INTRODUCTION

DESCRIPTION OF *EASTMAN* COLOR REVERSAL INTERMEDIATE FILM

EASTMAN Color Reversal Intermediate Film 5249/7249 is designed for making duplicate negatives in one printing stage from originals on EASTMAN Color Negative Film 5254/7254. The duplicate negatives are then printed on EASTMAN Color Print Film 5381/7381. EASTMAN Color Reversal Intermediate Film 5249/7249 has effective reproduction contrast near unity. It is characterized by excellent sharpness and high resolving power. Color-correcting masks are incorporated in the emulsion layers to make certain that good color reproduction will be achieved.

Film Characteristics

The required film characteristics are achieved through three fine-grain, high-resolution emulsion layers. A cross section of EASTMAN Color Reversal Intermediate Film is illustrated in Figure 200-1. In order to preserve color fidelity, the green- and red-sensitive layers contain yellow- and red-colored couplers which form masks to correct for unwanted absorptions of the magenta and cyan dyes formed in these layers. Additional color correction is achieved through interimage effects, which also contribute to sharpness. The green- and red-sensitive layers are separated by a gel interlayer while a yellow filter layer under the blue-sensitive emulsion prevents unwanted exposure of the lower layers by blue light. The film has an undercoat and a gel overcoat and the same jet-backed support as is used on other EASTMAN Color Negative and Intermediate Films.

Reversal processing causes the blue-, green- and red-sensitive layers to form yellow, magenta, and cyan dye in an inverse proportion to their exposure. The jet backing is removed and the antihalation and yellow filter layers are cleared during the process. In many ways the same principles for good results with EASTMAN Color Intermediate Film 5253 apply; however, certain different procedures are required.

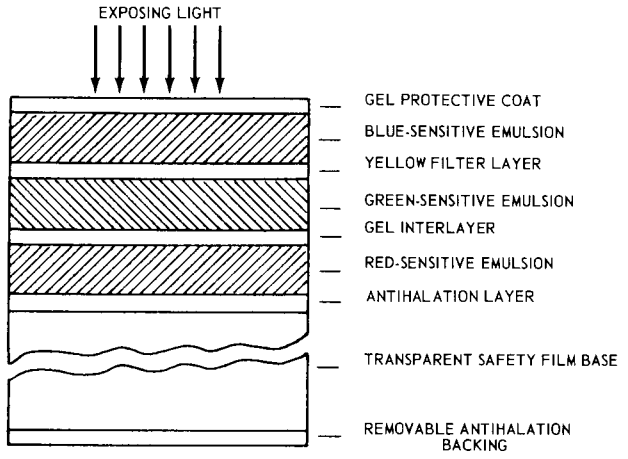


FIGURE 200-1
CROSS SECTION OF UNPROCESSED *EASTMAN* COLOR REVERSAL INTERMEDIATE FILM 5249/7249

This drawing illustrates only the relative layer arrangement of the film and is not drawn to scale.

With reversal intermediate film it is necessary to place the original (which might be a camera negative, duplicate negative, or composite of the two) base to emulsion in an optical printer when exposing the duplicate. This procedure is required to preserve orientation as well as to introduce effects or change picture format; also, modified techniques are required when introducing certain optical effects (such as fades) at this stage.

Color Image Formation During CRI-1 Processing

The following outline will serve as an aid in understanding the function of the various processing steps and the manner in which the color images are formed in the film during processing.

Process Step	*Function*
Prehardener	Hardens emulsion, thereby preventing excessive vertical and lateral swelling during processing. This permits processing at elevated temperatures with little danger of reticulation, and greatly reduces the chances for edge skiving of the emulsion by sides of machine rollers. There is then less chance for the emulsion to pick up dirt particles and to be damaged during processing. The prehardener also supplies an antifoggant to the film to prepare it for first development.
Neutralizer	Converts hardening agents in film to an inactive form before first development. Without this step, the hardening agents would react with the coupling agents as the film is developed in the alkaline developer. These coupling agents would then not be completely available for dye formation during color development.
Backing Removal	Removes rem-jet backing by use of a carbonate-sulfate dip and a water-spray scrubbing unit before entering the first developer.
First Developer	Develops exposed silver halide to a black-and-white negative silver image.
First Stop	Stops action of first developer carried over by the film and reduces emulsion swelling during the next wash.
Wash	Removes the acid solution from the film.
Color Developer	Contains a reversal agent which makes the remaining silver halide in the film developable, thus eliminating the necessity for reexposure by light. Develops the chemically sensitized silver halide to give dye images (and silver images) in the appropriate emulsion layers of the film.
Second Stop	Stops action of color developer carried over by the film and reduces emulsion swelling.
Wash	Removes the acid solution from the film.

Process Step	*Function*
Bleach	Converts all metallic silver to insoluble silver salts.
Fixer	Converts all silver salts to soluble compounds and removes them from the film.
Wash	Washes the fixer from the film.
Stabilizer	Suppresses water spots.
Dryer	Dries the film for windup and subsequent printing.

FILM PROCESSING EQUIPMENT

TABLE OF CONTENTS

PROCESSING MACHINE

Eastman Kodak Company does not market processing machines or auxiliary equipment for the process discussed in this manual. However, a list of manufacturers of processing equipment can be obtained on request from any regional office of the Motion Picture and Audiovisual Markets Division.

The film intended for Process CRI-1 is processed in a continuous strip in automatic processing machines.

If the processing machine is new and being started for the first time, a thorough cleanup using the sulfamic acid cleaning solution given on page 309 should be carried out.

All tanks and lines should be checked for metal chips, miscellaneous machine parts, or foreign material that can cause oxidation or catalytic decomposition of the developers (zinc, tin, copper, some phenolic plastics, etc), contamination of the prehardener or neutralizer (iron, brass, copper, tin, etc), or destruction of the bleach (iron, etc).

If the machine is old and has been used for other than Ektachrome or CRI-1 processes, the prehardener, neutralizer, and first and color developer sections should be disassembled and cleaned. All gaskets, plastic tubing, hoses, and software that can come in contact with the processing solutions should be replaced with inert, uncontaminated materials. This is especially true of converted processing machines in which the tanks have been separated and reassembled in a different order. Some chemicals used in other processes are totally incompatible with Process CRI-1 solutions and may only demonstrate their presence by a slow drift out of process control as they leach into the processing solution over a period of time. Replacement of the contaminated solution gives only temporary relief as the new solution is also soon contaminated. Eliminating the source of the contaminant is the only answer to the problem.

Practical materials of construction are discussed under the sections dealing with the various sections of the processing machine. A complete and accurate knowledge of what materials are present in every processing system is vital to preventing contamination from the use of incorrect materials. Incorrect types of plastic hose, pump impellers and liners, gaskets, filter media and cores, pipe metals, valve seals, bearings, and air filters, etc, can totally prevent any process from staying in control. The contamination effect may or may not be demonstrated analytically and the sensitometric change may be very rapid or take a long time (weeks) to occur, depending on the reaction and the amount of solution contact.

BACKING REMOVAL SCRUBBER

EASTMAN Color Reversal Intermediate Film 5249/7249 has a rem-jet backing that must be removed by the combined treatment of a rem-jet backing removal solution and a backing removal scrubber located between the neutralizer and the first developer. (The backing is not affected by the acidic prehardener and neutralizer.) After the film leaves the neutralizer, the backing is softened by a 3 to 10-second dip in the removal solution. Immediately following the dip, the backing is removed in the scrubber unit which consists of water sprays on either side of a buffer roller. It is very important to have a thorough sprayoff of the backing before it reaches the buffer. This must be done in such a manner that none of the spray effluent (laden with backing) encounters the buffer velour or the

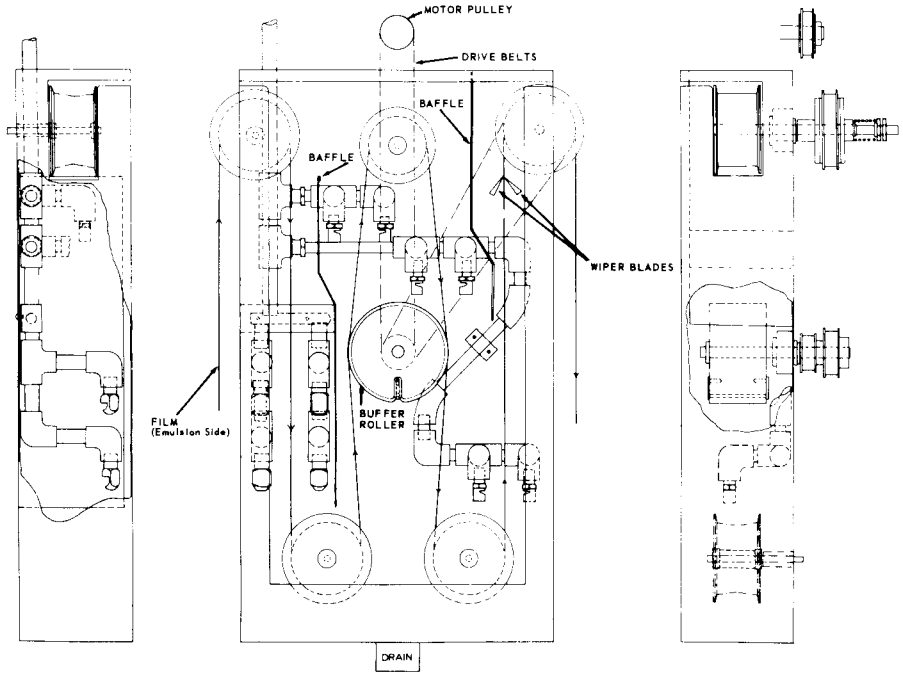


FIGURE 300-1
SCHEMATIC OF BACKING REMOVAL SCRUBBER

film emulsion surface. The film is then buffed to remove all haze, washed, squeegeed, and sent to the first developer.

The backing removal scrubber can be cleaned with hot water, if necessary.

Suitable backing removal scrubbers can be obtained from the processing machine manufacturers. A schematic of a scrubber is shown in Figure 300-1. In this unit, the 1/8K2* spray nozzles operate at 207 kN/m² (30 psig) and at 1.3 l/min (0.35 gal/min); the 1/4P5010* spray nozzles operate at 207 kN/m² (30 psig) and at 3.3 l/min (0.87 gal/min). These nozzles are aimed to flush the loosened particles of backing away from the emulsion and toward the back of the unit. The water and backing particles are then discharged through the drain. Nozzles of other design or nozzles from other manufacturers may also be satisfactory. Mohair velour is a satisfactory buffing material.† Other materials may also be satisfactory.

MACHINE TANKS

The processing machine should consist of a sufficient number of tank sections to provide for all of the solution and washing steps required by the process cycle. The tank sizes depend on the number and size of the film racks which in turn depend on the recommended solution times and the film speed. The steps for Process CRI-1 are shown in Figure 300-2.

The machine tanks for all solutions are made of stainless steel, AISI Type 316, except those used for the bleach. Titanium or Hastelloy C is preferred for construction of the bleach tanks. It is feasible to use certain plastics, rubbers, or elastomers with ferricyanide bleaches if the low-heat-transfer properties will not be of concern. Suggested materials are polyvinylchloride, polypropylene, hard rubber, or fiber glass reinforced with polyesters or epoxy. Fiber-glass materials can be used for all of the machine tanks, except for the color developer. If other types of plastics are to be used, tests should be made to determine that they will not produce any adverse photographic effects.

MACHINE RACKS

The machine racks are the units on which the film is threaded to allow its passage through the various processing solutions. They are designed to transport the film at a uniform rate and provide for regulation of the reaction time in any solution.

Although the design varies among processing machine manufacturers, the racks usually consist of a frame or assembly which fits into processing tanks. This frame or unit is removable for repair and periodic cleaning. The film travels on the rack on spools mounted on shafts at the top and bottom of the rack. Only the base side of the film is in contact with the spools. Either the top or bottom spool assembly may be easily raised or lowered in order to obtain proper treatment time in the various processing solutions. The drive may be either sprocket or friction type.

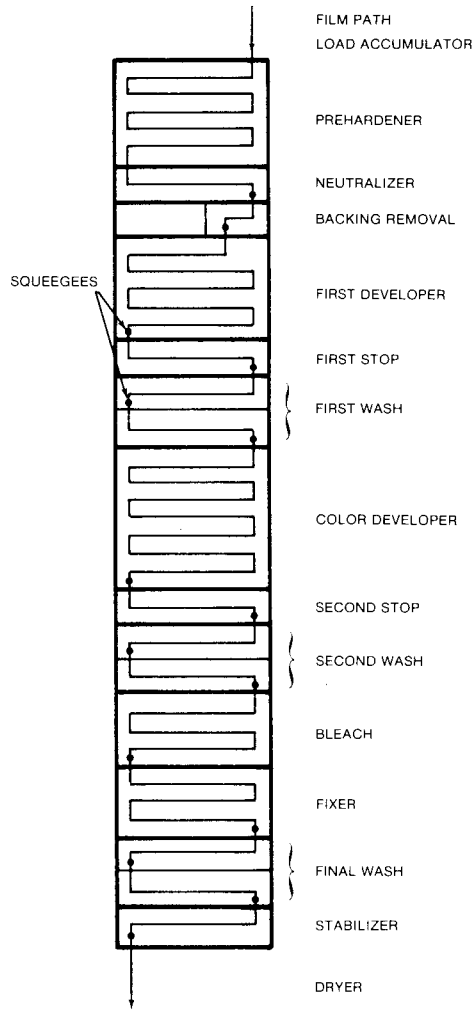


FIGURE 300-2
STEPS FOR PROCESS CRI-1

The machine racks are usually made of stainless steel, AISI Type 316, except those used for the bleach. Titanium or Hastelloy C is preferred for the construction of bleach racks. Spools for use in all solutions are generally made of nylon, polypropylene, or polyethylene.

CROSSOVER SQUEEGEES

An efficient squeegee is recommended for the exit strand from each machine tank including the double wash tanks. A wiper-blade squeegee should be positioned about 2.5 cm (1 inch) below the solution level on the entrance strand in the neutralizer tank. This submerged wiper blade is used to reduce streaking.

The removal of surface solution is desirable for processing uniformity and economy. As the film travels from one tank to another, a crossover squeegee removes the surface solution from both sides of the film and returns the solution to its machine tank. This action reduces the loss of processing solu-

*These numbers are catalog numbers of the Spraying Systems Co., 3201 Randolph St., Bellwood, Ill. 60104.

†Available from Collins-Eikman Corp., Ca Vel, N.C. 27512.

SOLUTION FILTRATION

Processing solutions and wash waters usually contain some insoluble material in the form of solids and tars. If this material is not removed, it may readily adhere to the film being processed, machine tank walls, rollers, lines, etc. Therefore, filtration systems are required in replenisher lines, recirculation systems, and wash-water lines. Properly designed mixing and processing equipment along with meticulous operating procedures and proper housekeeping will also minimize the formation of insoluble material.

The insoluble material may originate from a number of sources. The water supply can contribute in two ways. It can contain solids and also have hardness high enough to produce sludge when used for preparing processing solutions. The processing chemicals themselves may contain impurities that will not dissolve in water. Such impurities are at a minimum if the chemical is sold as photographic grade under American National Standards Institute specifications. Emulsion skivings and antihalation backing are also sources of dirt. The amounts of the materials in solution largely depend upon how well the processing equipment is designed and the attention paid to proper maintenance. Also, as a result of evaporation and aeration, solutions will contain some insoluble materials as tars and salts of crystallation. Some salts are slow to redissolve, while tars are usually insoluble.

The porosity rating of the filters should ideally be 10 microns, but the back pressure of a 10-micron filter in a system is sometimes too great to permit adequate flow unless oversized pumps are used. Increasing the filter area will decrease the back pressure, but this increases the cost of filters. Filters with porosity ratings larger than 30 microns will also produce low back pressure, but these filters are of little value in removing insoluble material.

A definite replacement schedule for filter cartridges should be established and followed. It is recommended that the filters be changed once every week, or more frequently if necessary.

One type of filter cartridge, suitable for photographic solution filtration, is the Fulflo Honeycomb Filter Tube.* (See table below.) The filter tube is used in a filter unit or shell (such as the Fulflo filter*) and placed in replenisher lines, recirculation systems, and wash-water lines. Metal components (heads, shells, and cores) for filters should follow the same recommendations made for piping. Suggested filters are listed below.

MAINTENANCE

A. Feed Section

It is very important that the feed section including the load accumulator be free of aluminum, magnesium, copper, and particularly zinc particles. If these metallic particles adhere to the dry, unprocessed film, they will cause a processing defect known as blue comets. Such particles usually come from abraded parts in cameras, film magazines, and load accumulators. These trouble areas should be vacuumed each day. An application of a thin plastic coating can also help. Such a coating can be easily applied from an aerosol container. One such product is marketed by Krylon Products, Norristown, Pa. 19401.

Periodically check all rollers in the feed section for alignment and freedom of rotation. Also check alarms for operation.

*Marketed by: The Carborundum Co., Commercial Filters Div., Lebanon, Ind. 46052; Commercial Filters Canada, Ltd., 1179 Caledonia Rd., Toronto, Ont., Canada

Solution	*Honeycomb Filter Tube*			
	Media	*Core Material*	*Nominal Porosity Rating (Microns)*	*Part No.*
Prehardener	Fiber Glass	Stainless Steel, AISI Type 316	15	K17R10S
Bleach	Polypropylene or Cotton	Polypropylene*	30	M13R10A 13R10A
Others (Includes: Neutralizer, First Developer, First Stop, Color Developer, Second Stop, and Fixer.)	Polypropylene or Cotton	Stainless Steel, AISI Type 316	30	M13R10S 13R10S

Other filters should be tested before use to determine whether they might produce any adverse photographic effects.

*Polypropylene has an upper operating temperature limit of 51.5 C (125 F). Therefore, it is important to use *only* stainless steel filter cores for filtered solutions other than the bleach, especially with washes that might encounter 82 C (180 F) before reaching the temperature mixing valve.

B. Squeegees

Check the squeegees often for proper operation, alignment, and cleanliness. If squeegees are not properly adjusted and maintained, they will not adequately remove solution from the film. They can also scratch the film and spray or drip processing solution, causing damage to the film and machine.

On weekly shutdowns, remove all air squeegees and soak them in water to remove any chemical deposits. Similar treatment might be periodically required for the other type of squeegees—i.e., wiper blades, vacuum, and wringer-sling. Any spools or rollers used with the squeegees should be lubricated once a week with a small amount of Vaseline or its equivalent. Rollers from rotary buffer squeegees should be washed in detergent, rinsed with water, air-dried, and fluffed.

C. Dryer Cabinet

Because the film is wet and tacky when it is in the dryer cabinet, it is essential that the dryer cabinet and air be free of dirt, lint, etc, for good quality film. It is, therefore, recommended that the following maintenance program be carried out at regular intervals. The inside of the cabinet is vacuumed and wiped down to remove any dust, lint, etc, that may have collected. All rollers are examined for buildup of emulsion or gelatin. Door cables and safety latches are checked. Rollers and floaters are checked for freedom of operation, and lubricated (sparingly) if necessary. All alarms are tested for proper working condition. Heating coils are inspected and checked for proper output. Air filters are checked and replaced if excessively dirty.

Any rubber roller rings that show signs of deterioration are replaced. Any flanges which show emulsion buildup are cleaned. The dryer cabinet drive roller assembly (outside of the dryer) is cleaned and any excess oil is carefully wiped off.

D. Wash Tanks—Algae and Fungi Control

Algae and fungi tend to form on the inside walls of the wash tanks. Their presence is indicated by a slippery and slimy feel on the tank walls. The formation of algae and fungi in the wash tanks usually can be controlled by draining and then immediately refilling the wash water tanks as part of the daily and weekly shutdown procedure. If algae and fungi form, add about 59 ml (2 fl oz) of a 5¼% solution of sodium hypochlorite to each tank as the tank is being refilled. This chemical is a common household bleaching solution, such as Clorox. Leave the bleaching solution in the tank. It will be removed by the normal replenishment during start-up. See start-up and shutdown procedures.

E. Lubrication

The processing machine, like any other mechanical equipment, requires lubrication.

All mechanical friction points on the machine are lubricated as required. The friction points include bushings, chain drive, idler rollers, bearings, etc.

Oil and grease are always used sparingly to avoid any excess oil or grease from being transferred onto the film.

F. Rack Cleaning

Solid materials and tars must be removed from the racks. Their presence could cause dirt, scratches, and abrasions on the film as well as interfere with the drive mechanism of the machine. A suggested method of cleaning removable machine racks is as follows (for racks that cannot be removed, see the section on Tank and Line Cleaning):

1. *Regular Racks*

   This rack cleaning procedure is for regular racks, *not buffer racks.*

   a. Remove the rack from the machine, and immediately rinse it with hot water for 2 minutes. If racks are permitted to stand without rinsing, chemicals will dry on them and make cleaning very difficult.

   b. Submerge the racks in the rack acid bath for 20 minutes. The formula for this bath is given below:

   Rack Acid Bath

Water	600 ml
Hydrochloric Acid (Conc.)	150 ml
Isopropyl Alcohol	250 ml

   Note: This bath is used at room temperature and the bath is gently agitated with air. Follow the safety precautions given below.

   c. Rinse the racks in hot water for 2 minutes.

   d. Scrub the racks with a stiff, bristle brush to remove any remaining deposits.

   e. Submerge the racks in the rack caustic bath for 15 minutes. The formula for this bath is:

   Rack Caustic Bath

Water	800	ml
Quadrafos	0.84	g
Sodium Hydroxide	16	g
Sodium Carbonate	16	g
Trisodium Phosphate	6.2	g
Water to make	1.0	liter

   Note: This bath is used at 49 C (120 F). The temperature can be maintained by steam coils. Moderate air agitation is used. Follow the safety precautions given below.

   f. Rinse the racks in hot water for 2 minutes.

   g. Inspect the racks and rewash ones that are not thoroughly clean.

2. *Buffer Racks*

   Buffer racks are cleaned in hot water *only*. They are never put in the acid or caustic baths.

3. *Safety Precautions*

   The isopropyl alcohol used in the acid bath is a flammable material. However, if the bath is made according to direc-

tions, the flash point of the bath will be well above ordinary building conditions. An increase in the alcohol or acid content of the bath will increase the hazard. The work area must be well ventilated, and an exhaust hood is recommended. Open flames must not be used. Under no circumstances should nitric acid or sulfuric acid be used in place of the hydrochloric acid. Neither should household cleaning agents be added to these recommended solutions.

Both the acid and caustic baths are harmful to skin and clothing. A hand spray, face spray, and shower must be available in the areas where these solutions are used. Goggles, rubber gloves, rubber boots, and aprons must be worn at all times by personnel using these solutions.

The residue on processing racks, especially the racks used in the color developer solution, may cause dermatitis.

G. Tank and Line Cleaning

Solid materials and tars must occasionally be removed from the processing tanks, recirculation systems, and supply lines. A suggested method of cleaning is as follows.

In general, dirt, sediment, and sludge are removed from the tanks and lines by flushing them with hot water. This treatment does not, however, remove carbonate scale. If carbonate scale is present, it must be removed by means of an acid solution. Acid cleanup, if not done correctly, can affect the processing results.

1. *Hot Water Cleanup of Machine Tanks and Lines*
   a. Disconnect or remove sensing elements of the temperature controller and any recording equipment to prevent damage.
   b. Drain the tanks and lines. Immediately fill the tanks with hot water (60 C/140 F), and scrub the tanks with long-handled bristle brushes.
   c. Drain the tanks and lines. Refill the tanks and lines with hot water and recirculate or air-agitate the water for 1 hour.
   d. Drain the water to the sewer.
   e. Check for carbonate scale. The frequency of an acid cleanup depends on the rate at which the scale forms.
   f. Change the filters and reassemble temperature controller and any recording equipment.

2. *Hot Water Cleanup of Replenisher Supply Lines*
   a. Disconnect the supply lines at the replenisher tank and the flowmeters, and then flush the lines with hot water for 1 hour.
   b. At convenient places, disconnect sections of the supply lines and check for carbonate scale. The frequency of an acid cleanup depends on the rate at which the scale forms.
   c. Drain the system and reconnect the lines.

3. *Acid Cleanup of Developer Tank and Lines*
   a. Drain the used developer solution to a holding tank. A portion of the used developer solution is used to prepare the "seasoning solution." See step i.
   b. Flush the system with water for about 1 hour.
   c. Fill the system with tank acid cleaning solution and recirculate the solution for about 1 hour through the filters. Change the filters as required. The formula for the acid cleaning solution is given below:

Tank Acid Cleaning Solution

Water	910 ml
Hydrochloric Acid (Conc.)	90 ml
Polyrad 1110-A (corrosion inhibitor)*	0.4 ml

   d. Drain the acid solution to the sewer.
   e. Flush the system with water for about ½ hour.
   f. Fill the system with the tank carbonate cleaning solution and recirculate the solution for about 1 hour through the filters. Change the filters as required. The formula for the carbonate cleaning solution is as follows:

Tank Carbonate Cleaning Solution

Water	1.0 liter
Sodium Carbonate	100 g

   Note: Safety precautions are used in handling cleaning solutions as given below:
   g. Drain the carbonate solution to the sewer.
   h. Flush the system with water for about ½ hour.
   i. Fill the system with the "seasoning solution," which is used developer solution diluted 1:1 with water.
   j. Drain the "seasoning solution" to the sewer, and then fill the tanks with fresh developer solution.

4. *Safety Precautions for Use with Tank Cleaning Solutions*

The work area must be well ventilated. Under no circumstances should nitric acid or sulfuric acid be used in place of the hydrochloric acid. Neither should household cleaning agents be added to these recommended solutions.

Both the acid and carbonate baths are harmful to skin and clothing. A hand spray, face spray, and shower must be available in the areas where these solutions are used. Goggles, rubber gloves, rubber boots, and aprons must be worn at all times by personnel using these solutions.

The residue on processing racks, especially the racks used in the color developing solution, may cause dermatitis.

5. *Ferricyanide Bleach and Prehardener Systems*

Only hot water is used in this equipment. Tanks and supply lines are flushed as described above.

*Available from Cellulose and Protein Products Dept., Hercules Inc., Wilmington, Del. 19899.

6. *Cleaning Central Mix Tanks*

Mix-tank cleaning is minimized by pumping solutions out as soon as possible. In this way, tar does not have time to form and adhere to the sides of the tank.

a. Remove the solutions from the mix tank as soon as possible.

b. Rinse the tank immediately with hot water (at 60 C/140 F).

c. Remove any residue which may remain in a tank by scrubbing the tank with a brush dipped in the acid cleaning solution.

d. Rinse with hot water (60 C/140 F).

7. *Alternative Cleaning Procedure Using Sulfamic Acid*

The use of sulfamic acid as the cleaning agent for tanks, lines, and recirculation systems in place of the above procedure may be preferred for the following advantages:

(1) easy and safe to handle, (2) no fumes, (3) noncorrosive, (4) photographically inert in small concentrations, and (5) eliminates the necessity of a carbonate neutralizing rinse.

Sulfamic Acid Cleaning Solution Formula

Water	800 ml
Sulfamic Acid*	50.0 g
Polyrad No. 1110-A (corrosion inhibitor)†	0.4 ml
Water to make	1.0 liter

a. Disconnect or remove sensing elements of the temperature controller and any recording equipment to prevent damage.

b. Pump replenisher and system solutions to respective storage tanks. Remove racks and turbulators from machines.

c. Mix sulfamic acid cleaning solutions in replenisher mix tank. Use hot water (60 C/140 F).

d. Pump cleaning solutions to any solution reserve tank and then to machine systems through the replenisher lines.

e. Recirculate cleaning solution in system for about 2 hours. Replenish cleaning solution at the rate of 250 ml per min per machine to maintain solution pH and temperature. Do not use filters while cleaning solution is being recirculated. Some brushing of machine tanks is advisable. If possible, adjust the temperature controller.

f. Dump cleaning solution to sewer. Flush mix and reserve tanks, replenisher lines, machine and recirculator system with water. Fill machine with water and recirculate for 30 minutes. Use recirculator system filters.

g. Dump water to sewer and change filters.

h. Fill recirculator system with "seasoning solution," which is used developer solution diluted 1:1 with water. Recirculate this solution for 30 minutes.

i. Discard the seasoning solution to sewer. Replace turbulators and racks. Change filters. Reassemble temperature control and recording equipment.

j. Fill system with fresh tank solution.

Note: It has been found expedient to clean the entire system, i.e., the mix tank to the recirculation system inclusive. The night before the cleanup, the sulfamic acid cleaning solution is mixed in the central mix tank and is pumped to the mix storage where it remains overnight. Steps d through j are then performed the following day. In this way, several systems can be cleaned at one time.

*Available from E. I. du Pont de Nemours & Co., Inc., Industrial and Biochemicals Dept., Wilmington, Del. 19898.

†Available from Cellulose & Protein Products Dept., Hercules Inc., Wilmington, Del. 19899.

PROCESS CONTROL

TABLE OF CONTENTS

INTRODUCTION

It is erroneous to assume that a color process can be started on a production basis without first establishing suitable standards of operation for the individual installation and without provision for adequate control procedures. It is of the utmost importance to realize at the outset that color processing demands much more rigid standards and more thorough planning in this respect than black-and-white processing.

In processing multilayer color films, it is evident that one must simultaneously control the chemical reactions taking place in the separate layers of the film. Not only must the correct reaction take place in each layer, but the interference of one reaction with another must also be held to a minimum, or at least constant. Further, the reactions must be allowed to proceed to that point, and only to that point, where the proper contrast relationships, minimum and maximum densities, permissible fog and stain levels, and the correct speed and color balance are obtained in the processed film.

Changes in time, temperature, agitation, composition of the processing solutions, and the like, do not, in general, affect each layer of the film in exactly the same manner. It is therefore never safe to assume than an off-standard condition can be compensated for by a change in some other condition and that such modifications in the process will yield satisfactory results for all emulsion numbers of the same film. There are also more steps in processing a multilayer color film than for a black-and-white film and each step must be carried out with a greater degree of precision and attention to detail than what is normally required in black-and-white processing.

Once the conditions that are known to produce satisfactory results have been established, very little opportunity for modification of the process is left. Adequate control equipment and procedures are considered to be an absolute requisite if consistently high quality results are to be expected.

The control of a chemical process demands first a knowledge of the characteristics of the product and process and the specific conditions that are required to obtain the desired result. Secondly, one must have means for continuous evaluation of the process to see that the status of the process remains unchanged and to provide that the characteristics in the finished product are being maintained. If changes do occur, one must have means for diagnosing the difficulty and locating the cause. Finally, the proper corrective action must be taken to restore the process to its original condition.

A complete process specification and evaluation system for use with the film(s) referred to in this manual call for (a) accurate mechanical data and control, (b) chemical specification and control by means of analysis, and (c) sensitometric tests, which relate quantitative relationships between photographic exposures and the image produced. During the research and development work on any film, various modifications in both film and process were tried. These modifications were evaluated and the film and process combination which gave the best results, in the opinion of a number of experienced observers, was selected. The mechanical, chemical, and sensitometric conditions for optimum processing of the film(s) were thereby determined. These became the "standard" specification for the process as recommended by Eastman Kodak Company and as outlined in this manual.

An excellent treatise on the subject of process control has been published by the Society of Motion Picture and Television Engineers titled, "Control Techniques in Film Processing (MP-2)."* While the book pertains to the control of processing of black-and-white films, the basic principles and methods are equally applicable to the control of color processing.

LABORATORY FACILITIES AND EQUIPMENT

A. Space Requirements and Location

For processors desiring to prepare their processing solutions from bulk chemicals and to prepare their own sensitometric control strips, it is recommended that two separate rooms be provided: one for the chemical laboratory and the other for making and evaluating sensitometric and other photographic tests. A space of about 9.3 square meters (100 square feet) for each of the rooms should be adequate in most laboratories. Air-conditioning of the rooms is desirable in the interests of minimizing troubles from chemical fumes and dust, as an aid in certain operations requiring temperature control, and for the general welfare and comfort of employees.

Since chemical analyses must be made on fresh mixes as well as on machine tank solutions, it is desirable to locate the chemical laboratory at a place that is convenient to both the mix room and the processing machine room. The photographic testing room is most conveniently located near the processing machine room, preferably near the mechanical control section or room.

B. The Chemical Laboratory

The floor should be constructed of acid-proof tile or brick with suitable wall aprons. A central sewer drain for the floor is recommended in case of trouble from accidental spillage of solutions. Walls should be covered with an acid-proof paint or some other chemically inert material to protect against accidental splashes.

Workbenches can be constructed from wood and the tops covered with Transite board or Formica sheets. Wall outlets for gas, air, and electric lines should be installed at convenient locations. Shelves and cabinets for storage of standard reagents can be located on adjacent walls.

An exhaust hood will be needed for some of the analytical work where there is danger from explosive or toxic vapors. This can be made with a metal or wood frame and sheets of Transite. A sliding door with shatterproof glass windows should be fitted to the front of the hood. The hood should be supplied with gas, air (low pressure), and electrical lines.

The exhaust fan and motor must be nonsparking types. The

*Available from SMPTE, 862 Scarsdale Ave., Scarsdale, N.Y. 10583.

fan should produce an air velocity through the face of the hood, with the door up, of at least 30.5 meters per minute (100 linear feet per minute). The electrical wiring should be of explosion-proof type in compliance with the National Electrical Codes for flammable liquids having a flash point below 26.5 C (80 F). All the metal parts of the hood, sink, drain, fan, and ductwork should be grounded.

Laboratory sinks can be made from stainless steel, AISI Type 316, or Alberene stone. The usual hot and cold water outlets will be required. Similar outlets will be needed for connections to a water bath to be used for samples on which measurements must be made at specified temperatures. For operations requiring suction filtering, a cold water outlet fitted with an aspirator pump will be satisfactory. For convenience in dispensing of distilled water, suitable tin piping, glass, or stainless steel lines and valves will be a useful addition.

An eyewash and a safety shower should be provided in an accessible place in the event that chemicals accidentally come in contact with laboratory personnel.

A list of the various types and sizes of laboratory glassware needed for the analytical work can be compiled by reference to the section titled "Analytical Procedures." This will include such items as beakers, graduated cylinders, flasks, burettes, transfer pipets, tip-up pipets, sample bottles, reagent bottles, etc. Other necessary equipment includes an analytical balance, a pH meter (with suitable electrodes), thermometers, hydrometers, magnetic stirrer, constant-temperature water bath, and possibly a spectrophotometer equipped for making measurements in the ultraviolet and visible regions of the spectrum.

C. Sensitometric and Miscellaneous Photographic Test Laboratory

The room should be equipped with standard tables and workbenches having tops covered with pressboard, linoleum, or Formica sheets. It is desirable to incorporate therein several "dark" drawers with lightproof sliding covers for temporary deposit of unexposed or exposed test strips when the occasion demands. Convenient electrical outlets for all instruments at appropriate places will be needed. The room should be equipped with a ceiling fixture for general room illumination and also with suitable ceiling and bench fixtures equipped with safelights for operations where they can be permitted. In order to prevent accidental exposure of film during periods when the room is dark and is being used for making photographic tests, the room should be provided with a double door with safety interlocks.

The laboratory should be equipped with a suitable intensity-scale-type sensitometer or scene tester, a photoelectric color densitometer, and ample storage cabinets for standard lamps, filters, and other accessories. It is also desirable to have an illuminator built into one of the workbenches or on the wall or else a portable one for use in the visual inspection of processed strips. Ample working space should be allowed in the room for plotting sensitometric and chemical control data. If desired, the room can also be used for storing printer control equipment and associated data.

D. Mechanical Control Facilities

In some installations, the mechanical controls for the processing machine will be located in the processing machine room itself, whereas, in other laboratories a separate control room may be provided. In either case, the equipment here will include accurate temperature control equipment and indicators for the various tank solutions, machine speed indicators, flowmeters, valves, and piping for replenishers and appropriate devices for sampling of the tank and replenisher solutions.

E. Personnel

For a small processing laboratory, it would appear that one properly trained person could handle all of the work associated with adjustment and control of the process. This would include sampling and analysis of fresh mixes and machine tank solutions, exposing and reading of sensitometric tests, tabulating mechanical operating data, plotting of control charts, and interpretation of the results. Since a considerable amount of responsibility would be associated with these combined duties, it would seem advisable to employ a chemist or chemical engineer for this position.*

In larger installations, where it seems feasible to employ two or more individuals for this work, the routine work associated with preparation of mixes, sampling of solutions, simple chemical analyses, exposing and evaluating sensitometric strips, etc, could be handled by a person of high-school-graduate level who has had some experience in chemical analytical work. The supervisory activities, however, including the responsibility of process adjustment, interpretation of control data, training of operators and analysts, etc, should be delegated to someone having considerably more training, preferably a chemical engineer or analytical chemist.

F. Laboratory Cleanliness and Personnel Training

In the interests of avoiding contamination of film products, analytical reagents, and tests, and in protecting employees from dermatitis and other hazards, it is recommended that both the chemical laboratory and the photographic testing room be kept spotlessly clean at all times. It is also suggested that all employees be instructed as to the importance of laboratory cleanliness and in the safe handling of various chemicals. The latter subject is discussed in detail on page 516.

ESTABLISHING A STANDARD PROCESS

It will be recognized that among various installations, differences will exist with regard to machine design, machine speed, agitation rates, recirculation and replenishment systems, extent of carry-over from one solution to the next, wash water rates,

*West, L. E., "The Role of the Chemist in the Processing Laboratory," *Journal of the SMPTE*, 65: 133-136, March 1956.

etc. Obviously, no single set of recommendations can be given that will be applicable for all individual installations. In each instance, therefore, a period of testing is required in order to arrive at the specific conditions necessary to obtain satisfactory results.

The ultimate goal is to produce color pictures of a quality level that will satisfy the largest percentage of viewers. On the average, the projected pictures should not look too blue, green, or red; they should have adequate contrast and saturation; there should be detail in both important shadows and highlights; and the extreme highlights should be clean and bright. Because of variations in individual tastes and preferences, judgments of quality cannot be based on the opinions of only one or two observers nor on looking at only one or two scenes. Instead, the ideal quality level must be finally determined by averaging the judgments of a number of different observers having normal color vision and by making such judgments on a variety of scenes and viewed under normal projection conditions. In general, most people tend to be particularly critical with respect to flesh-tone rendition, especially in close-ups. They are also critical with the reproduction of other familiar subjects such as blue skies, green grass, etc. For this reason, scenes containing such subjects should be included in pictures selected for quality evaluation.

During the initial testing stage, one must obtain all pertinent data relative to the mechanical and chemical conditions of the process so that, when the desired photographic quality has been obtained, the process can then be specified as completely as possible in these terms. Both sensitometric and picture tests should also be made, thus enabling one to include the film as well as the chemistry of the process in the complete specification. At later stages, when the process has been stabilized, it should be possible to hold the process in proper control with the aid of sensitometric tests and chemical analysis, without the aid of picture tests. However, it is not desirable to dispense entirely with the latter, since it is necessary to be able to check the sensitometric results, in some manner, occasionally. Such tests are also necessary for evaluation of subjective attributes such as sharpness and graininess.

MECHANICAL CONTROL

Solution times, replenisher flow rates, solution temperatures, and recirculation rates should be checked periodically and corrective adjustments should be made if necessary. The actual readings and any adjustments should be recorded on the process control chart to aid in the interpretation of any process fluctuations. The control chart will be described in the section on sensitometric control. A checklist such as shown in Figure 600-2 will be helpful in covering the important mechanical specifications of the process. During the early stages of operation, such readings should be made frequently, perhaps every half hour. Later, the readings can be made less frequently as indicated below:

A. Solution Times

Check the machine tachometer every day or every 8 hours during continuous operation. If the film racks are adjustable, check the position of the racks in the two developer solutions every day or every 8 hours during continuous operation.

Occasionally, check the machine speed and all solution times by using a mark on the leader or a splice in the leader and measuring the time of the mark in each solution with a stopwatch. Adjust the speed or times to meet $\pm 2\%$ of the recommended time.

B. Replenisher Flow Rates

Check the settings on the flowmeters for replenishers and wash waters every 2 hours.

The setting should be checked once a month (or whenever a flow rate problem is suspected) by measuring the flow by means of a graduated cylinder (500 ml) and a stopwatch. Break the replenisher or wash water line at a convenient place between the flowmeter and the machine. With the replenisher or wash water running and the flowmeter set at the recommended value, collect the solution or water in the graduated cylinder. Measure the volume of solution or water collected in 30 or 60 seconds. Compare this volume with the recommended volume. If the measured volume does not agree within 5% of this recommended volume, run a second check. If agreement is not obtained, clean the flowmeter and then recheck the rate. If the correct volume is not delivered in the specified time, then recalibrate the flowmeter by measuring the flow at four different settings about the desired flow. See Figure 600-1 for a typical flowmeter calibration curve. Plot the volumes obtained on one ordinate of graph paper and then plot the corresponding meter settings on the adjacent ordinate. Draw the best smooth curve through the points. Locate the desired flow on the graph, and then locate the point where this value meets the curve. This point then determines the proper setting for that flow as read on the adjacent coordinate.

C. Solution Temperatures

Check the temperatures every hour.

Use a good thermometer such as a KODAK Process Thermometer, Type 3. If necessary, adjust the temperature to the proper value.

D. Agitation

Check the air agitation and recirculation systems every 2 hours to make certain that they are operating properly.

E. Squeegees

Check the squeegees often for proper operation, alignment, and cleanliness.

If squeegees are not properly adjusted and maintained, they will not adequately remove solution from film. They may also scratch the film or drip processing solutions into the area around the squeegee station. In these ways, both film and equipment can be damaged.

F. Filters

Check the filtration system for proper operation. Processing solutions and wash waters usually contain some insoluble material. If this material is not removed, it will readily adhere to the film, machine tank walls, rollers, lines, etc.

The filters should be changed once every week or two. The filters should not be permitted to become clogged or be left out of the system.

G. Checklist

A checklist applicable to the machine and the installation should be used to start up and shut down a processing machine. See Figure 600-2. Gross errors in process control can be minimized by rigorously following a good checklist.

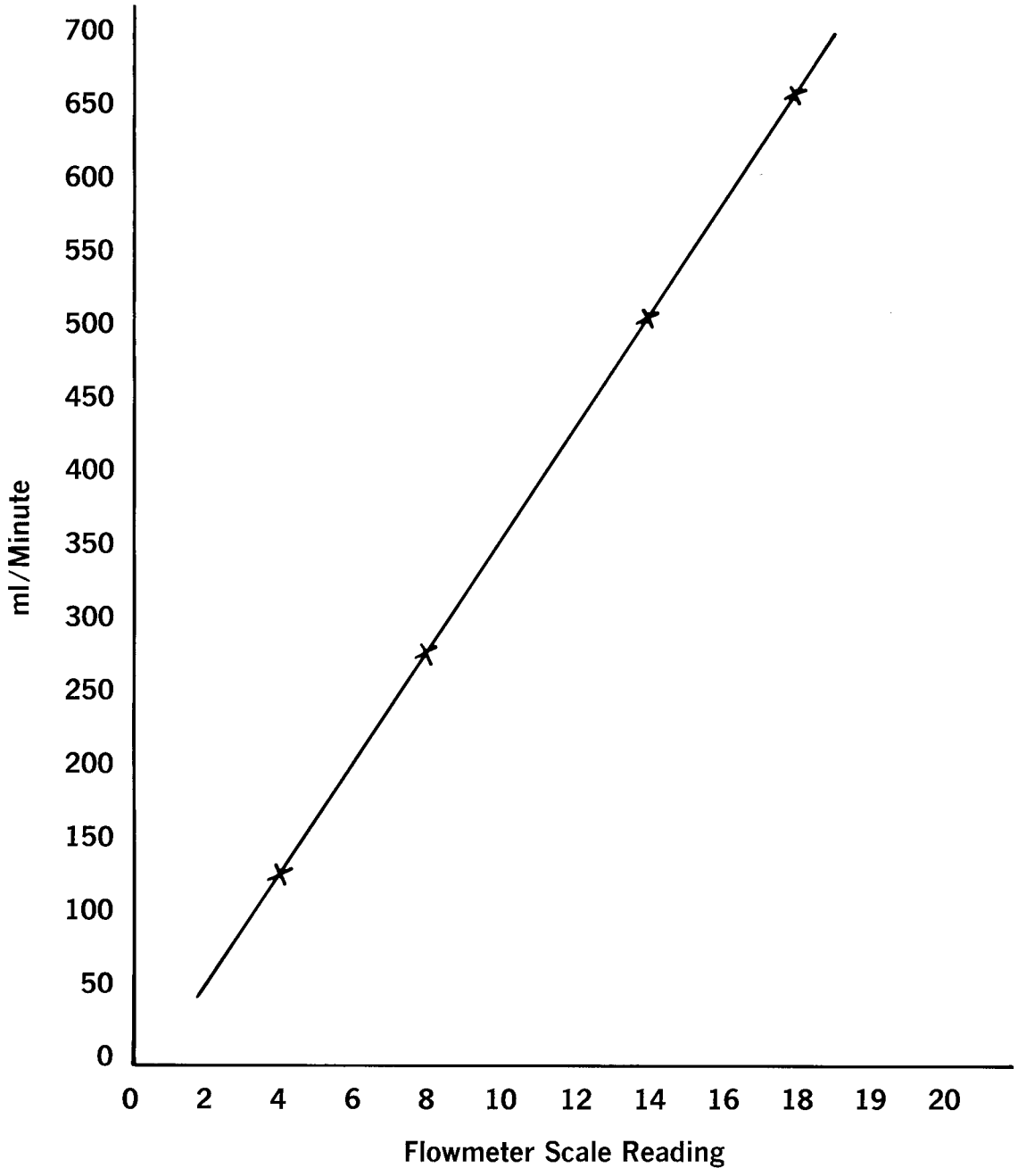


FIGURE 600-1
TYPICAL FLOWMETER CALIBRATION CURVE

FIGURE 600-2
CHECKLIST FOR DAILY OPERATION OF PROCESSOR

	Spec.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.	Sun.
1. Was shutdown strip in control?								
2. Turn on power, air, and water supplies, and the exhaust system.								
3. Check solution levels* in machine tanks.								
4. Check replenisher supply tanks and make mixes if necessary.								
Replenisher Solution: Prehardener								
Neutralizer								
Backing Removal								
First Developer								
First Stop								
Color Developer								
Second Stop								
Bleach								
Fixer								
Stabilizer								
5. Turn on recirculation pumps.								
6. Adjust wash water flowmeters to proper setting.								
7. Turn on and check air supply to air-agitated solutions and final squeegee.								
8. Turn on temperature control systems.								
9. Turn on replenishers. Use leader rates until film is being processed.								
10. Turn on dryer fan motor and heater.								
11. Start machine and check machine speed.								
12. Check final squeegee for cleanliness and clean if necessary.								
13. Check leader for twists.								
14. Check solution time in:								
Prehardener								
First Developer								
Color Developer								
15. Check solution temperature of:								
Prehardener								
First Developer								
Color Developer								

*Solution levels must be high enough in the weir boxes to prevent air from being drawn into the recirculation system when the recirculator pumps are turned on.

16. Check recirculation rate of:

    Prehardener
    First Developer
    Color Developer

17. Run control strips.

18. Proceed to production if in control.

19. Check replenisher flow rates:

    Prehardener
    Neutralizer
    Backing Removal
    First Developer
    First Stop
    First Wash
    Color Developer
    Second Stop
    Second Wash
    Bleach
    Fixer
    Final Wash
    Stabilizer

Spec.	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.	Sun.

CHEMICAL CONTROL

Regular chemical analyses of the processing solutions for their important constituents should be made according to the procedures given in the section entitled "Analytical Procedures." Some analytical methods for noncritical constituents are also included in this section. (These methods can be used as a basis for diagnosing processing troubles as they arise.)

At the start of operations, it is advisable to make frequent analyses, perhaps every 2 or 3 hours, to obtain the necessary data for replenishment requirements. Such a plan will also help laboratory personnel become thoroughly familiar with the analytical methods so that the analysis can be performed with greater speed and accuracy under routine conditions.

When conditions have become stabilized, the analyses can be made according to the definite schedule shown in Table 600-1. This schedule can be followed only when the photographic results indicate that the process is satisfactory in every respect. In the event of trouble, more frequent analyses (for critical items) will be required. For example, the accumulation of bromide in the First Developer may present a problem and require more frequent analyses in order to establish the proper replenishment rate.

Repeated chemical analyses of the same samples of solutions will not yield precisely the same results. The accuracy of an analysis will depend upon the accuracy of the method, measuring equipment, and analyst. One must be certain that a high or low result is indicative of the sample composition and not simply reflecting the variability of the analysis. The specification limits for each solution constituent must be broad enough to include this inherent variability. If a result is obtained which is outside the established specification limits, the analysis should be repeated, with a fresh sample, before attempting to modify the tank solution. Suggested specifications for the important contituents of processing solutions are given with the chemical formulas.

Table 600-1
Schedule of Analysis During Stable Operation

Analysis	Method Number: Once Per Day	Once Per Week	Every Two Weeks	Fresh Mixes
Prehardener				
pH		810		810
Specific Gravity	701D			701D
HA-2			1812A	1812A
Formalin			1812A	1812A
Anti-Fog, No. 6			1551A	1551A
Neutralizer				
pH		810		810
Specific Gravity			701D	701D
NA-1			1360B	1360B
Sodium Bromide			914	914
Rem-Jet Backing Removal Solution				
pH			810	810
Specific Gravity		701D		701D
First Developer				
pH		810		810
Specific Gravity			701D	701D
Hydroquinone			440	440
Phenidone			440	440
Potassium Iodide			929	929
Sodium Thiocyanate		1000F or 1001		1000F or 1001
Sodium Bromide		1001		
Total Alkalinity			702J	702J
First and Second Stop Baths				
pH		810		810
Color Developer				
pH	810			810
Specific Gravity			701D	701D
Benzyl Alcohol			1603D	1603D
Citrazinic Acid		1611C or 1612A		1611C or 1612A
CD-3			125C	125C
Sodium Bromide			930D	
Sodium Sulfite			1470B	1470B
RA-1			1470B	1470B
Total Alkalinity			702J	702J
Potassium Iodide			925A	925A
Bleach				
pH			810	810
Specific Gravity			701D	701D
Sodium Bromide				906G
Sodium Ferricyanide		1120, 1113B or 1100E		1120, 1113B or 1100E
Sodium Ferrocyanide			1101B	1101B
*Fixer**				
pH			810	810
Specific Gravity			701D	701D
Hypo Index		1308G		1308G

*Same analysis for both fixers.

These additional comments regarding processing solutions are also important to chemical control.

A. Dirt in processing solutions *cannot be tolerated,* especially in the prehardener, color developer, and bleach. This problem can be minimized by:
   1. Following proper mixing procedures and maintaining solutions at their analytical specifications. (For instance, improper mixing procedures can cause oiling out of CD-3 and benzyl alcohol in the color developer.)
   2. Noting (in any solution) the presence of threads caused by the film emulsion or base rubbing on something sharp and skiving.
   3. Checking wash tank dirt by draining the tanks every night. Regularly fill the wash tanks with a 3-5% solution of NaOH to remove slime growths; dump, spray-rinse, and refill with water.
   4. Cleaning machine and replenisher tanks as well as the machine and overhead areas.

B. Foam and air bubbles in processing solutions also *cannot be tolerated.* Most likely this could happen when:
   1. Air is leaking into the suction side of a recirculating pump.
   2. Solution is cascading over the weir and drawing air down the recirculation return line.
   3. The replenisher tank is empty when solution is being pumped.
   4. Large amounts of dissolved air are released as cold wash

water is warmed. To prevent air bubbles from sticking to the film and causing nonuniformity, the air must be allowed to leave the water before the water is used in a wash tank. A tempered-water holding tank or a 15-meter (50-foot) coil of 5 to 8-centimeter (2 to 3-inch) hose in the tempered-water supply *after* the last valve will help a great deal. Usage rates higher than 22.7 liters (6 gallons) per minute may require a larger, longer hose or holding tanks larger than 190 liters (50 gallons) if the problem is severe.

C. The following color changes in solutions are useful in determining whether or not a solution is normal:

1. Prehardener, neutralizer, first developer, and stop bath may change to a purple color because of chemicals leached out of the film. This is no cause for concern.
2. Washes should remain clear and colorless; if they do not, the carry-over is excessive, or the water flow rate is too low, or the tanks are not countercurrent.
3. If bleach turns green or dull, muddy brown in a small sample, it is probably being contaminated with iron.
4. If the fixer turns *dark* blue, it is too highly contaminated with bleach. It should be a light blue when seasoned.

This manual also contains analytical test procedures (Methods 1330A and 1707B) that can be used to predict the image stability of processed film. Each photographic film, when processed according to the film manufacturer's recommendations, has an intrinsic degree of image stability which generally is different for different films. If the processing conditions are not optimum for a film, the image stability of the film could be adversely affected to varying degrees, depending on the processing condition and the film being used. For example, excessive retention of sodium thiosulfate, normally associated with inadequate washing, is known to be harmful to image stability. However, its effect at any one concentration or level will vary with the film. Hence the results obtained with these test procedures and a particular film should be compared only with additional samples of that same kind of film. The result should not be compared with samples of other films.

SENSITOMETRIC CONTROL

The chemical reactions involved in the processing of color films are so complex that it is impossible to evaluate and control the process completely on the basis of mechanical and chemical data alone. The end results are photographic and include the characteristics of the sensitized material and the chemicals of the process. Actual picture tests can demonstrate how the process behaves photographically, and it is possible to use such tests for photographic control. Picture tests are always desirable because quality evaluations must be determined from the finished picture.

However, it is preferable to use methods that will furnish quantitative information about the process. A rapid and accurate means of evaluating the process photographically is provided by sensitometric strips that greatly simplify the evaluation and control of the process. These strips can be included in the process with regular production footage as often as desired and evaluated visually or, more precisely, by densitometric methods. The strips can be examined immediately after processing and the results can be plotted on charts near those on which the mechanical and chemical data are recorded. Such information gives an hour-to-hour check on whether accidents have occurred to move the process away from normal.

In using sensitometry for process control,* there are several operating assumptions that must be covered before proceeding with the details on making and evaluating sensitometric strips.

It must first be assumed that all sensitometric strips have identical exposure. This requires a sensitometer with constant light intensity and color temperature. The exposure timing mechanism of this instrument should consistently give precise and repeatable exposures. A sensitometer should be designed to provide the necessary precision, good regulation of power supply, and critical maintenance. If possible, frequent checks should also be made against a standard instrument to provide consistent exposure.

It is further assumed that the film is uniform throughout the length of a roll. This is a valid assumption as long as only a single roll number of one emulsion number of raw stock is used for making the strips. When the supply of the particular roll and emulsion number of film used for such strips has been depleted and a new one must be used, it will be necessary to revise the photographic standards to allow for possible differences between the batches.

Under ordinary conditions of temperature and humidity, film is not precisely constant, and as it ages, many of its characteristics change. In addition, after it has been exposed, the latent image changes with time. Fortunately, such changes can be greatly minimized by "seasoning" for 4 weeks at 21 C (70 F) before storing the film in taped cans at temperatures of −18 C (0° F) or lower, prior to processing. Such storage provisions also permit a number of sensitometric strips to be exposed at one time for use later on. Upon removal from storage, the can should be brought to room temperature before it is untaped. After the can is opened, strips from it should be processed promptly.

In order to be certain that the sensitometric results actually represent what will be obtained in the picture, it is important that the exposure conditions, i.e., the quality and intensity of the illumination and the exposure time, closely approximate those in the camera, printer, or other equipment used with the product in question. Such characteristics as contrast and speed of the individual layers in color films can vary considerably depending upon the exposure time. A time-scale exposure does

*More detailed information on the subject of color sensitometry is contained in "Principles of Color Sensitometry," published by the Society of Motion Picture and Television Engineers, 862 Scarsdale Ave., Scarsdale, N.Y. 10583.

not give the same results as an intensity-scale exposure. Furthermore, process variations may affect a film exposed for a short time in a very different manner than when the same film is exposed for a longer time. It is also not safe to assume that different emulsion numbers of the same film will behave in the same manner under nonstandard conditions. The best practice is to utilize an intensity-scale exposure with the exposure conditions as nearly identical as possible to those used in the camera, printer, etc.

The step wedge is a practical device for producing an intensity-scale exposure. Both photographic and colloidal graphite wedges are commercially available. Wedges with 0.15 density increment ($\sqrt{2}$ factor) or with 0.30 density increment (factor of 2) per step are satisfactory.

Preferably wedges should have a density range from nearly zero to at least 3.0. It is of importance to select an exposure time for a color sensitometer which will be nearly the same as that of the camera or printer which actually uses the film. An exposure of 1/50 second is probably close to an average motion picture camera exposure time.

When establishing a process and when picture tests indicate the process is giving satisfactory results, it is desirable to process a number of sensitometric strips at various intervals. From the processed sensitometric strips, the resulting integral densities to red, green, and blue light of the various exposure increments are determined by use of a densitometer. These density values are then plotted against their corresponding steps (log exposure), and the best smooth curve is drawn through each set of densities, i.e., one curve through the red densities, one through the green densities, and finally the blue. From these data, the average characteristic curves may be obtained which then represent the process aim point. Typical characteristic curves are shown in Figure 600-3. The complete curves give the clearest idea of the neutral scale results to be expected in the picture. For routine control, reading selected steps and plotting the densities on a control chart should be adequate to indicate any serious deviations from a normal process. A control chart method is described under "Photographic Control Method," Item F of this section. A typical control chart is shown in Figure 600-4.

A. Sensitometers

The number of commercially available instruments for making sensitometric exposures on color films is rather limited. Instruments which are suitable for use may be obtained from:

S.D.A. Industries, Inc.
7955 Haskell Ave.
Van Nuys, Calif. 91406

Kodak-Pathé
37-39 avenue Montaigne
75-Paris (8è), France

Macbeth Corp.
P.O. Box 950
Newburgh, N.Y. 12550

Where no sensitometer is available, exposures can be made in a printer which is provided with a full-frame step tablet made on 35mm black-and-white film. However, a printer used for this purpose must be controlled with the same precision as a sensitometer.* This calls for critical maintenance of lamp intensity and color temperature, printer speed, filter transmittance, etc.

B. Exposure of Sensitometric Strips

The sensitometric exposures for the film described in this manual should be color-balanced to give approximately neutral density images in the processed film.

The following conditions are recommended for EASTMAN Color Reversal Intermediate Film:

Lamp color temperature	2850 K
Exposure time	1/25 sec
Exposure modulation	intensity scale, 0.30 log E increments
Type of exposure	neutral scale

The filters required for exposure include the Special Series 1700 Filter† plus two thicknesses (total 8mm) of Pittsburgh No. 2043 Heat Absorbing Glass.

For routine control purposes, sensitometric strips should be processed along with production footage at 1-hour intervals. For this work, it will be preferable to use film of the same emulsion number as that used for the production footage. A large number of strips can be exposed at one time, sufficient to take care of operations over a period of 2 or 3 weeks, providing the strips were seasoned for 4 weeks at 21 C (70 F) and then kept in a deep-freeze refrigerator at −18 C (0° F) or lower until ready for use. As noted previously, strips should be packaged one or two to the can and the latter taped. The can should be warmed to room temperature after removal from cold storage before the tape is removed.

To determine whether there is any long-term upward or downward drift in the process, it is also desirable to expose and process one or two strips, once each day, using a "check emulsion." This is one selected as having average characteristics for the particular product being used and on which a number of repeated tests have been made to establish with certainty the results to be expected in a normal process. The raw stock used for this purpose should also be kept in a deep-freeze unit. Long before the supply has been exhausted, a single roll of a new check emulsion should be chosen, taking care to make a sufficient number of crossover tests to provide a proper correlation of the results.

C. Color Densitometers and Densitometric Measurements

To evaluate the processed control strips, it is necessary to

*Gale, R. O., and Graham, J. J., "Use of a Motion-Picture Printer as a Sensitometer," *Journal of the SMPTE*, 64: 123-125, March 1955.

†The Series 1700 Filter is a special combination of KODAK WRATTEN Filter, No. 2B, plus Corning Filter No. 3307 (approximately 1mm thickness) plus Jena RG 6 Filter (approximately 1mm thickness). It is designed to simulate the spectral transmittance characteristics of unexposed but processed EASTMAN Color Negative Film 5254.

measure the integral density of selected steps to red, green, and blue light. This requires the use of a photoelectric densitometer equipped with appropriate color filters. For general process control, it is sufficient to use an arbitrary set of red, green, and blue filters. For this purpose, it is suggested that a suitable set of filters referred to as KODAK Densitometer Filter Set AA (Certified) be used with Eastman and Kodak preprint and print films. For making density measurements more meaningful in relation to printing conditions, it is preferable to use a different set of filters [KODAK Densitometer Filter Set MM (Certified)]. These were referred to as "Status M" filters* and will yield density values closer to those values presented to the print films by the preprint films. Status M filters can also be used for process control.

A number of instruments of this type are commercially available from:

Bell & Howell
Professional Equipment Div.
7100 McCormick Rd.
Chicago, Ill. 60645

S.D.A. Industries, Inc.
7955 Haskell Ave.
Van Nuys, Calif. 91406

Macbeth Instrument Corp.
P.O. Box 950
Newburgh, N.Y. 12250

Westrex Corp.
390 N. Alpine Dr.
Beverly Hills, Calif. 90213

It should be noted that these instruments differ among themselves with regard to the characteristics of the photoreceptor, the spectral cut of the color filters, the amplifier linearity and sensitivity, the degree to which they approximate standard diffuse density readings, etc. Because of these differences, a given sensitometric strip will not yield the same density values when read on different makes of instruments. This is not significant for control work involving only one instrument provided that it is capable of giving the required precision and is stable in its operation. During the operation of the densitometer, stray light from fluorescent lights in the reading area should be eliminated—as it can adversely affect readings.

D. Sensitometer and Densitometer Maintenance

Both the sensitometer and the color densitometer require rigid instrument maintenance and control programs† to make sure that the results obtained from the sensitometric strips will truly represent the photographic condition of the process. Poor measurements may often be worse than none at all since their interpretation can lead to corrective action in the process that is entirely unwarranted. A definite schedule should be set up to check the operation of the sensitometer for repeatability, to check the filters, lamp intensity, voltage supply, etc. Similarly, the densitometer should be checked once each day to be sure that it remains calibrated during use. The recommended method involves the reading of highly stable references, such as the KODAK Transmission Densitometer Check Plaque. (Complete instructions for its use are included with the plaque.)

E. Photographic Control Method

As indicated earlier, sensitometry is employed only as a tool to evaluate and to control the photographic process. Naturally, it is desirable to use a method of control that will provide what is deemed to be acceptable photographic quality in the picture image. This requires careful correlation of picture judgments and sensitometric data to arrive at a set of aims and control limits expressed in terms of density values or color balance derived from the measured densities. When the sensitometric results are outside these control limits, the process is said to be out of control. Ideally, the control method should indicate an out-of-control process just before the process produces noticeable adverse results in the actual pictures. Therefore, the control method should have limits broad enough to include the inherent variability of the entire photographic system, including the manufacturing, exposing, storage, normal processing, and densitometry of the control strips. Also, the control method should have limits tight enough to detect an out-of-control process so that corrections can be made with reasonable cost and effort.

A suggested method of control that should be satisfactory for most processing laboratories is given below. This method uses sensitometric exposures made on EASTMAN Color Reversal Intermediate Film 5249 or 7249 to determine the condition of the process, and it uses a sensitometric reference level that must be obtained through picture correlation as described above. When the optimum picture process level is obtained, a control strip that is representative of other strips processed at the same time should become the reference control strip. A common type of sensitometric exposure utilizes a step-wedge in which the exposure difference between adjacent steps represents one camera stop (0.30 log E). The exposure level and balance selected should be such that the entire characteristic curve is generated and the net densities of the three color layers at any given step are approximately the same.

The processed sensitometric strips and control strips are evaluated against their respective reference strip by visual inspection and by densitometric comparison.

1. Visual Evaluation of Process Control Strip

   Using the illuminator, compare the dried processed control strip with the reference strip. A noticeable difference in overall density or in color balance between the two strips indicates that the process is out of control. Also check to determine whether the control strip is dirty, streaked, fogged, scratched, or if the emulsion has reticulated. Any of these adverse conditions can indicate that the process may be producing unsatisfactory product.

2. Establishing Control Chart Reference Readings

   a. Check the performance of the densitometer. If it is in control, place the reference control strip in the densi-

*Miller, O. E., and Powers, S. A., "Improved Printing Density Filters for Densitometry of Color Pre-print Materials," *Journal of the SMPTE*, September 1963.

†Brewer, W. L., Goddard, C., and Powers, S. A., "The Evaluation and Control of Direct Reading Color Densitometers," *Journal of the SMPTE*, 64: 561-565, October 1955. Powers, S. A., and Miller, O. E., "Pitfalls of Color Densitometry," *Journal of the SMPTE*, 72: 97-103, February 1963.

tometer. Then read the values of gray-scale steps No. 1, 4, 7, and 11 through the red, green, and blue filters in the densitometer.

b. Repeat step "a" (above) once per day for five days; then average the data. Do not use any values that do not appear to be part of the sample population—that is, any density reading that differs by more than 0.03 from the average.

For example, the averaged values for a typical Process CRI-1 reference control strip are:

	Filters		
Step Number	*R*	*G*	*B*
1	.08	.38	.85
4	.43	.76	1.33
7	1.33	1.67	2.34
11	1.92	2.21	2.64

c. Record the density values of the corresponding step numbers in the Reference-Reading areas provided by a KODAK Color Process Record Form, Y-55, as shown in Figure 600-4. The control limits for these specific portions of the characteristic curves or steps are given below. In addition to the limits for density for steps 4 and 7, a second set of limits or ranges is given for color balance spread.

Process CRI-1 Control Limits

Portion of Characteristic Curve	*Step No. of Control Strip*	*Limits About Reference Readings*	
		Density	*Color Balance Range*
D-minimum	1	+0.02 (no lower limit)	None
Density between 0.4 to 1.3	4	±0.05	0.06
Density between 1.3 to 2.3	7	±0.10	0.10
D-maximum	11	−0.08 (no upper limit)	None

Using dashed lines, mark the density control limits on the control chart. Fill in the process and machine information on the bottom of the form.

Underneath the Reference Readings for step 4 on the record form, mark "CB = 0.06," and underneath step 7 mark "CB = 0.10." "CB" is the abbreviation for "Color Balance," and the numbers 0.10 and 0.06 are control limits. There are no corresponding CB control limits for steps 1 and 11. If the spread between any two plotted points (for either gray-scale step) is greater than the CB value given for that step, or if a point falls outside the upper or lower density limits, the results are beyond the suggested control limits.

3. Establishing the Reference Characteristic Curves

Because the control chart described above uses only a portion of the control strip, it is desirable to establish the complete characteristic curves of the reference control strip.

These curves are very helpful in controlling the process because they employ the entire range of density measurements and corresponding exposures. By comparing the characteristic curves of the individual control strips to the reference characteristic curves, the density, contrast, color balance, and stain of the film can be estimated.

To prepare the characteristic curves, read all steps of the reference strip through the red, green, and blue filters and plot these density values against the corresponding steps on KODAK Curve Plotting Graph Paper or other suitable graph paper. Figure 600-3 shows a typical set of characteristic curves. Successive steps, as mentioned previously, are exposed to give log E increments of 0.30 or one camera stop. This procedure should be repeated for each new batch of control strips or different emulsion number.

4. Plotting of Process Control Strip

After a control strip has been processed and dried, the densities for the selected steps are measured through the red, green, and blue filters. The differences from the corresponding reference readings are then plotted on the control chart as shown in Figure 600-4.

After the density-difference values of each control strip have been plotted, count the density units separating the top and bottom plotted points for steps 4 and 7. If either of the resulting values exceeds the color balance (CB) control limit for that control step, mark the value underneath the plotted points.

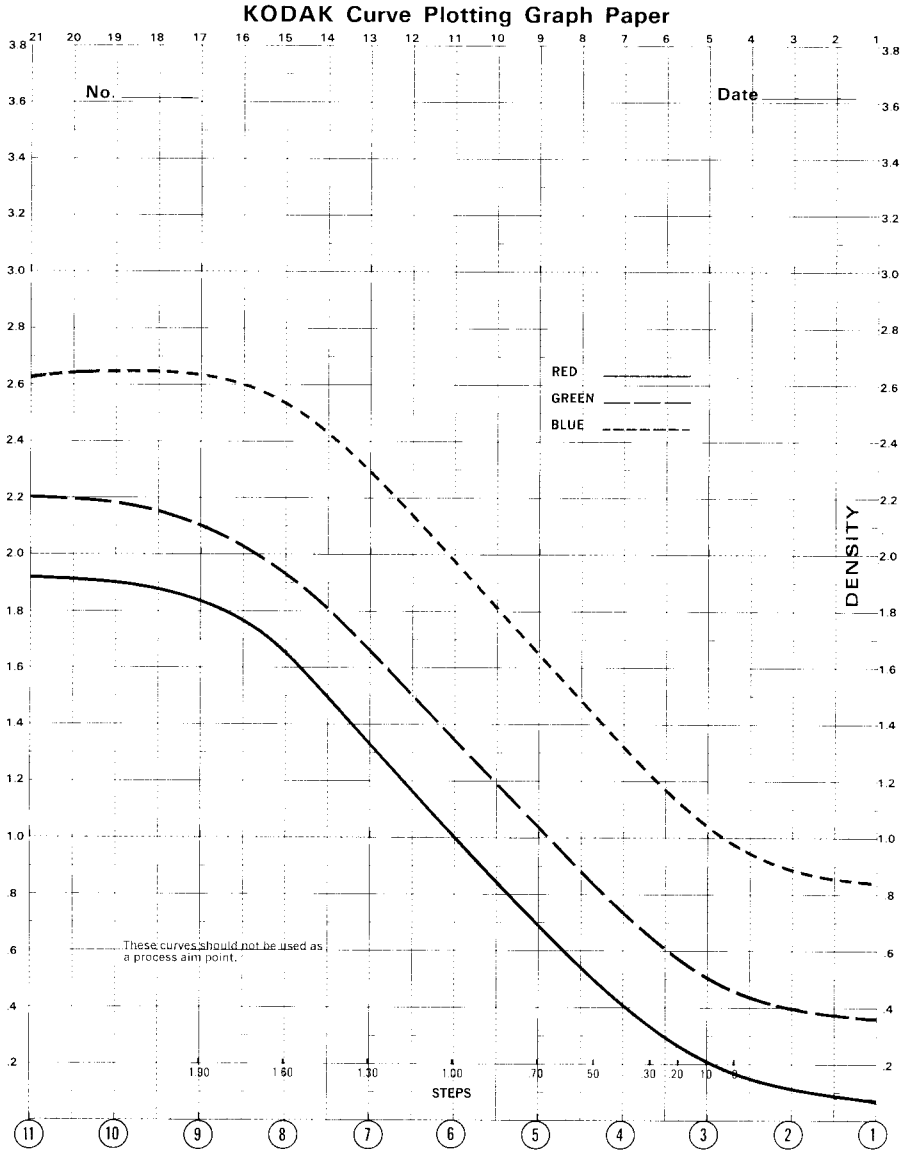
5. Interpretation of Control Chart

Visual examination of the strip can show, at a glance, whether the process is physically acceptable. However, it does not provide a permanent record of the sensitometric results obtained.

