

INTERNATIONAL
STANDARD

ISO
7766-1

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**Photography — Processing wastes —
Analysis of cyanides —**

Part 1:

**Determination of hexacyanoferrate(II) and
hexacyanoferrate(III) by spectrometry**

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ISO 7766-1:1993
Photographie — Effluents de traitement — Analyse des cyanures —
Partie 1: Détermination de l'hexacyanoferrate(II) et de
l'hexacyanoferrate(III) par spectrométrie



Reference number
ISO 7766-1:1993(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 7766-1 was prepared by Technical Committee ISO/TC 42, *Photography*.

ISO 7766 consists of the following parts, under the general title *Photography — Processing wastes — Analysis of cyanides*:

- Part 1: *Determination of hexacyanoferrate(II) and hexacyanoferrate(III) by spectrometry*

Further parts are in preparation.

Introduction

This part of ISO 7766 is one of a series devoted to the analysis of photographic wastes; it encompasses the field of 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; often the use of an outside laboratory will be required.

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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 part of ISO 7766 to provide a method giving an independent estimate of the cyanide present as complexes. Due to the chemical behaviour of cyanide complexes, it is not possible to specify a single method for the quantitative determination of complex cyanides in these effluents. This part of ISO 7766 provides an analytical procedure for the determination of the hexacyanoferrate complex.

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*;
- ISO 6703-4:1985, *Water quality — Determination of cyanide — Part 4: Determination of cyanide by diffusion at pH 6*.

NOTES

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

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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Photography — Processing wastes — Analysis of cyanides —

Part 1:

Determination of hexacyanoferrate(II) and hexacyanoferrate(III) by spectrometry

WARNING — Reagents and samples specified in this part of ISO 7766 contain cyanide. Although the cyanide is in a complexed form, it is possible for toxic hydrogen cyanide gas to form if the reagents are not treated correctly. Use these materials in a well-ventilated fume hood.

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1 Scope

This part of ISO 7766 establishes a test method for the determination of hexacyanoferrate(II) (ferrocyanide) and hexacyanoferrate(III) (ferricyanide), referred to hereafter as $\text{Fe}(\text{CN})_6$, in photographic processing effluents.¹⁾ Results are reported as hexacyanoferrate, $\text{Fe}(\text{CN})_6$.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 7766. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 7766 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 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 385-2:1984, *Laboratory glassware — Burettes — Part 2: Burettes for which no waiting time is specified.*

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

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

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

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

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

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

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

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 absorbance of the test. 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.

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

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 5667-3:1985, *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 by inter-laboratory tests.*

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.*

ISO 6703-4:1985, *Water quality — Determination of cyanide — Part 4: Determination of cyanide by diffusion at pH 6.*

3 Safety and hazards

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, rubber gloves and other protective apparel such as face masks or aprons where appropriate. Specific danger notices are given in the text 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 procedure section, 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 part of ISO 7766.

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

The hazard symbol system used in this part of ISO 7766 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.

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.

< 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.²⁾

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

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.

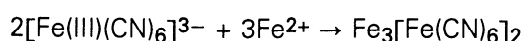
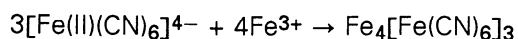
4 Principle

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

2) The flammable warning symbol < F > will not be used for quantities of common solvents under 1 litre.

1,0 mg/l to 10,0 mg/l of $\text{Fe}(\text{CN})_6$, 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



6 Reagents and materials

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 conform to applicable environmental regulations.

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. 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. See ISO 3696.

Strength of solutions: When a standardized solution is required, its concentration is expressed in moles per litre. The number of sufficient figures to which the molar concentration is known should be sufficient to ensure that the reagent does not limit the reliability of the test method. When a standardized solution is not required, its concentration is expressed in grams per litre to the appropriate number of significant figures.

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.

