she must be prepared for any possibility. The analysis must be accurate, for the results will have a direct bearing on the determination of guilt or innocence. It is crucial to know exactly what drug is present as well as its concentration. A chemist must also be able to defend the identification of a drug with the same amount of certainty.

Presented with a substance of unknown origin and composition, the forensic chemist must develop a plan of action that will ultimately yield the drug's identity. This is usually done in two phases. Since the possibilities are so plentiful, a chemist will first use screening tests to narrow down her search. There are several tests that forensic chemists normally rely on to perform a routine drug-identification analysis: color tests, microcrystalline test, chromatography, spectrophotometry, and mass spectrometry.



## Theory of Chromatography

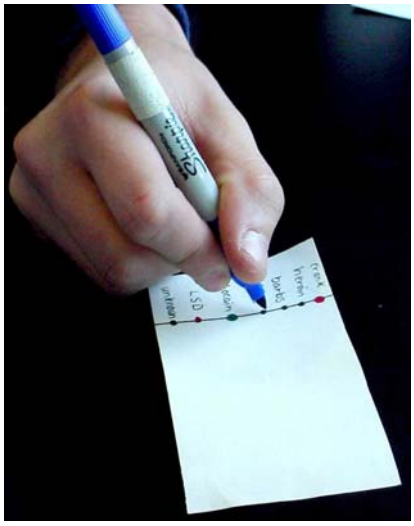
Chromatography is a technique for analyzing the multi-component samples that are frequently received in the crime laboratory. For example, illicit drugs sold on the street are not manufactured to meet government labeling standards; instead, they may be combined with any material that is at the disposal of a drug dealer. Hence, the task of identifying a drug from the street would be more difficult without the help of chromatography to first separate the mixture into its components.

## Thin-Layer Chromatography (TLC)

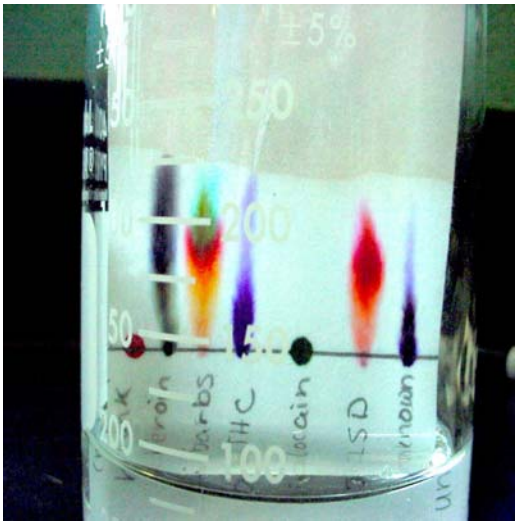
Chromatography itself covers a large range of applications from DNA to gas chromatography. Thin-layer chromatography incorporates a solid stationary phase and a moving liquid phase to cause a separation of the constituents of a mixture. Although simple test may be run by simply allowing a solvent to wick up a piece of porous paper, a more revealing test requires the preparation of a plate.

A thin-layer plate is prepared by coating a glass plate with a thin film of a granular material. Commonly, silica gel or aluminum oxide is used, but paper may suffice in simpler experiments. These serve as the solid stationary phase. If the sample to be analyzed is a solid, it must first be dissolved in a suitable solvent. A few micro liters of the solution are then applied to the lower edge of the plate. A liquid sample may be applied directly to the solid state in the same manner. The plate or paper is then placed upright into a closed chamber that contains a selected solvent.

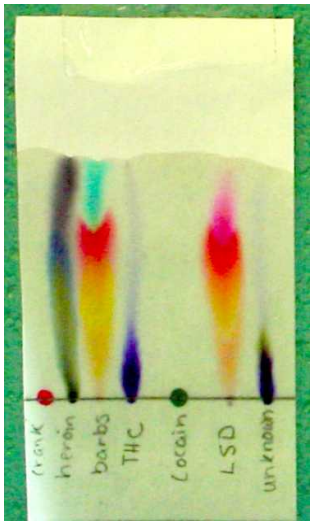
The solvent will slowly begin to wick up the plate by capillary action. It is the rising solvent that serves as the moving phase in thin-layer chromatography. As it moves past the sample spot, the components of the sample will become distributed between the stationary solid phase and the moving liquid phase. Those components with the greatest affinity for the moving phase will travel up the plate at a faster speed as compared to those that have greater affinity for the stationary phase. When the liquid front has moved a sufficient distance (usually 10 cm), the development is complete, and the plate is removed from the chamber and dried.



