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Photography — Determination of residual thiosulfate and other related chemicals in processed photographic materials — Methods using iodine-amylose, methylene blue and silver sulfide

Photographie — Détermination du thiosulfate résiduel et d'autres produits chimiques dans les produits photographiques traités — Méthodes à l'iode-amylose, au bleu de méthylène et au sulfure d'argent

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Contents

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 18917 was prepared by Technical Committee ISO/TC 42, *Photography*.

This first edition cancels and replaces the second edition of ISO 417 (ISO 417:1993) which has been technically revised. As in the second edition, it includes the iodine-amylose and methylene blue procedures, but the reactant levels have been modified to provide more reproducible results.

Annexes A, B, C and D of this International Standard are for information only.

Introduction

This International Standard is one of a series of specifications on photographic processing. Individuals without a working knowledge of analytical chemistry may occasionally use this International Standard. Hazard warnings have therefore been given using a system of symbols with letter codes designating the nature of the hazard. More detailed information regarding hazards, handling and use of these chemicals may also be available from the manufacturer.

Determination of residual thiosulfate and its decomposition products is of use in appraising the adequacy of washing and therefore the permanence of the silver image on photographic films, plates and papers. Inadequate washing can cause a loss in image density and the formation of stain in low-density areas. These deleterious effects are accelerated by improper storage conditions.

Determination of residual thiosulfate and related compounds, by itself, is not sufficient to insure the permanence of photographic records. Long term or archival storage requires proper attention to enclosure materials, storage environment, and the like. These considerations are specified in ISO 3897, ISO 5466, ISO 6051 and ISO 10602.

Photography — Determination of residual thiosulfate and other related chemicals in processed photographic materials — Methods using iodine-amylose, methylene blue and silver sulfide

1 Scope

1.1 This International Standard specifies test methods for the determination of residual thiosulfate and other related chemicals in processed photographic materials.

1.2 This International Standard applies to silver halide/gelatin products that have been processed with a final thiosulfate fixing bath and a water wash. This International Standard does not apply to stabilised black-and-white products, thermally processed films, or instant-type products. The procedures given in this International Standard measure residual thiosulfate, and the silver densitometric method measures residual related polythionate materials as well. Measurements carried out by the procedures in this International Standard may, within the limitations stated in annexes A and B, correlate with the image stabilities of processed photographs.

1.3 Film or plates with photographic-sensitive layers on both sides, or with a photographic sensitive layer on one side and a gelatin backing layer on the reverse side, may contain approximately twice as much thiosulfate after processing as samples having a coating on one side only. This situation will be true for materials for which residual thiosulfate is determined by the iodine-amylose or methylene blue procedures.

NOTE For the method of reporting such results, see figure 1, example 2.

1.4 The iodine-amylose can be used with fibre-based paper, resin-coated paper, films and plates. It is the method to be used with films and papers containing incorporated developing agents.

1.5 The methylene blue method can be used with fibre-based paper, resin-coated paper, films and plates but not with films and paper containing incorporated developing agents.

1.6 The silver sulfide densitometric method measures thiosulfates, polythionates and all other residual chemicals in a processed product that react with silver ion to form a silver "stain" under the conditions of the test.

1.7 A tabulated summary of methods, scope, etc. is given in annex B.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 5-3:1995, *Photography — Density measurements — Part 3: Spectral conditions.*

ISO 10349-1:1992, *Photography — Photographic-grade chemicals — Test methods — Part 1: General.*

3 General requirements

3.1 Safety and hazard concerns

3.1.1 Handling

Reagents shall be handled in conformity with health and safety precautions as shown on containers or as given in other sources of such information. Proper labelling of prepared reagents includes chemical name, date of preparation, expiration date, restandardization date, name of preparer, and adequate health and safety precautions. The discharge of reagents shall conform to applicable environmental regulations.

