BRITISH STANDARD

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Implementation of
ISO 6850:1994

Photography — Processing wastes — Determination of nitrate by a spectrometric method using brucine

Committees responsible for this British Standard

The preparation of this British Standard was entrusted to Technical Committee CPM/14, Photographic chemicals and processing, upon which the following bodies were represented:

British Institute of Non-Destructive Testing
British Photographic Association
Chemical Industries' Association
Department of the Environment (Water Directorate)
Royal Photographic Society

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Contents

National foreword

This British Standard reproduces verbatim ISO 6850:1994 and implements it as the UK national standard.

This British Standard is published under the direction of the Consumer Products and Services Sector Board whose Technical Committee CPM/14, has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international committee any enquiries on interpretation, or proposals for change, and keep UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the ISO title page, pages ii to iv, pages 1 to 6 and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

INTERNATIONAL STANDARD

ISO 6850

First edition
1994-12-15

Photography — Processing wastes — Determination of nitrate by a spectrometric method using brucine

Photographie — Effluents de traitement — Détermination de la teneur en nitrate par une méthode spectrométrique à la brucine

Reference number
ISO 6850:1994(E)

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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 6850 was prepared by Technical Committee ISO/TC 42, *Photography*.

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Introduction

This International Standard is one a series devoted to the analysis of photographic wastes; it encompasses the field of analysis of nitrate ions 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.

1 Scope

This International Standard specifies a spectrometric method for the determination of nitrates in photographic processing wastes. Pretreatment of the sample is necessary to remove interferences present in photographic processing wastes.

This method can be applied to samples containing nitrate in the concentration range 4,4 mg/l to 88 mg/l of nitrate (1 mg/l to 20 mg/l of nitrogen).

2 Normative references

The following 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 6353-1:1982, *Reagents for chemical analysis — Part 1: General requirements.*

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

The reaction between nitrate and brucine produces a yellow colour, the intensity of which is measured at 410 nm. The reaction rate between brucine and nitrate ions and hence the intensity of the colour formed is affected significantly by the amount of heat generated during the test. Thus the procedure seeks to control the heat by optimizing the reagent addition sequence and by subsequent incubation of the reaction mixture for a precise interval of time at a known temperature.

The sample is pretreated to remove interferences in photographic processing wastes. Sodium arsenite solution is added to the sample to eliminate any residual chlorine present in the sample. Sulfanilic acid in the brucine reagent eliminates nitrite interference. The sample is then reacted with brucine reagent, acidified with sulfuric acid, and incubated for exactly 20 min in a boiling water bath. The absorbance of the coloured sample is measured at 410 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 test and footnotes 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 material is noted in the test procedures, 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. 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 symbol will 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 code system defined 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.

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

5.1.3 ***Strength of solutions***

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

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

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

5.1.3.4 When a solution is to be diluted, its dilution 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

5.2.1 *Brucine reagent*

5.2.1.1 *Brucine/sulfanilic acid stock solution*

Dissolve 1,00 g ± 0,01 g of brucine sulfate $[(C_{23}H_{26}N_2O_4)_2.2H_2SO_4 \cdot 7H_2O]$ (DANGER: <<S>><C>) and 0,10 g ± 0,01 g of sulfanilic acid ($C_6H_7NSO_3 \cdot H_2O$) in 70 ml of hot water in a 150 ml beaker. Then add, from a tip-up pipette (**6.6**), 3 ml of hydrochloric acid, $\rho \approx 1{,}18$ g/ml (DANGER: <C><B>), cool and dilute to 100 ml. This stock solution shall be stored in a refrigerator, where it is stable for several months.

5.2.1.2 *Preparation*

Prepare the brucine reagent by mixing 25 ml of the brucine/sulfanilic acid stock solution (DANGER: <<S>><C<) (**5.2.1.1**) and 125 ml of the sodium chloride (**5.2.7**). This reagent shall be prepared fresh each day.

5.2.2 *Decolorizing charcoal*

5.2.3 *Filter aid* (diatomaceous earth).

5.2.4 *Standard nitrate solutions*

Prepare these from a stock solution of potassium nitrate containing 4,4 g/l nitrate ion (1 g/l of nitrogen) which is prepared from 7,175 g ± 0,001 g of dried potassium nitrate (KNO_3). (This should be dried in an oven at 100 °C to 105 °C for 2 h.) Transfer quantitatively to a 1 litre one-mark volumetric flask, dissolve in about 800 ml of water, and dilute to the mark. This solution is stable for 6 months.

NOTE 1 Experience in one laboratory shows that nitrate standards are subject to biodegradation (nitrification or denitrification) even with refrigeration and can be stabilized by the addition of 1 ml to 2 ml of chloroform per litre. Samples are stabilized by the adjustment of the pH to the range 1 to 2 by the addition of sulfuric acid.

