BRITISH STANDARD

BS ISO 7766:2003

Processing photographic wastes — Analysis of cyanides — Determination of hexacyanoferrate(II) and hexacyanoferrate(III) by spectrometry

ICS 13.030.30; 37.040.30

British Standards

National foreword

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Summary of pages

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INTERNATIONAL STANDARD

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Processing photographic wastes — Analysis of cyanides — Determination of hexacyanoferrate(II) and hexacyanoferrate(III) by spectrometry

Effluents de traitement photographiques — Analyse des cyanures — Détermination de l'hexacyanoferrate(II) et de l'hexacyanoferrate(III) par spectrométrie

Reference number
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Foreword

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Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 7766 was prepared by Technical Committee ISO/TC 42, *Photography*.

Introduction

This International Standard is devoted to the analysis of photographic wastes; it encompasses the analysis of complexed iron cyanides (hexacyanoferrates) in photographic effluents.

Some of the chemicals specified in the test procedures are caustic, toxic, or otherwise hazardous. Specific warning, caution and danger notices are noted but, in addition, the normal precautions required during the performance of any chemical procedure should be exercised at all times.

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

Complexed cyanides are used in the bleaching stage of colour photographic processing and it is, therefore, possible for the cyanide portion of the resulting photographic effluent to reach a reportable level. Complexed cyanides contribute to the total cyanides in those tests in which the sample preparation breaks down the complexed cyanides. It is the purpose of this International Standard to provide a method giving an independent determination of the cyanide present as hexacyanoferrate complexes. Due to the chemical behaviour of cyanide complexes, it is not possible to specify a single method for the quantitative determination of complexed cyanides in these effluents.

The analysis of cyanide is covered in various aspects in the following International Standards:

- ISO 6703-1:1984, *Water quality — Determination of cyanide — Part 1: Determination of total cyanide;*
- ISO 6703-2:1984, *Water quality — Determination of cyanide — Part 2: Determination of easily liberatable cyanide.*

NOTE 1 Easily liberatable cyanides are defined as substances with cyanide groups and a measurable hydrocyanic acid vapour pressure at pH 4 and room temperature.

NOTE 2 Cyanide diffuses as hydrogen cyanide (HCN) at room temperature from a solution at pH 6; the procedure determines cyanide from simple compounds of cyanide and easily dissociated complexes.

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Processing photographic wastes — Analysis of cyanides — Determination of hexacyanoferrate(II) and hexacyanoferrate(III) by spectrometry

1 Scope

This International Standard establishes a test method for the determination of hexacyanoferrate(II) (ferrocyanide) and hexacyanoferrate(III) (ferricyanide), referred to hereafter as $Fe(CN)_6$, in photographic processing effluents[1]. Results are reported as hexacyanoferrate, $Fe(CN)_6$.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

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 10349-1:2002, *Photography — Photographic-grade chemicals — Test methods — Part 1: General*

3 Safety and operational precautions

3.1 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 and, in some cases, other protective apparel such as rubber gloves, face masks and aprons. 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.

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1) Significant levels of thiosulfate (hypo) can result in interference. Significant levels of thiosulfate in processing-machine effluents result in oxidation of the thiosulfate by iron (III). Sulfur will form, increasing the spectrophotometric absorbance which is measured. Also, thiosulfate may deplete the added iron (III) leaving nothing for the colour reaction. The method is applicable to effluents from buildings where the thiosulfate would be diluted by the rest of the building wastes and this would eliminate the interference.

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 that 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.

Hazard warning symbols will not be used for common organic solvents when used in quantities of less than 1 l, 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 accordance with legal requirements.

The hazard code 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 pertinent information from the manufacturer about the hazards, handling, use and disposal of these chemicals.

3.2 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.
〈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.
〈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.

3.3 Safety precautions

ALL PIPETTE OPERATIONS SHALL BE PERFORMED WITH A PIPETTE BULB OR PLUNGER PIPETTE. Failure to observe this warning notice can result in cyanide poisoning. THIS IS A CRITICAL SAFETY WARNING!

