Chemistry 103 Lab: The Fresco Technique

Introduction. The fresco technique is one of the most ancient and widespread art forms in world. The raw materials--lime, sand, and colored clays--are geographically common, easy to collect, and process. In contrast to other painting techniques, the pigment used in frescoes is applied directly to the surface--wet plaster--without a binder. The wet slaked lime [$Ca(OH)_2$] plaster reacts with carbon dioxide, CO_2, in the air to become insoluble calcium carbonate, $CaCO_3$, which acts as the binder for the applied pigment. This consolidation of the pigment into the plastered wall itself makes fresco paintings extremely durable, but, at the same time, vulnerable to any deleterious environmental conditions to which the wall is subjected. In this lab, student will create small fresco paintings on tiles and explore the chemistry involved in fresco creation, degradation, and restoration. This lab is an adaptation and expansion of a similar one developed by Professor Sue Roper of Sacramento City College in California for a course on chemistry and art.

Terms used in fresco paintings.

fresco	fresh
giornata	one day's work, usually 3-5 m^2 (a saint's head)
arriccio	underlying coat of plaster applied directly to the wall
intonaco	last coat of plaster applied the day of painting
a secco	" when dry," painting the dry fresco pigments in organic binders such as egg, oils, or waxes
pentimenti	corrections added to the painting after the day's work
sinopia	stencil of the major shapes of the painting transferred to the wall before painting begins, sometimes called the cartoon

Preparing a Fresco. Preparation of the painting surfaces involves the construction of a wall coated with layers of plaster of increasingly finer texture. The first step in the preparation is the heating (calcination) limestone (calcium carbonate, $CaCO_3$) at 800-900ßC to make porous lime (calcium oxide, CaO).

$$\text{HEAT} + CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)} \qquad (1)$$

To form the plaster for fresco work, the lime is "slaked." The slaking process, which requires the addition of 2 or 3 moles of water for each mole of lime, yields calcium paste or lime putty, an aqueous gel of thin crystals of calcium hydroxide.

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(s)} + \text{HEAT} \qquad (2)$$

Excess water acts as a lubricant so that the crystals slide easily over one another. Historically, lime was slaked in pits or troughs over a period of at least six months to obtain lime putty of the desired consistency. Artisans in Michelangelo's time use plaster aged for as long as ten years. Fresco plaster itself is made from the slaked lime and varying portions of sand or marble dust. Generally, walls are plastered with several layers of such fresco plaster in order of decreasing proportions and particle size of sand. The first layer of plaster, the *arriccio* (1-2 cm thick), consists of one part slaked lime to two parts of sand; some fresco techniques use several layers of *arriccio*. Hardening of the *arriccio* on the wall includes several simultaneous physical and chemical process: the absorption of water into the wall, evaporation of water from the surface, and the carbonation of the slaked line by carbon dioxide, CO_2.

$$Ca(OH)_{2(s)} \quad + \quad CO_{2(g)} \longrightarrow \quad CaCO_{3(s)} \quad + H_2O_{(l)} \qquad (3)$$

On the dried *arriccio*, the artist sketches the *sinopia,* usually first with charcoal and then with a lime-compatible pigment mixed in water. The *sinopia* is then traced onto paper to serve as a guide for continued work. A final layer of plaster, the *intonaco* (0.5-1 cm thick) contains less sand than the underlying *arriccio* layer(s). In large fresco paintings, the artist applies the *intonaco* plaster over a portion to complete in a short time, the *giornata.* The paper *sinopia* is then placed over the fresh *intonaco* and the image transferred to it in one of two ways: (1) by gently incising the lines of the drawing through the paper into the plaster or (2) by dusting dry, dark pigments through perforations in the paper along the lines of the drawing ("pouncing"). To ensure that the pigment is incorporated into the plaster layer, the painting must be complete in the first hours of drying of the *intonaco.* Pigments are mixed with water, brushed onto the wet plaster, and fixed to the painting by carbonation of the slaked lime (equation 3). Overly wet plaster yields cloudy colors; whereas, a too dry plaster produces pale and dull hues. The integration of pigment into the dried plaster itself makes the fresco technique especially unforgiving.