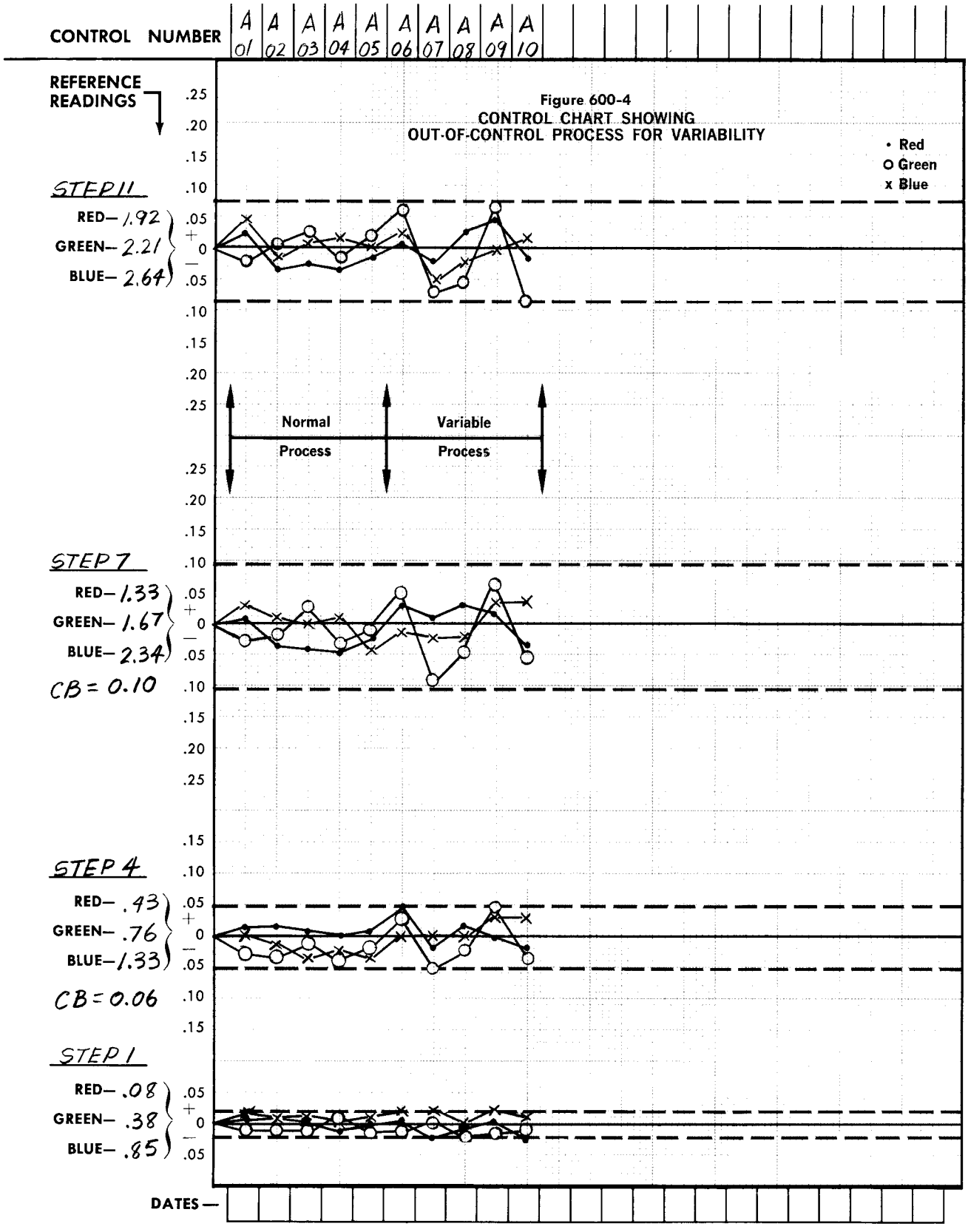
By using the densitometer, an accurate comparison with the reference strip can be made. When the comparative densities of several control strips have been plotted, the record forms will show the degree of uniformity of the process from run to run and day to day. In addition, further interpretation of the plotted points gives a numerical value to any shifts in color balance or density, the direction of such shifts, and a basis for determining what corrective action can be taken.

Theoretically, all correctly processed control strips should be identical to the reference strip and should plot on the reference (0) lines. In practice, neither process nor control measurements are perfect. Note that the nearer control strips plot to each reference line, and the smaller the color balance spread, the better the quality and uniformity of the process.

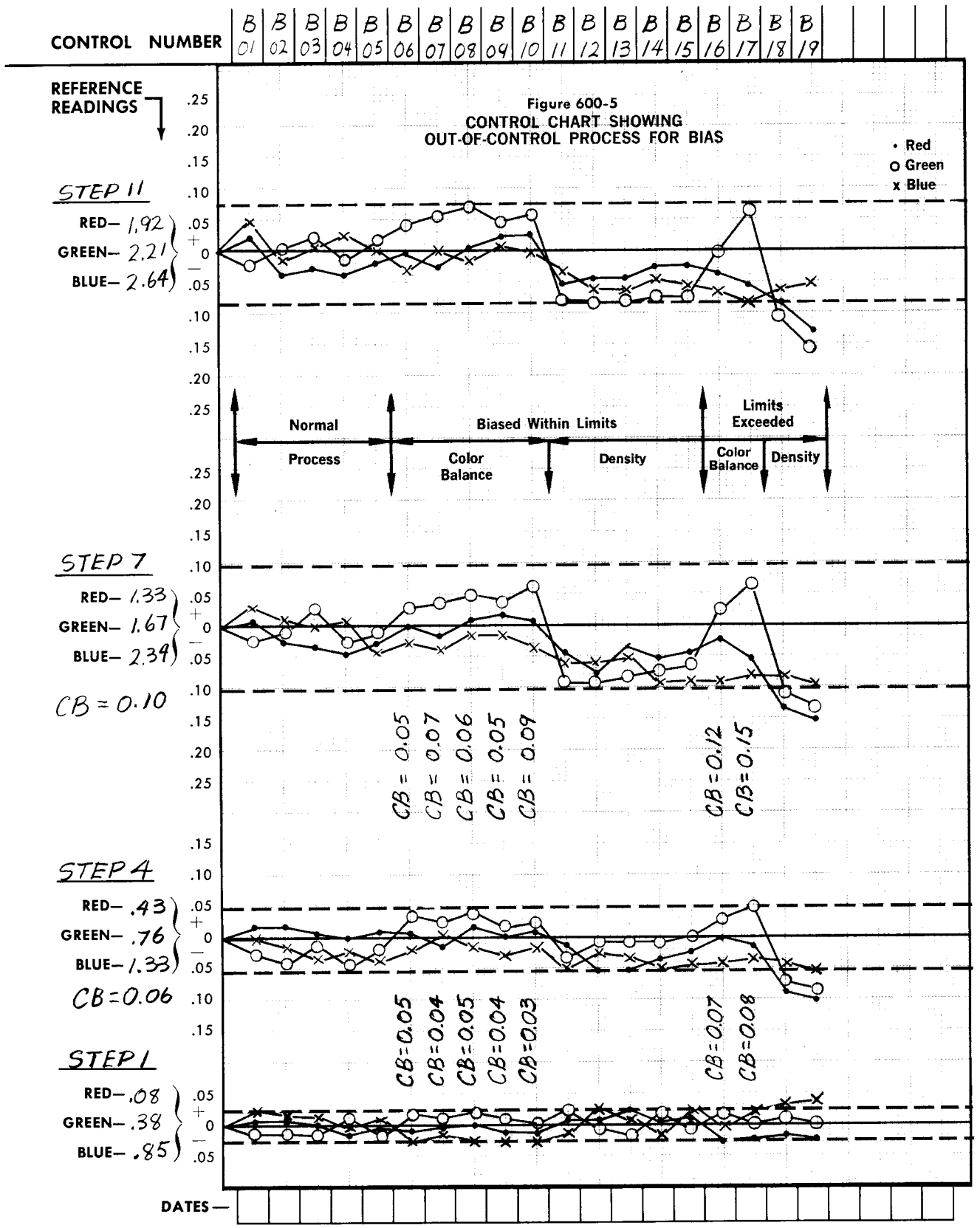
FIGURE 600-3
TYPICAL CHARACTERISTIC CURVES
FOR AN 11-STEP GRAY SCALE



The sensitometric curves and data in this publication represent product tested under the conditions of exposure and processing specified. They are representative of production coatings and, therefore, do not apply directly to a particular box or roll of photographic material. They do not represent standards or specifications which must be met by Eastman Kodak Company. The company reserves the right to change and improve product characteristics at any time.



Kodak Color Process Record Form **PROCESS** _____ **MACHINE** _____ Form No. Y-55



Kodak Color Process Record Form **PROCESS** _____ **MACHINE** _____ Form No. Y-55

Control charts illustrating both an in-control process and two possible out-of-control processes are shown in Figures 600-4 and 600-5.

In Figure 600-4, the plots of the first five control strips (A01 to A05) show satisfactory process performance. Each of the control strips in this series plots randomly about each reference line well within the control limits, without large fluctuations or variability. The next series of plots (A06 to A10) indicates a process with excessive variability. The process is averaging about the reference lines, but it is cycling from one limit to the other limit. Hence the film being processed during this time will also show these fluctuations.

Figure 600-5 demonstrates two process out-of-control conditions: (1) bias within the control limits, and (2) bias outside the limits. In Figure 600-5, the plots of the first five control strips (B01 to B05) again illustrate satisfactory process performance. In the next series of plots (B06 to B15), the control strips are within but near the limits for color balance and density. Whenever a series of five or six control strip plots is near a control limit even though all the strips plot within the control limits, the process should be considered to be out of control. In such a case, the closer the control strips plot near a limit, the more likely the process is producing unsatisfactory film.

In Figure 600-5, control strips B16 to B19 indicate an out-of-control process because the individual control strips have exceeded a control limit. In this series the process has moved considerably from the reference line; therefore, fewer than five or six control strips are required to indicate this out-of-control condition.

DIAGNOSING AND CORRECTING OUT-OF-CONTROL CONDITIONS

When picture tests and control strips indicate that the process has deviated from its specifications, the next phase of process control is the diagnosing of the cause of deviation and then taking the proper corrective action.

A. Control Action

The need for control action is usually first indicated when a control strip plots outside the tolerance limits for either density or color balance (CB), or when a series of control strips plot near a tolerance limit even though the control strips are within the limit. See "Interpretation of Control Chart," page 612. If corrective action is needed, the following investigational procedure should be followed:

1. Examine the control strip for physical defects such as fingerprints, scratches, streaks, fog, etc.
2. Reread the KODAK Transmission Densitometer Check Plaque to establish if the densitometer is in control.
3. Reread the control strip to eliminate measuring error as a possible cause of the out-of-control strip.
4. Process, read, and plot another control strip.
   a. If this strip plots within tolerance limits, the previous control strip may have been handled incorrectly before or during processing. Also, additive conditions may have been the cause of the out-of-control plot. When this is the case, it is very possible that the process is drifting toward an out-of-control condition. Therefore, it is advisable to process additional control strips in order to establish whether or not the process is approaching an out-of-control condition.
   b. If the out-of-control condition is confirmed by the plot of the additional control strip, proceed to the next sections, which describe suggested corrective actions.
5. If the corrective action involves chemical adjustment of a processing solution, refer to Method XVII, in the section on analytical procedures for instructions for the preparation of the adjustments.
6. If a solution constituent has been added and dissolved, the constituent and the pH should be redetermined. If a "cut" has been made, a complete analysis of the resulting solution should be made.

B. Correlation of Mechanical, Chemical, and Sensitometric Data

As experience is gained in the processing of the film to which this manual pertains, mechanical, chemical, and sensitometric data eventually will be accumulated that can serve as a reference source to indicate what may be expected in the photographic results when various mechanical and chemical changes occur.

Before experience is gained with Process CRI-1, it is important to know in a general way what photographic effects can usually be expected as a result of such variations and the approximate magnitude of changes that can produce a noticeable photographic effect. Such information is helpful in diagnosing the cause of a photographically off-balance condition. Photographic effects of mechanical and chemical variations on EASTMAN Color Reversal Intermediate Film are illustrated in Figures 600-6 through -16. Each plot illustrates the effect of changes in a process parameter (abscissa) on the dye density of the final film (ordinate). The recommended values for the various parameters are indicated by the letter S.

The magnitude of the changes shown in Figures 600-6 through -16 should not be considered as process control limits. Also, the data presented in Figures 600-6 through -16 are only qualitative and not quantitative. These photographic effects of chemical variations were obtained from experiments on small laboratory machines where all constituents were maintained constant except the variation being studied. Therefore, the figures should only be used as a trend chart and a guide. It should be noted that, if two or more process parameters are varied, the resulting photographic effect illustrated may not necessarily be additive. Interactions may take place that can produce effects other than those expected, thus causing contrast mismatches among the three dye layers, as well as other color balance shifts.

FIGURE 600-6
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

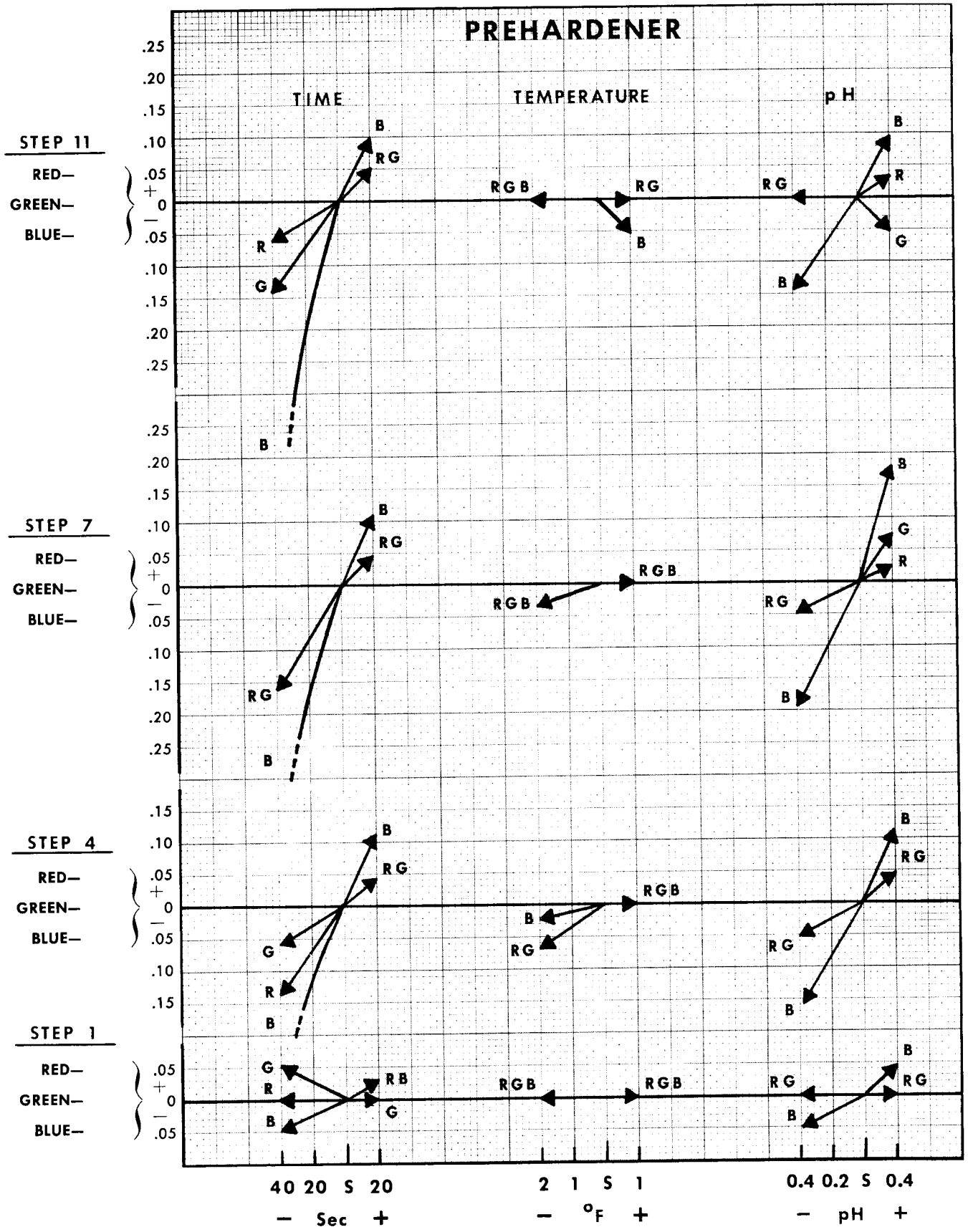


FIGURE 600-7
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

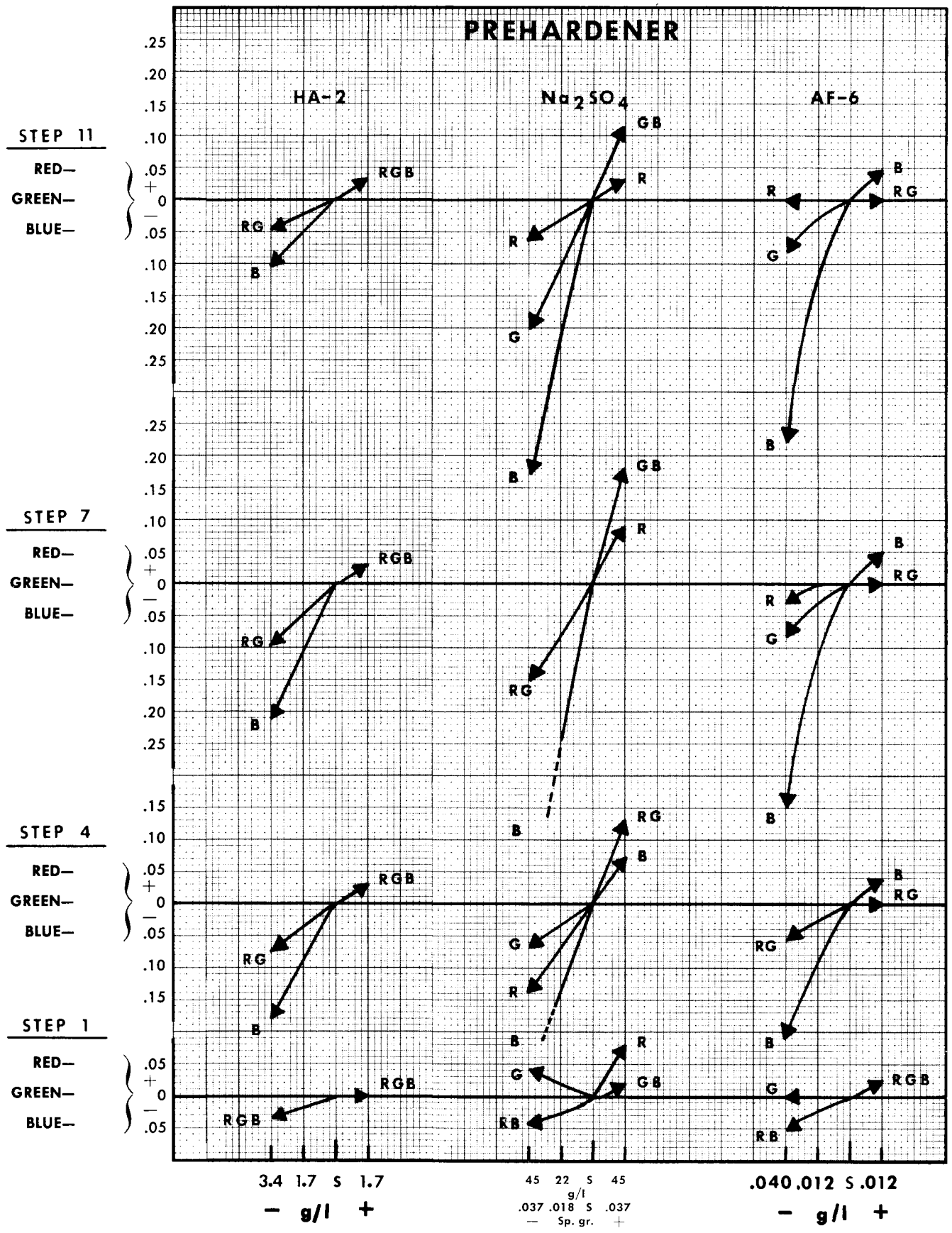


FIGURE 600-8
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

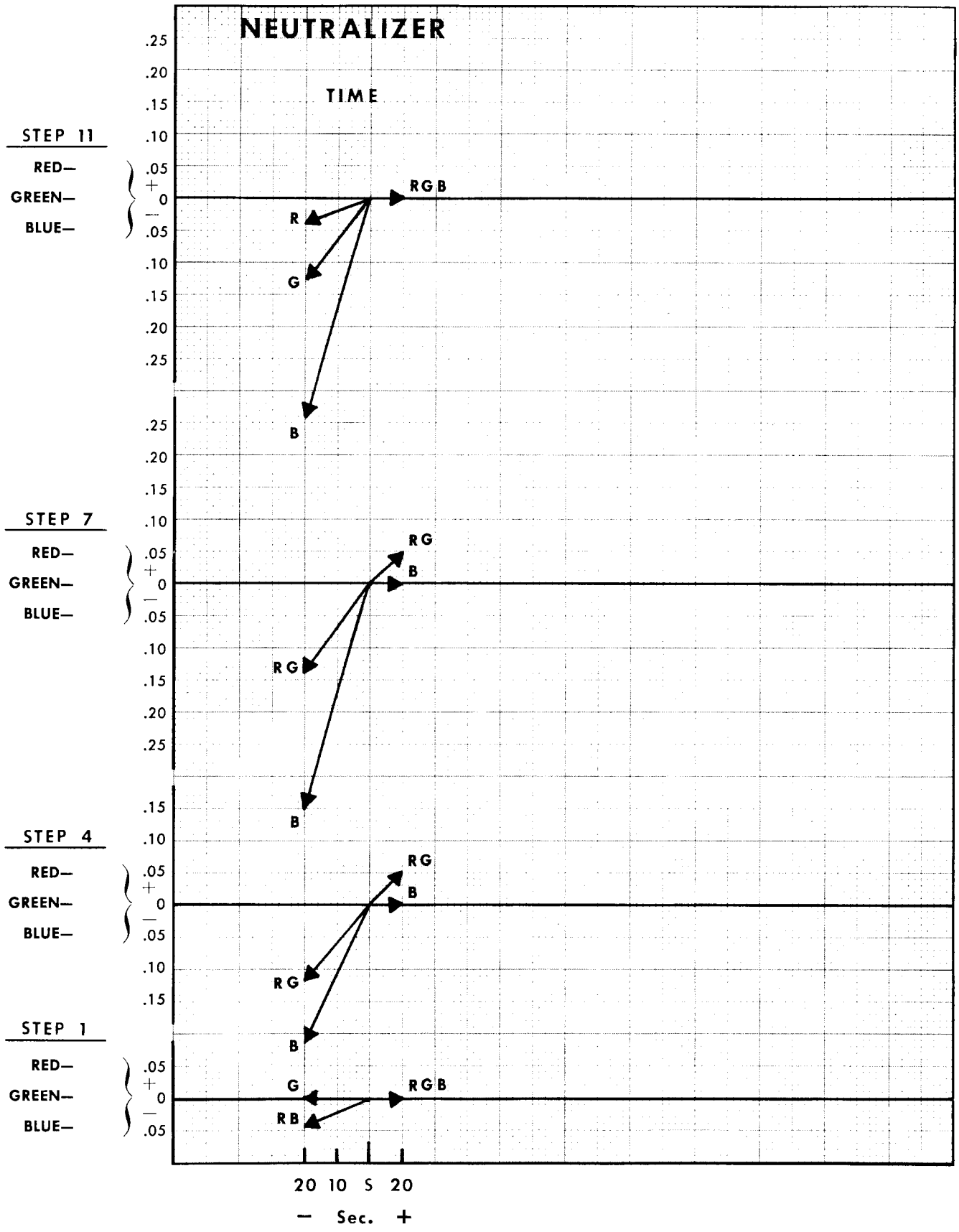


FIGURE 600-9
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

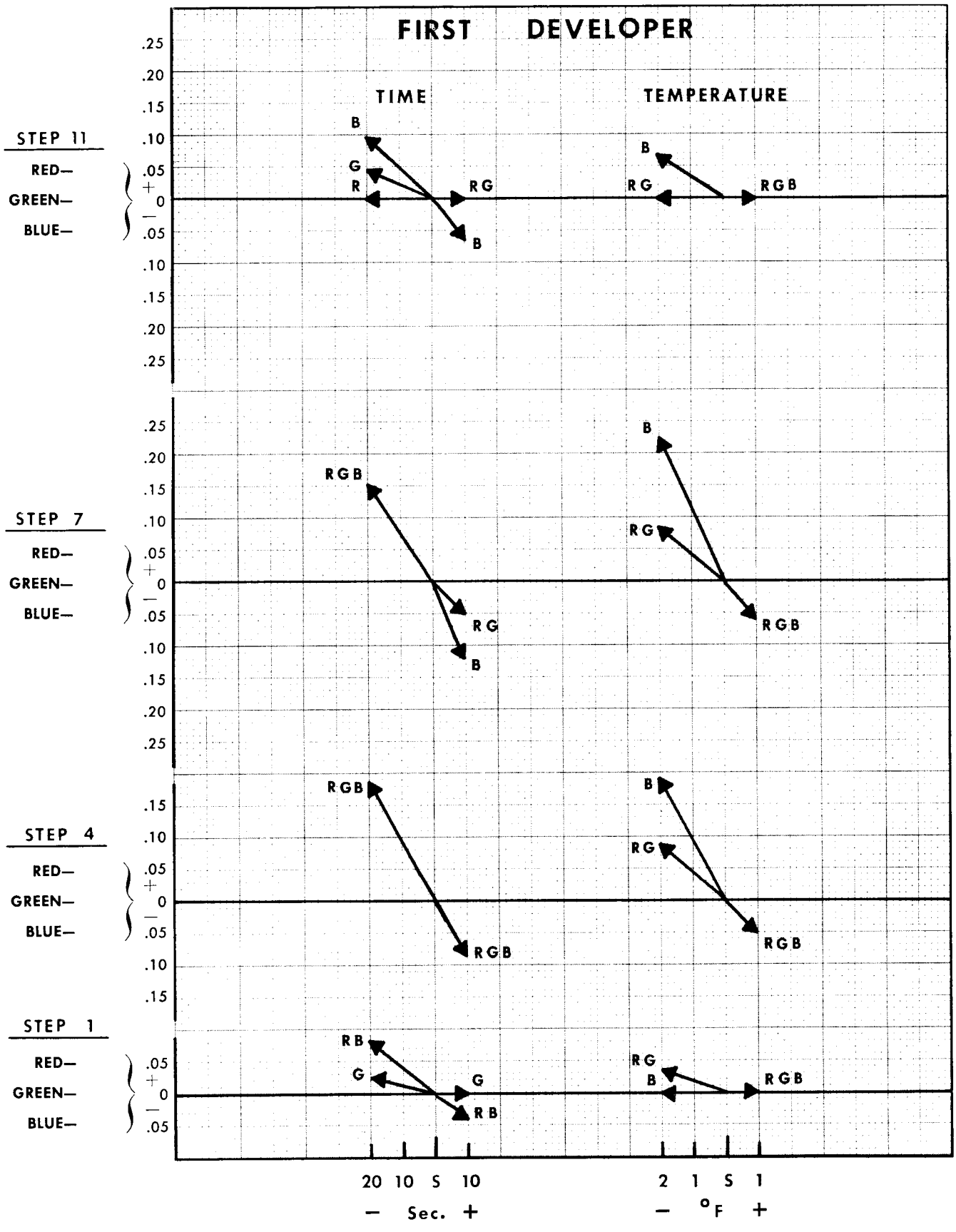


FIGURE 600-10
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

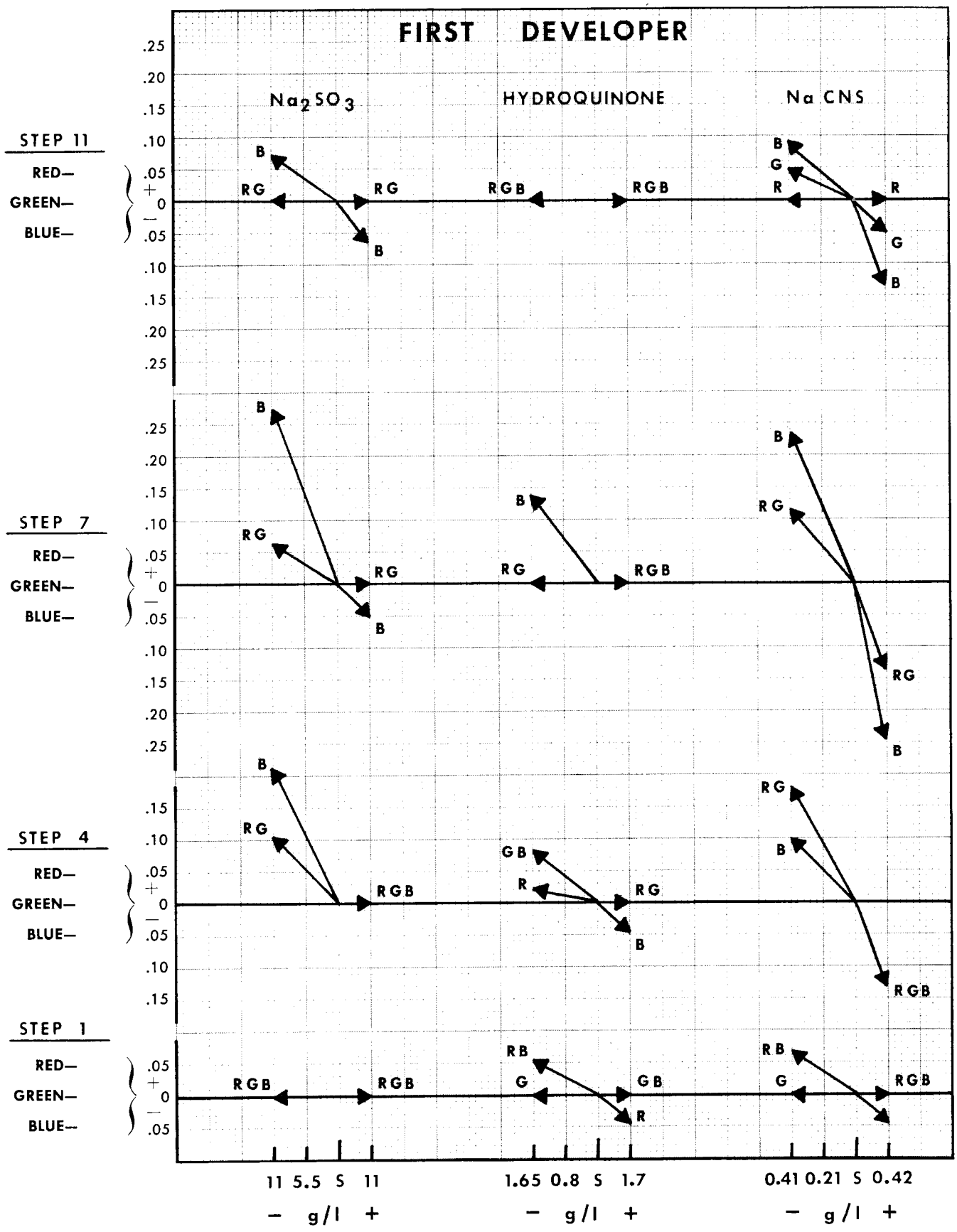


FIGURE 600-11
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

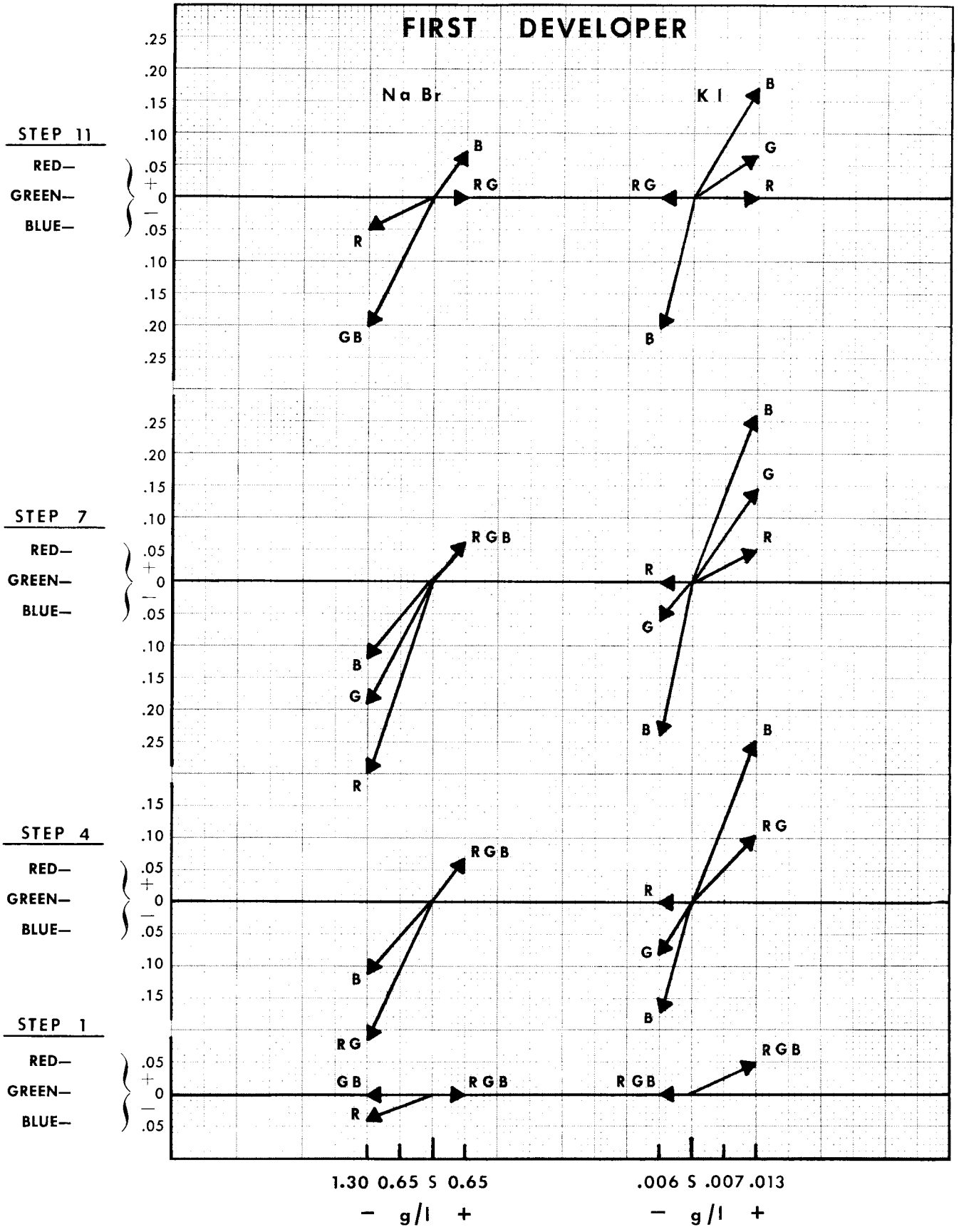


FIGURE 600-12
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

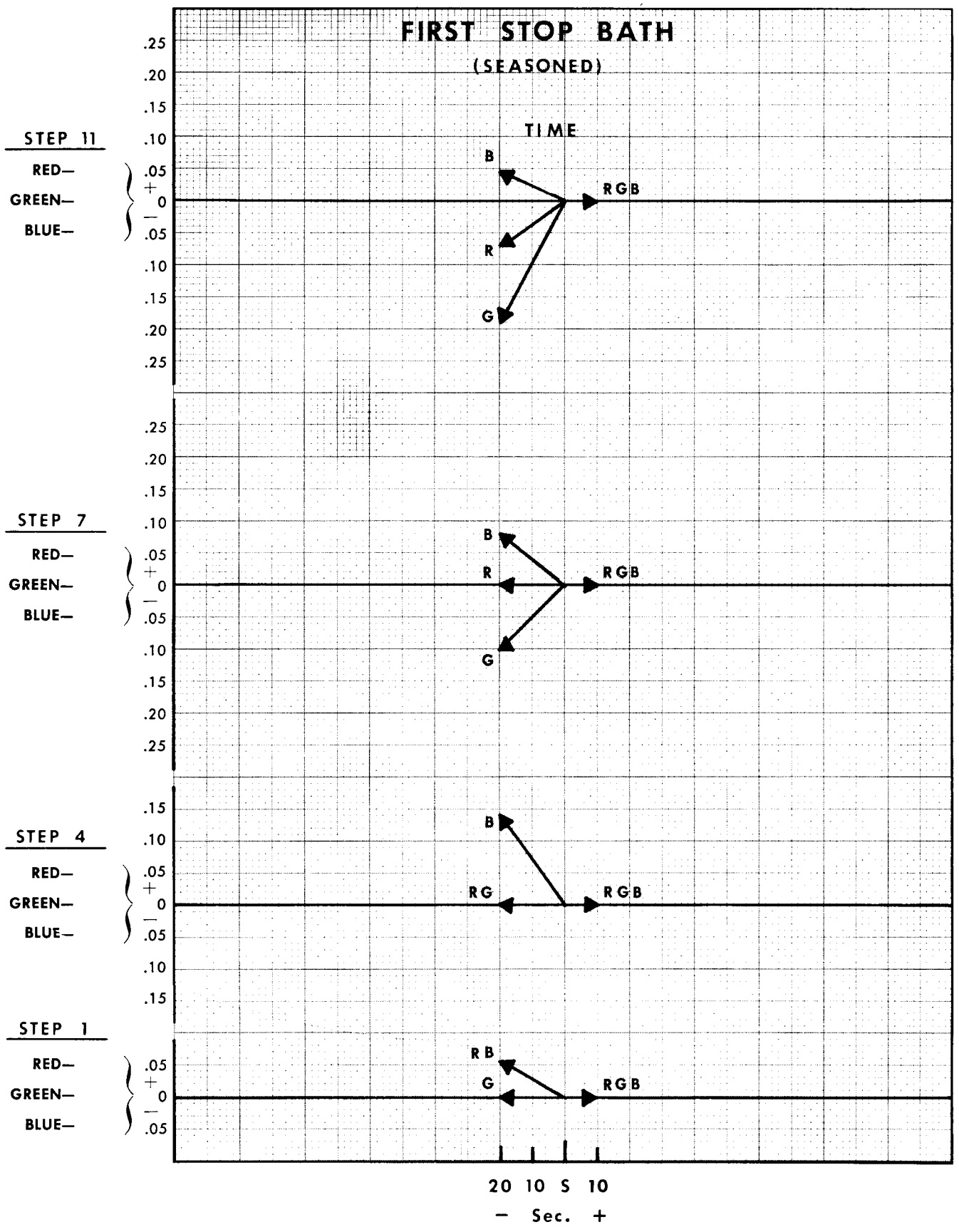


FIGURE 600-13
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

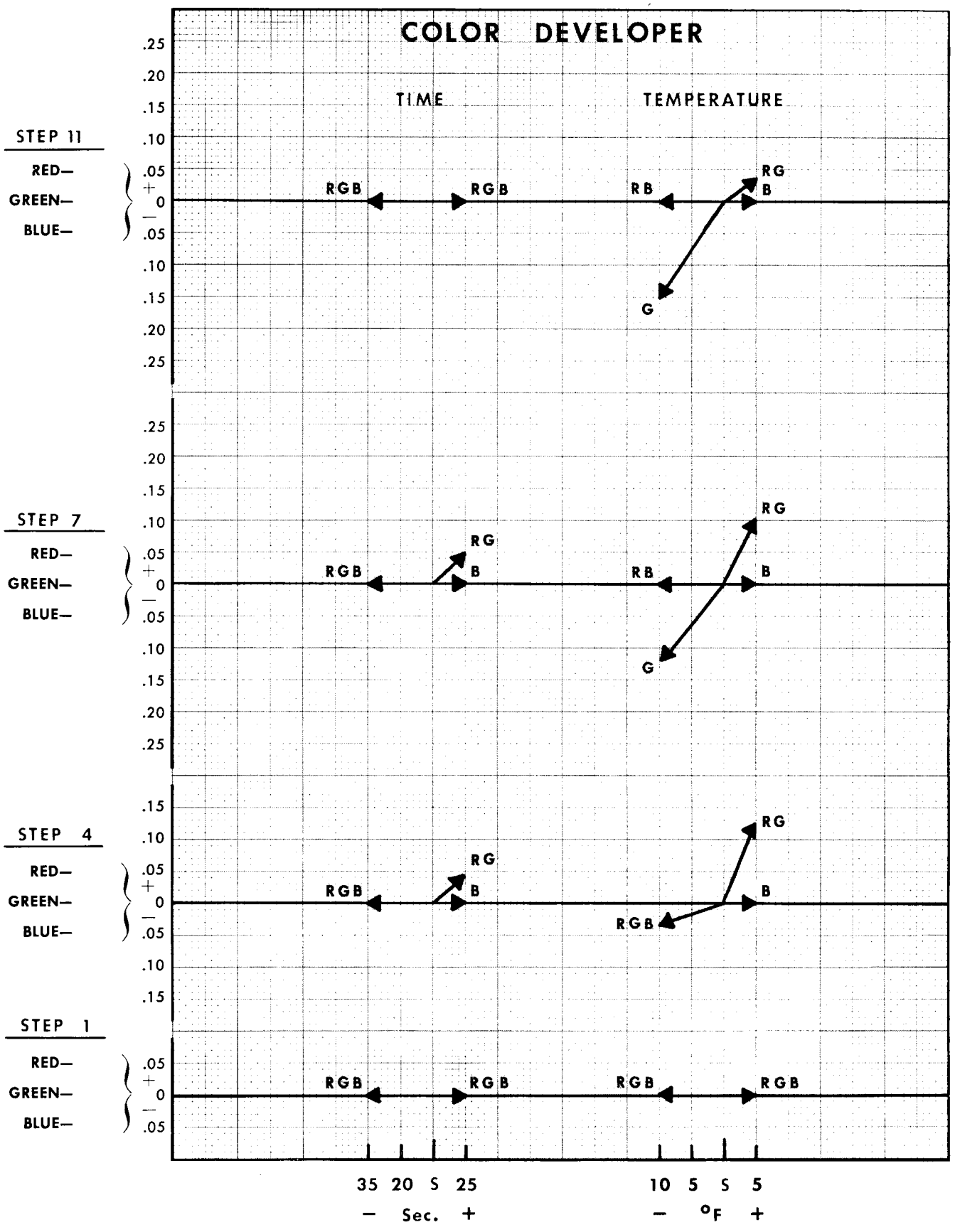


FIGURE 600-14
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

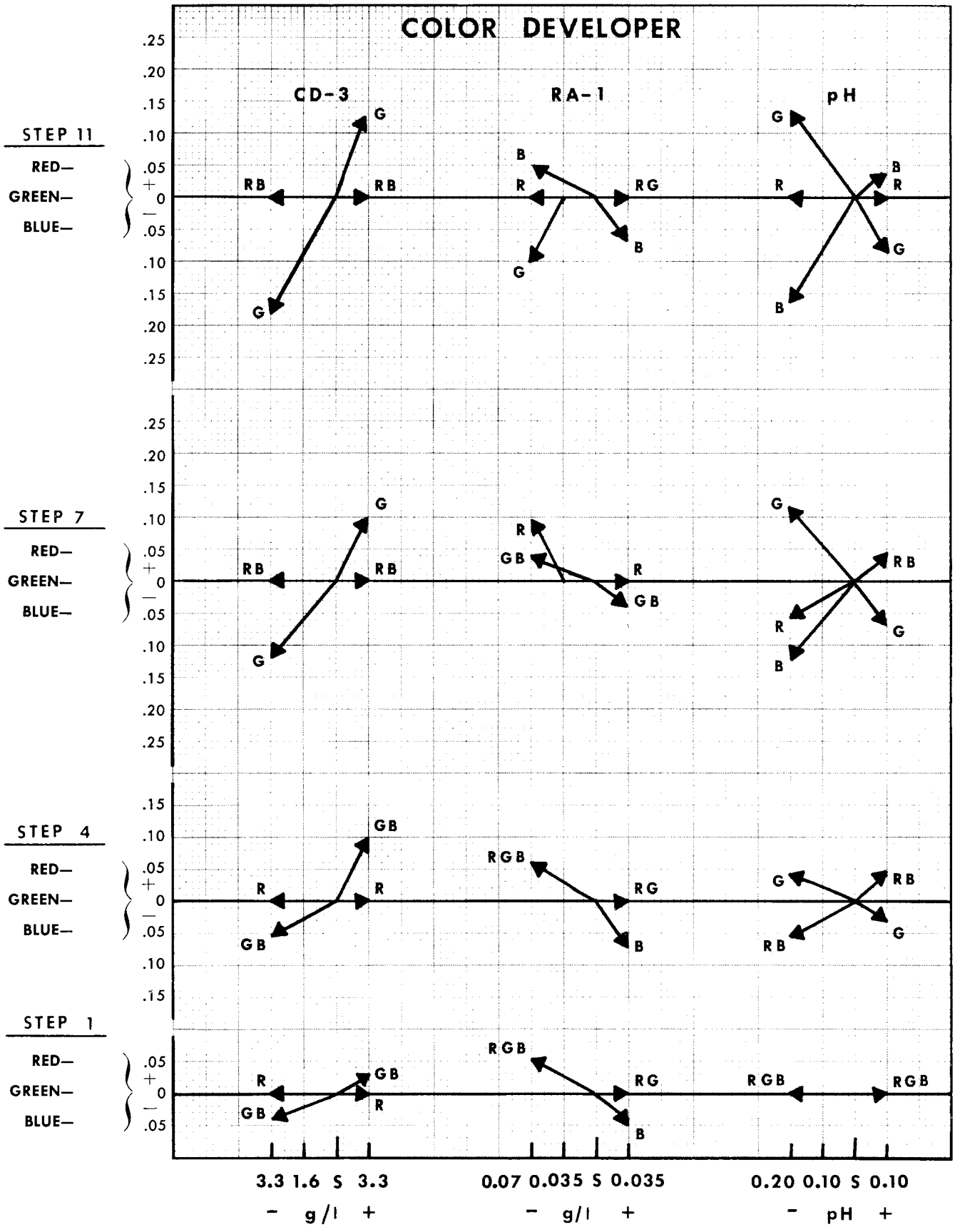


FIGURE 600-15
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1

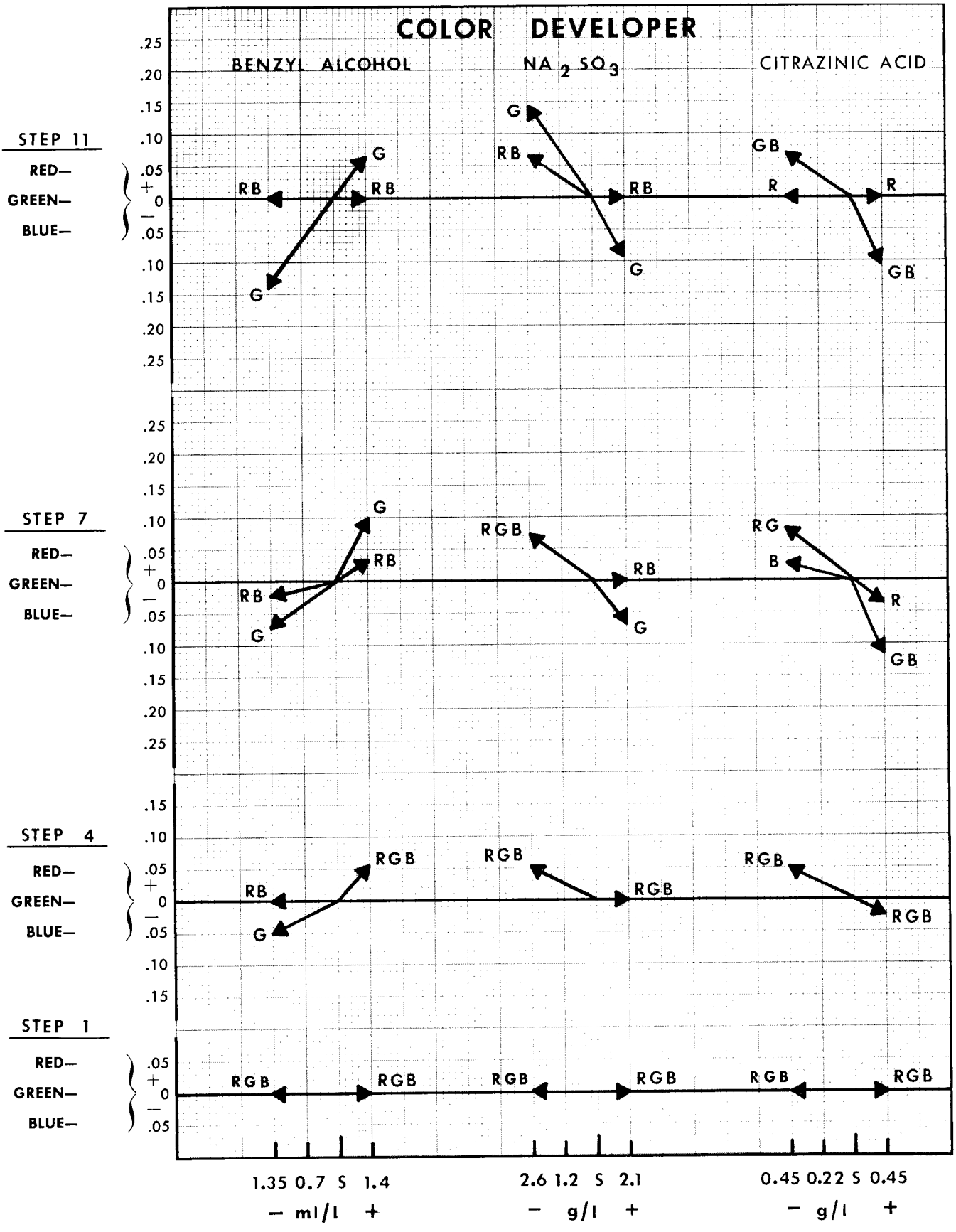
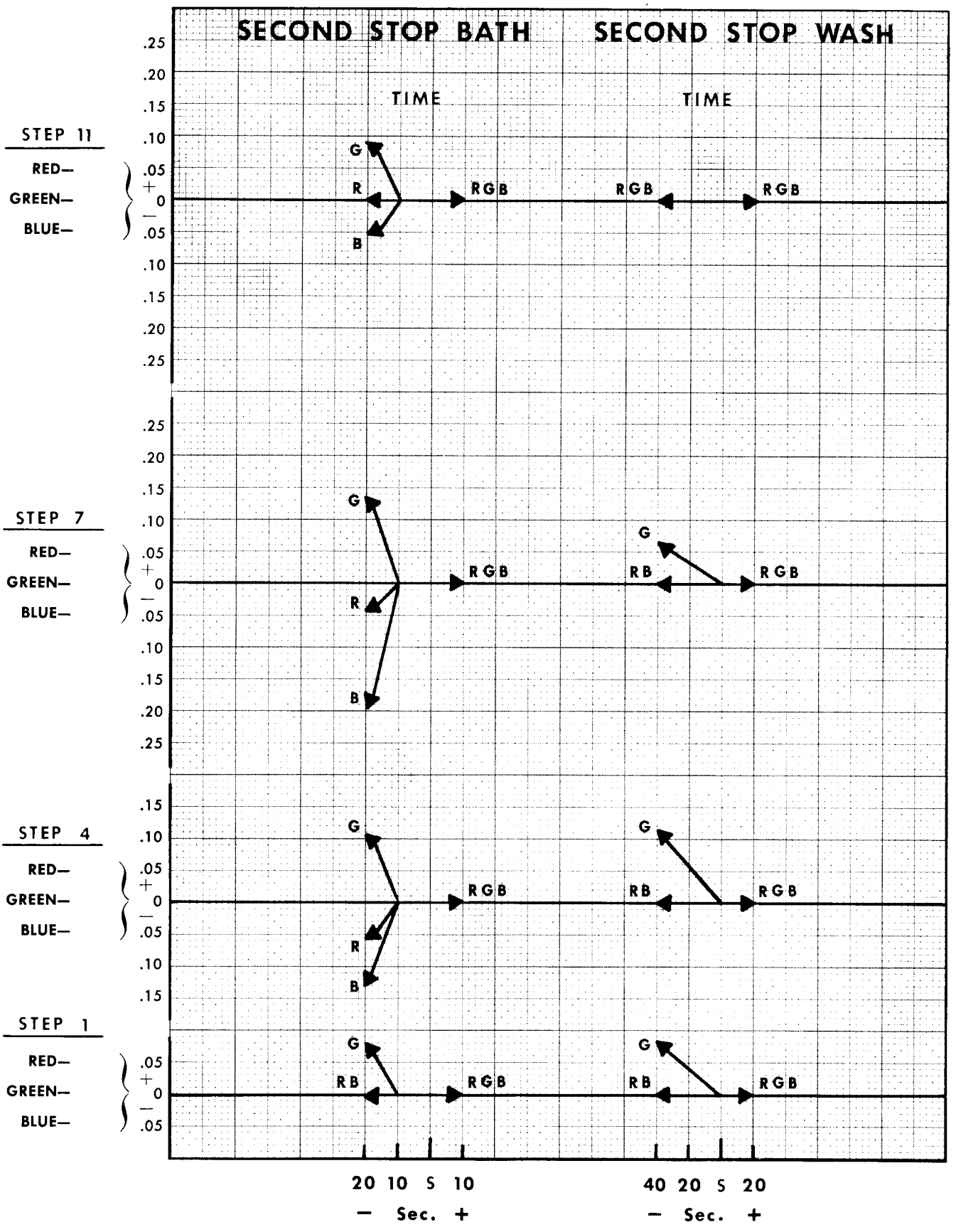


FIGURE 600-16
EFFECTS OF MECHANICAL AND CHEMICAL
VARIATIONS ON 7249 FILM IN PROCESS CRI-1



C. Corrective Action

Experience with Process CRI-1 has indicated that in general there are four types of out-of-control conditions that may take place, assuming that the processing solutions have been properly prepared. Some possible causes for these out-of-control conditions and corresponding corrective procedures are given below. The procedures are *not* to be used as process adjustments, but are items to be checked for adherence to published process specifications. Nonstandard adjustment of the process, using these procedures to compensate for some other undiscovered out-of-control condition, usually results in a quality loss as well as more complicated process control.

1. *Density Increase—No Significant Change in Color Balance*
   a. *First developer temperature too low.* Adjust the first developer temperature to specification. Check the temperature controller and the recirculation system for proper performance. Insufficient warm-up time can also be a cause of low temperature.
   b. *First development time too short.* Adjust first developer time or machine speed to specification.
   c. *Prehardener temperature too high.* Adjust prehardener temperature to specification. Check temperature controller and recirculation system for proper performance.
   d. *Prehardener time is too long.* Adjust prehardener time or machine speed to specification.
   e. *First developer replenishment rate too low.*
      (1) Adjust first developer replenisher flowmeter to appropriate specification for either leader or film run. To bring process into control rapidly, add first developer replenisher directly to first developer (tank) in increments of 3% of tank volume until control has been reestablished.
      (2) If the above action corrects the out-of-control condition but the condition recurs, clean and recalibrate the flowmeter for the first developer replenisher. See page 604.
   f. *First developer (tank solution) used instead of first developer replenisher.* Replace with proper solution.
   g. *Shelf life of first developer replenisher exceeded.* Replace replenisher with fresh replenisher. To bring process into control rapidly, add fresh replenisher directly to first developer (tank) in increments of 3% of tank volume until control has been reestablished.
   h. *Excessive aeration or exposure of first developer to air.* Locate cause and replace solution with fresh solution. (Extended downtime exposes the developer solution to air oxidation.)
      (1) Check developer overflow into the weir box. Solution must not cascade more than 12.7mm (1/2 inch) and there must be no vortex over the recirculation intake. Aeration problems due to vortices and entrained air can be minimized by returning 90% of the recirculating solution to the pump through an oversize pipe connected directly to an opening in the side of the machine tank. The opening should be well below the surface of the solution and completely separate from the weir.
      (2) Check piping and fittings of the recirculation system. The pump may be drawing air into the solution. Also check the pump seal.
   i. *Use of any films other than EASTMAN Color Reversal Intermediate Film 5249 or 7249 for seasoner and scratch tests.* Replenisher requirements for other black-and-white and color films are usually entirely different from those for 5249 or 7249 Film.
   j. *Excessive use of leader and leader replenisher rate.* Some of the processing solutions contain equilibria that are maintained only when "normally" exposed film is processed. Exposure variations average out, but use of leader, which requires no development at all, over a long period will cause control shifts.
   k. *Processing film with the feed-on area white lights on.* Totally flashed film makes excessive demands on the developer that are not easily averaged out.

2. *Density Decrease—No Significant Color Balance Change*
   a. *First developer temperature too high.* Adjust first developer temperature to specification. Check the temperature control system for proper performance and calibration.
   b. *First development time too long.* Adjust first developer time or machine speed to specification.
   c. *Prehardener temperature too low.* Adjust the prehardener temperature to specification. Check the temperature controller and the recirculation system for proper performance and calibration. Insufficient warm-up time can also be a cause of low temperature. Also check for normal recirculation.
   d. *Prehardener time is too short.* Adjust prehardener time or machine speed to specification.
   e. *First developer replenishment rate too high.* Adjust the first developer replenisher flowmeter to specification. Film replenishment rates may have been used instead of leader rates during a leader run. The flowmeter may need recalibration.
   f. *Leaking shutoff valve on first developer replenisher line.* Replace first developer with fresh solution. This trouble is difficult to detect. It can be checked by determining loss of replenisher during shutdown. To do this, mark the volume level on the replenisher tank at shutdown and check the level before the next start-up.
   g. *First developer replenisher used for tank solution.* Replace tank solution with fresh working solution.
   h. *First stop replenishment rate too low.* Adjust first stop replenisher flowmeter to standard. Add first stop replenisher to first stop (tank) in an amount of 50% of tank

volume or adjust pH of first stop. Flowmeter may need recalibration.

i. *First developer carry-over into first stop.* Adjust operation of squeegee after the first developer or adjust pH of first stop.

j. *Fogged film.* Review film handling procedures and check the machine magazine, room safelights, and machine lighttight covers.

k. *Prehardener replenishment rate too low.* Replace about 50% of the prehardener solution (tank) with prehardener replenisher and locate cause of low replenishment. This condition can also cause slow drying and insufficient hardening of emulsion.

3. *Changes in Color Balance—No Significant Change in Density*

a. *Low prehardener specific gravity.* Low prehardener sp. gr. causes a blue color balance in the film. The process may be rapidly returned to control by replacing the prehardener solution with a fresh tank mix. This procedure will give only temporary and partial control. Locate the cause of the low sp. gr. condition. Some possible causes are:

(1) Prehardener replenishment is too high.
Adjust flowmeter to specification.

(2) Prehardener replenisher used for tank.
Replace with fresh tank mix.

b. *Change in pH of color developer*

(1) *A magenta-blue color balance.* (Decrease in blue density with a slight increase in green density.) This is usually caused by a low pH of the color developer. The process can be rapidly returned to control by the addition of a sodium hydroxide solution to the color developer. Add 3 milliliters of 2.5 N sodium hydroxide* per liter of color developer to decrease the color balance spread by 0.10 density. This addition will raise the pH of the color developer 0.1 unit. (See "Analytical Procedures" for the determination of pH and "Analytical Reagents" for the preparation of 2.5 N sodium hydroxide.) This procedure will give only temporary and partial control. Locate the cause of the low pH condition. Some possible causes are:

(a) Color developer replenisher is too low. Adjust flowmeter to specification.

(b) Lack of a floating cover or use of an ineffective floating cover on color developer replenisher.

(c) Color developer tank solution used for color developer replenisher. Replace solution with fresh replenisher.

(d) Shelf life of color developer replenisher exceeded. Replace with fresh solution.

(e) Excessive exposure of color developer to air. Locate cause and replace with fresh solution. See part 1, h, (1), page 628, for corrective action.

(2) *A green-yellow color balance.* (Increase in blue density with a decrease in green density.) This is usually caused by a high pH of the color developer.

The process can be rapidly returned to control by the addition of an acid solution to the color developer. Add 3 milliliters of 2.5 N sulfuric acid* per liter of color developer to *decrease the color balance spread* by 0.10 density. This addition will lower the pH of the color developer 0.1 unit. See "Analytical Procedures" for the determination of the pH and "Analytical Reagents" for the preparation of 2.5 N sulfuric acid. This procedure will give only temporary and partial control. Locate the cause of the high pH condition. Some possible causes are:

(a) Color developer replenishment rate too high. Adjust the color developer replenisher flowmeter to specification. Film replenishment rates may have been used instead of leader rates during a leader run. The flowmeter may need recalibration.

(b) Leaking shutoff valve on color developer replenisher line. Replace color developer with fresh solution. This trouble is difficult to detect. It can be checked by determining a loss of replenisher during machine shutdown. To do this, mark volume level on replenisher tank at shutdown and check solution level before start-up.

(c) Color developer replenisher used for color developer. Replace with fresh solution.

c. *Stain*

Stain is an overall coloration of the film. It is first noticed in the minimum density area. Some possible causes and their effects are:

(1) Magenta-red stain (an increase in green density at Step No. 1). This condition results from the carry-over of CD-3 into the bleach where it is oxidized to a red compound. It appears in a print as a rapidly moving, blotchy, magenta-green color shift. It can be caused by:

(a) Underreplenishment of second stop.

(b) Inadequate wash-water flow rate of second stop wash.

continued on page 638

*If the volume of the required addition of 2.5 N sodium hydroxide is too large for the capacity of the color developer tank, it may be desirable to substitute 7 N sodium hydroxide. In this case, the addition of 1 milliliter of 7 N sodium hydroxide will raise the pH of the color developer 0.1 unit.

CAUTION: 7 N sodium hydroxide is a strong alkali and must be handled carefully. Use rubber gloves and safety goggles. See "Analytical Reagents" for its preparation.

*If the volume of the required addition of 2.5 N sulfuric acid is too large for the capacity of the color developer tank, it may be desirable to substitute 7 N sulfuric acid. In this case, the addition of 1 milliliter of 7 N sulfuric acid will lower the pH of the color developer 0.1 unit.

CAUTION: 7 N sulfuric acid is a strong acid and must be handled carefully. Use rubber gloves and safety goggles. See "Analytical Reagents" for its preparation.

