INTERNATIONAL STANDARD

ISO
18917

First edition
1999-06-01

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

Reference number
ISO 18917:1999(E)

Contents

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

Printed in Switzerland

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⟩⟩).

---

[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.

---

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 ($\mathrm{S_2O_3^{2-}}$), in grams per square metre, from an appropriate calibration curve (see 4.9).

$$\Delta A = A_\mathrm{s} - A_\mathrm{b}$$

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:

$$\rho_\mathrm{s} = \frac{10\rho_\mathrm{c}}{S}$$

where

ρ_c is the level of $\mathrm{S_2O_3^{2-}}$ 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)

---

(6) 1 $\mu g/cm^2 = 10^{-2}$ 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:

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

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

5.4 Reagents

5.4.1 Eluent

Dissolve 1,0 g ± 0,1 g of potassium iodide (KI) and 1,0 g ± 0,1 g of potassium dihydrogen phosphate (KH_2PO_4) in water in a 1 litre one-mark volumetric flask. Make up to the mark with water and mix well. This reagent is stable for at least one month.

5.4.2 Borohydride reagent

Dissolve 3,0 g of fresh potassium borohydride [7] (KBH_4) (DANGER: 〈C〉 〈B〉 〈F〉) in 100 ml of sodium hydroxide solution (5.4.6). This reagent is stable for 1 week in a cool place. Package solutions to be used beyond 1 week in small individual bottles which, once opened, shall be discarded at the end of the day.

DANGER: Potassium borohydride is hazardous in the following ways:

a) Personnel: Potassium borohydride is flammable and corrosive. It liberates hydrogen gas when in contact with water or acid, and poisonous gases in the presence of acid. In concentrated form, it causes severe skin burns. Handle with extreme care and store in a bottle with a loose stopper.

b) Sensitized materials: Potassium borohydride is a powerful fogging agent. Avoid contamination of unprocessed film, paper, and processing solutions. Thoroughly wash hands and equipment after the use of solid borohydride or borohydride reagent.

5.4.3 Acetone (DANGER: 〈F〉 〈B〉)

5.4.4 Ferric chloride reagent

To approximately 50 ml of water in a beaker, carefully add, while stirring, 37,5 ml of hydrochloric acid (HCl) ($\rho \approx$ 1,18 g/ml) (DANGER: 〈C〉). Dissolve 8,45 g ± 0,01 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in the diluted acid, cool to room temperature, and transfer to a 100 ml one-mark volumetric flask. Make up to the mark with water and mix well. This reagent is stable for at least 3 months.

5.4.5 NND Reagent

To approximately 50 ml of water in a beaker, carefully add, while stirring, 12,5 ml of hydrochloric acid (HCl) ($\rho \approx$ 1,18 g/ml) (DANGER: 〈C〉). Dissolve 3,00 g ± 0,01 g of *N*,*N*-dimethy-*p*-phenylenediamine sulfate[8] in the diluted acid, cool to room temperature, and transfer to a 100 ml one-mark volumetric flask. Make up to the mark with water and mix well. This reagent is stable for at least 1 week.

5.4.6 Sodium hydroxide solution, c(NaOH) = 0,20 mol/l (8,0 g/l)

Commercially available analysed reagent solution is recommended. A procedure for the preparation of this is given in annex C

5.5 Apparatus and glassware

See 4.5.2 for details of the cleaning of glassware.

5.5.1 Sample vials (scintillation vials), polyethylene, of 20 ml capacity with screw caps; nine are required.

---

[7] Also known as potassium tetrahydroborate.

