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R 417

METHODS FOR DETERMINING THIOSULPHATE AND TETRATHIONATE IN PROCESSED BLACK-AND-WHITE PHOTOGRAPHIC FILM, PLATES AND PAPERS

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BRIEF HISTORY

The ISO Recommendation R 417, *Methods for Determining Thiosulphate and Tetrathionate in Processed Black-and-White Photographic Film, Plates and Papers*, was drawn up by Technical Committee ISO/TC 42, *Photography*, the Secretariat of which is held by the American Standards Association, Inc. (ASA).

Work on this question by the Technical Committee began in 1956 and led, in 1958, to the adoption of a Draft ISO Recommendation.

In August 1961, this Draft ISO Recommendation (No. 392) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies:

Belgium	Germany	Romania
Brazil	Italy	Sweden
Canada	Japan	Switzerland
Chile	Netherlands	U.S.A.
France	New Zealand	U.S.S.R.

One Member Body opposed the approval of the Draft:

United Kingdom.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in March 1965, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 417 March 1965

METHODS FOR DETERMINING THIOSULPHATE AND TETRATHIONATE IN PROCESSED BLACK-AND-WHITE PHOTOGRAPHIC FILM, PLATES AND PAPERS

This ISO Recommendation contains two parts:

PART I

METHOD FOR DETERMINING THIOSULPHATE IN PROCESSED BLACK-AND-WHITE PHOTOGRAPHIC FILM AND PLATES

1. GENERAL

Determination of the amount of thiosulphate in processed black-and-white photographic film and plates is of interest in connection with studies of rate, efficiency and effectiveness of washing, and in connection with the problems of image stability with respect to storage.

The method described in this ISO Recommendation is reasonably accurate and very sensitive to thiosulphate. It is not at all sensitive to sulphite, bisulphite or thionates, such as tetrathionates.

The effectiveness of this test diminishes with elapsed time after the film or plates are processed. Residual thiosulphate decomposes fairly rapidly into substances which are not detected by this test, but which may still cause image deterioration. For this reason, it is prescribed that this test should be performed within 24 hours after completion of the processing steps.

For black-and-white film and plates processed more than 24 hours prior to testing, test methods chosen to indicate the image fading tendency may be used.

The method of this ISO Recommendation is not intended for use with colour film, but experience indicates that it may have some applicability.

2. SCOPE

This ISO Recommendation provides a method for determining quantitatively the thiosulphate content of freshly processed black-and-white photographic film and plates and is intended for use in the control or evaluation of processing.

3. METHOD

3.1 Outline of the test

The test depends upon the production of a degree of turbidity or opalescence in the test solution which is related to the amount of thiosulphate present in the sample. A measured area of the sample is immersed for a sufficient time in a given volume of the test solution. At essentially the same time as the sample is immersed, comparison solutions are prepared by adding known quantities of thiosulphate solution of specified concentration to the required volume of test solution. When thiosulphate is present, a precipitate is formed which rises to the upper part of the test solution. After standing undisturbed for a given period of time, the tubes are agitated to distribute the precipitates uniformly. The turbidity of the sample tube is compared with the turbidity of the comparison tubes, and matching turbidities are found. Since the quantity of thiosulphate in any comparison solution is known, the amount in the sample is thus quantitatively determined.

3.2 Sensitivity of the test

The lower limit of sensitivity of the test is 0.001 mg of anhydrous sodium thiosulphate ($Na_2S_2O_3$) per 10 ml of test solution. The test will therefore indicate down to this quantity in 5 cm^2 (0.78 in^2) of film or plate. The approximate reproducibility is shown in the Table, page 6.

3.3 Test solution

Prepare the following test solution from reagent quality chemicals:

Test solution for thiosulphate

Distilled water (20 to 50 °C)	750.0 ml
Potassium bromide	25.0 g
Mercuric chloride	25.0 g
Distilled water to make in total	1.0 litre

CAUTION: POISONOUS SOLUTION !

Allow the solution to stand overnight, before use. Keep in a glass-stoppered bottle, away from strong daylight or excessive heat. If a precipitate forms, the solution should be decanted or filtered. A completely clear solution is required for use.

