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# A Quantitative Study of Cuprous Oxide Photodismutation

Anne Dresden Bowman

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A QUANTITATIVE STUDY OF CUPROUS OXIDE PHOTODISMUTATION

by

Anne Dresden Bowman

A thesis submitted in partial fulfillment of the requirements for the degree of Bachelor of Science in the School of Photography in the College of Graphic Arts and Photography of the Rochester Institute of Technology

May, 1978

Thesis Advisor: Dr. Ronald Francis

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## ABSTRACT

A cuprous oxide emulsion was made using noodling and washing emulsion making techniques. An attempt to use phthalated gelatin and coagulation washing resulted in the formation of cuprous hydroxide and destruction of the phthalated gel molecule and lack of coagulation within the emulsion. Cuprous oxide was also slurried with water and coated onto unglazed porcelain plates. The density-log exposure relationship was linear for the cuprous oxide slurry and non-linear for the cuprous oxide emulsion. The cuprous oxide film gave a speed value twenty-five times greater than that obtained with the slurry. The cuprous oxide dismutation system possesses great variability and little repeatability.

## INTRODUCTION

Because of the rising price of silver (presently \$5.27 per troy ounce),<sup>1/</sup> its dwindling reserves, and its low recovery rate from photographic systems,<sup>2/</sup> interest in producing viable non-silver systems has increased over the past few years. Most non-silver materials used (copper, titanium dioxide) exist or can be produced in large, inexpensive quantities.<sup>3/</sup>

Upon exposure in a conventional silver-halide emulsion, interstitial silver ions present within the silver-halide crystals are photo-reduced to silver metal atoms at sensitivity specks forming latent image sites which serve as initiation sites for further amplification and development.<sup>4/</sup> If any metal ion could be photo-reduced in an image-wise fashion, nonsilver latent images would be formed. If these latent images were then capable of development and sufficient amplification to render a clear, discernible image, the process would constitute a viable nonsilver photographic system. The problems usually encountered with such systems, though, are lack of amplification as comparable to a silver system (which possesses an amplification factor of at least  $10^6$ ) and lack of speed.<sup>5/</sup>

P. J. Hillson and M. Ridgway published a paper in 1970 entitled "Dismutation: A New Development Reaction for Photographic Systems,"<sup>6/</sup> in which they discussed studies of several dismutations applicable to photographic systems. In each of these processes metal ions undergo a photo-induced dismutation to form

metal atoms and ions of higher valency. One such system is the cuprous oxide photodismutation:  $2\text{Cu}^+ \xrightarrow[\text{H}^+]{h\nu} \text{Cu}^0 + \text{Cu}^{++}$ . This system deserves a more quantitative study than that discussed by Hillson and Ridgway because of a purported quantum yield greater than one<sup>7/</sup> and the obvious cost advantage of copper over silver systems.

Cuprous oxide can be obtained by Fehling's reduction of a cupric salt or by adding alkali to a solution of cuprous ions, or reagent cuprous oxide may be used directly.<sup>8/</sup> Fehling's reduction results in a fine cuprous oxide precipitate<sup>9/</sup> suitable for use in a fine-grain emulsion. Once obtained, cuprous oxide can be slurried in water and brushed onto unglazed porcelain plates, or suspended in a colloidal matrix (such as gelatin) and coated onto film base and allowed to dry.<sup>10/</sup>

Normally cuprous oxide is unaffected by radiation.<sup>11/</sup> Sensitization is accomplished by immersing the cuprous oxide (dried slurry or emulsion) in a strong acid and exposing it while moist. This results in an image-wise photo-induced dismutation; the cuprous oxide remains unaltered in the unexposed areas.<sup>12/</sup> The resulting image consists of dark brown copper metal against a lighter brown cuprous oxide background. A stabilization of the image is accomplished by allowing the slurry/emulsion to dry before prolonged exposure to room lights.

Hillson and Ridgway state that the effective concentration limits of each acid developer depend upon the processing temperature and the concentration of the gelatin.<sup>13/</sup> As in

silver-halide emulsions, gelatin acts as a restrainer. The greater the gelatin concentration, the slower the diffusion rate of chemistry into the emulsion. Similarly, the higher the processing temperature, the less viscous and more fluid the gelatin becomes and the faster the diffusion rate of chemistry. The hydrogen ions liberated in the acid act as developer accelerators by bonding with the cupric ions liberated in the photodismutation,<sup>14/</sup> and thus displacing the equilibrium to the right. This produces the amplification factor for the cuprous oxide photodismutation system.

Too dilute an acid will not inhibit or prevent the dismutation.<sup>15/</sup> However, such dilution increases the development time and decreases the amplification obtained due to the decrease in developer activity. Too concentrated an acid shows no selectivity in development.<sup>16/</sup> Selectivity will also decrease in the acid developer forms a stable compound with the cupric ion as the formation of this stable compound will drive the dismutation reaction forward in a nonselective manner.<sup>17/</sup>

Hillson and Rdigway also found that as the time between application of acid developer to the cuprous oxide system and exposure increased, sensitivity decreased. This decrease in sensitivity was termed passivation.<sup>18/</sup> Passivation is reversible, though, and the sensitivity can be restored to its original level by allowing the acid-cuprous oxide to dry (even partially) and then reimmersing the slurry/emulsion in acid.<sup>19/</sup>

The lack of experimental data presented in the above-mentioned

paper makes it difficult to draw any substantive conclusions regarding the capabilities of the cuprous oxide photodismutation system. It is, then, desirable to investigate the system quantitatively and to determine its application as a photographic emulsion where cuprous oxide is precipitated directly into the gelatin as is done with conventional silver-halide emulsions.

If the speed and resolution of the cuprous oxide dismutation system are applicable under at least some special-purpose conditions, then the system is viable. Further experimentation can be devoted to refinements of the system such as increased sensitivity and resolution.



## EXPERIMENTAL

## Exposure Device:

A Kodak #2 uncalibrated step tablet was used to modulate the incident radiation. Because the cuprous oxide slurry/emulsion must be exposed while moist with acid, the step tablet was mounted one-half inch from the slurry/emulsion surface by means of a wooden frame two and one-eighth by six inches. The frame and step tablet sit directly on the unglazed porcelain plate..

The film is cut to two-by-five-inch strips and placed onto a piece of glass two and one-eighth by six inches which rests in an exposing frame. The step tablet frame is then placed on top of the film using spring clamps to hold the frame, film, and glass steady as a unit and to keep the film flat against the glass. A removeable piece of glass was used to facilitate cleaning.

## Sources:

The first source used was Philips mercury-cadmium-zinc gas discharge lamp (0.9 amp). The lamp-to-plate/emulsion distance was 15 inches for a 10-second exposure time, and eight and three-fourths inches for exposure times of one, two, and five minutes. To increase the amount of energy incident on the slurry/emulsion, a reflector of aluminum foil was mounted over the lamp parallel to the lamp surface at a distance of three-fourths inch. This latter configuration was used for an

exposure time of three minutes at a distance of eight and three-fourths inches.

The second source used was the 400 watt General Electric mercury vapor lamp. The diazo material exposing device, made by Colight, Inc., of Minneapolis, Minnesota, houses the lamp with surrounding reflectors to ensure that most of the emitted radiation is incident on a horizontal plane 15.5 inches from the lamp. Cuprous oxide coated procelain plates were exposed for 10 minutes at a distance of 15.25 inches, and for 15 minutes at a distance of 12.75 inches.

The energy output of the General Electric lamp was measured with the United Detector Technology, Inc., radiometer. The energy versus distance from the lamp plot for this lamp is presented in the results section.

#### Slurry Making:

1. measure out 20 grams of reagent grade cuprous oxide and place in a clean 400 milliliter beaker
2. slowly add five-milliliter portions of distilled water while grinding the cuprous oxide until a slurry is produced
3. using a natural bristle bursh, paint the slurry thickly onto unglazed porcelain plates and allow the slurry to dry

**Emulsion Making:**

Conventional emulsion making consists of five steps: precipitation, digestion, noodling, and washing or coagulation washing, redispersion, and coating. Only the final procedures for noodling and washing and coagulation washing methods are presented here. Previous formulations may be found in the author's notebook, along with lot numbers and serial numbers.

**-Noodling and Washing:**

1. measure out 15.00 grams inert gel and let soak for 10 minutes in 200 milliliters distilled water in a stainless steel beaker
2. place the beaker in a 65°C water bath and stir for 15 minutes using a Diagger Dial Speed stirrer with Powerstat veriac
3. add 3.00 drops Kodak antifoam  
21.00 grams  $\text{KNaC}_4\text{H}_4\text{O}_6$   
25.00 grams  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
12.00 grams NaOH  
and stir for 15 minutes
4. heat 250 milliliters distilled water to 90°C and place in a 250 milliliter separatory funnel with capillary tube attached to warm the separatory funnel (capillary tube delivers 3.42 milliliters per second)
5. measure out 7.50 grams  $\text{N}_2\text{H}_2\text{SO}_4$  and dissolve in 100 milliliters 90°C distilled water

6. drain the separatory funnel and fill it with the 100 milliliter  $\text{N}_2\text{H}_2\text{SO}_4$  solution
7. allow the  $\text{N}_2\text{H}_2\text{SO}_4$  solution to drain into the beaker thus precipitating the cuprous oxide in gelatin
8. stir for 20 minutes
9. add 20.00 grams inert gel and stir for 40 minutes
10. remove the beaker from the water bath and place it in the refrigerator to allow the emulsion to gel
11. after gelling, remove the emulsion from the beaker and noodle it; return the noodles to the beaker and wash them with distilled water using five 10-minute changes of water
12. drain the water from the emulsion
13. redisperse the emulsion at  $55^\circ\text{C}$ ; let stand 10 minutes in the water bath and then stir for 20 minutes (add no gelatin or water)
14. coat the emulsion onto film base