FIGURE 600-17

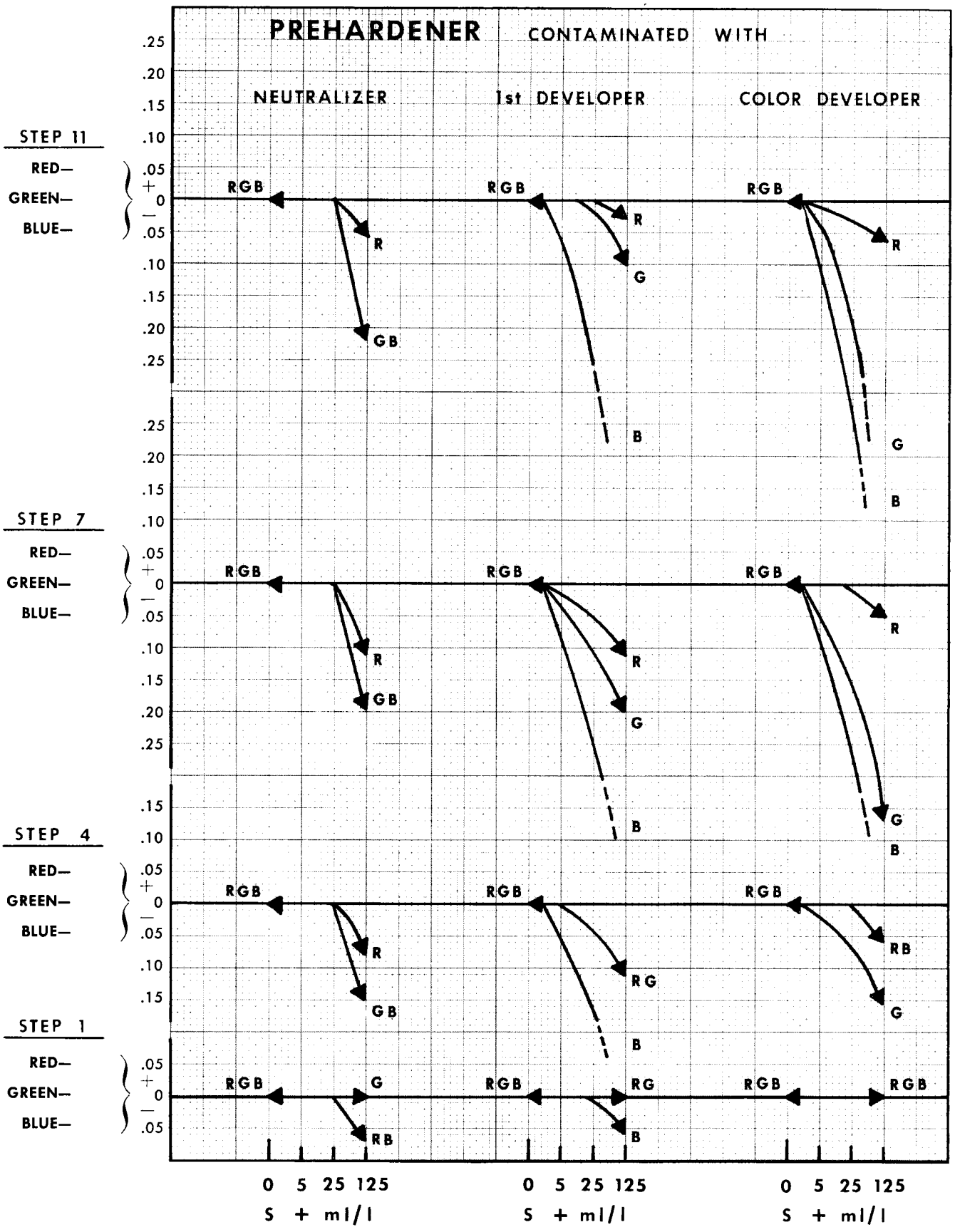


FIGURE 600-18

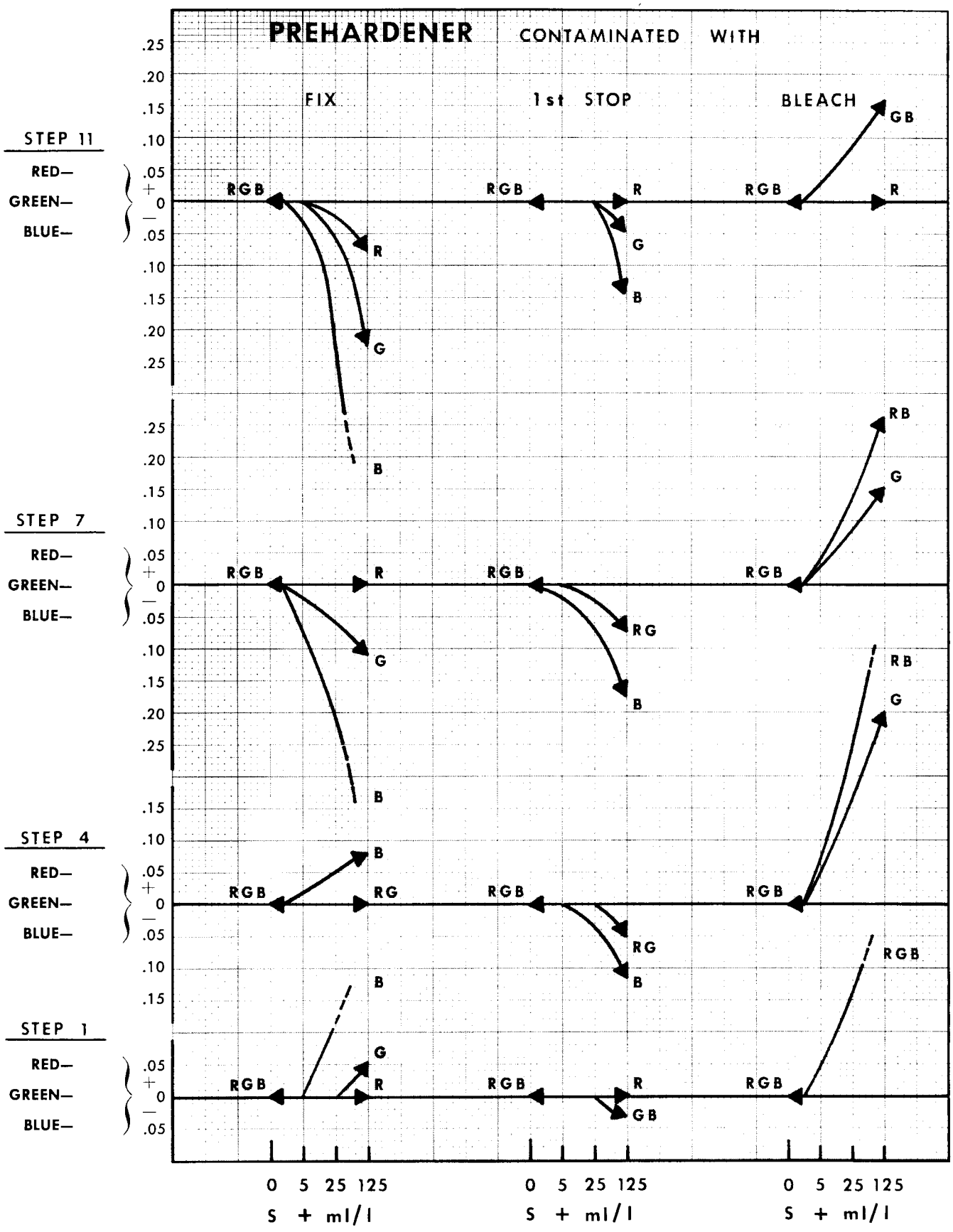


FIGURE 600-19

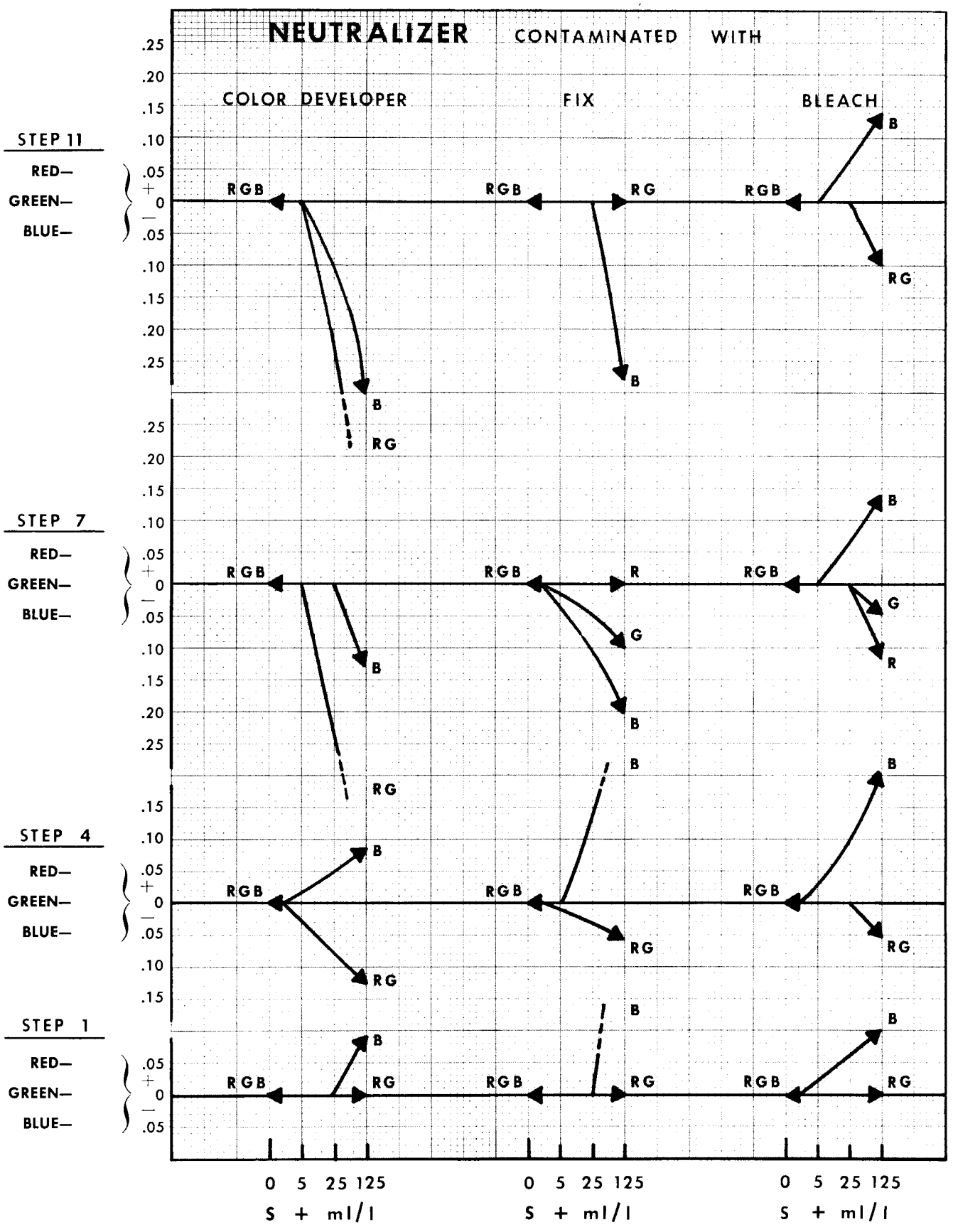


FIGURE 600-20

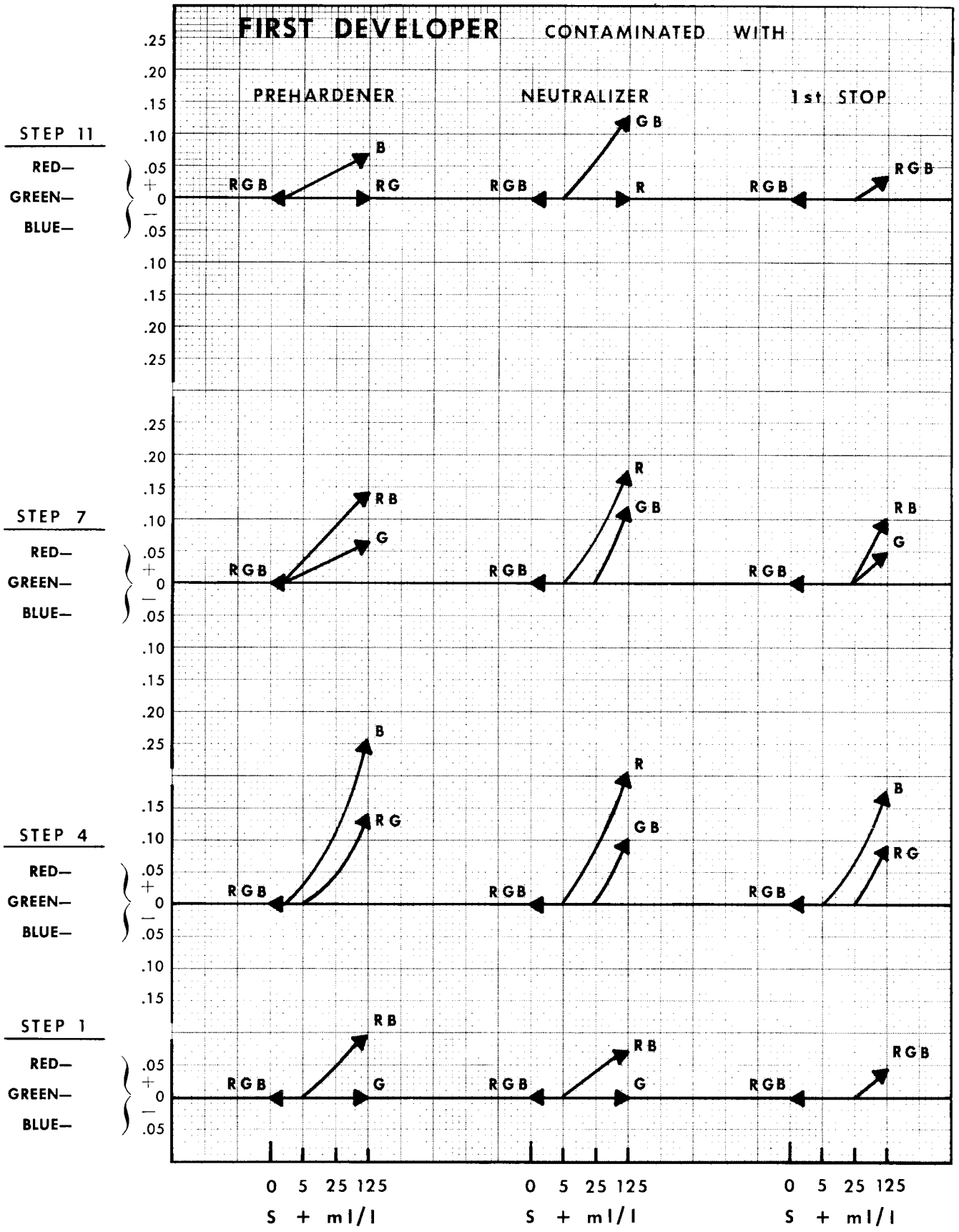


FIGURE 600-21

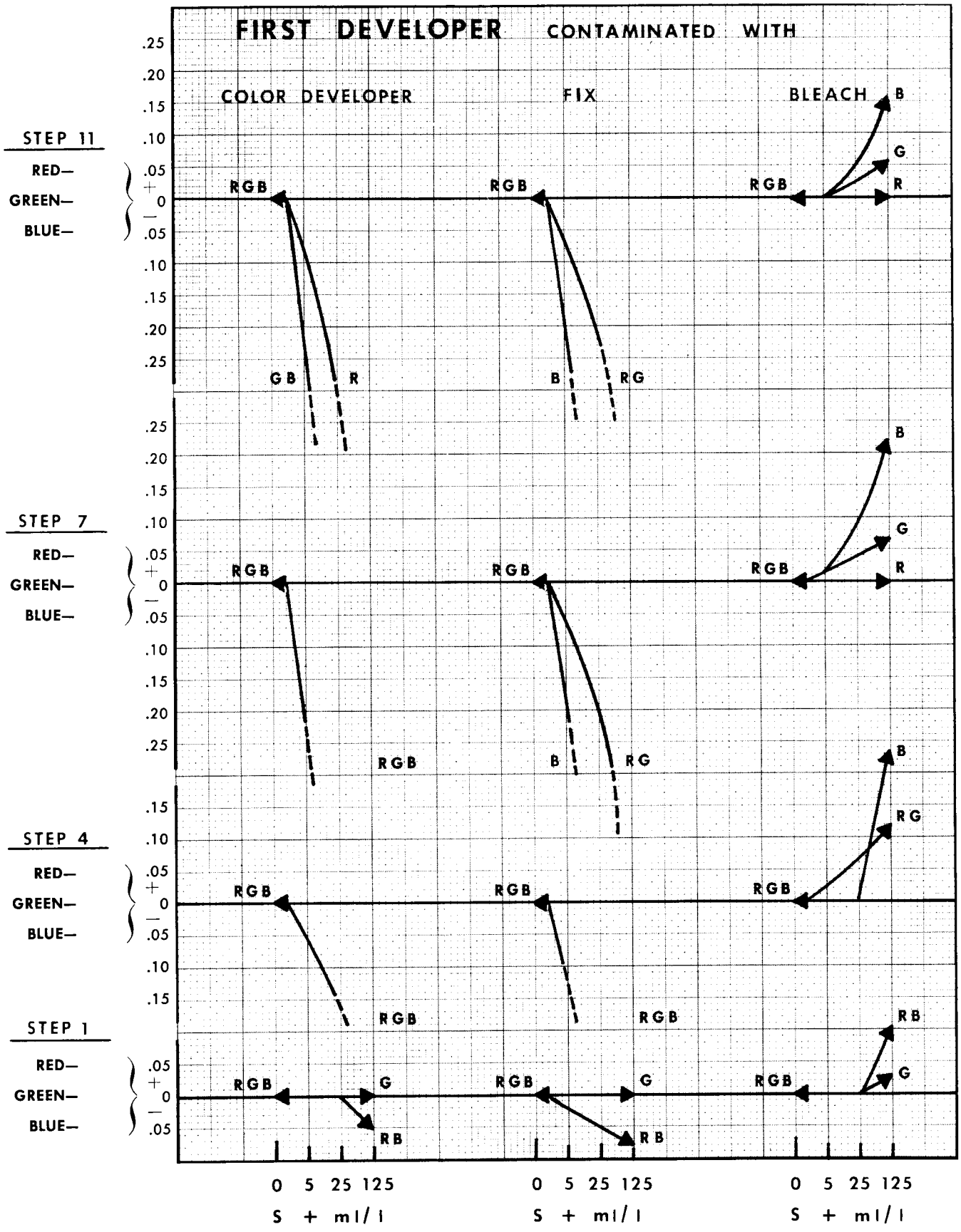


FIGURE 600-22

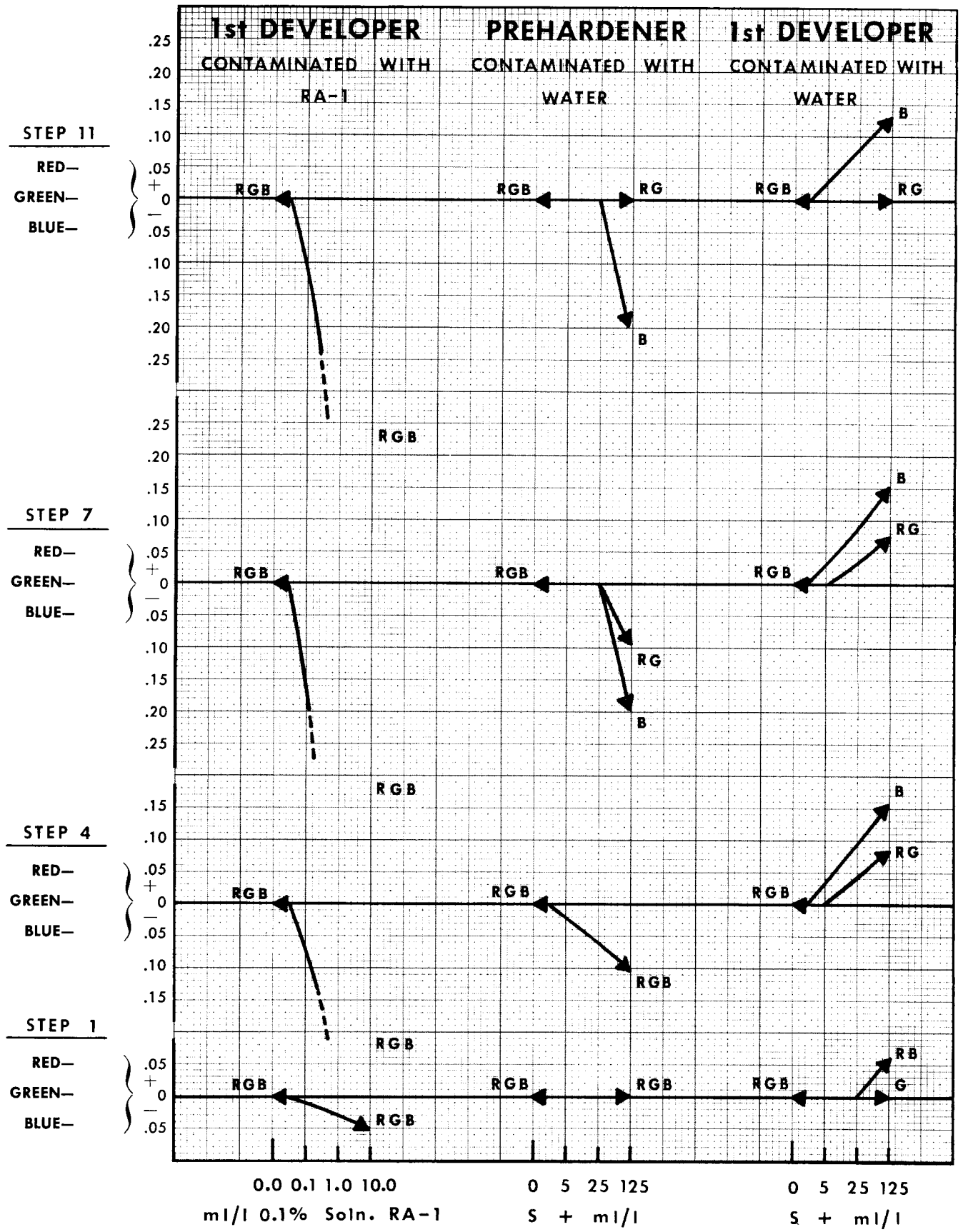


FIGURE 600-23

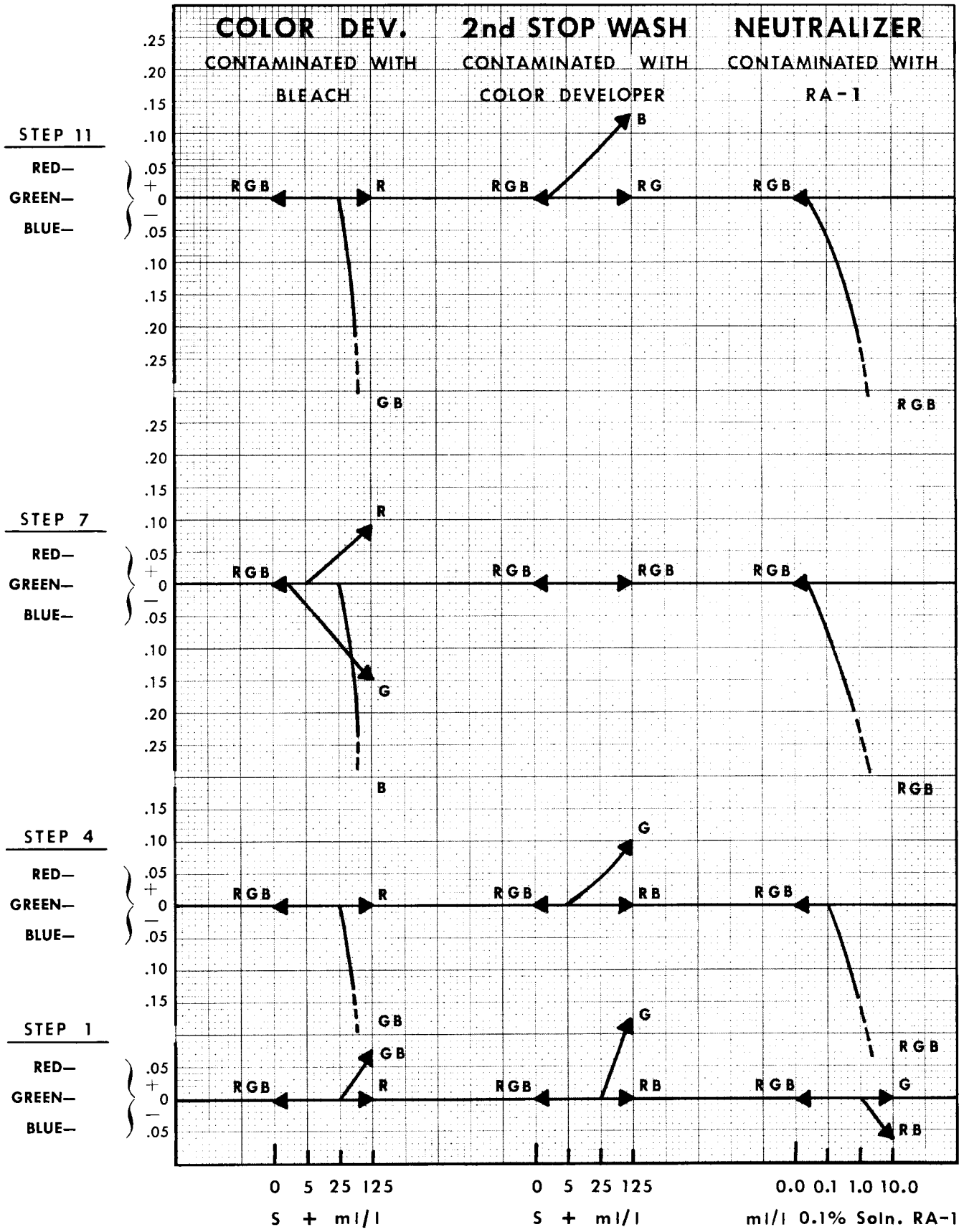
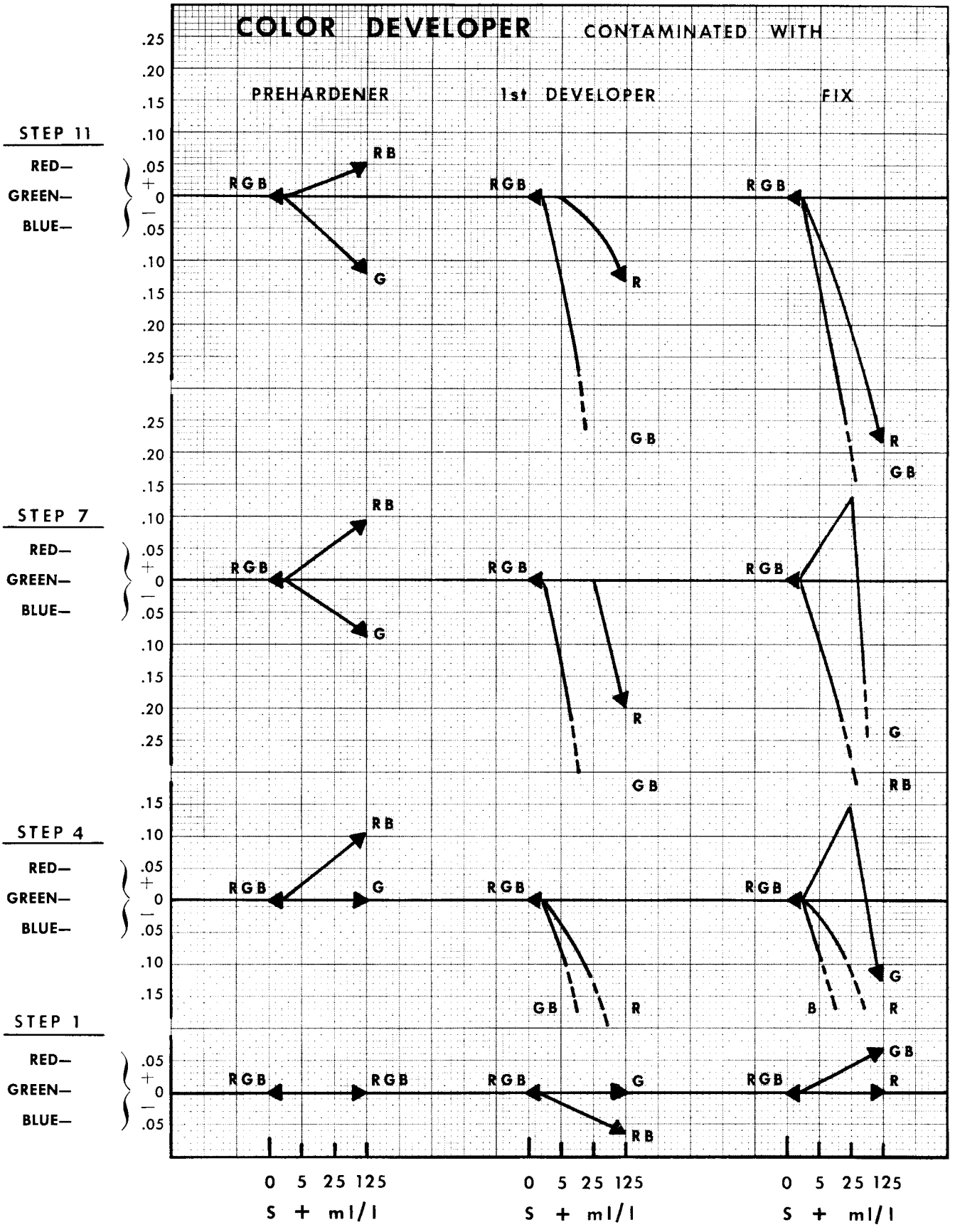


FIGURE 600-24



(c) Squeegee failure between color developer and second stop.

(2) Yellow stain (an increase in blue density at Step No. 1). This condition is caused by silver-halide retention due to inadequate fixing.

4. *Changes in Color Balance—Significant Change in Density*
Usually caused by contamination of processing solutions with other processing solutions.

D. Contamination

Contamination of one processing solution with another can cause serious out-of-control conditions. Therefore, extreme care must be taken when handling processing solutions and mixing equipment. The mixing tank and other mixing equipment must be thoroughly rinsed before and after each use. Precautions must be taken when transporting solutions so that no solution is pumped or splashed into another.

The effects of contamination of the prehardener, neutralizer, first developer, and color developer with other solutions are illustrated graphically in Figures 600-17 through 600-24, pages 630 to 637.

Each plot illustrates the effect of contamination of a processing solution (abscissa) on the dye density of the final film (ordinate).

The severity of the adverse photographic effect produced by contamination is dependent upon the amount of contamination and varies with the contaminant and the receiving solution. Use the data in the charts only as guides. Whenever contamination occurs, the source should be located and the contaminated solution replaced.

PHYSICAL DEFECTS ON PROCESSED FILM

A. Scratches

1. High-torque, high-speed take-up at dryer elevator causes cinch marks on the film base that appear as short, random, frequent, fine, dark lines in a projected print.
2. Backup rollers that do not turn easily and are not covered with a soft, nonscratch material cause long, fine scratches on the film base.
3. Too-rapid air movement in the dryer will cause strips on opposite sides of the same roller to slap together, giving intermittent scratched areas on the film base.
4. High machine tension or high friction roller bearings will cause excessive edge scratches on the film base.
5. Surfaces that intermittently contact the film, even gently, will scratch the base or emulsion if handling burrs are present. Sanding with #400 wet or dry emery paper will greatly decrease the problem where contact cannot be avoided.
6. Turbulator nozzles should be mounted flush with the surface of the feed pipe and then the whole assembly sanded with #400 wet or dry emery paper. Drilled header turbulators should also be sanded.
7. Crystal formations on wiper blade squeegees and in the orifices of venturi squeegees can scratch the base or emulsion surface.

B. Dirt

If general cleanliness is not the very best, dirt on the film will be unavoidable. The following comments should be helpful in minimizing this problem:

1. Dryer air filters for both recirculated and makeup air should be oil-free and of as fine porosity as possible.
2. If the ferricyanide bleach pH is very low, Prussian blue solids will form in the tank and stick to the film. Some Prussian blue precipitation will also occur, if the seasoned fixer pH is below 5.0.
3. If any stainless steel, iron, or yellow brass parts are present anywhere in the bleach system, dirt will appear until these parts are removed.
4. Prehardener dirt can settle to the bottom of the tank unless the recirculation geometry is designed to keep it in suspension and the recirculation rate high enough to filter it out.
5. If the wash tanks are not drained nightly, cleaned, and treated with 3-5% NaOH, slime organisms can stick to the film as well as the tanks and racks, causing streaks and scum marks on the film.

C. Spots and Streaks

1. See "Process-Related Physical Defects in EASTMAN Color Reversal Intermediate Film 5249/7249," on page 639.
2. See "B. Dirt" above.
3. Too low a level of wetting agent in the stabilizer can prevent elimination of water droplets, while an excess of wetting agent will increase the chances of scum on the film. These effects will be most noticeable when the final squeegee is dirty or not correctly adjusted.
4. Unshielded air squeegees can spray droplets or particles of processed solutions into the air and then onto unprocessed film to cause spots.

D. Nonuniformity

See "Process-Related Physical Defects in EASTMAN Color Reversal Intermediate Film 5249/7249," page 639.

E. Drying Problems

1. Tacky film and/or excessive "negative" cure (emulsion convex) may be symptoms of insufficient drying. Possible causes of insufficient drying are:
   a. Low dryer temperature.
   b. Inefficient final squeegee.
   c. Final wash too short.
   d. High pH of fixer, final wash, or stabilizer.

e. Prehardener temperature below normal.
f. Prehardener time below normal.

(Sensitometric changes will also be present.)

g. Dryer relative humidity too high.
h. Drying time too short.
i. Prehardener pH below normal.
j. Low sulfate or aldehyde concentration in prehardener.

(Sensitometric changes will also be present.)

2. Brittle film and/or excessive "positive" cure (emulsion concave) may be symptoms of excess drying. Possible causes of excess drying are:
   a. High dryer temperature.
   b. Low dryer relative humidity (too much makeup air).
   c. Drying time too long.
   d. Prehardener time, temperature, or pH above normal.

(Sensitometric changes will also be present.)

Process-Related Physical Defects in *Eastman* Color Reversal Intermediate Film 5249/7249

Defect	*Appearance in EASTMAN Color Reversal Intermediate Film*	*Appearance in Projected Print*	*Possible Source of Defect*	*Suggested Corrective Action*
Yellow Comets and Spots	Blue comets, splatters, dots; comets have tails opposite the direction of film travel.	Yellow comets, splatters, and dots; narrow; up to one 35mm frame in length, usually much smaller; dark yellow dot with long tail; short yellow streak.	Raw stock contaminated with metal dust (zinc, magnesium, etc); brass venturi squeegees used prior to color developer; oil in compressed air; brass eyelet splices; chemical dust or droplets in feed-on areas.	Use a damp sponge daily on areas where unprocessed film is handled; vacuum-clean printers, cameras, magazines often; do not use zinc, magnesium, or brass rewind equipment; paint galvanized duct work in film-handling areas; filter air in film-handling areas; use oil-free air; if problem persists, substitute wiper blades for air squeegees; use tape splices (fresh Scotch Electrical Tape #57, or equivalent); shield squeegees.
Yellow Fingerprints	Blue fingerprints, spots, and irregular areas.	Yellow fingerprints, spots, and irregular areas.	Handling unprocessed film with dirty hands; oil, antifoggant, developer, etc.	Supply acid soap, hand-wash, and towels in machine room; require clean hands.
Sparkle	Tiny granules stuck on the emulsion surface.	Fine, sharp, white dots on screen.	Dirt in prehardener or dryer.	Clean prehardener system, change filters to recommended porosity and use enough recirculation to keep solution clean; damp-sponge dryer at least once a week and use finest porosity oil-free filter available on both recirculated and makeup air.
Snowballs	Small, saucer-shaped depressions in emulsion surface.	Diffuse-edged, round, light spots randomly appearing.	Air in the final wash; splatter from final venturi squeegee returning to the emulsion surface before film enters the dryer.	Remove *all* apparent gas bubbles from the wash water; adjust final squeegee so it does not splatter; protect film from dirt and droplets before it enters the dryer.
Fine Mottle	Not readily apparent.	Diffuse, random motion on screen similar to grain but larger and much more diffuse.	Air in washes other than final wash.	Remove *all* apparent gas bubbles from the wash water.

(c) Squeegee failure between color developer and second stop.

(2) Yellow stain (an increase in blue density at Step No. 1). This condition is caused by silver-halide retention due to inadequate fixing.

4. *Changes in Color Balance—Significant Change in Density*
Usually caused by contamination of processing solutions with other processing solutions.

D. Contamination

Contamination of one processing solution with another can cause serious out-of-control conditions. Therefore, extreme care must be taken when handling processing solutions and mixing equipment. The mixing tank and other mixing equipment must be thoroughly rinsed before and after each use. Precautions must be taken when transporting solutions so that no solution is pumped or splashed into another.

The effects of contamination of the prehardener, neutralizer, first developer, and color developer with other solutions are illustrated graphically in Figures 600-17 through 600-24, pages 630 to 637.

Each plot illustrates the effect of contamination of a processing solution (abscissa) on the dye density of the final film (ordinate).

The severity of the adverse photographic effect produced by contamination is dependent upon the amount of contamination and varies with the contaminant and the receiving solution. Use the data in the charts only as guides. Whenever contamination occurs, the source should be located and the contaminated solution replaced.

PHYSICAL DEFECTS ON PROCESSED FILM

A. Scratches

1. High-torque, high-speed take-up at dryer elevator causes cinch marks on the film base that appear as short, random, frequent, fine, dark lines in a projected print.
2. Backup rollers that do not turn easily and are not covered with a soft, nonscratch material cause long, fine scratches on the film base.
3. Too-rapid air movement in the dryer will cause strips on opposite sides of the same roller to slap together, giving intermittent scratched areas on the film base.
4. High machine tension or high friction roller bearings will cause excessive edge scratches on the film base.
5. Surfaces that intermittently contact the film, even gently, will scratch the base or emulsion if handling burrs are present. Sanding with #400 wet or dry emery paper will greatly decrease the problem where contact cannot be avoided.
6. Turbulator nozzles should be mounted flush with the surface of the feed pipe and then the whole assembly sanded with #400 wet or dry emery paper. Drilled header turbulators should also be sanded.
7. Crystal formations on wiper blade squeegees and in the orifices of venturi squeegees can scratch the base or emulsion surface.

B. Dirt

If general cleanliness is not the very best, dirt on the film will be unavoidable. The following comments should be helpful in minimizing this problem:

1. Dryer air filters for both recirculated and makeup air should be oil-free and of as fine porosity as possible.
2. If the ferricyanide bleach pH is very low, Prussian blue solids will form in the tank and stick to the film. Some Prussian blue precipitation will also occur, if the seasoned fixer pH is below 5.0.
3. If any stainless steel, iron, or yellow brass parts are present anywhere in the bleach system, dirt will appear until these parts are removed.
4. Prehardener dirt can settle to the bottom of the tank unless the recirculation geometry is designed to keep it in suspension and the recirculation rate high enough to filter it out.
5. If the wash tanks are not drained nightly, cleaned, and treated with 3-5% NaOH, slime organisms can stick to the film as well as the tanks and racks, causing streaks and scum marks on the film.

C. Spots and Streaks

1. See "Process-Related Physical Defects in EASTMAN Color Reversal Intermediate Film 5249/7249," on page 639.
2. See "B. Dirt" above.
3. Too low a level of wetting agent in the stabilizer can prevent elimination of water droplets, while an excess of wetting agent will increase the chances of scum on the film. These effects will be most noticeable when the final squeegee is dirty or not correctly adjusted.
4. Unshielded air squeegees can spray droplets or particles of processed solutions into the air and then onto unprocessed film to cause spots.

D. Nonuniformity

See "Process-Related Physical Defects in EASTMAN Color Reversal Intermediate Film 5249/7249," page 639.

E. Drying Problems

1. Tacky film and/or excessive "negative" cure (emulsion convex) may be symptoms of insufficient drying. Possible causes of insufficient drying are:
   a. Low dryer temperature.
   b. Inefficient final squeegee.
   c. Final wash too short.
   d. High pH of fixer, final wash, or stabilizer.

e. Prehardener temperature below normal.
f. Prehardener time below normal.

} Sensitometric changes will also be present.

g. Dryer relative humidity too high.
h. Drying time too short.
i. Prehardener pH below normal.
j. Low sulfate or aldehyde concentration in prehardener.

} Sensitometric changes will also be present.

2. Brittle film and/or excessive "positive" cure (emulsion concave) may be symptoms of excess drying. Possible causes of excess drying are:

a. High dryer temperature.
b. Low dryer relative humidity (too much makeup air).
c. Drying time too long.
d. Prehardener time, temperature, or pH above normal.

} Sensitometric changes will also be present.

Process-Related Physical Defects in *Eastman* Color Reversal Intermediate Film 5249/7249

Defect	*Appearance in EASTMAN Color Reversal Intermediate Film*	*Appearance in Projected Print*	*Possible Source of Defect*	*Suggested Corrective Action*
Yellow Comets and Spots	Blue comets, splatters, dots; comets have tails opposite the direction of film travel.	Yellow comets, splatters, and dots; narrow; up to one 35mm frame in length, usually much smaller; dark yellow dot with long tail; short yellow streak.	Raw stock contaminated with metal dust (zinc, magnesium, etc); brass venturi squeegees used prior to color developer; oil in compressed air; brass eyelet splices; chemical dust or droplets in feed-on areas.	Use a damp sponge daily on areas where unprocessed film is handled; vacuum-clean printers, cameras, magazines often; do not use zinc, magnesium, or brass rewind equipment; paint galvanized duct work in film-handling areas; filter air in film-handling areas; use oil-free air; if problem persists, substitute wiper blades for air squeegees; use tape splices (fresh Scotch Electrical Tape #57, or equivalent); shield squeegees.
Yellow Fingerprints	Blue fingerprints, spots, and irregular areas.	Yellow fingerprints, spots, and irregular areas.	Handling unprocessed film with dirty hands; oil, antifoggant, developer, etc.	Supply acid soap, hand-wash, and towels in machine room; require clean hands.
Sparkle	Tiny granules stuck on the emulsion surface.	Fine, sharp, white dots on screen.	Dirt in prehardener or dryer.	Clean prehardener system, change filters to recommended porosity and use enough recirculation to keep solution clean; damp-sponge dryer at least once a week and use finest porosity oil-free filter available on both recirculated and makeup air.
Snowballs	Small, saucer-shaped depressions in emulsion surface.	Diffuse-edged, round, light spots randomly appearing.	Air in the final wash; splatter from final venturi squeegee returning to the emulsion surface before film enters the dryer.	Remove *all* apparent gas bubbles from the wash water; adjust final squeegee so it does not splatter; protect film from dirt and droplets before it enters the dryer.
Fine Mottle	Not readily apparent.	Diffuse, random motion on screen similar to grain but larger and much more diffuse.	Air in washes other than final wash.	Remove *all* apparent gas bubbles from the wash water.

Defect	*Appearance in* EASTMAN *Color Reversal Intermediate Film*	*Appearance in Projected Print*	*Possible Source of Defect*	*Suggested Corrective Action*
Shoreline	Emulsion ridges lengthwise on the film following the perforation contours.	Lines around the perforations that appear fuzzy on the screen, yet are standing still; not usually in picture area.	Nonuniform drying across the film surface and consequent emulsion distortion; excessive emulsion swelling during process.	Progressively lower the film drying temperature until the defect is minimized. Check prehardener.
Blue Edges	Not readily apparent.	Area around perforations tapers to blue balance compared to center of film strand.	Inadequate prehardener recirculation or processing machine speed.	Increase recirculation or machine speed.
Lines, Streaks, Spots, and Coarse Mottle	Barely visible on the emulsion side.	Light lines, streaks, etc.	Maladjusted final venturi squeegee allowing nonuniformly dry film emulsion surface to enter dryer.	Adjust final squeegee so emulsion surface is uniformly dry after squeegeeing.
Prussian Blue	Bluish-gray spot, streak, or smudge.	White or grayish spots.	Iron or stainless steel components in the bleach tank or bleach recirculation system, or low fixer pH.	Disassemble bleach recirculation system and look for Prussian blue. Replace iron or stainless steel parts with plastic, red brass, titanium, or Hastelloy C. Inspect filter, filter pot, and related components. Adjust pH to specification.
Blue spots	Yellow spots	Blue spots	Bleach splashed on film during or immediately after color development.	Locate and eliminate the source of bleach splatters.

Defect	*Appearance in EASTMAN Color Reversal Intermediate Film*	*Appearance in Projected Print*	*Possible Source of Defect*	*Suggested Corrective Action*
White Spots	Sharp-edged, round, black metallic silver deposits in film.	Sharp-edged, round white spots sometimes occurring in showers.	Air in washes, especially before the bleach; no squeegees before the bleach; inadequate bleach replenishment.	Remove *all* apparent gas bubbles from the wash water; install and adjust wiper blade before bleach; check bleach ferricyanide and bromide levels.
Reticulation	Ground-glass emulsion surface.	Depends on printing conditions.	Improper drying; inadequate final wash; high pH in fixer, wash, or stabilizer; inadequate prehardening; excessive emulsion swell.	Return process to recommended values.
Magenta-Green Stain	Appears on fully flashed film as pink areas.	Flashes intermittently on screen as pink or green balance changes.	Inadequate or contaminated stop or wash after the color developer.	Replace the second stop and wash; check the replenisher rates and be sure the wash is countercurrent.
Density Wedging	Not readily apparent.	Stable, edge-to-edge density gradient across screen; can be wedge- or bell-shaped; does not move.	Off-center turbulators in which nozzles do not hit center line of film; misalignment of printer aperture.	Realign nozzles; realign printer; consider use of drilled header turbulation system. See page 305 for details.
Dots Equally Spaced Apart, Repeating	Film base deformed or emulsion marked.	Repeated showers of dots in which the individual dots are always the same distance apart.	Transferable dirt on a soft-touch tire riding on the emulsion; film stopped in the dryer and heat distorted the film touching the tires.	Clean or replace the dirty or broken tires; do not let film stop in the dryer.
Fine Streaks	Not readily apparent.	Streaks and lines look like "rain"; are not apparent except in uniform density areas.	Nonuniform wiper blade action during process; worn or maladjusted blades.	Adjust or replace wiper blades.
Rem-Jet	Black spots or black areas on the film base.	White spots.	Defective rem-jet removal equipment, poor housekeeping, or low pH in backing removal solution.	Repair equipment; replace solutions and/or clean machine area; adjust pH to specification.
Curtains	Nonuniform density, oriented lengthwise on strip; hard to see.	Large vertical streaks on screen; moving side-to-side, usually neutral unless caused by color developer.	Inadequate agitation frequency and pressure in neutralizer, first developer, first stop, or color developer.	Increase agitation frequency or pressure; check for plugged nozzles; check alignment of nozzles.

ANALYTICAL REAGENTS

PREPARATION OF SPECIFIC REAGENTS

This section is an *alphabetical* listing of all reagents required by the analytical procedures used in chemical control.

For general background information on reagent preparation and standardization, refer to "Analytical Reagents for Chemical Control," Method I in the "Analytical Procedures."

For information on precautions and procedures for the safe handling of processing chemicals, see page series 500.

ACETIC ACID

CAUTION: Observe safety precautions for handling concentrated acids. Wear safety glasses and rubber gloves. Use care and always add acid to water.

Glacial CH_3COOH

Eastman grade (EASTMAN Organic Chemical 763) or reagent quality acetic acid, 99.7% CH_3COOH, sp gr 1.050, approx. 17.4 N.

2.0 N CH_3COOH

Add 115 ml of reagent quality glacial acetic acid, CH_3COOH (sp gr 1.050), to 500 ml of distilled water and dilute to 1 liter with distilled water.

---

6 N ACCELERATOR REAGENT [6 N NaOH-EDTA, (ETHYLENEDINITRILO) TETRA-ACETIC ACID]

1. Cautiously add and dissolve 240 g of reagent quality sodium hydroxide, NaOH, in 1 liter of tap or distilled water.
2. Add and dissolve 4.0 g of (ethylenedinitrilo) tetra-acetic acid (EDTA, EASTMAN Organic Chemical P5416).

ACETONE

Eastman grade (EASTMAN Organic Chemical 297) or reagent quality acetone. A clear colorless liquid with a characteristic odor. Acetone is highly flamable. Keep in tightly closed containers, in a cool place, away from flame.

AMMONIUM BIFLUORIDE

CAUTION: Observe safety precautions. Wear safety glasses and rubber gloves. Ammonium bifluoride is very corrosive to the skin, to glass, and to many metals.

20% $NH_4F \cdot HF$ Solution

Dissolve 20 g of technical quality ammonium bifluoride, $NH_4F \cdot HF$, (Baker and Adamson, Code 1277) in 80 ml of distilled water. Because of its corrosive action on glass, this solution should be mixed and stored in wax-lined or polyethylene-type containers.

AMMONIUM HYDROXIDE

CAUTION: Observe safety precautions. Wear safety glasses and rubber gloves. Excessive pressure may develop in containers. Store in a cool place.

Concentrated NH_4OH

Reagent quality ammonium hydroxide, NH_4OH, (28.0% minimum as NH_3) sp gr 0.90, approx. 15 N (Baker and Adamson, Code 1293).

4 N NH_4OH

Dilute 270 ml of reagent quality concentrated ammonium hydroxide (sp gr 0.90) to 1 liter with distilled water.

AMMONIUM NITRATE

1.0 M Ammonium Nitrate

Dissolve 80.0 g of reagent quality ammonium nitrate, NH_4NO_3, in distilled water and dilute to 1 liter with distilled water.

BORAX BUFFER

0.01 M Borax

Checking the Distilled Water. The experience of laboratories at Kodak Park indicates that borax buffer can be prepared in the manner outlined in the steps below. The National Bureau of Standards specifies that the distilled water used in the preparation of borax buffer must have a pH of "not less than 6.5 and not more than 7.5 . . . . obtained by boiling distilled water . . . . and cooling it under carbon dioxide-free conditions." (A soda-lime tube can be utilized when cooling the boiled water.) It is recommended that all laboratories follow the method of preparation found on the National Bureau of Standards certificate provided with the standard borax sample until data indicate that the distilled water being used is acceptable. However, in some instances distilled water that did not meet the above requirements has been found to be acceptable. A borax buffer prepared with this distilled water had the same pH as a buffer prepared with water that met the specifications.

Preparation of Borax Buffer

1. Add 600 ml of distilled water to a 1-liter volumetric flask.
2. Dissolve 3.8 $\pm$0.1 g of reagent quality crystalline sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$ (borax).
3. Dilute to volume with distilled water.

Preparation of Borax Buffer Using National Bureau of Standards Borax. Prepare a fresh *standard* borax buffer following Steps 1-3, using National Bureau of Standards borax sample No. 187a or subsequent Bureau of Standards pH standard. Use a torsion balance to weigh the sodium tetraborate. The preceding batch of standard buffer can be used only if it was prepared within one month of the time of use and if it is not moldy.

Testing Borax Buffer

1. Standardize the pH meter with the *standard* borax buffer, setting the pH scale dial according to Table I. Choose the setting that corresponds to the temperature at which the new buffer is to be used.

TABLE I

Temperature	Dial Setting
21.1 C (70 F)	9.21
23.9 C (75 F)	9.19
26.7 C (80 F)	9.16

The pH of the borax buffer is dependent on temperature. The effect of temperature over a wide range is shown in Table II.

2. Cross-check the electrode assembly by measuring the pH of a calcium chloride—calcium hydroxide buffer.
3. Determine the pH of the borax *buffer being tested* at the same temperature chosen in Step 1. (For tolerances, see Step 4.)
4. Determine the pH of the *standard* borax buffer at the same temperature chosen in Steps 1 and 3. (This serves as a check. The pH obtained on this *standard* borax buffer must

TABLE II

Effect of Temperature on Borax Buffer

C	F	pH	C	F	pH
15.6	60	9.27	21.7	71	9.21
16.1	61	9.26	22.2	72	9.20
16.7	62	9.26	22.8	73	9.20
17.2	63	9.25	23.3	74	9.19
17.8	64	9.25	23.9	75	9.19
18.3	65	9.24	24.4	76	9.18
18.9	66	9.23	25.0	77	9.18
19.4	67	9.23	25.6	78	9.18
20.0	68	9.22	26.1	79	9.17
20.6	69	9.22	26.7	80	9.16
21.1	70	9.21	27.2	81	9.16

not differ by more than 0.01 pH unit from the value at which the meter was standardized in Step 1.) The pH obtained on the *buffer being tested* in Step 3 must not differ by more than 0.02 pH unit from the pH at which the meter was standardized *and* from the pH obtained on the standard buffer in Step 4.

EXAMPLE: A buffer being tested at 21.1 C (70 F) is not acceptable if its pH in Step 3 is 9.23 when 9.20 is obtained in Step 4. However, 9.23 is acceptable if either 9.21 or 9.22 is obtained in Step 4.

5. If the pH of the standard buffer differs by more than ±0.01 pH unit from the value at which the meter was standardized (see Table I), restandardize the meter and repeat Steps 3 and 4.

If the pH reading of the new buffer differs by more than 0.02 pH unit from either the pH at which the meter was standardized or the pH obtained on the standard buffer in Step 4, obtain new samples of the two batches of buffer used above and repeat Steps 1 through 4. If the new buffer is still not acceptable, look for trouble with the electrodes or pH meter, or for contamination of the two buffer solutions.

It may be necessary to prepare a fresh standard buffer, using a previously unopened bottle of National Bureau of Standards borax (pH standard). If the two buffers continue to disagree, do not attempt to adjust the pH of the new batch. Discard the new batch of buffer and prepare another batch.

The Pyrex bottles in which the solution is stored should be stoppered except when actually in use, or a syphon system can be used with the solution being protected by a soda-lime tube, taking precautions that the soda-lime does not contaminate the buffer. Discard the solution after three months, or sooner if mold appears.

BORAX-PHOSPHATE BUFFER

pH 8.0 at 21.1 C (70 F) or 26.7 C (80 F)

1. Add 800 ml of distilled water to a 1-liter volumetric flask.
2. Add and dissolve 5.58 g of reagent quality potassium dihydrogen phosphate, KH_2PO_4.
3. Add and dissolve 9.00 g of reagent quality sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$ (borax).
4. Dilute to volume with distilled water.
5. The pH should be 8.00 ±.10 at 21.1 C (70 F) of 26.7 C (80 F). If not, add sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$, to raise the pH or potassium dihydrogen phosphate, KH_2PO_4, to lower the pH.

BOROHYDRIDE REAGENT

Dissolve 3.0 g of KBH_4 (available from Ventron Corp., Metal Hydrides Division, Congress St., Beverly, Mass. 01915) in 100 ml of approximately 0.2 N NaOH. This solution must be prepared fresh weekly. Store in a polyethylene dropping bottle (e.g., VWR Scientific, No. 16359-040).

CADMIUM NITRATE

CAUTION: Cadmium nitrate is poisonous; avoid any contact.

1.0 M $Cd(NO_3)_2$

Dissolve 308 g of reagent quality cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$, in distilled water and dilute to 1 liter with distilled water.

Acidified $Cd(NO_3)_2 \cdot 4H_2O$

1. Dissolve 200 g of reagent quality cadmium nitrate, $Cd(NO_3)_2 \cdot 4H_2O$, in 800 ml of distilled water.
2. Carefully (wear safety glasses and rubber gloves) add 20 ml of reagent quality concentrated nitric acid, HNO_3.
3. Dilute to 1 liter with distilled water.

CALCIUM CHLORIDE—CALCIUM HYDROXIDE BUFFER

(Containing 2 M Na^+, pH 11.770 at 27 C, pH 11.790 at 80 F)

4.0 N Hydrochloric Acid, HCl

See Hydrochloric Acid

Calcium Hydroxide, $Ca(OH)_2$

Reagent Grade, Baker and Adamson, Code 1522

Sodium Chloride, NaCl

Reagent Grade, Baker and Adamson, Code 2232

Determination of the Normality of the 4.0 N Hydrochloric Acid

1. Pipet (wipe) 10 ml of 4.0 N hydrochloric acid into each of two 125-ml conical flasks.
2. To one sample add 20 ml of distilled water and 4 drops of phenolphthalein indicator.
3. Using a 50-ml buret, titrate with standardized 1.000 N sodium hydroxide to a pink endpoint.
4. Calculation of the normality:

$$\frac{(\text{ml NaOH})(\underline{N}\ \text{NaOH})}{\text{ml HCl}} = 0.1000\ (\text{ml NaOH}) = \underline{N}\ \text{HCl}$$

5. Repeat Steps 2 through 4 using the second sample.
6. If the two values agree within 0.10, average them and label the bottle with the normality determined.

7. If the two values differ by more than 0.10, repeat Steps 2 through 4, using two fresh samples of the 4.0 N hydrochloric acid.

8. If three of the four values agree within 0.10, average them and label the bottle with the normality determined.

9. If three of the values do not agree within 0.10, check technique, reagents and equipment before continuing.

Preparation

1. Add approximately 750 ml of distilled water to a 1-liter volumetric flask; stir on a magnetic stirrer.

2. Using the normality determined above, calculate the necessary volume of hydrochloric acid as follows:

$$V\ HCl = \frac{400}{N\ HCl}$$

3. Pipet (wipe) 50 ml of the 4.0 N hydrochloric acid into the flask, and add the remainder from a 100-ml buret.

4. Add and dissolve 15 g of calcium hydroxide.

5. Add and dissolve 116 g of sodium chloride.

6. Dilute to volume with distilled water.

7. Add and dissolve 10 g of calcium hydroxide. (Excess calcium hydroxide should be present as a slurry for complete buffering.)

8. Store the buffer in a glass-stoppered Pyrex reagent bottle which has been cleaned with 3.0 N hydrochloric acid and rinsed with distilled water.

NOTE: Allow the buffer to stand for two weeks in the Pyrex bottle before using it.

CELITE

Celite (analytical filter aid) is available from Fisher Scientific Company, 585 Alpha Dr., Pittsburgh, Pa. 15238, Catalog No. C-211

CETYLTRIMETHYLAMMONIUM BROMIDE (CTAB)

1% (10 g/1) CTAB Solution

Add and dissolve 2.50 ±0.05 g of cetyltrimethylammonium bromide (EASTMAN Organic Chemical T 5650) in 200 ml of distilled water contained in a 250-ml volumetric flask. Dilute to volume with distilled water.

CHLOROFORM

CAUTION: Chloroform is toxic; use in exhaust hood or where there is adequate ventilation. Keep chloroform away from open flames and hot surfaces.

Spectro-Grade $CHCl_3$

EASTMAN Organic Chemical S 337.

CLEANING SOLUTIONS

Precautions

When mixing and handling the cleaning solutions, observe the safety precautions for handling concentrated acids, especially the wearing of rubber gloves and safety glasses, and the rule, "Always add acid to water."

The danger in pouring water into strong acid is from the large amount of heat generated. Dangerous fumes may result, and the heat may cause rapid evolution of steam and considerable spattering of hot acid.

If acid is spilled on the skin or clothing or splashed into the eyes, flush the affected parts with a large amount of water. The water will dilute the acid and wash it away. Secure competent medical treatment immediately.

Preparation

1. *"Sulfuric-Dichromate"*. Carefully dissolve approximately 30 g of sodium or potassium dichromate, $Na_2Cr_2O_7$ or $K_2Cr_2O_7$, in approximately 1 liter of concentrated sulfuric acid, H_2SO_4.

NOTES:

(a) The sodium salt is preferred because of its greater solubility.

(b) Technical quality salts and acid are satisfactory.

(c) The exact concentration of dichromate is not important. When an excess of dichromate is used, red crystals of chromium trioxide, CrO_3, separate from the solution. Decant the clear liquid, otherwise the crystals may clog buret or pipet tips during cleaning.

(d) Use undiluted. This solution may be reused until no longer effective. Discard when it becomes green.

2. *"Acid-Alcohol"*. Add carefully one volume of 3.0 N hydrochloric acid to one volume of methyl alcohol or isopropyl alcohol. Use undiluted. Discard the solution when it becomes highly colored.

ETHYL ACETATE

CAUTION: Flammable solvent; keep away from flame.

Absorbance Check. Ethyl acetate should be checked for ultraviolet absorbance before it is used. If the absorbance of a 1-cm silica cell filled with ethyl acetate exceeds 0.150, measured against an air blank at 295 and 315 nm, the ethyl acetate is not suitable for use in ultraviolet absorbance methods.

Anhydrous Ethyl Acetate

Anhydrous ethyl acetate absorbs water rapidly. Variations in its water content produce changes in volume when it is shaken with an aqueous sample. Since ethyl acetate cannot be assumed to be anhydrous and since the water content is unimportant provided it is always the same from one batch to another, it is recommended that it be saturated with water prior to use. 3.3 ml of water will dissolve in 90 ml of anhydrous ethyl acetate.

Water-Saturated Ethyl Acetate

Add 100 ml of distilled water to 900 ml of Eastman grade (EASTMAN Organic Chemical 13048) or spectro quality ethyl acetate. Shake well. Always leave an adequate air space at the top of the mixing vessel to allow for expansion. Decant the water-saturated ethyl acetate or withdraw the lower (aqueous) layer by using a length of glass tubing attached to an aspirator pump.

NOTE: If large volumes of this reagent are needed, a large mixing container can be used. If a power stirrer is used, it must be *air-driven* rather than electric in order to avoid the possibility of a spark igniting the flammable vapor.

EXTRACTANT SOLUTION

Potassium Iodide, KI

Reagent grade, Baker and Adamson, Code 2120

Potassium Bromide, KBr

Reagent grade, Baker and Adamson, Code 2100

Potassium Dihydrogen Phosphate, KH_2PO_4

Reagent grade, Baker and Adamson, Code 2130

Preparation

1. Place a 1-liter volumetric flask containing 800 ml of distilled water on a magnetic stirrer.
2. Add and dissolve 1.0 g of potassium iodide, 20.0 g of potassium bromide, and 1.0 g of potassium dihydrogen phosphate.
3. Dilute to volume with distilled water.

FERRIC CHLORIDE

1.8 M $FeCl_3$

Add and dissolve 500 g of reagent quality ferric chloride, $FeCl_3 \cdot 6H_2O$, in distilled water and dilute to 1 liter with distilled water.

FERRIC NITRATE

CAUTION: Acidified ferric nitrate is very corrosive to the skin and metals. Observe safety precautions for handling concentrated acids. Wear safety glasses and rubber gloves. Use caution and always add acid to water.

0.10 M Acidified Ferric Nitrate

1. Add cautiously 40 ml of colorless, reagent quality concentrated nitric acid, HNO_3, to 400 ml of distilled water. If the acid is colored, bubble nitrogen or air through it until the brown color has entirely disappeared, before diluting.
2. Dissolve 40.0 g of reagent quality ferric nitrate, $Fe(NO_3)_3 \cdot 9H_2O$, (Baker and Adamson, Code 1739) in the diluted acid and dilute to 1 liter with distilled water.

FERRIC SULFATE REAGENT

Ferric Sulfate, $Fe_2(SO_4)_3 \cdot X\ H_2O$

Reagent grade, Baker and Adamson, Code 1745

Concentrated Sulfuric Acid, H_2SO_4

Reagent grade, Baker and Adamson, Code 1180

Preparation

1. Measure and pour into a 250-ml beaker 89 ml of distilled water; stir on a magnetic stirrer.
2. Carefully add 15 ml of concentrated sulfuric acid.
3. Add and dissolve 3.0 g of ferric sulfate.

FERROUS AMMONIUM SULFATE

0.10 N $Fe(NH_4)_2(SO_4)_2$

Dissolve 39.2 g of reagent quality ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in 300 ml of distilled water. Add 25 ml of 7.0 N sulfuric acid and dilute to 1 liter with distilled water.

FOAMEX

Purchase from Glyco Products Co., Inc., Div. of Charles L. Huisking and Co., Inc., 417 Fifth Ave., New York, N.Y. 10016.

FORMALDEHYDE

37.5% Formaldehyde Solution, pH 3.9

Add formalin (approximately 37.5% CH_2O by weight) to a beaker. Using a pH meter (see Method 810 or any subsequent method for pH), adjust to pH 3.90 at 21.1 C (70 F) or 26.7 C (80 F) with 0.10 N sulfuric acid or 0.10 N sodium hydroxide using a buret or medicine dropper. (The volume required for the adjustment is expected to be small.)

6% Formaldehyde Solution, pH 3.9

Add 150 ml of formalin (approximately 37.5% CH_2O by weight) to 800 ml of distilled water. Using a pH meter (see Method 810 or any subsequent method for pH), adjust to pH 3.90 at 21.1 C (70 F) or 26.7 C (80 F) with 0.10 N sulfuric acid or 0.10 N sodium hydroxide using a buret or medicine dropper. (The volume required for the adjustment is expected to be small.) Dilute to 1 liter with distilled water.

FORMALIN

33-40% formaldehyde by weight, EASTMAN Organic Chemical P 450.

GELATIN

0.4% (4 g/l) Gelatin

1. Weigh 4 g of powdered gelatin (EASTMAN Organic Chemical P-1099) on a torsion balance.
2. Soak in a few ml of distilled water for approximately 5 minutes. The solution may be warmed to aid in dissolving the gelatin.
3. Dilute to 1 liter with distilled water.
4. This solution is stable for 5 days.

HYDROCHLORIC ACID

Concentrated Hydrochloric Acid, HCl

EASTMAN Organic Chemical No. 13061

Preparation

6.0 N hydrochloric acid
4.0 N hydrochloric acid
3.0 N hydrochloric acid
1.0 N hydrochloric acid

CAUTION: Observe safety precautions for handling concentrated acids. Wear safety goggles and rubber gloves. Use caution and always add acid to water.

1. Add approximately 400 ml of distilled water to a 1-liter

volumetric flask.

2. Add very cautiously, in an exhaust hood, the required amount of concentrated hydrochloric acid (see the table below) from a graduated cylinder.

Normality HCl Desired	Concentrated HCl, ml/l
6.0	498
4.0	333
3.0	249
1.0	83

3. Dilute to volume with distilled water.

NOTE: If possible, use a fresh unopened bottle of concentrated acid. The strength of the concentrated hydrochloric acid varies. The values given in the table are for 12.0 N hydrochloric acid and are intended to give slight over-concentrates which can be adjusted easily by addition of distilled water. Experience will help determine whether more or less of the concentrated acid is required to make HCl of the desired normality.

HYDROGEN PEROXIDE

CAUTION: 30% hydrogen peroxide is a strong oxidant. Avoid contact with skin, eyes, and combustibles. Store in a refrigerator. Protect from light and organic materials.

30% H_2O_2

Reagent quality 30% hydrogen peroxide, H_2O_2, (Baker and Adamson, Code 1802).

HYDROXYLAMINE SULFATE

2.5 M $(NH_2OH)_2 \cdot H_2SO_4$

Add and dissolve 410 g of Eastman grade (EASTMAN Organic Chemical 150) hydroxylamine sulfate, $(NH_2OH)_2 \cdot H_2SO_4$, in distilled water and dilute to 1 liter with distilled water.

INDICATORS

E-O-X

Color change when titrating with acid: green to purple at pH 4.3

Dissolve 1.5 g of ethyl orange (EASTMAN Organic Chemical 122) and 1.5 g of xylene cyanole FF (EASTMAN Organic Chemical T 1579) in 500 ml of distilled water contained in a 1-liter volumetric flask. Dilute to volume with distilled water.

Ferroin; 1,10(Ortho) - Phenanthroline Ferrous Sulfate, 0.025 Molar

Color change: red to green (except when affected by the presence of certain other materials).

Ferroin is available from G. Frederick Smith Chemical Co., Item No. 165.

Meta Cresol Purple (m-cresolsulfonephthalein)

Color change: yellow to purple, pH 7.5 to 9.0

Grind 0.1 g of m-cresolsulfonephthalein (EASTMAN Organic Chemical 2118) in a mortar with 26.2 ml of 0.01 N sodium hydroxide. Dilute to 250 ml with distilled water.

Methyl Red

Color change: red to yellow, pH 4.2 to 6.3

Grind 1.00 g of methyl red (EASTMAN Organic Chemical 431) in a mortar with 37 ml of 0.10 N sodium hydroxide. Dilute to 1 liter with distilled water.

Phenolphthalein

Color change: colorless to pink, pH 8.3 to 10.0

Dissolve 0.50 g of phenolphthalein (EASTMAN Organic Chemical 202) in 500 ml of methyl alcohol or isopropyl alcohol. Dilute to 1 liter with distilled water, or buy from vendor in solution (concentration not critical).

Potassium Chromate

Color change: yellow solution to reddish-brown precipitate

Dissolve 60 g of reagent quality potassium chromate, K_2CrO_4, (Baker and Adamson, Code 2105) in 100 ml of distilled water.

Sodium Diphenylamine Sulfonate, 0.01 M

Color change: colorless to red-violet

1. Dissolve 3.17 g of barium diphenylamine sulfonate (EASTMAN Organic Chemical 3104) in 1 liter of distilled water.

2. Dissolve 1 g of anhydrous sodium sulfate in a small amount of water and add it to the solution of barium diphenylamine sulfonate.

3. Stir the mixture and when the barium sulfate settles out, decant the clear solution and discard the precipitate.

Starch

Color change: blue to colorless

1. Add just enough cold distilled water to 10 g of reagent quality soluble starch (Baker and Adamson, Code 2352) to make a thin paste.

2. Slowly, while stirring, add the paste to 1 liter of rapidly boiling distilled water. Make a fresh starch solution each week.

3. Add 1 milligram (0.001 g) of mercuric iodide, HgI_2, per liter as a preservative if serious instability is encountered.

Thymol Blue

Grind 0.1 g of thymolsulfonephthalein (EASTMAN Organic Chemical 753) in a mortar with 21.5 ml of 0.10 N sodium hydroxide. Transfer to a 250-ml volumetric flask and dilute to volume with distilled water.

IODINE

1.0 N I_2 and 0.10 N I_2

Preparation

1. Add and dissolve reagent quality potassium iodide, KI, in distilled water in a 1-liter volumetric flask as indicated below.

2. Add and dissolve reagent quality iodine, I_2, as indicated below.

I_2 Solution	KI	Water	I_2
1.0 N	200 g	200 ml	127 g
0.10 N	40 g	40 ml	12.7 g

3. Stir until it is certain that the iodine has dissolved, and then dilute to volume with distilled water.

4. Store in a glass-stoppered bottle in the dark. Minimize exposure of iodine solutions to light and air.

Purchase

Purchase 1.0 N I_2 from:

Baker and Adamson, Code 1800.

Purchase 0.10 N I_2 from either:

Fisher Scientific Co., Catalog No. SO-1-86

or

Anachemia Chemicals Limited, P.O. Box 87, Champlain, N.Y. 12919.

Prepare according to the manufacturer's instructions. Store in a glass stoppered Pyrex bottle in the dark. Minimize exposure of iodine solutions to light and air.

Standardization Check

A. Preparation of Arsenious Oxide Stock Solution (see Sulfato Cerate)

1. Weigh, to 4 decimal places, 1.0 g of National Bureau of Standards arsenious oxide, As_2O_3, sample No. 83a or subsequent Bureau of Standards oxidimetric standard into a 125-ml Phillips beaker.

CAUTION: Arsenious oxide is poisonous.

2. Add 10 ml of 2.5 N sodium hydroxide from a tip-up pipet. Swirl to dissolve. Rinse down the sides of the beaker with distilled water from a wash bottle and swirl.

3. Add 30 ml of 1.0 N sulfuric acid from a tip-up pipet; cool to room temperature.

4. Transfer the solution to a 1-liter volumetric flask. Wash the beaker with a number of water rinses, transferring the rinses to the flask. Dilute to volume with distilled water.

B. Dilution of 1.0 N I_2

Pipet (wipe) 25.0 ml of 1.0 N I_2 into a 250.0-ml volumetric flask, dilute to volume with distilled water, and invert a few times to mix.

NOTE: Do not dilute 0.10 N I_2.

C. Titration

1. Add 50 ml of distilled water to a 250-ml Erlenmeyer flask.

2. Add and dissolve 2.0 g of reagent quality sodium bicarbonate, $NaHCO_3$.

3. Add 2 ml of starch indicator from a tip-up pipet.

4. Pipet (wipe the pipet before leveling) 100.0 ml of the arsenious oxide stock solution into the flask.

5. Using a 25-ml buret, titrate with the iodine being standardized. Add partial drops by rapidly twisting the stopcock and washing the tip of the buret with distilled water from a wash bottle. The end point is indicated by the appearance of the first blue color. Record this value to the nearest 0.01 ml.

D. Calculations,

1. $$\frac{(\text{aliquot of treated sample})(\text{g } As_2O_3)(1000)}{(\text{eq wt } As_2O_3)(\text{ml iodine})} =$$

$$\frac{\frac{(100)}{(1000)}(\text{g } As_2O_3)(1000)}{\frac{197.82}{(4)}(\text{ml iodine})} =$$

$$\frac{(\text{g } As_2O_3)(2.022)}{\text{ml iodine}} = \text{N of iodine}$$

2. Repeat the standardization using another stock solution of arsenious oxide.

3. To decide whether to accept the reagent or reject it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control." If the duplicate results from separate stock solutions of arsenious oxide are within the permissible range (refer to Table I or Figure 1), the arsenious oxide solutions may be used for further standardization procedures. If the 0.1000 N I_2 does not meet its specification, prepare a second batch. If the second batch still does not meet specifications, the 0.1000 N I_2 may be prepared by dissolving iodine in a KI solution as described above and then standardized as in the Standardization Check. Adjust or reject according to Method I.

ISOPROPYL ALCOHOL

98-99% isopropyl alcohol; EASTMAN Organic Chemical 212. Also available from Enjay Co. and Shell Chemical Corp.

MANNITOL

EASTMAN Organic Chemical 155.

MERCURIC CHLORIDE—POTASSIUM BROMIDE REAGENT

CAUTION: Mercuric chloride is extremely poisonous and also a powerful desensitizing agent for photographic materials. Do not pipet the solution by mouth and do not use it where it may contaminate unprocessed film and paper.

Preparation

1. Dissolve 25.0 g of reagent quality mercuric chloride, $HgCl_2$, (Baker and Adamson, Code 1966) in 800 ml of distilled water.

2. Add 25.0 g of reagent quality potassium bromide, KBr, (Baker and Adamson, Code 2100).

3. Dilute to 1 liter with distilled water.

4. Allow the solution to stand overnight before use. Keep in a glass-stoppered bottle away from strong daylight or excessive heat. This reagent should be discarded when turbidity develops.

METANIL YELLOW

EASTMAN Organic Chemical T766.

METHYL ALCOHOL

CAUTION: Keep away from flame. Flammable and poisonous.

Practical CH_3OH

EASTMAN Organic Chemical P467.

Methyl Alcohol Containing Thymol Blue

Add 25 ml of thymol blue indicator to each liter of practical grade methyl alcohol, CH_3OH. If the original solution is yellow, titrate with 0.25 N sodium hydroxide to the first *green* color. If the solution is green or blue, titrate with 0.10 N sulfuric acid to the first *yellow*.

NITRIC ACID

CAUTION: Observe safety precautions for handling concentrated acids. Wear safety glasses and rubber gloves. Use caution and always add acid to water.

Concentrated HNO_3

Reagent quality nitric acid, 69-71% HNO_3, approx. sp gr 1.42, approx. 15.8-16 N (Baker and Adamson, Code 1121).

N, N-DIMETHYL-p-PHENYLENE DIAMINE SULFATE

Place 89 ml of water in a beaker, carefully add 15 ml of concentrated sulfuric acid, and dissolve in it 1.0 g of N, N-Dimethyl-p-phenylene diamine Sulfate (EASTMAN Organic Chemical No. 1333). Add 5 g of Florisil (Floridin Co., 2 Gateway Ctr., Pittsburg, Pa. 15222) and stir the mixture until all colored material is adsorbed. Allow the adsorbant to settle and decant the supernatant solution.

OSMIC ACID

CAUTION: Osmic acid is a harmful, volatile substance. Avoid contact with skin or eyes. Avoid breathing vapors.

Dissolve 0.50 g of osmic acid (perosmic acid), OsO_4, (EASTMAN Organic Chemical 2119) in 200 ml of 0.10 N sulfuric acid.

NOTE: This solution is stable for approximately one month.

POTASSIUM ACETATE

5.0 M CH_3COOK

Add and dissolve 490 g of reagent grade potassium acetate, CH_3COOK, (Baker and Adamson, Code 2081) in approximately 600 ml of water. Bring to room temperature and dilute to one liter with distilled water.

POTASSIUM ACID PHTHALATE BUFFER

0.05 M Potassium Acid Phthalate

Checking The Distilled Water. The experience of laboratories at Kodak Park indicates that potassium acid phthalate buffer can be prepared in the manner outlined in the steps below. The National Bureau of Standards specifies that the distilled water used in the preparation of potassium acid phthalate buffer must have a pH of "not less than 6.5 and not more than 7.5 . . . . obtained by boiling distilled water . . . . and cooling it under carbon dioxide-free conditions." (A soda-lime tube can be utilized when cooling the boiled water.) It is recommended that all laboratories follow the method of preparation found on the National Bureau of Standards certificate provided with the standard potassium acid phthalate sample until data indicate that the distilled water being used is acceptable. In some instances distilled water which did not meet the above requirements has been found to be acceptable. A potassium acid phthalate buffer prepared with this distilled water had the same pH as a buffer prepared with water that met the specifications.

Preparation of Potassium Acid Phthalate Buffer

1. Add 600 ml of distilled water to a 1-liter volumetric flask.
2. Dissolve 10.2 ± 0.2 g of Eastman grade (EASTMAN Organic Chemical X538) or reagent quality potassium acid phthalate, $KHC_8H_4O_4$.
3. Dilute to volume with distilled water.

Preparation of Buffer Using National Bureau of Standards Potassium Acid Phthalate. Prepare a fresh *standard* potassium acid phthalate buffer following Steps 1-3 using National Bureau of Standards potassium acid phthalate sample No. 185d or subsequent Bureau of Standards pH standard. Use a torsion balance to weigh the potassium acid phthalate. The preceding batch of standard buffer can be used only if it was prepared within one month of the time of use and if it is not moldy.

Testing Potassium Acid Phthalate Buffer

1. Standardize the pH meter with the standard potassium acid phthalate buffer, setting the pH scale dial according to Table I. Choose the setting corresponding to the temperature at which the new buffer is to be used.

TABLE I

Temperature	Dial Setting
21.1 C (70 F)	4.00
23.9 C (75 F)	4.00
26.7 C (80 F)	4.01

The pH of this buffer is 4.00 between 10.0 C (50 F) and 24.4 C (76 F) and 4.01 between 25.0 C (77 F) and 30.0 C (86 F).

2. Cross-check the electrode assembly by measuring the pH of a borax buffer.
3. Determine the pH of the potassium acid phthalate *buffer being tested* at the same temperature chosen in Step 1. (For tolerances, see Step 4.)
4. Determine the pH of the *standard* potassium acid phthalate buffer at the same temperature chosen in Steps 1 and 3. (This serves as a check. The pH obtained on this *standard*

potassium acid phthalate buffer must not differ by more than 0.01 pH unit from the value at which the meter was standardized in Step 1.) The pH obtained on the *buffer being tested* in Step 3 must not differ by more than 0.01 pH unit from the pH at which the meter was standardized *and* from the pH obtained on the standard buffer in Step 4.

EXAMPLE: A buffer being tested at 21.1 C (70 F) is not acceptable if its pH in Step 3 is 4.01 when 3.99 is obtained in Step 4. However, 4.01 is acceptable if either 4.00 or 4.01 is obtained in Step 4.

5. If the pH of the standard buffer differs by more than ±0.01 pH unit from the value at which the meter was standardized (see Table I), restandardize the meter and repeat Steps 3 and 4.

If the pH reading of the new buffer differs by more than 0.01 pH unit from either the pH at which the meter was standardized or the pH obtained on the standard buffer in Step 4, obtain new samples of the two batches of buffer used above and repeat Steps 1 through 4. If the new buffer is still not acceptable, look for trouble with the electrodes or pH meter, or for contamination of the two buffer solutions.

It may be necessary to prepare a fresh standard buffer using a previously unopened bottle of National Bureau of Standards potassium acid phthalate (pH standard). If the two buffers continue to disagree, do not attempt to adjust the pH of the new batch. Discard the new batch of buffer and prepare another batch.

The solution should be stored in Pyrex bottles. Discard the solution after three months or sooner if mold appears.

POTASSIUM BORATE BUFFER

1. To 700 ml of distilled water in a 1-liter volumetric flask, add and dissolve 9.35 grams of reagent-grade potassium tetraborate, $K_2B_4O_7 \cdot 4H_2O$, (Baker and Adamson, Code 2098).

2. On a torsion balance, quickly weigh the amount of reagent-grade potassium hydroxide, KOH, (Baker and Adamson, Code 2069) calculated by the following equation:

$$\frac{3.02\ (100)}{\%\ \text{KOH}} = \text{grams of KOH}$$

The percent potassium hydroxide is usually given on the label of the container (for 85 percent KOH, weight 3.55 grams).

WARNING: Potassium hydroxide is corrosive. Avoid contact with skin, eyes, and clothing. *Do not weigh KOH in an aluminum dish.*

3. Add and dissolve the calculated amount of potassium hydroxide.

4. Dilute to 1 liter with distilled water.

5. Determine the pH of the solution. The pH should be 10.5 ±0.2 at 21.1 C (70 F), or 10.4 ±0.2 at 23.9 C (75 F) to 26.7 C (80 F). If the pH is not correct, adjust the buffer by adding and dissolving a small amount of solid potassium hydroxide to raise the pH, or solid potassium tetraborate to lower the pH; then redetermine the pH.

POTASSIUM BROMIDE

0.50 M KBr

Dissolve 59.5 grams of reagent quality potassium bromide, KBr*, in distilled water and dilute to 1 liter with distilled water.

1.0% KBr Solution

Dissolve 10.0 g of reagent quality potassium bromide, KBr,* in 800 ml of distilled water contained in a 1-liter volumetric flask. Dilute to volume with distilled water.

250 g/l KBr Solution

Dissolve 250 g of reagent quality potassium bromide, KBr,* in distilled water, warm to room temperature, and dilute to 1 liter with distilled water.

POTASSIUM CHLORIDE

Saturated KCl Solution

Dissolve 50 g of reagent quality potassium chloride, KCl, (Baker and Adamson, Code 2059) in 100 ml of distilled water. Stir for 5 minutes and warm to room temperature. Always maintain an excess of undissolved potassium chloride crystals in the reagent container.

3.5 M KCl Solution

1. Add approximately 800 ml of distilled water to a 1-liter volumetric flask; stir on a magnetic stirrer.

2. Add and dissolve 261 grams of reagent grade potassium chloride (Baker and Adamson, Code 2059).

3. Dilute to 1 liter with distilled water.

POTASSIUM CHROMATE

1. Weigh, on an analytical balance, 4.0000 ±.0001 g of potassium dichromate, $K_2Cr_2O_7$, (Oxidimetric Standard, U.S. Bureau of Standards).

2. Transfer the potassium dichromate to a 1-liter volumetric flask, and dilute to volume with 0.0100 N sulfuric acid. (See Sulfuric Acid.) Stopper and mix until completely dissolved. The solution will keep indefinitely.

3. Weigh 13.4 g of sodium monohydrogen phosphate (heptahydrate), $Na_2HPO_4 \cdot 7H_2O$, (Baker and Adamson, Code 2281). Transfer to a 1-liter volumetric flask.

4. Pipet (wipe the pipet before leveling) 5.00 ml of solution from Step 2 into the 1-liter volumetric flask. Dilute to volume with distilled water; stopper and mix thoroughly.

NOTE: The solution from Step 4 is intended to serve as a primary absorbance standard. However, if desired, an absorbance measurement of any given batch of reagent prepared can be crosschecked with that of any other batch of reagent. Batches which do not cross check, of course, are not valid as primary absorbance standards.

POTASSIUM FERRICYANIDE

0.1 M $K_3Fe(CN)_6$

Dissolve 33 g of reagent quality potassium ferricyanide,

* Baker and Adamson, Code 2100.

$K_3Fe(CN)_6$, (Baker and Adamson, Code 2109) in 800 ml of water and dilute to 1 liter.

0.2 M $K_3Fe(CN)_6$

Dissolve 66 g of reagent quality potassium ferricyanide, $K_3Fe(CN)_6$, in 800 ml of water and dilute to 1 liter.

POTASSIUM IODATE

0.1000 N KIO_3

Dissolve 3.5670 g of reagent quality potassium iodate (Baker and Adamson, Code 2119) (Note 1) in distilled water and dilute to volume in a 1-liter volumetric flask with distilled water. No standardization is required (Note 2).

