

Determination of Residual Thiosulfate in Processed Film

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The Crabtree-Ross procedure, employing the reaction of thiosulfate with mercuric chloride to form a turbid solution is the usual test for residual thiosulfate in processed film. Qualitative tests showed that in this procedure part of the precipitate remains in the gelatin layer of the film, causing the reported concentration of thiosulfate to be too low. When residual thiosulfate was measured in the presence of image silver, the image silver contributed an additional component to the turbidity. A new test procedure was developed which also employs mercuric chloride as the precipitant but which reveals 2 to 3 times as much residual thiosulfate as does the Crabtree-Ross procedure. Residual silver causes the formation of additional turbidity which is determined as residual thiosulfate. A trace of gelatin is dissolved from the film during the thiosulfate test, the amount depending on film type. The trace of gelatin had a pronounced effect on the amount of turbidity. The addition of a known amount of gelatin to the test solution masked the effect of dissolved gelatin, making it possible to prepare one calibration curve for all types of film. A new method of measuring the residual silver in processed film was developed. A photoelectric nephelometer was used to measure the turbidity.

1. Introduction

The reaction of thiosulfate with mercuric chloride to form a precipitate is the basis for a turbidity test which has been used for the past 30 years to determine the residual thiosulfate in processed film. The test is known in the literature as the Crabtree-Ross hypo test [1].¹ In the test a sample of film is immersed in a solution of mercuric chloride and potassium bromide and the turbidity is compared visually or by a photoelectric instrument with that produced in standard solutions containing known amounts of thiosulfate.

Analytical results have been reported [3, 4] to indicate that the Crabtree-Ross test measures all of the residual thiosulfate in processed film. However, the analysis of such small quantities of thiosulfate by chemical methods is subject to considerable error. It has been suspected that some of the precipitate formed in the reaction of thiosulfate with mercuric chloride remains in the gelatin layer, giving low values for the thiosulfate content. Also the comparison or standard solutions in the Crabtree-Ross test are not always reproducible and sometimes vary as much as 50 percent for the 5 μg standard, depending on how rapidly the thiosulfate was mixed in the preparation of the solutions.

It has been shown that potassium bromide can eliminate all of the thiosulfate from film after fixation [5]. A new thiosulfate test procedure has been

developed in which the residual thiosulfate is extracted from the film by treating the sample in a solution of potassium bromide. The mercuric chloride is added after removal of the film sample. In the new procedure, any residual silver in the form of a silver thiosulfate complex is removed by the potassium bromide. The silver then reacts with the halide present in the test solution to form a precipitate which adds to the turbidity formed by the thiosulfate. The effect of gelatin on the turbidity in the thiosulfate test procedure was determined.

Qualitative tests were made to show that part of the precipitate remains in the gelatin layer when the Crabtree-Ross test procedure is used. The effect of the image silver on the turbidity in the Crabtree-Ross test procedure was also investigated. A new test method was developed for determining the residual silver in processed film by measuring the transmission density of a silver image developed from the silver in the residual silver thiosulfate complex.

2. Test Methods

The solutions and experimental procedures used in this investigation for determining the residual thiosulfate in processed film are given below. The films were 35 mm. The area of the film test sample was 1 in.² Round samples were punched from unperforated film with a special punch and rectangular samples were cut from perforated film using a metal stencil. Two or more specimens were tested for each determination of residual thiosulfate content. Two or more standard solutions were made in each run

¹ Figures in brackets indicate the literature references at the end of this paper.

to determine the turbidity for each thiosulfate concentration and prepare a calibration curve. The tests were made at room temperature (23 to 27 °C).

The processing solutions used in preparing the film samples were the same as those described in a previous publication [5]. Samples of 35 mm film 10 in. in length were developed 5 min, treated in a stop bath 30 sec, fixed in a fresh acid hardening bath or one containing 8 g of silver per liter, and washed in running tap water for selected times at different water temperatures to obtain a range of residual thiosulfate concentrations in the processed film. The thiosulfate-free film samples used in the tests were obtained by fixing in a fresh bath and removing the residual thiosulfate in the washing process—no thiosulfate eliminators were used. The thiosulfate concentrations are expressed in terms of anhydrous sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) in micrograms per square inch ($\mu\text{g}/\text{in.}^2$).

2.1. New Thiosulfate Test Procedure

Solution A₀

Potassium bromide..... 50.00 g.
Water to make..... 1 liter.

Solution A

Potassium bromide..... 50.00 g.
Water to make..... 980 ml.
Filter and add 0.10% gelatin solution... 20 ml.

Solution B

Mercuric chloride..... 50.00 g.
Water to make..... 1 liter.

Solution A should be stored in a refrigerator and brought to room temperature before use.

The solutions were made up with distilled water and filtered through highly purified filter paper. The mercuric chloride was dissolved at room temperature. The potassium bromide, mercuric chloride, and the sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) used in the thiosulfate standard solutions were of reagent quality, meeting ACS specifications. The gelatin was photographic grade.