<u>Degradation and Conservation of Frescoes</u>. Deterioration of fresco paintings results from the open, porous nature of their support--walls and ceilings of buildings--and their interaction with the surrounding microclimates. The porous mortar backing provides an easy route for the movement of dilute salt solutions. Salts contained in the building materials or the surrounding area can be readily transported to the plaster underlying the painting. Volumetric expansion associated with crystallization of these salts disrupts the plaster-pigment adhesion and leads to disintegration of the surface. Such crystallization depends on the identity of the salts and the moisture content of masonry which is subject to seasonal variations in atmospheric humidity and rainfall.

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Conservation methods have been developed to remove salts formed from reactions of sulfate ion traveling through the mortar. When the sulfate ion reacts with calcium, it forms calcium sulfate, gypsum. Since gypsum is more soluble than calcium carbonate, it dissolves and re-crystallizes with changes in humidity. These cycles lead to severe damage when the gypsum crystallizes just beneath or throughout the paint layer. Florentine floods of 1966 spurred the development of a conservation treatment, the "Barium Method," in which a series of poultices are applied to such sulfate-damaged fresco paintings to form the less soluble barium sulfate from calcium sulfate The first step in this procedure solubilizes calcium sulfate. A poultice of rice paper pulp containing a supersaturated solution of ammonium carbonate [$(NH_4)_2CO_3$] is applied to the surface of the fresco so that the solution is absorbed by the wall. Any calcium carbonate forming on the surface of painting is swabbed away; whereas, that formed within the plaster helps re-establish cohesion.

$$CaSO_{4)} + (NH_4)_2CO_{3(aq)} \longrightarrow [(NH_4)_2SO_{4(aq)} + CaCO_{3(s)} \qquad (4)$$

Application of a second poultice containing barium hydroxide converts any remaining calcium sulfate present into the less soluble barium sulfate:

$$Ba(OH)_{2(aq} \quad + \quad CaSO_{4(s)} \longrightarrow BaSO_{4(s)} + Ca^{(}OH^{-})_2 \qquad (5)$$

The excess barium hydroxide is homogeneously absorbed into the *intonaco*. It reacts with any sulfate ion present to form barium sulfate and arrests further migration of this ion or with atmospheric carbon dioxide to act as a binding agent to consolidate the plaster and pigments:

$$Ba(OH)_{2(aq} \quad + \quad CO_2 \longrightarrow BaCO_{3(s)} \quad + \quad H_2O \qquad (6)$$

The scientific basis of this conservation rests on differences in the solubilities of several salts. In this lab, students will determine the relative solubilities of calcium carbonate, calcium sulfate, and barium sulfate.

The barium method was applied to restoration of the frescoes of Brancacci Chapel in Florence in which calcium sulfate had been shown to be the major agent of destruction. The second most common cause of deterioration of frescoes comes from previous conservation efforts in which early conservationists attempted to protect the fresco or brighten colors with glues, oils, egg white and/or waxes. In time, these organic materials darken, shrink, and lift off paint layers. In addition, they provide nutrients for the growth of microorganisms and prevent the exchange of moisture and air between the fresco and atmosphere. Recent restoration of the Sistine Chapel frescoes focused on removing the residues of early conservation efforts by treating the frescoes with a cleaning solution to solubilize glues and waxes. The cleaning solution contained ammonium bicarbonate, $(NH_4)_2CO_{3(aq}$ to remove calcium sulfate (equation 4). Consolidation of loose paint and *intonaco* was, however, done with polymeric injections as the paintings in the Sistine Chapel contained low levels of sulfates, but high levels of nitrates, a counter indication to barium hydroxide treatment Speculate on the reasons why the barium method would be inappropriate under these conditions.