-Coagulation Washing:

1. measure out 10.00 grams seven-percent phthalated gel and let soak 10 minutes in 400 milliliters distilled water in a stainless steel beaker
2. place the beaker in a  $65^\circ\text{C}$  water bath and stir for 10 minutes
3. add 21.00 grams  $\text{KNaC}_4\text{H}_4\text{O}_6$   
25.00 grams  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$   
12.00 grams NaOH

- and stir for 10 minutes
4. heat 250 milliliters distilled water to 90°C and place in a 250 milliliter separatory funnel with capillary tube attached to warm the separatory funnel
  5. measure out 7.50 grams  $N_2H_2SO_4$  and dissolve in 100 milliliters 90°C distilled water
  6. drain the separatory funnel and fill it with the 100 milliliter  $N_2H_2SO_4$  solution
  7. allow the  $N_2H_2SO_4$  solution to drain into the beaker thus precipitating the cuprous oxide in gelatin
  8. stir for 20 minutes and then remove the beaker
  9. add slowly sufficient 0.5N  $H_2SO_4$  to drop the pH to 5.8
  10. refrigerate the emulsion overnight
  11. draw off the water and soluble byproducts using a syringe
  12. measure out 12.00 grams inert gel and let soak 10 minutes in 250 milliliters distilled water
  13. dissolve the inert gel at 55°C with stirring for 10 minutes
  14. place the stainless steel beaker with the emulsion in a 55°C water bath
  15. pour the inert gelatin solution over the emulsion and stir for 20 minutes
  16. remove the beaker from the water bath and set the pH to 7 using 0.5N NaOH
  17. coat the emulsion onto film base

Determination of Isoelectric Point of Phthalated Gelatin:

1. measure out 2.00 grams phthalated gel and let soak for 10 minutes in 200 milliliters distilled water
2. heat the solution to 65°C with stirring to dissolve
3. titrate the solution with 0.5N H<sub>2</sub>SO<sub>4</sub> and plot the results; the observed properties of the isoelectric point occur roughly 0.45 pH units below the inflection point.

Determination of Isoelectric Point of Cuprous Oxide Precipitated in Phthalated Gelatin:

1. follow steps 1 through 8 as given above for coagulation washing
2. titrate the gel solution at 65°C with 0.5N H<sub>2</sub>SO<sub>4</sub>, plot the results and determine the isoelectric point graphically, or
3. cool the gel solution to room temperature and titrate with 0.5N H<sub>2</sub>SO<sub>4</sub> and visually observe the isoelectric properties to determine the isoelectric point

Exposure:

-Porcelain Plates

1. using a dropper, place drops of 0.125M H<sub>2</sub>SO<sub>4</sub> onto the plate covering the entire plate
2. continue placing acid onto the plate in this manner until the cuprous oxide remains moist
3. expose the plate immediately to a bright ultra-violet

radiation source using the step tablet frame

4. allow the plate to dry before moving it or exposing it for prolonged periods to room illumination
5. spray the plate with Krylon acrylic to protect the copper metal formed from aerial oxidation

-Film

1. Place 0.125M  $H_2SO_4$  in a 5x7 plastic tray
2. place the film in the acid for 12 seconds and squeegee the film
3. immediately place the film in the exposing device with step tablet frame and expose to a bright ultra-violet radiation source
4. remove the film from the frame and wash in distilled water for 30 seconds, squeegee the film after washing
5. allow the film to dry
6. spray the film with Krylon acrylic to protect the copper metal formed from aerial oxidation

Preparation of Phthalated Gelatin: 20/

1. measure out 7.00 grams phthalic anhydride and dissolve in a minimum of acetone (approximately 10 milliliters acetone per gram phthalic anhydride)
2. measure out 100 grams inert get and dissolve in 1.000 liter distilled water at 45°C to give a 10-percent gel solution
3. slowly add the phthalic anhydride solution to the 10-

- percent gel solution while maintaining the pH at 10
4. after addition, let the solution stand at 45°C with stirring for 15 minutes
  5. pour the solution into unused plastic trays and refrigerate to gel
  6. after gelling, break out the phthalated gelatin and place in a gelatin dryer for two to three days
  7. the percent phthalation is dictated by the percentage of phthalic anhydride used



## RESULTS

Initially Fehling's Reduction as given in chemistry texts (see Appendix A)<sup>21/</sup> was used to precipitate cuprous oxide in inert gel. This resulted in an emulsion with a pH in excess of 14 which would not gel. In view of the high pH, the limiting reagent in the formulation was found to be hydrazine sulfate and the other reagent quantities were calculated on this basis. This formulation resulted in an emulsion with a pH of approximately 8 which did gel. A comparison of reagent quantities may be found in Appendix A.

The first attempt at emulsion washing was done using noodling and washing as it was thought the cuprous oxide could not exist below a pH of 5.<sup>22/</sup> To have used phthalated gel would have meant lowering the pH to at least 3.5. The emulsion, however, was washed too long (twelve hours) and at coating, the emulsion was at most five-percent gel due to water-takeup during washing, loss of emulsion during washing, and the addition of water during redispersion. The emulsion was coated onto film base using the coating machine maintained by the Department of Photographic Science and Instrumentation at the Rochester Institute of Technology. The film was soaked 30 seconds in 0.125M sulfuric acid prior to exposure to the Philips mercury-cadmium-zinc gas discharge lamp. A five-minute exposure at a distance of 15 inches resulted in just discernible density (two steps). During the drying process the wetness of the emulsion became even more noticeable as the

copper metal image migrated within the emulsion to the lowest portion of the film curl. Also upon drying the copper metal image was aerially oxidized and the image destroyed.

Due to the difficulties encountered with the emulsion (stability and low density), a cuprous oxide-water slurry was made and painted onto unglazed porcelain plates in an attempt to repeat Hillson's and Ridgway's work. The plate was moistened with 0.125M sulfuric acid and exposed to the Philips lamp with foil reflector at a distance of eight and three-fourths inches for three minutes. A minute amount of copper metal, in the form of several small "dots," was formed in a non-image-wise fashion. It was also noticed that the lamp was not stable for times of use in excess of two minutes. After two minutes of use, the lamp appeared to burn brighter. In view of this and the lack of any density on the porcelain plate, a 400 watt General Electric mercury vapor lamp (housed in the Colight diazo material printer) was exchanged for the 0.9 amp Philips gas discharge lamp. The energy versus distance plot for the General Electric lamp is given below. Energy is given in terms of ergs per square centimeter per second which will be taken as the ultra-violet equivalent of illuminance. Then exposure, for this work, is defined as the product of energy and time of exposure in seconds.

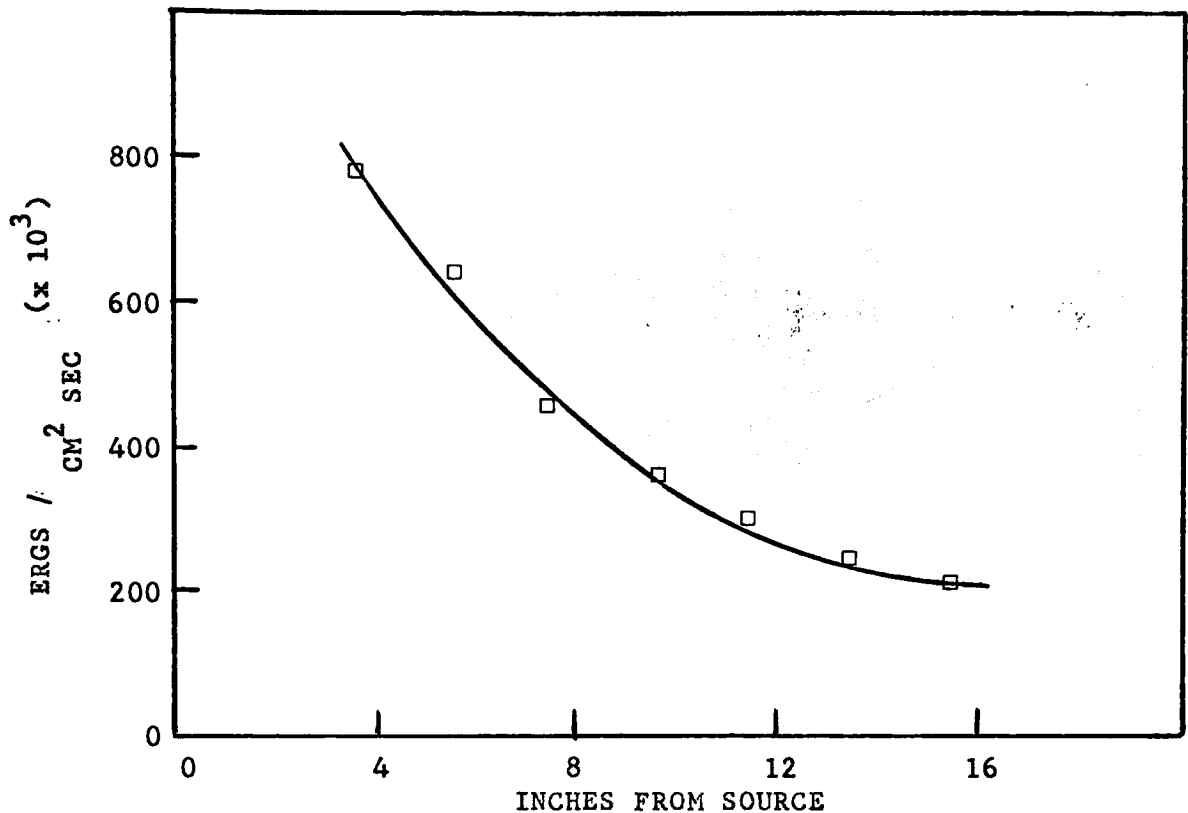


Figure 1. Energy versus Distance plot for the Mercury Vapor Lamp.