NOTES:

1. For work requiring an accuracy greater than 0.05%, the potassium iodate should be dried at 150 C for three hours and cooled in a desiccator before being weighed.
2. The solution is stable indefinitely.

Preparation of Larger Volumes. It is often necessary to prepare a larger volume of potassium iodate than the largest size volumetric flask. Prepare the required volume of the approximate strength and standardize the solution using the following procedure. The normality of the sodium thiosulfate is specified in the procedure but it does not enter into the calculations.

Standardization

1. Pipet 20.0 ml of primary standard 0.1000 N potassium iodate into a 125-ml Erlenmeyer flask.
2. Add 10 ml of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 15 ml of 0.6 M potassium iodide from a tip-up pipet.
4. Titrate the liberated iodine with approximately 0.1 N sodium thiosulfate, using a 25-ml buret. Titrate the solution to a light yellow color, add 5 ml of starch indicator from a tip-up pipet, and continue until the blue color is just discharged.
5. Repeat Steps 1-4 pipetting 20.0 ml of the potassium iodate being standardized.
6. Calculations:

$$\frac{\left(\begin{array}{c}\text{ml } Na_2S_2O_3 \text{ used against} \\ \text{solution being standardized}\end{array}\right)(0.1000)}{(\text{ml } Na_2S_2O_3 \text{ used against standard } KIO_3)}$$

= N of KIO_3 being standardized.

7. Repeat the standardization on another portion of the primary standard KIO_3 and the solution being standardized.
8. To decide whether to accept the reagent or adjust it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control."

NOTE: The data from the titration of the primary standard potassium iodate obtained during the standardization of sodium thiosulfate may also be used in the calculations for potassium iodate solutions. However, prepare the potassium iodate solution immediately after the sodium thiosulfate solution has been standardized. Do not allow portions of the standardized sodium thiosulfate to remain exposed to the air between the titrations of the primary standard potassium iodate and the potassium iodate being standardized.

POTASSIUM IODIDE

Preparation*

0.6 M KI

Dissolve 100 g of reagent quality potassium iodide, KI, in distilled water and dilute to 1 liter with distilled water.

0.10 N KI

Dissolve 16.7 g of reagent quality potassium iodide in distilled water and dilute to volume in a 1-liter volumetric flask with distilled water.

0.010 N KI

Dissolve 1.67 g of reagent quality potassium iodide in distilled water and dilute to volume in a 1-liter volumetric flask with distilled water.

0.0010 N KI

Dissolve 0.167 g of reagent quality potassium iodide in distilled water and dilute to volume in a 1-liter volumetric flask with distilled water.

0.00010 N KI

Dissolve 0.0167 g of reagent quality potassium iodide in distilled water and dilute to volume in a 1-liter volumetric flask with distilled water.

Alternative Preparation

Another way of preparing 0.01000 N, 0.00100 N, or 0.000100 N solutions is to dilute standardized solutions of greater normality:

0.0100 N KI

Pipet (wipe the pipet before leveling) 100.0 ml of standardized 0.1000 N solution into a 1-liter volumetric flask and dilute to volume with distilled water. If a precision of only 1 part in 100 is required, no standardization is necessary.

0.00100 N KI

Pipet (wipe) 100.0 ml of standardized 0.0100 N solution into a 1-liter volumetric flask and dilute to volume with distilled water. If a precision of only 3 parts in 100 is required, no standardization is necessary.

0.000100 N KI

Pipet (wipe) 100.0 ml of standardized 0.00100 N solution into a 1-liter volumetric flask and dilute to volume with distilled water. If a precision of only 10 parts in 100 is required, no standardization is necessary.

Standardization

0.1000 N KI

1. Pipet (wipe the pipet before leveling) 10.0 ml of the 0.1 N potassium iodide into a 125-ml Erlenmeyer flask.

* Using Crystal, KI, Reagent, ACS (Baker and Adamson, Code 2120).

2. Add approximately 50 ml of Eastman grade or reagent quality acetone.

3. Add 25 ml of 7.0 N sulfuric acid from a tip-up pipet.

4. Dilute the mixture to approximately 175 ml.

5. Add 1 drop of Ferroin indicator.

6. Titrate with 0.0500 N sulfato cerate until the pink color changes to pale blue.

7. Calculations:

$$\frac{(\text{ml cerate})(\text{N cerate})}{(\text{ml KI})(2)^*} =$$

$$(\text{ml cerate})(0.002500) = \text{N of KI}$$

8. Repeat the standardization on another 10-ml portion of the reagent.

9. To decide whether to accept the reagent or adjust it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control."

0.0100 N KI

Follow the same procedure as for 0.1000 N, using a 100.0-ml sample, 50 ml of acetone, and 25 ml of 7.0 N sulfuric acid, to give a total volume of 175 ml.

Calculations: (ml cerate)(0.0002500) = N of KI

0.00100 N KI

If a precision of greater than 3 parts in 100 is required, it will be necessary to standardize the solution by a potentiometric titration with silver nitrate.

1. Pipet (wipe the pipet before leveling) 20.0 ml of the 0.001 N KI into a 250-ml beaker.

2. Add 25 ml of distilled water from a tip-up pipet.

3. Add approximately 1 ml of 7.0 N sulfuric acid.

4. Place the silver and calomel electrodes in the solution. Add sufficient distilled water to immerse the electrodes properly, and turn on the mechanical stirrer.

NOTE: Use Corning Model 12 Research pH Meter (or equivalent), Beckman Fiber-Junction Calomel Electrode No. 39170 with saturated KNO_3 bridge (remove the saturated KCl solution and substitute saturated KNO_3 solution) and a silver bar electrode.

All titrations should be run with the reference electrode (Beckman Fiber-Junction Calomel Electrode) in the reference jack of the pH meter and the indicator electrode (Silver Bar Electrode) in the indicator jack of the pH meter.

5. Carefully titrate with 0.00100 N silver nitrate, recording the buret readings and the corresponding readings of the Corning meter. Use a 25-ml buret and make 0.1-ml additions of silver nitrate at the endpoint. (See Method XI for instructions on determining a potentiometric endpoint.)

NOTE: Prepare 0.00100 N silver nitrate by dissolving 0.1699 g of Eastman grade or reagent quality silver nitrate, $AgNO_3$, in chloride-free distilled water and by diluting to volume in a 1-liter volumetric flask with chloride-free distilled water.

6. Calculations:

$$\frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)}{(\text{ml KI})} =$$

$$(\text{ml } AgNO_3)(0.0000500) = \text{N of KI}$$

7. Repeat the standardization on another 20-ml portion of the reagent.

8. To decide whether to accept the reagent or adjust it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control."

0.000100 N KI

Follow the same procedure as for 0.00100 N potassium iodide, using a 200.0-ml sample in a 400-ml beaker, 10 ml of 7.0 N sulfuric acid, and titrate with 0.00100 N silver nitrate.

Calculations:

$$\frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)}{(\text{ml KI})} =$$

$$(\text{ml } AgNO_3)(0.00000500) = \text{N of KI.}$$

POTASSIUM MONOHYDROGEN—DIHYDROGEN PHOSPHATE BUFFER

(pH 7.9 at 26.7 C (80 F))

1. Add approximately 300 ml of distilled water to a 4-liter beaker and heat on a hot plate.

2. Add 1000 g of reagent quality potassium monohydrogen phosphate, $K_2HPO_4 \cdot 3H_2O$, (Potassium Phosphate, Dibasic, Baker and Adamson, Code 2131) and mix until the salt has dissolved.

3. Add 225 g of reagent quality potassium dihydrogen phosphate, KH_2PO_4. (Baker and Adamson, Code 2130)

4. Cool to room temperature. Transfer to a 1-liter volumetric flask and dilute to volume with distilled water.

5. Determine the pH on a Corning Model 12 Research pH Meter, or equivalent. The pH should be 7.90 ±.20 at 26.7 C (80 F).

POTASSIUM NITRATE

Saturated KNO_3 Solution

Dissolve 50 g of reagent quality potassium nitrate, KNO_3, (Baker and Adamson, Code 2122) in 100 ml of distilled water. Stir for 5 minutes and warm to room temperature. Always maintain an excess of undissolved potassium nitrate crystals in the reagent container.

POTASSIUM PERMANGANATE

0.41 M $KMnO_4$

Dissolve 65.0 g of reagent quality potassium permanganate, $KMnO_4$, (Baker and Adamson, Code 2128) in 900 ml of distilled water and dilute to volume in a 1-liter volumetric flask with distilled water.

POTASSIUM PHOSPHATE BUFFER

1. Add approximately 800 ml of distilled water to a 1-liter

*The reaction between sulfato cerate and potassium iodide in the presence of acetone requires 2 ceric ions for each iodide ion.

volumetric flask; stir on a magnetic stirrer.

2. Add and dissolve 6.8 grams of reagent grade potassium dihydrogen phosphate, KH_2PO_4, (Baker and Adamson, Code 2130).

3. Add 29.1 ml of standardized 1.000 Normal sodium hydroxide.

4. Dilute to 1 liter with distilled water.

5. Determine the pH. The pH of this buffer should be 7.00 ±0.20 at 27 C (80.6 F).

POTASSIUM THIOCYANATE

0.052 N KCNS

Preparation. Dissolve 5.1 g of reagent quality potassium thiocyanate, KCNS, (Baker and Adamson, Code 2144) in chloride-free distilled water and dilute to volume in a 1-liter volumetric flask with chloride-free distilled water.

NOTE: Do not standardize potassium thiocyanate solutions if they are to be used only for the method of standardization outlined for silver nitrate solutions. The normality does not enter into the calculations for the silver nitrate standardization and need not be exact.

Standardization

1. Pipet by bulb (wipe the pipet before leveling) 50.0 ml of primary standard 0.0500 N silver nitrate into a 250-ml glass-stoppered Erlenmeyer flask.

2. Add about 3 ml of 0.10 M acidified ferric nitrate.

3. Titrate with the thiocyanate solution being standardized. The endpoint is the first pink coloration which cannot be removed by vigorous shaking of the stoppered flask.

4. Calculations:

$$\frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)}{(\text{ml KCNS})} = \text{N of KCNS}$$

SILVER HALIDE DEVELOPER

NOTE: Use all possible care and keep air contact to a minimum once the hydroquinone is added to the flask.

1. Dissolve 50 g of *photographic grade* (ANSI Specification) sodium sulfite, Na_2SO_3, in 900 ml of 4 N ammonium hydroxide contained in a 1-liter beaker.

2. Add 50 g of hydroquinone to a dry, 1-liter volumetric flask using a dry powder funnel.

3. Add the sodium sulfite—ammonium hydroxide solution to the flask; bring to volume with 4 N ammonium hydroxide, stopper the flask and *then* shake to dissolve the hydroquinone.

4. Bottle the developer in rubber-stoppered 60-ml bottles. The solution should be colorless or light yellow. It should be discarded if it turns brown.

SILVER NITRATE

CAUTION: Silver nitrate is poisonous, causes burns, stains skin. Avoid contact.

0.0500 N $AgNO_3$

Preparation as a Primary Standard. Dissolve 8.495 g of reagent quality silver nitrate, $AgNO_3$,[1] in chloride-free distilled water and dilute to volume in a 1-liter volumetric flask with chloride-free distilled water. When Kodak or reagent quality silver nitrate is used and the solution is prepared as described, no standardization is required.

Preparation of Larger Volumes. It is often necessary to prepare a larger volume of silver nitrate than the largest volumetric flask will contain. Prepare the required volume of the approximate strength and standardize the solution using the procedure below.

The normality of the potassium thiocyanate is specified in the procedure. The normality does not enter into the calculations and need not be exact; however, it must be slightly greater than the normality of the silver nitrate solution being standardized.

Standardization

1. Pipet by bulb 50.0 ml of primary standard 0.0500 N silver nitrate into a 250-ml glass-stoppered Erlenmeyer flask.

2. Add about 3 ml of 0.10 M acidified ferric nitrate.

3. Titrate with approximately 0.052 N potassium thiocyanate to the first pink coloration which cannot be removed by vigorous shaking of the stoppered flask.

4. Repeat Steps 1, 2 and 3, pipetting 50.0 ml of the silver nitrate being standardized. (See note.)

5. Calculations:

$$\frac{\left(\begin{array}{c}\text{ml KCNS used against} \\ AgNO_3 \text{ being standardized}\end{array}\right)(0.0500)}{(\text{ml KCNS used against standard } AgNO_3)}$$

$$= \text{N of } AgNO_3 \text{ being standardized.}$$

6. Repeat the standardization on another portion of the primary standard silver nitrate and the solution that is being standardized.

7. To decide whether to accept the reagent or adjust it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control".

NOTE: By titrating two silver nitrate solutions alternately using the same equipment and technique, the titration errors cancel each other. This practice is preferred over the more common practice of standardizing a solution directly against a primary standard, where there is no such compensation of errors.

The data from the titration of the standard silver nitrate with thiocyanate may also be used to calculate the normality of the thiocyanate. The calculated normality can be used whenever a check of gross errors is desired for silver nitrate solutions prepared as primary standard solutions not requiring standardization. The approximate normality can be calculated as follows:

$$\frac{(\text{ml KCNS})(\text{N KCNS})}{(\text{ml } AgNO_3)} = \text{N of } AgNO_3$$

[1] EASTMAN Organic Chemical 491 (preferred material) or Baker and Adamson, Code 2179.

0.0100 N $AgNO_3$

Pipet 200.0 ml of 0.0500 N silver nitrate into a 1-liter volumetric flask and dilute to volume with chloride-free distilled water.

0.00500 N $AgNO_3$

Pipet 100.0 ml of 0.0500 N silver nitrate into a 1-liter volumetric flask and dilute to volume with distilled water.

0.00100 N $AgNO_3$

Pipet 20.0 ml of 0.0500 N silver nitrate into a 1-liter volumetric flask and dilute to volume with distilled water.

0.060 M $AgNO_3$—0.50 M CH_3COOH

1. Add and dissolve 30 ml of reagent quality glacial acetic acid, 99.7% CH_3COOH, sp gr 1.050 (Baker and Adamson, Code 1019 or EASTMAN Organic Chemical 763), in 750 ml of distilled water.
2. Add and dissolve 10 g of reagent quality silver nitrate, $AgNO_3$, (Baker and Adamson, Code 2179 or EASTMAN Organic Chemical 491).
3. Dilute to 1 liter with distilled water.
4. Store in a brown, glass-stoppered bottle away from strong light. Discard the solution if it has darkened.

SODIUM CARBONATE

Buffer, pH 11.1

Add 85.5 g of reagent quality sodium carbonate, Na_2CO_3, (Baker and Adamson, Code 2275) to distilled water and dilute to 1 liter.

SODIUM CHLORIDE

Crystalline NaCl

Reagent quality sodium chloride, NaCl, (Baker and Adamson, Code 2232).

Saturated NaCl Solution

Add 400 g of reagent quality sodium chloride, NaCl, to 1 liter of distilled water. Stir for 5 minutes. Always maintain an excess of undissolved sodium chloride crystals in the reagent container.

0.85 M NaCl

Add and dissolve 50 g of reagent quality sodium chloride, NaCl, in distilled water and dilute to 1 liter with distilled water.

0.10 N NaCl

Dissolve 5.85 g of reagent quality sodium chloride, NaCl, in distilled water and dilute to 1 liter with distilled water.

4.0 M NaCl—1.0 M HCl Reagent

Add and dissolve 234 g of reagent quality sodium chloride, NaCl, in 700 ml of distilled water. Add 85 ml of conc. reagent quality hydrochloric acid, HCl, and dilute to one liter with distilled water.

SODIUM FERROCYANIDE

0.20 M $Na_4Fe(CN)_6$

Add and dissolve 100 g of photographic grade sodium ferrocyanide decahydrate, $Na_4Fe(CN)_6 \cdot 10H_2O$, in 800 ml of distilled water, and then dilute to one liter with distilled water.

SODIUM HYDROXIDE

CAUTION: Sodium hydroxide is corrosive; avoid contact with skin or clothing. Do not weigh in an aluminum dish.

Preparation

16 N NaOH
10 N NaOH
2.5 N NaOH
1.0 N NaOH
0.10 N NaOH

1. Add (with extreme caution) in an exhaust hood, the indicated amount of reagent quality sodium hydroxide, NaOH, (Reagent quality, pellets, Baker and Adamson, Code 2255) to 800 ml of distilled water in a 2-liter Pyrex beaker.

Sodium Hydroxide Solution	Grams to Add Per Liter
16 N	656
10 N	410
2.5 N	102
1.0 N	41
0.10 N	4.1

2. Stir to dissolve; cool to room temperature. (Use care when handling the beaker of solution. It is safer to place the beaker in a polyethylene pail.)

NOTE: 16 N will contain a white sodium carbonate precipitate which need not be removed.

3. Transfer to a 1-liter volumetric flask and dilute to volume with distilled water.* The reagent does not require standardization unless it is to be used for preparing more dilute solutions.

0.2500 N NaOH

Pipet by bulb 100.0 ml of standardized 2.500 N NaOH into a 1-liter volumetric flask and dilute to volume with distilled water.*

Alternative Procedure; Pipet by bulb 100.0 ml of nonstandardized 2.5 N NaOH into a 1-liter volumetric flask and dilute to volume with distilled water.* Standardize the solution using the procedure below.

Standardization

1. Weigh, to four decimal places, the indicated amount of National Bureau of Standards potassium acid phthalate, $KHC_8H_4O_4$, sample No. 84H or subsequent Bureau of Standards acidimetric standard into a 125-ml Erlenmeyer flask. See Table.
2. Dissolve the sample in 50 ml of distilled water.
3. Add 3 drops of phenolphthalein indicator.

* Sodium hydroxide solutions should be stored in rubber-stoppered Pyrex bottles. If a solution is to be used in a dispensing system, there should be a soda-lime tube between the solution and the air.

Sodium Hydroxide Solution	Approximate Weight of Potassium Acid Phthalate
100 grams/liter	10 g
2.500 N	10 g
1.000 N	4 g
0.2500 N	1 g
0.1000 N	0.4 g

4. Using a 25-ml buret, titrate with the sodium hydroxide being standardized. The endpoint is indicated by a pink color which persists for one-half minute.

5. Calculations:

$$\frac{\text{(g potassium acid phthalate)(1000)}}{\text{(ml NaOH)(eq wt pot. acid phthalate)}} =$$

$$\frac{\text{(g potassium acid phthalate)(1000)}}{\text{(ml NaOH)(204.2)}} =$$

$$\frac{\text{(4.897)(g potassium acid phthalate)}}{\text{(ml NaOH)}} =$$

N of NaOH

6. Repeat the standardization on another sample of potassium acid phthalate.

7. To decide whether to accept the reagent or adjust it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control."

SODIUM HYDROXIDE—(ETHYLENEDINITRILO) TETRA-ACETIC ACID (EDTA) SOLUTION

1. Cautiously add and dissolve 40.0 g of reagent quality sodium hydroxide, NaOH, in 800 ml of distilled water.

2. Add and dissolve 2.0 g of (ethylenedinitrilo) tetraacetic acid (EDTA, EASTMAN Organic Chemical P 5416).

3. Dilute to 1 liter with distilled water.

SODIUM SULFATE

Anhydrous Na_2SO_4

Reagent quality, granular, anhydrous sodium sulfate, Na_2SO_4, (Baker and Adamson, Code 2295).

SODIUM SULFIDE

Crystalline Na_2S

Reagent quality sodium sulfide, $Na_2S{\cdot}9H_2O$, crystals (Baker and Adamson, Code 2297).

0.8 M Na_2S

Preparation. Dissolve 192 g of reagent quality sodium sulfide, $Na_2S{\cdot}9H_2O$, in distilled water and dilute to 1 liter with distilled water.

0.06 N Na_2S

Preparation

1. Add and dissolve 7.5 g of reagent quality sodium sulfide, $Na_2S{\cdot}9H_2O$, in 800 ml of distilled water, and dilute to 1 liter with distilled water.

2. Store the reagent in rubber-stoppered Pyrex bottles (60 ml, for example), filling the bottles to overflowing.

3. Standardize once a week. Avoid unnecessary air exposure of the reagent.

Standardization

1. Add, from a tip-up pipet, 30 ml of 0.10 N sodium chloride to a 600-ml beaker.

2. Pipet (wipe the pipet before leveling) 50.0 ml of 0.0500 N silver nitrate into the beaker.

3. Add 300 ml of 1.0 M sodium thiosulfate from a graduated cylinder.

4. Add 100 ml of sodium hydroxide-EDTA reagent from a tip-up pipet.

5. Add 10 ml of 0.4% (4 g/l) gelatin from a tip-up pipet.

6. Titrate with 0.06 N sodium sulfide. Follow the procedure for potentiometric titrations given in the manual, using a Corning Model 12 Research pH meter.

7. Calculations:

$$\text{(ml } AgNO_3)(\text{N } AgNO_3) = \text{(ml } Na_2S)(\text{N } Na_2S) =$$

$$\frac{(2.50)}{\text{(ml } Na_2S)} = \text{N of } Na_2S$$

8. Repeat the standardization, and average the results, if the range of two results does not exceed 0.00035 N. If the range exceeds this value, repeat the standardization. Follow Table I of "Sequential Analysis for Standardization of Reagents" (Method I) for 0.0500 N reagent to decide whether to accept the reagent. Do not attempt to adjust the reagent to its nominal value of 0.06 N; use the calculated normality.

SODIUM SULFITE

0.4 M Na_2SO_3

Add and dissolve 50.4 g of reagent quality sodium sulfite, Na_2SO_3 (Baker and Adamson, Code 2301), in 800 ml of distilled water, and dilute to 1 liter with distilled water.

0.10 M Na_2SO_3—2.5 M NaOH Reagent

Add and dissolve 12.6 g of reagent quality sodium sulfite, Na_2SO_3, in 800 ml of 2.5 N sodium hydroxide, NaOH, and then dilute to 1 liter with 2.5 N sodium hydroxide.

SODIUM TETRAPHENYLBORON

3% Sodium Tetraphenylboron Solution (NaTPB)

Weigh 3.0 g of reagent quality sodium tetraphenylboron (Baker and Adamson, Code 2329) in a 150-ml beaker. Add, from a graduated cylinder, 100 ml of 0.01 N sodium hydroxide. Stir for at least 5 minutes; then bottle.

NOTE: The solution will have a turbid appearance. This solution is stable for *three* days.

SODIUM THIOSULFATE

Crystalline $Na_2S_2O_3{\cdot}5H_2O$

Reagent quality sodium thiosulfate (Baker and Adamson, Code 2307).

1.0 M $Na_2S_2O_3$

Add and dissolve 248 g of sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, in 800 ml of distilled water, and dilute to 1 liter with distilled water. Do not use this reagent to prepare standard $Na_2S_2O_3$ reagents.

0.1000 N $Na_2S_2O_3$

Preparation. Dissolve 25 g of reagent quality sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, in freshly boiled and cooled distilled water and dilute to volume in a 1-liter volumetric flask with distilled water. Allow the solution to stand for one day before standardizing. Add 1 milligram (0.001 gram) of mercuric iodide, HgI_2, per liter as a preservative if serious instability is encountered.

Standardization

1. Pipet (wipe the pipet before leveling) 20.0 ml of primary standard 0.1000 N potassium iodate into a 125-ml Erlenmeyer flask.
2. Add 10 ml of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 15 ml of 0.6 M potassium iodide from a tip-up pipet.
4. Titrate the liberated iodine with the sodium thiosulfate being standardized, using a 25-ml buret. Titrate the solution to a light yellow color, add 5 ml of starch indicator from a tip-up pipet, and continue the titration until the blue color is just discharged.
5. Calculations:

$$\frac{(\text{N } KIO_3)(\text{ml } KIO_3)}{(\text{ml } Na_2S_2O_3)} = \text{N of } Na_2S_2O_3$$

6. Repeat the standardization on another 20-ml portion of the reagent.
7. To decide whether to accept the reagent or adjust it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control."

NOTE: The data from the titration of the primary standard potassium iodate obtained during the standardization of sodium thiosulfate may also be used in the calculations for potassium iodate solutions. However, prepare the potassium iodate solution immediately after the sodium thiosulfate solution has been standardized. Do not allow portions of the standardized sodium thiosulfate to remain exposed to the air between the titrations of the primary standard potassium iodate and the potassium iodate being standardized.

0.000063 N $Na_2S_2O_3$

1. Add 15.7 g (to the nearest 0.1 g) of reagent-quality sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, to a 1-liter volumetric flask and dilute with freshly boiled and cooled distilled water.
2. Pipet 1.00 ml of the above solution into a 1-liter volumetric flask and dilute with distilled water.
3. This second solution is stable for only two hours.

0.20 M $Na_2S_2O_3$—0.15 M Na_2SO_3 Reagent

1. Add and dissolve 19 g of reagent quality sodium sulfite, Na_2SO_3, in 750 ml of freshly boiled distilled water.
2. Add and dissolve 50 g of reagent quality sodium thiosulfate, pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$.
3. Dilute to 1 liter with freshly boiled distilled water.

SULFATO CERATE

0.0500 N Sulfato Cerate

Preparation

1. Weigh in a 150-ml beaker 27.413 g of ammonium hexanitrato cerate, $(NH_4)_2Ce(NO_3)_6$, GFS Certified (with certificate) Standard of Reference Purity, G. Frederick Smith Chemical Co., Item No. 15.

NOTE: The ammonium hexanitrato cerate is weighed in a glass beaker to avoid contamination by a metal dish.

Three-liter volumetric flasks are available from some laboratory supply houses. If more than three-liter quantities are prepared using a volumetric flask, do not exceed the load limit (150—200 g) recommended by the manufacturer of the analytical balance. Make the necessary number of weighings, and record each weight accurately.

It is acceptable procedure to make one weighing on another type balance if the capacity of the balance is adequate and if it has an actual operating capability of 1 part per 1,000.

2. Transfer the ammonium hexanitrato cerate to a 600-ml beaker.
3. Add (cautiously, wearing safety glasses and rubber gloves) 28 ml of reagent quality concentrated sulfuric acid, H_2SO_4, to the 600-ml beaker.
4. Dissolve the ammonium hexanitrato cerate and mix the constituents together for 1 minute.
5. Add (cautiously, in an exhaust hood, wearing safety glasses) 100 ml of distilled water and stir for 2 minutes.
6. Using distilled water, rinse off any ammonium hexanitrato cerate that has adhered to the weighing container, transfer funnel, etc, into the 600-ml beaker.
7. Add consecutive 100-ml portions of water with stirring until all the ammonium hexanitrato cerate has dissolved.
8. Place the beaker in a cooling bath and cool the solution to room temperature.
9. Transfer the solution quantitatively to a 1-liter volumetric flask and dilute to volume with distilled water.
10. No standardization is required when certified ammonium hexanitrato cerate is used and the solution is prepared as described. However, check the solution for gross errors by preparing and analyzing at least one fresh arsenious oxide stock solution. Follow the standardization procedure below. A repeat of the procedure is not necessary if one check indicates that the reagent falls within the limits of 0.0497 and 0.0503 N.
11. If the reagent is acceptable, use the nominal value of 0.0500 N. If the check indicates that the reagent requires adjustment, repeat the standardization using another arsenious oxide stock solution. Decide whether to accept or adjust

the reagent. See Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control."

Preparation of Larger Volumes. It is often necessary to prepare a larger volume of sulfato cerate than the largest volumetric flask will contain. The mixing vessel should be glass or of a ceramic material. Prepare the required volume of the approximate strength and standardize the solution, using the following procedure:

Standardization

A. Preparation of Arsenious Oxide Stock Solution

1. Weigh, to 4 decimal places, 1.0 g of National Bureau of Standards arsenious oxide, As_2O_3, sample No. 83a, or subsequent Bureau of Standards oxidimetric standard into a 125-ml Phillips beaker.

CAUTION: Arsenious oxide is poisonous.

2. Add 10 ml of 2.5 N sodium hydroxide from a tip-up pipet. Swirl to dissolve. Rinse down the sides of the beaker with distilled water from a wash bottle and swirl.

3. Add 30 ml of 1.0 N sulfuric acid from a tip-up pipet; cool to room temperature.

4. Transfer the solution to a 1-liter volumetric flask. Wash the beaker with a number of water rinses, transferring the rinses to the flask. Dilute to volume with distilled water.

B. Titration

1. Add, from a tip-up pipet, 50 ml of 2.5 N sulfuric acid to a 250-ml beaker.

2. Add 1 drop of osmic acid.

CAUTION: Osmic acid is a harmful, volatile substance. Avoid contact with skin or eyes. Avoid breathing vapors.

3. Add 1 drop of Ferroin indicator.

4. Stir on a magnetic stirrer.

5. Using a 50-ml buret, titrate with the sulfato cerate being standardized. Add partial drops by rapidly twisting the stopcock and washing the tip of the buret with distilled water from a wash bottle. The end point is indicated by the appearance of the first blue color. This first end point should require less than a drop. Record this blank value to the nearest 0.01 ml, and do not refill the buret. This is the blank value.

6. Pipet (wipe the pipet before leveling) 100.0 ml of the arsenious oxide stock solution into the indicator solution and again titrate to a colorless solution (loss of pink) using the partial drop addition technique near the end point. Record this volume to the nearest 0.01 ml.

7. Calculate the △ ml by subtracting the blank value in Step 5 from the value in Step 6.

C. Calculations:

$$1.\ \frac{(\text{aliquot of treated sample})(\text{g } As_2O_3)(1000)}{(\text{eq wt } As_2O_3)(\triangle \text{ ml sulfato cerate})} =$$

$$\frac{\frac{(100)}{(1000)}(\text{g } As_2O_3)(1000)}{\frac{(197.82)}{(\ 4\ )}(\triangle \text{ ml sulfato cerate})} =$$

$$\frac{(\text{g } As_2O_3)(2.022)}{(\triangle \text{ ml sulfato cerate})} = \underline{\text{N}} \text{ of sulfato cerate}$$

2. Repeat the standardization using another stock solution of arsenous oxide.

3. To decide whether to accept the reagent or adjust it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control." If the duplicate results from separate stock solutions of arsenious oxide are within the permissible range (refer to Table I or Figure 1), the arsenious oxide solutions may be used for further standardization procedures.

0.0100 N Sulfato Cerate

Pipet by bulb (wipe the the pipet before leveling) 200.0 ml of 0.0500 N sulfato cerate into a 1-liter volumetric flask. Add 115 ml of 7.0 N sulfuric acid from a graduated cylinder and dilute to volume with distilled water. No standardization is necessary.

Storage and Stability of Sulfato Cerate

This reagent is stable for at least seven weeks in a glass-stoppered bottle. *Never use rubber or similar materials for containers or stoppers.*

SULFURIC ACID

CAUTION: Observe safety precautions for handling concentrated acids. Wear safety glasses and rubber gloves. Use caution and always add acid to water.

Concentrated H_2SO_4

Reagent quality sulfuric acid, 95—98% H_2SO_4, sp gr 1.84, approx 36 N (Baker and Adamson, Code 1180).

18 N H_2SO_4
7.0 N H_2SO_4
2.5 N H_2SO_4
1.0 N H_2SO_4
0.50 N H_2SO_4
0.10 N H_2SO_4

Preparation

Add 500 ml of distilled water to a 1-liter *Pyrex* bottle. (See the Caution below for larger volumes.) While stirring the water with a magnetic stirrer, add slowly and cautiously the indicated amount of reagent quality concentrated (36 N) sulfuric acid to the water. Cool to room temperature and dilute to 1 liter with distilled water.

CAUTION: When preparing larger volumes of 18 N and 7 N acids, place the *Pyrex* bottle in a strong rubber or plastic pail. The bottles should not exceed 4 liters for 18 N and 9 liters for 7 N acid. Set a magnetic stirrer on the floor. The stirrer must have a platform and base as large as the bottle. Add the appropriate volume of distilled water to the bottle. Place a graduated cylinder on the floor, and measure the appropriate volume of acid. While stirring the water, slowly and cautiously, add the acid to the bottle. When the solution is throughly mixed, stopper the bottle and place the pail in a sink. Remove the stopper and cover the neck of

the bottle with a beaker. Cool to room temperature by first running warm water on the side of the bottle; then reduce the temperature of water. Dilute to volume with distilled water.

Sulfuric Acid Solution	ml to Add per Liter
18 N	500
7.0 N	200
2.5 N	70
1.0 N	28
0.50 N	14
0.10 N	2.8

0.1000 N H_2SO_4*

Preparation (Standardized). Pipet 100.0 ml of standardized 1.000 N H_2SO_4 into a 1-liter volumetric flask and dilute to volume with distilled water.

Standardization. Sulfuric acid must be standardized. There is no substance that can be used as a convenient primary standard for standardizing sulfuric acid. Therefore, it should be standardized against sodium hydroxide, which has in turn been standardized against National Bureau of Standards potassium acid phthalate sample No. 84d or subsequent Bureau of Standards acidimetric standard.

1. Pipet (use a bulb) 20.0 ml of the sulfuric acid being standardized into a 125-ml Erlenmeyer flask.
2. Add 25 ml of distilled water from a tip-up pipet.
3. Add 2 drops of methyl red indicator.
4. Using a 25-ml buret, titrate with the indicated standardized sodium hydroxide until the indicator changes from red to light yellow.

Sulfuric Acid Solution	N of Sodium Hydroxide
2.500 N	2.500
1.000 N	1.000
0.1000 N	0.1000

5. Calculations:

$$\frac{(\text{ml NaOH})(\text{N NaOH})}{(\text{ml } H_2SO_4)} = \text{N of } H_2SO_4$$

6. Repeat the standardization on another 20-ml portion of the reagent.
7. To decide whether to accept the reagent or adjust it, see Part G and Figure 1 of Method I, "Analytical Reagents for Chemical Control."

Alternative Procedure: Purchase item from Anachemia, Box 87, Champlain, N.Y. 12919. Prepare according to the manufacturer's instructions. No standardization is required.

THIOACETAMIDE

0.00926 ±0.0001 N Thioacetamide

Preparation. Dissolve 0.70 g of reagent quality thioacetamide (EASTMAN Organic Chemical 1719) in 2.00 liters of tap or distilled water. Add approximately 0.5 g of thymol (EASTMAN Organic Chemical 248). The thymol will not dissolve completely. This reagent is stable for two months when used with Method 1209D, Procedures I and III, and no standardization is required. However, standardization becomes necessary for the reliability of greater than ±5% required in Procedure II of that method.

Reagent quality thioacetamide is available with a minimum assay claim of 99% from one vendor and 95% from another. Limited experience has indicated that three lots of thioacetamide (including lots from the above two vendors and one nonreagent material) are all about 96% pure, as measured by the standardizing procedure below.

Standardization (Method 1209D, Procedure II). Pipet 5.00 ml of 0.0500 N silver nitrate into each of two 50-ml glass-stoppered graduated cylinders containing 3 ml* of 0.10 N sodium chloride. Swirl to mix the contents thoroughly. Add to each, 10 ml of 1 M sodium thiosulfate. Swirl to dissolve the precipitate. Add, stopper, and mix 10 ml of 6 N Accelerator Reagent. Add, from a buret, 26.70 ml of the thioacetamide to be standardized to one graduated cylinder and 27.30 ml to the other graduated cylinder. Stopper and shake vigorously 5 seconds. Filter approximately half the contents of each cylinder through a Whatman No. 3 (12.5 cm diameter) filter paper and collect each filtrate in a beaker containing approximately 5 ml of the thioacetamide solution.

The contents of the beaker from the cylinder containing 26.70 ml of the thioacetamide solution should turn color, and the contents of the beaker from the cylinder containing 27.30 ml of the thioacetamide solution should remain clear. If both conditions are met, the thioacetamide solution should be used without modification. If both conditions are not met, see "Adjustment":

Adjustment. If the filtrate was clear when 26.70 ml of the thioacetamide solution was used, the thioacetamide solution is too strong and must be diluted with water. Add 40 ml to what remains of the 2 liters, mix, and retest. Add 40-ml increments of water until the thioacetamide solution tests within the tolerances of 26.70 and 27.30 ml.†

If the filtrate was dark-colored when 27.30 ml of the thioacetamide solution was used, the thioacetamide solution is too weak. Discard it and prepare a new one using 0.73 g of thioacetamide.

WATER-SATURATED ETHYL ACETATE

See Ethyl Acetate.

ZINC SULFATE

50 gl/l $ZnSO_4$

Add and dissolve 89 g of reagent grade zinc sulfate,

* Add 1 milligram (0.001 gram) of mercuric iodide, HgI_2, per liter as a preservative if serious instability is encountered.

* Unless otherwise indicated, use cylinder markings for volume measurements.

† The nominal titration value for 0.00926 N thioacetamide is 27.00 ml. By accepting as limits 26.70 and 27.30 ml, an error of about ±1% is permitted. The sensitivity of the method is such that an increase in precision can be realized by decreasing these tolerances.

$ZnSO_4 \cdot 7H_2O$, (Baker and Adamson, Code 2452) in 800 ml of distilled water and dilute to volume in a 1-liter volumetric flask with distilled water.

$ZnSO_4$—7.0 N H_2SO_4 Reagent

Dissolve 250 g of reagent quality zinc sulfate, $ZnSO_4 \cdot 7H_2O$, in 500 ml of 7.0 N sulfuric acid and dilute to volume in a 1-liter volumetric flask with 7.0 N sulfuric acid.

ANALYTICAL PROCEDURES

ANALYTICAL METHODS FOR CHEMICAL CONTROL

Preface

Chemical analyses of the critical constituents in photographic processing solutions may be used routinely as a basis for discarding a solution or for adjusting the composition of a solution for further use. Examples of the routine use of analyses would include certification of replenisher solutions, start-up and daily tank analyses, and the measurement of silver in fixers. Chemical analyses are also used for determining proper replenisher formulas with their corresponding replenishment rates. The cost of the chemical analyses may be small as compared to the cost of using a substandard processing solution or the cost of process downtime.

All of the analytical methods contained in this section of the manual apply to Process ME-4, Process ECO-3, and Process CRI-1. The serial numbers assigned to the methods may be followed by a letter, A or B, etc, designating that the method is a revision of an earlier method. The first group of procedures is general, in that it applies to general principles and techniques. The page numbers of these methods are prefixed with GP (General Procedures). The second group of procedures is specific, in that it applies to the analyses of specific chemicals. The page numbers of these methods are prefixed with SP (Specific Procedures).

The methods are as short and simple as possible, commensurate with the accuracy and precision that is required for adequate chemical control. The analyses may be made by a trained technician.

Some methods for noncritical constituents are also included in the manual. These may be used as a basis for diagnosing processing troubles as they arise. This manual includes instructions for the preparation of the reagents (see "AR" page series, immediately preceding this section) and a collection of standard analytical practices which are not usually required for routine control. These practices are generally used by the supervisors and by those in charge of the maintenance of analytical equipment, etc.

TABLE OF CONTENTS

GENERAL PROCEDURES

ANALYTICAL REAGENTS FOR CHEMICAL CONTROL (I)

INTRODUCTION

A. Volumes of Reagents

Most of the instructions are written for the preparation of 1-liter quantities, but larger volumes should be prepared if they can be consumed before the reagent expiration date.

B. Volumetric Flask Measurements

Volumetric flasks are to be used only when specified. Approximate volumes can be measured with graduated cylinders.

C. Weight Measurements

When weighing a sample to a specified weight, the tolerance is ±1 unit in the last decimal place to the right. For example, 15.0 grams is understood to mean 15 g ±.1 g and 15.000 grams is understood to mean 15 g ±.001 g.

When the weight of a sample, in grams, is specified to two or more decimal places (e.g., 15.75) an analytical balance is to be used. A torsion balance or a triple-beam balance may be used for weighings which require less accuracy.

D. Water Quality

Use only distilled water in the preparation of standard reagents. Deionized water may be used if data are obtained that indicate reagents prepared with it are satisfactory.

E. Expiration Date

When no expiration date is given, it is implied either that the reagent is stable or that its proposed use is such that a critical concentration is not required.

F. Safety

See "Safe Handling of Color Processing Chemicals" in page series 500.

SEQUENTIAL ANALYSIS FOR STANDARDIZATION OF REAGENTS

A sequential test is one in which, after each analytical determination or standardization of the reagent, the analyst decides to:

1. Accept the reagent as conforming to the specifications, or
2. Alter the reagent concentration by adding water or other chemicals, or
3. Make further analyses to obtain sufficient information so that the reagent concentration may be accepted or altered.

The sequential test terminates according to simple definite rules, that is, when sufficient evidence for a decision has been accumulated. The basis for the plan is described here. A complete description of the plan may be found in *Sequential Analysis of Statistical Data,* Applications, Section V, Columbia University Press, New York, 1945.

A. Satisfactory Quality (Accuracy) Defined (permissible deviation from nominal value)

In order to use the plan it is necessary that "satisfactory" and "unsatisfactory" quality (accuracy) for the standardization of a reagent be defined. The quality (accuracy) of the standardized reagent is hereby defined as being satisfactory if it is equal to the nominal value (e.g., 0.1000 N, 1.000 N, etc) within an allowable tolerance of ±0.6%, 99% of the time. Thus two successive batches will never differ by more than 1.2%, and only one batch in 100 will ever differ from the nominal value by more than 0.6% even though, for convenience, the nominal value is used in all calculations. Thus the value 0.1000 may be used for control purposes even though the true normality may conceivably differ from it by as much as 0.6% (e.g., 0.1006 rather than 0.1000 N).

B. Precision (Repeatability) Requirement

The sequential plan is based on the use of the recommended methods, equipment, etc, and the ability of the analyst to replicate his standardizations well enough so that the standard deviation does not exceed 0.2% of the nominal normality. Rather than actually calculating the standard deviation from a series of successive standardizations, conformance to this precision requirement may be approximated sufficiently well by obtaining the range of the standardizations. The maximum permissible ranges between the highest and lowest values obtained in a series of replications are shown in Table I.

TABLE I

MAXIMUM PERMISSIBLE RANGE OF NORMALITIES OF REPLICATE STANDARDIZATIONS

Cumulative Number of Standardizations	0.0500 N Reagent	0.1000 N Reagent	1.000 N Reagent	2.500 N Reagent	General Case (% Nominal Value)
2	0.00035	0.0007	0.007	0.0175	0.7
3	.00040	.0008	.008	.0200	0.8
4	.00045	.0009	.009	.0225	0.9
5	.00045	.0009	.009	.0225	0.9
6	.00050	.0010	.010	.0250	1.0

If the range of the standardizations does not fall within these values, the assignable cause for the "excessive" variability should be sought and corrected. Unless the range conforms to Table I, the "out-of-control" values are useless for deciding whether the normality of the reagent is within the defined satisfactory limits. A careful analyst, well trained in the standardization procedures, should have no difficulty in obtaining results within the relatively broad tolerances.

C. The Risk of Accepting an Out-of-Specification Reagent

The sequential plan is also based upon a risk of accepting an out-of-tolerance reagent as being within tolerance. The risk is hereby set at 1% probability (0.01), or once in a hundred times an out-of-tolerance reagent is unknowingly accepted.

D. Risk of Adjusting a Within-Tolerance Reagent

There also exists the risk of adjusting, once in ten times, a reagent that is actually already within tolerance. This risk is set at a relatively large value because the magnitude does not determine the quality of the final product, since after retesting, the reagent is not used. Of course, the larger the percentage risk value that is assigned, the more costly the control because of the extra standardization, etc. Thus the 10% value was decided upon after considering economic factors.

E. Maximum Number of Standardizations

It is conceivable that a great number of replicates would be necessary before a decision is made. In order to avoid this, action is arbitrarily forced at the end of the sixth determination.

F. The Sequential Plan in Graphical Form

The foregoing plan covering:

a. Acceptable quality (accuracy)
b. Precision
c. Accepted risks, and
d. The limit on maximum number of standardizations

has been incorporated into a graphic form. This form can be used by an analyst who is responsible for the standardization of reagents. When he has completed two or more standardizations, the cumulative differences between each normality found, X_i, and the nominal value, M, are plotted for the appropriate replication number. The decision as to whether to accept, adjust, or to reanalyze is dependent upon whether the point plots below, above, or between the two diagonal parallel lines shown in the graph. See Figure 1. In the general case, the values on the ordinate are expressed as percentage of the nominal value. In specific cases, only the absolute values need be plotted; e.g., in case of 0.1000 N reagent when $|\Sigma (X_i - M)| = 0.0004$, this need not be converted to percentage as it was in the general case,

$$\frac{(0.0004)}{0.1000}(100) = 0.4\%$$

The three concentrations (0.0500, 0.1000, and 1.000 N) used most commonly in control laboratories are shown in Figure 1. The examples plotted are described later.

The two diagonal parallel lines on each graph are joined together because of the practical decision to never make more than six standardizations in order to decide whether to accept or adjust the solution.

If some concentration of reagent other than 0.05, 0.1, or 1.0 N is to be standardized, calculate the range of the values to be plotted in the ordinate, $|\Sigma (X_i - M)|$. The ordinate values will be proportional to the nominal values as may be noted on the three graphs in Figure 1.

The diagonal parallel lines are then constructed, again using the graphs for guidance. The parallel lines on each figure are then connected by drawing a horizontal line to the intersection of the lower parallel line with cumulative No. 6.

G. Procedure for Analyst

1. Run duplicate analyses for the standardization of the reagent and express results as normality.
2. Determine the range of the duplicates.
3. Refer to either Table I or Figure 1 to determine whether the duplicates are within the permissible range.

a. If *not within* the permissible range, search for assignable causes for the excessive variation. If the cause cannot be found and corrected, discard both values and repeat the standardizations until the resulting range is within the permissible range. (This plan does not apply to data with variability in excess of that indicated by the range limits.)

b. If *within* the acceptable limit, subtract the nominal value from each of the two values.

4. Add the two differences algebraically (take the sign of each value into account). (The sign of this sum, $|\Sigma (X_i - M)|$, is disregarded.)
5. Note in which of the three areas the point would plot and decide the next step accordingly.

a. If the point falls *above* the "adjust" line, reject the reagent. Adjust the concentration by adding either water or the chemical, basing all calculations on the average of the duplicates just obtained.

b. If the point falls below the "accept" line, accept the reagent as having the nominal value within tolerance.

c. If the point falls on or between the limit lines, restandardize the reagent.

6. If a third standardization is required, make the same type of calculations as above; i.e., determine the range of the three standardizations, and check for the conformance to Table I. If the range is within tolerance,

a. Determine the difference between the new (third) analysis and the nominal value;

b. Add this difference $(X_i - M)$ to the two preceding differences, taking into account the sign; and

c. Note in which of the three areas the sum of these values $\Sigma (X_i - M)$ would fall if plotted above the No. 3 (cumulative number of analyses) on the graph.

7. Again decide from the location of this point the next step. Accept the reagent, adjust the reagent, or continue testing. If more standardizations are required, proceed as above.

H. Example of Standardization of 0.1000 N NaOH

A 40-liter solution of approximately 0.1 N NaOH was prepared for standardization against potassium acid phthalate. The successive steps in the standardization are described here, keying the step numbers to the corresponding steps of Section G (Procedure for Analyst). The data are plotted in Figure 1, Example A, and tabulated in Table II.

1. Duplicate analyses (standardizations) were run and the normalities were calculated.

X_i (Standardization No. 1) = .1005 N
X_i (Standardization No. 2) = .1000 N

2. Range of duplicates is .0005.

TABLE II

EXAMPLE A (SEE FIGURE 1) OF STANDARDIZATION OF 0.1N NaOH

Replication No.	Normality Found (X_i)	Nominal Value (M)	X_i-M	$\Sigma (X_i-M)$	Action
1	.1005	.1000	+.0005		Restandardize
2	.1000*	.1000	+.0000	+.0005†	Restandardize
3	.1003*	.1000	+.0003	+.0008†	Restandardize
4	.1005*	.1000	+.0005	+.0013†	Restandardize
5	.1005*	.1000	+.0005	+.0018†	Adjust Reagent

* After each of these successive replications, it is noted that the range of the replications is within the maximum permissible range as listed in Table I and Figure 1.

† Ignore the sign when plotting.

3. From Table I, the maximum range of two standardizations when the nominal value is 0.1000 N is .0007. Since the normalities for standardizations No. 1 and 2 were within the permissible range, the nominal value was subtracted from each normality found.

$$X_i-M \text{ (No. 1)} = .1005 - .1000 = + .0005$$
$$X_i-M \text{ (No. 2)} = .1000 - .1000 = + .0000$$

4. +.0005 and +.0000 were added algebraically to make +.0005, $\Sigma (X_i-M)$; and .0005 was plotted above cumulative No. 2 in Example A, Figure 1. (If this value had been negative, it would nonetheless have been plotted as .0005, ignoring the sign.)

5. The point fell between the two limit lines indicating the need for a restandardization. (In practice the point need not be plotted. The graph would be referred to in order to decide the next step.)

6. X_i (Standardization No. 3) = .1003 N

The range of all three standardizations was .0005 which was less than the critical value, .0008 in Table I.

a. $(X_i-M) = .1003 - .1000 = + .0003$

b. $\Sigma (X_i-M) = + .0005$ (difference No. 1) + .0000 (difference No. 2) + .0003 (difference No. 3) = + .0008

c. plotted .0008 above the cumulative No. 3

7. The point fell between the two parallel lines indicating the need for a restandardization.

The fourth standardization, $|\Sigma (X_i-M)| = 0.0013$, indicated a further reanalysis was necessary.

The fifth standardization, $|\Sigma (X_i-M)| = 0.0018$, produced a point in the "adjust" section.

The concentration of the reagent was adjusted on the basis of the average normality (0.1004) obtained in the five standardizations. It is noted that the decision is to adjust the reagent even though the average of the five replications, 0.1004, was within the ±0.6% allowed tolerance as defined in paragraph A. The decision to adjust is because of the other aspects of quality which are incorporated in the sequential plan.

I. Adjustment of Concentration and Restandardization

For this illustration it is assumed that 200 ml of the reagent was consumed in the above titrations (Section H). The amount of water that is needed to reduce the normality from 0.1004 to 0.1000 N is calculated as follows:

$$(40,000-200)(0.1004) = (\text{final volume})(0.1000)$$

$$\text{final volume} = \frac{(39,800)(0.1004)}{0.1000} = 39,959 \text{ ml}$$

39,959 — 39,800 = 159 ml of water to be added. This amount was added, and the solution stirred thoroughly and retested. The data and action taken are shown in Table III and Example B of Figure 1.

TABLE III

EXAMPLE B (SEE FIGURE 1) OF STANDARDIZATION OF 0.1N NaOH AFTER ADJUSTMENT OF ITS CONCENTRATION

Replication No.	Normality Found (X_i)	Nominal Value (M)	X_i-M	$\Sigma (X_i-M)$	Action
1	.0999	.1000	−.0001	–	
2	.0997*	.1000	−.0003	−.0004†	Restandardize
3	.1002*	.1000	+.0002	−.0002†	Accept Reagent

* After each of these successive replications, it is noted that the range of the replications is within the maximum permissible range as listed in Table I and Figure 1.

† Ignore the sign when plotting.

J. Example of Standardization of 0.1000 N NaOH (Below Lower Tolerance)

A 40-liter solution of approximately 0.1 N sodium hydroxide is prepared and standardized as above. The average normality obtained from two successive analyses is 0.0990 N. The standardizations consumed 200 ml of solution. In this case, where the average of the determinations is lower than the nominal value, more sodium hydroxide is added to the solution. The amount necessary to raise the normality from 0.0990 N (average normality) to 0.1000 N (nominal normality) is calculated as follows:

$$\begin{pmatrix}\text{nominal}\\ \text{normality}\end{pmatrix} - \begin{pmatrix}\text{average}\\ \text{normality}\end{pmatrix} \begin{pmatrix}\text{liters of}\\ \text{solution}\end{pmatrix} \begin{pmatrix}\text{eq wt}\\ \text{of reagent}\end{pmatrix} = \begin{matrix}\text{grams NaOH}\\ \text{to be added}\end{matrix}$$

$$(0.1000 - 0.0990)(39.800)(40) = 1.6 \text{ g NaOH}$$

This amount of sodium hydroxide is added; the solution is added; the solution is stirred thoroughly and retested.

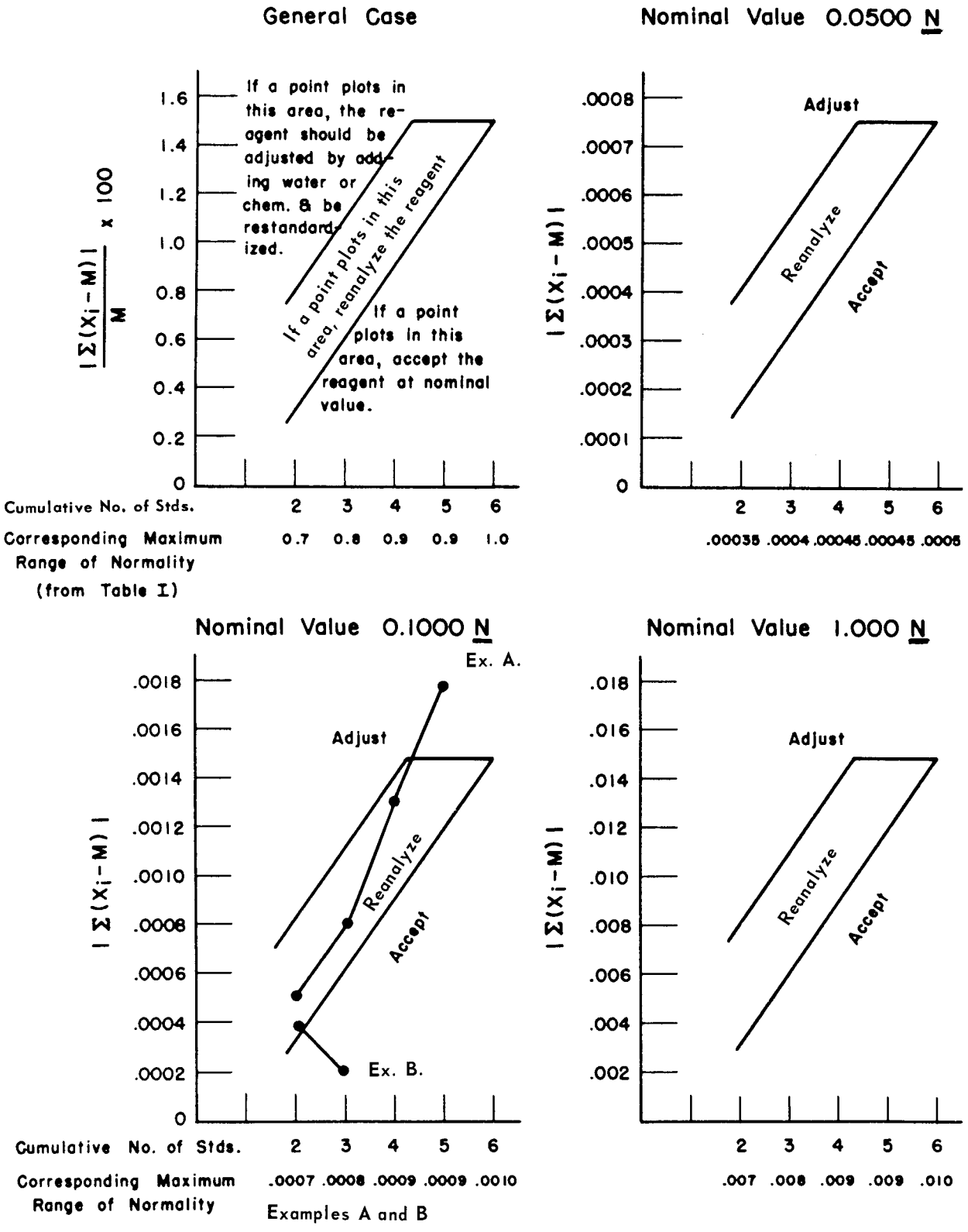

General Case
Nominal Value 0.0500 N
$\frac{|\Sigma(X_i - M)|}{M} \times 100$
If a point plots in this area, the reagent should be adjusted by adding water or chem. & be restandardized.
If a point plots in this area, reanalyze the reagent
If a point plots in this area, accept the reagent at nominal value.
Adjust
Reanalyze
Accept
$|\Sigma(X_i - M)|$
Cumulative No. of Stds.
Corresponding Maximum Range of Normality (from Table I)
Nominal Value 0.1000 N
Nominal Value 1.000 N
Ex. A.
Ex. B.
Examples A and B

FIGURE 1

THE SELECTION, CARE, AND USE OF VOLUMETRIC GLASSWARE AND WEIGHING EQUIPMENT (III)

VOLUMETRIC MEASURING EQUIPMENT

A. Introduction

The standard unit of volume in the metric system is the liter. It is defined as the volume occupied by the mass of one kilogram of water at its temperature of maximum density and under normal atmospheric pressure. On this basis, one liter is equal to 1.000028 cubic decimeters and one milliliter (1/1000 of a liter) equals 1.000028 cubic centimeters. Milliliters and cubic centimeters, therefore, are not synonymous but the difference between them is too small to be of consequence in most technical work. Volumetric glassware is calibrated in terms of liters or milliliters (ml) and not in terms of cubic centimeters.

A volumetric determination can be no better than the equipment and technique used in performing it. For that reason, those who make volumetric analyses should be familiar with the possible source of error in both the equipment and the technique of using it.

B. Selection and Tolerances

The volumetric glassware used must have adequate accuracy to avoid introducing a significant error to the analytical result. If a volume of solution is critical in an analytical procedure, pipets, burets, or volumetric flasks of high accuracy must be used. Other steps may require the measurement of only an approximate volume; thus either a graduated cylinder or a "tip-up-pipet" can be used.

The National Bureau of Standards Circular 602 has specified tolerances for volumetric glassware that meets the most precise requirements of the analytical procedures used in the control of photographic processing. This equipment is designated in Federal Specification DD-V-581 as "Class A." Glassware certified to meet these specifications is available from most manufacturers of laboratory glassware. The required tolerances are given in Table I.

C. Care of Volumetric Glassware

1. Cleaning Solutions. A piece of glass apparatus is not sufficiently clean unless its surface is uniformly wetted by distilled water. Grease prevents the glass walls from being uniformly wetted, causing drainage to be uneven and delivery not precise. To keep volumetric glassware scrupulously clean and free from grease, three types of cleaning solutions are recommended. These solutions are used undiluted and may be reused until no longer effective. Do not draw any of these cleaning solutions into pipets or burets by mouth. Use a rubber bulb.

a. Types

(1) Detergent—A Naccanol solution containing 50—100 grams per liter of Naccanol (Naccanol N.R. can be obtained from the National Aniline Company in Buffalo, N.Y.). This is a very effective material for most cleaning problems encountered. It is nontoxic and noncorrosive. Other detergents comparable to Naccanol may be used.

(2) Sulfuric-Dichromate—A solution of sodium dichromate ($Na_2Cr_2O_7$) in concentrated sulfuric acid (H_2SO_4) is most effective against grease. It is also the most dangerous because of its strong acid, oxidizing, and dehydrating properties.

Add about 30 grams of sodium dichromate to one liter of concentrated sulfuric acid. Technical grade is satisfactory, and the exact concentration of sodium dichromate is not important. After stirring the mixture a few minutes, decant the clear liquid from any sediment that may clog buret or pipet tips during cleaning.

The solution will become green as it loses its usefulness as a cleaning agent and should be discarded.

(3) Acid-Alcohol—A solution of one volume of 3 N hydrochloric acid (HCl) added to one volume of methyl alcohol is effective in removing cyan stains and in cleaning spectrophotometer cells.

> CAUTION: Do not mix this solution in a closed container. The heat produced may cause a dangerous increase in pressure.

b. Safety

When mixing and handling the sulfuric-dichromate or acid-alcohol cleaning solutions, wear rubber gloves and safety goggles and observe the other safety precautions for handling concentrated acids. Never add water to sulfuric-dichromate solution in a container because excessive heat and steam are likely to spatter the hot acid.

If acid is spilled on the skin or clothing or splashed into the eyes, flush the affected parts with a large amount of water. The water will dilute the acid, and wash it away. Secure competent medical treatment immediately.

2. Cleaning and Storing Glassware. Rinse glassware thoroughly with water before washing it with the cleaning solution. The cleaning solutions are best stored and used in polyethylene containers. Pipet jars, being tubular, are excellent for soaking and storing pipets and burets.

After treatment with a cleaning solution, the glassware should be thoroughly rinsed inside and out with distilled water. For reasons of economy ordinary tap water may be used for the preliminary rinsing, reserving the distilled water for the final rinsing. If water droplets adhere to the inside walls of the glassware after 1 minute of draining, it is not sufficiently clean. Only an unbroken film of water should remain.

Burets and pipets should drain in a vertical position. Volumetric flasks are inverted with the bottom at a slight angle from the horizontal, so that drops on the bottom will drain away.

If burets and pipets are clean, they generally do not have to be dried before being used with standard solutions. The slight amount of water which remains after rinsing and draining is removed by rinsing two or three times with small amounts of the solution to be used, allowing the buret or pipet to drain completely between rinses. If it is necessary to have volumetric vessels dry, a gentle stream of clean air can be

used. Acetone should not be used as a drying agent because trace amounts left in glassware cause unwanted absorption in spectrophotometric methods of analysis.

3. CAUTION: Heating Glassware. At no time should any piece of volumetric glassware be heated or rinsed with hot water. If heated above room temperature, the equipment may no longer be within the specified tolerance because such heating may cause a permanent change in volume.

D. Use of Volumetric Glassware

1. General Instructions

a. Effects of Temperature on Glassware and Solutions

(1) Glassware

The temperature at which volumetric vessels are calibrated is 20 C (68 F). For the greatest precision and accuracy all measurements should be made at this temperature. Since this condition may not be practicable, it is important to consider the magnitude of the errors introduced into volumetric procedures by using standard solutions at temperatures other than 20 C (68 F).

The change in *capacity* of glass volumetric apparatus with temperature is, at the most, only 1 part in 10,000 for each 5 C (9 F) change in temperature in the region of 20 C (68 F). This source of error generally may be disregarded.

(2) Solutions

Whereas the change in capacity of *glassware* with temperature generally may be disregarded, it is not to be confused with the change in volume of a *solution* with temperature. The effect of temperature on volume is shown in Table II. To attain accuracy of approximately 0.1% it is necessary that the solution be at 20 ±2 C (68 ±4 F) when measured.

The change in *concentration* of standard solutions is also affected by temperature. It may become of such magnitude as to introduce appreciable errors. In general, the more concentrated the solution, the more serious is the change. The coefficient of expansion of dilute aqueous solutions of different electrolytes is practically the same for similar concentrations; hence the values given in Table II serve as a general index of their behavior.

b. Meniscus

In the use of graduated cylinders, pipets, burets, and flasks, the lowest point of the meniscus should be taken as the reading. See Figures 1 and 2. Opaque solutions, however, must be measured by reading at the top of the meniscus. Another special case is the determination of specific gravity. The top of the meniscus is read because the hydrometer is calibrated on that basis.

In observing the lowest point of the meniscus it is very important that the line of vision be in the same horizontal plane as the bottom of the meniscus. This is easily ascertained if the graduations on the glassware extend at least halfway around the tube. The eye is correctly positioned when both front and back portions of the graduation coincide (Figures 1 and 2).

The meniscus may be seen more clearly if a small white card with a rectangular black patch is held behind the meniscus. Raise or lower the card until the bottom of the meniscus is clearly outlined (Figure 3).

2. Pipets. Most pipets are graduated to deliver (T.D.) known volumes of distilled water (not solutions of markedly different viscosity than water). The volume delivered will be within the tolerances for that pipet, provided it is used in accordance with the proper technique. The amount of liquid retained on the inside wall of a pipet depends in part upon the delivery time of the pipet. Class A pipets are required. See Table I for tolerances.

It is important that the analyst understand and practice the following instructions on the use of pipets:

a. Cleanliness—Use a clean pipet. The pipet does not have to be dry but must be perfectly clean and free from grease so that drops of the solution will not adhere to the walls causing the pipet to deliver less than the rated volume. Any contaminant may affect the results.

b. Perfect Tip—Use a pipet with a perfect tip. A pipet with a broken or chipped tip must be discarded since it will deliver a volume other than the rated volume when the tip is touched against the wall of the receiving vessel.

c. Rinsing—With one hand holding the pipet and the other hand holding a rubber bulb, squeeze the bulb, place it over the upper end of the pipet and release slowly. Draw a small portion of the solution into the pipet, i.e., about 20% of the volume of the pipet; then remove the bulb and cap the pipet with the forefinger. See Figure 4. Place the pipet in a horizontal position, and rotate it permitting the solution to wet the walls to a point about 2 inches above the calibration mark. Do not permit the top of the mouthpiece to become contaminated with solution, which in turn may contaminate the bulb. Discharge the solution through the tip, and repeat the rinsing with another portion of the solution.

> NOTE: If the solution being pipetted is a standardized reagent, the reagent is drawn into the pipet from a clean beaker which was rinsed once with reagent. To prevent contamination of the reagent, the pipet should not be placed into the stock bottle.

d. Filling—Using a bulb, draw the solution into the pipet to a point about 1 inch above the calibration mark; then remove the bulb and cap the pipet with the forefinger.

e. Wiping Outside—Before adjusting the liquid level to the mark, wipe off the drops adhering to the outside with a paper cleansing tissue. This prevents droplets on the outside from draining into the receiving vessel and affecting the results.

f. Lowering Meniscus to Mark—Hold the pipet in a vertical position at eye level over a waste container. Touch the tip of the pipet against the wall of the container. Hold the waste container at approximately a 30° angle so that the outflowing liquid makes continuous contact with the container. Carefully lower the meniscus to the mark. See Figure 5.

g. Movement of Pipet to Receiving Vessel—Carefully move pipet to the receiving vessel, avoiding rapid vertical

motion which might dispense part of the solution prior to reaching the receiving vessel.

h. Delivery—Keeping the pipet in a vertical position, place the tip against the wall of the receiving vessel (at approximately a 30° angle) just above the surface of the liquid; then remove the forefinger. Allow to drain at a vertical position until the continuous outflow ceases; then remove the pipet. A small amount of the solution will, and should, remain in the tip of the pipet. Do not blow it out.

i. Cleaning—If after usage a pipet has a film of liquid in it, not droplets of liquid, it may be reused immediately with the same solution without being cleaned in a cleaning solution. Merely rinse it with the solution to be pipetted. It is not necessary to rinse it with distilled water just prior to rinsing with the sample to be pipetted. However, if droplets of liquid are adhering to the inner surface of the pipet or if it is colored, it should be rinsed with a cleaning solution, then rinsed inside and out with tap water and flushed with distilled water for approximately 5 seconds. If drops of water remain in the pipet, it is contaminated and must be treated again with cleaning solution.

Store pipets in racks in a vertical position. Pipets must be recleaned immediately before use if allowed to stand more than an hour under ordinary conditions of air contamination.

3. Graduated Cylinders and Tip-up Pipets. In many cases the volume of a solution to be used in an analytical method need be only an approximation of the specified volume. For example, the method may prescribe 20 ml of a reagent whereas only slightly more than 15 ml would suffice. In these cases, graduated cylinders or tip-up pipets are used. Graduated cylinders are calibrated to deliver (T.D.) or to contain (T.C.). See Table I for tolerances. Tip-up pipets require less time for operation and are, therefore, preferable.

A portable tip-up pipet, shown in Figure 6, is available in different sizes. They may be purchased with either standard taper, ground glass, male joints, or for use with rubber stoppers. It is suggested that Erlenmeyer flasks of 250, 500, or 1000-ml capacity be selected with the ground glass joint to match. Tip-up pipets and flasks can be obtained from VWR Scientific, Rochester, N.Y. This glassware has the accuracy of a graduated cylinder.

4. Burets. Burets are graduated to deliver variable known volumes of liquids. Methods are generally developed to employ 30 to 50 ml of solution as measured from a buret. For such purposes, a 50-ml capacity buret is used. In those cases in which 10 to 20 ml of solution are measured from a buret, a 15 or 25-ml buret is used. Class A burets are required. See Table I for tolerances. Analysts should understand and apply the following specific instructions for the use of burets:

a. Cleanliness—Use a clean buret. The buret does not have to be dry before rinsing it with the solution to be used. If the buret is not perfectly clean, drops of the solution will adhere to the walls, and the buret will deliver less than the indicated volume. Furthermore, the contaminants (dirt) may affect the results.

b. Perfect Tip—Use a buret with a good tip. A buret with a broken tip may deliver a volume other than the rated volume when the tip is touched against the wall of the receiving vessel. A buret with a broken or chipped tip sometimes can be fire-polished and salvaged.

c. Stopcock Seal—Use a buret which will hold a constant reading for at least 5 minutes. If the stopcock seal is defective, the solution will leak and thus lower the buret reading. Teflon stopcocks do not require grease, and are preferred.

d. Rinsing—Rinse the entire inner surface of the buret two or three times with portions of the solution to be used.

e. Lowering Meniscus to the Zero Mark—Fill the buret well above the zero mark. With the buret zero mark at eye level, lower the meniscus to the zero mark. Allow a minute or two for drainage; then make the initial reading, or readjust the buret precisely to the zero mark. During the waiting period, check for leaks and make certain that air bubbles are expelled either at the top (or from the tip). After the meniscus has been adjusted, remove the final drop by touching the tip with the wall of a waste-solution beaker which is kept under the buret *except* during titration. One-second contact is adequate.

f. Position—The buret should be clamped in a vertical position during the readings and while the solution is being titrated.

g. Titration—After the initial reading is made and the final drop removed, the standard solution is added to the titration vessel with constant swirling. See Figure 7 for the proper way to turn a stopcock. As the end point is approached, the rate of addition is decreased, until finally the titrant is added dropwise or as split drops. At this point, tilt the vessel and remove each drop by touching the tip with the walls of the vessel at a level just above the surface of the liquid. Tilt the vessel slightly more to rinse in the drop. Generally, the end point is defined as a specified color change that persists for at least 15 seconds. When the end point has been reached, there should be no final drop to remove. *Exception:* For increased ease when titrating with a potentiometer or a pH meter, it is recommended that the tip of the buret be immersed in the liquid. There may be other exceptions that require a decision by the laboratory supervisor.

If an end point is not sharp, or if it is unfamiliar, it may be difficult to decide when the end point has been reached. In such case, record the buret reading after each drop as the end point is approached. Continue this procedure until the specified color change has occurred.

h. Drainage Error—Unless the titration to the end point has been slow and gradual, wait 30 seconds before taking the final reading of the meniscus, so that the effects of further drainage will be negligible. Read meniscus at eye level.

i. Cleaning Buret—Clean the buret with cleaning solution. Prevent the concentrated cleaning solution from coming into contact with the stopcock lubricant. A convenient way to clean burets without removing any of the stopcock lubricant is to invert them in a pipet jar containing enough cleaning solution to fill the buret to the stopcock. After a few minutes, rinse

inside and out with tap water; then rinse three times with small quantities of distilled water. Store in a vertical position.

j. Capping—Capping the buret with an inverted test tube will aid in preventing evaporation of the solution and contamination by dust. If the solution is not alkaline and does not contain fluorides or phosphates in acid solution, it is generally safe to allow the solution to stand in the buret. A full buret will stay clean longer than a dry or partially filled buret.

k. Greasing Stopcock (glass stopcocks)—If the stopcock sticks or leaks, remove the old lubricant by wiping with a cloth, using a solvent if desired. Replace with fresh lubricant. Both high-vacuum "Lubriseal"* and Dow Corning silicone stopcock grease† have been found adequate in this application. Apply only a thin film since too much lubricant may plug the hole. Unless the parts of the stopcock are dry before lubricating and sealing the plug, the seal may be defective. Teflon stopcocks are not to be greased.

l. Offset Tip—A buret with an offset tip is useful when titrating with a potentiometer or when the apparatus is crowded into a small space.

m. Plugged Tip—Occasionally a buret tip becomes plugged with a small amount of lubricant. The plug can be expelled in the following manner: Open the stopcock so that the pressure of the liquid column is on the plugged tip. Insert the tip in a beaker of warm water. If this treatment does not dissolve the plug, it will be necessary to disassemble the stopcock and thoroughly clean the buret with cleaning solution, after which the stopcock must be relubricated. In certain instances the use of a thin wire probe (pipet probe), sold in vials of 50 by most laboratory supply houses, is a satisfactory means of unplugging buret tips.

5. Volumetric Flasks. Volumetric flasks are generally graduated "to contain" (T.C.) known volumes of solutions and should never be used "to deliver" (T.D.) known volumes unless they have been so calibrated. Volumetric flasks are used to make up solutions to a given volume. Use Class A. See Table I for tolerances.

Analysts should understand and practice the following instructions for the use of volumetric flasks.

a. Safety—Volumetric flasks are fragile and, when shaken, should be held at both the neck and the bottom. A flask should never be shaken when held at the neck only. When inserting a stopper, hold at the neck rather than at the bottom.

b. Cleanliness—Use a clean flask. It usually does not have to be dry, but it must be clean. Rinse the entire interior of the flask two or three times with distilled water prior to use.

c. Diluting to Volume—Add the solution to be diluted into the flask, and add distilled water or specified diluent to bring to volume. While raising the meniscus to the graduation mark, hold the mark at eye level, and add the last few drops from a wash bottle or from a small pipet. Stopper and invert 6 to 12 times to achieve homogeneity.