3.1.2 Hazard warnings

Some of the chemicals specified in the test procedures are caustic, toxic or otherwise hazardous. Safe laboratory practice for the handling of chemicals requires the use of safety glasses or goggles, rubber gloves and other protective apparel such as face masks or aprons where appropriate. Specific danger notices are given in the text for particularly dangerous materials, but normal precautions are required during the performance of any chemical procedure at all times.

The first time that a hazardous is noted in the test procedure, the hazard shall be indicated by the word “DANGER” followed by a symbol consisting of angle brackets "〈 〉" containing a letter which designates the specific hazard. A double bracket "〈〈 〉〉" shall be used for particularly perilous situations.

In subsequent statements involving handling of these hazardous materials, only the hazard symbol consisting of the brackets and letter(s) shall be displayed. Furthermore, for a given material, the hazard symbols shall be used only once in a single paragraph.

Detailed warnings for handling chemicals and their diluted solutions are beyond the scope of this International Standard.

Employers shall provide training and health and safety information in conformance with legal requirements.

The hazard symbol system used in this International Standard is intended to provide information to the users and is not meant for compliance with legal requirements for labelling, as these vary from country to country.

It is strongly recommended that anyone using these chemicals obtain from the manufacturer pertinent information about the hazards, handling, use and disposal of these chemicals.

3.1.3 Hazard information code system

〈B〉 Harmful if inhaled. Avoid breathing dust, vapour, mist or gas. Use only with adequate ventilation.

〈C〉 Harmful if contact occurs. Avoid contact with eyes, skin or clothing. Wash thoroughly after handling.

〈S〉 Harmful if swallowed. Wash thoroughly after handling. If swallowed, obtain medical attention immediately.

〈〈S〉〉 May be fatal if swallowed. If swallowed, obtain medical attention immediately.

〈F〉 Will burn. Keep away from heat, sparks, and open flame. Use with adequate ventilation.

〈O〉 Oxidizer. Contact with other material may cause fire. Do not store near combustible materials.

The flammable warning symbol, 〈F〉, shall not be used for quantities of common solvents under 1 litre.

3.2 Reagents

Reagents used in the test procedures shall be certified reagent-grade chemicals and shall meet appropriate standards or be chemicals of purity acceptable for the analysis.

NOTE Further details are given in ISO 6353-1, ISO 6353-2 and ISO 6353-3 (see bibliography).

Whenever water is specified without other qualifiers in the test procedures, only distilled water or water of at least equal purity shall be used.

3.3 Glassware

All glassware subject to heating shall be of heat-resistant borosilicate glass.[1)]

Pipettes and other volumetric glassware shall meet the volume requirements of Class A or Class B glassware as specified in ISO 10349-1.

4 Iodine-amylose method

4.1 Use

The iodine-amylose method is applicable to the determination of residual thiosulfate ions in film and resin-coated photographic paper containing incorporated developing agents. The procedure covers the range from 0,002 μg/cm^2 to 0,40 μg/cm^2. The method is also applicable to measuring residual thiosulfate ion in fibre-based paper, film and plates. This method measures only thiosulfate ions and gives results comparable to those obtained by the methylene blue method.

The method gives results that correlate well with accelerated keeping tests of several processed microfilms and is applicable to colour as well as black-and-white products.

4.2 Principle

The eluent (4.4.4) is added to the sample to extract residual thiosulfate, tetrathionate and pentathionate ions. Formalin is added to form a complex with any sulfite ion present. Iodine is added to an amylose (fractionated linear potato starch) indicator to form a blue-coloured solution. The thiosulfate in the eluent, when added to the iodine-amylose solution, will react with the iodine and proportionately reduce the intensity of the blue colour. The loss in colour corresponds to the thiosulfate concentration.