<u>Experiments and Creation of Frescoes</u>. To be completed over a two-week period. .

Part A. Making a Tile Fresco.

<u>(Week 1) Preparation of the *Arriccio*</u>. Preparation of a wall for painting involves several layers of mortar, including an initial very rough layer of cement. By using a tile as the foundation, we will use only a single layer of lime plaster for the *arriccio* and forego the cement.

1. Mix the *arriccio* as two parts sand and one part slaked lime. (For two 2" x 2" tiles, measure out 50 ml of sand in a plastic beaker and then use 25 ml of slaked lime. Mix in 250-ml plastic beaker.) Mix well. You may need to add water if the lime sample was not wet; on the other hand, the plaster will crack if it is too wet.
2. Obtain a tile which has been soaked in water overnight. Dry it until the surface is no longer shiny.
3. Apply the plaster evenly over the rough side of the tile to a thickness of about 3 mm, thinner that for an *arriccio* on a wall. Save a small amount of the *arriccio* plaster for testing; label the beaker in which it was mixed and store until Week 2.
4, Let the plaster dry for 10 minutes; the tile will absorb the water.
5. Smooth the surface of the plaster with a spatula to give a relatively uniform surface.
6. Let the tile dry for a minimum of two days so that the plaster is converted to calcium carbonate (carbonation).

<u>Between Day1 and Day 2. Preparation of the *senopia*</u>.
Sketch your picture on tracing paper (provided). Use a tracing a pin to perforate the paper along the lines of your sketch. Plan the color scheme for your fresco and list pigments appropriate for it. (Large fresco wall paintings begin with a rough sketch on the *arriccio.* This sketch is then transferred to paper.)

<u>(Day 2) Preparation of the *intonaco* and *giornata*</u>.
1. Mix the *intonaco* as one part slaked lime and one part finely powdered sand. (For a two 2" x 2" tile, measure out 35 ml each of sand and of slaked lime. Mix in 250-ml plastic beaker.)
2. Thoroughly wet the *arriccio* and the tile. Then spread the plaster evenly to a thickness of about 2 mm. Let the tile dry about ten minutes.
3. "Polishing" the *intonaco* orients the sand and gives a smooth, polished surface. Smooth the surface in a single direction with a large, clean spatula. Remove any large granules that pop up and replace any miss plaster.
4. Apply a small brush stroke of water to ascertain if the surface is ready for painting. If the plaster readily absorbed the water, it is dry enough for painting.
5. Transfer the outline of your picture onto the plaster surface by laying the *sinopia* on the tile and pouncing with a lime-compatible pigment. Instead of pouncing, you may wish to gently incise the drawing into the plaster through the tracing paper.
6. Select the pigments and prepare them for painting by grinding a small amount in distilled with a flat spatula on a glass plate. The pigment preparation is ready when a small amount, dropped into water, mostly floats and does not sink. The pigment is applied as a dilute wash.
7. If you have prepared more than one tile, number each and record the name and formula of pigments used for each in your notebook. Paint a strip of the pigment for color reference as well.

8. Paint the tile. Shading with dark pigments is done first and then over-painted with lighter pigments. Since the colors are transparent, several thin layers of paint are needed to obtain bold colors. Wait 10 or 14 minutes between color layers to ensure that they do not mix.
9. When the painting has been completed, set the finished tile in a plastic bag, but leave the top open. (This procedure will ensure that the tile drives slowly and will minimize or eliminate crack formation.) Let the tile cure so for several days to consolidate the pigment with the newly formed calcium carbonate matrix of the fresco, a permanent and colorfast art object for generations to come.