Two plates were exposed using this source: one for 10 minutes at a distance of 15.25 inches, the other for 15 minutes at a distance of 12.75 inches. The exposure resulted in linear density versus log exposure curves with a  $\delta$  of 0.06. If speed is defined as the reciprocal of the exposure producing a net density of 0.10, the speed for the first plate is  $1.3 \times 10^{-9}$ , and for the second plate is  $2.5 \times 10^{-9}$ . The plates were sprayed with Krylon acrylic to protect the image from aerial oxidation. Density versus log exposure curves for the porcelain plates are presented below.

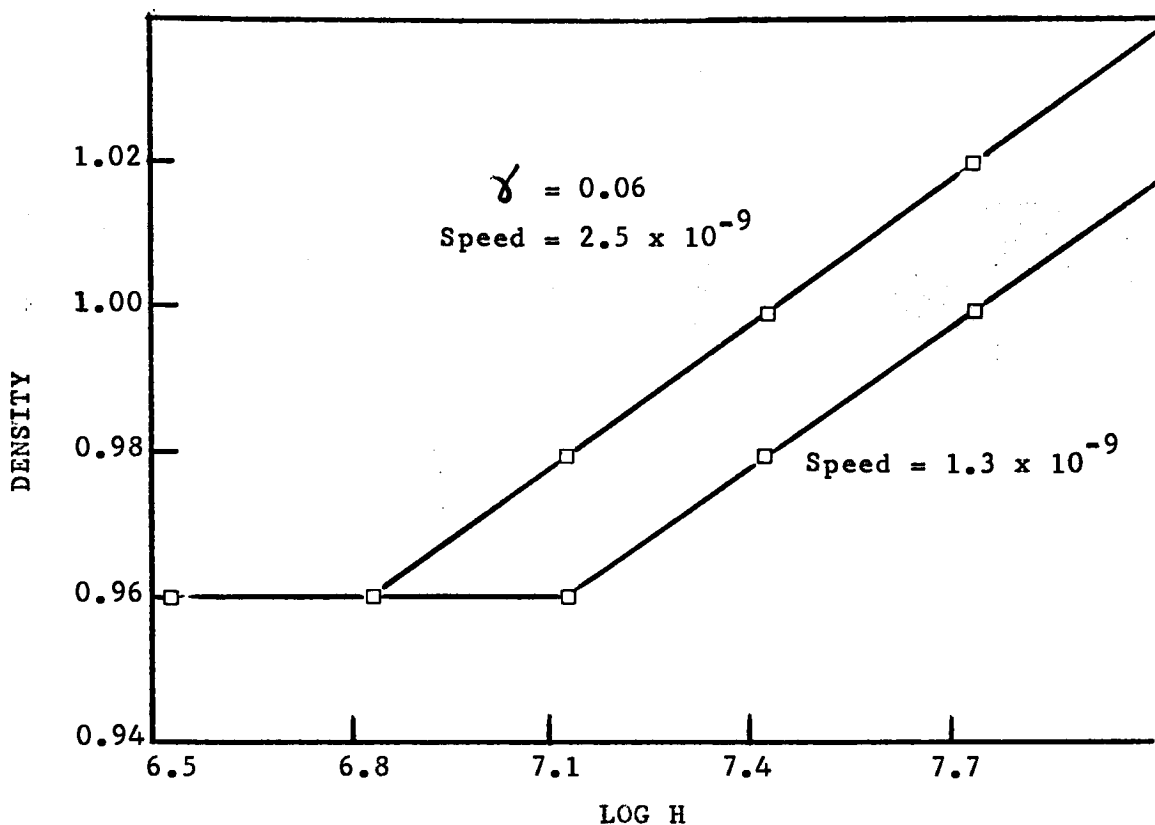


Figure 2. Density - Log H plot for Porcelain Plates.

Because of the severe water-takeup problem and the amount of handling of the emulsion encountered with noodling and washing, phthalated gel and coagulation washing were utilized. It was found that copper was formed in the emulsion below a pH of 3.4 when titrating the emulsion with 0.5N sulfuric acid. The apparent isoelectric point occurred at a pH of 5.8. A similar titration with phthalated gel alone resulted in an isoelectric point of 3.3; the inflection point of the titration occurred at a pH of 3.75 with the observed isoelectric point (definite coagulation) occurring in the pH range 3.2 to 3.4. See Figures 3 and 4, below.

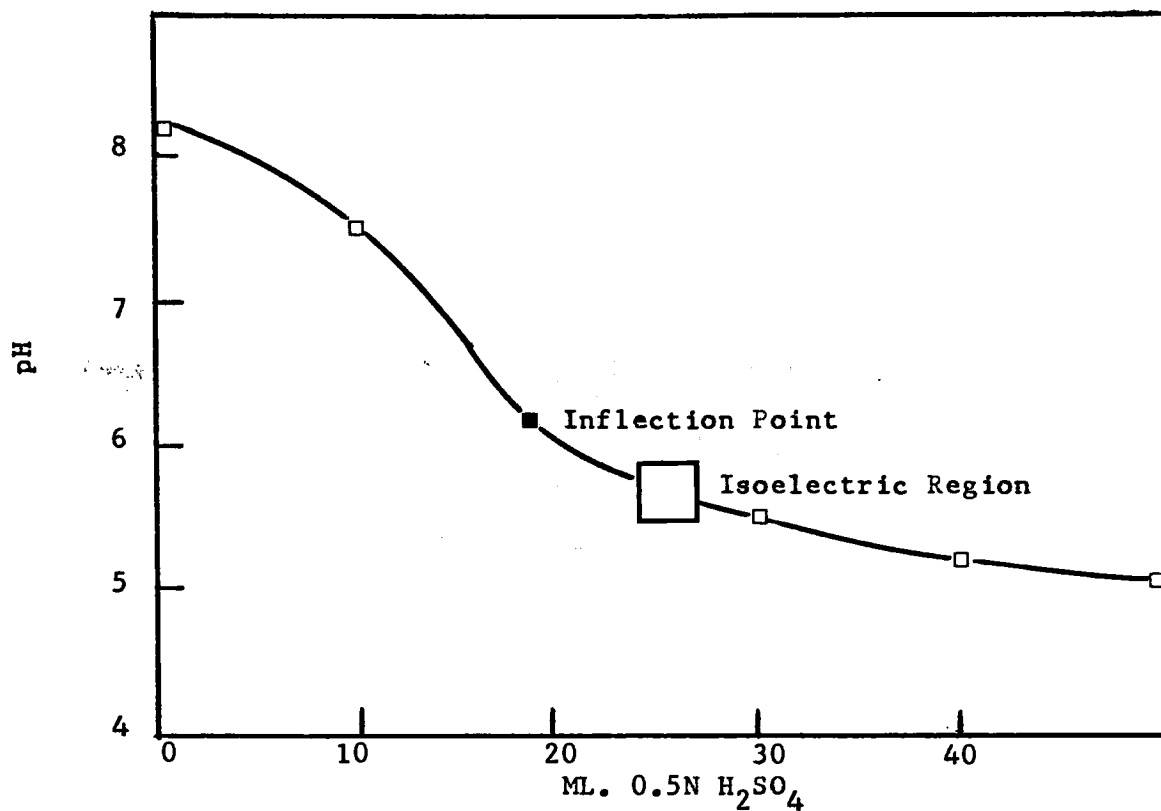


Figure 3. Titration curve for Cuprous Oxide Slurry.