Care should be taken when making the initial inversion. Some solutions have a tendency to effervesce, and loss of the solution may result if the stopper is not held firmly in place. If such is the characteristic of the solution being mixed, a momentary removal of the stopper (flask in an upright position) prior to the second inversion will release the gas pressure formed and avoid possible loss.

d. Cleaning and Storing—Clean the flask with a cleaning solution. It is not necessary to fill the volumetric flask with cleaning solution. If a generous portion is placed in the flask and the flask is stoppered, cleaning will be accomplished if the flask is shaken and inverted several times so as to keep the walls moistened with cleaning solution. After a thorough rinse inside and out with tap water, rinse 3 times with small quantities of distilled water. Store in an inverted position with the bottom slightly inclined. If the bottom is horizontal, the flask may not drain completely.

WEIGHING EQUIPMENT

A. Selection

When making analytical reagents or standard laboratory mixes, it is necessary to weigh the various constituents. Thus it is evident that the weighing operation is of fundamental importance.

If the weight of the chemical is specified in grams to two or more digits to the right of the decimal, e.g., 15.73, use an analytical balance and Class S weights. Do not use an analytical balance to weigh amounts greater than 150 grams.

A torsion balance and metric Class C weights are satisfactory for weighings from 0.1 to 100 grams, provided an accuracy of ±0.1 gram is sufficient. For measuring larger amounts than 100 grams, if the weight is not critical, a "trip" or "triple-beam" balance is adequate.

B. Care and Use of the Analytical Balance

1. Weighing Area. If possible, the balance should be kept in a room separate from the laboratory. It should be kept at a reasonably constant temperature and out of direct sunlight and air currents. The balance should be level, and it should be placed upon a solid support to protect it from vibration.

2. Protection of Knife Edges. To prevent injury to the agate knife edges and planes when the balance is not in use, the beam should be raised and the pan supports should be up. Nothing should be left on the pans. The door of the case should be closed. When weighing, raise the beam and arrest the pans before placing any object on the pans. To test for equilibrium, lower the beam and then release the pans. Before removing any object or weight from the pans, they must be arrested and the beam raised.

3. Protection of Pans. Never weigh chemicals directly on the pans since they may injure the pans. Never weigh chemicals on paper in an analytical balance. Weighing bottles, watch glasses, or aluminum laboratory dishes may be used as containers for weighing. The latter may be obtained from most laboratory supply houses. They should be used and then discarded.

* Available from Arthur H. Thomas Co., 254-60 N. 3rd St., Philadelphia, Pa. 19106.

† Available from Dow Corning Corp., S. Saginaw Rd., Midland, Mich. 48640

CAUTION: Sodium hydroxide should not be weighed in an aluminum dish.

4. Temperature. Objects to be weighed should be at room temperature. Differences in temperature will cause air currents which lead to errors in weighing.

5. Rest Point. Determine the zero rest point at each sitting.

6. Maximum Load. Do not overload the balance. The maximum capacity is 150 grams.

7. Cleanliness. Keep the balance clean. If any chemical is spilled, clean it up at once. Do not use liquids for cleaning the pans. Use a balance brush.

C. Care and Use of the Weights

Handle Class S weights only with forceps, preferably bone-tipped. To counterbalance an object try the large weights first, and then the smaller in systematic order. Always use the least number of weights possible, e.g., a 3 gram weight in preference to a 1 and a 2 gram weight. To avoid oscillation, place large weights in the center of the pan. Use great care to avoid dropping weights. Always doublecheck the result of a weighing by adding the values implied by the empty compartments in the box of weights and then recording immediately in a notebook.

TABLE I.
REQUIRED TOLERANCE FOR VOLUMETRIC GLASSWARE

	Tolerance of Glassware, ml			
Capacity, ml	Pipets, Vol. (Class A) TD*	Graduated Cylinders TD*	Burets (Class A) TD*	Volumetric Flasks (Class A) TC†
1	±0.006	± 0.1		±0.01
2	0.006			0.015
3	0.01			0.015
4	0.01			
5	0.01			0.02
10	0.02	0.1	±0.02	0.02
15	0.03			
20	0.03			
25	0.03	0.3	0.03	0.03
50	0.05	0.4	0.05	0.05
100	0.08	0.6	0.10	0.08
200	0.10	1.4		0.10
250		1.4		0.12
500		2.6		0.15
1000		5.0		0.30
2000		10.0		0.50
4000		50.0		

Suggested supplier:
Kimble Glass Co.
Div. of Owens-Illinois Glass Co.
22 S. Park Street
Montclair, N.J. 07042

Kimble Catalog No.	37010	20024	17027 or 17027F	28017A‡ 28014§

* Calibrated to deliver
† Calibrated to contain
‡ 1-ml to 3-ml
§ 5-ml to 2000-ml

TABLE II.
EFFECT OF TEMPERATURE UPON SOLUTIONS

	Volumes (ml) Occupied At				
Solution Composition	15 C (59 F)	20 C (68 F)	25 C (77 F)	30 C (86 F)	35 C (95 F)
1.0 N HCl	996.7	1000.0	1001.3	1002.8	1004.7
0.1 N HCl	997.1	1000.0	1001.2	1002.6	1003.8
Water	999.1	1000.0	1001.1	1002.5	1004.2

Reference: Fales and Kenney, "Inorganic Quantitative Analysis" (1940)

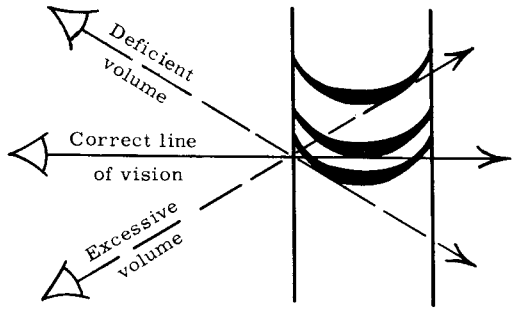


FIGURE 1 Reading the meniscus in pipet or volumetric flask

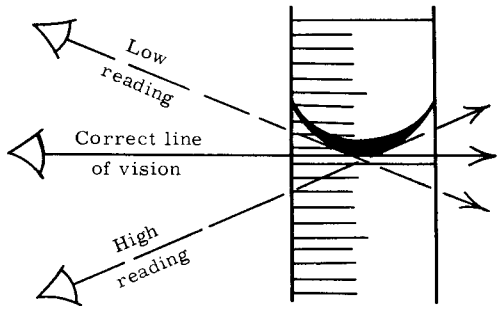


FIGURE 2 Reading the meniscus on buret

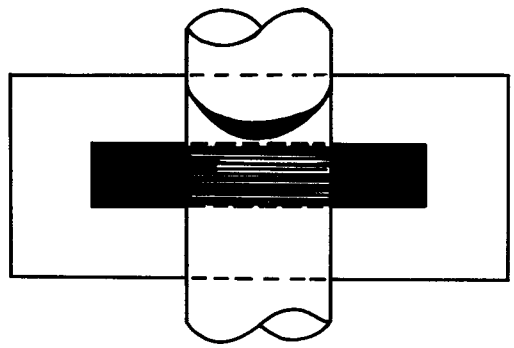


FIGURE 3 Outlining the meniscus

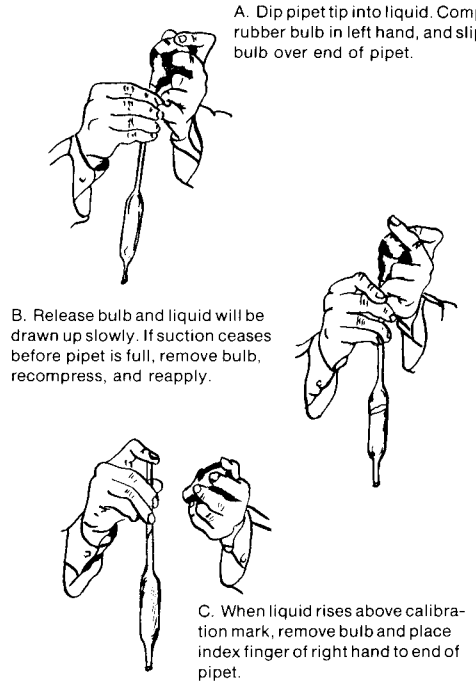


FIGURE 4 How to use a rubber bulb for pipeting

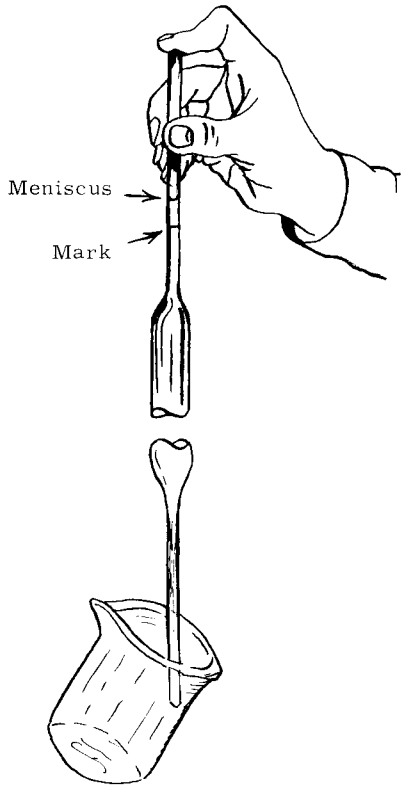


FIGURE 5 Lowering meniscus to mark

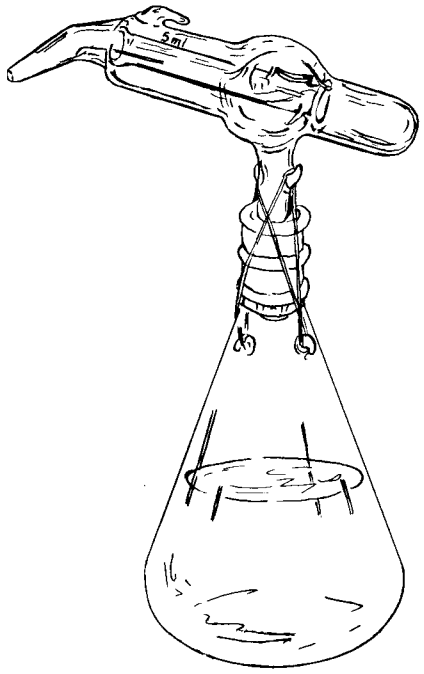


FIGURE 6 Tip-up pipet

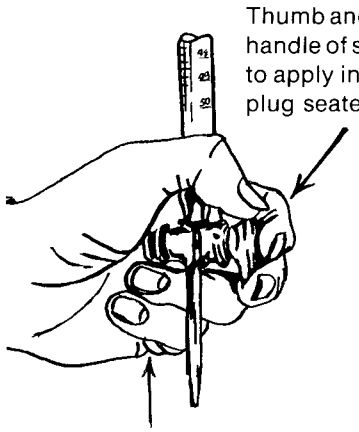


FIGURE 7 How to turn a stopcock

OPERATING INSTRUCTIONS FOR THE BECKMAN DU SPECTROPHOTOMETER (VI E)

INTRODUCTION

The methods contained in this manual specify the use of the Beckman DU spectrophotometer and a 1.00-cm silica cell with a density at 270 nm of 0.039 ±0.005 when filled with distilled water. The Beckman part number for this cell is 75170. If another spectrophotometer or cell is used, the calculation equations in the analytical methods may not apply.

A daily cell check is run using distilled water of high purity. A solution containing 26.4 mg/l potassium chromate in 0.05 M sodium monohydrogen phosphate is used daily to control and evaluate spectrophotometer performance. The absorbance measurement and the slit width used in obtaining the measurement are recorded either as a graph or table. While the average absorbances in Tables II and III are not necessarily accurate, they serve as useful control levels, especially with analyses that use precalibrated equations in the calculations. The optimal slit width at a given wavelength varies widely among spectrophotometers; however, a daily record of slit width provides a good relative measure of a spectrophotometer's performance for maintenance purposes.

The spectrophotometer is balanced against an air blank. The resulting absorbance measurement of the solution in the silica cell is due to the absorbance of both the solution and the cell. Only in certain methods, which involve the measurement of a blank, will the cell absorbance be canceled out.

The Beckman DU spectrophotometer can be fitted with either a hydrogen or deuterium or a tungsten lamp. The hydrogen or deuterium lamp is used to make measurements at wavelengths between 220 and 350 nm and the tungsten lamp between 320 and 1000 nm.

APPARATUS

1-cm Silica cell (Beckman Part No. 75170)
Cell holder (Beckman Part No. 100100)

REAGENTS

High-purity distilled water

NOTE: This water should contact only nonrusting metals, such as aluminum, stainless steel, or tin. Rubber or plastic tubing can lead to serious contamination. If such tubing is used to connect pieces of apparatus, the lengths of tubing should be as short as possible.

26.4 mg/l Potassium Chromate in 0.05 M Sodium Monohydrogen Phosphate

Acid-Alcohol cleaning solution

PROCEDURE

A. Preparing Instrument for Operation

NOTE: If the instrument is battery powered, the power supply should remain on. The charging rate should be the minimum value.

1. Attach the appropriate lamp to the spectrophotometer. See Table I.

a. Hydrogen or Deuterium Lamp:

Turn the hydrogen or deuterium lamp power supply switch to "on." Turn the filament control switch on the right to the extreme clockwise position. Allow 1 minute for the filaments to warm up.

Press the push-button switch to start the arc in the hydrogen or deuterium lamp. Observe the lamp to see that the discharge is not confined to the anode compartment of the lamp. If the lamp has not fired correctly, turn off the power supply switch, allow the lamp to cool, and repeat the start-up procedure.

WARNING: The hydrogen lamp can produce a severe burn on skin or to unprotected eyes. Do not look directly at the lamp. If it is necessary to examine or adjust the hydrogen lamp, use goggles that will absorb the dangerous ultraviolet radiation.

b. Tungsten Lamp:

The tungsten lamp should be powered by a 6-volt constant voltage transformer to prevent voltage fluctuations. A 5-minute warm-up is necessary for this lamp.

2. Set the selector switch at "Check."
3. Push the filter slide in as far as possible.
4. Select the appropriate phototube. Refer to Table I.
5. Set the sensitivity control knob at the appropriate position. See Table I.

B. Silica Cell Check

NOTE: Each cell, used for making sample measurements, must be checked daily.

1. A silica spectrophotometer cell should be stored submerged in distilled water when not in use.
2. Remove the cell from the water and clean it with a detergent solution (any mild dishwashing detergent can be used). Fill the cell with the detergent solution, and rub the window surfaces with a ball of cotton on a stick.

NOTE: Never touch the optical surfaces of a cell with fingers.

3. Rinse the cell several times with distilled water.
4. Fill the cell to 1/4 inch from the top with distilled water. Wipe the cell completely dry on all outside surfaces with tissue, making sure that all streaks and lint are removed.
5. Look through the cell toward a light, and be certain that there is absolutely no particulate matter either in the solution or on the optical surfaces of the cell. This includes tiny air bubbles, streaks, water marks, lint, or anything else that might become an obstacle in the optical path.
6. If there is any evidence of dirt on the inside surfaces of the cell, the cell should be cleaned. Refer to Procedure E, "Cleaning the Silica Cell." Then return to Step B, 2.

7. Place the cell very carefully in a cell holder. The correct cell position is determined in the initial cell check. In general, place the cell in the holder with the word "Beckman" facing the analyst. There should be no evidence of weak or misaligned springs, or corrosion in the cell holder that would prevent in *any* way a cell from fitting firmly and squarely into position. The cell must fit so that its optical surfaces are aligned perfectly normally (at right angles) to the light beam of the spectrophotometer.

8. Place the cell holder in the cell compartment of the spectrophotometer with the first position (blank position) empty.

NOTE: The side of the cell facing the slit width dial should be flush with the body of the cell holder. The spring side of the cell holder should face the phototube. This will allow light to pass through at right angles to the cell with minimum deflection. Replace the cover on the compartment.

9. Set the wavelength dial according to Table II for the hydrogen or deuterium lamp (220—350 nm) or Table III for the tungsten lamp (320—1000nm).

10. Turn the shutter switch "Off," and balance the instrument by returning the galvanometer needle to zero with the dark current knob.

11. Place the cell holder in the blank position, place the selector switch at "Check," turn the shutter switch to "On," and balance the instrument with the slit width knob.

12. Turn the shutter switch to"Off" and place the cell in the light beam.

13. Simultaneously set the selector switch at "1" and turn the shutter switch to "On"; balance the instrument with the density (absorbance) knob.

14. Turn the shutter switch to "Off," turn the selector switch to "Check," and record the absorbance reading. See Table II (hydrogen or deuterium lamp) or Table III (tungsten lamp) for control limits.

C. Instrument Check

1. Follow Silica Cell Check, procedure Steps B, 1, through B, 8, using 26.4 mg/l potassium chromate in 0.05 M sodium monhydrogen phosphate in place of distilled water.

2. Record the slit width used in obtaining the measurement. The tolerances for slit width at a given wavelength vary widely among instruments. Nevertheless, a daily slit width record does provide a meaningful relative measure of an instrument's performance for maintenance purposes.

3. Using the same cell, obtain a duplicate measurement.

4. If the absorbance values do not fall within the control limits, the instrument should be checked for a malfunction.

D. Measurement of Sample Absorbance

1. Follow Silica Cell Check, procedure Steps B, 1, through B, 8, but substitute the sample for distilled water, and set the wavelength dial at the wavelength indicated in the specific method.

2. Using the same cell, obtain a duplicate measurement.

3. The two absorbance readings should agree to within 0.003. If they do not agree to within 0.005, the cell should be cleaned thoroughly again, or replaced; the cell holder should be replaced; or a different spectrophotometer should be used on any subsequent attempt to obtain precise readings. (See Procedures B and C.)

NOTE: It has been established that duplicate readings are necessary to obtain precise measurements.

4. When the measurements have been completed, remove the cell from the holder, empty, and rinse with distilled water, and place the cell in water for storage.

5. Using the appropriate calibration equation or table, calculate the concentration of the compound being determined.

E. Cleaning the Silica Cell

1. Fill the cell with a detergent solution, and rub the window surfaces with a small ball of cotton on a stick.

2. Rinse the outside and inside of the silica cell with a solution composed of one part of 3 N hydrochloric acid and one part of either methyl or isopropyl alcohol.

NOTE: Dispense the acid-alcohol solution from either a plastic wash bottle or a dispenser as shown in Figure 1. The small tube inside the funnel is bent slightly to keep it from being expelled. Hold the inverted cell at the bottom edge over the small tube in the funnel. Press the rubber bulb gently. This forces a jet of cleaning solution into the silica cell and also cleans the outside surfaces. The cleaning solution must be replaced with fresh solution frequently.

TABLE I

PREPARATION OF THE INSTRUMENT FOR OPERATION

Lamp	Wavelengths Between 220 and 350 nm (Hydrogen or Deuterium)	Wavelengths Between 320 and 1000 nm (Tungsten)
Phototube	Rod out	320–625 nm–rod out 625–1000 nm–rod in
Sensitivity Knob	3 turns from the extreme counterclockwise position	½ turn from the extreme counterclockwise position

TABLE II

WAVELENGTH DIAL SETTINGS AND CONTROL LIMITS FOR THE HYDROGEN OR DEUTERIUM LAMP

Check	Wavelength Dial Setting	Control Limits
Cell (Water)	270 nm	0.039 ±0.005*
Instrument (26.4 mg/l potassium chromate in 0.05 M sodium monohydrogen phosphate)	274 nm	0.548 ±0.005

* If the reading is above 0.044, refer to Procedure E, "Cleaning the Silica Cell." If the reading continues above 0.044, investigate the purity of the distilled water or use another silica cell.

If the reading is below 0.034, reverse the position of the cell in the cell holder (the name "Beckman" facing away from the analyst) and repeat the cell check. If the reading continues below 0.034, use another silica cell.

TABLE III

WAVELENGTH DIAL SETTINGS AND CONTROL LIMITS FOR THE TUNGSTEN LAMP

Check	Wavelength Dial Setting	Control Limits
Cell (Water)	640 nm	0.030 ±0.005*
Instrument (26.4 mg/l potassium chromate in 0.05 M sodium monohydrogen phosphate)	373 nm	0.689 ±0.007

* If the reading is above 0.035, refer to Procedure E, "Cleaning the Silica Cell." If the reading continues above 0.035, investigate the purity of the distilled water or use another silica cell.

If the reading is below 0.025, reverse the position of the cell in the cell holder (the name "Beckman" facing away from the analyst), and repeat the cell check. If the reading continues below 0.025, use another silica cell.

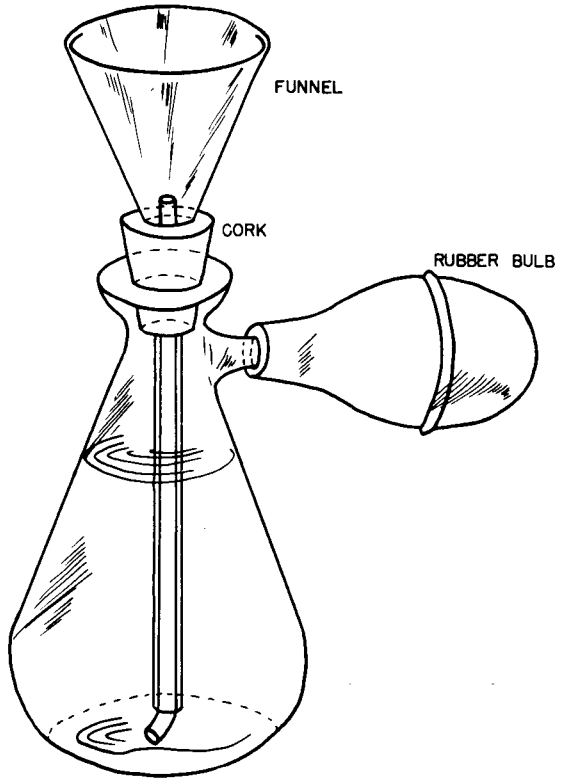


FIGURE 1 Dispenser for Acid-Alcohol Cleaning Solution

PREPARATION AND ANALYTICAL CONTROL OF MIX ROOM AND LABORATORY STOCK SOLUTIONS (IX)

INTRODUCTION

Certain chemicals are purchased in the form of an aqueous solution, to be used as stock solutions. They must be analyzed if differences between successive batches are large enough to cause processing difficulties.

Stock solutions are also prepared from solid chemicals in mix rooms or laboratories, when it is more practical to measure the volume of solution than to weigh out a small amount of the solid. For instance, for small-volume mixes, potassium iodide is used as a 1 g/l solution (0.1% solution). However, in the formulas in this manual, potassium iodide is stated in terms of mg/l.

Stock solutions may also be prepared from solids difficult to dissolve directly in a mix formula.

STABILITY

Unless noted otherwise, the solutions may be considered stable for at least 3 months when kept tightly stoppered at room temperature.

MEASURING LIQUIDS

In general, the weight of a material can be determined more accurately than its volume. With liquids, however, it is usually more convenient to measure the volume; this is sufficiently precise for most needs. Volumes up to 200 ml should be measured with an appropriate pipet; a buret should be used for intermediate volumes. Volumes from 200 ml up to 4 liters should be measured in graduated cylinders. Do not use pails with measuring sticks or marks.

Table I lists the liquids which may be added to mixes by volume and which may be expressed as milliliters of solution in official formulas. These liquids are of relatively constant composition, or are adjusted to the nominal value. Occasionally, other stock solutions (listed in Table II) may be purchased or prepared and measured by volume, but such chemicals appear in formulas as grams of the pure chemical, not as volume of a stock solution. For example, the concentration of sodium thiocyanate is expressed as grams of sodium thiocyanate even though an aqueous solution is usually used.

TABLE I

LIQUIDS IN FORMULAS EXPRESSED AS VOLUME (milliliters per liter)

1. Acetic Acid, Glacial (100%)
2. Ammonium Thiosulfate (58%)
3. KODAK Anti-Calcium, No. 4
4. Benzyl Alcohol
5. Formalin (37.5% formaldehyde in water)
6. Hexylene Glycol
7. Potassium Iodide; 1 g/l (0.1% solution)*
8. Sodium Hydroxide; 2.5 N
9. Sodium Hydroxide; 10 N
10. KODAK Stabilizer Additive, Processes E-4, ME-4, ECO-3, and CRI-1
11. Sulfuric Acid, 2.5 N

TABLE II

1. Carbowax 1540 solution
2. Sodium Thiocyanate; 250 g/l solution
3. Sodium Thiocyanate; 500 g/l solution
4. Ethylenediamine; ED (98% by weight)

STOCK SOLUTIONS

A. The following solutions are purchased already diluted to a specified concentration.

1. Ammonium Thiosulfate (58%). Ammonium thiosulfate can be purchased as a stock solution containing 57 to 61% of $(NH_4)_2S_2O_3$ by weight. Generally, it is not necessary to assay the solution. Assays of ten typical lots of the stock solution averaged 58.1%. The specific gravity of one lot, which assayed 58.6%, was 1.323.

2. Carbowax 1540 Solution. Carbowax 1540 can be purchased as a 50 to 60% (by weight) solution of Carbowax 1540 in water. It is assayed by Method 570 as grams of Carbowax 1540 per liter of solution.

3. Ethylenediamine

CAUTION: Ethylenediamine is toxic. Avoid breathing its vapors and contacting it with skin. Handle only in areas with good ventilation.

Ethylenediamine is a 98% (by weight) solution of ethylenediamine in water. It is stable for at least one year when stored in a stoppered bottle. It is assayed by Method 612C as grams of ethylenediamine per 100 g of solution (% by weight) or as g/l of ethylenediamine. The 95% confidence limits for an individual assay are ±5.4 g of ethylenediamine per liter. These data are based on 25 checks of one sample made throughout a year.

4. Formalin

CAUTION: Formalin is toxic. Avoid breathing its vapors and contacting it with skin. Handle only in areas with good ventilation.

Formalin is a 37.5% (by weight) solution of formaldehyde in water. The Formalin, as received, has been sufficiently close (±0.5%) to the 37.5 value, so that routine analysis is not necessary. The formula value and analytical methods are expressed in milliliters of Formalin. The stock solution is stable at least 3 months.

Formalin contains methyl alcohol as a preservative. The methyl alcohol concentration and the consequent specific gravity of the Formalin may vary from batch to batch.

B. The following solutions are prepared in the laboratory or mix room:

1. Potassium Iodide (1 g/l solution). Dissolve 1.00 g of

* Given as mg/l in formulas.

potassium iodide in approximately 750 ml of water; dilute to 1 liter. The solution is assayed by Method 924B and adjusted, if necessary, to 1.0 ±0.03 g/l. The average of 29 checks made in 10 periods on a standard sample of 1 g/l KI was 0.993 g/l; the standard deviation was 0.010 g/l. In these 10 periods no mix of 1 g/l KI required adjustment.

2. *Sodium Thiocyanate (500 g/l solution).* Dissolve 500 g of sodium thiocyanate (NaCNS) in approximately 750 ml of water; dilute to 1 liter. Fresh mixes are analyzed by Method 950 and adjusted to 500.0 ±2.5 g/l. The standard deviation of 26 checks made in 10 periods on a standard sample was 1.20 g/l; the standard deviation of 26 production mixes before adjustment was 23 g/l. In general, it is possible to meet the tolerance of ±2.5 on the first adjustment. It is sometimes convenient to prepare and use a stock solution containing 250 ±1.25 g/l of NaCNS.

3. *Sodium Hydroxide, 10 N.* To a 2-liter Pyrex beaker containing 800 ml of distilled water, slowly add 410 grams of sodium hydroxide (NaOH). Since heat and gases will be generated, mix the solution in an exhaust hood. (It is safer to place the beaker with water in a polyethylene pail before adding and mixing the sodium hydroxide.) Stir the solution carefully to dissolve the sodium hydroxide; cool to room temperature. (Use great care in handling the hot solution in the beaker.)

Transfer the cooled NaOH solution to a 1-liter bottle, and dilute to 1 liter with distilled water. Cap the bottle with a rubber stopper, and mix the solution thoroughly. No standardization of the solution is required.

4. *Sodium Hydroxide, 2.5 N.* To a 2-liter Pyrex beaker containing 800 ml of distilled water, slowly add 102 grams of sodium hydroxide (NaOH). Since heat and gases will be generated, mix the solution in an exhaust hood. (It is safer to place the beaker with water in a polyethylene pail before adding and mixing the sodium hydroxide.) Stir the solution carefully with a magnetic stirrer to dissolve the sodium hydroxide; cool to room temperature. (Use great care in handling the hot solution in the Pyrex beaker.)

Transfer the cooled NaOH solution to a 1-liter bottle, and dilute to 1 liter with distilled water. Cap the bottle with a rubber stopper, and mix the solution thoroughly. No standardization of the solution is required.

5. *Sulfuric Acid, 2.5 N*

CAUTION: OBSERVE SAFETY PRECAUTIONS FOR HANDLING CONCENTRATED ACIDS. WEAR SAFETY GOGGLES AND RUBBER GLOVES. USE CAUTION AND ALWAYS ADD ACID TO WATER.

Add 500 ml of distilled water to a 1-liter *Pyrex* bottle. (See the Caution below for larger volumes.) While stirring the water with a magnetic stirrer, add slowly and cautiously 70 ml of reagent quality concentrated (36N) sulfuric acid to the water. Cool to room temperature.

CAUTION: When preparing larger volumes of 2.5 N acid, place the *Pyrex* bottle in a strong rubber or plastic pail. The bottle should not exceed 4 liters. Set a magnetic stirrer on the floor. The stirrer must have a platform and base as large as the bottle. Add the appropriate volume of distilled water to the bottle. Place a graduated cylinder on the floor, and measure the appropriate volume of acid. While stirring the water, add the acid slowly and cautiously to the bottle. When the solution is thoroughly mixed, stopper the bottle and place the pail in a sink. Remove the stopper and cover the neck of the bottle with a beaker. Cool to room temperature by first running warm water on the side of the bottle; then reduce the temperature of the water.

POTENTIOMETRIC TITRATIONS (XIA)

INTRODUCTION

A titration involves the addition of measured amounts of a standardized reagent to a sample. The concentration of the constituent being titrated can be calculated from the amount of titrant used to reach the equivalence point of the reaction. The equivalence point or end point is most conveniently determined by using an indicator which changes color abruptly at the end point. However, there may be no suitable indicator for certain chemical reactions or for solutions which are highly colored. In such cases potentiometric titrations are generally used. In potentiometric titrations a pair of electrodes—an indicating electrode and a reference electrode—is inserted in the sample. The electrodes are chosen so that the drop in potential between the electrodes is a function of one or more of the ions present in the solution during the titration. As the titrant is added, the rate of change of potential reaches a maximum at the end point of the titration.

The indicating electrode for acid-base titrations is a glass electrode, because its potential is a function of the hydrogen ion concentration. A silver bar electrode is used as an indicating electrode for halide titrations, because its potential is a function of the silver ion concentration in the solution.

The reference electrode remains at a constant potential during the course of the titration. A calomel electrode, filled with potassium chloride solution, is used for acid-base titrations. A calomel electrode, filled with potassium nitrate instead of potassium chloride, is used for titrations of halides with silver nitrate. (The chloride ion is objectionable because some of the silver ions from the titrant diffuse into the wick, precipitating the chloride and plugging the electrode.)

The potential across the electrodes is measured and recorded manually when a potentiometer or a pH meter is used. These potential measurements may be read on a pH scale rather than a scale calibrated in volts, since the scales are proportional. If the instrument has been standardized against buffers of known pH, the readings will be true pH readings. Such standardization is not necessary for most titrations, however.

Mixtures of iodide, bromide, and chloride can be titrated potentiometrically because the solubilities of the silver halides are different enough that the three are precipitated one after another with little coprecipitation. As the precipitation of each halide approaches completion, there is a corresponding increase in the rate of change in the potential. Thus three inflection points are noted in the curve, which may be obtained by plotting potential measurements versus the volume of titrant consumed. Figure 1 illustrates such a case.

In the portion of the curve corresponding to a relatively large change in potential, there is a point at which the curve changes its direction of curvature. This point is an inflection point or "break" in the curve and ideally it occurs at the equivalence point of the titration. However, in certain cases, there may be a bias in the analysis, so that the breaks are slightly displaced from the true equivalence points of the reaction. The analyses of the known samples may indicate that the bias is large enough to require a correction.

One of the difficulties in titrations with silver nitrate is in knowing which particular halide caused the inflection points on the curve. The first break should be that of the iodide because it has the lowest solubility. However, if little or no iodide is present in the sample, the first break will be that of the bromide. When little or no chloride is present, the bromide and chloride breaks may almost merge. If so, one break may be easily confused with the other. This situation is avoided in several bromide methods by adding additional chloride to the sample before the titration.

DETERMINING THE INFLECTION POINT

A. Concentric Arcs Method

The easiest way of locating the inflection point of a titration curve is by using a concentric arcs template. This template is semirigid and transparent. There is a series of arcs scribed upon it, which are spaced ¼ inch apart. The grooves are filled with India Ink, and there is a small hole at their common center.

Locate the approximate position of the end point, which is in the part of the curve representing the greatest rate of potential change. See Figure 2. Place the template on the curve on one side of the approximate end point, so that one of the arcs is superimposed on the curve. Try different arcs to find the one that best fits the curve. Then make a dot on the graph through the small hole in the template.

Place the template on the curve on the other side of the approximate end point, and repeat the procedure. The arc that best fits this part of the curve is not necessarily the same arc that best fitted the first part of the curve. Draw a straight line between the two dots. The point where the straight line intersects the curve is the inflection point. Figure 2 illustrates the procedure.

B. "Delta" Method

This method may be used if the titration is run manually and if the tabulated date indicate a sharp end point. This method may give an incorrect end point if any one of the points is greatly in error. It is best applied to data which represent smooth, symmetrical curves. It is a rapid method because the data need not be manually plotted. During the titration, record the buret readings and corresponding meter readings for each added increment of titrant. The increment that causes the greatest change in meter reading indicates the end point. For most purposes the end point is assumed to be halfway between the two buret readings which showed the greatest difference. The procedure is explained by the example in Table I.

TABLE I

LOCATING THE END POINT BY THE "DELTA" METHOD

ml 0.0500 N $AgNO_3$	Meter Reading	Delta (Difference)
0	10.20	
0.50	10.18	
1.00	10.10	
1.50	10.01	
2.00	9.90	
2.20	9.86	.04
2.40	9.80	.06
2.60	9.73	.07
2.80	9.63	.10
3.00	9.48	.15
3.20	9.22	.26
3.40	8.92	.30
3.60	8.76	.16
3.80	8.67	.09
4.00	8.60	.07
4.20	8.57	.03
4.40	8.56	

Note that the greatest change in potential occurred when a total of 3.40 ml of titrant had been added. The end point is therefore 3.40 minus 0.20/2, or 3.30. (If the meter reading for 3.00 ml had been 9.52, there would have been two equal differences in column 3. In that case the end point would have been 3.20 ml.)

PROCEDURE FOR A POTENTIOMETRIC TITRATION USING THE CORNING MODEL 12 RESEARCH pH METER

This method is not applicable to acid-base titrations such as total alkalinity.

1. Turn the function knob to the STANDBY position.
2. Connect the power cord to the instrument and source of power, and allow 10 minutes for component stabilization.
3. Insert a calomel electrode (filled with saturated KNO_3 when titrating halides) into the reference jack and the proper indicating electrode (glass, platinum, silver, etc) into the glass electrode jack.

NOTE: A Corning adapter No. 477221 may be used to convert the glass electrode jack to a pin-type jack.

4. Turn the expand knob to the 0—14 position; lower the electrode assembly and a magnetic stirring bar into the sample to be titrated.
5. Turn on the stirrer and immerse the tip of the buret into the sample.
6. Turn the function knob to either the +mV or —mV range, as required, to bring the meter needle on scale for the particular titration.
7. From the lower meter scale, determine the mV interval where the sample titration will begin (e.g., between 3 and 4).
8. Turn the range knob to the lower value (e.g., at 3).
9. Turn the expand knob to 0—1 EXPAND position and plot or record the initial buret and meter reading.

NOTE: When the 0—1 EXPAND position is used, mV readings are composed of values taken from the range knob selector scale and the uppermost meter scale. The number from the range scale represents the hundreds of mVs; the number from the upper meter scale represents the tens, units, and tenths of mVs. (For example, see below.)

Range Value	Scale Value	Millivolt Reading
7	.572	757.2 mV
11	.368	1136.8 mV

10. Add the titrant in 0.20-ml increments unless otherwise indicated. After each addition, wait until the needle stops moving before plotting or recording the buret and meter readings. Bring the meter needle back on scale by turning the range knob in the appropriate direction.
11. Titrate until each succeeding 0.20-ml addition produces less change in the meter readings than the preceding addition. Add at least five more increments of titrant before ending the titration.

NOTE: In bromide titrations, titrate until the chloride end point has been passed unless more than 10 extra milliliters are required.

12. Draw a smooth curve through the plotted points and use the Concentric Arcs Method to determine the inflection point, or use the Delta Method when only recording.

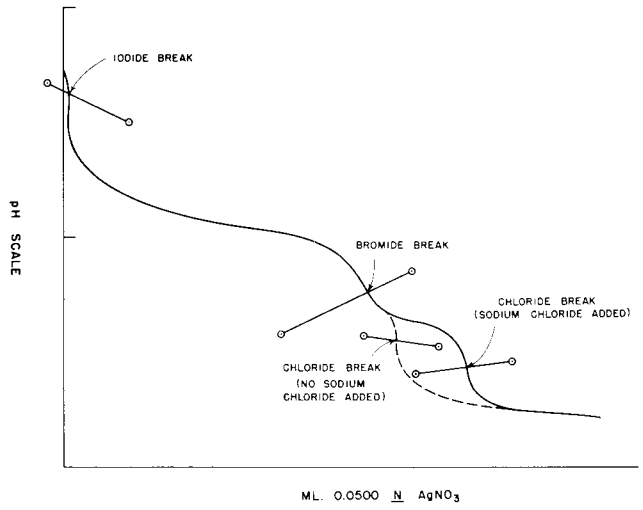


FIGURE 1 Typical Bromide Titration Curve

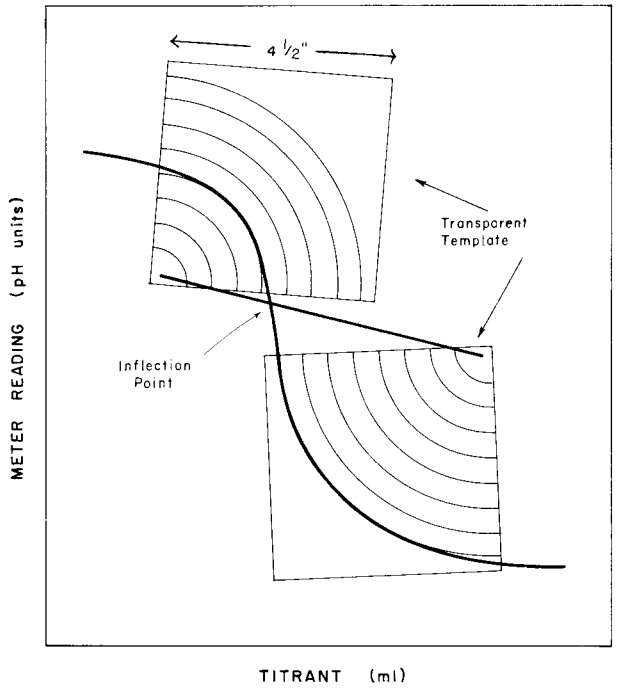


FIGURE 2 Use of Concentric Arcs Template to Determine the End Point of a Potentiometric Titration

SAMPLING OF PROCESSING SOLUTIONS (XIV)

INTRODUCTION

A. General Considerations

Control of a photographic process requires that the chemical concentration of the solutions be maintained at standard chemical levels. Chemical analyses that indicate concentration are of value for control action only when the samples analyzed are representative of the processing solutions. A correct analysis of a nonrepresentative sample may do more harm than good in controlling the process.

Processing solutions may be turbid or contain floating particles, dispersed oil droplets, or a precipitate. Even a clear solution may have a concentration gradient between different parts of the processing machine tank. For instance, the chemical composition where the film enters is not the same as in other parts of the tank even though the solution is agitated or recirculated. For such cases a prescribed procedure must be used, taking all samples from the same location, such as from a point near the tank overflow. These samples will be representative of the solution at the prescribed sampling point and successive analyses will indicate variations in concentration that will be useful for control action.

B. Sample Aliquot

Once a representative sample has been obtained from the processing solution, a representative aliquot must be taken from the sample bottle for analysis. For a volumetric analysis, the aliquot should be withdrawn 1 inch below the surface of the solution with a pipet. In general, no sample bottle should be shaken. However, the bottle should be allowed to stand for 10 minutes after taking the sample from the processing solution. This allows large particles to settle or allows turbidity due to aeration to clear. However, any turbidity due to benzyl alcohol in the processing solution will not disappear. An alternative procedure for obtaining samples free from sediment is to centrifuge the samples before taking an aliquot.

Handling of a sample may depend upon what is being measured in the processing solution. Occasionally, it is necessary to shake a sample bottle for a specific reason. An example would be when the concentration of a precipitate in a solution is being determined. Shaking the representative sample enables one to report the concentration of the precipitate in terms of grams per liter. Therefore, whenever a sample bottle is shaken, analysis of an aliquot will be indicative of the whole sample and not just the dissolved constituents.

SPECIAL APPARATUS

Polyethylene bottle and screw cap (for sampling, not for storage), or glass bottle with plastic screw cap or rubber stopper. Size to be determined by laboratory supervisor.

Bulb-type rubber syringe

Rubber gloves

PROCEDURE

A. General Instructions

1. Clean the syringes, bottles and caps with acid-alcohol cleaning solution (use caution), followed by a detergent solution. Then rinse with tap water and drain. The bottles need not be dry.

2. Each bottle must have adequate identification such as a label or an identification ticket.

NOTE: Some paints and inks contain solvents or ingredients which permeate polyethylene bottles and contaminate the inside. Such paints and inks should not be used for identification.

3. Use rubber gloves.

4. Rinse the bottle and syringe (if used) twice with the solution to be sampled.

5. Fill each sample bottle to overflowing to exclude air.

6. Cover immediately. Be sure the screw cap is put on tight to prevent the loss of volatile constituents.

7. For developers: Rinse the outside of the bottle with water to wash off the developer.

8. Use only one prescribed sampling procedure.

B. Sampling Mix-Tank Solutions by Surface Method

1. Take the sample immediately after the mixer is turned off, while the solution is moving.

2. Submerge the bottle 4 inches below the surface of the solution and as near the center of the tank as possible.

3. Rinse the bottle twice; then fill to overflowing with the final sample, being careful not to scoop in surface foam or small undissolved floating particles.

C. Sampling Mix-Tank Solutions by Tap-Off Method

The "tap-off" is a short nipple and valve installed in the side of the mix tank or outlet line.

1. Draw off and dispose of sufficient solution so that the final sample will be representative of the solution in the tank.

2. Rinse the sample bottle twice and fill to overflowing.

D. Sampling of Recirculated Solutions from Closed Systems

1. Sample by means of a valve in the line. The valve may be between the filters and the rotameters.

2. Open the valve fully, and permit the solution to flow until it is free of air bubbles.

3. Rinse the bottle twice. Then fill to overflowing with clear solution.

E. Sampling of Recirculated Solutions from Open Systems

1. Take a sample as described for solutions in closed systems (Part D).

2. As an alternative method take a sample from the ballast tanks using the surface technique described for mix tanks in Part B.

F. Sampling of Nonrecirculated Solutions

1. Insert a syringe 2 inches below the solution surface as close to the tank overflow as practicable.

2. Rinse both bottle and syringe twice with the solution being sampled. Do not aerate the solution while rinsing the syringe.

3. Draw a representative sample into the syringe and expel slowly close to the bottom of the bottle, avoiding aeration. Repeat until the sample bottle is filled to overflowing.

4. Use a separate syringe for each solution.

DIAGNOSING AND CORRECTING NONSTANDARD CHEMICAL COMPOSITION OF PROCESSING SOLUTIONS (XVII)

INTRODUCTION

This section describes tests that may be made to determine whether a mix meets the chemical control tolerances. This section also describes the method of calculating chemical adjustments, the proper method of their preparation, and the extent to which corrections are advisable.

The best prepared processing solution is one that requires no adjustment. In practice, measurable constituents are frequently adjusted to be within chemical tolerances. In some cases it is necessary to add more of certain materials than is called for in the formula and to restir the mix.

The variety and size of chemical adjustments and, in some cases, the instability of chemical additions, necessitates the preparation of chemical additions as they are needed.

This section assumes that the mixing tanks are properly calibrated and that the chemical analyses are reliable.

CRITERIA FOR EXAMINING PROCESSING SOLUTIONS

Before a processing solution is used, there are certain physical and chemical criteria that may be used to determine whether the solution will produce satisfactory photographic results. These criteria are (1) appearance of solution, (2) specific gravity, (3) pH, (4) total alkalinity, and (5) individual analyses. It is not necessary to evaluate all of these criteria for each solution. The extent to which these methods are used depends, in part, upon the risk the processor wishes to take in assuming that the processing solutions were prepared correctly. The more critical a constituent, the greater is the risk of faulty processing if an error has been made in mixing.

A. Appearance of Solution

Each processing solution has a characteristic appearance. Any deviation from its normal appearance is an indication that the solution may not produce satisfactory results. There are, in general, three such important deviations.

1. Color. A highly colored developer solution may indicate that the solution has been oxidized excessively. This may result from excessive stirring or exposure to air, or a low weir level on the process machine. It may also be possible that an insufficient amount of an antioxidant such as sulfite was added.

If the developer solution has deviated from its usual color, it is possible that an impure chemical was added.

2. Oily appearance. If a developer solution has an oily appearance, the developing agent or the benzyl alcohol has probably failed to dissolve completely. This condition generally results from the improper addition of the chemical or from insufficient mixing of the solution.

3. Undissolved particles. The presence of floating particles or a precipitate in the processing solution is usually caused by some deviation from the proper mixing technique:

a. Insufficient agitation of solution.

b. Wrong mixing order of constituents.

c. Wrong method of dissolving constituents.

d. Addition of a foreign chemical or an excess of a mix constituent.

e. Wrong addition of an acid or base greatly altering the pH of the solution.

B. Specific Gravity

The specific gravity determination is one of the most valuable single analyses for determining large errors in mix preparation. The test may also be used to detect mechanical trouble in the processing machine. With the recommended hydrometer it is possible to determine whether or not the total content of added materials is within 1 to 2 grams per liter of the proper amount.

The specific gravity of a mix cannot detect the presence or absence of materials present in small amounts (1.0 gram per liter or less). Neither can the specific gravity detect the accidental substitution of a wrong chemical, if added in a compensating amount, nor can it detect weighing errors that equally compensate each other. Some indications why the specific gravity of a mix does not meet its standard are:

1. A low specific gravity of a replenisher may indicate:

a. A constituent was omitted or too little of it added.

b. Certain constituents are not in solution.

c. The substitution by or the addition of too much of a constituent with a low specific gravity, such as benzyl alcohol.

d. The substitution of a hydrated chemical was made for the anhydrous material.

e. The solution was overdiluted.

2. A low specific gravity of a processing tank may indicate:

a. Underreplenishment.

b. Malfunctioning of air or water squeegees permitting excess water carry-in.

3. A high specific gravity of a replenisher may indicate:

a. Too much of a constituent with high specific gravity was added.

b. Too little of an ingredient with low specific gravity was added.

c. The substitution of an anhydrous chemical was made for the hydrated chemical.

d. Insufficient dilution.

4. A high specific gravity of a processing tank may indicate:

a. Overreplenishment.

b. Replenisher quick-fill valve open.

C. pH

The degree to which deviation of pH from standard can be tolerated depends on the sensitivity of the film to the pH of the solution. Developers generally require a high degree of pH stability and are thus designed to contain a buffer to resist changes in pH. A deviation of 0.2 pH unit in a developer may be an indication of very serious trouble in preparing the mix.

A pH adjustment of more than 0.2 to any developer is not advisable unless the reasons for it are known and unless the corrective constituent may be safely added at the end of the mixing operation.

The pH of the ferricyanide bleach is not critical; hence it does not need much buffering capacity nor pH control. It should be kept within its tolerances to prevent the formation of precipitates. The pH of the fixing bath is less critical than pH of the developers, but it must be maintained within its tolerances. The pH of this solution can be controlled with an automatic control device or with the use of a buffer (disodium phosphate).

A pH over 11 usually implies the presence of sodium hydroxide or trisodium phosphate in a solution. A pH as low as 10 for a color developer indicates trouble, probably an insufficient amount of hydroxide.

Amounts of sulfuric acid or sodium hydroxide required for adjusting the pH of a developer solution are shown in Table I. Note that 2.5 N sulfuric acid is specified because concentrated H_2SO_4, 96% or 35 N, if added directly to a replenisher, causes localized heating and chemical action on sulfite, carbonate, etc.

D. Total Alkalinity

This test measures the total contribution of the different constituents to the acid-neutralizing capacity of the solution. Most constituents contribute differently; thus a diagnosis of trouble is frequently possible with the aid of total alkalinity.

Sodium sulfite contributes substantially to total alkalinity. Thus an off-standard total alkalinity should be immediately followed by an analysis for sodium sulfite. If this is on standard, other alkaline constituents such as carbonate, hydroxide, or phosphate should be considered. Simple test methods are not available to measure the concentration of these chemicals in a processing solution. If the pH is above 12, at least some sodium hydroxide is present. By referring to the analytical method for the determination of total alkalinity and checking the contributions of each chemical toward total alkalinity, it is possible to calculate the probable error made in mixing the hydroxide or the carbonate. Note that some constituents have negative contributions. The mix is then brought to standard by making the proper addition of acid or base by considering the data given in Table I and the mentioned neutralization effects given in the total alkalinity determination.

E. Individual Analyses

The analyses of the individual constituents of a processing solution are, of course, most valuable in first determining whether a solution meets its control tolerances and secondly in determining any corrections that may be required. For routine control only the most photographically critical constituents are frequently measured as outlined in the "Chemical Control" section of Process Control, page series 600. The less critical constituents are measured occasionally, in order to maintain them at their most efficient concentrations.

RECOMMENDED MAXIMUM ADJUSTMENTS

Solutions found to have constituent concentrations seriously outside of control tolerance are usually the result of gross mixing errors or serious mechanical failure. It is impossible or impractical in some cases to correct the mix to standard. The maximum corrections recommended are:

Developers, $NaHSO_3$, Na_2SO_3	± 20%
Formalin	+ 20% to 0%
Acetic Acid, Anti-Fog, No. 6, Benzyl Alcohol, Citrazinic Acid, Ethylenediamine, KI, NA-1, NaBr, NaCNS, Na_2CO_3, Na_2SO_4, $Na_3PO_4 \cdot 12H_2O$, RA-1, SA-1, Sodium Acetate	+100% to −20%

Experience has shown that lowering the concentration of Formalin to standard has produced unsatisfactory photographic results.

CALCULATION OF "ADDITIONS" AND "CUTS" TO TANKS AND REPLENISHERS

The next step in the procedure of correcting a nonstandard solution is the calculation of the proper "addition" or "cut." An addition is a known amount of chemical, solid or in a solution, that must be added to a tank or replenisher to bring that constituent up to its standard level. A cut is a known volume of solution used to reduce the concentration of one or more constituents.

A. If Constituent is *Below* the Chemical Standard, an Addition is Needed.

Adjustments to processing solutions found to have one or more constituents below the chemical standards are made by the addition of the needed constituents. The resulting small change in volume is disregarded. The amount required to bring the constituent to the chemical standard is calculated from Equation #1.

$$\text{Total grams to be added} = \left[\left(\frac{\text{g/l}}{\text{chem std}}\right) - \left(\frac{\text{g l}}{\text{chem found}}\right)\right]\left[\frac{\text{liters}}{\text{of solution}}\right] \quad (1)$$

EXAMPLE:

A 1000-liter solution is found to contain 1.80 grams per liter of NaBr, and the chemical standard is 2.00 grams per liter. Then:

Total grams NaBr to add = (2.00 − 1.80)(1000) = 200 g

B. If Constituent is *Above* its Chemical Control Standard, A Cut is Needed.

Adjustment to processing solutions found to have one or more constituents above their chemical standards is accomplished by making a deliberate decrease in concentration of

the off-standard constituents while maintaining the others at their chemical standards.

Five cases are shown:

1. Only One Constituent Above the Upper Tolerance (Volume of mix cannot be increased.)

If a cut is needed for either a tank or a replenisher, but it is impossible to increase the volume of the solution due to the limited volume of the tank, then the following equation (#2) is used to determine the volume of the cut to be made. A volume of the out-of-standard solution, equal to the volume of the cut, must first be discarded.

$$\text{Liters of cut} = \left[\frac{(\text{g/l chem found}) - (\text{g/l chem std})}{\text{g/l chemical found}}\right]\left[\text{Liters of off-std sol'n}\right] \quad (2)$$

The amounts of chemicals to be added are as determined by Equation #3.

$$\text{Total of grams of each const to add} = (\text{Liters of cut})(\text{chem std of const}) \quad (3)$$

Usually a cut is prepared using the standard mixing procedures, but often it is necessary to prepare an odd-sized volume of solution, which necessitates a slight modification in the procedure. There are two suggested modifications. The selected modification usually depends upon the volume of the cut and the size of the available mixing tank.

a. The mix tank can be temporarily calibrated to the exact volume of the cut by adding water to the nearest calibration mark. Water is either added or discarded to meet the volume required by the cut. The tank is then marked at that volume. For example, a tank has calibrated marks at 90 and 100 liters. If a 91-liter cut is required, the tank is filled to 90 liters, and 1 more liter is added. If a 97-liter cut is required, the tank is filled to 100 liters and 3 liters are removed. The tank is marked at that volume. About 20 liters of water are discarded, leaving 80% of the water in order to dissolve the chemicals. The cut is then prepared according to standard procedures.

b. A cut can be prepared at the nearest known calibration mark that exceeds the volume needed. The extra volume of solution is then discarded. For example, a 91-liter cut is needed; a 100-liter mix is prepared. The extra 9 liters are discarded.

Equations #2 and #3 are explained by use of the following example:

A 1000-liter solution is found by analysis to contain 2.20 grams of hydroquinone per liter when the standard was 2.00 grams per liter. All the other constituents are on standard. (Quadrafos = 0.6 g/l, Na_2SO_3 = 72.0 g/l, added in two parts, ELON* = 4.00 g/l, Na_2CO_3 = 60.0 g/l, NaBr = 1.80 g/l, and KI = 25.0 ml of a 1 g/l solution).

* KODAK ELON Developing Agent (or p-Methylaminophenol Sulfate)

The volume of solution to be discarded =

$$\left(\frac{2.20 - 2.00}{2.20}\right)\left(1000\right) = 91 \text{ liters}$$

The volume of the cut is also 91 liters. The other constituents are added, in sequence, in the following amounts:

Water	= 73 liters		
Quadrafos	= (91) (0.6)	= 54.6	g
Na_2SO_3	= (91) (12)	= 1092	g
ELON	= (91) (4.00)	= 364.0	g
Na_2SO_3	= (91) (60)	= 5460	g
Na_2CO_3	= (91) (60)	= 5460	g
NaBr	= (91) (1.80)	= 163.8	g
KI	= (91) (25.0)	= 2275	ml of 1 g/l KI
Water to make	91 liters		

2. Several Constituents Above the Upper Chemical Tolerance (Volume of solution cannot be increased.)

The volume to discard is computed from Equation #2 and is based on the chemical requiring the greatest cut (the one present in the greatest percent excess). The chemicals which were originally on standard are added to the addition according to Equation #3 above. The second chemical (that requiring the next smaller cut) will now be present in too low a concentration until some more of that constituent is also added. The amount required is calculated as in Equation #4.

$$\text{Grams of chemical to add} = \left(\text{Final vol in liters}\right)\left(\text{g/l chem std}\right) - \left[\left(\text{Final vol in liters}\right) - (\text{liters of cut})\right]\left(\text{g/l chem found}\right) \quad (4)$$

EXAMPLE:

A solution was found to be the same as that described in the example of Part B, 1, above, except the NaBr tested 1.96 g/l with a standard of 1.80 g/l.

The HQ is adjusted by dilution as described above. All the other constituents are adjusted by additions as described above. Calculate the amount of NaBr to add which is based on the 91-liter cut from Equation #4.

grams of NaBr = (1000)(1.80) — (1000 — 91)(1.96)
= 18.4g

3. Only One Constituent Above the Upper Tolerance (Volume of mix may be increased.)

If a cut is needed, and it is possible to increase the volume of the total solution, then the following equation (#5) is used to determine the volume by which the mix must be diluted to bring the constituent back to standard.

$$\text{Final volume} = \left(\frac{\text{g/l chem found}}{\text{g/l chem std}}\right)\left(\text{original liters of solution}\right) \quad (5)$$

The volume of the cut to be made is the difference between the final volume and the original volume, Equation #6.

$$\text{Volume of cut} = \text{(final volume)} - \text{(original volume)} \quad (6)$$

It follows that if the solution were merely diluted with water, all the other constituents would be present in too-low concentrations. Therefore, these chemicals have to be added to make up this deficit. The amount of other constituents to be added is determined by Equation #3.

EXAMPLE:

Following the example described in B, 1, above:

$$\text{Final volume} = \left(\frac{2.20}{2.00}\right)(1000) = 1100 \text{ liters}$$

The volume of the cut = 1100 liters — 1000 liters = 100 liters.

Other constituents are added in the following amounts:

Water	= 80 liters		
Quadrafos	= 100 (0.6)	= 60	g
Na_2SO_3	= 100 (12.0)	= 1200	g
ELON	= 100 (4.00)	= 400.0	g
Na_2SO_3	= 100 (60.0)	= 6000	g
Na_2CO_3	= 100 (60.0)	= 6000	g
NaBr	= 100 (1.80)	= 180.0	g
KI	= 100 (25.0)	= 2500	ml
Water to make		100	l

4. Several Constituents Above the Upper Tolerance (Volume of mix may be increased)

This situation is similar to B, 2; however, the volume of the cut is computed from Equation #6 rather than Equation #2. The other chemical that requires the smaller cut is increased by Equation #7 rather than Equation #4.

$$\text{grams of chem to add} = \left[\left(\begin{matrix}\text{Final vol}\\ \text{in liters}\end{matrix}\right)\left(\begin{matrix}\text{g/l chem}\\ \text{std}\end{matrix}\right)\right] - \left[\left(\begin{matrix}\text{original vol}\\ \text{in liters}\end{matrix}\right)(\text{g/l chem found})\right] \quad (7)$$

EXAMPLE:

The following example is described above in B 1, 2, and 3. The HQ is adjusted by dilution as described above. All the other constituents are adjusted by addition as described above. The additional amount of NaBr is:

gram of NaBr = (1100)(1.80) — (1000)(1.96)
= 20.0 g

5. All Constituents Above Upper Tolerance

If all the measured constituents are found to be above the upper tolerance, the mix has probably been underdiluted. Specific gravity measurements are an aid in this diagnosis. The correction of this condition is a straightforward calculation of the amount of water needed.

PREPARATION OF CHEMICAL ADJUSTMENTS

Considerable care is needed in the preparation of individual chemical additions to a processing solution. This part describes the proper way to prepare these additions. It is divided into two groups, because different techniques are needed to make chemical additions to the tank solutions rather than to replenisher solutions. The difference is due to (1) the low rate of agitation found in tank systems, and (2) the necessity to maintain a constant pH of the tank solution.

After a constituent has been added and dissolved in the processing solution, the solution is reanalyzed for the constituent, and the pH is remeasured. If a cut (see previous section) has been made, a complete analysis of the resulting solution should be made.

A. Preparation of Replenisher Additions

1. Add and dissolve the following chemicals directly to the replenisher solution. Generally, no correction of pH is necessary because the addition will adjust the pH to standard.

Acetic Acid
Benzyl Alcohol
Citrazinic Acid
Ethylenediamine
Formalin
Hydroquinone
NA-1
Potassium Salts
RA-1
Sodium Salts

Water solutions such as Anti-Fog, No. 6, and CW-1540 (solution)

2. Phenidone*

Place the weighed amount of Phenidone into a suitable-sized beaker. For each gram of Phenidone, add 2 ml of methyl alcohol to make a slurry with the Phenidone. While stirring, add 20 ml of hot water (140 F), then 0.3 gram of sodium sulfite for each gram of Phenidone. Add 1 ml of 10 N sodium hydroxide for each gram of Phenidone. (See Table II.) At this point the Phenidone will start to go into solution.

NOTE: Do not use solid sodium hydroxide.

B. Preparation of Replenisher Cuts

1. Add 80% of the water calculated for the cut into a small mixing tank.
2. Add and dissolve the chemicals in the same manner as used when the solution was originally prepared.
3. Dilute to the calculated volume with water and mix.
4. Add this cut to the main solution and mix.

C. Preparation of Tank Additions

Most chemicals, being acidic or basic, will affect the pH of the processing solution when they are added to that solution. Table II shows the amounts of acid necessary to neutralize the chemical being added.

1. Anti-Fog, No. 6, 20 g/l

a. Measure the specified volume of the A.F., No. 6, solution in a graduated cylinder, and add it directly to the machine system.

* Phenidone is a registered trademark of Ilford, Ltd.

2. Citrazinic Acid

a. Weigh the specified amount of citrazinic acid.

b. For each gram of citrazinic acid, add 50 ml of water at 26.5 C (80 F) and stir to form a slurry.

c. Add slowly the appropriate volume of a sodium hydroxide solution as determined by using the factor given in Table II, and dissolve the citrazinic acid. If a precipitate forms during the addition of the hydroxide solution, add more water before adding the remainder of the hydroxide solution.

d. *Immediately add* the citrazinic acid solution to the machine system.

3. Developing Agents

a. (1) For each gram of *CD-3,* dissolve 0.4 g of sodium sulfite, *or* add 3 ml of 1.0 M sodium sulfite into 20 ml of water at 26.5 C (80 F).

(2) For each gram of *hydroquinone,* dissolve 0.4 g of sodium sulfite *or* add 3 ml of 1.0 M sodium sulfite into 20 ml of hot water at 60 C (140 F).

(3) For Phenidone, see separate part under Phenidone.

b. Weigh and dissolve the developing agent in the sulfite solution.

c. Measure the appropriate volume of either 2.5 N or 10 N NaOH solution as determined by using the factor given in Table II.

d. Add the NaOH solution to a volume of tank solution in the ratio of 20 ml per gram of developing agent, then add the Na_2SO_3—developer solution. Add this mixture to the machine system.

4. Ethylenediamine

a. Measure the specified volume of ethylenediamine in a graduated cylinder.

b. Using another graduated cylinder, measure 0.60 ml of 2.5 N sulfuric acid.

c. Add the ethylenediamine to the machine system. Then slowly add the sulfuric acid.

5. NA-1

a. Weigh the specified amount of NA-1.

b. Measure, in a graduated cylinder, the appropriate volume of 2.5 N or 10 N NaOH as determined by using the factor given in Table II.

6. Phenidone. Place the weighed amount of Phenidone into a suitable-sized beaker. For each gram of Phenidone, add 2 ml of methyl alcohol to make a slurry with the Phenidone. While stirring, add 20 ml of hot water at 60 C (140 F), then 0.3 gram of sodium sulfite for each gram of Phenidone. Add 1 ml of 10 N sodium hydroxide for each gram of Phenidone. (See Table II.) At this point the Phenidone will start to go into solution.

NOTE: Do not use solid sodium hydroxide.

7. Sodium Bisulfite. Dissolve the sodium bisulfite in water using the ratio of 5 g of sodium bisulfite to 50 ml of water.

8. Sodium Bromide. Dissolve the sodium bromide in water using the ratio of 5 g of bromide to 10 ml of water.

9. Sodium Thiocyanate, (500 g/l). Measure the appropriate amount of the sodium thiocyanate stock solution in a graduated cylinder, and add it directly to the machine system.

D. Preparation of Tank Cuts

1. Add 80% of the water calculated for the cut into a pail or small mixing tank.
2. Add and dissolve the chemicals in the same manner as used when the solution was originally prepared.
3. Dilute to the calculated volume with water, and mix.
4. Add this cut to the main tank system, and mix.

TABLE I

ADDITIONS TO CHANGE THE pH OF A SOLUTION

Developer	To LOWER pH, add ml 2.5 N H_2SO_4	pH Change	To RAISE pH, add ml 2.5 N NaOH
First	6.2	±0.10	5.5
Color	2.9	±0.10	3.1

TABLE II

NEUTRALIZATION FACTORS FOR ACIDIC-TYPE CHEMICAL ADDITIONS

Chemical	Neutralization Factor* per g or ml For Amounts of Chemicals less than 100 g use ml 2.5 N NaOH	greater than 100 g use ml 10 N NaOH
CD-3	5.0	1.3
Citrazinic Acid	5.0	1.3
Hydroquinone	2.5	0.63
NA-1	5.0	1.3
Phenidone	4.0	1.0

* Multiply grams, or milliliters, of chemical by factor to give amount of caustic solution to neutralize chemical.

EXAMPLE: 20 g Hydroquinone × 2.5 = 50 ml of 2.5 N NaOH.

CALIBRATION OF MIX TANKS (2210F)

FOREWORD

It is frequently necessary to determine accurately the volume of a mix tank or a recirculation system. This can be done either by a titration method or by a spectrophotometric method. The procedure is repeated for each volume or calibration mark being determined. It is only necessary to add the extra amount of solute and water between one volume and the next.

PRINCIPLE

The titration method involves weighing two portions of sodium chloride, dissolving the larger in the tank to be calibrated and the smaller in a volumetric flask. Samples are taken from both solutions and are titrated with silver nitrate, using potassium chromate as an indicator. The true volume of the tank is calculated from the ratio of the two volumes of silver nitrate.

Sodium chloride is used in the titration method because of its high uniformity of particle size and low cost. It is inert to carbon dioxide and oxygen and does not form hydrates. The small amount of sodium chloride used to prepare the reference solution must truly represent the large amount used to prepare the tank solution.

In the spectrophotometric method, accurately weighed amounts of metanil yellow are dissolved in the mix tank and in a volumetric flask. The absorbance of each solution is measured on a spectrophotometer, and the true volume of the tank is calculated from the ratio of the absorbances. This method has advantages, in that the amount of chemical required is smaller, and also an analytical balance may be used to measure both portions of the reagent, avoiding the use of less precise balances.

I. TITRATION METHOD

Reagents

Sodium Chloride, NaCl
Potassium Chromate, K_2CrO_4, indicator
0.05 N Silver Nitrate, $AgNO_3$

Procedure

A. Preparation of the Tank Solution of Sodium Chloride

1. Add water to the mix tank to bring the level nearly to the calibration mark. Stir thoroughly and withdraw approximately 3 liters for use in making a reference solution.

2. Accurately weigh sodium chloride to give a concentration of about 0.5 gram per liter in the mix tank (e.g., 500.0 grams for a 1000-liter calibration mark). Use the appropriate balance and weigh to the number of decimal places indicated.

Analytical Balance—For weights between 0.5000 and 49.500 g

Torsion Balance—For weights between 50.00 and 100.00 grams*

Torsion Balance—For weights between 100.50* and 499.50 g†

Triple Beam Balance—For weights between 500.0 and 2500 g.

3. Add the sodium chloride slowly in a fine stream to the mix tank, stir for a few minutes, and dilute to the calibration mark. Stir for approximately ½ hour.

B. Preparation of Reference Solution of Sodium Chloride

1. Weigh on an analytical balance 1.0000 gram from the same batch of sodium chloride used in the mix tank.

2. Transfer the sodium chloride to a 2-liter volumetric flask, dissolve it in approximately 1600 ml of the water taken from the mix tank and dilute to volume.

C. Titration of Two Samples of the Reference Solution

1. Pipet (wipe the pipet before leveling) 200.0 ml of the reference solution into a 500-ml glass-stoppered Erlenmeyer flask.

2. Add 3 drops of potassium chromate indicator.

3. Titrate with 0.05 N silver nitrate from a 50-ml buret, with constant swirling, until the precipitate has a slight orange tint.

4. Stopper the flask and shake vigorously for approximately 30 seconds.

5. Add more silver nitrate dropwise, with swirling, until the first permanent orange tint.

6. Titrate another 200.0 ml sample of the reference solution by repeating Steps C-1 through C-5, and average the two volumes of silver nitrate used.

D. Titration of Two Samples of the Mix Tank Solution

1. Withdraw a sample of the mix tank solution. Pipet (wipe the pipet before leveling) 200.0 ml into a 500-ml glass-stoppered Erlenmeyer flask, and repeat Steps C-2 through C-5.

2. Withdraw another sample from the mix tank and titrate a 200.0-ml portion as before.

3. Average the two volumes of silver nitrate obtained in Steps D-1 and D-2.

E. Calculations

$$\left[\frac{(2.0)(\text{ml } AgNO_3 \text{ for ref soln})}{(\text{ml } AgNO_3 \text{ for mix tank solution})}\right]\left[\begin{matrix}\text{g NaCl added}\\ \text{to mix tank}\end{matrix}\right] = \text{volume of mix tank in liters}$$

II. SPECTROPHOTOMETRIC METHOD

Special Apparatus

Beckman Model DU Spectrophotometer, or equivalent
1-cm Silica cell, Beckman Catalog No. 75170

* This value may be higher depending upon the load limit of the balance in use.

† Make multiple weighings for amounts in this range or for amounts larger than 2500 g if the total weight is a single addition to the tank. This will avoid overloading the balance.

Reagents

Metanil yellow

Procedure

A. Preparation of Tank Solution of Metanil Yellow

1. Add water to the mix tank to bring the level nearly to the calibration mark. Stir thoroughly and withdraw approximately 5 liters for use in making the reference solution and for use as a blank in the spectrophotometer measurements. (It is necessary that the same water at the same temperature be used for both solutions.)

2. Weigh to 4 decimal places on an analytical balance enough powdered metanil yellow to give a concentration of about 0.01 gram per liter in the mix tank (e.g., 10.0232 grams for a 100-liter calibration mark).

3. Add approximately 1 liter of water to the metanil yellow contained in a beaker, stir, and decant into the mix tank. Use care to keep any solid dye in the beaker. Repeat with 1-liter portions until all of the metanil yellow has been dissolved and added to the mix tank.

4. Dilute the solution to the calibration mark, and stir for approximately ½ hour.

B. Preparation of Reference Solution of Metanil Yellow

1. Weigh on an analytical balance 0.4000 gram from the same batch of metanil yellow used in the mix tank.

2. Transfer the metanil yellow to a 2-liter volumetric flask, dissolve it in part of the water taken from the mix tank, and dilute to volume.

3. Pipet (wipe the pipet before leveling) 50.0 ml of this solution into a 1-liter volumetric flask, and dilute to volume with water from the mix tank.

C. Measurement of the Absorbance of the Solutions Against an Air Blank

1. Measure the absorbance of the diluted reference solution at 425, 430, 435, 440, 445, and 450 nm (mμ). Use the tungsten lamp. See instructions for operation of the spectrophotometer, given in Method VI E.

2. Withdraw a sample of the mix tank solution, and measure its absorbance at each of the wavelengths listed in Step C-1.

3. Withdraw another sample from the mix tank, and repeat the measurements.

4. Average the two measurements at each wavelength for the mix tank solution.

D. Measurement of the Absorbance of the Water from the Mix Tank

Measure the absorbance of the water (refer to Step A-1) at each of the wavelengths listed in Step C-1.

E. Calculations

$$1.\left[\frac{(100)(A_{425}\text{ of ref soln} - A_{425}\text{ of water})}{(A_{425}\text{ of tank soln} - A_{425}\text{ of water})}\right]\left[\begin{array}{l}\text{grams of}\\ \text{metanil}\\ \text{yellow}\\ \text{added to}\\ \text{tank}\end{array}\right] = \text{volume of mix tank in liters}$$

2. Repeat the calculation using the absorbances of the solutions at each of the other wavelengths.

3. Average the six volumes obtained, and report the average value. The range of the six values is an indication of the precision of the work.

SPECIFIC PROCEDURES

DETERMINATION OF CD-3 IN COLOR DEVELOPERS (125C)

INTRODUCTION

The developing agent (CD-3) is extracted with chloroform from a sample of color developer. The chloroform layer is added to dilute sulfuric acid. The developing agent, which enters the acid layer, is titrated with sulfato cerate using Ferroin indicator. Benzyl alcohol is also extracted by chloroform but does not interfere in the titration.