The solutions were delivered from burets to 19 mm by 105 mm round cuvettes. The tip of the buret containing solution B was widened to permit delivery of 5 ml in about 5 or 6 sec. From the buret, 5 ml of solution A₀ or A was added to the cuvette. The test sample of film was folded twice with the emulsion side facing in and placed in solution A₀ or A for 15 min. The cuvette was agitated frequently during the immersion period. The sample was removed with a glass rod having a toe on the bottom end. The surface liquid was squeezed off as much as possible during removal. Then 5 ml of solution B was added from the buret and the cuvette was swirled immediately to insure rapid mixing of the solutions. The mixture was also stirred with the glass rod for a few seconds. The cuvette was wetted on the outside, wiped dry with soft tissue, and allowed to stand 30 min before the turbidity was measured.

Standard solutions were prepared by adding known amounts of sodium thiosulfate to 5 ml of solution A₀ or A, thoroughly mixing, adding 5 ml of solution B, and proceeding as described above in testing film. The standard solutions containing known amounts of thiosulfate were prepared as described in the American Standards Association method [2] for determining thiosulfate in processed film. No correction was made for the increase in volume of the test solution with the addition of the thiosulfate solution, since the error introduced is negligible.

2.2. Crabtree-Ross Thiosulfate Test Procedure

The following solution was made up with distilled water and filtered through highly purified filter paper:

Potassium bromide..... 25.00 g.
Mercuric chloride..... 25.00 g.
Water to make..... 1 liter.

The potassium bromide and mercuric chloride were of the same reagent quality as used above.

From a buret or pipet 10 ml of the above solution was added to a cuvette. The film sample was folded with the gelatin side in and immersed in the test solution for 15 min without agitation. Then the sample was removed, the solution was stirred with a glass rod, and the cuvette was allowed to stand 15 min before the turbidity was measured. The standard solutions containing known amounts of sodium thiosulfate were prepared and added as described in the American Standards Association method [2] referred to in section 2.1.

2.3. Turbidity Measurement

The turbidities of the test solutions were measured with a Coleman No. 9 nephelometer. In this instrument, a collimated beam of light from a tungsten lamp passes into the test solution, the light scattered at right angles to the exciting beam is detected by two photocells, and the output of the photocells is indicated on a meter. The nephelometer was calibrated by a Coleman turbidity standard of 74 units before each measurement. This standard did not change within a period of a year relative to other Coleman standards of 10, 18, 33, and 74 units. For readings above 130 units, the nephelometer was adjusted to make the standard of 74 units read 10 or 5 on the scale, making each unit on the scale equal to 7.4 or 14.8 units, respectively. The cuvettes were matched Coleman A grade. For the measurement, the cuvette was placed in a well containing sufficient distilled water to cover its three windows.

3. Results and Discussion

3.1. Effect of Time and Temperature on the Extraction of Thiosulfate From Processed Film

The treatment of processed microfilm and motion picture film for 15 min in solution A₀ at room temperature (23 to 27 °C) was found to be sufficient to

extract the residual thiosulfate and residual silver from the film sample. Clear (image-free) samples fixed in a fresh bath and in a bath containing 8 g of silver per liter were tested. Some of the samples were treated a second time in solution A₀ to determine if any measurable amount of thiosulfate remained. No thiosulfate was found in samples having a low residual thiosulfate concentration but 1 to 2 μg per in.² was found in microfilm and 1 to 5 μg per in.² was found in motion picture film having a residual thiosulfate concentration of 30 to 100 μg per in.² Most of the thiosulfate was removed during a 5-min treatment in solution A₀. Extending the time to 30 min did not yield more thiosulfate than a 15-min treatment. As an example of the rapidity of the removal of the thiosulfate from the film, one sample of microfilm, containing 29 μg of thiosulfate per in.² after fixation in a bath containing 8 g of silver per liter, tested 20 μg per in.² after treatment for 1 min in solution A₀. Any turbidity resulting from the residual silver adds to that formed by the residual thiosulfate and is determined in the new test procedure as thiosulfate.

Tests were made to determine the amount of residual thiosulfate extracted from film by distilled water. Clear (image-free) samples were treated in 5 ml of distilled water, removed, and 0.25 g of potassium bromide added to give a 5-percent solution of potassium bromide before the addition of the 5 ml of solution B. About 30 percent of the residual thiosulfate was extracted from samples of microfilm containing 8, 14, 17, 34, 54, and 59 μg of thiosulfate per in.² after fixation in a fresh bath. Only 1 to 3 μg of thiosulfate was extracted from samples of microfilm containing 14, 25, 31, 34, 44, and 46 μg of thiosulfate per in.² after fixation in a bath containing 8 g of silver per liter. The bromide ion in solution A₀ decomposed the residual silver thiosulfate complex making the thiosulfate and silver soluble.

