Environment

INFORMATION FROM KODAK

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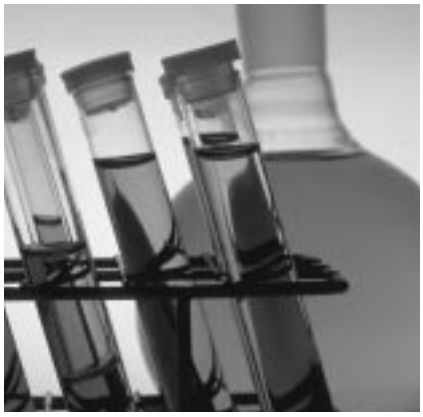
Measuring Silver in Photographic Processing Facilities



A number of techniques are available to measure silver in a photographic processing facility. These can range from simple on-site qualitative tests to a sophisticated analysis performed at an analytical laboratory. The type of test you use depends on both the material that is being tested and the purpose of the analysis.

The types of materials that are analyzed for silver in a photographic processing facility include photographic processing solutions and washwaters, photographic processing overflows and effluents, processor filters, and photographic films and papers. Photographic processing solutions and washwaters are analyzed for silver as a means of process control to ensure that replenishment rates are correct, in-line and terminal silver-recovery and regeneration systems are being operated properly, or processor rollers and squeegees are well maintained. Photographic processing effluents are analyzed as a compliance requirement for wastewater discharging or to characterize the material prior to off-site transportation for treatment or disposal. Processor filters and photographic films and papers are analyzed for silver to characterize the material prior to off-site transportation for refining, treatment, or disposal.

Whether you perform silver analysis for process control, regulatory compliance, or waste characterization, it is important that you be familiar with the uses and limitations of the available techniques for measuring silver.

SAMPLE COLLECTION

The first step in analyzing a material is collecting a sample. It is very important to be sure that any sample that you collect is representative of the material that you are analyzing. Take photographic processing solutions and washwater samples directly from the processor tanks. If the processor was recently turned on, give it adequate time to allow the tanks to reach equilibrium.

Sample collection points will often be specified in your wastewater discharge code or permit. Sampling may be required right after terminal silver-recovery equipment. If no sampling point is specified, sample at a point where all facility effluent is included. This point will result in a sample that is representative of the effluent from the entire facility.

Kodak's health, safety, and environmental publications are available to help you manage your photographic processing operations in a safe, environmentally sound and cost-effective manner. This publication is part of a series of publications on silver management designed to help you optimize silver recovery. It will help you understand the techniques available for measuring silver and which technique is right for your facility.

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Two types of wastewater samples are commonly taken.

Grab Sample—A grab sample is a single sample that is taken from a tank or effluent stream. This type of sample can be a good indicator of the typical character of the wastewater, but for processes that are not continuous, such as batch silver recovery, this may not be representative of actual total discharge.

Composite Sample—A composite sample is the accumulation of a series of grab samples collected at regular intervals over a long period of time, usually 24 hours. The interval of sampling can be either time or flow. Most photographic processing facilities do not run a 24-hour continuous business, therefore a flow proportional composite sample will result in a sample that more accurately characterizes the facility's discharge. Automatic composite sampling equipment can be expensive and difficult to install in some facilities.

Some large facilities may have continuous sampling equipment. This equipment typically draws small samples for continuous on-line monitoring. This equipment is very expensive and may require trained personnel to operate it.

Carefully collect all samples in clean, unused containers; immediately cap and properly label the containers. Photographic processing solutions and effluents can undergo chemical or physical changes after collection and may need stabilization. Traditionally, the stabilization technique for silver has been the addition of nitric acid. This method should *not* be used for photographic processing solutions and effluents because it results in the precipitation of silver sulfide due to the decomposition of thiosulfate in the photographic processing solutions and effluents. For analysis of other parameters where stabilization is required, you should collect separate samples and preserve accordingly.

Send samples to the analytical laboratory for analysis as soon as possible after you collect them. You should not hold samples that are being analyzed for silver longer than six months.