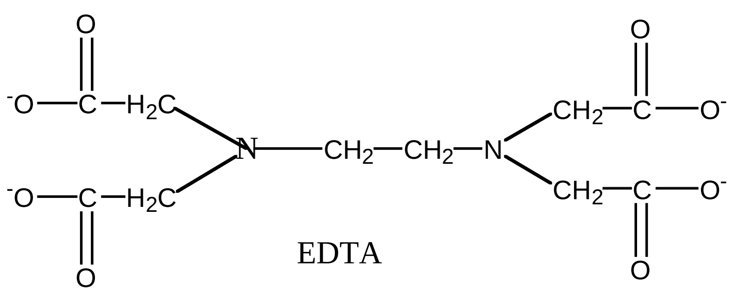
Chemistry of Frescoes (Week 1 or 2).
A. Acid-base Chemistry. Use pH test papers as demonstrated by the instructor.
1. Chip a piece of the *intonaco/arriccio* from a sample fresco tile or from your hardened excess *arriccio* plaster and put it in a disposable test tube. Carefully add a drop of 3 M HCl to it. Repeat with a sample of fresh lime plaster.
2. Determine the pH of the slaked lime and pure $CaCO_3$ suspended in water.
3. Add a pinch of calcium oxide to a disposable test tube. Add about 1 ml to the test tube and test it for heat evolution. Determine the pH of the resultant mixture.
4. Add about 20 ml of water to a 100-ml plastic beaker. Measure the pH of the water. Carefully add crushed dry ice, solid CO_2, to the beaker. After most of the solid has disappeared, measure the pH again.

Write equations for any reactions that occurred above and discuss the results of the pH tests.

B. (Week 1) Evaluation of the relative solubilities of $CaCO_3$, $CaSO_4$, and $BaSO_4$.
Dissolution of these salts can be represented generically as follows:

$$MX_{(s)} \longrightarrow M^{2+}{}_{(aq)} + X^{2-+}{}_{(aq)} \qquad (7)$$

The calcium and barium ions are represented by M^{2+} and the carbonate and sulfate ions, by X^{2-}. In this experiment, students will prepared saturated solutions of each of the three salts and determine the amount dissolved by measuring the concentration of the cation, $M^{2+}{}_{(aq),}$ in this solution. This measurement will be done by following the reaction of the cations with the reagent EDTA whose structure is shown below.


EDTA

Although EDTA appears to have a complicated structure, it can be represented by Y^{4-} as shown in the following equation for its reaction with cations:

$$M^{2+} + Y^{4-} \longrightarrow MY^{2-} \qquad (7)$$

The reaction of EDTA with either calcium or barium ions will be followed by a process called titration in which an indicator changes color when the number of moles of EDTA molecules (in an aqueous solution) added equals that of the cations. Students will practice their titration technique with a solution of known calcium ion concentration.

Procedure (Students will work in pairs).

1. Preparation of saturated solutions of $CaCO_3$, $CaSO_4$, and $BaSO_4$. Use a spatula to transfer an amount equivalent to about 2 teaspoons of each solid to each of three separate 50 ml capped centrifuge tubes. Add approximately 40 ml of distilled water. Put the 3 tubes on the wrist-action shaker and shake vigorously for at least a half-hour. Remove the tubes from the shaker and allow the undissolved solid to settle to the bottom of the tube. The aqueous layers are saturated with the appropriate salts.

2. Titration procedure. Note that each student pair will do four sets of 3 titrations: From the Ca^{2+} standard and from the three saturated solutions ($CaCO_3$, $CaSO_4$, and $BaSO_4$).

Working with standard. Pour about 20 ml of the Ca^{2+} standard (2.50×10^{-3} M) into a labeled 50 ml plastic beaker. In a separate labeled 50 ml plastic beaker, pour 20 ml of 1.5×10^{-2} M EDTA Obtain and label a 5 ml syringe (with needle): "Calcium standard."