The effect of temperature on the extraction of the residual thiosulfate by solution A₀ was investigated. Tests were made at room temperature and a lower temperature on the same strip of film at the same time. After extraction, the specimens at the lower temperature were brought to room temperature before the addition of solution B. One sample of microfilm extracted at 7 to 9 °C tested 14 μg of thiosulfate per in.² and at 26°, 17½ μg/in.²; and a second sample at 13 °C tested 13 μg/in.² of thiosulfate and at 26 °C, 15 μg/in.² Both samples had been fixed in a bath containing 8 g of silver per liter. From the above data it may be inferred that a change of 3 °C in solution A₀ would cause an error of about ½ μg of thiosulfate per in.²

3.2. Effect of Gelatin on the Turbidity in the Thiosulfate Test

Solution B was added to solutions of A₀ containing 5, 10, 20, and 40 μg, respectively, of sodium thiosulfate. Then the tests were repeated, except that 1-in.² samples of clear (image-free) thiosulfate-free film were immersed in solution A₀ for 15 min and

removed before the addition of the thiosulfate and solution B. The turbidities are shown in table 1 for different types of film and the above thiosulfate concentrations. For solutions containing more than 5 μg of thiosulfate, the turbidity of the solutions treated with film were much higher than the controls. The turbidities for microfilm specimens differed from those for motion picture film. The results suggested that the turbidity might be increased by an agent extracted from the film such as gelatin, causing a more highly dispersed precipitate. Turbid test solutions treated with film appeared bluer than those not treated. The turbidities in table 1 were reproducible to within 5 percent for each type of film. It appeared at first that a calibration curve would have to be prepared for each type of film, but this would have made the test procedure impractical.

Tests were then made to determine the effect of gelatin on the turbidity of the test solutions. Small concentrations of gelatin were added to solution A₀ containing known concentrations of sodium thiosulfate after which the required amount of solution B was added. It was found that traces of gelatin significantly increased the turbidity in the thiosulfate test solution. As little as 3 parts of gelatin in a billion caused a detectable change of the turbidity in the thiosulfate test solution!

TABLE 1. Effect of different films on the turbidity in the thiosulfate test when solution A₀ was treated with 1 square inch of image-free thiosulfate-free film

Thiosulfate added after removal of film	No film treatment. Data taken from calibration curve	Turbidimetric units				
		Microfilm			Motion picture film	
		A	B	C	A	B
<i>Micrograms</i>						
5-----	11	14	13	13	9	12
10-----	42	96	86	75	114	123
20-----	146	333	325	296	245	263
40-----	339	632	610	614	488	562

In order to evaluate the effect of gelatin concentration on turbidity, a 0.10-percent gelatin solution was made up as follows: About 10 g of photographic grade gelatin were heated in 600 ml of distilled water at 50 to 60 °C for 1 hr with frequent stirring. About 200 ml of the warm solution were filtered through 2 layers of highly purified filter paper. The solid content of the filtrate was determined by pipeting 10 ml into a tared 20 ml beaker, heating in an oven at 100±2 °C for 24 hr, and weighing the beakers and residue. From the weight of the solid residue in the 10 ml aliquot the volume of the filtrate containing 1 g of gelatin was calculated and this volume of filtrate was diluted to 1 liter with distilled water to obtain the 0.10-percent gelatin solution. A commercial food gelatin gave the same results as the above photographic gelatin, but it developed a fungus growth after storage for 8 weeks in a refriger-

ator, while the photographic grade has remained stable for 8 months in a refrigerator.

The effect of gelatin concentration on the turbidity in the thiosulfate test was determined for 10, 20, and 40 μg of sodium thiosulfate by adding different amounts of gelatin to solution A_0 . Solution A_0 was made up to 1000 ml less the volume of gelatin solution to be added, filtered, and the gelatin solution added. The gelatin solution was added after filtration to avoid any effect of the filter paper on the concentration of the gelatin. In the tests, the thiosulfate was added to solution A_0 containing gelatin, followed by solution B. In figure 1 the gelatin concentrations are plotted against turbidimetric units for the 3 thiosulfate concentrations. These curves show that very low concentrations of gelatin in the test solution (1 to 10 μg per 10 ml of test solution) have a large effect on measured turbidity in the thiosulfate test. Between 50 and 200 μg per 10 ml of test solution, however, the change in measured turbidity is very slight. The data in figure 1 suggest that the effects of different amounts of gelatin dissolved from different types of film might be eliminated by increasing the gelatin concentration in the test solution.

A concentration of 100 μg of gelatin in 5 ml of the extracting solution A_0 was selected for the new thiosulfate test procedure and is hereafter designated solution A. Tests were then made to determine if treatment of different types of clear (image-free) thiosulfate-free film in solution A would give the same turbidity for a given thiosulfate concentration. Samples of 1 in.² of film were immersed in solution A for 15 min and then removed before the addition of thiosulfate and solution B. Samples of three different microfilms and two motion picture films were tested at 5 thiosulfate concentrations (5, 10, 20, 40, and 80 μg per 10 ml of test solution). The measured turbidities for each concentration agreed within experimental error with the corresponding turbidities obtained for each of the above thiosulfate concentrations when solution A was not treated with a film. These results demonstrated conclusively that the effect on measured turbidity of gelatin dissolved from the film had been eliminated.

