Chemistry 103
Labs on Paint and Blue Pigments

Goals: Learn properties of pigments, paint, and paintings
-How paint is made
-Characteristics of components: Pigments and binders
-Identification of pigments

Experiments /Activities

1. Make paint by grinding pigments and media. Each pair of two students will work with two blue pigments and use each of the following media: tempera, casein, acrylic, gum Arabic, linseed oil. Paint strips of each paint on water color paper and wooden stick. Let dry for 1 week, varnish half of each sample, and characterize by the following techniques:

    a. Visual appearance. Use a magnifying glass to examine the texture more closely. Compare the appearance of the varnished and unvarnished areas.

    b. Obtain the visible reflectance spectra (400-740 nm) of two paint samples (two pigments with the same binder). Goal: Decide how the spectra can be correlated with the visual appearance of paint and be used in identifying the pigment component of the paint.

    c. Obtain the infrared reflectance spectra (4000-900 cm^{-1}) of two paint samples (two pigments with the same binder). Obtain the infrared reflectance spectra of the two pigments under the same conditions. The instructor will demonstrate the techniques for collecting these data. Goal: Decide how the spectra can be correlated with the visual appearance of paint and be used in identifying the pigment component of the paint.

2. Characterizing and identifying pigments.
    a. Microchemical testing. Each pair of two students will examine all blue pigments to microchemical testing. Goal: Decide how one might identify one pigment from all other blues based on unique reactions.

    b. Obtain infrared spectra of two pigments Goal: Decide how one might identify one pigment from all other blues based on unique infrared spectrum.

Each student pair will choose one of the following two pigments to study during this two-week experiment. .

Pair 1: Indigo and Ultramarine
Pair 2. Indigo and Prussian Blue
Pair 3. Ultramarine and Azurite
Pair 4. Ultramarine and Phthalocyanine blue
Pair 5. Azurite and Smalt
Pair 6. Azurite and Prussian Blue

Structures of most widely used blue pigments

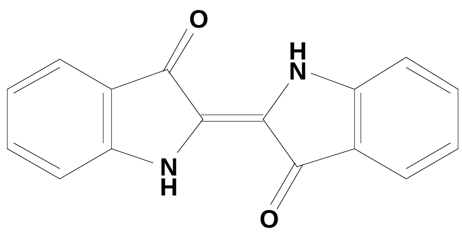
Azurite: $2CuCO_3{}^{\cdot}\ Cu(OH)_2$ (artificial or synthetic = Blue Verditer or blue bice)

Ultramarine: $Na_6[Al_6Si_6O_{24}]S_xCa$, X > 1

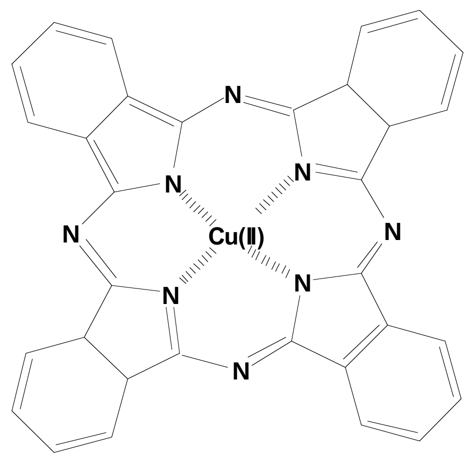
Prussian Blue: $NH_4Fe(III)[FeCN_6]$, $KFe(III)[FeCN_6]$, or Fe $(III)_4[FeCN_6]$

Smalt: Glass (SiO_2, K_2O) containing CoO

Cobalt Blue: $CoO{}^{\cdot}Al_2O_3$

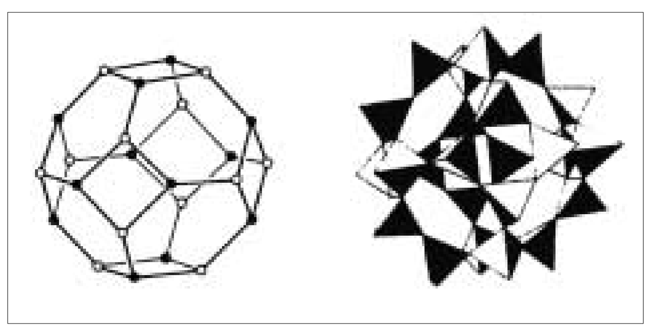


Indigo



Phthalocyanine blue
Phthalo Blue

Structure of Ultramarine



¥ Left: Silicon oxygen framework

¥ Right: Bridging oxygens

¥ Cage structure holds cations and sulfur

Blue color arises from trisulfide radical anion: S_3^-

Less widely used blue pigments:

Cerulean Blue: **$CoO{}^{\cdot}nSnO_2$**
Egyptian Blue: $CuO/CaO/SiO_2$--glass
Manganese Blue: $BaMnO_4$

