INTERNATIONAL
STANDARD

ISO
6849

First edition
1996-11-01

Photography — Processing wastes — Determination of boron

Photographie — Effluents de traitement — Détermination du bore

Reference number
ISO 6849:1996(E)

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 6849 was prepared by Technical Committee ISO/TC 42, *Photography*.

Annex A of this International Standard is for information only.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Introduction

This International Standard is one of a series devoted to the analysis of photographic wastes; it encompasses the field of analysis of boron in photographic effluents.

This International Standard is intended for use by individuals with a working knowledge of analytical techniques, which may not always be the case. Some of the procedures utilize caustic, toxic or otherwise hazardous chemicals. 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. Normal precautions required in the performance of any chemical procedure are to be exercised at all times but care has been taken to provide warnings for hazardous materials. Hazard warnings designated by a letter enclosed in angle brackets, ⟨ ⟩, are used as a reminder in those steps detailing handling operations and are defined in clause 4. More detailed information regarding hazards, handling and use of these chemicals may be available from the manufacturer.

In the case of effluents, the photographic laboratory can best establish its conformity to regulations by appropriate chemical analysis. In some cases, in-house analyses will be possible; often the use of an outside laboratory will be required.

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Photography — Processing wastes — Determination of boron

1 Scope

This International Standard specifies two methods for the determination of boron in photographic processing wastes. The first method is the estimation of borates by titration of the boric acid-mannitol complex, which is a stronger acid than the boric acid from which it is formed. It is suitable for boron concentrations of 0,1 mg/l and higher. In the range 0,1 mg/l to 5 mg/l, phosphate is removed by precipitation by lead acetate. In the range 1 mg/l to 100 mg/l, the sample is diluted 25 times; this eliminates phosphorous interference if the phosphorous concentration is below 500 mg/l.

The second and alternative method is a spectrophotometric technique using methylene blue and is useful in the boron range of 0,1 ml/l to 1,0 mg/l, this being the concentration likely to be encountered in photographic processing wastes.

2 Normative references

The following International Standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

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

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

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

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

3 Principle

In the method using boric acid-mannitol complex, sodium acetate is added to stabilize the pH. The sample is then acidified with sulfuric acid and boiled to expel carbon dioxide. Upon cooling, the pH is adjusted to 7 with sodium hydroxide. Mannitol is added to form a complex acid with any boric acid present. The mixture is then titrated back to pH 7 with 0,02 mol/l sodium hydroxide. Interference by atmospheric carbon dioxide is minimized by titrating both the sample and a blank in a specified time. This method should not be used in the presence of ammonia gas, acetic acid vapours, or hydrochloric acid fumes since these may be absorbed into the sample and change the pH.

In the spectrophotometric method using methylene blue, sulfuric acid and hydrofluoric acid are added to form the tetrafluoroborate ion (BF_4^-). Methylene blue is then added and the complex formed is extracted with 1,2-dichloroethane. The absorbance of the extract is measured at a wavelength near 660 nm.

4 Safety and operational precautions

4.1 Hazard warnings

Some of the chemicals specified in the test procedures are caustic, toxic or otherwise hazardous. Specific danger notices are given in the text and footnotes, but normal precautions are required during the performance of any chemical procedure at all times. The first time that a hazardous material is handled in a procedure, the hazard will be indicated by the word "DANGER" followed by a symbol consisting of angle brackets "⟨ ⟩" containing a letter which designates the specific hazard and a statement of the hazard. A double bracket "⟨⟨ ⟩⟩" will 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) will be displayed. Furthermore, for a given material, the hazard symbols will be used only once in a single paragraph. Hazard symbols will not be used for common organic solvents when used in quantities of less than 1 litre unless they are particularly hazardous.

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 any 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.

4.2 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.

4.3 Safety precautions

All pipette operations shall be performed with a pipette bulb or plunger pipette. This is a critical safety warning!

Safety glasses shall be worn for all laboratory work.

5 Materials and reagents

5.1 General

5.1.1 Handling and labelling

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 comply with applicable environmental regulations.

5.1.2 Purity

Reagents used in the test procedures shall be certified reagent-grade chemicals and shall meet appropriate standards or be chemicals of a purity acceptable for the analysis. For details see ISO 6353-1, ISO 6353-2 and ISO 6353-3.