The titration itself. **RECORDING THE EXACT WEIGHT OF THE TITRATION BOTTLE AND ITS CONTENTS AT EACH STEP OF THIS PROCEDURE ARE CRITICAL. MAKE SURE YOU UNDERSTAND THE PROCEDURE COMPLETELY.** The most efficient and convenient form for organizing your titration is a table. Here is a suggested format (report the exact concentration of EDTA):

Table 1. Titration of Ca^{2+} standard (2.50×10^{-3} M) with 1.5×10^{-2} M EDTA

	Trial 1	Trial 2	Trial 3
Sample	Weight, grams	Weight, grams	Weight, grams
Empty Bottle			
Bottle + standard			
Bottle + standard + reagents			
Bottle + standard + reagents + EDTA			

a. Weigh a small titration bottle and record its weight (or if no others students are using the same balance, tare the bottle.)
b. Remove the bottle from the balance, and use the 5 ml syringe to add between 4 and 5 ml of the calcium standard to the bottle. **Weigh the bottle again** to determine the exact amount of calcium standard added.
c. Add 2-3 drops of the pH 10 ammonia buffer and 1 drop of the Calmagnite indicator to the titration bottle and **weigh the bottle again**. The solution should be red at this point.
d. Remove the bottle from the balance. Take a disposable Pasteur pipette and add the EDTA solution dropwise to the bottle and swirl it carefully after each addition. Continue to add EDTA until the solution turns blue. This point is called the endpoint in the

titration and signals that all the Ca^{2+} has reacted with EDTA. **Weigh the bottle** to determine the exact amount of EDTA added.

e. Dispose of the solution in the titration bottle and wash it with distilled water. Repeat the procedure at least three times or until you are confident of your titration skills. In order to evaluate these skills, you will need to do some arithmetic calculations: The simplest way to check your skills is to calculate the number of grams of EDTA solution/grams of Ca^{2+} solution for each trial. They should be nearly the same for all three titration trials.

Determining the concentration of M^{2+} (as a measure of solubilities) in saturated solutions of salts. The titration procedure is nearly identical to that used for the calcium standard. For these solutions, it is necessary to filter them to ensure that no solid is transferred. After filling a syringe (use a separate labeled syringe for each solution) with solution, remove the needle and attach a 0.45 μm disposable filter to the syringe. Push the solution through this filter into the titration bottle. The same filter may be used for all the titration trials for a particular solution. **Record the weights at all stages in the titration.**

If you find that the amount of EDTA used is too small to measure accurately for any of the solutions, you may wish to do additional titration trails with a more dilute (1.25×10^{-3} M) EDTA solution.

Analysis of titration data to evaluate relative solubilities.

1. Organize the titration data in a table similar to the one below (with similar entries for the solutions of $CaSO_4$ and $BaSO_4$):

Sample and Trials	Trial 1	Trial 2	Trial 3
	grams	grams	grams
A. Saturated solution of $CaCO_3$			
Weight of Sample			
Weight of EDTA used			
Weight of EDTA/Weight of sample			
Moles of M^{2+} in solution			

2. From the titration results [average of the three values for Weight of EDTA/Weight of sample), determine the relative solubilities of the three compounds. Which one is the most soluble? The least soluble?

3. From number of moles of M^{2+} (average of three trials), express the solubilities in moles/liter, grams/liter, and grams/100 ml. Compare your results with values you find in the *CRC Handbook* (Note that the CRC Handbook includes numerical values for solubilities in g/100 mL only in editions before 1998.).

4. Conclusions. Write a short paragraph summarizing your findings regarding the solubility of these three salts and the implications of your findings for the protection of outdoor monuments carved in limestone ($CaCO_3$) from the detrimental effects of acid rain, primarily dilute solutions of sulfuric acid.

D. Effects of acid rain on Frescoes (Optional, extra credit). Devise and carry out an experiment to test the effects of dilute solutions (1×10^{-3} or 1×10^{-4} M) of HCl and H_2SO_4 (acid rain) on the stability of fresco paintings. Dilute acid solutions will be available.