Digestion procedures shall be performed in a fume hood. Hydrogen cyanide or other toxic substances may be evolved.

Safety glasses shall be worn for all laboratory work.

4 Principle

A sample of effluent, or diluted effluent, is treated with a mixture of iron(II) and iron(III) ions. If $Fe(CN)_6$ is present, a blue suspension will form. In the range 1,0 mg/l to 10,0 mg/l of $Fe(CN)_6$, this suspension is stable and its absorbance is linear with its concentration. The absorbance is measured with a spectrometer, and the concentration determined from a previously established calibration.

5 Reactions

$$3[Fe(II)(CN)_6]^{4-} + 4Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3$$

$$2[Fe(III)(CN)_6]^{3-} + 3Fe^{2+} \rightarrow Fe_3[Fe(CN)_6]_2$$

6 Reagents and materials

6.1 General

6.1.1 Handling and labelling

Reagents shall be handled in accordance 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.

6.1.2 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, as specified in ISO 6353-1, ISO 6353-2 and ISO 6353-3.

6.1.3 Water

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

6.1.4 Strength of solutions

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

6.1.4.2 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.

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

6.1.4.4 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 water (6.1.3).

6.2 Reagents

6.2.1 Ferrous-ferric reagent

Dissolve with continuous stirring, using a magnetic stirrer, 0,75 g of iron(II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), 0,75 g of iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and 3 ml of concentrated hydrochloric acid (6.2.2) (DANGER: ⟨B⟩, ⟨C⟩) in 20 ml of water contained in a 50 ml beaker. Dilute to 30 ml.

6.2.2 Hydrochloric acid (HCl), concentrated $\rho \approx 1{,}18$ g/ml (DANGER: ⟨B⟩, ⟨C⟩)

6.2.3 Hydrochloric acid solution, 1 mol/l

To about 500 ml of water in a 1 l beaker, add 31 ml of concentrated hydrochloric acid (6.2.2) (⟨B⟩, ⟨C⟩) with constant stirring. Dilute to 1 l with water.

6.2.4 Potassium ferrocyanide standard solution, corresponding to 0,040 g/l of $Fe(CN)_6$

Prepare a solution containing 4,0 g/l of $Fe(CN)_6$ by adding 8,0 g of potassium ferrocyanide trihydrate $[K_4Fe(CN)_6 \cdot 3H_2O]$ (DANGER: ⟨⟨S⟩⟩) to a 1 l one-mark volumetric flask. Add water to dissolve and make up to the mark. Pipette 10 ml of this solution into a 1 l one-mark volumetric flask. Make up to the mark with water. This solution contains 0,040 g/l of $Fe(CN)_6$. This dilute standard solution should be prepared fresh daily.

6.2.5 Sodium hydroxide solution, 100 g/l

Slowly add 100 g of sodium hydroxide pellets (DANGER: ⟨⟨C⟩⟩) to 800 ml of cold water in a 2 l container. Extreme caution shall be exercised in this operation as considerable heat will be evolved. The procedure should be carried out under an exhaust hood. It is also advisable to place the container in a polyethylene pail. Stir until dissolved, cool and dilute to 1 l. This concentration is not critical.

6.3 Materials

6.3.1 Filter paper, pre-folded, medium porosity (8 µm particle retention); medium flow (55 s for 100 ml prefiltered water); 15 cm^2 folded paper[2].

6.3.2 Litmus paper, blue

7 Apparatus

7.1 General

All glassware subject to heating shall be heat-resistant borosilicate glass[3].

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

7.2 Spectrometer, capable of absorbance at 700 nm.

7.3 Cells, of optical path length 1 cm.

8 Sampling and sample preparation

It is necessary that the analysis be carried out on a representative sample. The sampling of a process effluent or a plant effluent can encompass many difficulties and due care shall be exercised, as specified in ISO 5667-1, ISO 5667-2 and ISO 5667-3.

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2) Whatman® No. 41 and 2V filter paper are examples of suitable products available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these products.

3) 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.