Making Paint

Tempera. The simplest tempera technique is the one that uses pure egg yolk as a binder. Egg yolk is a natural emulsion, containing fatty oils, watery material, and the emulsifying agents, lecithin and albumen. The egg yolk technique is uncomplicated and has proven its durability in the many paintings that have survived in good condition for more then six hundred years.
-Grind each pigment with pure water to make a stiff paste and set aside.
-Break the egg and separate the white from the yolk by passing the yolk between shells. Transfer the intact yolk to a paper towel and roll it about to remove any remaining white. Roll the yolk to the edge of the paper and hold it over a clean or beaker. Puncture sac and let the contents run into the container. Add about 1/3 teaspoon full of water to the yolk and stir.
-Combine the pigment/water paste and with an equal amount of yolk binder and mix thoroughly. The egg tempera paint is ready to use.

Casein. Casein is prepared in skim milk. It can be obtained from chemical supply houses in the form of a yellowish white powder, which is dissolved in water by means of a strong alkali to make an adhesive syrup. The casein you will be using to prepare paint is premixed in syrup form. Milk paint, with casein powder, differs from other water-based paints, as it dries to become water insoluble. Although it takes a week or month to cure completely, it dries very quickly to the touch so that many successive layers can be painted in a single session.

Obtain a small amount (1/2 tsp, 1-2 grams) of pigment. Using the prepared casein (syrup) solution, carefully add a very small amount (five or six drops) of casein to the pigment. A thick paste should form when the pigment and casein are mixed. If this paste appears too thick (the muller or pallet knife does not glide smoothly along the surface) add a few more drops of casein. The casein paint is ready to use. In case it begins to dry out, it may be diluted with water.

Acrylic Paint. Grind the pigment with water to make a stiff paste. Combine the pigment paste with acrylic polymer in a 1:1 ratio. Use at once.

Water Color Paint. Grind the pigment with water to make a stiff paste. Combine the pigment paste with gum Arabic binder in a 1:1 ratio. Use at once. In case it begins to dry out, it may be diluted with water.

Oil Paint. Place a small amount (1/2-tsp., 1-2 grams) of pigment on flat non-porous surface. Add a small amount of linseed oil (or other oil) and work the pigment and oil together with a palette knife in a circular motion to disperse the pigment. The ideal consistency for the paint is one containing no lumps of pigment and that has a buttery feel. If the mixture is too stiff and dry, add more oil; if too runny, add more pigment. When the right consistency is reached the paint is ready to be used.

Additional material on pigments and making paint may be obtained *from The painter's guide to studio methods and materials*, Reed Kay, Englewood Cliffs, N.J.: Prentice-Hall, c1983 and from Web site of Sinopia: http://www.sfo.com/~sinopia/geninfo.html.

Chemistry 103: Microchemical Characterization of Blue Pigments

Class work will focus on five blue pigments: azurite, indigo, ultramarine, Prussian blue, and phthalocyanine blue. The structures and chemical formula of these materials are shown at the end of this document. You will note that most of these pigments are inorganic compounds; phthalocyanine blue, a 20th century material, and indigo, used from ancient times, are organic compounds.

Microchemical testing provides an inexpensive method for aiding in pigment identification based on the differences in reactions between specific reagents and each pigment. In this section of our study of paint and pigments, students will mix each of the above five pigments with different reagents to ascertain the how this tool is used in characterizing the blues of paintings. Careful observation and recording keeping data is, as usual, key to understanding the use of this tool in examining works of art.

Experimental Procedures.

General. Very small amounts of pigment are needed for the test procedure. The instructor will demonstrate how to transfer the amount needed to the test plate (or porcelain spoon). Then a drop or few drops of the reagent is added to the pigment. The simplest way to carry out the testing is to use a single reagent with all five pigments and then proceed to the next test reagent. Carefully record your observations of the reaction (or lack thereof) of each pigment with the reagent. Although most reagents are designed to be most diagnostic in its reaction with a particular pigment (noted in bold), it is important to compare its action of all five materials.

Specific tests

Hydrosulfite test, $Na_2S_2O_4$, (most specific for indigo which acts both as dye as well as a pigment). Add one or more drops of reagent (50 g sodium dithionite, 50 g of NaOH in 1 liter of water) to the pigment, mix, and let sit for a few minutes. Note any color change. Dip a small cotton thread or swatch in the solution and remove and allow to dry in air. Carefully note color changes.

Heat resistance: Dip a small platinum wire in the flame of a Bunsen and heat to redness. Cool and observe. Alternatively heat some of the pigment in a porcelain spoon.

Test with acid. Add one or more drops of 3 M HCl (3 M) to the pigment and mix. Look carefully for any gas evolution or color change. Note any odor as well.