Prepare the following standard solutions by dilution from the stock solution using one-mark pipettes and one-mark volumetric flasks.

5.2.4.1 *Nitrate standard,* 440 mg/l of nitrate ion.

Dilute 50 ml of stock solution (**5.2.4**) to 500 ml.

5.2.4.2 *Nitrate standard,* 8,8 mg/l of nitrate ion.

Dilute 10 ml of 440 mg/l standard solution (**5.2.4.1**) to 500 ml.

5.2.4.3 *Nitrate standard,* 44 mg/l of nitrate ion.

Dilute 50 ml of 440 mg/l standard solution (**5.2.4.1**) to 500 ml.

5.2.4.4 *Nitrate standard,* 79,2 mg/l of nitrate ion.

Dilute 90 ml of 440 mg/l standard solution (**5.2.4.1**) to 500 ml.

5.2.5 *Silver sulfate/ammonia solution*

Add 23 g of silver sulfate (Ag_2SO_4), weighed to the nearest 0,1 g, to 250 ml of water in a 1 litre one-mark volumetric flask. Stir on a magnetic stirrer, and add 700 ml of ammonium hydroxide (NH_4OH), $\rho \approx 0{,}91$ g/ml (DANGER: <C><B>), stirring until all is dissolved. Remove the stirring bar and dilute to the mark with ammonium hydroxide, $\rho \approx 0{,}91$ g/ml (<C><B>). This reagent shall be stored in a tightly stoppered brown reagent bottle.

5.2.6 *Sodium arsenite,* $NaAsO_2$, 5 g/l solution.

Weigh, to the nearest 0,1 g, 5 g of sodium arsenite (DANGER: <<S>>) and add to 800 ml of water in a 1 litre one-mark volumetric flask. Dissolve by stirring on a magnetic stirrer, and dilute to the mark with water.

5.2.7 *Sodium chloride,* NaCl, 300 g/l solution.

Weigh, to the nearest 0,1 g, 300 g of sodium chloride and dissolve it in about 700 ml of water in a one-mark 1 litre volumetric flask. Mix well and dilute to the mark with water.

5.2.8 *Dilute sulfuric acid,* H_2SO_4 (3 + 1) (DANGER: <C>).

Prepare by slowly adding 750 ml of concentrated sulfuric acid, $\rho \approx 1{,}84$ g/ml (DANGER: <<C>>) to the 250 ml of water in a 1 litre heat-resistant borosilicate beaker, stirred on a magnetic stirrer. Cool and dilute to 1 litre with water.

6 Apparatus

All glassware subject to heating shall be of heat-resistant borosilicate glass[1]. Pipettes and other volumetric glassware shall meet the requirements specified in ISO 10349-1.

All glassware shall be cleaned with hot 1 mol/l hydrochloric acid[2] (DANGER: <C>) and rinsed thoroughly before use.

6.1 *Spectrometer,* for measurements at a wavelength of 410 nm, and fitted with two matched silica cells of optical path length 1 cm.

6.2 *Microfiltration equipment,* using glass fibre filters about 47 mm in diameter.

6.3 *Water bath,* capable of being maintained between 14 °C and 18 °C.

6.4 *Water bath,* capable of being maintained at 95 °C ± 1 °C.

6.5 *Alarm timer*

6.6 *Pipettes* (see **4.3**).

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. Guidance on sampling programmes and techniques can be found in parts 1 to 3 of ISO 5667. Sampling shall be carried out in conformance with regulatory requirements. Sampling should be 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 flowrate. Samples taken during a sudden discharge or during another non-routine operation will not yield results representative of the normal operation.

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

[2] This may be prepared from concentrated hydrochloric acid, $\rho \approx 1{,}18$ g/ml (DANGER: <C><B>).

Nitrate can be unstable as it is subject to biodegradation (see note 1 in **5.2.4**). Other than filtration and pretreatment to remove possible interferences as described below, the sample needs no other special handling or preservation requirements.

8 Procedure

NOTE 2 Pretreatment of the sample is a time-consuming process. However, running several samples at once can reduce the time to 10 min to 15 min per sample.

8.1 Sample pretreatment to remove interferences

Pipette 10,0 ml of the effluent sample into a 100 ml one-mark volumetric flask and dilute to the mark with water. Stopper, mix well by inverting, then pour the contents of the flask into a 250 ml beaker. Using a tip-up pipette (**6.6**), add 15 ml of freshly opened silver sulfate/ammonia solution (**5.2.5**), and swirl. Cover the beaker with a watch glass, place on a hot plate and bring the solution to a boil for 5 min using the timer (**6.5**). Remove the beaker from the hot plate and place it in the cold water bath (**6.3**). Cool the contents to between 14 °C and 18 °C.