5.1.3 Water

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

5.1.4 Strength of solutions

5.1.4.1 Acids and ammonium hydroxide are full strength unless otherwise specified.

5.1.4.2 When a standardized solution is required, its concentration is expressed in moles per litre (mol/l). The number of significant figures to which the molarity (mol/l) is known shall be sufficient to ensure that the reagent does not limit the reliability of the test method.

5.1.4.3 When a standardized solution is not required, its concentration is expressed in grams per litre (g/l) to the appropriate number of significant figures.

5.1.4.4 When a solution is to be diluted, its solution is indicated by (X + Y), meaning that X volumes of reagent, or concentrated solution, are to be diluted with Y volumes of distilled or deionized water.

5.2 Reagents for method using boric acid-mannitol complex

5.2.1 Lead acetate solution, $c[Pb(C_2H_3O_2)_2 \cdot 3H_2O] \approx 0{,}5$ mol/l.

Add approximately 750 ml of water to a 1 litre volumetric flask. Add and dissolve 190 g ± 1 g of lead acetate trihydrate (DANGER: ⟨⟨S⟩⟩) and dilute to volume with water. If the solution is not clear, filter it through a filter paper [1] (prefolded; medium flow — 100 ml prefiltered water in 55 s; medium porosity — 8 µm particle retention).

5.2.2 Mannitol ($C_6H_{14}O_6$).

5.2.3 Sodium acetate solution, $c(NaC_2H_3O_2) \approx 0{,}1$ mol/l.

Add approximately 750 ml of water to a 1 litre volumetric flask. Add and dissolve 8,2 g ± 0,1 g of sodium acetate (anhydrous), dilute to volume with water, stopper and mix well.

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[1] Whatman 2V is an example of a suitable filter paper 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.

5.2.4 Sodium hydroxide, standard volumetric solution, $c(\mathrm{NaOH}) = 0{,}020\,0$ mol/l.

Pipette 100,0 ml of standard sodium hydroxide solution (0,100 0 mol/l) into a 500 ml volumetric flask. Dilute to volume with boiled distilled water which has been cooled to room temperature. Avoid unnecessary exposure to air. This solution is stable for about one week.

5.2.5 Sodium hydroxide, saturated solution.

Slowly dissolve 60 g of sodium hydroxide (DANGER: ⟨C⟩) in 50 ml of freshly boiled, distilled water in a polyethylene or polypropylene bottle. Allow this solution to stand for 48 h before using it. When using this solution, care should be taken not to disturb it. Decant the amount needed to avoid contamination from sodium carbonate which has settled to the bottom of the container.

DANGER — If the water has not cooled before adding the sodium hydroxide, the heat of solution may cause the mixture to boil and erupt.

5.2.6 Sodium hydroxide, approximately 0,5 mol/l solution (carbonate free).

Add from a graduated cylinder, 3 ml of the decanted saturated sodium hydroxide (DANGER: ⟨C⟩) (5.2.5) to a 150 ml beaker. Dilute to approximately 100 ml with freshly boiled distilled water and store in a polyethylene or polypropylene bottle. Avoid prolonged and unnecessary exposure to air. The solution is stable for two days only.

5.2.7 Sodium sulfate solution, $c(\mathrm{Na_2SO_4}) \approx 0{,}5$ mol/l.

Add approximately 750 ml of water to a 1 litre volumetric flask. Add and dissolve 71 g ± 1 g of sodium sulfate (anhydrous), dilute to volume with water, stopper and mix well.

5.2.8 Sulfuric acid solution, $c(\mathrm{H_2SO_4}) = 0{,}05$ mol/l.

5.2.9 Thymol blue solution, 0,04 % in water.

5.3 Reagents for methylene blue method

5.3.1 Boron standard solution, boron = 0,1 g/l.

Dissolve 0,572 g ± 0,001 g of orthoboric acid in water, transfer to a 1 litre volumetric flask, add water up to the mark, stopper and mix well. This solution can be kept for 6 months after preparation.

5.3.2 Boron standard solution, boron = 0,001 g/l.

Pipette 10 ml of boron standard solution (0,1 g/l) (5.3.1) into a 1 litre volumetric flask, add water up to the mark, stopper and mix well. This solution should be used within 10 days after preparation.