Emulsions tend to form between the chloroform and water layers during the extraction of certain highly seasoned samples. The addition of an anti-emulsification agent, cetyltrimethylammonium bromide (CTAB) solution, before the chloroform extraction minimizes the formation of this emulsion. Occasionally, a narrow emulsion layer may be present. If the layer is transferred to the sulfuric acid, a significant error will be introduced. The CTAB causes no interference in this analysis, and it is added to all samples for uniformity.

Spectro-grade chloroform is recommended because practical grade chloroform has produced a different and indistinct color change with results which were approximately 20% high on some samples. However, if spectro-grade cannot be obtained, practical grade should be tried.

The equations which are shown for the developer calculations are expected to be valid for all laboratories. However, if standard mixes are prepared, the average result should be within $\pm 5\%$ of the formula amount of the developing agent.

Developing agents dissolved in water may cause dermatitis and are more likely to cause it when dissolved in chloroform. Therefore, use extra caution while running this analysis to keep the chloroform solution from the skin.

> CAUTION: Chloroform is toxic; therefore, the extractions must be performed in an exhaust hood or where there is adequate ventilation. Keep chloroform away from open flames and hot surfaces. Chlorinated materials may break down to give toxic and irritating gases such as phosgene and hydrogen chloride. Waste chloroform should be disposed of according to locally acceptable practices.

RELIABILITY

The determination of developing agents is stoichiometric. The value of the blank (0.25) is subtracted from the volume of sulfato cerate used in the titration.

SPECIAL APPARATUS

Magnetic stirrer (VWR Scientific)
Teflon-covered stirring bar (Catalog No. 58949-061)

REAGENTS

Cetyltrimethylammonium Bromide (CTAB), 1% solution
Chloroform, $CHCl_3$, spectro-grade
7.0 N Sulfuric Acid, H_2SO_4
Ferroin indicator
0.0500 N Sulfato Cerate

PROCEDURE

A. Extraction of the CD-3 with Chloroform

1. Pipet 25.0 ml of developer into a 125-ml separatory funnel.
2. Add 1 ml of 1% CTAB solution from a tip-up pipet and mix by gently swirling.
3. Add, from a tip-up pipet, 25 ml of spectro-grade chloroform, and shake the funnel vigorously for 30 seconds.
4. Allow 1 minute for complete separation of the layers.

> NOTE: If any globules of chloroform are seen floating on the water layer, swirl the funnel until the globules drop back into the chloroform layer.

5. Pour approximately 400 ml of distilled water from a graduated cylinder into a 1-liter beaker.
6. Add, from a tip-up pipet, 25 ml of 7.0 N sulfuric acid, and mix thoroughly using a magnetic stirrer.
7. Carefully drain the lower (chloroform) layer into the dilute sulfuric acid, holding the tip of the funnel against the inside of the beaker. Drain off all but the *last few drops* of chloroform. Do not drain off any of the aqueous layer.
8. Extract the CD-3 remaining in the water layer by repeating Steps 3, 4, and 7.

B. Titration of the Acid-Chloroform Mixture

1. Add 4 drops of Ferroin indicator to the acid-chloroform mixture.
2. Turn on the magnetic stirrer so that the solution is mixing vigorously.
3. Titrate the solution with 0.0500 N sulfato cerate to the *first pale green color which persists for 15 seconds.* Add the titrant dropwise when within an estimated 2 ml of the end point, allowing sufficient time for complete mixing before making another addition.
4. After the titration, dispose of the chloroform according to locally acceptable practices.

C. Calculations

1. $$\frac{(\text{ml cerate} - \text{ml blank})(\text{N cerate})(\text{eq wt CD-3})}{(\text{ml sample})} =$$

2. $$\frac{(\text{ml cerate} - 0.25)(0.0500)(218.0)(1000)}{(25.0)(1000)} =$$

$$(\text{ml cerate} - 0.25)(0.436) = \text{CD-3, g/l}$$

TITRIMETRIC DETERMINATION OF HYDROQUINONE AND PHENIDONE* IN FIRST DEVELOPER (440)

PRINCIPLE

Most of the Phenidone and a small amount of hydroquinone are extracted from an acidified (pH 4.7) sample into chloroform. The hydroquinone that is extracted is washed out of the chloroform with a distilled water wash. The Phenidone is then reextracted from the chloroform into an acid solution of ferric chloride where the Phenidone reduces the ferric chloride to an equivalent amount of ferrous ions. The amount of ferrous ions formed is determined with a cerimetric titration as a measure of the Phenidone.

In aged mixes, an emulsion may be formed at the solvent-aqueous interface after the first extraction. This emulsion must be transferred along with the solvent.

The hydroquinone which was left in the original acidified water layer is extracted into ethyl acetate. It is then determined directly with a cerimetric titration.

RELIABILITY

Ten ME-4 first developer laboratory standard mixes were prepared with different combinations of Phenidone (0.100 to 0.500 g/l) and hydroquinone (3.00 to 7.00 g/l) to determine the calibration curves and the effect of one compound on the analysis of the other. Two analysts produced 19 analyses which showed complete separation of the two compounds.

The same conclusion was indicated by the 10 analyses of five ECO-3 first developer laboratory standard mixes containing 0.100 to 0.300 g/l of Phenidone and 2.00 to 6.00 g/l of hydroquinone.

A comparison of the individual calibration curves showed that there was no significant difference between them for each solution. Therefore, the data were pooled to obtain only one calibration equation for each compound. Based on these data, the 95% confidence limits for a set of analyses are ±0.01 g/l of Phenidone and ±0.10 g/l of hydroquinone.

REAGENTS

Chloroform, $CHCl_3$
Glacial Acetic Acid, CH_3COOH
Water
1.8 M Ferric Chloride, $FeCl_3$
3.0 N Hydrochloric Acid, HCl
Ethyl Acetate, water saturated
Methyl Alcohol, CH_3OH
Ferroin indicator
0.0500 N Sulfato Cerate
7.0 N Sulfuric Acid, H_2SO_4

* Phenidone is a registered trademark of Ilford, Ltd.

PROCEDURE

A. Extraction of Phenidone

1. Set up and label three separatory funnels as indicated:

   Funnel #1—500-ml funnel
   Funnel #2—250-ml funnel
   Funnel #3—250-ml funnel

2. Add, from a tip-up pipet, 150 ml of chloroform to funnel #1.

   CAUTION: Chloroform is toxic; therefore, the extractions must be performed in an exhaust hood or where there is adequate ventilation. Keep chloroform away from open flames and hot surfaces. Chlorinated materials may break down to give toxic and irritating gases such as phosgene and hydrogen chloride. Waste chloroform should be disposed of according to locally acceptable practices.

3. Add, from a tip-up pipet, 4 ml of glacial acetic acid to funnel #1.
4. Add, from a tip-up pipet, 100 ml of distilled water to funnel #2.
5. Add, from a tip-up pipet, 2 ml of 1.8 M ferric chloride to funnel #3.
6. Add, from a tip-up pipet, 10 ml of 3.0 N hydrochloric acid to funnel #3.
7. Pipet 50.0 ml of sample into funnel #1.
8. Do not stopper funnel #1. Swirl the funnel for several seconds to allow the rapidly forming gases to escape. Stopper and shake the funnel for 30 seconds, venting occasionally through the stopper.
9. After the phases separate, drain the chloroform (lower) layer into funnel #2. Retain the water layer in funnel #1.

   NOTE: If there is an emulsion at the solvent interface, carefully transfer the emulsion with the chloroform.

10. Add, from a tip-up pipet, 100 ml of ethyl acetate, water-saturated, to funnel #1.
11. Stopper and shake *both* funnel #1 and #2 for 30 seconds, venting occasionally as above. Retain funnel #1 for Part D.

    NOTE 1: The HQ is extracted from the remaining mix constituents into the ethyl acetate.

    NOTE 2: Any HQ that was extracted into the chloroform (funnel #2) is removed by this water wash and is discarded.

B. Selective Oxidation of Phenidone

1. After the phases separate, drain the chloroform (lower) layer from funnel #2 into funnel #3.
2. Stopper and shake separatory funnel #3 vigorously for 2 minutes, venting occasionally as above.
3. After the layers separate, discard the chloroform (lower) layer.

NOTE: In this step, the Phenidone is oxidized by ferric chloride. The ferrous ions which were produced remained in the water phase while most of the oxidized Phenidone was discarded in the chloroform. The remaining oxidized Phenidone is removed by the following chloroform wash.

4. Add, from a tip-up pipet, 50 ml of chloroform to funnel #3.

5. Stopper and shake funnel #3 for 30 seconds, venting occasionally as above. After the layers separate, discard the chloroform (lower) layer.

6. Repeat Steps 4 and 5.

C. Titration of Ferrous Ions (Indirect Measurement of the Original Phenidone)

1. Add approximately 300 ml of distilled water to a 600-ml beaker.

2. Add, from a tip-up pipet, 25 ml of 7.0 N sulfuric acid to the beaker.

3. Add 3 drops of Ferroin indicator.

4. Drain the water solution from funnel #3 into the beaker. Rinse the funnel and its stopper with distilled water from a wash bottle, allowing the wash water to go into the beaker.

5. Stir on a magnetic stirrer and titrate with 0.0500 N sulfato cerate to a green-yellow which persists for 30 seconds.

NOTE: There is very little end-point warning, so the titration must be done slowly.

D. Isolation of HQ

1. Discard the water (lower) layer from funnel #1 (from Step A-11).

2. Add, from a tip-up pipet, 10 ml of distilled water to funnel #1.

3. Stopper and shake funnel #1 for 10 seconds. After the phases separate, discard the water (lower) layer.

4. Drain the ethyl acetate layer into a 200-ml volumetric flask. Rinse funnel #1 with methyl alcohol, adding it to the flask. Dilute the contents of the flask to volume with methyl alcohol. Stopper the flask and mix the contents by inverting it several times.

NOTE: A long-stemmed funnel in the flask may help in transferring the contents from the separatory funnel.

E. Titration of HQ

1. Pipet a 50.0-ml aliquot of the solution in the flask into a 150-ml beaker.

2. Add 10 ml of 3 N hydrochloric acid from a tip-up pipet.

3. Stir on a magnetic stirrer, add 3 drops of Ferroin indicator, and titrate with 0.0500 N sulfato cerate to a green-yellow which persists for 30 seconds.

NOTE: There is very little end-point warning, so the titration must be done slowly.

F. Calculations

1. For Phenidone:
   0.0757 (ml sulfato cerate) — 0.020 = Phenidone, g/l
   For convenience, use Table I.

2. For Hydroquinone:
   0.243 (ml sulfato cerate) — 0.07 = HQ, g/l
   For convenience, use Table II.

TABLE I

PHENIDONE IN FIRST DEVELOPER

ml	Phenidone g/l	ml	Phenidone g/l	ml	Phenidone g/l
.5	.02	3.0	.21	5.5	.40
.6	.03	3.1	.21	5.6	.40
.7	.03	3.2	.22	5.7	.41
.8	.04	3.3	.23	5.8	.42
.9	.05	3.4	.24	5.9	.43
1.0	.06	3.5	.24	6.0	.43
1.1	.06	3.6	.25	6.1	.44
1.2	.07	3.7	.26	6.2	.45
1.3	.08	3.8	.27	6.3	.46
1.4	.09	3.9	.28	6.4	.46
1.5	.09	4.0	.28	6.5	.47
1.6	.10	4.1	.29	6.6	.48
1.7	.11	4.2	.30	6.7	.49
1.8	.12	4.3	.31	6.8	.49
1.9	.12	4.4	.31	6.9	.50
2.0	.13	4.5	.32	7.0	.51
2.1	.14	4.6	.33	7.1	.52
2.2	.15	4.7	.34	7.2	.53
2.3	.15	4.8	.34	7.3	.53
2.4	.16	4.9	.35	7.4	.54
2.5	.17	5.0	.36	7.5	.55
2.6	.18	5.1	.37	7.6	.56
2.7	.18	5.2	.37	7.7	.56
2.8	.19	5.3	.38	7.8	.57
2.9	.20	5.4	.39	7.9	.58

(0.0757)(ml cerate) — 0.020 = Phenidone, g/l

TABLE II

HYDROQUINONE IN FIRST DEVELOPER

ml	HQ, g/l	ml	HQ, g/l	ml	HQ, g/l
13.0	3.09	14.0	3.33	15.0	3.58
13.1	3.11	14.1	3.36	15.1	3.60
13.2	3.14	14.2	3.38	15.2	3.62
13.3	3.16	14.3	3.40	15.3	3.65
13.4	3.19	14.4	3.43	15.4	3.67
13.5	3.21	14.5	3.45	15.5	3.70
13.6	3.23	14.6	3.48	15.6	3.72
13.7	3.26	14.7	3.50	15.7	3.75
13.8	3.28	14.8	3.53	15.8	3.77
13.9	3.31	14.9	3.55	15.9	3.79

0.243 (ml cerate) — 0.07 = HQ, g/l

ml	HQ, g/l	ml	HQ, g/l	ml	HQ, g/l	ml	HQ, g/l	ml	HQ, g/l	ml	HQ, g/l
16.0	3.82	19.5	4.67	23.0	5.52	26.5	6.37	30.0	7.22	33.5	8.07
16.1	3.84	19.6	4.69	23.1	5.54	26.6	6.39	30.1	7.24	33.6	8.09
16.2	3.87	19.7	4.72	23.2	5.57	26.7	6.42	30.2	7.27	33.7	8.12
16.3	3.89	19.8	4.74	23.3	5.59	26.8	6.44	30.3	7.29	33.8	8.14
16.4	3.92	19.9	4.77	23.4	5.62	26.9	6.47	30.4	7.32	33.9	8.17
16.5	3.94	20.0	4.79	23.5	5.64	27.0	6.49	30.5	7.34	34.0	8.19
16.6	3.96	20.1	4.81	23.6	5.66	27.1	6.52	30.6	7.37	34.1	8.22
16.7	3.99	20.2	4.84	23.7	5.69	27.2	6.54	30.7	7.39	34.2	8.24
16.8	4.01	20.3	4.86	23.8	5.71	27.3	6.56	30.8	7.41	34.3	8.26
16.9	4.04	20.4	4.89	23.9	5.74	27.4	6.59	30.9	7.44	34.4	8.29
17.0	4.06	20.5	4.91	24.0	5.76	27.5	6.61	31.0	7.46	34.5	8.31
17.1	4.09	20.6	4.94	24.1	5.79	27.6	6.64	31.1	7.49	34.6	8.34
17.2	4.11	20.7	4.96	24.2	5.81	27.7	6.66	31.2	7.51	34.7	8.36
17.3	4.13	20.8	4.98	24.3	5.83	27.8	6.69	31.3	7.54	34.8	8.39
17.4	4.16	20.9	5.01	24.4	5.86	27.9	6.71	31.4	7.56	34.9	8.41
17.5	4.18	21.0	5.03	24.5	5.88	28.0	6.73	31.5	7.58	35.0	8.44
17.6	4.21	21.1	5.06	24.6	5.91	28.1	6.76	31.6	7.61	35.1	8.46
17.7	4.23	21.2	5.08	24.7	5.93	28.2	6.78	31.7	7.63	35.2	8.48
17.8	4.26	21.3	5.11	24.8	5.96	28.3	6.81	31.8	7.66	35.3	8.51
17.9	4.28	21.4	5.13	24.9	5.98	28.4	6.83	31.9	7.68	35.4	8.53
18.0	4.30	21.5	5.15	25.0	6.01	28.5	6.86	32.0	7.71		
18.1	4.33	21.6	5.18	25.1	6.03	28.6	6.88	32.1	7.73		
18.2	4.35	21.7	5.20	25.2	6.05	28.7	6.90	32.2	7.75		
18.3	4.38	21.8	5.23	25.3	6.08	28.8	6.93	32.3	7.78		
18.4	4.40	21.9	5.25	25.4	6.10	28.9	6.95	32.4	7.80		
18.5	4.43	22.0	5.28	25.5	6.13	29.0	6.98	32.5	7.83		
18.6	4.45	22.1	5.30	25.6	6.15	29.1	7.00	32.6	7.85		
18.7	4.47	22.2	5.32	25.7	6.18	29.2	7.03	32.7	7.88		
18.8	4.50	22.3	5.35	25.8	6.20	29.3	7.05	32.8	7.90		
18.9	4.52	22.4	5.37	25.9	6.22	29.4	7.07	32.9	7.92		
19.0	4.55	22.5	5.40	26.0	6.25	29.5	7.10	33.0	7.95		
19.1	4.57	22.6	5.42	26.1	6.27	29.6	7.12	33.1	7.97		
19.2	4.60	22.7	5.45	26.2	6.30	29.7	7.15	33.2	8.00		
19.3	4.62	22.8	5.47	26.3	6.32	29.8	7.17	33.3	8.02		
19.4	4.64	22.9	5.49	26.4	6.35	29.9	7.20	33.4	8.05		

0.243 (ml cerate) — 0.07 = HQ, g/l

SPECTROPHOTOMETRIC DETERMINATION OF CARBOWAX 1540 IN BLEACH (560)

INTRODUCTION

The Carbowax 1540 is precipitated with ferrocyanide from an acidified sample of the bleach. The Carbowax-ferrocyanide precipitate is dissolved in alkali, and the Carbowax 1540 is then determined indirectly by the spectrophotometric measurement of the ferrocyanide. Although there is usually ferrocyanide in a bleach, ferrocyanide is added to produce an excess. The addition of solid sodium chloride and the use of a sodium chloride-hydrochloric acid wash improves the formation of the Carbowax-ferrocyanide precipitate.

Some iron hydroxide is present in the bleach solution as finely divided particles of ferric hydroxide and ferrous hydroxide. If the iron hydroxide is allowed to remain in the bleach sample, the acidification of the sample will cause Prussian blue, ferric ferrocyanide, and ferrous ferrocyanide to precipitate. The subsequent caustic treatment used to dissolve the Carbowax-ferrocyanide precipitate will also dissolve the iron ferrocyanides. Additional ferrocyanide is then released which will then increase the reported Carbowax concentration since the Carbowax is measured indirectly from the ferrocyanide level.

Usually the bleach filtration system is adequate for the removal of the iron hydroxide. If it is inadequate, the sample of the bleach must then be filtered through a fritted Pyrex disc Büchner funnel of fine porosity before the analyst begins the procedure.

RELIABILITY

The calibration curve was calculated from the data obtained by 2 analysts who analyzed 5 standard laboratory mixes containing 2 to 10 g/l of Carbowax 1540 and constant amounts of the other constituents. The absorbance values determined by following the analytical procedure were plotted against the corresponding concentrations of the Carbowax. The best straight line was determined from the data of 10 analyses. The equation for this line is found in the calculations. Based on these data, the 95% confidence limits for an individual determination are ± 0.16 g/l of Carbowax 1540.

APPARATUS

Beckman DU Spectrophotometer, or equivalent

1-cm Silica cell

Fritted Pyrex Disc Büchner Funnel, 60mm dia. fine porosity (VWR Scientific, Catalog No. 30301-120, or Corning No. 36060)

REAGENTS

0.2 M Sodium Ferrocyanide, $Na_4Fe(CN)_6 \cdot 10H_2O$

Sodium Chloride, NaCl

3.0 N Hydrochloric Acid, HCl

4 M Sodium Chloride—1 M Hydrochloric Acid Reagent, 4 M NaCl—1 M HCl

0.1 M Sodium Sulfite—2.5 N Sodium Hydroxide Reagent, 0.1 M Na_2SO_3—2.5 N NaOH

PROCEDURE

A. Precipitation and Collection of Carbowax-Ferrocyanide Precipitate

1. Pipet 10.0 ml of sample into a 125-ml Phillips beaker, and stir on a magnetic stirrer.
2. Add 10.0 ml of 0.2 M sodium ferrocyanide from a tip-up pipet.
3. Add and dissolve 2.0 g of sodium chloride.
4. Add 10 ml of 3.0 N hydrochloric acid from a tip-up pipet.
5. Stir for 10 minutes; then filter the mixture through a fritted Pyrex disc Büchner funnel, 60mm dia. fine porosity catching the filtrate in a 250-ml filter flask.
6. Disconnect the aspirator hose. Rinse, from a tip-up pipet, the Phillips beaker and then the sides of the funnel with 10.0 ml of 4 M NaCl—1 M HCl reagent. Reconnect the aspirator hose to filter the solution.
7. Repeat Step 6.

B. Dissolution of Carbowax-Ferrocyanide Precipitate

1. Disconnect the aspirator hose. Thoroughly rinse the 250-ml flask, the rubber adapter, and the inside and outside of the funnel stem with distilled water. Reassemble the cleaned apparatus without the aspirator hose.
2. Rinse, from a tip-up pipet, the Phillips beaker, and then the sides of the funnel with 20.0 ml of 0.1 M Na_2SO_3—2.5 N NaOH reagent. After the solution has been in contact with the sintered surface for one minute, connect the aspirator hose and draw the solution into the 250-ml flask.
3. Disconnect the aspirator hose, and repeat Step 2.
4. Quantitatively transfer the filtrate with water rinses to a 100-ml volumetric flask and dilute to volume with water.

C. Measurement of Absorbance

Measure the absorbance of the diluted filtrate at 322 nm (mμ) with the spectrophotometer. Use the ultraviolet lamp. See instructions in Method VI E.

D. Calculations

$$(9.88)(A_{322}) - 0.66 = \text{g/l CW-1540}$$

DETERMINATION OF CARBOWAX 1540 IN STOCK SOLUTIONS BY SPECIFIC GRAVITY (570B)

INTRODUCTION

The concentration of Carbowax 1540 (CW-1540) in stock solution is based on the specific gravity of the solution.

RELIABILITY

The attached Table I was determined by measuring the specific gravity at 27 C (80 F) of five standard stock solutions containing 300 to 800 g/l of CW-1540 and of eight stock solutions containing 370 to 485 g/l of CW-1540. There is curvature at the higher concentrations. The 95% confidence limits are estimated to be ±10 g/l CW-1540 in the region of greatest interest.

SPECIAL APPARATUS

Taylor Permax Quality Hydrometer or equivalent:

Specific Gravity Range	Taylor Number
1.000 — 1.050	H-4140
1.050 — 1.100	H-4141
1.100 — 1.150	H-4142

Hydrometer cylinder or 250-ml graduated cylinder.

PROCEDURE

1. Fill the hydrometer cylinder with the sample.
2. Adjust the temperature of the sample to 27 ±0.5 C (80 ±1°F).
3. Dry the hydrometer thoroughly and carefully lower it into the sample, being sure that the stem of the hydrometer is dry to within ⅛ inch of the surface of the liquid. Make sure the bulb of the hydrometer is floating freely and is not sticking to the inside wall of the cylinder while the specific gravity is being determined.

NOTE: For an illustration of the hydrometer apparatus see Method 701D, "Determination of the Specific Gravity of Processing Solutions."

4. After the hydrometer has stopped settling in the liquid, read it at the top of the meniscus as seen along the side of the hydrometer stem.
5. Determine the concentration of CW-1540 from Table I.

TABLE I

CW-1540 IN STOCK SOLUTIONS

Specific Gravity	g/l	Specific Gravity	g/l	Specific Gravity	g/l
1.047	297	1.071	450	1.095	618
1.048	304	1.072	457	1.096	626
1.049	310	1.073	463	1.097	634
1.050	317	1.074	470	1.098	642
1.051	323	1.075	476	1.099	650
1.052	330	1.076	483	1.100	658
1.053	336	1.077	490	1.101	665
1.054	342	1.078	497	1.102	672
1.055	349	1.079	504	1.103	681
1.056	355	1.080	510	1.104	690
1.057	361	1.081	517	1.105	700
1.058	367	1.082	524	1.106	710
1.059	373	1.083	530	1.107	720
1.060	380	1.084	537	1.108	730
1.061	386	1.085	544	1.109	741
1.062	393	1.086	551	1.110	752
1.063	399	1.087	558	1.111	763
1.064	406	1.088	564	1.112	777
1.065	412	1.089	571	1.113	792
1.066	418	1.090	578	1.114	808
1.067	425	1.091	586	1.115	825
1.068	431	1.092	594	1.116	850
1.069	437	1.093	602	1.117	877
1.070	444	1.094	610	1.118	905

DETERMINATION OF THE PURITY OF ETHYLENEDIAMINE (612C)

INTRODUCTION

The purity of ethylenediamine, which may range from 75 to 100%, is determined by titration with standard sulfuric acid using E-O-X as the indicator.

REAGENTS

E-O-X indicator
2.500 N Sulfuric Acid, H_2SO_4

PROCEDURE

A. Titration of Sample with 2.500 N Sulfuric Acid

1. Add 100 ml of distilled water from a graduated cylinder to a 250-ml Erlenmeyer flask.
2. Pipet by bulb (wipe the pipet before leveling) 4.00 ml of the ethylenediamine solution into the flask. Allow the pipet to drain for 10 seconds.
3. Add 5 drops of E-O-X indicator.
4. Titrate with 2.500 N sulfuric acid from green through gray to the first gray-purple coloration.

B. Calculations

$$\frac{(\text{ml } H_2SO_4)(\text{N } H_2SO_4)(\text{eq wt ethylenediamine})(1000)}{(\text{ml sample})(1000)} =$$

$$(\text{ml } H_2SO_4)(18.78) = \text{ethylenediamine, g/l of solution}$$

DETERMINATION OF ETHYLENEDIAMINE IN COLOR DEVELOPERS (617B)

INTRODUCTION

A sample of the developer is first acidified to a given pH. Formalin is then added to react with the ethylenediamine to release hydronium ions (H_3O^+) as shown.

$$H_2N(CH_2)_2NH_3^+ + CH_2O \longrightarrow$$

$$CH_2{=}N(CH_2)_2NH_2 + H_3O^+$$

The hydronium ions that are released are then titrated with base to give an indirect measure of ethylenediamine.

RELIABILITY

The calibration curve was calculated from the 40 results obtained by two analysts who analyzed standard laboratory mixes for various Ektachrome processes. The mixes contained from 1.50 to 3.40 g/l of ethylenediamine. The volumes of base required in the titrations were used to calculate, by the method of least squares, the best straight line for the universal calibration curve. The equation for this line is found under Calculations. The 95% confidence limits for an individual determination are ±0.04 g/l of ethylenediamine.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent
Corning No. 476022, or Leeds & Northrup Standard Black-Dot Glass Electrode, No. 117169
Beckman Fiber-Type Calomel Electrode, No. 39170 (filled with saturated potassium chloride solution)

REAGENTS

Potassium Acid Phthalate Buffer, 0.05 Molar
Borax Buffer, 0.01 Molar
Foamex
1.0 N Sulfuric Acid, H_2SO_4
0.1000 N Sodium Hydroxide, NaOH
37.5% Formaldehyde solution, pH 3.9

PROCEDURE

A. Preparation of the Meter

1. Follow Method 810 (or any subsequent pH method) for making pH measurements below 9.
   a. Adjust the temperature of the buffers.
   b. Adjust the meter.
   c. Standardize the meter with potassium acid phthalate buffer.
   d. Cross-check the electrodes with borax buffer.

B. Titration of the Sample

1. Pipet 50.0 ml of sample into a 250-ml beaker.
2. Immerse the electrode assembly in the sample and add sufficient distilled water to cover the tips of the electrodes.
3. Add 1 drop of Foamex, and stir the solution with a magnetic stirrer.
4. Add, from a squeeze bottle or buret, 1.0 N sulfuric acid to attain a pH equal to or slightly less than 3.8. (This volume does not have to be measured.)
5. Adjust the solution to pH 3.90 with 0.1000 N sodium hydroxide from a squeeze bottle or an eyedropper.
6. Add 25 ml of 37.5% formaldehyde solution, pH 3.9, from a tip-up pipet.
7. Titrate to pH 3.90 with 0.1000 N sodium hydroxide.

C. Calculations

1. Substitute the buret reading recorded in Step B, 7 in the following equation:

(0.116)(ml) + 0.26 = ethylenediamine, g/l

or for convenience use Table I.

TABLE I

ETHYLENEDIAMINE IN *EKTACHROME* COLOR DEVELOPERS

ml NaOH	g/l	ml NaOH	g/l	ml NaOH	g/l
8.0	1.18	11.0	1.53	14.0	1.88
8.1	1.20	11.1	1.54	14.1	1.89
8.2	1.21	11.2	1.56	14.2	1.90
8.3	1.22	11.3	1.57	14.3	1.91
8.4	1.23	11.4	1.58	14.4	1.93
8.5	1.24	11.5	1.59	14.5	1.94
8.6	1.25	11.6	1.60	14.6	1.95
8.7	1.27	11.7	1.61	14.7	1.96
8.8	1.28	11.8	1.62	14.8	1.97
8.9	1.29	11.9	1.64	14.9	1.98
9.0	1.30	12.0	1.65	15.0	2.00
9.1	1.31	12.1	1.66	15.1	2.01
9.2	1.32	12.2	1.67	15.2	2.02
9.3	1.34	12.3	1.68	15.3	2.03
9.4	1.35	12.4	1.69	15.4	2.04
9.5	1.36	12.5	1.70	15.5	2.05
9.6	1.37	12.6	1.72	15.6	2.06
9.7	1.38	12.7	1.73	15.7	2.08
9.8	1.39	12.8	1.74	15.8	2.09
9.9	1.40	12.9	1.75	15.9	2.10
10.0	1.42	13.0	1.76	16.0	2.11
10.1	1.43	13.1	1.78	16.1	2.12
10.2	1.44	13.2	1.79	16.2	2.13
10.3	1.45	13.3	1.80	16.3	2.15
10.4	1.46	13.4	1.81	16.4	2.16
10.5	1.47	13.5	1.82	16.5	2.17
10.6	1.49	13.6	1.83	16.6	2.18
10.7	1.50	13.7	1.84	16.7	2.19
10.8	1.51	13.8	1.86	16.8	2.20
10.9	1.52	13.9	1.87	16.9	2.22

(0.116)(ml NaOH) + 0.26 = ethylenediamine, g/l

ml NaOH	g/l	ml NaOH	g/l	ml NaOH	g/l	ml NaOH	g/l	ml NaOH	g/l	ml NaOH	g/l
17.0	2.23	19.5	2.52	22.0	2.81	24.5	3.10	27.0	3.39	29.5	3.68
17.1	2.24	19.6	2.53	22.1	2.82	24.6	3.11	27.1	3.40	29.6	3.69
17.2	2.25	19.7	2.54	22.2	2.83	24.7	3.12	27.2	3.41	29.7	3.70
17.3	2.26	19.8	2.55	22.3	2.84	24.8	3.13	27.3	3.42	29.8	3.72
17.4	2.27	19.9	2.56	22.4	2.85	24.9	3.14	27.4	3.43	29.9	3.73
17.5	2.28	20.0	2.57	22.5	2.86	25.0	3.15	27.5	3.44	30.0	3.74
17.6	2.30	20.1	2.59	22.6	2.88	25.1	3.17	27.6	3.45	30.1	3.75
17.7	2.31	20.2	2.60	22.7	2.89	25.2	3.18	27.7	3.47	30.2	3.76
17.8	2.32	20.3	2.61	22.8	2.90	25.3	3.19	27.8	3.48	30.3	3.77
17.9	2.33	20.4	2.62	22.9	2.91	25.4	3.20	27.9	3.50	30.4	3.79
18.0	2.34	20.5	2.63	23.0	2.92	25.5	3.21	28.0	3.51		
18.1	2.35	20.6	2.64	23.1	2.93	25.6	3.22	28.1	3.52		
18.2	2.37	20.7	2.66	23.2	2.95	25.7	3.23	28.2	3.53		
18.3	2.38	20.8	2.67	23.3	2.96	25.8	3.25	28.3	3.54		
18.4	2.39	20.9	2.68	23.4	2.97	25.9	3.26	28.4	3.55		
18.5	2.40	21.0	2.69	23.5	2.98	26.0	3.27	28.5	3.57		
18.6	2.41	21.1	2.70	23.6	2.99	26.1	3.28	28.6	3.58		
18.7	2.42	21.2	2.71	23.7	3.00	26.2	3.29	28.7	3.59		
18.8	2.44	21.3	2.72	23.8	3.01	26.3	3.30	28.8	3.60		
18.9	2.45	21.4	2.74	23.9	3.03	26.4	3.32	28.9	3.61		
19.0	2.46	21.5	2.75	24.0	3.04	26.5	3.33	29.0	3.62		
19.1	2.47	21.6	2.76	24.1	3.05	26.6	3.34	29.1	3.64		
19.2	2.48	21.7	2.77	24.2	3.06	26.7	3.35	29.2	3.65		
19.3	2.49	21.8	2.78	24.3	3.07	26.8	3.36	29.3	3.66		
19.4	2.50	21.9	2.79	24.4	3.08	26.9	3.37	29.4	3.67		

(0.116)(ml NaOH) + 0.26 = ethylenediamine, g/l

THE DETERMINATION OF THE SPECIFIC GRAVITY OF PROCESSING SOLUTIONS (701D)

INTRODUCTION

Specific gravity is the ratio of the mass of a body to the mass of an equal volume of water at the same temperature. It is used as a measure of the total amount of dissolved material in a solution.

The temperature of measurement should be specified and controlled in all specific gravity measurements because the specific gravity of a solution is affected by temperature. An increase of 2.8 C (5 F) causes a decrease of 0.001 in the specific gravity of most processing solutions. Standards of specific gravity for processing solutions are set by preparing standard mixes at 27 C (80 F) because many processing solutions are used at that temperature.

The variability of measurements is expected to fall within ±0.002 99% of the time.

CALCULATIONS OF SPECIFIC GRAVITY OF A MIX AT 27 C (80 F)

An empirical approximation of specific gravity for a fresh mix may be determined by adding or subtracting the contribution of each chemical constituent to the specific gravity. Table I lists the constants for most of the processing chemicals. Calculations may be made as follows:

1. Using Table I, calculate the contribution of each chemical in a mix by multiplying its specific gravity constant by its concentration in the mix. Add all the values so obtained, taking the sign into account.
2. Subtract 0.003. This empirical constant includes a correction factor for reporting the specific gravity at 27 C (80 F) rather than 20 C (68 F).
3. Add 1.000, a constant for water.

SPECIAL APPARATUS

The hydrometers recommended for determining specific gravity are calibrated for reference to distilled water at 15.5 C (60 F), although measurements are made at 27 C (80 F).

Taylor Permax Quality Hydrometer or equivalent:

Sp Gr Range	Taylor Number
1.000 – 1.050	H-4140
1.050 – 1.100	H-4141
1.100 – 1.150	H-4142
1.150 – 1.200	H-4143

Hydrometer cylinder.

PROCEDURE

1. Fill the hydrometer cylinder with the sample so that it overflows upon insertion of the hydrometer.
2. Adjust the temperature of the sample to 27 ±0.6 C (80 ±1° F).
3. Dry the hydrometer thoroughly and carefully lower it into the sample, being sure that the stem of the hydrometer is dry to within ⅛ inch of the surface of the liquid.
4. Read the hydrometer at the top of the meniscus as seen along the side of the hydrometer stem. See the diagram below.

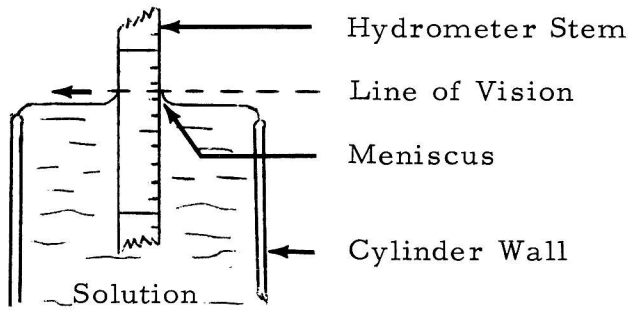


TABLE I

CONSTANTS FOR CALCULATING SPECIFIC GRAVITIES—20 C (68 F)

Constituent	Formula	Specific Gravity Units per gram of Constituent per liter of Proc. Solution
Acetic Acid	CH_3COOH	0.00014/ml
Benzyl Alcohol	$C_6H_5CH_2OH$	0.00020/ml
CD-3	--------	0.00060/g
Formalin, 37.5% formaldehyde	HCHO (in water)	0.00026/ml
Hypo (sodium thiosulfate pentahydrate)	$Na_2S_2O_3 \cdot 5H_2O$	0.00050/g
Potassium Ferricyanide	$K_3Fe(CN)_6$	0.00061
Potassium Persulfate	$K_2S_2O_8$	0.00090
Sodium Acetate	$NaOOCCH_3$	0.00042
Sodium Bisulfite	$NaHSO_3$	0.00068
Sodium Bromide	NaBr	0.00078
Sodium Carbonate (soda ash)	Na_2CO_3	0.00094
Sodium Ferrocyanide, decahydrate	$Na_4Fe(CN)_6 \cdot 10H_2O$	0.00050
Sodium Hydroxide	NaOH	0.00094
Sodium Phosphate, dibasic	Na_2HPO_4	0.00080
Sodium Phosphate, tribasic	$Na_3PO_4 \cdot 12H_2O$	0.00045
Sodium Sulfate	Na_2SO_4	0.00082
Sodium Sulfite	Na_2SO_3	0.00086
All other chemicals (estim.)	--------	0.00066

DETERMINATION OF THE TOTAL ALKALINITY OF DEVELOPER SOLUTIONS (702J)

FOREWORD

A critical appraisal of the pH, specific gravity, and total alkalinity of a mix is useful in detecting incorrect amounts of the inorganic constituents and certain of the organic constituents.

PRINCIPLE

The total alkalinity (T. Alk.) of a processing solution is defined as the milliliters of 0.1000 N sulfuric acid required to adjust a specified volume of processing solution to pH 4.3. That pH was selected because most salts derived from weak acids show an inflection point in their titration curves near pH 4.3.

Colored and some clear samples, when titrated visually, do not give a clear end point, thus causing excessive variability. For this reason, potentiometric titrations are recommended. Complete titration curves need not be plotted routinely.

Either an automatic titrator or a pH meter can be used with glass and calomel electrodes. The instruments are standardized at the nominal temperature at which pH measurements are obtained. The temperature is usually 27 C (80 F).

The approximate total alkalinity of a fresh developer solution can be calculated from the formula and the alkalinity contribution of each solution constituent. The alkalinity contribution of a constituent is the amount of 0.1000 N acid required to adjust one gram of that constituent to pH 4.3. Table I lists the various constituents and their respective alkalinity contributions.

The numerical value for the total alkalinity of 1 liter of a processing solution is calculated by summing the amounts of acid which will bring each of the constituents, considering the concentrations used in the solution, to approximately pH 4.3. The sum for 1 liter of solution is then corrected for the sample size normally used in the analysis by using the following equation:

$$\frac{\left[\begin{array}{c}\text{proposed sample}\\ \text{size, ml}\end{array}\right]\left[\begin{array}{c}\text{ml 0.1000 N } H_2SO_4\\ \text{for 1 liter}\end{array}\right]}{1000} = \text{the T. Alk. for a specific sample size}$$

The sample size is so chosen that the total volume of sulfuric acid consumed falls between 25 and 45 ml. The sample sizes must be specified with all total alkalinity analyses.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent
Corning No. 476022, or Leeds & Northrup Black-Dot Glass Electrode, No. 117169
Beckman Fiber-Junction Calomel Electrode, No. 39170 (filled with saturated potassium chloride solution)

REAGENTS

0.1000 N Sulfuric Acid, H_2SO_4
Potassium Acid Phthalate Buffer
Borax Buffer

PROCEDURE

A. Preparation of the pH Meter

Follow Method 810 (or any subsequent pH method) for making pH measurements below pH 9, Parts A through D:

1. Adjust the temperature of the buffers and the sample.
2. Adjust the meter.
3. Standardize the meter with potassium acid phthalate buffer.
4. Cross-check with borax buffer.

B. Titration of the Sample and Reporting Results

1. Pipet the sample volume indicated below into a 150-ml beaker containing 50 ml of distilled water. The water should be approximately the same temperature as the buffer used in the cross-check.
   a. For First Developer, use a 4.00-ml sample.
   b. For Color Developer, use a 10.0-ml sample.
2. Place the electrode assembly and stirrer in the solution. Turn on the stirrer and immerse the tip of the buret into the sample.
3. Titrate to a pH of 4.3 with 0.1000 N sulfuric acid, zeroing the needle with the pH scale dial as the acid is slowly added. When the region of pH 5 is reached, add the titrant in 0.10-ml increments, zeroing the needle in the pH scale dial after each addition.
4. Report the ml of acid required to reach a pH of 4.3.

   NOTE: This is, by definition, the total alkalinity. Always indicate the sample size when reporting the results.

5. Remove the sample and rinse the electrode assembly with distilled water. If rinsing does not completely remove sample deposits, wipe the assembly with a cleansing tissue, and rerinse. Replace in potassium acid phthalate buffer.

TABLE I

ALKALINITY OF PROCESSING CHEMICALS

Constituent	Formula	Mole Wt.	Eq. Wt.	Alkalinity Contribution by Experiment*
Benzyl Alcohol	$C_6H_5CH_2OH$	107	---	0
Borax, pentahydrate	$Na_2B_4O_7{\cdot}5H_2O$	291	146	70
CD-3†	---------	---	---	– 44
Citrazinic Acid†	-N=C(OH)CH=C(COOH)CH=C(OH)–	155	---	–150
Ethylenediamine	$NH_2CH_2CH_2NH_2$	60	30	330‡
Hydroquinone	$C_6H_4(OH)_2$	110	---	0
Phenidone	---------	---	---	0
Potassium Bromide	KBr	119	---	0

* The ml of 0.1000 N sulfuric acid required to adjust 1.00 gram of constituent to pH 4.3.

† These chemicals make a negative contribution to the T. Alk.; i.e., they have a pH less than 4.3.

‡ $\frac{(1000)}{(\text{Eq. Wt.})(\text{N Acid})} = \frac{(1000)}{(\text{Eq. Wt.})(0.1000)} = \frac{(10{,}000)}{(\text{Eq. Wt.})}$ = Calculated alkalinity contribution

Constituent	Formula	Mole Wt.	Eq. Wt.	Alkalinity Contribution by Experiment*
Potassium Iodide	KI	166	---	0
Quadrafos	---------	---	---	24
Sodium Bisulfite	$NaHSO_3$	104	0	1
Sodium Bromide	NaBr	103	---	0
Sodium Carbonate (Soda Ash)	Na_2CO_3	106	53	189‡
Sodium Carbonate, monohydrate	$Na_2CO_3 \cdot H_2O$	124	62	163.2
Sodium Hydroxide	NaOH	40	40	250‡
Sodium Sulfate	Na_2SO_4	142	---	0
Sodium Sulfite	Na_2SO_3	126	126	76
Sodium Thiocyanate	NaCNS	81	---	5.3
Sulfuric Acid†	H_2SO_4	98	49	–360 per ml‡
Trisodium Phosphate, 12-mole	$Na_3PO_4 \cdot 12H_2O$	380	190	60.4

* The ml of 0.1000 N sulfuric acid required to adjust 1.00 gram of constituent to pH 4.3.

† These chemicals make a negative contribution to the T. Alk.; i.e., they have a pH less than 4.3.

$$\ddagger \frac{(1000)}{(\text{Eq. Wt.})(\text{N Acid})} = \frac{(1000)}{(\text{Eq. Wt.})(0.1000)} = \frac{(10{,}000)}{(\text{Eq. Wt.})} = \text{Calculated alkalinity contribution}$$

TABLE II

CONTRIBUTION OF CONSTITUENTS TO TOTAL ALKALINITY OF TYPICAL DEVELOPER REPLENISHER SOLUTIONS

Developer	Constituent	Concentration g/l	Contribution ml	Contribution %
ECO-3 First	Quadrafos	2.0	0.2	0.6
	$NaHSO_3$	3.3	0.0	0.0
	Phenidone	0.20	0.0	0.0
	Na_2SO_3	38.4	11.8	33.3
	HQ	5.5	0.0	0.0
	Na_2CO_3	31.0	23.5	65.8
	NaCNS	2.7	0.1	0.3
	KI	0.005	0.0	0.0
	Cal. T. Alk.; 4.00-ml sample		35.6	100.0
ECO-3 Color	Anti-Calcium, No. 4	3.0*	3.0	6.8
	Benzyl Alcohol	5.1*	0.0	0.0
	Na_2SO_3	7.75	5.9	13.3
	$Na_3PO_4 \cdot 12H_2O$	37.5	22.7	51.0
	NaBr	0.1	0.0	0.0
	KI	0.04	0.0	0.0
	NaOH	4.60	11.5	25.9
	Citrazinic Acid	1.60	— 2.4	— 5.3
	CD-3	12.0	— 5.0	—11.6
	Ethylenediamine	3.05	8.8	19.9
	RA-1	0.1	0.0	0.0
	Cal. T. Alk.; 10.0-ml sample		44.5	100.0
ME-4 First	Quadrafos	2.0	0.2	0.5
	$NaHSO_3$	2.9	0.0	0.0
	Phenidone	0.4	0.0	0.0
	Na_2SO_3	44.0	13.4	37.7
	HQ	7.0	0.0	0.0
	Na_2CO_3	28.9	21.9	61.8
	NaCNS	1.4	0.0	0.0
	NaBr	0.2	0.0	0.0
	KI	0.007	0.0	0.0
	Cal. T. Alk.; 4.00-ml sample		35.0	100.0
ME-4 Color	Anti-Calcium, No. 4	3.0*	3.0	6.8
	Benzyl Alcohol	5.1*	0.0	0.0
	Na_2SO_3	7.75	5.9	13.3
	$Na_3PO_4 \cdot 12H_2O$	37.5	22.7	51.0
	NaBr	0.1	0.0	0.0
	KI	0.04	0.0	0.0
	NaOH	4.60	11.5	25.9
	Citrazinic Acid	1.60	— 2.4	— 5.3
	CD-3	12.0	— 5.0	—11.6
	Ethylenediamine	3.05	8.8	19.9
	RA-1	0.1	0.0	0.0
	Cal. T. Alk.; 10.0-ml sample		44.5	100.0
CRI-1 First	Quadrafos	2.0	0.2	0.5
	$NaHSO_3$	2.9	0.0	0.0
	Phenidone	0.4	0.0	0.0
	Na_2SO_3	44.0	13.4	37.7
	HQ	7.0	0.0	0.0
	Na_2CO_3	28.9	21.9	61.8
	NaCNS	1.4	0.0	0.0
	KI	0.013	0.0	0.0
	Cal. T. Alk.; 4.00-ml sample		35.5	100.0
CRI-1 Color	Anti-Calcium, No. 4	3.0*	3.0	6.8
	Benzyl Alcohol	5.1*	0.0	0.0
	Na_2SO_3	7.75	5.9	14.0
	$Na_3PO_4 \cdot 12H_2O$	37.5	22.7	51.0
	NaBr	0.1	0.0	0.0
	KI	0.04	0.0	0.0
	NaOH	4.60	11.5	25.9
	Citrazinic Acid	1.60	— 2.4	— 5.3
	CD-3	12.0	— 5.2	—11.6
	Ethylenediamine	3.05	8.8	19.9
	RA-1	0.1	0.0	0.0
	Cal. T. Alk.; 10.0-ml sample		44.5	100.0

* ml/liter

cross-check should be placed in the pH 10.4 buffer for storage.

b. If after 2 days in the pH 10.4 buffer the electrode still fails to give a satisfactory cross-check, use the following regeneration procedure:

(1) Remove the electrode from the assembly and immerse it in 3 N hydrochloric acid for 30 seconds.

(2) Rinse the electrode immediately with running water, and soak it in pH 10.4 potassium borate for 16 hours.

(3) If the electrode still fails to produce a satisfactory cross-check, immerse the lower portion of the electrode in a 200 g/l ammonium bifluoride solution (use this solution in a polyethylene container) for 1 minute, rinse with running water, and again immerse the electrode in 3 N hydrochloric acid for 30 seconds. Rinse the electrode with distilled water, and place it in the pH 10.4 buffer until a satisfactory cross-check can be made.

WARNING: Ammonium bifluoride is very toxic; it is corrosive to skin and glass. If this solution is spilled on the skin, immediately flush the area with plenty of water. Mix, store, and use this solution in polyethylene containers.

4. Beckman No. 39170 Calomel Reference Electrodes with Fiber Junctions (Care and Storage)

a. A new electrode has two rubber caps, one on the side and one on the end, to prevent loss of potassium chloride solution. Both of the rubber caps should be removed before the electrode is inserted into the electrode assembly.

b. The 3.5 N potassium chloride has been substituted for saturated potassium chloride as the filling solution for reference electrodes. At the beginning of each day of use, the electrode should be emptied, then rinsed and refilled with new 3.5 N potassium chloride; water is no longer used for rinsing. Performance of electrodes in general has been more reliable and more stable with this new change.

c. If the pH reading for the cross-check buffer is above the specified tolerance, the calomel electrode is probably plugged. To check this, place the fiber tip end of the electrode firmly on a dry paper towel at least four times (in different areas of the towel). If the tip is not plugged, a tiny wet spot will be visible on the towel, as the electrode is lifted each time. If an electrode becomes plugged on the outside at the bottom end of the wick, rub the end of the electrode across the flat surface of a fine-toothed file or a waterproof 320-grit silicon carbide paper.

d. It has been common practice when performing potentiometric titrations, using silver nitrate as titrant, to flush a calomel electrode and then refill it with saturated potassium nitrate solution. Since it is difficult to obtain a complete flushing, it is now recommended that a separate calomel electrode be kept filled with saturated potassium nitrate solution for use with such titrations.

e. To store the electrode for an extended period of time, out of the storage buffer, fill the electrode completely with 3.5 N potassium chloride and replace the rubber caps.

C. Temperature Control of Solutions

The pH values of processing solutions and buffers, as well as the responses of electrodes, are dependent upon temperature. Therefore, to obtain reproducible pH values, it is necessary to standardize the temperature at which the measurements are to be made. Usually, pH measurements are made at 27 C (80.6 F). In a processing solution originally at pH 10.5, a temperature change of 6 C produces a pH change of approximately 0.10 unit; in a processing solution originally at pH 13.0, the pH change is approximately 0.20 units. Temperature control is more important at the higher pH values.

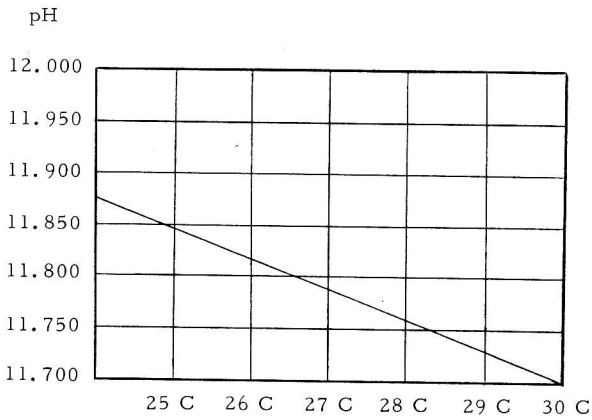


FIGURE 1 Effect of Temperature on the pH of Calcium Chloride-Calcium Hydroxide Buffer

As an example, Figure 1 shows the effect of temperature on the pH of the calcium chloride-calcium hydroxide buffer. A temperature change of 1 C from 27 C causes a pH change of 0.028 units. An error of 1 C in the buffer temperature would shift the pH enough to cause many good electrodes to exceed the control limits of the cross-check procedure.

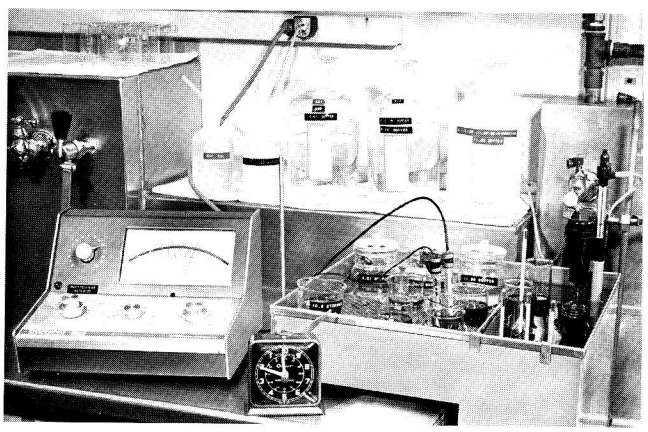


FIGURE 2 Constant-Temperature Water Bath

D. Constant-Temperature Bath

In order to achieve temperature control, store all buffers, the samples, and electrodes in a water bath controlled to maintain a sample temperature of 27 ±0.25 C. A water bath (1 cubic foot, self-contained reservoir of approximately 28 liters) can be controlled to this tolerance using a Bronwill

Model 22 Constant Temperature Circulator, Jr. (Catalog No. 21517-059) coupled with a Bronwill Mercury Contact Regulator (Catalog No. 21517-081), which are available from VWR Scientific. Figure 3 shows the control device in detail.

FIGURE 3 Bronwill Model 22 Constant Temperature Circulator, Jr.

The water bath should have a raised grid or other support (see Figure 2) for the beakers so that the water circulating underneath will bring the solutions to equilibrium more rapidly. The water level should be approximately 1½ inches above the grid. Arrange the water input and overflow so that there is no appreciable temperature gradient in the bath. An accurate thermometer should be mounted in the water bath in order to check the temperature periodically.

REAGENTS

A. pH Buffers

1. *Potassium Acid Phthalate (0.05 M)*
2. *Borax (0.01 M)*
3. *Calcium Chloride-Calcium Hydroxide*

B. Electrode Treatment and Storage Solutions

1. *A pH 7.0 Phosphate Buffer*
2. *A pH 10.4 Potassium Borate Buffer*
3. *A 3.5 N Potassium Chloride Solution; KCl*
4. *A 3.0 N Hydrochloric Acid Solution; HCl*
5. *A 200 g/l Ammonium Bifluoride Solution; $NH_4F{\cdot}HF$*

C. Standard Developer Samples

The specific developers selected for standards should be in a pH range consistent with that of the samples measured routinely. Each standard developer should be prepared in a 5 or 10-liter batch, and then bottled in glass-stoppered 125-ml reagent bottles. Each bottle should be filled completely and tightly stoppered. Each batch is assumed to be stable, with respect to pH, for periods up to one month from preparation.

PROCEDURE

A. Temperature Adjustments of Buffers and Sample(s)

1. To separate 150-ml beakers, add approximately 100 ml of each of the following solutions.
   a. 0.05 M potassium acid phthalate buffer
   b. calcium chloride-calcium hydroxide buffer
   c. 0.01 M borax buffer
   d. the sample(s) to be tested
2. Place the beakers in the constant-temperature water bath which is controlled to give a solution temperature of 27 ±0.25 C; allow the solutions to reach temperature equilibrium before testing the pH.

B. Adjustment of the pH Meter

1. Set the function switch to the standby position.
2. Set the temperature compensator knob at 27 C.
3. Connect the power-line cord to the pH meter and source of power; allow 10 minutes for component stabilization.

C. Standardization of the Meter Electrode System

1. Rinse the electrode assembly with distilled water.
2. Lower the electrode assembly into the beaker containing the appropriate standardizing buffer (see Table I), keeping the buffer in the water bath.
3. Set the timer for *2 minutes,* and turn the function knob to the pH position.
4. Turn the range knob to the position indicated in Table I.
5. Turn the expand knob to the "0—1" position.
6. Turn the calibration knob to set the meter needle, on the upper meter scale, at the pH of the buffer indicated in Table I. (e.g., the upper scale should read 0.163 at 27 C for the borax buffer).
7. Adjust the calibration knob, and lock it in place *at the end of 2 minutes.*
8. Turn the expand knob to the "0—14" position.
9. Remove the electrode assembly from the buffer, and rinse it with distilled water.

D. Cross-Check of the Meter Electrode System

1. Lower the electrode assembly into the beaker containing the appropriate cross-check buffer (see Table II), keeping the buffer in the water bath.

2. Set the timer at *2 minutes.*

3. Turn the range knob to the position shown in Table II.

4. Turn the expand knob to the "0—1" position.

Calcium Chloride-Calcium Hydroxide Buffer (pH 11.770)	Borax Buffer (pH 9.163)
5. At the end of *1 minute,* the buffer pH should read no less than 11.740 and no more than 11.880. During the second minute, the buffer reading should drift no more than 0.010, and never in a downward direction. In any case, *at the end of 2 minutes,* the reading should be between 11.740 and 11.800.	5. The control limits for this buffer are between 9.113 and 9.213.

NOTES:

a. If the reading does not fall within the control limit, reject any results obtained since the last staisfactory cross-check, and try another glass electrode, repeating Sections C and D.

b. If the buffer reading falls within the control limits, go on to Step 6.

6. Turn the expand knob to the "0—14" position.

7. Remove the electrode assembly from the buffer and rinse it with distilled water.

E. Determination of the pH of the Sample(s)

1. With expand knob in the "0—14" position, lower the electrode assembly into the sample beaker still in the water bath.

2. Set the timer for *2 minutes.*

3. From the lower meter scale, determine the pH interval in which the sample pH lies (e.g., between 9 and 10).

4. Turn the range knob to the position of the lower value (e.g., at 9).

5. Turn the expand knob to the "0—1" position.

6. At *exactly 2 minutes,* record the pH of the sample.

7. Turn the expand knob to the "0—14" position.

8. Remove the electrode assembly from the beaker, and rinse it with distilled water.

9. If only one sample is to be analyzed, record the pH of the sample; repeat the cross-check as in Section D.

10. For additional pH measurements, continue by repeating Section E, Steps 1 through 9, always ending with the cross-check of Section D.

NOTE: One to four samples may be analyzed between cross-checks.

TABLE I

pH OF THE STANDARDIZING BUFFERS AT 27 C

Sample pH	Buffer	pH	Setting of Range Knob
Below 9	Potassium Acid Phthalate	4.010	4
Above 9	Borax	9.163	9

TABLE II

CONTROL LIMITS OF THE CROSS-CHECK BUFFERS AT 27 C

Sample pH	Buffer	Control Limits	Setting of Range Knob
Below 9	Borax	9.113 to 9.213	9
Above 9	Calcium Chloride-Calcium Hydroxide	11.740 to 11.800	11

POTENTIOMETRIC DETERMINATION OF BROMIDE IN BLEACH (906G)

INTRODUCTION

The ferricyanide and ferrocyanide ions in the bleach sample are precipitated as the cadmium salts, and then are removed by centrifuging or filtering. A portion of the resulting solution is then titrated potentiometrically with silver nitrate.

The bleach has no chloride in its formula. However, chloride ions may be present in the water, or as an impurity in other chemicals. Because there is usually only a small amount of chloride present, the chloride and bromide inflection points tend to merge and be confused. To separate them satisfactorily, more chloride must be added prior to titration.

SPECIAL APPARATUS

Centrifuge with head to accommodate 40 or 50-ml centrifuge tubes

40 or 50-ml centrifuge tubes

Corning Model 12 Research pH Meter, or equivalent

Beckman Fiber-Junction Calomel Electrode, No. 39170. (Remove the saturated potassium chloride solution, and substitute saturated potassium nitrate solution.)

Silver bar electrode (Precision Scientific Co., Catalog No. 68865)

REAGENTS

Celite

Acidified Cadmium Nitrate, $Cd(NO_3)_2$

0.10 N Sodium Chloride, NaCl

0.0500 N Silver Nitrate, $AgNO_3$

PROCEDURE

A. Treatment of the Sample

1. Pipet 5.00 ml of bleach into a 100-ml volumetric flask.

2. Add 25 ml of acidified cadmium nitrate from a tip-up pipet.

CAUTION: Cadmium nitrate is poisonous; avoid contact with skin.

3. Dilute to volume with distilled water. Stopper and invert the flask 6—12 times.

4. Pour nearly equal amounts of the mixture into two 40 or 50-ml centrifuge tubes. Do not fill the tubes to more than within 1 inch from the top.

NOTE: If more convenient, delete Steps 4—6 and filter the treated sample through fluted, 32-cm Whatman No. 12 filter paper to which 2 g of Celite was first added.

5. Place the tubes in opposite positions and centrifuge at maximum speed for at least 2 minutes. (Observe safety precautions for use of centrifuge.)

6. Carefully transfer the liquid phase from both centrifuge tubes to a 150-ml beaker.

7. Pipet 50.0 ml of the liquid phase or filtrate into a 250-ml beaker.

8. Add 1 ml of 0.10 N sodium chloride from a tip-up pipet.

B. Titration

1. Once daily, clean the silver bar electrode to brightness with a small amount of ordinary household cleansing powder placed upon a damp tissue. Rinse the electrode with distilled water. Wipe and rinse.

2. Titrate the solution with 0.0500 N silver nitrate using a pH meter. See instructions in Method XIA.

C. Calculations

$$\frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)(\text{eq wt NaBr})(1000)}{(\text{fraction of treated sample})(\text{ml sample})(1000)} =$$

$$\frac{(\text{ml } AgNO_3)(0.0500)(102.91)(1000)}{(50/100)(5.00)(1000)} =$$

$$(\text{ml } AgNO_3)(2.058) = \text{NaBr, g/l}$$

DETERMINATION OF BROMIDE IN NEUTRALIZER (914)

INTRODUCTION

The sample of neutralizer is treated with 7.0 N sulfuric acid and titrated potentiometrically with standard silver nitrate. A silver electrode is used to follow the progress of the titration.

The chloride ion present in the sample precipitates after the bromide ion. Because there is only a small amount of chloride in many samples, the chloride and bromide breaks tend to merge in the titration curve. When this happens, the chloride break can be easily mistaken for the bromide end point. Therefore, more chloride is added to the sample before the titration in order to separate the two inflection points.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent

Beckman Fiber-Type Calomel Electrode, No. 39170 (Remove the saturated potassium chloride solution and substitute saturated potassium nitrate solution.)

Silver bar electrode (Precision Scientific Co. Bulletin 640, Catalog No. 68865)

REAGENTS

7.0 N Sulfuric Acid, H_2SO_4

0.10 N Sodium Chloride, NaCl

0.0500 N Silver Nitrate, $AgNO_3$

PROCEDURE

A. Treatment of Sample

1. Pipet 10.0 ml of sample into a 150-ml beaker.
2. Add slowly 5 ml of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 1 ml of 0.10 N sodium chloride from a tip-up pipet.
4. Add distilled water until the electrodes are immersed 1 inch into the solution.

B. Titration

1. Once daily, clean the silver bar electrode to brightness with a small amount of ordinary household cleansing powder placed upon a damp tissue. Rinse the electrode with distilled water.
2. Titrate the sample with 0.0500 N silver nitrate, using a pH meter. See instructions in Method XIA.

C. Calculations

$$\frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)(\text{eq wt NaBr})(1000)}{(\text{ml sample})(1000)} =$$

$$(\text{ml } AgNO_3)(0.5145) = \text{NaBr, g/l}$$

POTENTIOMETRIC DETERMINATION OF POTASSIUM IODIDE IN STOCK SOLUTIONS (924B)

INTRODUCTION

The most common stock solution of potassium iodide, KI, contains 1 gram of potassium iodide per liter and is referred to as 1 g/l KI solution. The preparation and control of this solution are described in Method IX, "Analytical Control of Mix Room and Laboratory Stock Solutions."

The iodide concentration is determined by a potentiometric titration with standard silver nitrate, the progress of which is indicated by a silver electrode. See Method XIA, "Potentiometric Titrations."

Small amounts of chloride ion are present in the water used in preparing most stock solutions. The iodide and chloride inflection points may be confused as a single, combined point. The addition of 2 ml of 0.5 molar potassium bromide solution gives a distinct separation of the iodide end point. The iodide end point is the first significant inflection point obtained, and is the one on which the calculations are based.

As a further aid in selecting the proper inflection point and detecting instrument trouble and analytical errors, a standard titration curve should be kept on file. Such a curve can be compared against the general shape and relative position of any routine titration curve. Figures 1 and 2 show typical titration curves for a 1 g/l potassium iodide stock solution.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent
Sargent Model D Recording Titrator, or equivalent
Beckman Fiber-Junction Calomel Electrode, No. 39170. (Remove the saturated potassium chloride solution and substitute saturated potassium nitrate solution.)
Silver bar electrode (Precision Scientific Co. Bulletin 640, Catalog No. 68865)

REAGENTS

0.0500 N Silver Nitrate, $AgNO_3$
0.5 M Potassium Bromide, KBr

PROCEDURE

A. Treatment and Titration of Sample

1. Pipet (wipe before leveling) 100.0 ml of stock solution into a 250-ml beaker.

2. Add 2 ml of 0.5 M potassium bromide from a tip-up pipet.

3. Titrate the sample with 0.0500 N silver nitrate using either a titrator or a pH meter. See instructions, Method XI.

NOTE: All titrations should be run with the reference electrode (Beckman Fiber-Junction Calomel Electrode) in the reference jack of the pH meter and the indicator electrode (Silver Bar Electrode) in the indicator jack of the pH meter.

B. Calculations

$$\frac{(\text{ml } AgNO_3)(\underline{N}\ AgNO_3)(\text{equiv wt KI})(1000)}{(1000)(100)} =$$

$$(\text{ml } AgNO_3)(0.0830) = \text{KI, g/l of stock solution}$$

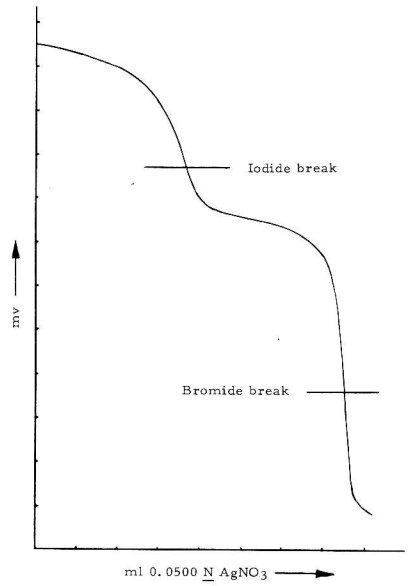


FIGURE 1 Typical Iodide Titration Curve, 1 g/1 KI Stock Solution, Beckman Model G pH Meter

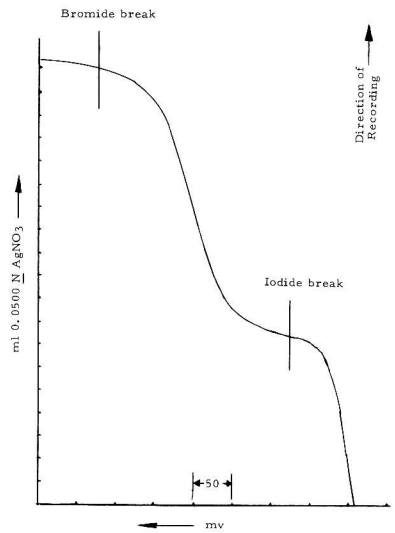


FIGURE 2 Typical Iodide Titration Curve, 1 g/1 KI Stock Solution, Sargent Model D Recording Titrator

POTENTIOMETRIC DETERMINATION OF IODIDE IN *EKTACHROME* COLOR DEVELOPERS (925A)

PRINCIPLE

A sample of developer is made highly alkaline to prevent the formation of an emulsion during the extraction of CD-3 and RA-1 with chloroform. After the extraction, the aqueous phase is acidified with glacial acetic acid. The solution is then titrated potentiometrically with a silver nitrate solution using silver-bar and calomel electrodes. The inflection point is determined by applying the concentric arcs technique.

The addition of sodium chloride alters the shape of the potentiometric curve such that the end point determined by this technique is slightly beyond the actual inflection point. However, the concentric arcs technique is used because it produces more reliable results than other techniques for determining the location of the end point. The difference between the determined end point and the actual inflection point is fairly constant and is calibrated out.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent

Beckman Fiber-Junction Calomel Electrode, No. 39170. (Remove the saturated potassium chloride solution and substitute saturated potassium nitrate solution.)

Silver bar electrode (Precision Scientific Co., Catalog No. 68865)

REAGENTS

10 N Sodium Hydroxide, NaOH
Chloroform, $CHCl_3$
Acetic Acid, Glacial, CH_3COOH
Sodium Chloride, NaCl
0.00500 N Silver Nitrate, $AgNO_3$

RELIABILITY

Three standard ECO-3 color developer mixes containing 20, 50 and 80 mg/l of potassium iodide were analyzed in duplicate by two analysts. For the first analysis of each mix the analyst added RA-1, equivalent to 56 mg/l, to the sample before treatment. The second analysis was performed with 168 mg/l RA-1. The RA-1 was added prior to the analyses because of its tendency to decompose in developer solutions during storage. The procedure was repeated the next day using three standard ME-4 color developer mixes. The least mean square line and 95% confidence limits for individual results are based on these data. The 95% confidence limits are ±1.71 mg/l of KI.

PROCEDURE

A. Extraction of Developing Agents

1. Add 250 ml of developer, from a graduated cylinder, to a 500-ml separatory funnel.

2. Add 25 ml of 10 N sodium hydroxide from a tip-up pipet.

3. Add 100 ml of chloroform from a tip-up pipet.

CAUTION: Chloroform is toxic; use in an exhaust hood or where there is adequate ventilation. Keep chloroform away from open flames and hot surfaces. Chlorinated materials may break down to give toxic and irritating gases such as phosgene and hydrogen chloride. Waste chloroform should be disposed of according to locally acceptable practices.

4. Stopper and shake the funnel a few times; then vent through the stopper. Continue to shake the funnel for 30 seconds, venting occasionally.

5. Discard the lower (chloroform) layer and any emulsion present at the interface.

6. Repeat *twice* Steps 3, 4, and 5.

B. Titration of Aqueous Layer

1. Once daily, clean the silver bar electrode to brightness with a small amount of ordinary household cleansing powder placed upon a damp tissue. Rinse the electrode with distilled water. Wipe and rinse.

2. Drain the remaining (aqueous) layer into a 400-ml beaker.

3. While stirring on a magnetic mixer, add 35 ml of glacial acetic acid from a tip-up pipet.

4. Add and dissolve 10 g of sodium chloride.

5. Titrate the sample with 0.00500 N silver nitrate contained in a 25-ml buret. Use a pH meter with silver bar and calomel electrodes. See instructions for potentiometric titrations in Method XIA.

6. Determine the end point using the concentric arcs method.

C. Calculation

3.54 (ml 0.00500 N $AgNO_3$) — 3.43 = mg/l, KI

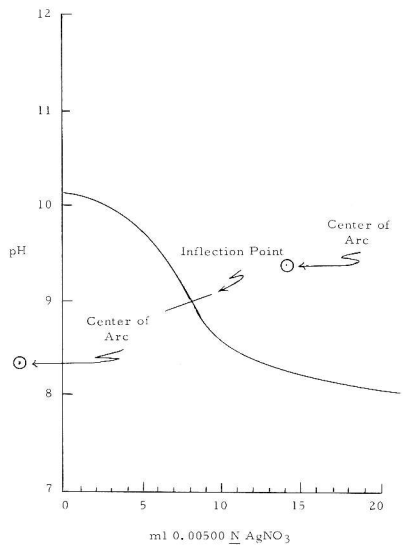


FIGURE 1 Typical Titration Curve for Iodide in EKTACHROME Color Developer

POTENTIOMETRIC DETERMINATION OF IODIDE IN FIRST DEVELOPER (929)

INTRODUCTION

The potentiometric titration of iodide with silver nitrate can be made only in a limited range of iodide-to-bromide and iodide-to-thiocyanate ratios. The ratios in the first developers are unfavorable. They are improved in the analysis by adding silver nitrate in a slight molar excess in order to precipitate all the iodide and only a small amount of bromide and thiocyanate. The silver precipitate is then collected on a filter and treated with an ammoniacal solution of hydroquinone to dissolve all of the iodide with only a reduced amount of bromide and thiocyanate present. The iodide is then titrated potentiometrically with silver nitrate.

It is necessary to first treat the tank samples with a boiling alkali solution to destroy any gelatin before the silver salts are precipitated. If gelatin were present, it would change the surface characteristics of the silver precipitate, thus affecting the rate of filtration. For consistency, the replenisher samples are also treated in the same manner.

RELIABILITY

The calibration curve was prepared by analyzing four standard laboratory mixes of each developer by two analysts. The mixes contained 3.00 to 15.0 mg/l of potassium iodide and constant amounts of the other constituents. The volumes of silver nitrate required in the titrations were plotted against the corresponding concentrations of potassium iodide. The best straight line was determined from the data of 16 analyses. Based upon these data, the 95% confidence limits for an individual determination are ± 0.7 mg/l of potassium iodide.

The calibration mixes contained 3.00—15.0 mg KI/l, 0.0—1.3 g NaBr/l, and 1.4—2.6 g NaCNS/l. If the concentration of these components is changed appreciably, the calibration equation should be reestablished.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent

Beckman Fiber-Junction Calomel Electrode, No. 39170 with a saturated potassium nitrate bridge. (Remove the saturated potassium chloride solution and substitute saturated potassium nitrate solution.)

Silver bar electrode (Precision Scientific Co. Bulletin 640, Catalog No. 68865). (Do not use a silver button electrode.)