The nephelometer calibration curve shown in figure 2 was prepared by plotting measured turbidities as a function of thiosulfate concentration. The plotted values were an average of five or more determinations. In this new test procedure the rapid mixing of solutions, A and B, and the added gelatin formed a reproducible turbidity. The curve in figure 2 shows a sharp change between 6 and 8 μg of thiosulfate, but is linear from 9 to 100 μg . Figure 3 is an enlarged scale of a portion of figure 2 showing more clearly the sharp change in the calibration curve for the lower thiosulfate concentrations, those of chief concern in microfilm practice. In the Crabtree-Ross test procedure the turbidity readings for the standard solutions were not always reproducible and sometimes varied as much as 50 percent for the 5 μg standard. The rate of mixing of the thiosulfate in the test solution appears to affect the particle size of the precipitate.

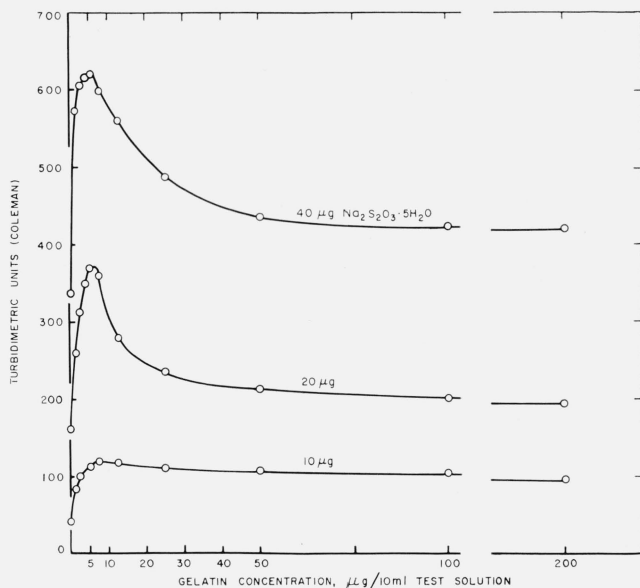


FIGURE 1. Effect of gelatin concentration on the turbidity formed by the reaction of mercuric chloride with thiosulfate after the addition of 5 ml of solution B to 5 ml of solution A_0 for 3 thiosulfate concentrations.

The concentration of sodium thiosulfate is shown on the curves.

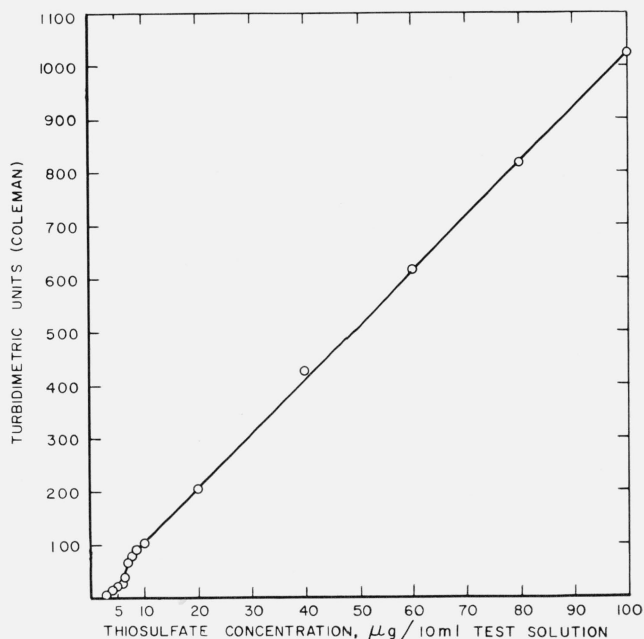


FIGURE 2. Nephelometer calibration curve showing the turbidity formed by the reaction of mercuric chloride with thiosulfate after the addition of 5 ml of solution B to 5 ml of solution A.

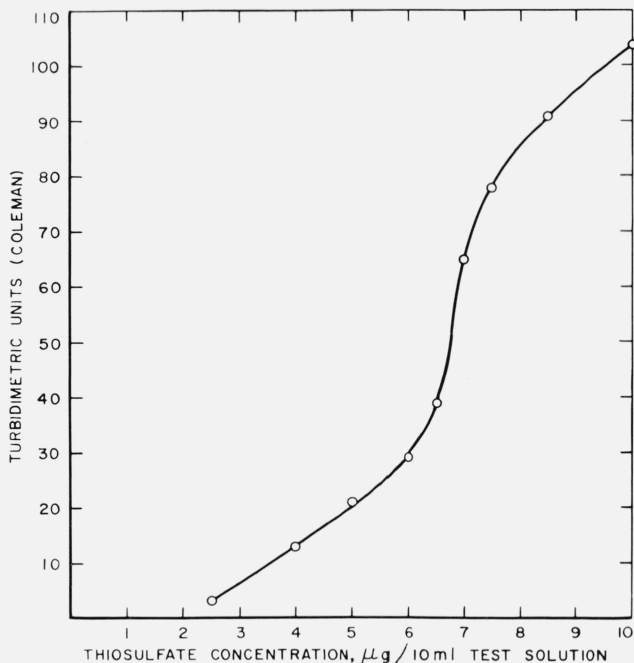


FIGURE 3. An enlarged scale of the calibration curve in figure 2 for the low sodium thiosulfate concentrations.

