Potentiometric Determination of Potassium Iodide in First Developers
ECR-929C

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<th>ECN-2</th>
<th>ECP-2D</th>
<th>VNF-1/LC</th>
<th>RVNP</th>
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<td>DR-100/101</td>
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**PRINCIPLE**

A potentiometric titration of iodide can be done successfully only in a limited range of iodide to bromide and iodide to thiocyanate ratios. If the bromide and thiocyanate concentrations are considerably higher than the iodide concentration, poor titration curves result due to small potential changes and co-precipitation. The ratios in VNF-1 and RVNP first developers are unfavorable, being in excess of 1000:1. Through a precipitation enrichment process, these ratios can be improved.

The iodide is precipitated with silver nitrate over a five-minute period. Only a small amount of bromide precipitates under experimental conditions. The precipitate is collected on a filter and washed. The iodide is then solubilized in a hydroquinone silver-halide developer. It is filtered twice to remove the silver metal generated during development that can interfere with the analysis. The iodide in the filtrate is titrated potentiometrically with silver nitrate.

This method requires handling potentially hazardous chemicals. Consult the Material Safety Data Sheet for each chemical before use. MSDS’s are available from your chemical supplier.

**RELIABILITY**

All calibration mixes were made to current specifications. Any considerable change in salt content, particularly bromide, may necessitate recalibration. Four standard mixes containing 5.00, 10.00, 15.00, and 20.00 mg/L potassium iodide, respectively, were analyzed by three analysts in two laboratories. The 95 percent confidence limits were determined to be ±0.6 mg/L potassium iodide. The iodide additions to the calibration mixes were made with a potassium iodide stock solution that was assayed to be 1.00 g/L potassium iodide.

**SPECIAL APPARATUS**

- pH Meter
- Reference Electrode, Double Junction, Orion No. 900200 or equivalent
- Indicator Electrode, Silver Billet, Beckman No. 39261 or equivalent
- Millipore Filter apparatus
- Millipore Filter membrane, 0.45 micron porosity

**REAGENTS**

Use ACS Reagent Grade reagents unless specified otherwise.
- 18 N Sulfuric Acid, \( \text{H}_2\text{SO}_4 \)
- Celite filter aid
- 0.001 N Silver Nitrate, \( \text{AgNO}_3 \) (standardized to 5 decimal places)
- 1.0 M Ammonium Nitrate, \( \text{NH}_4\text{NO}_3 \)
- Silver Halide Developer

**PROCEDURE**

**Apparatus Preparation**

1. Avoidance of contamination is essential. All glassware should be cleaned with sulfuric-dichromate cleaning solution prior to use.
2. A double junction/silver billet electrode pair should be used for the potentiometric titrations. The electrode pair may be stored in distilled water when not in use.
Silver Iodide Precipitation

1. Pipet, wipe the pipet before leveling. 200.0 mL of sample into a 1-litre conical flask.
2. Set the 1-litre conical flask in an exhaust hood and stir moderately on a magnetic stirrer.
3. While stirring add very slowly, from a tip-up pipet, 50 mL of 18 N sulfuric acid to the conical flask.

**Caution**

ACID. Avoid contact with skin and eyes. In case of contact, flush with water.

**Note:** Do not add Foamex to control the foaming action.

4. Add approximately 0.3 to 0.4 grams of Celite to the flask. (Two scoops from a Coors No. 2 porcelain spoon is about 0.3 to 0.4 grams.)
5. Add, from a graduated cylinder, 50 mL of standardized 0.001 N silver nitrate to the solution as it stirs. Immediately set a timer for five minutes and continue to stir for that period.
6. As the solution stirs, assemble a Millipore filter holder and filter membrane (type HAWP 0.45 micron porosity) on a 500-mL filter flask.
7. At the end of the five-minute stirring period, connect the aspirator hose and filter the solution through the Millipore apparatus, retaining the stirring bar in the conical flask by means of another mag-bar outside the flask. Do not discard the conical flask. When filtering is completed, disconnect the aspirator hose.
8. Rinse the sides of the original 1-litre conical flask with 25 mL of 1.0 M ammonium nitrate from a tip-up pipet. Retaining the stirring bar in the conical flask, rinse the sides of the Millipore funnel by pouring the solution through a long-stemmed glass funnel. Reconnect the aspirator hose and filter the solution into the 500-mL filter flask. Disconnect the aspirator hose when the filtering is completed. Save both the long-stemmed funnel and the 1-litre conical flask.
9. Only rinse the inside and outside of the stem of the Millipore funnel with distilled water from a squeeze bottle. Do not disassemble the filter holder and membrane. Discard the filtrate and place the filter holder and membrane on a clean 250-mL filter flask.