Millipore filter holder, Pyrex, Catalog No. XX1004700, Millipore Corp., Bedford, Mass. 01730

Millipore filter membrane, unmounted, HA type, white, plain, 47mm

Constricted-tip funnel (made by drawing out and breaking off part of a short-stem funnel)

Exhaust hood

REAGENTS

16 N Sodium Hydroxide, NaOH

18 N Sulfuric Acid, H_2SO_4

Celite

0.00100 N Silver Nitrate, $AgNO_3$

1.0 M Ammonium Nitrate, NH_4NO_3

Silver halide developer (Do not use a solution which has turned brown.)

PROCEDURE

A. Preparation of Apparatus

1. This is a micro-method. Clean glassware and avoidance of contamination are especially important. It may be necessary to clean all of the apparatus with sulfuric-dichromate cleaning solution.

2. Before each analysis, clean the silver bar electrode to brightness with a small amount of ordinary household cleansing powder placed upon a damp tissue. Rinse the electrode with distilled water. Wipe and rerinse.

B. Elimination of Gelatin

1. Pipet 200.0 ml of sample into a 500-ml Erlenmeyer flask.

2. Add 10 ml of 16 N sodium hydroxide from a graduated cylinder.

3. Boil the alkaline sample for 5 minutes.

4. Cool to room temperature.

C. Precipitation of Silver Iodide

1. Set the flask in an exhaust hood, and rapidly stir with a magnetic stirrer.

2. Add slowly, from a graduated cylinder, 50 ml of 18 N sulfuric acid to the solution while it is being stirred.

NOTE: Even though the solution foams, Foamex *should not* be used because of its solvent action on the Millipore filter.

3. Add approximately 0.3—0.4 g of Celite.

NOTE: It may be convenient to add two level scoops of Celite from a Coors No. 2 porcelain spoon.

4. By immersing a 50-ml pipet beneath the foam, add 50 ml of 0.00100 N silver nitrate into the solution while it is being rapidly stirred. Continue to stir for 5 minutes.

NOTE: The volume of silver nitrate does not need to be accurately measured, but the technique of addition is important.

5. Place a Millipore filter holder and filter membrane on a 500-ml filter flask. Apply full suction and filter the solution while retaining the stirring bar in the flask with another bar on the outside of the flask. Disconnect the aspirator hose after filtration.

6. Rinse the sides of the flask with 25 ml of 1.0 M ammonium nitrate from a tip-up pipet. While retaining the stirring bar in the flask, rinse the sides of the Millipore funnel by pouring the solution from the flask through a constricted-tip

funnel. Reconnect the aspirator hose and draw the solution into the filtering flask.

7. Disconnect the aspirator hose and rinse the inside and outside of only the stem of the Millipore funnel with water from a wash bottle.

NOTE: Do not disassemble the filter and membrane.

8. Discard the filtrate and thoroughly rinse the filtering flask. Reassemble the apparatus.

D. Developing the Silver Iodide

1. Add, from a graduated cylinder, 20 ml of silver halide developer to the 500-ml Erlenmeyer flask.

NOTE: Do not expose the silver halide developer to air any longer than necessary. A developer that has turned brown should not be used. However, it is still usable if it has a light yellow color.

2. Swirl the Erlenmeyer flask slightly and immediately rinse the sides of the Millipore funnel (no applied suction) by pouring the developer through a constricted-tip funnel. (Always retain the stirring bar in the flask during a transfer.)

3. Allow the solution to remain in the Millipore funnel for 5 minutes. After the first 30 seconds and again after 1 minute, swirl the solution to cause new contact between the developer and precipitate.

4. After 5 minutes, reconnect the aspirator hose and draw the solution into the clean filtering flask, taking care not to lose any solution down the hose. Disconnect the hose.

5. Add from a tip-up pipet 50 ml of distilled water to the 500-ml Erlenmeyer flask.

6. Rinse the sides of the Millipore funnel by pouring the water through the constricted-tip funnel. Reconnect the aspirator hose and draw the solution into the flask. Disconnect the apparatus and pour the solution into a 250-ml beaker. Rinse the filtering flask with two 10-ml portions of distilled water.

7. Add, from a graduated cylinder, 50 ml of 18 N sulfuric acid to the beaker.

E. Titration

1. Stir the solution moderately with a magnetic stirrer.

2. Equilibrate a calomel-silver bar electrode pair by immersing them into the solution and waiting for 2—5 minutes until the galvanometer is steady before proceeding to Step 3.

3. Titrate the sample with 0.00100 N silver nitrate, using a pH meter. See instructions in Method XIA.

F. Calculations

$$(0.855)(\text{ml } AgNO_3) + 1.29 = KI, \text{ mg/l}$$

G. Reporting Results on Tank Samples

1. Report no results above 40 mg/l of potassium iodide, except as "greater than 40 mg/l."

2. Report the 95% confidence limits (±0.7 mg/l for individual results) along with the result. Report no answer below 1.3 mg/l except as "less than 1.3 mg/l."

POTENTIOMETRIC DETERMINATION OF BROMIDE IN COLOR DEVELOPER (930D)

PRINCIPLE

The sample is acidified to remove the sulfite and also inactivate the developing agent. The treated sample is then titrated potentiometrically with standard silver nitrate solution. See Method XIA, "Potentiometric Titrations."

RELIABILITY

The calculations are based on stoichiometry.

Any iodide ion present in the sample precipitates before the bromide ion. In the color developer, the iodide is of sufficient concentration to make the bromide results approximately 0.06 grams per liter high.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent

Beckman Fiber-Junction Calomel Electrode, No. 39170. (Remove the saturated potassium chloride solution and substitute saturated potassium nitrate solution.)

Silver bar electrode (Precision Scientific Co. Bulletin 640, Catalog No. 68865)

REAGENTS

Foamex

7.0 N Sulfuric Acid, H_2SO_4

0.10 N Sodium Chloride, NaCl

0.0500 N Silver Nitrate, $AgNO_3$

PROCEDURE

A. Treatment of Sample

1. Pipet 200.0 ml of sample into a 600-ml beaker. Add 1 drop of Foamex.

2. Add slowly 100 ml of 7.0 N sulfuric acid from a tip-up pipet.

3. Add 1 ml of 0.10 N sodium chloride from a tip-up pipet.

B. Titration

1. Once daily, clean the silver bar electrode to brightness with a small amount of ordinary household cleansing powder placed upon a damp tissue. Rinse the electrode with distilled water.

2. Titrate the sample with 0.0500 N silver nitrate, using a pH meter. See instructions in Method XIA.

C. Calculations

$$\frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)(\text{eq wt NaBr})(1000)}{(\text{ml sample})(1000)} =$$

$$(\text{ml } AgNO_3)(0.02573) = \text{NaBr, g/l}$$

For convenience, use Table I.

TABLE I

SODIUM BROMIDE IN DEVELOPER

200-ml Sample Size

$AgNO_3$ ml	NaBr g/l	$AgNO_3$ ml	NaBr g/l	$AgNO_3$ ml	NaBr g/l
10.0	0.26	20.0	0.51	30.0	0.77
10.4	0.27	20.4	0.53	30.4	0.78
10.8	0.28	20.8	0.54	30.8	0.79
11.2	0.29	21.2	0.55	31.2	0.80
11.6	0.30	21.6	0.56	31.6	0.81
12.0	0.31	22.0	0.57	32.0	0.82
12.4	0.32	22.4	0.58	32.4	0.83
12.8	0.33	22.8	0.59	32.8	0.84
13.2	0.34	23.2	0.60	33.2	0.85
13.6	0.35	23.6	0.61	33.6	0.86
14.0	0.36	24.0	0.62	34.0	0.87
14.4	0.37	24.4	0.63	34.4	0.89
14.8	0.38	24.8	0.64	34.8	0.90
15.2	0.39	25.2	0.65	35.2	0.91
15.6	0.40	25.6	0.66	35.6	0.92
16.0	0.41	26.0	0.67	36.0	0.93
16.4	0.42	26.4	0.68	36.4	0.94
16.8	0.43	26.8	0.69	36.8	0.95
17.2	0.44	27.2	0.70	37.2	0.96
17.6	0.45	27.6	0.71	37.6	0.97
18.0	0.46	28.0	0.72	38.0	0.98
18.4	0.47	28.4	0.73	38.4	0.99
18.8	0.48	28.8	0.74	38.8	1.00
19.2	0.49	29.2	0.75	39.2	1.01
19.6	0.50	29.6	0.76	39.6	1.02

(ml $AgNO_3$)(0.02573) = NaBr, g/l

TITRIMETRIC DETERMINATION OF SODIUM THIOCYANATE IN STOCK SOLUTIONS (950C)

PRINCIPLE

Crystalline sodium thiocyanate, NaCNS, is extremely deliquescent. Therefore, stock solutions of sodium thiocyanate are prepared in the production chemical mix room and in service laboratories for use in making mixes, instead of weighing the solid chemical each time. Stock solutions are prepared to contain 500 g or 250 g of sodium thiocyanate per liter.

When preparing standard laboratory mixes for analytical purposes, it is frequently more accurate and convenient to use the more dilute solution containing 250 grams of sodium thiocyanate per liter. See "Analytical Control of Mix Room and Laboratory Stock Solutions" in another part of this manual for the preparation and control of sodium thiocyanate solutions.

The analysis consists of a titration of the sodium thiocyanate solution against standard silver nitrate, with acidified ferric nitrate as the indicator.

REAGENTS

0.0500 N Silver Nitrate, $AgNO_3$
0.10 M Acidified Ferric Nitrate, $Fe(NO_3)_3$

PROCEDURE

A. Treatment of the Sample

1. Pipet (wipe the pipet before leveling) 100.0 ml of 0.0500 N silver nitrate into a 250-ml glass-stoppered Erlenmeyer flask.
2. Add 3 ml of 0.10 M acidified ferric nitrate from a tip-up pipet.
3. Pipet (wipe) 20.0 ml of the sodium thiocyanate solution to be analyzed into a volumetric flask; dilute to volume and mix by inverting 20 times.

a. For solutions containing approximately 500 g/l, dilute 20.0 ml to 500 ml.

b. For solutions containing approximately 250 g/l, dilute 20.0 ml to 250 ml.

B. Titration of the Diluted Sample

1. Fill a 25-ml buret with the diluted stock solution.
2. Titrate the silver nitrate with the sodium thiocyanate. When near the expected end point, add the titrant *dropwise* until the first reddish-brown color appears.
3. Stopper the flask and shake vigorously. If the reddish-brown color disappears, add one additional drop of titrant and reshake. Continue until the reddish-brown color cannot be removed by shaking.

C. Calculations

1. Solutions containing approximately 500 g NaCNS/l:

$$\frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)(\text{eq wt NaCNS})(500)}{(\text{ml NaCNS used in titration})(20.0)} =$$

$$\frac{(100.0)(0.0500)(81.08)(500)}{(\text{ml NaCNS used in titration})(20.0)} =$$

$$\frac{10{,}135}{\text{ml NaCNS used in titration}} = \text{NaCNS, g/l}$$

2. Solutions containing approximately 250 g NaCNS/l:

$$\frac{(100.0)(0.0500)(81.08)(250)}{(\text{ml NaCNS used in titration})(20.0)} =$$

$$\frac{5{,}068}{\text{ml NaCNS used in titration}} = \text{NaCNS, g/l}$$

COLORIMETRIC DETERMINATION OF THIOCYANATE IN FIRST DEVELOPERS (1000F)

PRINCIPLE

The sample is reacted with acidified ferric nitrate reagent to produce the red-colored ferri-thiocyanate complex. The absorbance of this solution is measured at 460 nm (mμ) on a spectrophotometer. The temperature of the reagent affects the intensity and the stability of the color-forming complex and must therefore be controlled.

RELIABILITY

The calibration curve was prepared by the analysis of 32 standard laboratory mixes. The levels of sodium thiocyanate in the respective developers and replenishers ranged from 0.90 g/l to 3.00 g/l. They were analyzed by four analysts employing two spectrophotometers. No significant statistical or analytical difference was found between ME-4 and ECO-3 developers or replenishers; therefore, a universal calibration curve was determined by the method of least squares. The equation for this curve is found in the calculations. Some statistically significant differences were noted between analysts and also between spectrophotometers. These differences were not analytically significant, however, and their inclusion in the calibration led to slightly inflated confidence limits. This calibration is valid between 24—27 C (75—80 F). If it is necessary to run the determination at another temperature, a recalibration at that temperature must be performed.

The 95% confidence limits for each determination are ±0.055 g/l of sodium thiocyanate based on 128 analyses.

SPECIAL APPARATUS

Beckman DU Spectrophotometer, or equivalent

TABLE I

SODIUM THIOCYANATE IN FIRST DEVELOPER

A_{460}	g/l	A_{460}	g/l	A_{460}	g/l	A_{460}	g/l	A_{460}	g/l	A_{460}	g/l
0.200	0.58	0.320	1.05	0.440	1.52	0.560	1.99	0.680	2.46	0.800	2.92
0.204	0.60	0.324	1.07	0.444	1.54	0.564	2.00	0.684	2.47	0.804	2.94
0.208	0.62	0.328	1.08	0.448	1.55	0.568	2.02	0.688	2.49	0.808	2.96
0.212	0.63	0.332	1.10	0.452	1.57	0.572	2.04	0.692	2.50	0.812	2.97
0.216	0.65	0.336	1.11	0.456	1.58	0.576	2.05	0.696	2.52	0.816	2.99
0.220	0.66	0.340	1.13	0.460	1.60	0.580	2.07	0.700	2.53	0.820	3.00
0.224	0.68	0.344	1.15	0.464	1.61	0.584	2.08	0.704	2.55	0.824	3.02
0.228	0.69	0.348	1.16	0.468	1.63	0.588	2.10	0.708	2.57	0.828	3.03
0.232	0.71	0.352	1.18	0.472	1.65	0.592	2.11	0.712	2.58	0.832	3.05
0.236	0.73	0.356	1.19	0.476	1.66	0.596	2.13	0.716	2.60	0.836	3.06
0.240	0.74	0.360	1.21	0.480	1.68	0.600	2.14	0.720	2.61	0.840	3.08
0.244	0.76	0.364	1.22	0.484	1.69	0.604	2.16	0.724	2.63	0.844	3.10
0.248	0.77	0.368	1.24	0.488	1.71	0.608	2.18	0.728	2.64	0.848	3.11
0.252	0.79	0.372	1.26	0.492	1.72	0.612	2.19	0.732	2.66	0.852	3.13
0.256	0.80	0.376	1.27	0.496	1.74	0.616	2.21	0.736	2.67	0.856	3.14
0.260	0.82	0.380	1.29	0.500	1.75	0.620	2.22	0.740	2.69	0.860	3.16
0.264	0.83	0.384	1.30	0.504	1.77	0.624	2.24	0.744	2.71	0.864	3.17
0.268	0.85	0.388	1.32	0.508	1.79	0.628	2.25	0.748	2.72	0.868	3.19
0.272	0.87	0.392	1.33	0.512	1.80	0.632	2.27	0.752	2.74	0.872	3.21
0.276	0.88	0.396	1.35	0.516	1.82	0.636	2.28	0.756	2.75	0.876	3.22
0.280	0.90	0.400	1.36	0.520	1.83	0.640	2.30	0.760	2.77	0.880	3.24
0.284	0.91	0.404	1.38	0.524	1.85	0.644	2.32	0.764	2.78	0.884	3.25
0.288	0.93	0.408	1.40	0.528	1.86	0.648	2.33	0.768	2.80	0.888	3.27
0.292	0.94	0.412	1.41	0.532	1.88	0.652	2.35	0.772	2.82	0.892	3.28
0.296	0.96	0.416	1.43	0.536	1.89	0.656	2.36	0.776	2.83	0.896	3.30
0.300	0.97	0.420	1.44	0.540	1.91	0.660	2.38	0.780	2.85	0.900	3.31
0.304	0.99	0.424	1.46	0.544	1.93	0.664	2.39	0.784	2.86	0.904	3.33
0.308	1.01	0.428	1.47	0.548	1.94	0.668	2.41	0.788	2.88	0.908	3.34
0.312	1.02	0.432	1.49	0.552	1.96	0.672	2.43	0.792	2.89	0.912	3.36
0.316	1.04	0.436	1.50	0.556	1.97	0.676	2.44	0.796	2.91	0.916	3.37

$(3.90)(A_{460}) - 0.20 = NaCNS, g/l$

1-cm Silica cell, Beckman Catalog No. 75170
Constant temperature bath at 24—27 ±0.5 C (75—80 ±1.0 F)

REAGENTS

0.10 M Acidified Ferric Nitrate, $Fe(NO_3)_3$

PROCEDURE

A. Treatment of the Sample

1. Pipet 200.0 ml of 0.10 M acidified ferric nitrate into a dry, glass-stoppered, 250-ml Erlenmeyer flask. The temperature of the reagent must be the same as that used in the calibration, 24—27 ±0.5 C (75—80 ±1.0 F).

NOTE: It may be more convenient to use a dry 200-ml volumetric flask to measure *and* contain the 200 ml of 0.10 M acidified ferric nitrate.

2. Pipet a 1.00 ml sample of the developer into the flask.
3. Note the time (see Step B).
4. Stopper the flask and mix the contents thoroughly by swirling or inverting.

B. Measurement of the Absorbance at 460 nm (mμ)

Measure the absorbance of the solution vs air at 460 nm (mμ) exactly 2 minutes after the sample is added to the reagent. Use the tungsten lamp, and pull the phototube rod out. See instructions in Method VI E.

CAUTION: This reagent is very corrosive to the skin and metals. If the reagent is spilled, flush the area with water. If any drops spill into the spectrophotometer cell compartment, the phototube housing must be removed and cleaned.

C. Calculations

For the developers and replenishers use:

$(3.90)(A_{460}) - 0.20 =$ NaCNS, g/l, or for convenience use Table I.

POTENTIOMETRIC DETERMINATION OF BROMIDE AND THIOCYANATE IN FIRST DEVELOPER* (1001)

PRINCIPLE

The determination of bromide is contained in Part A of the procedure. Acetone is added to a sample of the developer solution to eliminate the interference of thiocyanate. The sample is then acidified to remove the sulfite and carbonate and also inactivate the developing agents. The treated sample is then titrated potentiometrically with standard silver nitrate solution. See Method XIA, "Potentiometric Titrations."

If the sample were acidified and then titrated with silver nitrate, the silver bromide and silver thiocyanate would precipitate together since their solubilities are nearly the same in an aqueous solution. Acetone is added to reduce the solubility of silver bromide relative to the solubility of silver thiocyanate. This change in their solubilities is great enough to avoid the interference from the thiocyanate.

The determination of thiocyanate is Part B of the procedure. A second sample is acidified and titrated with standard silver nitrate solution. As indicated above, this titration measures both the bromide, if present, and the thiocyanate. The thiocyanate content is then calculated by subtracting the volume of silver nitrate used in Part A from that used in Part B.

SPECIAL APPARATUS

Corning Model 12 pH Meter, or an Automatic Titrator

Beckman Fiber-Junction Calomel Electrode, No. 39170. (Remove the saturated potassium chloride solution and substitute saturated potassium nitrate solution.)

Silver bar electrode (Precision Scientific, Inc., Catalog No. 68865)

REAGENTS

Acetone, CH_3COCH_3

18 N Sulfuric Acid, H_2SO_4

0.10 N Sodium Chloride, NaCl

0.0500 N Silver Nitrate, $AgNO_3$

* The CRI-1 First Developer Replenisher does not contain sodium bromide. Therefore, Part A need not be run.

PROCEDURE

A. Determination of Bromide

1. Treatment of Sample

a. Pipet 100.0 ml of developer solution into a 1-liter beaker.

b. Add 400 ml of acetone from a graduated cylinder.

CAUTION: Acetone is volatile and highly flammable. Do not use it near an open flame.

c. Cautiously add 200 ml of 18 N sulfuric acid from a graduated cylinder.

2. Titration

a. Once daily, clean the silver bar electrode to brightness with a small amount of ordinary household cleansing powder placed upon a damp tissue. Rinse the electrode with distilled water.

b. Titrate the sample with 0.0500 N silver nitrate. See instructions in Method XIA.

3. Calculations

$$\frac{(\text{ml } AgNO_3)(\text{N } AgNO_3)(\text{eq wt NaBr})(1000)}{(\text{ml sample})(1000)} =$$

$$(\text{ml } AgNO_3)(0.05145) = \text{NaBr, g/l}$$

B. Determination of Thiocyanate

1. Treatment of Sample

a. Pipet 100.0 ml of developer solution into a 1-liter beaker.

b. Add 400 ml of distilled water from a graduated cylinder.

c. Cautiously add 200 ml of 18 N sulfuric acid from a graduated cylinder.

d. Add 5 ml of 0.10 N sodium chloride from a tip-up pipet.

2. Titration

a. Once daily clean the silver bar electrode to brightness with a small amount of ordinary household cleansing powder placed upon a damp tissue. Rinse the electrode with distilled water.

b. Titrate the sample with 0.0500 N silver nitrate. See instructions in Method XIA.

3. Calculations

a. Subtract ml of silver nitrate obtained in Part A from ml of silver nitrate obtained in Part B.

$$(\text{ml } AgNO_3, \text{ Part B}) - (\text{ml } AgNO_3, \text{ Part A}) = \triangle \text{ ml}$$

b. $(\triangle \text{ ml})(0.040535) = \text{NaCNS, g/l}$

IODOMETRIC DETERMINATION OF FERRICYANIDE IN A FERRICYANIDE BLEACH (1100E)

PRINCIPLE

Excess iodide ions and a zinc reagent are added to the bleach sample. The ferricyanide reacts with the iodide to produce an equivalent amount of iodine. The iodine is titrated with standard sodium thiosulfate. The reaction of ferricyanide and iodide is quantitative as long as zinc ions are present in excess. Any ferrocyanide initially present in the bleach, as well as the ferrocyanide produced by the reduction of ferricyanide, is precipitated as zinc ferrocyanide.

Persulfate ions and some other oxidizing agents will also oxidize iodide and hence, will be measured as ferricyanide by this method.

REAGENTS

0.6 M Potassium Iodide, KI
Zinc Sulfate— 7.0 N Sulfuric Acid reagent
0.1000 N Sodium Thiosulfate, $Na_2S_2O_3$
Starch indicator

PROCEDURE

A. Removal of the Interfering Constituents

1. Pipet 5.00 ml of sample into a 250-ml Erlenmeyer flask.
2. Add 25 ml of 0.6 M potassium iodide from a tip-up pipet.
3. Add 20 ml of zinc sulfate— 7.0 N sulfuric acid reagent from a tip-up pipet.
4. Mix thoroughly.

B. Titration with Sodium Thiosulfate

1. Titrate with 0.1000 N sodium thiosulfate to a light yellow color.
2. Add 5 ml of starch indicator from a tip-up pipet, and continue the titration until the blue color disappears.

C. Calculations

$$\frac{(\text{ml } Na_2S_2O_3)(\text{N } Na_2S_2O_3)(\text{eq wt } K_3 \text{ or } Na_3Fe(CN)_6)(1000)}{(\text{ml sample})(1000)} =$$

1. $(5.619)(\text{ml } Na_2S_2O_3) = Na_3Fe(CN)_6$, g/l
2. $(6.585)(\text{ml } Na_2S_2O_3) = K_3Fe(CN)_6$, g/l

TITRIMETRIC DETERMINATION OF FERROCYANIDE IN A FERRICYANIDE BLEACH (1101B)

INTRODUCTION

Ferrocyanide is determined by its oxidation in an acid solution by means of sulfato cerate using sodium diphenylamine sulfonate indicator. This reaction is:

$$Ce^{++++} + Fe(CN)_6^{----} \longrightarrow Ce^{+++} + Fe(CN)_6^{---}$$

The indicator has a blank of 0.1 ml of 0.0500 N sulfato cerate. This value is used in the calculations.

RELIABILITY

It is difficult to see the color change of the indicator in dark-colored seasoned samples. Thus, the resulting analyses may vary by approximately ±3 g/l of ferrocyanide.

REAGENTS

7.0 N Sulfuric Acid, H_2SO_4
0.01 M Sodium Diphenylamine Sulfonate indicator
0.0500 N Sulfato Cerate

PROCEDURE

A. Treatment of Sample

1. Add approximately 250 ml of distilled water to a 500-ml Erlenmeyer flask.

TABLE I
SODIUM FERROCYANIDE DECAHYDRATE, $Na_4Fe(CN)_6 \cdot 10H_2O$, g/l IN FERRICYANIDE BLEACH

5.00-ml sample						5.00-ml sample					
ml 0.0500 N Cerate	g/l	ml 0.0500 N Cerate	g/l	ml 0.0500 N Cerate	g/l	ml 0.0500 N Cerate	g/l	ml 0.0500 N Cerate	g/l	ml 0.0500 N Cerate	g/l
0.0	0.0	6.0	28.6	12.0	57.6	18.0	86.6	24.0	115.7	30.0	144.7
0.2	0.5	6.2	29.5	12.2	58.6	18.2	87.6	24.2	116.7	30.2	145.7
0.4	1.4	6.4	30.5	12.4	59.5	18.4	88.6	24.4	117.6	30.4	146.7
0.6	2.4	6.6	31.5	12.6	60.5	18.6	89.6	24.6	118.6	30.6	147.6
0.8	3.4	6.8	32.4	12.8	61.5	18.8	90.5	24.8	119.6	30.8	148.6
1.0	4.3	7.0	33.4	13.0	62.4	19.0	91.5	25.0	120.5	31.0	149.6
1.2	5.3	7.2	34.4	13.2	63.4	19.2	92.5	25.2	121.5	31.2	150.6
1.4	6.3	7.4	35.3	13.4	64.4	19.4	93.4	25.4	122.5	31.4	151.5
1.6	7.3	7.6	36.3	13.6	65.4	19.6	94.4	25.6	123.4	31.6	152.5
1.8	8.3	7.8	37.3	13.8	66.3	19.8	95.4	25.8	124.4	31.8	153.5
2.0	9.2	8.0	38.2	14.0	67.3	20.0	96.3	26.0	125.4	32.0	154.4
2.2	10.2	8.2	39.2	14.2	68.3	20.2	97.3	26.2	126.3	32.2	155.4
2.4	11.1	8.4	40.2	14.4	69.2	20.4	98.3	26.4	127.3	32.4	156.4
2.6	12.1	8.6	41.1	14.6	70.2	20.6	99.2	26.6	128.3	32.6	157.3
2.8	13.1	8.8	42.1	14.8	71.2	20.8	100.2	26.8	129.2	32.8	158.3
3.0	14.0	9.0	43.1	15.0	72.1	21.0	101.2	27.0	130.2	33.0	159.3
3.2	15.0	9.2	44.0	15.2	73.1	21.2	102.1	27.2	131.2	33.2	160.2
3.4	16.0	9.4	45.0	15.4	74.1	21.4	103.1	27.4	132.2	33.4	161.2
3.6	17.0	9.6	46.0	15.6	75.0	21.6	104.1	27.6	133.1	33.6	162.2
3.8	17.9	9.8	46.9	15.8	76.0	21.8	105.0	27.8	134.1	33.8	163.1
4.0	18.9	10.0	47.9	16.0	77.0	22.0	106.0	28.0	135.1	34.0	164.1
4.2	19.8	10.2	48.9	16.2	77.9	22.2	107.0	28.2	136.0	34.2	165.1
4.4	20.8	10.4	49.9	16.4	78.9	22.4	107.9	28.4	137.0	34.4	166.0
4.6	21.8	10.6	50.8	16.6	79.9	22.6	108.9	28.6	138.0	34.6	167.0
4.8	22.7	10.8	51.8	16.8	80.8	22.8	109.9	28.8	138.9	34.8	168.0
5.0	23.7	11.0	52.8	17.0	81.8	23.0	110.9	29.0	139.9		
5.2	24.7	11.2	53.7	17.2	82.8	23.2	111.8	29.2	140.9		
5.4	25.6	11.4	54.7	17.4	83.7	23.4	112.8	29.4	141.8		
5.6	26.6	11.6	55.7	17.6	84.7	23.6	113.8	29.6	142.8		
5.8	27.6	11.8	56.6	17.8	85.7	23.8	114.7	29.8	143.8		

$(4.841)(\text{ml sulfato cerate} - 0.10) = Na_4Fe(CN)_6 \cdot 10H_2O$, g/l

2. Pipet (wipe the pipet before leveling) 5.00 ml of sample into the flask.

3. Add 10 ml of 7.0 N H_2SO_4 from a tip-up pipet.

B. Titration with Sulfato Cerate

1. Add, with swirling, 20 drops (approximately 1 ml) of sodium diphenylamine sulfonate indicator.

2. Titrate immediately with 0.0500 N sulfato cerate to the first scarlet color which persists for 1 minute.

C. Calculations

Sodium ferrocyanide decahydrate:

$$\frac{\left(\begin{matrix}\text{ml}\\ \text{sulfato}\\ \text{cerate}\end{matrix} - \text{Blank}\right)\left(\begin{matrix}\text{N}\\ \text{sulfato}\\ \text{cerate}\end{matrix}\right)\left(\begin{matrix}\text{eq wt}\\ Na_4Fe(CN)_6\\ \cdot 10H_2O\end{matrix}\right)(1000)}{(\text{ml sample})(1000)} =$$

$$\frac{(\text{ml sulfato cerate} - 0.10)(0.0500)(484.1)(1000)}{(5.00)(1000)} =$$

$$(4.841)(\text{ml sulfato cerate} - 0.10) = Na_4Fe(CN)_6 \cdot 10H_2O, \text{ g/l}$$

For convenience, refer to Table I

POTENTIOMETRIC DETERMINATION OF BORAX IN FERRICYANIDE BLEACH (1107C)

INTRODUCTION

A sample of bleach is adjusted to pH 6.0 with sulfuric acid, thus converting the borax to boric acid:

$$Na_2B_4O_7 + H_2SO_4 + 5\ H_2O \longrightarrow 4\ H_3BO_3 + Na_2SO_4$$

Boric acid is such a weak acid that it cannot be titrated accurately with alkali. However, mannitol is added which complexes with boric acid forming a much stronger acid than boric acid, thus allowing a satisfactory titration:

$$4\ H_3BO_3 \cdot \text{complex} + 4\ NaOH \longrightarrow 4\ NaH_2BO_3 \cdot \text{complex} + 4\ H_2O$$

Four equivalents of alkali are required for each equivalent of borax. The sample is titrated potentiometrically because the dark color of the ferricyanide masks any indicator change.

Any substance that will react with alkali will be measured by this test method. To correct for this interference, a sample of seasoned bleach with no borax was titrated. The titration required 2.4 ml of 0.1000 N sodium hydroxide; this volume is recommended as a blank value in the titrations. The blank cannot be checked in any system that already contains borax.

RELIABILITY

Two mixes were prepared by adding known amounts (1.0 and 5.0 g/l) of borax, $Na_2B_4O_7 \cdot 5H_2O$, to a freshly regenerated ferricyanide bleach. They were analyzed according to the procedure below. The sample containing 1.0 g/l borax was analyzed at 1.1 g/l while the sample containing 5.0 g/l was analyzed at 5.0 g/l.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent
Corning No. 476022, or Leeds & Northrup No. 117169 Glass Electrode
Beckman No. 39170 Calomel Electrode, (filled with saturated potassium chloride solution)

REAGENTS

Mannitol
0.1000 N Sodium Hydroxide, NaOH
1.0 N Sulfuric Acid, H_2SO_4

PROCEDURE

A. Preparation of the pH Meter

Follow Method 810 (or any subsequent pH method for making pH measurements below pH 9).

1. Adjust the temperature of the buffers.
2. Adjust the meter.
3. Standardize the meter with potassium acid phthalate buffer.
4. Cross-check the electrodes with borax buffer.

B. Treatment of Sample

1. Pipet 100.0 ml of bleach into a 250-ml beaker; wipe the tip of the pipet before leveling to the mark.
2. Adjust the pH of the sample to 6.0 ±0.1 with 1.0 N sulfuric acid, using a pH meter.
3. Add and dissolve 5 g of mannitol.
4. Titrate with 0.1000 N sodium hydroxide to pH 8.2.
5. For further instructions on the use of a pH meter, see Method 810.

NOTE: All titrations should be run with the reference electrode (calomel electrode) in the reference jack of the pH meter, and the indicator electrode (glass electrode) in the indicator jack of the pH meter.

C. Calculations

$$\frac{[(N\ NaOH)(ml\ NaOH - 2.4^*)]\ (eq\ wt\ borax)(1000)}{(ml\ sample)(1000)} =$$

$$(0.073)(ml\ NaOH - 2.4) = Na_2B_4O_7 \cdot 5H_2O,\ g/l$$

* This value, 2.4 (blank), was the volume of sodium hydroxide used to titrate a sample of seasoned bleach, before any borax was added to the bleach system.

TITRIMETRIC DETERMINATION OF FERRICYANIDE AND PERSULFATE IN FERRICYANIDE BLEACH (1113B)

PRINCIPLE

Cadmium nitrate is added to a sample of ferricyanide bleach to precipitate the ferricyanide and ferrocyanide. The persulfate remains in solution. The mixture is then centrifuged and the supernatant liquid is decanted.

The combined cadmium ferricyanide and ferrocyanide precipitate is dispersed in acid and excess potassium iodide. Iodide equivalent to the amount of ferricyanide present is oxidized to iodine. A titration of the liberated iodine with standard sodium thiosulfate gives an indirect measure of the ferricyanide content. This ferricyanide determination is valid in the presence of persulfate and other oxidizing agents. Although sodium ferricyanide is usually purchased as a hydrate, it is reported here as anhydrous sodium ferricyanide, $Na_3Fe(CN)_6$.

The persulfate remaining in the decanted supernatant liquid is determined by treatment with a known excess of ferrous ion. The unoxidized ferrous ion is titrated in an acid solution with 0.0100 N sulfato cerate using Ferroin indicator.

RELIABILITY

The reliability required in detecting low levels of persulfate is attained by using 0.0100 N sulfato cerate rather than 0.0500 N sulfato cerate. If 0.0500 N sulfato cerate is used, the difference in titration volume, the A — B term, in the calculations which corresponds to 1 g/l of potassium persulfate is only 0.74 ml. This volume difference increases fivefold to 3.7 ml when 0.0100 N sulfato cerate is used, thus increasing the reliability of the test method.

SPECIAL APPARATUS

Centrifuge, with head to accommodate 50-ml centrifuge tubes

50-ml Centrifuge Tubes, glass- or rubber-stoppered

REAGENTS

7.0 N Sulfuric Acid, H_2SO_4

1.0 M Cadmium Nitrate, $Cd(NO_3)_2$

Potassium Iodide, KI

0.1000 N Sodium Thiosulfate, $Na_2S_2O_3$

Starch Indicator

0.10 N Ferrous Ammonium Sulfate, $Fe(NH_4)_2(SO_4)_2$

NOTE: The concentration of the ferrous ammonium sulfate must be determined daily since its strength decreases because of aerial oxidation.

Ferroin Indicator

0.0100 N Sulfato Cerate

PROCEDURE

A. Separation of Ferricyanide and Ferrocyanide from Persulfate

1. Pipet (wipe the pipet before leveling) 5.00 ml of sample into a 50-ml centrifuge tube.
2. Add 3 ml of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 20 ml of distilled water from a tip-up pipet.
4. Add 5 ml of 1.0 M cadmium nitrate from a tip-up pipet.
5. Stopper the tube and shake it vigorously for 15 seconds. Rinse down the stopper with distilled water into the centrifuge tube.
6. Stopper the tube and centrifuge for 2 minutes.
7. Carefully decant the supernatant liquid into a 250-ml conical flask. (Do not pour the solution too slowly since this promotes a greater loss of precipitate.)
8. Add from a tip-up pipet 20 ml of distilled water to the precipitate.
9. Stopper and shake the tube until the precipitate has completely broken up. Shake for an additional 10 seconds. Rinse down the stopper with distilled water into the centrifuge tube.
10. Stopper the tube and centrifuge for 2 minutes.
11. Carefully decant the rinse into the conical flask containing the previously decanted liquid. (Do not pour the solution too slowly since this promotes a greater loss of precipitate.) Save the decanted liquid for the determination of persulfate.

B. Determination of Sodium Ferricyanide

1. Add from a tip-up pipet 5 ml of 7.0 N sulfuric acid to the precipitate remaining after step A 11.
2. Add 6 g of potassium iodide crystals.
3. Stopper the tube and shake it until the precipitate is completely dispersed.
4. Transfer the mixture into a 250-ml conical flask.
5. Rinse the stopper and sides of the centrifuge tube with distilled water and add the rinses to the flask.
6. Add 100 ml of distilled water from a graduated cylinder.
7. Titrate with 0.1000 N sodium thiosulfate to a light yellow color.
8. Add 5 ml of starch indicator and continue the titration until the blue color just disappears. Any precipitate present does not interfere.
9. Calculations (for convenience, use Table I)

$$\frac{(\text{ml } Na_2S_2O_3)(\text{N } Na_2S_2O_3)[\text{eq wt } Na_3Fe(CN)_6](1000)}{(\text{ml sample})(1000)} =$$

$$(\text{ml } Na_2S_2O_3)(5.619) = Na_3Fe(CN)_6, \text{ g/l}$$

C. Determination of Persulfate

1. Pipet (wipe the pipet before leveling) 4.00 ml of 0.10 N ferrous ammonium sulfate into the 250-ml conical flask containing the decanted liquid from step A 11.
2. Swirl the flask and allow it to stand for one minute.
3. Add 10 ml of 7.0 N sulfuric acid from a tip-up pipet.
4. Add 4 drops of Ferroin indicator to the flask.
5. Titrate with 0.0100 N sulfato cerate to the first blue color that persists for 15 seconds. (If the volume of titrant required for the decanted liquid is 5 ml or less, repeat sections A and C, pipetting 10.0 ml of 0.10 N ferrous ammonium

sulfate.) The volume of sulfato cerate required is "B" in the calculations below.

6. Once daily determine the strength of the ferrous ammonium sulfate using approximately 20 ml of distilled water in place of the decanted liquid. Repeat steps 1—5 of section C as with the decanted liquid. Record the volume of sulfato cerate required. This volume is "A" in the calculations.

7. Calculations

Potassium Persulfate, $K_2S_2O_8$ (for convenience, use Table II)

$$\frac{(A - B)(\underline{N} \text{ sulfato cerate})(\text{eq wt } K_2S_2O_8)(1000)}{(\text{ml sample})(1000)} =$$

$$(A - B)(0.2703) = K_2S_2O_8, \text{ g/l}$$

Ammonium Persulfate, $(NH_4)_2S_2O_8$ (for convenience, use Table III)

$$\frac{(A - B)(\underline{N} \text{ sulfato cerate})[\text{eq wt } (NH_4)_2S_2O_8](1000)}{(\text{ml sample})(1000)} =$$

$$(A - B)(0.2280) = (NH_4)_2S_2O_8, \text{ g/l}$$

TABLE I

SODIUM FERRICYANIDE IN FERRICYANIDE BLEACH (5.00-ml SAMPLE)

ml 0.1 $\underline{N}$ $Na_2S_2O_3$	$Na_3Fe(CN)_6$ g/l	ml 0.1 $\underline{N}$ $Na_2S_2O_3$	$Na_3Fe(CN)_6$ g/l
13.0	73	18.0	101
13.2	74	18.2	102
13.4	75	18.4	103
13.6	76	18.6	105
13.8	78	18.8	106
14.0	79	19.0	107
14.2	80	19.2	108
14.4	81	19.4	109
14.6	82	19.6	110
14.8	83	19.8	111
15.0	84	20.0	112
15.2	85	20.2	114
15.4	87	20.4	115
15.6	88	20.6	116
15.8	89	20.8	117
16.0	90	21.0	118
16.2	91	21.2	119
16.4	92	21.4	120
16.6	93	21.6	121
16.8	94	21.8	122
17.0	96	22.0	124
17.2	97	22.2	125
17.4	98	22.4	126
17.6	99	22.6	127
17.8	100	22.8	128
23.0	129	30.0	169
23.2	130	30.2	170
23.4	131	30.4	171
23.6	133	30.6	172
23.8	134	30.8	173
24.0	135	31.0	174
24.2	136	31.2	175
24.4	137	31.4	176
24.6	138	31.6	178
24.8	139	31.8	179
25.0	140	32.0	180
25.2	142	32.2	181
25.4	143	32.4	182
25.6	144	32.6	183
25.8	145	32.8	184
26.0	146	33.0	185
26.2	147	33.2	187
26.4	148	33.4	188
26.6	149	33.6	189
26.8	151	33.8	190
27.0	152	34.0	191
27.2	153	34.2	192
27.4	154	34.4	193
27.6	155	34.6	194
27.8	156	34.8	196
28.0	157	35.0	197
28.2	158	35.2	198
28.4	160	35.4	199
28.6	161	35.6	200
28.8	162	35.8	201
29.0	163	36.0	202
29.2	164	36.2	203
29.4	165	36.4	205
29.6	166	36.6	206
29.8	167	36.8	207

TABLE II
POTASSIUM PERSULFATE IN FERRICYANIDE BLEACH (5.00-ml SAMPLE)

(A – B) ml cerate	$K_2S_2O_8$ g/l	(A – B) ml cerate	$K_2S_2O_8$ g/l	(A – B) ml cerate	$K_2S_2O_8$ g/l
0	0	3.00	0.81	6.00	1.62
0.10	0.03	3.10	0.84	6.10	1.65
0.20	0.05	3.20	0.86	6.20	1.68
0.30	0.08	3.30	0.89	6.30	1.70
0.40	0.11	3.40	0.92	6.40	1.73
0.50	0.14	3.50	0.95	6.50	1.76
0.60	0.16	3.60	0.97	6.60	1.78
0.70	0.19	3.70	1.00	6.70	1.81
0.80	0.22	3.80	1.03	6.80	1.84
0.90	0.24	3.90	1.05	6.90	1.87
1.00	0.27	4.00	1.08	7.00	1.89
1.10	0.30	4.10	1.11	7.10	1.92
1.20	0.32	4.20	1.14	7.20	1.95
1.30	0.35	4.30	1.16	7.30	1.97
1.40	0.38	4.40	1.19	7.40	2.00
1.50	0.41	4.50	1.22	7.50	2.03
1.60	0.43	4.60	1.24	7.60	2.05
1.70	0.46	4.70	1.27	7.70	2.08
1.80	0.49	4.80	1.30	7.80	2.11
1.90	0.51	4.90	1.32	7.90	2.14
2.00	0.54	5.00	1.35	8.00	2.16
2.10	0.57	5.10	1.38	8.10	2.19
2.20	0.59	5.20	1.41	8.20	2.22
2.30	0.62	5.30	1.43	8.30	2.24
2.40	0.65	5.40	1.46	8.40	2.27
2.50	0.68	5.50	1.49	8.50	2.30
2.60	0.70	5.60	1.51	8.60	2.32
2.70	0.73	5.70	1.54	8.70	2.35
2.80	0.76	5.80	1.57	8.80	2.38
2.90	0.78	5.90	1.59	8.90	2.41

(A — B)(0.2703) = $K_2S_2O_8$, g/l

TABLE III
AMMONIUM PERSULFATE IN FERRICYANIDE BLEACH (5.00-ml SAMPLE)

(A – B) ml cerate	$(NH_4)_2S_2O_8$ g/l	(A – B) ml cerate	$(NH_4)_2S_2O_8$ g/l
0	0	1.00	0.23
0.10	0.02	1.10	0.25
0.20	0.05	1.20	0.27
0.30	0.07	1.30	0.30
0.40	0.09	1.40	0.32
0.50	0.11	1.50	0.34
0.60	0.14	1.60	0.36
0.70	0.16	1.70	0.39
0.80	0.18	1.80	0.41
0.90	0.21	1.90	0.43
2.00	0.46	6.50	1.48
2.10	0.48	6.60	1.50
2.20	0.50	6.70	1.53
2.30	0.52	6.80	1.55
2.40	0.55	6.90	1.57
2.50	0.57	7.00	1.60
2.60	0.59	7.10	1.62
2.70	0.62	7.20	1.64
2.80	0.64	7.30	1.66
2.90	0.66	7.40	1.69
3.00	0.68	7.50	1.71
3.10	0.71	7.60	1.73
3.20	0.73	7.70	1.76
3.30	0.75	7.80	1.78
3.40	0.78	7.90	1.80
3.50	0.80	8.00	1.82
3.60	0.82	8.10	1.85
3.70	0.84	8.20	1.87
3.80	0.87	8.30	1.89
3.90	0.89	8.40	1.92
4.00	0.91	8.50	1.94
4.10	0.93	8.60	1.96
4.20	0.96	8.70	1.98
4.30	0.98	8.80	2.01
4.40	1.00	8.90	2.03
4.50	1.03	9.00	2.05
4.60	1.05	9.10	2.07
4.70	1.07	9.20	2.10
4.80	1.09	9.30	2.12
4.90	1.12	9.40	2.14
5.00	1.14	9.50	2.17
5.10	1.16	9.60	2.19
5.20	1.19	9.70	2.21
5.30	1.21	9.80	2.23
5.40	1.23	9.90	2.26
5.50	1.25	10.00	2.28
5.60	1.28	10.10	2.30
5.70	1.30	10.20	2.33
5.80	1.32	10.30	2.35
5.90	1.35	10.40	2.37
6.00	1.37	10.50	2.39
6.10	1.39	10.60	2.42
6.20	1.41	10.70	2.44
6.30	1.44	10.80	2.46
6.40	1.46	10.90	2.49

(A — B)(0.2280) = $(NH_4)_2S_2O_8$, g/l

IODOMETRIC DETERMINATION OF FERRICYANIDE IN BLEACH CONTAINING CARBOWAX 1540 (1120)

INTRODUCTION

Excess iodide ions and a zinc reagent are added to the bleach sample. The ferricyanide reacts with the iodide to produce an equivalent amount of iodine. The iodine is then titrated with standard sodium thiosulfate. The reaction of ferricyanide and iodide is quantitative as long as zinc ions are present in excess. Any ferrocyanide initially present in the bleach, as well as the ferrocyanide produced by the reduction of ferricyanide, is precipitated as zinc ferrocyanide.

Carbowax 1540 interferes with the iodine end point and, therefore, must be removed prior to the formation of the iodine. This is accomplished by acidifying the sample and adding an excess of ferrocyanide which forms a precipitate with the Carbowax. The excess ferrocyanide is then removed with zinc ions as mentioned above.

Persulfate ions and some other oxidizing agents also oxidize iodide and, hence, are measured as ferricyanide by this method.

REAGENTS

Sodium Ferrocyanide Decahydrate, $Na_4Fe(CN)_6 \cdot 10H_2O$
7.0 N Sulfuric Acid, H_2SO_4
0.6 M Potassium Iodide, KI
Zinc Sulfate— 7.0 N Sulfuric Acid reagent
Starch indicator
0.1000 N Sodium Thiosulfate, $Na_2S_2O_3$

RELIABILITY

An estimate of the reliability can be obtained from the following data of one analyst.

	(1)	(2)	(3)
g/l $K_3Fe(CN)_6$ mixed at	70.0	100.0	160.0
g/l $K_3Fe(CN)_6$ found	69.9	100.0	159.2
	69.8	99.7	159.6

PROCEDURE

A. Removal of the Interfering Constituents

1. Pipet 100.0 ml of sample into a 200-ml volumetric flask.
2. Add approximately 1 gram of sodium ferrocyanide decahydrate using one level #3 Coors spoon. Swirl to dissolve.
3. Add 10 ml of 7.0 N sulfuric acid from a tip-up pipet.
4. Dilute to volume with distilled water, and mix thoroughly.
5. Filter about 50 ml of the treated sample through a #12 Whatman filter paper.
6. Pipet 15.0 ml of filtrate into a 250-ml Erlenmeyer flask.
7. Add 25 ml of 0.6 M potassium iodide from a tip-up pipet.
8. Add 20 ml of zinc sulfate— 7.0 N sulfuric acid reagent from a tip-up pipet.
9. Mix thoroughly.

B. Titration with Sodium Thiosulfate

1. Titrate with 0.1000 N sodium thiosulfate to a light yellow color.
2. Add 5 ml of starch indicator from a tip-up pipet, and continue the titration until the blue color disappears.

C. Calculations

$$\frac{(\text{ml } Na_2S_2O_3)(\text{N } Na_2S_2O_3)[\text{eq wt } Na_3Fe(CN)_6](1000)}{(\text{fraction of treated sample})(\text{ml sample})(1000)} =$$

$$\frac{(\text{ml } Na_2S_2O_3)(0.1000)(280.95)(1000)}{(15/200)(100.0)(1000)} =$$

$$3.75\ (\text{ml } Na_2S_2O_3) = Na_3Fe(CN)_6,\ g/l$$

POTENTIOMETRIC DETERMINATION OF SILVER IN FIXING BATHS (1208C)

PRINCIPLE

The sample containing silver is titrated potentiometrically using sodium sulfide. The potential change of the system is followed with a silver and calomel electrode pair.

The sample is made alkaline to prevent the decomposition of sodium thiosulfate which occurs in acid solutions. (Ethylenedinitrilo) tetra-acetic acid, EDTA, is added to minimize interference of other metal ions. However, the EDTA reagent does not prevent interference from zinc ions. Gelatin is added to prevent the coagulation of the silver sulfide which is formed. Otherwise, the coagulated silver sulfide would occlude the silver ions.

Changes in volumes of the sample and the sodium hydroxide-EDTA reagent affect the silver results. If small samples are used, the sample volume must be brought to about 300 ml with 1.0 M sodium thiosulfate. The standardization of the sodium sulfide is also done in this manner.

RELIABILITY

Four fixing baths containing known amounts of silver, Ag, were analyzed by two analysts. The concentration of these samples ranged from 0.100 to 1.00 g/l Ag. The 95% confidence limits for an individual analysis are ±0.01 g of Ag per liter.

The recording automatic titrators, when used, may produce results higher than stoichiometric equivalence. The instrument should be checked for this bias by analyzing several standard laboratory mixes. All fixing baths should be given this check, and if a bias is found, the correction for bias should be applied to the silver results.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent

Beckman Inverted Sleeve-Junction Calomel Electrode, No. 43462, or Beckman Fiber-Junction Calomel Electrode, No. 39170, with a saturated potassium nitrate bridge. (Remove the saturated potassium chloride solution and substitute saturated potassium nitrate solution.)

Silver-Silver Sulfide electrode (See Procedure for preparation.)

REAGENTS

Sodium Sulfide, $Na_2S \cdot 9H_2O$

1.0 N Sodium Hydroxide, NaOH

1.0 M Sodium Thiosulfate, $Na_2S_2O_3$

Sodium Hydroxide—(Ethylenedinitrilo) Tetra-Acetic Acid reagent, NaOH—EDTA

0.4% Gelatin solution*

0.06 N Sodium Sulfide, Na_2S (standardized)

* 10 g/l = 1%

PROCEDURE

A. Preparation of the Silver-Silver Sulfide Electrode

1. Thoroughly clean a silver bar electrode (Precision Scientific Co. Bulletin 640, Catalog No. 68865) with household cleaning powder. Rinse well with distilled water.

2. Place the clean electrode in 1.0 N sodium hydroxide containing a few crystals of sodium sulfide for a period of 10 minutes.

3. Remove the electrode from the solution for 5 minutes (for air oxidation).

4. Replace the electrode in 1.0 N sodium hydroxide containing crystals of sodium sulfide for 15 minutes.

5. Repeat Steps 3 and 4 several times during a 2—3 hour period until the electrode has darkened. Make sure that there are always sodium sulfide crystals in the solution.

NOTE: The performance of this electrode improves with age. It *does not* require cleaning or regeneration other than a rinse with distilled water after each use.

B. Treatment of the Sample

1. a. For samples containing *1 g/l of silver or less,* carefully measure 300 ml of sample in a graduated cylinder, and add it to a 600-ml beaker.

b. For samples containing *1 to 3 g/l of silver:*

(1) Pipet 100.0 ml of sample into a 600-ml beaker.

(2) Add, from a graduated cylinder, 200 ml of 1.0 M sodium thiosulfate to the beaker.

c. For samples containing *more than 3 g/l of silver:*

(1) Pipet 50.0 ml of sample into a 600-ml beaker.

(2) Add, from a graduated cylinder, 250 ml of 1.0 M sodium thiosulfate to the beaker.

2. Add 100 ml of the NaOH—EDTA reagent from a 50-ml tip-up pipet.

3. Add 10 ml of 0.4% gelatin from a tip-up pipet.

C. Titration of the Sample

Titrate the sample with standardized 0.06 N sodium sulfide, using a pH meter (or an automatic titrator). See instructions in Method XIA; however, use the following settings:

NOTE: All titrations should be run with the reference electrode (Beckman Fiber-Junction Calomel Electrode) in the reference jack of the pH meter and the indicator electrode (Silver Bar Electrode, Leeds and Northrup Black-Dot Glass Electrode, Beckman Platinum Inlay Electrode) in the indicator jack of the pH meter.

1. Turn the pointer knob to "—MV."

2. Place the silver-silver sulfide electrode in the upper jack.

NOTE: Avoid unnecessary exposure of the standardized sodium sulfide to the air. The reagent should be standardized once a week. Discard all unused reagent that remains in an open bottle at the end of each day. A 60-ml bottle is suggested.

D. Calculations:

1. $$\frac{(\text{ml } Na_2S)(\underline{N}\ Na_2S)(108)(1000)}{(\text{ml sample})(1000)} = \text{silver, g/l}$$

2. For a 300-ml sample,

   $$(\text{ml } Na_2S)(\underline{N}\ Na_2S)(0.360) = \text{silver, g/l}^*$$

3. For a 100-ml sample,

   $$(\text{ml } Na_2S)(\underline{N}\ Na_2S)(1.08) = \text{silver, g/l}^*$$

4. For a 50-ml sample,

   $$(\text{ml } Na_2S)(\underline{N}\ Na_2S)(2.16) = \text{silver, g/l}^*$$

* Apply the correction for bias (if any) to the results.

DETERMINATION OF SILVER IN THIOSULFATE FIXERS WITH THIOACETAMIDE (1209D)

PRINCIPLE

The technique is based on the work of Bush, Zuehlke, and Ballard,* but no instrument is required. The silver in a fixer is titrated, in effect, by adding graduated amounts of a thioacetamide solution to samples of the bath that have been adjusted to a pH greater than 12. At this alkalinity, thioacetamide decomposes to sulfide which immediately precipitates a chemically equivalent amount of silver sulfide. The silver sulfide is filtered and the filtrate is tested for completeness of silver precipitation by adding more thioacetamide.

It is probable that this method will be used most frequently to determine the amount of silver in a fixer before and/or after the fixer has passed through the KODAK Chemical Recovery Cartridge and associated KODAK Circulating Unit. A fix which has passed through this silver recovery unit contains moderate amounts of ferrous iron (II) ions which will interfere unless they are removed by the addition of ferricyanide. This step is included for all samples on the assumption that they will contain some iron II.

The fixer must not have very much color, although some can be tolerated provided a suitable blank is used.

The practical extremes of the technique are presented as Procedures I and II. Procedures III and IV illustrate very useful specific modifications.

Procedure I—Rapid Determination of Silver Concentration Range in Thiosulfate Fixers (Results are reported to nearest gram per liter.)

Procedure II—Determination of Silver in Thiosulfate Fixers (This is a more precise procedure making use of pipets and burets. Results are reported to nearest 0.1 gram per liter.)

Procedure III—Rapid Determination of Silver in Thiosulfate Fixers when Concentration of Silver is Less than 0.5 gram per liter (Results are reported to nearest 0.5 gram per liter.)

Procedure IV—Special Application of Procedure III for Determination of Exhaustion of KODAK Chemical Recovery Cartridge

RELIABILITY

Eight fixing baths were prepared containing known amounts of silver and varying in pH from 4 to 10. Each contained some of the following items: conventional sequestering agents, sulfite (bisulfite), carbonate (bicarbonate), thiosulfate (sodium or ammonium), formaldehyde, acetate, borate, potassium alum, antifoamants, and citrate.

The fixers were analyzed using Procedure II. End points were determined to 0.05 g/l. Of the 30 results in the range from 0.50 to 6.00 g/l, all were within 0.10 g/l of the nominal value and there appeared to be no bias.

Ten acid hardening fixes were prepared to contain either 0.50 g or 5.00 g of silver and 0.1 to 10 g of Iron II ions. These were analyzed according to Procedure II and all results were within ±0.2 g/l of the mix level.

SPECIAL APPARATUS

100-ml glass-stoppered graduated cylinder (VWR Scientific, Catalog No. 24760-100)
10-ml graduated cylinder (VWR Scientific, Catalog No. 24710-044)
Filter paper, Whatman No. 3, dia. 12.5 cm (VWR Scientific, Catalog No. 28456-101)
Balance, torsion, sensitivity 0.01 g

REAGENTS FOR PROCEDURES

6.0 N Accelerator reagent
0.00926 N Thioacetamide
0.1 M Potassium Ferricyanide
0.2 M Potassium Ferricyanide

REAGENTS FOR STANDARDIZATION OF 0.00926 N THIOACETAMIDE

0.10 N Sodium Chloride
0.0500 N Silver Nitrate
1.0 M Sodium Thiosulfate

PROCEDURE I—RAPID DETERMINATION OF SILVER CONCENTRATION RANGE IN THIOSULFATE FIXERS

A. Treatment of Sample

NOTE: Use cylinder markings for all measurements.

1. Add to each of three 100-ml glass-stoppered graduated cylinders, labeled 2, 4, and 6, 10 ml of fixer sample, 10 ml of 0.1 M potassium ferricyanide, and 10 ml of 6 N accelerator reagent. Swirl to mix. If the resulting color is:

a. *reddish-brown,* proceed to step 2.

b. *black,* add 10 ml more of 0.1 M potassium ferricyanide and swirl to mix. Proceed to step 2 if the resulting color is reddish-brown. If not, start over again, using a fresh sample and a 0.2 M potassium ferricyanide reagent.

2. Using a polyethylene squeeze bottle, add to the cylinders the following volumes of 0.00926 N thioacetamide:

Cylinder No. 2—20 ml
Cylinder No. 4—40 ml
Cylinder No. 6—60 ml

3. Stopper and shake all cylinders vigorously 5 seconds.

4. Filter approximately 20 ml of the contents of each cylinder through a Whatman No. 3 (12.5-cm diameter) filter paper and collect the filtrates in beakers containing approximately 5 ml of 0.00926 N thioacetamide.

5. Observe the appearance of the beakers' contents, and refer to Table I.

*D. G. Bush, C. W. Zuehlke, and A. E. Ballard, *Analytical Chemistry,* 31, 1368 (1959).

B. Reporting Results

1. The results from these three cylinders will identify the silver concentration range of the fix as:

a. less than 2 g/l

b. between 2 and 4 g/l

c. between 4 and 6 g/l, or

d. over 6 g/l*

2. One more trial will suffice to establish the silver content between two silver concentrations 1.0 g/l apart (see Procedure II).

PROCEDURE II—DETERMINATION OF SILVER IN THIOSULFATE FIXING BATHS

Procedure I has established the silver concentration range. If it is desirable to determine the concentration more precisely, it is necessary to zero in on the end point by measuring volumes with pipets and burets and by using smaller increments of 0.00926 N thioacetamide in the end point region.

This procedure establishes the silver content to the nearest 0.1 g/l, with three or fewer trials.

A. Treatment of Sample

1. Pipet into four 100-ml glass-stoppered graduated cylinders 10.0 ml of fixer. Using the markings on the cylinders, add to one 10 ml of 0.1 M potassium ferricyanide and 10 ml of 6 N accelerator reagent. Swirl to mix. If the resulting color is:

a. *reddish-brown,* proceed to Step 2.

b. *black,* add 10 ml more of 0.1 M potassium ferricyanide. Swirl to mix. Proceed to step 2 if the resulting color is reddish-brown. If not, start over again using a fresh sample and a 0.2 M potassium ferricyanide reagent. Prepare the remaining cylinders similarly.

2. Add from a buret the appropriate amount of 0.00926 N thioacetamide to each cylinder.

> NOTE: The appropriate amounts of 0.00926 N thioacetamide are selected from Table II and are based on the silver concentration range found in Procedure I. For example, if the range was found to be more than 2 but less than 3 grams per liter, the region to explore is between 2 and 3. Increments shown are in 1.0 ml 0.00926 N thioacetamide (equivalent to 0.1 g Ag/l). To obtain greater efficiency, the end point may be approached by trying one at about 2.5 g/l and then one at 2.3 g/l or 2.7 g/l, depending on the result obtained with 2.5 g/l.

3. Stopper and shake each cylinder vigorously 5 seconds.

4. Filter approximately 20 ml of the contents of each cylinder through a Whatman No. 3 (12.5-cm diameter) filter paper and collect the filtrates in beakers containing approximately 5 ml of 0.00926 N thioacetamide each.

* If the silver content is more than 6 g/l, dilute the sample with an equal volume of water and rerun the determinations corresponding to cylinders 2, 4, and 6. *Remember to multiply any final answer by 2.*

B. Reporting Results

Observe the appearance of the contents of the beakers, and refer to Table II for decisions and details of further trials, if necessary.

PROCEDURE III—DETERMINATION OF SILVER IN THIOSULFATE FIXERS WHEN CONCENTRATION OF SILVER IS LESS THAN 0.5 g/l

When the concentration of silver is less than 0.5 g/l, it is possible to establish the silver content between two concentrations 0.05 g/l apart, using only graduated cylinders and the markings on the cylinders for all measurements. Because this is expected to be an area of great interest, Procedure III is included.

A. Treatment of Sample

1. Obtain several 100-ml glass-stoppered graduated cylinders. Add to each 40 ml of fixer sample, 20 ml of 0.2 M potassium ferricyanide, and 20 ml of 6 N accelerator reagent. Stopper and shake to mix.

2. Add from a polyethylene squeeze bottle to one of the cylinders, 20 ml of 0.00926 N thioacetamide, and to a second cylinder, add 10 ml.

> NOTE: 20 ml of 0.00926 N thioacetamide is equivalent to 0.5 g/l of silver, and 10 ml is equivalent to 0.25 g/l of silver.

3. Stopper, and shake the cylinders vigorously 5 seconds.

4. Filter approximately 20 ml of the contents of each cylinder through a Whatman No. 3 (12.5-cm diameter) filter paper, and collect the filtrates in a beaker containing approximately 5 ml of 0.00926 N thioacetamide each.

5. Observe the appearance of the contents of the beakers, and refer to Table III to make the next decision.

B. Reporting Results

1. These two trials determine that:

a. The procedure is not applicable (silver content is greater than 0.5 g/l).

b. The silver content is below 0.25 g/l.

c. The silver content is between 0.25 and 0.5 g/l.

2. If the procedure is applicable, three or fewer trials will establish the silver concentrations 0.05 grams per liter apart.

PROCEDURE IV—(SPECIAL APPLICATION) DETERMINATION OF EXHAUSTION OF KODAK CHEMICAL RECOVERY CARTRIDGE

When the concentration of silver in the effluent from the recovery cartridge exceeds 0.25 grams of silver per liter, it can be assumed that the capacity of the cartridge has been exceeded. By using 10 ml of 0.00926 N thioacetamide (equivalent to 0.25 g/l of silver) and making only the one trial, a decision on exhaustion can be reached.

A. Treatment of Sample

1. Place in a 100-ml glass-stoppered graduated cylinder 40 ml of fixer sample, 20 ml of 0.2 M potassium ferricyanide,

and 20 ml of 6 N accelerator reagent. Stopper and shake to mix.

2. Add 10 ml of 0.00926 N thioacetamide, stopper, and shake for 5 seconds.

3. Filter approximately 20 ml of the mixture through a Whatman No. 3 filter paper into a beaker containing approximately 5 ml of 0.00926 N thioacetamide.

B. Decision

If the resulting solution is:

a. *colored*— the recovery cartridge is exhausted;

b. *clear*— the recovery cartridge is still serviceable.

TABLE I

DECISION SHEET FOR DETERMINING SILVER CONCENTRATION RANGE (10-ml SAMPLE) PROCEDURE I

Cylinder No.	0.00926 N Thioacetamide Added	If the Contents of the Beaker Turn Color,* Amount of Silver in Fix is More Than	If the Contents of the Beaker Remain Clear,† Amount of Silver in Fix is Less Than
1	10	1.0 g/l	
2	20	2.0	
3	30	3.0	
4	40	4.0	
5	50	5.0	
6	60	6.0	

* The color in the beaker is greater than that of a blank—consisting of appropriate amounts of sample, potassium ferricyanide, 6 N accelerator reagent and water (in place of 0.00926 N thioacetamide)— that was filtered and collected in about 5 ml of water.

† The color in the beaker is not greater than a blank prepared as above.

TABLE II

DECISION SHEET FOR DETERMINING SILVER CONCENTRATION (10.0-ml SAMPLE) PROCEDURE II

Range g/l	0.00926 N Thioacetamide Added	If the Contents of the Beaker Turn Color, Amount of Silver in Fix is More Than	If the Contents of the Beaker Remain Clear, Amount of Silver in Fix is Less Than
0	1.00	0.1 g/l	
	2.00	0.2	
	3.00	0.3	
	4.00	0.4	
	5.00	0.5	
	6.00	0.6	
	7.00	0.7	
	8.00	0.8	
	9.00	0.9	
1	10.0	1.0	
	11.0	1.1 g/l	
	12.0	1.2	
	13.0	1.3	
	14.0	1.4	
	15.0	1.5	
	16.0	1.6	
	17.0	1.7	
	18.0	1.8	
	19.0	1.9	
2	20.0	2.0	
	21.0	2.1	
	22.0	2.2	
	23.0	2.3	
	24.0	2.4	
	25.0	2.5	
	26.0	2.6	
	27.0	2.7	
	28.0	2.8	
	29.0	2.9	
3	30.0	3.0	
	31.0	3.1	
	32.0	3.2	
	33.0	3.3	
	34.0	3.4	
	35.0	3.5	
	36.0	3.6	
	37.0	3.7	
	38.0	3.8	
	39.0	3.9	
4	40.0	4.0	
	41.0	4.1	
	42.0	4.2	
	43.0	4.3	
	44.0	4.4	
	45.0	4.5	
	46.0	4.6	
	47.0	4.7	
	48.0	4.8	
	49.0	4.9	
5	50.0	5.0	

TABLE II

DECISION SHEET FOR DETERMINING SILVER CONCENTRATION (10.0-ml SAMPLE) PROCEDURE II

Range g/l	0.00926 N Thioacetamide Added	If the Contents of the Beaker Turn Color, Amount of Silver in Fix is More Than	If the Contents of the Beaker Remain Clear, Amount of Silver in Fix is Less Than
	51.0		5.1 g/l
	52.0		5.2
	53.0		5.3
	54.0		5.4
	55.0		5.5
	56.0		5.6
	57.0		5.7
	58.0		5.8
	59.0		5.9
6	60.0		6.0

TABLE III

DECISION SHEET FOR PROCEDURE III (40-ml SAMPLE)

ml of 0.00926 N Thioacetamide Added	If the Contents of the Beaker Turn Color, Amount of Silver in Fix is More Than	If the Contents of the Beaker Remain Clear, Amount of Silver in Fix is Less Than
2		0.05 g/l
4		0.10
6		0.15
8		0.20
10		0.25
12		0.30
14		0.35
16		0.40
18		0.45
20		0.50

DETERMINATION OF TOTAL SULFITE IN FIRST DEVELOPER (1305L)

INTRODUCTION

The developer sample is added to an excess of iodine, formed by acidifying standard potassium iodate solution and adding potassium iodide. Part of the iodine is reduced to iodide by the sulfite in the sample; the unreduced part is measured by titrating it with standard sodium thiosulfate using starch indicator. Since the quantity of sulfite is equivalent to the quantity of reduced iodine, and since the quantity of sodium thiosulfate used in the titration is equivalent to the quantity of unreduced iodine, the difference between the total iodine and the volume of standard sodium thiosulfate is a measure of the sodium sulfite concentration.

In the preparation of the first developer solution, both sodium sulfite and sodium bisulfite are used. This method measures the total sulfite content of a sample; thus it reports the bisulfite as sodium sulfite.

RELIABILITY

Photographic grade sodium sulfite is usually less than 100% pure (ANSI PH4.275-1972 specifies 97.0% minimum Na_2SO_3). Photographic grade sodium bisulfite is a mixture of $NaHSO_3$ and $Na_2S_2O_5$ (sodium metabisulfite). ANSI PH4.276-1972 for photographic grade sodium bisulfite calls for a minimum assay, as determined by an iodine titration and expressed as $Na_2S_2O_5$, of 97.0%. One gram of photographic grade $NaHSO_3$ is equivalent to 1.30 grams of Na_2SO_3 (100%).

In some mixes containing a relatively small amount of sulfite, an appreciable portion of the sulfite is oxidized during mixing, thus leading to sulfite analyses that are lower than mix level.

REAGENTS

0.1000 N Potassium Iodate, KIO_3
7.0 N Sulfuric Acid, H_2SO_4
0.6 M Potassium Iodide, KI
0.1000 N Sodium Thiosulfate, $Na_2S_2O_3$
Starch indicator

PROCEDURE

A. Treatment and Titration of Sample

1. Pipet 50.0 ml of 0.1000 N potassium iodate into a 250-ml Erlenmeyer flask.
2. Add 25 ml of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 25 ml of 0.6 M potassium iodide from a tip-up pipet.

TABLE I

SULFITE IN FIRST DEVELOPER (5.00-ml SAMPLE SIZE)

ml 0.1 N $Na_2S_2O_3$	Na_2SO_3 g/l	ml 0.1 N $Na_2S_2O_3$	Na_2SO_3 g/l	ml 0.1 N $Na_2S_2O_3$	Na_2SO_3 g/l	ml 0.1 N $Na_2S_2O_3$	Na_2SO_3 g/l	ml 0.1 N $Na_2S_2O_3$	Na_2SO_3 g/l	ml 0.1 N $Na_2S_2O_3$	Na_2SO_3 g/l
7.5	53.6	10.0	50.4	12.5	47.3	15.0	44.1	17.5	41.0	20.0	37.8
7.6	53.5	10.1	50.3	12.6	47.2	15.1	44.0	17.6	40.9	20.1	37.7
7.7	53.3	10.2	50.2	12.7	47.0	15.2	43.9	17.7	40.7	20.2	37.6
7.8	53.2	10.3	50.1	12.8	46.9	15.3	43.8	17.8	40.6	20.3	37.5
7.9	53.1	10.4	49.9	12.9	46.8	15.4	43.6	17.9	40.5	20.4	37.3
8.0	53.0	10.5	49.8	13.0	46.7	15.5	43.5	18.0	40.4	20.5	37.2
8.1	52.8	10.6	49.7	13.1	46.5	15.6	43.4	18.1	40.2	20.6	37.1
8.2	52.7	10.7	49.5	13.2	46.4	15.7	43.2	18.2	40.1	20.7	36.9
8.3	52.6	10.8	49.4	13.3	46.3	15.8	43.1	18.3	40.0	20.8	36.8
8.4	52.4	10.9	49.3	13.4	46.1	15.9	43.0	18.4	39.8	20.9	36.7
8.5	52.3	11.0	49.2	13.5	46.0	16.0	42.9	18.5	39.7	21.0	36.6
8.6	52.2	11.1	49.0	13.6	45.9	16.1	42.7	18.6	39.6	21.1	36.4
8.7	52.1	11.2	48.9	13.7	45.8	16.2	42.6	18.7	39.5	21.2	36.3
8.8	51.9	11.3	48.8	13.8	45.6	16.3	42.5	18.8	39.3	21.3	36.2
8.9	51.8	11.4	48.7	13.9	45.5	16.4	42.4	18.9	39.2	21.4	36.1
9.0	51.7	11.5	48.5	14.0	45.4	16.5	42.2	19.0	39.1	21.5	35.9
9.1	51.6	11.6	48.4	14.1	45.3	16.6	42.1	19.1	39.0	21.6	35.8
9.2	51.4	11.7	48.3	14.2	45.1	16.7	42.0	19.2	38.8	21.7	35.7
9.3	51.3	11.8	48.2	14.3	45.0	16.8	41.9	19.3	38.7	21.8	35.6
9.4	51.2	11.9	48.0	14.4	44.9	16.9	41.7	19.4	38.6	21.9	35.4
9.5	51.1	12.0	47.9	14.5	44.8	17.0	41.6	19.5	38.5	22.0	35.3
9.6	50.9	12.1	47.8	14.6	44.6	17.1	41.5	19.6	38.3	22.1	35.2
9.7	50.8	12.2	47.7	14.7	44.5	17.2	41.4	19.7	38.2	22.2	35.1
9.8	50.7	12.3	47.5	14.8	44.4	17.3	41.2	19.8	38.1	22.3	34.9
9.9	50.6	12.4	47.4	14.9	44.3	17.4	41.1	19.9	38.0	22.4	34.8

4. Pipet 5.00 ml of sample into the flask.

5. Titrate with 0.1000 N sodium thiosulfate to a light yellow color. Then add 5 ml of starch indicator from a tip-up pipet, and continue the titration until the blue disappears.

