19th century photography in a modern chemistry lab

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Abstract

College courses focusing on the interface of chemistry and art are increasingly popular at many academic institutions where they are seen as an attractive way to engage non-science majors. However, there are very few courses that seek to engage science majors in the art world. An upper-level course was recently developed at Rice University for chemistry and chemical engineering majors that introduced students to the chemistry of 19th century photographic processes and conservation science. Working with Toshiaki Koseki, the photograph conservator at the Museum of Fine Arts, Houston, the students learned to identify 19th century processes. They then made cyanotypes, van Dyke brown prints, gum bichromate prints, and salted paper prints using negative/positive processes or cliché-verre. They were also introduced to toning methods, which included sepia, selenium, and gold toning. The students learned the importance of non-destructive analytical techniques and successfully used x-ray fluorescence spectroscopy (XRF) to identify toning or stabilizing materials on salted paper and van Dyke brown prints. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR) was used to identify organic binders on a selection of study collection prints. Students also had an opportunity to look at the size and constituents of the image particles using scanning electron microscopy coupled with energy dispersive x-ray spectroscopy (SEM-EDX). The course was well received by the students, none of whom had ever had the opportunity to make photographic images or interact with the museum and conservation worlds. In addition they had never used many of the instruments before and so learned new analytical techniques as well. The authors have published the salted paper print exercise in the *Journal of Chemical Education* ("An investigation into the creation, stability and X-ray fluorescence analysis of early photographic processes: an upper-level undergraduate laboratory," Web published July 8, 2011). This poster presents a holistic overview of this advanced course to the conservation field and discusses the full scope of experiments covered.

Course Format

Day 1

♦ **Introductions**

The instructors introduced themselves and explained the format of the course. It met three hours a week for 11 weeks and was worth 1 credit hour.

♦ **Construction of darkroom boxes**

The laboratory took place in a chemistry department that did not have darkroom facilities. In order to prevent fogging of light sensitive papers each student constructed a darkroom box based upon a design suggested by Mark Osterman from the George Eastman House. A large cardboard box had a window cut out on one side leaving a 2-inch lip. (Figure 1). The bottom of the box was lined with duct tape to make it easier to clean. To provide working light the top of the box had a small window cut into it and a 5x7 inch amber safelight filter taped over it. A length of black fleece was used for the dark cloth.