Add about 0,6 g of decolorizing charcoal (**5.2.2**), mix well by swirling, then filter the mixture through the filtration apparatus (**6.2**). If the filtrate (labelled A) is not clear and colourless, repeat the charcoal and filtration treatment. Rinse the beaker several times with water, shaking out as much excess water as possible and discard the rinsing water. Return the filtrate A to the beaker. Carefully add 1 ml of the sodium chloride (**5.2.7**) from a tip-up pipette (**6.6**) and mix well by swirling. Carefully add 4 ml of sulfuric acid (**5.2.8**) (DANGER:<C>) from a tip-up pipette and mix well by swirling. Add about 0,6 g of filter aid (**5.2.3**) and mix well by swirling. Then cover the beaker with a watch glass and return it to the cold water bath (**6.3**), allowing enough time for the temperature to equilibrate.

Set up the filtration apparatus (**6.2**) and prepare the filter. Add about 1,2 g of filter aid to the filtration apparatus, followed by approximately 100 ml of water. Mix the contents of the filter well by swirling and then filter the water from the apparatus with an aspirator. Discard the filtrate.

Add the contents of the beaker equilibrated in the cold water bath to the filtration apparatus and filter, labelling the filtrate as B. Rinse the beaker with water and shake out the excess water. Discard the rinsing water. Return the filtrate B to the beaker. Add 1 ml of sodium chloride (**5.2.7**) from a tip-up pipette (**6.6**). If the filtrate is cloudy, it shall be discarded and the sample pretreatment shall be repeated using a fresh aliquot from the 10 % solution of the sample. If repetition fails to produce a clear filtrate, check all reagents, equipment and sample handling techniques. When the final filtrate (labelled C) is clear, the pretreatment is finished.

8.2 Colour development and spectrometric measurements

Pipette 10,0 ml of pretreated sample C into an 18 mm × 150 mm test tube. Add 2 drops of the sodium arsenite (DANGER: <<S>>) (**5.2.6**) and then 2,5 ml of brucine reagent (DANGER: <<S>><C>) (**5.2.1**) from a burette. Mix well by swirling and stopper the test tube. Place the stoppered test tube in a rack cooled in the cold water bath (**6.3**) and add 10 ml of sulfuric acid (**5.2.8**) (DANGER: <C>) from a burette. Return the stoppered test tube to the cold water bath and allow to cool.

Remove the stoppers from the tubes and place the rack containing the samples in a boiling water bath (**6.4**) for exactly 20 min. The temperature of the water bath shall not drop below 95 °C. Remove the rack from the boiling water bath and return it to the cold water bath (**6.3**) to stop colour development. When the samples have cooled to between 14 °C and 18 °C, remove the rack from the cold water bath and allow the samples to equilibrate to room temperature.

Measure the absorbance of the sample at 410 nm using a 1 cm cell. If sample is too cold, water will condense on the exterior of the cell causing erroneous results.

If the absorbance is above 0,550, repeat the whole determination with a diluted sample. Note the sample absorbance Y.

8.3 Preparation of calibration graph

Carry out the entire procedure including pretreatment daily on the three nitrate standard solutions (**5.2.4.2**, **5.2.4.3** and **5.2.4.4**). Record the absorbance of the standard solutions in the following way:

Y_2 is the absorbance of the 8,8 mg/l of nitrate solution (2,0 mg/l of nitrogen);

Y_{10} is the absorbance of the 44,0 mg/l of nitrate solution (10,0 mg/l of nitrogen);

Y_{18} is the absorbance of the 79,2 mg/l of nitrate solution (18,0 mg/l of nitrogen).

Plot the absorbance values Y_2, Y_{10} and Y_{18} versus the nitrogen values on graph paper and draw the best straight line through the three points and the origin.

9 Expression of results

The nitrate or nitrogen content of the sample, in milligrams per litre, can be read directly from the graph constructed in **8.3**. Alternatively, either of the following two equations can be used to determine the sample content:

nitrate content =

$$= \frac{4,4\left[10 + Y - (Y_2 + Y_{10} + Y_{18})\right]}{3} \times \frac{16}{(Y_{18} - Y_2)} \text{ mg/l}$$

or

nitrogen content =

$$= \frac{\left[10 + Y - (Y_2 + Y_{10} + Y_{18})\right]}{3} \times \frac{16}{(Y_{18} - Y_2)} \text{ mg/l}$$

10 Precision

In an interlaboratory test, carried out in accordance with ISO 5725, twelve standards and four effluent samples were analysed by two operators in two different laboratories using two different spectrometers (a Beckman model B and a Beckman model DU). A linear relationship exists between the concentration of nitrate and the absorbance.
The 95 % confidence limits for an individual determination in the range of 0 mg/l to 88 mg/l of nitrate (0 mg/l to 20 mg/l of nitrogen) were found to be ± 4,4 mg/l of nitrate (± 1,0 mg/l of nitrogen).

Annex A (informative)
Bibliography

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

ISO 5667-2:1982, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1985, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method using inter-laboratory tests.*

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