B. Calculations

$$\frac{[(\text{ml} \times \underline{\text{N}} \text{ of } KIO_3) - (\text{ml} \times \underline{\text{N}} \text{ of } Na_2S_2O_3)] \left[\begin{matrix} \text{Eq wt} \\ Na_2SO_3 \end{matrix} \right]}{(\text{ml sample})} =$$

$$\frac{(50.0 - \text{ml } Na_2S_2O_3)(6.302)}{(\text{ml sample})} = Na_2SO_3, \text{ g/l, or}$$

for convenience, use Table I.

DETERMINATION OF HYPO INDEX, AND THE SULFITE, BISULFITE, AND THIOSULFATE CONTENT OF A FIXER (1308G)

PRINCIPLE

The hypo index (H.I.) of a fixer is defined as the milliliters (ml) of 0.1000 N iodine consumed by the sulfite, bisulfite, and thiosulfate in a specified volume of the fixing bath. In Part A of the Procedure, the hypo index is determined by adding the sample to an excess of iodine (formed by acidifying potassium iodate and adding an excess of potassium iodide) and titrating this excess with standard sodium thiosulfate. The difference between the ml of 0.1000 N potassium iodate added originally and the ml of 0.1000 N sodium thiosulfate used in the titration is, therefore, the hypo index of the sample.

Ferrocyanide is present in fixers as a carry-in from the bleach. This ferrocyanide interferes in the determination of the hypo index. Zinc sulfate is added to remove the ferrocyanide.

The theoretical consumption of iodine by sulfite, bisulfite, and thiosulfate is a close approximation of the actual consumption (see Table I). The "theoretical" hypo index is calculated from a consideration of the equivalent weights of ammonium thiosulfate, sodium sulfite, sodium bisulfite, and sodium thiosulfate pentahydrate. Photographic grade ammonium thiosulfate is supplied as a water solution having an assay of 58 ±2.0% and containing a maximum of 1.0% ammonium sulfite and 0.5% free ammonia (E.K. Specification 3464-5). Photographic grade sodium sulfite is usually less than 100% pure (ANSI PH4.275-1972 specifies 97% minimum Na_2SO_3). Photographic grade sodium bisulfite is a mixture of $NaHSO_3$, $Na_2S_2O_5$ (sodium metabisulfite), and water. Its purity, as determined by an iodine titration and expressed as $Na_2S_2O_5$ should be at least 97% (ANSI PH4.276-1972). If it were pure $NaHSO_3$, it would assay 91% as $Na_2S_2O_5$. Table II shows the contributions of the constituents of typical fixing baths to hypo index.

In order to determine only the thiosulfate content, follow Procedure, Part B. A separate sample is first adjusted to pH 8.5. Formalin is then added to form a complex with the sulfite. At this pH the complex forms rapidly. The solution is then made acid to prevent the complex from reacting with iodine, which is subsequently used to titrate the thiosulfate.

The sulfite content is calculated in Procedure, Part C, by subtracting the volume of iodine consumed by the thiosulfate from the volume of iodine consumed by the sum of sulfite, bisulfite, and thiosulfate (the hypo index). A factor appears in the calculations to compensate for differences in sample size between Parts A and B of the procedure.

REAGENTS

0.1000 N Potassium Iodate, KIO_3
2.0 N Acetic Acid, CH_3COOH
50 g/l Zinc Sulfate, $ZnSO_4$
0.6 M Potassium Iodide, KI
0.1000 N Sodium Thiosulfate, $Na_2S_2O_3$
Starch indicator
Formalin
Phenolphthalein indicator
1.0 N Sodium Hydroxide, NaOH
0.1000 N Iodine, I_2

PROCEDURE

A. Hypo Index (Total Bisulfite, Sulfite, and Thiosulfate)

1. Treatment and Titration of Sample

a. Pipet (wipe before leveling) 50.0 ml of 0.1000 N potassium iodate into a 250-ml Erlenmeyer flask.

b. Add 10 ml of 2.0 N acetic acid from a tip-up pipet.

c. Add 5 ml of 50 g/l zinc sulfate from a tip-up pipet.

d. Stir the solution with a magnetic stirrer, and add 25 ml of 0.6 M potassium iodide from a tip-up pipet.

e. Immediately pipet (wipe) 3.00 ml (if from tank) or 1.00 ml (if fresh recirculated replenisher) of fixer into the flask while the solution is stirring.

f. Titrate with 0.1000 N sodium thiosulfate to a light yellow color. Add 5 ml of starch indicator from a tip-up pipet and continue the titration until the blue color disappears.

2. Calculations

(50.00 — ml $Na_2S_2O_3$) = Hypo Index

NOTE: Always specify the sample size when reporting results.

B. Thiosulfate (Hypo)

1. Treatment of Sample

a. Pipet 3.00 ml of sample into a 250-ml conical flask.

b. Add 5 ml of Formalin from a tip-up pipet.

c. Add 3 to 4 drops of phenolphthalein indicator.

d. (1) If the solution is pink, titrate with 1.0 N sulfuric acid to colorless.

(2) If the solution is colorless, titrate with 1.0 N sodium hydroxide to the first light pink.

e. Let the solution stand for 2 minutes.

f. Add 10 ml of 2.0 N acetic acid from a tip-up pipet.

g. Add 5 ml of 50 g/l zinc sulfate from a tip-up pipet.

2. Titration with Iodine

a. Add, from a tip-up pipet, 5 ml of starch indicator to the sample.

b. Titrate with 0.1000 N iodine to the first distinct blue color.

3. Calculations

a. Sodium Thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$

$$\frac{(\text{ml } I_2)(\text{N } I_2)(\text{eq wt } Na_2S_2O_3 \cdot 5H_2O)(1000)}{(\text{ml sample})(1000)} =$$

TANK (3-ml sample)

$$(\text{ml } I_2)(8.273) = Na_2S_2O_3 \cdot 5H_2O, \text{ g/l}$$

REPLENISHER (1-ml sample)

$$(\text{ml } I_2)(24.82) = Na_2S_2O_3 \cdot 5H_2O, \text{ g/l}$$

b. Ammonium Thiosulfate, $(NH_4)_2S_2O_3$[58.6%]*

$$\frac{(\text{ml } I_2)(\underline{N}\ I_2)[\text{eq wt } (NH_4)_2S_2O_3](1000)(100)}{(\text{ml sample})[\%\ (NH_4)_2S_2O_3][\text{sp gr } (NH_4)_2S_2O_3](1000)} =$$

TANK (3-ml sample)

$$(\text{ml } I_2)(6.38) = (NH_4)_2S_2O_3[58.6\%], \text{ ml/l}$$

REPLENISHER (1-ml sample)

$$(\text{ml } I_2)(19.14) = (NH_4)_2S_2O_3[58.6\%], \text{ ml/l}$$

C. Bisulfite and Sulfite (as Na_2SO_3)

1. Tank (3-ml sample used for Hypo Index)

$$[(\text{H.I.}) - (\text{ml } I_2 \text{ for hypo})]\ 2.10 = Na_2SO_3, \text{ g/l}$$

2. Replenisher (1-ml sample used for Hypo Index)

$$[(3)(\text{H.I.}) - (\text{ml } I_2 \text{ for hypo})]\ 2.10 = Na_2SO_3, \text{ g/l}$$

* The average of nine typical lots of ammonium thiosulfate stock solution tested was 58.6% as $(NH_4)_2S_2O_3$ and contained 0.7% as $(NH_4)_2SO_3$.

TABLE I

REDUCING CAPACITY OF FIXER CONSTITUENTS (ml of 0.1000 N Iodine Consumed by 1.00 g or ml of Constituent)

Constituent	Theoretical	By Experiment
Ammonium thiosulfate solution, ml	53.1	53.5*
$NaHSO_3$, g	192	207†
Na_2SO_3, g	159	156‡
$Na_2S_2O_3 \cdot 5H_2O$, g	40.3	40.3§

* Using a sample of solution having an assay of 58.5% and containing 0.86% $(NH_4)_2SO_3$. They contributed to theoretical value to the extent of 52.1 and 0.98 respectively, and to the experimental value by 52.1 and 1.4 respectively.

† Using sodium bisulfite which assayed 97.0% as $Na_2S_2O_5$ (PH4.276-1972).

‡ Using photographic grade sodium sulfite which has a minimum assay of 97.0% as Na_2SO_3. (PH4.275-1972)

§ Using photographic grade sodium thiosulfate (crystalline) which has an assay between 99.0 to 101.0% as $Na_2S_2O_3 \cdot 5H_2O$ (ANSI PH4.251-1960, Reviewed 1966).

TABLE II

CONTRIBUTION OF CONSTITUENTS TO HYPO INDEX OF FIXER REPLENISHERS

Fixer Replenisher	Constituent	Mix Value	ml 0.1 N I_2 Consumed Theoretical
Fresh, nonrecirculated	$Na_2S_2O_3 \cdot 5H_2O$	220.0 g/l	26.6
	Na_2SO_3	10.0 g/l	4.7
			31.3 (3-ml sample)
Fresh, recirculated	$Na_2S_2O_3 \cdot 5H_2O$	250.0 g/l	10.1
	Na_2SO_3	40.0 g/l	6.2
			16.3 (1-ml sample)
Fresh, recirculated	$(NH_4)_2S_2O_3$*	130.0 ml/l	20.8
	Na_2SO_3	25.0 g/l	11.7
	$NaHSO_3$	12.5 g/l	7.8
			40.3 (3-ml sample)

* 58.6% solution

COLORIMETRIC DETERMINATION OF RESIDUAL THIOSULFATE IN PROCESSED FILM (METHYLENE BLUE) (1330A)

INTRODUCTION

This analytical method is based on the work of Warburton and Przybylowicz[1] employing borohydride as the reductant and methylene blue absorbance as the parameter. The method offers advantages over Pope's modification[2] of the Ross-Crabtree procedure in simplicity, time per analysis, and an approximate sevenfold increase in sensitivity.

In film containing silver, the true value of the thiosulfate can be obtained only by analysis immediately after processing. This time dependence is markedly diminished when the sample is taken from a minimum density area. Since image deterioration of marginally washed film is observed only in the low-density areas, this is a proper sample for forecasting image stability.

Film with photographic layers on both sides, or with a photographic layer on one side and a noncurl backing layer on the reverse side, will contain approximately twice as much thiosulfate after processing as film having a photographic layer on one side and nothing on the other. This higher level of thiosulfate will require the use of Procedure II for analysis. The results must be interpreted according to ANSI Standard, "Photographic Films for Permanent Records," PH 1.28-1969.

PRINCIPLE

Residual thiosulfate is extracted from the film, and reduced by potassium borohydride to sulfide in an alkaline solution. Acetone is added prior to acidification with ferric sulfate reagent to minimize the loss of sulfide as hydrogen sulfide concurrent with the evolution of hydrogen from the hydrolysis of borohydride. The ferric sulfate is added in excess to oxidize N, N-Dimethyl-p-phenylenediamine whose oxidation product reacts with the initially produced sulfide to form methylene blue. The absorbance of the solution is then read on a photometer or spectrophotometer.

An absorbance of 0.8 represents a thiosulfate ion, $S_2O_3^{--}$, level near 1.0 $\mu g/cm^2$ which is the upper limit measurable by the use of Procedure I. If higher levels are found or anticipated, two courses of action are open: (1) the sample size may be reduced or, (2) a larger volume of extractant solution can be used and an aliquot taken for the test. Procedure II, contained in Appendix II, employs the second choice and permits analysis over the range of 1 to 500 μg of thiosulfate per square centimeter of film.

RELIABILITY

Each laboratory must prepare and use a calibration curve (instructions are included in Appendix I). A typical calibration curve obtained and verified by several laboratories is illustrated in Figure 1.

REAGENTS

Extractant solution
Borohydride reagent
Acetone
Ferric Sulfate reagent
N, N-Dimethyl-p-phenylenediamine Sulfate reagent

SPECIAL APPARATUS

Visible Range Photometer or Spectrophotometer
1-cm Silica cell, Beckman Catalog No. 75170
Three-dram Opticlear Vial with Polyethylene Cap (Fisher Scientific, Catalog No. 3-339 or E. H. Sargent, Catalog No. F-83230E)

PROCEDURE I

A. Extraction of Residual Thiosulfate

1. Place a 10.0 cm^2 sample of film (equal to a 6.25 cm length of unperforated 16mm film) in a 3-dram shell vial by folding into a "W" shape.
2. Pipet (wipe the pipet before leveling) 5.00 ml of extractant solution into the vial and allow to stand for 10 minutes with occasional swirling.
3. Remove the sample with forceps, carefully draining it.

B. Reduction of Thiosulfate to Sulfide and Formation of Methylene Blue

NOTE: Fill all medicine droppers in readiness for reagent additions.

1. Add 5 drops of the borohydride reagent to the vial and swirl.

NOTE: Complete the next step within 15 seconds; then make the remaining additions in rapid succession and cap the vial immediately.

2. Add 10 drops of acetone and swirl.

CAUTION: Acetone is volatile and highly flammable. Do not use it near an open flame.

3. Add 5 drops of ferric sulfate reagent; immediately add 5 drops of N, N-Dimethyl-p-phenylenediamine sulfate reagent.
4. Cap the vial tightly and shake vigorously for 30 seconds. Vent the pressure formed by evolved hydrogen.
5. Repeat the 30-second shake, vent, and recap. Allow the solution to stand until the red color (Würster's salt) disappears (3 to 5 minutes).

NOTE: If the red color fails to form, the high level of thiosulfate has exhausted a reagent, and Procedure II found in Appendix II must be used.

C. Measurement of the Absorbance

1. Using a small portion (0.5 ml) of the solution, rinse a previously cleaned 1-cm silica cell.

---

[1] C. D. Warburton and E. P. Przybylowicz, *Phot. Sci. and Eng.*, 10:86, March-April, 1966.

[2] C. I. Pope, *J. Res. Natl. Bur. Std.*, 67C:237, July-September, 1963.

2. Read the absorbance of the solution at 665 nm (mμ) versus air on a photometer or spectrophotometer.

NOTE: If the absorbance is greater than 0.800, refer to Appendix II.

D. Calculations

1. Referring to a current calibration curve, find the resulting absorbance on the vertical axis.

2. Proceed horizontally until intersecting the curve. From that point, proceed vertically until intersecting the horizontal axis.

3. Divide the value found at this point (μg $S_2O_3^{--}$ per five ml of test solution) by the sample size in cm^2 (usually 10), and report the result as $\mu g/cm^2$. See Illustration I in Appendix III.

NOTE: One μg of $S_2O_3^{--}$ is equivalent to: 1.4 μg of sodium thiosulfate, anhydrous, $Na_2S_2O_3$; or 2.2 μg of sodium thiosulfate, pentahydrate, $Na_2S_2O_3 \cdot 5H_2O$.

APPENDIX I
CALIBRATION PROCEDURE

The calibration curve is prepared using known amounts of thiosulfate and plotting the absorbances against the thiosulfate used.

A. Preparation of the Standard Thiosulfate Solution (Prepare fresh daily.)

Pipet (wipe before leveling) 25.0 ml of 0.1000 N thiosulfate into a 500-ml volumetric flask and dilute to volume with distilled water. Stopper and invert to mix 8 to 10 times. Pipet 5.00 ml of the resulting solution into a 250-ml volumetric flask and dilute to volume with distilled water. Stopper and invert to mix 8 to 10 times. The resulting standard solution contains 11.2 μg of thiosulfate per ml.

B. Procedure

1. Fill a 10-ml buret with the 11.2 μg/ml standard thiosulfate solution.

2. Fill a 25-ml buret with the extractant solution.

3. Add the appropriate volume (see Table I) of standard thiosulfate solution to a 3-dram vial.

TABLE I
PREPARATION OF SAMPLES FOR CALIBRATION

Volumes of Reagents		Content of Calibration Solutions
Standard Solution $S_2O_3^{--}$ (ml)	Eluent* (ml)	(μg $S_2O_3^{--}$/5 ml)
0.20	4.8	2.2
0.40	4.6	4.5
0.60	4.4	6.7
0.80	4.2	9.0

* Extractant.

4. Add the appropriate volume (see Table I) of extractant solution. Swirl to mix.

5. Continue with Parts B and C of Procedure I.

6. Plot the absorbances versus the thiosulfate contents (Table I). Compare the curve with the curve in Figure 1. The slope and variability should approximate those shown.

APPENDIX II
TREATMENT OF SAMPLES CONTAINING MORE THAN 1.0 MICROGRAM THIOSULFATE PER SQUARE CENTIMETER OF FILM

For film containing high levels of thiosulfate, a larger volume of extractant solution is necessary to adequately remove the thiosulfate and to provide a satisfactorily dilute test solution for subsequent absorbance readings.

The three dilutions chosen will yield absorbances below 0.8 for 10 cm^2 samples containing between 1.0 and 500 $\mu g/cm^2$ of film. Values can then be read from the calibration curve which when multiplied by the appropriate dilution factor will equal the number of μg of thiosulfate per sq cm of film. The three dilutions are equivalent to extracting the 10 cm^2 sample in 25, 250, and 2500 ml of extractant solution.

PROCEDURE II

A. 25-ml Dilution of Test Solution

1. Place a 10.0 cm^2 film sample (equal to a 6.25 cm length of unperforated 16mm film) in a 100-ml beaker.

2. Pipet (wipe) 25.0 ml of extractant solution into the beaker. Be certain the film is completely immersed. Allow the sample to stand for 10 minutes with occasional swirling.

3. Pipet (wipe) 5.00 ml of the test solution into a 3-dram shell vial and continue, using Procedure I, Parts B and C.

4. If the resulting absorbance is below 0.8, read the corresponding number of μg of thiosulfate per 5 ml of test solution from the calibration curve and multiply by 0.5. This product is the number of μg $S_2O_3^{--}$ per cm^2 of film.

B. 250-ml Dilution of Test Solution

1. If the resulting absorbance (Step A, 4) is above 0.8, pipet (wipe) 10.0 ml of the 25-ml dilution test solution into a 100-ml volumetric flask. Dilute to volume with extractant solution, and mix.

2. Pipet (wipe) 5.00 ml of this test solution into a 3-dram shell vial and continue, using Procedure I, Parts B and C.

3. If the resulting absorbance is below 0.8, read the corresponding number of μg of thiosulfate per 5-ml test solution from the calibration curve and multiply by 5.0. This product is the number of μg $S_2O_3^{--}$ per cm^2 of film.

C. 2500-ml Dilution of Test Solution

1. If the resulting absorbance (Step B, 3) is above 0.8, pipet (wipe) 10.0 ml of the 250-ml dilution test solution into a 100-ml volumetric flask. Dilute to volume with extractant solution, and mix.

2. Pipet (wipe) 5.00 ml of this test solution into a 3-dram vial and continue, using Procedure I, Parts B and C.

3. From the calibration curve, read the number of μg of thiosulfate per 5-ml test solution which corresponds to the absorbance. Multiply this number by 50. This product is the number of μg $S_2O_3^{--}$ per cm^2 of film.

APPENDIX III

Illustration I

If, when a 10 cm^2 sample was used, and an absorbance of 0.632 resulted from Procedure I, it can be seen from the calibration curve (Figure 1) that 7.2 μg $S_2O_3^{--}$ were present in the 5 ml of test solution. Since the 5 ml of test solution contained all the thiosulfate extracted (7.2 μg) and the thiosulfate was extracted from 10 cm^2 of film, then 1 sq cm of film contained 1/10 of the thiosulfate or 0.7 μg.

Illustration II

High Thiosulfate Level

If a 10 cm^2 sample produces an absorbance above 0.8 using Procedure I, this indicates the sample contains more than 1.0 μg thiosulfate per sq cm and that Procedure II must be used. If Procedure II, Part B, produces an absorbance of 0.520, this indicates on the calibration curve (Figure 1) that 5.9 μg of thiosulfate are present in the 5 ml of test solution. Since this 5 ml of test solution contains 1/50 (i.e., $\frac{5}{25} \cdot \frac{10}{100}$) of all the thiosulfate extracted from the 10 cm^2 film sample, then 1 sq cm contains 29.5 μg thiosulfate. Using the equation in Procedure II, Part B, Step 3, for the illustration we have (5.0) (5.9 μg per 5 ml test solution) = 29.5 $\mu g/cm^2$ thiosulfate.

APPENDIX IV
SOURCES OF EXPERIMENTAL DIFFICULTY

In the event that a new calibration curve differs greatly from Figure 1 or that a new set of reagents produces points off the old calibration curve, the following items should be investigated: (1) impurities such as copper in the distilled water used for reagents, (2) too great a time lapse after addition of acetone or between addition of ferric sulfate reagent and N, N-dimethyl-p-phenylenediamine sulfate reagent, (3) a borohydride reagent which has expired, or was prepared from low-assay material.

Distilled water prepared from metal stills may contain copper. Levels of 1 ppm copper will reduce the methylene blue formation by 50%. Water for reagents should contain no more than 0.01 ppm copper. Water demineralizers* sold for use with steam irons can produce such water.

* Deem-X Demineralizing Filter and Squeeze Bottle (Crystal Research Laboratories, Inc., Hartford, Conn.), or equivalent.

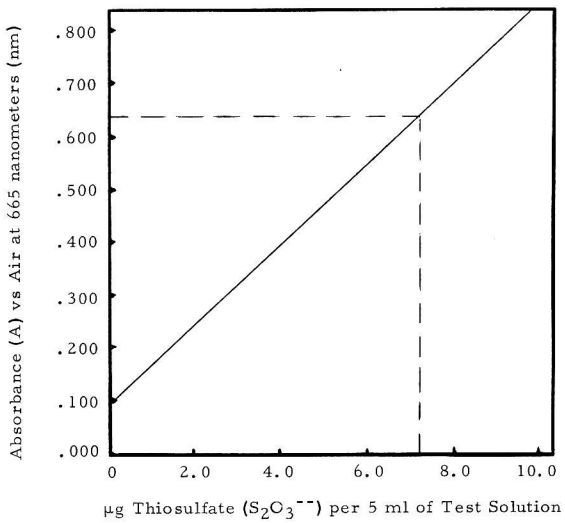


FIGURE 1 A Typical Calibration Curve for the Methylene Blue Test Method

DETERMINATION OF KODAK NEUTRALIZING AGENT, NA-1, IN THE NEUTRALIZER (1360B)

PRINCIPLE

A sample of the neutralizer is first acidified to a given pH. Formalin is then added to react with the KODAK Neutralizing Agent, NA-1, to release hydronium ions (H_3O^+).

The hydronium ions that are released are then titrated with base to give an indirect measure of the NA-1 concentration.

RELIABILITY

The calibration curve was calculated from the data obtained by three analysts. They analyzed five standard laboratory mixes containing 4.00 to 20.00 g/l of NA-1 (100%) and constant amounts of the other constituents. The volumes of base required in the titrations were plotted against the corresponding concentrations of NA-1. The best straight line was determined from the data of 15 analyses. The equation for this line is found in the calculations. The 95% confidence limits for an individual determination are ±0.11 g/l of NA-1.

SPECIAL APPARATUS

Corning Model 12 Research pH Meter, or equivalent
Beckman General Purpose Glass Electrode, No. 40498, or Leeds & Northrup No. 117169 Glass Electrode
Beckman Fiber-Junction Calomel Electrode, No. 39170 (filled with saturated potassium chloride solution)

REAGENTS

Potassium Acid Phthalate Buffer, 0.05 Molar
Borax Buffer, 0.01 Molar
1.0 N Sulfuric Acid, H_2SO_4
0.1000 N Sodium Hydroxide, NaOH
6% Formaldehyde solution, pH 3.9

PROCEDURE

A. Preparation of the Meter

Follow Method 810 (or any subsequent pH method) for making pH measurements below 9.

a. Adjust the temperature of the buffers.
b. Adjust the meter.

TABLE I

NA-1 IN NEUTRALIZER

ml NaOH	NA-1 g/l	ml NaOH	NA-1 g/l	ml NaOH	NA-1 g/l	ml NaOH	NA-1 g/l	ml NaOH	NA-1 g/l	ml NaOH	NA-1 g/l
13.5	11.37	16.0	13.47	18.5	15.58	21.0	17.68	23.5	19.79	26.0	21.89
13.6	11.45	16.1	13.56	18.6	15.66	21.1	17.77	23.6	19.87	26.1	21.98
13.7	11.54	16.2	13.64	18.7	15.75	21.2	17.85	23.7	19.96	26.2	22.06
13.8	11.62	16.3	13.73	18.8	15.83	21.3	17.93	23.8	20.04	26.3	22.14
13.9	11.70	16.4	13.81	18.9	15.91	21.4	18.01	23.9	20.12	26.4	22.23
14.0	11.79	16.5	13.89	19.0	16.00	21.5	18.10	24.0	20.21	26.5	22.31
14.1	11.87	16.6	13.98	19.1	16.08	21.6	18.19	24.1	20.29	26.6	22.40
14.2	11.96	16.7	14.06	19.2	16.17	21.7	18.27	24.2	20.38	26.7	22.48
14.3	12.04	16.8	14.15	19.3	16.25	21.8	18.36	24.3	20.46	26.8	22.57
14.4	12.13	16.9	14.23	19.4	16.34	21.9	18.44	24.4	20.54	26.9	22.65
14.5	12.21	17.0	14.31	19.5	16.42	22.0	18.52	24.5	20.63	27.0	22.73
14.6	12.29	17.1	14.40	19.6	16.50	22.1	18.60	24.6	20.71	27.1	22.82
14.7	12.38	17.2	14.48	19.7	16.59	22.2	18.69	24.7	20.80	27.2	22.90
14.8	12.46	17.3	14.57	19.8	16.67	22.3	18.78	24.8	20.88	27.3	22.99
14.9	12.55	17.4	14.65	19.9	16.76	22.4	18.86	24.9	20.97	27.4	23.07
15.0	12.63	17.5	14.74	20.0	16.84	22.5	18.95	25.0	21.05	27.5	23.16
15.1	12.71	17.6	14.82	20.1	16.92	22.6	19.03	25.1	21.13	27.6	23.24
15.2	12.80	17.7	14.90	20.2	17.01	22.7	19.11	25.2	21.22	27.7	23.32
15.3	12.88	17.8	14.99	20.3	17.09	22.8	19.20	25.3	21.30	27.8	23.41
15.4	12.97	17.9	15.07	20.4	17.18	22.9	19.28	25.4	21.39	27.9	23.49
15.5	13.05	18.0	15.16	20.5	17.26	23.0	19.37	25.5	21.47	28.0	23.58
15.6	13.14	18.1	15.24	20.6	17.35	23.1	19.45	25.6	21.56	28.1	23.66
15.7	13.22	18.2	15.32	20.7	17.43	23.2	19.53	25.7	21.64	28.2	23.74
15.8	13.30	18.3	15.41	20.8	17.51	23.3	19.62	25.8	21.72	28.3	23.83
15.9	13.39	18.4	15.49	20.9	17.60	23.4	19.70	25.9	21.81	28.4	23.91

0.842 (ml NaOH) = NA-1, g/l

c. Standardize the meter with potassium acid phthalate buffer.

d. Cross-check the electrodes with borax buffer.

B. Titration of the Sample

1. Pipet 10.0 ml of sample into a 150-ml beaker.

2. Add 100 ml of distilled water, and immerse the electrode assembly in the sample.

3. Stir the solution on a magnetic stirrer.

4. Add, from a pipet or buret, 1.0 N sulfuric acid to attain a pH of approximately 3.5. (This volume does not have to be measured.)

5. Bring to pH 3.90 with 0.1000 N sodium hydroxide from a fine-tipped polyethylene "squeeze bottle."

6. Add 10 ml of 6% formaldehyde solution, pH 3.9, from a tip-up pipet.

7. Titrate to pH 3.90 with 0.1000 N sodium hydroxide. Record the volume used in this titration for the calculation.

8. Remove the electrodes from the sample, and rinse them with distilled water. If rinsing does not completely remove the sample deposits, wipe the electrodes with a paper tissue and rerinse. Replace the electrodes in the potassium acid phthalate buffer.

C. Calculation

0.842 (ml NaOH) = KODAK Neutralizing Agent, NA-1, g/l, or for convenience, use Table I.

IODOMETRIC DETERMINATION OF RA-1 AND SODIUM SULFITE IN COLOR DEVELOPER (1470B)

INTRODUCTION

KODAK Reversal Agent, RA-1, is a strong reductant in both acidic and alkaline solutions. Extra precautions, therefore, are needed to protect the developer sample from air oxidation. The ease by which RA-1 is oxidized by air is the basis of these determinations.

PRINCIPLE

A sample of developer is diluted and acidified to pH 3—4. At this pH the sulfite in the sample is converted to bisulfite which then reacts to form a compound with RA-1. The rate of the reaction depends upon the pH, temperature, and concentrations of bisulfite, RA-1, and oxygen.

This reaction product of RA-1 and bisulfite is a stronger reductant than either the RA-1 or bisulfite; hence it is highly reactive to the oxygen in the air. To prevent interference from oxygen, the system is placed in an atmosphere of nitrogen. In the absence of oxygen, the compound is titrated along with the excess bisulfite to give a measure of RA-1 plus bisulfite. This titration, however, is not equal to the sum of the individual titrations of RA-1 and bisulfite.

A second sample is similarly acidified, but stirred in air. This system gives a lower iodine titration. It has been determined that this decrease is due to air oxidation of a RA-1-bisulfite reaction product. Therefore, there is less bisulfite and no RA-1 left to consume iodine. These two titration values can then be used to calculate the concentrations of sulfite and RA-1 in the original sample.

The acidity of the system is maintained at pH 3—4 to prevent the formation of hydrogen sulfide which would occur if the pH decreased to pH 2 or less. Also at pH 3—4, there is no interference from the developing agent which would occur at a higher pH.

RELIABILITY

The calibration equations for the ECO-3 Color Developer were calculated from 12 analyses obtained by two analysts who analyzed six standard laboratory mixes containing 3.50 to 7.00 g/l of sodium sulfite, 0.03 to 0.10 g/l of RA-1, and constant amounts of the other constituents. The 95% confidence limits for an individual determination are ±0.05 g/l of sodium sulfite, and ±0.0058 g/l of RA-1.

The calibration equations for the ME-4 Color Developer were also calculated from the data of 12 analyses obtained by two analysts who analyzed six standard laboratory mixes. These mixes contained 5.00 to 10.00 g/l of sodium sulfite, 0.04 to 0.11 g/l of RA-1, and constant amounts of the other constituents. The 95% confidence limits for an individual determination are ±0.06 g/l sodium sulfite, and ±0.0063 g/l RA-1.

SPECIAL APPARATUS

Parafilm "M," Marathon, Division of American Can Co., Wenaska, Wis.; Dow Saran Wrap; or equivalent.

Nitrogen Cylinder (water-pumped nitrogen). "High purity" water-pumped nitrogen was used in the development and calibration of this method. Possibly a lower purity of nitrogen would suffice. Oil-pumped nitrogen (left-hand threaded cylinder) cannot be used with the recommended regulator valve (right-hand thread) but can be used if a left-hand threaded regulator valve is available.

Gas Pressure Regulator and Reducing Valve for nitrogen cylinders. The flowmeter should measure 0 to 15 liters per minute. The regulator must be constructed to withstand a pressure of 3000 psi.

REAGENTS

7.0 N Sulfuric Acid, H_2SO_4
Starch indicator
0.1000 N Iodine, I_2

NOTE: The same batch of all reagents must be used for both titrations in this procedure.

PROCEDURE

A. Sampling

1. a. To sample a *mix tank,* follow Method XIV, "Sampling of Processing Solutions," Procedure Parts B and C. Use a 250-ml glass-stoppered Erlenmeyer flask.

b. To obtain a sample from a *machine tank,* fill a siphon tube with developer solution. Rinse the tube by allowing sufficient volume of the tank solution to flow through the tube. Remove the stopper from a 250-ml glass-stoppered Erlenmeyer flask, and *immediately* place the tube to the bottom of the flask. Fill to overflowing; then stopper it tightly as quickly as possible.

NOTE: Do not use a syringe.

2. Wash the outside of the flask with water.

3. Whenever an aliquot is taken from the sample flask, a rapid stream of nitrogen should be running into the sample flask through a glass tube positioned at least an inch below the top of the flask.

CAUTION: Comply with the Safety Precautions for Use of Gas Cylinders included with this method.

B. Titration of Sulfite and of the Reaction Product of RA-1 and Bisulfite

NOTE: Part C can be run during the nitrogen bubbling time in Part B, Step 5.

1. Add 800 ml of water to a 2-liter Erlenmeyer flask from a graduated cylinder.

NOTE: The type and size of the flask are critical.

2. Add 15 ml of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 10 ml of starch indicator from a tip-up pipet.
4. Place a Teflon-coated stirring bar in the flask.

5. Vigorously bubble the solution with nitrogen for at least 10 minutes through a glass tube.

NOTE: Do not use a gas dispersion tube.

6. While the solution is bubbling, obtain a 3 × 3-inch sheet of Parafilm "M" or Dow Saran Wrap, and also fill a 50-ml buret with 0.1000 N iodine.

7. Remove the tube with the nitrogen still flowing, and *within 1 second,* cover the top of the flask tightly with the sheet of Parafilm, or the plastic.

8. Slowly stir the solution on a magnetic stirrer.

9. Pipet 25.0 ml of sample into the flask close to the liquid surface by pushing the pipet through the plastic sheet.

CAUTION: Whenever an aliquot is taken from the sample flask, a rapid stream of nitrogen should be running into the sample flask through a glass tube positioned at least an inch below the top of the flask.

10. *Immediately* after the sample addition, increase the stirring rate to avoid local excess of iodine and push the buret tip through the plastic sheet. Titrate the sample with 0.1000 N iodine to a blue color which persists for 5—10 seconds.

11. Record to the nearest 0.01 ml. This is Volume A in the calculations.

C. Titration of Sulfite

1. Add 800 ml of water to another 2-liter Erlenmeyer flask from a graduated cylinder.

NOTE: The type and size of the flask are critical.

2. Add 15 ml of 7.0 N sulfuric acid from a tip-up pipet.

3. Add 10 ml of starch indicator from a tip-up pipet.

4. Stir the solution slowly on a magnetic stirrer.

5. Pipet 25.0 ml of sample into the flask adding it close to the surface of the solution.

CAUTION: Whenever an aliquot is taken from the sample flask, a rapid stream of nitrogen should be running into the sample bottle through a glass tube positioned at least an inch below the top of the flask.

6. Cover the flask tightly with a sheet of Parafilm, or plastic, and stir the solution rapidly for 5 minutes.

NOTE: The Parafilm or plastic sheet is used to prevent the loss of sulfur dioxide gas. There is sufficient volume of air in this flask to oxidize the reaction product of bisulfite and RA-1.

7. Make a small hole in the Parafilm or plastic sheet, and titrate the solution with 0.1000 N iodine to a blue color which persists for 5—10 seconds.

8. Record to the nearest 0.01 ml. This is Volume B in the calculations.

D. Calculations

$$0.04383\ A - 0.04374\ B + 0.0034 = \text{RA-1 g/l}$$

$$0.142\ A + 0.115\ B = Na_2SO_3,\ g/l$$

ADDENDUM TO METHODS REQUIRING COMPRESSED GAS AND CYLINDER SAFETY PRECAUTIONS

1. Storage and Handling of Cylinder

Store compressed gas cylinders in cool and well-ventilated areas away from sources of heat (hot plates, ovens, radiators, etc) and protect from physical shock. A rack chain, clip, or similar device should be used to secure the cylinder in an up-right position. Replace valve covers when cylinders are not in use. Use hand truck as an aid in moving cylinders and to prevent physical shock to the cylinder.

2. Connections

Never force connections or fittings. Never use makeshift connections or fittings.

3. Pressure-Adjusting Devices

When regulators are connected, but are not in use, close the cylinder valve, open the pressure-adjusting device to drain the gas, and release (close) the pressure-adjusting device.

Never open the cylinder valve until the pressure-adjusting device on the regulator has been fully released (closed). Never try to stop the flow of gas with a finger or any portion of your body.

CAUTION: The gas may have sufficient velocity to pierce the skin.

4. Identification

Do not accept any cylinder that is not clearly identified as to its contents by the manufacturer of the gas. Do not depend on the color of a cylinder for identification, because there is not full agreement among vendors on a standardized color code.

SPECTROPHOTOMETRIC DETERMINATION OF KODAK ANTI-FOG, NO. 6, IN PREHARDENER (1551A)

PRINCIPLE

KODAK Anti-Fog, No. 6, is precipitated as a complex with tetraphenylboron, filtered, and washed to remove the excess tetraphenylboron. The complex is treated with potassium bromide which by mass-action dissolves the Anti-Fog—tetraphenylboron complex and simultaneously precipitates a potassium—tetraphenylboron complex. The liquid phase is adjusted to volume and refiltered through the precipitate to cause complete replacement and to avoid possible turbidity. The absorbance of the final solution is determined at 277 nm (mμ) with a Beckman DU spectrophotometer.

RELIABILITY

Because of the rapid initial decomposition of KODAK Anti-Fog, No. 6, in the prehardener, it was added to the otherwise complete mixes as a 0.04% stock solution immediately prior to analysis.

Five standard laboratory mixes containing 0.004 to 0.040 g/l of KODAK Anti-Fog, No. 6, were analyzed by 3 analysts. The data of 15 analyses were used to derive the calibration equation by the method of least squares and to predict that the 95% confidence limits for an individual determination are ±0.001 g/l KODAK Anti-Fog, No. 6.

Investigation shows seasoned samples with a high potassium ion concentration may give results low to the extent of 0.001—0.002 g/l KODAK Anti-Fog, No. 6.

SPECIAL APPARATUS

Beckman DU Spectrophotometer, or equivalent
Millipore filter holder, Pyrex, Catalog No. XX 1004700, Millipore Corp., Bedford, Mass. 01730
984H Ultra filter, glass paper 4.25 cm, H. Reeve Angel & Co., Inc., Clifton, N.J.
Teflon-covered stirring bar, VWR Scientific, Catalog No. 58949-061
1-cm Silica cell, Beckman Catalog No. 75170

REAGENTS

Glacial Acetic Acid, CH_3COOH
Chloroform, $CHCl_3$
1% Potassium Bromide solution, KBr
250 g/l Potassium Bromide solution, KBr
3% Sodium Tetraphenylboron solution

PROCEDURE

A. Removal of the Precipitation Suppressant

1. Prepare a Millipore filtration setup with a 250-ml filter flask and 984H Ultra glass filter paper, 4.25 cm.
2. Pipet 100.0 ml of sample into a clean 250-ml separatory funnel.
3. Add 5 ml of 1% potassium bromide solution to the separatory funnel from a tip-up pipet.
4. Add 10 ml of glacial acetic acid from a tip-up pipet.
5. Add 100 ml of chloroform from a tip-up pipet.

CAUTION: Chloroform is toxic; therefore, the extractions must be performed in an exhaust hood or where there is adequate ventilation. Keep chloroform away from open flames and hot surfaces. Chlorinated materials may break down to give toxic and irritating gases such as phosgene and hydrogen chloride. Waste chloroform should be disposed of according to locally acceptable practices.

6. Stopper and shake the separatory funnel for a few seconds; then vent through the stopper. Continue to shake the funnel for 30 seconds, venting occasionally.
7. Allow the layers to separate.

NOTE: There may be some bubbles suspended in the aqueous phase; it is not necessary to wait for these to separate out.

8. Discard the (lower) chloroform layer.

B. Precipitation of the Anti-Fog, No. 6—Tetraphenylboron Complex

1. Drain the aqueous layer into a 250-ml Phillips beaker containing a magnetic stirring bar.
2. Add 25 ml of distilled water to the separatory funnel from a tip-up pipet. Stopper and shake the funnel several times and add the rinse to the Phillips beaker.
3. Rinse down all splashings on the walls of the beaker using a wash bottle.
4. Place on a magnetic stirrer and stir rapidly without splashing. While stirring, add (pipet) 5.00 ml of 3% sodium tetraphenylboron solution. Continue stirring for 2 minutes. (Use a timer.)

C. Removal of Excess Tetraphenylboron

1. With full suction on the filter setup, slowly transfer the contents of the Phillips beaker to the filter funnel, holding the magnetic bar in the beaker.
2. When the solution has been completely filtered, add, from a tip-up pipet, 25 ml of distilled water to the Phillips beaker, rinsing down the sides with the water; then transfer the rinse to the filter funnel with suction still on. Hold the stirring bar in the beaker.
3. When the rinse water has been completely drawn through the filter, break the suction. Remove the filter funnel assembly without dismantling it. Rinse the stem with distilled water from a wash bottle. Discard the filtrate and wash the filter flask thoroughly with distilled water. Reassemble the filter setup. *Do not turn suction on.*

D. Dissolution of the Anti-Fog, No. 6—Tetraphenylboron Complex

1. Add 25 ml of 250 g/l potassium bromide solution to the Phillips beaker from a tip-up pipet, rinsing down the sides during the addition.

2. *With suction off,* transfer the contents of the beaker, except the stirring bar, to the filter funnel. Let it stand for 1 minute. (Use a timer.)

3. Connect and turn suction on full, and draw the solution into the filter flask. When the filtration is complete, break suction by removing the tubing from the filtering flask *before* turning off the water.

4. Repeat Steps 1 through 3 and then remove the filter funnel assembly *without* dismantling it.

5. Carefully transfer the contents of the filtering flask to a 100-ml volumetric flask.

NOTE: A small transfer funnel may be used to assist in the transfer but if used, it also must be rinsed in the next steps.

6. Rinse the filtering flask with repeated small volumes of distilled water, transferring each rinse to the volumetric flask. (Do not go over volume.) Make final volume adjustment with the aid of a wash bottle. Stopper the flask and invert it 6— 10 times to mix.

7. Reinsert the filter funnel into the filter flask; connect and turn the suction on full.

8. Transfer the contents of the volumetric flask to the filter funnel washing down the sides of the funnel during the transfer. Draw all of the solution into the filtering flask. When the filtration is complete, break suction by removing the tubing from the filtering flask *before* turning off the water.

E. Measurement of the Absorbance

Rinse and fill a 1-cm silica cell with solution from the filtering flask and determine the absorbance of the solution vs air at 277 nm (mμ) on a Beckman DU Spectrophotometer.

F. Calculations

$(62.33)(A_{277}) - 1.26 =$ mg/l KODAK Anti-Fog, No. 6

or, $(3.166)(A_{277}) - 0.063 =$
ml/l of 20 g/l solution of KODAK Anti-Fog, No. 6

DETERMINATION OF BENZYL ALCOHOL IN COLOR DEVELOPER (1603D)

INTRODUCTION

The benzyl alcohol in the alkaline developer is oxidized to benzoic acid with a solution of permanganate at room temperature. The excess permanganate is reduced with hydroxylamine sulfate in an acid solution and nitrogen is bubbled through the treated sample to eliminate interfering organic materials. The benzoic acid is extracted with chloroform and the chloroform is washed with a saturated sodium chloride solution to eliminate acids stronger than benzoic acid. Methanol is added to the chloroform extract, and the single phase is titrated with standard sodium hydroxide.

Critical steps in the procedure are the bubbling with nitrogen and the separations. Insufficient bubbling causes volatile organics to remain in solution thereby giving high results. On the other hand, violent bubbling and foaming may cause loss of sample. Because of the latter, a pipet is preferable to gas dispersion tubes. It is also possible to use a drawn-out glass tube. If the chloroform layers are drawn off too rapidly and/or too soon after the shaking, they will be contaminated and high results will occur. Any transfer of the aqueous phase affects the neutralization.

A calibration curve was prepared by analyzing several standard laboratory mixes containing varying known amounts of benzyl alcohol and constant amounts of the other constituents. The volumes of sodium hydroxide required in the titrations were plotted against the corresponding concentrations of benzyl alcohol. The best straight line was determined from the data. The equation for this line is found in the calculations.

RELIABILITY

Five standard laboratory mixes were prepared and analyzed by three analysts. Three mixes contained 1, 4, and 6 ml/l of benzyl alcohol and constant amounts of other constituents at tank level. Two mixes contained 1 and 6 ml/l of benzyl alcohol, but the other constituents were at replenisher level. The benzyl alcohol was added to a beaker by buret and weighed. The volume for calibration was then corrected for 20 C using Lange's specific gravity of 1.043 $\frac{20^\circ}{4^\circ}$. Based upon these data, the 95% confidence limits for individual determinations are ± 0.16 ml of benzyl alcohol per liter.

SPECIAL APPARATUS

Gas pressure regulator and reducing valve. The flowmeter should measure 0 to 15 liters per minute. The regulator must be constructed to withstand a pressure of 3000 pounds per square inch.

Nitrogen cylinder (water-pumped nitrogen). "High purity" water-pumped nitrogen is not required but can be used. Oil-pumped nitrogen (left-hand threaded cylinder) cannot be used with the recommended regulator valve (right-hand thread) but can be used if a left-hand threaded regulator valve is available.

Exhaust hood

REAGENTS

0.41 M Potassium Permanganate, $KMnO_4$
2.5 M Hydroxylamine Sulfate, $(NH_2OH)_2 \cdot H_2SO_4$
18 N Sulfuric Acid, H_2SO_4
Chloroform, $CHCl_3$, practical grade
Saturated Sodium Chloride, NaCl, solution
Methyl Alcohol containing Thymol blue
0.1000 N Sodium Hydroxide, NaOH

PROCEDURE

A. Treatment with Potassium Permanganate

1. Adjust the sample to room temperature.
2. Pipet 20.0 ml of sample (at room temp.) into a 500-ml separatory funnel.
3. Insert a long-stem funnel into the separatory funnel.

NOTE: The funnel prevents the potassium permanganate from adhering to the stopper of the separatory funnel when it is added in the next step.

4. Add 40 ml of 0.41 M potassium permanganate using a 20-ml tip-up pipet.
5. Swirl the separatory funnel vigorously for 15 seconds, but avoid splashing the liquid high on the sides.
6. Let the funnel stand for 5 minutes.
7. Add 5 ml of 18 N sulfuric acid from a tip-up pipet, and swirl the funnel to mix.
8. Add 10 ml of 2.5 M hydroxylamine sulfate from a tip-up pipet.

CAUTION: Make certain that the funnel is not pointing at anyone because there may be considerable foaming.

9. Swirl the separatory funnel until all of the MnO_2 (brown precipitate) disappears.

NOTE: The MnO_2 on the sides of the separatory funnel can be removed by carefully tipping the funnel on its side.

10. Bubble nitrogen through the solution vigorously, but without splashing, for 5 minutes. Use a pipet as a bubbling tube.

NOTE #1: Comply with the Safety Precautions for Use of Gas Cylinders included with this method.

NOTE #2: If nitrogen is not available, clean compressed air may be substituted.

11. Cool the solution to room temperature if excessive pressure is found to occur in Step B, items 2 and 4.

B. Extraction with Chloroform

1. Add 25 ml of chloroform, from a tip-up pipet, washing down the pipet used for nitrogen bubbling.

CAUTION: Chloroform is toxic. Therefore, the extraction must be performed in a hood or where there is adequate ventilation. Keep chloroform away from open flames and hot surfaces. Chlorinated materials may break down to give toxic gases such as phosgene and hydrogen chloride. Waste chloroform should be disposed of according to locally acceptable practices.

2. Shake the funnel for 30 seconds *venting* the funnel as necessary. Avoid opening the stopcock (to prevent acid contamination).

3. Let stand 3 minutes. Swirl the funnel gently so that any chloroform floating on the surface of the water layer will drop into the chloroform layer. Then slowly drain the lower (chloroform) layer into a 125-ml separatory funnel. Allow 1/3—2/3 cm (1/8—1/4 inch) of chloroform to remain in the bottom of the 500-ml funnel.

4. Add 25 ml of chloroform from a tip-up pipet to the aqueous layer in the 500-ml separatory funnel and extract again by shaking 30 seconds. It is not necessary to vent the funnel.

5. Repeat Step B, 3.

6. Add 5 ml of saturated sodium chloride solution from a tip-up pipet to the 125-ml separatory funnel. Shake for 30 seconds.

7. Allow the layers to separate for 3 minutes. Then slowly drain the lower (chloroform) layer into a 250-ml Erlenmeyer flask. Allow 1/3—2/3 cm (1/8—1/4 inch) of chloroform to remain in the separatory funnel.

TABLE I

BENZYL ALCOHOL IN COLOR DEVELOPER

ml 0.1 N NaOH	ml/liter	ml 0.1 N NaOH	ml/liter
5.50	3.05	8.50	4.74
5.60	3.10	8.60	4.80
5.70	3.16	8.70	4.85
5.80	3.22	8.80	4.91
5.90	3.27	8.90	4.97
6.00	3.33	9.00	5.02
6.10	3.38	9.10	5.08
6.20	3.44	9.20	5.13
6.30	3.50	9.30	5.19
6.40	3.55	9.40	5.25
6.50	3.61	9.50	5.30
6.60	3.67	9.60	5.36
6.70	3.72	9.70	5.42
6.80	3.78	9.80	5.47
6.90	3.84	9.90	5.53
7.00	3.89	10.0	5.59
7.10	3.95	10.1	5.64
7.20	4.01	10.2	5.70
7.30	4.06	10.3	5.76
7.40	4.12	10.4	5.81
7.50	4.17	10.5	5.87
7.60	4.23	10.6	5.93
7.70	4.29	10.7	5.98
7.80	4.34	10.8	6.04
7.90	4.40	10.9	6.10
8.00	4.46	11.0	6.15
8.10	4.51	11.1	6.21
8.20	4.57	11.2	6.26
8.30	4.63	11.3	6.32
8.40	4.68	11.4	6.38

0.5647 (ml 0.1000 N NaOH) — 0.0603 = benzyl alcohol, ml/l

C. Titration with Sodium Hydroxide

1. Using a tip-up pipet, rinse down the sides of the flask with 50 ml of methyl alcohol containing thymol blue.

2. Using a 25-ml buret, titrate with 0.1000 N sodium hydroxide to the *first* persistent yellow-green color. Approach the end point dropwise. Read the buret to the nearest hundredth ml.

3. After the titration, dispose of the chloroform according to locally acceptable practices.

D. Calculations

$$0.5647 \text{ (ml 0.1000 N NaOH)} - 0.0603 = \text{benzyl alcohol, ml/l}$$

For convenience, use Table I.

ADDENDUM TO METHODS REQUIRING COMPRESSED GAS AND CYLINDER SAFETY PRECAUTIONS

1. Storage and Handling of Cylinder

Store compressed gas cylinders in cool and well-ventilated areas away from sources of heat (hot plates, ovens, radiators, etc) and protect from physical shock. A rack chain, clip, or similar device should be used to secure the cylinder in an upright position. Replace valve covers when cylinders are not in use. Use hand truck as an aid in moving cylinders and to prevent physical shock to the cylinder.

2. Connections

Never force connections or fittings. Never use makeshift connections or fittings.

3. Pressure-Adjusting Devices

When regulators are connected, but are not in use, close the cylinder valve, open the pressure-adjusting device to drain the gas; then release (close) the pressure-adjusting device.

Never open the cylinder valve until the pressure-adjusting device on the regulator has been fully released (closed). Never try to stop the flow of gas with a finger or any portion of your body.

CAUTION: The gas may have sufficient velocity to pierce the skin.

4. Identification

Do not accept any cylinder that is not clearly identified as to its contents by the manufacturer of the gas. Do not depend on the color of a cylinder for identification, because there is not full agreement among vendors on a standardized color code.

DETERMINATION OF CITRAZINIC ACID IN COLOR DEVELOPER (1611C)

INTRODUCTION

Citrazinic acid can be determined by measuring the absorbance of its sodium salt solution on a spectrophotometer at 345 nm (mμ). Since the decomposition products of the developer also absorb at this wavelength and vary with usage and air exposure, the citrazinic acid must first be separated from the rest of the mix. Citrazinic acid has very low solubility in an acidic solution, but can be dissolved by forming the sodium salt. Therefore, it can be separated from the mix by acid precipitation and filtration. The precipitate is then dissolved and measured in an alkaline solution.

CALIBRATION

The calibration curve was prepared by analyzing several standard laboratory mixes containing varying known amounts of specially purified citrazinic acid and constant amounts of the other constituents. The absorbance values determined by following the analytical procedure were plotted against the corresponding concentrations of citrazinic acid. The best straight line was determined from the data.

RELIABILITY

The individual results obtained by this method have 95% confidence limits of ±0.08 g/l. These limits are based upon 35 individual analyses of standard laboratory mixes.

SPECIAL APPARATUS

Fritted Pyrex Disc Büchner Funnel, 40mm dia. fine porosity (VWR Scientific, Catalog No. 30301-120 or Corning No. 36060)

Beckman Model DU Spectrophotometer, or equivalent

1-cm Silica cell, Beckman Catalog No. 75170

REAGENTS

Celite filter-aid

7.0 N Sulfuric Acid, H_2SO_4

0.10 N Sulfuric Acid, H_2SO_4

0.10 N Sodium Hydroxide, NaOH

PROCEDURE

A. Precipitation and Filtration of Citrazinic Acid

1. Add about 1 gram of Celite to a 150-ml beaker.
2. Pipet (wipe the pipet before leveling) 20.0 ml of sample into the beaker.
3. Add 2 ml of 7.0 N sulfuric acid from a tip-up pipet. Swirl the beaker to mix the Celite, sample, and acid thoroughly.
4. Allow 10 minutes for complete precipitation.
5. Prepare an aspirator-filter assembly. Use a 250 or 500-ml filtering flask and a fine porosity, 40mm, fritted-glass Büchner funnel.
6. After 10 minutes have elapsed, filter the reacted sample.
7. Rinse the beaker with two 10-ml portions of 0.10 N sulfuric acid, and transfer the rinses to the funnel.
8. Disconnect the aspirator-filter assembly. Discard the filtrate and rinse the inside of the flask three times with distilled water.

B. Formation of the Sodium Salt of Citrazinic Acid

1. Mount the funnel in the filtering flask. Add, from a tip-up pipet, 20 ml of 0.10 N sodium hydroxide to the beaker, and then transfer the solution to the funnel. Retain the beaker.
2. Mix the contents of the funnel by gently swirling the funnel for 1 minute.
3. Apply suction and filter the dissolved precipitate.
4. Rinse the beaker, then the funnel with four 15-ml portions of distilled water from a tip-up pipet.
5. Quantitatively transfer the filtrate to a 100-ml volumetric flask. Dilute to volume with distilled water. Stopper and invert 6 to 12 times.
6. Pipet 10.0 ml of the dilution into a 250-ml volumetric flask. Dilute to volume with distilled water. Stopper and invert 6 to 12 times.

C. Measurement of the Absorbance

Measure the absorbance of the dilution with the spectrophotometer at 345 nm. Use the hydrogen lamp. See instructions given in Method VI E.

D. Calculations

$$2.53\ (A_{345}) + 0.09 = \text{citrazinic acid, g/l}$$

TITRIMETRIC DETERMINATION OF CITRAZINIC ACID IN COLOR DEVELOPERS (1612A)

PRINCIPLE

The citrazinic acid is removed from solution by precipitation with acid. Celite is added to aid the precipitation by acting as a collecting agent. A known excess of sodium hydroxide is added, and a portion of it reacts with an equivalent amount of the precipitate. The excess hydroxide is then titrated with sulfuric acid.

RELIABILITY

The calibration equations were calculated by the method of least squares from the data obtained by three analysts who analyzed four laboratory standard mixes of each developer. The range of calibration for developers is from 1.00 to 2.00 g/l citrazinic acid. Based on 12 analyses, the 95% confidence limits for an individual determination are ±0.07 g/l citrazinic acid in the developers.

SPECIAL APPARATUS

Millipore filter holder, Pyrex, Catalog No. XX 1004700, Millipore Corp., Bedford, Mass. 01730

984H Ultra filter, glass paper 4.25 cm, H. Reeve Angel & Co., Inc., 9 Bridewell Place, Clifton, N.J.

REAGENTS

Celite filter-aid

7.0 N Sulfuric Acid, H_2SO_4

Foamex

0.1000 N Sodium Hydroxide, NaOH

Meta Cresol Purple indicator

0.1000 N Sulfuric Acid, H_2SO_4

PROCEDURE

A. Precipitation and Filtration of Citrazinic Acid

1. Add 3 to 4 g of Celite to a 400-ml beaker.
2. Pipet 100.0 ml of sample into the beaker.
3. Add 10 ml of 7.0 N sulfuric acid from a tip-up pipet.
4. Stir on a magnetic stirrer for 15 minutes.
5. Prepare a filtration setup using a Millipore filter holder and a 500-ml filtering flask. Place the glass-fiber filter paper in the filter holder.
6. After 15 minutes have elapsed, apply full suction. Transfer the mixture onto the filter paper using a glass rod; filter the solution. (The precipitate will be easier to wash if it does not collect on the holder.) Retain the stirring bar in the beaker by placing a second bar on the outside of the beaker.
7. Rinse the beaker, stirring bar, and glass rod with two 10-ml portions of distilled water. Transfer each rinse to the Millipore holder.
8. Disconnect the aspirator filter assembly and discard the filtrate. Rinse the flask and the tip of the Millipore holder three times with distilled water. Discard the rinses.

B. Formation of the Sodium Salt of Citrazinic Acid

1. Add 1 drop of Foamex to the flask. Reassemble the apparatus, but do not apply suction.
2. Pipet 50.0 ml of 0.1000 N sodium hydroxide into the beaker. Swirl the beaker to dissolve any citrazinic acid that may still be in the beaker.
3. Cautiously transfer the sodium hydroxide to the Millipore holder.

NOTE: *Do not* rinse the beaker; the strength of hydroxide must not be reduced at this time. (See Step 6.)

4. Swirl the Millipore holder for 1 minute.

NOTE:The Celite and citrazinic acid material must become suspended during the swirling action.

5. Apply suction and filter the solution.
6. Rinse the beaker with distilled water, and cautiously transfer the rinses to the holder. All solid material must be transferred to the holder.
7. Cautiously rinse the holder and the Celite with at least two 20-ml portions of distilled water.
8. Disconnect the suction line, and *quantitatively* transfer the filtrate to a 400-ml beaker.

C. Titration

1. Add 6 drops of meta cresol purple indicator to the beaker.
2. While stirring on a magnetic stirrer, titrate the solution with 0.1000 N sulfuric acid to the first clear yellow.
3. Determine the acid-base blank by pipetting 50.0 ml of 0.1000 N sodium hydroxide into a 150-ml beaker. Proceed by repeating Steps 1 and 2.

D. Calculations

Subtract the buret reading recorded in Step C, 2 from the reading in Step C, 3. Substitute the difference, △ ml, in the equation:

$$0.0831\ (\triangle\ \text{ml}) + 0.01 = \text{citrazinic acid, g/l}$$

DENSITOMETRIC INDICATOR OF IMAGE STABILITY (DIIS) (1707B)

INTRODUCTION

Inadequate washing allows certain chemicals to be retained in processed photographic materials. Some of these chemicals contribute to poor keeping characteristics of the photographic image. This method produces results that correlate with keeping as measured by accelerated keeping tests* and therefore appears to be measuring residual chemicals of interest. One of these residual chemicals is thiosulfate, which, depending on the product involved and degree of washing, may be the major contribution to the density values that are measured with this test. This method applies to aged as well as to recently processed films. Suggested upper limits for residual chemicals are given after the procedure section.

PRINCIPLE

A film sample is immersed half its length in an acidified silver nitrate reagent, converting certain residual chemicals in the sample into brown silver sulfide. The sample is then immersed completely in a sodium chloride solution, converting the unused silver ion reagent into insoluble silver chloride. The silver chloride is then removed by total immersion in a thiosulfate reagent. After washing and drying, the densities of the stained and the unstained halves of the sample are read. The difference in the densities, reported as a DIIS value, is a measure of residual chemicals and an indicator of image stability.

RELIABILITY

This method measures thiosulfate. It must also measure polythionates since the results (level of residual chemicals) do not change appreciably as the sample ages. It does not measure sulfite, thiocyanate, or thiourea.

To extend the sensitivity of the test into low amounts of residual chemicals, the densities of film samples are read through two thicknesses. Differences as small as 0.02 density can be detected. A difference of 0.03 corresponds to approximately 1 microgram of sodium thiosulfate per square centimeter of sample.

SPECIAL APPARATUS

Transmission densitometer
KODAK Status "Z" Densitometer Filter,† or equivalent

REAGENTS (No standardization is required.)

0.060 M Silver Nitrate — 0.50 M Acetic Acid reagent
0.85 M Sodium Chloride, NaCl
0.20 M Sodium Thiosulfate — 0.15 M Sodium Sulfite

*D. C. Hubbell, R. G. McKinney, and L. E. West, *Phot. Sci. and Eng.*, 11:295-305, September-October, 1967.

†Available from densitometer manufacturers.

PROCEDURE

A. Treatment of Sample

1. Cut a strip of processed film approximately 1.5 × 12 cm from a minimum density area, and fold it at the midpoint with the emulsion side out.

NOTE: To avoid contamination of the sample through handling, wear gloves, or use tweezers or film clips.

2. Immerse the folded end of the film sample one-half its length, in 20 ml of 0.060 M silver nitrate — 0.50 M acetic acid reagent, for 4 minutes, agitating from time to time.

NOTE: For convenience, a number of samples can be suspended from film clips supported by a rod over a tray of the reagent.

3. Immerse the entire sample in 20 ml of 0.85 M sodium chloride reagent for 4 minutes. Occasionally agitate the sample.

4. Immerse the entire sample in 20 ml of 0.20 M sodium thiosulfate — 0.15 M sodium sulfite reagent for 4 minutes. Occasionally agitate the sample.

5. Wash the sample in running tap water for 5 or 10 minutes, and dry.

B. Measurement of Density

1. Refold the dry strip, emulsion out. Measure to the nearest hundredth the density of the double thickness of film in both the stained (Density A) and unstained (Density B) areas. Use a transmission densitometer equipped with a KODAK Status "Z" Densitometer Filter, or equivalent.

NOTE: If the stained area density is greater than 2.00, take a second reading, using only one thickness. In this case, the density result must be doubled, to correspond with values obtained by using a double thickness of film.

C. Reporting the Results

Report the differences in densities between the stained and the unstained areas as the DIIS value.

Density A — Density B = DIIS

SUGGESTED UPPER LIMITS FOR RESIDUAL CHEMICALS

Film Type	DIIS Value, D
Fine-grain black-and-white copy, duplicating, and printing films	Not sufficiently sensitive
Medium-grain camera films, negative and reversal	+0.08
Color motion picture films	+0.14

DETERMINATION OF FORMALIN IN STABILIZER (1803G)

INTRODUCTION

In this method the sample is added to an excess of hypoiodite (formed by acidifying standard potassium iodate, adding an excess of potassium iodide, and making the solution alkaline). Part of the hypoiodite is reduced by the formaldehyde in the sample, and the unreduced part is converted to iodine by acidifying the solution. The iodine is then titrated with sodium thiosulfate using starch indicator.

Formalin is a solution of formaldehyde, CH_2O, in water. The formulas for processing solutions are based on Formalin which is 37.5% formaldehyde by weight and with a specific gravity of 1.095. The percent by weight and the specific gravity enter into the calculations for this determination. The specific gravity varies slightly depending on the concentration of methyl alcohol present as an antifreeze and preservative.

NOTE: The stabilizer of Process CRI-1 does not contain formalin; hence, this method does not apply.

RELIABILITY

The equation for determining the Formalin content should be checked by preparing several standard laboratory mixes containing the particular strength of the Formalin stock solution used in the processing solution. Normally, the results obtained are somewhat below the amount added to the mix.

The results obtained on standard mixes should be within 5% of the mix value. If this is not the case, the concentration and the specific gravity of the Formalin stock solution must be determined. The concentration can be found by using the ANSI specification test method for this chemical.

REAGENTS

0.1000 N Potassium Iodate, KIO_3
7.0 N Sulfuric Acid, H_2SO_4
0.6 M Potassium Iodide, KI
2.5 N Sodium Hydroxide, NaOH
0.1000 N Sodium Thiosulfate, $Na_2S_2O_3$
Starch indicator

PROCEDURE

A. Treatment of Sample with Hypoiodite

1. Pipet (wipe the pipet before leveling) 50.0 ml of 0.1000 N potassium iodate into a 250-ml glass-stoppered Erlenmeyer flask.
2. Add 5 ml of 7.0 N sulfuric acid from a tip-up pipet.
3. Add 25 ml of 0.6 M potassium iodide from a tip-up pipet. Swirl to mix.
4. Pipet (wipe the pipet before leveling) 20.0 ml of sample into the flask.
5. Add 25 ml of 2.5 N sodium hydroxide from a tip-up pipet.
6. Stopper the flask, swirl the contents, and allow it to stand approximately 1 minute.
7. At the end of 1 minute add 10 ml of 7.0 N sulfuric acid from a tip-up pipet.

B. Titration of Sample with Sodium Thiosulfate

1. Titrate immediately with 0.1000 N sodium thiosulfate to a light yellow color.
2. Add 5 ml of starch indicator from a tip-up pipet and continue the titration to the disappearance of the blue color.

C. Calculations

$$\frac{\left[\left(\begin{matrix}\text{ml}\\ KIO_3\end{matrix}\right)\left(\begin{matrix}\text{N}\\ KIO_3\end{matrix}\right) - \left(\begin{matrix}\text{ml}\\ Na_2S_2O_3\end{matrix}\right)\left(\begin{matrix}\text{N}\\ Na_2S_2O_3\end{matrix}\right)\right]\left(\begin{matrix}\text{eq wt}\\ CH_2O\end{matrix}\right)(100)}{(\text{ml sample})(\%\ CH_2O\ \text{by wt})(\text{sp gr of } CH_2O)} =$$

$$\frac{\left[(50.0)(0.1000) - \left(\begin{matrix}\text{ml}\\ Na_2S_2O_3\end{matrix}\right)(0.1000)\right](15.015)(100)}{(20.0)(37.5)(1.095)} =$$

$$9.15 - 0.183\ (\text{ml } Na_2S_2O_3) = \text{Formalin, ml/l}$$

DETERMINATION OF HA-2 AND FORMALIN IN PREHARDENERS CONTAINING MAGNESIUM SULFATE (1812A)

PRINCIPLE

The sodium bisulfite in the prehardener solution is released from the aldehyde complexes by the addition of sodium hydroxide. The formation of magnesium hydroxide in the presence of excess magnesium ions provides a buffered solution at pH 9—10. In this system, iodine can be used to oxidize the sulfite without oxidizing the aldehydes. This serves to remove the bisulfite.

The solution is then adjusted to pH 4 and treated with a known quantity of excess sodium bisulfite for a few minutes to form the bisulfite complex of all the aldehydes. An iodine titration of the excess bisulfite then indirectly measures the total aldehydes.

After the excess bisulfite is removed, the conditions—such as pH, temperature, time, and quantity of reactants, including a known excess of iodine—are adjusted to promote the differential rates of dissociation of the complexes. Under these conditions, the HA-2 complex dissociates at a much faster rate than does the formaldehyde complex. The iodine reacts with the bisulfite as fast as it is released. The dissociation reaction is then stopped by decreasing the pH after a given time. The excess iodine is titrated with thiosulfate. This gives an indirect measure of the bisulfite released and furnishes a second value for two simultaneous equations from which the concentration of each aldehyde is calculated.

RELIABILITY

The calculating equations and 95% confidence limits in the procedure are specifically for SA-1 at 1.0 g/l. The concentration ranges for HA-2 and Formalin included in the calibration mixes were 5.5 to 11.5 g/l and 18.0 to 36.0 ml/l respectively. The confidence limits for individual determinations based on the data obtained are:

g HA-2/l = ± 0.45

ml Formalin (37.5%)/l = ± 0.39

SA-1 is known to produce high results for the HA-2 determination. The calculation equation and reliability data have been corrected for this effect. Should any changes be made in the SA-1 concentration, a recalibration at the new level will be necessary.

APPARATUS

Constant temperature bath at 26.5 ±.5 C (80 ±1° F) with circulating water
Timer

REAGENTS

Obtain large enough quantities of all reagents to use the same batch of each reagent for standardizations and analyses.

Glacial Acetic Acid, CH_3COOH
0.4 M Sodium Sulfite, Na_2SO_3
Starch indicator
1.0 N Sodium Hydroxide, NaOH
1.0 N Sulfuric Acid, H_2SO_4
7.0 N Sulfuric Acid, H_2SO_4
5.0 M Potassium Acetate, CH_3COOK*
1.000 N Iodine, I_2
0.1000 N Iodine, I_2*
0.1000 N Thiosulfate, $Na_2S_2O_3$

NOTE: The supplies of iodine should be kept stoppered in brown bottles to avoid a change of normality during use. Also, old or partially full bottles should be restandardized before using. If they are out of tolerance, discard them.

PROCEDURE

A. Standardization of 0.4 M Sodium Sulfite

NOTE: This standardization must be made immediately before Part B is started for each sample. Care should be taken to minimize air contact with the sodium sulfite solution.

1. Add 150 ml of distilled water to a 500-ml Erlenmeyer flask from a graduated cylinder.
2. Pipet (wipe the pipet before leveling) 5.00 ml of glacial acetic acid into the flask.
3. Pipet (wipe) 35.0 ml of 1.000 N iodine into the flask.
4. Pipet (wipe) 40.0 ml of 0.4 M sodium sulfite into the flask.
5. Titrate with 0.1000 N thiosulfate to light yellow. Add 25 ml of starch indicator from a tip-up pipet, and titrate from blue to colorless solution.
6. Record this as Volume A.

NOTE: If Volume A exceeds 50 ml, prepare a fresh batch of 0.4 M sodium sulfite and restandardize.

B. Determination of Sodium Bisulfite and Complete Formation of the Bisulfite Complexes of the Aldehydes

1. Add, from a graduated cylinder, 150 ml of distilled water to a glass-stoppered, 500-ml Erlenmeyer flask and stir on a magnetic stirrer.
2. Pipet (wipe) 25.0 ml of sample into the flask.
3. Add 25 ml of starch indicator from a tip-up pipet to the flask.
4. Pipet (wipe) 10 ml of 1.0 N sodium hydroxide into the flask. (A precipitate of $Mg(OH)_2$ will form.)
5. Titrate with 0.1000 N iodine to the first blue color which persists for at least 5 seconds. This is Volume B. Continue stirring for the next two additions.
6. Pipet (wipe) 40.0 ml of *standardized* 0.4 M sodium sulfite solution.
7. Pipet (wipe) 5.00 ml of glacial acetic acid into the flask.

* Keep the supply bottles of these reagents in a 26.5 C (80 F) bath.

8. Immediately stopper the flask and place it in a 26.5 ±.5 C (80 ±1° F) bath for 10 minutes.

C. Measurement of Total Aldehydes

1. After the 10 minutes, stir the solution on a magnetic stirrer, and titrate with 1.000 N iodine to a deep purple.

2. Back-titrate with 0.1000 N sodium thiosulfate to the disappearance of the purple color.

NOTE: Avoid overshooting the end point.

3. Record as Volume C, ml =

$$\frac{(\text{ml } 1.0\ \underline{N}\ I_2)}{1} - \frac{(\text{ml } 0.1\ \underline{N}\ Na_2S_2O_3)}{10}$$

NOTE: If Volume C is less than 4.0 ml, this procedure does not apply to the sample.

D. Separation of the Aldehydes

1. From a 50-ml buret, add to the flask a volume of 1.0 N sulfuric acid (ml) equal to:

$$35.0 - 1.5\ (\text{Volume C} + \frac{\text{Volume B}}{10})$$

2. Pipet (wipe) 10.0 ml of glacial acetic acid into the flask.

3. Pipet (wipe) 50.0 ml of 5.0 M potassium acetate at 26.5 C (80 F) into the flask.

4. Set, but do not start, a timer for 30.0 minutes.

5. Pipet (wipe) 35.0 ml of 0.1000 N iodine into the flask at 26.5 C (80 F). Start the timer at the beginning of the iodine addition.

6. Immediately after the iodine addition, stopper the flask and place it in the 26.5 ±.5 C (80 ±1° F) temperature bath.

7. At the end of the 30.0 minutes, add 20 ml of 7.0 N sulfuric acid from a tip-up pipet, and stir on a magnetic stirrer.

NOTE: The 30 minutes between the first contact with 0.1000 N iodine and the addition of 7.0 N sulfuric acid must be controlled to ±1.0 minute. If these limits are exceeded, discard the solution.

8. Titrate the solution with 0.1000 N thiosulfate to colorless.

NOTE: To avoid overshooting the end point, the rate of titration must be slower than normal, and a strong source of backlighting (such as a flashlight) must be used.

9. Record this as Volume D.

NOTE: If Volume D is less than 3 ml, this procedure does not apply to the sample.

E. Calculations

$$Y_1 = 35.00 - 0.1\ (\text{Volume A}) - (\text{Volume C})$$

$$Y_2 = 35.00 - \text{Volume D}$$

$$\text{g/l HA-2} = 0.597\ (Y_2) - 0.040\ (Y_1) - 2.102$$

$$\text{ml/l Formalin} = 1.562\ (Y_1) - 0.312\ (Y_2) + 0.19$$

INDEX

Only chemicals that are used in the preparation of processing solutions are listed in the index. Analytical reagents used in analytical control are alphabetically listed in the "Analytical Reagents" section of this manual. Analytical procedures are referenced by page number and parenthetically by method number.