A trace of thiosulfate is held by the film in the thiosulfate test. It was found that the 1-in.² microfilm samples removed 0.03 to 0.05 ml of solution A. This loss was determined by weighing, in a tared glass stoppered bottle, three 1-in.² samples, before and after treatment in solution A. The loss of this amount of solution does not introduce any significant error, especially for the low residual thiosulfate concentrations. Tests were made by treating solutions of A containing 10 to 70 μg of thiosulfate with clear (image-free) thiosulfate-free microfilm to determine the error caused by removing the film sample from solution A. There was a loss of about 1 μg of thiosulfate per in.² regardless of the thiosulfate concentration. If the film sample was not removed before the addition of solution B, the sample sometimes interfered with the formation of the precipitate giving low turbidity values. Evidently the film absorbed the thiosulfate in the emulsion or on the film base. A correction of 1 μg might be applied. This correction is not significant for high thiosulfate concentrations, but it may be desirable to add it at concentrations below 20 μg per in.² for accurate determination of residual thiosulfate.

3.3. Comparison of the New Test Procedure With the Crabtree-Ross Test Procedure

Unexposed strips of 35-mm film, cut 10 in. in length, were developed, treated in a stop bath, fixed, and washed at different water temperatures and for different times to obtain image-free samples with a range of residual thiosulfate concentrations. The film strips were stored about 2 to 3 weeks before testing. Analysis of the residual thiosulfate content

was made by the two procedures at the same time on the same strip of film in each run. A calibration curve was prepared for the Crabtree-Ross test procedure and calibration curves for the new procedure are shown in figures 2 and 3. Samples of 1 in.² of film were cut or punched from the strip, alternate samples 1 and 3 being used in one procedure and 2 and 4 in the other. The duplicate in both procedures generally gave the same residual thiosulfate content, occasionally differing by $\frac{1}{2}$ to 1 μg in the low thiosulfate concentrations and 1 to 2 in the high. The average residual thiosulfate concentrations of the duplicate samples for the two procedures are given in table 2 for microfilm and motion picture film after fixation in a fresh bath and a bath containing 8 g of silver per liter. The thiosulfate concentrations for the new procedure were not corrected for the 1 μg of thiosulfate per in.² which is normally absorbed by the film. As shown in table 2, the new test procedure measured 2 to 3 times as much residual thiosulfate in processed film as the Crabtree-Ross test procedure.

TABLE 2. Comparison of residual thiosulfate concentrations obtained from the new thiosulfate test and the Crabtree-Ross thiosulfate test for the same sample of image-free film

Thiosulfate, micrograms per square inch					
Microfilm			Motion picture film		
Film brand	New procedure	Crabtree-Ross procedure	Film brand	New procedure	Crabtree-Ross procedure
Fixed in a fresh bath					
A-----	2	0	A-----	28	11
A-----	7	4 $\frac{1}{2}$	A-----	87	28
A-----	19	6 $\frac{1}{2}$	A-----	110	32
A-----	22	12	B-----	16	7
A-----	55	27	B-----	50	18
B-----	5	2	B-----	78	28
B-----	7 $\frac{1}{2}$	4			
B-----	19	10 $\frac{1}{2}$			
B-----	43	19			
B-----	90	42			
Fixed in a bath+8 g of silver per liter					
A-----	9 $\frac{1}{2}$	3	A-----	64	18
A-----	25	7	A-----	88	23
A-----	38	12	B-----	6 $\frac{1}{2}$	4 $\frac{1}{2}$
A-----	62	18	B-----	52	19
B-----	8	2 $\frac{1}{2}$	B-----	78	28
B-----	39	10			
B-----	70	18			

The lower residual thiosulfate concentrations measured by the Crabtree-Ross procedure may be attributed to the precipitation of some of the reaction product from the thiosulfate and mercuric chloride within the gelatin layer of the film. Thus, only a part of the thiosulfate is extracted to form a precipitate in the test solution. The presence of a precipitate in the gelatin layer after treatment in the Crabtree-Ross test solution was determined qualitatively by dissolving the gelatin and observing the turbidity of the solution. One-in.² samples from clear (image-free) microfilm containing 0 and 50 to 70 μg of residual thiosulfate were treated in the Crabtree-Ross test solution for 15 min, washed 10

min, and treated in 10 ml of a 1/2-percent solution of pancreatic enzyme at about 55 °C for 30 min to dissolve most of the gelatin. On visual inspection, there was considerably more turbidity in the enzyme solution for films containing residual thiosulfate than the one containing none. The precipitate in the enzyme solutions for films containing thiosulfate appeared bluish, but the blank was brownish gray. In other tests on microfilm having a high residual thiosulfate concentration, the turbidity remaining after solution of the gelatin roughly corresponded to the difference of residual thiosulfate content measured by the new test procedure and the Crabtree-Ross test procedure. In another test, 1-in. samples of clear (image-free) microfilm containing 17, 39, and 51 µg of thiosulfate were treated in 10 ml of the Crabtree-Ross test solution for 15 min, washed 10 min, and heated in 10 ml of a 5-percent solution of citric acid at 70 to 80 °C for about 1 hr to dissolve the emulsion. There was considerably more turbidity in the solutions for films containing residual thiosulfate than for the one containing none. The degree of turbidity was in the same order as the residual thiosulfate concentrations of the films whether estimated visually or measured with the nephelometer. Again the precipitate in the solutions for the films containing residual thiosulfate was bluish, but the blank was brownish to gray. When the above solutions were made alkaline with concentrated ammonium hydroxide, most of the turbidity in the sample containing no thiosulfate was eliminated while the solutions for films containing thiosulfate became quite bluish and the turbidities were in the same order as the residual thiosulfate contents when estimated visually or measured with nephelometer.

