Determination of Residual Thiosulfate in Processed Black-and-White Films as Methylene Blue

ULM-0004/1

INTRODUCTION

This method is a modification of the procedure developed by Warburton and Przybylowicz for the determination of residual thiosulfate in processed black-and-white films. Thiosulfate is extracted from the processed film with a solution containing potassium phosphate and potassium iodide. The thiosulfate in the extract is reduced by borohydride to sulfide, which is then reacted with N,N-dimethyl-p-phenylenediamine in the presence of ferric ion. The product of this reaction, methylene blue, is measured spectrophotometrically.

Use of this method requires handling of potentially hazardous chemicals. Material Safety Data Sheets should be consulted for each chemical before use. These can be obtained from each chemical supplier.

PERECISION AND BIAS

Six processed black-and-white film samples were each analyzed, in duplicate, by four analysts, on each of two different days using two different instruments. All results reported below are expressed as micrograms $S_2O_3^{=}/cm^2$.

Customer Standard Deviation, $1s_c$

The customer standard deviation is an estimate of the variability a customer could expect when submitting a sample to any Photoprocessing Quality Services Laboratory, where any analyst could test the sample using any instrument on any day.

95 Percent Confidence Estimate

The 95 percent confidence estimate (calculated using the customer standard deviation) around a single test result will include the mean component concentration level 95 percent of the time.

Sample	n	Mean	$1S_c$	95% CE
TMG/RA-458	16	2.2	0.18	± 0.4
PFC/RA XO541	16	2.8	0.36	± 0.8
MRM-758	16	4.3	0.44	± 0.9
EHN-731	16	6.6	0.45	± 1.0
XRP-539	16	11.5	0.99	± 2.1
TMH/RA-443	16	13.8	0.54	± 1.2

Bias

Bias is a statistically significant deviation of the mean from the known analyte level at the 95 percent confidence level. Bias was not determined for this method, since the thiosulfate content of the samples was not known.

APPARATUS

All volumetric glassware should meet all “Class A” specifications, as defined by the American Society for Testing and Materials (ASTM) Standards E 287, E 288, and E 969, unless otherwise stated.

- Film punch, with 1 cm^2 die calibrated to nearest 0.001 cm^2
- Scintillation vials, polyethylene, with screw caps, 20-mL
- Repeating dispenser, 10-mL, Oxford Model 1063 or equivalent
- Pipettor, 5-mL, VWR CAT No. 53499-605
- Repeating dispenser, adjustable, 1-mL capacity, EM Science Optifix, or equivalent (4 required)
- Spectrophotometer, visible wavelength
- Spectrophotometer cells, 1-cm

REAGENTS

All reagents used are ACS Reagent Grade unless otherwise stated.

- Water, Type I Reagent – This method was developed using reagent water equivalent to or purer than Type I Grade, as defined in ASTM Standard D 1193. Other grades of water, e.g., reverse osmosis (RO), demineralized, or distilled water, may give equivalent results, but the effects of water quality on method performance have not been studied.
- Extractant
- Borohydride Reagent
- Acetone
- Ferric Chloride Reagent
- N, N-Dimethyl-p-phenylenediamine Sulfate (NND) Reagent

PROCEDURE

Preparation for Analysis

1. Zero the spectrophotometer vs air at 665 nm.
2. Transfer some of the extractant to the reservoir for the 10-mL repeating dispenser. Transfer the borohydride reagent, acetone, ferric chloride reagent and NND reagent to separate reservoirs for the 1-mL repeating dispensers. Flush each reagent dispenser by dispensing and discarding at least 10 aliquots of reagent before the first determination of the day.

Extraction of Residual Thiosulfate

1. Inspect the film to be tested for streaking, spots, and fingerprints. Choose an area free from these defects, at least 1" from the sheet edge, for the sample.

   Note: It is recommended that the analyst wear clean, white cotton gloves when handling film samples.

2. Cut a 1-cm² piece of the film to be tested, using a calibrated punch, and place the film piece in a clean, dry 20-mL plastic scintillation vial.
3. Dispense 10.0 mL of extractant into the vial, using the 10-mL repeating dispenser.
4. Cap the vial and allow to stand for 10 minutes, swirling occasionally (once every 1-3 minutes).

Formation and Measurement of Methylene Blue

1. Transfer 5.0 mL of the film extract from step 4 of the *Extraction of Residual Thiosulfate* procedure, to another clean, dry 20-mL plastic scintillation vial with the 5-mL pipettor.

   Note: All of the following reagent additions are made without delay between additions.

2. Add 0.25 mL of borohydride reagent and mix the solution.
3. Add 0.50 mL acetone and mix the solution.
4. Add 0.25 mL ferric chloride reagent. DO NOT MIX THE SOLUTION.
5. Add 0.25 mL NND reagent and immediately cap the vial.
6. Shake the vial vigorously for 1 minute, then immediately proceed to the next step.
7. Using a small portion of the solution (maximum 1.5 mL), rinse a 1-cm spectrophotometer cell, then fill the cell with the remainder of the solution. Rinse the outer surface of the cell with deionized water and wipe dry with a tissue. Ensure that gas bubbles are absent from the cell. If necessary, tap the cell to dislodge gas bubbles adhering to the cell walls.
8. Immediately read the absorbance at 665 nm vs air. (The absorbance should be measured within 1 minute or low results may be obtained.)
9. Analyze a reagent blank by following steps 1 through 8 of this procedure, substituting extractant solution for the film extract in step 1.