Processor filters and photographic films and papers are analyzed to characterize the materials prior to transportation for refining, treatment, or disposal. Be sure to collect enough of a sample for the analysis, and make sure that the sample is representative of all of the materials that are being characterized.

MEASUREMENT TECHNIQUES

A number of techniques are available to measure silver in a photographic processing facility. There are on-site techniques that you can perform in most photographic processing facilities, and there are tests performed by analytical laboratories. In general, the on-site techniques tend to be qualitative and less accurate than those performed by an analytical laboratory. On-site results cannot typically be used to demonstrate regulatory compliance. However, on-site techniques are relatively inexpensive and easy to perform, and are ideal for frequent process control checks.

On-Site Techniques

The two most commonly used on-site measurement techniques for silver in a photographic processing facility are qualitative test strips and colorimetry.

Qualitative Test Strips—This technique involves using a strip of paper that is impregnated with a silver-sensitive material or a strip of polished copper. The strip is dipped into the sample for a short period of time. Discoloration indicates the presence of soluble silver in the sample. Varying levels of discoloration indicate different concentrations of silver. This technique is qualitative; you can use it to estimate silver concentrations greater than 1 gram/litre.

The most common qualitative test strip is KODAK Silver Estimating Test Paper. This is a yellow paper strip that changes to a brown color in the presence of silver. A color comparison chart is provided with the test strips to estimate silver concentration. Strongly colored solutions, such as bleach-fix, may also add color to the paper, making the estimation more difficult to accurately read. You can use these test strips to monitor electrolytic silver-recovery equipment or to test a Metallic Replacement Cartridge* (MRC) for silver breakthrough.

Soaking test strips for longer periods of time in the test sample can give an indication of silver present at concentrations lower than 1 gram/litre. This technique is extremely qualitative and is not reliable to quantify low levels of silver in photographic processing solutions.

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*Cartridges used in the metallic replacement process for recovering silver have been described as chemical recovery cartridges (CRCs), metallic recovery cartridges (MRCs), and silver recovery cartridges (SRCs).

The photographic industry has avoided the term SRC to prevent theft of the cartridges during shipment. The term CRC is closely associated with the original Kodak product which was protected by a U.S. Patent. Therefore, we will use MRC as a generic term to refer to metallic replacement.

Colorimetry—This technique involves adding a chemical to a sample that contains silver. The silver reacts with the chemical to form a specific color. The color intensity of the treated sample is compared to a reference sample. The difference in color corresponds to the silver concentration in the solution.

Most commercially available colorimetric tests for silver are performed using visual observation. This makes these tests very qualitative and accurate only to several hundred parts per million (ppm) silver. Kodak has developed a colorimetric test for silver that uses a spectrometer. The KODAK Colorimetric Silver Test Kit can detect silver as low as 30 ppm in most photographic processing solutions with an accuracy that is within 10% of analytical laboratory techniques. Photographic processing solutions that contain high levels of iron, such as a bleach-fix, have a higher silver detection limit of 60 ppm. The instrumentation is portable, relatively inexpensive, and easy to operate. You can complete the analysis in less than three minutes.

This technique is ideal for process control by monitoring in-line and terminal silver recovery to insure proper operation.

KODAK Colorimetric Silver Test Kit

ANALYTICAL LABORATORIES

Samples requiring precise analysis for silver, such as those required for demonstrating regulatory compliance, will normally be sent off-site to an analytical laboratory. Some large facilities may have an in-house analytical laboratory due to the large number of samples that need to be analyzed. Testing for regulatory compliance requires sophisticated equipment, trained personnel, and adherence to United States Environmental Protection Agency (USEPA) protocol. The laboratory may also need to be certified to perform the analysis.

Sample Preparation

Once a sample is received at an analytical laboratory, it is prepared for the silver analysis. The preparation method depends on the type of analysis that is needed. There are three types of silver analysis commonly performed at an analytical laboratory:

- *Total Recoverable Silver*—This is an analysis of all silver that is present in the sample. Silver, which may exist in suspended or particulate forms, will need to be solubilized prior to analysis. The preferred method of solubilizing silver in photographic processing solutions or effluents is the use of cyanogen iodide (CNI). The CNI solubilizes any silver present in the solid phase. This is performed using EPA Method 272.1.