Placing Samples



Ink samples on the move



Finished Test

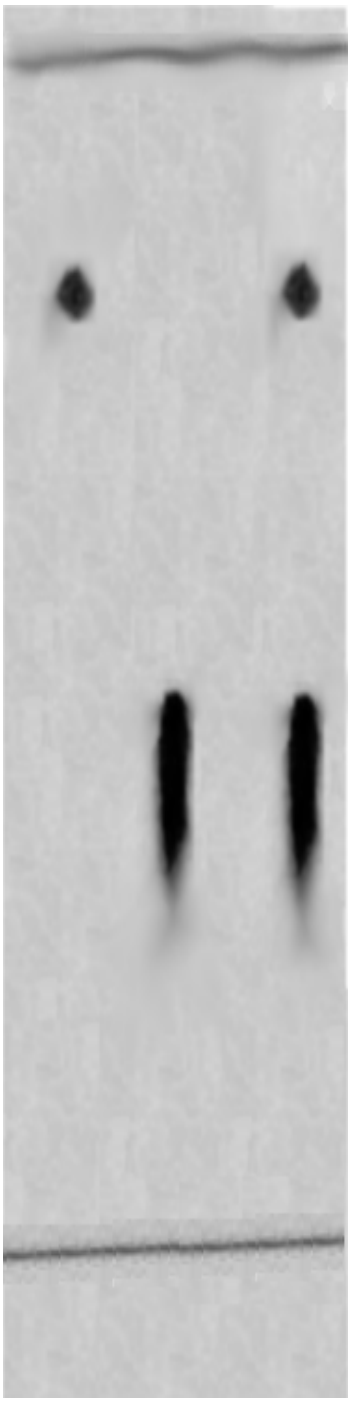
Because most compounds are colorless, no separation will be noticed after development unless the materials are *visualized*. This is may be done by:

- Exposing to UV light
- Exposing to fluorescent dyes
- Exposing to iodine
- Spraying with a reagent

These procedures may be used alone or in conjunction to make the components of a sample visible.

The distance a component has traveled up a plate can be assigned a numerical value known as the $R_f$ value. $R_f$ is defined as the distance traveled by the component divided by the distance traveled by the solvent. In the example to the right, the solvent was allowed to travel 10 cm up the plate before the plate was removed from the tank. After visualization, the heroin spot moved 8 cm. This indicates an $R_f$ value of 0.8; the quinine migrated 4 cm and has a $R_f$ value of 0.4. Note the third sample, which is a combination of quinine and heroin.

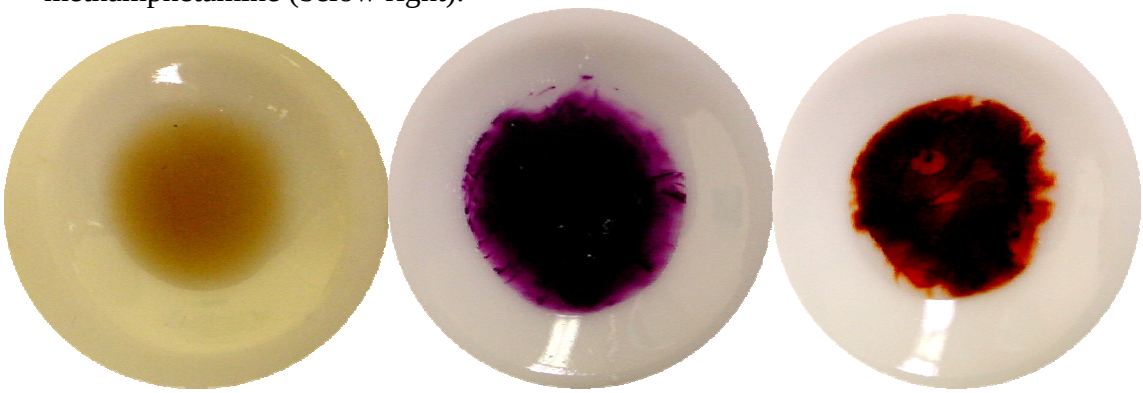
Although chromatography is fairly accurate on most drugs, inks, and some other chemicals, it is often necessary to be more precise. Some drugs and poisons require a very small quantity to be active. Such small amounts of chemical will not show up on a chromatography test. It is then that quantitative analysis is utilized.



## Color Test

Most color tests are used in initial screening. Although these tests are fairly accurate, they are often conducted in the field and are not the final test used as evidence in court. These tests are less expensive than the final tests performed in the lab. Most color tests are extremely simple and only require the addition of a prepared solution followed by a visual observation. The following simple color tests are only a few of the mainstays used in forensics:

- *Marquis* is a solution of 2% formaldehyde in sulfuric acid (below left). The reagent turns purple in the presence of heroin, morphine, and most opium derivatives (below center). Marquis will also become orange-brown when mixed with amphetamines and methamphetamine (below right).



- *Dillie-Koppanyi* (below left) is a two step test. First, cobalt acetate 1% in methanol is added to a suspect material. Then 5% isopropylamine in added in methanol. The presence of barbiturates causes the solution to turn violet-blue (below-right).


- *Duquenois-Levine* is a three step test administered to a plant or plant material to test for the presence of marijuana. The first solution is a mixture of 2% vanillin and 1% acetaldehyde in ethyl alcohol. Next, a solution of concentrated hydrochloric acid is added. Finally, chloroform is added. A positive result is shown by a purple color upon addition of the chloroform.