3.4 Thiosulphate solutions for preparing comparison solutions

Weigh 1.570 ± 0.010 g of crystalline sodium thiosulphate ($Na_2S_2O_3 \cdot 5H_2O$) of reagent quality. Dissolve in about 750 ml of distilled water at room temperature, then add distilled water to make 1 litre and mix well. This is equivalent to a 1: 1000 solution of anhydrous sodium thiosulphate. Remove a 200 ml portion of this 1: 1000 solution and dilute with distilled water to 1 litre to make a 1: 5000 solution and, similarly, dilute a 50 ml portion of the original solution to 1 litre to make a 1: 20 000 solution. Dilute 500 ml of the 1: 20 000 solution to 1 litre to make a 1: 40 000 solution. For accurate work, volumes should be measured with pipettes and volumetric flasks. The original 1: 1000 solution may be used for 5 or 6 days and should be kept in a glass-stoppered bottle. The more dilute thiosulphate solutions should be prepared within two hours of use.

3.5 Test procedure

3.5.1 *Test tubes.* Select for uniformity and clarity a number of glass vials or test tubes approximately 18 mm × 150 mm (0,71 in × 5.91 in), so that a 10 ml volume of solution gives essentially the same height in each. Ordinarily, to determine an unknown thiosulphate content, 8 tubes are required for the comparison solutions, with an additional tube for each sample tested.

3.5.2 *Preparation of film or plate sample.* Cut accurately a 5 cm² (0.78 in²) ± 5 per cent sample of film or plate from a representative image area (see Appendix to Part I, page 9). Place the sample in one of the tubes in a manner which allows free access of test solution to both sides of the film or plate. This sample should be taken from a film or plate which has been processed within the preceding 24 hours.

3.5.3 *Performance of the test.* Into each film or plate sample tube and the 8 comparison tubes introduce 10 ml of the perfectly clear test solution (prepared as in clause 3.3).* Introduce into the comparison tubes the respective volumes, indicated in the Table, page 6, of 1: 1000, 1: 5000, 1: 20 000, and 1: 40 000 sodium thiosulphate solutions (prepared as in clause 3.4), using either a 1 ml measuring pipette having 0.1 ml division marks or an automatic pipette suitable for dispensing 0.1 ml quantities accurately. The thiosulphate solutions should be delivered directly into the test solution, employing equipment and technique which prevent retention of drops on the tip of the pipette or the wall of the tube. The volume of thiosulphate solution added to 10 ml of test solution should not exceed 0.2 ml. One of the 8 tubes should be free of thiosulphate in order to serve as a blank.

Allow the film or plate sample and the comparison tubes to stand without agitation for 15 min (minutes). Then agitate to distribute uniformly any precipitate which may have formed. Remove the film or plate before evaluation.

NOTE.—If considerable thiosulphate is present, 5 min instead of 15 min may be permitted to elapse before the samples are agitated and examined.

3.5.4 *Evaluation of turbidity.* Compare the turbidity or opalescence in the solutions by viewing toward a black or dark background, with the test tubes uniformly illuminated from the side opposite to that of the observer, and with the light source elevated or depressed from the line of sight by 30 to 90°. A preferable light source for direct visual comparison consists of a daylight-type fluorescent lamp fitted with an opaque shield or placed in an illuminator to prevent direct light from reaching the observer ** (see Fig. 1, 2 and 2 (a), page 10, for suggested illuminators). Light from a bright sky also may be used. After obtaining a match of turbidity or opalescence, the corresponding quantities of sodium thiosulphate in microgrammes per square centimetre, microgrammes per square inch and milligrammes per square inch of the film or plate sample are found by reference to the Table, page 6. The 8 comparison solutions specified in the Table are sufficient for most purposes, but, for determination of intermediate quantities in a given range, other comparison solutions can be prepared, as suggested in the Note following the Table, or the size of the film or plate sample can be changed.

3.5.5 *Films or plates with layers on both sides.* Values for thiosulphate content as taken from the Table should be divided by two for films or plates having

(1) image layers on both sides, or

(2) an image layer on one side and a similar non-image layer on the reverse side.

* An automatic pipette is desirable for dispensing this poisonous solution. The equipment chosen should deliver precisely the same quantity each time.

** For readings made by instrumental methods, such as in photoelectric instruments, the use of a mercury vapour lamp in a housing is permitted as an alternative light source.