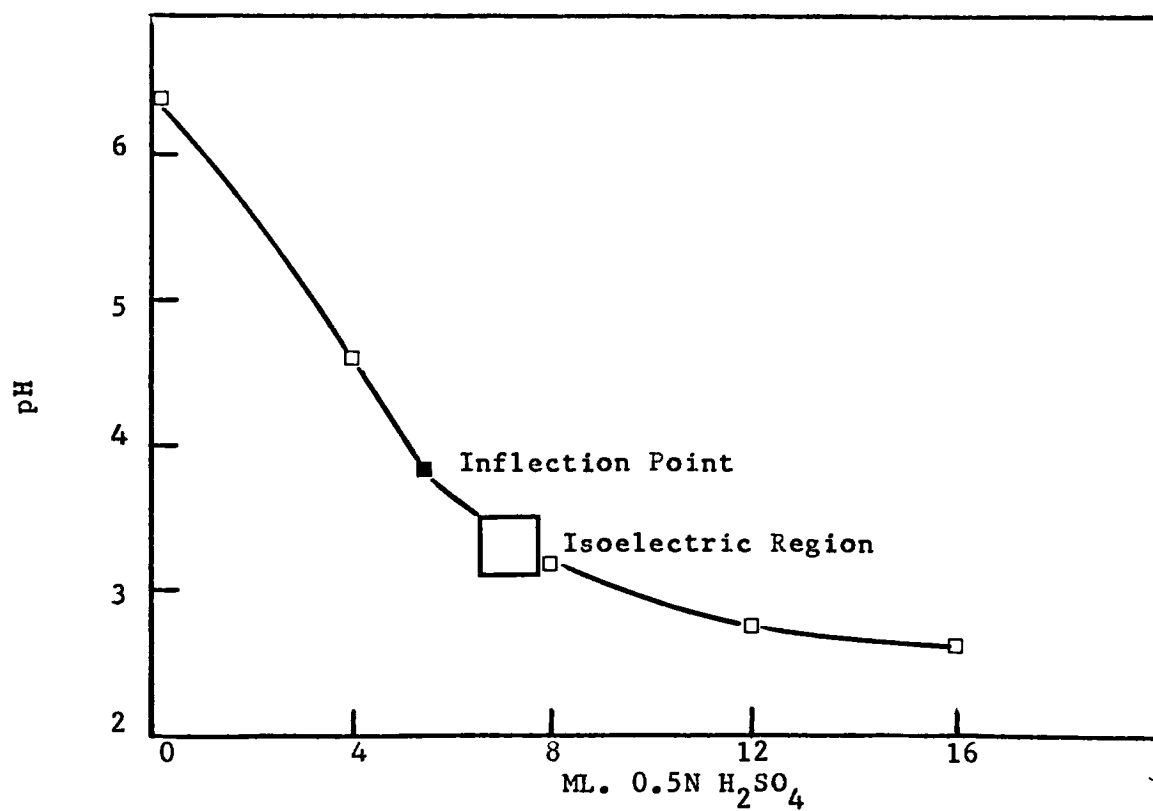


Figure 4. Titration curve for Phthalated Gelatin

Repeated titrations of the cuprous oxide emulsions indicated that the emulsion would not coagulate, but that the region of heaviest precipitation occurred at a pH of 5.8. It was thought initially that differing degrees of phthalation might control the coagulation process within the cuprous oxide emulsion and a 40-percent phthalated gel was made. This approach was abandoned after speaking to Dr. B. H. Carroll who advised that gelatin is phthalated to saturation by a ten-percent phthalation formulation. Therefore, noodling and washing were again utilized in the emulsion making.

The same procedure used to produce the gelled emulsion above was followed. This resulted in an emulsion that was 11.7-percent in gel. During washing the emulsion was found to increase its weight by 40-percent. The emulsion was redispersed without the addition of either water or gelatin resulting in an emulsion that was seven-percent in gel at coating. After the film was removed from the dryer, gas bubbles<sup>23/</sup> were noticed in the emulsion.

Prior to exposure the film was soaked in 0.125M sulfuric acid. A soaking time of 10 seconds resulted in little development activity, while a time of 15 seconds resulted in non-selective development. A soaking time of 12 seconds was chosen as optimum. Upon immersion in the acid, the emulsion contracted from the base dimensions and cracked. It was also found that the amount of acid absorbed by the emulsion varied greatly as two four-minute exposures at a distance of 13.5 inches each exhibited different degrees of development as indicated by the step tablet densities

obtained and the resulting  $\gamma$ 's and speeds. One four-minute exposure produced a  $\gamma$  of 1.29 and a speed of  $6.3 \times 10^{-8}$ , while the other produced a  $\gamma$  of 0.42 and a speed of  $1.9 \times 10^{-8}$ .

The first film strips were merely dunked in acid, placed in the exposing frame and exposed. After exposure the film was sprayed with Krylon acrylic to prevent aerial oxidation. Images remained for approximately 30 minutes before destruction by the cupric ion.<sup>24/</sup> To increase the uniformity of immersion, a film squeegee was used before placing the film in the exposing frame. Under these conditions, the image remained for an hour before the cupric ion was formed in visible excess, and the quantity of cupric ion formed was not as great as in the first case. By squeegeeing the film before exposure, rinsing in distilled water for 30 seconds after exposure and then squeegeeing the film, allowing it to dry, and then spraying the film with Krylon acrylic, the image remains stable for at least 15 hours with the cupric ion formation (as evidenced by an overall green hue) just noticeable.

The emulsion grain size was found to be 4.5 micrometers by using a measuring microscope.<sup>25/</sup>

## CONCLUSIONS AND DISCUSSION

## Sources:

The Philips mercury-cadmium-zinc gas discharge lamp did not put out sufficient energy to expose a porcelain plate (using equal times) to the same degree as the General Electric 400 watt mercury vapor lamp. Nor was the Philips lamp as stable as the General Electric lamp -- no measurable difference was found in the General Electric source for operating times up to two and one-half hours.

## Cuprous Oxide Slurry on Porcelain Plates:

The method of slurring cuprous oxide with water and then painting it onto unglazed porcelain plates and then exposing to obtain an image proved an easy, though variable, process. Once the two acceptable images were obtained, more plates were coated, moistened with acid and exposed, but with no discernible results. An image could not be obtained after five attempts, and this approach was abandoned in favor of emulsion making and the use of film.

## Emulsion Making:

1. As mentioned above, phthalated gel alone exhibited an isoelectric point in the pH range 3.2 to 3.4, while the cuprous oxide emulsion did not coagulate but did exhibit a point of maximum precipitation at a pH of 5.8. Figure 5, below, is a



schematic representation of the formation of phthalated gel.<sup>26/</sup>

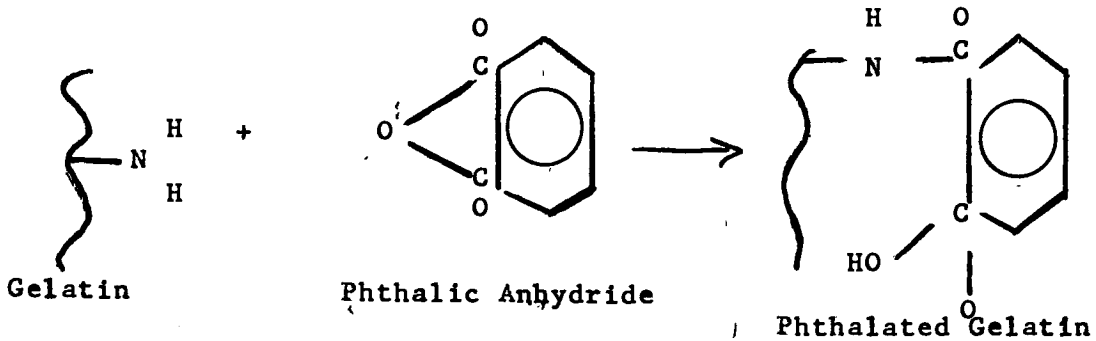


Figure 5. Formation of phthalated gelatin.

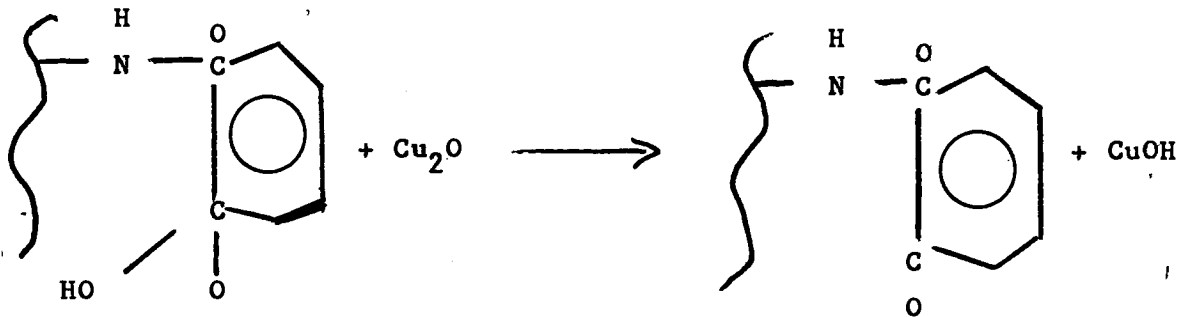


Figure 6. Formation of Cuprous Hydroxide.

At the isoelectric point the gelatin possesses an equal number of positive and negative charges, in the absence of binding of foreign ions, and the molecule possesses no net charge.<sup>27/</sup> At this point the gelatin also possesses minimum solubility<sup>28/</sup> and falls out of solution.

It is possible to titrate the number of terminal carboxyl groups on the phthalated gel molecule with an acid. The inflection point and isoelectric region may be located graphically as the carboxyl groups ionize at a pH lower than that for the other

groups and produce the strongest inflection point.<sup>29/</sup> As indicated in Figure 4, the inflection point for the phthalated gel occurs at pH 3.75 with the isoelectric region in the pH range 3.2 to 3.4.

As noted in the results, precipitation of cuprous oxide in the phthalated gel solution and subsequent titration resulted in an apparent isoelectric region around pH 5.8. It would seem reasonable that two hydroxides of copper (cuprous and cupric) would exist, but there is no evidence to suggest the existence of cuprous hydroxide.<sup>30/</sup> Because coagulation does not occur, it can be postulated that cuprous hydroxide is formed upon precipitation of cuprous oxide and prevents coagulation by either removing or complexing with the terminal carboxyl group of the phthalated gel molecule.<sup>31/</sup>

The existence of cuprous hydroxide or a complexed form thereof would explain the elevated pH corresponding to the isoelectric region of cuprous oxide precipitated in phthalated gelatin. With fewer carboxyl groups to titrate, the isoelectric region and inflection point would occur at higher pH values. Also, the next group of the gel molecule to ionize, the  $\alpha$ -amino imidazole group, does so at a pH 2.5 units greater than that for the ionization of carboxyl groups.<sup>32/</sup> This fact corresponds well with the observed data.

2. The emulsion must not be so wet as to allow migration of the image (less than five-percent in gel) nor so dry (seven-percent in gel) that soaking in acid pulls the existing water out of the emulsion shrinking and cracking it.

3. Due to the variability encountered due to differences in the diffusion rate of acid into the emulsion, a more controlled method of film immersion in the acid should be developed. It is expected that this would increase the repeatability and decrease the variability presently involved with cuprous oxide film.