[8] Bis (*N*,*N*-dimethy-*p*-phenylenediamine sulfate), M.W. 370,47. An equivalent commercially available salt, with one equivalent of amine per mole (M.W. 234,28) can also be used and if so use 3,78 g of amine per 100 ml of solution

5.5.2 Repeating dispensers adjustable, of 1 ml capacity[9]; four are required.

5.5.3 Visible photometer or spectrophotometer, with 1 cm **cells**

5.6 Procedure

5.6.1 Analysis of test sample

Analyse samples within 2 weeks of photographic processing

5.6.1.1 Cut a 1 cm^2 sample of film, paper or plate from an area of minimum density; a 1,0 cm^2 punch may be used for film or paper samples. Place the sample in a clean, dry sample vial (5.5.1). Add 10,0 ml of eluent (5.4.1) and allow the mixture to stand for 10 min with occasional swirling (once every 1 min to 3 min). Pipette 5,0 ml of the extract into another sample vial.

NOTE If destruction of the plate is undesirable, immerse the entire plate in a tray slightly larger than the plate (0,5 cm on each side) and elute as above but use a larger volume of eluent (5.4.1), keeping the proportion of eluent volume to plate area constant. After elution, pipette 5,0 ml of the resulting test solution into a sample vial (5.5.1). Continue with the procedure given in 5.6.1.2. Wash the plate with water after testing, to remove the residual eluent.

5.6.1.2 Transfer the following four reagents to separate reservoirs for the repeating dispensers; set each dispenser for the requisite volume.

Borohydride reagent (5.4.2)	0,25 ml
Acetone (5.4.3)	0,50 ml
Ferric chloride reagent (5.4.4)	0,25 ml
NND reagent (5.4.5)	0,25 ml

Flush each dispenser by dispensing and discarding at least 10 aliquots of reagent before the first determination of the day.

Complete all of the following reagent additions without delay between additions.

a) Add 0,25 ml of the borohydride reagent (5.4.2). Swirl to mix.

b) Add 0,50 ml of acetone (5.4.3). Swirl to mix.

c) Add 0,25 ml of the ferric chloride reagent (5.4.4) and 0,25 ml of the NND reagent (5.4.5).

Immediately cap the vial securely. Shake the vial vigorously for 1 min. Then carefully vent the pressure formed by evolved hydrogen, making sure that the vial is pointed away from the face. Proceed immediately with the next step.

5.6.1.3 Measure the absorbance of the test solution at 665 nm in a 1 cm cell versus air (no cuvette in the light beam) using the photometer (5.5.3).

5.6.1.4 Analyse a reagent blank by substituting 5,0 ml of eluent instead of the extract in 5.6.1.1. Calculate the net absorbance of the test solution by subtracting the blank absorbance from the test solution absorbance obtained in 5.6.1.3.

5.6.2 Expression of results

Obtain the results according to 5.6.2.1 or 5.6.2.2.

---

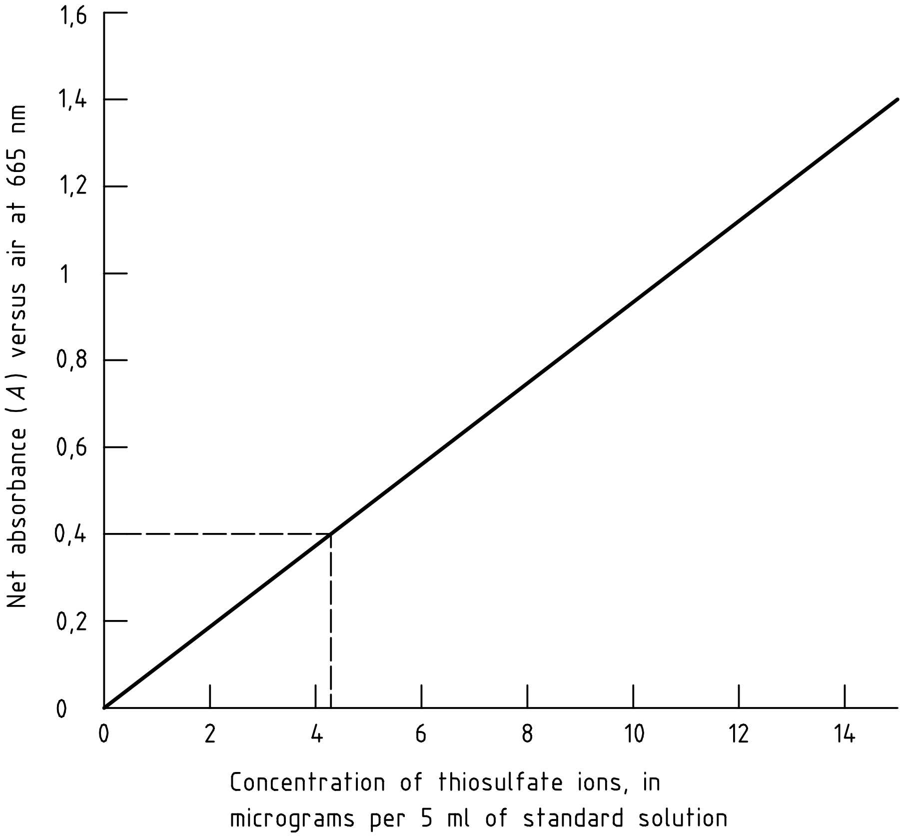
[9] The EM Science OPTIFIX dispenser is an example of a suitable product available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product