6.1 Ferrous-ferric reagent

Dissolve with continuous stirring, using a magnetic stirrer, 0,75 g of iron(II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), 0,75 g of iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and 3 ml of hydrochloric acid (6.2) (DANGER: < C > < B >) in 20 ml of water contained in a 50 ml beaker. Dilute to 30 ml.

6.2 Hydrochloric acid (HCl), $\rho \approx 1,18$ g/ml (DANGER: < C > < B >).

6.3 Potassium ferrocyanide standard solution, corresponding to 0,040 g/l of $\text{Fe}(\text{CN})_6$.

Prepare a solution containing 4,0 g/l of $\text{Fe}(\text{CN})_6$ by adding 8,0 g of potassium ferrocyanide trihydrate [$\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$] (DANGER: << S >>) to a 1 litre one-mark volumetric flask. Add water to dissolve and make up to the mark. Pipette 10 ml of this solution into a 1 litre one-mark volumetric flask. Make up to the mark with water. This solution contains 0,040 g/l of $\text{Fe}(\text{CN})_6$. This dilute standard solution should be prepared fresh daily.

6.4 Sodium hydroxide solution, 100 g/l

Slowly add 100 g of sodium hydroxide (DANGER: << C >>) pellets to 800 ml of cold water in a 2 litre 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 litre. This concentration is not critical.

6.5 Filter paper, pre-folded³⁾; medium porosity (8 μm particle retention); medium flow (55 s for 100 ml prefiltered water); 15 cm^2 folded paper.

6.6 Litmus paper, blue.

7 Apparatus and glassware

All glassware subject to heating shall be heat-resistant borosilicate glass⁴⁾.

Pipettes and other volumetric glassware shall meet the volume requirements of Class A glassware as specified in ISO 385-1, ISO 648, ISO 835-1, ISO 835-2, ISO 835-3, ISO 835-4, ISO 1042 and ISO 4788.

7.1 Spectrometer, to measure absorbance at 700 nm.

7.2 Cells, of optical path length 1 cm.

8 Sampling

It is necessary that 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. See es-

3) Whatman® No. 2V filter paper is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 7766 and does not constitute an endorsement by ISO of this product.

4) Pyrex® is an example of suitable glassware available commercially. This information is given for the convenience of users of this part of ISO 7766 and does not constitute an endorsement by ISO of this product.

pecially 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 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 acid⁵⁾ 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 (6.4). Mix well, wait 5 min, and then filter using medium-porosity filter paper³⁾. Acidify the filtrate by adding hydrochloric acid (6.2) (<C>) dropwise using litmus paper (6.6) as indicator. Transfer two 40 ml lots 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 (6.1) 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 (7.1), measure the absorbances at 700 nm in 1 cm cells (7.2) 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.

5) This can be prepared from the hydrochloric acid (6.2) (<C>).

9.4 Calibration

Prepare a series of calibration solutions from the standard potassium ferrocyanide solution (6.3) (<<S>>) by running from a 25 ml burette into 100 ml one-mark volumetric flasks the volumes given in table 1. Make up each flask to the mark with water.

Table 1

| Volume of standard solution ml | Concentration of Fe(CN) ₆ mg/l |
|-----------------------------------|--|
| 0 | 0 |
| 2,5 | 1,0 |
| 6,25 | 2,5 |
| 12,5 | 5,0 |
| 25,0 | 10,0 |

Treat these 100 ml standard solutions in the same way as the 100 ml of Solution B. However, only one blank need 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 3 For a 1 cm cell, this 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 the effluent of Fe(CN)₆, c , in milligrams per litre, is calculated from the equation

$$c = (A_S - A_B) \cdot F_c \cdot D$$

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 the absorption vs. concentration and the analysis values read from the plot.

11 Test report

The test report shall include the following information:

- the results and method of expression used;
 - any unusual features noted during the determination;
 - details of any operating procedures not specified elsewhere in this part of ISO 7766, or regarded as optional, together with any incidents likely to have affected the results.
- the method used;

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