5.3.3 Boron standard solution, boron = 0,000 1 g/l.

Pipette 10 ml of boron standard solution (0,001 g/l) (5.3.2) into a 100 ml volumetric flask, add water up to the mark, stopper and mix well. Prepare this solution at the time of use. This solution should be used within 8 h after preparation.

5.3.4 1,2-Dichloroethane (DANGER: ⟨F⟩⟨C⟩).

5.3.5 Hydrofluoric acid (1 + 9).

Prepare the solution in a fume hood. **(EXTREME DANGER: ⟨⟨C⟩⟩⟨⟨S⟩⟩. Concentrated hydrofluoric acid is extremely corrosive.)**

5.3.6 Methylene blue solution.

Dissolve 0,40 g ± 0,01 g of methylene blue in water to make 100 ml of solution. Add 10 ml of this solution to a 100 ml volumetric flask, add water to the mark, stopper and mix well.

5.3.7 Silver sulfate solution, 0,3 g/l.

Dissolve 0,15 g ± 0,01 g of silver sulfate in water to make 500 ml of solution.

5.3.8 Sodium carbonate, Na_2CO_3, anhydrous.

5.3.9 Sodium hydroxide, $c(\mathrm{NaOH}) \approx 1$ mol/l.

5.3.10 Sulfuric acid (3 + 97).

While stirring, slowly and cautiously add 3 parts of sulfuric acid to 97 parts of water (DANGER: ⟨C⟩⟨B⟩).

6 Apparatus

All glassware subject to heating shall be of heat-resistant borosilicate glass[2].

Pipettes and other volumetric glassware shall meet the requirements specified in ISO 10349-1.

6.1 Special apparatus for method using boric acid-mannitol complex

6.1.1 Electronic pH-meter, complete with pH electrodes and capable of reading to three decimal places, i.e. 0,001 pH units.

6.1.2 Alarm stop-clock.

6.2 Special apparatus for methylene blue method

6.2.1 Separating funnel, polyethylene or polypropylene, of capacity 50 ml.

6.2.2 Photometer, spectrophotometer measuring in the visible portion of the electromagnetic spectrum.

7 Sampling and sample preparation

It is necessary that the analysis be carried out on a representative sample and the sampling of a process effluent or a plant effluent can encompass many difficulties and due care shall be exercised. See ISO 5667-1, ISO 5667-2 and ISO 5667-3. Sampling shall be carried out in conformance with regulatory requirements. Sampling should be carried out under typical operating conditions and the sample normally should be representative of the overall plant effluent. Daily samples that are truly representative of the effluents require sampling over 24 h and sampling that is proportional to flow rate. Samples taken during a sudden discharge or during another non-routine operation will not yield results representative of the normal operation.

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[2] 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 product.

8 Procedure

NOTE — In the method using boric acid-mannitol complex, if the pH-meter does not have automatic temperature compensation, standardization of electrodes and pH measurements shall be carried out at 23 °C ± 2 °C. Do not use buffer solutions containing boron.

8.1 Procedure for method using boric acid-mannitol complex for levels of boron from 0,1 mg/l to 5 mg/l

8.1.1 Removal of phosphate

Add, from a graduated cylinder, 400 ml of sample to a 600 ml beaker. Using a pipette, add 10 ml of lead acetate solution (DANGER: ⟨⟨S⟩⟩) (5.2.1). Place on a magnetic stirrer and stir moderately. Using a pipette, add 10 ml of sodium sulfate solution (5.2.7). Remove the stirring bar and allow the beaker to stand for 2 min. Decant 250 ml of the supernatant liquid into a graduated cylinder and discard the excess. Transfer the liquid to a 400 ml beaker. Add 5 drops of thymol blue solution (5.2.9).

8.1.2 Removal of carbonate

Add sulfuric acid solution (5.2.8) to the solution, drop by drop, until the thymol blue changes colour. Cover the beaker with a watch glass and boil gently for 2 min. Place the beaker in a water bath and cool the contents to room temperature.