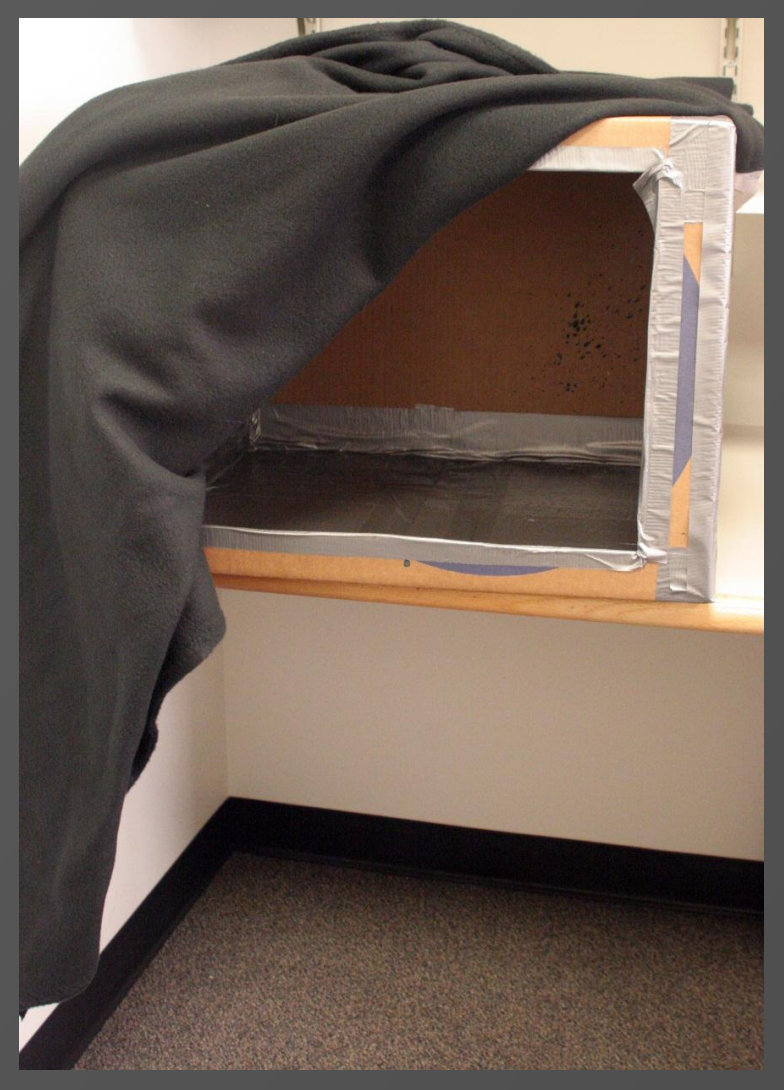

Figure 1. A darkroom box

♦ **Introductory lecture**

This lecture introduced the students to the history of photography, beginning with Johann Heinrich Schulze's discovery that silver chloride and silver nitrate salts darken upon exposure to light and covering the Daguerreotype, salted paper, calotype, ambrotype, and tintype processes. The differences between printing out and developing out processes were also discussed.

♦ **Assigned reading**

Students were required to read chapters 1-4 of Care and Identification of 19th Century Photographic Prints by James M. Reilly, Eastman Kodak Company, 1986.

Day 2

♦ **Visit to the Museum of Fine Arts Houston (MFAH)**

Mr. Toshiaki Koseki, the photograph conservator at the MFAH, provided an introduction to the use of a stereomicroscope for identification of photographic processes. He provided a series of 'known' photographs from his study collection and taught the students how to identify them using the identification flow chart in Care and Identification of 19th Century Photographic Prints (Figures 2 and 3). The students were then challenged to identify 'unknown' photographs using this methodology.