- *Van Urk* consists of a 1% solution of p-dimethylaminobenzaldehyde in 10% concentrated hydrochloric acid and ethyl alcohol. This reagent turns blue-purple in the presence of LSD.

- *Scott Test* requires a specific response in each of three parts. First, a solution of 2% cobalt thiocyanate is dissolved in water and glycerin (scott solution). A cocaine-containing powder will turn blue in this solution. The solution is then added to concentrated hydrochloric acid. If cocaine is present, the solvent dissolves the powder while leaving the solution pink. Finally, with the addition of chloroform, a portion of the solution should turn a blue color. It is important to note that each color must appear in each step. Some non-cocaine chemicals may yield one of the colors in one of the steps, but not all three.


**Concaine Powder**

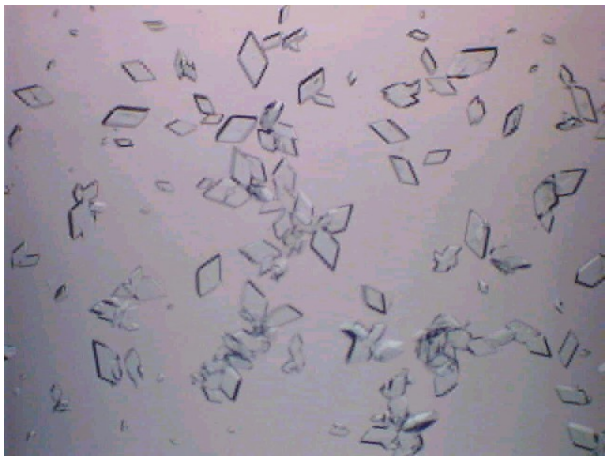
**Additon of Scott Soln**

**Additon of HCl**

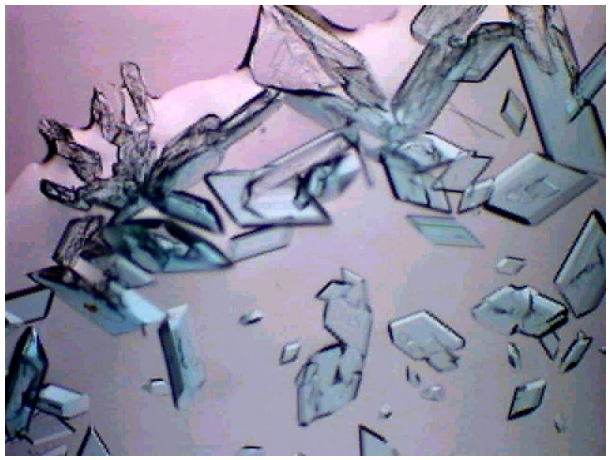
**Addition of Chloroform**

## Microcrystalline Test

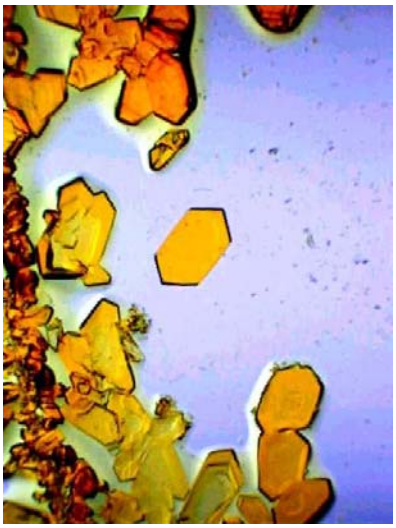
A technique considerably more specific than color tests is the microcrystalline test. Here, a drop of a suspected chemical solution is added to a small quantity of the chemical on a slide. Under such conditions, the solution will begin to re-crystallize. Under microscopic examination, the size and shape of the crystals are characteristic of the specific chemical. These tests are rapid, cheap, and often do not require the isolation of a chemical from its diluents. The following photographs are microcrystalline tests for some common chemicals which could be found at a crime scene or in a public place.