Effect of 2 M NaOH. Add drop of 2 M NaOH to small amount of pigment on porcelain spoon. Note any color change. Then warm the mixture over a Bunsen burner.

Ferrocyanide test: Add one drop of 5% potassium ferrocyanide [$K_4Fe(CN)_6$] to cover pigment. The add one small drop of 3 M HCl. Note that Cu^{2+} reacts with ferrocyanide to form salmon-red cupric ferrocyanide, $Cu_2 Fe(CN)_6$.

Chemistry 103: Infrared Spectroscopy of Pigment

Background and introduction. Atoms, excited by light or electrical energy, emit energy in the form of light, often in the visible range. In the first lab of the semester, students found that the wavelength of the light emitted, corresponding to the transition of an electron between two energy levels (see p. 2 of the lab manual, was characteristic of each element. The characteristic wavelength (and color) of the emitted light provided a tool for identifying an unknown. The second lab explored the absorption of visible light by molecules in solution, in particular colored dyes. These molecular transitions correspond also involve the excitation from a ground state to an excited state.

Molecules may also absorb light in the infrared region of the electromagnetic spectrum to excite rotations and vibrations. The resultant infrared absorption spectra are characteristic of the particular molecule absorbing the light and, in fact, often provide a finger print for identification purposes. The infrared radiation of greatest use in such molecular foot printing ranges from around 2.5-15 x 10^{-6} meters or 2,500-15,000 nanometer, the mid-infrared. As seen before, the energy of a transition is inversely related to the wavelength, λ, of the absorbed light:

$$\Delta E = hc/\lambda = h\nu \qquad (1)$$

Electromagnetic radiation can be characterized both by the wavelength and by the number of waves per unit length, the wave number, given the symbol $\bar{\nu}$:

$$\bar{\nu} = 1/\lambda \qquad (2)$$

The common unit for wavenumbers is the cm^{-1}. Because of the simple inverse relationship of equation 2, wavenumbers can be readily converted to wavelength units when needed. For example, 1000 wavenumbers (cm^{-1}) is the same as the wavelength of 0.001 cm, 0.01 μm (microns or 10^{-6} meters) or 10 nm. Infrared spectra are most usually displayed as percent transmittance %T (y-axis) (or, % reflectance if the reflected light is collected) as a function of wavenumber in cm^{-1}(x-axis). Infrared spectra, in combination with microscopic examination, provide one of the most powerful tools for identifying pigments in art objects. In this part of the study of paints and their composition, students will obtain the infrared spectra of pigments to gain an understanding of the use of this technique in art conservation studies. Infrared spectra of the major blue pigments (as attenuated total reflectance, ATR, spectra) are attached. Students will prepare samples for analysis using the yellow stickies to hold the pigments in place; consequently, the infrared spectrum of this backing material is also included.

See case studies in Chapter 6 of Michele R. Derrick, Dusan Stulik, and James M. Landry (1999). *Infrared Spectroscopy in Conservation Science,* Chapter 6. Los Angeles, CA: Getty Conservation Institute.

Chemistry 103: Practical Aspects of Infrared Spectroscopy of Pigments
Preparing Samples and Obtaining Spectra with
Nicolet Fourier Transform Infrared (FTIR) Spectrophotometer

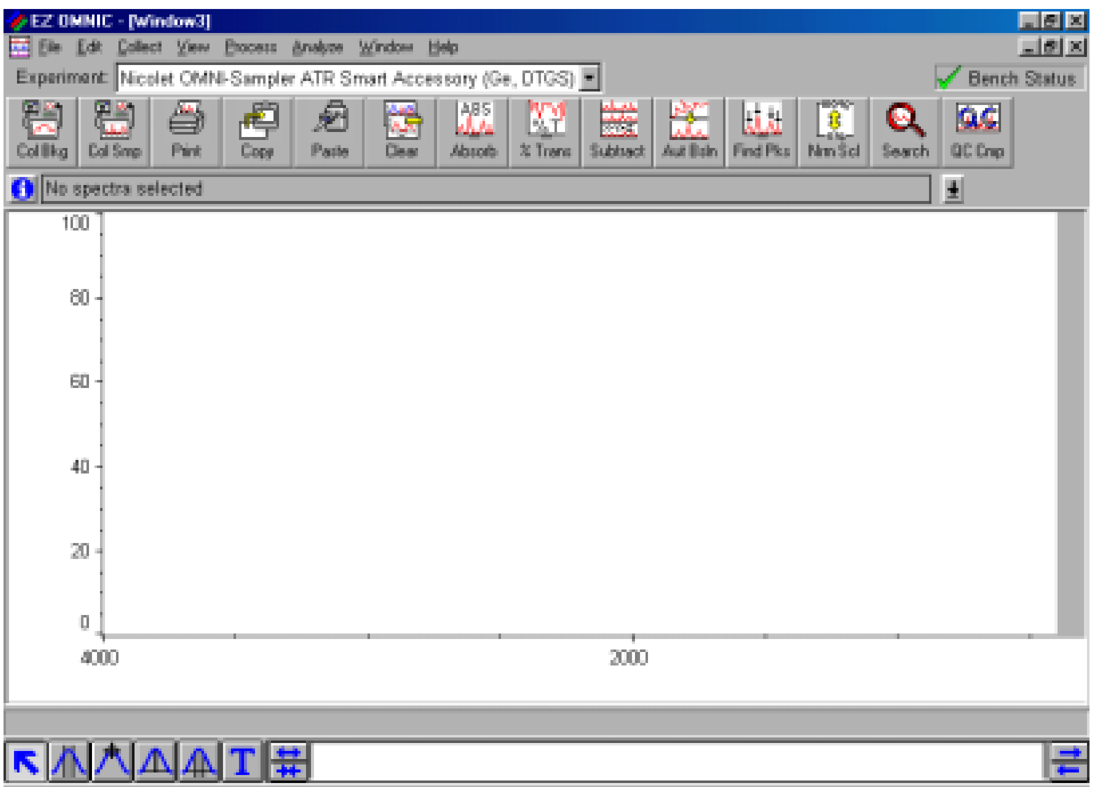
Goal: Understand how infrared (IR) spectroscopy is used in pigment identification and in characterizing paintings.