8.1.3 Preparation for titration

Standardize the pH electrodes (see 6.1.1). Stir the sample moderately on a magnetic stirrer. Adjust the pH of the sample to 7,00 using 0,5 mol/l and 0,020 0 mol/l sodium hydroxide solutions (5.2.6 and 5.2.4). Allow 1 min for equilibration and make any final adjustments to give pH 7,00 ± 0,05 [sulfuric acid solution (5.2.8) may be used if the pH is too high]. If the drift is more than 0,004 in 30 s, wait another minute and readjust the pH of the sample.

8.1.4 Titration

Fill and level a 10 ml burette with 0,020 0 mol/l sodium hydroxide (5.2.4). Record the pH of the sample to three decimal places, i.e. 0,001 pH unit. Set the alarm stop-clock (6.1.2) for 2 min and add 5,0 g ± 0,1 g of mannitol (5.2.2). Immediately titrate with the sodium hydroxide solution to the recorded pH value. Finish the titration before the alarm sounds.

When the alarm sounds, wait 5 s and record the pH. The pH should be 0,005 of the recorded value. If not, discard the results and start again from 8.1.1. Record the titrant volume; this is V_1.

8.1.5 Obtaining a blank reading

Repeat the procedure described in 8.1.1 to 8.1.4 using 250 ml of water instead of the sample. The burette reading in 8.1.4 now becomes V_2. The blank reading should be taken at least once daily by the technician performing this analysis. If V_2 is greater than 0,12 ml, the analysis should be repeated using fresh reagents.

8.2 Procedure for method using boric acid-mannitol complex for high levels of boron (5 mg/l to 100 mg/l)

8.2.1 Removal of carbonate

Pipette 10,0 ml ± 0,1 ml of sample into a 400 ml beaker. Add 240 ml of water from a graduated cylinder. Pipette 10 ml of sodium acetate solution (5.2.3) and 5 ml of sulfuric acid solution (5.2.8). Cover the beaker with a watch glass and boil gently for 2 min. Place the beaker in a water bath and cool the contents to room temperature.

8.2.2 Preparation for titration

Standardize the pH electrodes (see 6.1.1). Stir the sample moderately on a magnetic stirrer. Adjust the pH of the sample to 7,00 using 0,5 mol/l and 0,020 0 mol/l sodium hydroxide solutions (5.2.6 and 5.2.4). Allow 1 min for equilibration and make any final adjustments to give pH 7,00 ± 0,05 [sulfuric acid solution (5.2.8) may be used if the pH is too high]. If the drift is more than 0,004 in 30 s, wait another minute and readjust the pH of the sample.

8.2.3 Titration

Fill and level a 10 ml burette with 0,020 0 mol/l sodium hydroxide solution (5.2.4). Record the pH of the sample to three decimal places, i.e. 0,001 pH unit. Set the alarm stop-clock (6.1.2) for 2 min and add 5,0 g ± 0,1 g of mannitol (5.2.2). Immediately titrate with the sodium hydroxide solution to the recorded pH value. Finish the titration before the alarm sounds. When the alarm sounds, wait 15 s and record the pH. The pH should be 0,005 of the recorded value. If not, discard the results and start again from 8.2.1. Record the titrant volume; this is V_1.

8.2.4 Obtaining a blank reading

Repeat the procedure in 8.2.1 to 8.2.3 using 250 ml of water instead of the sample. The burette reading in 8.2.3 now becomes V_2. The blank reading should be taken at least once daily by the technician performing this analysis. If V_2 is greater than 0,15 ml, the analysis should be repeated using fresh reagents.

8.2.5 Expression of results; method using boric acid-mannitol complex

8.2.5.1 Method of calculation – low levels of boron

The boron concentration, in milligrams per litre, is given by the formula

$$\rho_B = (V_1 - V_2) \times 0{,}99$$

8.2.5.2 Method of calculation – high levels of boron

The boron concentration, in milligrams per litre, is given by the formula

$$\rho_B = (V_1 - V_2) \times 24{,}5$$

8.2.6 Precision

Four standard mixes, ranging in boron concentrations from 5 mg/l to 100 mg/l, were prepared and eight analyses were performed by two analysts. The 95 % confidence limit for a single analysis was ± 7 mg/l.

Five standard mixes, ranging in boron concentrations from 0,4 mg/l to 5 mg/l, were prepared and ten analyses were performed by two analysts. The 95 % confidence limit for a single analysis was ± 0,2 mg/l.