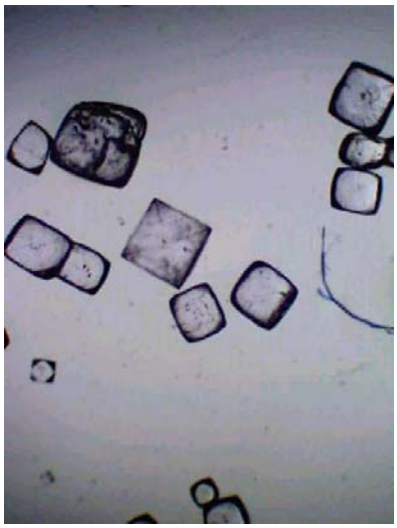
Copper II Sulfate x40



Copper Sulfate x100

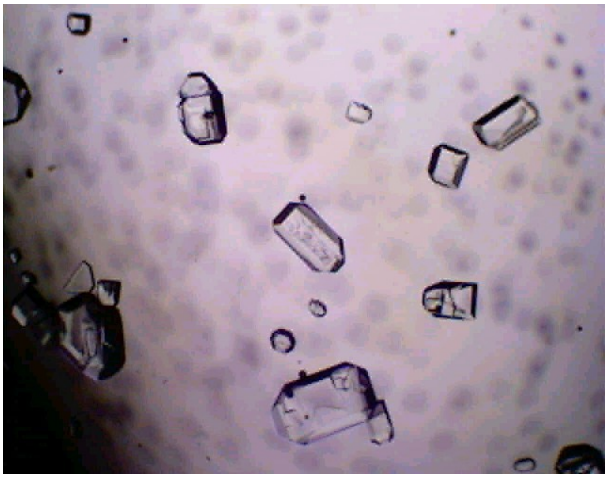


Potassium Ferricyanide x40



Salt Crystals x40

Aspirin x100

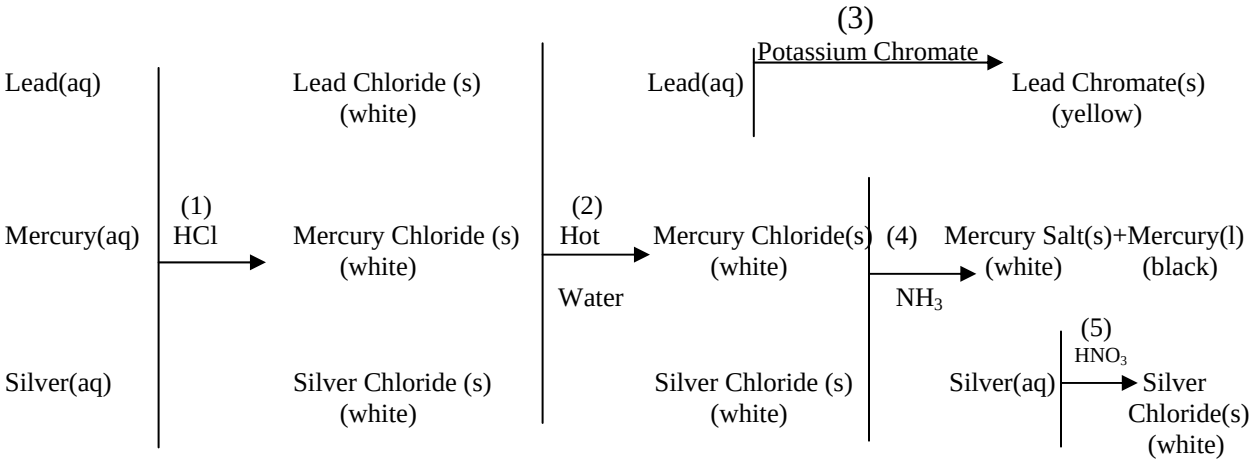


Sugar x40

Sugar x100

## Qualitative Analysis

Through the process of an organized order of reactions it is possible to separate, eliminate, and identify many different drugs and poisons. This type of analysis is often used to detect poisons and contaminates in liquids. It can also be adapted to identify multiple poisons or contaminants at once. Below is a flow chart of a simple chemical procedure which may be used to detect a few different types of poisons. This specific procedure may be used to separate and identify one of three different chemicals. Given the number of possibilities, it is a fairly simple procedure. These types of procedures can be organized to separate and test as many as 10 to 15 chemical simultaneously. The quantities such a test is designed to discover would not be visible in tests such as chromatography or micro-crystallization.




The details of each of these types of procedures are different. The basic premise however is the same. Initial steps in the procedures are used to separate and isolate each chemical by the use of differing properties such as solubility and reactivity. As each chemical is isolated, it is then added to a reagent which confirms the presence or absence of the chemical.

Below-left: A centrifuge is used to compact a precipitate, a solid powder, into the bottom of a test tube for separation.