The presence of a precipitate in the gelatin layer was also shown by measuring the transmission density of the film sample after treatment in the Crabtree-Ross test solution. Clear (image-free) microfilm samples containing 0, 60, 70, 103, and 150 µg, of residual thiosulfate per in.² were treated for 15 min in the Crabtree-Ross test solution, washed 15 min, dried, and the transmission density of the samples measured. The untreated microfilm had a density of 0.07. The control sample having 0 µg of thiosulfate per in.² had a density of 0.08; 60 µg, 0.09; 70 µg, 0.10; 103 µg, 0.11; and 150 µg 0.13. The above data showed that a precipitate was present in the gelatin layer and its density increased from 0.01 to 0.05 above that of the control.

The above results explain why the Crabtree-Ross test procedure gave low values for the residual thiosulfate content in processed film. The gelatin effect on the turbidity was not investigated for the Crabtree-Ross test procedure, but it is probably small since the test solution is acid.

3.4. Effect of the Image Silver on the Crabtree-Ross Test Procedure

Residual thiosulfate contents determined by the new test procedure and the Crabtree-Ross test pro-

cedure in the silver image of processed film did not show the same difference as those determined for clear (image-free) film. Flash-exposed strips of 35-mm film, cut 10 in. in length, were developed, treated in a stop bath, fixed, and washed for different times to obtain samples with a range of residual thiosulfate concentrations. The thiosulfate tests were made within 4 hr after processing. The samples were tested by the two test procedures as described in section 3.3. The comparative results for a microfilm fixed in a fresh bath and a bath containing 8 g of silver per liter are given in table 3 for an image density of 5. The residual thiosulfate contents from the two test procedures were about the same for thiosulfate concentrations of 20 µg per in.² and higher, but the Crabtree-Ross test procedure gave higher thiosulfate contents in the range of 10 µg of thiosulfate per in.² Other tests on microfilm for image densities of 0.02, 0.72, 1.62, and 2.48 showed that the thiosulfate contents from the Crabtree-Ross procedure were about one-half the value obtained from the new procedure at a density of 0.02, but approached those from the new procedure as the image density increased. Thiosulfate contents indicated by both procedures became about equal at image densities of 4 to 5. The above results show that the Crabtree-Ross test procedure gives higher residual thiosulfate contents in the presence of image silver than in clear (image-free) film and this difference may result from the addition of silver to the test solution forming a turbidity of silver halide. In the Crabtree-Ross test procedure the silver in the image is bleached by the mercuric chloride, forming silver halide in the film. Any residual thiosulfate present could form a soluble silver thiosulfate complex which migrates into the test solution where it decomposes to form an additional turbidity of silver halide and is measured along with that formed by the reaction of thiosulfate with mercuric chloride.

TABLE 3. Comparison of residual thiosulfate concentrations obtained from the new thiosulfate test and the Crabtree-Ross thiosulfate test for microfilm having a density of 5.

Fixed in a fresh bath		Fixed in a bath +8 g of silver per liter	
New procedure	Crabtree-Ross procedure	New procedure	Crabtree-Ross procedure
Thiosulfate, µg/in. ²			
9.....	14.....	11.....	16.....
12.....	16.....	20.....	21.....
18.....	21.....	31.....	29.....
24.....	23.....	57.....	43.....

Different amounts of silver as silver nitrate were added to the Crabtree-Ross test solution and the turbidities measured. The standard silver solutions were made up and added by the same method used for the standard thiosulfate solutions. Figure 4 shows the calibration curve obtained by plotting the turbidimetric units against the silver concentration in the Crabtree-Ross test solution. The calibration curve showed that the turbidity of the silver halide varied linearly with the silver concentration and also

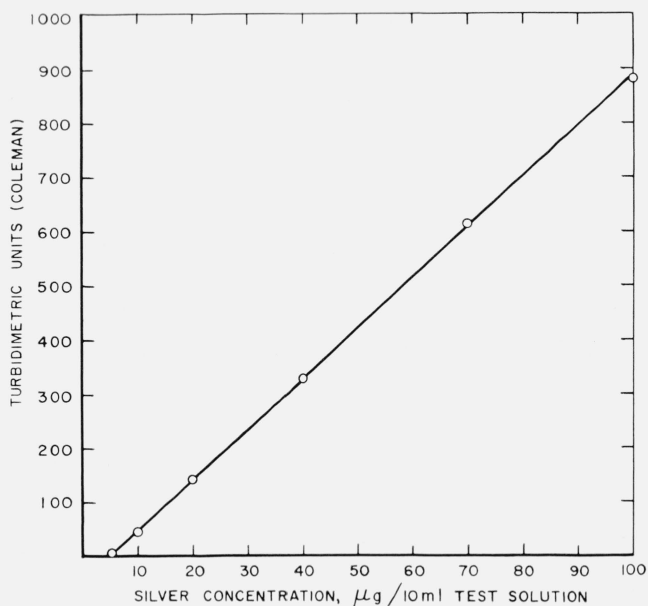


FIGURE 4. Calibration curve showing the turbidity formed by silver added as silver nitrate to 10 ml of the Crabtree-Ross thiosulfate test solution.

that a small amount of silver in the test solution would add appreciably to the turbidity in the thiosulfate test. For example, 20 μg of silver gave a turbidity reading of 142 as compared to 204 for 20 μg of thiosulfate shown in figure 2.