  Silver in the solid phase can also be solubilized by a nitric acid digestion or a nitric/hydrochloric acid digestion. Nitric acid microwave digestion can also be used for sample preparation and digestion; however, this method is *not* approved by USEPA for silver analysis in wastewaters.

- *Dissolved Silver*—This is an analysis of soluble silver in the sample. The sample is filtered prior to analysis to remove all silver that exists as a particulate or suspended solid. Some wastewater discharge codes are now being adopted using dissolved silver as the regulated parameter or using a translator to estimate dissolved silver based on total silver. Be sure that you request the correct silver analysis as required by your local discharge regulations or permit.
- *Leachable Silver*—This is an analysis of the amount of silver that will leach from a solid or the amount of silver that is present in a liquid. The leaching test is used to determine if the material is a hazardous waste by using the Toxicity Characteristic Leaching Procedure (TCLP). Solids are reduced in size and subjected to a dilute acid solution. The leachate is then analyzed to determine the amount of silver extracted from the solid. Liquids are directly analyzed for total recoverable silver.

Instrumental Tools

Silver can be detected by absorption or emission of radiant energy which is read at specific wavelengths by a spectrophotometer. There are three spectroscopic methods commonly used by analytical laboratories to measure silver:

- *Flame Atomic Absorption Spectroscopy (FAA) [EPA Method 272.1]*—FAA measures metals in solution by flame ionization. Photo-multiplier tubes are used to detect specific metals in solution by measuring the energy absorbed when the metal ions come in contact with the flame. This procedure is only capable of measuring one metal at a time. Silver can be measured as low as 10 parts per billion (ppb).

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)

- *Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) [EPA Method 200.7]*—ICP-AES works using a principle opposite to that of FAA. It measures the energy emitted from metal ions in solution using an argon-plasma instead of a flame. The ICP-AES unit has the ability to measure multiple elements in solution; therefore, it has greater flexibility and economic advantages than the FAA unit when multi-element analysis is required. Silver can be measured as low as 2 ppb.

- *Graphite Furnace Atomic Absorption Spectroscopy (GFAA) [EPA Method 272.2]*—GFAA works on the same principle as the FAA unit but has a lower detection limit. This is achieved through a smaller sample size and total sample utilization, and gives the GFAA unit greater sensitivity for all metals. GFAA is also limited to one metal at a time. Silver can be measured as low as 0.3 ppb.

Data Validity and Quality Control

Analytical laboratories that are performing chemical analyses are required to perform quality control procedures and to keep records to ensure that the reported data is correct. If you receive data from an analytical laboratory that looks suspect or may indicate a compliance problem, you may want to have the laboratory recheck the data or retest the sample to make sure that the report is correct.

Photographic processing solutions and effluents can present several unique problems for laboratories not familiar with matrix effects encountered during the analysis of silver. High levels of dissolved solids can cause spectral and matrix interferences, and the use of nitric or hydrochloric acids can produce insoluble silver sulfides and chlorides during sample preparation. Laboratories that are not aware of these potential problems may be using EPA-approved methods for silver but report data that is not valid.

Methods of Silver Analysis Commonly Used by Analytical Laboratories

Digestive Technique	Nitric Acid	Nitric/Hydrochloric Acid	Nitric Acid Microwave	CNI Complexation
Instrumental Tools	FAA [EPA Method 272.1]	FAA [EPA Method 272.1]	FAA [EPA Method 272.1]	FAA [EPA Method 272.1]
	ICP-AES [EPA Method 200.7]	ICP-AES [EPA Method 200.7]	ICP-AES [EPA Method 200.7]	ICP-AES [EPA Method 200.7]
	GFAA [EPA Method 272.2]	GFAA [EPA Method 272.2]	GFAA [EPA Method 272.2]	GFAA [EPA Method 272.2]
Pro's and Con's	Can cause silver to precipitate as silver sulfide in sample. This method is normally used when silver exists in organic matter or is attached to particulate matter.	Can cause silver to precipitate as silver chloride/sulfide in sample. This method is normally used when silver exists in organic matter or is attached to particulate matter.	This method is not approved by USEPA for silver analysis in waste waters.	This method is ideal for measuring silver in photographic processing solutions and effluents. CNI complexes all forms of silver into solution and prevents precipitation.