#### Fixing the Image:

Spraying the copper-cuprous oxide images produced on the porcelain plates proved an acceptable method of fixing the image and protecting it from aerial oxidation. This approach is not acceptable for use with cuprous oxide film because the acid developer is sealed into the emulsion allowing continued development. The cupric ion is formed in the development process and it is expected that for normal development (i.e., production of image) the green color of the cupric ion is not noticeable but that over an extended time as more cupric ions are produced and development begins to become non-selective, the amount of cupric ion increases drastically resulting in a visually noticeable green color overall. Washing the film in water and then drying it greatly diminishes this problem.

The images produced on porcelain plates retain their dark brown image on light brown background because the acid sinks to the bottom of the porous plate. It is expected that after repeated use of the plate (washing, recoating with slurry, moistening with acid) that the content and physical level of acid would increase and eventually result in a green color overall as in the film.

### Development Mechanism:

The linear relationship observed in the density versus log exposure curves for the cuprous oxide slurry on porcelain plates suggests a simple, one-step photographic mechanism and possible quantum yield equal to or greater than one.<sup>33/</sup> The non-linear relationship observed between density and log exposure for the cuprous oxide emulsion suggests a more complicated photographic mechanism similar perhaps to that observed in a silver halide emulsion. This phenomenon may also be a function of the diffusion of acid developer into the emulsion.

Once the top most layers of the porcelain plate are moist with acid, the dry cuprous oxide forms a thin layer on top of the acid on top of the plate. Some of the acid evaporates and the rest diffuses down into the plate away from the image so that the rate of diffusion will determine (along with the exposure) the maximum density obtainable but will not affect the development mechanism itself.

With the film, the acid remains in contact with the image for a greater period of time and the development mechanism may become autocatalytic to some extent. More dismutation or developer activity may result where there is more density. This effect would level off as the maximum density is approached due to the dwindling amount of cuprous ions remaining to dismutate.

It was also found that the film possessed a speed value approximately 25 times greater and a  $\delta$  14 times greater than those obtained for the cuprous oxide-coated porcelain plates.

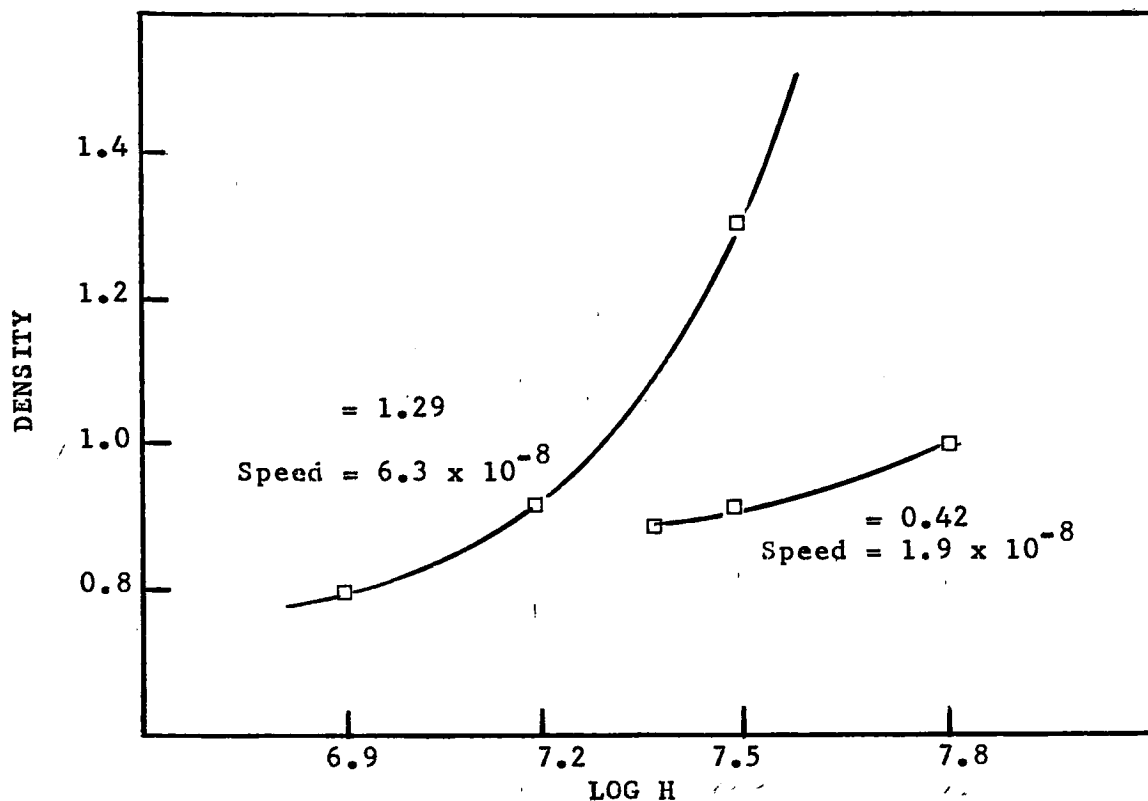


Figure 7. Density-Log H curves for four minute exposure, Cuprous Oxide film.

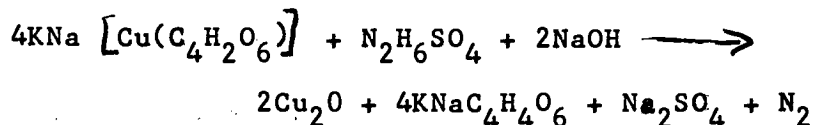
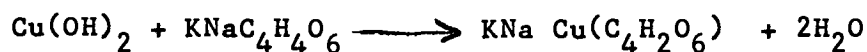
#### The Cuprous Oxide System:

The cuprous oxide system is a viable, though extremely slow, photographic system able to produce variable  $\gamma$ 's. As such, the system may have application in both reducing extremely high contrast originals and rendering low contrast originals to images with normal contrast ranges. To decrease the long exposure times involved, a smaller lamp-to-film-plane distance and/or a more powerful source should be tried.

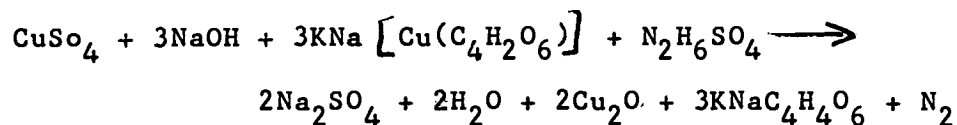
### Recommendations for Future Work:

1. Optimize the emulsion system taking into account processing time and temperature, and gelatin, acid and cuprous oxide concentrations.
2. Design a more reliable method of immersing film prior to exposure to decrease the variability in diffusion rate of acid developer into the emulsion.
3. Determine the quantum yield of both systems utilizing the analyses for copper, cuprous oxide, and cupric oxide utilized by S. B. Seeger and W. A. Escobar and found in the translated paper appearing in Appendix B.

APPENDIX A

Fehling's Reduction

Take 75 grams potassium sodium tartrate mixed with 75 grams NaOH in 600 milliliters warm water, add 50 grams  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and dissolve to give Fehling's solution of the copper tartrate complex. Take 7 to 8 grams hydrazine sulfate in 100 milliliters hot water and add slowly with stirring. Heat the entire reaction mixture to boiling with continuous agitation. Maintain the heating for 10 minutes. The blue color will disappear and give way to a brick-red precipitate of cuprous oxide. Wash the residue repeatedly with distilled water.

Overall ReactionComparison of Reagent Quantities

Old	Formulation	New
75.00 grams	$\text{KNaC}_4\text{H}_4\text{O}_6$	21.00 grams
50.00 grams	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	25.00 grams
75.00 grams	NaOH	12.00 grams
7.50 grams	$\text{N}_2\text{H}_6\text{SO}_4$	7.50 grams



APPENDIX B

The following is a synopsis (Introduction) and translation (remainder of the paper) of "Analysis of Mixtures of Copper Metal, Copper (I) Oxide, and Copper (II) Oxide," S. B. Seeger and W. A. Escobar, Rev. Real. Acad. Cienc. Exactus, Fis. Natur. Madrid, 62(1), 205 (1968). The translation was performed by Anne Dresden Bowman, April 10, 1978.

#### INTRODUCTION

Semi-Reactions	$E_o$ (v)
$Cu^+ + e^- \longrightarrow Cu_s$	+0.521
$Cu^{++} + 2e^- \longrightarrow Cu_s$	+0.337
$Cu^{++} + e^- \longrightarrow Cu^+$	+0.153

The volumetric determination of similar systems generally has basis in the previous dissolution or successive oxidation of one or two components. The difficulty of in situ analysis lies in having the reagent oxidize or dissolve in a specified and adequate manner to the diverse components and in the dismutation of the cuprous ion to copper metal and the cupric ion.

#### EXPOSITION and RESULTS

The problem of the analysis of copper and its oxides is very old; in the Handbook of Quantitative Chemical Analysis, 1905, Classen described a method for determining cuprous oxide in black copper (4).

According to the procedure used, the previous methods can be arranged in the following form:

A. Method to successively separate the components by dissolution:

Crisan (5) separated the copper (I) in 3N ammonium chloride; then separated the copper (II) in 6N sulfuric acid; and finally the copper metal in 6N nitric acid.

B. Method to first separate the copper (I) oxide and determine copper metal in the presence of copper (II) oxide with one oxidizing mixture:

Lavrukina (6) dissolved copper (I) oxide in hydrochloric acid, hydrazine sulfate, and potassium chloride; and Baker and Gibbs (7) used a solution of alcohol of hydrochloric acid and tin (II) chloride. Both determine in succession by titration of copper metal in the presence of copper (II) oxide by oxidation with ferric chloride and titrating the ferrous ion formed with cerium (IV).

Hurd and Clark (8) dissolved the copper (I) oxide in ammonium chloride, alcohol, and phenylhydrazine, and then determined in the filtrate the copper metal in the presence of copper (II) oxide by oxidation with ferric chloride and titrating the ferrous ion formed with dichromate.

