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10348

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1993-02-01

**Photography — Processing wastes —
Determination of silver content**

iTeh STANDARD PREVIEW
*Photographie — Effluents de traitement — Détermination de la teneur
en argent*
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ISO 10348:1993

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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 10348 was prepared by Technical Committee ISO/TC 42, *Photography*.

Annex A forms an integral part of this International Standard.

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Introduction

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

Analysis for silver in photographic products and effluents presents unique problems in sampling, handling and treatment. These problems are not always adequately covered in standard references. It is the purpose of this International Standard to provide methodology both for sample handling and for the analysis of silver in effluents. Some of the chemicals specified in the test procedures are caustic, toxic or otherwise hazardous. Specific warning, caution and danger notices are noted for particularly hazardous materials but normal precautions required during the performance of any chemical procedure shall be exercised at all times.

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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Silver in photographic processing wastes originates as a soluble thiosulfate or other complex. Other waste components, however, may interact, resulting in an unstable system containing varying amounts of soluble forms of silver. Waste samples to be analysed for heavy metals are normally stabilized by acidification with nitric acid. This treatment is unsatisfactory for silver in effluents containing photographic processing wastes. Since thiosulfate is unstable in acid solutions, the conventional treatment can actually promote the formation of insoluble silver. Cyanogen iodide (CNI) solution is the effective preservative for silver in these effluents.¹⁾

This International Standard includes flame atomic absorption spectroscopy (AAS) and two potentiometric iodide titration (PT) methods of analysis. The method employed will dictate the way in which the sample is preserved and treated. Samples to be analysed by the AAS method are normally ready for analysis, once stabilized with CNI solution. The iodide titration methods, however, require a digestion to solubilize the silver and remove interfering species followed by a boiling step (for Digestion A) to concentrate the sample. The standard digestion methods for AAS, which recommend the use of hydrochloric acid, are not suitable for the preparation of samples for silver analysis.

1) Owerbach, D. The use of cyanogen iodide (CNI) as a stabilizing agent for silver in photographic processing effluents. *Journal of Applied Photographic Engineering*, **4**(1), pp. 2-24, 1978.

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Photography — Processing wastes — Determination of silver content

1 Scope

This International Standard gives methods for determining the silver content in photographic effluents from photographic processing wastes. Sampling, sample preservation and analytical methodology are included.

Three analytical procedures are given with two supporting sample treatment methodologies:

- a) a flame atomic absorption spectroscopy (AAS) method;
- b) two potentiometric iodide titration (PT) methods.

The choice of treatment is dependent on the analysis method and form of sample. Where AAS is the chosen method for analysis, cyanogen iodide-treated or preserved samples may be analysed directly. For the PT method, two digestion procedures are given: Digestion A for effluents with low salt content, and Digestion B for samples with high solids content.

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

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.*

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:—²⁾, *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.*

2) To be published. (Revision of ISO 5667-3:1985)

3 Principle

3.1 Flame atomic absorption spectroscopy (AAS) methodology

A silver-containing lamp, when heated to excitation, generates a spectrum which includes the ultraviolet emission bands of the silver atom. The silver ions in a solution aspirated into a flame will absorb the silver emission bands when light from the lamp is passed through the flame, according to a Beer's law relationship:

$$c_{\text{Ag}} = k \cdot \log(\tau/\tau_0)$$

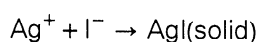
where

- c_{Ag} is the concentration of silver ions;
- τ is the transmittance of light through the flame at the specified wavelength aspirated with the sample;
- τ_0 is the transmittance of light through the flame at the specified wavelength aspirated with a silver-free reference sample;
- k is a constant.

A calibration curve is normally generated to define the relationship specifically.

3.2 Potentiometric titration (PT) methodology

The titration of a solution containing silver ions with an iodide solution will form a precipitate of silver iodide in accordance with the reaction:



A silver electrode, either prepared from a silver billet (11.1.2) or an iodide-selective electrode, with an appropriate reference electrode will generate a potential in the presence of a solution containing silver ions in accordance with the Nernst equation:

$$E = E_0 + 0,023(RT/nF) \cdot \log(c_{\text{Ag}})$$

where

- E is the measured potential, in volts;
- E_0 is the base potential, including the reference electrode contribution, in volts;
- R is the universal gas constant;
- T is the thermodynamic temperature;
- n is the number of electrons transferred;

F is the Faraday constant;

c_{Ag} is the concentration of silver ions.

