

INTERNATIONAL STANDARD

ISO
10348

First edition
1993-02-01

Photography — Processing wastes — Determination of silver content

*Photographie — Effluents de traitement — Détermination de la teneur
en argent*



Reference number
ISO 10348:1993(E)
AVA Documents
Document Sharing Hub

Contents

	Page
1 Scope	1
2 Normative references	1
3 Principle	2
3.1 Flame atomic absorption spectroscopy (AAS) methodology ..	2
3.2 Potentiometric titration (PT) methodology	2
4 Reliability	2
5 Safety and operational precautions	2
5.1 Hazard warnings	3
5.2 Hazard information code system	3
5.3 Safety precautions	3
5.4 Operational precautions	3
6 Reagents	4
7 Glassware	5
8 Sampling and sample pretreatment	5
8.1 Sampling and preservation	5
8.2 Sample size and pretreatment	6
9 Preparation of test sample	7
9.1 Cyanogen iodide (CNI) treatment	7
9.2 Concentration and digestion (Digestion A)	8
9.3 Vigorous digestion (Digestion B)	8
10 Analysis by atomic absorption spectroscopy (AAS)	9
10.1 Special apparatus	9
10.2 Procedure	9
11 Analysis by potentiometric iodide titration (PT)	9
11.1 Special apparatus	10

© ISO 1993

All rights reserved. No part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

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

Printed in Switzerland

11.2	Procedure	10
11.3	Calculations for titration methods	10

Annex

A	Preparation of reagent solutions	12
A.1	Preparation of cyanogen iodide solution (CNI) (DANGER: << S >> < B > < C >)	12
A.2	Preparation of silver standard solutions (0,5 mg/l, 1,0 mg/l, 3,0 mg/l and 5,0 mg/l) for AAS method	12
A.3	Preparation of silver nitrate standard solutions (0,100 mol/l, 0,010 mol/l and 0,001 mol/l) for PT methods	13
A.4	Preparation of potassium iodide standard solutions (0,1 mol/l, 0,01 mol/l and 0,001 mol/l)	13

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.

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.

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.

This page intentionally left blank

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:

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

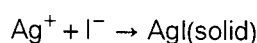
where

- 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.