The effect of image silver on the turbidity in the Crabtree-Ross test procedure was further investigated by adding a known amount of thiosulfate to processed microfilm. A 0.05 ml solution containing 20 μg of sodium thiosulfate was pipeted onto 1-in.² samples of thiosulfate-free film punched from clear (image-free) strips and strips having an image density of 5, evaporated to dryness in an oven at 50 °C, and the residual thiosulfate determined at the same time by the two test procedures. Duplicate samples were used for each test in the clear and image areas. The amount of residual thiosulfate found by the new test procedure in exposed film (image density 5) was about the same as that found in clear film. In one run 19 μg of sodium thiosulfate were measured in the clear film and 17 μg in the exposed film; in a second run, there was 17 μg in the clear film and 16 μg in the exposed film. The above results showed that the residual thiosulfate was accurately determined in the presence of image silver if allowance is made for some loss of thiosulfate due to its tendency to react with silver to form silver sulfide. A trace of thiosulfate may also be oxidized by exposure to air during oven drying.

The amount of residual thiosulfate found by the Crabtree-Ross procedure in exposed film (image density 5) was more than that found in an unexposed film. In one run, 11 μg of sodium thiosulfate were measured in the clear film and 17 μg in the exposed film. In a second run, there were 12 μg in the clear

film and 19 μg in the exposed film. The results show that the exposed film tested higher in residual thiosulfate than the clear film, indicating that some of the silver in the bleached image had migrated into the test solution. The amount of thiosulfate found by the Crabtree-Ross test procedure in the clear film was less than was found by the new test procedure, due to the retention of some of the precipitate in the gelatin layer, as shown in section 3.3.

3.5. Test for Residual Silver in Processed Film

Residual silver in processed film is present as a silver thiosulfate complex. Appreciable amounts of residual silver may cause fading or yellowing of the image due to the formation of silver sulfide. A large concentration of residual silver in the film would indicate that the fixing bath contained too much silver for adequate removal of the silver thiosulfate complex during a normal washing procedure. A fresh fixing bath leaves no measurable residual silver in the film, but as silver accumulates in the fixing bath the tendency for the silver thiosulfate complex to remain in the film increases. The silver thiosulfate complex is more difficult to remove in the washing process than the thiosulfate. As the fixing bath approaches exhaustion the residual silver in the film becomes high and some of it remains after prolonged washing.

The test for residual silver in processed film [6] now in use is only qualitative. In this test the film is treated with a 0.2-percent solution of fused sodium sulfide and a yellow stain is produced if sufficient residual silver is present. Tests showed that at high residual silver concentrations a stain density of only 0.02 was produced in microfilm and 0.04 in motion picture film. A more sensitive and quantitative test was needed to indicate the amount of residual silver present in processed film. It has been shown [5] that a 0.1-percent solution of potassium iodide will react with the residual silver thiosulfate complex in processed film to precipitate silver iodide in the film. An investigation was made to determine if the silver in the silver thiosulfate complex could be converted to silver in the film and the amount of residual silver indicated by measuring the transmission density of the silver.

Samples of unexposed microfilm and motion picture film were fixed in a bath containing 8 g of silver per liter and washed for different times to obtain a range of residual thiosulfate concentrations accompanied by high residual silver concentration. It was found that the residual silver in the silver thiosulfate complex could be converted to a silver image by treating it in a developer containing 2 g of potassium iodide per liter, while exposing it to light. The optimum concentration of potassium iodide was 1½ to 3 g per liter of developer solution. If there was less than 1½ g of potassium iodide per liter, not all of the residual silver was converted to image silver and if above 3 g, some of the silver iodide passed into solution before development. For the test procedure, 2 g of potassium iodide per liter of developer solution was used. The following developers were used in the experimental work and gave the same results:

Developer A

Amidol, 2,4-diaminophenol dihydrochloride	5.0 g.
Sodium sulfite, anhydrous	30.0 g.
Potassium iodide	2.0 g.
Water to make	1 liter.

Developer B

Monomethyl <i>p</i> -aminophenol sulfate	3.1 g.
Sodium sulfite, anhydrous	45.0 g.
Hydroquinone	12.0 g.
Sodium carbonate, anhydrous	67.5 g.
Potassium iodide	2.0 g.
Water to make	1 liter.