Sampling shall be carried out in accordance with regulatory requirements. Sampling should be done under typical operating conditions and 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 the flow rate.

Samples taken during a sudden discharge or during another non-routine operation will not yield results representative of the normal operation.

9 Procedure

9.1 Pretreatment of glassware

Pretreat all glassware with 1 mol/l hydrochloric acid (6.2.3) and rinse thoroughly with water before use.

9.2 Sample treatment

9.2.1 Test samples of effluent for this determination require no special treatment for preservation. If necessary, they should be well agitated before initial pipetting and during subsequent dilution. A 100 ml test sample of effluent should be collected and labelled “Solution A”. Pipette 25,0 ml of this sample into a 250 ml one-mark volumetric flask and make up to the mark with water. Label this “Solution B”.

9.2.2 Transfer 100 ml of Solution B to a 250 ml conical flask. Make the solution alkaline with 10 drops of sodium hydroxide solution (6.2.5). Mix well, wait 5 min, and then filter using medium-porosity filter paper (6.3.1). Acidify the filtrate by adding concentrated hydrochloric acid (6.2.2) (⟨B⟩, ⟨C⟩) dropwise using litmus paper (6.3.2) as the indicator. Transfer two 40 ml aliquots of the filtrate to 150 ml beakers, labelling one as “Test solution” and the other as “Blank.”

9.3 Formation of colour and measurement of absorbance

Add two drops of the ferrous-ferric reagent (6.2.1) to the “Test solution” beaker and allow to stand for 15 min. If no colour is produced, repeat the sample treatment procedure of 9.2.2 using Solution A instead of Solution B.

Using the spectrometer (7.2), measure the absorbances at 700 nm in 1 cm cells (7.3) against air, including each corresponding blank. If the absorbance of the test solution derived from Solution B is greater than 0,80, dilute Solution B by an additional factor of 10 and repeat the sample preparation (see 9.2.2) and measurement.

9.4 Calibration

Prepare a series of calibration solutions from the potassium ferrocyanide standard solution (6.2.4) (⟨⟨S⟩⟩) by transferring the volumes given in Table 1 from a 25 ml class a pipette into 100 ml one-mark volumetric flasks.

Table 1 — Calibration solutions

Volume of standard solution ml	Concentration of $Fe(CN)_6$ mg/l
0	0
2,0	0,8
5,0	2,0
15,0	6,0
25,0	10,0

Treat each of these 100 ml standard solutions in the same way as the 100 ml of Solution B. However, only one blank needs to be measured.

Subtract the absorbance of the blank from the absorbance of each of the standard solutions at 700 nm. Then divide these values into the corresponding $Fe(CN)_6$ concentration values to obtain a set of calibration factors. Average the factors to obtain a mean calibration factor F_c.

NOTE For a 1 cm cell, the mean calibration factor should be between 22 and 29. A value of 25 may be taken for rough analyses.

10 Expression of results

10.1 Calculation of total $Fe(CN)_6$ concentration

The concentration, in milligrams per litre, of hexacyanoferrate [$Fe(CN)_6$] is

$$\left(A_S - A_B\right) \cdot F_c \cdot D$$

where

A_S is the absorbance of the test solution at 700 nm;

A_B is the absorbance of the blank at 700 nm;

F_c is the calibration factor;

D is the factor by which the original test sample was diluted (e.g. D = 10 if Solution B was used).

10.2 Calibration curve

Alternatively, a plot can be made of absorption versus concentration and the analysis values read from the plot.

11 Test report

The test report shall include the following information:

- the method used;
- the results and method of expression used;
- any unusual features noted during the determination;
- details of any operating procedures not specified elsewhere in this International Standard, or regarded as optional, together with any incidents likely to have affected the results.

Bibliography

[1] ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

[2] ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility for a standard measurement method*

[3] ISO 6703-1:1984, *Water quality — Determination of cyanide — Part 1: Determination of total cyanide*

[4] ISO 6703-2:1984, *Water quality — Determination of cyanide — Part 2: Determination of easily liberatable cyanide*

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