8.3 Procedure for methylene blue method

NOTE — The chromate ion interferes. However, adding several drops of hydrogen peroxide (1 + 100), followed by heating to decompose the excess hydrogen peroxide, removes the interference.

8.3.1 Direct sample preparation

If the sample is not neutral, neutralize with sulfuric acid (3 + 97) (5.3.10) or sodium hydroxide (5.3.9).

Place a 10 ml aliquot of the sample (containing 0,001 mg or less as boron) in a separating funnel (5.1.5.2) and dilute to 15 ml with water, add 3 ml of sulfuric acid (3 + 97) (5.3.10), 3 ml of methylene blue solution (5.3.6) and 10 ml of 1,2-dichloroethane (DANGER: ⟨F⟩⟨C⟩) (5.3.4). (This will extract materials such as anionic surface active agents.) Mix by shaking for 1 min and allow to stand.

NOTE — A considerable period of time is necessary for the separation of the 1,2-dichloroethane (DANGER: ⟨F⟩⟨C⟩) and aqueous layers.

Discard the 1,2-dichloroethane layer (DANGER: ⟨F⟩⟨C⟩), slowly add 3 ml of hydrofluoric acid (DANGER: ⟨⟨C⟩⟩⟨⟨S⟩⟩) (5.3.5) and allow to stand for 1 h.

Slowly add 10 ml of 1,2-dichloroethane (DANGER: ⟨F⟩⟨C⟩), mix by vigorous shaking for 1 min and allow to stand.

Proceed to 8.3.3.

8.3.2 Fusion sample preparation

In the case where fluoride ions or a large amount of organic substances are present, place a definite amount of sample in a platinum dish, add 0,1 g of sodium carbonate (5.3.8), evaporate to dryness, and then fuse the mass. After cooling, add water, heat to dissolve the residue and, after neutralizing with sulfuric acid (3 + 97) (5.3.10), dilute the solution to a definite volume.

Place an aliquot of this solution containing 0,000 1 mg to 0,001 mg of boron in a separating funnel (6.2.1), and dilute with water to 15 ml. Add 3 ml of sulfuric acid (3 + 97) (5.3.10) and 3 ml of hydrofluoric acid (1 + 9) (DANGER: ⟨⟨C⟩⟩⟨⟨S⟩⟩) (5.3.5), mix by shaking and allow to stand for about 1 h. Then add 3 ml of methylene blue solution (5.3.6), and mix by shaking. Then add 10 ml of 1,2-dichloroethane (DANGER: ⟨F⟩⟨C⟩) (5.3.4), and mix by vigorous shaking for 1 min to extract the boron complex. Thereafter, proceed to 8.3.3.

8.3.3 Completion of sample preparation

Transfer the 1,2-dichloroethane (DANGER: ⟨F⟩⟨C⟩) layer into another separating funnel, add 5 ml of silver sulfate solution (5.3.7), mix by shaking for 1 min to wash the 1,2-dichloroethane layer and allow to stand.

Transfer a part of the 1,2-dichloroethane (DANGER: ⟨F⟩⟨C⟩) layer into a 1 cm absorption cell and measure the absorbance at a wavelength near 660 nm using 1,2-dichloroethane as a reference solution. Since methylene blue can coat the walls of the absorption cell, it is recommended that the cells be balanced using a double-beam spectrophotometer.

NOTE — When methylene blue adheres to the separating funnel, absorption cells, etc., they shall be cleaned with ethanol.

Prepare a blank test using 15 ml of water and carrying out the procedures specified in the first two paragraphs of 8.3.1 to provide an absorbance correction for the sample.

8.3.4 Calibration curve

Run a series of analyses, step by step, adding 1 ml to 10 ml of boron standard solution (0,000 1 g/l) to the separating funnels and carry out the procedure specified in the second paragraph of 8.3.2 then in the first and second paragraphs of 8.3.3. Construct a curve for the relation between absorbance and quantity of boron.

8.3.5 Expression of results

Determine the amount of boron from the calibration curve and calculate the concentration, in grams per litre, of the boron in the sample.

9 Test report

The test report shall include the following information:

a) an identification of the sample;

b) the reference of the method used;

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard, or regarded as optional.