5.6.2.1 Film or plates having gelatin on only one side

From the calibration curve, read the concentration of thiosulfate ions. in micrograms per 5 ml of test solution, corresponding to the net absorbance. To obtain the level of thiosulfate ions, ρ_S, in micrograms per square centimetre of the film or plate, multiply the concentration of thiosulfate ions, in micrograms per 5 ml of test solution, by 2 because of the 10 ml eluent volume (see figure 1, example 1).

5.6.2.2 Film or plates having gelatin on both sides

Report the results as instructed in figure 1, exemple 2.



Example 1: If a film sample produces an absorbance of 0,400, it corresponds to 4,4 µg of $S_2O_3^{2-}$ per 5 ml of test solution. The film then contains (4,4 × 2) or 8,8 µg/cm^2 (0,088 g/m^2) of $S_2O_3^{2-}$.

Example 2: If the sample has gelatin on each side, it is assumed that the residual $S_2O_3^{2-}$ is equally divided between the two sides (but this is in fact dependent on the gelatin coating weight on the two sides which may significantly differ). Therefore, the level of $S_2O_3^{2-}$ on each side will be one-half the total. For example, if the sample in example 1 had a gelatin backing, the level of $S_2O_3^{2-}$ would be 4,4 µg/cm^2 (0,044 g/m^2) per side.

Figure 1 — Typical calibration curve for the methylene blue method

5.7 Calibration curve for the methylene blue method

Prepare a new calibration curve when new reagents are used. Check the curve at regular intervals (e.g. once a week).

5.7.1 Preparation of standard sodium thiosulfate solution, 11,2 µg/ml

Prepare this on the day it is to be used.

Pipette 25,0 ml of 0,1 mol/l thiosulfate solution (4.4.6) into a 500 ml one-mark volumetric flask and make up to the mark with water. Stopper the flask and invert to mix 8 to 10 times. Pipette 5,0 ml of the resulting solution into a 250 ml one-mark volumetric flask and make up to the mark with water. Stopper the flask and invert to mix 8 to 10 times. The resulting solution contains 11,2 µg/ml of thiosulfate.

5.7.2 Calibration procedure

Pipette the appropriate volumes of standard thiosulfate solution (5.7.1) into the corresponding one-mark volumetric flasks (see table 2), make up to the mark with eluent and mix. Analyse a 5 ml aliquot of each calibration solution according to the procedure in 5.6.1. Plot the net absorbance obtained versus the corresponding thiosulfate concentration. The slope of the data should approximate that shown in figure 1.

The calibration procedure is based on the standard thiosulfate solution having a titre of exactly 0,100 mol/l. Correction in the calibration values or adjustment of the solution shall be made to accommodate any difference.