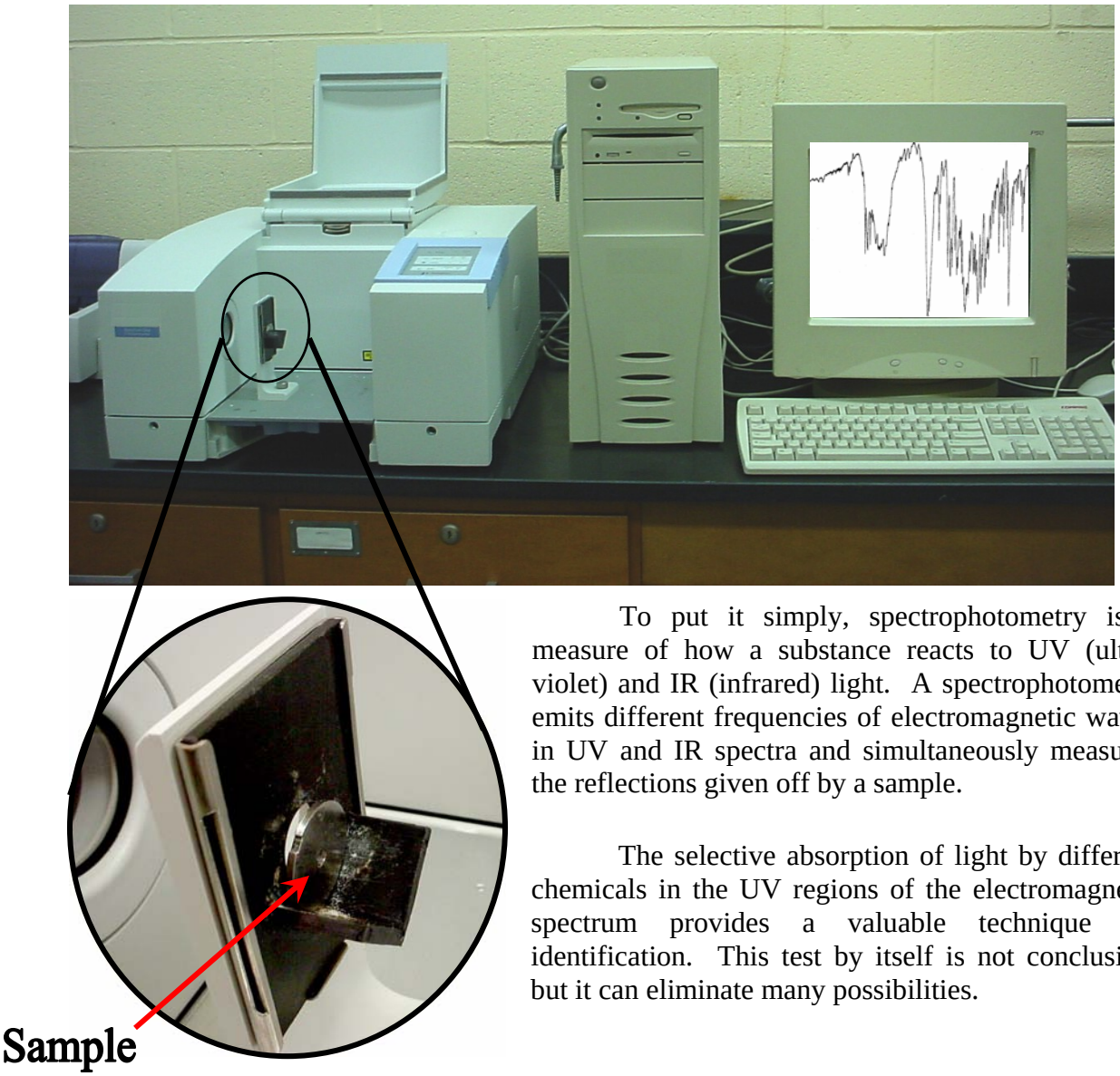
Below-right: A solution in a test tube after extraction from the centrifuge.

# Instrumental Analysis

Technological advances have made it possible to identify most chemicals as specifically as fingerprints. These methods often are expensive, but extremely accurate. Often these tests are used only after a simpler, cheaper test is performed initially as a screening process. There also exist a large number of samples to be run on these machines. It is not uncommon for a chemist to have a six to twelve months backlog of samples to be tested.

The details of how these instruments work is tedious at best. Each machine requires constant calibration and upkeep. This book will give only a light overview of some of the more common instruments and how they work. For further information on this subject try an internet search on "spectrophotometer," "mass spectrometry," and "gas chromatography."