Matha and Bharucha (9) dissolved the copper (I) oxide in a warm, saturated potassium iodide solution, and subsequently determined in two separate samples of copper and copper (II) oxide the total copper and the copper metal by oxidation with ferric chloride.

- C. Methods to determine copper metal in the presence of its oxides by selective oxidation:

Fitzpatrick (10) oxidized copper metal to the cupric ion with silver sulfate and continued the dissolution of the oxides in a ten-percent solution of sulfuric acid. Like the copper oxide dismutation, the cupric ion and copper metal are formed; then separate the products and perform an iodometric determination.

- D. Methods to selectively dissolve the oxides and subsequently determine copper metal:

Ubaladini and Guerrieri (11) first insolubilized the copper metal and transformed it into copper sulfide with sulfur dissolved in carbon sulfide and later dissolved the oxides in one sample with hydrochloric acid and potassium chloride. Bonner and Kaura (12) separated the two oxides by dissolving the sample in 0.5M sodium cyanide and then determined the copper metal by residual iodometric analysis.

A more complete description is found in the optical methods:

- E. Optical Methods:

Lerfass and Willard (13) calculated the particulars of copper metal, copper (I) oxide, and copper (II) oxide using microscope polarization by which they differentiated by means of density, color, and crystallization in the different systems; they related the numbers with the concentration of each component.

The basic method in A. and B. above is a previous separation of copper (I) oxide by dissolution. But from previous considerations, it is difficult to dissolve the sample in sufficient quantity to obtain the oxide without affecting the copper metal and copper (II) oxide. The error with this method is relatively high. In effect, Baker and Gibbs (7) point out the method of Hurd and Clark (8) -- the difficulty of dissolving copper (I) oxide without affecting the copper (II) oxide. Those authors indicate the results depend on the ability of the operator to recognize the moment in which all the copper (I) oxide is totally dissolved, which depends on the precision and velocity of introducing carbon dioxide which affects the solubility of copper (I) oxide which is moreover influenced by time and temperature. Methods 6, 7, and 9 also begin with selective dissolution of copper (I) oxide and present the disadvantages outlined above.

Crisan's (5) method is the most recent (1950) but makes no comment. Reliable tests in this paper show that 3N ammonium chloride dissolves some copper (II) oxide, and 6N sulfuric acid some of the copper metal -- an error which indicates too high values for copper (I) oxide and too low values for copper metal in the table values presented.

The selective dissolution of the two oxides accomplished in the two methods of D. is difficult to realize due to some of the copper metal being ultimately dissolved. Bonner and Kaura (12) solubilized the two oxides in a 0.5M sodium cyanide solution which was left in contact with the sample for 90 to 120 minutes

and which has no effect on copper metal. Notwithstanding, Hurd and Clark (3) have studied the method and affirmed the extraction with sodium cyanide of the contained oxides nicely divided, as occurs in the commercial sample, originally a serious loss of copper, which depends on the quantity of copper (II) oxide present and the volume of the cyanide solution used.

On the other hand, the dissolution of copper metal with soluble cyanides is described by many authors. Feinberg (14) found that a three-percent potassium cyanide solution dissolved the native copper and cuprite (cuprous oxide). Mostovitch (15) found that a seven-percent (approximately 1N) potassium cyanide solution in a hydrogen atmosphere dissolved 85.86 percent of the copper in 24 hours, and Abetician (16) found that all the copper was dissolved.

In this work, the same conditions as stipulated by Bonner and Kaura (50 milliliters of 0.5M sodium cyanide in contact with the sample for 20 to 25 minutes) resulted in the following percentages of dissolution of copper and its oxides; using separate samples of 0.20 grams each and a contact time of 20 minutes:

15.37 percent of the copper was dissolved

79.10 percent of the cuprous oxide was dissolved

95.20 percent of the cupric oxide was dissolved

The studied methods do not advise to begin with the selective dissolution of copper (I) oxide. Rather to begin with the dissolution of the oxides is advantageous in the presence of copper metal, as in the example of the dissolution with cyanides

and as can verify the experimental numbers obtained in different conditions. The total dissolution of the oxides becomes inevitable, accompanied by a decrease of copper metal. It is good to insolubilize the copper to the point where it is transformed to copper sulfide, as Ubaldini and Guerrieri (11) did; the treatment ought to affect the oxides by the superficial formation of sulfide.

In the method which develops in this paper, the following considerations are made:

1. The determination of each one of the components is the result of smaller things, three different reactions.
2. Reactions which offer certainty of a stoichiometric displacement in the desired way are preferred; by example, a total oxidation to copper (II) is preferred to an extraction of one of the components.
3. The inevitable reactions, whose magnitude of displacement offers doubts, should be selected in order to maximize the most advantages of their application.
4. In order to prevent the error of a reaction in the other reactions, work each time with individual samples..
5. The techniques used should be easily handled and done with the aim of a minimum of reactions.
6. As in the determination of copper metal, it is most important that the copper metal should be in direct form.

One of the determinations is that of total copper. After the dissolution of this sample in concentrated nitric acid and

the elimination of nitrogen vapors with urea or sulfamic acid, the total copper can be determined very exactly with an iodometric determination.

Another determination carries out the oxidation of copper metal and copper (I) oxide to the cupric ion with one sample of a potential of sufficient redox elevation. The other possibility is the total reduction to copper metal as is used, for example, in the determination of the iron oxides with the help of hydrogen (18 and 19). But it already involves the use of the most complicated equipment which is necessary for the volumetric determination.

The third stage, following the statement of 6., above, is the direct determination of copper metal.

#### Determination of the Reducing Power of the Sum of Copper Metal and Copper (I) Oxide:

The determination of the reducing power of copper metal and copper (I) oxide is possible with any oxidizing agent with a redox potential of sufficient elevation. The oxidizing agent, moreover, ought to be stable for use as a liquid in an acid medium and in heat with an endpoint obtained in a rapid dissolution of the sample. Execution requires the use of cerium (IV), iron (III), and dichromate.

The experiments done in the present paper with cerium (IV) sulfate offer no proof of advantage over the use of dichromate due to the inconvenience of the formation of insoluble sediments;



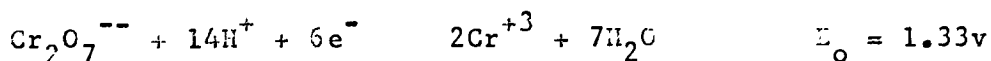
there is no major importance for this reaction.

In the experiment with ferric ammonium sulfate, no satisfactory results were obtained, as they had been with the use of dichromate. In 14 determinations the values obtained fluctuated between 86 and 95 percent of the theoretical oxidation when the dichromate was used.

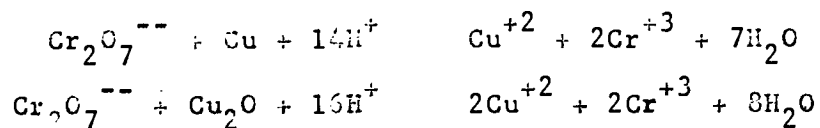
The techniques used are the following: Dissolve the sample of three milligrams copper and 30 milligrams copper (I) oxide in 25 milliliters 0.1N ferric ammonium sulfate and 20 milliliters five-percent sulfuric acid and agitate for 30 minutes in reduced temperatures, titrate the ferrous ion formed with 0.1N dichromate in the presence of 10 milliliters one-to-four phosphoric acid using diphenylamine sulfonic acid as an indicator.

#### Oxidation with Potassium Dichromate:

According to the potential of the redox of the half-reaction:



the reactions:



are realized in this stoichiometric form.

In practice, after a number of experiments, Seeger and Escobar obtained good results with the following technique.

According to the quantity of the sample (50-150 milligrams) treat with 40 to 60 milliliters of 0.1N dichromate, measure out 40 milliliters 6N sulfuric acid and heat with low agitation using

a magnetic stirrer until there is total dissolution of the sample, which should occur in less than 25 minutes. After the solution has cooled, measure out 10 milliliters of one-to-four phosphoric acid, two drops of 25-percent diphenylamine sulfonic acid as an indicator, and an excess of 0.1N iron (II) solution (20-25 milliliters). Titrate the excess ferrous ion with dichromate until the solution becomes violet.

The dichromate can also directly titrate the ferrous ion, but in the first case the endpoint is very neat.

The results of the determinations with this procedure are given in tables 2, 3, and 4.

(Results of Tables 2, 3, and 4:

Table 2. Oxidation of copper with 0.1N  $K_2Cr_2O_7$  (copper purity is 99.05%)

--  $\bar{x}$  = 98.67% of copper present was oxidized

Table 3. Oxidation of copper (I) oxide with 0.1N  $K_2Cr_2O_7$  (copper (I) oxide purity of 99.46%)

--  $\bar{x}$  = 99.33% of copper (I) oxide present was oxidized

Table 4. Oxidation of copper and copper (I) oxide with 0.1N  $K_2Cr_2O_7$  (copper purity of 99.05%; copper (I) oxide purity of 99.46%)

--  $\bar{x}$  = 98.50% of the copper and copper (I) oxide present was oxidized

Selective Oxidation of Copper Metal in the Presence of Its Oxides:

The selective oxidation of copper metal in the presence of its oxides, especially copper (I) oxide, is difficult to accomplish as the redox potentials for the system are very close, as shown in the beginning.