Table 1 — Preparation of calibration solutions

Volume of standard thiosulfate solution (5.7.1) ml	**Volumetric flask** ml	**Concentration of calibration solution** µg of $S_2O_3^{2-}$ per 5 ml
1,00	200	0,28
2,00	100	1,12
2,00	50	2,24
4,00	50	4,48
7,00	50	7,84
10,00	50	11,20
15,00	50	16,80

6 Silver densitometric method

6.1 General

The silver densitometric method measures thiosulfate, polythionates and other sulfur-containing residual chemicals in a processed product. It may therefore be used at least several months after processing, since it measures degradation products of thiosulfate. A silver sulfide stain is formed and the results are usually reported as the density difference between the stained and unstained portions from a minimum-density (D_{min}) area. Optical density is measured with a standard densitometer. The method should be restricted to samples where this difference is 0,03 or greater. This typically corresponds to residual thiosulfate levels of 0,009 g/m^2 (0,9 µg/cm^2) or greater. The sensitivity can be significantly increased by using a suitable filter10) in the light path. When the densitometer uses a solid-state detector, the use of the filter may lead to erroneous results.

---

10) Kodak Wratten No. 18A filter 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.

The density differences can be converted to residual thiosulfate concentrations if a calibration curve is run for the type of product under test. This implies the availability of unexposed, unprocessed material to generate the calibration samples by processing and washing over a range of thiosulfate concentrations.

The method is not applicable to film or paper containing incorporated developing agents, since erroneously high results will be obtained from a contribution by the developing agents.

Experience has shown that products with a high level of residual chemicals are often unevenly washed. Variations within a sheet of film or paper can exceed a factor of 5 in residual thiosulfate levels. Samples of 1 cm^2 area may therefore not be representative. Manufacturers of processing equipment, chemicals and the like can evaluate processing systems by applying the sulfide densitometric (stain) test in three trays, using full-size sheets or pieces cut down from the original so as to fit the trays. This method supplies both a visual and a quantitative analysis of the completeness and uniformity of washing.

6.2 Principle of the test

A sample strip of film, plate or paper is immersed to half its length in an acidified silver nitrate reagent. Thiosulfate and certain other ions, if present, will produce a yellow-brown stain. The complete sample is then immersed in a sodium chloride solution followed by a thiosulfate-sulfite fix to remove excess silver ions. After washing and drying, the densities on the stained and unstained areas of the sample are measured. On film and plate samples, two thicknesses are used for the density measurement. The difference in these densities is a measure of the residual chemicals.

6.3 Chemical reactions

The following group of reactions occurs:

$$S_2O_3^{2-} \text{ and / or } S^{2-} + AgNO_3 \overset{H^+}{\to} Ag_2S \text{ and silver-sulfur compounds (yellow-brown)}$$

6.4 Reagents

6.4.1 Silver nitrate/acetic acid reagent

Dissolve 10 g of silver nitrate ($AgNO_3$) (DANGER: 〈C〉) in a solution containing 30 ml of glacial acetic acid (DANGER: 〈C〉) in 750 ml of water in a 1 litre one-mark volumetric flask. Make up to the mark with water and store in a brown, glass-stoppered bottle away from strong light. Discard the reagent if it is darkened.

6.4.2 Sodium chloride reagent

Dissolve 50 g of sodium chloride (NaCl) in water and dilute to 1 litre.

6.4.3 Sodium thiosulfate/sodium sulfite reagent

Dissolve 19 g of sodium sulfite (Na_2SO_3) and 50 g of sodium thiosulfate pentahydrate, ($Na_2S_2O_3 \cdot 5H_2O$) in 750 ml of freshly boiled and cooled water in a 1 litre one-mark volumetric flask and make up to the mark with water.

6.5 Apparatus

The silver densitometric method of measuring residual chemicals involves the measurement of the blue density of a brown stain on a minimum-density or non-image area of processed photographic material.

This method requires a densitometer capable of operating in both the transmittance and reflectance modes.