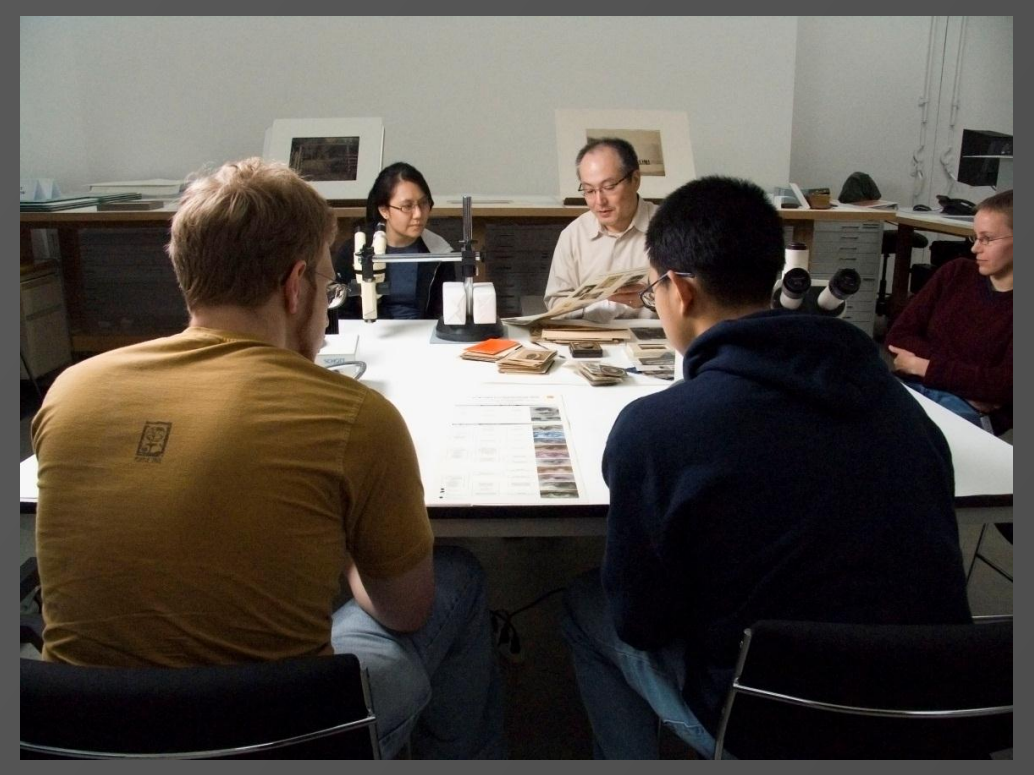

Figure 2. Toshiaki Koseki explaining how to identify 19th Century photographic processes (photo taken by Karen Willis)

Figure 3. Toshiaki Koseki helping the students to identify their unknown photographs (photo taken by Karen Willis)

Day 3

♦ **Introduction to X-ray fluorescence spectroscopy (XRF) and its application to photograph identification**

As none of the students had encountered XRF spectroscopy before an introductory lecture was given on the theory behind this technique. This was followed by a practical introduction to the Bruker Tracer III instrument. The students then used this method to identify their unknowns from Day 2 in order to determine if their visual identification was correct.

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Day 4

♦ **Lecture on iron based photographic processes**

This lecture introduced the students to the chemistry behind cyanotype, van Dyke brown and platinum/palladium processes.

♦ **Contact printing frames**

Commercial contact printing frames are prohibitively expensive so we constructed simple ones from wooden frames, latex tubing, velara and foam-core [1, 2] (Figure 4).

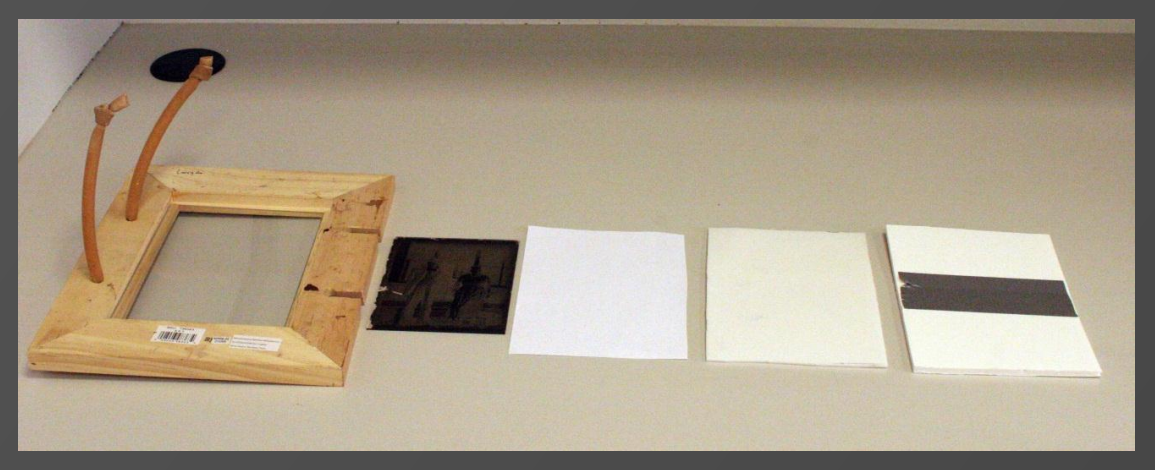


Figure 4. Deconstructed contact printing frames. Image taken from [2].

♦ **Cyanotypes**

The students made cyanotypes using the traditional iron(III) citrate and potassium ferricyanide [3] recipe and compared them to those created by Dr. Mike Ware's modification that uses iron(III) oxalate and potassium ferricyanide [4]. They determined proper exposure time by performing trial exposures with transmission step wedges. They were also introduced to toning processes and used trisodium phophate or tea to create yellow or brown prints, respectively (Figure 5).