One reaction which works well with the copper metal is the oxidation by use of silver, as  $\text{Cu}_s + 2\text{Ag}^+ \longrightarrow \text{Cu}^{+2} + 2\text{Ag}_s$ , utilized to obtain the silver molecule by Walden's reduction (20). The reaction is realized because of stoichiometry -- the potential  $E_{\text{O Ag/Ag}^+} = +0.79\text{v}$ , and is of sufficient elevation for the total oxidation to copper metal, but also affects the copper (I) oxide.

Though thermodynamically the oxidation reaction should affect both the copper metal and copper (I) oxide with sufficient magnitude, copper (I) oxide possesses different kinetics such that the reaction only affects the copper metal which reacts with sufficient velocity to allow quantitative analysis, leaving the copper (I) oxide permanently unaltered.

Now formerly, the determination of manganese, developed in the Department of Analytical Chemistry (21), made possible the study of better conditions to provide for one of the reactions in an equilibrium.

a. Experiment with silver sulfate

In Scott's Handbook, Standard Methods of Chemical Analysis (10), he describes a method developed by E. F. Fitzpatrick in which he oxidizes the copper metal with a solution of

saturated and neutralized silver sulfate by boiling for 10 minutes. He does not present a table of values, and the method is the only well-known one which uses a direct determination of copper metal; he did numerous experiments with this method, but in the conditions described by the author, copper (I) oxide is also dissolved. Of 88.4 milligrams copper (I) oxide, 7.26 milligrams (8.21%) were dissolved; of 61.1 milligrams, 5.08 milligrams (8.32%) were dissolved; of 70.4 milligrams, 5.83 milligrams (8.28%) were dissolved. In the same time, not all the copper dissolved.

For copper treated with silver sulfate in 10 minutes of boiling, of 59.0 milligrams, 18.7 milligrams (37.9%) dissolved; of 94.0 milligrams, 39.1 milligrams (41.6%) dissolved; of 83.2 milligrams, 30.2 milligrams (36.3%) dissolved.

b. Experiment with silver nitrate

The silver nitrate is more accessible than silver sulfate and has greater solubility and so permits prepared solutions of greater concentrations. As there is no apparent motive for not using silver nitrate instead of silver sulfate, Scott performed experiments for studying the oxidizing action upon copper metal and copper (I) oxide, with the end result the range in which he obtained a very complete first oxidation and a minimal second oxidation. We ought, then, first investigate the influence of time and temperature upon the dissolution of two reducing components.

c. Influence of Time and Temperature

We used for every experiment a 0.1N silver nitrate solution prepared by simple dissolution of the salt in water with the pH controlled (no less than 5) in order to avoid the dissolution of the two oxides by the acid.

The experiments were done by the following procedure:

The sample was formed of 50 to 150 milligrams and left in contact with 30 milliliters of the 0.1N silver nitrate solution with mild agitation, then filtered, and the filtrate analyzed iodometrically with thiosulfate for the cupric ion. The silver iodide formed in these conditions does not present difficulties. Seeger and Escobar also performed experiments where the excess silver ions were titrated by Volhard's method (the results are not important), but the determination presents no advantages over the previous one, and requires an increased number of dissolutions. As in the preparation of silver nitrate, in order to maintain a constant pH, add a few drops of 0.1N sodium hydroxide until a precipitate just begins to form and use the filtered liquid; the iodometric method is also an unnecessary control of the silver dissolution.

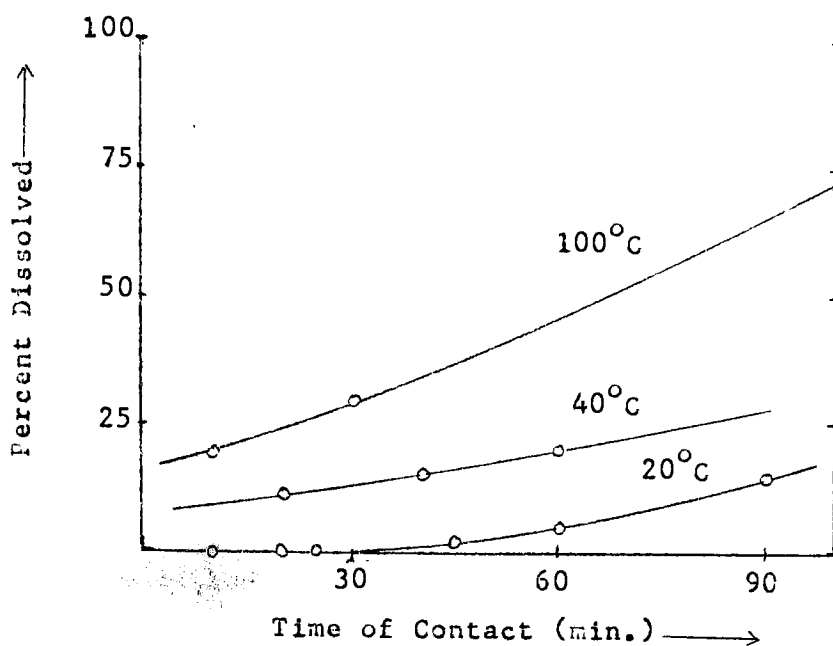


Fig. 1. Effect of time and temperature on the dissolution of  $\text{Cu}_2\text{O}$  with  $0.1\text{N AgNO}_3$

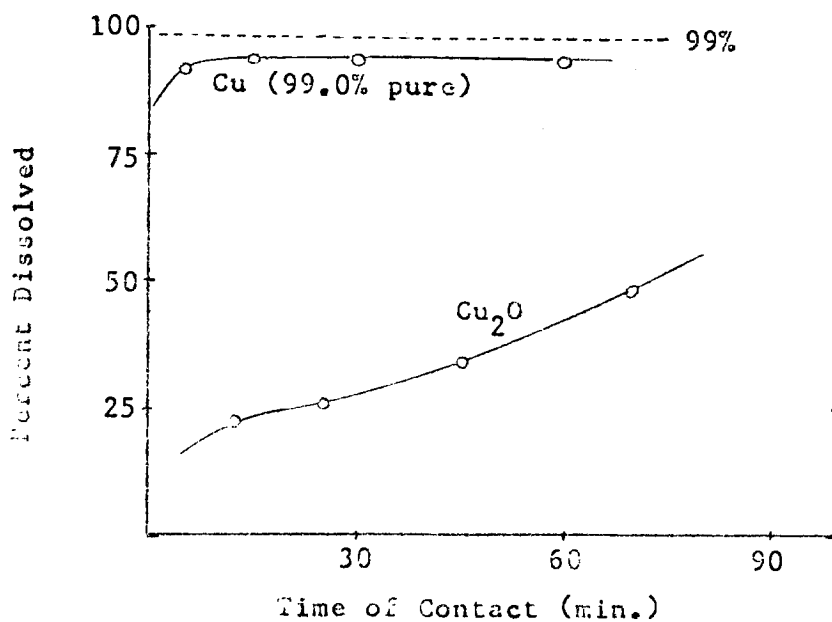


Fig. 2. Dissolution of Cu and  $\text{Cu}_2\text{O}$  with  $0.1\text{N AgNO}_3$  at  $20^\circ\text{C}$

In Fig. 1., the effect of time and temperature on the dissolution of copper (I) oxide within the sample is shown. The results indicate that only a temperature of 20°C and short time of contact results in a minimal dissolution of copper (I) oxide; the dissolution increases appreciably at higher temperatures. In the following experiments we studied the differences in the oxidizing action of silver nitrate upon copper metal and copper (I) oxide at a temperature of 20°C (Fig. 2.). We can observe that, in spite of the difference in the dissolution of the two components, the copper does not overtake to dissolve in stoichiometric form. In the previous results the sample was agitated occasionally; for constancy of this factor use a magnetic stirrer. The greatest agitation ought to contribute to a major dissolution of copper (I) oxide.

d. Dissolution experiments of silver nitrate and hydrated alcohol

The particles of copper present resistance and interference in view of those which easily remain floating on the surface of the solution. This can be a cause of the low values obtained in the treatment with silver nitrate which does not come up to react with every particle of the metal. A substantial condition which promotes the dampening of copper to favor a very complete reaction. With this end, we proceed with experiments in which the sample is previously dampened with ethyl alcohol before adding the 30 milliliters of 0.1N silver nitrate. Effectively, the dissolution of copper in

these conditions is most complete and comes to almost the theoretical ninety-nine-percent corresponding to the purity of the sample.

To also measure the particles of copper (I) oxide that float easily in the solution, the addition of alcohol has the interesting effect of diminishing the dissolution in an appreciable manner.

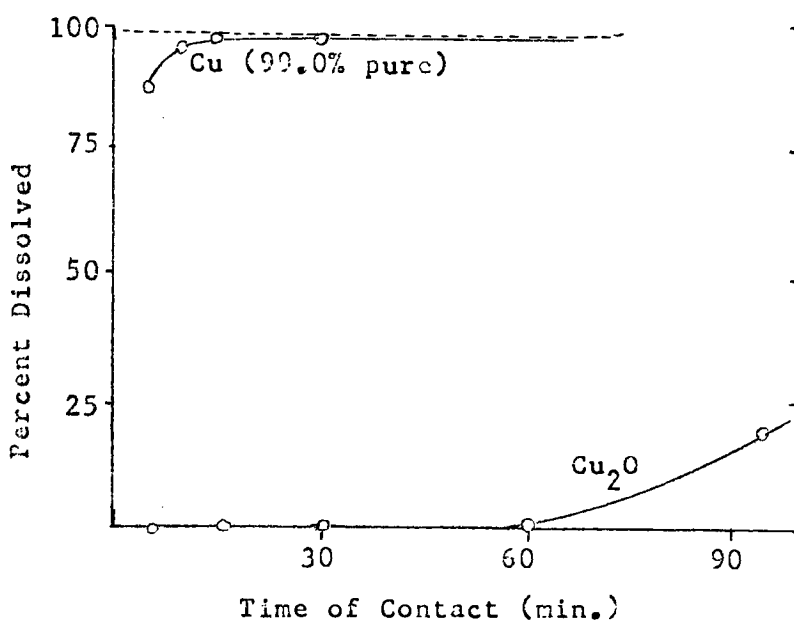


Fig. 3. Dissolution of Cu and Cu<sub>2</sub>O with 0.1N AgNO<sub>3</sub> in Hydrated Alcohol at 20°C

From Fig. 3., we can deduce the conditions under which it is possible to determine the copper metal without interference from cuprous oxide. To this end, we selected a contact time of 15 minutes for further determinations.