For transmission measurements on film and plates, ISO status A density, $D_T\,(S_H\!:\!A_{\mathrm{B}})$, shall be used (see ISO 5-3).

For reflection measurements on paper, ISO status A density, $D_R(S_A\!:\!A'_{\mathrm{B}})$, shall be used (see ISO 5-3).

6.5.1 Transmission densitometer, equipped with the ISO status A blue spectral product (ISO 5-3).

6.5.2 Reflection densitometer, equipped with the ISO status A blue spectral product (ISO 5-3).

6.6 Preparation of test sample

6.6.1 Film

Cut a strip of film approximately 1,5 cm × 6 cm from a minimum-density area and fold at the midpoint with the emulsion side out. With films coated on two sides, take care that the fold does not restrict solution access.

6.6.2 Plates

Cut two samples approximately 1,5 cm × 3 cm from a minimum-density area.

6.6.3 Paper

Cut a sample approximately 1,5 cm × 3 cm from a minimum-density area.

6.7 Procedure

6.7.1 Immersion and washing

Immerse one-half of the sample (for film, folded end down) in 20 ml of silver nitrate/acetic acid reagent (6.4.1) for 4 min. Agitate occasionally.

NOTE For convenience, a number of samples may be suspended from film clips and supported by a rod over a tray containing appropriate volumes of reagent.

Immerse the entire sample in 20 ml of the sodium chloride reagent (6.4.2) for 4 min. Agitate occasionally. Immerse the entire sample in 20 ml of sodium thiosulfate/sodium sulfite reagent (6.4.3) for 4 min. Agitate occasionally. Wash the sample under running tap water for 5 min to 10 min and dry.

6.7.2 Measurement of sample density

6.7.2.1 Film

Refold the dry strip, with the emulsion outwards. Measure, to the nearest hundredth, the density of the double thickness of film in both the stained and unstained areas, using the transmission densitometer (6.5.1).

6.7.2.2 Plates

Measure, to the nearest hundredth, the density of the two superimposed plate samples in both the stained and unstained areas, using the transmission densitometer (6.5.1).

6.7.2.3 Paper

Measure the reflection density of a single thickness, to the nearest hundredth, on both stained and unstained areas, using the reflection densitometer (6.5.2).

6.7.3 Expression of results

6.7.3.1 As density differences, ΔD

Subtract the density of the unstained area from that of the stained area and report the difference as ΔD (for example, $\Delta D = 0{,}13$). Report a density difference of 0,03 or less as ΔD equal to or less than 0,03.

6.7.3.2 As level of thiosulfate ions

Although there may not be universal correlation between the silver density produced and the thiosulfate level (as measured by the methylene blue method or iodine-amylose method) for all products, it is reasonable to believe that such a relationship could be developed for a specific product on freshly processed materials. The user may wish to prepare such a calibration curve for a particular product. Figure 2 represents such a correlation on five colour films. Although the correlation appears reasonable, there is not yet enough experience to conclude that the relationship applies to all products. It is probable that the relationship would decrease in reliability as the product ages and thiosulfate is converted to polythionates.