4.3 Chemical reactions

a) Starch $(C_6H_{10}O_5)_n$ + I_2 (in KI solution) → Blue-coloured solution

b) Blue-coloured solution + $S_2O_3^{2-}$ → Decrease in blue colour intensity

4.4 Reagents

4.4.1 Potassium iodate, $c(KIO_3)$ = 0,000 017 mol/l (0,003 57 g/l)

Prepare a 0,0167 mol/l solution of potassium iodate by weighing 0,357 g of potassium iodate (DANGER:⟨O⟩) and placing it in a 100 ml one-mark volumetric flask, making up to the mark with water and mixing well. Pipette 1,0 ml of the 0,016 7 mol/l potassium iodate solution into a 1 litre one-mark volumetric flask, making up to the mark with water.

[1)] Pyrex® is an example of suitable glassware available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this brand.

4.4.2 Formate buffer, pH 2,0

Add, from a graduated cylinder, 110 ml of formic acid (HCO_2H)) (88-90 %) (DANGER: ⟨C⟩ ⟨B⟩ ⟨S⟩ ⟨F⟩) to a 1 litre one-mark volumetric flask containing 500 ml to 600 ml of water, and make up to the mark with water. Using a pH meter, adjust the solution to pH 2,0 ± 0,1 at 21 °C with 10 mol/l sodium hydroxide solution (4.4.8) (DANGER: ⟨⟨C⟩⟩) from a dropping pipette.

4.4.3 Formate buffer, pH 2,8

Pipette 10,0 ml of pH 2,0 formate buffer (4.4.2) into a 1 litre one-mark volumetric flask and make up to the mark with water.

4.4.4 Eluent

Dissolve 1,0 g ± 0,1 g of potassium iodide (KI) and 1,0 g ± 0,1 g of potassium monohydrogen phosphate trihydrate ($K_2HPO_4 \cdot 3H_2O$) and dilute to 1 litre with water. Using a pH meter, adjust to pH 8,5 at 21 °C by adding 0,5 mol/l sulfuric acid (4.4.9) drop by drop from a dropping pipette.

4.4.5 Cadmium iodide-amylose reagent (CdI_2-amylose)

NOTE Batches should be limited to 1 litre volumes.

Add and dissolve 11,0 g ± 1 g of cadmium iodide (CdI_2) (DANGER: Carcinogen[2]) in 400 ml of water, and boil gently for 15 min. Add a further 400 ml of water and heat to boiling. Continue boiling and slowly add, while stirring, 5,0 g of amylose[3]. Boil and stir for 5 min. Continue boiling and slowly add, with stirring, 5,0 g of acid-washed analytical filter aid[4]. Boil and stir for 5 min.

While the solution is still hot, filter it under a high vacuum, using a Buchner funnel (4.5.1.5) with the fine porosity filter paper (4.5.1.6) into a 1 litre vacuum flask. Transfer the filtrate to a 1 litre volumetric flask. Rinse the vacuum flask with water and add the rinsings to the volumetric flask. Dilute to 1 litre with water.

4.4.6 Sodium thiosulfate, $c(Na_2S_2O_3)$ = 0,100 0 mol/l (15,8 g/l)

Commercially available analysed reagent solutions are recommended. Annex D provides a procedure for the preparation of standard sodium thiosulfate solution using sodium thiosulfate penthahydrate ($Na_2S_2O_3 \cdot 5H_2O$).

4.4.7 Formalin (DANGER:⟨B⟩ ⟨C⟩ ⟨S⟩)

4.4.8 Sodium hydroxide, c(NaOH) = 10 mol/l (DANGER:⟨⟨C⟩⟩)

This solution may be prepared from sodium hydroxide (DANGER:⟨⟨C⟩⟩).

4.4.9 Sulfuric acid, $c(H_2SO_4)$ = 0,5 mol/l

This solution may be prepared from sulfuric acid (1,84 g/ml approx.) (DANGER:⟨⟨C⟩⟩).

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[2] Zinc iodide (ZnI_2) has reportedly been used in at least two laboratories to avoid the use of cadmium iodide (CdI_2). An equimolar amount of zinc iodide (9,59 g) is to be used.