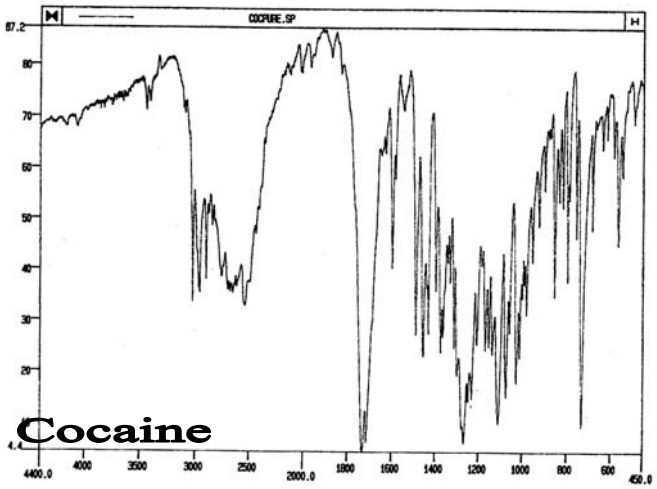
## Spectrophotometry

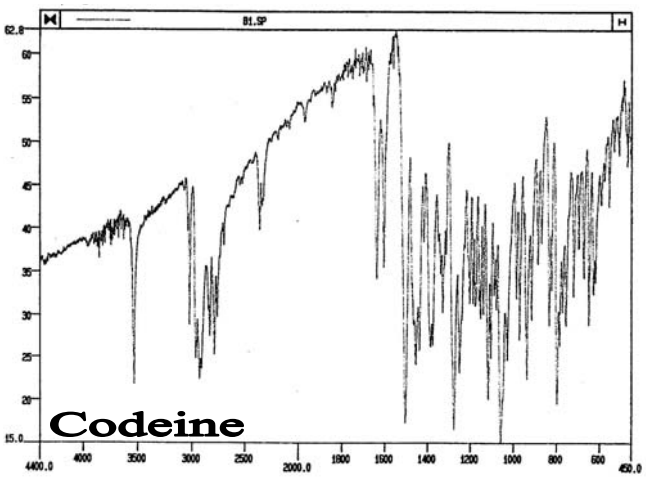


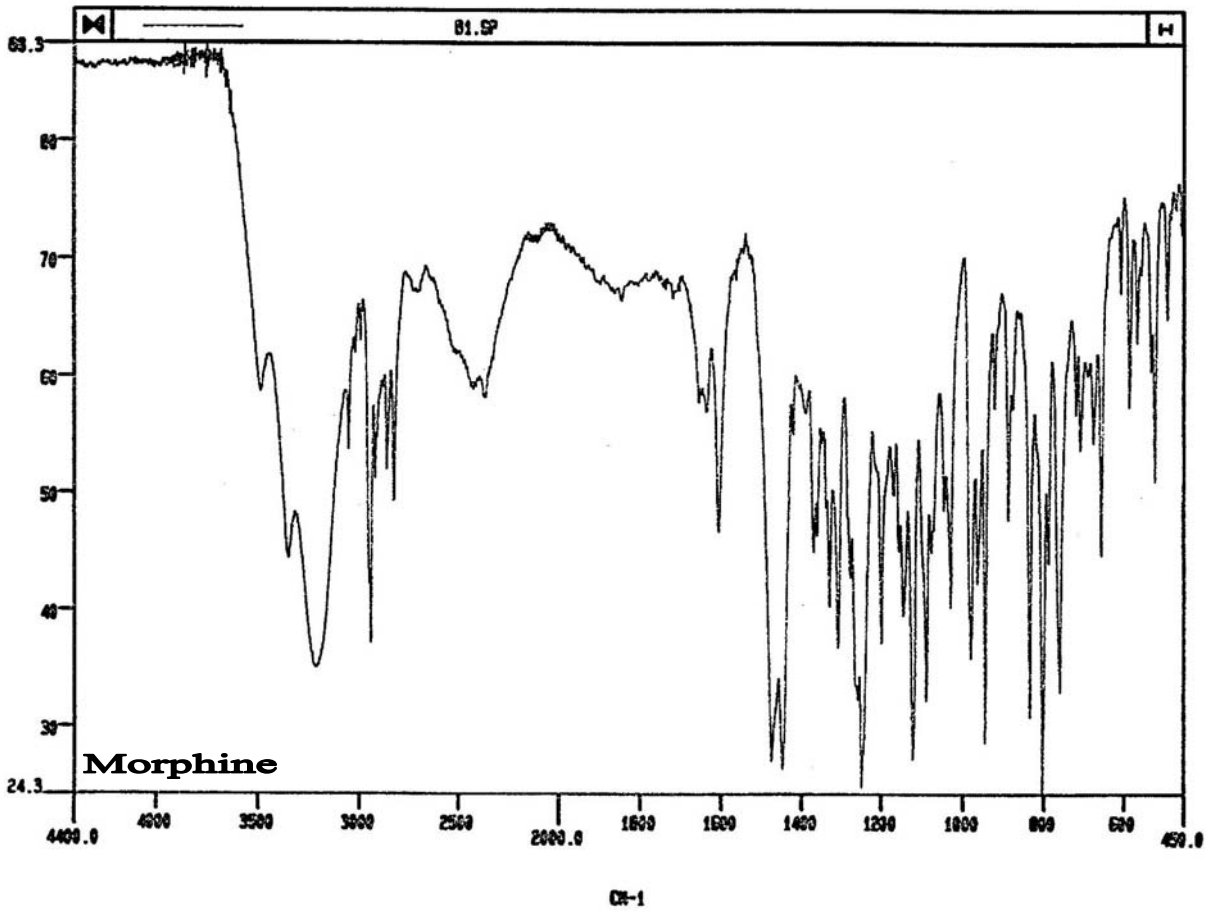

To put it simply, spectrophotometry is a measure of how a substance reacts to UV (ultra-violet) and IR (infrared) light. A spectrophotometer emits different frequencies of electromagnetic waves in UV and IR spectra and simultaneously measures the reflections given off by a sample.

The selective absorption of light by different chemicals in the UV regions of the electromagnetic spectrum provides a valuable technique for identification. This test by itself is not conclusive, but it can eliminate many possibilities.