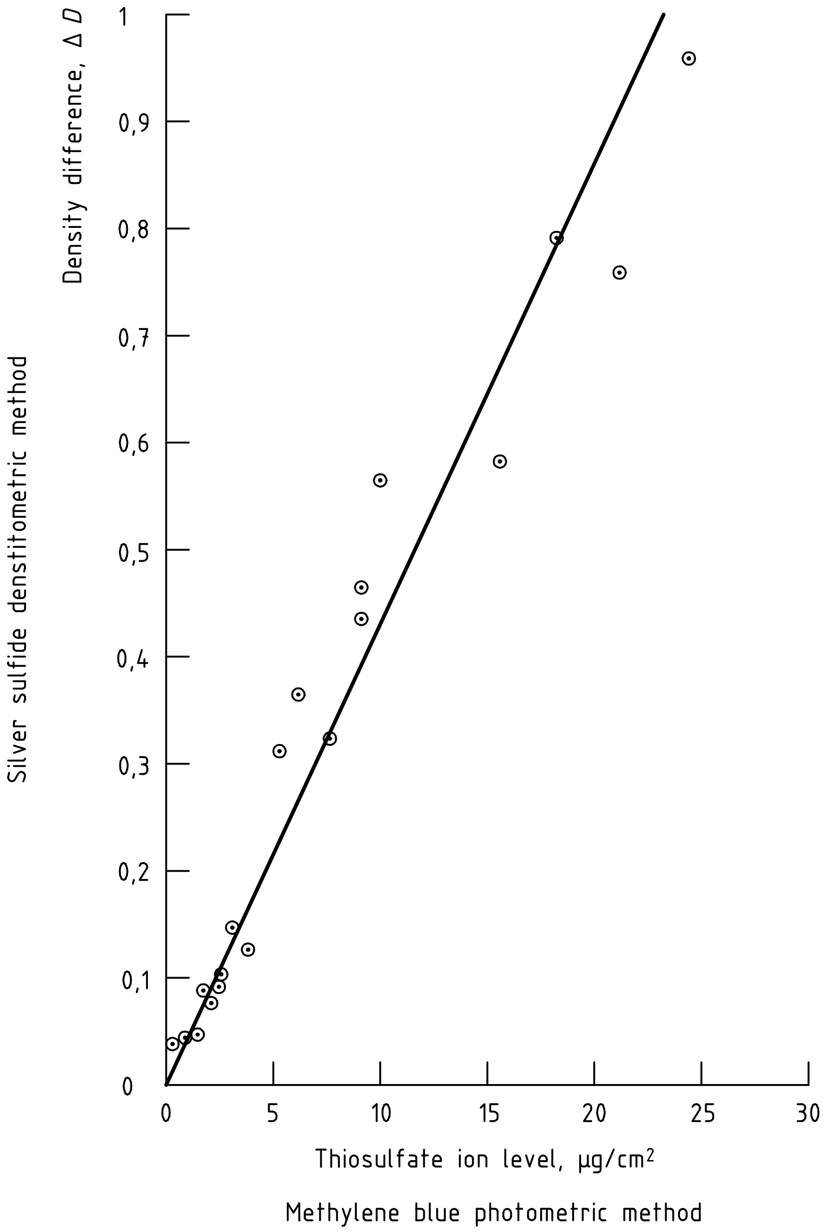


Figure 2 — Illustrative correlation between the silver densitometric method and the methylene blue or iodine-amylose method for measuring thiosulfate ion levels

Annex A
(informative)

Appraisal of keeping characteristics

Having a quantitative measure of residual chemicals in a film or paper does not tell, *a priori*, how long the product will be useful, even if the conditions of storage and use are specified. The effects of residual chemicals differ among types of products and within a given type of product.

In order for any measure of residual chemicals to be useful, it is necessary to have a correlation between the test results of the chemicals and the keeping characteristics of the particular product. Actual use and storage tests on some products may require years before there are measurable image and background changes. Further difficulties in appraising the keeping characteristics arise owing to the discontinuation of some products and the continuous introduction of new products. Changes in the components of photographic emulsion may have no effect on the sensitometric properties, but may have a long-term effect on the performance of a photographic material. A practical approach is therefore required not only to collect keeping characteristics data under good storage conditions, but also to appraise keeping qualities under accelerated conditions. Hopefully, good correlation will be observed between the chemical test results and the keeping qualities of the various products. Although there are risks attendant with accelerated tests, the results may furnish valuable guidelines for predicting the keeping qualities of a product for several years.

The distribution of residual thiosulfate in the larger sizes of film and paper products is not always uniform. It therefore seems prudent to make tests from several sections of large-sized film and paper samples to determine which areas are likely to have the highest concentration of thiosulfate ions. Testing of production samples should be made from the areas most likely to contain the highest concentration.