The developer should be fresh and developer A should be made up just before use. The film sample was treated in the developer solution for 20 min with occasional stirring while exposed to a 100-w tungsten lamp located 6 in. from the surface of the solution, treated 1 min in a stop bath containing 12 ml of glacial acetic acid per liter, and washed 15 min. The densities of the silver images obtained for the different thiosulfate concentrations were very reproducible and correlated well with the thiosulfate concentrations. Silver in the image was identified qualitatively by dissolving the image in nitric acid and obtaining a precipitate of silver chloride after the addition of sodium chloride. Film samples of the silver image were immersed in water for 5 min and, after removal of the surface water, they were bleached over concentrated hydrochloric acid, dried, and redeveloped with light in developer A. The same density could be redeveloped, indicating that the image was silver.

One set each of unexposed 35 mm samples, cut 10 in. in length, from a microfilm and a motion picture film, respectively, were fixed in a bath containing 8 g of silver per liter and washed at 25° C for different times to obtain a range of residual thiosulfate concentrations. Then samples from strips having different residual thiosulfate concentrations were developed together in Developer A, one set being run for microfilm and one for motion picture film. The transmission densities of the developed samples were measured and the density of the film base subtracted from the density readings. The density of the silver image for each sample was plotted against its respective residual thiosulfate concentration and curves for the microfilm and the motion picture film are shown in figure 5. The data in the curves show that the silver density developed from the residual silver is proportional to the residual thiosulfate concentration for the lower thiosulfate concentrations and becomes nearly constant at the higher concentrations. The test method may be used to study the exhaustion of a fixing bath under controlled conditions, since the appearance of appreciable concentrations of residual thiosulfate will signal difficulty in removing the silver thiosulfate complex in the washing process.

In a microfilm with a residual thiosulfate concentration of 130 μg per in.², a density of 0.16 was obtained, while in the sodium sulfide test [6] a stain

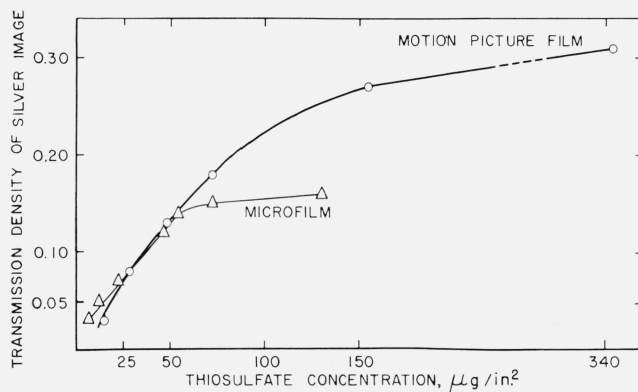


FIGURE 5. Density of silver image formed from the silver in the silver thiosulfate complex versus the thiosulfate concentration.

density of only 0.02 was found. In a motion picture film for a residual thiosulfate concentration of 154 μg per in.², a density of 0.27 was obtained while in the sodium sulfide test a stain density of only 0.04 was found. Clearly, the new test method is much more sensitive than the sodium sulfide test.

Tests were made for residual silver on microfilm and motion picture film fixed in a fresh bath by the new test method and no residual silver could be detected in microfilm samples containing up to 240 μg of residual thiosulfate per square inch and motion picture samples containing up to 500 μg per in.²

4. Summary

A new test procedure was developed for the determination of residual thiosulfate in processed film. This procedure indicates that the residual thiosulfate present in clear (image-free) processed film is 2 to 3 times that indicated by the Crabtree-Ross test procedure. In the course of development of the new test procedure, it was found that a trace of gelatin dissolved from the film sample produced a considerable change in the measured turbidity. The amount of gelatin dissolved depended on the type of film being tested. A separate nephelometer calibration curve might have been prepared for each type of film, but such a procedure would be impractical. Instead the effect of gelatin concentration in the test solution was investigated. The data showed that the addition of 100 μg of gelatin to the test solution would eliminate the effect of gelatin dissolved from the film, thus making it possible to prepare a single calibration curve for all types of film. For accurate results at low thiosulfate concentrations a correction of 1 μg per in.² should be added to the value obtained turbidimetrically.

In the new procedure the thiosulfate was extracted from 1 in.² of film by treatment in 5 ml of a 5-percent solution of potassium bromide solution containing 100 μg of gelatin, and 5 ml of a 5-percent solution of mercuric chloride was added after removal of the film sample. A nephelometer was used to measure the turbidities. A calibration curve was prepared at 25 °C \pm 2 °C. The temperature of the solutions

during the thiosulfate test should be the same as that at which the calibration curve was prepared.

Qualitative tests showed that some of the precipitate in the Crabtree-Ross test procedure remained in the film during the test, causing low values of residual thiosulfate concentration to be reported.

When a silver image containing residual thiosulfate was tested by the Crabtree-Ross test procedure, there was evidence that some of the image silver migrated into the test solution, adding a turbidity of silver halide.

The new test procedure may be used for determining the residual thiosulfate in film containing image silver. However, it has been shown [5] that the test for residual thiosulfate in film should be made with an image-free area of film.

A new test method was developed for determining the residual silver in processed film. The silver in the silver thiosulfate complex was developed to a silver image and its transmission density measured.

(Paper 67C3-134)

5. References

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