Infrared spectrophotometry, on the other hand, can confirm the specific identity of a substance. The pattern of an infrared spectrum is unique for each compound. Unfortunately, for this test, the substance must be nearly pure. This poses a problem, since most substances found at a crime scene are not pure. The following are sample IR spectrums for three common drugs.

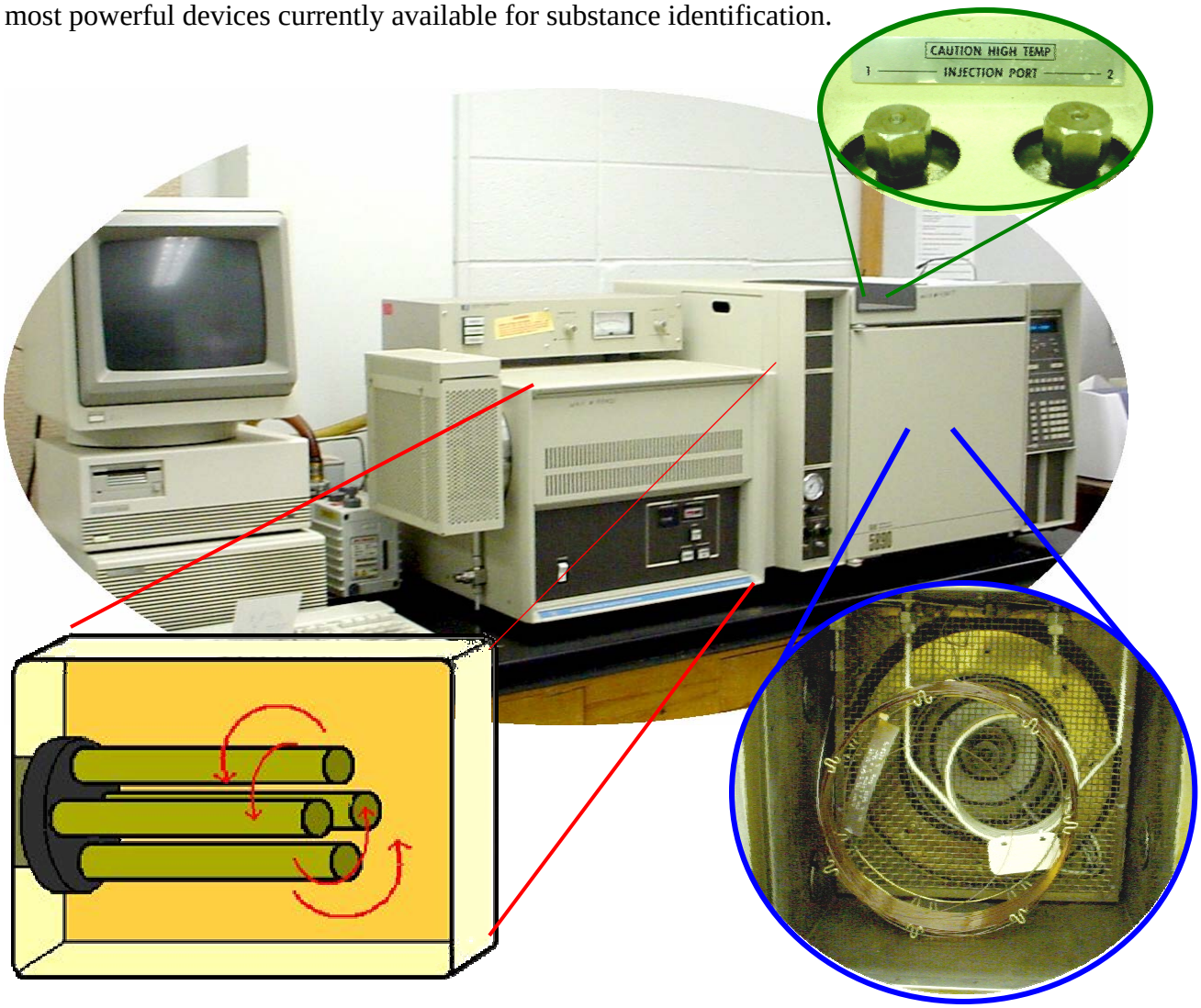


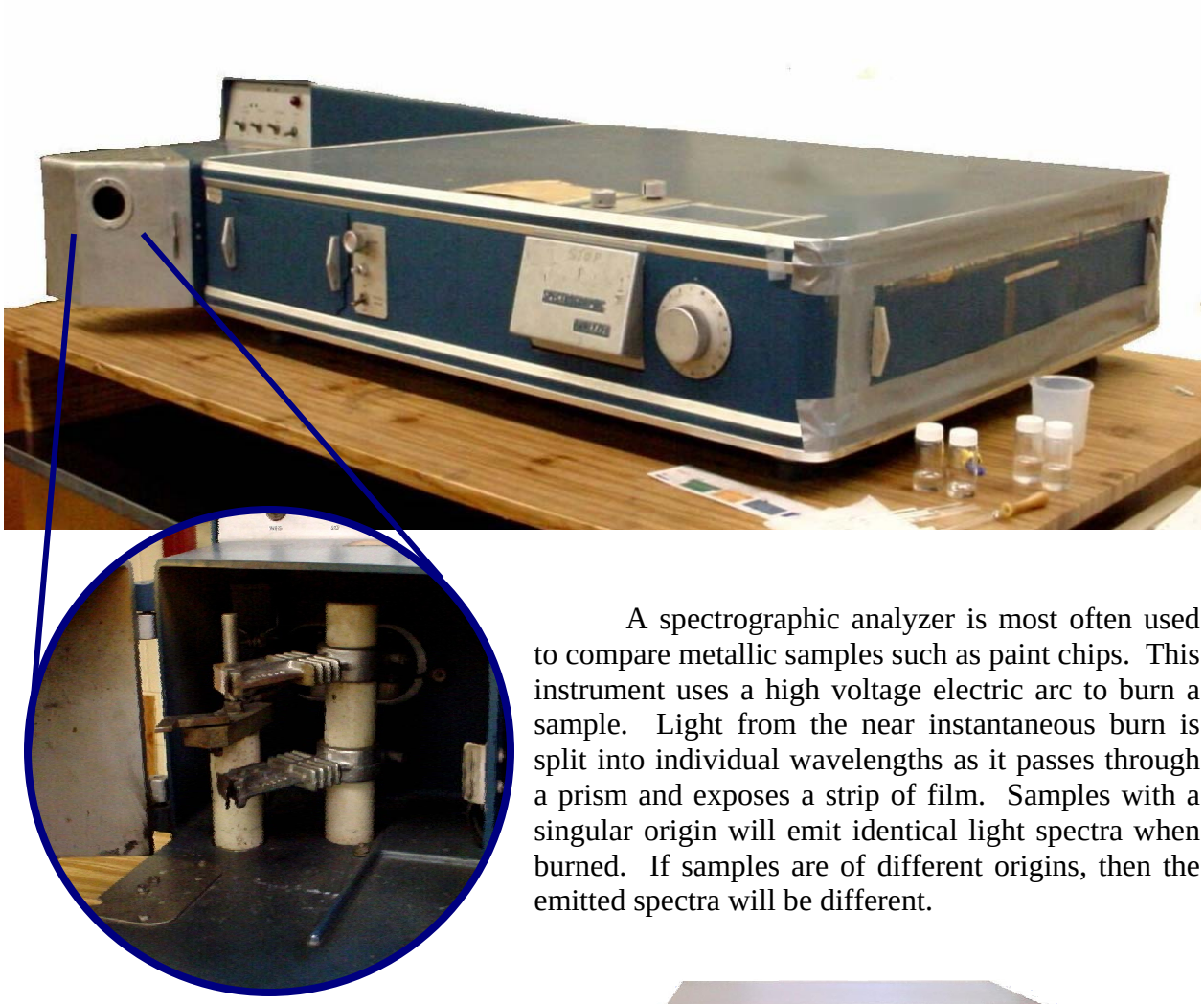
## Mass Spectrometry

The technique of gas chromatography is particularly suited for analyzing drugs, explosives, and poisons, since it can readily separate a chemical from other substances present. Gas chromatography, however, cannot provide a specific identification of a sample. To solve this problem, scientists have combined a gas chromatograph and a mass spectrometer. The resultant instrument, known as a gas chromatography/mass spectrometry (GC/MS) is one of the most powerful devices currently available for substance identification.




When a sample is **injected** into this device, it first enters the gas chromatograph (GC). The GC uses substances with varied densities to separate a sample into components. The concept is similar to throwing two rocks into a river. A heavier, denser rock moves slower down the river, while a lighter, less dense rock is swept away by the moving water. When a sample is placed into the GC, each component moves through the instrument at a speed relative to its singular density. As a sample exits the GC, it enters the mass spectrometer (MS). The sample is then exposed to high-energy electrons, causing the sample's molecules to fragment. No two substances fragment in exactly the same way. Therefore, this device has the ability to identify specifically the components of a sample. Moreover, the sample doesn't need to be pure; the MS will identify the impurities and the drugs alike.

## Spectrographic Analyzer



A spectrographic analyzer is most often used to compare metallic samples such as paint chips. This instrument uses a high voltage electric arc to burn a sample. Light from the near instantaneous burn is split into individual wavelengths as it passes through a prism and exposes a strip of film. Samples with a singular origin will emit identical light spectra when burned. If samples are of different origins, then the emitted spectra will be different.

## Automation

Advancements in chemical analyses procedures and instrumentation continue to emerge. However, the underlying premise of these basic instruments has changed little in the past several years. There is an increasing quantity of samples to be analyzed. So, improvements in technology are focused on ways to improve the consistency of results and to speed analysis. At right, an auto sampler which, when integrated into a system, may hold and automatically analyze up to ninety samples.