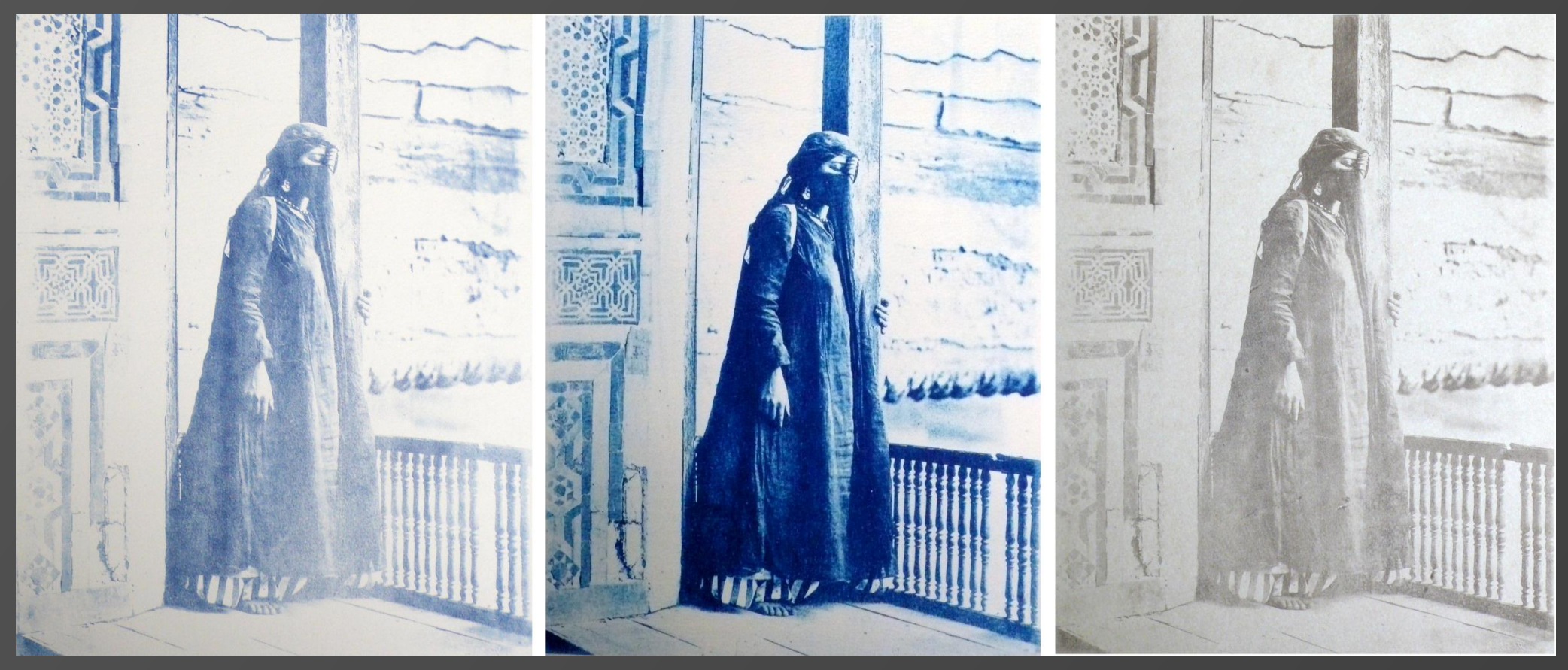


Figure 5. From left to right: traditional cyanotype, Ware cyanotype and tea-toned traditional cyanotype; note the denser tonality of the Ware method print.

♦ **Paper sizing**

To investigate the role paper sizing plays in tonality of salted paper prints each student sized a series of papers with arrowroot starch, gelatin, acrylic matte medium or gum Arabic with potassium dichromate.

Day 5

♦ **Halide stabilized and thiosulfate fixed salted paper prints**

The students created halide stabilized and thiosulfate fixed salted paper prints using their sized papers (Figure 6). When improper stabilization methods were used the prints deteriorated over a very short time period providing a dramatic example of the notorious instability of this method [5].