CALCULATIONS

$$\text{Net A} = A_s - A_b$$

Where:

A_s = absorbance of the sample solution at 665 nm
A_b = absorbance of the blank solution at 665 nm

$$\text{Residual thiosulfate } (S_2O_3^{=}),\ \mu g/cm^2 = \frac{m(\text{net A}) + b}{\text{Area}}$$

Where:

m = the slope obtained from the calibration equation
b = the intercept obtained from the calibration equation
Area = actual area of die on film punch (cm²)

The slope and intercept are obtained from a calibration equation derived according to *APPENDIX A*.

Note: Each laboratory should establish its own calibration equation based on analysis of standards. *APPENDIX A* details this calibration procedure. Due to differences among spectrophotometers, each equation may be different. A significant bias may occur from use of an equation which was not established on the spectrophotometer used for the test.

RESULTS

The results from this analysis should be reported to the nearest µg/cm².

APPENDIX A

Calibration Procedure

This appendix is used to establish the initial calibration, whenever equipment has been adjusted, or to recheck response every six months.

Preparation of Standards (prepare fresh daily)

1. Pipet 25.0 mL of standardized 0.1 N sodium thiosulfate into a 500-mL volumetric flask, dilute to volume with extractant, and mix. This is the first dilution.
2. Pipet 5.00 mL of the first dilution into a 250-mL volumetric flask, dilute to volume with extractant, and mix. This is the second dilution.
3. Referring to the table below, pipet the specified volumes of the second dilution into the corresponding volumetric flasks, dilute each to volume with extractant, and mix.

Volume of Second Dilution (mL)	Volumetric Flask (mL)	Approximate Concentration (μg/cm²)
1.00	200	0.56
2.00	100	2.2
2.00	50	4.5
4.00	50	9.0
7.00	50	15.7
10.0	50	22.4
15.0	50	33.6

Analysis of Standards

1. Analyze the standards by performing steps 1 through 8 of the *Formation and Measurement of Methylene Blue* procedure, substituting each standard for the film extract in step 1.
2. For the 0.0 μg/cm² standard, analyze a blank by performing step 9 of the *Formation and Measurement of Methylene Blue* procedure.
3. Repeat the analysis of each standard, including the blank, once.

Derivation of Calibration Equation

1. Calculate the actual concentrations of the standards, expressed as micrograms thiosulfate/cm² of film, as follows:

$$\mu g\ S_2O_3^{=}/cm^2 = \frac{N \times V1 \times 1121.3}{V2}$$

Where:

N = Normality of standardized $Na_2S_2O_3$, meq/mL
V1 = Volume of second dilution pipetted, mL
V2 = Volumetric flask size for standard, mL
1121.3 = 112.13 x 1000 x 0.001 x 10
112.13 = Formula weight of thiosulfate ($S_2O_3^{=}$) mg/meq
1000 = Factor to convert mg to μg
0.001 = Dilution factor, first and second dilutions (25 mL/500 mL x 5 mL/250 mL)
10 = Dilution factor, film extract (10 mL/1 cm²)

2. For each standard, calculate net absorbances as follows:

$$\text{Net } A = A_s - A_b$$

Where:

A_s = absorbance of the sample solution at 665 nm
A_b = absorbance of the blank solution at 665 nm

For the 0.0 μg/cm² standard (the blank), the net absorbance is 0.

3. Determine the calibration equation by least-squares linear regression of the μg/cm² thiosulfate and the corresponding net absorbance data obtained above. Include the data for the 0.0 μg/cm² standard. The regression equation should follow the form $y = m(x) + b$,

Where:

y = thiosulfate concentration in μg/cm²
m = slope of the calibration line (the relationship between thiosulfate concentration and absorbance at 665 nm)
x = Net A, the net absorbance at 665 nm
b = the intercept of the calibration line with the y (concentration) axis

Example Raw Data

μg $S_2O_3^{=}$/cm²	Absorbance	Net Absorbance
0 (blank)	0.0849	0
0 (blank)	0.0821	0
0.5561	0.1196	0.0361
0.5561	0.1205	0.0370
2.224	0.1895	0.1060
2.224	0.1823	0.0988
4.449	0.3000	0.2165
4.449	0.2986	0.2151
8.898	0.5175	0.4340
8.898	0.5088	0.4253
15.571	0.7841	0.7006
15.571	0.8007	0.7172
22.245	1.1138	1.0303
22.245	1.1058	1.0223
33.367	1.5542	1.4707
33.367	1.5661	1.4826

From the data above, a linear regression yields:

m (slope) = 22.467 μg $S_2O_3^{=}$/(cm² • net A)

b (intercept) = – 0.309 μg $S_2O_3^{=}$/cm²

μg $S_2O_3^{=}$/cm² = 22.467 (net A) – 0.309