Silver Iodide Development

1. Add, from a graduated cylinder, 20 mL of silver-halide developer to the original 1-litre flask.

**Note:** Do not expose the silver-halide developer to air any longer than necessary. When not in use, store the silver-halide developer in a cool, dark place. A developer that has turned brown should not be used. The developer is still usable if it has a light tan color.

2. Swirl the conical flask and immediately rinse the sides of the Millipore funnel (with no applied suction) by pouring the developer through the long-stemmed funnel. Set a timer for five minutes and allow the developer to stay in the Millipore funnel for that period. At one-minute intervals, swirl the Millipore funnel for several seconds.
3. During the five-minute waiting period, add, from a tip-up pipet, 50 mL of distilled water to the 1-litre conical flask and swirl.
4. At the end of the five-minute waiting period, connect the aspirator hose to the Millipore filter apparatus and filter the solution into the clean 250-mL filter flask. (Care must be taken to prevent loss of the filtrate through the aspirator hose.) Disconnect the aspirator hose when the filtration is completed.
5. Swirl the 1-litre conical flask and wash the sides of the Millipore funnel by pouring the solution from the flask through the long-stemmed funnel. Connect the aspirator hose and filter the solution. Disconnect the aspirator hose when the filtration is completed.
6. Assemble a Millipore filter holder and filter membrane (type HAWP 0.45 micron porosity) on a 250-mL filter flask.
7. Quantitatively transfer the filtrate from Step 5 into the Millipore apparatus set up in Step 6. Connect the aspirator hose and filter the solution. Disconnect the aspirator hose when the filtration is completed.
8. Quantitatively transfer the filtrate into a 250-mL beaker.
9. Slowly add 50 mL of 18 N sulfuric acid to the beaker from a tip-up pipes or graduated cylinder.

**Caution**

ACID. Avoid contact with skin and eyes. In case of contact flush with water.
Titration

Note: For preparation of the electrode pair, refer to *Apparatus Preparation* at the beginning of the procedure.

1. Stir the solution moderately on a magnetic stirrer.
2. Equilibrate an electrode pair by immersing them into the solution and waiting several minutes for the meter to settle down.
3. Titrate potentiometrically with standardized 0.001 N silver nitrate using a 50R-mL buret.

Note: Because of the relatively low iodide level, the system may take several minutes to equilibrate between additions, particularly at or near the end point. Taking potential readings at specific intervals, such as three minutes, in the vicinity of the end point, will result in uniform results. This is generally only necessary near the end point. Faster equilibration times at the beginning and end of the titration do not require a time interval quite as long. A potential change of less than 5 mV over a three-minute period can generally be regarded as a sign of equilibrium conditions.

These titrations may be done on automatic titrators equipped with controls for slow titration speeds. In any case, results from automated titrations should be checked against those from manual titrations prior to using an automatic titrator routinely. Refer to Figure 1 for a typical titration curve.

4. Determine the inflection point using the Concentric Arcs from Method ULM-0003-01, *Potentiometric Titrations for Photoprocessing Solutions*, or any subsequent revision.

Figure 1 Typical Iodide Titration Curve in Reversal First Developers

Calculation

Potassium Iodide, mg/L =

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878(N\text{ AgNO}_3)(mL\text{ AgNO}_3) + 0.52
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