The infrared spectra will be collected in the reflectance mode using an attenuated total reflectance (ATR) accessory, shown on the next page. The resultant spectra, called ATR-IR spectra, are displayed as % Reflectance VS wavenumber (cm^{-1}).

Spectra to be obtained:

- -Of two pure blue pigments
- -At least one of the pigments in one or more binders on water color paper
- -Of binder and/or water color paper to evaluate the effect of the binder and/or support on the infrared spectrum of pigment

Experimental Procedures:
Pigment samples. The instructor will demonstrate the technique for placing a pigment sample on a yellow sticky. The spectra of these samples (and of the paints) will be collected using the Nicolet software EZ OMNIC, which can be opened from the icon on the desktop to give a window as shown:

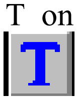


Under the **Collect** menu, select **Collect Background** (reference). In response to the directive to Prepare to Collect Background, make sure there is no sample on the

germanium crystal and then click **OK.** Wait for completion of this operation and then click **No** in response to the inquiry about adding the spectrum to the window.
Next place the sample on the germanium crystal as demonstrated by the instructor. Then click on the **Collect Sample** button to obtain the spectrum of your sample. In the window asking for a spectrum title, enter a descriptive name such as AzuriteTempera. In response to the directive to Prepare to Collect Sample Spectrum, click **OK.** Wait for completion of this operation and then click **Yes** in response to the inquiry about adding the spectrum to the window.

Peak Picking To find and label the peaks, auto click on the Find Peaks button under the **Analyze** menu. (The instructor will demonstrate how to set the threshold and replace original spectrum with annotated one) or manually.

To do this operation manually, click the button at the bottom of the screen with the blue T on it:



Then place the cursor on a peak and click. The frequency in wavenumbers will appear with a line to the point on the spectrum. If you hold down the mouse button, you can drag the writing to a different part of the spectrum.

Save the spectrum. Under the **File** menu, select the **Save As** and select the Chem 103 Folder. Then select Set filename to spectrum title and add your initials to this name; e.g., AzuriteTemperaMM and click the **Save** button.

Print the spectrum. Under the **File** menu, select **Print.**

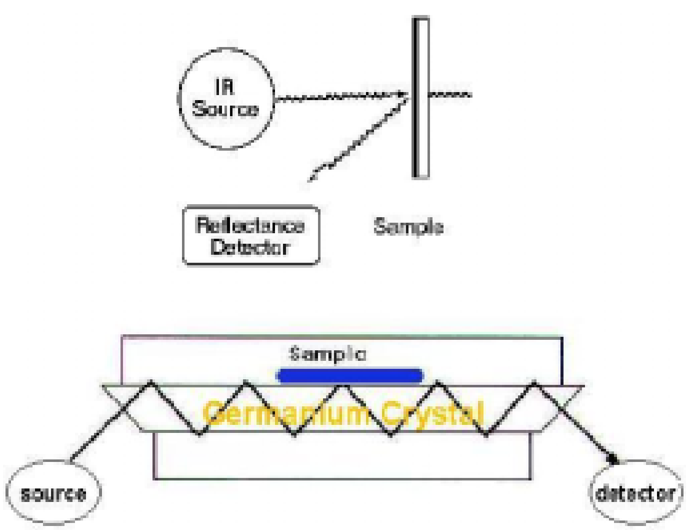


Figure 1. Infrared Reflectance Measurements. Top, general; bottom, attenuated total reflectance, ATR.