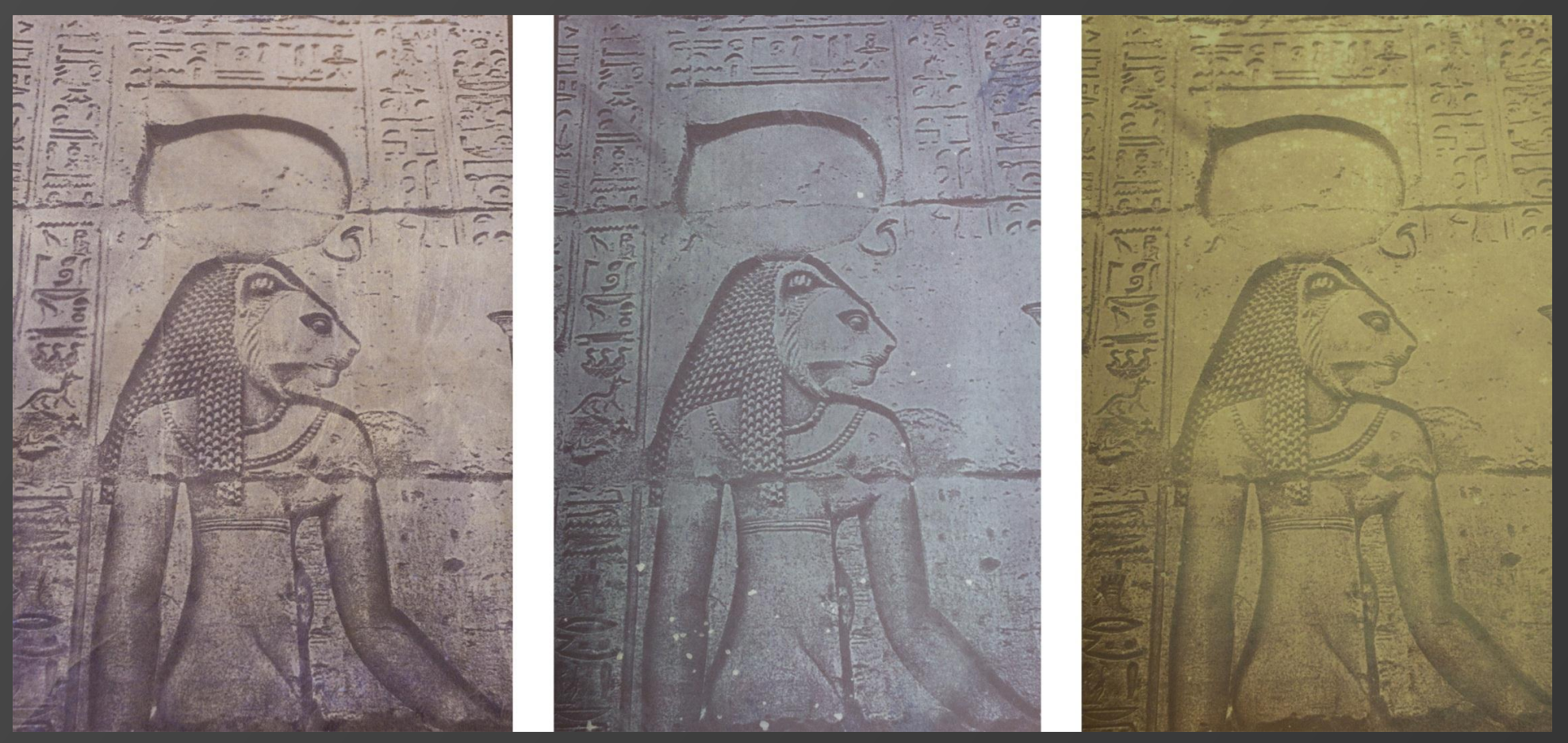


Figure 6. From left to right: chloride, bromide and iodide stabilized salted paper prints. Image taken from [2]

Day 6

♦ **XRF analysis of salted paper prints**

In addition to being able to detect the presence of halide stabilizers as shown in [2] the stabilized prints can also be distinguished from thiosulfate fixed prints due to equal levels of silver present in the light and dark areas of the halide-stabilized prints (Figure 7).