In the presence of an excess of iodide ions, the silver ion concentration, c_{Ag} , is given by

$$c_{\text{Ag}} = K_{\text{SP}}/c_{\text{I}}$$

where

K_{SP} is the solubility product for silver iodide;

c_{I} is the concentration of iodide ions.

A sharp change in potential is obtained during the titration as the solution progresses from one with silver ions in excess to one with iodide ions in excess.

4 Reliability

The practical lower limits (approximate) for silver analyses are the following

Direct flame AAS	0,1 mg/l
PT, Digestion A (sample 500 ml; titrant 0,001 mol/l potassium iodide)	0,2 mg/l
PT, Digestion B (sample 1,0 ml; titrant 0,001 mol/l potassium iodide)	100 mg/l

The 2σ confidence limits for Digestion A, as determined through inter-laboratory tests, are equal to $\pm 0,12$ mg/l for samples containing 0,2 mg/l to 4,0 mg/l of silver in effluent samples. These results are based on seventeen data points obtained from six different laboratories³⁾. This value is true for both potentiometric iodide titration methods using either the manual method (pH-meter) or the automatic titrimeter method with a titrant addition rate of 0,1 ml/min.

The 2σ confidence limits for the flame AAS method are equal to $\pm 0,007$ mg/l for samples containing 0,02 mg/l to 0,05 mg/l of silver in photographic effluents, when directly aspirated after a five-fold sample volume reduction.

5 Safety and operational precautions

The test procedure for silver analysis given in this International Standard requires careful technique by an experienced operator. It requires care in sample storage and safe handling of both the sample and reagent solutions due to the hazards and/or toxicity of the cyanogen iodide stabilizing agent and other solutions. Due to the vigorous agitation and possible loss by splashing in the potentiometric iodide titration, careful monitoring of the procedure is required. The unique requirements and the large number of items

3) For an explanation on how the data were treated, see the *ASTM Handbook on Statistical Methods*. Copies are available from ASTM, 1916 Race Street, Philadelphia, PA 19103, USA.

in separate categories result in the following safety and operational precautions.

5.1 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 symbols 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 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.

5.2 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.

5.3 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 can be evolved.

Safety glasses shall be worn for all laboratory work.

Cyanogen iodide may be decomposed by treatment with sodium hypochlorite.

5.4 Operational precautions

5.4.1 The cyanogen iodide (CNI) silver solvent shall be added to the bulk sample a sufficient time before the test sample is taken, to ensure complete dissolution of occluded or precipitated silver. If a bulk sample is acidic, it shall be neutralized before CNI is added. The minimum reaction time after CNI addition is 1 h. CNI may be added at the bulk sampling time. The treated sample is stable indefinitely.

5.4.2 Bulk samples containing large quantities of silver, to be dissolved by the addition of large volumes of CNI (up to 20 % addition), shall have the original bulk sample volumes recorded at the bulk sampling time before the addition of CNI. When tested, the dilution factor given in 8.2.3 shall be used with the AAS value to find the true concentration of the sample. The recommended reaction time is overnight for samples with large silver concentrations resulting from particulate matter. Representative samples, including solids and particulate matter, shall be taken for true silver values. Representative sampling shall also take into account adsorption of silver or precipitation of silver species on the container walls. Appropriate treatment of the container when removing the sample is necessary.

5.4.3 Where CNI preservation is used, the sample container material is not of significant concern. In these cases, plastic containers are preferred to avoid breakage. In any event, sample containers shall be properly cleaned (see 5.4.5).

5.4.4 Analyses of samples for dissolved silver require immediate filtration after sampling and the use of support apparatus that will not affect the silver concentration after filtration. A 0,45 µm membrane filter medium with a stainless steel support is an acceptable system. Fritted glass and ceramic filter elements may absorb silver from the filtrate and are not recommended.

5.4.5 All glassware and containers shall be cleaned by soaking with a 1 % to 2 % CNI solution or concentrated nitric acid for a minimum of 4 h to prevent absorbed silver from being released from the container walls and becoming part of the sample during digestion. The containers shall then be rinsed several times with distilled water.

5.4.6 Digestions shall be carried to completion in order to eliminate interfering materials that react with the potassium iodide titrant.

5.4.7 The titration rate with potassium iodide shall not exceed 0,1 ml/min until the end-point is approached. The final titration rate shall not exceed 0,05 ml/min. In cases of low silver concentrations and, therefore, slow chemical reaction rates, faster titration rates will result in apparent high values. These titration rates apply to automatic titration equipment as well.