Experience indicates that the higher the level of residual chemicals, the poorer the image stability. The quantitative effects of residual chemicals in colour products are not well known, but accelerated heat and humidity-keeping test methods [16] (see bibliography) that are basically those specified in this International Standard have permitted correlations for some products [17-21] (see bibliography).

It is not possible to establish a universally applicable level of residual chemicals that will result in the longest life for all products. This is because of differences among types of products, differences between products of the same type, and variations in the combination of chemicals, even when they contain the same level of certain residual chemicals.

Annex B
(informative)

Guidance in the selection of test method

See table B.1.

Table B.1 — Analytical method for determining thiosulfate ion in specific photographic materials

Materials for testing	Method	Detectable levels of thiosulfate ions g/m^2	Time weeks
Films, plates, fibre-based papers, RC paper	Iodine-amylose	0,002 – 0,40	$\leqslant 2$
Films, plates, fibre-based papers, RC paper with no incorporated developing agents	Methylene blue	0,005 – 0,30	$\leqslant 2$
Films, plates, fibre-based papers, RC paper with no incorporated developing agents	Silver densitometric	$\geqslant 0,009$	Less affected by time than other methods
Note 1 $1\ \mu g/cm^2 = 10^{-2}\ g/m^2$ Note 2 Storage conditions have been found to have an effect on residual thiosulfate stability. Samples should be stored at – 4 °C, if possible, and be allowed to come to room temperature prior to analysis. Limited studies have shown that residual thiosulfate is stable for up to 3 to 7 weeks, depending on the product type, when the film is stored at – 4 °C.			

Annex C
(informative)

Preparation for 0,2 mol/l sodium hydroxide solution

C.1 Preparation of solution (non-standardized) or purchased standard material

Use the following procedure if the sodium hydroxide solution that is purchased is less than 0,2 mol/l or if the laboratory wants to prepare its own solution.

a) Add (with extreme care), in a fume hood, 8,2 g ± 0,1 g of reagent-quality sodium hydroxide to 800 ml of distilled water in a 2 litre glass beaker

b) Stir to dissolve; cool to room temperature. (Use care when handling the beaker of solution.)

c) Transfer to a 1 litre one-mark volumetric flask and make up to the mark with water

C.2 Alternative procedure

Pipette, using a bulb (wipe), 200,0 ml of standard 1 mol/l sodium hydroxide into a 1 litre one-mark volumetric flask and make up to the mark with distilled water.

Annex D

(informative)

Preparation of 1,000 mol/l sodium thiosulfate solution

D.1 Preparation of solution

Add about 800 ml of freshly boiled and cooled distilled water to a 1 litre one-mark volumetric flask; stir on a magnetic stirrer.

Add and dissolve 25 g of sodium thiosulfate pentahydrate.

Make up to the mark with distilled water.

NOTE 1 Allow the solution to stand for 1 day before standardizing.

NOTE 2 Add 1 mg of mercuric iodide[11] (HgI_2) (DANGER: 〈C〉 〈〈S〉〉) per litre after standardizing if serious instability problems are encountered.

D.2 Standardization

D.2.1 Materials required:

a) Potassium iodate solution, $c(KIO_3)$ = 0,0167 mol/l (3,5 g/l)

b) Sulfuric acid solution, $c(H_2SO_4)$ = 3,57 mol/l [may be prepared from sulfuric acid, density ≈ 1,84 g/ml (DANGER: 〈〈C〉〉)]

c) Potassium iodide solution, $c(KI)$ = 0,6 mol/l (99,6 g/l)

d) Starch indicator solution

D.2.2 Procedure

Pipette (wipe) 20,0 ml of primary standard 0,016 7 mol/l potassium iodate solution into a 125 ml conical flask.

Add 10 ml of 3,5 mol/l sulfuric acid solution from a tip-up pipette

Add 15 ml of 0,6 mol/l potassium iodide solution from a tip-up pipette or graduated cylinder.