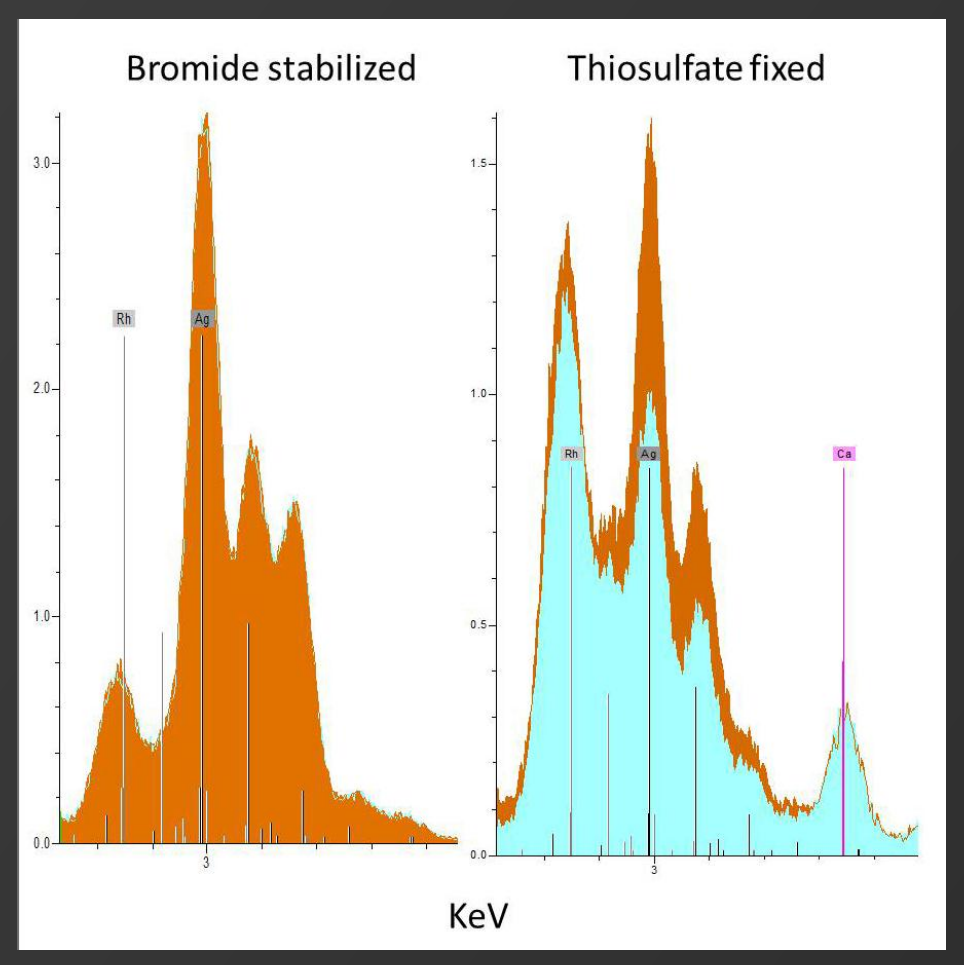


Figure 7. Comparison of the intensity of the silver peaks in the light and dark areas of bromide stabilized and thiosulfate fixed prints. Orange- dark; Blue- light. The light and dark areas of the halide stabilized prints cannot be distinguished by XRF.

Day 7

♦ **Toning of thiosulfate fixed salted paper prints**

The students toned their prints using Kodak Professional Sepia II Warm Toner, Kodak Rapid Selenium Toner, Clerc's thiourea gold toner [6] or gold borax toner [6].

♦ **XRF analysis of toning materials**

As described in [2] XRF can determine if a print has been toned with selenium or gold. The issue of sulfur (sepia) toning is more complex because the detection of sulfur by XRF could also indicate incomplete removal of the thiosulfate fixer.