The difference in the magnitude of the dissolution of copper and of copper (I) oxide can be attributed to a different mechanism of dissolution. In the copper (I) oxide, the



dissolution. In the copper (I) oxide, the dissolution begins with the ionization  $\text{Cu}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{Cu}^+ + 2\text{OH}^-$ , favored because of the dielectric properties of dissolving; production of cupric ions after the oxidation displaces the equilibrium to the right.. Likewise, the equilibrium can be displaced to the right by adding hydrogen ions. This ionization is seriously reduced by the alcohol. In the copper, on the other hand, because the metal is insoluble in water, the dissolution is produced by direct oxidation of copper by silver ions upon the surface of the copper particles; this reaction is favored by the alcohol and the greater contact between hydrophobic copper and the hydrated silver ion.

The results of the dissolution of copper with silver nitrate in the presence of alcohol is contained in table 5.

Results of Table 5: time of contact is 15 minutes

copper is 99.05% pure

percent copper dissolved is  $x = 97.41\%$

In the presence of oxides the results are very good and fluctuate around the theoretical value.

Combining these two reaction studies, the oxidation of copper and copper (I) oxide and the selective oxidation of copper, it is possible to determine each one of the components in a sample of unknown composition.

#### Determination of Copper-Copper (I) Oxide-Copper (II) Oxide Components in Unknown Composition Sample

Weigh out three samples, each 0.200 grams.

1. determine the total copper by dissolution in concentrated nitric acid, eliminate the nitrogen vapors with urea or sulfamic acid and titrate iodometrically with 0.1N thiosulfate
2. determine the reducing power of copper and copper (I) oxide by taking them to dichromate in a sulfuric-phosphoric medium and titrating the excess dichromate with ferrous sulfate
3. selectively oxidize the copper metal with 0.1N silver nitrate in a solution of hydrated alcohol

For part 1, use a milliliters 0.1N thiosulfate

part 2, use b milliliters 0.1N dichromate

part 3, use c milliliters 0.1N thiosulfate,

then the copper (milligrams) =  $6.354\underline{c}$

cuprous oxide (milligrams) =  $\underline{b} - 7.154(2\underline{c})$

cupric oxide (milligrams) =  $\underline{a} - \underline{b} + 7.954\underline{c}$ .

With this method, the determination of each of the three components is greater than 97.4 percent.

## EXPERIMENTAL SECTION

### Solutions

#### a. total copper determination

1. weigh out 25 grams sodium thiosulfate pentahydrate and dissolve in distilled water; and 0.1 grams sodium carbonate and bring the volume to 1.000 liter. Let the solution set for 24 hours before using it to titrate.
2. weigh out 125 grams of ammonium thiocyanate and bring the volume to 250 milliliters.

b. copper and copper (I) oxide determination

1. use potassium dichromate, which has been dried at  $120^{\circ}\text{C}$  for two hours; weight out 4.904 grams potassium dichromate and dissolve it in 1.000 liter distilled water.
2. weigh out 27.8 grams ferrous sulfate septahydrate and 3.2 milliliters hydrochloric acid (density of 1.19) and bring the volume to 1.000 liter.
3. weigh out 2 grams barium diphenylamine sulfate and dissolve in 50 milliliters distilled water and saturate with carbon dioxide; when the liquid clears, use it as and indicator.

c. copper metal determination

1. weigh out 16.988 grams silver nitrate and dissolve it in 1.000 liter distilled water, and neutralize with 0.1N sodium hydroxide until precipitation begins.

-Burets

Use 25 and 50 milliliter burets with scale divisions of 0.1 milliliters, estimate fractions.

-Buret for Reduction of Silver

To the buret assigned to the ferrous dissolution, add to the bottom of the buret fiberglass and cover to a depth of about 3 centimeters with finely divided silver. The silver metal is to make an approximately ten-percent silver nitrate solution acidulous with nitric acid by precipitation by means of a layer of copper electrolyte. In order to eliminate the cupric ions present, wash the precipitate with dilute sulfuric acid until the

cupric ion is emitted. To measure the elapsed time the reducing column of silver is obscured because of the decomposition of silver chloride formed in the reduction of ferric ion by silver metal.

**-Titration Vessel**

Use 250 milliliter Erlenmeyer flasks and magnetic stirrers.

**-Determination by dissolution of sodium thiosulfate**

Weigh out 3.177 grams of copper metal in sheets and dissolve in 20 milliliters concentrated nitric acid; eliminate the nitrogen vapors with urea or sulfamic acid and flush successively with 500 milliliters acid. Liquify and cover with 25 milliliters (using pipet) and titrate with thiosulfate. The titration yields a solution of thiosulfate in milligrams of copper per milliliter.

**-Determination by titration of solution of ferrous sulfate**

The titration of the 0.1N ferrous sulfate with excess dichromate in a sulfuric-phosphoric acid medium in the presence of diphenylamine sulfonic acid as an indicator is used in the same way for the experimental determination of copper metal and copper (I) oxide.

**-Control of utilized reactions**

Copper metal, copper (I) oxide, and copper (II) oxide in this work are like Merck mixtures without indication of purity. In order to control their purity and its affect on the analysis of copper, we have used iodometric and electrolytic methods, as presented in tables 7, 8, and 9.

Results of Table 7: Copper metal found to be 99.05% pure by both iodometric and electrolytic methods.

Results of Table 8: To calculate the percentage of copper (I) oxide, multiply the copper value obtained (milligrams) by 1.1259; copper (I) oxide found to be 98.46% pure by both iodometric and electrolytic methods.

Results of Table 9: To calculate the percentage of copper (II) oxide, multiply the copper value obtained (milligrams) by 1.2518; copper (II) oxide was found to be 99.57% pure by the iodometric method, and 99.30% pure by the electrolytic method.

Table of values for Fig. 1.:

<u>Time(min.)</u>	<u>% Cu<sub>2</sub>O dissolved with 0.1N AgNO<sub>3</sub></u>	<u>Temperature</u>
10	----	
25	----	
25	0.11	
45	3.68	20°C
60	4.70	
90	14.80	
-----		
20	11.14	
40	15.90	40°C
60	20.10	
-----		
10	19.70	
30	30.04	100°C
100	73.00	

Table values for Fig. 2.: Dissolution with 0.1N  $\text{AgNO}_3$ ,  $20^\circ\text{C}$ 

<u>Time(min.)</u>	<u>%Cu</u>	<u>Dissolved</u>	<u>%Cu<sub>2</sub>O</u>
5	91.80		
12			22.80
15	93.90		
25			26.00
30	94.00		
45			34.00
60	93.80		
70			47.80

Table values for Fig. 3: Dissolution with 0.1N  $\text{AgNO}_3$  in hydrated alcohol at  $20^\circ\text{C}$ 

<u>Time(min.)</u>	<u>%Cu</u>	<u>Dissolved</u>	<u>%Cu<sub>2</sub>O</u>
5	87.72		-----
10	96.30		
15	97.40		-----
30	97.66		-----
60			3.10
95			19.90

## CONCLUSIONS

1. The analysis of copper metal-copper (I) oxide- copper (II) oxide mixtures presents great interest in metallurgy of the elements in numerous industrial processes. With a few methods described in the bibliography, one can obtain variable results, examples of which may be found in the present work.
2. The copper metal-copper (I) oxide-copper (II) oxide system is difficult to analyse volumetrically because of the small separation in redox potentials; this makes quantitative separation by redox reactions of one component without affecting the other components, producing dismutations, and yielding impossible results difficult.
3. In the present paper, the reactions are carried out on separate samples which may displace totally without adverse affects, like the dissolution and determination by iodometric means with dichromate.
4. In the selective oxidation of copper metal in the presence of copper (I) oxide -- a reaction not previously pursued -- we studied the conditions in which the oxidation of copper is facilitated and the oxidation of copper (I) oxide is diminished. This is obtained with a solution of hydrated alcohol with 0.1N silver nitrate which is left in contact with the sample for 15 minutes under agitation and room temperature.

5. It is possible to determine each component of the copper metal-copper (I) oxide-copper (II) oxide system by doing one different determination on each of three samples.
6. The method is easy to perform and presents the advantage of determining all three components, rather than just copper metal, as previously done.



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## FOOTNOTES

1/ The New York Times, April 10, 1978.

2/ Kodak Publication J-10, "Recovering Silver from Photographic Materials," 1972; p. 3.

3/ The price of copper is presently \$0.04 per troy ounce. The New York Times, April 10, 1978.

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7/ Dr. Ronald Francis, personal communication.

8/ Hillson and Ridgway, op. cit.

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22/ R. Bartonicek and M. Lukasovska, "A Potential - pH Diagram for the System Cu - NH<sub>3</sub> - Cl - H<sub>2</sub>O," Corrosion Science, 9, 35 (1969).

23/ Dr. Burt H. Carroll, personal communication.

24/ Dr. Ronald Francis, personal communication.

25/ Dissolve the emulsion in trypsin, remove the base, wash the grains with distilled water, decant off the excess water, and prepare a microscope slide.

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