Titrate the liberated iodine with the sodium thiosulfate solution being standardized, using a 25 ml burette. Titrate the solution to a light yellow colour, add 5 ml of starch indicator from a tip-up pipette, and continue the titration until the blue colour is just discharged.

---

[11] The use of small amounts of sodium carbonate (0,1 g/l) has been reported as effective in inhibiting sulfur precipitation. Its use as a replacement for mercuric iodide is because of the toxicity effects of mercury.

D.2.3 Calculation

The concentration of $Na_2S_2O_3$, c_T, in moles per litre, is calculated as follows:

$$c_T = \frac{120 c_1}{V}$$

where

c_1 is the concentration, in moles per litre, of the standard potassium iodate solution (KIO_3);

V is the volume, in millilitres, of the sodium thiosulfate ($Na_2S_2O_3$) solution used to reach the endpoint;

120 is the factor including 6 molar equivalents of thiosulfate per molar equivalent of iodate and the volume of the standard potassium iodate solution, i.e. 20 ml.

Repeat the standardization on another 20 ml portion of the reagent.

The average of the two standardization is the concentration, in moles per litre, of $Na_2S_2O_3$.

Bibliography

[1] ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

[2] ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

[3] ISO 835-1:1981, *Laboratory glassware — Graduated pipettes — Part 1: General requirements.*

[4] ISO 835-2:1981, *Laboratory glassware — Graduated pipettes — Part 2: Pipettes for which no waiting time is specified.*

[5] ISO 835-3:1981, *Laboratory Glassware — Graduated pipettes — Part 3: Pipettes for which a waiting time of 15 s is specified.*

[6] ISO 835-4:1981, *Laboratory glassware — Graduated pipettes — Part 4: Blow-out pipettes.*

[7] ISO 1042:1998, *Laboratory glassware — One-mark volumetric flasks.*

[8] ISO 3897:1997, *Photography — Processed photographic plates — Storage practices*.

[9] ISO 4788:1980, *Laboratory glassware — Graduated measuring cylinders.*

[10] ISO 5466:1996, *Photography — Processed safety photographic films — Storage practices*.

[11] ISO 6051:1997, *Photography — Processed reflection prints — Storage practices*.

[12] ISO 6353-1:1982, *Reagents for chemical analysis — Part 1: General test methods*.

[13] ISO 6353-2:1983, *Reagents for chemical analysis — Part 2: Specifications — First series*.

[14] ISO 6353-3:1987, *Reagents for chemical analysis — Part 3: Specifications — Second series*.

[15] ISO 10602:1995, *Photography — Processed silver-gelatin type black-and-white film — Specifications for stability.*

[16] HUBBELL, D.C., MCKINNEY, R.G. and WEST L.E. Methods for testing image stability of colour photographic products. *Photographic Science and Engineering*, **11**(5), 1976, pp. 295-305.

[17] LARSON, G.W., HUBBELL, D.C. and WEST, L.E. Application of two analytical test methods to predict processed image stability. *Journal of the Society of Motion Picture and Television Engineers*, **71**(7), 1962, pp. 495-501.

[18] KOPPERL, D.F., LARSON, G.W., HUTCHINS, B.A. and BARD, C.C. A method to predict effect of residual thiosulfate content on the long-term image-stability characteristics of radiographic films. *Journal of Applied Photographic Engineering*, **8**(2), 1982, pp. 83-89.

[19] WEST, L.E. Water conservation in photographic processing*. Image Technology*, **11**, 1969, pp. 15-22.

[20] OWERBACH, D. A colorimetric determination of residual thiosulfate (hypo) in processed paper. *Journal of Applied Photographic Engineering*, **9**(2), 1983, pp. 66-70.

[21] KOPPERL, D.F. and HUTTEMANN, T.J. Effect of residual thiosulfate on the image stability of microfilms. *Journal of Imaging Technology*, **12**(4), 1986, pp. 173-180.

ICS 37.040.99

Price based on 21 pages