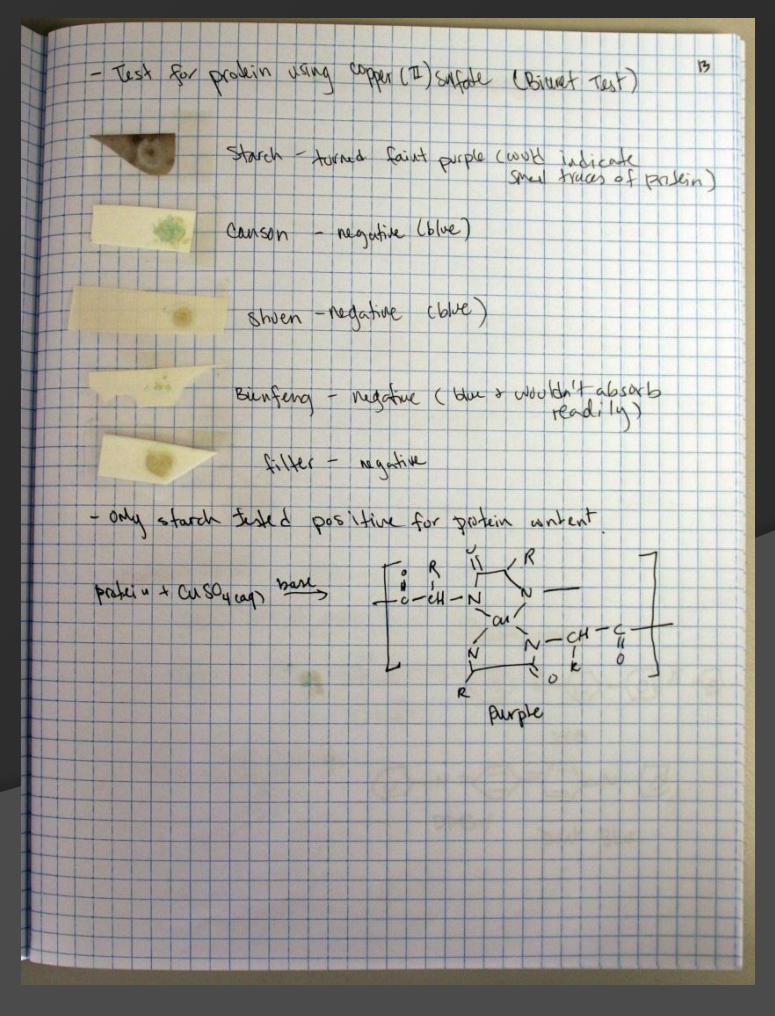
Day 8

♦ **Identification of binders and paper sizes by attenuated total reflection spectroscopy (ATR)**

The students learned how to use the ATR instrument for non-destructive analysis of photographs. Albumen, silver-gelatin and salted paper prints (binderless) were used as examples. The students then analyzed the paper they had sized.

♦ **Identification of binders and paper sizes by microchemical tests**

Using Nancy Odegaard's text [7] as a reference the students analyzed the papers they had sized as well as the 'unknown' photographs from day 2 (Figure 8).



- Test for protein using copper (II) sulfate (Biuret Test)

Starch - turned faint purple (could indicate small traces of protein)

Canson - negative (blue)

Shoen - negative (blue)

Binfeng - negative (blue & wouldn't absorb readily)

filter - negative

- only starch tested positive for protein content

protein + $CuSO_4$(aq) $\xrightarrow{base}$

Purple

Figure 8. A page from a student notebook showing their microchemical test results.

Day 9

♦ **van Dyke brown prints**

Coming back to iron-based photography the students made van Dyke brown prints and toned them using the same techniques they had learned for salted paper prints (Figure 10).