5.4.8 The specified silver electrode cleaning and coating procedure shall be performed to provide the correct coating depth of sulfide. Excess time in the sulfide reagent can overcoat the electrode, resulting in slow reaction and apparent high values.

5.4.9 The digested sample volume, immediately before titration, should be 150 ml or less. A larger volume may degrade the potentiometric break required for determining the end-point of the titration, especially for samples low in silver.

5.4.10 The sample shall be stirred vigorously during titration to assist reaction completion. Failure to do so can result in invalid values for the analysis.

5.4.11 All containers shall be labelled and dated. Appropriate warning labels shall be affixed to the containers.

6 Reagents

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 should be expressed in moles per litre. The number of significant 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 should be 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, is to be diluted with Y volumes of distilled or deionized water.

6.1 Reagents for atomic absorption spectroscopy (AAS)

6.1.1 Cyanogen iodide solution (CNI) (DANGER: <<S>><C>)⁴⁾

6.1.2 Silver (Ag) standard solutions, 0,5 mg/l, 1,0 mg/l, 3,0 mg/l and 5,0 mg/l.⁴⁾

6.2 Reagents for potentiometric titrations (PT)

6.2.1 Acetic acid (CH₃COOH), glacial, $\rho \approx 1,05$ g/ml (DANGER: <C>).

6.2.2 Ammonium hydroxide (NH₄OH), $\rho \approx 0,91$ g/ml (DANGER: <C>).

6.2.3 Hydrogen peroxide (H₂O₂), 30 % (m/m) (approximately) (DANGER: <C> <O>).

6.2.4 Nitric acid (HNO₃), 70 % (m/m) (approximately) (DANGER: <C> <O>).

6.2.5 Potassium iodide standard solutions (KI), 0,1 mol/l, 0,01 mol/l and 0,001 mol/l.⁴⁾

6.2.6 Potassium nitrate solution (KNO₃), saturated.

Add 50 g of potassium nitrate to 100 ml of water. Stir for 5 min then warm to room temperature. Maintain

4) Procedures for the preparation of these solutions are given in annex A.

an excess of undissolved potassium nitrate crystals in the reagent container.

6.2.7 Silver nitrate (AgNO₃) standard solutions, 0,100 mol/l, 0,010 mol/l and 0,001 mol/l.⁴⁾

6.2.8 Sulfuric acid (H₂SO₄), $\rho \approx 1,84$ g/ml (DANGER: << C >>).

7 Glassware

All glassware subject to heating shall be of heat-resistant borosilicate glass.⁵⁾

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.

8 Sampling and sample pretreatment

This International Standard covers a choice of analytical methods and sample preparation procedures. In order to ensure that the analysis yields a meaningful result, it is necessary that the proper choices and decisions are made from among the options. It is, therefore, the intent of this clause to provide a systematic and rational approach to making the choices consistent with the material type and analysis technique for

- representative sampling;
- sample size determination;
- sample preparation.

Table 1 provides an overview of the choices based on sample type treatment and analysis method. For AAS, any sample treatment is useable but CNI is preferred for simplicity where applicable. PT requires a digestion

treatment, and the less vigorous Digestion A method is preferred where applicable. Samples with a high solids content require the more vigorous Digestion B method for PT and AAS when the CNI method is not suitable for the latter.

8.1 Sampling and preservation

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

The method of analysis and desired result will determine the need for sample preservation. It is generally recommended that all effluent samples intended for silver analysis be treated with CNI. It should be noted that samples treated with CNI, intended for shipment, may be in violation of transport regulations and, if so, the CNI treatment can be carried out after arrival. It is only necessary that the treatment be carried out at least 1 h before the analysis. Normal treatment with CNI for stabilization requires the addition of CNI at a rate of 1,0 ml of CNI solution per 100 ml of sample.

CNI is used to stabilize samples for AAS analysis. After CNI stabilization, such samples can normally be directly used for aspiration. CNI is used for PT samples to prevent loss of material by absorption to the container walls. Since PT analysis requires a digestive procedure, CNI stabilization is not required, provided that there is no loss of silver due to absorption.

Table 1 — Operational flowchart

Sample type	Analysis method	Subclause	Treatment	Subclause
Low-salt effluents	AAS	10.2	CNI	8.2.2 or 8.2.3
	AAS or PT	10.2 or 11.2	Digestion A	9.2
	AAS or PT	10.2 or 11.2	Digestion B	9.3
High-solids effluents	AAS or PT	10.2 or 11.2	Digestion B	9.3

5) 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.