[3] Examples of suitable commercially available amylose are Aldrich Chemical Company No. 85573-1, ICN Biomedical Inc. No. 100669 and Sigma No. A0512 (Type 3 from potato). This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

[4] A diatomaceous earth such as Aldrich Chemical Company No. 16,743-6 or BDH 33134-2K are examples of suitable materials. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

4.5 Apparatus and glassware

4.5.1 Apparatus

4.5.1.1 Transmission spectrometer, suitable for recording optical absorbance over the wavelength range of interest, and a 5 cm cell.

4.5.1.2 pH meter

4.5.1.3 Interval timer

4.5.1.4 Dropping pipettes (also known as medicine droppers) (as required).

4.5.1.5 Buchner funnel

4.5.1.6 Filter paper, 11,0 cm diameter: ashless; fine porosity (2,5 µm particle retention); slow flow [240 s for 100 ml prefiltered water)]; smooth surface; dense.[5)]

4.5.2 Glassware

All glassware shall be free from reducing or oxidizing materials. One way to assure this is to rinse the glassware with an iodide-iodine solution made from the following reagents. (see. 3.3).

Mix 10 ml of potassium iodate solution (4.4.1), 5 ml of pH 2,0 formate buffer (4.4.2), 5 ml CdI_2-amylose reagent (4.4.5), and about 100 ml of water for a rinsing solution. Rinse glassware first with this solution and then with water.

4.6 Absorbance of blank solution

Run a reagent blank before and after the analyses of the samples. If the group of samples is large (greater than six), also run blanks in the middle of the group.

NOTE In developmental and experimental work, absorbances of the blank have been between 0,70 and 0,80.

The blank absorbance is obtained by adding all the following reagents to a 50 ml one-mark volumetric flask:

— 10 ml of eluent (4.4.4)

— 1 ml of formalin (4.4.7) (⟨B⟩ ⟨C⟩ ⟨S⟩)

— 3 ml of pH 2,8 formate buffer solution (4.4.3)

— 5,0 ml of potassium iodate solution (4.4.1)

— 5 ml of cadmium iodide-amylose reagent (4.4.5)

— 5 ml of pH 2,0 formate buffer solution (4.4.2)

Swirl to mix, and make up to the mark with water. Stopper the flask and mix thoroughly. After 3 min, measure the absorbance of this solution as described in 4.8.3 and 4.8.4.

4.7 Preparation of test sample

Analyze samples within 2 weeks of photographic processing.

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5) Whatman ® No. 42 filter paper is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

4.7.1 Cut a 10 cm^2 strip of paper or film, obtained from a non-image area or an area of minimum density. Fold the strip into a "W" with the emulsion side inwards. Place the folded sample in a dry 30 ml beaker.

4.7.2 Add 10 ml of eluent (4.4.4) to the beaker. Swirl the beaker until the sample is completely immersed. Swirl again after 1 min and 5 min. Total elution time shall be 10 min for resin-coated (RC) paper, lightweight paper, and single-weight paper. For medium-weight or double-weight paper, the contact time with the eluent shall be increased to 20 min.

4.7.3 Add 1 ml of formalin (4.4.7) (⟨B⟩ ⟨C⟩ ⟨S⟩) to the beaker. Swirl, making sure that the solution reaches any droplets on the beaker wall. Allow a reaction time of 1 min.

4.7.4 Add 3 ml of pH 2,8 formate buffer (4.4.3). Swirl to reach any droplets on the 30 ml beaker wall and allow 2 min for completion of the reaction. During these 2 min, carry out the following steps in a 50 ml volumetric flask: Pipette 5,0 ml of potassium iodate solution (4.4.1); add 5 ml of cadmium iodide-amylose reagent (4.4.5) and swirl the flask; add 5 ml of pH 2,0 formate buffer (4.4.2) and swirl the flask.