Selecting an Analytical Laboratory

Because of the complexity that is associated with analyzing materials from photographic processing facilities for silver, you must be careful when selecting an analytical laboratory to perform silver analysis. There are several questions that you should ask when making this selection:

- Is the analytical laboratory capable of performing the analysis correctly for the type of sample or effluent matrix?
- Does the analytical laboratory use approved analytical methods and know how to apply that methodology to the sample type in order to obtain the correct answer?
- Are complete records and documentation supporting the analysis available and can you get access to that information; is the data reliable?
- Does the lab participate in EPA proficiency testing on an annual basis and are they certified by their own state, if required?

It is important that the laboratory understand the unique nature of photographic processing solutions and effluents as they relate to silver analysis. The laboratory you select should have a good understanding of, and experience in, analyzing these types of materials. The laboratory should also have a good data management system that allows quick access to your past analysis. Some states require laboratories that perform analysis for regulatory compliance purposes to be certified. This certification requires the laboratory to demonstrate their capabilities on a regular basis. Make sure you are using a certified laboratory if your state requires certification.

Environmental Analytical Services from Kodak make the testing process simple, economical, and accurate. You can benefit from Kodak's extensive expertise in analyzing complex photographic processing solutions and effluents. Strict adherence to EPA-approved testing methods and laboratory certification yield accurate analytical results that can be submitted for regulatory compliance demonstration purposes in most states.

For more information about **Environmental Analytical Services** from Kodak, call 1-800-283-4173.

A COMPARISON OF MEASURING TECHNIQUES FOR SILVER

Measuring Technique	Qualitative Test Strips	KODAK Colorimetric Silver Test Kit	Flame Atomic Absorption (FAA)	Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)	Graphite Furnace Atomic Absorption (GFFA)
Test Range	>1000 ppm	>30 ppm	>0.01 ppm	>0.002 ppm	>0.0003 ppm
Accuracy of Results	Poor	Good (±10%)	Excellent	Excellent	Excellent
Expertise Required	Low	Low	High	High	High
Equipment Cost	None	<$1K	$30–40K	$170–250K	$60–70K
Typical Cost per Test	<$ .01	<$3.00	$35.00	$35.00	$35.00
Advantages	Inexpensive; easy to use; immediate results	Simple, accurate; wide range; immediate results	High-accuracy; wide range	High-accuracy; wide range	High-accuracy; wide range
Disadvantages	Qualitative; not usable at low concentrations	Limited use at low concentrations	Off-site testing	Off-site testing	Off-site testing
Best Use	Rough check of silver-recovery equipment operation	Process control; adjusting in-line silver recovery	Compliance testing; verify on-site tests	Compliance testing; verify on-site tests	Compliance testing; verify on-site tests

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MORE INFORMATION

If you have environmental or safety questions about Kodak products or services, contact Kodak Environmental Services at 1-716-477-3194, between 8 a.m. and 5 p.m. (Eastern time).

Kodak also maintains a 24-hour health hotline to answer questions about the safe handling of photographic chemicals. If you need health-related information about Kodak products, call 1-716-722-5151.

The products and services described in this publication may not be available in all countries. In countries other than the U.S., contact your local Kodak representative, or your usual supplier of Kodak products.

Kodak has many publications to assist you with information on Kodak products, equipment, and methods. To obtain a list of Kodak publications, send your request for a copy of KODAK Publication No. L-1, *KODAK Index to Photographic Information*, with $1 to Eastman Kodak Company, Department 412-L, Rochester, New York 14650-0532.

The following publications are available from dealers who sell Kodak products, or you can order them directly from Kodak through the order form in KODAK Publication No. L-1.

J-210 *Sources of Silver in Photographic Processing Facilities*

J-212 *The Technology of Silver Recovery for Photographic Processing Facilities*

J-213 *Refining Silver Recovered from Photographic Processing Facilities*

J-214 *The Regulation of Silver in Photographic Processing Facilities*

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