3.5.6 *Film or plate sample size, when excessive thiosulphate content is found.* Determination of thiosulphate content in excess of that provided for in the Table is seldom of interest. However, films or plates having such higher content can be tested by using 0.5 cm^2 (0.08 in^2) instead of 5 cm^2 (0.78 in^2). The corresponding thiosulphate content will then be 10 times that of a given value shown in the Table. Comparison solutions containing greater quantities of thiosulphate than the maximum shown in the Table should not be used, since the turbidity differences gradually diminish with addition of the thiosulphate above the maximum quantity shown.

Table.—Volumes of sodium thiosulphate solutions required to give varying degrees of turbidity for comparison

(The volumes are calculated for 5 cm^2 (0.78 in^2) film or plate samples and 10 ml of test solutions for thiosulphate).

Thiosulphate solution to be added	Concentration of thiosulphate solution to be used	Content of thiosulphate as anhydrous sodium thiosulphate ($Na_2S_2O_3$)		
millilitres		Micrograms per square centimetre	Micrograms per square inch	Milligrammes per 5 square centimetres (0,78 square inch)
—	—	Zero	Zero	Zero
0.1	1 : 40 000	0.5 ± 0.16	3.2 ± 1.0	0.0025 ± 0.001
0.1	1 : 20 000	1.0 ± 0.2	6.3 ± 1.0	0.005 ± 0.001
0.2	1 : 20 000	2.0 ± 0.4	12.5 ± 2.0	0.01 ± 0.002
0.1	1 : 5000	4.0 ± 0.8	25.0 ± 5.0	0.02 ± 0.005
0.2	1 : 5000	8.0 ± 1.6	50.0 ± 10.0	0.04 ± 0.010
0.1	1 : 1000	20.0 ± 4.0	125.0 ± 25.0	0.1 ± 0.025
0.2	1 : 1000	40.0 ± 8.0	250.0 ± 50.0	0.2 ± 0.050

NOTE.—Values for thiosulphate content between any two shown in the last three columns can be obtained by the use of volumes intermediate to those shown in the first column or by employing thiosulphate solutions of concentrations intermediate to those given in the second column.

PART II

METHOD FOR DETERMINING THIOSULPHATE AND TETRATHIONATE IN PROCESSED PHOTOGRAPHIC PAPERS

1. GENERAL

Determination of the amount of residual thiosulphate in processed photographic paper prints is of interest in studies of thoroughness of fixation, rate, efficiency and effectiveness of washing, and in connection with the problems of image stability with respect to storage.*

The determination of tetrathionate which may be formed by mild oxidation of thiosulphate is of value in studies of " hypo eliminators " and also of interest in studies of image stability during storage. Tetrathionates (for example, sodium tetrathionate, $Na_2S_4O_6$), like soluble thiosulphate, can cause sulphiding of the silver image during humid storage conditions.

The method described in this ISO Recommendation is very sensitive, reasonably accurate, and convenient to use. It determines soluble or insoluble thiosulphate, together with any tetrathionate which may be present.

2. SCOPE

2.1 Processed and washed prints

This ISO Recommendation provides a method for quantitatively determining the thiosulphate content of processed photographic paper prints. The method is intended for use in the selection of prints with reference to their probable permanency and in the control or evaluation of processing.

2.2 Prints treated with hypo eliminators

The method given in this ISO Recommendation is also valid and preferable as a means for determining any residual thiosulphate (and tetrathionate) in prints which have been treated with hypo eliminators. Thus, the effectiveness of a given hypo eliminator can be determined.

3. METHOD

3.1 Principle of test

The test given in this ISO Recommendation depends upon the production of insoluble brown silver sulphide in the print itself by the quantitative reaction between the thiosulphate or tetrathionate and silver nitrate (silver ion) occurring in situ, when the print is bathed for 4 min in an acid solution, containing an excess of a soluble silver salt. To prevent possible subsequent darkening of the treated area, the treatment is followed by bathing in a solution of sodium chloride to completely convert the excess silver nitrate into insoluble white silver chloride, removing the silver chloride in a suitable fixing solution, and finally washing and drying. The transmission density of the treated area is then read.

The transmission density of the untreated area is read and subtracted from that of the treated area. The resulting value representing the transmission density of the silver sulphide is compared with the standard curve of Figure 3, page 12, from which the corresponding equivalent content of thiosulphate or tetrathionate as $Na_2S_2O_3$ in milligrammes per 5.0 cm^2 (0.78 in^2) is found. The method is valid for papers between 0.07 mm (0.0026 in) and 0.48 mm (0.0190 in) in thickness.