4.8 Colorimetric Measurement

4.8.1 Set a timer for 3 min.

4.8.2 Transfer the liquid from the 30 ml beaker (see 4.7.4) to the 50 ml volumetric flask containing the iodine-amylose solution (4.7.4). Rinse the sample and beaker with 10 ml of water and transfer the rinsings to the 50 ml volumetric flask containing the reagent mixture (see 4.7.4). Make up to the mark with water and mix well.

4.8.3 After 3 min from the time of transfer, measure the absorbance of the solution at 610 nm in a 5 cm glass cell versus air using the spectrometer (4.5.1.1).

4.8.4 Convert the absorbance obtained into the level, ρ_s, of thiosulfate ions ($S_2O_3^{2-}$), in grams per square metre, from an appropriate calibration curve (see 4.9).

$$\Delta A = A_s - A_b$$

where

ΔA is the absorbance difference;

A_b is the absorbance of the blank solution;

A_s is the absorbance of the test solution.

If A_s falls below 0,090, re-extract the sample using a smaller sample. Correct the result then obtained from the calibration curve as follows:

$$\rho_s = \frac{10\rho_c}{S}$$

where

ρ_c is the level of $S_2O_3^{2-}$ ions read from the calibration curve, in grams per square metre;

S is the sample area, in square centimetres.

Low levels of thiosulfate (0,001 g/m^2 to 0,009 g/m^2) are generally achieved only in well-washed, fine-grain, black-and-white films.[6)]

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6) 1 µg/cm^2 = 10^{-2} g/m^2

4.9 Calibration, including blank

4.9.1 Prepare a stock sodium thiosulfate solution (0,001 0 mol/l) by pipetting 1,00 ml of 0,100 0 mol/l sodium thiosulfate (4.4.6) into a 100 ml one-mark volumetric flask. Make up to the mark with water.

4.9.2 Assuming a 10 cm^2 sample, pipette the volumes of stock solution given in table 1 into appropriately labelled 30 ml beakers.

Table 1 — Preparation of samples for calibration

Volume of stock solution	Equivalent ρ_s	
µl	g/m^2	$\mu g/cm^2$
50	0,005 6	0,56
100	0,011	1,1
300	0,034	3,4
None	Blank	Blank

4.9.3 Analyse the samples starting at 4.7.2 by adding the eluent (4.4.4) and continuing the procedure steps up to and including 4.8.3. The sample sizes given in 4.7.1 are replaced by the pipetted quantities given in 4.9.2. If the sample has a gelatin coating on each side of the base, it may contain twice the level of thiosulfate ions as a sample coated on one side only.

4.9.4 Plot ΔA against ρ_s, in grams per square metre (for a 10 cm^2 sample).

5 Methylene blue method

5.1 Use

The methylene blue method determines only thiosulfate ions. The procedure as specified covers the range from 0,005 g/m^2 to 0,34 g/m^2 (0,5 $\mu g/cm^2$ to 34 $\mu g/cm^2$) of thiosulfate for fibre-based paper, resin-coated paper, film or plates.

5.2 Principle

Residual thiosulfate that is extracted (eluted) from the sample is reduced by potassium borohydride to sulfide. The sulfide reacts with oxidized N,N-dimethyl-*p*-phenylenediamine (DP) to form methylene blue (MB). The absorbance of the blue colour is measured with a photometer or spectrometer. The thiosulfate level is determined from a calibration curve. A curve is to be prepared in each laboratory to eliminate errors due to variations in the reagents, equipment or technique, but it should approximate to the curve in figure 1.

NOTE The curve shown in figure 1 is only an example and is not to be used as a working calibration curve. A working calibration curve is to be established only by following the procedures described in this International Standard.

5.3 Chemical reactions

The following reactions occur:

$$3H_2O + S_2O_3^{2-} + BH_2^- \rightarrow HS^- + 2HSO_3^- + H_2BO_3^- + 2H_2$$

$$HS^- + 12FeCl_3 + 2DP \rightarrow MB$$