Figure 10. Gold borax toned van Dyke brown print made from an antique glass plate negative

♦ **Cliché-verre**

The students smoked a glass plate over a candle flame, lightly sprayed it with Krylon workable fixative, and then drew on the plate (Figure 11). They were permitted to print their plate and tone the resulting image in a method of their choosing

Day 10

♦ **Gum-bichromate prints**

The students made single color gum bichromate prints using a variety of inorganic pigments from Kremer. To determine proper exposure times they performed test exposures using transmission step wedges. This is important as different pigments accelerate or retard the crosslinking reaction

Figure 11. Cliché-verre plate and van Dyke brown print made from the plate

Day 11

♦ **Analysis of photographs by scanning electron microscopy and energy dispersive x-ray analysis**

Sections of cyanotypes (both traditional and Ware method) and thiosulfate fixed salted paper prints were taken from dark areas and carbon coated. Image particles were located and their sizes measured. This provided graphic evidence for the nanoscale size of the particles and the fibrous nature of the paper.

Chemical principals covered

Every photographic technique introduced in the laboratory was accompanied by a handout describing the chemical principles underlying the method as well as the methodology and history. Some of the major principles covered and example reactions from the photographic techniques covered include:

♦ **Photochemistry**

Photochemistry is the ubiquitous process underlying all photographic processes and yet is usually not covered in most chemistry curriculum.

In cyanotypes exposure to light causes citrate to break down forming carbon dioxide and acetone:
$C_5H_5O_7^{2-}$ + light → $3CO_2(g) + C_3OH_6(l) + H^+ + e^-$
and creating the electrons which reduce potassium ferricyanide to ferrocyanide

In salted paper prints the silver halide is reduced photochemically:
$2AgCl(s)$ + light → $2Ag(s) + Cl_2(g)$

♦ **Thermodynamics and equilibrium constants**

The formation of silver halides from metallic silver and halogen gas is thermodynamically favored. Therefore scavenging of the halogen produced by the reaction above is necessary if metallic silver is to remain. This occurs via the reaction $X_2(g) + H_2O(l) \rightarrow X^-(aq) + HOX(aq) + H^+(aq)$, where X is a halogen. The equilibrium constant, K, is 500, 0.01 and 10^{-9} for Cl_2, Br_2 and I_2, respectively [8] suggesting that in the absence of other reactions recombination of iodine with Ag to reform AgI is favored. The fact that this reaction is not seen by the students leads to a discussion of what this implies, namely another reaction that removes the HOI or HOBr formed:
$3HOX(aq) \rightarrow 2X^-(aq) + XO_3^-(aq) + 3H^+(aq)$ therefore driving the first reaction forward.

♦ **Electrochemical series**

Gold toning, where exposure of the print to a solution of oxidized gold cations causes electrochemical replacement of some of the silver image particles with gold, is a good example of the importance played by reduction/oxidation potentials: $3Ag(s) + [AuCl_4]^- \rightarrow Au(s) + 3AgCl(s)$

The differences between redox potentials are also exploited in van Dyke brown prints, where the photochemically produced iron(II) reduces silver nitrate to metallic silver.

♦ **Complex ion formation**

The formation of complex metal ions occurs during thiosulfate fixing:
$2Na_2S_2O_3^{2-}(aq) + AgCl(s) \rightarrow [Ag(S_2O_3)_2]^{3-}(aq) + 2NaCl(aq)$

And in the formation of the 'ammonio nitrate' solution of silver used by Talbot:
$AgNO_3(aq) + NH_3(aq) \rightarrow [Ag(NH_3)_2]NO_3(aq)$
This is a particularly graphic example because the initial addition of ammonia to the silver nitrate solution results in the formation of insoluble Ag_2O, which re-dissolves upon complex ion formation

♦ **Polymer crosslinking and solubility**

In gum bichromate prints exposure to light causes the potassium dichromate to crosslink gum Arabic polymers together, increasing their average molecular weight and reducing their solubility.

Conclusions

The instructors felt that this course successfully introduced the applicability of science to photograph and the art museum world. The students learned several new techniques that they would not otherwise have been exposed to and a great deal about photography, something than none of them had though of chemically before. The students themselves appreciated the history behind the techniques and the 'non theoretical' nature of the experiments- the actual production of images made the chemistry real to them.

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