3.2 Sensitivity of the test

With ordinary care, it is possible to determine quantities of thiosulphate in photographic prints as low as 0.003 mg per 5.0 cm^2 (0.78 in^2), as $Na_2S_2O_3$. The visual threshold of the test appears to be about 0.002 mg per 5 cm^2. Quantities up to 0.3 mg per 5 cm^2 (0.78 in^2) are indicated in the standard curve of Figure 3, page 12.

* See also ISO Recommendation R 421, *Method for indicating the stability of the images of processed black-and-white photographic films, plates and papers.*

3.3 Test solutions

The following solutions are required. In stoppered bottles they keep for at least 6 months at 20 °C (68 °F). Unused solutions should be employed for each set of tests.

Solution A	Water	750.0 ml
	Acetic acid (glacial)	30.0 ml
	Silver nitrate	10.0 g
	Water to make in total	1.0 litre

Store in a brown or blackened glass-stoppered bottle away from strong light.

Solution B	Water	750.0 ml
	Sodium chloride	45.0 g
	Water to make in total	1.0 litre
Solution C	Water	750.0 ml
	Sodium sulphite (anhydrous)	15.0 g
	Sodium thiosulphate (crystalline)	45.0 g
	Water to make in total	1.0 litre

3.4 Blue-green (cyan) filter

The blue-green (cyan) filter for use in making the visual transmission densitometric readings should be similar to one having the following transmission characteristics:

Wavelength	Transmittance %	Wavelength	Transmittance %
400	0.44	500	55.8
410	0.36	510	50.9
420	0.63	520	42.1
430	3.63	530	30.5
440	13.1	540	18.6
450	25.4	550	8.99
460	36.5	560	3.59
470	46.5	570	0.80
480	53.6	580-680	Nil
490	56.8	690	0.18
		700	1.60

3.5 Test procedure

To determine the thiosulphate (or tetrathionate) in the paper, a non-image portion (unexposed margin, etc.) at least 0.6 cm × 2.5 cm (¼ in × 1 in) in size is removed and approximately one-half of it dipped and allowed to remain submerged or the whole immersed*, with occasional agitation, in an excess of Solution A for 4 min, then totally immersed with treatment successively in Solution B for 4 min and Solution C for 4 min, washed 5 to 10 min, and dried. In tests of batch washing, unexposed paper of the same mass and general size processed with the lot can be used to give representative tests, provided the agitation is uniform.

Following the preparation of the print samples for indication of thiosulphate, the transmission densities of corresponding treated and untreated samples are determined by means of a visual transmission densitometer. All readings for the purpose of this ISO Recommendation are made using a suitable blue-green (cyan) filter placed over the eyepiece of the densitometer. The filter should be similar to that described in clause 3.4. If other types, such as photoelectric densitometers, are employed, specific calibration curves should be determined. Procedure for obtaining the necessary calibration data for such other types of densitometers is given under reference 6 of Bibliography, page 11.

The difference between the density readings of the treated and untreated areas is the visual transmission density (through the filter) or the silver sulphide produced by the thiosulphate (or tetrathionate) in the paper and is a quantitative measure of the thiosulphate which the paper contained. The corresponding thiosulphate content in terms of anhydrous sodium thiosulphate ($Na_2S_2O_3$) in milligrammes per 5.0 cm^2 (0.78 in^2) is obtained by reference to the standard curve in Figure 3, page 12.

* When print samples are totally immersed in Solution A, agitate them using rubber gloves, a glass rod or clean print tongs of inert material (stainless steel, plastic or lacquered wood), so as not to allow the silver nitrate solution to contact the hands, otherwise black silver stains will be produced.

APPENDICES

for informative purposes only

APPENDIX TO PART I
EFFECT OF DENSITY OF SAMPLE

Careful users of the method given in this ISO Recommendation have observed that at low thiosulphate content, more thiosulphate is sometimes indicated by the test, when the samples are taken from areas of high silver density as compared with low density. For most purposes, the effect is insignificant, unless the density is greater than 2.0 in more than 25 per cent of the area. In order to avoid possible error from this source, it is prescribed in clause 3.5.2 that the sample of film or plate for test should be taken from a representative image area. Thus, the sample should not include any greater or lesser area of high or low density than is normal for the type of subject matter.

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